Workshop sobre Química Inorgânica Sintética

Workshop on Synthetic Inorganic Chemistry

Hotel Dall'Onder Vittoria - Bento Gonçalves - RS - Brazil
September, 21st-24th, 2011

Support:

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FAPERGS

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PROGRAMA DE PÓS-GRADUAÇÃO EM QUÍMICA
Universidade Federal de Santa Maria

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Editorial

The Department of Chemistry at UFSM celebrates this year the 15th anniversary of the Laboratory of Inorganic Materials (LMI). Many landmarks certainly have been achieved during this successful period and we are now willing to take part in a major effort to improve both the level and scope of inorganic synthesis in Brazil. The first part of this endeavor is the WQIS meeting, which has found huge support in the Inorganic Chemistry community mainly because the number of researchers and groups in the field decreased a lot in recent years.

The WQIS has been organized focusing on two main points and expectations; the first one is to foster the exchange of experiences between young students and renowned scientists. During the meeting, students will have the opportunity to attend a number of conferences and talks of researchers working in inorganic synthesis, and thus discuss not only scientific issues at the highest level, but also better understand the broad scope and implications of inorganic chemistry in contemporary research.

The second point will be the composition of a written document aimed at highlighting the relevance of basic inorganic synthesis in materials research. Such document will be sent to CNPq, CAPES and other research sponsoring agencies. We have a strong believe that novel advanced materials – possibly with immediate applications – are to be discovered through fundamental research. It is therefore in the best interest of the Nation to improve investments specifically in the inorganic synthesis area.

Why are we making this effort?

Nowadays Brazilian economic development is based mainly on the export of commodities. We can do much better developing new materials. The ages of ancient civilization are remembered by the materials men discovered and used: the Stone Age, the Bronze Age, the Iron Age. It is possible that the present time will be remembered as the Nanomaterials Age. New materials bring new knowledge and new fields of science, which in turn evolve into new technologies. Without the development of inorganic (and organic) synthesis we have no chance of taking part of history.

What is our main desire? What do we have to do at this moment?

We are working hard to develop science and knowledge at a high level, but this is not enough. If we compare the number of chemists engaged in inorganic synthesis in Brazil and in many other countries, we will conclude that Brazilian numbers are astonishingly small. In this context, we must urgently act in favor of bringing more students and young scientists to this field. Whilst it is difficult to quantify the impact of these efforts in the short term, they will surely improve the quality of chemistry research and science in Brazil in the years to come s to come. Perception and understanding by the financial support agencies is required to support this challenge.

We sincerely hope the WQIS will contribute to this cause.

Ernesto S. Lang
Chairman of the WQIS

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  Universidade Federal do Paraná UFPR
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  Universidade de São Paulo Campus São Carlos - USP/São Carlos
- **Dr. Sailer Santos dos Santos**
  Universidade Federal do Paraná UFPR

Program of activities

Wednesday, September 21st, 2011

14:30 - 18:00 - Reception of participants and delivery of materials

18:00 - 20:00 – Dinner

20:00 - 20:30 - Opening Cerimony:
Prof. Dr. Ernesto Lang - Universidade Federal de Santa Maria - UFSM – Brazil

20:30 - 21:30 - Plenary lecture:
Prof. Dr. Ulrich Abram - Freie Universität Berlin - Germany
"Oligonuclear complexes of tellurium and other metals as building blocks for supramolecular assemblies."

21:30 - 22:30 - Cocktail

Thursday, September 22nd, 2011

8:30 - 8:50 - Short-presentation:
Prof. Dr. Manfredo Horner - Universidade Federal de Santa Maria – UFSM - Brazil
"Bistriazenes: Macrocyclic systems and metal complexes derivatives."

8:50 - 9:10 - Short-presentation:
Dr. Adelheid Hagenbach - Freie Universität Berlin - Germany
"Synthesis and structure of tecnetium halides."

9:10 - 9:30 - Short-presentation:
Prof. Dr. Maurício Lanznaster - Universidade Federal Fluminense - UFF - Brazil
“Synthesis and study of electronic and magnectic properties of coordination compounds of naphtoquinones and transition metals.”

9:30 - 9:50 - Short-presentation:
MSc. Juan Castillo - Freie Universität Berlin - Germany
“Tc(V) and Re(V) Complexes with Thiocarbamoylbenzamidines as Tetradentate Ligands for Bioconjugation.”

9:50 - 10:40 - Plenary lecture:
Prof. Dr. Ezequiel Vázquez-López - Universidad de Vigo - Spain
“Schiff bases for the design of metal-supramolecular derivatives.”

10:40 - 11:10 - *Coffee-break*

11:10 - 12:00 - Plenary lecture:
Prof. Dr. Sandra Signorella - Universidade Nacional de Rosário - Argentina
“Design, synthesis and activity of catalysts inspired by manganese based enzymes.”

12:00 - 12:50 - Plenary lecture:
Prof. Dr. Koiti Araki - Universidade de São Paulo - USP - Brazil
“From molecules to supermolecules and hibrid nanomaterials and interfaces.”

12:50 - 14:30 - Lunch

14:30 - 18:00 - Touristic session: *Stone ways (Caminho de Pedras)*

18:00 - 20:00 - Dinner

20:00 - 21:00 - Plenary lecture:

Prof. Dr. Ademir Neves - Universidade Federal de Santa Catarina - UFSC - Brazil

"Synthesis of multinuclear complexes with applications for bioinorganic chemistry."

21:00 - 22:00 - Poster session

Friday, September 23rd, 2011

8:30 - 8:50 - Short-presentation:

Prof. Dr. Victor Deflon - Universidade de São Paulo/Campus São Carlos - USP/São Carlos - Brazil

"Group 10 Metals Thiosemicarbazone Complexes with Anti-Mycobacterium tuberculosis Activity."

8:50 - 9:10 - Short-presentation:

MSc. Jecob Jegatesh - Freie Universität Berlin - Germany

"Host-Guest Chemistry on Bi- and Tetranuclear Oxorhenium(V) Compounds."

9:10 - 9:30 - Short-presentation:

Dr. Sailer Santos - Universidade Federal do Paraná - UFPR - Brazil

"Chalcogen Chemistry during the 15 years of the Laboratory of Inorganic Materials."

9:30 - 9:50 - Short-presentation:

Invited researchers

9:50 - 10:40 - Plenary lecture:

Prof. Dr. Heloisa Beraldo - Universidade Federal de Minas Gerais - UFMG - Brazil

"Synthesis of ligands and metallic complexes for Inorganic Medicinal Chemistry."

10:40 - 11:10 - *Coffee-break*

11:10 - 12:00 - Plenary lecture:

Prof. Dr. Jaísa Soares - Universidade Federal do Paraná - UFPR - Brazil

"Homo- and heterometallic alcoxides of vanadium, titanum and iron: synthesis, structural and spectroscopic characterization."

12:00 - 12:50 - Plenary lecture:

Prof. Dr. Alzir Batista - Universidade Federal de São Carlos - UFSCar - Brazil

"On new metal complexes with anticancer activity."

12:50 - 14:30 – Lunch

14:30 - 18:00 - Touristic session: *Vineyard Valley (Vale dos Vinhedos)*

18:00 - 20:00 – Dinner

20:00 - 21:00 - Plenary lecture:

Prof. Dr. Maria Vargas - Universidade Federal Fluminense - UFF – Brazil

"Synthetic challenges in the investigation of problems related to Bioinorganic and Medicinal Chemistry."

21:00 - 22:00 - Roundtable

Brazilian researchers

"Discussion about the Brazilian Synthetic Inorganic Chemistry."

Saturday, September 24th, 2011

Transportation to Porto Alegre.

Plenary Lectures

“Oligonuclear complexes of tellurium and other metals as building blocks for supramolecular assemblies.”

Prof. Dr. Ulrich Abram

***ulrich.abram@fu-berlin.de**

Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstraße 34-36, D-14195 Berlin, Germany;

Abstract

Aroylthioureas are versatile S,O chelating ligands, the coordination behavior of which is well known with almost all transition metals and with many main group elements. The assembly of two or more of such chelating groups around a structural template gives access to multinuclear building blocks with two up to six metal atoms. The ligands H_2L^1 to H_3L^2 have been reacted with a large number of each two metal salts comprising metal ions such as K^+, Cs^+, Ag^+, Tl^+, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Hg^{2+}, Ca^{2+}, Ba^{2+}, UO_2^{2+}, In^{3+}, Fe^{3+}, various lanthanides (Ln^{3+}), ReO^{3+} and different Te(II) and Te(IV) aryl compounds. The metal ions in the complexes are strictly organized following the ‘concept of hard and soft acids and bases’ between the O, N and S donor atoms in a way that ‘soft’ and thiophilic metal ions such as Hg^{2+}, Zn^{2+} or $PhTe^+$ are strictly coordinated by the benzoylthioureato chelating unit, while ‘hard’ metal ions are directed to the central O,N,O cavity. ‘Borderline’ metal ions such as Ni^{2+}, Co^{2+} or ReO^{2+} can be coordinated either by the central O,N,O donor set or the peripheral S,O positions depending on the (‘harder’ or ‘softer’) properties of the competing metal ions. The number of the coordinated metal ions and ligands depend on the sizes of the metal ions or cavities (different for H_2L^1 and H_2L^2) and the preferred coordination numbers and polyhedra of the metal ions (octahedral vs. five-coordinate or tetrahedral). Thus, a variety of discrete oligonuclear metal complexes can be synthesized, the structural and magnetic properties of which can be controlled over a wide range by a simple concept. Figure 1 shows some examples with the ligand H_2L^1.

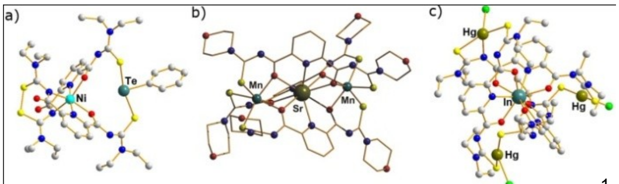

Figure 1. Typical structures of a) bi-, b) tri- and c) tetrameric complexes with $\{L^1\}^{2-}$.

Aggregation of such defined building blocks to supramolecular assemblies succeeds by means of bonding forces of different strengths: strong and weak coordinate bonds, hydrogen bonds, π-π interactions, or long-range Te…I bonds (Figure 2).

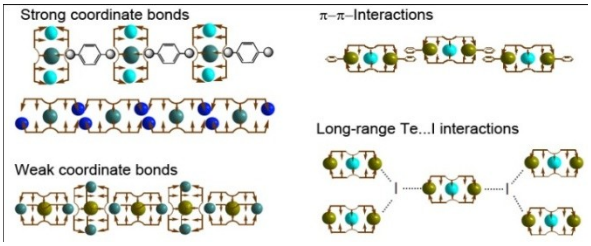

Figure 2. Typical aggregation patterns of the oligonuclear complexes

A series of oligonuclear metal complexes was prepared on the basis of aroylthiourea ligands. The multinuclear units can be designed in a way that supramolecular assemblies are formed by means of different types of intermolecular interactions.

We thank DAAD for travel support.

“Schiff bases for the design of metal-supramolecular derivatives.”

Prof. Dr. Ezequiel Vázquez-López

Departamento de Química Inorgánica, Universidade de Vigo, E-36310 Vigo, Galicia - Spain.

Abstract

Ligands based on Schiff bases are widely used in coordination chemistry. This group of compounds include those based on the fragment hydrazone (C = N-N-) to which a wide variety of additional groups may be anchored to provide different properties and coordination capacities. Many hydrazones present interesting biological properties that sometimes are amplified when complexed to a metal. Although the most studies have been subject of analytical chemistry as selective metal extracting agents and/or in spectroscopic determination of certain transitions metals.

Recently, it has been tested the dynamic behavior of metal-hydrazone link in some derivatives so that there is a growing interest in incorporating of this group in systems which are intended design of smart materials [1]. However, there are still major problems in predicting the final structure of material [2] and consequently, much of the research in this field is aimed at analyzing the factors that may be decisive in the production of a defined aschitecture.

The present contribution includes the results obtained in our laboratory at the time to design and synthesize different metal complexes with this kind of ligands. Studies show not only the high degree of variability of the systems when forming a structure, which is often determined by the presence of additional weak interactions (hydrogen bonding, pi-pi stacking) or solvents.

[1] Chow C.-F., Fujii S., Lehn, J.L. *Angew. Chem. Int. Ed*. **2007**, *46*, 5007
DOI: 10.1002/anie.200700727.
[2] Hutchinson, Hanton, L.R., Moratti, S.C. *Inorg. Chem.* **2011**, *50* 7637 DOI:10.1021/ic200670w

"Design, synthesis and activity of catalysts inspired by manganese based enzymes."

Prof. Dr. Sandra Signorella

signorella@iquir-conicet.gov.ar

Departamento de Química Física / IQUIR-CONICET, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, S2002LRK Rosario, Argentina

Abstract

The major biological roles of Mn are related to oxygen metabolism; *i.e.* making oxygen in photosystem II and as the cofactor for antioxidant defense enzymes. The number and type of ligands, the charges of surrounding protein residues, more than one manganese ion clustered together, are among the factors that introduce a way of tuning the redox potential of the metal center to face redox challenges that arise as a consequence of aerobic lifestyles. The redox function of Mn is reflected in the active site of specialized enzyme systems, such as catalases, superoxide dismutases and the oxygen evolving center of photosystem II. Biomimetic compounds provide a unique way to rationalize the catalytic mechanisms in these enzymes and dictate the critical features for obtaining efficient catalysts for ROS scavenging and water oxidation.

We have evaluated the activity of several families of manganese complexes with a number of polydentate ligands with N/O ratios and different donor site gaps, to catalyze ROS scavenging and water oxidation, and correlated their catalytic acitivity with the geometrical motif of the metal center and electronic properties modulated by the ligands. Our results provide some clues that contribute to delineate more effective mimics that could find applications as therapeutic agents against oxidative stress and as catalysts of water oxidation in artificial photosynthesis.

"From molecules to supermolecules and hibrid nanomaterials and interfaces."

Prof. Dr. Koiti Araki
koiaraki@iq.usp.br

Institute of Chemistry, University of Sao Paulo, Brazil

Abstract

Among the traditional areas of Chemistry, Inorganic Chemistry probably is the one with the broadest scope and view, long been responsible for the systematization and correlation of theory and properties, from bonding, structure, kinetic and thermodynamics to spectroscopic, redox, catalytic, electron transfer, conduction, magnetic, etc., properties of compounds and solid state materials. However, it was shadowed particularly after the emergence of Organic Chemistry with polymers, pharmaceutics and pesticides, and the creation of divisions such as Catalysis and Materials, inducing a perception that probably there won't be anything else relevant to develop in Inorganic Chemistry. The advent of coordination, bioinorganic and, more recently, supramolecular chemistry showed interesting new possibilities, leading to the realization of several supramolecular systems based on the coordination chemistry approach. Thus, the properties (p.ex., of metalloporphyrins) were shown to be improved/modified by the combination with suitable transition metal complexes, where the ancillary groups can play several roles: a) by modifying the local environment by steric effects, b) improving the solvation properties, c) acting as cofactors and relays in redox, electron and energy transfer processes, d) inducing electronic effects dependent on the oxidation states, and e) by providing important sites for intra- and intermolecular interactions, allowing the assembly of higher order supramolecular structures and materials. This scenario was further improved as the outcome of nanoscience and nanotechnology, because the development of stabilized engineered functional nanomaterials is depending on the control of the bonding with metal and metal ions and of the interaction of their molecular and nano-components, the natural realm of inorganic chemists. Accordingly, the molecular chemistry evolved to the development of nanotechnology based on the supramolecular coordination chemistry approach, aiming the large-scale production of nanomaterials and devices.

"Synthesis of multinuclear complexes with applications for bioinorganic chemistry."

Prof. Dr. Ademir Neves

ademir@qmc.ufsc.br

[1]Labinc - Laboratory of Bioinorganic and Crystallography, Department of Chemistry, UFSC, Florianópolis-SC, Brazil

Keywords: Inorganic Synthesis, Hydrolase, Catecholase, Promiscuity

Abstract

The synthesis of structural and functional biomimetic systems for a variety of metalloenzymes, certainly constitutes one of the most attractive area of investigation in bioinorganic chemistry.[1] For example, the proposed mechanism for the hydrolysis of phosphate diester and monoester bonds (catalytic promiscuity) by mammalian and plant Purple Acid Phosphatases (PAPs) enzymes has been strongly supported by spectroscopic and kinetic data of synthetic model complexes.[2]

In this work, we intend to present the importance and success of some organic and inorganic procedures adopted to generate suitable structural and functional ligands and model complexes for the metalloenzymes hydrolases and catechol oxidases. In addition, we will also report synthetic routes for the preparation of modified catalytic complex-anchored systems as DNA-intercalators and generation of new hydrolases and possible anti-cancer drugs as shown in Fig. 1.

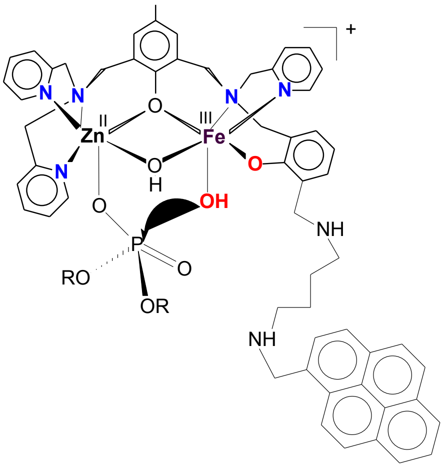

Fig. 1. Proposed mechansm for hydrolysis of DNA promoted by the $Fe^{III}Zn^{II}$ complex.[2]

Acknowledgment: This talk is dedicated to all students of LABINC. CNPQ and INCT-catálise

1. Neves, A.; Schenk, G. *et al*, *Chem. Rev.* **2006,** *106*, 3338.

2. (a) Schenk, G.; Henge, A. *et al J. Am. Chem. Soc.* **2007**, *129*, 9550. (b) Neves, A.; Schenk, G. *et al J. Am. Chem. Soc.* **2007**, *129*, 7486. (b) Neves and Pacheco, *et al* unpublished results.

“Synthesis of ligands and metallic complexes for Inorganic Medicinal Chemistry.”

Prof. Dr. Heloisa de Oliveira Beraldo
hberaldo@ufmg.br
Universidade Federal de Minas Gerais - UFMG - Brazil

Abstract

The syntheses of some bioactive organic compounds which can be used as ligands of metal complexes presenting antimicrobial, anti-inflammatory and antitumor properties will be discussed. The syntheses of a variety of metal complexes with pharmacological activity will be discussed as well. Some aspects such as the choice of substituents in organic ligands and the choice of the metals for metal-based drugs will also be shown. The design and syntheses of organic ligands for coordination with metals in the therapy of Alzheimer disease will be presented.

“Homo- and heterometallic alcoxides of vanadium, titanum and iron: synthesis, structural and spectroscopic characterization.”

Prof. Dr. Jaísa Fernandes Soares

jaisa.soares@pq.cnpq.br

Universidade Federal do Paraná - UFPR - Brazil

Abstract

We have been interested in structural features and reactivity patterns of *single-source alkoxide precursors* (SSP), that is, molecules containing different metal elements in well-defined stoichiometric proportions, and also in their sol-gel processing to give mixed-metal oxides. We reported the first examples of structurally-characterised double alkoxides of Ti/Fe, V/K and V/Fe, as well as their homonuclear analogues. Complexes containing both titanium and iron were prepared by reaction of $[Ti(OPr^i)_4]$ with $KOPr^i$ in toluene, followed by addition of $FeCl_n$ (n = 2, 3). Preparations involving iron(II) gave $[FeCl\{Ti_2(OPr^i)_9\}]$ (**A**) and the ionic $[Ti_3(OMe)_2(OPr^i)_9]$ $[Fe_4TiCl_4(O)(OPr^i)_9]$ (**B**). With $FeCl_3$, products were $[Ti_3(OPr^i)_{11}][FeCl_4]$ (**C**), $[Fe_5(\mu_5\text{-}O)(\mu\text{-}OPr^i)_8Cl_5]$ (**D**) and $[FeCl_2(Pr^iOH)_4]$ (**E**). Reactions involving non-oxo vanadium(IV), on the other hand, gave high yields of thermochromic $[V_2(\mu\text{-}OR)_2(OR)_6]$, R = Pr^i (**F**), Nep (**G**) and Cy (**H**). Complexes **F** and **G** were employed as starting materials for the synthesis of heteronuclear $[FeI_2(\mu\text{-}OPr^i)_2V(OPr^i)_2(HOPr^i)]$ (**I**) and $[V(ONep)_3(\mu\text{-}ONep)_2Li(thf)_2]$ (**J**). Structural patterns and general spectroscopic features of these products will be discussed.

Keywords: alkoxide, heteronuclear, single-source precursor.

"On new metal complexes with anticancer activity"

Prof. Dr. Alzir Batista

daab@power.ufscar.br

Universidade Federal de São Carlos - UFSCar - Brazil

Abstract

Cancer is a highly prevalent disease that poses an increasing public health threat worldwide. However, the low selectivity and high toxicity of most currently used anti-cancer drugs compromise the beneficial treatment effects of these agents [1-2]. The use of cisplatin is severely limited by its toxic side-effects. These problems have also prompted chemists to develop alternative strategies based on different metals and aimed at different targets. This has spurred chemists to employ different strategies in the development of new metal-based anticancer agents with different mechanisms of action. Medicinal inorganic chemistry can exploit the unique properties of metal ions for the design of new drugs. These include the more selective delivery and/or activation of cisplatin-related prodrugs and the discovery of new non-covalent interactions with the classical target, DNA. Thus, in this work we will discuss on the strategies that can be used to obtain metal complexes with anticancer activity and low toxicity, which are desired properties for drug candidates.

1. Novotny L, Szekers T. Cancer therapy: new targets for chemotherapy. Hematology, 2003, 8,129-127
2. Honea N, Brant J, Beck S.L. Treatment-related symptom clusters. Semin Oncol Nurs, 2007, 23, 142-151

“Synthetic challenges in the investigation of problems related to Bioinorganic and Medicinal Chemistry.”

Prof. Dr. Maria Vargas

mdvargascp@gmail.com

Universidade Federal Fluminense - UFF - Brazil

Short - presentations

“Bistriazenes: Macrocyclic systems and metal complexes derivatives.”

Prof. Dr. Manfredo Horner

Universidade Federal de Santa Maria - UFSM - Brazil

Abstract

The presentation deals with the synthesis and structure of macrocyclic bistriazenes derivatives and complexes with transition metal ions. The strategy of the synthesis of the macrocyclic bis-catena triazenes will be presented in connection with their ability to perform supramolecular arrangements in the solid state due to secondary non-covalent bonding.

"Synthesis and Structure of Technetium Halides."

Adelheid Hagenbach (PQ)*, Samundeeswari M. Balasekaran (PG), Eda Yegen (PQ), Ulrich Abram (PQ)

***hagenb@zedat.fu-berlin.de**

Freie Universität Berlin, Institute of Chemistry and Biochemistry, Fabeckstr. 34-36, D-14195 Berlin.

Keywords: Technetium, Halides, Complexes.

The structural chemistry of technetium(IV) halides is relatively less explored. There are only structural reports about $TcCl_4$ and $TcBr_4$ and some $[TcX_6]^{2-}$ salts (X = Cl, Br, I). More knowledge, however, is required to understand the geological chemistry of this radioactive metal as well as for the development of new radiopharmaceuticals on the basis of technetium(IV) compounds. Technetium(IV) chloride readily dissolves in a number of donor solvents such as THF, acetonitrile, DMSO, thioxane (1-oxa-4-thiacyclohexane) or phosphines.[1] The reaction results in cleavage of the polymeric chain of the $(TcCl_4)_n$ polymer and the formation of $[TcCl_4(L)_2]$ complexes.

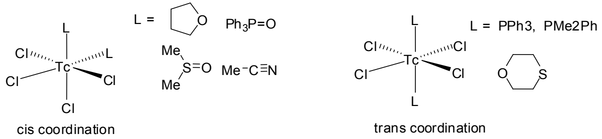

Figure 1. Dependence of the conformation of $[TcCl_4(L)_2]$ complexes on the donor atoms of the ligands.

The conformation of the products depends on the donor atoms in a way that *trans*-coordination is established with 'soft' donor atom such as sulfur or phosphorus, while *cis*–complexes are established with the 'harder' donors like oxygen or nitrogen (see Fig. 1). The *trans*-complexes are air-stable and resistant against hydrolysis. The *cis*-complexes undergo a stepwise hydrolysis, during which complexes of the composition $[Cl_3(L)_2TcOTc(L)_2Cl_3]$ (L = H_2O, DMSO, CH_3CN) are formed. The isolation of the stepwise hydrolysis products of $[TcCl_4]_n$ was possible in moist dioxane. The aqua-complex $[TcCl_4(H_2O)_2]$ and also the dimeric species are stabilized by frameworks of hydrogen bonds between the water ligands and the donor solvent dioxane (Fig. 2).[2]

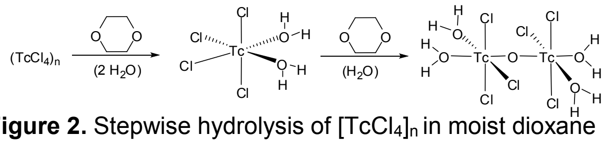

Figure 2. Stepwise hydrolysis of $[TcCl_4]_n$ in moist dioxane

The reactivity of fluorine compounds is different to the reactivity of the chlorine compounds. Hexachlorotechnetate rapidly hydrolyzes under the formation of amorphous $(TcO_2)_n$, while hexafluorotechnetate is fairly stable in aqueous solutions and hydrolysis and formation of the oxo-bridged anion $[Tc_2OF_{10}]^{3-}$ was only obtained during reactions in aqueous ammonia. More complex reaction patterns were found during reactions of $(TcCl_4)_n$ with dimethylsulfoxide and alkyl isocyanides. Solutions of $[TcCl_4(DMSO)_2]$ isomerize and yield the ionic product $[TcCl_3(DMSO)_3]_2[TcCl_6]$. Similar ion pairs, e.g. $[TcCl_5(C{\equiv}N\text{-}R)][TcCl_2(C{\equiv}N\text{-}R)_5]$, were obtained during reactions of $[TcCl_4]_n$ with alkyl isocyanides (Fig. 3).

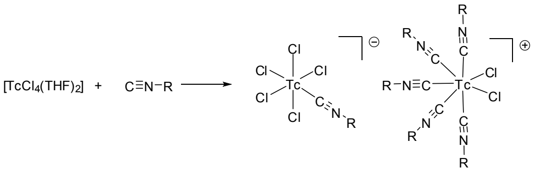

Figure 3. Reaction of $(TcCl_4)_n$ with alkyl isocyanides in THF.

The resulting products were characterized by spectroscopic methods and X-ray crystallography. Reactions of the polymeric $(TcCl_4)_n$ with small donor molecules ends in the cleavage of the polymeric framework and the formation of small $[TcCl_4(L)_2]$ complexes. The conformation of the products depends on the donor atoms. Traces of water during the reactions results in the formation of hydrolysis products. Fluoro complexes are more water-resistant and hydrolysis is only observed under drastic conditions.

We gratefully thank the DFG, GRK 1582/1, and DAAD for financial support.

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[1] A. Hagenbach, E. Yegen, U. Abram, Inorg. Chem. **2006**, 45,7331.

[2] E. Yegen, A. Hagenbach, U. Abram, Chem. Commun. **2005**, 557.

"Synthesis and study of electronic and magnetic properties of transition metal complexes with naphthoquinones."

Mauricio Lanznaster

ml@id.uff.br

Universidade Federal Fluminense, Instituto de Química, 24020-141, Niterói, RJ

Resumo

Quinones are an important class of naturally occurring molecules with a great variety of physiological functions, which includes electron transfer in the respiratory chain by coenzyme Q and blood coagulation by vitamin K.[1] A large number of synthetic and naturally occurring quinones also show biological activities against some fungi, protozoa, viruses and cancer.[1,2] Their mechanism of action has been associated with its redox activity, in which a quinone can be reversible reduced by one or two electrons.[1] When coordinated to metal ions, quinone containing complexes may present intra-molecular electron transfer equilibrium (valence tautomerism), which can be induced by an external stimuli (e.g. heat and light).[3] Among several valence tautomeric systems identified until now, cobalt compounds with 1,2-benzoquinones are the most extensively studied. These complexes undergo thermally and sometimes light induced interconversion between two valence tautomers: Co(III)(*cat*) ⇄ Co(II)(*SQ*) (were *cat* and *SQ* are the two and one electron reduced forms of a quinone, respectively).[4] Such systems are expected to be applied in the development of new materials for molecular based devices in quantum computing.[4] Nonetheless, to have a better control the properties that govern the valence-tautomeric equilibrium, new classes of complexes must be synthesized and studied.[5] Therefore, our go is to develop a new family of coordination compounds with 2-hydroxy-1,4-naphthoquinones, a class of electroactive ligands with redox properties similar those found in 1,2-benzoquinones. Such complexes are rare in the literature and only one report with evidence of valence tautomerism was found so far.[6] In this work, we present some results of a systematic study on the coordination of 2-hydroxy-1,4-naphthoquinones to first row transition metal ions, as well as structural, spectroscopic, electrochemical and magnetic data.

Acknowledgements: CNPq, CAPES, FAPERJ, LDRX/UFF and LabCri/UFMG.

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“Tc(V) and Re(V) Complexes with Thiocarbamoylbenzamidines as Tetradentate Ligands for Bioconjugation.”

***MSc. Juan* Daniel Castillo Gómez**

***castillogo@hotmail.com**

[1]Freie Universität Berlin, Fabeckstr. 34/36, D-14195, Berlin, Germany

Re and Tc complexes are of particular importance for nuclear medicine because of the diagnostic use of ^{99m}Tc and the therapeutic use of ^{186}Re and ^{188}Re. One main focus of current research is bioconjugation.The tetradentate thiocarbamoylbenzamidines **L1** and **L2** can be easily synthesized from benzimidoyl chlorides and o-phenylene diamine[1,2]. They have been shown to be suitable ligands for Re(V) and Tc(V) oxo and nitrido cores. It was possible to synthesize a similar ligand with an additional carboxylic group for conjugation (**L3**). Reactions of the carboxyl-substituted ligand **L3** with oxorhenium(V) cores gave complexes, in which a third weak co-ligand was needed for stabilization (**C5** and **C6**). This problem could be avoided using ReN and TcN cores (**C7** and **C8**). The ligand itself and its nitrido complexes could be coupled to propargyl amine via standard amide coupling prodecures (**L4**, **C9**, **C10**).

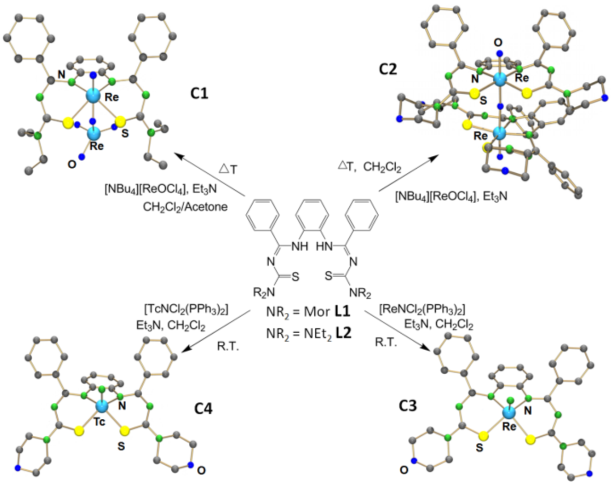

Figure 1. Prototype Complexes of **L1** and **L2.**

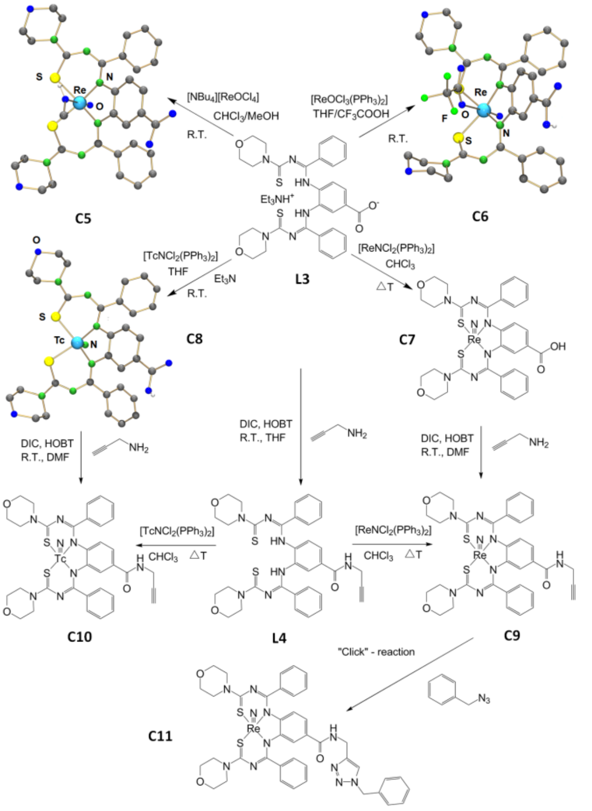

Figure 2. Complexes of **L3** and further coupling reactions.

A model “Click”-coupling reaction was made with **C10** and benzyl azide forming complex **C11**. Stable oxo and nitrido complexes of Re and Tc with tetradentate thiocarbamoylbenzamidines were synthesized. Nitrido complexes of the ligands **L3** and **L4** can be coupled to small organic molecules through amide- and „Click“-coupling reactions.

We thank DAAD for financial support.

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"Group 10 Metals Thiosemicarbazone Complexes with Anti-Mycobacterium tuberculosis Activity."

Prof. Dr. Victor Deflon

Universidade de São Paulo/Campus São Carlos - USP/São Carlos - Brazil

Abstract

Square planar analog complexes of the type [MCl(L1)], where M represents Ni(II), Pd(II) or Pt(II) and L1 the monovalent anion of 2-acetylpyridine-N(4)-phenyl-thiosemicarbazone, as well as octahedral Ni(II) complexes of the type [Ni(L1,3)2] (HL3 represents 2-acetylpyridine-N(4)-methyl-thiosemicarbazone have been prepared and characterized and had their ani-Mycobacterium tuberculosis activity evaluated.

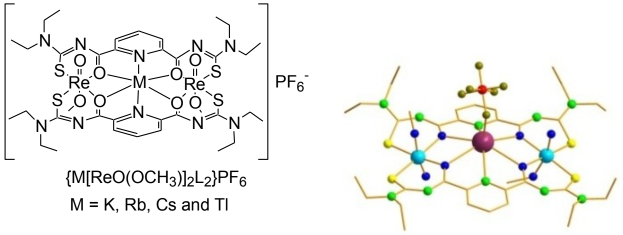
"Host-Guest Chemistry on Bi- and Tetranuclear Oxorhenium(V) Compounds."

MSc. Jecob. J. Jegathesh

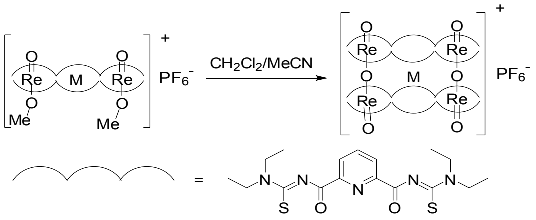
jecob07@chemie.fu-berlin.de

Freie Universität Berlin, Institute of Chemistry and Biochemistry, Fabeckstr. 34/36, 14195 Berlin, Germany

A number of mono- and binuclear oxorhenium(V) complexes with benzoylthiourea ligands have been isolated and structurally characterized.[1] Moreover, bi- and tetranuclear oxorhenium(V) complexes with bipodal aroylthiourea derivatives of type (**I**) have recently been reported showing cage-like, oxo-bridged structures (**II**).[2] In the present work, we extend this chemistry with pyridine-2,6-dicarbonyl-bis(N,N-diethylthiourea) (H_2L) (**III**) in order to accommodate metal ions in the centre of the formed cage. $(NBu_4)[ReOCl_4]$ and H_2L react rapidly in MeOH under formation of a wine-red solution in the presence of a metal chloride MCl (M= K, Rb, Cs and Tl). Stable complexes of the composition $\{M[ReO(OCH_3)]_2L_2\}$–(PF_6) (type 1) are isolated after the addition of $(NBu4)PF_6$ to the reaction mixture (Scheme 1). Each $\{O{=}Re{-}OMe\}^{2+}$ core coordinates two mono-anionic thiourea moieties from two different ligands as is observed in complexes described for (**I**).[2] Additionally, both pyridine-2,6-diacetyl centres of the ligand coordinate to the central metal cation.Recrystallization of type 1 complexes from a 1:1 mixture of CH_2Cl_2/MeCN produces tetranuclear, cage-like, oxo-bridged complexes (Scheme 2). Formation of $\{O{=}Re{-}O{-}Re{=}O\}^{4+}$ via the intermediate $\{O{=}Re{-}OH\}^{2+}$ core is already observed in previous works.[1,2]



Scheme 1. Synthesis of binuclear oxorhenium(V) complexes with additional metal cation (type 1)



Scheme 2. Formation of tetranuclear oxorhenium(V) complexes with an additional metal cation (type 2)

A metal-metal exchange inside the cage is possible. This exchange depends on the size of the cations. Bigger cations like Cs^+ are more stable inside the cages. The rate of exchange is estimated by means of the β^- emitting isotope ^{204}Tl (Scheme 3).

Scheme 3. Exchange of $^{204}Tl^+$ with K^+, Rb^+ and Cs^+

Almost no exchange of $^{204}Tl^+$ with K^+ is observed, while about 50 per cent of $^{204}Tl^+$ is replaced by the larger Rb^+ ions, and the highest exchange rate is found for Cs^+. Tetranuclear oxorhenium(V) cages containing an additional metal cation were synthesized and structurally characterized. An exchange of the central metal ions is possible. The rate of the exchange depends on the size of the metal ions and was estimated by means of radiochemical techniques.

We would like to thank the Center of Supramolecular Interactions of FU Berlin (CSI) and DAAD for the financial support.

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"Chalcogen Chemistry during the 15 years of the Laboratory of Inorganic Materials."

Dr. Sailer Santos

sailer.santos@gmail.com

Laboratório de Projetos e Processos Ambientais , Departamento de Química, Universidade Federal do Paraná, Curitiba - PR - Brazil

Abstract

Chalcogen chemistry has different applications mainly related to the preparation of semiconductors, biochemistry and synthetic organic chemistry. It is also a traditional research topic in Brazil, but just a few groups work with the development of new organochalcogen metal complexes, essential compounds for several methodologies to produce semiconductors. The strategic importance of this sector is evident because this kind of products is essential for improving quality of life. The Brazilian chemical trade deficit peaked at the amount of US$ 6.7 billion in 2004, showing the need for investment in research to obtain these materials. In an attempt to develop techniques for preparing these materials, research efforts on organochalcogen metal complexes have been developed at the Laboratory of Inorganic Materials (Laboratório de Materiais Inorgânicos – LMI) since 1996. Synthetic and structural aspects of cluster compounds prepared from the building block $M(EPh)_2$ (M= metal, E= Se, Te) and also for organochalcogen halides complexes will be discussed.

Poster Abstracts

Titles Index

Bio-Inorganic Chemistry - BI

BI-01 Characterization and antibacterial assays of a gold(I) complex with rimantadine

BI-02 Synthesis, Characterization and Reactivity of a dinuclear manganese complex $Mn^{III}(\mu OAc)2Mn^{II}py_3mff]ClO_4$

BI-03 Synthesis and characterization of biomimetic Manganese complexes with N,O ligands

BI-04 Platinum complexes with dithiocarbazate derivatives of β-diketones aiming new trypanocidal agents

BI-05 Diruthenium(II,III) complex of □-linolenic acid synthesis, characterization and inhibition of C6 rat glioma cell proliferation.

BI-06 On the ability of the *cis*-$[RuCl_2(dppb)(bipy)]$ complex to coordinate with nucleobases synthesis and structural aspects

BI-07 Synthesis and characterization of a ruthenium complex with djenkolic acid

BI-08 Synthesis and characterization of Cu(II)-glutamate complex

BI-09 Synthesis of a New Mononuclear Copper(II) Complex with a N_2O-purine-containing Ligand

BI-10 Synthesis and characterization of Cu(II)-nicotine complex

BI-11 Synthesis and structural characterization of the new complex of manganese

BI-12 Synthesis and antitubercular activity of paladium (II) complexes with dithiocarbazate Schiff bases

BI-13 Synthesis and characterization of dipyridophenazine ruthenium(II) complexes promising metallodrugs against cancer

BI-14 Synthesis, characterization and cytotoxic activities of ruthenium(II) complexes containing folic acid as ligand

BI-15 A new manganese complex of a pyridoxal derivative

BI-16 Chelate complexes of vanadium (+IV) and (+V) and rhenium (+V) with a pyridinone ligand derivated from maltol and isoniazid

BI-17 Synthesis and characterization of ruthenium (II) complexes with dithiocarbazate Schiff bases: Potential antitumoral.

Catalysis - CT

CT-01 Synthesis of solids based on inorganic supports and anionic iron(III) porphyrin for oxidation heterogeneous catalysis.

CT-02 Nickel(II) complexes with pyrazolyl-imidazolium ligands and their catalytic behavior in ethylene oligomerization

CT-03 Synthesis and characterization of ruthenium (III) complexes studied in hydrogenation reactions.

CT-04 Poly(ε-caprolactone) produced using $[Ti_3(\mu_3\text{-OPri})_2(\mu\text{-OPri})_3(OPri)_6][FeCl_4]$ as catalyst

CT-05 Ruthenium(II) Carbonyl Complexes with Amine and Imine Ligands Synthesis, Characterization and Catalytic Activity.

CT-06 Ruthenium(II) Hydride Complexes Synthesis, Characterization and Catalytic Activity.

Interface and Surface Chemistry - IS

IS-01 Sensor based on electrostatic assembled tetraruthenated free-base and zinc meso-tetra(4-pyridylvinylphenyl)porphyrins films

IS-02 The use of superparamagnetic Carbon Electrodes: a new approach for analysis of mercury ions

IS-03 Surface chemistry of oxidized charcoal fines with metal ion adsorption capacity.

IS-04 APTES-Modified Silicas in the Reaction with Essential Oil of Citronella

Structural and Coordination Chemistry - SC

SC-01 Tc(V) and Re(V) Complexes with Thiocarbamoylbenzamidines as Tetradentate Ligands for Bioconjugation

SC-02 X-ray Crystallography and Luminescence Studies for a New Complex of Eu with Ligand derived from 2,6-diformylpyridine

SC-03 Building Hg(II)Cu(I) multinuclear compounds from mercury bis(phenylselenolate).

SC-04 Non-oxo vanadium(IV) alkoxides synthetic and structural trends

SC-05 Synthesis, structure and optical features of single adamantanoid Hg-SePh-X anionic clusters stabilized by octahedral complexes. (Ph = phenyl; X = Cl, Br, I)

SC-06 Rhenium(I) and Technetium(I) Tricarbonyl Halogeno Complexes Containing a N,S-Bidentate Dithiocarbazate as Ligand

SC-07 New Oxotechnetium(V) Complex Containing a Dithiocarbazate Ligand Synthesis, Characterization and Crystal Structure

SC-08 Synthesis and characterization of a mononuclear nickel complex

SC-09 Organoindium(III) one-dimensional polymers with alkyl diphosphine oxide spacers

SC-10 Copper Complex with a Thiosemicarbazone Derivative Ligand

SC-11 Synthesis and characterization of metal-organic frameworks containing a mixture of metals

SC-12 Synthesis and structural characterization of the tetranuclear palladium chalcogenolato-acetato complex $[Pd(TeC_6H_3(CH_3O)_2)(O_2CCH_3)]_4$

SC-13 Synthesis and structural features of new aryltellurenyl iodides.

SC-14 Synthesis and structure of new aryltellurenyl halides with mixed or uncommon valences.

SC-15 Synthesis, structure and luminescence studies of new Eu(III) complex with 2,6-Diformylpyridine derivative.

SC-16 Synthesis and crystal structure of 2,6-Diacetylpyridin-bis(benzoylhydrazine)lanthanide(III) complexes

SC-17 Synthesis, characterization and supramolecular assemblies of novel ditelluroethers iodides

SC-18 Lamellar crystal structure of $[Mn(O_2Se\text{-}4\text{-}C_6H_4Cl)_2(H_2O)_4]$ formed by by hydrogen bonds

SC-19 Synthesis and characterization of the 2,6-bis(imidazol-2-yl)pyridine complex with copper(II)

SC-20 Synthesis, characterization and study of coordination chemistry of new compounds containing Indium and Tellurium

SC-21 Synthesis and structural characterization of a new macrocyclic compound containing Tellurium

SC-22 Synthesis and structural characterization of new coordination polymers containing Mercury

SC-23 New Dioxomolybdenum Dithiocarbazate Complex

SC-24 Supramolecular assembly of new heteropolymetalic molecules based on tetraiminodiphenolate macrocycle and hexacyanometallate anions

SC-25 Synthesis and characterisation of oxazolinylthiophenolate complexes of vanadium(III)/(IV)

SC-26 Synthesis and characterization of a new porphyrin nitrosyl ruthenium complex

SC-27 Synthesis and Crystal Structure of a New Binuclear Gold(I) complex with thiocarbamoyl-pyrazoline ligand.

SC-28 Synthesis and structural analysis of lead(II) compounds with pyrimidine-2-thione

SC-29 Synthesis and X-ray Structure of a New Organoselenium Cluster Based on Se–Hg Adamantane Cages.

SC-30 A New Copper-Phenylselenolate Cluster, $[Cu_6(bpy)_2(\mu\text{-}SePh)_2(\mu_3\text{-}SePh)_4]$, Synthesis and Structural Analysis.

SC-31 Thiosemicarbazones complexes with first row transition metals

SC-32 Rhenium mixed complexes involving a *S,N,S*-tridentate thiosemicarbazone and pseudo halogeno ligands

SC-33 Synthesis and structural analysis of new polymeric M−NCS−HgSePh compounds (M = Co, Ni).

Poster Abstracts I:
Bio-Inorganic Chemistry

Workshop sobre Química Inorgânica Sintética – WQIS (Workshop on Synthetic Inorganic Chemistry - WSIC)

Characterization and antibacterial assays of a gold(I) complex with rimantadine

Suelen F. Sucena (PG)[1], Ives I.B. Mattos (PG)[2], Débora D. Camargo (IC)[1], Raphael E.F. Paiva (IC)[1], Marcelo Lancellotti (PQ)[2], André L.B. Formiga (PQ)[3], Pedro P. Corbi (PQ)[1*].
*** ppcorbi@iqm.unicamp.br**

1 – Bioinorganic and Medicinal Chemistry Research Laboratory - LQBM, Institute of Chemistry, University of Campinas. P.O. BOX 6154, 13083-970, Campinas, São Paulo, Brazil. 2 – Laboratory of Biotechnology, Institute of Biology, University of Campinas. Campinas, São Paulo, Brazil. 3 – Coordination Chemistry Laboratory - LQC, Institute of Chemistry, University of Campinas. P.O. BOX 6154, 13083-970, Campinas, São Paulo, Brazil

Keywords: Metal complexes, rimantadine, gold(I), antibacterial agent

Introduction

Metal-based drugs have been used for the diagnosis and treatment of different human malignancies. Particularly, chrysotherapy is the medicinal term for treatments based on gold compounds. Such compounds have been investigated as antibacterial agents since the middle ages. There are reports of prescriptions of gold mixtures for the treatment of a wide range of conditions and also as an elixir of youth since the 8th century.[i] In the 19th century, Koch scientifically documented the bacteriostatic properties of gold(I) dicyanoaurate.[ii]

Recently, the application of gold compounds in medicine has been mainly centered on the treatment of inflammatory processes, with emphasis on rheumatoid arthritis. The most used compound in the treatment is auranofin. Solganol and myochrysine are other examples of gold(I) compounds used for the treatment of arthritis. More recently, novel gold(I) complexes exhibiting antibacterial activities against pathogenic bacteria have been reported in the literature.[iii]

Rimantadine ($C_{12}H_{21}N$, rtd) is an antiviral agent which specifically inhibits the replication of *Influenza A* virus. The compound is obtained by functionalization of adamantane with an ethanamine group. The presence of a NH_2 group confers to rimantadine the ability to coordinate metal ions through the nitrogen atom. The present work deals with the synthesis, spectroscopic characterization and antibacterial activities of a gold(I) complex with rimantadine.

Results and Discussion

The gold(I) complex with rimantadine (Au-rtd) was synthesized by the reaction of an aqueous solution of rimantadine hydrochloride (4.60×10^{-4} mol) with an aqueous solution of potassium dicyanoaurate(I) (4.60×10^{-4} mol) under stirring and at room temperature. The white precipitate obtained was collected by filtration, washed with water and dried in a desiccator with P_4O_{10}. Elemental analysis led to a 1:1 metal/ligand composition plus a cyanide group. Anal. Calc. for $[Au(C_{12}H_{21}N)(CN)]$ (%) C. 66.8, H. 10.3. Found (%) C. 66.5, H. 10.1. The thermogravimetric data confirmed the 1:1 molar composition (M:L) of the complex. A comparative study between the infrared spectra (IR) of the ligand and the gold(I) complex show differences in the NH_2 stretching frequencies, which indicates coordination of rimantadine to Au(I) through the nitrogen atom. The IR spectra of the complex also presents an absorption band at 2140 cm^{-1} which confirms the presence of cyanide coordinated to gold(I). The ^{13}C and ^{15}N NMR data also indicates coordination through the nitrogen atom.

A typical antibiogram assay was carried out in order to evaluate the antibacterial activity of the Au-rtd complex. In this study, Gram-positive and Gram-negative pathogenic bacteria (*Staphylococcus aureus* Rib1 and BEC 9393 MRSA and *Pseudomonas aeruginosa*) were selected. The obtained results indicated the antibacterial activity of the gold(I) complex with rimantadine at a concentration of 20 μg of the compound.

Conclusions

Molar composition of the gold(I) complex with rimantadine was found to be 1:1 (metal/ligand). IR and NMR spectroscopic measurements indicate coordination of the ligand to the metal center through the nitrogen atom of the NH_2 group. The compound presents antibacterial activities against methycillin resistant *S. aureus* (Rib1 and BEC 9393) and *P. aeruginosa* bacterial strains.

Acknowledgements

This study was supported by grants from FAPESP (proc. n° 2006/55367-2), CNPq (proc. n° 472468/2010-3) and CAPES (Brazilian agencies).

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Synthesis, Characterization and Reactivity of a dinuclear manganese complex $[Mn^{III}(\mu OAc)_2Mn^{II}py_3mff]ClO_4$.

***Claudia Pereira (IC), Rosely A. Peralta (PQ)**

*** claudiakrauser@hotmail.com**

Universidade Federal de Santa Catarina- Departamento of Chemistry, Laboratório de Bioinorgânica e Cristalografia – Campus Universitário-CEP-88040-900-Florianópolis-SC-Brazil.

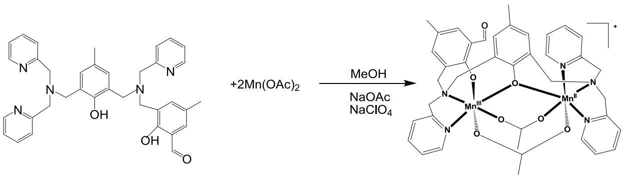
Keywords: *Catalases, Model complex, X-ray Structure.*

Introduction

Models for manganese enzymes, such catalase, are important, considering biotechnological application[1,2]. In the present work was synthesized, characterized a dinuclear manganese complex **$[Mn^{III}(\mu OAc)_2Mn^{II}py_3mff]ClO_4$ (1)** The reactivity towards the 3,5-di-tert-butylcatechol oxidation is also presented.

Results and Discussion

The ligand was synthesized according to the synthetic route described in literature[3]. With this ligand we synthesized a mixed valence manganese complex **(1),** according Scheme 1.



Scheme 1 Synthesis of **(1)**.

The complex was characterized by Infrared and UV-Vis spectroscopies and X-ray analysis. In the IR spectrum of the complex it is possible to see the bands also present in the ligand. The bands at 1570 and 1430 cm^{-1} with a difference of 130 cm^{-1} is characteristic of bridging acetato groups. The band at 1090 cm^{-1} is attributed Cl-O bond stretching of the perchlorate counter ion.

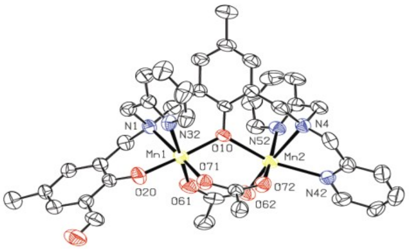


Figure 1 Molecular structure of **(1)**.

Brown-red crystal consists of a binuclear cation, **(1)** (Figure 1) and one counter anion perchlorate. In the hard side of the ligand, the Mn^{III} ion is coordinated octahedrally by two oxygen atoms (from the central and terminal phenolate), two N atoms (from the tertiary amine and a pyridine) and by two oxygen atoms from the bridging acetate groups. The Mn^{II} ion is coordinate by three N atoms (two pyridine groups and a tertiary amine) and by the three bridging groups.

The catecholase activity of complex was determined using the substrate 3,5-di-*tert*-butylcatechol by following spectrophotometrically the absorbance increase due to the formation of 3,5-di-*tert*-butylquinone (λ_{max}= 400 nm), under conditions of excess substrate. The pH-dependence of the oxidation reaction of 3,5-dtbc was evaluated from pH 4.5 to 9.0 and, can be observed a sigmoidal-shape profile (Figure 2, left).

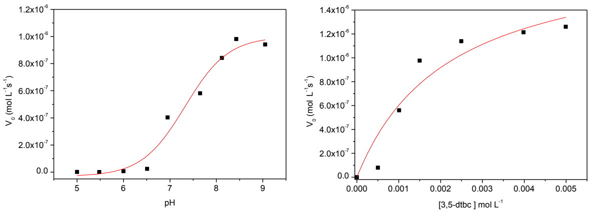


Figure 2 pH dependence (left) and [3,5-dtbc] dependence (right) on the oxidation of substrate 3,5-di-tert-butylcatechol promoted by **(1)**.

The dependence of the initial rates on the concentration of 3,5-dtbc using complex as the catalyst was investigated at 25 ºC at pH 8.5 and revealed saturation kinetics with Michaelis-Menten-like behavior (Figure 2, right). The kinetic parameters were obtained from Michaelis-Menten nonlinear treatment were: $V_{max}=1.93\times10^{-6}$ mol L^{-1} s^{-1}, $K_M=2.21\times10^{-3}$ mol L^{-1} and $k_{cat}=8.08\times10^{-2}$ s^{-1}.

Conclusions

We synthesized, characterized a manganese dinuclear complex with the ligand H_2py_3mff. This complex promotes the oxidation of 3,5-di-*tert*-catechol.

Acknowledgements

The authors thank to CNPq, CAPES, FAPESC, UFSC and Prof. Dr. Ademir Neves.

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Synthesis and characterization of biomimetic Manganese complexes with N,O ligands

Camila A. Wegermann* (PG), Sueli M. Drechsel (PQ), Fábio S. Nunes (PQ), Stela Maris M. Romanowski (PQ) and Ronny R. Ribeiro (PQ)**
***caw.weg@gmail.com; **drechsel@ufpr.br**

Departamento de Química, UFPR, Centro Politécnico, Cx.Postal 19081, 81531-990 Curitiba, PR, Brazil.

Keywords: *manganese, biomimetic complexes, bioinorganic chemistry*

Introduction

Polydentate ligands, especially those with N,O donor groups, stabilize mono and polinuclear structures with manganese in various oxidation states (Mn^{II}, Mn^{III}, Mn^{IV}, Mn^{II}_2, $Mn^{II}Mn^{III}$, Mn^{III}_2, $Mn^{III}Mn^{IV}$, Mn^{IV}_2). These complexes can act as structural and functional models for the catalytic sites of numerous metaloproteins[1]. The coordination groups present in the ligand, and their basicity, determinate the number of metal centers and the oxidation states of the manganese atoms[2], their electrochemical potentials e consequently, their redox reactivity[3]. In this work we are presenting three manganese compounds with N,O donating ligands:
Htpeten [N,N,N' – tris(2-methypyridyl) - N' – hydroxyethyl-ethylenediamine] (**MnL1**), H_2bbpeten [N-(2-hydroxybenzyl) - N,N' - bis(2-methylpyridyl) - N' -hydroxyethyl -ethylenediamine] (**MnL2**) e H_3bpeten [N,N' - (2-hydroxybenzyl) – N - (2-methylilpyridyl) - N' - hydroxyethyl-ethylenediamine] (**MnL3**). The ligands have growing numbers of phenol groups in order to observe their influence in the nuclearity of the formed structures and the oxidation states of the manganese atoms.

Results and Discussion

The compounds were synthesized by the mixture of $Mn(OAc)_2.4H_2O$ and the ligands (**L1, L2** and **L3**) in methanol. The solution was kept under reflux with magnetic stirring for 30 minutes followed by the addition of NH_4PF_6. All the systems produced brown solids which were isolated and characterized. In the FTIR spectra of the compounds the characteristics bands of the ligands were observed: 756 cm^{-1} $\delta_{C\text{-}H}$, 840 cm^{-1} $\nu_{P\text{-}F}$, 1240 cm^{-1} $\nu_{C\text{-}O}$ e 1400 e 1600 cm^{-1} $\nu_{C=C}$ e $\nu_{C=N}$. The EPR spectra for all the compounds (acetonitrile solution at 77K) have shown large signals around g = 2 normally observed for Mn^{II} or Mn^{IV} centers, with small signals between g = 3-5 typical of zero field splitting. The appearance of signal discard the formation of Mn^{III} mononuclear or $Mn^{III}Mn^{III}$ binuclear compounds, which are EPR silent. Similar spectra have been also observed for mononuclear Mn^{II} and $Mn^{II}Mn^{III}$ compounds. In cyclic voltammetry experiments for **MnL1** and **MnL3** three processes were observed: **MnL1** (E_1 = 1,4V; E_2 = 1,7V e E_3 = -1,1V vs Ag/AgCl) and **MnL3** (E_1 = 1,0V; E_2 = 1,4V e E_3 = -0,93V vs Ag/AgCl). We tentatively attribute the observed waves in positive potentials to $Mn^{II} \leftrightarrow Mn^{III} \leftrightarrow Mn^{IV}$ redox processes. The waves observed around -1 V were attributed to ligand reduction processes and have also been observed for other ligands with phenol groups. Conductivity analysis in MeCN solutions indicated the presence of 2:1 electrolytes for **MnL1** and **MnL3** (274 and 285 $S.cm^{-2}.mol^{-1}$) and 3:1 electrolyte for **MnL2** (386 $S.cm^{-2}.mol^{-1}$)[4]. This observation is consistent with the CHN analysis confirming the formation of mononuclear structures for **MnL1**, $[Mn(Htpeten)\ MeOH](PF_6)_2.4H_2O$ (Calc. C-33.43 H-4.76 N-8.47; Exp. C-33.3 H-3.23 N-8.59); and **MnL3**, $[Mn(H_3bpeten)\ MeOH](PF_6)_2.2H_2O$ (Calc. C-36.60 H-4.55 N-5.12 Exp. C-36.62 H-4.51 N-5.03), and a binuclear complex for **MnL2**, $[Mn_2(Hbbpeten)_2\ MeOH](PF_6)_3.2H_2O$ (Calc. C-40.51 H-4.29 N-8.22; Exp. C-40.57 H-4.66 N-8.80). The complexes were also characterized by electronic spectroscopy and showed intense absorptions in the range of 300-400 nm characteristic of charge transfer transitions.

Conclusions

Three new complexes of manganese with N,O ligands were synthesized. Based on the characterization results we are proposing the formation of mononuclear complexes for **MnL1** and **MnL3** $[M(L)S]^{n+}$ (S = solvent), and a binuclear valence mixed structure for **MnL2**, $Mn^{II}Mn^{III}$, $[Mn_2(Hbbpeten)_2](PF_6)_3.3H_2O$.

Acknowledgements

CNPq, Capes, Fundação Araucária, DQUI, UFPR.

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Platinum complexes with dithiocarbazate derivatives of *β*-diketones aiming new trypanocidal agents

Zumira A. Carneiro (PG), Pedro Ivo da S. Maia (PG) and Victor M. Deflon (PQ)[*]

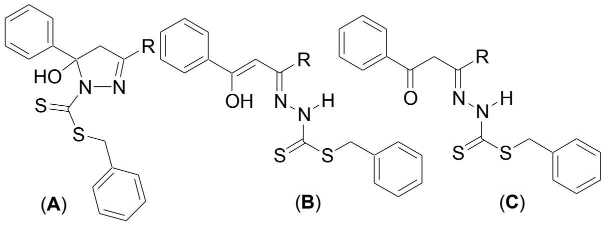
*** deflon@iqsc.usp.br**

University of São Paulo, Institute of Chemistry of São Carlos, São Carlos, Brazil

Keywords: *Platinum, Dithiocarbazate Complexes and Trypanossoma cruzi.*

Introduction

Very recently, a new type of dithiocarbazates derived from β-diketones as well as their Pt(II) and Pd(II) complexes with high trypanocidal activity (H_2L) were reported.[1] As mentioned, these dithiocarbazates derivatives may undergo cycle-chain equilibrium and can exist in several distinct isomeric forms (see **Scheme 1**).



Scheme 1. Some isomeric forms of H_2L.

In order to get further insight into the trypanocidal activity of these kind of compounds, herein we describe the synthesis and characterization of a series of new Pt(II) complexes containing H_2L (R = Me and Ph) and imidazole.

Results and Discussion

Reactions of benzydithiocarbazate and symmetric *β*-diketones lead to the formation of different isomers due to the presence of a chiral center (C19 and C29) as shown for the adduct presented in **Fig. 1**.

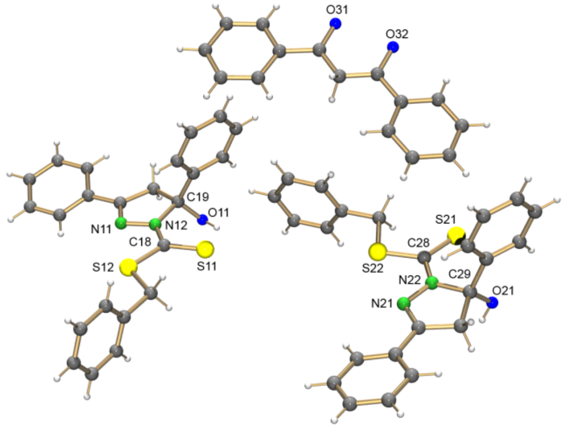
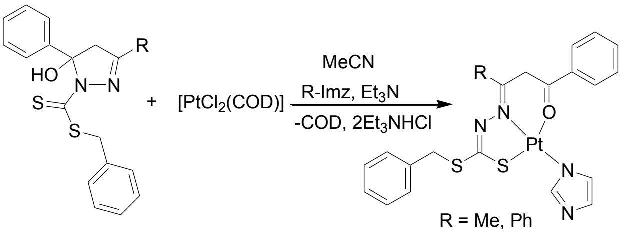


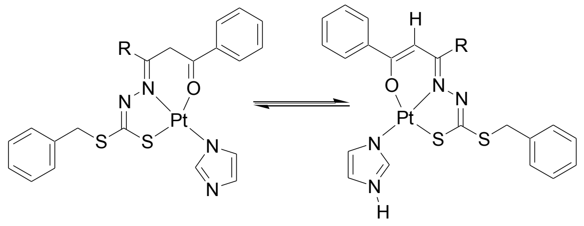
Figure 1. Dithiocarbazate isomers derived from dibenzoylmethane.

$[PtCl_2(COD)]$ readily reacts with H_2L in MeCN solutions and imidazole derivatives (R-Imz) in the presence of a supporting base (Et_3N) (**Scheme 2**). The yellow precipitates formed have been characterized by spectroscopic methods like IR, UV-Vis, elemental analyses and ^{1}H-NMR.



Scheme 2. Synthesis of [Pt(L)(RIMZ)].

No IR bands related to ν(O–H) or ν(N–H) are observed upon complex formation, which is in agreement with the coordination of the oxygen atom to the Pt(II) center, with double deprotonation of H_2L, and of the imidazolate ligand. However, a new band appearing around 1680 cm^{-1}, assignable as ν(C=O), suggests the coordination assuming the isomeric form C (see **Scheme 1**). On the other hand, ^{1}H-NMR results indicate the presence of isomers, showing duplicated peaks, which is proposed to be due to the equilibrium shown in **Scheme 3**.



Scheme 3. Tautomeric equilibrium of the [Pt(HL)(Imz)] complexes in $CDCl_3$ solution.

Conclusions

The several numbers of isomeric forms of H_2L as well as their ability to form chelates with many metal complexes may be related to their remarkable trypanocidal activity. Presently, studies with further systematic variations of H_2L and the influence of the second ligand (imidazole) are underway in our laboratories intending to improve the understanding of the biological activity of this kind of compounds.

Acknowledgements

Fapesp, Capes and CNPq

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Diruthenium(II,III) complex of γ-linolenic acid: synthesis, characterization and inhibition of C6 rat glioma cell proliferation.

Geise Ribeiro (PQ)[1,2*], Marcel Benadiba (PQ)[3], Alison Colquhoun (PQ)[3] and Denise de O. Silva (PQ)[1].

***geise@unifei.edu.br**

[1] *Department of Fundamental Chemistry, University of São Paulo, São Paulo, SP, Brazil.*
[2] *Present address: Department of Physics and Chemistry, Federal University of Itajubá, Minas Gerais, MG, Brazil.*
[3] *Department of Cell and Developmental Biology, University of São Paulo, São Paulo, SP, Brazil.*

Keywords: *γ-linolenic acid , ruthenium, carboxylate*

Introduction

Ruthenium compounds exhibit anti-tumour activity with lower cytotoxicity compared to cisplatin and its analogs. In particular, we are interested in the study of ruthenium - ruthenium bonded complexes with paddle-wheel type structure and general formula $[Ru_2Cl(RCOO)_4]$. Polyunsaturated fatty acids, including γ-linolenic acid (GLA), have been reported to exert anti-tumour effects in several tumour types. GLA is an inhibitor of glioma cell proliferation and its effects have been observed both *in vitro* and *in vivo* animal studies and in human clinical studies. The present study reports the synthesis, the characterization and the anti-proliferative action in the C6 rat glioma model of the novel diruthenium(II,III) - GLA complex, $[Ru_2Cl(GLA)_4]$.

Results and Discussion

The starting complex, $[Ru_2Cl(CH_3COO)_4]$, reacted with γ-linolenic acid (GLA) giving a novel compound of formula $[Ru_2Cl(GLA)_4]$ (Ru_2GLA) according to elemental analysis data. The electronic spectrum of this compound is typical of a mixed valent diruthenium(II,III) carboxylato. Two absorption bands involving the dimetal core were found in ethanol solution: one band at 429 nm assigned to a π (Ru-O, Ru_2) $\rightarrow \pi$ (Ru_2) electronic transition and one near-IR band at about 950 nm that can be ascribed to a δ (Ru_2) $\rightarrow \delta$ (Ru_2) electronic transition. The vibrational FTIR spectrum of Ru_2GLA shows the main bands of the GLA: ν (CH): 3008, 2956, 2917 and 2853 cm^{-1}; ν (C=C): ~1656 cm^{-1} and $\rho(CH_2)$: 724 cm^{-1}. The absence of the ν (C=O) carbonyl stretching (1740 cm^{-1}, for GLA) indicates that there is no free acid present in the Ru_2GLA product. The novel complex, instead, exhibits new bands related to deprotonated –COO groups. Two strong bands: $\nu_{as}(COO)$ at 1530 cm^{-1}, with shoulder at 1556 cm^{-1}, and $\nu_s(COO)$ at 1424 cm^{-1}, with shoulder at 1463 cm^{-1}, can be assigned to the four bridging carboxylates coordinated to the dimetal unit. These results indicate that the complex $[Ru_2Cl(GLA)_4]$ exhibits a paddle-wheel type structure where a mixed valent Ru_2(II,III) is stabilized by four equatorial carboxylato bridging ligands derivated from the γ-linolenic acid. The axial positions are occupied by chlorido ligands that bridge two $[Ru_2(GLA)_4]^+$ dimetal unities and neutralize their positive charges. Biologic assays *in vitro* show that anti-proliferative action in C6 rat cells depends on the time of exposing the cell culture to the complex. While GLA caused inhibition of cell proliferation at 48 h this effect was greatly reduced after 72 h as the surviving cells adapted to the presence of the fatty acid. Opposing effects were seen in the presence of GLA after 24 h where low concentrations (25–50 mM) were stimulatory while higher concentrations (200 mM) were inhibitory to cell proliferation. The precursor complex showed inhibitory effects after 72 h showing a cumulative effect of ruthenium upon C6 cells. Ru_2GLA caused increasing effects on tumour cell number over time becoming gradually more inhibitory to the increasing in cell number at 24, 48 and 72 h seen for control cells. The EC_{50} for the precursor and Ru_2GLA decreased with increasing time of exposure while that of GLA decreased at 48 h and increased again at 72 h as the cells adapted to the presence of the polyunsaturated fatty acids. The 72 h EC_{50} values for Ru_2GLA, precursor complex and GLA were 81.4 mM, 206 mM and 1152 mM, respectively. Thus after 72 h drug exposure the effects of Ru_2GLA were more inhibitory than GLA when a comparison was made between 50 mM Ru_2GLA and 200 mM GLA which takes into account the difference in mol numbers of the two treatments.

Conclusions

The present study reported the synthesis and characterization of the $[Ru_2Cl(GLA)_4]$ complex. The coordination of four carboxylato bridging ligands derivated from the γ-linolenic acid in Ru_2 (II,III) core led to synergistic effects that increased significantly the inhibition of C6 rat glioma proliferation in relation to the organic acid.

Acknowledgements

FAPESP and CNPq.

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On the ability of the *cis*-[RuCl$_2$(dppb)(bipy)] complex to coordinate with nucleobases: synthesis and structural aspects

Rodrigo S. Corrêa (PG)[1,*], João Paulo Barolli (PG)[1], Javier Ellena (PQ)[2], Alzir A. Batista (PQ)[1]. *e-mail: rodrigocorrea@ufscar.br

[1] Departamento de Química, Universidade Federal de São Carlos, UFSCar, Rodovia Washington Luiz, KM 235 CP 676, CEP 13561-901, São Carlos-SP, [2]Instituto de Física de São Carlos - USP, Cx. P. 369, 13560-970, São Carlos-SP.

Keywords: *Ruthenium complex, nucleobases, ^{31}P{^{1}H} NMR, X-ray analysis.*

Introduction

In the last two decades we have investigated the synthesis and characterization of ruthenium with dipyridyl and bisphosphines ligands.[1-2] An interesting precursor commonly used by our research group is the *cis*-[RuCl$_2$(dppb)(bipy)] complex,[3] [dppb = 1,4-bis(diphenilphosphine)butane and bipy = 2,2'-bipyridine]. As part of our ongoing study on reactivity of *cis*-[RuCl$_2$(dppb)(bipy)] with ligands presenting biological interest, we have explored the ability of this precursor to coordinate with nucleobases. Here, cytosine (cyt) has been used as a bioligand. This molecule presents chemical versatility that can be evidenced by possibility of exiting in tautomeric equilibrium and also be deprotonated [4] deserving special attention in the coordination chemistry field. Therefore, in this report is presented the reactivity and structures for cyt coordinated with *cis*-[RuCl$_2$(dppb)(bipy)].

Results and Discussion

The synthesis procedures of *cis*-[RuCl$_2$(dppb)(bipy)] with cyt are described in the scheme 1.

Scheme 1. Reaction of *cis*-[RuCl$_2$(dppb)(bipy)] with cytosine in different conditions.

Synthesis

$$cis\text{-}[RuCl_2(dppb)(bipy)] + cyt \xrightarrow[\text{MeOH/NH}_4\text{PF}_6 \; 25^{\circ}\text{C}]{\text{1) With Et}_3\text{N} \;\; \text{2) Without Et}_3\text{N} \;\; \text{3) pH 4-5}} [Ru(cyt)(dppb)(bipy)]PF_6$$

These three reactions were followed through ^{31}P{^{1}H} NMR, in methanol. In the synthesis 1 and 2, the ^{31}P{^{1}H} NMR spectrum indicated the presence of four doublets, suggesting the existence of a mixture containing two products. In 1 (with Et$_3$N) there is a pair of doublets at 43.47 and 46.23 ppm (^{2}J = 33.21 Hz) [hereafter called Isomer 1] and another one in the region of 41.16 and 42.93 ppm (^{2}J= 36.45 Hz) [hereafter called isomer 2]. The crystallographic analysis of this mixture presented two complexes in a same crystal (co-crystal) (Fig. 1).

As depicted in Figure 1, the nucleobase is coordinated to the metal as bidented (O, N) ligand. In both isomers the oxygen is coordinated *trans* to the nitrogen of bipy and the endocyclic nitrogen of cytosine is *trans* to a phosphorus of the dppb ligand. The main difference in the structures is that the isomer 1 presents the N1 linked at the metal center, whereas the isomer 2 shows the coordination involving N2 of the cyt.

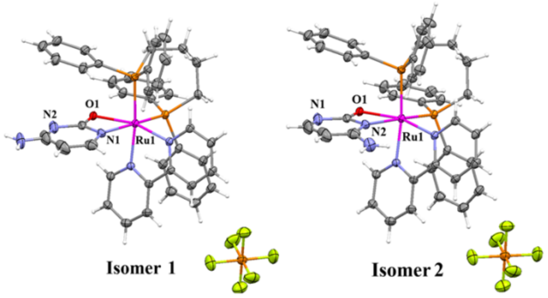

Figure 1. Crystal structure of the co-crystal showing the two isomers of [Ru(cyt)(dppb)(bipy)]PF$_6$.

In the synthesis 2 (without Et$_3$N), a significant displacement of the chemical shift of one pair of doublet in the ^{31}P{^{1}H} NMR [41.10 and 45.25 ppm (^{2}J = 33.30 Hz)]. On the other hand, the other pair of doublet at 43.48 e 47.22 ppm (^{2}*J*= 32.43 Hz) is kept almost unchanged (isomer 2). Also, the X-ray diffraction of this sample confirmed the presence of co-crystal where a protonated ligand is present (a cation with charge 2+ instead of 1+). Finally, in the reaction 3 (pH 4-5), it was possible to isolate only one product that presents two pair of doublets at 42.82 and 46.83 ppm (^{2}J = 32.49 Hz), and compared with the data of reaction 1 and 2, this complex presents chemical shift closer to that one exhibited by the isomer 2.

Conclusions

In summary, the present study contribute to better understand of the reactivity of *cis*-[RuCl$_2$(dppb)(bipy)] with the cytosine and in the exploration of further possibilities of Ru-DNA linkage in the biological environment.

Acknowledgements

FAPESP, CNPq and CAPES/PROEX. RSC acknowledges FAPESP (grant No. 2009/08131-1) for a PhD fellowship.

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Synthesis and characterization of a ruthenium complex with djenkolic acid

J. L. Dutra(IC)[1], M.I.F. Barbosa(PG)[1] and A.A. Batista(PQ)[1]

[1] *Universidade Federal de São Carlos,São Carlos, Brasil*

e-mail: jocely.dut@hotmail.com

Keywords: *djenkolic acid, ruthenium complexes*

Introduction

Amino acids occupy a special place in the coordination chemistry of transition metal ions[1-3]. This fact and the excellent results obtained by our researcher group with ruthenium complexes as potential drugs, led us to synthesize new complexes of ruthenium with amino acids. In the present work we described the syntheses and characterization of complexes with general formula "*cis*-[Ru(A-A)(P-P)(N-N)]PF_6" where A-A = djenkolic acid, Figure 1, dppb = 1,4-*bis*(diphenylphosphino)butane and bipy = 2,2-bipyridine. The obtained compounds were characterized by infrared spectroscopy, cyclic voltammetry, molar conductivity and nuclear magnetic resonance $^{31}P\{^1H\}$.

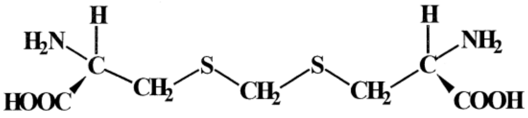

Fig. 1. Structural formula of djenkolic acid.

Results and Discussion

Synthesis: the precursor *cis*-$RuCl_2$(dppb)(bipy)] compound was dissolved in 30 mL (methanol/water (2:1)) and the amino acid was added, in a proportion of 2:1,5 (precursor / amino acid). The solution was stirred under argon for 48h and hexane was added to precipitate the resulting yellow powder, which was filtered, washed well with water and dried under vacuum. The complexes were characterized by the $^{31}P\{^1H\}$ NMR spectroscopy, showing the presence of diastereoisomers, Figure 2.

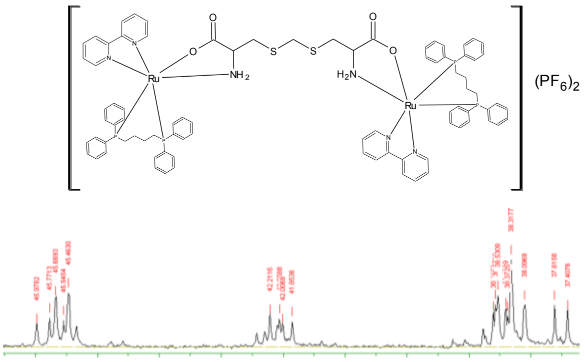

Fig. 2. Proposed structure for the ruthenium djenkolic acid complex and $^{31}P\{^1H\}$ spectrum, in $CDCl_3$.

Molar conductivity data suggest the formation of an eletrolite 1:2 in methanol. The cyclic voltammograms of the complex present a first anodic wave around 1.1 V (1) attributed to the oxidation of $Ru^{II} \rightarrow Ru^{III}$, while the second anodic wave, which appears around 1.3 V (2), is referent to the oxidation of the COO^- group of the aminoacid ligand, Figure 3.

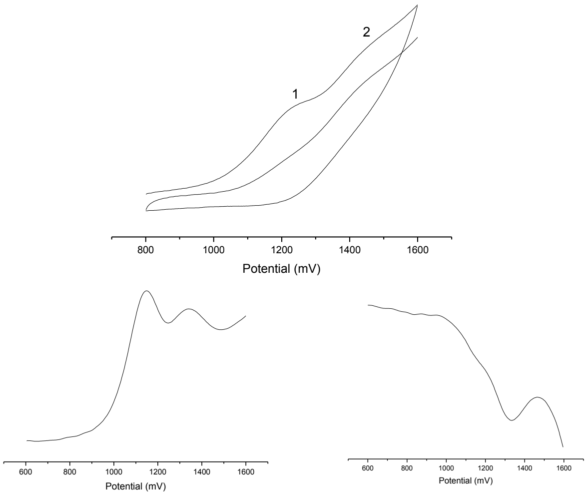

Fig. 3. cyclic voltammogram and diferential pulse, (CH_2Cl_2, 0.1 mol L^{-1} TBAP).

The IR spectrum of the complex show characteristic NH_2 and (COO^-) stretching bands, which are found to be shifted to higher frequencies when compared to the free aminoacid, as expected (1631 cm^{-1} and 3432 cm^{-1}, respectively).

Conclusion

The NMR spectra showed the presence of diastereoisomers, wich are formed due to the presence of chiral carbon of the aminoacid.

Acknowledgements

_________Capes, Cnpq and Fapesp_________

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Synthesis and characterization of Cu(II)-glutamate complex

Eduardo J. Arruda (PQ)[1*], Thiago A.D. Rodrigues (PG)[1], Gleison Casagrande (PQ)[1], Claudio T. Carvalho (PQ)[1] and Cleusa R.G. Gaban (PG)[1]**

***eduardoarruda@ufgd.edu.br; ** thiagoadrodrigues@gmail.com**

[1] *UFGD - Universidade Federal da Grande Dourados - FACET - C.P. 533, 79804-970, Dourados-MS*

Keywords: *Insert insecticides, Aedes aegypti, oxidative stress*

Introduction

Dengue, yellow fever and viral infectious diseases are transmitted by the bite of female mosquito *Aedes aegypti*. The incidence of dengue is a serious public health problem worldwide and it is estimated that up 3.5 billion people are at risk of disease. Recent study has showed the potential use of Cu(II) in the form of complex for controlling the population of *Ae. aegypti*[1].

Copper is an essential element for living organisms and has two concentration ranges of activity *in vivo*: an effect biotic and other toxic. It was published the biological activity of Schiff bases and carboxylic acid as well as their metal complexes. In addition, it has been demonstrated the biological activity of Cu(II)-glutamate[2]. These complexes were shown to be potentially toxic and have biological activity. In this context, the synthesis of coordination compound of copper, its characterization and the study of its bioactivity is extremely important for the development of pharmaceutical and insecticides uses.

Results and Discussion

The coordination compound formed by Cu(II) and L-glutamate was obtained by reacting 5.6 mmol of L-glutamic acid and 3.0 mmol Cu(II) ($Cu(NO_3)_2.3H_2O$) in water, which were heated to 50°C for 1 hour, then ethanol was added, the precipitate was washed with ethanol and left to dry. There was precipitation of a light blue solid and the reaction yield was 70.2%. The biological activity is being conducted by toxicity experiments to determine the lethal concentrations (LC) for 3rd *instar* larvae of *Ae. aegypti* and antibiograms according to WHO[3] and CLSI[4] methods.

The UV-Vis spectra of complex and $Cu(NO_3)_2.3H_2O$ was caried out in aqueous solution in a concentration 1.10^{-3} mol L^{-1}. Absorption bands were detected at 712nm and 806nm, indicating that the the d-d transitions were changed at the Cu^{2+} spectra. An electrical conductivity of the compound of 43.04 μS/c was measured in a conductivity meter model mCA 150.1 Tecnopon at a concentration of 1.10^{-3} $mol.L^{-1}$ in water solution. This value, when compared to that obtained for the aqueous solution of metal salt (206.7 μS/cm) and glutamic acid (56.24 μS/cm), shows the formation of coordination compound. The biological assays and antibiograms for the compound are underway and results will be presented later.

Table 1*. IR bands for the complex and free ligand.

Acid/Complex	$V_{as}(COO^-)$	$V_s(COO^-)$
L-Glutamic acid	1663 m, 1638 s	1436 m, 1420 s
Complex	1588 vs	1400 s, 1384 s

* Table1: comparison of the typical carboxylate stretching bands of the free amino acid and the respective Cu(II) complexes (infrared data, values cm^{-1}; vs, very strong; s, strong; m, medium.

Conclusions

The coordination compound formed by Cu(II) and L-glutamate was synthesized and its physicochemical properties determined. The initial results showed that the Cu(II)-glutamate has larvicidal activity for *Ae. aegypti* and bactericidal activity against *Gram-positive* and *Gram-negative*. The Cu(II)-glutamate at the concentrations used for controlling *Ae. aegypti* and microorganisms has no toxicity to human beings and environment.

Acknowledgements

CNPq, CAPES, FUNDECT e REDE DENGUE MS

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Synthesis of a New Mononuclear Copper(II) Complex with a N_2O-purine-containing Ligand

Tiago P. Camargo (PG) Ademir Neves (PQ)

***tiago83@ymail.com**

Laboratório de Bioinorgânica e Cristalografia, Departamento de Química, Universidade Federal de Santa Catarina – Campus Universitário Trindade, Florianópolis – SC, CEP 88040-900, Brazil.

Keywords: *Copper(II) Complex, Bioinorganic Chemistry.*

Introduction

The sequence-specific recognition of double-stranded DNA by proteins is a key step in several cellular processes and under certain conditions, pyrimidine oligonucleotides can bind to complementary purine sequences in homopurine-homopyrimidine segments of duplex DNA to form triple helical structures. Besides having biological implications *in vivo,* this property has been exploited in molecular biology applications.[1,2]

In this sense, here we report the synthesis, spectroscopic and electrochemical behavior of a new mononuclear copper(II) complex with the ligand HL^{purine} for further studies with DNA-complex interactions.

Results and Discussion

The ligand HL^{purine} was prepared by a reductive amination between the *N*'-6-Purinyl-ethylenediamine and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde as shown below and characterized by IR and NMR spectroscopies.

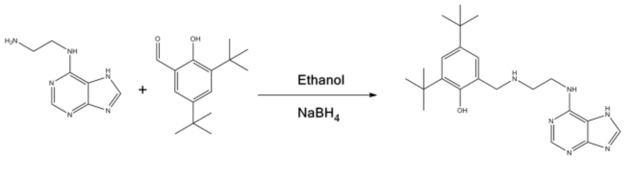

Figure 1 Synthetic path for the Ligand HL^{purine}.

The mononuclear copper(II) complex (**1**) was synthesized adding the HL^{purine} upon a copper(II) perchlorate acetonitrile solution according the figure **2**.

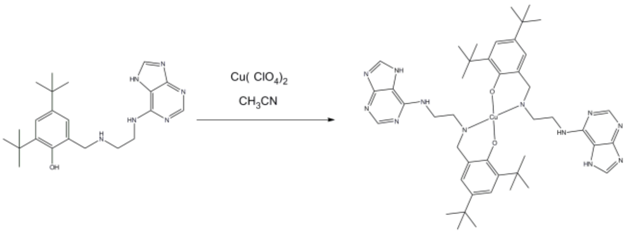

Figure 2 Synthesis of **1**.

The infrared spectra of $[Cu(L^{purine})_2]$ has shown similar absorption bands if compared with the free ligand. The absence of the perchlorate anion absorption at 1090 cm^{-1} supports a electrically neutral complex motif. The electronic spectrum has presented an intense band at 463 nm (ε = 525 $M^{-1}.cm^{-1}$), which can be attributed to the phenolate-to-copper(II) charge transfer process and another broad band in 650 nm (ε = 67 $M^{-1}.cm^{-1}$) which, most probably, arises from a copper(II) *d*-*d* transition with a d^9 electronic system. Electrochemical study (cyclic voltammetry) of **1** revealed one irreversible redox processes at -890 mV vs ? attributed to the Cu^{II} / Cu^{I} couple (Figure **3**).

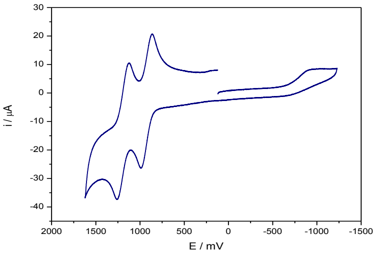

Figure 3 Cyclic voltammogram of **1** in $CHCl_3$ with 0.1 M $(n\text{-}Bu)_4NPF_6$ at 100 $mV.s^{-1}$. Ferrocene/ferrocinium redox pair was used as an internal standard.

At the positive side, two additional *quasi*-reversible processes could be observed (1208 and 943 mV) respectively, which can be ascribed probably to the successive phenoxyl radicals formation.

Conclusions

The new $[Cu(L^{purine})_2]$ was synthesized and characterized by electrochemical and specytroscopic techniques. Studies of DNA-complex interaction are being carried out and will be the subject of future publications.

Acknowledgements

To UFSC, Cnpq, CAPES, FAPESC and INCT.

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Workshop sobre Química Inorgânica Sintética – WQIS (Workshop on Synthetic Inorganic Chemistry - WSIC)

Synthesis and characterization of Cu(II)-nicotine complex

Hellenicy V. Rezende (PG)[1*], Gleison Casagrande (PQ)[1] , Eduardo J. Arruda (PQ)[1], Cleusa R.G. Gaban (PG)[2] and Lincoln C.S. De Oliveira (PQ)[2]

***hellenicy.rezende@gmail.com**

[1] *UFGD - Universidade Federal da Grande Dourados - FACET - C.P. 533, 79804-970, Dourados-MS*

[2] *UFMS - Universidade Federal do Mato Grosso do Sul - Química - C.P. 549, 79074-460, Campo Grande-MS*

Keywords: *New insecticides, Aedes aegypti, oxidative stress*

Introduction

Dengue is a viral infection transmitted by the mosquito *Aedes aegypti*. The incidence of dengue is a serious public health problem in the world. The disease control considers the population reduction of *Ae. aegypti* by use of insecticides convencionais. In this scenario, the use of Cu(II) in the form of complex has been proposed as an alternative to control the population of mosquito Ae. aegypti in th immature forms[1].

Copper is an essential element for living organisms and has a narrow range of toxicity. Nicotine is an alkaloid of plants (*Solanaceae*), constitutive approximately 0.6-3.0% of dry weight of tobacco and has chemical specify to insects[2].

The synthesis of alkaloidal insecticide and fungicide of Cu(II)-nicotine, their characterization and study of their bioactivity is important for the control of eggs and larvae of *Ae. aegypti* and consequently dengue.

Results and Discussion

The coordination compound formed by Cu(II) and nicotine was obtained by reacting 2.0 mmol of nicotine and 1.0 mmol Cu(II) ($CuCl_2.2H_2O$) in methanol, the reaction was carried out at room temperature for 15 minutes. After quantitative precipitation, the dark yellow solid was filtered, washed with methanol and dried (yield: 70%). The UV-Vis. spectra of Cu(II)-nicotine complex was performed in the concentrations (10^{-3}, 10^{-4}, 5.10^{-5}) in aqueous solution, the main bands that appears at the spectra is related with d-d transitions of the metal center. The IR spectra of the ligand and complex is summarized at the Table 1. The ν(C=N) vibration of the pyridinic ring is increased to higher frequencies indicating the complexation of the nitrogen at the metal center. The vibration of the ν(C–N)-pyrrole group does not show any significant displacement in the IR spectra due to non-involvement of this group in the coordination. The electrical conductivity of the complex was performed in a MCA model 150 conductivity, at a concentration of 10^{-3} mol.L^{-1} in water and the value was 222.3 uS/cm. This value, when compared to that obtained for the solution of metallic salt (248.00 uS/cm) and nicotine (21.37 uS/cm), indicates the formation of coordination compound. The biological activity is being conducted by means of experiments to determine the toxicity and lethal concentrations (LC) to the 3rd *instar* larvae *Ae. aegypti* and antibiograms conducted for determination of the inhibition halos according to WHO[3] and NCLSI[4] methods. The biological assays and antibiograms for the synthesized compound are underway and results will be presented later.

Table 1. Displacement of the bands in the IR spectra

Nicotine / Complex	**ν(C=C) arom. ring**	**ν(C–N) pyrrole ring.**	**ν(C=N) arom. ring**
Nicotine	1570 m	1315 f	1425 s
Complex	1600 f	1316 f	1435 s

* Table1: Comparison of C=C, C-N and C=N bonds and the nicotine ligand complex Cu. (Infrared data, the values cm^{-1}; s, strong; f, weak, m medium).

Conclusions

The complex Cu(II)-nicotine was synthesized and its physicochemical properties determined. The results showed this complex has the larvicidal activity for *Ae. aegypti* and bactericidal against *Gram-positive* and *Gram-negative*.

Acknowledgements

CNPq, PPSUS, CAPES, FUNDECT REDE DENGUE MS

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Synthesis and structural characterization of the new complex of manganese.

Cristiéli Rossini Kopp (PG)[1*], Roger Kober (IC)[1], Davi F. Back (PQ)[1] Sandra Signorella[2] (PQ), Verónica Daier[2] (PQ), Sebastián Bellú[2] (PQ), Claudia Palopoli[2] (PQ), Gabriela N. Ledesma[2] (PQ) Paula de Oña[2] (IC)

***cristielikopp@gmail.com**

[1] *Laboratório de Materiais Inorgânicos - Universidade Federal de Santa Maria – RS - Brazil*

2- Universidade Nacional de Rosario -Argentina/ IQUIR (Instituto de Química Rosario) - CONICET, Facultad de Ciencias Bioquímicas y Farmacéuticas.

Keywords: pyridoxal, manganese complex and x Ray diffraction.

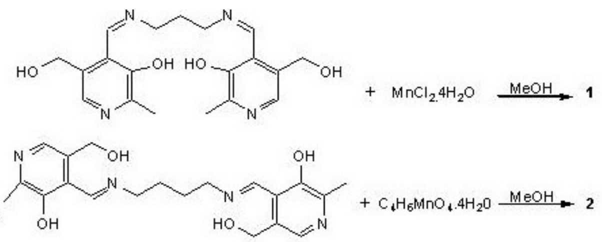
Introduction

It is know that manganese plays an essential and versatile role in the biochemistry of many microorganisms, plants and animals[1,2]. Already compounds resulting from vitamin B6 as pyridoxal, can offer a wide variety of coordination sites, with different hard and soft character, allowing a rich coordination chemistry[3,4]. Based on this we developed two new complexes of pyridoxal with manganese, characterized by x-ray diffraction in order to study the redox capacity of manganese and its application as mimetic of superoxide dismutase(SOD-Mn).

Results and Discussion

The synthesis to obtain the compounds **1** and **2** is described in the scheme below.

Scheme 1: Synthesis of complexes **1** and **2**.



Reactions of these crystals were obtained with a yield of 45% for compound **1** and 40% for compound **2**.

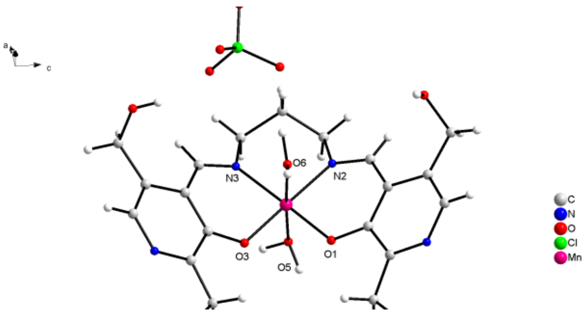


Figure 1: Structure of complex **1**.

It can be seen in Figure 1, two water molecules are directly coordinated to the metal center, which can provide rapid availability of an orbital metal center when the compound is soluble.

It is observed that in complex 2, shown in Figure 2, the manganese atom is coordinated to two molecules of ligand by two connections to the imino nitrogen, the three phenolic oxygen atoms and one nitrogen atoms from the 1.4-diaminobutane that is used as connector between the two units that make up the molecule, giving the metal center geometry of an almost perfect octahedron. With the increase of carbon chain, we obtained a dimeric structure one of the rare examples in the literature.

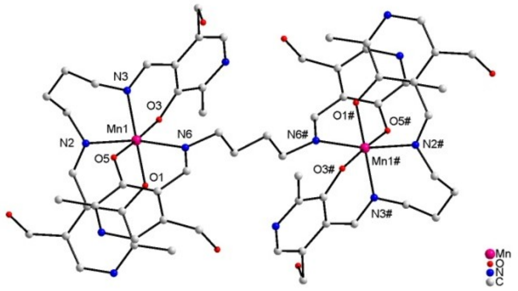


Figure 2: Structure of complex **2**.

Conclusions

The results were satisfactory regarding the synthesis and characterization of the complexes. Future studies will evaluate the antioxidant activity of these derivatives, since similar structures appear to be very promising.

Acknowledgements

CAPES, CNPq, FAPERGS and EDITAL PRPGP/UFSM 07 /2011

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Synthesis and antitubercular activity of paladium (II) complexes with dithiocarbazate Schiff bases

Lucas V. Pozzi (PG)[1]*, Angelica E. Graminha (PG)[1], Rodrigo Correa (PG)[1], Javier Ellena(PQ)[2] e Alzir A. Batista (PQ)[1] Daisy N. Sato (PQ)[3] Clarice Q. F. Leite (PQ)[3]

***pozzi.lucas@gmail.com**

[1] Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brasil,

[2] Departamento de Física, Universidade São Paulo, São Carlos, SP, Brasil

[3] Departamento de Ciências Biológicas, Faculdade de Ciências Farmacêuticas, UNESP, Araraquara, SP, Brasil,

Keywords: *Schiff base, palladuim, phosphine.*

Introduction

Metal complexes with Schiff Bases derived of S-benzyl and S-methyldithiocarbazate are been used as antimular agents, antibacterial and antifungal[1]. Palladium complexes has been shown antibacterial and antifungal activities[2]. In some cases theses complexes are active against resistant bacteria[3].In this work we prepared a serie of palladium (II) complexes containing triphenylphosphines and dithiocarbazate derived from 2-acetylpyridine.

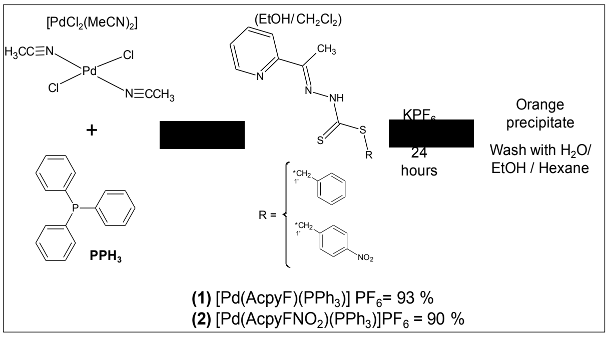

Figure 1. Representative scheme of the synthetic route of palladium complexes with dithiocarbazate.

Results and Discussion

Conductivity measurements suggest the formation of anionic complexes and microanlyses data indicate the formation of the [Pd(L)(PPh$_3$)]PF$_6$ (L = AcpyBzNO$_2$ and AcpyBz, desprotonated N(2)). NMR ^{31}P data for the complexes show a singlet at about δ28 assigned to phosphorus *trans* the nitrogen (Figure 2).

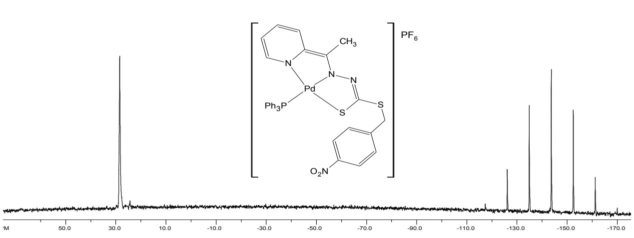

Figure 2. ^{31}P NMR spectrum of [Pd(AcpyBzNO$_2$)(PPh$_3$)]PF$_6$ in CH$_2$Cl$_2$.

The cyclic voltammogram of the complexes shows a irreversible processes assigned to the Pd^{II}/Pd^{I} reduction followed by oxidation (Table 1).

Table 1. Data of cyclic voltammetry for the palladium complexes (DMF, 0.1 mol L^{-1} PTBA).

Compound	Pd^{II}/Pd^{I} Ep$_c$ (V)	Pd^{I}/Pd^{II} Ep$_a$ (V)
(1)	-1,01	0,28
(2)	-1,02	0,35

The compounds were investigated for *in vitro* antimycobacterial activity against M. tuberculosis H37Rv strains by the REMA method. The minimum inhibitory concentrations (MICs) found for the free ligands, palladium complexes and rifampicin are shown in Table 2.

Tabela 2. MIC value of antimycobacterial of free ligands, palladium complexes and reference drug.

Compound	MIC*	MIC**
AcpyF	62.5	207.4
AcpyFNO$_2$	31.2	90.2
(1)	15.6	19.2
(2)	15.6	18.2
Rifampicin	< 0.015	0.02

* (μg mL^{-1}) / ** (μmol L^{-1})

Conclusions

Two new palladium complexes were synthesized and their characterization confirm the proposed structures. Their biological assays indicated a significant antituberculosis activity.

Acknowledgements

FAPESP, CNPq and Capes

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Synthesis and characterization of dipyridophenazine ruthenium(II) complexes: promising metallodrugs against cancer.

Barolli, J.P. (PG)[1*], Miranda, F.S. (PQ)[2]; Correa, R.S. (PG)[1] and Batista, A.A. (PQ)[1]*.

***jpbarolli@yahoo.com.br**

[1]*Laboratório de Estrutura e Reatividade de Compostos Inorgânicos, Departamento de Química, Universidade Federal de São Carlos, CP 676, São Carlos, SP, Brasil.*

[2]*Laboratório de Fotoquímica Molecular, Instituto de Química, Universidade Federal Fluminense, Niterói, RJ, Brasil.*

Keywords: *ruthenium, phosphines, dipyridoquinoxalinoquinoxaline.*

Introduction

Ruthenium complexes with phenanthroline derivatives exhibit relevant photochemical properties[1]. This class of ligands act as bidentate, presenting a rigid and planar structure highly conjugated. Many ruthenium(II) complexes with phenazine derivatives show to be a promising DNA-linkers, which can interact with nucleobase pairs[2].

Thus, aiming to obtain compounds with potential biological activity, the purpose of this study is the syntheses and characterization of ruthenium complexes containing phosphine and dipyridoquinoxalinoquinoxaline [3] (dpqQX) ligand and evaluate their cytotoxicities in several tumor cells line.

Results and Discussion

The complexes, *trans*-[$RuCl_2(PPh_3)_2$(dpqQX)] **(1)**, *trans*-[$RuCl_2$(dppb)(dpqQX)] **(2)** and *cis*-[$RuCl_2$(dppb)(dpqQX)] **(3)** were obtained from the precursors [$RuCl_2(PPh_3)_3$] and [$RuCl_2$(dppb)(PPh_3)].

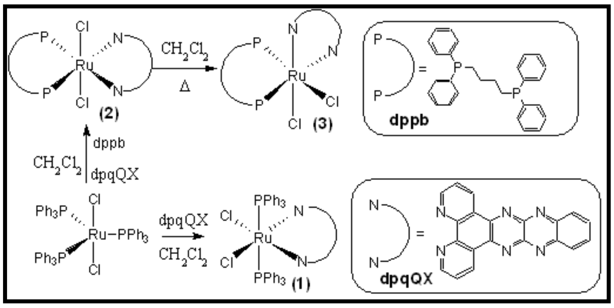

Figure 1. General procedure of the syntheses of the complexes.

To a 1:1 mixture of CH_2Cl_2 were added dpqQX and $RuCl_2(PPh_3)_3$ (**complex 1**) or $RuCl_2$(dppb)(PPh_3) (**complex 2**) and the solutions were stirred for 1 h under argon. The resulting brown solutions were concentrated to 1 ml and hexane (10 ml) added. The brown precipitates were collected, washed with hexane, and dried under vacuum. The *cis* complex (**complex 3**) was isolated by refluxing the mixture in CH_2Cl_2, (40 ml) for 60 h under Ar. The solution was cooled and 20 mL of hexane was added. Elementary analyses and yield for all complexes were satisfactory. The conductivity in dichloromethane suggests that the complexes are neutral species. The structure of the **1** was confirmed by single-crystal X-ray diffraction. The main data of this study are summarized in table 1.

Table 1. Data for the complexes.

	$E_{1/2}$ (V) (Ru^{III}/Ru^{II})	**$^{31}P\{^1H\}$ δ (ppm)**	**$^2J_{p-p}$ (Hz)**	**IC_{50} MDA-MB-231 (μmol.L^{-1})**
1	0.55	22.6	-	3.09 ± 0.64
2	0.64	32.6	-	28.72 ± 0.34
3	0.76	30.8 and 43.5	33.8	6.04 ± 0.27

The presence of *cis/trans* geometries were confirmed by the techniques $^{31}P\{^1H\}$ NMR, cyclic voltammetry and differential pulse. The cyclic voltammograms of complexes **1-3** show one-electron, chemically reversible wave corresponding to the $Ru^{III/II}$ redox couple. The isomers, *trans* **(2)** *and cis* **(3)** presented reduction potential at 0.64 V and 0.76 V, respectively. The $^{31}P\{^1H\}$ NMR spectrum of the *cis* complex, in CH_2Cl_2, present a well-defined AX system with chemical shifts at 30.8 ppm (d) and at 43.5 ppm (d), while for the isomer *trans* only a siglet in 32.6 ppm, was observed. The cytotoxicity assays in tumor mammalian cells (MDA-MB-231) were performed with the compounds **1-3 (Table 1)**. Low values of IC_{50} were found compared with the metallodrug reference, cisplatin (88 *μ*M).

Conclusions

New ruthenium(II) complexes containing the dpqQX as ligand in cis/trans isomers were obtained. The preliminary results obtained for these complexes point out potentials metallodrugs for studies *in vitro* and *in vivo* against human tumor cells.

Acknowledgements

PPGQ-UFSCar, CAPES-PROEX, CNPQ, FAPESP.

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Synthesis, characterization and cytotoxic activities of ruthenium(II) complexes containing folic acid as ligand

Barolli, J.P. (PG)[1*], Ribeiro, J.U. (PQ)[1]; and Batista, A.A. (PQ)[1].

***jpbarolli@yahoo.com.br**

[1]*Laboratório de Estrutura e Reatividade de Compostos Inorgânicos, Departamento de Química, Universidade Federal de São Carlos, CP 676, São Carlos, SP, Brasil.*

Keywords: *ruthenium, phosphines, folic acid.*

Introduction

The study of the transition metals chemistry has attracted interests of researchers, also due to their importance as antitumor and antimicrobial agents. Platinum drugs have been strongly studied in recent decades. However, drug resistance and accumulation effects of drugs have restricted their clinical uses[1]**.** Thereby, ruthenium is one of the most studied metals aiming the preparation of the potentials metallodrugs with higher selectivity and less toxicity. It is emphasized by many derivatives exhibiting cytotoxic activity, in which ruthenium complexes containing phosphines and other ligands have shown promising results *in vitro* when tested in tumor mammalian cells[2].

On the other hand, antagonists of the folic acid are used on some cancer treatments. Small structural and conformation changes in this folic acid leads to the impediment of its main biological functions as hindrance cells multiplication. The folic acid, deserve major attention in medicinal chemistry because it has a crucial role in the formation of structural proteins, hemoglobin and synthesis of DNA and RNA. Thus, aiming to obtain new complexes, the purpose of this study is the syntheses and characterization of ruthenium complexes containing folic acid, and evaluate their cytotoxicities in tumor cells line MDA-MB-231.

Results and Discussion

The compounds $[Ru(FO)(dppb)(bipy)]PF_6$ (**1**), $[RuCl_2(FO)(dppb)]$ (**2**) and $[RuClCO(FO)(dppb)]PF_6$ (**3**) were obtained from the ruthenium precursors *cis*-$[RuCl_2(dppb)(bipy)]$ and $[RuCl_2(dppb)(PPh_3)]$. The structures of these complexes were proposed based mainly usual spectroscopic techniques: Multinuclear (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$) NMR, ESI-Q-TOF/MS, voltammetric techniques and microanalysis. The cytotoxicity tests in tumor cells (MDA-MB-231) were performed with the complexes, with the aim to study the influence of the bioligand on the cell viability of the complexes.

The reactivity of the folic acid with ruthenium precursors were similar. For example, in the compound **1** the $^{31}P\{^1H\}$ NMR spectrum showed two dublets: 38.3 ppm and 34.8 ppm (^2J = 34 Hz), pointing out the non-equivalence of phosphorus atoms, in which one atom, probably, is *trans* to N-pyridine and the other one is *trans* to N-pterinic. Also, in the $^{13}C\{^1H\}$ NMR experiment it was observed a shift of the pterinic carbonyl to low field, comparing to the free and coordinated ligand[4]. The cyclic voltammetry of the complex showed an irreversible process (Ru^{II}/Ru^{III}), at 1.1 V. In all cases the results elemental analysis are satisfactory.

Table 1. Analysis data and IC_{50} ($\mu mol.L^{-1}$) for the complexes in study.

	ESI-Q-TOF/MS*	E_{pa} Ru^{II}/Ru^{III}	IC_{50} $\mu mol.L^{-1}$
(1)	1124.277 (1124.272)	1.1 V	43,89 ± 0,77
(2)	1004.174 (1004.179)	0.83 V	81,6 ± 0,39
(3)	1004.174 (1004.179)	1.2 V	13,96 ± 0,81

*Theoretical values in parenthesis.

From the $^{31}P\{^1H\}$ NMR and ESI-Q-TOF/MS data for the compounds **2** and **3**, were observed the formation of dimmers units, which may be explain by possible peptide bonds between units of folic acid π-π,affecting slightly the change in the Tolman angle of diphosphine[4]. The cytotoxicity assays in tumor mammalian cells (MDA-MB-231) were performed with the ruthenium complexes. Low value of IC_{50} was found compared with the metallodrug reference, cisplatin (88 μM).

Conclusions

Three new folic acid complexes were prepared and characterized by several techniques. The preliminary biological results obtained for folic acid ruthenium complexes were satisfactory.

Acknowledgements

PPGQ-UFSCar, CAPES-PROEX, CNPQ, FAPESP.

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A new manganese complex of a pyridoxal derivative. Synthesis and structural analysis.

Roger Kober (IC)[1*], Cristiéli Rossini Kopp (PG)[1], Davi F. Back (PQ)[1] Sandra Signorella[2] (PQ), Verónica Daier[2] (PQ), Sebastián Bellú[2] (PQ), Claudia Palopoli[2] (PQ), Gabriela N. Ledesma[2] (PQ) Paula de Oña[2] (IC)

***roger_kober@hotmail.com**

[1] Laboratório de Materiais Inorgânicos (LMI) - Universidade Federal de Santa Maria – RS - Brasil

[2] Universidade Nacional de Rosario -Argentina/ IQUIR (Instituto de Química Rosario) - CONICET, Facultad de Ciencias Bioquímicas y Farmacéuticas.

Keywords: *Manganese complex, bioinorganic chemistry, X-ray diffraction.*

Introduction

Manganese complexes have a high interesting in the bioinorganic fields[1,2], because the transition metal is present in catalase (two manganese ions at its active site) while manganese superoxide dismutase, MnSOD [3], is a mononuclear enzyme. Both of these enzymes play a role in protecting an organism from the potential deleterious effects of the reduced forms of dioxygen, hydrogen peroxide and superoxide, respectively. On the other hand, it is known that the compounds deriving from pyridoxal can provide a great variety of coordination sites with different charges and hard/soft character[4], allowing the assumption of a rich coordination chemistry.
Based in this information, we report now the synthesis and the structural characterization of (ligand (L1), together with the synthesis and the structural features of its chelate complexes of manganese, (Complex(1)).

Results and Discussion

First, we promote the condensation of benzohydrazide and the pyridoxal, thus obtaining a ligand L1. This ligand is shown in the figure 1.

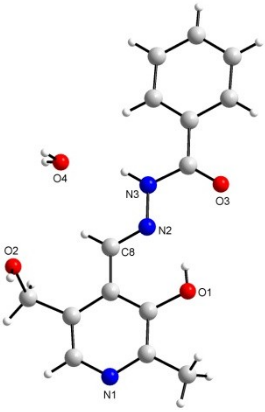

Figure 1. Structure of the ligand 3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methyl) benzohydrazide and a water solvate.

Giving sequence to our experiments about the metallation of biologic ligands and to those involving the synthesis and the structural characterization of complex (chelate) salts of manganese with compounds derived from the vitamin B6. The manganese centers in complex 1 adopt a six-coordinate configuration, already observed in literature examples. This leads to more or less distorted octahedral structure, completed, by one perchlorate molecule, and two molecules of DMSO (one of these DMSO molecules shows a disorder between the sulfur atoms). Figure 2 shows the structure of this complex.

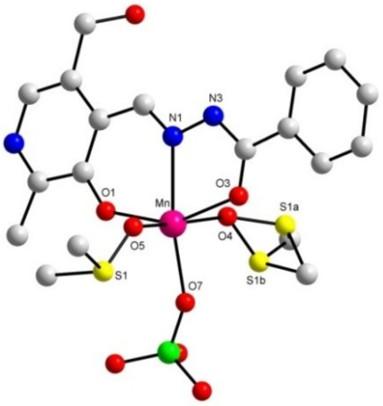

Figure 2. Representation of the molecular structure for the complex 1. The hydrogen atoms were omitted for clarity.

Conclusions

The reactions reported in this work make evident that pyridoxal derivatives present a remarkable chemical ability to react with $[Mn]^{2+}$, should also represent a qualitative contribution to the research potential of the vitamin B6 family with its chemical ability to form stable chelate complexes.

Acknowledgements

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Chelate complexes of vanadium (+IV) and (+V) and rhenium (+V) with a pyridinone ligand derivated from maltol and isoniazid

Murilo C. Carroccia (PG)[a]*, André G. A. Fernandes (PG)[a], Pedro I. da S. Maia (PG)[a], Ulrich Abram (PQ)[b] and Victor M. Deflon (PQ)[a] *muriloccar@iqsc.usp.br

[a] Institute of Chemistry of São Carlos, University of São Paulo - Brazil;
[b] Institute of Chemistry and Biochemistry, Freie Universität Berlin – Germany.

Keywords: *vanadium(+IV) and (+V), rhenium (+V), pyridinones, biologic potential*

Introduction

The coordination chemistry of vanadium and rhenium has been receiving increased attention in the last years since the discovery of the vanadium presence in enzymes of some organisms and due to its complexes' insulin enhancing properties[1], as well as the potential application of rhenium complexes in nuclear medicine[2].

Maltol, a pyrone type ligand, forms a complex with vanadium, bis-maltolate-oxovanadium(IV) (BMOV), that shows high activity in the insulin mimesis[1]. In the other hand, isoniazid, a hydrazone type ligand, is the most important first line medicine used in the treatment of tuberculosis. On the other hand, isoniazid can present severe side effects and develops relatively often and quickly resistance, being necessary the development of new drugs for tuberculosis treatment.

Pyridinones represent a class of organic compounds derivate from pyrones that have been used as ligands with some metals, generating stable complexes[3].

Results and Discussion

A new pyridinone ligand, H_2maiso, was prepared and characterized. Complexation reactions were carried out to obtain new complexes of vanadium, [V(IV)O(Hmaiso)$_2$] (**1**) and [V(V)O(Hmaiso)$_2$(OMe)] (**2**), and rhenium, ([ReO(Cl)(Hmaiso)] (**3**).

The complexes' characterization performed (Tables 1-4) indicate that in all products, the new H_2maiso ligand coordinates as expected for a maltolate-like ligand, *O,O*-bidentate and monoanionically.

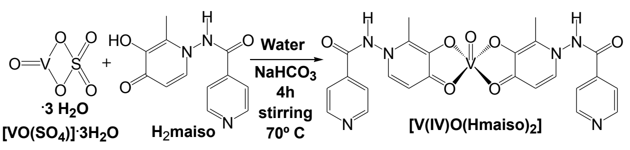

Figure 1. Synthesis of [V(IV)O(Hmaiso)$_2$] (**1**).

Table 1. CHN for H_2maiso((Found), Calculated):

C (%)	H (%)	N (%)
58,26 (58,77)	4,43 (4,52)	15,05 (17,13)

Table 2. IR data from KBr pellets (cm^{-1}):

	ν(O-H)	ν(C=O)	ν(V=O)	ν(Re=O)
H_2maiso	3098	1692 / 1626	--------	--------
1	--------	1670	980	--------
2	--------	1690	953	--------
3	--------	1703	--------	974

Table 3. ^{1}H-NMR data for H_2maiso, 400 MHz, ppm):

CH_{iso}	CH_{iso}	CH_{ma}	CH_{ma}	OH	CH_3
8,84(dd)	7,85(dd)	7,73(d)	6,21(d)	5,75(s)	2,14(s)

*(s): simplet, (d): duplet and (dd): double duplet

Table 4. MS-ESI data, (m/z):

	[M]$^+$	[M+H]$^+$	[M+Na]$^+$
H_2maiso	--------	246,09	268,07
1	--------	--------	578,08
2	555,08	--------	--------
3	691,10	--------	--------

*M = Molecular mass of the compound.

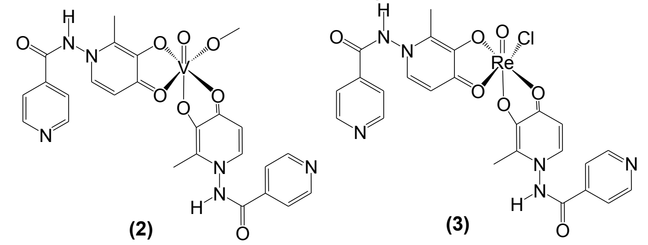

Figure 2. Structures proposals for (**2**) and (**3**).

Conclusions

A new pyridinone ligand of biological interest (H_2maiso) was synthesized and used for preparing two new oxovanadium complexes and one oxorhenium complex. The ligand coordinates *O,O*-bidentate, monoanionically, as a maltolate type ligand.

Acknowledgements

CNPq, FAPESP, IQSC-USP and FU Berlin.

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Synthesis and characterization of ruthenium (II) complexes with dithiocarbazate Schiff bases: Potential antitumoral.

Angelica E. Graminha (PG)[1]*, Rodrigo Correa (PG)[1], Javier Ellena(PQ)[2], Heloisa Selistre de Araujo[3] e Alzir A. Batista (PQ)[1]. *angelicagraminha@yahoo.com.br

[1] *Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brasil*

[2] *Departamento de Física, Universidade São Paulo, São Carlos, SP, Brasil*

[3] *Departamento de Ciências Fisiológicas, Universidade Federal de São Carlos, São Carlos, SP, Brasil*

Keywords: *Schiff base, ruthenium, phosphine.*

Introduction

The biological activity of Schiff base has been known since 1946 when its bactericidal activity was found *in vivo*[1]. Since then a wide range of biological activities of these ligands was observed[2,3]. Ruthenium compounds have attracted increasing interest over the last 20 years as potential antitumor drug. These new ruthenium-based compounds, in some cases, have shown to be less toxic and able to overcome the resistance induced by platinum drugs in cancer[4]. In this work we prepared a series of ruthenium (II) complexes containing phosphines and dithiocarbazate derived from 2-acetylpyridine (Figure 1).

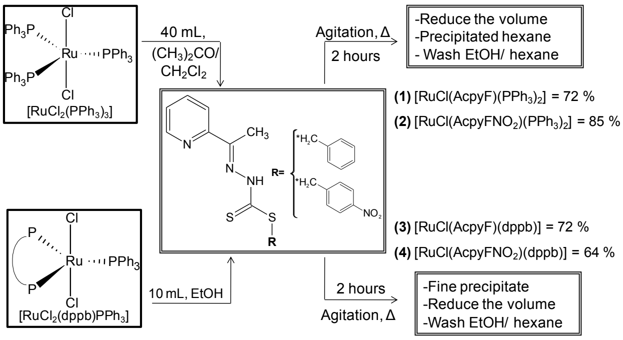

Figure 1. Representative scheme of the synthetic route of ruthenium complexes with dithiocarbazate.

Results and Discussion

Microanalyses and conductivity data suggest the formation of neutral complexes of type $[RuCl(L)(PPh_3)_2]$ (**1** and **2**) and $[RuCl(L)(dppb)]$ (**3** and **4**) (L = AcpyBz and $AcpyBzNO_2$, deprotonated N(2)). NMR ^{31}P data for the complexes **1-2** show a singlet at about δ 25 assigned to phosphorus in *trans*. The spectrum of the complexes **3-4** show two doublets at about δ 45 e 35 indicating the nonequivalence of phosphorus (Figure 2).

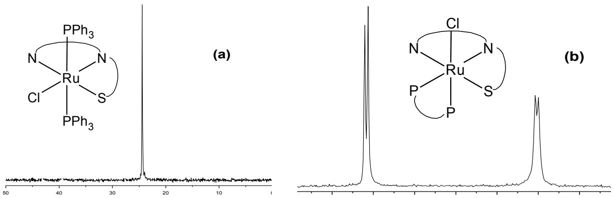

Figure 2. ^{31}P NMR spectrum of (a) **1-2** and (b) **3-4** (CH_2Cl_2).

The cyclic voltammograms of the complexes shows a quasi-reversible processes assigned to the Ru^{II}/Ru^{III} oxidation (Table 1)

Table 1. Data of cyclic voltammetry for the ruthenium complexes (CH_2Cl_2, 0.1 mol L^{-1} PTBA).

	E_{pa} (V)	E_{pc} (V)	E ½ (V)	I_{pa}/I_{pc}
(1)	0,59	0,34	0,47	1,07
(2)	0,52	0,37	0,44	1,02
(3)	0,49	0,42	0,45	1,09
(4)	0,59	0,40	0,49	1,04

Cytotoxicity assay antitumoral show that the complexes 3 and 4 exhibit activity in the three cell lines studied. The complexes 1 and 2 exhibit activity only in the cell line MDA-MB-231. In all case the complexes are more active than standard drug *cisplatin* (Table 2).

Table 2. Values of IC_{50} of the ruthenium complexes and their respective ligands.

	IC_{50} (μmol L^{-1})		
	S180	K562	MDA-MB-231
AcpyBz	0,6 ± 0,8	3,5 ± 1,3	1,8 ± 2,1
AcpyBzNO	3,4 ± 0,4	5,7 ± 0,7	1,5 ± 1,1
(1)	>200	>200	3.3 ± 3.1
(2)	>200	>200	5.5 ± 2.9
(3)	6.7 ± 3.8	2.1 ± 7.1	0.4 ± 0.8
(4)	1.6 ± 1.4	1.8 ± 3.1	0.8 ± 0.9
cisplatin	40.2±15.7	na	87.5 ± 12.6

Conclusions

The characterization of the complex indicate the acquisition of four new ruthenium complexes and the cytotoxicity assay show that the complexes 1 and 2 exhibit selectivity for line of breast cancer.

Acknowledgements

FAPESP, CNPq andCapes

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Poster Abstracts II: Catalysis

Workshop sobre Química Inorgânica Sintética – WQIS (Workshop on Synthetic Inorganic Chemistry - WSIC)

Synthesis of solids based on inorganic supports and anionic iron(III) porphyrin for oxidation heterogeneous catalysis.

Guilherme S. Machado (PG)[1,2]*, Fernando Wypych (PQ)[2] and Shirley Nakagaki (PQ)[1]*.

***guismachado@yahoo.com.br**

[1] Bioinorganic and Catalysis Laboratory, [2] Solid State Chemistry Laboratory. Federal University of Parana, Chemistry Department, CP 19081, CEP 81531-980, Curitiba, Paraná, Brazil.

Keywords: *Porphyrins, Layered Hydroxide Salts, Catalysis.*

Introduction

Porphyrins are high conjugated macrociclic compounds presents in a great diversity of proteins and live organisms[1]. The first synthesis of porphyrins in laboratory was reported by Rothemund[2], but with very low reaction yields. Lindsay and co-workers[3] published a new method to porphyrin synthesis based on the pyrrole and aldehyde condensation under mild and controlled experimental conditions, using different catalysts. The modifications resulted in reaction yields up to 50 %.The immobilization of metalloporphyrins in different inorganic matrixes has become an interesting strategy to obtain solids for catalytic heterogeneous process, in particular for oxidation reactions. We have been observed that small modifications in the experimental process to prepare these inorganic solids have been resulted in different supports for metalloporphyrins immobilization with unusual catalytic activity. This work describes the synthesis of one anionic iron(III) porphyrin and your immobilization on different layered hydroxide salts obtained by a precipitation methodology[1].

Results and Discussion

The initial step consists in the porphyrin macrociclic synthesis using an adaptation of the Lindsay's method[3], where the 2-chloro-6-fluoro-benzaldehyde was utilized, and borotrifluorodietil etherate was used as acid catalyst. A reaction yield of approximately 40-60 % was obtained. The synthetized tetrakis (2-chloro-6-fluorophenyl) porphyrin [H_2(TCFPP)] was submitted to a sulfonation process using a methodology described by Turk[4], in order to obtain the anionic tetrasodium-5,10-15,20-tetrakis (2-chloro-6-fluoro-3-sulfonato phenyl) porphyrinate [H_2(TCFSPP)]$^{4-}$, with a reaction yield of 70 %. This anionic porphyrin was submitted to a metallation process with $FeCl_2$ in dimethylformamide in a system under reflux and magnetic stirring in argon atmosphere by 10 hours, the Fe(III) coordination to porphyrin ring was accompanied by UV-Vis spectroscopy and tin layer chromatography. All obtained compounds were characterized by infrared and UV-Vis spectroscopy.

In sequence, the tetrasodium-5,10,15,20-tetrakis (2-chloro-6-fluoro-3-sulfonatophenyl) porphyrinate iron(III) [Fe(TCFSPP)Na_4]$^+$ (FeCF), was immobilized on two layered hydroxide salts, zinc hydroxide nitrate (ZHN) and zinc hydroxide chloride (ZHC), obtained by a precipitation method[1]: a knowledge mass of $Zn(NO_3)_2.6H_2O$ or $ZnCl_2$ was dissolved in water and drops of NH_4OH solution (28 %) were added to the system, generating the precipitation of ZHN and ZHC solids. The obtained solids were characterized by X ray diffraction, infrared spectroscopy and electronic paramagnetic resonance that confirmed the structural arrangement. The solids were used as catalyst in cyclohexane oxidation: 23 % of cyclohexanone were obtained for FeCF-ZHN and 22 % of cyclohexanol was obtained for FeCF-ZHC. This interesting behavior can be attributed to the immobilization form of FeCF on each synthesized support: for ZHN, the nitrate ions can be changed by the FeCF and for ZHC, although it showed a similar structure in comparison to ZHN, the chloride ion can be not changed by the complex and the immobilization occurred only in the layer's edges. These generate different oxidation mechanisms to immobilized FeCF, showing the importance of synthesized inorganic support on immobilization process[1].

Conclusions

The anionic iron(III) porphyrin [Fe(TCFSPP)] was successful synthetized following the Lindsay's methodology and the Turk's method for sulfonation. The iron(III) porphyrin was immobilized in two layered hydroxide salts, showing catalytic activity for cyclohexane oxidation with interesting results.

Acknowledgements

CNPq, CAPES, Fundação Araucária, FUNPAR and UFPR.

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Nickel(II) complexes with pyrazolyl-imidazolium ligands and their catalytic behavior in ethylene oligomerization

Ana Helena D.P.S. Ulbrich (PG)[1] and Osvaldo de L. Casagrande (PQ)[1]*

***osvaldo.casagrande@ufrgs.br**

[1] *Universidade Federal do Rio Grande do Sul, Bento Gonçalves, 9500, Porto Alegre, Brasil.*

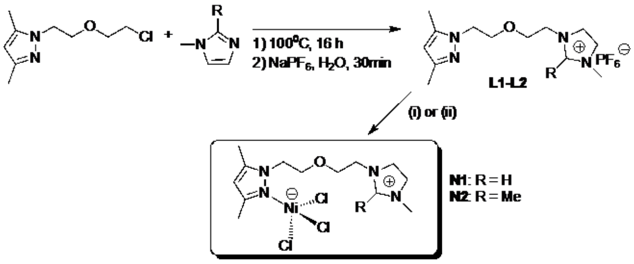
Keywords: *Nickel complexes, ethylene oligomerization, pyrazolyl-imidazolium ligands.*

Introduction

Olefin oligomerization is a major industrial process[1]. The commercial oligomerization of ethylene is predominately carried out using transition-metal catalysts that produce a broad distribution of linear α-olefins (LAOs). Many efforts are still devoted to the development of highly selective ethylene oligomerization catalysts. Herein, we report the synthesis and characterization of a new series of Ni(II) complexes bearing pyrazolyl-imidazolium ligands which in association with MAO, afford active catalysts for selective dimerization of ethylene to 1-butene.

Results and Discussion

The pyrazolyl-imidazolium ligands **L1-L2** were prepared in high yields (85-95%), and their identity were established by ^{1}H and ^{13}C{1H} NMR spectroscopy (Scheme 1). The reaction of nickel starting compound with the appropriate ligand affords the corresponding complexes $NiCl_2L$ (**Ni1-Ni2**)) (Scheme 1), which were isolated as yellow solids (yield 88-96%).



(i) $Ni(OAc)_2$, 55ºC, 20 h, DMF, LiCl; (ii) [$NiCl_2$(DME)], 25ºC, 48 h, CH_2Cl_2;

Scheme 1. Synthesis of ligands and catalysts

Single crystals of nickel complexes suitable for X-ray diffraction analysis were obtained from slow diffusion of ether into an acetonitrile or ethanol solution of **Ni1/Ni2** at 25ºC. The molecular geometry and atom-labeling scheme of **Ni1** are shown in Figure 1. The crystal structure of **Ni1** and **Ni2** confirm both the monomeric nature of the complexes and κ^1-coordination of the pyrazolyl-imidazolium ligands with the pyrazolyl units bonded to the metal centers. The nickel centers are in a distorted tetrahedral geometry, as evidenced by the N–Ni–Cl_{av} 105,9° (**Ni1**) and 107,4° (**Ni2**) and Cl–Ni–Cl_{av} bond angles 111,9° (**Ni1**) and 111,6° (**Ni2**). The Ni–Cl (Ni-Cl_{av} = 2.251 Å (**Ni1**) and 2.254 Å (**Ni2**)) bond distances are comparable to that found in related nickel compound having bifuncional imidazolium ligand, such as [$NiCl_3(PPh_2$-Imi)] (Ni–Cl_{av} = 2.260 Å).[2]

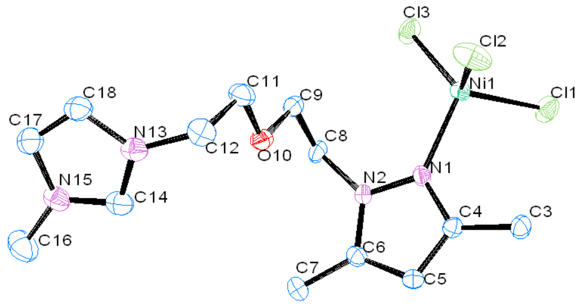


Figure 1. Molecular structure of compounds **Ni1** (thermal ellipsoids are drawn at the 30% probability level; hydrogen atoms are omitted for clarity).

The ethylene oligomerization behavior of nickel complexes **Ni1-Ni2** (conditions: 30°C, 15 min, MAO as cocatalyst, 250 [Al]/[Ni], toluene as solvent) has been evaluated and **Ni2** had higher turnover frequency (TOF - Mol of ethylene converted (mol of Ni)$^{-1}$ h^{-1}) – 19 900 h^{-1} – than **Ni1** – 1.200 h^{-1}. For both, the selectivity for butane-1 is up to 83%.

Conclusions

A series of new nickel complexes $NiCl_2$(L) based pyrazolyl-imidazolium ligands were synthesized and characterized. These new catalysts show activity in ethylene oligomerization.

Acknowledgements

This research was in part financially supported by the CNPq (Brazil), CNRS (France), and Petrobrás (Brazil).

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Synthesis and characterization of ruthenium (III) complexes studied in hydrogenation reactions.

Claudia Rodrigues (PG)[1*], Lucas Miranda (IC)[1] and Alzir Azevedo Batista (PQ)[1].

***claudinha_rod@yahoo.com.br**

[1] *Federal University of São Carlos.*

Keywords: *Ruthenium complexes, catalysis and hydrogenation reactions.*

Introduction

Ruthenium complexes are attracting interests in catalysis, specifically in hydrogenation reactions, once their results present great conversion (%) and TOF (h^{-1}) (*turnover frequency*) values [1,2]. In the present study, new complexes *mer*-[$RuCl_3$(dppb)(L)], [L= pyridine (py), 4-*terc*-butilpyridine (4^tBupy), 4-phenylpyridine (4-Phpy) and pirazine (pz) and 1,4-bis(diphenylphosphino)butane (dppb)] were synthesized and characterized. In the catalytic studies of hydrogenation reactions it was observed the conversion of cyclohexene (CXE) to cyclohexane (CXA), with conversion values around 85%.

Results and Discussion

All the *mer*-[$RuCl_3$(dppb)(L)] complexes (L= pyridine (py) **(1)**, 4-*terc*-butilpyridine (4^tBupy) **(2)**, 4-phenylpyridine (4-Phpy) **(3)** and pirazine (pz) **(4)** and 1,4-bis(diphenylphosphino)butane (dppb)) were prepared from *mer*-[$RuCl_3$(dppb)H_2O] [3] with the N-heterocyclic ligands (Figure 1).

Data of conductivity and elementar analysis show that the complexes are neutrals. Magnetic susceptibility suggests the paramagnetism of the complexes with one unpaired electron. The IR spectroscopy present the ν(Ru-P), ν(Ru-N) and ν(Ru-Cl) bands showing the coordination of the ligands with the ruthenium metallic center.

Cyclic voltammograms of the complexes in CH2Cl2 solution, at room temperature reveal an irreversible RuIII → RuII process (only one electron involved). In the first cycle, starting from around 0.40 V, after inversion of the scan rate (at 1.0 V) a reduction process is observed at –0.07 V. In the second cycle, two poorly defined oxidation processes appears, with Epa around 0.42 V and 0.54 V (peaks 2 and 3, respectively). This electrochemical behavior can be explained considering that after the reduction of RuIII/II, at –0.07 V (in the first cycle), the species [Ru_2Cl_5(dppb)$_2$] (equation 2), [Ru_2Cl_4(dppb)$_2$(4-VPy)] (equation 3) and [$RuCl_2$(dppb)(4-VPy)$_2$] (equation 4) are generated at the electrode surface, according to Figure 2 as shown below [4]. All the complexes **(1-4)** present the same cyclic voltamogram perfil.

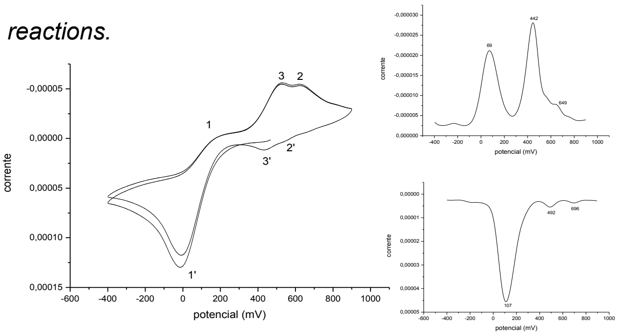

Figure 2. Cyclic voltammograms and differential pulses of *mer*-[$RuCl_3$(dppb)(4^t-Bupy)], for potentials between -0.8 and 1.0 V, vs. Ag/AgCl, recorded in 1x10^{-3} mol L^{-1} in 0.1 mol L^{-1} TBAP in CH_2Cl_2; sweep rate 100 mV s^{-1}.

$$[RuCl_3(dppb)(L)] + e^- \longrightarrow [RuCl_2(dppb)(L)] + Cl^- \quad (1)$$

$$[RuCl_3(dppb)(L)] + [RuCl_2(dppb)(L)] \longrightarrow [Ru_2Cl_5(dppb)_2] + 2\,L \quad (2)$$

$$2[RuCl_2(dppb)(L)] \longrightarrow [Ru_2Cl_4(dppb)_2(L)] + L \quad (3)$$

$$[RuCl_2(dppb)(L)] + L \longrightarrow [RuCl_2(dppb)(L)_2] \quad (4)$$

All the complexes were tested in hydrogenation reactions of cyclohexene using 52 psi H_2 and 80°C of temperature. Results of conversions are in Table 1.

Table 1. Conversion (CXE to CXA) and TOF values of the ruthenium (III) complexes.

Complexes	Conv. (%)	TOF (h^{-1})
(1)	84	43
(2)	83	42
(3)	76	25
(4)	83	40

*CXE = cyclohexene and CXA = cyclohexane

Conclusions

Ruthenium (III) complexes were synthesized, characterized and their catalytic activities show good results in hydrogenation reactions [around 85 % of conversion and TOF 40 (h^{-1})].

Acknowledgements

CNPq, CAPES and Fapesp

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Poly(ε-caprolactone) produced using $[Ti_3(\mu_3\text{-}OPr^i)_2(\mu\text{-}Pr^i)_3(OPr^i)_6][FeCl_4]$ as catalyst

Thaiane Gregório[1] (IC)*, Siddhartha Om Kumar Giese (PG), Davi Back[2] (PQ), Andersson Barison[1] (PQ), Eduardo Lemos de Sá[1] (PQ), Ronny R. Ribeiro[1] (PQ), Arion Zandoná Filho[1] (PQ), Sônia Faria Zawadzki[1] (PQ), Jaísa Fernandes Soares[1] (PQ), Giovana Gioppo Nunes[1] (PQ). *nunesgg@ufpr.br*

[1] *Departamento de Química – Universidade Federal do Paraná – Centro Politécnico – Curitiba/PR.*
[2] *Departamento de Química – Universidade Federal de Santa Maria – Camobi – Santa Maria/RS*

Keywords: *Poly(ε-caprolactone), Alkoxides, Titânium, Biodegradable polymer*

Introduction

The Poly(ε-caprolactone) (PCL) has been used extensively in the biomaterials field mainly in drug-delivery devices[1]. For this purpose, titanium and iron akoxides are attractive as catalyst because they are considered eco-friendly and nontoxic metals. In this work the heterometallic alkoxide $[Ti_3(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_3(OPr^i)_6][FeCl_4]$ **(A)** was applied as catalyst of polymerization of ε-caprolactone.

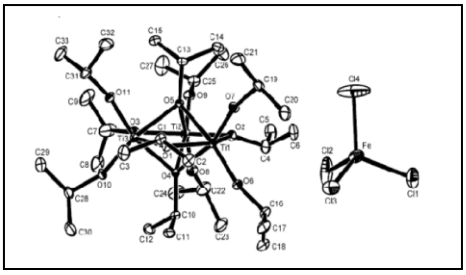

Figure 1: ORTEP representation of $[Ti_3(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_3(OPr^i)_6][FeCl_4]$ **(A)**.

Results and Discussion

Polymerisations of ε-caprolactone were carried out in a Schlenk tube under $N_{2(g)}$ in toluene varying temperature, reaction time and catalyst:monomer rate. The polymers were precipitated in methanol and dried under vacuum. Polymerization results are deposited in Table 1.

Table 1. Polimerization of poly(ε-caprolactone) under different conditions using **A** as catalyst.

	A:CL (m/m)	**Temp. (°C)**	**Time (h)**	**Yield (%)**	**M_n (g/mol)**	**PDI**
1	1:1000	90	17	50	9157	1.5
2	1:200	90	23	100	9777	1.5
3	1:200	90	6	29	5934	2.2
4	1:200	90	3	25	7193	1.8
5	1:200	60	20	86	10411	1.6
6	1:200	30	20	56	9773	1.5
7	1:100	110	16	95	-	-
8	1:100	90	32	95	-	-
9	1:100	90	16	100	15581	1.5

M_n = Molecular weight; PDI = polydispersity index

The IR spectra of polymers are characterized by absorptions of esters groups in 1720; ν(C=O), 1104; ν_{as}C(C=O)O and 1042 cm^{-1}; ν_{as}(COC). The comparison of ^1H RMN spectra, recorded in $CDCl_3$, for monomer and polymer shown a chemical shift of peaks at δ = 2.6 and 4.3 ppm assigned to methylenes of monomer to δ = 2.3 and 4.1 ppm in the polyester. The presence of signals at 1.1 and 5.0 ppm were assigned to hydrogens of isopropoxide groups in the end of polymeric chain. This points to a ring open polymerization mechanism.

Powder X-ray diffracctograms of solids are typical for crystalline poly(ε-caprolactone) with peaks of high intensity at 2θ in 21.56 and 23.82 and smaller peaks in 15.85 and in the region ranging 30 to 50°. This diffraction pattern suggests relative low molecular weight for all samples. These results were confirmed by the medium molecular weight and polydispersity index (PDI) obtained from GPC analysis. Compoud **A** was found to be moderately active at 30 °C, however the yield increase for longer reaction time. High tempertaure (90 °C) leads to 100 % of conversion for a catalyst:monomer ratio of 1:100 and 1:200 after 16 and 23 h. Interestingly, the higher molecular weight and lower PDI were obtained for sample 9, showing good control over the polymerisation process. DSC curves from -100 to 120 °C shown glass transition at –60 °C and melting point at 55 °C.

Powder EPR spectra of polymers at 77 K exhibits iron(III) signals at g = 4.3 and 2.0 due rhombic species and $[FeCl_4]^-$ anion. Following reactions over 22 h, it was observed the degradation of catalyst from the appearance of additional lines in spectra.

Conclusions

Compound **A** was applied to produced monodisperse poly(ε-caprolactona) in higher molecular weight than other titanium alkoxides.

Acknowledgements

Fundação Araucária, CNPq, UFPR

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Ruthenium (II) Carbonyl Complexes with Amine and Imine Ligands: Synthesis, Characterization and Catalytic Activity.

Deividi A. Cavarzan (PG)[1]*, Otávio Fuganti (PG)[1], Francisco D. Fagundes (PG)[1], Carlos B. Pinheiro (PQ)[2] and Márcio P. de Araujo (PQ)[1].

***deividi.cavarzan@gmail.com**

[1] Departamento de Química, Universidade Federal do Paraná, 81531-980 Curitiba-PR, Brazil.

[2] Departamento de Física, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte-MG, Brazil.

Keywords: *Carbonyl Ruthenium Complexes, Catalytic Activity.*

Introduction

The interest in the chemistry of ruthenium is constantly renovated during the years; since its discovery in 1844, ruthenium has gained an increasing attention due to its application in several aspects of chemistry, for example, supramolecular and material chemistry,[1] catalysis[2] and medicinal inorganic chemistry.[3] Ruthenium complexes have an important role in catalysis, especially in hydrogen-transfer and hydrogenation reactions for reduction of polar bonds, C=X (X= O or N).[2] In this work, we present the syntheses and characterization of complexes with general formula [$RuCl_2(CO)(PPh_3)(N\text{-}N)$]; N-N= bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me-bipy), 2,2'-dipyridylamine (bam), 2-aminomethylpyridine (ampy) and ethylenediamine (en).

Results and Discussion

The complexes were synthesized from the complex [$RuCl_2(CO)(dmf)(PPh_3)_2$] and the appropriate N-N ligands, Scheme 1. The characterization of the complexes was made by FTIR, NMR, (Table 1) and X-ray diffraction (Figure 1).

Scheme 1

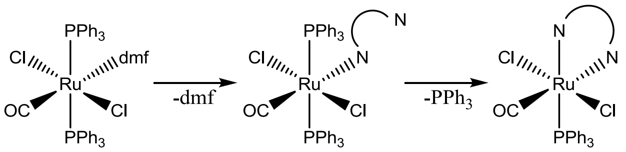

Table 1. FTIR, $^{31}P\{^1H\}$ NMR data and conversion for the reduction of acetophenone.

N-N	ν cm^{-1a}	δ (ppm) $^{31}P\{^1H\}$	%^{b}	%^{c}
bipy	1951	42,1	80%	82%
Me-bipy	1955	42,4	83%	88%
bam	1945	41,5	77%	78%
ampy	1942	51,0	81%	92%
en	1949	52,3	81%	96%

[a] In KBr pellets.
[b,c] General conditions: Isopropanol, acetophenone, KOH, 82°C.
[b] Catalyst:base:substrate = 1:20:1000; 24h.
[c] Catalyst:base:substrate = 1:20:500, 4h.

The reduction of acetophenone was perfomed in hydrogen transfer conditions, using isopropanol as hydrogen source and KOH as co-catalyst. The reduction was tested in two proportions Ru:base:substrate, 1:20:1000 and 1:20:500. The conversions were up to 83% for the former in 24h and up to 96% for the later in 4h, Table 1.

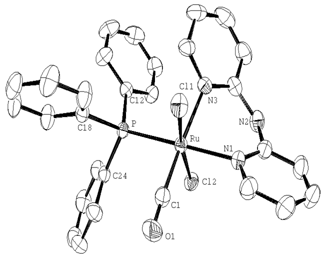

Figure 1 . Structure of X-ray diffraction for [$RuCl_2(CO)(PPh_3)(bipy)$].

Conclusions

Complexes with general formula [$RuCl_2(CO)(PPh_3)_2(N\text{-}N)$], were synthesized successfully. The characterization by FTIR and NMR are consistent with X-ray diffraction, indicating a structure in which a PPh_3 is trans with the pyridine N- or NH_2. The catalytic studies show that the presence of NH_2 increases the activity of the complex.

Acknowledgements

The authors gratefully acknowledge the financial support of CAPES, CNPq and Fundação Araucária.

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Ruthenium (II) Hydride Complexes: Synthesis, Characterization and Catalytic Activity.

Deividi A. Cavarzan (PG)[1]*, Otávio Fuganti (PG)[1], Francisco D. Fagundes (PG)[1] and Márcio P. de Araujo (PQ)[1].

***deividi.cavarzan@gmail.com**

[1] Departamento de Química, Universidade Federal do Paraná, 81531-980 Curitiba-PR, Brazil.

Keywords: *Hydride Ruthenium Complexes, Catalytic Activity.*

Introduction

Transition metals hydrides are of great importance in coordination chemistry due their participation in catalyzed reduction reactions. In this way, ruthenium (II) hydride complexes have attracted much attention, since ruthenium complexes are very active in hydrogenation and transfer hydrogenation reactions.[1] In this work, we present the complexes with general form $[Ru(H)(CO)(PPh_3)_2(N\text{-}N)]Cl$ – N-N= bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (Me-bipy), o-phenanthroline (phen), 2,2'-dipyridylamine (bam) and ethylenediamine (ampy) were worked.

Results and Discussion

The complexes were synthesized from the complex *cis*-$[Ru(H)Cl(CO)(PPh_3)_3]$[2] and the appropriate N-N ligands, Scheme 1. The complexes were characterized by FTIR and NMR. Structural elucidation of the complexes was performed by analysis of HMQC, COSY and nOe.

Scheme 1

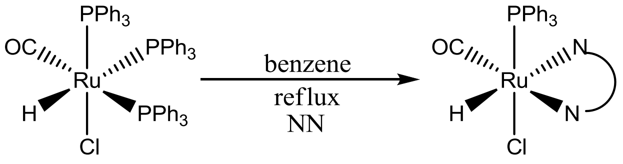

Table 1. $^{31}P\{^1H\}$ and ^1H NMR data for the $[RuH(CO)(PPh_3)_2(N\text{-}N)]Cl$.

N-N	δ (ppm) $^{31}P\{^1H\}$	δ (ppm) ^1H hydride
bipy	46,5 (s)	-11,3 (t) $^2J_{P\text{-}H}$=19,8Hz
Me-bipy	47,3 (s)	-11,3 (t) $^2J_{P\text{-}H}$=19,7Hz
phen	47,6 (s)	-12,3 (t) $^2J_{P\text{-}H}$=19,5Hz
bam	46,7 (s)	-11,2 (t) $^2J_{P\text{-}H}$=19,3Hz
ampy	46,2 (s)	-11,3 (t) $^2J_{P\text{-}H}$=20,1Hz

The reduction of acetophenone was perfomed in hydrogen transfer conditions, using isopropanol as hydrogen source and KOH as co-catalyst, according to Scheme 2. The reduction was tested in two conditions Ru:base:substrate, 1:20:1000 and 1:20:500. The conversions were up to 81% for the former in 24h and up to 86% for the later in 4h, Table 2.

Scheme 2

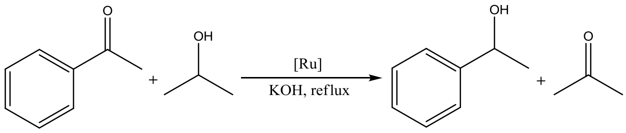

Table 2. Data for reduction of acetophenone with different N-N ligands.

Complexes	%[a]	%[b]
$[Ru(H)(CO)(PPh_3)_2(bipy)]Cl$	70%	84%
$[Ru(H)(CO)(PPh_3)_2(Me\text{-}bipy)]Cl$	78%	78%
$[Ru(H)(CO)(PPh_3)_2(bam)]Cl$	75%	86%
$[Ru(H)(CO)(PPh_3)_2(fen)]Cl$	77%	65%
$[Ru(H)(CO)(PPh_3)_2(ampy)]Cl$	81%	86%

General conditions: Isopropanol, acetophenone, KOH, 82°C.
[a] Catalyst:base:substrate = 1:20:1000; 24h.
[b] Catalyst:base:substrate = 1:20:500, 4h.

Conclusions

Complexes with general formula $[Ru(H)(CO)(PPh_3)_2(N\text{-}N)]^+$, were synthesized and characterized by FTIR and NMR (1D and 2D) and their structures were proposed. The complexes were tested as pre-catalysts for the reduction of acetophenone, and studies are ongoing in order to find out the effect of the N-N ligands on the activity of the catalyst.

Acknowledgements

The authors gratefully acknowledge the financial support of CAPES, CNPq and Fundação Araucária.

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Poster Abstracts III: Interface and Surface Chemistry

Sensor based on electrostatic assembled tetraruthenated free-base and zinc *meso*-tetra(4-pyridylvinylphenyl)porphyrins films

Bernardo A. Iglesias (PG)[1*], Paulo R. Martins (PG)[1], Henrique E. Toma (PQ)[1], Koiti Araki (PQ)[1]

***iglesias@iq.usp.br**

[1]*Universidade de São Paulo, USP, CP 26077, São Paulo, SP 05513-970, Brazil.*

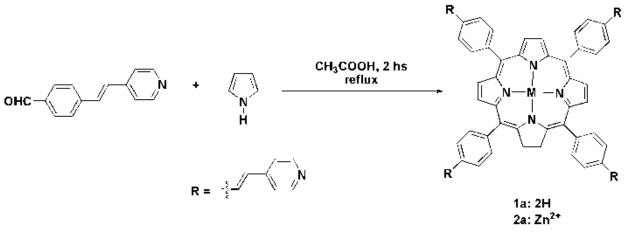
Keywords: *Porphyrins, Ruthenium Complexes, Electrocatalysis.*

Introduction

The chemistry of polymetallic porphyrins and other supermolecules has attracted the attention of many research groups interested in molecular devices and multi-electron transfer catalysis[1]. It should be noted that porphyrin-modified electrodes have been employed, with increasing interest, in analytical and bioanalytical chemistry[2,3]. In this work, the investigation of synthesis of vinyl-porphyrins electrochemical behavior and of the modified electrodes containing tetraruthenated zinc or free-base porphryin was directed to the detection of reducing analytes, particulary those which are not suitable for conventional electroanalytical monitoring, such as the nitrite and sulfite ions, due of their poor electrochemical activity on bare electrodes.

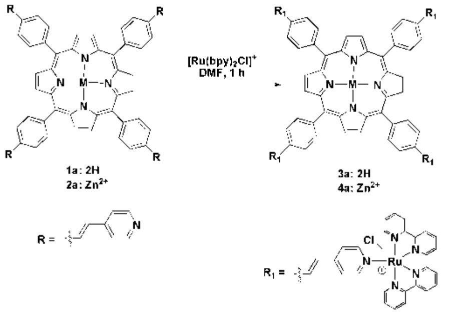
Results and Discussion

The vinylpyridyl-porphyrin **(1a)** was obtained in glacial acetic acid by the direct reaction of the precursor 4-vinylpyridylbenzaldehyde and pyrrole (4: 4.05 ratio), in reflux for 2 hours. The zinc(II) porphyrin (**2a**) was obtained by reaction of porphyrin with $Zn(OAc)_2.H_2O$, in DMF solution for 1 hour (**Scheme 1**). The tetraruthenated porphyrin complexes (free-base **3a** and zinc complex **4a**) were obtained by reaction between vinyl-porphyrin and $[Ru(bpy)_2Cl]^+$, in DMF for 1 hour (**Scheme 2**).



Scheme 1. Scheme of the synthesis of *meso*-(4-pyridylvinylphenyl)porphyrin **(1a)** and its zinc complex **(2a)**.

The cyclic voltammograms was registered in potentiostat/galvanostat Autolab PGSTAT 30, using a conventional system three electrodes, an platinum wire as auxiliar electrode, a reference electrode Ag/AgCl (KCl 1mol/L) and glass carbon electrodes modified with free-base **3a** and zinc complex **4a** was previously described by Martins et al.[3]. The sulfite and nitrite solutions were prepared with buffer phosphate solution (0.1 mol/L; pH 6.8), also used as electrolyte solution.



Scheme 2. Scheme of the synthesis of tetraruthenated free-base porphyrin **(3a)** and its zinc complex **(4a)**.

In the range +0.22 – +1.22 V (E *vs* SHE) the cycle voltammograms of glass carbon modified presented a reversible pair of waves at E_{pa}= +0.98V and E_{pc}= +0.93V relative to redox process Ru(II)/(III).

The glass carbon modified with (**3a**) and (**4a**) in presence of sulfite and nitrite ions presented an electrochemical signal around +0.99V and +1.02V respectively and the current intensity was proportional to the concentration of added analytes.

Conclusions

The glass carbon electrodes modified with tetraruthenated free-base porphyrin and its zinc complex presented a good responses to sulfite an nitrite ions in aqueous solution, can be excellent amperometric sensors to determination of reducing analytes in food or FIA (Flow Injection Analysis).

Acknowledgements

Were thanks the FAPESP and CNPq for the financial support.

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The use of superparamagnetic Carbon Electrodes: a new approach for analysis of mercury ions

Ulisses Condomitti (PG)[1*], André Zuin (PG)[1], Alceu Totti (PG)[1], Koiti Araki (PQ)[1] and Henrique Eisi Toma (PQ)[1]

***ulissesc@usp.br**

[1]*Universidade de São Paulo, USP, CP 26077, São Paulo, SP 05513-970, Brazil.*

Keywords: *Magnetoelectrochemistry, mercury, square wave, magnetic carbon*

Introduction

Mercury ions represent a critical species in the biosphere, originating from both natural and anthropogenic sources[1]. Its common chemical forms are toxic, persistent species in the environment, exhibiting a great tendency to accumulate in biota. Current analytical methods for mercury involve amalgamation pre-concentration[2] with gold, followed by heating in an inert gas stream and subsequent metal detection, using for instance [2] cold vapor atomic fluorescence (CVAF). In this work we have demonstrated that Mercury ions can be captured with superparamagnetic carbon powder substrates and transported to the electrode surface using an external miniature magnet. The magnetic carbon substrate is electronically conducting, and more than promoting efficient preconcentration of the element at the electrode, the presence of the external magnet also allows to perform direct electrochemical analysis, leading to a very strong enhancement of the analytical signals for the reduction of the Hg(II) ions.

Results and Discussion

Superparamagnetic nanoparticles of magnetite of about 10-20 nm were obtained by the method of co-precipitation. After treating with carbon powder (1:4 MagNp:carbon, 100 mesh, from Aldrich) suspended in toluene, the mixture was sonicated for 60 min. The power was separated with a magnet and stored dry under vacuum. The suspensions were always freshly prepared by redispersing 10 mg of superparamagnetic carbon powder into 0.5 M KNO_3 aqueous solution containing the analytes. A SEM image of material is showed in figure 1.

The square wave voltammograms of the magnetically confined particles previously treated with $2 \times 10^{-6} - 4 \times 10^{-3}$ mol L^{-1} Hg^{2+} ions are shown in Fig. 2. There is a sharp enhancement of the signals, due to the high local concentration of the Hg^{2+} ions, exhibiting a good linearity with the concentration of the mercury ions.

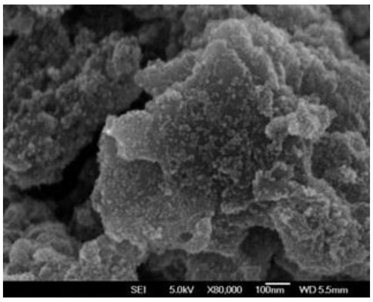

Figure 1. SEM image of carbon powder impregnated with superparamagnetic nanoparticles

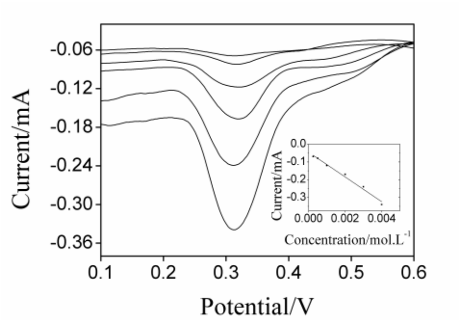

Figure.2 Square wave voltammograms of superparamagnetic carbon electrode, in the presence of the external magnet for Hg^{2+} ions in the range of $2 \times 10^{-6} - 4 \times 10^{-3}$ mol L^{-1}

Conclusions

Magnetic Carbon powder can be employed to capture mercury ions and transport them to the electrode surface using an external miniature magnet promoting the improve of analytical signals for the reduction of analytes such as the Hg(II) ions.

Acknowledgements

Were thanks the FAPESP, PETROBRÁS and CNPq for the financial support.

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Surface chemistry of oxidized charcoal fines with metal ion adsorption capacity.

Liliam C. Angelo (PG), Karen M. Mantovani (IC), Sailer S. dos Santos (PQ), Antonio S. Mangrich* (PQ). mangrich@ufpr.br

Departamento de Química da Universidade Federal do Paraná. Centro Politécnico da UFPR, CP 19081, Jardim das Américas, CEP 81531-980.

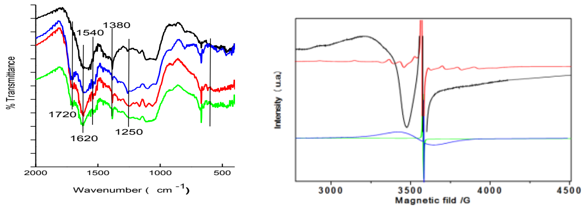
Keywords: *charcoal oxidation, metal ion adsorption, EPR spectra.*

Introduction

Charcoal fines (CCF), reject of the metallurgical industry have a great ability to sequester carbon. However it is a potential environmental pollutant and must be chemically modified to perform activities similar to natural organic matter (NOM) in the environment, including capacity of metal ions adsorption. Nitric acid is among the most widely used chemical reagents to obtain functionalized coal.[1] The CCF treated with HNO_3 in air resulted in bulk quantity of oxidized charcoal (CCFN). The types of metal-binding sites in CCFN were studied by reactions with aqueous solutions of vanadyl, VO^{2+}, and Cu^{2+} ions. FT-IR and EPR spectroscopy were employed for the characterization of prepared CCFN and the VOCCFN and CuCCFN solid complexes.

Results and Discussion

Figure 1 A shows the FT-IR spectra Fig. 1 B the EPR spectra of the different studied materials.



A **B**

Figure 1. A) FTIR spectra of CCF (black), CCFN (blue), VOCCFN complex (red) and CuCCFN complex (green). B) EPR spectra of CCF (blue), CCFN (green), CuCCFN complex (black) and VOCCFN complex (red).

The FTIR CCF is typical for carbonaceous material with the G and D bands around 1600 and 1380 cm^{-1}, respectively. These are normally IR-forbidden vibrations but became actives when the sp^2 symmetry of the graphitic rings is broken by heteroatom in the lattice.[2] The oxidation/nitration reaction of the CCF with nitric acid makes appear absorption bands at 1720 cm^{-1}, and 1250 cm^{-1} attributed to carboxylic acids, that had their intensity diminished by the complexation reactions with Cu^{2+} or VO^{2+} ions suggesting metal ions coordination with oxygen atoms from carboxylic groups. The complexation reactions produce also the evidence of the broad band around 600 cm^{-1} attributed to the graphitic sp^2 bonds vibration.

The EPR CCF experimental spectrum (Fig. 1B blue) shows a sharp absorption line with g = 2.0032 proper for organic free radical (OFR) with unpaired electron density on carbon atoms. The sharp line is above a broad line from Fe^{3+} ions in a concentrated or cluster domain. The nitric acid treatment leached the Fe^{3+} from the CCFN material but the OFR sharp line remains. Parallel and perpendicular spectra for the CUCCFN (Cu(II), $S = 1/2$, $I = 3/2$) and VOCCFN (VO(II), $S = 1/2$, $I = 7/2$) are also shown in Fig. 1 B. The spin Hamiltonian parameters values for the CuCCFN and VOCCFN prepared complexes are shown in table 1.

Table 1. Spin Hamiltonian parameters.

EPR Parameters	CuCCFN	VOCCFN
$A_{\perp}(10^{-4}\ cm^{-1})$	25	66
$A_{\parallel}(10^{-4}\ cm^{-1})$	145	175
$g_{\perp}$	2.0850	1.9350
$g_{\parallel}$	2.3400	1.9800
$g_{\parallel}/ A_{\parallel}$	161 cm	
$\langle g \rangle$		1.965
$\langle A \rangle 10^{-4}\ cm^{-1}$		102

The $A_{\parallel}$ and $g_{\parallel}$ values for the CUCCFN complex are concordant with at least two oxygen atoms coordination, indicating chelation. The isotropic parameters $\langle g \rangle$ and $\langle A \rangle$ for the VOCCFN complex point to oxygen as equatorial donor atoms of C_{4v} symmetry site, $VO(O)_2$.

Conclusions

A carbonaceous material for metal ions adsorption was prepared by nitric acid oxidation of charcoal powder. The material presents free radical with g = 2.0032 proper for OFR with unpaired electron density on carbon atoms. The EPR data indicate that in both the complexes oxygen atoms are the donor sites.

Acknowledgements

CNPq, CAPES, FINEP and DQ/UFPR. K.M.M., L.C.A. and S.S.S thank UFPR/TN (1989002133), CNPq (149087/2010-1) and INCT-E&A/CNPq (150948/2011-5) for a research fellow, respectively.

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APTES-Modified Silicas in the Reaction with Essential Oil of Citronella

Lara M. P. Montenegro (PG)*, Fabiele Tavares (IC), Jordana Griep (IC) and Daniela Bianchini (PQ).

***mp_lara@yahoo.com.br**

Universidade Federal de Pelotas, Campus Capão do Leão s/n, 96010-900 – CCQFA – LASIR – RS - BRAZIL

Keywords: *Silica; APTES; essential oil of citronella.*

Introduction

Synthesis of SiO_2 by sol-gel process using alkoxysilane precursors such as 3-aminopropyltriethoxysilane (APTES) and tetraethylorthosilicate (TEOS), allows modification of the surface by adding of organic moieties in its structure, thereby providing properties covering a wide range of applications, including the use of this material as heterogeneous catalysts and solid adsorbent[1]. The aim of this study is evaluate the use of APTES-modified silica as a scavenging agent of carbonyl compounds, such as citronellal present in the essential oil of citronella (*Cymbopogon nardus*). Citronellal reacts with the amine groups of the modified silica, leading to the formation of imines groups[2]. The sol-gel process involves two steps, hydrolysis of alkoxysilane and its condensation. In this work, three silicas were synthesized by sol-gel process: silica without modification as a reference, R1, silica modified with APTES, R2, and APTES-modified silica impregnated with essential oil of citronella, R3. In the Schlenk flasks, it was added anhydrous EtOH, distilled H2O, concentrated HCl, and TEOS. In addition to these reagents, it was added APTES in the R2 flask reaction, and essential oil of citronella before the TEOS in the R3 flask reaction. The samples were characterized by FT-IR, the BET method and SEM.

Results and Discussion

According to the FT-IR spectra in the Figure 1, we observe that the silica surface was modified by amine groups of APTES, R2. It is evidenced by δNH_2 band at 1547 cm^{-1}.

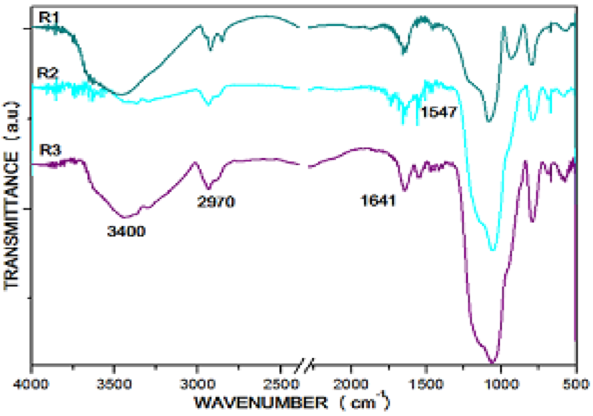

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Figure 1: FT-IR spectra of the synthesized silicas.

It was not possible to visualize the formation of imines, whose υC=N should be observed around 1640 cm^{-1} in the R3 spectrum. Probably, the υC=N is overlapped by the δ(HOH) observed at 1641 cm^{-1}.

Table 1: Textural properties of the silicas.

sample	**S_{BET}* (m^2/g)**	**$V_{p\text{- BJH}}$* (cm^3/g)**	**$d_{p\text{- BJH}}$* (Ǎ)**
R1	166	0.005	24
R2	31	0.002	91
R3	108	0,02	75

* S_{BET}: specific surface area; Vp: pore volume; dp: pore diameter.

We observe that the addition of essential oil during sol-gel process leads to an increase of the specific surface area and the pore volume. The decreasing of the pore diameter suggests that the pores of R3 silica are deeper than the pores of R2 silica. The specific surface area of non-modified silica, R1, is higher than that observed for R2 and R3 silicas.

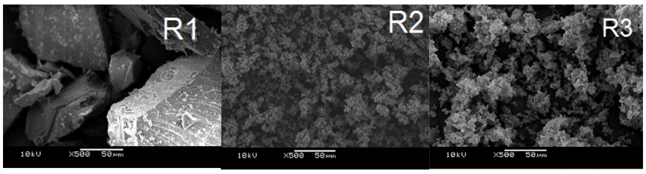

Figure 2: SEM images of the samples (x500).

The Figure 2 shows that the synthesized silicas have no definite morphology. However, R1 silica presents a compact structure, while modified silicas, R2 and R3, are formed for an agglomerated of particles.

Conclusions

Silica modified with APTES was synthesized efficiently, but the imine formation by the addition of essential oil of citronella could not be detected with the techniques employed in this study. On the other hand, the effect of essential oil on the textural properties was observed by BET method.

Acknowledgements

To CAPES for the scholarship granted and to FAPERGS for financial support.

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Poster Abstracts IV: Structural and Coordination Chemistry

Tc(V) and Re(V) Complexes with Thiocarbamoylbenzamidines as Tetradentate Ligands for Bioconjugation

Juan Daniel Castillo Gómez (PG)[1]*, Nguyen Hung Huy (PQ)[2], Ulrich Abram (PQ)[1]

castillo@zedat.fu-berlin.de

[1]*Freie Universität Berlin, Fabeckstr. 34/36, D-14195, Berlin, Germany*
[2]*Hanoi University of Science, 19 Le Thanh Tong, Hanoi, Vietnam*

Keywords: *Technetium, Rhenium, Complex synthesis, Bioconjugation*

Introduction

Re and Tc complexes are of particular importance for nuclear medicine because of the diagnostic use of ^{99m}Tc and the therapeutic use of ^{186}Re and ^{188}Re. One main focus of current research is bioconjugation.

Results and Discussion

The tetradentate thiocarbamoylbenzamidines **L1** and **L2** can be easily synthesized from benzimidoyl chlorides and o-phenylene diamine[1,2]. They have been shown to be suitable ligands for Re(V) and Tc(V) oxo and nitrido cores.

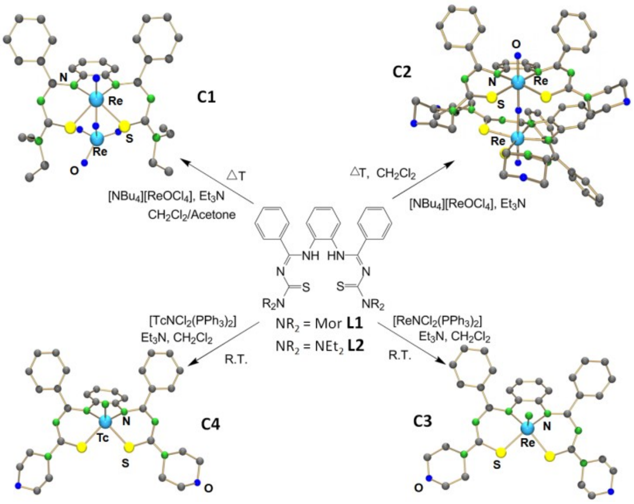

Figure 1. Prototype Complexes of **L1** and **L2**.

It was possible to synthesize a similar ligand with an additional carboxylic group for conjugation (**L3**). Reactions of the carboxyl-substituted ligand **L3** with oxorhenium(V) cores gave complexes, in which a third weak co-ligand was needed for stabilization (**C5** and **C6**). This problem could be avoided using ReN and TcN cores (**C7** and **C8**). The ligand itself and its nitrido complexes could be coupled to propargyl amine via standard amide coupling procedures (**L4**, **C9**, **C10**). A model "click"-coupling reaction was made with **C10** and benzyl azide forming complex **C11**.

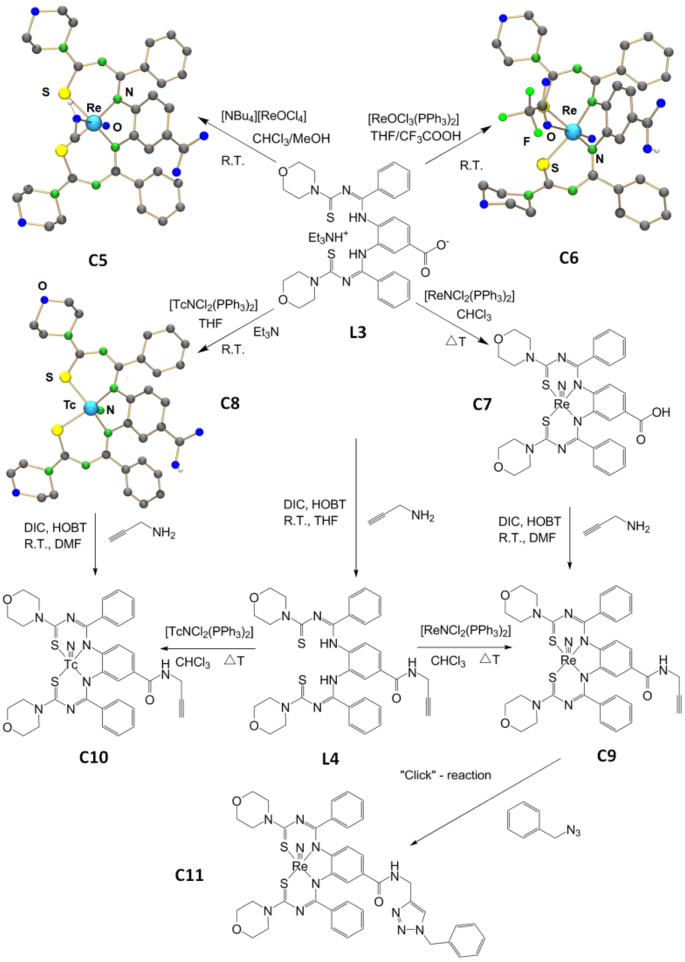

Figure 2. Complexes of **L3** and further coupling reactions.

Conclusions

Stable oxo and nitrido complexes of Re and Tc with tetradentate thiocarbamoylbenzamidines were synthesized. Nitrido complexes of the ligands **L3** and **L4** can be coupled to small organic molecules through amide- and „click"-coupling reactions.

Acknowledgements

We thank DAAD for financial support.

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X-ray Crystallography and Luminescence Studies for a New Complex of Eu with Ligand derived from 2,6-diformylpyridine

Aline Machado (PQ)[1*], Gelson Manzoni de Oliveira (PQ)[2], Ulrich Abram (PQ)[3] and Geraldo Wachholz Gomes (IC)[2]

***quimica.aline@gmail.com**

[1] *Instituto Federal Farroupilha – Campus Panambi*

[2] *Universidade Federal de Santa Maria*

[3] *Frei Universität Berlin*

Keywords: lanthanide, X-ray, luminescence

Introduction

The polydentate ligands derived from 2,6-diformylpyridine and 2,6-diacetylpyridine are mostly symmetric and good chelating agents for lanthanide ions, but so far they have not been outstanding by their fluorescent activities, still less by their ability to transfer energy to a lanthanide ion and so excite its luminescence. In this work we attempt to enlarge the performance of this kind of compounds, by exploiting the optical properties of novel, uncommon structures.

Results and Discussion

We report a new result on the complex structural chemistry of lanthanides and ligand derived from 2,6-diformylpyridine, together with luminescence studies carried outwith the new chelate [Eu(dfpbpsc-H$^+$)$_2$]NO$_3$ (**1**) (dfpbpsc= 2,6-diformylpyridinebis(4-phenylsemicarbazone).

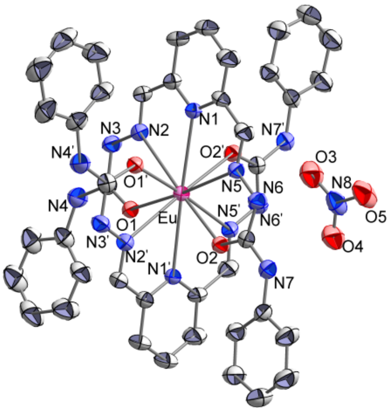

Figure 1. Complex [Eu(dfpbpsc-H$^+$)$_2$]NO$_3$ (**1**).

The metal center in the europium complex **1** presents coordination number 10, and its coordination polyhedron is clearly a bicapped cube, or elongated square dipyramid.

The emission spectrum of **1**, (Figure 2) shows the characteristic transitions of the europium ion, $^5D_0 \rightarrow {}^7F_J$; J = 0, 1, 2, 3 and 4. The transition (0-2) appears with the highest intensity, and the high intensity of the (0-4) transition can be an indicative of high symmetry around the europium ion, as well as a long range effect. The number of (0-0) lines is equal to the number of different non centrosymmetric sites around the metal center, and the absence of this transition should be an indicative that the europium ion would lie in a symmetric site. There is at least one line for this transition for complex **1**, therefore the europium ion lies in a non centrosymmetric site.

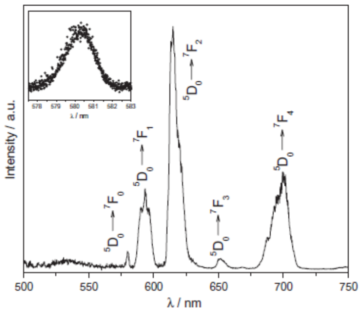

Figure 2. Emission spectrum of **1**, with λ_{ex} = 329 nm at ~77K. The inserted signal amplification covers the range 577-583nm and shows the $^5D_0 \rightarrow {}^7F_0$ transition.

Conclusions

The new complex synthesized show coordination number uncommon for lanthanide chelates. The investigation of the spectroscopic parameters of the complex, by calculating the group state geometry using the Sparkle/AM1 method, as well as the intensity parameters, transfer and back transfere rates and energy levels populations.

Acknowledgements

CNPq, UFSM, IFFarroupilha – *Campus* Panambi, FAPERGS, CAPES.

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Building a Hg(II)/Cu(I) multinuclear compounds from mercury bis(phenylselenolate).

Rafael Stieler (PG)[1,2*], Ernesto S. Lang (PQ)[2], Robert A. Burrow (PQ)[2], Paulo Piquini (PQ)[3]

***rafaelstieler@hotmail.com**

[1] Universidade Federal da Fronteira Sul, Realeza-PR, Brazil
[2] Departamento de Química, Universidade Federal de Santa Maria, Santa Maria-RS, Brazil
[3] Departamento de Física, Universidade Federal de Santa Maria, Santa Maria-RS, Brazil

Keywords: *mercury(II), copper(I), multinuclear cluster compounds.*

Introduction

The synthesis of new ternary clusters has been attracting considerable attention due to their potential use in different areas. The quantum-dot effect demonstrated in these compounds gives them interesting and unique optical properties, that are not present in simple molecules. As these compounds present size-dependent optical properties, interest in the study of such compounds lies in the characterization of their structures by single-crystal X-ray diffractometry analysis.[1,2]

Results and Discussion

Focusing to contribute for the research in this area, we present here the synthesis, structure and optical properties of four new ternary Hg-Cu-Se clusters. These results were correlated with data calculated by Density Functional Theory calculations. The compunds $[(Ph_3P)_2XCu(SePh)Hg(SePh)CuX(PPh_3)_2]$ X= Cl(**1a**), Br(**1b**), I(**1c**) (Figure 1) and $[Hg_6Cu_4(SePh)_{16}]$ (**2**) (Figure 2) were obtained from the reaction between $Hg(SePh)_2$ and $[Ph_3PCuX]_4$ in dimethylformamide (DMF).

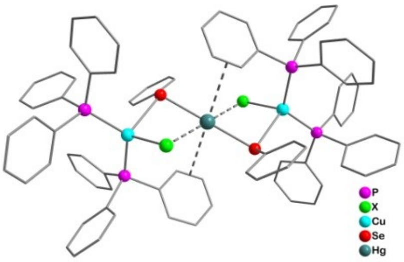

Figure 1. Molecular structure of the compound 1.

The compounds **1a**, **1b** and **1c** are iso-structural. In this compounds, the mercury atom, located at the center of the complex, is linked to the copper atoms through two μ-SePh bonds. The coordination sphere of the mercury atom is completed by two more η^2-π-aryl interaction with the phenyl ring of the PPh_3 and two halide atoms, bonded to the copper atoms. The coordination sphere of each copper is formed by two PPh_3, an halide atom and a SePh (Figure 1).

In the compound **2**, the core of the cluster is formed by six mercury and four copper atoms. Four mercury atoms presented a nearly trigonal-planar coordination environment. The other two mercury and four copper atoms are disordered over six symmetricaly-equivalents positions, and present a distorted tetrahedral coordination. All the metalic centers are bridging through μ-SePh ligands (Figure 2).

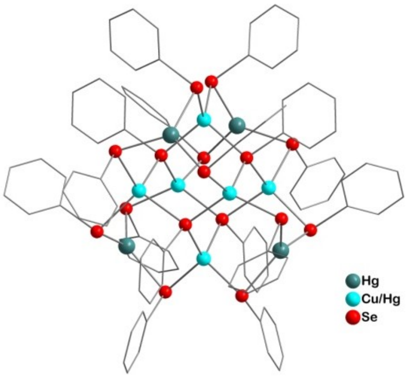

Figure 2. Molecular structure of the compound **2**.

The UV-Vis absorption spectra of **1**(**a**-**c**) and **2** in the solid state at room temperature were measured, and the estimated band-gaps found are 2.80 eV (443 nm) (**1a**), 2.66eV (467 nm) (**1b**), 2.60 eV (478 nm) (**1c**), and 2.22eV (560 nm) (**2**).

Conclusions

The reaction of $Hg(SePh)_2$ and $[Ph_3PCuX]_4$ reported here is a promissory route for the synthesis of ternary nanoclusters. Their unique optical properties give them a potential use in different areas.

Acknowledgements

We are grateful to CNPq and Capes.

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Non-oxo vanadium(IV) alkoxides: synthetic and structural trends

Giovana G. Nunes (PQ)[1], Dayane M. Reis (PQ)[2], Kátia C. M. Westrup (PG)[1], Danilo Stinghen (PG)[1], Thaiane Gregório (IC)[1], Peter B. Hitchcock (PQ)[3], David L. Hughes (PQ)[4], Davi F. Back (PG)[5], Ronny R. Ribeiro (PQ)[1], Eduardo L. de Sá (PQ)[1] and Jaísa F. Soares (PQ)[1]* ***jaisa.soares@ufpr.br**

[1] Departamento de Química, UFPR, Curitiba/PR. [2] Departamento de Química e Biologia, UTFPR, Curitiba/PR. [3] Department of Chemistry, University of Sussex, Brighton BN1 9QJ, England. [4] School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, England. [5] Departamento de Química, UFSM, Santa Maria/RS.

Keywords: *vanadium(IV), non-oxo, alkoxide.*

Introduction

Our interest in the chemistry of non-oxo vanadium alkoxides stems from their intriguing spectroscopic and magnetic properties,[1] thermochromic behaviour in solution[2] and high reactivity towards hydrolysis/condensation, which in turn leads to the synthesis of technologically relevant homo- and heterometal oxides.[3]

Our research work in this area spans the last 15 years and reveals structural and reactivity patterns that are likely to facilitate the access of other groups to this interesting and yet poorly known chemical system. Synthetic and theoretical challenges we face involve *(i)* the stabilization of non-oxo metal centres in coordinatively unsaturated environments, *(ii)* the establishment of magneto-structural correlations in alkoxo-bridged, non-oxo V^{IV} dimers and *(iii)* the development of theoretical models to rationalise the magnetic behaviour of these dimers.

Results and Discussion

We have synthesised several homoleptic, non-oxo vanadium(IV) alkoxides of general formula $\{V(OR)_4\}_n$ (Table 1). They can be liquid or solid, monomeric or dimeric compounds depending on the bulk of the alkyl (R) group. The monodentate nature of the ligands leads to four- or five-coordinate metal centres and highly air-sensitive products (Fig. 1).[1,4] Six-coordination has been described, but only with polydentate ligands.[5] Fine tuning of ligand bulk allows observation of reversible thermochromic behaviour in a variety of organic solvents.[1,2]

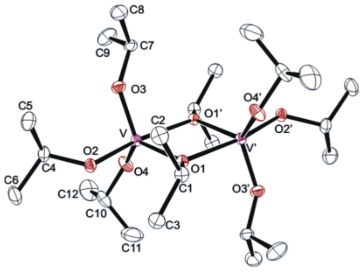

Figure 1. Representation of complex **5**. Products **4** and **6** have very similar structures.

From complexes **5** and **6** as starting materials, we have also obtained the heterometal products **8** (Fe^{II}+V^{IV}) and **9** (Li^{I}+V^{IV}, Fig. 2).[6,7] Compound **8** is a *single-molecule magnet* (SMM) and **9** has an unusually rhombic *g* tensor as revealed by EPR spectroscopy.[7] Product **9** is also useful as starting material for the preparation of other heterometal complexes by salt elimination reactions.

Table 1. V^{IV} alkoxides synthesised in our laboratory.

Complex	R group	Aspect at RT
$[V(OBu^t)_4]$, **1**	*tert*-butyl	Royal blue liquid
$[V(OPe^t)_4]$, **2**	*tert*-pentyl	Emerald green liquid
"$V(OBu^s)_4$", **3**	*sec*-butyl	Deep green liquid (*)
$[V_2(OCy)_8]$, **4**	cyclohexyl	Dark yellow crystals (*)
$[V_2(OPr^i)_8]$, **5**	isopropyl	Deep green crystals (*)
$[V_2(ONep)_8]$, **6**	neopentyl	Olive green crystals (*)
"$V_2(OBz)_8$", **7**	benzyl	Deep green crystals (**)

* Thermochromic behaviour in solution. (**) Recently prepared.

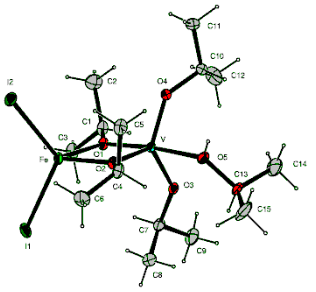

Fig. 2a. Product **8**, $[Fe^{II}I_2(\mu\text{-}Pr^i)_2V^{IV}(OPr^i)_2(HOPr^i)]$.

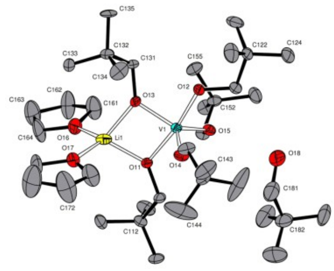

Fig. 2b. Product **9**, $[V(ONep)_3(\mu\text{-}ONep)_2Li(thf)_2]$.

Conclusions

In all crystalline complexes we obtained so far, the non-oxo V^{IV} centre adopts trigonal bipyramidal (TBP) geometry. Recent studies of magnetic behaviour indicate that such TBP environment leads to an orbitally quasi-degenerate ground state for the d^1 ions, which confers uncommon magnetic properties to the products. These studies are progressing, as well as the synthesis of new compounds to expand the series.

Acknowledgements

UFPR, FINEP/CT-INFRA, CAPES, CNPq.

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Synthesis, structure and optical features of single adamantanoid Hg-SePh-X anionic clusters stabilized by octahedral complexes. (Ph = phenyl; X = Cl, Br, I)

Fabrício Bublitz (IC)[1*], Rafael Stieler (PG)[1,2], Ernesto S. Lang (PQ)[1], Gelson M. de Oliveira (PQ)[1]

***fbublitz@hotmail.com**

[1] *Departamento de Química, Universidade Federal de Santa Maria, Santa Maria-RS, Brazil*
[2] *Universidade Federal da Fronteira Sul, Realeza-PR, Brazil*

Keywords: *mercury(II), selenium, adamantanoid cluster, Complex salts of IIA elements.*

Introduction

Clusters compounds derivated from $M(RE)_2$ (R = aryl; E = Se, Te; M = metals of IIb subgroup) with halogenides and others ligands seems to accuire preferentialy adamantane like forms. These compounds normally appear as polymers or fused cages.[1-3] However, in a halogen rich medium, it's possible to obtain single adamantanoid anions, like $[Hg_4X_4(SePh)_6]^{2-}$, as we are reporting in this work. The driving force supporting the formation of the title compounds seems to be the hardness of the interaction Hg-X (X = Cl, Br, I) allied to the chelate effect of the bis(diphenylphosphine)methane dioxide ($dppmo_2$) ligand, which force the migration of the halides from the hard metal to the adamandanoid system.

Results and Discussion

Focusing to contribute for the research in this area, we present here the synthesis, structure and optical properties of six new compounds with general formula $[M(dppmo_2)_3][Hg_4X_4(SePh)_6].4dmf.H_2O$ where M = Mg and X = Cl (**1a**), Br (**1b**), I (**1c**); X = Br and M = Fe (**2**), Co (**3**), Ni (**4**).

The products were obtained through the reaction of $Hg(SePh)_2$ with the respective metal halide ($MgCl_2.6H_2O$, $MgBr_2$, MgI_2, $FeBr_2$, $CoBr_2$ and $NiBr_2$) and $dppmo_2$ in dimethylformamide (dmf).

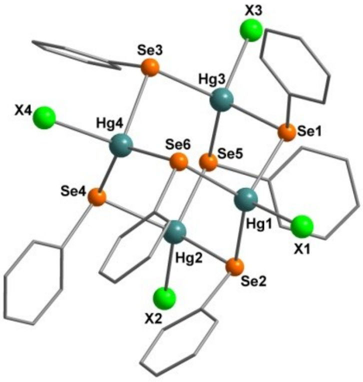

Figure 1. Adamantane like structure of the anions $[Hg_4X_4(SePh)_6]^{2-}$.

The structures of the compounds **1a**, **1b**, **1c**, **2**, **3** and **4** are represented in Figures 1 and 2. The cation and anion are displayed separately for clarity, and also for this reason the hydrogen atoms and the solvate molecules (dmf and water) are not shown. All the compounds are iso-structural.

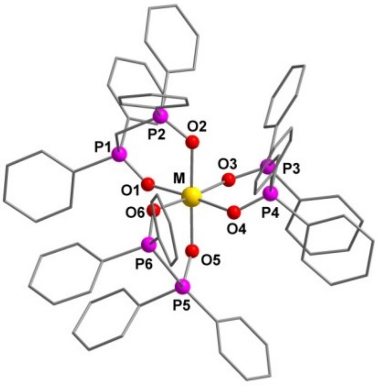

Figure 2. Structure of the cations $[M(dppmo_2)_3]^{2+}$.

The UV-Vis absorption spectra of **1**(**a**-**c**) **2**, **3** and **4** in the solid state at room temperature were measured, and the estimated optical band-gaps found are 2.76 eV (449 nm) for **1a**, 2.72 eV (456 nm) for **1b**, 2.75 eV (451 nm) for **1c**, 2.71 eV (457 nm) for **2**, 2.71 nm (457 nm) for **3** and 2.75 eV (451 nm) for **4**, respectively.

Conclusions

The reaction of $Hg(SePh)_2$, MX_2 and $dppmo_2$ reported here is a promissory route for the synthesis of single adamantanoid anionic clusters. Their unique optical properties give them a potential use in different areas.

Acknowledgements

We are grateful to CNPq and CAPES.

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Rhenium(I) and Technetium(I) Tricarbonyl Halogeno Complexes Containing a *N,S*-Bidentate Dithiocarbazate as Ligand

André Gustavo de Araujo Fernandes (PG)[1]*, Juan Daniel Castillo Gómez (PG)[2], Adelheid Hagenbach (PQ)[2], Ulrich Abram (PQ)[2], Victor M. Deflon (PQ)[1],

***agaf@iqsc.usp.br**

[1] *Institute of Chemistry, University of Sao Paulo, Sao Carlos, Brazil*

[2] *Institute of Chemistry and Biochemistry, Free University of Berlin, Berlin, Germany*

Keywords: *rhenium(I), technetium(I), dithiocarbazates, carbonyl compounds, and nuclear medicine.*

Introduction

The traditional synthesis of carbonyls by autoclave reactions are time-consuming and causes numerous problems in terms of radiations protection when radioactive materials are used.[1] However, a protocol which produces M(I) tricarbonyl (M = Re or Tc) in a one-pot synthesis using carbon monoxide at normal pressure as established by Alberto and co-workers[2] is a breakthrough which opens up to the aqueous coordination chemistry of *fac*-$[M(CO)_3]^+$ core.

On the other hand, dithiocarbazates are very versatile ligands that may act neutral or anionic and link metal ions by different coordination modes.[3]

Results and Discussion

Two new carbonyl complexes, $[ReBr(L)(CO)_3]$ (**1**) and $[TcCl(L)(CO)_3]$ (**2**), L being the neutral and dehydrated form of H(HO)L, 5-hydroxy-3-methyl-5-phenyl-pyrazoline-1-(S-benzyldithiocarbazate), were synthesized and characterized by IR, ^{1}H-NMR. Elemental analysis and MS-ESI measurements were done for complex **1**.

The complexes present facial geometry for the carbonyl groups, with the neutral dithiocarbazate Ligand occupying trans positions to two carbonyls, coordinating in a *N,S*-bidentate form.

Synthesis of $[ReBr(L)(CO)_3]$:

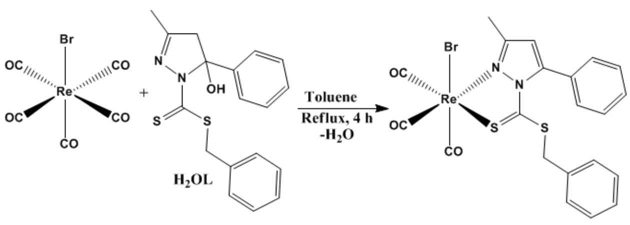

Table 1. Elemental analysis for **1**.

	C	H	N	S
Found	37.25	1.98	3.83	9.19
Calculated	37.39	2.85	3.96	9.07

Table 2. MS-ESI data for **1**, $[m/z]^+$.

	$[M-Br]^+$	$[M+Na]^+$	$[M+K]^+$
1	595.02	696.93	712.90

Table 3. IR data from KBr pellets (cm^{-1}).

	ν(CO)	ν(C=N)	ν(C_6H_5)
1 / 2	2024 / 2025 1926* / 1909* 1902* / **	1608 / 1600	695 / 696

* = broad band, ** = unidentified

Table 4. ^{1}H-NMR data for **1** and **2** ($CDCl_3$, 400 MHz, ppm).

	CH_3	CH_2	CH	phenyl ring
1	2.77 (s)	4.48 (d)	6.51 (s)	7.52-7.16 (m)
2	2.32 (s)	4.34 (d)	6.23 (s)	7.36-7.26 (m)

(s): simplet, (d): duplet and (m): multiplet

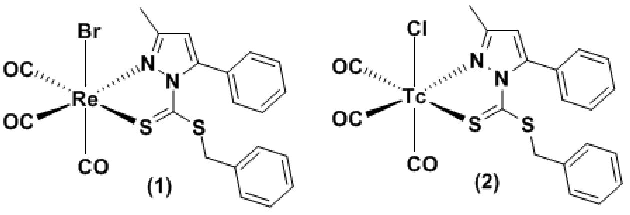

Figure 1. Structure proposals for **1** and **2.**

Conclusions

The complexes were obtained in satisfactory yield and high purity.

The stability of the complexes and the high synthetic potential of dithiocarbazate ligands justify the use of this class of compounds in further experiments and trials, particularly, such as for the synthesis of bioconjugates with ^{99m}Tc or ^{186,188}Re.

Acknowledgements

This work was supported by FAPESP, CNPq and CAPES-PROBRAL

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New Oxotechnetium(V) Complex Containing a Dithiocarbazate Ligand: Synthesis, Characterization and Crystal Structure

André Gustavo de Araujo Fernandes (PG)[1*], Adelheid Hagenbach (PQ)[2], Ulrich Abram (PQ)[2], Victor M. Deflon (PQ)[1],

***agaf@iqsc.usp.br**

[1] *Institute of Chemistry, University of São Paulo, São Carlos, Brazil*

[2] *Institute of Chemistry and Biochemistry, Free University of Berlin, Berlin, Germany*

Keywords: *technetium(V), dithiocarbazates and nuclear medicine.*

Introduction

The nuclear medicinal chemistry of technetium has been studied for some decades and the metastable nuclear isomer, γ-emitting ^{99m}Tc has been established as the ‘‘work horse’’ of diagnostic nuclear medicine (more than 80% of the diagnostic studies in routine nuclear medicine are done with this nuclide).[1]

On the other hand, dithiocarbazates are very versatile ligands. They may act neutral or anionic and link metal ions by different coordinative modes.[2]

Results and Discussion

The new complex [TcO(bdtc)Cl] (**1**), bdtc being the bideprotonated form of 5-hydroxy-3-methyl-5-phenyl-pyrazoline-1-(S-benzyldithiocarbazate), was characterized by FTIR and ^{1}H-NMR spectroscopies and the technetium analyses were done by liquid scintillation counting. The crystal and molecular structure of (**1**) was determined by X-ray diffraction.

The overall geometry around the technetium atom is best described as distorted square pyramidal, with dianionic *O,N,S*-tridentate (bdtc)$^{2-}$ ligand occupying three positions of the equatorial plane. The chlorine atom occupies the remaining equatorial position to form a distorted square pyramidal.

Synthesis of [TcO(bdtc)Cl]:

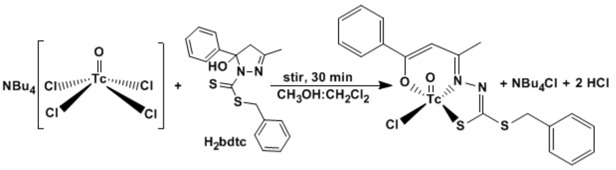

Table 1. IR data from KBr pellets (cm^{-1}):

	ν(Tc=O)	ν(C=N)	ν(OH)
[TcO(bdtc)Cl]	976	1547 1527	-----
(NBu$_4$)[TcOCl$_4$]	1026	-----	-----
H$_2$bdtc	-----	1628	3359

Table 2. Tc analyses - scintillation counting:

	% Tc (calculated / founded)
(1)	20.0 / 19.5

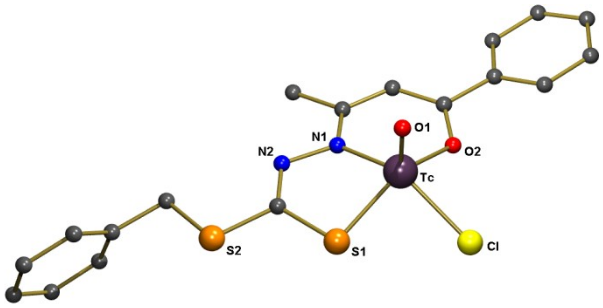

Figure 1. X-ray molecular structure for [TcO(bdtc)Cl], omitting the hydrogen atoms.

Table 3. ^{1}H-NMR data for [TcO(bdtc)Cl] and H$_2$bdtc (CDCl$_3$, 400 MHz, ppm):

	CH$_3$	CH$_2$	OH
[TcO(bdtc)Cl]	2.87 (s)	4.54 (s)	-----
H$_2$bdtc	2.10 (s)	4.35 (d)	6.47 (s)
(s): simplet and (d): duplet			

Conclusions

The complex was obtained in good yield and high purity. The tridentate dithiocarbazate used is able to form an air stable complex with technetium(V) center, with potentiality for the medicinal radiochemistry, once substitutions in their periphery are possible to be made, without changing its donor abilities, but changing some properties of the complex formed, such as lipophilicity, solubility or polarity.

Acknowledgements

This work was supported by FAPESP, CNPq and CAPES-PROBRAL

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2904.

Synthesis and characterization of a mononuclear nickel complex

*** Laís S. Matos (IC)[1], Claudia Pereira (IC)[2], Rosely A. Peralta (PQ)**

*** laissottili@hotmail.com**

Universidade Federal de Santa Catarina- Departamento de Química, Laboratório de Bioinorgânica e Cristalografia – Campus Universitário-CEP-88040-900-Florianópolis-SC-Brazil.

Keywords: *Biomimetic Synthetic, Antioxidant Enzyme.*

Introduction

Cells within the brain, particularly neurons, are highly vulnerable to the detrimental effects of reactive oxygen species (ROS). This occurs because of their high metabolic rate, rich composition of fatty acids prone to peroxidation, high intracellular concentrations of transition metals capable of catalyzing the formation of reactive hydroxyl radicals, low levels of antioxidants, and reduced capability to regenerate. The Mn-catalase enzyme present inside the cells is a natural antioxidant that combats this process. For this reason, researchers are continuously developing manganese complexes to act as biomimetic of this natural enzyme.

Results and Discussion

The ligand **H_2L1** was synthesized in two stages.

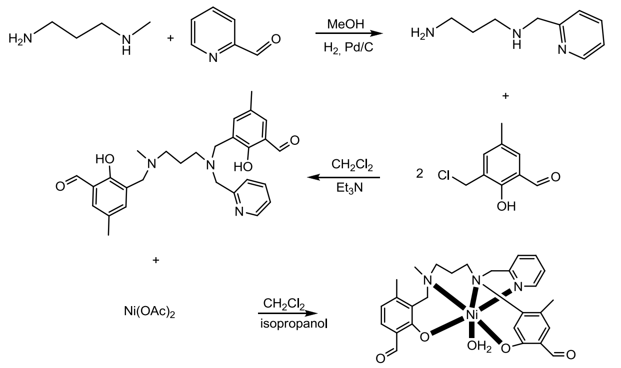

Figure 1 Schematic overview of ligand and complex.

In the first stage, 5 mmol of *N*-methyl-1,3-propanediamine were dissolved in methanol. To this solution, it was added 2-pyridinecarboxaldehyde previously dissolved in methanol. The reaction mixture stayed in agitation by 24 hours. The formed imine was reduced with H_2/Pd/C. In the second stage, the amine was slowly added to 2.9 mmol of triethylamine and 7.62 mmol of cmff previously dissolved in dichloromethane. The reaction mixture was maintained under reflux for 12 hours. The organic layer was washed with an aqueous $NaHCO_3$ solution (6x20 mL). With this ligand was synthesized a mononuclear nickel(II) complex **(1)**.

The synthesis of the complex was formed by adding 0.5 mmol of the ligand in a dichloromethane/isopropanol 3:1 v/v containing 0.5 mmol of nickel(II) acetate, under stirring and mild heating (40°C). Finally, 1 mmol of triethylamine were added. The ligand and the complex (**1**) were characterized by infrared. The band at 2850 cm^{-1} is characteristic of stretching of C-H bond of aldehyde and the band at 1684 cm^{-1} is assigned to C=O of aldehyde. The band at 1619 cm^{-1} is attributed to the stretching of C=C and C=N bonds. The band at 1371 cm^{-1} is attributed to stretching of O-H bond of phenol[2]. The infrared absorptions of (1) showed the same characteristic bands due to the complexation of the ligand, as expected. The value obtained for the conductivity was 7.23 $mS.cm^{-1.}$ According Geary[1], molar conductivity values below 120 $\Omega^{-1}.mol^{-1}.cm^2$ are typical of neutral substances. The electronic spectrum of the complex NiL1 presented two bands. The first one has a maximum wavelength about 606 nm, with ε of 14 $L.mol^{-1}.com^{-1}$ that is characteristic from d-d electronic transitions of the ion Ni(II). The second one has maximum wavelength about 389 nm with ε of 5148 $L.mol^{-1}.cm^{-1}$ shows the charge transfer from the phenolate to the Ni(II).

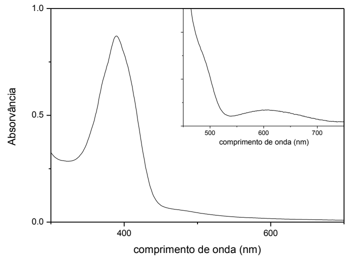

Figure 2 Electronic spectrum of (1), in acetonitrile solution. (6.67 x 10-5 mol L-1) and (1.0 x 10-5 mol L-1 in detail)

Conclusions

The mononuclear nickel(II) complex with the ligand H_2L1 was synthesized and characterized by Infrared and electronic UV-Vis spectroscopies and conductivity. In order to use the coordination compounds synthesized in the degradation of reactive oxygen species, other characterizations are still needed.

Acknowledgements

The authors thank CNPq, CAPES, FAPESC, UFSC.

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Organoindium(III) one-dimensional polymers with alkyl diphosphine oxide spacers

Rafael P. das Chagas (PQ)[1]*, Clovis Peppe (PQ)[2], Robert A. Burrow (PQ)[2], Liérson B. de Castro (PQ)[3], Felipe C. Wouters (IC)[2], Jaqueline P. Vargas (PG)[1], Melina A. Mello (PG)[2]

***rafael.pchagas@gmail.com**

[1] *Universidade Federal do Rio Grande do Sul, Porto Alegre-RS, Brazil*
[2] *Universidade Federal de Santa Maria, Santa Maria-RS, Brazil*
[3] *Universidade Federal da Fronteira Sul, Erechim-RS, Brazil*

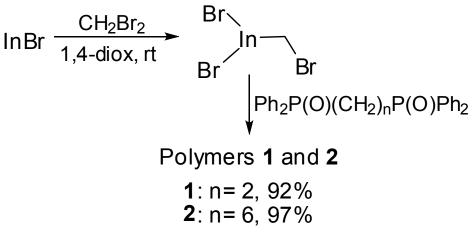
Keywords: *indium, halogenomethylene complexes, one-dimensional polymers.*

Introduction

The ability of the Br_2InCH_2Br to coordinate independently to hard and soft bases through its two different electrophilic sites suggests that these indium halogenomethylene complexes are potential starting materials to obtain novel metal organic frameworks (MOF's).[1,2] In this work we investigated the conditions to prepare adducts of Br_2InCH_2Br using diphosphine oxides acting as hard ligands, and now we report the synthesis and molecular structure of two organoindium(III) one-dimensional polymers with alkyl diphosphine oxide spacers.

Results and Discussion

Br_2InCH_2Br, obtained from the oxidative insertion of indium(I) bromide into a carbon–halogen bond of dibromomethane, was reacted with the hard donor ligands $Ph_2PO(CH_2)_nPOPh_2$ to afford the corresponding linear coordination polymers $[Br_2(CH_2Br)In\{OP(Ph)_2(CH_2)_n(Ph)_2PO\}]_\eta$, where n = 2, **1** and n = 6, **2** (Scheme 1).



Scheme 1. Preparation of polymers **1** and **2**.

Compounds **1** and **2** were produced as white solids in 92% and 97% of yield, respectively. The molecular formulae of both compounds were established by elemental analysis. The crystal structures of **1** and **2** were determined using single crystal X-ray diffractometry, showing that both are one-dimensional polymers interlinked by diphosphine oxide molecules. Also, for both, the indium center is five-coordinated with trigonal bipyramidal geometry, where the equatorial positions are occupied by two bromine atoms and one bromomethylene ligand and the apical positions by the oxygen atoms of two different molecules of the diphosphine oxide spacer ligands (Figures 1 and 2).

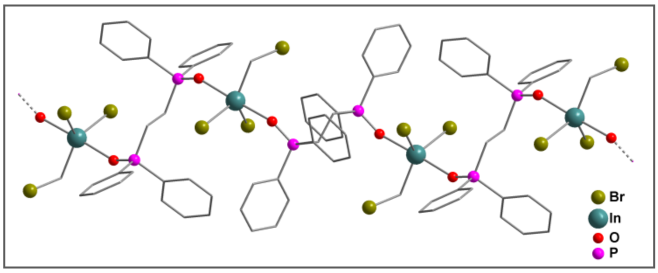


Figure 1. Polymeric structure of $[Br_2(CH_2Br)InOP(Ph)_2(CH_2)_2(Ph)_2PO]_\eta$

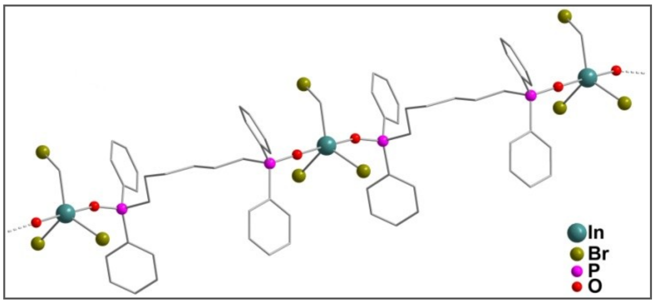


Figure 2. Polymeric structure of $[Br_2(CH_2Br)InOP(Ph)_2(CH_2)_6(Ph)_2PO]_\eta$

Conclusions

We have synthesized and characterized two new organoindium(III) one-dimensional polymers with alkyl diphosphine oxide spacers. We expect to use the full coordinating ability of the Br_2InCH_2Br, in reactions with bidentate soft and hard ligands, to synthesize some new one- and two-dimensional metal organic frameworks (MOF's) of indium, which we shall report briefly.

Acknowledgements

We are grateful to CNPq and CAPES.

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Copper Complex with a Thiosemicarbazone Derivative Ligand

Mónica Soto Monsalve (PG)[1], Pedro Ivo da S. Maia (PG)[1], Claudia C. Gatto (PQ)[2], Davi F. Back (PQ)[3], Victor M. Deflon (PQ)[1]*

***deflon@iqsc.usp.br**

[1] *Institute of Chemistry, University of São Paulo, São Carlos, Brazil*
[2] *Institute of Chemistry, University of Brasília, Brasília, Brazil*
[3] *Department of Chemistry, Federal University of Santa Maria, Santa Maria, Brazil*

Keywords: *copper(II) complex, thiosemicarbazone, crystal structure.*

Introduction

Thiosemicarbazones embody a class of *N,S*-donor ligands, which can present diverse coordination modes to metal centers and can possess different biological activities[1,2]. Various references evidence an enhancement of the aforementioned thiosemicarbazones's activity by coordination to metal ions in different oxidation states[3].

Results and Discussion

The complex [(apct)Cu(μ-Cl)$_2$Cu(apct)] (**1**), where apct represents the monoanion of 2-acetylpyridine-N(4)-cyclohexyl-thiosemicarbazone, was synthesized and characterized by IR, elemental analysis and X-ray diffraction.

Methanol solutions of copper chloride (0.20 mmol) and Hapct (0,20 mmol) where mixed with posterior addition of three drops of triethylamine. The reaction mixture was refluxed for four hours.

A binuclear complex was obtained in 86 % yield, the copper center presents a distorted square pyramidal coordination geometry, with the anionic thiosemicarbazone coordinated in a *N,N,S*-tridentate form and two bridging chloro ligands completing the coordination sphere of the metal. Melting points for the complex and for the Hapct ligand are in the range of 215-219 °C and 152-155 °C, respectively.

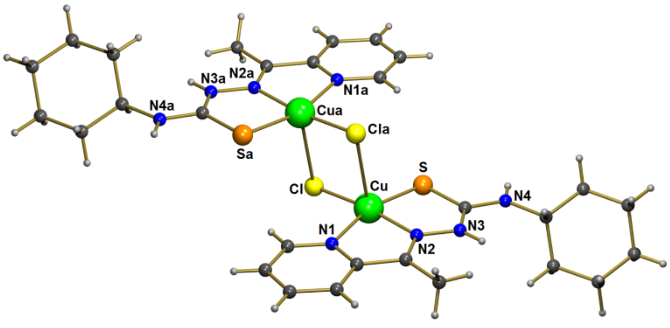

Figure 1. X-ray molecular structure of complex 1.

Table 1. Elemental analysis for 1 (%).

	C	H	N
Found	43,65	5,54	13,77
Calculated	44,91	5,13	14,97

Table 2. IR data from KBr pellets (cm^{-1}).

Compound	ν(C=N)	ν(N-H)	ν(C-H)
Hapct	1580	3329 3222	2932 2850
1	1600	3262	2926 2851

Table 3. X-Ray refinement data for 1.

Molecular formula	$Cu_2Cl_2S_2N_8C_{28}H_{40}$
crystal system	triclinic
space group	$\bar{1}$
a, b, c	8.1423(4),10.3081(5), 10.3733(5)
α, β, γ	98.102(2), 106.910(2), 92.316(2)
R_1/wR_2	0.0246/0.0686

Conclusions

The complex was obtained in satisfactory yield and high purity.

The stability of the complex and the high synthetic potential of thiosemicarbazone ligands justify the use of this class of compounds in further experiments, particularly involving studies of biological activity.

Acknowledgements

This work was supported by FAPESP, CNPq and CAPES-PROBRAL

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Synthesis and characterization of metal-organic frameworks containing a mixture of metals

Ricardo B. Ferreira (PG)[1]*, Perry M. Scheetz (IC)[2] and André L. B. Formiga (PQ)[1]

***ricardobferreira@gmail.com**

[1]*Instituto de Química, Universidade Estadual de Campinas – UNICAMP, P.O.Box 6154, Zip Code 13083-970, Campinas – SP, Brazil.*
[2] *Bard College, 30 Campus Road, Annandale-on-Hudson – NY 12054, USA.*

Keywords: *MIL-101, porous materials, metal-organic frameworks.*

Introduction

M*etal-organic frameworks* (MOFs) are 3D porous structures produced by the junction between transition metal ions or clusters and rigid organic linkers.[1] Usually, these materials are porous solids which feature high surface area and low density,[2] being applied to processes such as gas separation and storage and heterogeneous catalysis.

In 2005, Férey *et al.* reported the synthesis of a new MOF called MIL-101, formed by trinuclear clusters of Cr(III) and terephtalic acid anions, obtaining a crystalline structure with surface area in the order of 5900 $m^2.g^{-1}$.[3]

In the present study, we aim to obtain materials with crystalline structures analogous to MIL-101 using a system composed by a mixture of chromium and ruthenium trivalent cations in order to incorporate ruthenium in some metal sites in the framework.

Results and Discussion

The results have been achieved substituting a percentage of the amount of chromium nitrate used in original synthesis by an amount of ruthenium chloride. We have obtained samples using reaction media composed by 100, 67, 33, 25, 20, 11 and 6% of ruthenium.

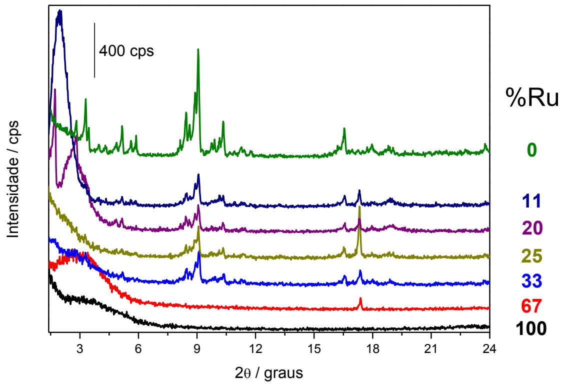

Figure 1. PXRD patterns of the samples obtained using a mixture of chromium and ruthenium salts. The ruthenium percentages used in the preparation of the samples are indicated.

The powder X-ray diffraction pattern of each sample is presented in Figure 1, where we can conclude that using systems with higher ruthenium amount generates lower crystalline materials. Moreover, the samples produced in the 100% and 67% of ruthenium input have not presented evidences supporting the formation of the MIL-101 structure.

The samples were also characterized by infrared spectroscopy and the resulting spectra are presented in Figure 2. The spectra present two characteristic strong bands in the 1600-1350 cm^{-1} range, which can be assigned to asymmetrical and symmetrical stretching vibrational modes of coordinated carboxylates.

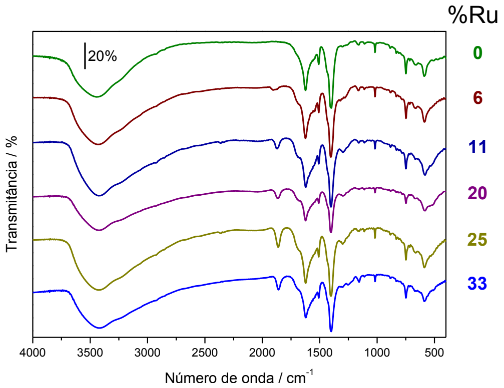

Figure 2. IR spectra of the samples obtained using different percentages of ruthenium.

Conclusions

Materials showing MIL-101 structure have been produced using systems with mixtures of Cr(III) and Ru(III). Further analyses are necessary to indicate the incorporation of ruthenium in the structure.

Acknowledgements

We thank to FAPESP (process #2010/13914-2), CNPq (process #479415-2009-9) and National Science Foundation (NSF-FAPESP program).

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Synthesis and structural characterization of the tetranuclear palladium chalcogenolato-acetato complex $[Pd(TeC_6H_3(CH_3O)_2)(O_2CCH_3)]_4$

Bárbara Tirloni (PG)[1]*, Vânia D. Schwade (PG)[1], Ernesto S. Lang (PQ)[1], Vinicius R. de M. Ferro (IC)[1]

***batirloni@yahoo.com.br**

[1] *Laboratório de Materiais Inorgânicos, Depto. de Química, Universidade Federal de Santa Maria, Santa Maria, Brasil.*

Keywords: *crystal structure, tellurium, palladium.*

Introduction

The study of transition metal chalcogenolate complexes is one of the most actively explored fields of inorganic/metal organic chemistry, mainly due to the bonding diversity, reactivity, and potential application of respective compounds as precursors for metal chalcogenide phases *via* low temperature routes. This bridge to material sciences due to the well-known opto-eletronic properties, catalytic and certain biological activities of numerous metal chalcogenides.[1-4]

In this communication, we are reporting the synthesis and properties of the tetranuclear palladium chalcogenolato-acetato complex $[Pd(TeC_6H_3(CH_3O)_2)(O_2CCH_3)]_4$ (**1**).

Results and Discussion

The compound **1** was synthesized by reaction of $[Hg(TeC_6H_3(CH_3O)_2)_2]$ with palladium(II) acetate in tetrahydrofuran at room temperature (Scheme 1). Dark red crystals of **1** were obtained.

$$2\,[Hg(TeC_6H_3(CH_3O)_2)_2] + 4\,[Pd(O_2CCH_3)_2] \xrightarrow[\text{room temperature}]{\text{tetrahydrofuran, stirring for 4 hours}} [Pd(TeC_6H_3(CH_3O)_2)(O_2CCH_3)]_4 + 2\,[Hg(O_2CCH_3)_2]$$

(**1**, 48%)

dark red crystals

Scheme 1. Synthesis of compound **1**.

The compound **1** shows paddle-wheel type geometry with a square planar coordination environment at the palladium atoms. Each of the divalent palladium cations being surrounded by two oxygen atoms of the acetate and two tellurium atoms of the tellurolate ligands (Figure 1).

Owing to a heteroleptic bridging mode by two (O_2CCH_3) or two $(TeC_6H_3(CH_3O)_2)$ units, respectively, the four Pd atoms form a rectangle with two $[Pd_2(O_2CCH_3)_2]^{2+}$ units (Pd-Pd 2.925(7) Å, within the range of known bonds in d^8 Pd compounds), being linked by four $(TeC_6H_3(CH_3O)_2)^-$ groups at two longer, non-bonding Pd···Pd contacts (3.753(2) Å).

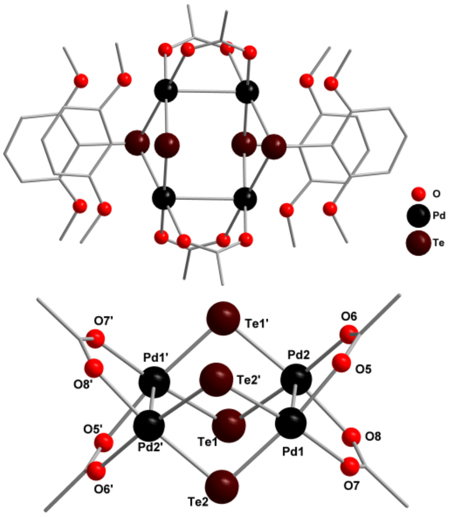

Figure 1. Molecular structure of **1** in two different views. Hydrogen atoms were omitted (bottom: $(TeC_6H_3(CH_3O)_2)$ groups were omitted).

The UV-Vis absorption spectrum of **1** was measured in the solid state and at room temperature. The estimated HOMO-LUMO gap found is 1.93 eV (643 nm). This energy value is typical optical band gap in solid state for palladium-chalcogenolato complex, and is in agreement with data from literature.[1,3]

Conclusions

The reaction of $[Hg(TeC_6H_3(CH_3O)_2)_2]$ and palladium(II) acetate offers a facile way to yield palladium-chalcogenolato complex.

The optical properties of **1** are dictated primarily by the identity of the core metal ions, and these properties give it a potential use in different areas.

Acknowledgements

CAPES, CNPq and FAPERGS.

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Synthesis and structural features of new aryltellurenyl iodides.

Cesar B. Pereira (PG)[1], Eliandro Faoro (PG)[1*], Gelson M. de Oliveira (PQ)[1] and Ernesto S. Lang (PQ)[1]

***e_faoro@yahoo.com.br**

[1] *Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, Santa Maria, RS, Brazil.*

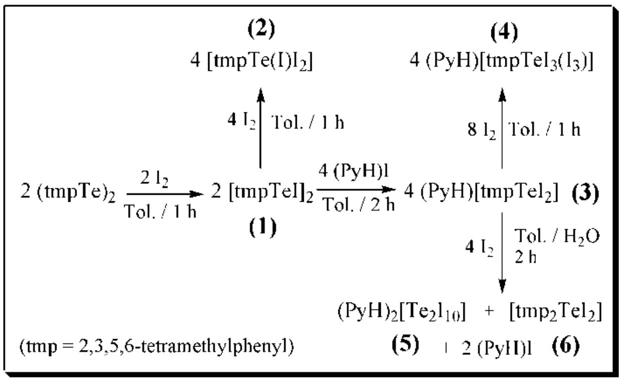
Keywords: *Polymeric organotellurium iodides, Hypervalent complexes of Te^{II}, Secondary interactions.*

Introduction

The increasingly interesting and attractive chemistry of organyltellurenyl iodides affords, worldwide, the emergence of new experimental routes to achieve compounds with innovative architectural designs. The reactions of diarylditellurides $(RTe)_2$ with iodine have been experimentally studied with the purpose of obtaining Te^{II} and Te^{IV} compounds, as well as mixed-valent aryltellurenyl iodides and related charge-transfer complexes. It is well known that uncommon compositions and configurations are characteristic for these types of compounds.[1,2] Almost as a rule, tellurium(II) and tellurium(IV) iodide compounds attain all possible combinations of secondary, interionic interactions. As part of our research on further effects of the ligand R on the stabilization and structure of aryltellurenyl iodides, we describe in this work the syntheses and the structural characterization of the intermediary $[tmpTeI]_2$ (**1**) and of the new complexes $[tmpTe(I)I_2]$ (**2**), $(PyH)[tmpTeI_2]$ (**3**), $(PyH)[tmpTeI_3(I_3)]$ (**4**), $(PyH)_2[TeI_4(\mu\text{-}I)_2TeI_4]$ (**5**) and $[tmp_2TeI_2]$ (**6**) (tmp = 2,3,5,6-tetramethylphenyl).

Results and Discussion

The preparation of all complexes mentioned and discussed in this work is resumed in Scheme 1. The syntheses and recrystallizations of compounds **1**–**4** were carried out under Ar atmosphere. Structurally, these compounds were characterized by single crystal x-ray diffraction, which showed the presence of intra- or intermolecular secondary bonds Te···Te, Te···I, I···I, beyond hydrogen bonds N–H···X.



Scheme 1. Reactions of $(tmpTe)_2$ (tmp = 2,3,5,6-tetramethylphenyl).

As is also depicted in Scheme 1, our reaction of $(tmpTe)_2$ with I_2 affords initially 2 equiv of $[RTeI]_2$ (**1**), (figure 1) which reacts with 4 equiv of iodine which causes the splitting of the Te–Te bond to give $[tmpTe(I)I_2]$ (**2**).

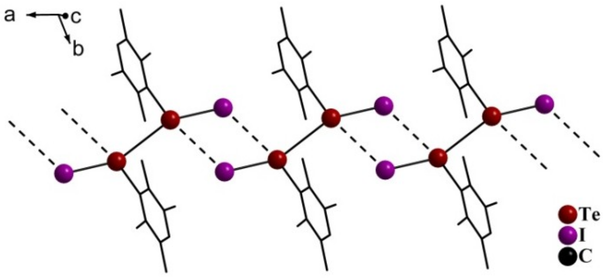


Figure 1. Molecular structure of $[tmpTeI]_2$ (**1**) and the one-dimensional assembling along the *a* axis.

The hypervalent, 3c–4e T-shaped compound $(PyH)[tmpTeI_2]$ (**3**) can be represented by 10–Te–3, according to the N-X-L notation proposed by Martin.[3]

The complex $(PyH)[tmpTeI_3(I_3)]$ (**4**) represents a rare example of Te^{IV} compound in which a I_3^- chain appears as component of the complex and not as solvate, as normally occurs.[4]

Complex $(PyH)_2[TeI_4(\mu\text{-}I)_2TeI_4]$ (**5**), represents the first main product of this work obtained in the presence of water. The aryltellurenyl iodides synthesized in these conditions undergo stoichiometric rearrangement of the R–Te^{II} bond, with its partial cleavage under oxidation to Te^{IV} and subsequent addition of the R group to a Te^{II} substract $\{R_2Te{\cdot}I_2$ (**6**)$\}$.

Conclusions

These new products corroborate to the versatility of aryltellurenyl iodides, regarding reactivity and structure, as well as the close dependence of these factors with the substituent R.

Acknowledgements

This work was supported with funds from PRONEX-CNPq/FAPERGS (Brazil).

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Synthesis and structure of new aryltellurenyl halides with mixed or uncommon valences.

Eliandro Faoro (PG)[1*], Gelson M. de Oliveira (PQ)[1], Ernesto S. Lang (PQ)[1] and Douglas G. Ribas (IC)[1]

***e_faoro@yahoo.com.br**

[1] *Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, Santa Maria, RS, Brazil.*

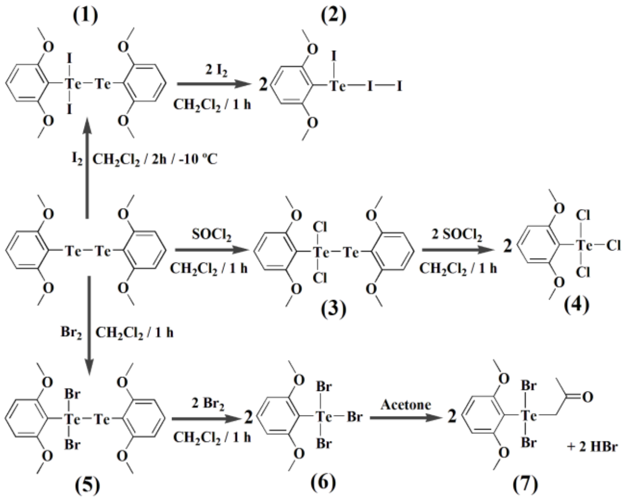
Keywords: Organyltellurium halogenides, Secondary interactions, Supramolecular assemblies.

Introduction

The halogenation of diarylditellurides $(RTe)_2$ has been experimentally studied in recent years with the purpose of obtaining Te^{II} and Te^{IV} compounds, as well as mixed-valent aryltellurenyl halides and related charge-transfer complexes.[1,2] Since the chemistry of organotellurium halides is becoming more and more interesting and attractive, we have developed new experimental routes to reach compounds with innovative architectural designs. Thus, in this work will be reported synthetic routes used for the synthesis of new aryltellurenyl halides, based on the $(RTe)_2$ (R = 2,6-dimethoxyphenyl).

Results and Discussion

The reactions of bis(2,6-dimethoxyphenyltellurium) under different conditions presented in this work are summarized in Scheme 1. The syntheses and recrystallizations of compounds **1**–**7** were carried out under Ar atmosphere. Structurally, that compounds were characterized by single crystal x-ray diffraction, which showed the presence of intra- or intermolecular secondary bonds Te···Te, Te···O, Te···X and X···X (X = halogen), responsible for the organization of supramolecular assemblies in the solid state.

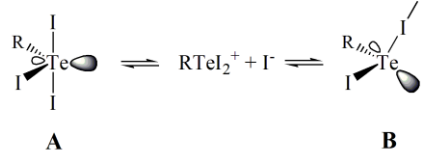


Scheme 1. Reactions of $(RTe)_2$ (R = 2,6-dimethoxyphenyl).

The compounds **1**, **3** and **5** with vicinal, asymmetrically substituted Te atoms with oxidation numbers 1+ and 3+, exemplifies the steric effect of the 2,6-dimethoxyphenyl group in regard to the stabilization of unusual structures, as well as the selective oxidative character obtained for these species.

The subsequent addition of two more equivalents of halogen (I and Br) or $SOCl_2$, has led to the formation of compounds **2**, **4** and **6**, respectively.

The open Te–I–I angle [171.15(18)°] of **2** allows us to consider the species $RTe(I)I_2$ as a RR'E·X_2, three-coordinated molecular complex (MC).[3] The hypervalent 3c–4e atoms in Te–I–I (MC) are represented by 10–I–2, according to the N-X-L notation proposed by Martin and co-workers.[4] An alternative configuration for **2** would be the TBP $RTeI_3$ (10–Te–4). Probably, this realizable form was hindered by the interactions with bulky neighbor molecules, forcing the preferential three-coordinated configuration (B, Scheme 2) because the increased bulkiness around Te prefers MC to TBP.



Scheme 2. TBP and MC configurations for $RTeI(I_2)$.

The dissolution of complex **6** in acetone and further recrystallization leads to the substitution of Br by one $CH_3COCH_2^-$ anion, with HBr elimination and formation of $[RTeBr_2(CH_2–C(O)–CH_3)]$ (**7**).

Conclusions

Based on the results obtained, we can presume that the two methoxy groups of 2,6-dimethoxyphenyl are particularly able to stabilize tellurium iodides in mixed-valent, unusual compositions.

Acknowledgements

This work was supported with funds from PRONEX-CNPq/FAPERGS (Brazil).

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Synthesis, structure and luminescence studies of new Eu(III) complex with 2,6-Diformylpyridine derivative.

Geraldo W. Gomes (IC)[1*], Gelson M. de Oliveira (PQ)[1], Tiago Bessega (PG)[1], Gustavo R. Bolzan (IC)[1].

***geraldowg@hotmail.com**

[1] *Universidade Federal de Santa Maria, UFSM, Departamento de Química, 97105-900 Santa Maria, RS, Brazil*

Keywords: *Coordination Chemistry, Lanthanide Complexes, Eu(III) Luminescence.*

Introduction

Reactions of lanthanides with polydentate oxygen and nitrogen ligands have attracted great interest because of the ability of these (hard base) sites to realize stable chelate complexes with high coordination numbers.[1,2] In addition, we have already shown that some polydentate nitrogen ligands are able to transfer energy to a lanthanide ion, thus exciting its luminescence – the so-called "antenna" effect.[3] We report now a result on the complex structural chemistry of lanthanides and ligands derived from 2,6-diformylpyridine, together with luminescence studies carried out with the new chelates [Eu(dfpbpsc–H$^+$)$_2$]NO$_3$ **(1)**, where dfpbpsc is 2,6-Diformylpyridin-bis(4-phenylsemicarbazine)

Results and Discussion

To a suspension of 0.0401 g (0.1 mmol) of dfpbpsc in 10 mL of ethanol, a solution of 0.0214 g (0.05 mmol) of $Eu(NO_3)_3.5H_2O$ in 5 mL of ethanol was added. After addition of three drops of triethylamine the suspension was refluxed by 3 h. The red mixture was then cleaned by filtration. The slow evaporation of the solvent led to the formation of yellow crystals. Yield: 53% based on $Eu(NO_3)_3.5H_2O$.

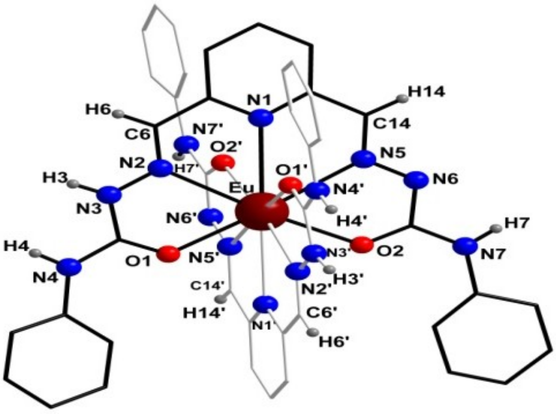

Figure 1. [Eu (dfpbpsc-H)$_2$] NO$_3$

Properties: yellow crystalline substance. Melting point: 276 ºC. Anal. Calc. for $C_{42}H_{36}EuN_{16}O_{10}$ (1076.82): C, 49.69%; H, 7.42%; N, 14.74%. Found: C, 49.71%; H, 7.58%; N, 14.85%. IR (KBr): 3384.2 [ms(N–H), strong], 1597.1 [ms(C=C), medium], 1693.2 [ms(C=O), strong], 1237.6 [ms(N=C), medium], 1163.6 cm^{-1} [ms(N–N), medium].

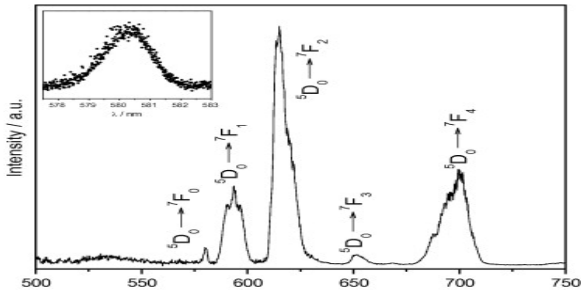

Figure 2. Emission spectrum of [Eu(dfpbpsc–H$^+$)$_2$]NO$_3$.

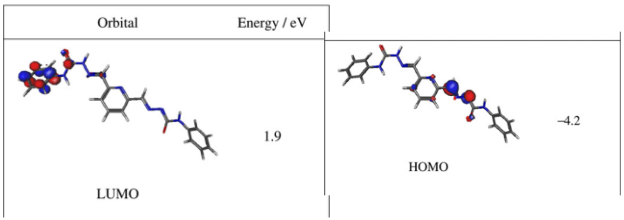

Figure 3: HOMO and LUMO of the coordinated ligand dfpbpsc–H+.

The energy gap ranges from _4.2 to 1.9 eV and the HOMO are localized manly in the deprotonated side of the ligand, embracing the C=N–N¯C=O atoms/bonds, whereas the LUMO are located on the carbonyl group and on the terminal phenyl rest of the protonated ligand side.

Conclusions

The new synthesized complexe show that coordination can not be considered unusual for lanthanide chelates. The low level of covalence in the coordinated bonds of europium-ligand could also be calculated. The geometry of the ground state calculated from Sparkle/AM1 is in good agreement with the geometry from data obtained by X-ray diffraction on single crystal. The Eu(III) complexe showed luminescent properties.

Acknowledgements

This work was supported with funds from CAPES, CNPq, FAPESP and FAPERGS

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Synthesis and crystal structure of 2,6-Diacetylpyridin-bis(benzoylhydrazine)lanthanide(III) complexes.

Tiago Bessega (PG),[1]* Gelson M. de Oliveira (PQ),[1] Gustavo R. Bolzan (IC),[1] Geraldo W. Gomes (IC).[1]

***tiagobessega@gmail.com**

[1]Laboratório de Materiais Inorgânicos, Departamento de Química, Universidade Federal de Santa Maria, UFSM, 97105-900, Santa Maria, RS, Brazil

Keywords: *Coordination Chemistry, Lanthanide Complexes.*

Introduction

The photoluminescence properties of lanthanide compounds have been fascinating researchers for decades. An attractive feature of luminescent lanthanide compounds is their line-like emission, which results in a high color purity of the emitted light.[1] Polydentate oxygen and nitrogen ligands have attracted great interest because of the ability of these sites to realize stable chelate complexes.[2] In addition, it has been shown that some polydentate nitrogen ligands are able to transfer energy to a lanthanide ion, thus exciting its luminescence.[3] We report some results on structural chemistry of lanthanides complexes with 2,6-diacethylpyridine based ligands: Bis(2,6-diacetylpyridin-bis-enzoylhydrazine)lanthanide(**III**)-chloride Ethanol/Wather-Solvat $[Ln(H_2L_1{}^a)_2]Cl_3 \cdot 2H_2O \cdot 3EtOH$ where Ln = Gd **(1)**, Dy **(2)** and Ho **(3)**.

Results and Discussion

All the complexes were synthesized following the same standard procedure. A solution of 0.25 mmol of hexahydrated lanthanide(**III**) chloride in 10 mL of ethanol was added to a solution of 0.5 mmol of H_2L_1 in 15 mL of ethanol. The solution was stirred under reflux by 3 h and then filtered. The solvent slow evaporation yielded yellow crystals of **1**, **2** and **3**. Yield: 36%, 83% and 88% respectively based on Ln salt.

The complexes **1**, **2** and **3** were analyzed by single crystal X-ray diffraction, which showed that three isostructural complexes **(Table 1)**. The lanthanide ions is decacoordenated by two chelate ligands. Some bond lengths are listed in **Table 2.** Lanthanide ion charge is balanced by three chloride ions.

Table 2: Main bond lengths of compounds **1**, **2** and **3**.

	1	**2**	**3**
Ln-O	2.464(7)*	2.3871(14)**	
Ln-N(py)	2.626((8)*		2.606(4)**
Ln-N(A)	2.574(8)*	2.4949(16)**	

* longer and **shorter

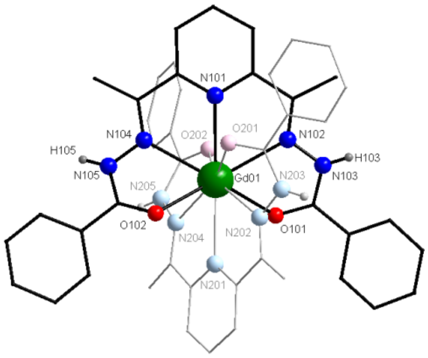

Figure 1: Cristal structure of compound **1**.

Table 1: Crystal data refinement for **1**, **2** and **3**.

	1	**2**	**3**
	$C_{52}H_{64}Cl_3Gd N_{10}O_9$	$C_{52}H_{64}Cl_3Dy N_{10}O_9$	$C_{52}H_{64}Cl_3Ho N_{10}O_9$
a (Å)	12.3293(16)	12.2796(5)	12.369(2)
b (Å)	13.6456(17)	13.4021(5)	13.587(2)
c (Å)	17.822(2)	17.6417(7)	17.825(4)
α (˚)	106.814(8)	106.601(2)	106.970(12)
β (˚)	94.946(9)	96.805(2)	94.840(13)
γ (˚)	95.236(9)	93.803(2)	95.061(12)
V ($Å^3$)	2838.2(6)	2747.36(19)	2834.8(9)

Conclusions

The synthesized complexes have an ideal structure for a luminescent material with a lanthanide emitter ion and a energy transfer ligand. The standard synthesis procedure was efficient for complexes with promising luminescent properties.

Acknowledgements

This work was supported from CAPES, CNPq, FAPESP and FAPERGS.

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Synthesis, characterization and supramolecular assemblies of novel ditelluroethers iodides.

Roberta Cargnelutti (PG)[1*] and Ernesto Schulz Lang (PQ)[1]

***rocargnelutti@yahoo.com.br**

[1] *Departamento de Química, Laboratório de Materias Inorgânicos, Universidade Federal de Santa Maria, Campus-Camobi, 97105-900 Santa Maria, RS, Brazil.*

Keywords: *ditelluroethers iodides, secondary interactions, supramolecular assemblies.*

Introduction

Several classes of organotelluronium halide compounds are known, including species of general formula $RTeX_3$, R_2TeX_2 and R_3TeX.[1] Compounds of organotelluronium halides have been an interesting field to research, due to the occurrence of secondary interactions Te···X, that can result in pseudo-polimeric[2] and supramolecular[3] assemblies. Among these organotelluronium halide compounds, stand out the ditelluroethers iodides, characterized by the formation of unusual arrangements, thus establishing an open field for further research.[4]

Results and Discussion

In the present work, two new compounds of ditelluroethers iodides are described. In order to examine the secondary interactions between Te/I, and the effect of these in coordination geometry of tellurium, crystallographic analysis by X-ray diffraction were used.

For the synthesis of compounds **1** and **2**, CH_2Cl_2 and THF were used as solvents, respectively, under N_2 atmosphere at room temperature, as the following equation.

$$RTe(CH_2)_4TeR + 2I_2 \xrightarrow{\text{solvent / r.t.}} RTeI_2(CH_2)_4TeI_2R$$

R= 4-$MeOC_6H_4$ (**1**) 59.23%; 2,6-$MeOC_6H_3$ (**2**) 30.5%

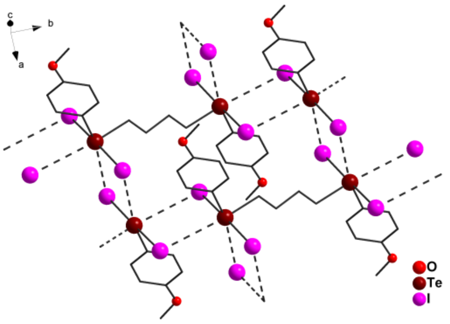

Fig. 1. Pseudo-polymeric projection for compound **1**.

In **Fig. 1** we observed the formation of a two-dimensional pseudo-polymer composed of molecules $\{4\text{-}MeOC_6H_4TeI_2(CH_2)_2\}_2$ through the secondary interactions Te···I, represented by the dashed lines. These distance bonds for Te···I are in the order of 3.865 Å – 3.886 Å.

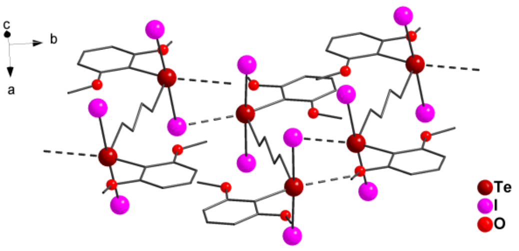

Fig. 2. Pseudo-polymeric projection for compound **2**.

The **Fig. 2** shows the formation of a pseudo-polymer between molecules of $\{2,6\text{-}MeOC_6H_3TeI_2(CH_2)_2\}_2$ that are connected through the secondary interactions Te···I. The dashed lines were used to represent them and the distance bonds are in order of 3.747 Å.

In **Table 1** are presented the some crystallographic data for the synthesized compounds.

Tab. 1. Crystallographic data of compouds **1** e **2**.

Compound	**1**	**2**
Empirical formula	$C_{18}H_{22}I_4O_2Te_2$	$C_{20}H_{26}I_4O_4Te_2$
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P2₁/c*
a/Å	11.5587(4)	13.9341(3)
b/Å	11.6679(4)	11.5256(3
c/Å	21.4250(7)	8.8825(2)
α/Å	90	90
β/Å	90.770(2)	100.311(1)
γ/Å	90	90
R_1;wR_2	0.0371, 0.0801	0.0347; 0.0827

Conclusions

Through the obtained results, we can conclude that ditelluroethers iodides show to be important precursors for the formation of supramolecular assemblies through secondary interactions.

Acknowledgements

CNPq / CAPES.

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Lamellar crystal structure of $[Mn(O_2Se\text{-}4\text{-}C_6H_4Cl)_2(H_2O)_4]$ formed by hydrogen bonds.

Giancarlo Z. Belmonte (PG)[1*] and Robert A. Burrow (PQ)[1]

***giancarlobelmonte@yahoo.com.br**

[1]*Universidade Federal de Santa Maria, Laboratory of Inorganic Materials (LMI), Santa Maria, Rio Grande do Sul, Brazil.*

Keywords: *seleninatos ligands, manganese(II) supramolecular compounds, crystal structure, hydrogen bonds.*

Introduction

Compounds with organylseleninato ligands are interesting since they can form supramolecular lamellar compounds in the form of coordination polymers or by intermolecular interactions.[1] This work presents the crystallized lamellar structure of $[Mn(O_2Se\text{-}4\text{-}C_6H_4Cl)_2(H_2O)_4]$ **1** formed by hydrogen bonds. The dehydration of **1** forms a crystalline powder $[Mn(O_2Se\text{-}4\text{-}C_6H_4Cl)_2]$ **2**.

Results and Discussion

Light brown plates of $[Mn(O_2Se\text{-}4\text{-}C_6H_4Cl)_2(H_2O)_4]$ **1** suitable for X-ray single crystal analysis were obtained by hydrothermal reaction in an oven with computerized temperature control programmed with a slow cooling ramp. The crystal structure was determined by X-ray diffraction on single crystal. Further characterization of the compound was performed by elemental and thermogravimetric analysis, infrared spectroscopy and X-ray diffraction powder diffraction. The structure of compound **1** was determined in space group $P2_1/c$. Some crystallographic parameters are presented in Table 1.

Table 1. Crystallographic parameters.

Molecular formula	$C_{12}H_{16}Cl_2MnO_8Se_2$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	16.262(8)
b (Å)	5.071(2)
c (Å)	12.010(6)
β (°)	108.78(2)
Volume (Å^3)	937.71(8)

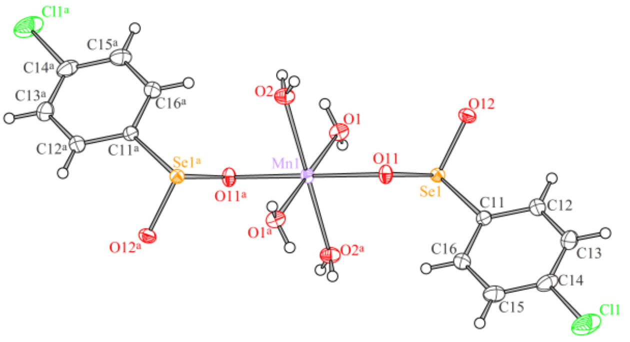

Figure 1. Molecular structure of **1**, showing the octahedral geometry of the Mn(II). Symmetry operation ^{a}: $1-x$, $1-y$, $1-z$.

In the crystal structure of **1**, the Mn(II) atom is situated on a center of inversion with half the molecule of **1** in the asymmetric unit. The complete molecule of **1** has a Mn(II) atom with octahedral geometry formed by two *trans* oxygen atoms, each from a 4-chlorophenylseleninato ligand, and four oxygen atoms from four water ligands, Figure 1. Hydrogen bonding creates a two-dimensional structure which extends parallel to the *bc* crystallographic plane, Figure 2. Compound **1** has a topology similar to the compound described by Schiødt *et al*[2] which shows interesting magnetic properties.

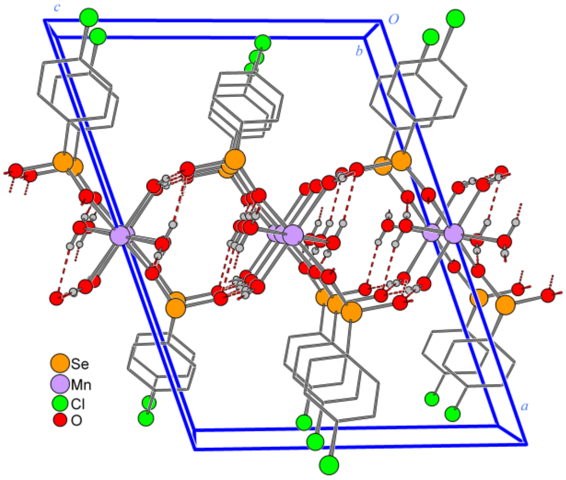

Figure 2. Projection of a lamellar structure in the direction of the crystallographic direction *b*.

Dehydration of **1** at 120 °C for 4 hours gave a light brown crystalline powder, $[Mn(O_2Se\text{-}4\text{-}C_6H_4Cl)_2]$ **2**. The powder shows a powder diffraction powder indicates a lamellar structure of higher symmetry than **1**. We believe that **2** is a two dimensional coordination polymer.

Conclusions

Two new supramolecular compounds with seleninato ligands was synthesized and characterized. Compounds **1** and **2** are a strong candidates for materials with useful magnetic properties due to the Mn(II) center. Also luminescent studies are planned.

Acknowledgements

CNPq, FAPERGS, CAPES and FINEP.

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Workshop sobre Química Inorgânica Sintética – WQIS (Workshop on Synthetic Inorganic Chemistry - WSIC)

Synthesis and characterization of the 2,6-bis(imidazol-2-yl)pyridine complex with copper(II)

Eduardo G. R. de Arruda[1]* (IC), Stella de Almeida Gonsales[1] (PG), André L. B. Formiga [1] (PQ).

*** earruda@gmail.com**

[1] *Laboratório de Química de Coordenação do Instituto de Química da Universidade Estadual de Campinas (UNICAMP). Cidade Universitária Zeferino Vaz, CP 6145, Barão Geraldo, Campinas-SP, Brazil.*

Keywords: *New ligands, metal complex, coordination chemistry.*

Introduction

The ligands based on 1H-imidazole are very interesting due to their high similarity with biological systems that enable their use in synthesis of complexes with potential biological activity. In the literature, many new complexes with these ligands are being studied[1,2]. In this work we synthesized and characterized the complex of 2,6-Bis (imidazol-2-yl) pyridine with Cu(II).

Results and Discussion

The ligand was synthesized from a nitrile in a "one-pot" reaction[3], the product was characterized by ^1H and ^{13}C NMR and UV-Vis spectroscopy and the results were consistent with those described before.[1]

The complex was synthesized by reacting a stoichiometric ratio of 2:1 ligand to metal, using copper(II) chloride as ions source.[1,2]

The ligand was dissolved in methanol and added to an aqueous solution of copper(II) chloride. After 20 minutes of stirring, the solution changed color to a dark green, indicating the reaction, and the complex was precipitated with the addition of ammonium hexafluorophosphate. After quantitative precipitation, the solid was filtered, washed with ethyl ether and dried.

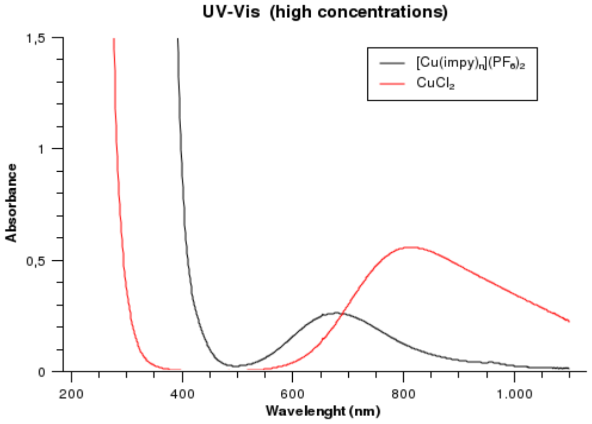
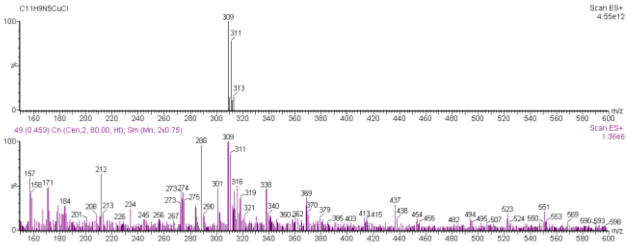


Figure 1. UV-Vis spectra of the copper(II) chloride and the complex.

Using UV-Vis spectroscopy (Fig.1) the copper(II) chloride was compared with the product obtained, and it was possible to observe a band shift indicating the reaction.



ESI-MS analysis indicated that the complex has a 1:1 Cu:L ratio with chloride completing the coordination sphere.

Figure 2. ESI-MS of the copper salt with the hypothesis of a 1:1 ligand-metal complex.

Others analyses are being made to complete the characterization.

Conclusions

The ligand and the complex were synthesized following the procedures described in the literature. Analyses indicate the coordination of copper with one 2,6-bis(imidazole-2-yl)pyridine and one chloride, following the 1:1 metal-ligand ratio.

Acknowledgements

The authors thanks the agencies FAPESP (2006/55367-2), CAPES and CNPq (Proc. 479415/2009-9)

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Synthesis, characterization and study of coordination chemistry of new compounds containing Indium and Tellurium

Thomaz A. Wioppiold (IC)[1], Melina de A. Mello (PG)[1]*, Ernesto S. Lang (PQ)[1], and Liérson B. de Castro (PQ)[2].

***melquimica@mail.ufsm.br**

[1] *Universidade Federal de Santa Maria, Santa Maria – RS, Brazil.*

[2] *Universidade Federal da Fronteria Sul, Erechim – RS, Brazil.*

Keywords: *indium(III) halides, tellurium species, coordination chemistry.*

Introduction

The search for new III/VI semiconductor materials has driven many research groups to study new synthetic methodologies that lead to this type of material and also to characterize them.[1]

According to research conducted in the database "*Cambridge Structural Database*" (CSD)[2] on August 20th, 2011, there are only 36 characterized compounds containing In and Te. This number is lower than compounds containing S and Se. This fact can be attributed to the different behavior of chalcogens towards indium.

Results and Discussion

This work is based on the reactive system shown in Scheme 1.

$$\mathbf{InX_3 + nL_{\mathit{hard}} + PhTeX_3 \xrightarrow{(\mathit{i})} [InX_2(L_{\mathit{hard}})_n]^+[PhTeX_4]^-}$$

(*i*) = MeOH, r.t.

1 = 74%
2 = 68%
3 = 87%
4 = 68%

Scheme 1. Reactive system proposed.

Indium(III) halides - InX_3 (X = Cl, Br) - react with phenyltellurium(IV) trihalides - $PhTeX_3$ (X = Cl, Br) - and hard ligands such as $OPPh_3$, 1,10-phenantroline (1,10-phen) and DMSO, to yield $[InX_2(OPPh_3)_4]^+[PhTeX_4]^-$ (X = Cl, **1**; X = Br, **2**), $[InBr_2(1,10\text{-phen})_2]^+[PhTeBr_4]^-$ (**3**) and $[InBr_2(DMSO)_4]^+[PhTeBr_4]^-$ (**4**). In Table 1 are shown the compounds **1** – **4** that were obtained according to the Scheme 1.

Table 1. Compounds $[InX_2(L)_n]^+[PhTeX_4]^-$.

Compound	X	*n*	L_{hard}
1	Cl	4	$OPPh_3$
2	Br	4	$OPPh_3$
3	Br	2	1,10-phen
4	Br	4	DMSO

The crystalline structure of all compounds was determined by X-ray diffraction. In all compounds, the halogen was dislocated from the indium coordination sphere to the tellurium coordination sphere by the hard ligand and all compounds are formed by an indium octahedral cation and a tellurium pyramidal quadratic anion as shown in the Figure 1.

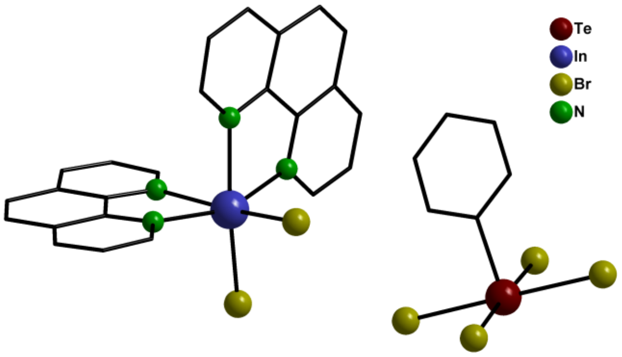

Figure 1. Molecular structure of compound **3**.

Conclusions

In this work were described 4 compounds containing In and Te in which tellurium shows a more pronounced metallic behavior towards indium. Eventually, the compounds obtained can be used as precursors in synthesis routes of semiconductors.

Acknowledgements

We are grateful to CNPq, CAPES and FAPERGS.

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Synthesis and structural characterization of a new macrocyclic compound containing Tellurium.

Poliana Reckziegel (PG)[1]*, Vânia D. Schwade (PG)[1], Davi F. Back (PQ)[1], Ernesto S. Lang (PQ)[1]
***poliziegel@yahoo.com.br**

1-Laboratório de Materiais Inorgânicos - LMI/ Universidade Federal de Santa Maria – RS – Brazil

Keywords: *Crystal structure, macrocycle, tellurium.*

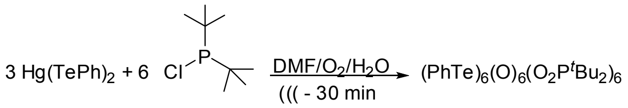
Introduction

Organotellurium ligands have applicability in organic chemistry[1], precursors of semiconducting materials[2], and biochemistry[3]. Over recent years, considerable effort has been directed towards the synthesis of macrocyclic ligands containing tellurium. Although the macrocyclic selenium compounds are known, derivatives containing tellurium in its constitution still have a few examples in the literature[4,5].

As examples of the literature involving macrocyclic tellurium formed by associations are phosphinoxide are uncommon[6], this work, so original, is directed to the development of synthetic methodologies and characterization by X-ray diffraction of these compounds.

Results and Discussion

The synthetic route to obtain the compound **1** is described in the Scheme 1, below:



Scheme 1. Reaction to obtain the compound **1**.

After the complete dissolution of mercury bis(phenyltelurolate) with the addition of phosphine, the solution was kept in ultrasound for 30 minutes and reserved for a period of two weeks. From reaction were obtained colourless crystals with a yield of approximately 70%, suitable for analysis by single crystal X-ray diffraction.

The crystal structure of **1**, shown in the Figure 1, reveals the formation of a 12 membered macrocycle involving six atoms of tellurium(IV) and six oxo ligands. The tellurium atoms are still connected in pairs by the di-*tert*-buthylphosphinate ligands, which are formed from the oxidation of phosphine, with consequent generation of $HgCl_2$. There was a positional disorder observed for the tellurium atoms, where it was possible to establish a proportion of 86/14% for both. The crystallographic data obtained for this new compound of tellurium are given in the table 1.

Table 1. Crystallographic data obtained for the compound **1**.

Compound	1
Formula	$C_{84}H_{138}O_{18}P_6Te_6$
Molecular weight	2387.34
Crystal system	Trigonal
Space group	R-3
a (Å)	28.7898(8)
b (Å)	28.7898(8)
c (Å)	11.0792(3)
γ (°)	120.00
R$_1$; *wR*$_2$	0.0646; 0.1997

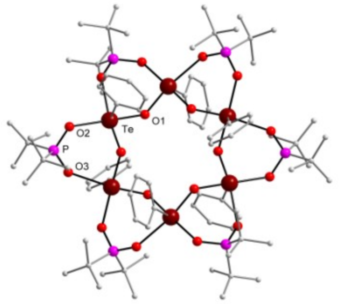


Figure 1. Representation of the molecular structure of the compound **1**. The hydrogen atoms were omitted for a better view.

Conclusions

This result shows that the methodology is very versatile for the elimination of mercury from the starting material. In addition, it should be noted that it is the first example of the literature with such structural form. Further studies will be performed by modifying the phosphines in order to increase the internal cavities of new products.

Acknowledgements

CNPq, CAPES and FAPERGS

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Synthesis and structural characterization of new coordination polymers containing Mercury.

Poliana Reckziegel (PG)[1]*, Davi F. Back (PQ)[1], Ernesto S. Lang (PQ)[1]

***poliziegel@yahoo.com.br**

1-Laboratório de Materiais Inorgânicos - LMI/ Universidade Federal de Santa Maria – RS – Brazil

Keywords: *Structure, coordination polymers, mercury.*

Introduction

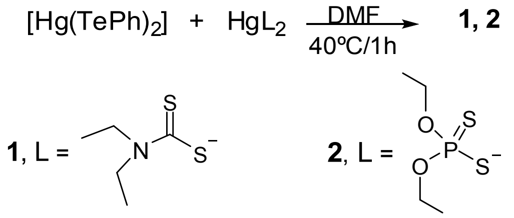
Coordination polymers has aroused great interest in the fields of supramolecular chemistry and crystallochemical due to its variety of architectures[1], wide potential application in catalysis[2], gas storage[2,3], magnetism[3] and electric conductivity[4].

These polymers can be considered a supramolecular arrangement originated in the reactions of self organization of organic ligands an metal units, where the repeating units extend through metal-ligand interactions in one-, two-, and tridimensional structures.

Organic ligands, such as carbamate derivatives[5], are very important in building this structural species, since some changes can lead to formation of a class of materials with different architectures and functions. This work is directed to the replacement of ligands.

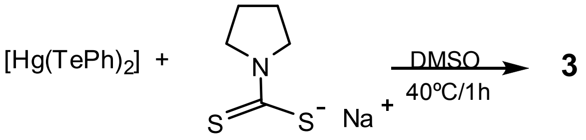
Results and Discussion

The synthetic route to obtain compounds **1** and **2** is described in Scheme 1, while the synthesis of compound **3** is shown in Scheme 2:



$$[Hg(TePh)_2] + HgL_2 \xrightarrow[40ºC/1h]{DMF} \mathbf{1, 2}$$

Scheme 1. Reaction to obtain the compounds **1** and **2**.



$$[Hg(TePh)_2] + \text{pyrrolidine-}N\text{-}C(=S)S^- Na^+ \xrightarrow[40ºC/1h]{DMSO} \mathbf{3}$$

Scheme 2. Reaction to obtain the compound **3**.

From these reactions were obtained crystals in good yields, suitable to analysis by X-ray diffraction on single crystal. The Figure 1 shows the crystal structures of the compounds.

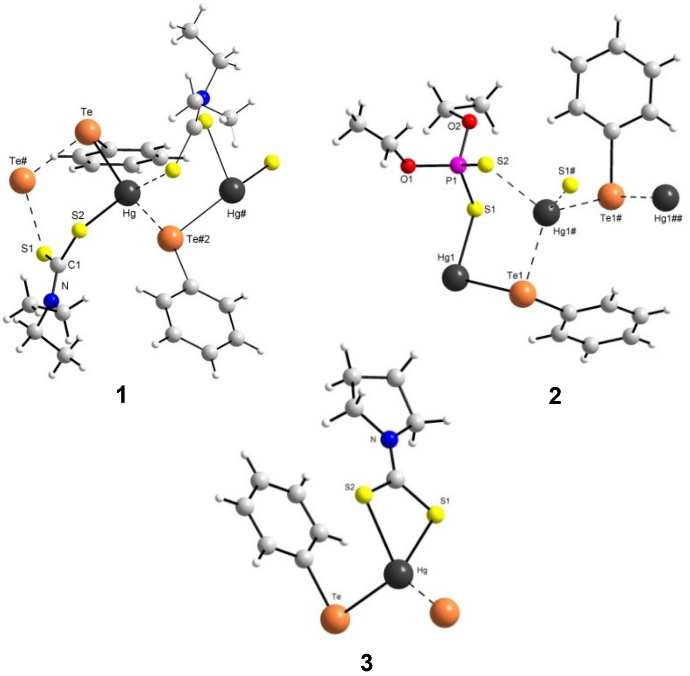


Figure 1. Representation of the molecular structure of compounds **1**, **2** and **3**.

Conclusions

Three new coordination polymers with different polymeric characteristics were synthesized and structurally characterized. The use of different carbamate derivatives proves to be versatile enough to achieve these polymeric structures. Future studies will be linked to obtain other tellurium polymeric derivatives as well of selenium and sulfur chalcogenides.

Acknowledgements

CNPq, CAPES and FAPERGS

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New Dioxomolybdenum Dithiocarbazate Complex

Rafaela B. P. Pesci (PG)[1]*, André G. de A. Fernandes (PG)[1], Davi F. Back (PQ)[2], Victor M. Deflon (PQ)[1].
***rafa_ppesci@iqsc.usp.br**

[1] *Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970, São Carlos – SP, Brazil*
[2] *Departamento de Química, Universidade Federal de Santa Maria, Santa Maria – RS, Brazil*

Keywords: *Dioxomolybdenum, dithiocarbazate, crystal structure.*

Introduction

Molybdenum is widely available to biological systems and the coordination chemistry of Mo(VI) has aroused considerable interest in view of its biochemical significance[1].

Dithiocarbazate and its substituted derivatives have been synthesized and investigated over the past few decades. Interest remains high in these compounds since the intriguing observation that they sometimes show different biological properties, although they may differ only slightly in their molecular structures. Transition metal complexes of these ligands are widely studied because of their potential for therapeutic use[2].

In view of this, we are reporting the synthesis and characterization of a new neutral Mo(VI) complex, $[MoO_2(bmdt)(MeOH)]$, where H_2bmdt = Benzoylacetone-(S-parametoxi-enzyldithiocarbazate.

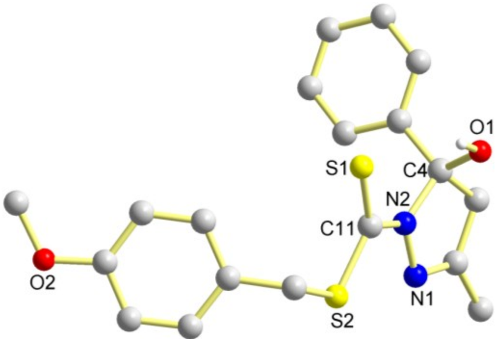

Figure1- Crystal structure of H_2bmdt.

Results and Discussion

The dioxomolybdenum complex was obtained through a stoichiometric quantitative reaction of the precursor $[MoO_2(acac)_2]$ with the ligand H_2bmdt in MeOH. The new complex was characterized on the basis of elemental analysis, IR, ^{1}H-NMR and by X-ray diffraction on single crystal.

Table 1- Results of the elemental analysis.

	$H_2bdtcOMe$	$[MoO_2(bdctOMe)(MeOH)]$
C%(Calc/Found)	61.26/ 61.20	45.28/ 45.52
H%(Calc/Found)	5.41/ 5.22	4.18/ 3.18
N%(Calc/Found)	7.52/ 7.48	5.28/ 5.36
S%(Calc/Found)	17.21/17.72	12.10/ 12.92

The formation of a *cis*-dioxomolybdenum complex is confirmed by the presence of two IR bands related to ν(Mo=O), 939 and 905 cm^{-1}. ^{1}H-NMR (ppm): 2.81 (s, 3H, OCH_3), 3.21 (s, 3H, CH_3), 4.33 (s, 2H, CH_2), 6.38 (s, 1H, CH), 6.84-7.30 (m, 4H, PhOMe), 7.80–7.42 (m, 5H, Ph). The recrystallization of the complex in dimethylsulfoxide resulted in red crystals with the change in the coordination sphere of a molecule of methanol per one of DMSO.

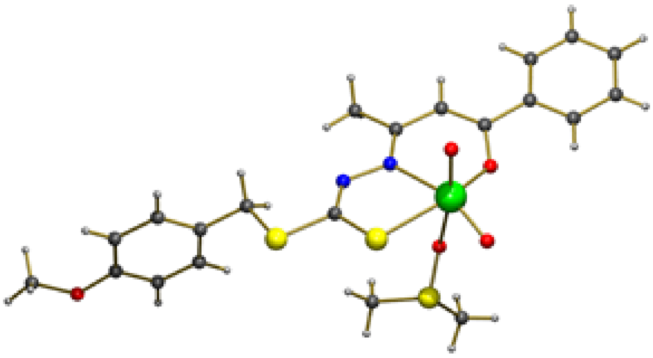

Figure 2- Crystal structure of $[MoO_2(bmdt)(DMSO)]$

Conclusions

The complex $[MoO_2(bdtcOMe)(MeOH)]$ is formed in high yield and mild conditions. The structural analogy of the ligand H_2bmdt with the bioactive H_2bdtc[3] place the new dioxomolybdenum complex as a good candidate for performing future test of antibacterial activity.

Acknowledgements

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Supramolecular assembly of new heteropolymetalic molecules based on tetraiminodiphenolate macrocycle and hexacyanometallate anions.

Júlio César da Rocha[1](PG), Rafael Block Samulewski[1](PG), Rafael Stieler[2](PG), Ernesto Schulz Lang[2](PQ), David John Evans[3](PQ), Giordano Poneti[4](PQ), Otaciro Rangel Nascimento[5](PQ), Ronny Rocha Ribeiro[1](PQ), *Fábio Souza Nunes[1](PQ)
***fsnunes@ufpr.br**

[1] Departamento de Química, Universidade Federal do Paraná Cx.Postal 19081, 81531-990 Curitiba, PR, Brazil
[2] Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil
[3] Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Norwich NR4 7UH, UK
[4] Laboratory of Molecular Magnetism (LAMM), Department of Chemistry, Ugo Schiff and INSTM Research Unit, University of Florence, Via della Lastruccia, 3-13,50019 Sesto Fiorentino, Florence,Italy
[5] Instituto de Física de São Carlos, Universidade de São Paulo, Cx.Postal 369, 13560-970 São Carlos, SP, Brazil

Keywords: *coordination polymers, supramolecular chemistry, crystal structure*

Introduction

Magnetic and spectroscopic properties of coordination polymers are intimately related to the crystal structure and depend upon the nature of the building blocks, their relative orientation in the crystal lattice and interactions such as H-bonding and van der Waals. Herein we report on the preparation, characterization and properties of three new heteropolynuclear metal complexes of the Robson family.

Results and Discussion

The macrocyclic ligand *tidf* was prepared by condensation of 2,6-diformyl-4-methylphenol and 1,3-diaminepropane in the presence of magnesium acetate and magnesium nitrate. The polynuclear compounds $[\{Cu_2(tidf)(H_2O)\}_2(\mu\text{-}CN)_2Fe(CN)_4]\cdot 6H_2O$ **(1)**, $[Cu_2(tidf)(H_2O)_2][Ni(CN)_4]$ **(2)** and $[Cu_2(tidf)(H_2O)_2][Fe(CN)_5NO].H_2O$ **(3)** were prepared from reactions between $[Cu_2(tidf)(ClO_4)_2(H_2O)_2]$ and $K_4[Fe(CN)_6]\cdot 3H_2O$, $K_2[Ni(CN)_4]\cdot H_2O$ and $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, respectively, in water [1]. Single crystals suitable for crystal structure determination were formed in very good yields (87–96%) by the following procedure. A monolayer of isopropyl alcohol was added slowly over concentrated aqueous solutions of the cyanometallate compounds. Then, the dicopper complex in acetonitrile were added very slowly. The systems with apparent three layers were left the dark for many days. Therefore, the starting materials always reacted in a mixture of polar solvents and in molar ratios that would favor the formation of neutral species and that was the outcome observed in all cases. The compounds are fairly stable and were characterized structurally and spectroscopically. Selected bonds of complexes 1-3 are showed at Table 1.

In complex **1** two units of $[Cu_2(tidf)(H_2O)]^{2+}$ are linked by a hexacyanoferrate(II) ion through two cyano-bridges in a *trans* configuration. In complexes **2** and **3,** $[Ni(CN)_4]^{2-}$ and $[Fe(CN)_5(NO)]^{2-}$ are not directly bound to the copper(II) ion, although they play an essential role to maintain the 3D-molecular structures through elaborated hydrogen-bonding interactions between the cyano groups and the coordinated water molecules.

Table 1 Selected bond lengths (Å) for complexes

Complexes	1	2	3
Cu–N	1.986(3)	1.9624(13)	1.9821(17)
Cu–O	2.006(2)	1.9792(11)	1.9716(14)
Cu–N’	2.214(3)	-	-
Cu–O	2.367(3)	2.1964(13)	2.2596(16)
N≡C	1.158(4)	-	-
Fe–C	1.924(3)	1.9352(18)	-
Cu...Cu	3.133	3.109	3.114
Ni–C	-	-	1.867(2)

The vibrational and electronic spectra of complexes **1–3** showed splittings of the ν(C≡N) and ligand field transitions, respectively, all exhibiting a good correlation with the crystallographic bond distances and angles.

The variable-temperature (2–300K) magnetic measurements for **1-3** showed isotropic magnetic interactions between the two copper ions through the diphenolate bridge within the tidf ligand, with strong antiferromagnetic interactions (2J values at -783(29), -913(2) and -905(1) cm^{-1}).

Conclusions

The results show a very interesting case of self-assembly of the building molecules into extended structures in the solid state, maintained by intricate hydrogen-bonding interactions.

Acknowledgements

CNPq, Fundação Araucária, FINEP, UFPR

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Synthesis and characterisation of oxazolinylthiophenolate complexes of vanadium(III)/(IV)

Maria Carolina Chaves (PG)[1,*], Samuele Ciattini (PQ)[2], Rúbia Camila R. Bottini (PQ)[1], Ronny R. Ribeiro(PQ)[1], Rogério A. Gariani (PG)[3], Fábio Simonelli (PQ)[1], Eduardo L. de Sá (PQ)[1], Giovana G. Nunes(PQ)[1], Jaísa F. Soares (PQ)[1]. *carolinaquimica@yahoo.com.br

[1]Departamento de Química, UFPR, Centro Politécnico, Curitiba/PR. [2]Centro di Cristallografia, Università degli Studi di Firenze, Sesto Fiorentino, Firenze/FI, Italy. [3]Instituto de Química, Universidade de São Paulo, São Paulo/SP.

Keywords: oxazoline, vanadim(III)/(IV), thiophenolate.

Introduction

Vanadium(IV) complexes are promising homogeneous catalysts for the epoxidation de non-functionalized olefins and allylic alcohols, hydroxylation of alkanes and arenes and oxidation of sulphides and alcohols.[1] Among these examples, the preparation of epoxides has attracted attention because of their application in the synthesis of natural products and biologically active substances. Literature reports have shown that vanadium(IV) complexes with *N,C*-donor ligands can be employed as catalysts in these reactions.[2]

The aim of the present work is the synthesis and characterisation of coordination compounds of vanadium (in oxidation states from +II to +V) with *S,N*-donors, to be tested as reaction catalysts. This Abstract describes our first results.

Results and Discussion

Two vanadium complexes (oxidation states +III and +IV) were prepared from lithium 2-(4',4'-dimethyloxazolin-2'-yl)thiophenolate, Li(*N,S*-ox), in 1:2 M:L proportion. The vanadium starting materials were [VCl_3(thf)$_3$] and [VO(acac)$_2$] for products **I** and **II**, respectively (acac = acetylacetonate). Reactions were carried out in toluene at room temperature under $N_{2(g)}$, giving dark red crystals of **I** and yellowish-green crystals of **II**.

Infrared (FTIR) spectra recorded for the two products (Table 1) support the coordination of the thiophenolate to the metal.

Table 1. FTIR data obtained for **I** and **II**

Vibrational mode	Wavenumber (cm^{-1})	
	Complex I	**Complex II**
ν(C=N)	1585	1589
ν(C-N)	1371	1372
δ(C–O–C)	1054	1056
ν(C–O)	1030	1030
ν(V=O)	-----	996
ν(C–S)	738	785
ν(C–CH_3)	690	689
ν(V–N)	526	526

Results of X-band EPR analysis in toluene solution at 77 K are compatible with the expected metal oxidation states. Thus, product **I** did not give any EPR signal, while **II** presented a well-resolved hyperfine spectrum, typical of mononuclear oxo-vanadium(IV) in frozen solution.

The electronic spectrum of **I** in CH_3CN solution contains bands compatible with LLCT transitions (248, 264, 279 and 350 nm) as well as absorptions at 382 and 448 nm assigned to LMCT. These assignments are based in TDDFT calculations carried out for Fe^{II} and Zn^{II} analogues of **I**.[3] The spectrum of **II** in toluene solution is significantly different, with a band at 343 nm attributed to LMCT and four lower energy absorptions (434, 560, 712 and 810 nm) with intensities compatible with d-d transitions.

The structures of **I** and **II**, determined by single crystal X-ray diffractometry, are very similar. Two oxazolinylthiophenolate ligands are coordinated to the metal and the coordination geometry about the vanadium ion is trigonal bipyramidal. In **I**, [VCl(*N,S*-ox)$_2$], the chloride ligand occupies one of the equatorial positions of the pyramid, while in **II**, [VO(*N,S*-ox)$_2$], this position is taken by the oxo ligand (Figure 1).

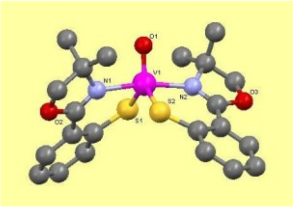

Figure 1. Representation of the molecular estruture of **II**, [VO(*N,S*-ox)$_2$].

Conclusions

Next steps of this work include comparative studies of the catalytic activity of **I** and **II** in vegetable oil epoxidation, as well as the synthesis of an analogue of **I** and **II** with non-oxo vanadium(IV), to allow studies on the influence of the vanadyl group and the coordination geometry on the catalytic results.

Acknowledgements

UFPR, FINEP/CT-INFRA, CAPES, CNPq.

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Synthesis and characterization of a new porphyrin nitrosyl ruthenium complex

M.I.F. Barbosa(PG)*[1] and A.A. Batista(PQ)[1]
***e-mail: mariliaifrazaob@yahoo.com.br**

[1]Laboratório de Estrutura e Reatividade de Compostos Inorgânicos,Departamento de Química, Universidade Federal de São Carlos, CP 676, São Carlos, SP, Brasil.

Keywords: *porphyrin, nitrosyl ruthenium complexes*

Introduction

Nitric oxide (NO) is one of the most fascinating substances in biological chemistry. The action of NO has also been found in a variety of physiological and pathological processes in different cells and tissues, such as neurotransmission, blood pressure control, inhibition of platelet aggregation and immunological responses [1]. Despite the great importance of NO in the biological system, its pharmacological studies have been limited due to its high reactivity and short half-life [2]. The development of molecules that can release NO and overcome this kind of problem, and also be potential therapeutic agents of interest. Accordingly, in this work, a new porphyrin nitrosyl ruthenium complex was synthesized.

Results and Discussion

The synthesis of the porphyrin complex, Figure 1, was accomplished by a previously established procedure [3]. Analytical techniques as elemental analysis, UV-Vis and infrared spectroscopies, nuclear magnetic resonance of ^1H and HPLC were realized and confirm the proposed structure for the compound. The electronic spectra of the porphyrin complex are typical of porphyrin macrocycles giving a very intense soret band at 423 nm and four less intense Q-bands, ranging from 500 to 700 nm, Figure 2. The porphyrin complex was characterized by ^1H NMR and HPLC and showing a clear indication of the purity of it.

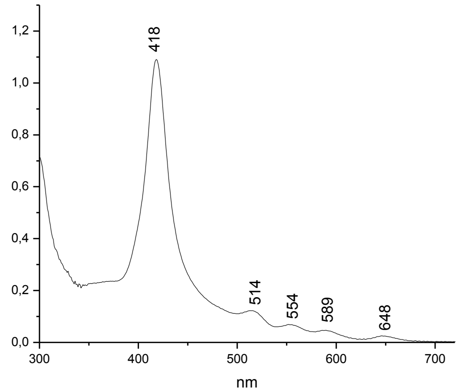

Fig. 2. Electronic absorption spectra, in CH_2Cl_2.

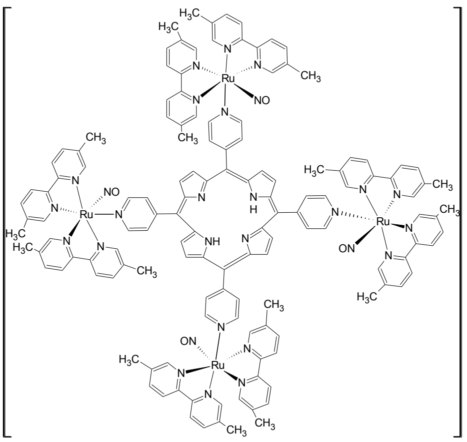

Fig. 1. Proposed structure to the $\{TPyP[Ru(5,5'\text{-}bipy)(NO)]_4\}(PF_6)_{12}$

In the IR spectrum of the complex a characteristic νNO stretching band is observed at 1940 cm^{-1}. In the cyclic voltammetry, the process are centered in the nitrosyl group ($NO^+ \rightarrow NO^0$ (464 mV), $NO^0 \rightarrow NO^-$ (-404 mV), $NO^- \rightarrow NO^0$ (-355 mV), and $NO^0 \rightarrow NO^+$ (540 mV)), Figure 3,

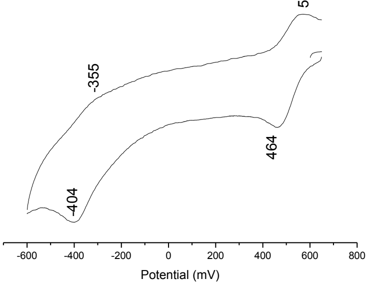

Fig. 3. Cyclic voltammogram of the the $\{TPyP[Ru(5,5'\text{-}bipy)(NO)]_4\}(PF_6)_{12}$ in 0.1M PTBA, in CH_3CN

Conclusions

A new supramolecular specie was obtained, based on the characterization analysis. This complex can be used to deliver NO to a specific target and also can be potentially used as therapeutic agent.

Acknowledgements

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Synthesis and Crystal Structure of a New Binuclear Gold(I) complex with thiocarbamoyl-pyrazoline ligand.

Gleison Antônio Casagrande (PQ)[a*], Bruna Pereira Kuhn (IC)[a], Andressa Ferle(PG)[a] , Simone D. Inglez (PQ)[a], Lucas Pizzuti (PQ)[a], Ernesto S. Lang (PQ)[b] , Davi F. Back (PQ)[b]

***gleisoncasagrande@ufgd.edu.br**

[a]*Laboratório de Síntese e Caracterização Molecular– Universidade Federal da Grande Dourados-UFGD-MS*

[b]*LMI – Universidade Federal de Santa Maria- UFSM-RS*

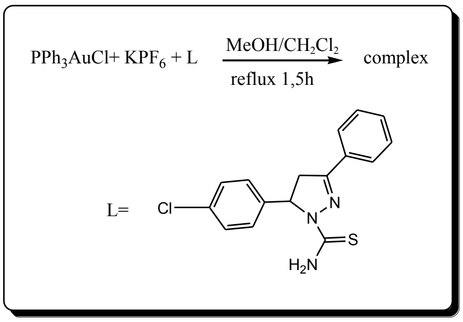
Keywords: Gold(I) complexes, pyrazolines

Introduction

The synthesis of transition metal complexes with pyrazoline ligands has been investigated and widely widespread in the inorganic synthesis field. It is assigned due to its potential uses in drug design, such as antipyretics and antirheumatics as well as in fungicides and herbicides[1]. Gold(III) complexes with thiocarbamoil-pyrazoline-*type* ligands were synthesized by Wang e co-workers on 2010. These complexes have presented higher cytotoxic effects against two cells lines[2]. On the other hand, gold(I) complexes with thiocarbamoil-pyrazolines ligands were not synthesized so far. The literature has been reported the involvement of gold(I) complexes containing pyrazolate ligands with luminescence properties based in LMCT transitions. In this work we present the synthesis and crystal structure of a new binuclear gold(I) complex whit a pyrazoline ligand.

Results and Discussion

The gold(I) complex was synthesized in agreement with de outline bellow:



The Figure 1. shows the crystal structure of the complex. The Table 1. summarizes the crystal data and refinements cycles for the synthesized complex.The IR spectra of the complex confirms that the ligand act as a monodentade form. The complexation was performed by the sulfur atom of the ligand. The ν(C=S) band that appears at 1360 cm^{-1} at the free ligand, was decreased to 1358 cm^{1} in the complex. The ν(N–H) bands do not change at the IR spectra of the complex, indicating the non-involvement of the (N–H) groups with hydrogen bonds in the solid state. The binuclear structure was achieved by a short contact Au(I)···Cl of 3.660Å. These types of short contacts are involved in a dimeric association of gold(I) complexes and were reported in the literature in previous works[3] .

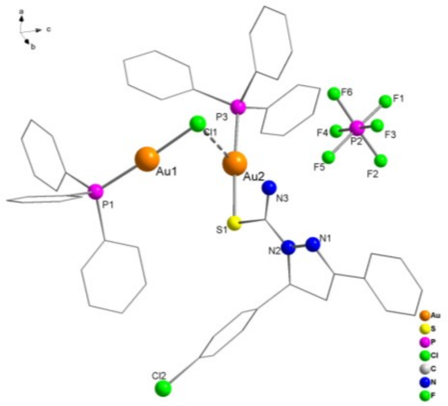


Table 1: Crystal data for the gold(I) complex.

Empirical formula	$C_{52}H_{44}Au_2Cl_2F_6N_3P_3S$
Formula weight	1414.71
Wavelength (λ/ Å)	0.71073
Crystal system, space group	Triclínic $P\bar{1}$
Unit cell dimensions	
a (Å)	9.8851(13)
b (Å)	16.420(2)
c (Å)	16.891(2)
α(˚)	73.485(7)
β(˚)	81.600(8)
γ(˚)	87.597(8)
Final *R* Indices [I>2σ(I)]	R1 = 0.0694, wR2 = 0.1437
R Indices (all data)	R1 = 0.2468, wR2 = 0.2079

Conclusions

A new binuclear gold(I) complex was synthesized and fully characterized by X-ray diffraction and IR analysis.

Acknowledgements

We gratefully acknowledge to the CNPq and Fundect-MS by the financial support.

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Synthesis and structural analysis of lead(II) compounds with pyrimidine-2-thione

Vânia Denise Schwade (PG)[1]*, Bárbara Tirloni (PG)[1], Luana Floriano (IC)[1], Ernesto Schulz Lang (PQ)[1]

***vaniaschwade@gmail.com**

[1] *Laboratório de Materiais Inorgânicos, Depto. de Química, Universidade Federal de Santa Maria, Santa Maria, Brasil.*

Keywords: *crystal structure, lead(II) compounds, pyrimidine-2-thione.*

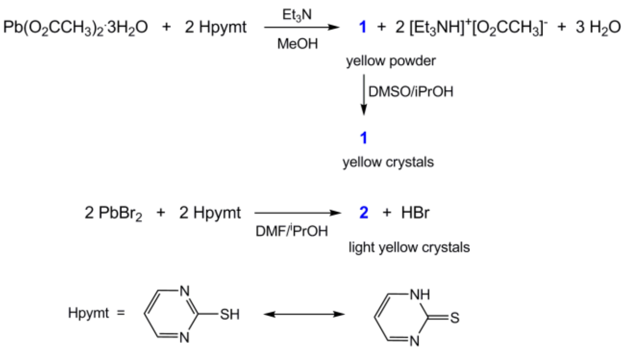
Introduction

The chemistry of metal-sulfur complexes is interesting due to its relevancy as models of active sites in metalloenzymes and the ability to adopt structurally complex arrangements.[1,2]

In this communication, we present two lead(II) complexes obtained in different conditions and starting lead(II) salts with the pyrimidine-2-thione ligand.

Results and Discussion

The compounds $[Pb(pymt)_2]_n$ (**1**) and $[Pb_2(Hpymt)_2Br_3(OH)]_n \cdot H_2O$ (**2**) were obtained from the reaction of pyrimidine-2-thione ligand with lead(II) acetate or lead(II) bromide in the conditions presented in the Scheme bellow:



The crystal structure of the compound **1** reveals the S_4N_4 coordination sphere for the lead(II) atoms. Each Pb atom is linked to a S and to a N atom from four pyrimidine-2-thionate ligands. The S atoms of the ligands act as bridges μ_2–S and the N atoms are connected to neighboring Pb atoms, forming a tridimensional arrangement, as is shown in Figure 1.

In the compound **2**, the crystal structure shows the formation of a polymeric chain along the crystallographic axis *a*. Each lead(II) atom is connected to 4 Br atoms, to the S and N atom from one pyrimidine-2-thione and to the O atom from the hydroxo ligand. Differently of **1**, in this compound the pyrimidine-2-thione is only coordinated to one discrete lead(II) atom by S and N atoms, according the Figure 2. Another interesting fact is that this ligand remains in the protonated form, which leads to the formation of hydrogen bonds.

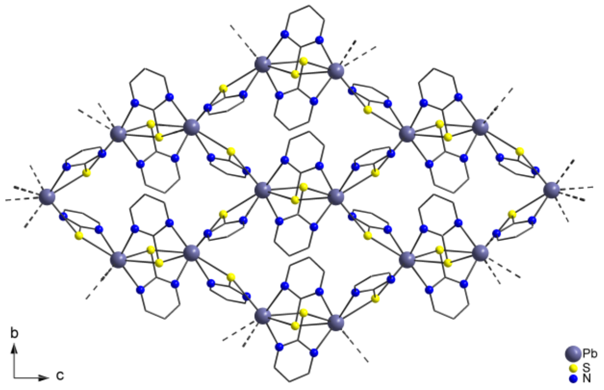


Figure 1. View of the compound **1** in the *bc* crystallographic plane. Hydrogen atoms were omitted.

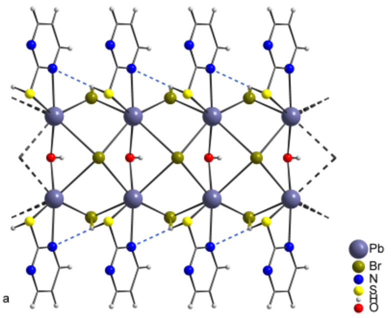


Figure 2. View of the compound **2**. The solvent water molecule was omitted.

Conclusions

These results show that the pyrimidine-2-thione ligand can be remaining, in the complexes, either in the protonated form or in the anionic form. We believe that it depends strongly with the lead(II) salts used in the synthesis. This ligand can exhibit different coordination modes, leading to diverse arrangements.

Acknowledgements

CNPq, CAPES, FAPERGS.

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Synthesis and X-ray Structure of a New Organoselenium Cluster Based on Se–Hg Adamantane Cages.

Simone Finoto (PG)[a], Eduardo J. de Arruda (PQ)[a], Cristiano Raminelli (PQ)[a], Gleison A. Casagrande (PQ)[a*] , Davi F. Back (PQ)[b].

***gleisoncasagrande@ufgd.edu.br**

[a]*Laboratório de Síntese e Caracterização Molecular – Universidade Federal da Grande Dourados- UFGD –Dourados-MS*
[b]*LMI – Universidade Federal de Santa Maria-UFSM-RS*

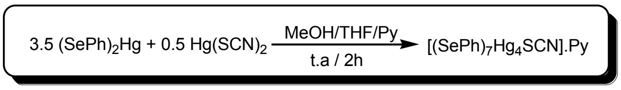
Keywords: Selenium, Clusters, X-ray Diffraction

Introduction

The potential uses of organoselenium clusters in materials chemistry among other areas, has contributed for a large and extensive search of new molecules this class of compounds[1]. For this reason, the selenium mercury clusters have received special attention due to optical and electronic properties. In this context, the control of the shape and size of the synthesized structures is very important, once the optic and electronic properties of this class of compounds are in agreement with these variables. In order to improve and to extend the comprehension about the preparative chemistry of organoselenium clusters, we present in this work, the synthesis and structural characterization by X-ray diffraction of a new organoselenium cluster based on Se–Hg adamantane cages.

Results and Discussion

The Cluster was synthesized in agreemente with the equation below:



$$3.5\ (SePh)_2Hg + 0.5\ Hg(SCN)_2 \xrightarrow[\text{t.a / 2h}]{\text{MeOH/THF/Py}} [(SePh)_7Hg_4SCN].Py$$

The molecular structure obtained from the X-ray data is shown in the Figure(1).

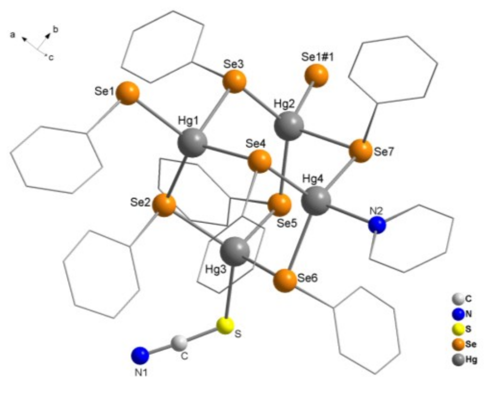


Figure 1. Molecular structure of the $[(PhSe)_7Hg_4(SCN)].Py$ cluster.

The Table 1. summarizes the crystal data and refinement cycles for the cluster. The asymmetric unit of the cluster presents an adamantane cage structure formed by Se–Hg bonds. These bond lengths are in the range of 2.600Å to 2.730Å and this is in agreement with the literature data[2,3]. On the other hand, a polymeric chain is achieved by one intermolecular bond μ_2–Se(1)–Hg(2)#1 of 2.693Å along of the *c* crystallographic axis. The Hg(II) atoms present a tetrahedral coordination geometry at the central cage. The vibrational spectra of the cluster show a very strong band at 2104 cm^{-1} attributed to the symmetric stretching mode of the SCN group.

Table 1. Crystal data and structure refinement for the cluster.

Empirical formula	$C_{48}H_{40}Hg_4N_2SSe_7$
Formula weight	2031.96
Wavelength (λ/ Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	13.9991(5)
b (Å)	24.2237(8)
c (Å)	15.2676(6)
α (˚)	90
β (˚)	101.814(2)
γ(˚)	90
Final *R* Indices [I>2σ(I)]	$R_1 = 0.0550$, $wR_2 = 0.1160$
R Indices (all data)	$R_1 = 0.1008$, $wR_2 = 0.1284$

Conclusions

A new cluster featuring adamantane (Se–Hg) cage was synthesized and fully characterized by X-ray difratometry. The structure reveals a polymeric organization in the solid state.

Acknowledgements

We gratefully acknowledge to the CNPq and Fundect-MS by the financial support.

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A New Copper-Phenylselenolate Cluster, $[Cu_6(bpy)_2(\mu\text{-}SePh)_2(\mu_3\text{-}SePh)_4]$, Synthesis and Structural Analysis.

Bruno N. Cabral (IC)[1*], Sailer S. dos Santos (PG) and Ernesto Schulz Lang (PQ)[1]

***brunonoschang@bol.com.br**

[1] *Universidade Federal de Santa Maria, Laboratório de Materiais Inorgânicos – RS, Brazil*

Keywords: *Phenylselenolate, copper(I), cluster*

Introduction

Clusters of the late transition metals have become progressively important due to their semiconductor potentialities[1]. There are several examples on literature covering the clusters CuSe with ancillary ligands[2,3,4], using mainly the methodology **1** (Scheme **1**).

In this work, we describe the synthesis of 2,2-bipyridine stabilized copper–phenylselenolate cluster, using the methodology **2**, resulting in a cluster with new bonding features (Scheme **1**).

$$\textbf{(1)}\ L_nCu(I)X + Me_3SiSeR \longrightarrow \boxed{L_nCu(I)\text{-}SeR} + XSiMe_3$$

$$\textbf{(2)}\ L_nCu(II)X_2 + 2\,NaSeR \longrightarrow \boxed{L_nCu(I)\text{-}SeR} + 2\,NaX + 0.5\,(PhSe)_2$$

Scheme 1: Methodologies used in literature.

Results and Discussion

All operations were carried out under argon atmosphere and with dried solvents.

Diphenyldiselenide (50 mg; 0.16 mmol) was dissolved in a mixture of THF/EtOH. Reduction with $NaBH_4$ (12 mg; 0.32 mmol), resulted in a colorless solution. Phenylselenolate generated *in situ* was transferred with a syringe to a suspension of $Cu(bpy)Cl_2$ (46 mg; 0.16 mmol) in 10 ml of THF. The color of the solution changed to red opalescent. Precipitate was removed by filtration and the clear solution gave after 3 days, dark red crystals of the compound **1**. The reaction led to a new cluster (Fig.**1**), determined by single-crystal X-ray diffraction. Crystallographic data are found in Table 1.

Table 1. Crystallographic Parameters

Compound	1
Empirical Formula	$C_{56}H_{46}N_4Se_6Cu_6$
Crystal System	Monoclinic
Space Group	$P2_1/c$
a/Å; b/Å; c/Å	13.981; 15.218; 29.222
α/Å; β/Å; γ/Å	90; 101.457; 90
R_1; wR_2	0.0848; 0.2545

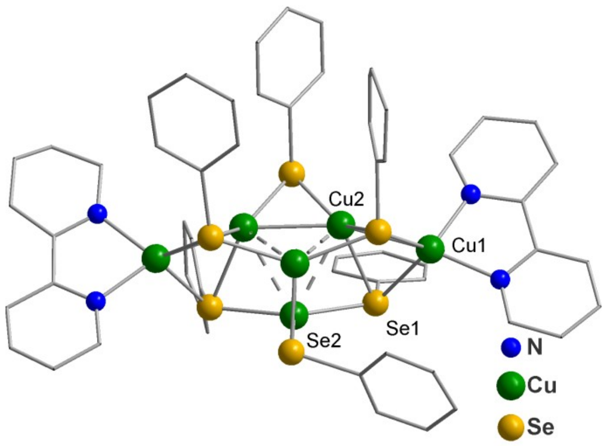

Figure 1. Cluster $[Cu_6(bpy)_2(\mu\text{-}SePh)_2(\mu_3\text{-}SePh)_4]$.

The core of the cluster is composed by six atoms of selenium and six atoms of copper. The Cu1 atoms are coordinated by a 2,2-bipyridine (bpy), two μ_3–PhSe (Se1 ligands) and also exhibit an intermetallic Cu1–Cu2 bond (2.480 Å). The coordination environment for Cu2 atoms is built up by two μ_3–PhSe (Se1) ligands, one μ_2–PhSe (Se2) moiety and two intermetallic bonds (Cu1–Cu2, 2.480 Å; Cu2–Cu2, 2.609 Å). Two secondary Cu2···Cu2 interactions (2.738 Å) provide a tetrahedral array for the central metallic atoms.

Conclusions

Here we presented an unexplored methodology to obtain new metallic-chalcogenide clusters, which can be extended to another transition metals with intermediary oxidation states. More analysis need to be done to evaluate possible semiconductor properties.

Acknowledgements

This work was supported with funds from PRONEX-CNPq/FAPERGS (Brazil). B.N.C. and S.S.S. thank CNPq for a research fellow (Processes 026646 and 140349/2007-3 respectively).

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Thiosemicarbazones complexes with first row transition metals

Carolina G. Oliveira (PG)[1], Pedro Ivo S. Maia (PG)[1], Victor M. Deflon (PQ)[1*] *deflon@iqsc.usp.br

[1]*Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, São Carlos-SP*

Keywords: *thiosemicarbazones, transitions metals, crystal structure.*

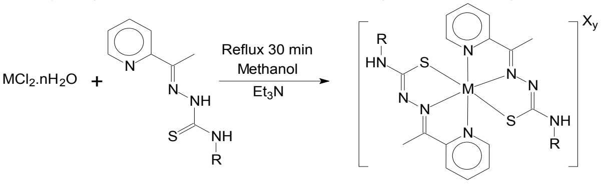
Introduction

It has been observed that octahedral nickel(II) complexes with thiosemicarbazones (Tsc's) present relevant anti-*Mycobacterium tuberculosis* (MTB) activity and low cytotoxicity against healthy cells.[1]

In this study a series of octahedral thiosemicarbazone complexes was prepared varying the metal center, aiming to evaluate the relation between the metal centers (Co, Fe, Mn) as well as the variation of the group R in the Tscs (Htsc-R) moiety with the anti-MTB activity.

Results and Discussion

Reactions of Htsc-R and $MCl_2{\cdot}nH_2O$ in MeOH and some drops of supporting base (Et_3N) yields solids of composition $[M(tsc\text{-}R)_2]Cl_y$ (M= Mn, Fe, y=0; M= Co, y=1), after reflux for 30 min (**Scheme 1**).



M = Co (X = Cl ;y = 1), Mn (y = 0), Fe (y = 0)
R = Etyl, phenyl

Scheme 1. Synthesis of the complexes.

The IR spectra of Htsc-R exhibit two bands related to ν(N-H) in the range 3350-3200 cm^{-1}. In the spectra of the complexes only one ν(N−H) band is observed around 3100 cm^{-1}. This is compatible with a single deprotonation of the ligands.

The presence of the counter ion (Cl^-) in the cobalt complexes $[Co(tsc\text{-}R)_2]Cl$ was confirmed by conductivity measurements, displaying values of 34.5 µS/cm in dichloromethane (R = Ph) and 131.4 µS/cm in water (R = Et), in accord to an 1:1 electrolyte. The measurements for the Mn and Fe complexes indicated neutral species.

The $[Mn(tsc\text{-}R)_2]$ compounds are paramagnetic in the extension of one unpaired electron (d^5) with values of μ_{exp} = 1.16 BM (R = Et) and 1.29 (R = Ph). The Co and Fe complexes showed values consistent with diamagnetic species.

Differently from what was reported for $[Fe(tsc\text{-}Ph)_2]$, which exhibits a totally reversible Fe^{II}/Fe^{III} couple at 0.063 V,[2] the analog complex $[Mn(tsc\text{-}Ph)_2]$ shows two quasi-reversible processes in CV (**Fig. 1**). The first oxidation occurs at 0.470 V (Mn^{II}/Mn^{III}), the second occurs at 1.080 V (Mn^{III}/Mn^{IV}), while the reduction processes are observed at 0.929 V (Mn^{IV}/Mn^{III}) and 0.309 V (Mn^{III}/Mn^{II}).

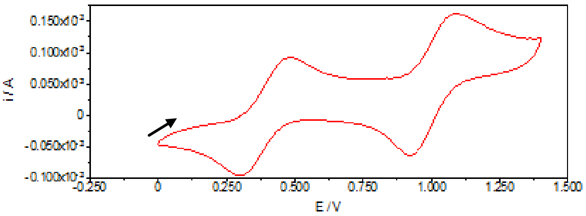


Figure 1. Cyclic voltammogram of $[Mn(tsc\text{-}Ph)_2]$.

The crystal structures of $[Mn(tsc\text{-}Et)_2]$ and $[Co(tsc\text{-}Ph)_2]Cl$ were determined (**Fig. 2** and **Table 1**). In both cases the metal centers are coordinated to monodeprotonated *N,N,S*-tridentate ligands in octahedral environments. Differently from the Mn complex, the Co complex is cationic, with a Cl^- as counter ion, confirming the oxidation state +III.

Table 1. Refinement data for $[Mn(tsc\text{-}Et)_2]$ and $[Co(tsc\text{-}Ph)_2]Cl$

	$[Mn(tsc\text{-}Et)_2]$	**$[Co(tsc\text{-}Ph)_2]Cl$**
Crystalline system (*Z*)	Monoclinic (2)	Monoclinic (4)
Space group	$P2_1$	$P2_1/n$
a/*b*/*c*	8.8196(2)/ 14.7506(4)/ 9.3757 (2)	9.8287(3)/ 23.4347(7)/ 13.1980(4)
β	102.357(1)°	98.462(2)°

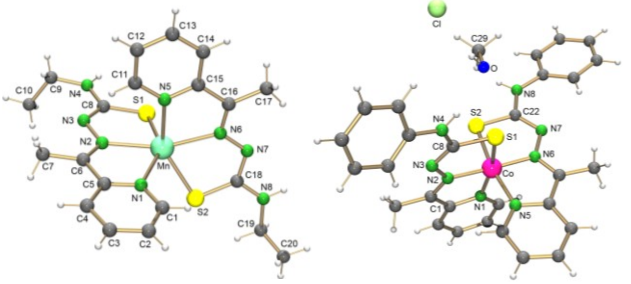


Figure 2. Molecular Structures of $[Mn(tsc\text{-}Et)_2]$ (left) and $[Co(tsc\text{-}Ph)_2]Cl{\cdot}MeOH$ (right).

Conclusions

Octahedral complexes of Tscs and first row transition metals have been prepared. The chemical properties of these complexes can be changed according to the metal center with the goal to get better biological activity against MTB.

Acknowledgements

FAPESP, CAPES and CNPq.

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Rhenium mixed complexes involving a *S,N,S*-tridentate thiosemicarbazone and pseudo halogeno ligands

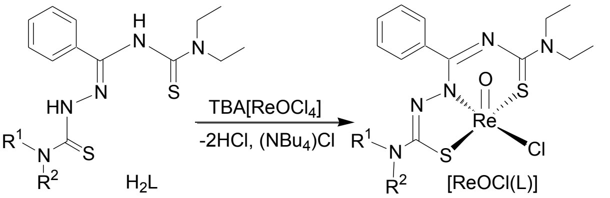
Pedro Ivo S. Maia (PG)[1*], Ulrich Abram (PQ)[2] and Victor M. Deflon (PQ)[1] *pedovivo@iqsc.usp.br

[1] *Instituto de Química de São Carlos, Universidade de São Paulo, CP 780 São Carlos - São Paulo*
[2] *Free University of Berlin, Institute of Chemistry and Biochemistry, Fabeckstrasse 34-36, D-14195 Berlin*

Keywords: *thiosemicarbazones, rhenium, pseudohalides.*

Introduction

A new class of *S,N,S*-tridentate thiosemicarbazones (H_2L1) with antitumoral properties has recently been prepared. H_2L1 readily reacts with $(NBu_4)[ReOCl_4]$ in MeOH under the formation of oxorhenium(V) complexes of composition [ReOCl(L1)].[1]



In the present work it's described the synthesis and characterization of new oxorhenium(V) complexes by replacing the chloro ligand and/or the remaining sixth position of the [ReOCl(L1)] compounds in order to change the chemical as well as biological properties of this type of complex.

Results and Discussion

Reactions of [ReOCl(L1)] with $NH_4(SCN)$ and KCN give complexes of the type [ReO(NCS)(L1)] (**1a**) and [ReO(CN)(L1)] (**1b**), respectively. Surprisingly, the reaction of [ReOCl(L1)] with KSeCN doesn't lead to the formation of the isoselenocyanato derivative but to [ReO(CN)(L1)] under formation of elemental selenium (**Scheme 1**).

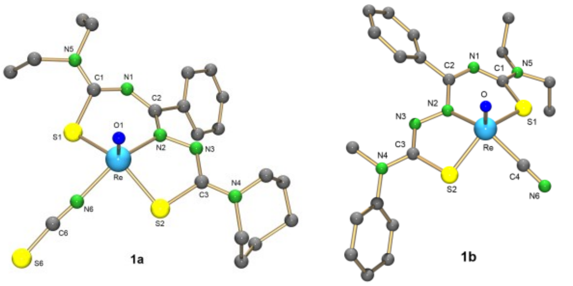
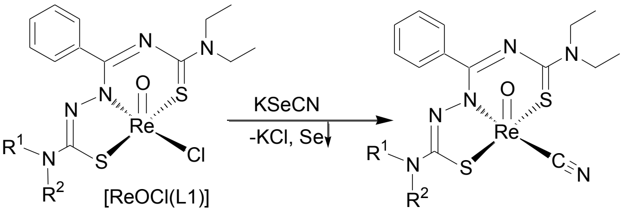
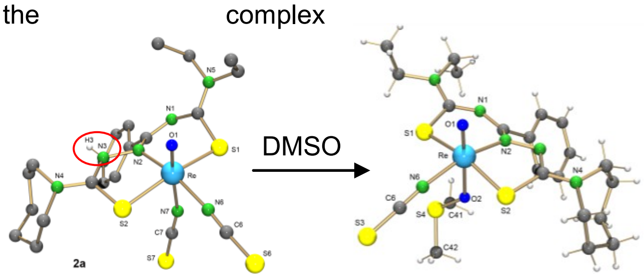


Figure 1. Molecular Structure of [ReO(NCS)(L)] (**1a**) e [ReO(CN)(L)] (**1b**).

Scheme 1. Synthesis of [ReO(CN)(L1)].



On the other hand, by reacting $(NBu_4)[ReOCl_4]$ with H_2L1 and two equivalents of $NH_4(SCN)$ in a *one pot* reaction, H_2L1 reacts as a monodeprotonated ligand, forming complexes of the type $[ReO(NCS)_2(HL1)]$ (**Scheme 2**). Interestingly, it was observed that in the presence of a neutral ligand like DMSO, the thiosemicarbazone ligand in $[ReO(NCS)_2(HL1)]$ suffers a second deprotonation and the NCS^- ligand *trans* to the oxo group is replaced by DMSO to form the complex [ReO(NCS)(L1)(DMSO)] (**Scheme 2**).



Scheme 2. Replacement of isothiocyanato in the $[ReO(NCS)_2(HL1)]$ complex by DMSO.

Furthermore, dimeric complexes were obtained by reactions with NaN_3, like the complex $[\{ReN(HL1)\}_2(O)]$ showed in **Fig. 2**.

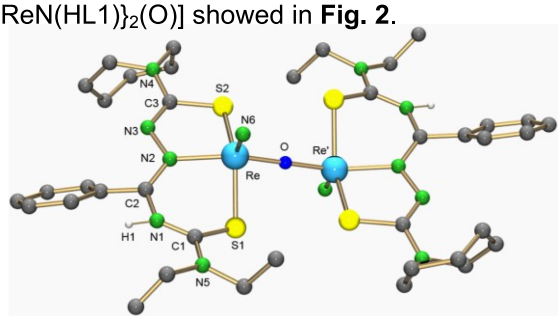


Figure 2. Molecular Structure of $[\{ReN(HL1d)\}_2(O)]$.

Conclusions

The reactions described on this work involve quite simple synthetic approaches that lead to interesting and sometimes unexpected products. The chemical and biological properties of the [ReOCl(L1)] may be completely changed by replacing the Cl^- ligand.

Acknowledgements

FAPESP, CAPES (PROBRAL) and CNPq.

Nguyen, H.H.; Jegathesh, J.J.; Maia, P. I. S.; Deflon, V. M.; Gust, R.; Bergemann, S.; Abram, U. *Inorg. Chem.* **2009**, *48*, 9356-9373.

Synthesis and structural analysis of new polymeric M−NCS−HgSePh compounds (M = Co, Ni).

Camila N. Cechin (IC)[1], Rafael Stieler (PG)[1,2]*, Ernesto S. Lang (PQ)[1] and Davi F. Back (PQ)[1]

***rafaelstieler@hotmail.com**

[1] *Departamento de Química, Universidade Federal de Santa Maria, Santa Maria-RS, Brazil*
[2] *Universidade Federal da Fronteira Sul, Realeza-PR, Brazil*

Keywords: *polymeric compound, selenium, mercury(II).*

Introduction

The syntheses of organochalcogenide compounds have attracting considerable attention due their interesting structure and optical properties. Chalcogenide clusters, for example, have been employed as new strategies for the synthesis of well defined nano-sized materials. Although we can find a wide literature describing binary compounds, ternary organochalcogenide polymeric compounds are rare, and it can be a good strategy to the development of new supramolecular architectures, with different arrangement and physical properties.[1,2]

Results and Discussion

In this work, we present the synthesis of new ternary organochalcogenide polymeric compounds $[M(dmf)_2(NCS)_4(HgSePh)_2]_n$ where M = Co (**1**), Ni (**2**). Figure 1 shows the asymmetric unit of the title compounds.

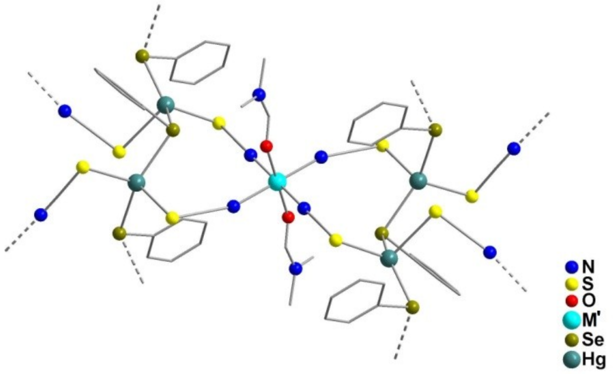


Figure 1. Molecular structure (asymmetric unit) of $[M(dmf)_2(NCS)_4(HgSePh)_2]$ where M = Co (**1**), Ni (**2**).

The compounds were obtained through the reaction of a equivalent amount $Hg(SePh)_2$ with $Hg[M(SCN)_4]$ in dmf, by layering isopropanol on the mother solution.
The crystal structure of the compounds shows that the mercury atoms have a tetrahedral $Hg(SCN)_2(SePh)_2$ environment, while the M atoms present a $M(NCS)_4(dmf)_2$ octahedral environment. The compound assembles in a polymeric bidimensional lattice, where the mercury atoms are linked to the M atom through a SCN bridge. The structure shows a quasi linear Hg-SePh-Hg chains along the crystallographic axis *b*, connected each other through a SCN-Co-NCS bridges. This coordination system is similar to the observed for the tellurium derivative, as reported earlier.[3]

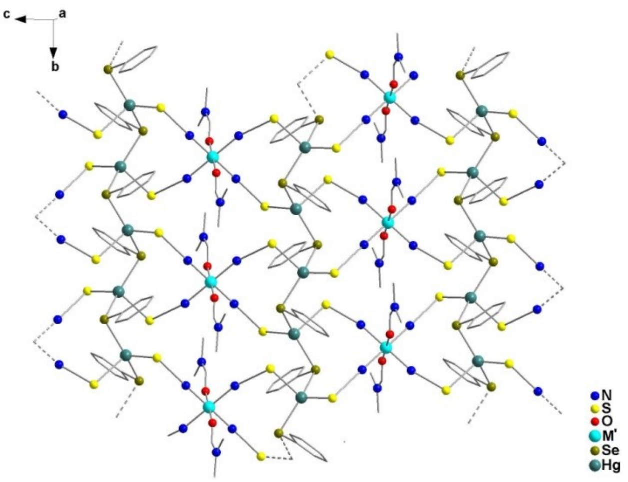


Figure 2. Polymeric assembly of $[M(dmf)_2(NCS)_4(HgSePh)_2]_n$ (M = Co (**1**), Ni (**2**)) along the crystallographic plane *bc*.

Conclusions

The reaction of $Hg(SePh)_2$ with $Hg[M(SCN)_4]$ complexes reported here is a promissory route for the synthesis of ternary polymeric compounds. These compounds show interesting molecular structures that can result interesting physical properties.

Acknowledgements

The authors are grateful to CNPq and Capes.

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Authors Index

Authors Index