

07-Crystallography of Organometallic and Coordination Compounds

241

At the moment we are not able to establish if compound **1** would be a monohydride or a dihydride. Infrared and NMR spectra suggest that **1** may rather be a monohydride. On the contrary the low magnetic moment (0.7 BM) of **1** do not support spectroscopic data. Then the following questions need an answer: is it **1** a mixture of isostructural Ir^{IV} monohydride and Ir^V dihydride complexes? Is it a low μ_{eff} , sometimes, a peculiar characteristic of paramagnetic hydrides? At present definite evidences on the basis of the IR and NMR spectra are not in favour of **1** as non classical dihydrogen Ir^{III} complex.

PS-07.05.09 CRYSTAL STRUCTURE OF $\{[Ni(CHO)]_2L\}-(ClO_4)_4$. A NICKEL(II) DIMER WITH CARBONYL-OXIME PYRIMIDINE BRIDGES. By R. Kivekäs* and M. Klinga, Division of Inorganic Chemistry, University of Helsinki, Finland; A. Romerosa, J.M. Dominguez-Vera and E. Colacio, Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Spain

Studies of magnetic exchange interactions in polynuclear metal complexes are of continuing interest to coordination chemists. One of the recent subjects in this field is to seek new bridging systems which can mediate a strong antiferromagnetic spin-coupling between two different paramagnetic centers in order to obtain ferrimagnetic materials. Spin exchange through oximate bridges is strongly antiferromagnetic and is able to cause complete or nearly complete spin-coupling even at room temperature.

In attempts to prepare oxime bridged Ni-Cu-Ni complexes by reacting $[CuL(ClO_4)_2]$ with $[Ni(CHO)](ClO_4)_2$ an unexpected product, analysed as $\{[Ni(CHO)]_2L\}(ClO_4)_4$, was formed. This paper deals with the structure of this unusual compound.

Abbreviations: H₂L is α,ω -bis(1,3-dimethyl-5-nitroso-uracil-4-ylamine)butane and CHO is *d*,1-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclo-tetradecane.

Crystal data: monoclinic with $a=18.083(6)$, $b=12.225(3)$, $c=15.775(5)$ Å, $\beta=98.50(3)^\circ$, $V=3449(2)$ Å³, $P2_1/c$, $Z=2$, $R=0.065$ ($R_w=0.044$) for 2965 reflections and 415 parameters.

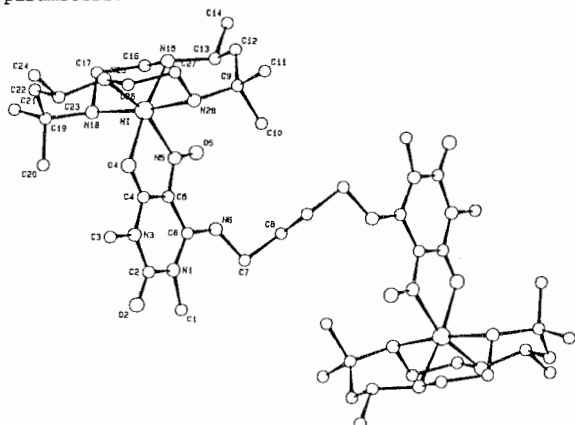
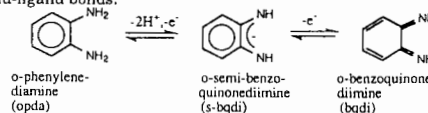


Fig. 1. $\{[Ni(CHO)]_2L\}^{4+}$

The dimeric complex unit is situated across a crystallographic center of inversion between C8 and C8'. The metal environment has distorted octahedral geometry. The tetrapodant ligand CHO provides four coordination sites with Ni-N bond lengths of 2.083(5) to 2.157(6) Å. The Nickel(II) atom is also coordinated through the N5 atom of the nitroso group [Ni-N5=2.135(8) Å] and the carbonyl oxygen atom O4 of the uracil group [Ni-O4=2.135(5) Å].

PS-07.05.10 Eclipsed Cofacial Dimers of Metal Complexes Containing Rh^I-Rh^I and Ir^I-Ir^I Bonds. Crystal Structure of Bis(semibenzoquinonediimine)dicarbonylrhodium(I) and Bis(semibenzoquinonediimine)dicarbonyliridium(I) Ming-Chi Liaw* and Shie-Ming Peng Department of Chemistry, National Taiwan University Taipei, Taiwan

π - π interactions between highly conjugated molecules, e.g. TTF-TCNQ (TTF=tetrathiafulvalene, TCNQ=7,7,8,8-tetracyano-*p*-quinodimethane) complexes, play important roles in their electron transport processes but only a few examples of strongly attractive bonding interactions of those molecules have been reported. Two requirements are necessary for these attractive interactions—the close cofacial approach of the planar molecules and the odd electron population attributed to π or π^* orbitals of the molecules. Here we report two novel crystal structures of metal complexes of semi-quinonediimine-type ligands which contain synergic metal-metal and ligand-ligand bonds.



The reaction of $[Rh(CO)_2Cl]_2$ with o-phenylenediamine(opda) yields a green solution, from which the dark green crystals are obtained. It was characterized by IR, EA, and X-ray diffraction as $[Rh(s-bqdi)(CO)_2]_2$. The green crystals were found to crystallize in the monoclinic space group $P2_1/n$ with $a=13.248(3)$, $b=10.796(3)$, $c=13.249(3)$ Å, $\beta=112.819(2)$, $Z=4$; The final $R=0.046$ and $R_w=0.044$ for 896 observations and 235 parameters.

The reaction of $[Ir(CO)_2(acac)]$ with o-phenylenediamine(opda) yields a green solution, from which dark green crystals are obtained. It was characterized by IR, EA, and X-ray diffraction as $[Ir(s-bqdi)(CO)_2]_2$. The green crystals were found to crystallize in the triclinic space group $P1$ with $a=9.516(6)$, $b=11.929(2)$, $c=12.662(3)$ Å, $\alpha=116.80(2)$, $\beta=91.5019(2)$, $\gamma=103.34(2)$, $Z=2$; The final $R=0.043$ and $R_w=0.041$ for 2890 observations and 317 parameters. These two structures have a number of unusual features.

- 1) they contain Rh^I-Rh^I and Ir^I-Ir^I bond (d^8-d^8)
- 2) the two semibenzoquinonediimine ligands are arranged in an eclipsed fashion and are separated by only 3.0 Å.
- 3) the ligands have delocalized bond character and contain a δ type bond between the two parallel semibenzoquinonediimine ligands.

PS-07.05.11 CRYSTAL STRUCTURE OF A BARIUM FLUORINATED ALKOXIDE $Ba_5(OH)(OCH(CF_3)_2)_9(THF)_4 \cdot H_2O$, FOR USE AS PRECURSOR FOR HIGH T_C SUPRACONDUCTORS CVD. By H. Vincent*, ENSPG/LMGP BP 46, 38402 St Martin d'Hères, F. Labrize and L. Hubert, Labo. de Chimie Moléculaire, Université. de Nice, 06034 Nice, France.

MOCVD (Metal-Organic Chemical Vapor Deposition) is potentially well suited for the obtaining of thin films, but needs volatile precursors. To date, β -diketonates based on bulky or fluorinated ligands have generally been used as a source of metal oxides. For heavy electropositive metals such as barium, problems due to a poor volatility and/or stability are often encountered and result in a lack of reproductibility for the deposits.

07-Crystallography of Organometallic and Coordination Compounds

Metal alkoxides might represent an alternative, especially as they are generally more attractive for the design of mixed metal species. Barium alkoxides involving fluorinated groups, namely perfluoroisopropoxide $\text{OCH}(\text{CF}_3)_2$ (ORf) have been obtained either by direct reaction between the metal and the alcohol or by alcoholysis reactions. Crystal structure and chemical formula of one of them, crystallized from hexane/tetrahydrofuran (THF), have been determined by single crystal X-ray diffraction at 220 K.

Crystal data are as follows: monoclinic symmetry; space group $P2_1/C$; cell parameters at 220 K: $a = 24.667(7) \text{ \AA}$, $b = 13.925(3) \text{ \AA}$, $c = 25.856(9) \text{ \AA}$, $\beta = 113.15(3)^\circ$; asymmetric unit: one $\text{Ba}_5(\text{OH})(\text{OCH}(\text{CF}_3)_2)_9 (\text{THF})_4 \text{H}_2\text{O}$ molecule + one not bonded THF molecule; $Z = 4$. The molecular structure consists of a classical pentanuclear cluster of barium atoms, arranged in a square based pyramid. A μ_5 -oxo ligand lies at the center of the pyramid squared basis; 5 μ_3 -ORf ligands, 4 μ_2 -ORf ligands, 4 THF and 1 H_2O ligands are surrounding the cluster. Thus, each barium atom has 7 to 11 oxygen or fluor atoms as neighbours. Such a high coordination number for barium atoms explains the relative stability of this alkoxide

PS-07.05.12 THE MODULATED CRYSTAL STRUCTURE OF A METALLOPORPHYRIN π -CATION RADICAL.

Kenneth J. Haller* and A. David Rae, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington N.S.W. 2033, Australia.

The hexachloroantimonate salt of chloroiron tetramesityl porphyrin radical monocation crystallizes as a modulated structure with a tetragonal $I4/m$ parent space group; $a = 18.008$, $c = 9.028 \text{ \AA}$, $Z = 2$. A commensurate modulation exists corresponding to $h+k+l = 2n+1$ data being weakly present. The absence condition $h+k = 2n+1$ is maintained for the $l = 0$ data. There are also weak satellite reflections corresponding to a modulation wave vector $0.46 c^*$.

A hierarchical approach to structure elucidation was used, starting with a disordered average structure in $I4/m$ and progressing to structure refinement attempts in $P4_2/n$, and $P4/n$ to try to identify the nature of the modulation. The cation was located on a $4/m$ site in $I4/m$ with the mesityl groups on four separate cations defining a channel about the 4_2 axis which contains the SbCl_6^- counterions. These ions appear streaked along c and individual atoms are not resolved. Reduction of symmetry to $P4_2/n$ or $P4/n$ allows the cation to adopt either a $\bar{4}$ or 4 symmetry respectively. Packing requires the SbCl_6^- to have a 2 axis between adjacent Cl coincident with a 2 fold crystal axis parallel to c . In either spacegroup symmetry creates a second anion 90° rotated translated along the same axis. Both of these cannot fit in the axial repeat and one is not required by chemistry. Ordering to lower the spacegroup to $P\bar{4}$ causes the n glide absence condition to be violated. The anions appear to contribute very little to the $h+k+l = 2n+1$ data. The $h+k+l = 2n+1$ data has intensity distributed in h and k rather than l . This appears to correspond to a correlated rotation of the mesityl groups which provides a mechanism for creating the necessary correlation between columns to see the incommensurate reflections. The c repeat distance would appear to be determined by contacts between the mesityl groups of different molecules but there appears to be a three atom contact between adjacent cations along c . This is consistent with having an asymmetric Cl_3^- ion linking Fe atoms rather than a Cl^-

Dimensions are compatible. This would further enhance the necessary communication for the incommensurate modulation to be observed. Resolution of the structure options requires an ability to model the anions. The anions were initially included in the model, as a series of spherically averaged SbCl_6^- spaced at $1/8c$ with large U_{33} thermal parameters. Subsequent to this fractional oriented anions streaked along c have been used. The progress of refinement has been monitored by assessing data of different index condition. Refinement was kept in control using RAELS89 to refine rigid body thermal parameters and impose localised symmetry constraints. The anions appear to have restricted orientation and be clustered around the same z heights as the cations, $1/2c$ apart in the average structure. Refinement is continuing. The observed incommensurate modulation appears to be the result of the c axial length being longer than required to have anions touching. This allows extra species, presumably solvent, to be fitted into the channels.

We wish to thank Professor W. Robert Scheidt and Dr. Hungsun Song of The University of Notre Dame, IN for providing the data for this problem.

PS-07.05.13 STRUCTURAL CHEMISTRY STUDIES ON RARE EARTH AMINOACID COMPLEXES

By Y.H.Lin*, Y. Xin, A.Z.Ma, L.M.Li and S.Q.Xi, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, China

This report gives a brief account of some of structural chemistry studies on rare earth aminoacid (REA). During the past years, our research group has succeeded in synthesizing a series of REA. These complexes respectively belong to $([\text{Er}(\text{pro})_2(\text{H}_2\text{O})_2\text{Cl}_2])_n$ (Ma, Li, Lin and Xi, Acta Cryst. (1993), C49) $\text{Sm}(\text{ClO}_4)_2(\text{Val})_n \cdot 4\text{H}_2\text{O}$, $\text{Sm}(\text{ClO}_4)_2(\text{ASP})_n \cdot n\text{H}_2\text{O}$, $\text{Sm}(\text{ClO}_4)_2(\text{Gly}) \cdot 4\text{H}_2\text{O}$, $\text{YbCl}_2(\text{Ala}) \cdot 4\text{H}_2\text{O}$, $\text{YbCl}_2(\text{pro}) \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{ClO}_4)_2(\text{pro}) \cdot n\text{H}_2\text{O}$, $\text{La}(\text{ClO}_4)_2(\text{Ala}) \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{ClO}_4)_2(\text{Gly}) \cdot 4\text{H}_2\text{O}$, $\text{Sm}(\text{ClO}_4)_2(\text{Ala}) \cdot 3\text{H}_2\text{O}$ and $\text{Er}(\text{ClO}_4)_2(\text{His}) \cdot 5\text{H}_2\text{O}$. The chemical structures of these complexes have been identified by elemental analyses, IR and mass spectra. Among them, the molecular configuration and the bond parameters of eleven typical complexes have been determined by careful X-ray structural analyses.

The characteristics of the molecular structure of REA have been summarized. First, the amino groups in REA are protonated and not coordinated. Secondly, rare earth atoms are separated from each other by a distance about 4 \AA , so that there are no metal-metal bonds between them. Thirdly, the coordination number of rare earth metals are 8-10, their coordinate configuration forming square antiprism, tricapped trigonalprism and bicapped square antiprism respectively. Finally, these structure can be divided into infinite three-dimensional network, one-dimensional chain and binuclear bridge three classes.

PS-07.05.14 CRYSTAL STRUCTURES OF $(\text{AdeH}_2)\text{SbCl}_5\text{H}_2\text{O}$ AND $(\text{AdeH})_2\text{SbCl}_5\text{H}_2\text{O}$ (Ade = ADENINE). By Tu Lian-Dong* and Hu Sheng-Zhi, Chemistry Department, Xiamen University, Xiamen, China.