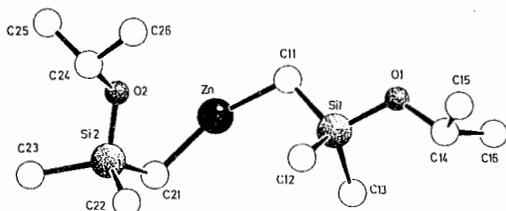


07-Crystallography of Organometallic and Coordination Compounds

$b=11.672(2)$, $c=20.342(1)$ Å. $R(R_w)=0.054(0.055)$, 2737 observed reflections, 135 refined parameters, $\text{MoK}\alpha$ radiation, $D_{\text{cal}}=1.137\text{g}\cdot\text{cm}^{-3}$, $F(000)=704$ (G. Bülow, H.-J. Gais, G. Raabe, 1993, *Organometallics*, submitted). In addition to two covalently bonded C atoms Zn is coordinated by an oxygen atom of a neighbouring molecule. As a result of this complexation the C-Zn-C moiety is significantly bent ($152.3(3)^\circ$) and the molecules are arranged in helices perpendicular to the bc plane. The metal atom lies in a chiral plane and is in contact with another oxygen atom belonging to one of its covalently bonded ligands. The influence of complexation on the geometry of the C-Zn-C segment is substantiated by quantum chemical *ab initio* and semiempirical calculations. In addition the computational results indicate that the energy of complexation is rather low (≈ 3 kcal/mol).



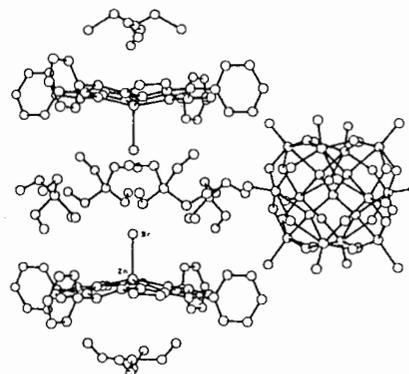
PS-07.05.07 A NEW TERNARY POLYOXOMETALATE CHARGE-TRANSFER SALT. By D. Attanasio, F. Bachechi* and L. Suber*, Istituto di Chimica dei Materiali, Istituto di Strutturistica Chimica, Area della Ricerca di Roma, C.N.R., C.P. 10, 00016 Monterotondo Staz., Roma, Italy.

Recently, a type of organic-inorganic charge-transfer compounds has received considerable attention. These materials consist of polyoxoanions as electron acceptors and a variety of organic molecules as donors.

As part of a study concerning polyoxoanions of the early transition metals in the α -Keggin structure and alkyl amines as organic donors, several ternary CT salts were synthesized and the crystal structure of one of them, $[(\text{C}_2\text{H}_5)_4\text{N}]_5[(\text{ZnTPP})_2\text{SiMo}_{12}\text{O}_{40}\text{Cl}]$, with ZnTPP = tetraphenylporphyrinatozinc(II), was determined.

These compounds contain two photoactive molecular entities, the metallo macrocycles and the α -Keggin units, which can give rise to electron transfer processes. This unexpectedly stable molecular association is made possible by the presence of the halide ion as third component.

The structure (space group $I\bar{4}$) is built by $\text{SiMo}_{12}\text{O}_{40}$ units at the origin of the I lattice. The two ZnTPP are located on the four-fold axis and are related by an inversion centre. Also the Br atom, coordinated to the Zn, and one molecule of $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ lie on the four-fold axis and are disordered on two centrosymmetric positions. The other molecules of $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ appear forming a layer which interposes between the two ZnTPP.



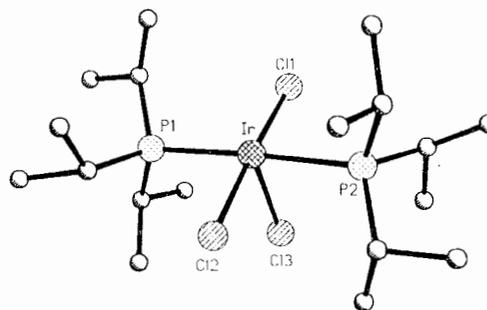
PS-07.05.08 CRYSTAL AND MOLECULAR STRUCTURE OF $[\text{Ir}(\text{H})_x(\text{Cl})_3(\text{P}^+\text{Pr}_3)_2]_x$, $x=1$ or 2 : ANOTHER EXAMPLE OF Ir^{IV} PARAMAGNETIC HYDRIDE OR AN IRIDIUM(V) COMPLEX, TRANSIENT INTERMEDIATE OF $[\text{Ir}^{\text{IV}}(\text{H})_2(\text{Cl})_2(\text{P}^+\text{Pr}_3)_2]$, 2 ? By D. Capitani P. Mura* (I.S.C. "G. Giacomello" - Area della Ricerca C.N.R. Monterotondo Stazione Roma - Italy), and D. Ajò (I.C.T.R. Area della Ricerca C.N.R. Padova - Italy).

We recently reported on the unusual paramagnetic behaviour of Ir^{IV} and Rh^{IV} dihydrido complexes (D. Ajò, D. Attanasio, S. Lucente, P. Mura, A.L. Segre, F. De Zuane, J. Mag. and Magnetic Materials, 1992, 104-107, 1997-1998). Till now we have not a definitive explanation why the synthesis of 2 (P. Mura, A.L. Segre, S. Sostero, *Inorg. Chem.*, 1989, 28, 2853-2858) sometimes give rise to samples having different μ_{eff} , and the magnetic moment of recrystallized samples show always lower values ($\mu_{\text{eff}} < 1$ BM) than spin only for a d^5 , Ir^{IV} species. Complex 1 probably may help us to clarify the problem. The crystal structure of 1 show a slightly distorted octahedral geometry with the two P^+Pr_3 phosphines in trans position as well as two chlorine atoms; the third Cl is in trans to the hydride(s) ligand(s).

Crystal data for 1 .

Cryst. Syst. Triclinic, space group $P1$.

$a=8.761(2)$ Å $b=8.823(1)$ Å $c=9.808(2)$ Å
 $\alpha=100.66^\circ(1)$ $\beta=91.20^\circ(1)$ $\gamma=119.72^\circ(1)$
 $V=641.39\text{Å}^3$ $F(000)=309.00$ $\rho=5.64\text{mm}^{-3}$
 $R=0.0588$ $wR=0.0706$ for 2993 data ($F_o > 8\sigma(F_o)$)



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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 $\{[Ni(CHO)_2]_2L\}-(ClO_4)_4$. 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 $[Ni(CHO)_2](ClO_4)_2$ an unexpected product, analysed as $\{[Ni(CHO)_2]_2L\}(ClO_4)_4$, 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, $\beta=98.50(3)^\circ$, $V=3449(2)\text{Å}^3$, $P2_1/c$, $Z=2$, $R=0.065$ ($R_w=0.044$) for 2965 reflections and 415 parameters.

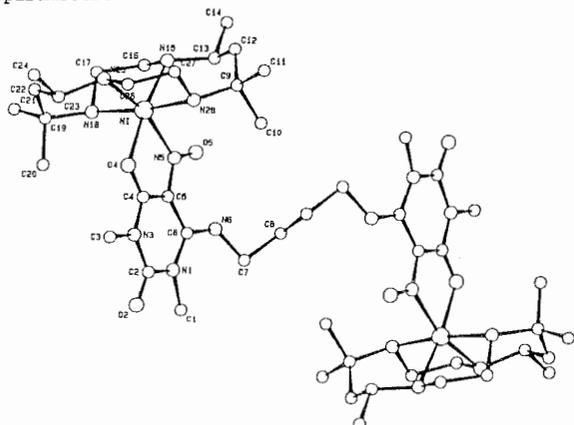
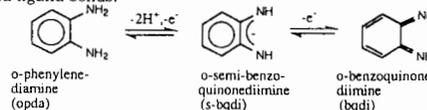


Fig. 1. $\{[Ni(CHO)_2]_2L\}^{4+}$

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(semibenzoquinonedimine)dicarbonylrhodium(I) and Bis(semibenzoquinonedimine)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-quinonedimine-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 semibenzoquinonedimine 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 semibenzoquinonedimine 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.