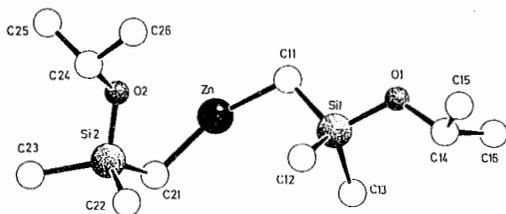


07-Crystallography of Organometallic and Coordination Compounds

$b=11.672(2)$, $c=20.342(1)$ Å. $R(R_w)=0.054(0.055)$, 2737 observed reflections, 135 refined parameters, $\text{MoK}\alpha$ radiation, $D_{\text{calc}}=1.137\text{g}\cdot\text{cm}^{-3}$, $F(000)=704$ (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).



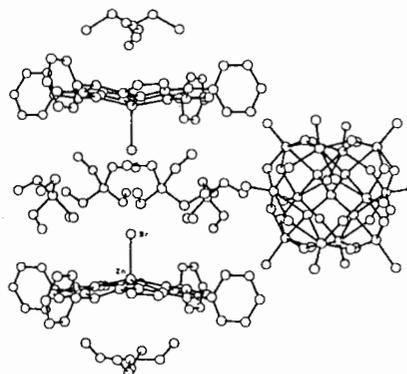
PS-07.05.07 A NEW TERNARY POLYOXOMETALATE CHARGE-TRANSFER SALT. By D. Attanasio, F. Bachechi* and L. Suber*, Istituto di Chimica dei Materiali, Istituto di Strutturistica Chimica, Area della Ricerca di Roma, C.N.R., C.P. 10, 00016 Monterotondo Staz., Roma, Italy.

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 $[\text{Ir}(\text{H})_x(\text{Cl})_3(\text{P}^i\text{Pr}_3)_2]$, $\underline{1}$ ($x=1$ or 2): ANOTHER EXAMPLE OF Ir^{IV} PARAMAGNETIC HYDRIDE OR AN IRIDIUM(V) COMPLEX, TRANSIENT INTERMEDIATE OF $[\text{Ir}^{\text{IV}}(\text{H})_2(\text{Cl})_2(\text{P}^i\text{Pr}_3)_2]$, $\underline{2}$? 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 $\underline{2}$ (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 $\underline{1}$ probably may help us to clarify the problem. The crystal structure of $\underline{1}$ show a slightly distorted octahedral geometry with the two P^iPr_3 phosphines in trans position as well as two chlorine atoms; the third Cl is in trans to the hydride(s).

Crystal data for $\underline{1}$.

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 ($F_o > 8\sigma(F_o)$)

