

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

conclusions are drawn: (a) (*s-cis*- $\eta^4$ -diene) $MCP_2$  complexes are best described as  $\sigma^2, \pi$ -complexes (b) the  $\sigma/\pi$  ratio in the metal diene bonding increases from 1 to 5 and is greater for 7 than for 6, (c) in the Hf complexes the ligands are more  $\sigma$  bonded than in the Zr complexes, and (d) Zr-C bonds are slightly longer than their Hf counterparts. These findings are important for an understanding of different reaction rates (e.g. in carbonylation) and automerization barriers of these complexes.

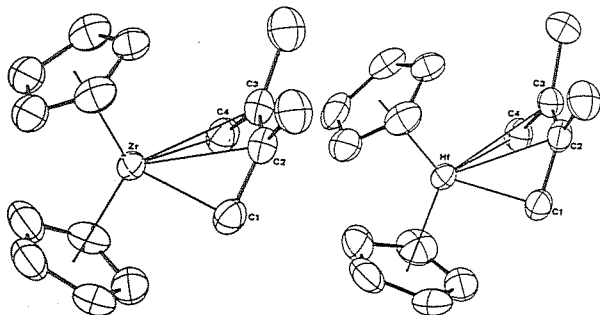


Fig.: Perspective views of the Zr complex 3 and the Hf complex 6.

## 09.4-16 THE CRYSTAL AND MOLECULAR STRUCTURE OF AZIDO-COBALAMIN

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As part of our investigations of the trans-influence of upper axial ligands in vitamin B<sub>12</sub> derivatives we have determined the crystal and molecular structure of azido-cobalamin. Suitable single crystals were obtained by slow evaporation of a methanol/water solution and prepared together with their mother liquor in Lindemann glass capillaries. The space group is  $P2_12_12_1$  with lattice parameters  $a = 2585.6(9)$ ,  $b = 2252.2(9)$  and  $c = 1586.1(5)$  pm.

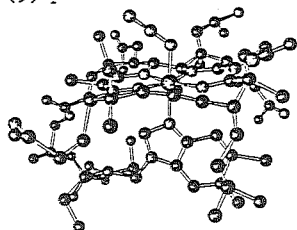


Figure: Plot of azido-cobalamin

The terminal azide ligand is bent with an Co-N-N angle of  $\sim 120^\circ$ . The N atoms of the azide group are linear and asymmetric. Disorder in the ligand is not observed.

09.4-17 STRUCTURES OF SOME ADDUCTS OF HEXACYANOFERRATES WITH POLYCYCLIC TERTIARY AMINES. By J. Pickardt, Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D 1000 Berlin 12, W. Germany.

Hexacyanoferrates of the alkali metals and alkaline earth metals form addition compounds with various amines. Some adducts of hexacyanoferrates(III) of these ions with polycyclic tertiary amines, e.g. hexamethylenetetramine ("HMTA"), quinuclidine ("QUIN"), and 1,4-diazabicyclo[2.2.2]octane ("DABCO") have been obtained as crystals and their structures have been determined by X-ray structure analyses:

$Li_3[Fe(CN)_6] \cdot 2HMTA \cdot 5H_2O$ , orthorhombic,  $I2mm$ ,  $a=9.094(5)$ ,  $b=10.461(5)$ ,  $c=14.558(5)$  Å,  $Z=2$ .

$K_3[Fe(CN)_6] \cdot 2HMTA \cdot 4.5H_2O$ , triclinic,  $P\bar{1}$ ,  $a=14.125(7)$ ,  $b=17.808(9)$ ,  $c=14.116(7)$  Å,  $\alpha=114.14(5)$ ,  $\beta=94.91(5)$ ,  $\gamma=108.36(5)^\circ$ ,  $Z=4$ .

$Be_3[Fe(CN)_6]_2 \cdot 4HMTA \cdot 8H_2O$ , orthorhombic,  $Pc2_1b$ ,  $a=14.368(6)$ ,  $b=14.439(6)$ ,  $c=14.128(5)$  Å,  $Z=2$ .

In the lithium as well as in the beryllium compound the cations are disordered. Lithium hexacyanoferrate(III) also forms an adduct with quinuclidine,  $Li_2H[Fe(CN)_6] \cdot 2QUIN \cdot 3H_2O$ , the crystals are orthorhombic,  $Pn2_1a$ ,  $a=9.580(5)$ ,  $b=18.221(9)$ ,  $c=14.175(6)$  Å, and  $Z=4$ , and also an adduct  $Li_3[Fe(CN)_6] \cdot 2DABCO \cdot xH_2O$ , the structure of which is still under investigation. The crystal structures of these compounds are discussed and compared.

09.4-18 STEREOCHEMICAL FEATURES OF EFFICIENT Ru-BASED O<sub>2</sub> OXIDATION CATALYSTS. By J. D. Oliver, L. C. Strickland, and D. P. Riley, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, OH 45247, USA.

The use of Ru(II) complexes with organosulfur ligands to catalyze the oxidation of dialkylsulfides to dialkylsulfoxides with molecular oxygen has recently been investigated.<sup>1</sup> An array of Ru(II) complexes were tested for catalytic activity using decylmethylsulfide as the substrate. Only complexes containing two anionic ligands were active and among these, the complex, trans-RuBr<sub>2</sub>(DMSO)<sub>4</sub>(1), was the most active.

In an effort to prepare more stereochemically rigid complexes having high catalytic activities, the ligands  $[EtS(CH_2)_3]_2SO$  (2) and  $[EtSO(CH_2)_3]_2S$  (3) were synthesized and their complexes with Ru(II) were isolated. The crystal structures of 1 and the complexes with ligands 2 and 3 have been determined and will be described in terms of their catalytic activities. Complex 1 has a trans arrangement of bromide ligands; however, the Ru(II) complexes of ligands 2 and 3 have a cis arrangement of the bromide ligands. Additional physico-chemical data for Ru(II) complexes of this type will be presented.

1) D. P. Riley, *Inorg. Chem.*, **22**, 1965-67(1983) and D. P. Riley and R. F. Shumate, *J. Am. Chem. Soc.*, in press.

2) D. P. Riley, in preparation.