conclusions are drawn: (a) (s-cis-\(\eta^1\)-dime)Ni(dp) complexes are best described as \(\eta^1\), \(\eta^1\)- complexes; (b) the \(\sigma/\pi\) ratio in the metal diene bonding increases from 1 to 5 and is greater for \(\sigma\) than for \(\pi\); (c) in the Hf complexes the ligands are more \(\sigma\) bonded than in the Zr complexes; and (d) Zr–O 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.

**Figure:** Perspective views of the Zr complex \(\mathbf{1}\) and the Hf complex \(\mathbf{2}\).

**09.4–16** The Crystal and Molecular Structure of Azido-cobalamin


As part of our investigations of the trans-influence of upper axial ligands in vitamin B12 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 Liebig glass capillaries. The space group is \(\text{P}2_1\text{P}2_1\text{P}2_1\) with lattice parameters \(a = 2385.6(9)\) A, \(b = 2252.2(3)\) A, and \(\gamma = 1586.4(5)\) °.

![Figure: Plot of azido-cobalamin](image)

The terminal azide ligand is bent with an O–N–H 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.

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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:

- Li₃[Fe(CN)₆]·2H₂O, orthorhombic, \(\text{P}2_1\text{P}2_1\text{P}2_1\), \(a = 9.094(5)\) A, \(b = 10.461(5)\) A, \(c = 14.558(5)\) A, \(Z = 2\).
- K₃[Fe(CN)₆]·2H₂O, triclinic, \(\text{P}\), \(a = 14.125(7)\) A, \(b = 17.808(9)\) A, \(c = 14.116(7)\) A, \(\alpha = 114.14(5)\) °, \(\beta = 94.91(5)\) °, \(\gamma = 108.36(5)\) °, \(Z = 4\).
- Be₂[Fe(CN)₆]·4H₂O·Br₂, orthorhombic, \(\text{P}2_1\text{P}2_1\text{P}2_1\), \(a = 14.368(6)\) A, \(b = 14.439(6)\) A, \(c = 25.85(2)\) A, \(Z = 2\).

In the lithium as well as in the beryllium compound the cations are disordered. Lithium hexacyanoferrate(III) also forms an adduct with quinuclidine. Li₃[Fe(CN)₆]·2QUIN·3H₂O, the crystals are orthorhombic, \(\text{P}2_1\text{P}2_1\text{P}2_1\), \(a = 9.580(5)\) A, \(b = 18.221(9)\) A, \(c = 14.175(6)\) A, \(Z = 4\), and also an adduct Li₃[Fe(CN)₆]·2DABCO·xH₂O, the structure of which is still under investigation. The crystal structures of these compounds are discussed and compared.