09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

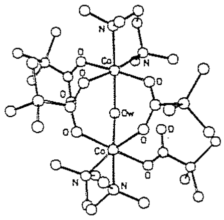
09.4–13 X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF A WATER OXYGEN AND CARBOXYLATO BRIDGED BINUCLEAR COBALT(II) COMPLEX, $Co_2(Cl_3C_2O_2)_4(C_6H_{16}N_2)_2H_2O$.

By U. Turpeinen, R. Hämäläinen and M. Ahlgrén, Division of Inorganic Chemistry, University of Helsinki, Finland

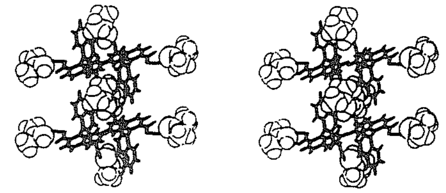
Crystals of the title compound were obtained by slow evaporation of ethanol solution containing cobalt(II) trichloroacetate and N,N,N′,N′-tetramethylethylenediamine. The compound crystallizes in the space group $P2_1/c$ with a=23.610(7), b=10.439(2), c=17.920(4) Å, β=110.43(4)° and Z=4. The structure was solved by direct methods and refined to a final R=0.087 for 2189 reflections. The structure consists of discrete binuclear molecules. The octahedral coordination of each Co atom is achieved by a bridging water molecule, two bridging carboxylate ions, a chelating diamine molecule and a monodentate carboxylate ion, with Co-N distances of 2.18(2)-2.21(2) Å and Co-O distances of 2.06(1)-2.18(1) Å. The Co-Co distance is 3.696(3) Å and the Co-O-Co and the average Co-O-C-O-Co potential magnetic exchange pathways are 4.36 and 6.59 Å, respectively. The Co-O-Co angle is 116.1(6)°.

The binuclear structure is additionally stabilized by strong intramolecular hydrogen bonds formed between the two noncoordinated carboxylate oxygen atoms and the bridging water molecule. Some trichloroacetate chlorine atoms are disordered, which is not unexpected.

The magnetic susceptibility was measured between 93 and 303 K. The effective magnetic moment per Co ion decreases from 4.96 BM at 303 K to 4.59 BM at 93 K. However, this does not necessarily imply antiferromagnetism since even monomeric octahedral cobalt(II) complexes show such a decrease because of the extensive spin-orbit coupling.

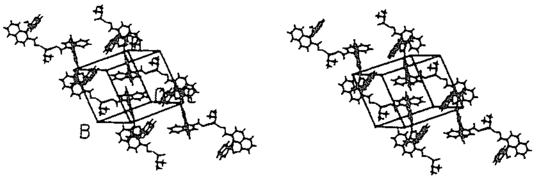


play an important role in the complexation in both structures. In the BIN-DMF 1:2 clathrate the DMF guests are encapsulated in nearly rectangular cages of the BIN host lattice and are also held fixed by H-bonds, each to one of the carboxyl groups.



BIN-DMF 1:2 clathrate

In the BIN-DMSO 1:1 clathrate, each DMSO molecule is a H-bond acceptor from two carboxyl groups belonging to two different BIN molecules, resulting in infinite H-bonded BIN-DMSO-BIN-DMSO.... chains running parallel to each other.



BIN-DMSO 1:1 clathrate

Further structural details, comparison with related structures, and characteristic aspects on the mode of complexation will be discussed.

09.4–14 CRYSTAL STRUCTURES OF TWO COORDINATOCLATHRATES: 1,1′-BINAPHTHYL-2,2′-DICARBOXYLIC ACID HOST WITH EITHER DIMETHYLFORMAMIDE OR DIMETHYL SULFOXIDE AS GUEST.

By Ingeborg Csöregh and Agneta Sjögren, Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, Sweden; Mátyás Czugler, Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary, and Edwin Weber, Institut für Organische Chemie und Biochemie der Universität Bonn, FR Germany.

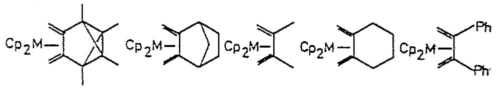
1,1′-Binaphthyl-2,2′-dicarboxylic acid (BIN) is known to act as a clathrate host for a number of small organic molecules. The structures of five BIN clathrates with alcoholic guests have been recently studied by X-ray diffraction (Weber, Csöregh, Stensland, Czugler, J. Am. Chem. Soc. (1984) in press). The aim of the present investigation was to obtain information about the mode of complexation with BIN of guests lacking a hydroxyl group.

The crystal structures of the title compounds have been determined from single crystal X-ray diffraction data and refined by least-squares methods to R values of 0.066 (2550 reflections) and 0.080 (1932 reflections) for the clathrates with dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as the guest molecules, respectively. The unit cells were monoclinic with Z = 4 in both structures. The DMF clathrate crystallizes in space group $P2_1/c$ with a = 14.916(13) Å, b = 9.882(10), c = 17.128(13) and β = 90.45(7)°. The structure with DMSO guests has the space group $P2_1/n$ with a = 12.912(5) Å, b = 17.979(15), c = 9.702(7) and β = 110.79(7)°. Hydrogen bonds

09.4–15 σ VS. π BONDING IN (S-CIS-η^4-BUTADIENE) COMPLEXES OF ZIRCONOCENE AND HAFNOCENE.

By G. Müller, Anorg.-chem. Institut der TU München, Garching, FRG, G. Erker, Abteilung f. Chemie d. Ruhr-Universität, Bochum, FRG, and C. Krüger, MPI f. Kohlenforschung, Mülheim a.d. Ruhr, FRG.

The molecular structures of five (s-cis-η^4-1,3-diene)$ZrCp_2$ complexes 1-5 and two analogous -$HfCp_2$ complexes 6,7 are compared.



M = Zr (1) M = Zr (2) M = Zr (3) M = Zr (4) M = Zr (5)
Hf (6) Hf (7)

As the figure shows, the η^4 coordination of the double bonds of the cisoid 1,3-diene ligands to the bent MCp_2 fragment leads to a pseudotetrahedral geometry of the metal centers. There are pronounced differences in bond lengths between the bonds to the diene termini C1/C4 and those to the internal C atoms C2/C3. This is indicative of a decrease in π bonding compared to that in late transition metal conjugated diene complexes, where approximately equal metal diene bounds are found. The M-C1/C4 bonds resemble closely M-C σ bonds of the respective metals, whereas the M-C2/C3 bonds are essentially π in nature. (M-C1/C4 for 1-5: 2.279(2)-2.329(2)Å; 6: 2.268(5)Å; 7: 2.255(8) Å. M-C2/C3 for 1-5: 2.550(5)-2.714(5)Å; 6: 2.646(5)Å; 7: 2.72(1)Å). By comparison of the various geometrical parameters the following conclusions are drawn: (a) (s-cis-η^4-diene)MCp$_2$ complexes are best described as σ^2, π-complexes (b) the σ/π 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 σ 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.

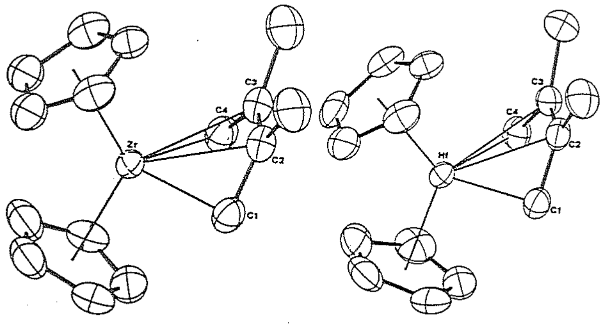


Fig.: Perspective views of the Zr complex 3 and the Hf complex 6.

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

By W. Hinrichs, G. Klar, J. Kopf and J. Wiese,
Institut für Anorg. und Angew. Chemie,
Universität Hamburg, Martin-Luther-King-Platz 6,
D-2000 Hamburg 13, Federal Republic of Germany.

As part of our investigations of the trans-influence of upper axial ligands in vitamin B_{12} 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 theit 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.

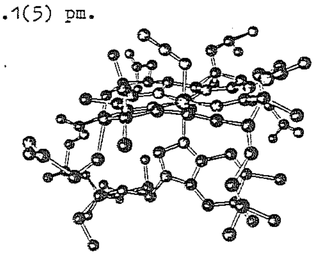


Figure: Plot of azido-cobalamin

The terminal azide ligand is bent with an Co-N-N angle of ~120°. 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
α=114.14(5), β=94.91(5), γ=108.36(5)°, 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_2 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.[1] 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-$RuBr_2(DMSO)_4$(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 physicochemical 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.