09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-13 X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF A WATER OXIDE AND CARBOXYLATE BRIDGED BINUCLEAR COBALT(II) COMPLEX, CO$_2$(C$_5$H$_4$)$_2$(CO$_3$)$_2$(N$_2$)$_2$, by U. Turenen, R. Hämäläinen and K. Shigden, Division of Inorganic Chemistry, University of Helsinki, Finland.

Crystals of the title compound were obtained by slow evaporation of ethanol solution containing cobalt(II) trichloracetate 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, V=1107.3(3) Å$^3$ and Z=4. The structure was solved by direct methods and refined by least-squares to R values of 0.087 for 2189 reflections. The structure consists of discrete binuclear molecules. The octahedral coordination of each cobalt ion is achieved by the bridging water molecule, two bridging carboxylate ions, one chelating C$_5$H$_4$N$_2$ 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 angle Co-O-Co is 116.1(6)°.

The binuclear structure is additionally stabilized by intermolecular hydrogen bonds arising from the noncoordinated carboxylate oxygen atoms and the bridging water molecule. Some trichloracetate chlorine atoms are disordered, which is not unexpected. The magnetic susceptibility was measured between 93 and 303 K. The effective magnetic moment per cobalt ion decreases from 4.96 BM at 303 K to 4.59 BM at 93 K. However, this is not unexpected as a decrease because of the extensive spin-orbit coupling.

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.

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 COORDINATE-CLATHRATES: 1,1-BINAPHTHYL-2,2-DICARBOXYLIC ACID HOST WITH EITHER DIMETHYLFORMAMIDE OR DIMETHYL SULFOXIDE AS GUEST. By Ingeborg Csoregh and Erik Weber, Institut für Anorganische Chemie, Archenheim Laboratory, University of Stockholm, Sweden; Mátécs Csuzgler, 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, Csoregh, 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 hydroxy 1 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=16.018(4) Å, b=8.883(10) Å, c=17.283(13) Å, and α=90.46(7)°. The structure with DMSO guests has the space group P2$_1$/c with a=15.918(4) Å, b=17.978(16) Å, c=9.708(7) Å and β=110.79(7)°. Hydrogen bonds play an important role in the complexation in both structures. In the BIN-DMP 1:2 clathrate the DMP 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.


The molecular structures of five (s-cis-1,1'-butadiene)ZrCP$_2$ complexes, 1-5, and two analogous HCP$_2$ complexes, 6 and 7, are compared.

As the figure shows, the ν coordination of the double bonds of the cisoid 1,3-diene ligands to the metal fragment leads to a pseudo-tetrahedral geometry of the metal centers. There are pronounced differences in bond lengths between the bonds to the diene termini 1C/04 and those to the internal C atoms 02/03. This is indicative of a decrease in ν bonding compared to that in late transition metal conjugated diene complexes, where approximately equal metal diene bounds are found. The M-C1/04 bonds resemble closely M-O bonds of the respective metals, whereas the M-02/03 bonds are essentially μ in nature. (ν of 04 for 1: 2.579(2)-2.529(2) Å; 2: 2.658(5) Å; 3, 4, 5: 2.525(5) Å).