

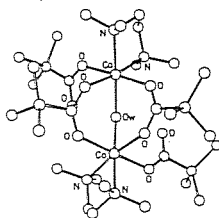
09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-13 X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF A WATER OXYGEN AND CARBOXYLATE BRIDGED BINUCLEAR COBALT(II) COMPLEX, $\text{Co}_2(\text{Cl}_2\text{C}_2\text{O}_2)_4(\text{C}_6\text{H}_{16}\text{N}_2)_2\text{H}_2\text{O}$. By U. Turpeinen, R. Hämmäläinen and M. Ahlgren, 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, $\beta=110.43(4)^\circ$ 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-C potential magnetic exchange pathways are 4.36 and 6.59 Å, respectively. The Co-O-Co angle is $116.1(6)^\circ$.

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 anti-ferromagnetism since even monomeric octahedral cobalt(II) complexes show such a decrease because of the extensive spin-orbit coupling.

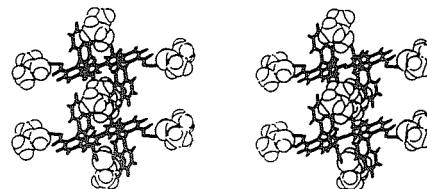


09.4-14 CRYSTAL STRUCTURES OF TWO COORDINATION-CLATHRATES: 1,1'-BINAPHTHYL-2,2'-DICARBOXYLIC ACID HOST WITH EITHER DIMETHYLFORMAMIDE OR DIMETHYL SULFOXIDE AS GUEST. By Ingeborg Csöreg and Agneta Sjögren, Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, Sweden; Mátyás 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, Csöreg, 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.

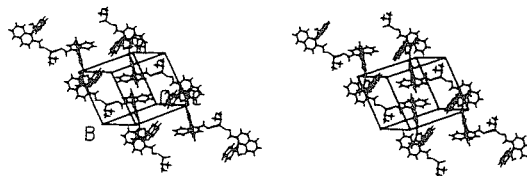
The crystal structures of the title compounds have been determined from single crystal X-ray diffraction data and refined by least-squares methods to R values of 0.066 (2550 reflections) and 0.080 (1932 reflections) for the clathrates with dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as the 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 $a = 14.916(13)$, $b = 9.882(10)$, $c = 17.128(13)$ and $\beta = 90.45(7)^\circ$. 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 $\beta = 110.79(7)^\circ$. Hydrogen bonds

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.

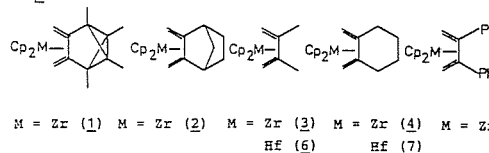


BIN-DMSO 1:1 clathrate

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

09.4-15 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)ZrCp₂ complexes 1-5 and two analogous -HfCp₂ complexes 6,7 are compared.



As the figure shows, the η^4 coordination of the double bonds of the cisoid 1,3-diene ligands to the bent MCp₂ 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 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 bonds 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