

07-Crystallography of Organometallic and Coordination Compounds

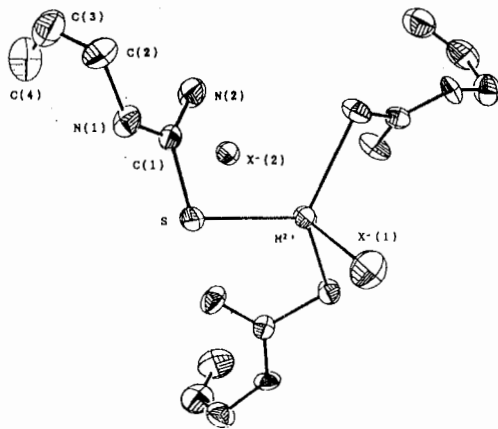
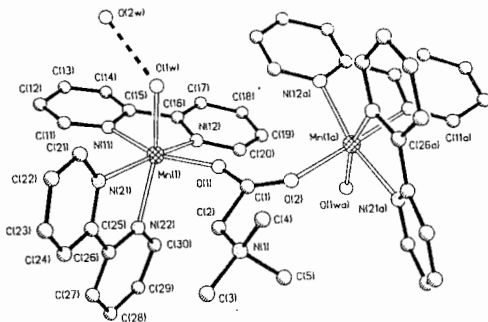


Fig.1 Molecular Structure

PS-07.04.02 CRYSTAL STRUCTURE OF A NEW DINUCLEAR Mn(II) COMPLEX BRIDGED BY A SINGLE CARBOXYLATO-0,0' GROUP.

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A novel Mn(II) complex $[\text{Mn}_2(\text{bpy})_2(\text{bet})(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$, isolated from a mixture of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 1,1'-bipyridine (bpy) and betaine (bet, $\text{Me}_3\text{N}^+\text{CH}_2\text{CO}_2^-$) in water-ethanol solution, has been characterized by X-ray crystallography. The yellow crystals are in monoclinic, space group C_2 with $a = 16.321(5)$, $b = 13.354(5)$, $c = 13.298(2) \text{ \AA}$, $\beta = 96.55(2)^\circ$, $V = 2879(2) \text{ \AA}^3$, and $Z = 2$. The structure comprises discrete dinuclear Mn cations, in which a pair of Mn atoms, separated at a non-bonded distance of $5.670(2) \text{ \AA}$, are bridged by a single carboxylato-0,0' group of the bet ligand in the *syn-anti* mode. No singly carboxylato-0,0'-bridged dinuclear manganese complex has been reported so far. Each Mn atom is in a distorted octahedral environment, surrounded by two chelate bpy ligands [$\text{Mn}-\text{N} = 2.240(8) \sim 2.261(8) \text{ \AA}$], one aqua ligand [$\text{Mn}-\text{O} = 2.158(7) \text{ \AA}$] and one oxygen atom of the two-foldly disordered carboxylato group of the bet ligand [$\text{Mn}-\text{O} = 2.085(10)$ or $2.213(10) \text{ \AA}$].



PS-07.04.03 STRUCTURES OF BIS(2-METHOXYETHYL-CYCLOPENTADIENYL) COMPLEXES OF LANTHANIDE CHLORIDES. By Pei-Ju Zheng*, Jian Chen and Guang Wu, Research Center of Analysis & Measurement, Fudan University, Shanghai, P.R.China, 200433; Dao-Li Deng, Ji-Qian Hu and Chang-Tao Qian, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Biscyclopentadienyl lanthanide chlorides are of importance in the synthetic chemistry of organolanthanides. We think that the good coordination environment and the oxophilicity of the metal greatly enhance the stability of the complex formed. The ether-substituted cyclopentadienyl ligand Cp' ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4$) has been used and shown to be an efficient ligand for stabilizing biscyclopentadienyl complexes of lanthanide chlorides (Deng, Qian, Wu and Zheng, J. Chem. Soc., Chem. Commun., 1990, 880). The molecular structure of $[\text{Cp}'_2\text{La}(\mu\text{-Cl})_2]$ is shown in Fig.1. The lanthanum atom is ten coordinated by two cyclopentadienyl ligands, two oxygen and two chlorine atoms with a distorted octahedral coordination geometry.

Recently a new series of $\text{Cp}'_2\text{LnCl}$ ($\text{Ln}=\text{DY}$, Er and Yb) complexes has been studied. $\text{Cp}'_2\text{ErCl}$ crystallized in space group Pnma with $a=12.269(0)$, $b=11.742(6)$, $c=11.197(2) \text{ \AA}$, $z=4$, $R=0.043$ for 1796 observed [$I > 3\sigma(I)$] reflections. The molecular structure of the complex is shown in Fig.2. The atom Er and atoms C(3),C(4),C(5),O(1) and C(6) of one Cp' ligand are located on the mirror plane and the other atoms of this Cp' ligand are symmetrically arranged on the both sides of the mirror plane. While the atom Cl and all atoms of another Cp' ligand except C(16) and C(16') reside neither on the mirror plane nor symmetrically around the plane, it implies that these atoms are disordered with occupancy of 0.5 each. There are two equivalently favourable sites for them as shown in Fig.2(a) and Fig.2(b). Thus the crystal structure retains a crystallographic mirror plane. The Er atom is coordinated by one Cl atom, two cyclopentadienyl rings and two oxygen atoms of the Cp' groups with a pseudo-trigonal bipyramid coordination. Its coordination number of nine is lower than that of La atom due to its smaller radius. The average Er-O bond distance compares reasonably with the axial one in $\text{CpErCl}_2(\text{THF})_3$ (Cp denotes C_5H_5) (Cynthia, Organometallics, 1982, 1,998), but differs from the "equatorial" one in $\text{CpErCl}_2(\text{THF})_3$ and the bridge linkages in $[\text{Cp}'\text{ErOH}]_2$ (to be published). It can readily be presumed that the difference in metal-ligand bond lengths are associated with specific structural alternations. It has been found that $\text{Cp}'_2\text{DyCl}$, $\text{Cp}'_2\text{ErCl}$ and $\text{Cp}'_2\text{YbCl}$ are isomorphous compounds.

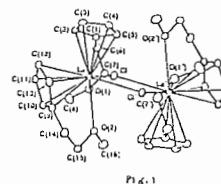


Fig. 2(a)

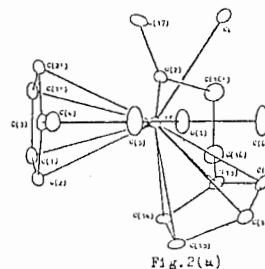


Fig. 2(b)

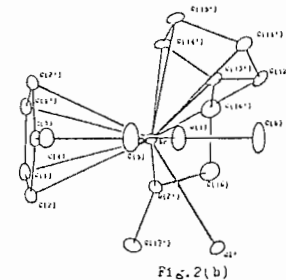


Fig. 2(c)