07-Crystallography of Organometallic and Coordination Compounds

PS-07.04.02 CRYSTAL STRUCTURE OF A NEW DINUCLEAR Mn(II) COMPLEX BRIDGED BY A SINGLE CARBOXYLATO-0',0'-GROEP.
By Xiao-Ming Chen*, Department of Chemistry, Zhejiang University, Hangzhou 310027, China, and Thomas C. M. Mak, Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong.

A novel Mn(II) complex \( [\text{Mn} \cdot \text{ppy}] \cdot \text{bet} \cdot (\text{H}_2 \text{O}) \cdot \text{ClO}_4 \), -2H_2O, isolated from a mixture of MnClO_4, 5H_2O, 1,1'-bipyridine (bpy) and betaine (bet, Me_3NCH_2CO_2) in water-ethanol solution, has been characterized by X-ray crystallography. The yellow crystals are in monoclinic, space group \( C2 \) with \( a = 16.321(5) \) Å, \( b = 13.35(4) \) Å, \( c = 13.298(2) \) Å, \( \beta = 96.15(2) \)°, \( V = 2879(2) \) Å³, and \( Z = 2 \). The structure comprises discrete dicobalt ions, in which a pair of Mn atoms, separated by a non-bonded distance of 3.670(2)Å, 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 \( \{\text{Mn} - \text{N} = 2.240(8) - 2.261(8) \AA\} \), one aqua ligand \( \{\text{Mn} - \text{O} = 2.158(7) \AA\} \) and one oxygen atom of the two-foldly disordered carboxylato group of the bet ligand \( \{\text{Mn} - \text{O} = 2.085(10) \text{ or } 2.213(10) \AA\} \).

PS-07.04.03 STRUCTURES OF BIS-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.

Bis(cyclopentadienyl) lanthanide chlorides are of importance in the synthetic chemistry of organolanthanides. We think that the good coordination environment and the exo-phobicity of the metal greatly enhance the stability of the complex formed. The ether-substituted cyclopentadienyl ligand CP'(CH_3OCH_2CH_2CH_2CH_2) has been used and shown to be an efficient ligand for stabilizing bis(cyclopentadienyl) complexes of lanthanide chlorides (Deng, Qian, Wu and Zheng, J. Chem. Soc., Chem. Commun., 1990, 880). The molecular structure of [CP'La(μ-Cl)]_2 is shown in Fig.1. The lanthanum atom is tetrahedrally coordinated by two cyclopentadienyl ligands, two oxygen and two chlorine atoms with a distorted octahedral coordination geometry.

Recently a new series of CP'ECl (E= Dy, Er and Yb) complexes have been studied. CP'ECl crystallized in space group Pnma with \( a = 12.269(6) \) Å, \( b = 11.742(6) \) Å, \( c = 11.972(7) \) Å, \( \beta = 90.043 \)° for 1996 observed (I>5σ(I)) reflections. The molecule structure of the complex is shown in Fig.2. The atoms Er and atoms C(15), 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 other side of the mirror plane. While the atom C1 and all atoms of another CP' ligand except C(16) and C(17) locate 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 equally favourable sites for them as shown in Fig.2(a) and 2(b). Thus the crystal structure retains a crystallographic mirror plane. The Er atom is coordinated by two CP'Cl atoms, two cyclopentadienyl rings and two oxygen atoms of the CP' groups with a pseudo-trigonal bipyramidal 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 CP'ECl(THF)_2; (CP' denotes CP'(CH_3OCH_2CH_2CH_2)) (Conn, Organomechanics, 1982, 1998) but differs from the "equatorial" one in CP'ECl(THF)_2 and the bridge linkages in [CP'E(OH)_2]_2 (to be published). It can readily be presumed that the difference in metal-ligand bond lengths is associated with specific structural alternations. It has been found that CP'DyCl, CP'ErCl and CP'TbCl are isomorphous compounds.