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-O,O' GROEP.
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A novel MnII(II) complex $[\text{Mn(bpy)}_2\text{Cl}_2]$ isolated from a mixture of $\text{MnCl}_2\cdot\text{H}_2\text{O}$, $\text{Cl}_2\text{O}_4$, and $\text{H}_2\text{O}$ solution is characterized by X-ray crystallography. The yellow crystals are monoclinic, space group $\text{P}2_1$ with $a = 16.321(5)$, $b = 13.354(5)$, $c = 13.298(2)$ Å, $\beta = 96.35(2)^\circ$, $\gamma = 87.90(2)^\circ$, and $Z = 2$. The structure consists of discrete Mn cations, in which a pair of Mn atoms, separated by a non-bonded distance of 3.670(2) Å, are bridged by a single carboxylato-O,O' group of the bidentate ligand in the sym-anti mode. No singly carboxylato-O,O'-bridged dinuclear manganese complex has been reported so far. Each Mn atom is in a distorted octahedral environment, surrounded by two chelate bpy ligands $[\text{Mn} - \text{N} = 2.28(8) - 2.26(8)$ Å], one aqua ligand $[\text{Mn} - \text{O} = 2.158(7)$ Å] and one oxygen atom of the two-fold disordered carboxylato group of the bidentate ligand $[\text{Mn} - \text{O} = 2.085(10)$ or 2.213(11)$Å].

Recently, a new series of $\text{Cp}^\text{II}^\text{LnCl}$ ($\text{Ln} = \text{Dy}, \text{Er}$ and $\text{Yb}$) complexes has been studied. $\text{Cp}^\text{II}^\text{ErCl}$ crystallizes in space group $\text{Pnm}$ with $a = 12.269(6)$, $b = 11.742(6)$, $c = 11.975(7)$ Å, $Z = 4$, and $R = 0.043$ for 1996 observed (I>3$\sigma$(I)) reflections. The molecule structure of the complex is shown in Fig.2. The atom Er and atoms C(1), C(4), C(5), O(1) and O(6) of one Cp ligand are located on the mirror plane and the other atoms of the Cp ligand are symmetrically arranged on the both sides of the mirror plane. While the atom C(2) 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 sets 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 two 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 $\text{Cp}^\text{II}^\text{Cl}(\text{THF})$ (Cp denotes $\text{C}_5\text{H}_{5}$, Organometallics, 1982, 1,968), but differs from the equatorial one in $\text{Cp}^\text{II}^\text{ErCl}(\text{THF})$, and the bridge linkages in $\text{Cp}^\text{II}^\text{ErOH}_2$ (to be published). It can readily be presumed that the difference in metal-ligand bond lengths is associated with specific structural alterations. It has been found that $\text{Cp}^\text{II}^\text{LaCl}$, $\text{Cp}^\text{II}^\text{ErCl}$ and $\text{Cp}^\text{II}^\text{YbCl}$ are isomorphous compounds.