

## 07-Crystallography of Organometallic and Coordination Compounds

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**PS-07.03.23** STRUCTURAL CHARACTERIZATION OF TETRANUCLEAR CLUSTER  $(Et_4N)_2[Fe_4S_4(S-p-tol)_4]$ . By Li Li, Xiaofeng Zheng, Yuguo Fan, Yan Liu\*, and Jiqing Xu\*, Key Laboratory for Molecular Spectra and Structure and \*Department of Chemistry of Jilin University, Changchun 130023, PRC.

$(Et_4N)_2[Fe_4S_4(S-p-tol)_4]$  (tol=tolyl),  $M_r=552.44$ , tetragonal,  $P4_2,2, a=12.227(2) \text{ \AA}, c=36.15(2) \text{ \AA}, V=5405(3) \text{ \AA}^3, Z=4, D_x=1.358 \text{ g cm}^{-3}, \lambda(\text{MoK}\alpha)=0.71069 \text{ \AA}, \mu=13.92 \text{ cm}^{-1}, F(000)=2312, T=293(2) \text{ K}$ . The coordinates and anisotropic thermal parameters of the Fe and S atoms, and the coordinates and isotropic parameters of all remaining non-hydrogen atoms were refined by full matrix least-squares procedure on  $F^2$ , which converged to the final  $R=0.054, (\Delta/\sigma)=0.05, (\Delta\rho)_{\text{max}}=0.186, (\Delta\rho)_{\text{min}}=-0.184 \text{ e \AA}^{-3}$ .

The structural characterization reveals that the configuration of the title compound exhibits a tetranuclear cubane-type  $(Fe_4S_4)$  core with six Fe-Fe distances in the range of 2.750–2.761 Å (Fig.1). The cluster anion has distorted  $D_{2d}$  symmetry with the inverse four-fold axis passing the midpoint of bonds  $Fe_1-Fe_2$  and  $Fe_{1a}-Fe_{2a}$ , which is very similar to the configurations of the clusters  $[Fe_4S_4(\text{Sph})_4]^{2-}$  (L. Que, Jr., M.A. Bobrik, J.A. Ibers, and R.H. Holm, 1974),  $[Fe_4S_4(\text{Sph})_4]^{3-}$  (E.J. Laskowski, R.B. Frankel, and J.A. Ibers, 1978), and  $[Fe_4S_4(\text{SCH}_2\text{ph})_4]^{2-}$  (B.A. Averill, T. Herskovitz, R.H. Holm, and J.A. Ibers, 1973). The cation  $(Et_4N)^+$  is disordered with two possible sites of equal occupation factors.

## References

- B.A. Averill, T. Herskovitz, R.H. Holm, and J.A. Ibers, *J. Am. Chem. Soc.*, **95**, 3523 (1973).  
E.J. Laskowski, R.B. Frankel, and J.A. Ibers, *J. Am. Chem. Soc.*, **100**, 5322 (1978).  
L. Que, Jr., M.A. Bobrik, J.A. Ibers, and R.H. Holm, *J. Am. Chem. Soc.*, **96**, 4168 (1974).

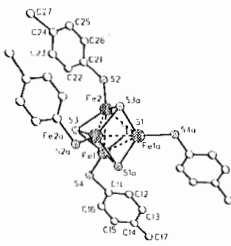


Fig.1

**PS-07.03.24**

**PLANAR TRINUCLEAR COBALT CARBONYL CLUSTER CONTAINING NEW CYCLO-THIOPHOSPHATO LIGAND.** By L. Qi Wang\*, H. Xiang, L. Shutang, Z. Liping, W. Baoshan, State Key Laboratory of Structural Chemistry; Department of Chemistry, Inner Mongolia University, China, and S. Jianqiu, Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou, China.

Most of the known  $Co_3$  carbonyl cluster derivatives were capped with a main-group atom to have a tetrahedral  $Co_3E$  framework, but here we report that the reaction of  $Cl_2PSCH_2CH_2OPCl_2$  with  $Co_2(CO)_8$  yields a non-capped planar  $Co_3$  cluster  $(Co_3(\mu-PSCH_2CH_2O)_3(CO)_6)$  I. The molecular structure of I determined by x-ray diffraction is shown in Figure 1 and indicates that this non-capped planar  $Co_3$  molecule is symmetrical ( $C_{3v}$ ) with six terminal carbonyl and three bridging phosphor-containing  $P \begin{matrix} S \\ / \backslash \\ O \end{matrix}$  ligands.

Fragmentation of the linear reactant  $Cl_2PSCH_2CH_2OPCl_2$  followed by a cyclic formation led to the first reported cyclo-thiophosphato ligand  $PSCH_2CH_2O$ , in which the P atom is a three-electron donating bridging atom, linked to each of the three Co-Co edges of the  $Co_3$  triangle. The analytical data, IR( $\nu_{CO}$ ),  $^1H$  NMR and MS spectra are consistent with the molecular structure of I.

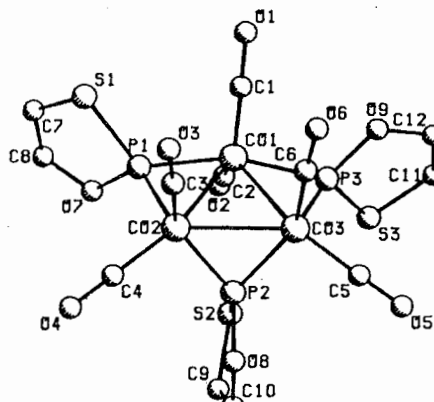


Fig 1

(Keller, E., & Vahrenkamp. (1977), *Angew. Chem. Intern. Eng.* **16**, 731).

## 07.04 – Metal Coordination Analysis

**PS-07.04.01** CRYSTAL STRUCTURES OF  $[M(C_4H_8N_2S)_3X]X$  WHERE  $M=Cd, Hg, X=Cl, Br$ . By Wen-Tao Yu\*, D.R. Yuan, D.Xu and M.H. Jiang, Institute of Crystal Materials, Shandong University, Jinan, Shandong, 250100, China.

In a search for organometallic compounds which have nonlinear optical properties in the solid state, the four compounds have been prepared. They all have NLO properties and their crystal structures have been solved. Four compounds crystallized in the trigonal space group  $R\bar{3}c$ . All cells take hexagonal setting. The main crystallographic data are:

- (1):  $[Cd(C_4H_8N_2S)_3Cl]Cl$ ,  $M_r=531.9$ ,  $a=11.527(4)$ ,  $c=27.992(4) \text{ \AA}, V=3221.1 \text{ \AA}^3, Z=6, D_c=1.65 \text{ g cm}^{-3}, T=296 \text{ K}, R=0.028$  for 940 observed reflections.
  - (2):  $[Cd(C_4H_8N_2S)_3Br]Br$ ,  $M_r=620.8$ ,  $a=11.621(2)$ ,  $c=28.659(7) \text{ \AA}, V=3351.7 \text{ \AA}^3, Z=6, D_c=1.85 \text{ g cm}^{-3}, T=296 \text{ K}, R=0.036$  for 924 observed reflections.
  - (3):  $[Hg(C_4H_8N_2S)_3Cl]Cl$ ,  $M_r=620.1$ ,  $a=11.436(3)$ ,  $c=28.106(8) \text{ \AA}, V=3183.2 \text{ \AA}^3, Z=6, D_c=1.94 \text{ g cm}^{-3}, T=296 \text{ K}, R=0.048$  for 912 observed reflections.
  - (4):  $[Hg(C_4H_8N_2S)_3Br]Br$ ,  $M_r=708.9$ ,  $a=11.579(2)$ ,  $c=28.917(8) \text{ \AA}, V=3357.6 \text{ \AA}^3, Z=6, D_c=2.10 \text{ g cm}^{-3}, T=296 \text{ K}, R=0.066$  for 840 observed reflections.
- All data were measured on a Nicolet R3m/E diffractometer using graphite monochromatized  $MoK\alpha$  radiation (0.71069 Å). Four structures were solved by Patterson and difference electron syntheses and refined by the block-diagonal matrix least-squares method. The results of these structure analyses show that four compounds are fully isostructural and each molecule consists of  $[M^{2+}(C_4H_8N_2S)_3X^-]$  complex cation and  $X^-$  anion. The  $M^{2+}$  and  $X^-$  ions occupy a special position (6a) of the space group. In all four structures, the  $M^{2+}$  cations are four-coordinated by one  $X^-$  anion and three sulphur atoms belonging to three allylthiourea ligands.

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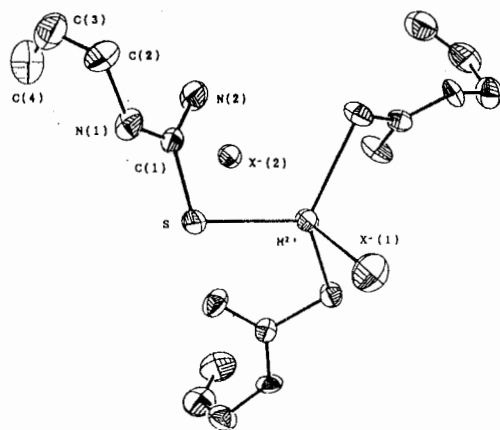
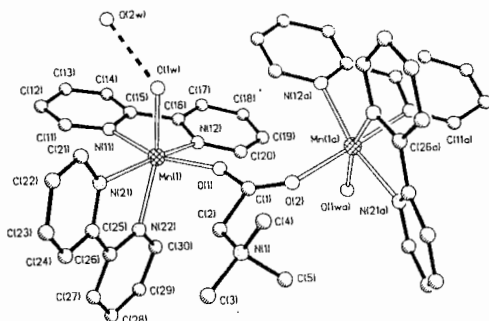


Fig.1 Molecular Structure

PS-07.04.02 CRYSTAL STRUCTURE OF A NEW DINUCLEAR Mn(II) COMPLEX BRIDGED BY A SINGLE CARBOXYLATO-*O,O'* 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-*O,O'* group of the bet ligand in the *syn-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 [ $\text{Mn}-\text{N} = 2.240(8) \sim 2.261(8) \text{ \AA}$ ], 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  $\text{Cp}'$  ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4$ ) 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  $\text{Pnma}$  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  $\text{Cp}'$  ligand are located on the mirror plane and the other atoms of this  $\text{Cp}'$  ligand are symmetrically arranged on the both sides of the mirror plane. While the atom Cl and all atoms of another  $\text{Cp}'$  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  $\text{Cp}'$  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  $\text{C}_5\text{H}_5$ ) (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.

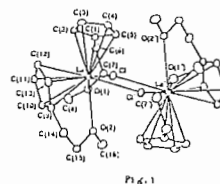


Fig. 2 (a)

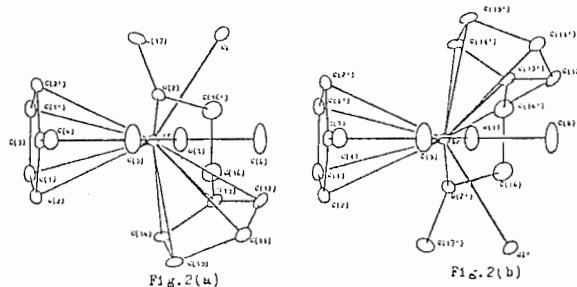


Fig. 2 (b)