

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, $P4_2,2,2$, $a=12.227(2) \text{ \AA}$, $c=36.15(2) \text{ \AA}$, $V=5405(3) \text{ \AA}^3$, $Z=4$, $D_x=1.358 \text{ g cm}^{-3}$, $\lambda(\text{MoK}\alpha)=0.71069 \text{ \AA}$, $\mu=13.92 \text{ cm}^{-1}$, $F(000)=2312$, $T=293(2) \text{ K}$. 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).

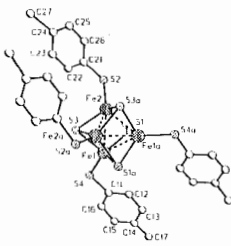


Fig.1

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(ν_{CO}), 1H NMR and MS spectra are consistent with the molecular structure of I.

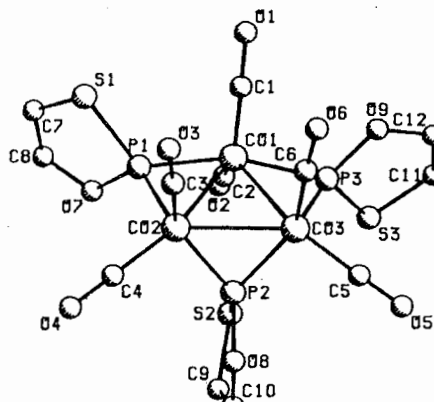


Fig 1

(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 \AA). 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.