

09.5-3 CRYSTAL AND MOLECULAR STRUCTURE OF SOME CUBANE-LIKE TETRANUCLEAR MOLYBDENUM CLUSTERS. By J.L. Huang and J.Q. Huang, (Department of Chemistry, Fuzhou University), S.F. Lu, H. H. Zhang, D.M. Wu, Y.H. Lin, X.M. Zhang and J.X. Lu, (Fujian Institute of Research on the Structure of Matter, Chinese Academic of Science), Fuzhou, People's Republic of China.

In the investigation of molybdenum clusters with diethyldithiophosphate(dtp) anion ligands, some tetranuclear molybdenum clusters were synthesized and structurally characterized. The crystal parameters for each compound are given below:

1. $\text{Mo}_4(\mu_3\text{-S})_3(\mu_3\text{-O})(\mu\text{-dtp})_3(\text{dtp})_3 \cdot 3\text{CH}_3\text{CN}$, R^3 , $a=12.852(3)\text{\AA}$, $\alpha=108.37(2)^\circ$, $Z=1$, $R=0.072$.
2. $\text{Mo}_4(\mu_3\text{-S})_3(\mu_3\text{-O})(\mu\text{-dtp})_3(\text{dtp})_3$, $a=13.387(3)$, $b=13.997(4)\text{\AA}$, $c=16.281(3)\text{\AA}$, $\alpha=72.84(2)^\circ$, $\beta=87.92(2)^\circ$, $\gamma=84.87(2)^\circ$, $P\bar{1}$, $Z=2$, $R=0.092$.
3. $\text{Mo}_4(\mu_3\text{-S})_3(\mu_3\text{-O})(\mu\text{-dtp})_2(\text{dtp})_4$, $P2_1/n$, $Z=4$, $a=12.827(2)\text{\AA}$, $b=17.206(3)\text{\AA}$, $c=13.507(2)\text{\AA}$, $\beta=93.07(1)^\circ$, $R=0.069$.
4. $\text{Mo}_4(\mu_3\text{-S})_4(\mu\text{-dtp})_2(\text{dtp})_4$, $P2/n$, $a=12.827(2)$, $b=17.206(3)\text{\AA}$, $c=17.503(2)\text{\AA}$, $\beta=97.12(2)^\circ$, $Z=4$, $R=0.069$, ($\text{dtp}=\{\text{S}_2\text{P}(\text{OEt})_2\}$).

The structure determination shows that the cluster skeleton of all the compounds has cubane-like configuration with either four S atoms or three S atoms and one O atom as triple bridging atoms capping each Mo triangle respectively. Table below gives the average value for

CLUSTER	Mo-Mo (Å)	Mo- μ_3 -S	Mo- μ_3 -O	Mo-S _t	
1	2.700*	2.831#	2.356Å	2.036Å	2.556Å
2	2.709	2.841	2.351	2.050	5.564
3	2.726	2.817	2.344	2.005	2.562
4		2.819	2.333		2.569

* Mo-Mo bond in the triangle capped by S atom.
Mo-Mo bond in the triangle capped by O atom.

some important bond lengths within the cluster skeleton. It is interest to note that the Mo-Mo distances in the Mo triangle capped by O atom are considerably larger than those capped by S atom. Among the four cluster compounds, there are two different arrangements for the six dtp ligands around cluster skeleton, as shown in Fig. 1 and Fig. 2. Cluster 1 and 2 have three bridging dtp ligands and three chelate dtp ligands, while in the cluster 3 and 4, two dtp ligands are bridging and four are chelate. All the cluster compounds have ten cluster electrons to form the metal-metal bonds:

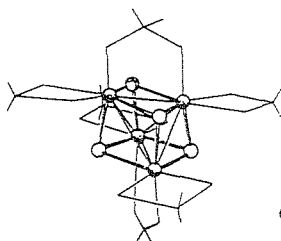


Fig. 1

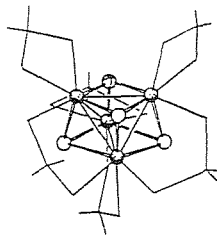


Fig. 2

09.5-4 STRUCTURAL-BONDING ANALYSIS OF SEVERAL UNUSUAL MOLYBDENUM CLUSTERS: CONSTRAINED REFINEMENTS OF DISORDERED AND THERMALLY LIBRATING LIGANDS. By Diana R. Tomchick, Charles P. Gibson, Kenneth J. Haller, and Lawrence F. Dahl, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, USA.

Our investigations of the photolytic reactions of the 30-electron acetylene-like $\text{Mo}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\text{CO})_4$ with various organometallic nitrosyl or carbonyl species have produced a wide variety of intriguing molybdenum-based clusters. Isolated triangular-metal clusters include $(\eta^5\text{-C}_5\text{Me}_5)_3\text{Mo}_3(\text{CO})_4(\mu_3\text{-N})(\text{O})$ containing trimetal-bound "T-shaped" nitride and terminal oxygen ligands, $(\eta^5\text{-C}_5\text{Me}_5)_3\text{Mo}_3(\text{CO})_4(\mu_2\text{-H})(\mu_3\text{-O})$ containing a localized monoprotonated Mo-Mo double bond, and $(\eta^5\text{-C}_5\text{Me}_5)\text{MoFe}_2(\text{CO})_x(\text{NO})_y(\mu_3\text{-O})$ containing disordered carbonyl-nitrosyl ligands. The combined use of crystallographic-spectroscopic-electrochemical measurements to determine their stereophysical properties will be illustrated. Advantages in carrying out least-squares refinements via RAELS with appropriate constraints (Rae, A.D. *Acta Cryst.* 1975, 31A, 560-570; 570-574) in the treatment of highly librating and disordered ligands will be given.