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

1. \[ \text{Mo}_4\left(\text{dtp}\right)_3 \text{NO}_3 \]
   \[ a=12.852(3)\, \text{\AA}, \quad \beta=108.372(2)^\circ, \quad Z=1, \quad R=0.072. \]

2. \[ \text{Mo}_4\left(\mu_3\text{S}\right)_3\text{O} \left(\mu\text{dtp}\right)_3 \]
   \[ a=13.997(3)\, \text{\AA}, \quad \beta=16.881(5)^\circ, \quad \gamma=72.842(4)^\circ, \quad Z=1, \quad R=0.092. \]

3. \[ \text{Mo}_4\left(\mu_3\text{S}\right)_3\text{O} \left(\mu\text{dtp}\right)_2 \text{dtp} \]
   \[ a=12.827(2)\, \text{\AA}, \quad b=17.206(3)\, \text{\AA}, \quad c=13.507(2)\, \text{\AA}, \quad \beta=93.07(1)^\circ, \quad R=0.069. \]

4. \[ \text{Mo}_4\left(\mu_3\text{S}\right)_3\text{O} \left(\mu\text{dtp}\right)_2 \text{dtp} \]
   \[ a=12.700(2)\, \text{\AA}, \quad b=17.206(3)\, \text{\AA}, \quad c=17.505(2)\, \text{\AA}, \quad \beta=97.12(2)^\circ, \quad Z=2, \quad R=0.069. \]

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 some important bond lengths within the cluster skeleton. It is interesting 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.

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**CLUSTER** | **Mo-Mo (\text{\AA})** | **Mo-S (\text{\AA})** | **Mo-O (\text{\AA})** | **Mo-S (\text{\AA})**
---|---|---|---|---
1 | 2.700 | 2.831 | 2.956 | 2.036
2 | 2.700 | 2.841 | 2.951 | 2.050
3 | 2.726 | 2.817 | 2.344 | 2.005
4 | 2.819 | 2.333 | 2.956 | 2.956

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

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Fig. 1

Fig. 2