

Structure and reactivity of molybdenum clusters with loose coordination site, $\text{Mo}_3\text{S}_4[\text{S}_2\text{P}(\text{OEt})_2]_4\text{L}$

J. Q. Huang J. L. Huang M. Y. Shang S. F. Lu X. T. Lin Y. H. Lin
M. D. Huang H. H. Zhuang J. X. Lu

Fujian Institute of Research on the Structure of Matter, Academia Sinica
Fuzhou, Fujian, P.R.C.

Abstract - The trinuclear Mo cluster $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ has been synthesized in an EtOH/HCl medium, using $\text{MoCl}_3 \cdot 3\text{H}_2\text{O}$ as starting material. The structure of the cluster skeleton consists of a mono-capped trinuclear cluster core in which each of the three $\mu_2\text{-S}$ atoms bridges a pair of Mo atoms and each of the three dtp ligands chelates a Mo atom and the fourth dtp ligand spans a pair of Mo atoms, leaving the other Mo atom to possess a loose coordination site. Some structural regularities for this type of clusters are discussed. Several reactions, including ligand substitution reaction, addition reaction and oxidative reaction of the cluster $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ are given along with a discussion of the relation between the structure and reactivities.

INTRODUCTION

Transition metal cluster chemistry continues to be one of the most rapidly growing areas of inorganic chemistry. Interest in this area arises from its widespread occurrence in biological system, possible applications in homogeneous and heterogeneous catalysis, development of theories concerning bonding, reactivity, and synthetic strategy, and being model systems for metal surface chemistry.

Among the molybdenum clusters obtained so far, the trinuclear ones exhibit rather wide variety of structure and chemistry. The first example of trinuclear molybdenum clusters may be traced to the McCarroll's work on ternary compound $\text{Zn}_2\text{Mo}_3\text{O}_8$ in solid state as early as in 1957(ref. 1). Nevertheless, the existence of the trinuclear molybdenum clusters as a stable discrete form in aqueous solution was not recognized until 1978(ref. 2). Since then the amount of the compounds with Mo_3 core has increased rapidly. In 1980 Müller et al (ref. 3) gave a report on the trinuclear clusters of the early transition metals, in which the importance of this area was emphasized.

Several years ago, our research group found that in an acidic ethanol medium and in the presence of air, Mo(III) has a variety of cluster formation modes, and thus found a new route to a series of new Mo clusters (ref. 4). In our investigation, much attention has been paid to a new kind of compounds with the formula $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$, which is customarily called by us Mo clusters with loose coordination site, because these compounds exhibit rather fascinating structure, bonding character, and chemical reactivity.

It must be pointed out that the first example of this kind of cluster skeleton was found by Hemmut Keck (ref. 5) in the compound $[\text{Mo}_3\text{S}_4(\text{R}_2\text{PS}_2)_4]$, which was called by them coordination-unsaturated cluster.

This paper will give a general account of our research work in this area with emphasis on their reactivities.

CLUSTER CONFIGURATION

The common feature of this type of cluster is illustrated in Fig. 1. In this structure, three triangularly distributed Mo atoms and a triply bridging atom form a trigonal pyramid. Each pair of Mo atoms is connected further by a doubly bridging atom so as to complete a cluster core " Mo_3S_4 ". In addition, each Mo atom is also chelated by a dtp ligand, while the fourth dtp ligand spans two Mo atoms, resulting in two different coordination environments for the three Mo atoms. In other words, although the coordination of every Mo atom is all distorted octahedron, the coordination atoms for each Mo atom are somewhat different. There are five coordination atoms, namely, one $\mu_3\text{-S}$ atom, two $\mu_2\text{-S}$ atoms, and two S atoms from a

chelating dtp ligand, which are similar for every Mo atom. But only two of the sixth coordination sites are occupied by two terminal S atoms of the bridging dtp ligand. As a result the third Mo atom leaves its sixth coordination site to be occupied by a monodentate ligand.

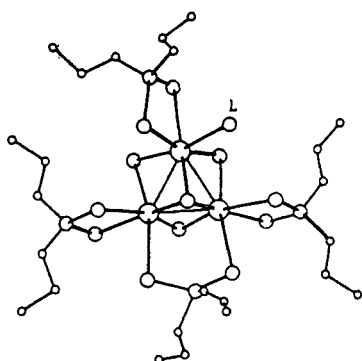


Fig.1 Configuration of cluster with loose coordination site

TABLE 1 Important bond lengths (in Å) of clusters with loose coordination site

No	Cluster	Mo-Mo	μ_3 Mo- μ_3	μ_2 Mo- μ_2	Mo-Stc	Mo-Std	L Mo-L
1	Mo ₃ S ₄ (dtp) ₄ (H ₂ O)	2.734, 2.763, 2.766	S	2.346	S	2.283	2.571 2.586 O 2.361
2	Mo ₃ S ₄ (dtp) ₄ {SC(NH ₂)(NHC ₃ H ₅)}	2.744, 2.760, 2.761	S	2.341	S	2.286	2.582 2.608 S 2.618
3	Mo ₃ S ₄ (atp) ₄ (py)	2.743, 2.758, 2.761	S	2.339	S	2.282	2.573 2.623 N 2.360
4	Mo ₃ S ₄ (dtp) ₄ (PNC ₂ H ₂ CN)	2.750, 2.753, 2.768	S	2.341	S	2.284	2.577 2.654 N 2.250
5	[Mo ₃ S ₄ (dtp) ₄ (SbCl ₃)(EtOH)]EtOH	2.722, 2.740, 2.744	S	2.337	S	2.308	2.560 2.576 O 2.241
6	Mo ₃ (S, O) ₆ S ₃ (dtp) ₄ {SC(NH ₂) ₂ }	2.669, 2.684, 2.690	O	2.202	S	2.282	2.568 2.610 S 2.633
7	Mo ₃ (μ_3 -O)S ₃ (dtp) ₄ (imidazole)	2.658, 2.646, 2.649	O	2.052	S	2.280	2.598 2.622 N 2.232
8	Mo ₃ S ₄ (dtp) ₄ (dmf)	2.703, 2.743, 2.778	S	2.337	S	2.303	2.525 2.569 O 2.278
9	Mo ₃ S ₄ (dtp) ₄ (PPh ₃)·(0.86C ₂ H ₂ Cl) ₂	2.731, 2.748, 2.753	S	2.333	S	2.288	2.592 2.592 P 2.647
10	Mo ₃ S ₄ (dtp) ₄ (PhCH ₂ SH)	2.742, 2.760, 2.762	S	2.337	S	2.282	2.568 2.643 S 2.734
11	Mo ₃ S ₄ (dtp) ₄ (oxazole)	2.752, 2.760, 2.767	S	2.337	S	2.282	2.573 2.617 N 2.316
12	Mo ₃ S ₄ (dtp) ₄ (C ₆ H ₅ CH ₂ CN)	2.743, 2.757, 2.763	S	2.344	S	2.281	2.572 2.633 N 2.306
13	Mo ₃ S ₄ (dtp) ₄ (SbCl ₃)(oxazole)	2.729, 2.743, 2.751	S	2.338	S	2.315	2.553 2.551 N 2.271
14	Mo ₃ (μ_3 -O)S ₃ (dtp) ₄ (oxazole)	2.644, 2.628, 2.642	O	2.027	S	2.282	2.590 2.584 N 2.283
15	[Mo ₃ S ₄ (dtp) ₄ (py) ₂ (H ₂ O)]	2.706, 2.741, 2.777	S	2.343	S	2.289	2.523 2.593 N 2.365
16	[Mo ₃ S ₄ (dtp) ₃ (imidazole) ₂](dtp)	2.756, 2.762, 2.763	S	2.339	S	2.287	2.571 N 2.266
17	Mo ₃ S ₄ (μ_2 -O ₂ CCH ₂ CH ₃)(dtp) ₃ (py)	2.747, 2.763, 2.684	S	2.335	S	2.288	2.549 N 2.372
18	Mo ₃ S ₄ (μ_2 -O ₂ CH)(dtp) ₃ (py)	2.700, 2.747, 2.774	S	2.332	S	2.287	2.545 N 2.385
19	Mo ₃ S ₄ (μ_2 -O ₂ CCH ₃)(dtp) ₃ (py)	2.687, 2.762, 2.769	S	2.334	S	2.293	2.549 N 2.385
20	[Mo ₃ S ₄ (dtp) ₃ (bipy)] ⁺ (dtp) ⁻	2.729, 2.755, 2.769	S	2.337	S	2.275	2.589 S 2.573
21	Mo ₃ S ₄ (dtp) ₃ (μ_2 -OAc)CuI(H ₂ O)	2.692, 2.762, 2.770	S	2.334	S	2.330	2.527 O 2.295

* Stc : S atom from terminal cheleting group ; Std : S atom from bridging cheleting group

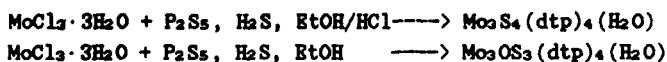
It is this coordination site that exhibits somewhat specific character. Any ligand located in this site is bonded to the Mo atom considerably weaker than the corresponding single covalent bond as can be seen from Table 1. Therefore, this Mo-L bond is very active towards substitution reaction. That is the reason why we call it loose coordination site.

Each Mo atom in this cluster has a formal oxidation state of +4. Therefore, three Mo atoms as a whole may contribute six electrons to the formation of the M-M bonds. This is basically in accord with the Mo-Mo distances obtained from the structure determination, although the Mo-Mo distance in a cluster compound also depends on the ligating atoms, particularly, on the μ_3 - and μ_2 -bridging atoms. We shall discuss this matter later.

SYNTHETIC ROUTE

In most of our synthetic work, MoCl₃·3H₂O was used as the starting material. Reactions were carried out under atmospheric condition in EtOH or EtOH/HCl media. To prepare MoCl₃·3H₂O, MoO₃ was dissolved in concentrated hydrochloric acid and then the solution was reduced in a diaphragm electrolytic cell equipped with a mercury cathod and a graphite anode until the solution turned dark red. The solid product obtained by evaporating the solution under reduced pressure at a temperature of 95-100°C was dark brown instead of copper red as reported in the literature (ref. 6), in which the evaporation temperature was 70-80°C. Our experiments have shown that the former has a more suitable oxidation state for forming Mo

clusters. The synthetic procedures are schematically shown below.



REACTIVITY

We have chosen the cluster compounds $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$ as the object for a systematic investigation of their reactivity mainly on account of the fact that they have five different coordination modes, which, without any doubt, must engender different reactivities and reaction modes. The reaction was carried out in appropriate solvents with chosen reagent and the products were identified by IR spectroscopy as well as by X-ray diffraction work. Some results are schematically given below.

1. Replacement of the ligand in loose coordination site

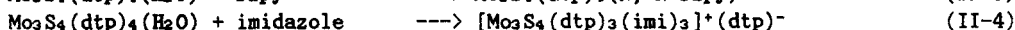
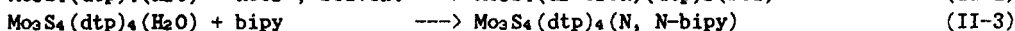
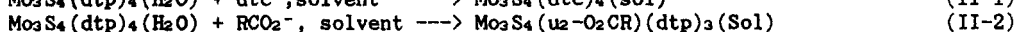
The terminal ligand L in loose coordination site of $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$ is liable to be replaced by other ligands or solvent molecules containing atoms with lone-pair electrons such as O, S, N, P.



The reaction takes place smoothly at room temperature, which shows well that the Mo-O(H₂O) bond is remarkably active towards substitution.

2. Replacement of dtp ligand

There are three terminal chelating dtp ligands and one bridging dtp ligand in the molecule $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{H}_2\text{O}$. How different the reactivities and reaction modes of these two kinds of coordination dtp ligands will be is an important matter concerning the chemical behavior of the molecule. Several reactions conducted in our group are chemically given below.



In order to make the change of cluster configuration more intuitive after the reaction happened, the following figures give only the coordination groups that have undergone changes in the course of reaction, while those remaining intact upon reactions are omitted.

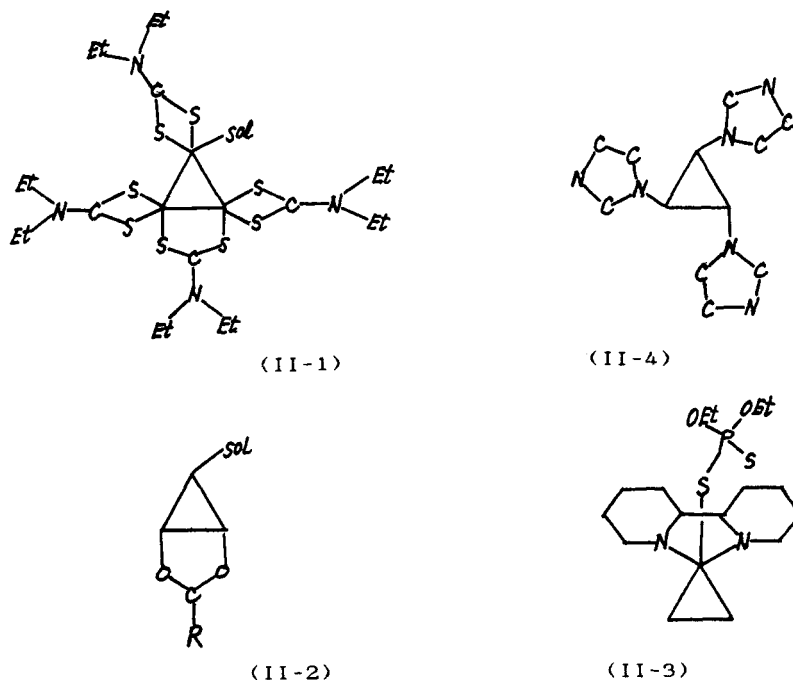


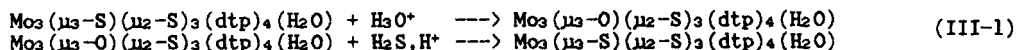
Fig.2 Simplified figure of the products obtained from the replacement reactions

The results show that when dtp^- ligands are used, all the four dtp ligands can be replaced by the dtp^- ligands, while in Reaction II-2 only the bridging dtp group is selectively replaced by RCO_2^- ($\text{R}=\text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{Ph}$) ligand. In case that the bidentate 2, 2'-bipyridine (bipy) ligands are used, the substitution reaction can take place only on the Mo atom with loose coordination site and the product is shown in Fig. II-3.

Reaction II-4 was conducted by using excess imidazole, which led to the replacement of the bridging dtp ligand and the terminal H_2O . This result shows clearly the difference in the reactivities of these two kinds of dtp ligands with different coordination geometries.

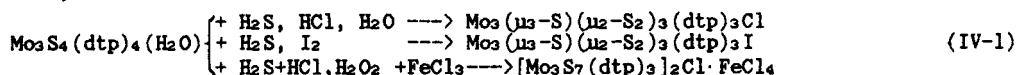
3. Replacement of μ_3 -S atom

The μ_3 -S atom can be exchanged with a μ_3 -O atom under certain conditions. Experiments have indicated that in the presence of some source of S^{2-} , $\text{Mo}_3\text{OS}_3(\text{dtp})_4(\text{H}_2\text{O})$ can be readily converted to $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ in an acidic solution, while the reverse reaction can take place only when it is refluxed in an acidic medium for a long period of time.

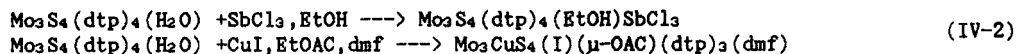


4. Addition reaction

Although no replacement reaction has been observed so far on the three μ_2 -S atoms in $\text{Mo}_3\text{S}_4(\text{dtp})_4$, their concerted action tends to induce the following two characteristic addition reactions. The first one is the addition of S atoms to the μ_2 -S bridging atoms to give a μ_2 -S₂ species, as shown in Formula IV



The second type of addition reaction is by using the surplus of lone-pair electrons in S atoms to another metal atom to complete a distorted cubane-like structure.



5. Oxidative reaction

Like most of dtp -containing clusters, crystals of $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ are stable in air, being without any noticeable change for several months. But in solution two kinds of oxidative reactions have been observed unexpectedly. One of the oxidative reactions leads to the rupture of one side of the Mo_3 triangle along with the formation of two $\text{M}=\text{O}$ bonds at both ends on a long exposure of the $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ solution to air.

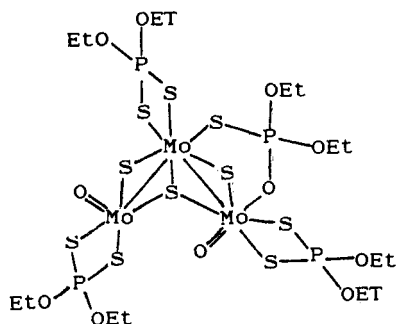
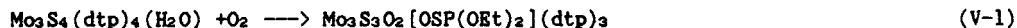


Fig. 3 The configuration of $\text{Mo}_3\text{S}_3\text{O}_2[\text{OSP}(\text{OEt})_2]_2(\text{dtp})_3$

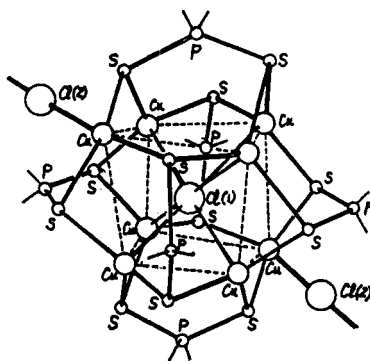
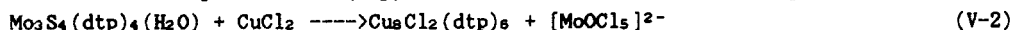


Fig. 4 The configuration of $\text{Cu}_8\text{Cl}_2(\text{dtp})_6$

The molecular configuration of the product is shown in Fig. 3. The result was confirmed by IR spectroscopy ($\nu_{\text{Mo}=\text{O}}: 890\text{cm}^{-1}$) and X-ray diffraction work. At the same time one of the dtp ligands becomes $[\text{SOP}(\text{OEt})_2]^-$ and the average formal oxidation state of the Mo atoms is raised from +4 to $+4^{2/3}$. A simple electron counting shows that the number of cluster core electrons is reduced from 6 to 4. This is in coincidence with the fact that only two Mo-Mo bonds are retained.

Another oxidative reaction leading to the destruction of the cluster skeleton was observed in an attempt to carry out addition reaction of CuCl_2 to $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$. As an excess CuCl_2 was used, pale yellow crystals were obtained and characterized by X-ray diffraction work to be an octa-nuclear Cu compound $\text{Cu}_8\text{Cl}_2(\text{dtp})_6$ with the structure shown in Fig. 4.



In the reaction Cu(II) was reduced to Cu(I), while Mo(IV) was oxidized to Mo(V) and remained in the solution.

DISCUSSION

Some structural regularities concerning the M_1 -type structure

The cluster skeleton of $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$ belongs to the M_1 -type structure, which is used by us to denote a kind of mono-capped trinuclear species, such as $\text{Zn}_2\text{Mo}_3\text{O}_8$ (ref. 1) and $[\text{Mo}_3(\mu_3\text{-O})-(\mu_2\text{-Cl})_3(\text{O}_2\text{CH})_3\text{Cl}_3]^-$ (ref. 7) as shown in Fig. 5. Before turning to discuss the reactivities of different types of ligands, it would be interesting to survey their bonding characters and to see how metal-metal bonds are affected by some structural characters, such as cluster electrons and different ligating atoms it has.

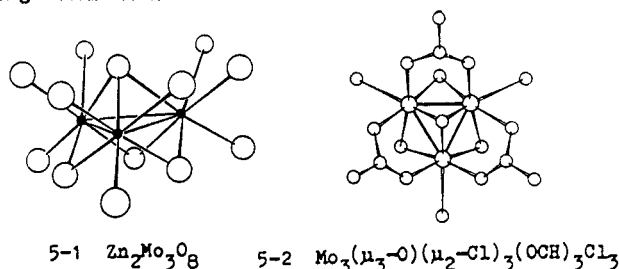


Fig. 5 The configuration of M_1 -type cluster

It is evident that the metal-metal interaction is due first to the overlap of valent shell orbitals of the metal atoms, and also to the number of cluster electrons (c.e.), which will occupy the molecular orbitals so formed. Therefore, for a given type of structure, the M-M distance depends on the cluster electrons they possess. This will be made clear from a comparison of the M-M bond lengths with different c.e. numbers as given in Table 2.

TABLE 2 M-M Bond lengths with different cluster electrons

Cluster	μ_3	μ_2	c.e.	Mo-Mo (in Å)
$\text{Zn}_2\text{Mo}_3\text{O}_8$	0	0	6	2.524(2)
$\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$	S	S	6	2.754
$\text{LiZn}_2\text{Mo}_3\text{O}_8$	0	0	7	2.578(11)
$\text{Zn}_3\text{Mo}_3\text{O}_8$	0	0	8	2.580(2)
$[\text{Mo}_3\text{O}(\text{CMe})_3(\text{NO})_3(\text{CO})_6]^{2-}$	0	OMe	12	3.297(2)
$[\text{Mo}_3(\text{OCH}_3)_4(\text{NO})_3(\text{CO})_3]^-$	OMe	OMe	12	3.428
$\text{Mo}_3\text{S}_3\text{O}_2(\text{dtp})_3[\text{SOP}(\text{OEt})_2]$	S	S	4	2.808, 2.839, 3.337(1)

From Table 2 it can be seen that the compound $\text{Zn}_2\text{Mo}_3\text{O}_8$ with six c.e. has the shortest Mo-Mo distance (2.524 Å). Increase of the c.e. leads to lengthening the Mo-Mo distance as found in $\text{LiZn}_2\text{Mo}_3\text{O}_8$ and $\text{Zn}_3\text{Mo}_3\text{O}_8$ reported by McCarley (ref. 8). When the number of c.e. reaches 12 as found in $[\text{Mo}_3\text{O}(\text{CMe})_3(\text{NO})_3(\text{CO})_6]^{2-}$ and $[\text{Mo}_3(\text{CMe})_4(\text{NO})_3(\text{CO})_6]^-$ (ref. 9), the Mo-Mo distances are up to 3.3-3.4 Å, which are indicative no metal-metal interaction. In the case of $\text{Mo}_3\text{S}_3\text{O}_2(\text{dtp})_3[\text{SOP}(\text{OEt})_2]$ (ref. 10) with only four c.e., there are two Mo-Mo bonds retained and the third side of the Mo_3 triangle has been opened up.

As to the influence of the ligating atoms, the investigation shows that for a given number of c.e. the M-M bond lengths depend mainly on the triply and doubly bridging atoms. A systematic comparison of the structures gives some interesting conclusions. As can be found from Table 1, the replacement of $\mu_3\text{-O}$ by $\mu_3\text{-S}$ in $\text{Mo}_3\text{XS}_3(\text{dtp})_4\text{L}$ (X=O or S) causes the Mo-Mo bonds to be lengthened by ca. 0.1 Å. Similarly, the compounds listed in Table 1 with the cluster core " $\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-S})_3$ " have an average Mo-Mo distance of 2.645 Å. This is longer by about 0.12-0.15 Å than those with with the cluster core " $\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-O})_3$ " such as in ZnMo_3O_8 .

TABLE 3 Comparison of bond lengths for different kinds of coordinations

$[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$	Mo-($\mu_3\text{-O}$) 2.020 Å	Mo-($\mu_2\text{-O}$) 1.916 Å	Mo-O(trans to μ_2) 2.26 Å	Mo-O(trans to μ_3) 2.163 Å
$\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$	Mo-($\mu_3\text{-S}$) 2.346 Å	Mo-($\mu_2\text{-S}$) 2.283 Å	Mo-S(trans to μ_2) 2.586 Å	Mo-S(trans to μ_3) 2.571 Å

From the point of view of steric effect it is understandable that as the bridging atoms become bigger, there should be some stretching of the Mo-Mo bonds in order to accommodate them. However, the steric requirement of the bridging atoms could never be regarded as the sole contribution to the increase of the Mo-Mo distance on account of the fact that the Mo-Mo distances in $[\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-Br})_3(\text{OAc})_3\text{Cl}_3]^-$ (ref. 11) are larger than those in $[\text{Mo}_3(\mu_3\text{-O})(\mu_2\text{-Cl})_3(\text{OAc})_3\text{Cl}_3]^-$ (ref. 12) only by about 0.018Å. Therefore, we are led to the conclusion that the increase of the M-M separation is not only due to the steric effect of the bridging atoms, but also to their electronic effect. Considering that S atom is a good π donor, it may donate part of its $p\pi$ electrons to fill in the Mo-Mo antibonding orbitals so as to weaken the bonding interaction.

It is noticeable that the Mo-(μ_2 -S) distances are the shortest (2.288Å) in this compound as compared with the Mo-(μ_3 -S) bonds (2.340Å) and Mo-S_t bond (2.566Å). Investigation shows that for a typical Mo-S bond, the bond length is ca. 2.08Å (ref. 13), while the bond length of Mo-S single bond amounts to 2.4Å (ref. 14). Therefore the Mo-(μ_2 -S) bond length is intermediate between the single and double bonds. This must be an indication that the sulfur $p\pi$ electrons have taken part in the formation of the Mo- μ_2 -S bond. In other words, although the $p\pi$ electrons of the μ_2 -S atoms weaken the Mo-Mo bonds, they do enhance the Mo-(μ_2 -S) bonds and as a result they will strengthen the cluster skeleton.

The order of reactivity for different ligands towards substitution

The experimental results mentioned above indicate the following order of reactivity for different kinds of coordination bonds in $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ towards substitution. That is: Mo-O_t(H₂O) > Mo-S_b(dtp) > Mo-S_t(dtp) > Mo-(μ_3 -S) > Mo-(μ_2 -S). This order is similar to that reported by Rodgers (ref. 15) for different kinds of oxygen-containing ligands in $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ towards H_2^{18}O isotopic exchange reaction.

In the cluster anion $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$, each Mo atom has three terminal H₂O ligands, two of which are located in two positions trans to the μ_2 -O atoms and the third is trans to the μ_3 -O atom. The former having larger bond lengths than the latter showed higher reactivity. In cluster $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$, apart from these sites there is a loose coordination site that is especially active towards substitution. As mentioned above, the four dtp ligands may be divided into two kinds. Three are chelating and one is bridging. Since the chelating dtp has a "bite" trans to μ_3 -S atom and the other trans to the μ_2 -S atom, its reactivity is lower than the bridging dtp ligand, which has two "bite" all trans to the μ_2 -S atoms. A comparison of the bond lengths for different kinds of coordinations shows that there is a good correlation between the substitution reactivity of the Mo-L bond and its corresponding bond length, namely, the longer the bond length is, the more active it is towards substitution. The substitution reactions indicate that all the dtp ligands in the $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ can be replaced by either monodentate or by bidentate ligands.

The products of reaction are related not only to the substitution reactivities of different coordinations, but also to the substituents used. When imidazole is used, substitution reactions of the loose coordination site and the bridging dtp ligand will happen concurrently. This is also an indication that the bridging dtp ligand is more active than the chelating. Nevertheless, when $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$ reacts with bidentate reagents, such as $\text{Et}_2\text{NCS}_2^-$, RCO_2^- and bipy, the reaction modes are first governed by the geometric factor of the substituents. In all Mo_3 clusters reported so far with Mo atoms coordinated octahedrally, the two oxygen atoms of a RCO_2^- ligand are always coordinated to two adjacent Mo atoms, thus forming a bridge without any exception. This may be interpreted by a simple bonding scheme as given in Fig. 2, which shows the geometry of the bridging coordination and the supposed chelating coordination of a RCO_2^- group to the metal atoms. It is obvious that octahedrally coordinated Mo atoms demand that the \angle Mo-Mo'-O bond angle approach 90°, while the sp^2 hybridized carbon atoms demands an angle of about 120° for \angle OCO angle. When bridging RCO_2^- group forms a five-membered ring "Mo₂O₂C", the \angle Mo-O-C angle may approach 120° (122° and 124° observed in $\text{Mo}_3\text{S}_4(\mu\text{-O}_2\text{CH})(\text{dtp})_3\text{py}$ and $\text{Mo}_3\text{S}_4(\mu_2\text{-O}_2\text{Et})(\text{dtp})_3\text{py}$ respectively), which is suitable to having a good π bonding. However, if a chelating four-membered ring were formed the \angle MoOC angle would have been about 75°, departing far from the value suitable to a good π bonding for O atom. That is the reason why the substitution of $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$ for a carboxyl group happens only in the bridging dtp ligand, while other parts of the molecule remain unchanged. Similarly, it is also impossible for bipy ligand to form effectively a six-membered ring "Mo₂N₂C₂" so as to bridge two Mo atoms in this regard. In addition, that the substitution reaction of bipy happens in ambient coordinations on the Mo atom which is not bridged by dtp ligand also shows that the coordination bonds of this metal atom are more active than those of the other two. On the contrary, since d orbitals of S atoms may participate in bonding interaction, bond angle of S atoms in bidentate ligands such as dtp and $\text{Et}_2\text{NCS}_2^-(\text{dte}^-)$ groups can vary over a wide range, so that these groups are able to act either as bridging or as chelating ligands. Therefore, the dte^- ligands can replace all the dtp ligands in $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ dissolved in dimethylformamide(dmf) to give the cluster $\text{Mo}_3\text{S}_4(\text{dte})_4(\text{dmf})$. As for capping and bridging atoms, an important empirical rule is often observed governing over our synthetic

system, that is, in a highly acidic medium, μ_3 -S capping atoms are rather easy to be introduced, while low acidity tends to introduce μ_3 -O atoms. For example, differences of synthetic conditions for the following pairs of clusters, $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ and $\text{Mo}_3\text{OS}_3(\text{dtp})_4(\text{H}_2\text{O})$, $[\text{Mo}_3\text{S}_7(\text{dtp})_3]^+$ and $[\text{Mo}_3\text{OS}_6(\text{dtp})_3]^+$, $[\text{Mo}_4\text{S}_4(\text{dtp})_6]$ and $[\text{Mo}_4\text{OS}_3(\text{dtp})_6]$ are only in the acidity of media. It is reasonable to think that in the conditions of high acidity and the presence of S_2^{2-} source, Mo-O bonds are easy to be converted to Mo-S bonds as mentioned above.

The similarity between the " Mo_3S_3 " cluster core and the benzene ring

The substitution reactions show that except the three μ_2 -S atoms all other ligands in the $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ can be replaced by suitable groups. The stability of Mo-(μ_2 -S) bonds towards substitution stimulates us to ponder over the bonding character of the cluster core. The Mo- μ_2 -S bond distances are about 2.29Å, which is shorter than the Mo-S single bond distance (2.4-2.5Å), but longer than the Mo=S double bond distance (2.07Å), indicating that in addition to the σ bond there may also exist the $d\pi$ - $p\pi$ interaction between the Mo and μ_2 -S atoms. Therefore, if one focuses his attention on the " Mo_3S_3 " ring and neglects the other ligands for the time being, it would be reminiscent of the Kekule's model for the benzene molecule. Of course, the " Mo_3S_3 " core is not actually planer, but the π bonding character is similar to that in the benzene to some extent. Nevertheless, in the case of " Mo_3S_3 " contribution to the π -bonding system comes from the $d\pi$ -orbitals of the Mo atoms and the lone pair $p\pi$ electrons of the μ_2 -S atoms. This differs obviously from that well known in the benzene ring.

The similarity is also manifested in their chemical behavior. In substitution reaction the benzene molecule strives to reserve its aromatic character, namely, to keep the " C_6 " unit unchanged even all the H atoms are replaced by other atoms or groups. This is obviously similar to that found for the $\text{Mo}_3\text{S}_4(\text{dtp})_4\text{L}$.

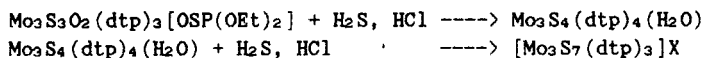
On this basis, we are going further to survey the other reaction. The hydrogenation of benzene takes place with concurrent addition of three H_2 molecule to the C_6H_6 molecule. As a result the coordination number of the C atoms has changed from three to four and cyclohexane is obtained. For a comparison, it is convenient to look at the addition reaction of S atoms to $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$, which is added to at the same time by three S atoms, resulting in a new compound $[\text{Mo}_3\text{S}_7(\text{dtp})_3]\text{X}$ and the coordination number of the Mo atoms may be considered as changing from six to seven.

Comment on the addition reaction and oxidative reaction

The cluster compound $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ can be converted to a "sulfur-rich" compound with the cluster core " Mo_3S_7 " by addition reaction of S atoms to three μ_2 -S atoms. It can also be converted to a cubane-like tetranuclear cluster with the skeleton " Mo_3MS_4 " by addition of an appropriate metal ion M^+ . It is obviously owing to that μ_2 -S atoms carrying lone-pair electrons are potent in coordination and owing to full use of the valent shell orbitals of the metal atoms. Thus after the addition reaction has given rise to the " Mo_3S_7 " compound the coordination number of Mo atoms is changed from six to seven. In the case of the formation of " Mo_3CuS_4 ", three additional Mo-Cu bonds are formed, which shows that the Mo atom has changed from coordination unsaturate to saturate. It follows that the lone-pair electrons of the S atoms are essential to induce the above addition reaction.

Experiments undertaken have already shown that two kinds of metal atoms can be involved in addition reaction. The one is from the main group, such as Sb^{3+} . Being lack of valent electrons, Sb atom is not able to form Mo-Sb bond (Mo...Sb: ca. 3.8Å). The other one is from the late transition metals such as Cu^+ , which indeed forms Mo-Cu bonds.

The knowledge on the two kinds of oxidative reaction of $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$, namely, the partial oxidation and that leading to the destruction of cluster skeleton, is far from completion yet, but some useful information can be provided. Evidence has been gathered that the loose coordination bond Mo-O(H_2O) in $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ has bearing on the partial oxidative reaction. Once Mo-O(H_2O) bond is converted to Mo-N(py) bond or other Mo-L bond the oxidation can be effectively prevented. Besides, an attempt to reconstruct the broken Mo-Mo bond caused by partial oxidation has been realized. Thus, in the presence of HX, bubbling H_2S into a solution of the partially oxidized product, $\text{Mo}_3\text{S}_3\text{O}_2(\text{dtp})_3[\text{OSP}(\text{OEt})_2]$, can convert it to $[\text{Mo}_3\text{S}_7(\text{dtp})_3]\text{X}$ (X=Cl or I), which is obviously formed by a further sulfur-addition reaction.



The destruction of $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ by reaction with CuCl_2 is rather interesting. In the process the Cu(II) atoms usurp the dtp ligands from the Mo cluster and oxidize Mo(IV) to Mo(V) at the same time. Further research has also shown that this kind of oxidation is not unique. CuCl_2 may react with other dtp-containing Mo clusters in a similar manner.

Structural fluxion of dtp ligands in the molecule

Upon a careful comparison of the structure of $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$ with its substitution products, which happened in the loose coordination site, it was found that the positions the reagents entered are not always the same as those having been occupied previously by the ligands to be replaced. For example, upon replacement of the terminal H_2O , PPh_3 group entered the site that had been occupied by an end-atom of dtp group instead of that occupied by H_2O , as shown in Fig. 6. This may indicate that the two ends of the dtp ligand are capable to rotate around the metal atoms. The same reason may also be used to explain the coexistence of the two structural isomers of tetranuclear Mo clusters $[\text{Mo}_4\text{OS}_2(\text{dtp})_6]$ (ref. 16).

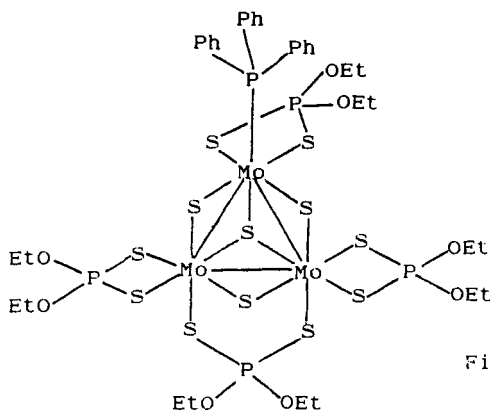


Fig. 6 The configuration of $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{PPh}_3)$

The reaction regularities mentioned above may be grafted to other related clusters. For example, several reactions of the cluster $\text{Mo}_3\text{OS}_3(\text{dtp})_4(\text{H}_2\text{O})$ are quite similar to those observed on $\text{Mo}_3\text{S}_4(\text{dtp})_4(\text{H}_2\text{O})$. In addition, the bridging dtp ligands in the tetranuclear cluster $\text{Mo}_4\text{S}_4(\mu_2\text{-dtp})_2(\text{dtp})_4$ can also be replaced by OAc^- group to yield $\text{Mo}_4\text{S}_4(\mu_2\text{-OAc})_2(\text{dtp})_4$.

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