A Neutral Trinuclear Molybdenum-Sulfur(Oxygen) Cluster Complex with [$Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3$] Core

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A neutral molybdenum cluster $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(DTP)_4(H_2O)$ (DTP = diethyl dithiophosphate) is rationally synthesized and structurally characterized. Its molecules are linked via hydrogen bonding and supramolecular interactions, leading to an infinite one-dimensional chain structure.

Trinuclear molybdenum cluster compounds have been extensively studied for their potential application in some catalytic processes.[1] Previous researches have been focused on those compounds with discrete Mo_3S_4 core[2] and limited results have been reported on those with $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_n(\mu\text{-}S)_{3\text{-}n}$ (n = 1, 2, 3) cores,[3] especially on their potential macromolecular or supramolecular chemistry. By selecting appropriate ligands, some interesting structures have been reported on the dimers and oligmers of Mo_3X_4 (X=S, O) incomplete and complete cubane-type complexes, but they are all achieved by introducing multi-functional ligands and some of them are linked via S···S interaction together with H-bonds.[4] Herein we report the synthesis and structure of the first neutral molybdenum complex with $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3$ core: $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(DTP)_4(H_2O)$ **A**. Its molecules are assembled into an infinite one-dimension structure without introducing multi-functional ligands.

Under a dinitrogen atmosphere, 8 mL HDTP was added into a Schlenk flask containing 50 mL $[Mo_3O_3S(H_2O)_9]^{4+}$ (0.25 M per trimer, 6 M HCl solution), which was prepared and concentrated according to the literature.[3b,5] After vigorous stirring for 2 h, a great deal of brown-green precipitates deposited. The precipitates were filtered and dried in vacuum, and recrystallized from acetone, giving dark red rectangular crystals of $[Mo_3O_3S(DTP)_4(H_2O)]$ (2.25 g, 2.0 mmol, yield 16.0% referred to $[Mo_3O_3S(H_2O)_9]^{4+}$) after two weeks. (Found: C, 17.46; H, 4.08%. Calcd. for $C_{16}H_{42}Mo_3S_9O_{12}P_4$: C, 17.05; H, 3.76%.).

The crystal structure has been determined by X-ray crystallography[6] and the ORTEP drawing of complex **A** is shown in Figure 1 together with the selected atomic distances.

The molecular structure of complex **A** reveals a typical incomplete cubane-type structure, just like the analogue $[Mo_3S_4(DTP)_4(H_2O)]$.[2a] Each Mo in oxidation state IV is octahedrally coordinated with hard distortion. The bridging DTP, the coordinated H_2O molecule and the μ_3-S are all at the same side referred to the plane constructed by three Mo atoms. Both the Mo–Mo(av) and the Mo–(μ-O)(av) bond lengths are much shorter than those in $[Mo_3S_4(DTP)_4(H_2O)]$. The bond length Mo2–O (of H_2O) in complex **A** is obviously shorter (0.115 Å) than that in $[Mo_3S_4(DTP)_4(H_2O)]$. Because inside Mo_3X_4 core, S attracts less electrons than O since it has lower electronegativity than O; π-electrons can be delocalized over the no-planar puckered $Mo_3(\mu\text{-}S)_3$ ring. Comparatively, there is no such electron delocalization effect in $Mo_3(\mu\text{-}O)_3$. The Mo atom in $Mo_3(\mu\text{-}O)_3$ is electron-less than in $Mo_3(\mu\text{-}S)_3$ and it can draw more electrons from other ligands such as O (of H_2O), leading to the stronger bonding of Mo with the other ligands.

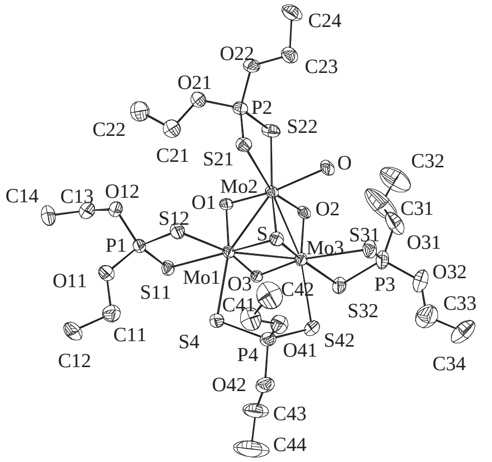

Figure 1. ORTEP drawing of complex **A** at 30% probable thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected atomic distances (Å): Mo1–Mo2 = 2.5966(8); Mo1–Mo3 = 2.6006(8); Mo2–Mo3 = 2.6083(8); Mo–Mo(av) = 2.6018(8); Mo1–O1 = 1.931(4); Mo1–O3 = 1.944(4); Mo2–O1 = 1.877(4); Mo2–O2 = 1.915(4); Mo3–O2 = 1.910(4); Mo3–O3 = 1.928(4); Mo–(μ-O)(av) = 1.918(4); Mo2–O = 2.246(5).

Reported crystal structural results show that the average bond length of Mo–(μ-S) in Mo_3S_4 falls between single bonds and double bonds.[7] However, in this compound, the Mo–(μ-O)(av) bond length falls in the single bond range, as in the case of Mo_3O_4.[8]

As shown in Figure 2, multiple H-bonds and weak S···S, S···O contacts co-exist in the solid state of complex **A**. O–H···O

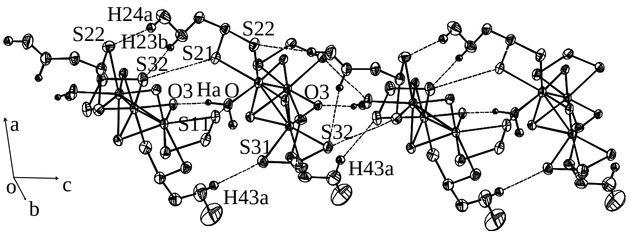

Figure 2. O–H···O and C–H···S hydrogen bonds (indicated by dashed lines) in crystal **A**. Mostly hydrogen atoms and DTP ligands are omitted for clarity.

Table 1. Hydrogen bonds in the crystal packing of complex **A**

D–H···A	Distance/Å			D–H–A
	D–H	H–A	D–A	Angle/°
O–HA···O3[a]	0.95(3)	1.85(4)	2.737(6)	153(6)
C24–H24A···S22[a]	0.959	2.775	3.712(9)	165.7
C23–H23B···S32[a]	0.971	2.921	3.884(9)	170.3
C43–H43A···S31[b]	0.970	2.805	3.730(11)	159.6

[a] Symmetry code: x, 1.5 − y, −0.5 + z.
[b] Symmetry code: x, 1.5 − y, 0.5 + z.

hydrogen bond is found between O (of H_2O) and O3 (a μ-O belongs to the neighbor molecule) with atomic distance 2.737(6) Å. Three C–H···S hydrogen bonds are formed between DTP ligands of adjacent molecules, corresponding atomic distances and angles are listed in Table 1.

The (C–)H···S distances are obviously shorter than the sum of their Van der Waals radii, indicating weak hydrogen bonding. The O···S11 distance is 3.245(5) Å, slightly shorter than the sum of their Van der Waals radii but no O–H···S H-bond is found between them. The intermolecular O–H···O hydrogen bonds make other intermolecular weak contacts possible, including the weak S32[a]···S21 contacts (3.695 Å). We consider that the bridging DTP ligand in complex **A** is flexible enough so that the molecules can approach each other, making the supramolecular interactions possible. The cooperation of all these interactions results in the formation of infinite one-dimension chains along the *c* axis, forming a zigzag network structure, inside which, the incomplete cubane-type $Mo_3O_3S(DTP)_4(H_2O)$ is acting as the building block.

In complex A, one μ-O atom of Mo_3O_3S core acts as the proton acceptor and the loosely-coordinated ligand H_2O acts as the donor. The hydrogen bond formed between them makes it possible that $Mo_3O_3S(DTP)_4(H_2O)$ molecules are stranded into an infinite array without introducing multi-functional ligands. To our knowledge, this type of infinite structure in complex **A** is initially found here among reported Mo_3X_4 analogues.

The different atoms in μ-positions of Mo_3X_4 core between complex **A** and $[Mo_3S_4(DTP)_4(H_2O)]$ lead to the great differences of the physical and chemical properties. $[Mo_3S_4(DTP)_4(H_2O)]$ is stable in air and in appropriate solvent. However, the crystals of **A** tend to deliquesce in air, its acetone solution is more labile in air with the color changing from dark red to green within two weeks. Structurally, Mo_3O_3S core is more closely packed than Mo_3S_4 core, which can be seen clearly by comparing the corresponding bond lengths. For the reactivity, $[Mo_3S_4(H_2O)]^{4+}$ can combine many metals to give cubane-type complexes, even the neutral complex $[Mo_3S_4(DTP)_4(H_2O)]$ can also react with Cu, Pb, Cd, and so on.[9] Nevertheless, no metal additive product has been reported concerning either $[Mo_3O_3S(H_2O)_9]^{4+}$ or its neutral derivative so far.

Further study on the synthesis, structure and property of these complexes is in progress.

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6 The Crystal data for compound **2**: $Mo_3S_9P_4O_{12}C_{16}H_{42}$, $Mr = 1126.74$, Monoclinic $P2(1)/c$, $a = 22.2584(5)$ Å, $b = 12.7795(2)$ Å, $c = 15.4231(2)$ Å, $\beta = 109.097(1)^\circ$, $U = 4145.68(13)$ Å^3, $Z = 4$, $D_c = 1.805\,\mathrm{g{\cdot}cm^{-3}}$, $\mu(\mathrm{Mo\ K}\alpha) = 1.546\,\mathrm{mm^{-1}}$, $F(000) = 2256$, $T = 293(2)$ K, 7258 reflections measured, 4768 unique ($R_{\mathrm{int}} = 0.0477$) which were used in all calculations. The final $R = 0.0476$, $wR = 0.1004$ for 4768 reflections $[I > 2\sigma(I)]$. Crystal reflections were collected on a CCD diffractometer, the structure was refined with the Shelxl-97 program (F^2). Most hydrogen atoms were added by geometry, the hydrogen atoms belonging to loosely-coordinated H_2O were added by difference Fourier synthesis.

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