Dimerization of Incomplete Cuboidal Mo_3S_4 Units via α,ω-Dicarboxylates, and Their Supramolecular Architectures through Intermolecular S···S and C–H···S Interactions

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Two novel hexanuclear molybdenum cluster compounds $[Mo_3S_4(dtp)_3(L)]_2[\eta^2$-$\mu$-$OOC(CH_2)_nCOO$-$\mu$-$\eta^2]$ (n = 4, L = DMF for **1**; n = 3, L = DMSO for **2**) have been synthesized by reaction of $Mo_3S_4(dtp)_3(ClCH_2COO)(Py)$ with α,ω-dicarboxylates. Intermolecular S···S and C–H···S interactions are observed, yielding two different two-dimensional supramolecular structures.

Cluster compounds with $Mo_3O_nS_{4-n}$ (n = 0, 1, 3, 4) cores have been extensively studied over the past twenty years due to their relevance in biological systems[1] and catalytic processes.[2] The previous research has focused on the chemistry of the discrete tri- and tetranuclear species,[3] and little is known about their potential macromolecular or supramolecular chemistry.[4] We have recently reported the reactions of $Mo_3O_nS_{4-n}(dtp)_3(L')(L)$ (n = 0, 1) (dtp = diethyldithiophosphate, L′ = dtp, $ClCH_2COO$, CCl_3COO; L = H_2O, Py) with oxidized 1,2-bis(diphenylphosphino)ethane,[5] phthalate[6] and malonate[5] to oligomerize $Mo_3O_nS_{4-n}$ cluster complexes. Herein we use the long-chain dicarboxylic acids as the substitution ligands and successfully crystallize the clusters $[Mo_3S_4(dtp)_3(L)]_2[\eta^2$-$\mu$-$OOC(CH_2)_nCOO$-$\mu$-$\eta^2]$ (n = 4, L = DMF for **1**; n = 3, L = DMSO for **2**). These two cluster polymers are achieved by the joint effect of covalent bonding, intermolecular S···S and C–H···S interactions.

The mixture of $Mo_3S_4(dtp)_3(ClCH_2COO)(Py)$ (prepared according to the literature method[7]) (0.10 g, 0.088 mmol), adipic acid (0.01 g, 0.068 mmol) and DMF (10.0 cm^3) was stirred at 80 °C for 1 h. After filtration, 20.0 cm^3 anhydrous ethanol was added, well-shaped crystals precipitated when the red-brown solution was kept at room temperature for two weeks (Yield: 61%). The preparation of complex **2** is similar to **1** but using glutaric acid and DMSO instead of adipic acid and DMF (Yield: 74%). Satisfactory results of elemental analysis were obtained for both complexes.[8] X-ray crystallography[9] demonstrates the two complexes are isostructural. The molecular structure of complex **2** is depicted in Figure 1 together with the selected bond lengths.

The two hexanuclear Mo(IV) complexes are the first structurally characterized dimers, in which two incomplete cubane-type units are connected by only one dicarboxylate group. The coordination pattern of the dicarboxylate contrasts with that of their analogue substituted by phthalate[6] or malonate,[5] in which one of the two carboxyl groups bridges two Mo atoms and the other carboxyl group interacts, through strong H-bonds, with the carboxyl from the adjacent molecule. As shown in Figure 1, compound **2** consists of two Mo_3S_4 units linked by one glutarate, whose $–CO_2$ chelating groups bridge Mo(2), Mo(3) and Mo(5), Mo(6), respectively. DMSO molecules are coordinated to Mo(1) and Mo(4) via O atom by substituting the loosely-coordinated Py ligand in the precursor (In compound **1**, the counterpart is DMF group). Thus, every Mo atom has a distorted octahedral coordination by five S atoms from the core and dtp ligand and one O atom from dicarboxylate or DMSO. Compound **1** has a similar structure to **2**, in which two Mo_3S_4 units are linked by an adipate ligand. The principal bond parameters of compounds **1** and **2** are consistent with the monocarboxylate-coordinated complexes $Mo_3S_4(dtp)_3(RCOO)(Py)$ (R = H, CH_3, CH_3CH_2).[10,11] However, despite their similar structures and coordination patterns, the relative positions of two Mo_3 planes in compounds **1** and **2** are different from each other. The dihedral angle between two Mo_3 planes in **1** is 7.5°, showing good coplanarity, while **2** shows not owing to the bigger dihedral angle 31.7°.

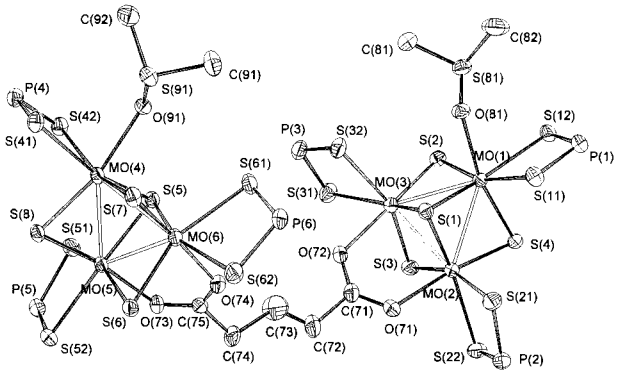

Figure 1. ORTEP drawing of compound **2** at 20% probable thermal ellipsoids. The EtO groups of dtp ligands were omitted for clarity. Selected bond lengths (Å): Mo(1)-Mo(2) 2.7520(11), Mo(1)-Mo(3) 2.7698(11), Mo(2)-Mo(3) 2.6905(11), Mo(4)-Mo(5) 2.7522(11), Mo(4)-Mo(6) 2.7623(12), Mo(5)-Mo(6) 2.6890(11), Mo(1)-S(1) 2.335(2), Mo(1)-S(3) 2.307(2), Mo(1)-S(4) 2.276(2), Mo(1)-O(81) 2.235(6), Mo(2)-S(1) 2.333(2), Mo(2)-S(2) 2.292(3), Mo(2)-S(4) 2.280(2), Mo(2)-O(71) 2.197(7), Mo(3)-S(1) 2.331(2), Mo(3)-S(2) 2.301(3), Mo(3)-S(3) 2.289(2), Mo(3)-O(72) 2.241(7), Mo(4)-S(5) 2.334(2), Mo(4)-S(6) 2.272(2), Mo(4)-S(8) 2.301(2), Mo(4)-O(91) 2.276(2), Mo(5)-S(5) 2.331(2), Mo(5)-S(7) 2.289(3), Mo(5)-S(8) 2.289(3), Mo(5)-O(73) 2.230(8), Mo(6)-S(6) 2.285(2), Mo(6)-S(7) 2.297(2), Mo(6)-O(74) 2.218(6).

It is noteworthy that intermolecular C–H···S hydrogen bonds (See Table 1), with the geometrical parameters falling within the limits suggested by Taylor and Kennard,[12] and S···S interactions

Table 1. Geometric parameters of hydrogen bonds

	D–H···A	D–H /Å	H···A /Å	D···A /Å	D–H···A /deg.
1	C(74b)–H74A···S(21)[a]	0.97	2.89	3.69(2)	141.0
	C(42c)–H42A···S(7b)[b]	0.96	2.79	3.68(2)	154.3
	C(44a)–H44B···S(61b)[c]	0.96	2.67	3.58(2)	158.5
2	C(81)–H81B···S(2a)[d]	0.96	2.74	3.59(1)	148.0
	C(81)–H81C···S(41b)[e]	0.96	2.99	3.49(1)	113.4

Symmetry codes: [a]2–x, 1–y, 1–z. [b]2–x, 1–y, –z. [c]1+x, y, z. [d]0.5–x, 5.0+y, 0.5–z. [e]1–x, 2–y, 1–z.

are observed for the two compounds. Although S···S interactions are common in Mo–S clusters, the intermolecular C–H···S hydrogen bond has never been reported for trimolybdemum compounds, nor for the analogue bridged by aromatic dicarboxylate such as *o*-phthalate or by short-chain aliphatic dicarboxylate such as malonate. We consider that the hydrocarbon chain lengths of these binary acids play an important role in the formation of C–H···S hydrogen bonds. The flexibility of long-chain adipate and glutarate ligand makes the molecules packed more compactly, so as to enable the formation of diversiform intercluster interactions. Nevertheless, the two clusters show different packing diagrams resulting from the different distribution of C–H···S and S···S interactions. In crystal **1**, the S atoms from Mo_3S_4 cores and dtp ligands form five S···S contacts (3.358(6)–3.664(5) Å) between two adjacent molecules to result in oligomerization. One-dimensional infinite chains are formed by linking the oligomers through intermolecular C–H···S hydrogen bonds (C(74b)···S(21) 3.69(2) Åand C(44a)···S(61b) 3.58 (2) Å). All the molecules are finally packed as a two-dimensional network by linking the chains through a class of intermolecular C(42c)···S(7b) hydrogen bonds (C···S = 3.68(2) Å) (Figure 2). Compared to **1**, molecules of compound **2** are packed in a different way. Both (rather than only one in **1**) the Mo_3S_4 cores in **2** are involved in

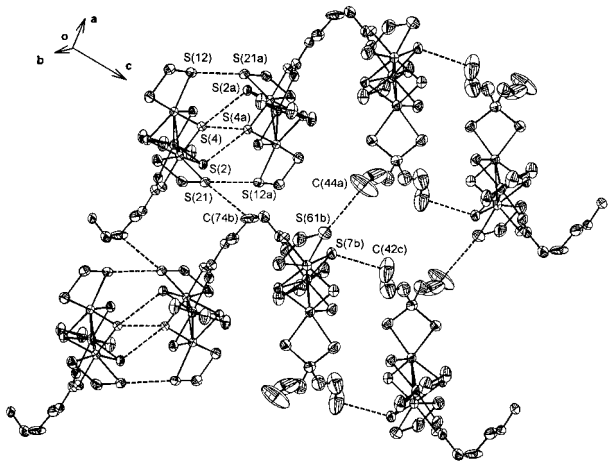

Figure 2. S···S and C–H···S interactions (indicated by dashed lines) in crystal **1**. S(12)–S(21a) 3.664(5), S(4)–S(4a) 3.358(6), S(2)–S(4a) 3.461(4) Å. Symmetry code: 3–x, 1–y, 1–z.

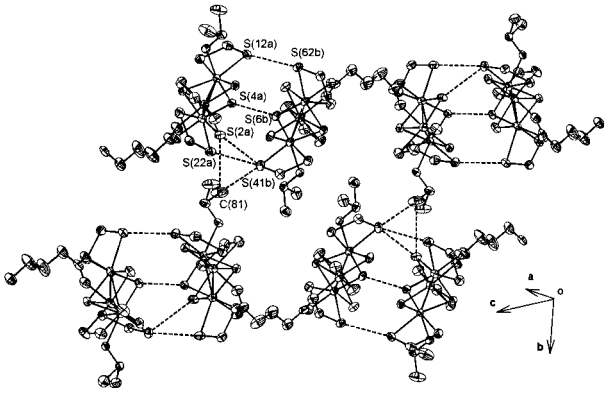

Figure 3. S···S and C–H···S interactions (indicated by dashed lines) in crystal **2**. S(12a)–S(62b) 3.490(4), S(4a)–S(6b) 3.175(3), S(2a)–S(41b) 3.615(4), S(22a)–S(41b) 3.572(4) Å. Symmetry code: 0.5+x, 1.5–y, 0.5+z.

S···S interactions, by which the molecules are stringed together to form one-dimensional infinite chains. The polymeric chains interact with each other through intermolecular C–H···S interactions originated from the C atoms (of DMSO ligands) and the S atoms (of Mo_3S_4 cores and dtp ligands), resulting in the formation of a supramolecular framework as shown in Figure 3.

Although the versatile reactivity of incomplete cuboidal Mo_3 compounds has been well appreciated and many new derivatives have been prepared from them, it is the first time to report their two-dimensional cluster polymers. Furthermore, by choosing ligands with different chelating properties and functional groups, we can design compounds with novel structures and specific functions. This will extend the trinuclear molybdenum chemistry into a new field of metallic polymers, which are very important in material sciences and functional molecules.

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References and Notes

1 a) D. Coucouvanis, *Acc. Chem. Res.*, **24**, 1 (1991). b) D. C. Rees, M. K. Chan, and J. Kim, *Adv. Inorg. Chem.*, **40**, 89 (1994).
2 a) R. R. Chianelli, *Catal. Rev. Sci. Eng.*, **26**, 361 (1991). b) A. Müller, *Polyhedron*, **5**, 323 (1986). c) M. Draganjac and T. B. Rauchfus, *Angew. Chem., Int. Ed. Engl.*, **24**, 742 (1985).
3 For example: a) T. Shibahara, K. Hashimoto, and G. Sakane, *J. Inorg. Biochem.*, **43**, 280 (1991). b) G. Sakane and T. Shibahara, *Inorg. Chem.*, **32**, 777 (1993). c) D. M. Saysell and A. G. Sykes, *J. Cluster Sci.*, **6**, 499 (1995).
4 a) A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, **101**, 3842 (1979). b) F. A. Cotton and R. W. Schwotaer, *Inorg. Chim. Acta*, **155**, 231 (1989). c) V. P. Fedin, A. V. Virovets, M. N. Sokolov, D. N. Dybtsev, O. A. Gerasko, and W. Clegg, *Inorg. Chem.*, **39**, 2227 (2000).
5 Y. G. Yao, work to be published.
6 L. Wu, J. B. Xia, C. N. Chen, X. Y. Huang, Y. G. Yao, and J. X. Lu, *Polyhedron*, **17**, 4203 (1998).
7 Y. G. Yao, H. Akashi, G. Sakane, T. Shibahara, and H. Ohtaki, *Inorg. Chem.*, **34**, 42 (1995).
8 Anal. Calcd for $C_{36}H_{82}N_2Mo_6S_{20}P_6O_{18}$ **1**: C, 19.36; H, 3.70; N, 1.25%. Found: C, 20.28; H, 3.94; N, 1.39%. Calcd for $C_{33}H_{78}Mo_6S_{22}P_6O_{18}$ **2**: C, 17.78; H, 3.53; S, 31.57%. Found: C, 18.16; H, 3.67; S, 31.28%.
9 Crystal data for **1**: $C_{36}H_{82}N_2Mo_6S_{20}P_6O_{18}$, M_r = 2233.70, triclinic, *P*-1, a = 12.9283(7), b = 13.5782(7), c = 25.4202(13) Å, α = 90.4030(10), β = 98.3110(10), γ = 109.7380(1)°, V = 4186.6(4) Å^3, Z = 2, D_c =1.788 g·cm^{-3}. 14496 unique reflections, R_1 = 0.0770, wR_2 = 0.1235 ($I > 2\sigma(I)$). **2**: $C_{33}H_{78}Mo_6S_{22}P_6O_{18}$, M_r = 2229.73, monoclinic, $P2_1/n$, a = 12.398(3), b = 20.533(3), c = 31.896(5) Å, β = 97.717(11)°, V = 8046(2) Å^3, Z = 4, D_c = 1.841 g·cm^{-3}. 14085 unique reflections, R_1 = 0.0580, wR_2 = 0.1647 ($I > 2\sigma(I)$). Data were collected on a Siemens SMART CCD diffractometer ($\lambda_{Mo\ K\alpha}$ = 0.71073 Å), T = 293(2) K, full-matrix least-squares refinements on F^2 using all data with SHELXL programs. Hydrogen atoms were generated geometrically and refined with isotropic thermal parameters.
10 S. F. Lu, J. Q. Huang, M. D. Huang, and J. L. Huang, *Acta Chim. Sin.* (English Edition), **1**, 24 (1989).
11 J. Hu, Y. F. Zheng, J. Q. Huang, and J. X. Lu, *Chinese J. Struct. Chem.*, **8**, 6 (1989).
12 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, **104**, 5063 (1982).