Syntheses, Crystal Structures of Mo–S Clusters $[Mo_3S_4(dtp)_3(L)]_2[\mu\text{-}OOC(CH_2)_nCOO\text{-}\mu]$ (L = dmf, dmso; $n = 3, 4$) and Their Supramolecular Architectures

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The substitution reaction of $[Mo_3S_4(dtp)_3(ClCH_2COO)(py)]$ (dtp = diethyl dithiophosphate) or $[Mo_3S_4(dtp)_4(H_2O)]$ with adipic acid or glutaric acid in *N*,*N*′-dimethylformamide (dmf) or dimethyl sulfoxide (dmso) dimerized two discrete Mo_3S_4 clusters into novel Mo(IV) cluster compounds $[Mo_3S_4(dtp)_3(L)]_2[\mu\text{-}OOC(CH_2)_nCOO\text{-}\mu]$ (L = dmf, $n = 4$ for **1**, $n = 3$ for **2**; L = dmso, $n = 3$ for **3**). Their structures have been determined by X-ray crystallography and spectroscopically characterized. Each molecule of these clusters consists of two incomplete cubane-type $[Mo_3S_4(dtp)_3(L)]$ units, and each unit is respectively coordinated to one dicarboxylate group of the same dicarboxylic acid. Intermolecular S⋯S and C–H⋯S contacts, observed in the crystal packing diagram, establish three infinite two-dimensional supramolecular architectures.

The synthesis and reactivity of cluster compounds with $Mo_3O_nS_{4-n}$ ($n = 0, 1, 3, 4$) cores have been extensively studied over the past twenty years.[1] The previous researches have been focused on the chemistry of discrete tri- and tetranuclear species,[2] and little is known about their macromolecular or supramolecular chemistry. So far, only a few compounds with two or more $Mo_3O_nS_{4-n}$ units, such as $Na_4[(Mo_3O_4)_2(edta)_3]\cdot 14H_2O$,[3] $[Mo_3S_4(HBpz_3)_2]_2(\mu\text{-}O)(\mu\text{-}C_3H_3N_2)_2$,[4] $Na_2M_2[Mo_3O_4(O_2CEt)_8]_2$ (M = Fe, Cr, V),[5] and $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](pyH)(C_{36}H_{36}N_{24}O_{12})\}Cl_4\cdot 17H_2O$,[6] have been reported. The synthetic strategy included the reduction of Mo_3X_4 (X = S, O) clusters with metals,[7–10] the replacement of the coordinated ligand H_2O with the multidentate ligands[3,5] and the self-assemblage with corresponding metal compounds.[6] Recently, we have developed a rational synthesis to convert $[Mo_3O_nS_{4-n}]^{4+}$ aqua ion species into the neutral compounds $[Mo_3O_nS_{4-n}(dtp)_3(L')(L)]$ (L′ = -dtp, -HCOO, $-ClCH_2COO$; L = H_2O, py).[11] Both L′ and L in $[Mo_3O_nS_{4-n}(dtp)_3(L')(L)]$ can be easily replaced by other ligands with stronger coordinating capability. Based on these reactions, we have initiated an effort to oligomerize $Mo_3O_nS_{4-n}$ complexes through multidentate ligands. In this research, we used the long-chain dicarboxylic acids as the substituting ligands and successfully crystallized the clusters $[Mo_3S_4(dtp)_3(L)]_2[\mu\text{-}OOC(CH_2)_nCOO\text{-}\mu]$ (L = dmf, $n = 4$ for **1**,[12] $n = 3$ for **2**; L = dmso, $n = 3$ for **3**[12]). These three Mo_3S_4 cluster polymers are constructed by the joint effect of covalent bonds and intermolecular S⋯S or C–H⋯S interactions.

Experimental

General Procedures and Measurements. All experiments were carried out under air. $[Mo_3S_4(dtp)_4(H_2O)]$ and $[Mo_3S_4(dtp)_3(ClCH_2COO)(py)]$ were prepared according to the literature procedure.[13] Other reagents were purchased commercially and used without further purification. Infrared spectra were recorded on a Nicolet Magna 750FT-IR spectrophotometer in KBr pellets (4000–400 cm^{-1}). Elemental analyses were performed on an EA1110 Elemental Analyzer.

Preparation of $[Mo_3S_4(dtp)_3(dmf)]_2[\mu\text{-}OOC(CH_2)_4COO\text{-}\mu]$ (1). The mixture of $[Mo_3S_4(dtp)_3(ClCH_2COO)(py)]$ (0.10 g, 0.088 mmol), $HOOC(CH_2)_4COOH$ (0.01 g, 0.068 mmol), and DMF (10.0 cm^3) was stirred at 80 °C for 1 h. After filtration, anhydrous ethanol (20.0 cm^3) was added; well-shaped crystals precipitated in good yield (61%) when the red-brown solution was kept at room temperature for two weeks. Found: C, 20.28; H, 3.94; N, 1.39%. Elemental analysis Calcd for $C_{36}H_{82}Mo_6N_2O_{18}P_6S_{20}$: C, 19.36; H, 3.70; N, 1.25%.

Preparation of $[Mo_3S_4(dtp)_3(dmf)]_2[\mu\text{-}OOC(CH_2)_3COO\text{-}\mu]$ (2). The preparation of complex **2** is similar to that of **1** but using glutaric acid instead of adipic acid as the substituting reagent. Yield: 58%. Found: C, 19.83; H, 3.39; N, 1.21%. Elemental analysis Calcd for $C_{35}H_{80}Mo_6N_2O_{18}P_6S_{20}$: C, 18.94; H, 3.63; N, 1.26%.

Preparation of $[Mo_3S_4(dtp)_3(dmso)]_2[\mu\text{-}OOC(CH_2)_3COO\text{-}\mu]$ (3). The mixture of $[Mo_3S_4(dtp)_4(H_2O)]$ (0.10 g, 0.085 mmol), 4,4′-bipyridine (0.01 g, 0.065 mmol), and EtOH (20.0 cm^3) was refluxed at 80 °C for 30 min. Then to the suspended solution was added glutaric acid (0.01 g, 0.076 mmol) and the mixture was further refluxed for 20 min. After cooling, DMSO (10.0 cm^3) was added to dissolve the precipitate. The solution, after several days' standing, produced dark crystals with 30% yield. Found: C, 18.16; H, 3.67; S, 31.28%. Elemental analysis Calcd for $C_{33}H_{78}Mo_6O_{18}P_6S_{22}$: C, 17.78; H, 3.53; S, 31.57%.

Crystal Structural Determination. Data were collected at 293(2) K on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with ome-

Table 1. Crystallographic Data for Clusters **1**–**3**

Compounds	**1**	**2**	**3**
M_r	2233.70	2219.67	2229.73
$F(000)$	2236	2220	4456
Crystal dimensions/mm^3	0.36 × 0.18 × 0.08	0.44 × 0.14 × 0.04	0.70 × 0.36 × 0.22
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a/Å	12.9283(7)	13.9819(6)	12.398(3)
b/Å	13.5782(7)	14.2625(7)	20.533(3)
c/Å	25.4202(13)	21.9735(10)	31.896(5)
$\alpha/^\circ$	90.4030(10)	76.4190(10)	90.00
$\beta/^\circ$	98.3110(10)	86.6750(10)	97.717(11)
$\gamma/^\circ$	109.7380(10)	78.7720(10)	90.00
V/Å^3	4148.6(4)	4177.5(3)	8046(2)
Z	2	2	4
$\rho_{calcd}/g\,cm^{-3}$	1.788	1.765	1.841
μ/mm^{-1}	1.552	1.540	1.649
θ range/°	0.81–25.03	1.48–25.02	1.18–25.04
No. of rflns. (measd.)	21692	21848	28470
No. of rflns. (indep.)	14496	14615	14085
No. of rflns. (obsd.)	7159	4877	9416
No. of parameters	792	769	766
R_1 ($I > 2\sigma(I)$)	0.0778	0.0960	0.0580
wR_2 (all data)	0.1811	0.2336	0.2070
GOF	1.028	0.932	1.241

$$\left.\begin{array}{c} Mo_3S_4(dtp)_3(CH_2ClCOO)(py) \\ HOOC(CH_2)_nCOOH \end{array}\right\} \xrightarrow{dmf} \begin{array}{c} [\,Mo_3S_4(dtp)_3(dmf)][OOC(CH_2)_nCOO] \\ (n = 3, 4) \end{array} \quad (1)$$

Scheme 1.

ga scans; an empirical absorption correction was applied. The structures were refined by full-matrix least-squares on F^2 through the use of the SHELXL programs.[14] The positions of the molybdenum atoms were determined by direct methods, and successive difference electron density maps located the remaining non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically except C74 in **1** and some C atoms of dtp ligands in **2**. The positions of the hydrogen atoms were generated geometrically (C–H bond fixed at 0.96 or 0.97 Å), assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms before the final cycle of least-squares refinements.

The crystallographic data for clusters **1**–**3** are summarized in Table 1.

Results and Discussion

Synthesis. The syntheses of clusters **1** and **2** can be depicted with Scheme 1. Each dicarboxylate group of the dicarboxylic acid replaced the μ-CH_2ClCOO ligand in the precursors, leading to the dimerization of two Mo_3S_4 units. At the same time, the loosely-coordinated py ligand was replaced by the solvent molecule dmf. The cluster **3** can also be prepared by reaction (1) using dmso instead of dmf. In all syntheses, the trinuclear molybdenum compounds are soluble in many polar solvents. Nevertheless, the dimeric complexes reported here can only be dissolved in highly polar solvents such as dmf and dmso.

Crystal Structure. These three isostructural clusters: **1**, **2**, and **3** have been characterized by X-ray crystallography. The ORTEP drawings of **1** and **3** are shown in Fig. 1. The structure of **2** is similar to that of **3** except the coordinated solvent molecule is dmf instead of dmso, so the drawing of **2** is not included in Fig. 1. Selected bond lengths and angles of these three clusters are listed in Table 2. A comparison of important average bond lengths among these three complexes and other related clusters is given in Table 3.

These Mo–S complexes are the first structurally characterized compounds dimerized by only one dicarboxylate. Both two carboxylate groups of adipate or glutarate coordinate to Mo atoms in bridging modes, resulting in the covalent dimerization of Mo_3S_4 moieties. This kind of coordination pattern contrasts with that of their analogues substituted by *o*-phthalate,[15] in which one of the two carboxylates coordinates to two Mo atoms from one Mo_3S_4 moiety, while the other carboxylate interacts through H-bonds with the carboxylate from the adjacent dicarboxylic acid. The flexibility of the longer hydrocarbon chain of these dicarboxylic acids is responsible for these unique molecular configurations.

By consulting the geometrical parameters as listed in Table 3, we will find that the coordination environment around each Mo_3S_4 core of clusters **1**, **2**, and **3** is essentially identical to that of the discrete trinuclear molybdenum clusters coordinated by monocarboxylate.[16,17] The averaged Mo–Mo, Mo–(μ-S), Mo–(μ_3-S), and Mo–O(in L or L′) bond lengths are similar to those of the monocarboxylate-coordinated com-

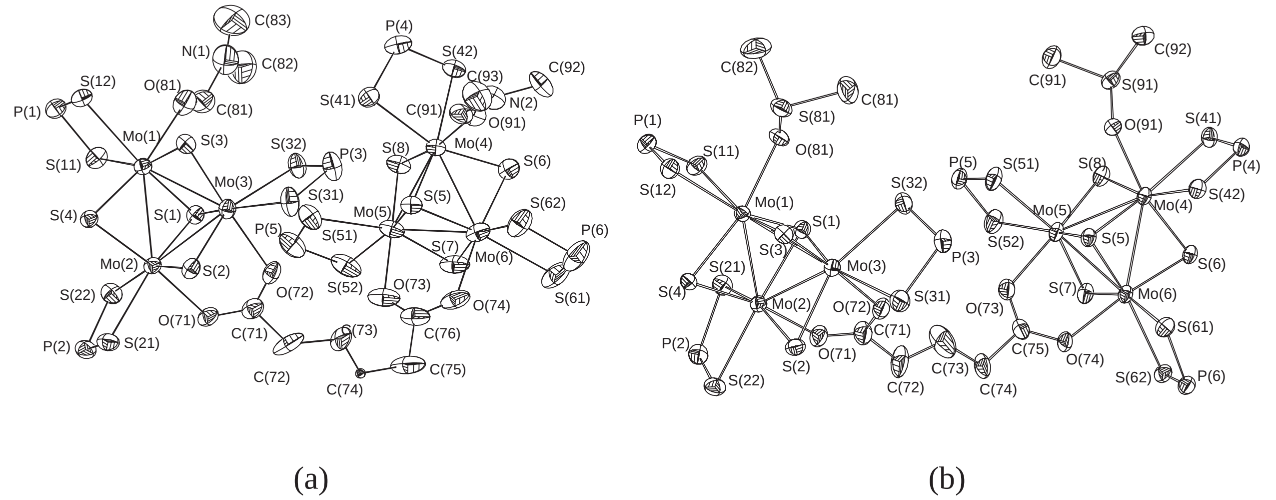

Fig. 1. ORTEP drawings of **1** (a) and **3** (b) at 20% probable thermal ellipsoids. The EtO groups of dtp ligands were omitted for clarity.

Table 2. The Selected Bond Lengths and Angles (Å, °)

	Cluster **1**	Cluster **2**	Cluster **3**		Cluster **1**	Cluster **2**	Cluster **3**
Mo(1)–Mo(2)	2.7515(14)	2.767(2)	2.7520(11)	Mo(3)–S(3)	2.298(3)	2.279(5)	2.289(2)
Mo(1)–Mo(3)	2.7552(15)	2.758(2)	2.7698(11)	Mo(3)–O(72)	2.258(9)	2.249(11)	2.241(7)
Mo(2)–Mo(3)	2.6798(15)	2.685(2)	2.6905(11)	Mo(4)–S(5)	2.331(3)	2.332(5)	2.334(2)
Mo(4)–Mo(5)	2.7568(16)	2.754(2)	2.7522(11)	Mo(4)–S(6)	2.299(4)	2.294(5)	2.272(2)
Mo(4)–Mo(6)	2.7481(17)	2.750(2)	2.7623(12)	Mo(4)–S(8)	2.271(3)	2.271(5)	2.301(2)
Mo(5)–Mo(6)	2.689(2)	2.675(2)	2.6890(11)	Mo(4)–O(91)	2.247(9)	2.247(19)	2.276(6)
Mo(1)–S(1)	2.339(3)	2.326(5)	2.335(2)	Mo(5)–S(5)	2.317(3)	2.337(5)	2.331(2)
Mo(1)–S(3)	2.295(3)	2.292(5)	2.307(2)	Mo(5)–S(7)	2.310(4)	2.291(5)	2.299(3)
Mo(1)–S(4)	2.277(3)	2.272(5)	2.276(2)	Mo(5)–S(8)	2.293(4)	2.287(5)	2.289(3)
Mo(1)–O(81)	2.329(11)	2.208(12)	2.235(6)	Mo(5)–O(73)	2.204(11)	2.248(11)	2.230(8)
Mo(2)–S(1)	2.333(3)	2.327(5)	2.333(2)	Mo(6)–S(5)	2.336(3)	2.329(5)	2.336(2)
Mo(2)–S(2)	2.285(3)	2.295(5)	2.292(3)	Mo(6)–S(6)	2.283(4)	2.288(5)	2.285(2)
Mo(2)–S(4)	2.294(3)	2.295(5)	2.280(2)	Mo(6)–S(7)	2.289(4)	2.304(5)	2.297(2)
Mo(2)–O(71)	2.193(8)	2.213(11)	2.197(7)	Mo(6)–O(74)	2.197(11)	2.198(11)	2.218(6)
Mo(3)–S(1)	2.343(3)	2.346(4)	2.331(2)	C(81)–O(81)	1.16(2)	1.24(2)	
Mo(3)–S(2)	2.287(3)	2.295(5)	2.301(3)	C(91)–O(91)	1.235(16)	1.08(5)	
Mo(1)–Mo(2)–Mo(3)	60.95(4)	60.75(5)	61.17(3)	S(5)–Mo(5)–S(7)	108.32(15)	108.96(17)	108.58(9)
Mo(1)–Mo(3)–Mo(2)	60.81(4)	61.10(6)	60.51(3)	S(5)–Mo(6)–S(6)	105.73(13)	105.70(19)	104.58(9)
Mo(2)–Mo(1)–Mo(3)	58.24(4)	58.15(5)	58.32(3)	S(5)–Mo(6)–S(7)	108.39(15)	108.78(17)	108.48(9)
Mo(4)–Mo(5)–Mo(6)	60.59(4)	60.84(6)	61.00(3)	S(6)–Mo(6)–S(7)	93.21(14)	92.41(18)	92.85(9)
Mo(4)–Mo(6)–Mo(5)	60.92(4)	61.01(6)	60.63(3)	S(6)–Mo(4)–S(8)	98.20(14)	96.52(18)	97.74(9)
Mo(5)–Mo(4)–Mo(6)	58.49(5)	58.15(6)	58.37(3)	S(7)–Mo(5)–S(8)	94.33(14)	94.06(18)	93.62(10)
S(1)–Mo(1)–S(3)	105.16(12)	105.20(16)	104.47(8)	O(71)–Mo(2)–S(4)	172.9(2)	173.6(3)	171.2(2)
S(1)–Mo(1)–S(4)	105.56(11)	104.81(17)	105.10(9)	O(71)–Mo(2)–S(2)	85.1(2)	84.7(3)	84.5(2)
S(1)–Mo(2)–S(2)	108.81(12)	108.98(17)	108.56(9)	O(71)–Mo(2)–S(1)	81.9(2)	82.3(3)(3)	83.7(2)
S(1)–Mo(2)–S(4)	105.23(11)	104.05(17)	105.02(9)	O(72)–Mo(3)–S(3)	173.1(2)	173.2(3)	171.4(2)
S(1)–Mo(3)–S(2)	108.39(12)	108.29(17)	108.33(9)	O(72)–Mo(3)–S(2)	82.3(2)	82.3(3)	81.7(2)
S(1)–Mo(3)–S(3)	104.94(12)	104.93(16)	105.17(9)	O(72)–Mo(3)–S(1)	81.9(2)	81.8(3)	82.9(2)
S(2)–Mo(2)–S(4)	92.64(11)	93.70(18)	93.35(10)	O(73)–Mo(5)–S(8)	172.8(3)	172.5(3)	171.1(2)
S(2)–Mo(3)–S(3)	94.89(12)	93.98(17)	92.94(10)	O(73)–Mo(5)–S(7)	82.3(3)	83.0(3)	82.1(2)
S(3)–Mo(1)–S(4)	97.76(11)	97.59(18)	97.74(9)	O(73)–Mo(5)–S(5)	82.7(3)	83.0(3)	83.3(2)
S(5)–Mo(4)–S(6)	105.39(13)	105.38(18)	105.05(9)	O(74)–Mo(6)–S(6)	172.4(3)	172.1(3)	171.86(18)
S(5)–Mo(4)–S(8)	104.63(12)	105.22(18)	104.97(9)	O(74)–Mo(6)–S(7)	83.9(4)	83.7(3)	83.63(19)
S(5)–Mo(5)–S(8)	104.39(12)	104.55(18)	105.46(9)	O(74)–Mo(6)–S(5)	81.9(3)	82.1(3)	83.52(18)

Table 3. A Comparison of Averaged Bond Lengths (Å) in Clusters **1**–**3** and Related Compounds

	Mo–Mo (av.)	Mo–(μ-S) (av.)	Mo–(μ_3-S) (av.)	Mo–O(in L′) (av.)	Mo–L (av.)	Ref.
$[Mo_3S_4(dtp)_3(DMF)]_2$(adipate) **1**	2.7301	2.290	2.333	2.213	2.288 (O)	This work
$[Mo_3S_4(dtp)_3(DMF)]_2$(glutarate) **2**	2.731	2.289	2.333	2.227	2.227 (O)	This work
$[Mo_3S_4(dtp)_3(DMSO)]_2$(adipate) **3**	2.7367	2.283	2.333	2.222	2.255 (O)	This work
$Mo_3S_4(dtp)_3(HCOO)(Py)$ **4**	2.741	2.287	2.332	2.224	2.385 (N)	16
$Mo_3S_4(dtp)_3(CH_3COO)(Py)$ **5**	2.740	2.293	2.334	2.205	2.385 (N)	16
$Mo_3S_4(dtp)_3(CH_3CH_2COO)(Py)$ **6**	2.731	2.288	2.335	2.224	2.372 (N)	17
$Mo_3S_4(dtp)_3(CH_2ClCOO)(Py)$ **7**	2.725	2.275	2.341	2.271	2.353 (N)	17
$Mo_3S_4(dtp)_4(H_2O)$ **8**	2.754	2.283	2.346		2.361 (O)	18
$[Mo_3S_4(dtp)_3(phthalate)(Py)]_2 \cdot EtOH \cdot CH_2Cl_2$ **9**	2.737	2.294	2.336	2.242	2.358 (N)	13

plexes **4**–**6**. In cluster **3**, the substitution of glutarate for μ-dtp in the starting material **8** shortens the bridged Mo–Mo distances from 2.734 Å to 2.6905 Å and 2.6890 Å, respectively, and the average Mo–Mo bond length (2.7367 Å) is also shorter than that of cluster **8** by 0.017 Å.[18] The mean Mo–Mo and Mo–(μ-S) distances of cluster **1**, **2** are only slightly different from their precursor **7**. However, the mean Mo–(μ_3-S) and Mo–O(carboxylate) distances of **7** are longer than those of **1** and **2**; this should be attributed to the electron density decreasing of Mo_3S_4 caused by the strong electron-withdrawing ability of -Cl group in μ-CH_2ClCOO ligand in cluster **7**.

The Mo–O(O from dmf or dmso) bond lengths of clusters **1**–**3** fall in the regular Mo–O bond range and are obviously shorter (by ~0.12 Å) than those of Mo–N(py) of clusters **4**–**7** and **9**. This result indicates that dmf and dmso are tightly bonded to Mo. The coordination of dmf and dmso is not the case of H_2O and py, which are often called the loosely-coordinated ligands. So the replacement of py by dmf and dmso can take place.

Although these three complexes have almost the same composition and coordination pattern, the relative positions of the two Mo_3 planes inside the molecule are different. There is good coplanarity (7.5°) between the two Mo_3 planes in **1**. The dihedral angle between the two Mo_3 planes is 18.1° for **2** and 31.7° for **3**, showing not so good coplanarity.

Infrared Spectra. The asymmetric and symmetric stretching vibrations (ν_{asym} and ν_{sym}) of the dicarboxylate group are: 1512 cm^{-1} and 1408 cm^{-1} (**1**), 1514 cm^{-1} and 1406 cm^{-1} (**2**), 1516 cm^{-1} and 1407 cm^{-1} (**3**), respectively. So their corresponding $\Delta\nu(OCO)$ ($\nu_{asym} - \nu_{sym}$) (104 cm^{-1} (**1**), 108 cm^{-1} (**2**) and 109 cm^{-1} (**3**), respectively) are far smaller than that of free carboxylate (210–250 cm^{-1})[19] because these carboxylates bridge to Mo atoms. The IR bands of Mo–O (in dicarboxylate and dmf or dmso) are assigned as follows: 791 cm^{-1} and 643 cm^{-1} (**1**); 787 cm^{-1} and 643 cm^{-1} (**2**); 792 cm^{-1} and 644 cm^{-1} (**3**). The strong vibration at 1645 cm^{-1} for **1** and 1643 cm^{-1} for **2**, respectively, can be assigned to the stretching vibration of C–O in dmf.

S···S Interactions and C–H···S Interactions. Carbon atoms act as proton donors in C–H···X hydrogen bonds (X denotes a hydrogen bond acceptor atom, i.e., O, N, Cl, or S). These bonds have been well established in many systems[20] and a great many reports of such C–H···O hydrogen bonds have been published.[21] Iwaoka and Tomoda demonstrated a C–H···Se "hydrogen bond".[22] However, as their analogue, the C–H···S hydrogen bonding is less reported[23] and less well understood.[24] It is noteworthy that, in our compounds **1**–**3**, several C–H···S interactions between the C atoms (from dtp ligands and the coordinated dmf or dmso groups) and S atoms (from cluster cores and dtp ligands) are observed and are significant in the crystal packing. Their hydrogen bond parameters are presented in Table 4. The parameters of C–H···S interactions as listed in Table 4 fall within the limits suggested by Taylor and Kennard[24] and their H···S and C···S distances are shorter than the corresponding van der Waals radii sum (3.05 and 3.70 Å, respectively).[25,26] The intermolecular S···S interactions (<3.70 Å), which are common in molybdenum polychalcogenide compounds,[15,27] are also found in these three compounds (Table 5).

As shown in Figs. 2–4, the combined interactions of Mo–O

Table 4. Hydrogen-Bonding Geometry (Å) of Compounds **1**–**3**

	D–H···A	D–H	H···A	D···A	D–H···A
1	C(42c)–H42A···S(7a)[a)]	0.96	2.79	3.68(2)	154.2
	C(44a)–H44B···S(61b)[b)]	0.96	2.66	3.56(2)	156.5
2	C(63)–H63B···S(61c)[c)]	0.97	3.01	3.59(2)	120.0
	C(83b)–H83C···S(51a)[d)]	0.96	2.95	3.69(2)	135.1
3	C(81)–H81B···S(2a)[e)]	0.96	2.74	3.59(1)	148.0
	C(81)–H81C···S(41b)[f)]	0.96	2.99	3.49(1)	113.4

Symmetry codes: a) $2-x$, $1-y$, $-z$; b) $1+x$, y, z; c) $-x$, $1-y$, $1-z$; d) $-x$, $1-y$, $-z$; e) $0.5-x$, $5.0+y$, $0.5-z$; f) $1-x$, $2-y$, $1-z$.

Table 5. S···S Interactions (Å) of Compounds **1**–**3**

1[a)]	S(2)···S(4a)	3.460(4)	S(4)···S(4a)	3.357(6)	S(12)···S(21a)	3.663(5)
2[b)]	S(6)···S(7a)	3.259(7)	S(6)···S(6a)	3.213(10)	S(62)···S(41a)	3.583(8)
	S(6)···S(8a)	3.424(7)	S(7)···S(41a)	3.468(7)		
3[c)]	S(6b)···S(4a)	3.175(3)	S(41b)···S(22a)	3.572(4)	S(41b)···S(2a)	3.615(4)
	S(62b)···S(12a)	3.490(4)				

Symmetry codes: a) $3-x$, $1-y$, $1-z$; b) $-x$, $-y$, $1-z$; c) $0.5+x$, $1.5-y$, $0.5+z$.

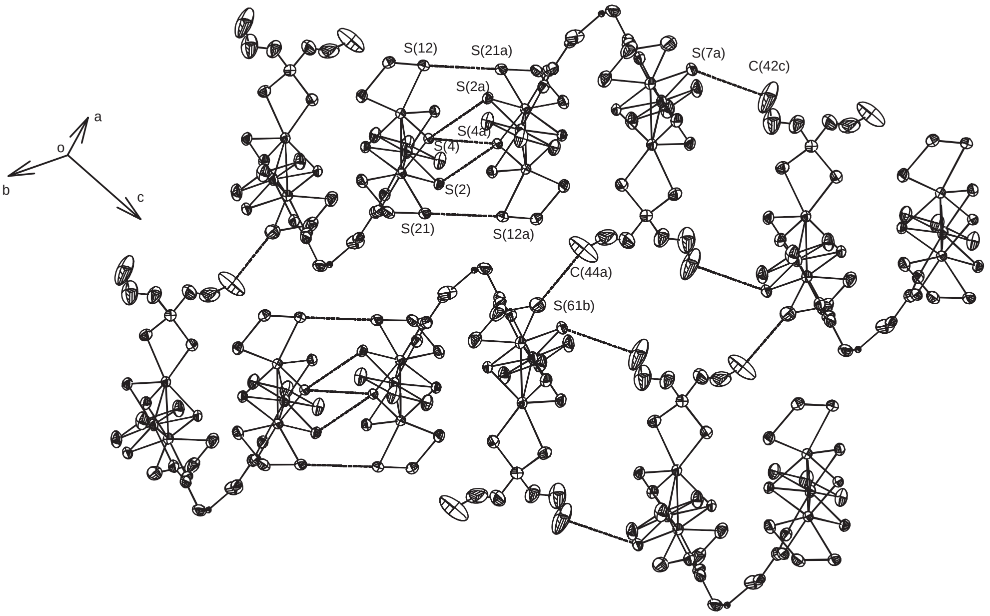

Fig. 2. The packing of **1** with partial atom-numbering scheme at 20% probable thermal ellipsoids. All H atoms and most periphery atoms are omitted for clarity. Hydrogen bonding interactions and S···S interactions are indicated by dashed lines.

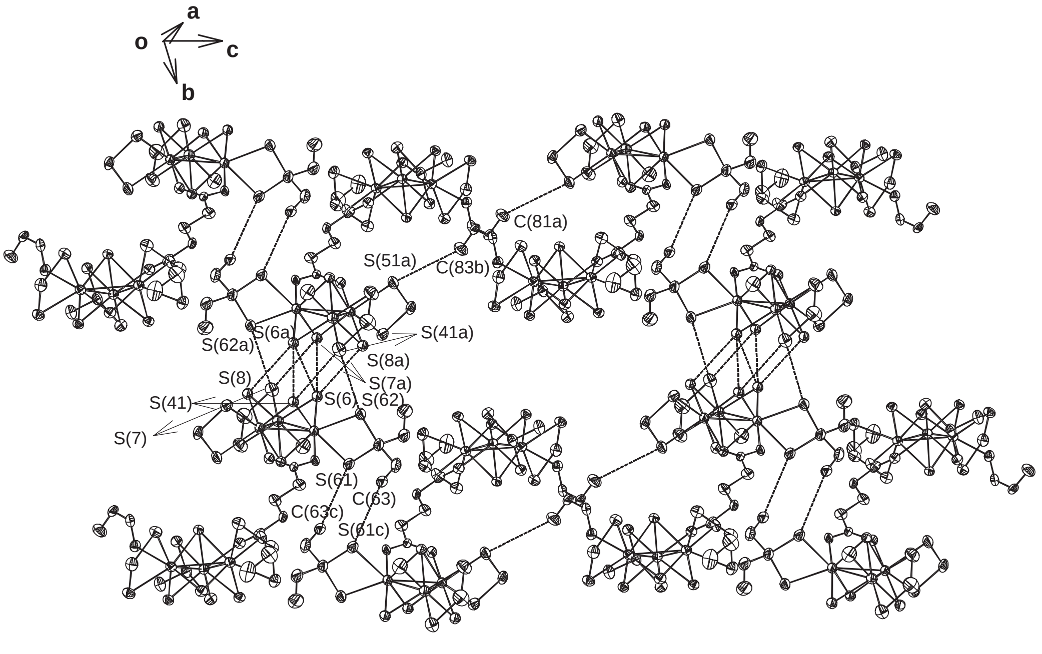

Fig. 3. The packing of **2** with partial atom-numbering scheme at 20% probable thermal ellipsoids. All H atoms and most periphery atoms are omitted for clarity. Hydrogen bonding interactions and S···S interactions are indicated by dashed lines.

covalent bonds from the bridging carboxylates of adipate and glutarate, the S···S interactions and C–H···S hydrogen bonding have assembled the incomplete cuboidal Mo_3S_4 cores into novel infinite extended network structures. Their crystal architectures are different from each other, although their molecular formulas are almost the same.

In crystal **1**, five S···S interactions between Mo_3S_4 cores draw two molecules together to form a dimer. One-dimensional infinite chains are formed by linking the dimers through intermolecular C(44a)···S(61b) contacts. All the molecules are finally packed as a two-dimensional structure by linking the chains through a class of intermolecular C(42c)···S(7a) contacts (Fig. 2). Compared to **1**, molecules of compound **2** are packed in another way. As shown in Fig. 3, the alternate dimers through the linkage of nine S···S interactions are joined together by C(63)···S(61c) and C(83b)···S(51a) via hydrogen bonding to form a two-dimensional polymeric network. Despite their identical configuration, the S···S interaction mode of **3** is quite different from those of **1** and **2**. Both (rather than only one in **1** and **2**) Mo_3S_4 cores in **3** participate in S···S interactions, stringing the molecules together to form one-dimensional infinite chains. The polymeric chains interact with

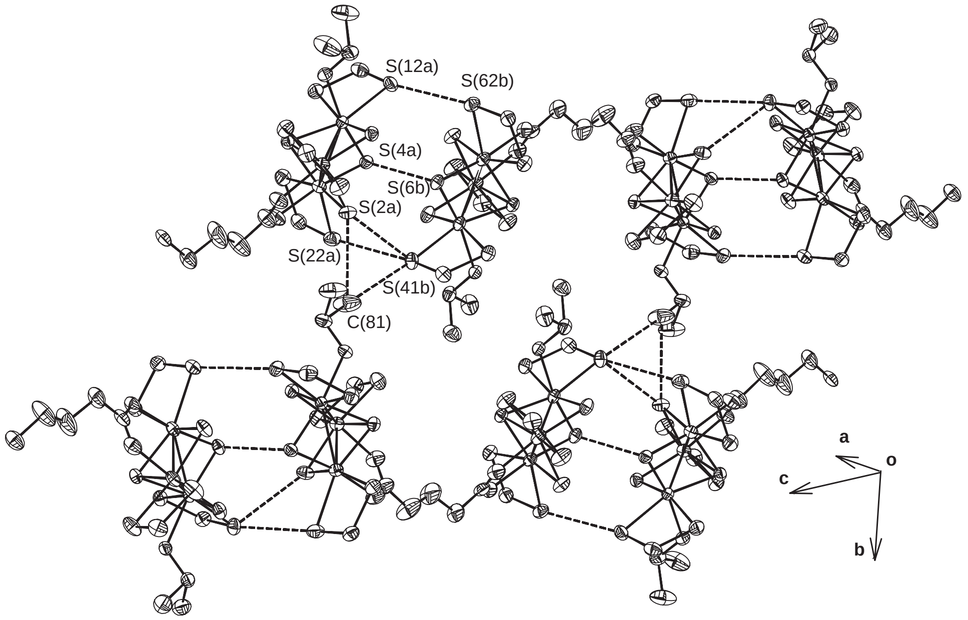

Fig. 4. The packing of **3** with partial atom-numbering scheme at 20% probable thermal ellipsoids. All H atoms and most periphery atoms are omitted for clarity. Hydrogen bonding interactions and S···S interactions are indicated by dashed lines.

each other through C–H···S interactions that originate 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 Fig. 4.

Conclusion

The crystal engineering of supramolecular architectures has attracted intense interest in recent years. Most of the work is focused on the assemblage from simple metal salts with multidentate organic ligands. This work has synthesized the metallic supramolecules using trinuclear Mo cluster complexes as the starting materials. These Mo_3S_4 complexes are good building blocks, considering their versatile reactivity and chemical stability. Our study indicates that not only the multidentate ligands but also the S atoms from the cluster core and the ligands are involved in the coordination and intermolecular interactions, leading to interesting supramolecular cluster polymers such as **1**, **2**, and **3**. Up to now, we have synthesized ten more complexes with Mo_3S_4 cores. They show unique supramolecular structures, owing to the diverse combinations of covalent bonds, S···S interactions, C–H···S and/or O–H···O hydrogen bonds.

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