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Synthesis, crystal structures and calculated nonlinear optical properties of seven di-nuclear metal (0, I) carbonyl cyclohexanthiolates, $[M_2(\mu-SC_6H_{11})_x(CO)_y]^{n-}$ (M = Mo, W; x = 2, 3; y = 6, 8; n = 0, 1, 2)

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Abstract

Seven novel di-nuclear molybdenum and tungsten metal cluster complexes with cyclohexanthiolate ligand, $[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$ (1), $[Et_4N]_Mo_2(SC_6H_{11})_3(CO)_6]$ (2), $[Ph_4P]_Mo_2(SC_6H_{11})_3(CO)_6]$ (3), $[(CH_3)_3PhCH_2N]_Mo_2(SC_6H_{11})_3(CO)_6]$ (4), $[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$ (5), $[W_2(SC_6H_{11})_2(CO)_8]$ (6) and $[Et_4N]_W2(SC_6H_{11})_3(CO)_6]$ (7) have been synthesized and characterized. The crystal structure determinations reveal that 1 and 5 contain a planar $[M(0)_2S_2]$ unit, 6 contains a planar $[M(I)_2S_2]$ unit and 2, 3, 4 and 7 contain a $[M(I)_2S_3]$ core with a planar M_2S_2 unit coordinated by a third chair form SC_6H_{11} bridging ligand (M = Mo, W). IR of these seven complexes was measured. Theory calculation indicated that compounds 2 and 7 possess large first-order hyperpolarizability of 13×10^{-30} esu and 8×10^{-30} esu, respectively, which could be an IR second-order nonlinear optical candidate materials.

Keywords: M (Mo,W)₂S_{2,3} unit; De-carbonylation; Crystal structures; Nonlinear optical property

1. Introduction

With the development of laser technique, optical communication, optical signal processing and transmission, optical data acquisition and storage, optical computing, optical electronic modulation, and especially optical limiting effects utilized in the protection of optical sensors, tremendous interest has been aroused to search for new nonlinear optical (NLO) materials, so the design and synthesis of new NLO materials become the subject of the current research interest, and represent a new active research field [1,2]. And transition-metal cluster nonlinear optical (NLO) materials have attracted increasing interest recently

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owing to the potential device applications in IR spectroscopic region [3]. Recently, transition-metal sulfur clusters have grown into a new promising class of NLO material [4], and have gradually been paid attention to by virtue of their possessing the combined advantages of both organic polymers and inorganic semiconductors [5,6]. The multinuclear molybdenum and tungsten complexes are one of the systems that having been investigated [7]. The binuclear molybdenum carbonyl complexes containing thiolate bridges, with a planar [Mo₂S₂] core were synthesized in 1984 by reaction of $Mo(CO)_6$ with thiolate ligands[8]. These metal-carbonyl complexes undergo reversible two-electron oxidation accompanied by metalmetal bond formation [9,10]. Decarbonylation of $[M_2]$ $(\mu$ -SR)₂(CO)₈]^{2-,0} and the subsequent reaction of its core $[M_2S_2]$ (M = Mo, W) are attractive because it may be used to further synthesize a variety of multinuclear metal

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complexes. In order to discuss the influence of R ligand on the $[M_2S_2]$ -core in these compounds, and the difference between Mo analog and W analog with cyclohexanthiolate ligand, in this paper we report the synthesis, structure, spectroscopic characterization and primary theoretical calculation of seven new metal thiolate carbonyl compounds by introducing a new chair-form C₆H₁₁S-ligand which is different from aryl and alky to M2S2 unit: [Et4N]2[Mo2 $(SC_6H_{11})_2(CO)_8$ (1), $[Et_4N][Mo_2(SC_6H_{11})_3(CO)_6]$ (2), $[Ph_4P]$ $[Mo_2(SC_6H_{11})_3(CO)_6]$ (3), $[(CH_3)_3PhCH_2N]$ $[Mo_2(SC_6H_{11})_3]$ $(CO)_{6}$ (4), $[Et_{4}N]_{2}[W_{2}(SC_{6}H_{11})_{2}(CO)_{8}]$ (5), $[W_{2}(SC_{6}H_{11})_{2}]$ $(CO)_{8}$ (6) and $[Et_{4}N][W_{2}(SC_{6}H_{11})_{3}(CO)_{6}]$ (7). The structure determinations indicate that there are three modes of structure in these complexes. (i) $M_2(0)$ -S₂ core without M...M bonding (in 1 and 5) (A); (ii) $M_2(I)-S_2$ core with M-M bonding (in 6) (B) and (iii) $M_2(I)$ -S₃ core with M-M bonding (in 2, 3, 4 and 7) (C). Two of the seven compounds have been theoretically predicted to have considerable molecular NLO activity. And, furthermore, these two compounds are non-centrosymmetric, so, they may be promising second-order nonlinear optical materials which can be applied in IR region.



2. Results and discussion

2.1. Synthesis and synthetic reaction of compounds 1–7

The synthesis and synthetic reaction for compounds 1-7 is described in Schemes 1 and 2. As is shown in Scheme 1,

 $Mo(CO)_6$ reacts with $C_6H_{11}SNa$ in the presence of Et_4NCl at 50 °C affording [Et₄N]₂[Mo₂(SC₆H₁₁)₂(CO)₈] (1) (Reaction 1), 1 undergoes oxidation by I_2 to give $[Mo_2(SC_6H_{11})_2]$ $(CO)_{8}$ (1') and $[Mo_{2}(SC_{6}H_{11})_{2}(CO)_{6}(CH_{3}CN)_{2}]$ (1") when toluene and MeCN were used as solvent (Reactions 2 and 3), respectively [11,12]. 1' or 1" reacts with $C_6H_{11}SNa$ in the presence of Et₄NCl resulting in [Et₄N][Mo₂(SC₆ $H_{11}_{3}(CO)_{6}$] (2) (Reactions 4 and 5). Interestingly and unexpectedly, both reaction of $Mo(CO)_6$ with $C_6H_{11}SNa$ in the presence of Et₄NCl at 85 °C for 24 h and the solution of 1 in MeCN standing in refrigerator at 4 °C for 3 months can afford compound 2 also (Reactions 6 and 7). It is obvious that reactions 6 and 7 involve with an oxidation of Mo atom, although not any oxidant have been added in these two reactions. The oxidation may be attributed to a small amount of air, which remains in the Schlenk tube because the degassing is not thorough. The remainder air is too less to influence the synthetic reaction at room temperature and in short reaction time, but the remainder air may become an oxidant at high temperature and even at low temperature in long reaction time. So, the reaction 6 should contain formation of $[Mo_2(SC_6H_{11})_2(CO)_8]^{2-}$ (Reaction a), oxidation of $[Mo_2(SC_6H_{11})_2(CO)_8]^{2-}$ by O₂ (Reaction b) and substitution of MeCN in Mo₂(SC₆H₁₁)₂(CO)₆ $(CH_3CN)_2$ by $SC_6H_{11}^-$ (Reaction c), and the real reaction 7 should involve oxidation of $[Mo_2(SC_6H_{11})_2(CO)_8]^{2-1}$ (Reaction a), decomposition of $[Mo_2(SC_6H_{11})_2(CO)_8]^{2-1}$ to generate ligand $SC_6H_{11}^-$ (Reaction d) and substitution of MeCN in $Mo_2(SC_6H_{11})_2(CO)_6(CH_3CN)_2$ by $SC_6H_{11}^-$ (Reaction c)

$$Mo(CO)_6 + SC_6H_{11}^{-1} \frac{85^{\circ}C}{MCN} [Mo_2(SC_6H_{11})_2(CO)_8]^{2-}$$
 (a)

$$[Mo_{2}(SC_{6}H_{11})_{2}(CO)_{8}]^{2-}$$

$$\xrightarrow{O_{2}}{MeCN}Mo_{2}(SC_{6}H_{11})_{2}(CO)_{6}(CH_{3}CN)_{2}$$
(b)







Scheme 2.

$$Mo_{2}(SC_{6}H_{11})_{2}(CO)_{6}(CH_{3}CN)_{2} + SC_{6}H_{11}^{-} \rightarrow [Mo_{2}(SC_{6}H_{11})_{3}(CO)_{6}]^{-} + MeCN$$
 (c)

$$[Mo_2(SC_6H_{11})_2(CO)_8]^{2-} \xrightarrow{\text{acc}} SC_6H_{11}^- + Mo - SC_6H_{11}^- - CO \quad (d)$$

As a matter of fact, compound 1 in MeCN underwent oxidation to give compound 2 in about 4 weeks at room temperature when a certain amount of air was injected in the Schlenk tube (Reaction 8). The phenomenon of air infiltration leading to the valence enhancement of Mo atom has been reported in our previous paper [13,14]. Compound 4, [(CH₃)₃PhCH₂N] [Mo₂(SC₆H₁₁)₃(CO)₆], can be synthesized according to Reaction 1 and Reaction 7 by using (CH₃)₃PhCH₂NBr instead of Et₄NCl.

It is worth pointing out that compound **3**, $[Ph_4P]$ -[Mo₂(SC₆H₁₁)₃(CO)₆] was obtained from the reaction of [Mo₂(SC₆H₁₁)₂(CO)₈] with Ph₄PBr and CH₃CH₂CH₂-COONa at 50 °C in 24h (Reaction 9). This implies that the presence of CH₃CH₂CH₂COONa may accelerate the decomposition of [Mo₂(SC₆H₁₁)₂(CO)₈] to generate SC₆H₁₁ and the SC₆H₁₁ is more easy to react with [Mo₂(SC₆H₁₁)₂(CO)₈] giving [Mo₂(μ -SC₆H₁₁)₃(CO)₆]⁻ than CH₃CH₂CH₂COO⁻ giving [Mo₂(μ -SC₆H₁₁)₂(μ -CH₃-CH₂CH₂COO)(CO)₆]⁻.

As is shown in Scheme 2, the synthesis and synthetic reaction of tungsten analogs **5**, **6** and **7** are similar to those

of molybdenum analogs. The only difference is: high temperature is required for reaction of W-analog.

2.2. Molecular structures of compounds 1–7

The structures of the anion of 1, 2, 5 and 7 are shown in Figs. 1–3 and 5, respectively. The molecular structure of 6 is depicted in Fig. 4. Selected bond lengths and angles are listed in Table 1–7, respectively.

Compound 1 consists of three discrete structural fragments, two Et_4N^+ cations and an di-anion $[Mo_2 (SC_6H_{11})_2(CO)_8]^{2-}$. As is shown in Fig. 1 and Table 1, the $[Mo_2(SC_6H_{11})_2(CO)_8]^{2-}$ is centrosymmetric and is comprised of two equivalent Mo atoms, each of which bonds to four terminal carbonyls and two bridging chair-form SC_6H_{11} ligands in *trans*-arrangement on the different sides of the $[Mo_2S_2]$ plane, the geometry of each molybdenum (0) atom is a distorted octahedron with two coordinated sulfur atoms and four coordinated carbon atoms and a small SMoS angle of 81.69° . The large $Mo \cdots Mo$ distance of 3.94 Å implies non-bonding of metal \cdots metal which meets the requirement of an 18-electron configuration of each Mo atom for stabilization. The bimetal core unit



Fig. 1. The structure of the anion of compound 1 with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.



Fig. 2. The structure of the anion of compound 2 with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.



Fig. 3. The structure of the anion of compound 5 with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

 MoS_2Mo is a plane with a Mo–S bond distance of 2.6063 Å.

Compound **2** consists of two discrete structure fragments, an Et_4N^+ cation and an anion $[Mo_2(SC_6H_{11})_3$ $(CO)_6]^-$. As is shown in Fig. 2 and Table 2, the $[Mo_2(SC_6H_{11})_3(CO)_6]^-$ has a $[Mo_2S_3]$ core with a planar Mo_2S_2 unit and is comprised of two equivalent Mo⁺ atoms each of which bonds to three terminal carbonyls and three bridging chair-form SC_6H_{11} ligands two of them are located on the same side of the planar Mo_2S_2 -unit in *cis*arrangement and the third one is on the other side with a longer Mo–S bond length. The anion of **2**, $[Mo_2(SC_6H_{11})_3$ $(CO)_6]^-$, is centrosymmetric and the geometry of each



Fig. 4. The structure of the compound **6** with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.



Fig. 5. The structure of the anion of compound 7 with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

molybdenum (I) atom is distorted octahedron with three coordinated sulfur atoms and three coordinated carbon atoms. The bond angle of Mo–S–Mo is 70.81°and the Mo–Mo distance is 2.8562(7) Å indicating an interaction between two metal atoms.

Compounds 3 and 4 are similar to compound 2 except their cations, $[Ph_4P]^+$ (for 3) and $[(CH_3)_3PhCH_2N]^+$ (for 4). The anion of 3 and 4 are the same as that of 2.

Table 1

Table 2

Selected bond lengths (Å) and bond angles (°) for $[Et_4N]_2[Mo_2(SC_6H_{11})_2-(CO)_8]$ (1)

(00)			
Mo(1)–C(1)	1.943(3)	Mo(1)–C(3)	2.033(3)
Mo(1)-C(4)	1.957(3)	Mo(1) - S(1)	2.6039(7)
Mo(1)–C(2)	2.007(3)	Mo(1)-S(1')	2.6087(7)
S(1)-Mo(1)-S(1')	81.69(2)	Mo(1)-S(1)-Mo(1')	98.31(2)

Selected bond lengths (Å) and bond angles (°) for $[Et_4N][Mo_2(SC_6H_{11})_3-(CO)_c](2)$

$(CO)_{6}$ (2)			
Mo(1)-C(1)	1.933(8)	Mo(1)-C(2)	2.006(8)
Mo(1)-C(3)	1.982(10)	Mo(1) - S(3)	2.455(2)
Mo(1)-S(4)	2.482(2)	Mo(2)-C(5)	2.017(9)
Mo(1)-S(5)	2.6096(18)	Mo(2)-S(3)	2.456(2)
Mo(1)-Mo(2)	2.8562(7)	Mo(2)-S(4)	2.468(2)
Mo(2)–C(6)	1.919(8)	Mo(2)-S(5)	2.5801(19)
Mo(2)–C(4)	1.987(9)	S(3)-Mo(1)-S(4)	107.97(6)
S(3)-Mo(1)-S(5)	77.57(6)	S(4)-Mo(2)-Mo(1)	54.99(5)
S(4)-Mo(1)-S(5)	73.66(7)	S(5)-Mo(2)-Mo(1)	57.10(4)
S(3)-Mo(1)-Mo(2)	54.45(5)	Mo(1)-S(3)-Mo(2)	71.12(6)
S(4)-Mo(1)-Mo(2)	54.52(5)	Mo(2)-S(4)-Mo(1)	70.49(6)
S(5)-Mo(1)-Mo(2)	56.12(4)	Mo(2)-S(5)-Mo(1)	66.78(4)
S(4)-Mo(2)-S(5)	74.41(6)	S(3)-Mo(2)-S(4)	108.40(7)
S(3)-Mo(2)-Mo(1)	54.43(4)	S(3)-Mo(2)-S(5)	78.12(6)

Table 3 Selected bond lengths (Å) and bond angles (°) for $[Ph_4P][Mo_2(SC_6H_{11})_3-(CO)_2](3)$

$(CO)_{6}(3)$			
Mo(1)-C(3)	1.933(6)	Mo(2)-C(4)	1.935(6)
Mo(1)-C(2)	2.004(5)	Mo(2)–C(5)	2.003(5)
Mo(1)-C(1)	2.021(5)	Mo(2)–C(6)	2.014(5)
Mo(1)-S(2)	2.4558(13)	Mo(2)-S(2)	2.4689(14)
Mo(1) - S(1)	2.4593(16)	Mo(2)-S(1)	2.4741(14)
Mo(1)-S(3)	2.596(2)	Mo(2)-S(3)	2.5623(18)
Mo(1)-Mo(2)	2.8691(10)	S(1)-Mo(2)-Mo(1)	54.20(4)
S(2)-Mo(1)-Mo(2)	54.58(3)	S(3)-Mo(2)-Mo(1)	56.78(4)
S(1)-Mo(1)-Mo(2)	54.68(3)	Mo(1)-S(2)-Mo(2)	71.27(4)
S(3)-Mo(1)-Mo(2)	55.64(4)	S(2)-Mo(1)-S(1)	108.78(4)
S(2)-Mo(2)-S(1)	107.89(5)	S(2)-Mo(1)-S(3)	77.05(5)
S(2)-Mo(2)-S(3)	77.47(5)	S(1)-Mo(1)-S(3)	70.95(6)
S(1)-Mo(2)-S(3)	71.30(6)	Mo(1)-S(1)-Mo(2)	71.12(4)
S(2)-Mo(2)-Mo(1)	54.15(3)	Mo(2)-S(3)-Mo(1)	67.58(4)

Table 4

Selected bond lengths (Å) and angles (°) for $[(CH_3)_3PhCH_2N]\![Mo_2-(SC_6H_{11})_3(CO)_6]$ (4)

Mo(1)–C(1)	1.85(2)	Mo(2)–S(3)	2.573(5)
Mo(1)–C(3)	2.04(2)	Mo(1)-Mo(2)	2.8818(10)
Mo(1)-C(2)	2.09(2)	Mo(2)-C(4)	1.86(2)
Mo(1)-S(2)	2.431(5)	Mo(2)-C(6)	1.93(3)
Mo(1)-S(1)	2.440(5)	Mo(2)–C(5)	1.99(2)
Mo(1)-S(3)	2.598(5)	Mo(2)-S(2)	2.447(5)
Mo(2)-S(1)	2.465(5)	S(2)-Mo(2)-S(1)	106.12(16)
S(2)-Mo(1)-S(1)	107.41(16)	S(2)-Mo(2)-S(3)	78.69(15)
S(2)-Mo(1)-S(3)	78.48(16)	S(1)-Mo(2)-S(3)	72.30(16)
S(1)-Mo(1)-S(3)	72.27(16)	S(2)-Mo(2)-Mo(1)	53.54(11)
S(2)-Mo(1)-Mo(2)	54.04(11)	S(1)-Mo(2)-Mo(1)	53.61(12)
S(1)-Mo(1)-Mo(2)	54.43(12)	S(3) - Mo(2) - Mo(1)	56.55(11)
S(3)-Mo(1)-Mo(2)	55.72(11)	Mo(1)-S(1)-Mo(2)	71.97(15)
Mo(1)-S(2)-Mo(2)	72.42(14)	Mo(2)-S(3)-Mo(1)	67.72(11)

Table 5

Selected bond lengths (Å) and bond angles (°) for $[Et_4N]_2[W_2(SC_6H_{11})_2-(CO)_8]\,(\textbf{5})$

W(1)–C(21)	1.955(13)	W(1)–S(1)	2.596(3)
W(1)-C(24)	1.919(12)	S(1)-W(1')	2.599(3)
W(1)-C(23)	1.985(13)	W(1) - S(1')	2.599(3)
W(1)-C(22)	2.016(15)	S(1')-W(1)-S(1)	80.81(9)
W(1')-S(1)-W(1)	99.19(9)		

Table 6 Selected bond lengths (Å) and bond angles (°) for $[W_2(SC_6H_{11})_2(CO)_8]$ (6)

W(1)-C(4)	2.01(2)	W(2)–C(8)	1.986(17)
W(1)–C(1)	2.014(17)	W(2)–C(5)	2.001(15)
W(1)-C(3)	2.040(19)	W(2)–C(6)	2.03(2)
W(1)-C(2)	2.044(17)	W(2)–C(7)	2.055(17)
W(1)-S(2)	2.481(4)	W(2)–S(2)	2.477(4)
W(1) - S(1)	2.484(4)	W(2)-S(1)	2.478(4)
W(1)–W(2)	2.9762(9)	S(2)-W(2)-W(1)	53.17(9)
S(2)-W(1)-S(1)	106.09(13)	S(2)-W(2)-S(1)	106.41(13)
S(2)-W(1)-W(2)	53.05(9)	S(1)-W(2)-W(1)	53.24(9)
S(1)-W(1)-W(2)	53.05(9)	W(2)-S(1)-W(1)	73.71(12)
W(2)-S(2)-W(1)	73.79(12)		

Table 7 Selected bond lengths (Å) and bond angles (°) for $[Et_4N][W_2(SC_6H_{11})_3-(CO), 1/7]$

$(CO)_{6}(7)$			
W(1)–C(13)	1.932(15)	W(2)–C(21)	1.949(15)
W(1)-C(12)	2.021(14)	W(2)-C(22)	1.946(19)
W(1) - C(11)	2.015(16)	W(2)–C(23)	1.975(15)
W(1) - S(3)	2.459(3)	W(2) - S(3)	2.452(3)
W(1)–S(2)	2.474(3)	W(2)-S(2)	2.464(4)
W(1) - S(1)	2.583(4)	W(2) - S(1)	2.577(3)
W(1) - W(2)	2.8614(8)	S(3)-W(2)-S(1)	77.74(11)
S(3)-W(1)-S(2)	107.72(12)	S(2)-W(2)-S(1)	73.72(11)
S(3)-W(1)-S(1)	77.50(11)	S(3)-W(2)-W(1)	54.48(8)
S(2)-W(1)-S(1)	73.45(11)	S(2)-W(2)-W(1)	54.76(8)
S(3)-W(1)-W(2)	54.24(8)	S(1)-W(2)-W(1)	56.41(9)
S(2)-W(1)-W(2)	54.42(9)	W(2)-S(3)-W(1)	71.27(9)
S(1)-W(1)-W(2)	56.22(8)	W(2)-S(2)-W(1)	70.82(9)
S(3)-W(2)-S(2)	108.29(13)	W(2)-S(1)-W(1)	67.36(8)

Compound 5 consists of three discrete structural fragments, two Et₄N⁺ cations and an anion $[W_2(SC_6H_{11})_2]$ $(CO)_8]^{2-}$ which is comprised of 2 equiv. W atoms, each bonds to four terminal carbonyls and two bridging chairform SC_6H_{11} ligands in *trans*-arrangement on the different sides of the $[W_2S_2]$ plane. As is shown in Fig. 3 and Table 5, the anion of 5, $[W_2(SC_6H_{11})_2(CO)_8]^{2-}$, is centrosymmetric and the geometry of each tungsten(0) atom is distorted octahedron with two coordinated sulfur atoms and four coordinated carbon atoms. The S-W-S bond angle is 80.81°. The large W...W distance of 3.956 Å implies nonbonding of metal ... metal which meets the requirement of an 18-electron configuration of each W atom for stabilization. The bimetal core unit WS₂W is a plane with a W-S bond distance of 2.598 Å. The axial W-C distance (2.001 Å) is longer than the equatorial one (1.937 Å), so the C–O distance of the equatorial carbonyl is obviously different from that of the axial carbonyl. This is obviously due to the opposite effect.

Compound 6 is centrosymmetric, the geometry around each W atom is a distorted octahedron with two S atoms from bridging chair-form SC₆H₁₁ ligands and four carbon atoms from carbonyls. As is shown in Fig. 4 and Table 6, the distance of W-S and bond angle of W-S-W are 2.483 Å and 73.75°, respectively. The W-W distance is 2.9762 Å indicating an interaction between two metal atoms. Like the compound 5, the four carbonyls coordinated to each tungsten atom are unequal in the W-C bond distances. The axial W–C distance (2.042 Å) is longer than the equatorial one (2.012 Å), so the C–O distance of the equatorial carbonyl is obviously different from that of the axial carbonyl, also the average W-C distance (2.027 Å) of compound 6 is longer than that of the compound 5 (1.969 Å). This implies that the donation of electrons of W to carbonyls for compound 6 is more than that for compound 5.

Compound 7 consists of two discrete structure fragments, an cation, Et_4N^+ , and an anion $[W_2(SC_6H_{11})_3$ $(CO)_6]^-$ which has a $[W_2S_3]$ core containing a planar W_2S_2 unit with W–S of 2.467 Å and is comprised of 2 equiv. W⁺ atoms, each of which bonds to three terminal carbonyls and three bridging chair-form SC_6H_{11} ligands. As is shown in Fig. 5 and Table 7, two of the $SC_6H_{11}^-$ ligands are located on the same side of the planar W_2S_2 unit in *cis*-arrangement and the third one is on the other side with a longer W–S bond length of 2.583 Å. The anion of 7, $[W_2(SC_6H_{11})_3(CO)_6]^-$, is centrosymmetric and the geometry of each tungsten (I) atom is distorted octahedron with three coordinated sulfur atoms and three coordinated carbon atoms. The bond angle of W–S–W is 69.82°, and the W–W distance of 2.8614 Å indicates an interaction between two metal atoms.

Comparison of μ -C₆H₁₁ ligand containing-Mo(0), W(0) compounds 1 and 5 with Ph and alkyl ligands containing compounds $[Et_4N]_2[Mo_2(SPh)_2(CO)_8][10]$, $[Et_4N]_2[Mo_2$ $(SC_6H_{13})_2(CO)_8$ [15], $[Et_4N]_2[W_2(SPh)_2(CO)_8]$ [16] and $[Et_4N]_2[W_2(SEtO_2CH_3)_2(CO)_8][17]$ (Table 8). It can be found that M–C and M–S distances of the M_2S_2 (M = Mo, W) core for all those complexes are comparable. While the M–S–M angles of 1 (98.31°) and 5 (99.19°) with C_6H_{11} ligand are smaller than that of $[Et_4N]_2[Mo_2(SC_6H_{13})_2]$ $(CO)_{8}$ (99.72°), $[Et_{4}N]_{2}[W_{2}(SEtO_{2}CH_{3})_{2}$ (CO)₈] (100.3°) $[Et_4N]_2[Mo_2(SPh)_2 (CO)_8] (102.55^\circ)$ and $[Et_4N]_2[W_2(SPh)_2]$ $(CO)_8$ (103.10°). In terms of the results derived from a theoretical study [18], the electronic structure for d⁶-d⁶ complexes, $[M_2(CO)_8(\mu-SR)_2]^{2-}(M = Mo, W)$, is $\pi^{*2}\delta^{*2}\sigma^2\delta^2$ $\pi^2 \sigma^{*2}$ and the occupied π^* and σ^* levels, especially the σ^* level, rise sharply with a decrease of the M-S-M bridging angle. So the smaller M-S-M angle leads to the rise of the occupied σ^* level and thus the electrons filled in the σ^* orbital become more unstable and can be taken out easily resulting in the two-electron oxidation of the M(0)dimer to the M(I) dimer accompanied by formation of the M-M bond in order to satisfy the 18-electron configuration around each d⁵ M atom if certain conditions such as the presence of oxidant (I_2 for example) or electrolysis are provided. The fact that the M-S-M angles of compounds 1 and 5 with C_6H_{11} -ligand are smaller than that of the analogs with phenyl and other alkyl ligands implies that compounds 1 and 5 are easier to be oxidized than the analogs with Ph and other alkyl ligands. In fact, 1 and 5 are very

sensitive to air. Their color turned green from yellow quickly if exposed in air for a while. This is the reason why the compound $[Et_4N][M_2(SC_6H_{11})_3(CO)_6]$ could be obtained easily without additional oxidant, but $[Et_4N]-[M_2(SPh)_3(CO)_6]$ could not.

In Table 8, it also can be found that the W–W, W–S, W– C distances and W–S–W angles of the W_2S_2 core for W(I) compounds $[W_2(SC_6H_{11})_2(CO)_8]$, $[W_2(SPh)_2(CO)_8][19]$, $[W_2(S-t-Bu)_2(CO)_8]$ [20] and $[W_2(SMe)_2(CO)_8]$ [21] are comparable although compound **6** contains $SC_6H_{11}^-$ ligand. The Mo analog compounds have the same phenomenon. So we may come to a conclusion that introduction of C_6H_{11} group has much more influence to $M(0)-S_2-M(0)$ core than to $M(I)-S_2-M(I)$ core. Also, inspecting 2, 7 and Ph-ligand containing-compound $[Et_4N][Mo_2(SPh)_3(CO)_6]$ [19], it is found that Mo-S distance of the $Mo(I)-S_{2-}$ Mo(I) core for these three compounds are comparable, while the Mo-Mo distances and Mo-S-Mo angles of 2 and 7 are smaller than those of $[Et_4N][Mo_2(SPh)_3(CO)_6]$, this may attribute to the larger stereo hindrance of the chair-form C_6H_{11} ligand than Ph ligand.

2.3. IR spectra

IR data of compounds 1, 5, $[Et_4N]_2[Mo_2(SPh)_2(CO)_8]$, $[Et_4N]_2[W_2(SPh)_2(CO)_8]$, $[Et_4N]_2[Mo_2(SC_6H_{13})_2(CO)_8]$ and $[Et_4N]_2[W_2(SEtO_2CH_3)_2(CO)_8]$ are listed in Table 9. Obviously, only four absorptions in 1727–2073 cm⁻¹ which are assigned to v_{co} could be observed in compounds $[Et_4N]_2[Mo_2(SPh)_2(CO)_8]$ and $[Et_4N]_2[W_2(SPh)_2(CO)_8]$ and 6–8 absorptions could be found in $[Et_4N]_2[Mo_2(SC_6H_{13})_2(CO)_8]$, $[Et_4N]_2[W_2(SEtO_2CH_3)_2(CO)_8]$, compound 1 and compound 5. This shows that the character of chair-form C_6H_{11} -ligand is more similar to alkyl ligand than to Ph ligand.

2.4. Theory calculation of compounds 2 and 7

The *ab initio* study on the first hyperpolarizability of 2 (Fig. 6 shows the molecular model and its orientation)

Table 8

Selected bond distances (Å) and bond angles (°) of $[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$ (1), $[Et_4N]_2[Mo_2(SPh)_2(CO)_8]$, $[Et_4N]_2[Mo_2(SC_6H_{13})_2(CO)_8]$, $[Et_4N]_2[W_2(SPh)_2(CO)_8]$, $[Et_4N]_2[W_2(SEt_02CH_3)_2(CO)_8]$, $[W_2(SC_6H_{11})_2(CO)_8]$ (6), $[W_2(SPh)_2(CO)_8]$, $[W_2(S-t-Bu)_2(CO)_8]$, $[W_2(SMe)_2(CO)_8]$, $[Et_4N]_4M[Mo_2(SC_6H_{11})_3(CO)_6]$ (2), $[Et_4N]_4W_2(SC_6H_{11})_3(CO)_6]$ (7), $[Et_4N]_4M[Mo_2(SPh)_3(CO)_6]$

Compound	M–M	M–S	M-S-M	M–C	M-S'	M-S'-M	Ref.
$[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$ (1)	3.944	2.6063	98.31	1.985			This work
$[Et_4N]_2[Mo_2(SPh)_2(CO)_8]$	4.069	2.608	102.55	1.985			[10]
$[Et_4N]_2[Mo_2(SC_6H_{13})_2(CO)_8]$	3.979	2.6023	99.72	1.985			[15]
$[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$ (5)	3.955	2.598	99.19	1.969			This work
$[Et_4N]_2[W_2(SPh)_2(CO)_8]$	4.056	2.591	103.10	1.981			[16]
$[Et_4N]_2[W_2(SEtO_2CH_3)_2(CO)_8]$	3.962	2.580	100.33	1.985			[17]
$[W_2(SC_6H_{11})_2(CO)_8]$ (6)	2.976	2.483	73.75	2.023			This work
$[W_2(SPh)_2(CO)_8]$	2.969	2.477	73.66	2.028			[19]
$[W_2(S-t-Bu)_2(CO)_8]$	2.988	2.477	74.20	2.028			[20]
$[W_2(SMe)_2(CO)_8]$	2.970	2.473	73.79	2.014			[21]
$[Et_4N][Mo_2(SC_6H_{11})_3(CO)_6](2)$	2.856	2.469	70.81	1.974	2.610	66.78	This work
$[Et_4N][W_2(SC_6H_{11})_3(CO)_6](7)$	2.861	2.467	71.05	1.973	2.583	67.36	This work
[Et ₄ N][Mo ₂ (SPh) ₃ (CO) ₆]	2.877	2.468	71.32	1.95	2.585	67.65	[19]

Table 9

IR data for $[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$ (1), $[Et_4N]_2[Mo_2(SPh)_2(CO)_8]$, $[Et_4N]_2[Mo_2(SC_6H_{13})_2(CO)_8]$ and $[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$ (5), $[Et_4N]_2[W_2(SPh)_2(CO)_8]$, $[Et_4N]_2[W_2(SPh)_2(CO)_8]$ (5), $[Et_4N]_2[W_2(SPh)_2(CO)_8]$ (7), $[Et_4N]_2[W_2(SPh)_2(C$

Compounds	$v(co) (cm^{-1})$	Ref.
$[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$ (1)	1755, 1813, 1882, 1946, 1996, 2029, 2040, 2073	This work
$[Et_4N]_2[Mo_2(SPh)_2(CO)_8]$	1770, 1840, 1900, 2000	[10]
$[Et_4N]_2[Mo_2(SC_6H_{13})_2(CO)_8]$	1738, 1770, 1835, 1870, 1940, 1980	[15]
$[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$ (5)	1755, 1811, 1874, 1936, 1973, 1986, 2025, 2038	This work
$[Et_4N]_2[W_2(SPh)_2(CO)_8]$	1794, 1839, 1886, 1988	[16]
$[Et_4N]_2[W_2(SEtO_2CH_3)_2(CO)_8]$	1727, 1774, 1835, 1874, 1980, 2038	[17]



Fig. 6. Theoretical model and molecular orientation of complex 2.

has been carried out using the finite-field method at HF/ LANL2DZ level. The first hyperpolarizability of the anion and the molecule of compound **2** have been calculated, respectively, and the results are shown in Table 10. The β value can be expressed as

$$\begin{split} \beta_{xyz} &= -\text{Lim}_{F \to 0} \frac{\partial^3 E}{\partial F_x \partial F_y \partial F_z}, \\ \beta_i &= \frac{1}{3} \sum_j (\beta_{ijj} + \beta_{jji} + \beta_{jij}), \quad i, j = x, y, z \\ \beta_0 &= \beta_x + \beta_y + \beta_z \end{split}$$

The cation is placed in z-axes in the calculation. The spatial average value of the first-order hyperpolarizability along z direction is found quite large, $\beta_z = 13 \times 10^{-30}$ esu indicating the potential applications of this cluster for NLO processes. The theoretical analysis shows that the charge-transfer inside the [Mo₂S₃] metal core plays the crucial role in NLO response and the joint effect of metal core and organic ligands (C₆H₁₁)₃s also contribute to nonlinear

Table 10

First-order hyperpolarizability value of the compounds **2** and **7** (β , 10^{-30} esu)

Compound	β_x	β_y	β_z	β_0
$[Mo_2(SC_6H_{11})_3(CO)_6]^-$	2	3	2	4
[Et ₄ N][Mo ₂ (SC ₆ H ₁₁) ₃ (CO) ₆]	2	3	13	13
$[Et_4N][W_2(SC_6H_{11})_3(CO)_6]$	0	6	5	8

optical polarizability. In addition, the organic ion group, $[\text{Et}_4\text{N}]^+$, situated in z-direction tends to enhance the β_z value by a long way. Further study about influence of the cation on hyperpolarizability is very interesting and significant, in order to search some cations which tend to enhance the β_0 value of the molecule. From Table 10, it is found that the first-order hyperpolarizability of **2** is larger than that of **7**. The complex **2** and **7** belong to non-centrosymmetric space group and the X-ray crystallography experiments have showed favorite orientations of the constituent clusters in a unit cell. The theoretical results suggest they would be promising candidates for the second-order NLO effect in medium/far IR region.

The anions of compound **2–4** are the same, $[Mo_2 (SC_6H_{11})_3(CO)_6]^-$, the only difference is that they contain the cation: $[Et_4N]^+$, $[Ph_4P]^+$ and $[(CH_3)_3PhCH_2N]^+$, respectively. This difference leads to the three compounds to have different space group: non-centrosymmetric *Pna2*(1) and centrosymmetric *P2*(1)/*c*, respectively. As the centrosymmetric space group compound has not secondorder NLO effect, to change the compound's space group from centrosymmetric to non-centrosymmetric by introducing different cations, may be a much more significant way to compose NLO material.

3. Experimental

3.1. Materials and methods

All experimental procedures including synthetic reaction, structure determination, physical and chemical measurements were carried out under nitrogen atmosphere by using standard Schlenk technique and all solvents and reagents were dried and degassed before use. NaC₆H₁₁ was prepared by the reaction of C₆H₁₁SH with NaOCH₃ (which was obtained from the reaction of Na with CH₃OH) in CH₃OH. IR spectra were recorded on a Nicolet-Magna 750 Fourier transform IR spectrometer or Digilab FTS-20E/D-V Fourier transform IR spectrometer. Elemental analysis was performed on a CARLD ERBA instrumentation elemental analyzer MOD 1106.

3.2. Synthesis of $[Et_4N]_2[Mo_2(SC_6H_{11})_2(CO)_8]$ (1)

To the solid mixture of $Mo(CO)_6$ (2.64 g, 10 mmol), Et₄NCl (1.655 g, 10 mmol) and NaSC₆H₁₁ (1.38 g, 10 mmol) was added 50 ml MeCN. The reaction mixture was stirred at 50°C for 24 h resulting in orange-yellow solution with small amount of white residue in it, accompanied by vigorous CO evolution. After filtration and concentration, 20 ml of isopropanol was added and then the resulting solution was concentrated at room temperature until a great deal of yellow crystalline product came out. After filtering, washed with acetonitrile–isopropanol and isopropanol in turn and dried in vacuum, 2.25 g of 1 was obtained (yield 49.6% based on the Mo(CO)₆ used). Anal. Calc. for C₃₆H₆₂N₂O₈S₂ Mo₂, C, 47.63; H, 6.84; N, 3.09; S, 7.06. Found: C, 47.20; H, 6.96; N, 3.52; S, 6.52%; IR (KBr pellet): 1755(s), 1813(s), 1882(s), 1946(s), 1996(s), 2029(m), 2040(m), 2073(w) cm⁻¹ (ν_{co}).

3.3. Synthesis of $[Et_4N][Mo_2(SC_6H_{11})_3(CO)_6]$ (2)

- (a) To the solid mixture of $Mo_2(SC_6H_{11})_2(CO)_8$ [11] $(0.634 \text{ g}, 1 \text{ mmol}), \text{ Et}_4 \text{NCl} (0.166 \text{ g}, 1 \text{ mmol}) \text{ and}$ NaSC₆H₁₁ (0.138 g, 1 mmol) was added 20 ml acetone. The green solution immediately turned brown, accompanied with vigorous CO evolution. The reaction mixture was stirred at 50 °C overnight, yielding a brown solution, which was evaporated under vacuum to 5 ml. Isopropanol (10 ml) was added forming lots of dark precipitate. After filtering, washed with acetonitrile and dried under vacuum, 0.412 g of 2 was obtained (yield 49.3% based on the $Mo_2(SC_6)$ $H_{11}_{2}(CO)_8$ used). Anal. Calc. for $C_{32}H_{53}NO_6S_3Mo_2$, C, 45.94, H, 6.34, N, 1.68. Found: C, 46.00, H, 6.35, N, 1.68%. IR (KBr pellet): 1809(s), 1828(s), 1907(s), 1923(s), 1936(s), 1990(m) cm⁻¹ (v_{co}). The filtrate was allowed to stand at 4 °C for several days to obtain crystals for X-ray single-crystal diffraction analysis.
- (b) To the solid mixture of $Mo_2(SC_6H_{11})_2(CO)_6(CH_3)$ CN)₂[12] (0.323 g, 0.5 mmol), Et₄NCl (0.083 g, 0.5 mmol) and NaSC₆H₁₁ (0.069 g, 0.5 mmol) was added 20 ml acetone resulting in grass green solution which immediately turned brown. The reaction mixture was stirred at 50 °C overnight, yielding a brown solution which was evaporated under vacuum to 5 ml. 8 ml of isopropanol was added forming dark precipitate. After filtering the filtrate was allowed to stand at 4 °C for several days to obtain crystals for X-ray single-crystal diffraction analysis. The resulting dark precipitate was washed with acetonitrile and dried under vacuum to yield 0.121 g of pure product, which had been recognized as compound 2 by IR, elemental analysis and X-ray crystallography (28.9% yield based on the $Mo_2(SC_6H_{11})_2(CO)_6(CH_3CN)_2$ used).
- (c) To the solid mixture of $Mo(CO)_6$ (1.32 g, 5 mmol), Et₄NCl (0.83 g, 5 mmol) and NaSC₆H₁₁ (0.69 g, 5 mmol) was added 30ml MeCN. The reaction mixture was stirred at 85 °C for 10 min, the solution turned to straw yellow, and then about 30 min later turned to saffron, accompanied with a lot of CO

evolution. After stirring for 24 h, the resulting brown solution was evaporated under vacuum to 5 ml. Isopropanol (10 ml) was added and the resulting solution was filtered and the filtrate allowed to stand at $4 \,^{\circ}$ C for several weeks crystalline products were obtained. Verified by IR and X-ray crystallography, the product is compound **2**.

- (d) A solution of compound 1 in MeCN was placed in refrigerator (at 4 °C). Some yellow crystals formed in 2 weeks later and the yellow crystals turned to dark crystals in about 3 months. The dark crystals were verified to be the compound 2 by IR measurement and X-ray crystallography.
- (e) To a solution of compound 1 (0.0907 g, 0.1 mmol) in MeCN was injected 5.5 ml air, then the solution was stood at 4 °C for several weeks and crystalline products were obtained. Verified by IR and X-ray crystallography, the crystalline product is compound 2.

3.4. Synthesis of $[Ph_4P][Mo_2(SC_6H_{11})_3(CO)_6]$ (3)

To the solid mixture of $Mo_2(SC_6H_{11})_2(CO)_8$ (0.178 g, 0.28 mmol), Ph₄PBr (0.118 g, 0.28 mmol) and CH₃CH₂-CH₂COONa (0.031 g, 0.28 mmol) was added 20 ml acetone resulting in green solution which immediately turned brown, accompanied with vigorous CO evolution. The reaction mixture was stirred at 50 °C overnight yielding a brown solution, which was evaporated under vacuum to 5 ml. Isopropanol (8 ml) was added forming dark precipitate. 0.044 g of pure dark product 3 (yield 15.0% based on the $Mo_2(SC_6H_{11})_2(CO)_8$ used) was obtained after filtering, washed with MeCN and dry in vacuum. Anal. Calc. for C₄₈H₅₃PO₆S₃Mo₂, C, 54.29, H, 5.08. Found: C, 54.70, H, 5.15%. IR (KBr pellet): 1836(m), 1915(m), 1938(m) cm⁻¹ (v_{co}). The mother liquid was stood at 4 °C for several weeks to obtain single crystals suitable for X-ray crystallography.

3.5. Synthesis of $[(CH_3)_3PhCH_2N][Mo_2(SC_6H_{11})_3-(CO)_6]$ (4)

A solid mixture of $Mo(CO)_6$ (1.32 g, 5 mmol), $(CH_3)_3PhCH_2NBr$ (1.15 g, 5 mmol) and $NaSC_6H_{11}$ (0.69 g, 5 mmol) in 20 ml MeCN was stirred at 50 °C for 24 h resulting in orange-yellow solution with small amount of white residue in it, accompanied with vigorous CO evolution. After filtration and concentration 10 ml of isopropanol was added and then the resulting solution was put in refrigerator (4 °C), 2 weeks later, getting some yellow crystals, about 3 months later, the yellow crystals turned to dark crystals. The dark crystals were collected and recognized as compound 4 by IR, elemental analysis and X-ray crystallography. Anal. Calc. for $C_{34}H_{49}NO_6S_3Mo_2$, C, 47.67, H, 5.73, N, 1.64. Found: C, 47.82, H, 5.78, N, 1.58%. IR (KBr pellet): 1828(m), 1915(m), 1936(m) cm⁻¹ (v_{co}).

3.6. Synthesis of $[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$ (5)

A solid mixture of $W(CO)_6$ (3.52 g, 10 mmol), Et₄NCl (1.65 g, 10 mmol) and $\text{NaSC}_6\text{H}_{11}(1.38 \text{ g}, 10 \text{ mmol})$ in 50 ml MeCN was stirred at 85 °C for 24 h resulting in orange-yellow solution with small amount of white residue in it, accompanied with vigorous CO evolution. After cooling to room temperature and filtering off the residue, the filtrate was concentrated to 10 ml, then 15 ml of siopropanol was added forming a great deal of yellow microcrystalline product, 2.26 g of yellow microcrystalline 5 was obtained. After filtering, washed with acetonitrile-isopropanol and isopropanol in turn and dried in vacuum (vield 42% based on the W(CO)₆ used). Anal. Calc. for $C_{36}H_{62}N_2O_8S_2$ W₂, C, 39.93; H, 5.73; N, 2.59; S, 5.92. Found: C, 39.53; H, 5.81; N, 2.51; S, 5.82%; IR (KBr pellet): 1755(s), 1811(s), 1874(s), 1936(s), 1973(m), 1986(s), 2025(m), 2038(m) cm⁻ (v_{co}) . The orange-yellow filtrate was concentrated slightly and then cooled at 4 °C for several days yellow crystals of 5 suitable for X-ray crystallography were obtained.

3.7. Synthesis of $[W_2(SC_6H_{11})_2(CO)_8]$ (6)

A solid mixture of $[Et_4N]_2[W_2(SC_6H_{11})_2(CO)_8]$ (2.71 g, 2.5 mmol) and $I_2(0.64$ g, 2.5 mmol) in 30 ml toluene was stirred at room temperature under CO for 5 h resulting in a dark green solution with white solid in it. After filtering, the dark green filtrate was concentrated and cooled at 4 °C for several days, 1.64 g of dark green crystalline product **6** was collected (yield 80.0% based on the $[Et_4N]_2[W_2$ $(SC_6H_{11})_2(CO)_8]$ used). Anal. Calc. for $C_{30}H_{33}O_9S_3W_3$,

Table 11

Crystal data and collection and refinement details for $1\cdot 2\text{CH}_3\text{CN}_2,\,2\text{--}7$

C, 29.20; H, 2.68; S, 7.79. Found: C, 28.88; H, 2.73; S, 7.81%. IR (KBr pellet): 1932(s), 1982(s), 2027(s) cm⁻¹ (v_{co}).

3.8. Synthesis of $[Et_4N][W_2(SC_6H_{11})_3(CO)_6]$ (7)

- (a) A solid mixture of $W_2(SC_6H_{11})_2(CO)_8$ (0.411 g, 5 mmol), Et₄NCl (0.083 g, 5 mmol) and NaSC₆H₁₁ (0.069 g, 5 mmol) in 20 ml acetone was stirred at 85 °C overnight, resulting in brown solution. The reaction solution was evaporated under vacuum to 5 ml. 10 ml of isopropanol was added forming some dark precipitate, 0.15 g of pure product 7 was obtained after filtering, washed with acetonitrile and dried under vacuum (yield 30.0% based on the $W_2(SC_6H_{11})_2(CO)_8$ used). Anal. Calc. for $C_{32}H_{53}$ NO₆S₃W₂, C, 36.4; H, 5.02; N, 1.38. Found: C, 36.8; H, 5.05; N, 1.42%. IR (KBr pellet): 1801(s), 1822(s), 1924(s) cm⁻¹ (v_{co}). The mother liquid was allowed to stand at 4 °C for several days to obtain crystals for X-ray single-crystal diffraction analysis.
- (b) A solution of compound 5 in acetone was placed in refrigerator (4 °C), 2 weeks later, some yellow crystals came out and about 2 months later, the yellow crystals turned to dark crystals, which were verified to be compound 7 by IR and X-ray crystallography.

3.9. X-ray crystallography

The single crystal samples were mounted on the glass fiber and coated with epoxy cement. The samples of 1, 2, 5 and 6were mounted on Siemens Smart CCD diffractometer

Compounds	$1\cdot 2\text{CH}_3\text{CN}_2$	2	3	4	5	6	7
Empirical formula	$C_{40}H_{68}Mo_2N_4O_8S_2\\$	$C_{34}H_{53}Mo_2NO_6S_3$	$C_{48}H_{53}Mo_2O_6PS_3$	$C_{34}H_{49}NO_6S_3Mo_2$	$C_{36}H_{62}N_2O_8S_2W_2\\$	$C_{20}H_{22}O_6S_2W_2$	$C_{32}H_{53}NO_6S_3W_2$
Formula weight	988.98	835.81	1044.93	855.80	1082.70	822.20	1011.63
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P2(1)/n	Pna2(1)	P2(1)/c	P2(1)/c	C2c	P2(1)/c	Pna2(1)
Unit cell dimensions							
a (Å)	14.4322(11)	20.5805(10)	10.725(4)	12.1427(10)	15.5168(1)	18.1140(8)	20.570(2)
b (Å)	10.2536(7)	9.3127(5)	26.550(10)	14.1618(10)	16.5943(3)	9.4416(4)	9.280(1)
c (Å)	17.1182(13)	20.2955(10)	17.808(7)	23.414(2)	17.0890(3)	21.4963(10)	20.240(4)
$\beta(^{\circ})$	100.7310(10)	90	103.768(4)	99.752(4)	101.6290(10)	90.0950(10)	90
Volume (Å3)	2488.9(3)	3889.8(3)	4925(3)	3968.1(5)	4309.93(11)	3674.0(3)	3863.6(10)
Ζ	2	4	4	4	4	6	4
Density (Mg m ⁻¹)	1.320	1.427	1.409	1.433	1.669	2.230	1.739
<i>F</i> (000)	1032	1728	2144	1760	2144	2316	1984
Crystal size (mm)	$1.00 \times 0.40 \times 0.24$	$0.40 \times 0.15 \times 0.20$	$0.50\times0.30\times0.15$	$0.40\times0.20\ \times0.20$	$0.80\times0.60\times0.52$	$0.62 \times 0.58 \ \times 0.20$	$0.44 \times 0.40 \times 0.32$
θ Range for data collection (°)	2.04-25.07	1.98-25.09	2.48-27.48	3.10-25.03	1.82-25.07	1.12-25.06	2.41-27.48
Reflections collected	7890	12476	36803	24915	6764	12433	28619
Independent reflections	4381	6570	11126	7007	3811	6462	8712
	$(R_{\rm int} = 0.0319)$	$(R_{\rm int} = 0.0545)$	$(R_{\rm int} = 0.0335)$	$(R_{\rm int} = 0.0443)$	$(R_{\rm int} = 0.0423)$	$(R_{\rm int} = 0.0694)$	$(R_{\rm int} = 0.1112)$
Data/restraints/ parameters	4381/0/254	6570/1/397	11,266/0/541	7007/0/415	3811/0/266	6462/0/433	8712/1/397
Goodness-of-fit on F^2	1.072	1.042	1.065	1.075	1.003	1.052	1.002
Final R indices	R = 0.0688,	R = 0.0469,	R = 0.0699,	R = 0.1042,	R = 0.0541,	R = 0.0639,	R = 0.0603,
$(I \ge 2\sigma(I))$	Rw = 0.1739	Rw = 0.0665	Rw = 0.1726	Rw = 0.2808	Rw = 0.1180	Rw = 0.1591	Rw = 0.1165
Largest difference	0.906 and	0.488 and	2.000 and	1.698 and	1.836 and	2.250 and	1.795 and
in peak and hole $(e \text{ Å}^{-3})$	-0.601	- 0.367	-1.077	-2.567	-1.878	- 2.586	-1.739

equipped with a graphite monochromator (Mo K α radiation $\lambda = 0.71073$ Å) at 293 K for data collection. The samples of **3**, **4** and **7** were mounted on Rigaku Mercury CCD diffractometer equipped with a graphite monochromator (Mo K α radiation $\lambda = 0.71073$ Å) at 293 K for data collection. The data were corrected for absorption using semi-empirical scan data. The structures were solved by direct methods and refined by full-matrix least-squares method. All non-hydrogen atoms were refined an isotropically, and hydrogen atoms were refined as riding model with fixed isotropic U. All calculations were carried out with the Siemens SHELXTL PLUS package [22] and Rigaku/MSC CRYSTAL CLEAR package [23], respectively. Crystallographic data for clusters 1–7 are summarized in Table 11.

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Appendix A. Supplementary material

CCDC 232061, 232060, 243545, 621665, 243543, 243540 and 621666 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5**, **6** and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam. ac.uk.

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