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Notes

Syntheses and Characterizations of the Novel Dodecanuclear Heterobimetallic Cage Clusters: $[Et_4N]_2[(M_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (M = Mo, W; edt = $^-SC_2H_4S^-$)

Ping Lin, Xintao Wu,* Qun Huang, Quanming Wang, Tianlu Sheng, Wenjian Zhang, Jun Guo, and Jiaxi Lu

State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of Matter,
The Chinese Academy of Sciences, Fuzhou, Fujian 350002,
People's Republic of China

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Introduction

Heterometallic cluster compounds containing $[MS_4]^{2-}/Cu^+$ (M = Mo, W) have been extensively studied.[1] Apart from the possible relevance to the Mo−Cu biological antagonism,[1a] some complexes also show potential applications as materials with nonlinear physical properties.[2] At present, some polynuclear $M^{VI}/Cu^I/S$ (M = Mo, W) cluster compounds such as $[Cu_6S_6W_2(SCMe_3)_2(O)_2(PPh_3)]$ (double cubane-like),[3] $[Et_4N]_2[M_4Cu_4S_{12}O_4]$, $[M_4Cu_4S_{12}O_4(CuTMEN)_4]$ (TMEN = *N,N,N′,N′*-tetramethylethylenediamine),[4] and $[Et_4N]_4[Cu_{12}M_8S_{28}O_4]\cdot DMF$ (M = Mo, W),[5] have been characterized. A few $M^V/Cu^I/S$ complexes such as $[M_2Cu_2S_4edt_2(PPh_3)_2]$ (cubane-like),[6] $[Cu_2S_4W_2(SCN)_8]^{4-}$ (cubane-like),[7] and $[M_2CuS_4edt_2(PPh_3)]^-$ (incomplete cubane-like)[8] have been reported. A single example of dodecanuclear cluster containing (μ_6−S), $[Et_4N]_2[Mo_6Cu_6S_6(\mu_6\text{−}S)O_6(S_2)_6]$, has been obtained by our group.[9]

Herein, we report the syntheses and characterizations of the novel dodecanuclear clusters $[Et_4N]_2[(M_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (M = Mo, W; edt = $^-SC_2H_4S^-$), which are the new molybdenum(V) (or tungsten(V))−copper(I) clusters containing a μ_6−S_2 ligand.

Table 1. Crystallographic Data and Refinement Details for the Structures of **1** and **2**

	1	**2**
empirical formula	$N_2C_{29}H_{66}O_6Cl_2S_{20}Cu_6Mo_6$	$N_2C_{29}H_{66}O_6Cl_2S_{20}Cu_6W_6$
mol wt	2207.87	2735.23
a, Å	13.2861(1)	13.20(8)
c, Å	38.1583(2)	38.04(3)
V, Å^3	6735.72(8)	6635(3)
space group	$P4_12_12$ (No.92)	$P4_32_12$ (No.96)
Z	4	4
diffractometer	Siemens smart CCD	Rigaku AFC5R
T, K	293	296
λ (Mo Kα), Å	0.710 73	0.710 73
crystal dimens, mm	0.2 × 0.2 × 0.1	0.4 × 0.4 × 0.25
μ(Mo Kα), cm^{-1}	36.254	131.9
d_{calcd}, g/cm^3	2.177	2.74
no. of unique data	4829	3464
no. of obs data	4066 ($I > 2((I)$)	2041 ($I > 3((I)$)
no. of variables refined	218	238
R^a	0.0594	0.056
R_w	0.1386[b]	0.059[c]
GOF	1.190	1.12
max shift in final cycle	0.001	0.01

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$ for **1** and **2**. [b] $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 46.0727P]$, where $P = (F_o^2 + 2F_c^2)/3$ for cluster **1**. [c] $R_w = \{\sum[w(F_o - F_c)^2]/\sum[wF_o^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.010F_o)^2 + 1.000]$ for cluster **2**.

Experimental Section

All experiments were carried out in air. $[Et_4N]_2[Mo_2O_2S_2edt_2]$ was prepared according to ref 10, and $[Et_4N]_2[W_2S_4edt_2]$ was obtained by published procedures.[11] Other chemicals were purchased. Infrared spectra were recorded on a Magna 750 spectrometer using KBr pellets. Electronic spectra were obtained on a Shimadzu UV-3000 spectrophotometer in DMF solution between 600 and 200 nm. Elemental analyses were performed by the Elemental Analysis Laboratory in our Institute.

Preparation of $[Et_4N]_2[(Mo_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (1). To a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.242 g, 1 mmol in 30 mL of CH_3CN and 30 mL of CH_2Cl_2) was added $NaBH_4$(0.038 g, 1 mmol) with stirring. After 30 min, $[Et_4N]_2[Mo_2O_2S_2edt_2]$ (0.356 g, 0.5 mmol) was added to the suspension, the mixture was stirred for a while, and then 2 drops of $(NH_4)_2S_x$ solution (10% S^{2-} + 6% S) were added. The reaction mixture was stirred for another 10 min, and then the black precipitate was removed by filtration. The dark red filtrate was allowed to stand at ambient temperature in the air for 1 day, and the resulting brown precipitate was removed by filtration. After another 7 days, 0.08 g of black crystals was obtained. Yield: 21.7%. Anal. Calcd (found): C, 15.78 (16.03); H, 3.01 (2.96); N, 1.27 (1.36). IR (KBr pellet, cm^{-1}): Mo−(μ_3-S), 430.1 (m); S−S, 530.3 (m); Mo−O, 952.7 (vs). UV (DMF solution, λ, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 275 (1.54 × 10^4).

Preparation of $[Et_4N]_2[(W_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (2). To a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.242 g, 1 mmol in 20 mL of CH_3CN and 30 mL of CH_2Cl_2) was added $NaBH_4$ (0.038 g, 1 mmol). After

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(10) Preparation of $[Et_4N]_2[Mo_2O_2S_2edt_2]$. H_2S gas was bubbled into a 20 mL aqueous solution of Na_2MoO_4 (4.84 g, 20 mmol); 3 min later, the solution turned to red, the solution was then heated to 85 °C, and $Na_2S_2O_4$ (0.469 g, 3.3 mmol) and $H_6S_2C_2$ (3.2 mL, 20 mmol) were added. After being stirred for 2 h, 4.2 g of $[Et_4N]Br$ (20 mmol) was added to the solution, the solution was cooled in the air, and a lot of red precipitate appeared. The precipitate was collected and washed by C_2H_5OH and Et_2O three times, and 6.5 g of $[Et_4N]_2[Mo_2O_2S_2edt_2]$ was obtained. Yield 91.3%. Anal.: C, 32.80; H, 6.7; N, 3.81.

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10.1021/ic9704142 CCC: \$15.00

Table 2. Atomic Coordinates for $[(Mo_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]^{2-}$ (**1**)

atom	x	y	z	U_{eq} (Å^2)[a]
Mo1	0.18304(10)	−0.03575(10)	0.26106(4)	0.0396(4)
Mo2	−0.12656(11)	0.22727(11)	0.15295(4)	0.0412(4)
Mo3	−0.05933(11)	0.37224(10)	0.20419(4)	0.0408(4)
Cu1	0.0158(2)	0.0478(2)	0.30987(5)	0.0472(6)
Cu2	0.07845(15)	0.2032(2)	0.23366(5)	0.0456(5)
Cu3	−0.1488(2)	0.26760(15)	0.28860(5)	0.0462(5)
S	−0.0508(3)	0.1422(3)	0.26629(10)	0.0345(8)
S1	0.1192(3)	−0.0621(3)	0.20426(10)	0.0432(10)
S2	0.2320(3)	0.1232(3)	0.23438(11)	0.0456(10)
S3	0.1917(3)	0.0660(3)	0.31461(11)	0.0464(10)
S4	0.0924(3)	0.3789(3)	0.24136(12)	0.0501(11)
S5	−0.2841(3)	0.1312(3)	0.15002(11)	0.0483(11)
S6	−0.0549(3)	0.0649(3)	0.13666(11)	0.0491(11)
S7	−0.2243(3)	0.3146(3)	0.19461(11)	0.0441(10)
S8	−0.1395(3)	0.4201(3)	0.25937(12)	0.0502(11)
S9	0.0376(3)	0.2482(3)	0.17544(11)	0.0456(10)
O1	0.2953(8)	−0.1069(8)	0.2615(3)	0.052(3)
O2	−0.1246(9)	0.2936(9)	0.1138(3)	0.055(3)
O3	−0.0523(9)	0.4882(9)	0.1792(3)	0.059(3)
C1	0.3046(13)	0.1861(13)	0.2699(5)	0.053(5)
C2	−0.0403(16)	0.4862(15)	0.2843(5)	0.069(6)
C3	0.0548(14)	0.4241(14)	0.2840(5)	0.059(5)
C4	−0.1608(14)	0.0007(14)	0.1129(5)	0.061(5)
C5	−0.2504(14)	0.0026(14)	0.1352(5)	0.060(5)
C6	0.2407(14)	0.1919(15)	0.3031(5)	0.059(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized tensor $\mathbf{U}_{ij}$.

being stirred for 30 min, suspension i was produced. Four drops of H_2O_2 water solution (containing 30% H_2O_2) were added to a solution of $[Et_4N]_2[W_2S_4edt_2]$ (0.470 g, 0.5 mmol in 20 mL of CH_3CN and 20 mL of CH_2Cl_2), and stirring for 1 h produced solution ii. This solution was added to suspension i, and the mixture was stirred for 0.5 min before 2 drops of $(NH_4)_2S_x$ solution (10% S^{2-} + 6% S) were added. The reaction mixture was stirred for another 20 min, and the brown precipitate was removed by filtration. The orange filtrate was allowed to stand at ambient temperature in the air for 1 day. The resulting brown precipitate was removed by filtration. After another 7 days, 0.10 g of red crystals was obtained. Yield: 21.9%. Anal. Calcd (found): C, 12.73 (13.18); H, 2.43 (2.30); N, 1.02 (1.06). IR (KBr pellet, cm^{-1}): W−(μ_3-S), 416.6 (m); S−S, 520.7 (m); W−(O, 966.2 (vs). UV (DMF solution; ϵ, nm (λ, dm^3 mol^{-1} cm^{-1})): 278 (3.5×10^4).

Crystal Structure Determination. Crystals of **1** and **2** were selected and mounted on glass fibers for single-crystal X-ray diffraction. The crystallographic data were given in Table 1. Diffraction data were collected on a Siemens smart CCD three-circle area diffractometer for **1** and on a Rigaku AFC5R four-circle diffractometer for **2** by Mo Kα radiation.

The structures were solved by direct methods using SHELXS[12a] for **1** and MolEN[12b] for **2**, and the positions of heavy atoms were obtained from E maps. The structure of compound **1** was refined on F^2 using SHELXTL-93, and the structure of compound **2** was refined on F using MolEN. The remaining non-hydrogen atoms were located from difference Fourier maps. No attempt was made to locate hydrogen atoms for each structure determination. Absolute structures of clusters **1** and **2** have been determined (absolute structure parameter for **1** is 0.02; the data of enantiomer for **2**: $R = 0.061$, $R_w = 0.066$). Atomic scattering factors were taken from ref 13. Coordinates of cluster atoms for **1** and **2** are listed in Tables 2 and 3.

Results and Discussion

Table 3. Atomic Coordinates for $[(W_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]^{2-}$ (**2**)

atom	x	y	z	B_{eq} (Å^2)[a]
W1	−0.1805(1)	−0.0335(1)	0.01120(4)	2.27(3)
W2	0.3739(1)	0.0596(1)	0.04476(4)	2.54(3)
W3	0.2302(1)	0.1268(1)	0.09654(4)	2.47(3)
Cu1	−0.0110(4)	0.0512(4)	0.0596(1)	3.9(1)
Cu2	0.1509(4)	0.2690(4)	0.0380(1)	4.0(1)
Cu3	−0.0777(4)	0.1995(4)	−0.0155(1)	3.7(1)
S	0.0541(8)	0.1438(8)	0.0160(3)	3.4(2)
S1	−0.0591(8)	−0.1182(8)	0.0458(2)	3.1(2)
S2	−0.2327(8)	0.1260(9)	−0.0155(3)	3.1(2)
S3	−0.1890(9)	0.0673(9)	0.0647(3)	3.8(3)
S4	0.1349(9)	0.2850(8)	0.1004(3)	3.6(2)
S5	0.3787(9)	−0.0924(9)	0.0077(3)	3.8(3)
S6	0.4241(8)	0.1396(9)	−0.0098(3)	3.6(2)
S7	0.2506(8)	−0.0388(8)	0.0743(3)	3.1(2)
S8	0.0680(8)	0.0578(9)	0.1139(2)	3.1(2)
S9	0.3183(8)	0.2268(8)	0.0558(3)	3.1(2)
O1	−0.286(2)	−0.101(2)	0.0116(6)	3.2(6)
O2	0.480(2)	0.051(2)	0.0698(8)	4.9(7)
O3	0.300(2)	0.123(2)	0.1352(6)	3.5(6)
C1	−0.309(3)	0.187(3)	0.0204(9)	3.0(8)
C2	0.000(3)	0.163(3)	0.137(1)	3.6(9)
C3	0.006(3)	0.260(4)	0.116(1)	4.52(7)
C4	0.487(3)	0.044(3)	−0.035(1)	4(1)
C5	0.430(3)	−0.054(4)	−0.035(1)	4.62(6)
C6	−0.248(3)	0.196(3)	0.0542(9)	3.1(8)

[a] $B_{eq} = (^4/_3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

Table 4. Selected Bond Distances (Å) of $[Et_4N]_2[(Mo_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (**1**)[a]

atom	atom	distance	atom	atom	distance
Mo1	O1	1.765(11)	Cu1	S6a	2.306(5)
Mo1	S1	2.354(4)	Cu1	S3	2.358(5)
Mo1	S1a	2.358(4)	Cu1	S1a	2.365(5)
Mo1	S2	2.433(5)	Cu2	S	2.271(4)
Mo1	S3	2.453(4)	Cu2	S2	2.300(5)
Mo1	Mo1a	2.893(3)	Cu2	S4	2.361(5)
Mo2	O2	1.735(12)	Cu2	S9	2.364(5)
Mo2	S7	2.358(5)	Cu3	S	2.279(4)
Mo2	S9	2.360(5)	Cu3	S8	2.316(5)
Mo2	S6	2.439(5)	Cu3	S5a	2.364(5)
Mo2	S5	2.454(5)	Cu3	S7a	2.366(5)
Mo2	Mo3	2.886(2)	Cu3	Mo2a	3.094(2)
Mo3	O3	1.813(12)	S	Sa	2.119(7)
Mo3	S7	2.350(5)	S1	Mo1a	2.358(4)
Mo3	S9	2.362(5)	S1	Cu1a	2.365(5)
Mo3	S8	2.444(5)	S5	Cu3a	2.364(5)
Mo3	S4	2.467(5)	S6	Cu1a	2.306(5)
Cu1	S	2.263(4)	S7	Cu3a	2.366(5)

[a] a: $(-y, -x, {}^1/_2 - z)$.

Syntheses of Clusters 1 and 2. $(NH_4)_2S_x$ together with $[Et_4N]_2[Mo_2O_2S_2edt_2]$ and $[Et_4N]_2[W_2S_4edt_2]$ were used as starting materials for syntheses of **1** and **2** with the $[W_2S_4edt_2]^{2-}$ anion being oxidized by H_2O_2 to produce $[W_2O_2S_2edt_2]^{2-}$. Cu^+ cations were introduced through the reduction of $Cu(NO_3)_2\cdot 3H_2O$ by $NaBH_4$. After a while, $(NH_4)_2S_x$ was added. Anions **1** and **2** are possibly derived from an initially formed $[Mo_2O_2S_2edt_2]^{2-}/2Cu^+$ (M = Mo, W) fragment; three $[Mo_2O_2S_2edt_2]^{2-}/2Cu^+$ fragments were then assembled by an S_2^{2-} ion to form a cage with the S_2 group at the center. The S_2^{2-} coordinated to six Cu atoms using two S atoms to form a μ_6-S_2. The two cluster compounds are stable in the air, insoluble in CH_3CN or CH_2Cl_2, but soluble in DMF.

Structure of the cluster $[Et_4N]_2[(Mo_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (1). Cluster **1** is isomorphous with the corresponding tungsten cluster **2** and only the structure of **1** is thus

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Table 5. Selected Bond Angles (deg) for $[Et_4N]_2[(Mo_2Cu_2S_2O_2edt_2)_3(\mu_6\text{-}S_2)]\cdot CH_2Cl_2$ (**1**)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O1	Mo1	S1	103.5(4)	S3	Cu1	S1a	81.7(2)
O1	Mo1	S1a	108.6(4)	S	Cu2	S2	120.0(2)
S1	Mo1	S1a	101.61(14)	S	Cu2	S4	110.1(2)
O1	Mo1	S2	104.1(4)	S2	Cu2	S4	112.7(2)
S1	Mo1	S2	80.8(2)	S	Cu2	S9	115.6(2)
S1a	Mo1	S2	145.6(2)	S2	Cu2	S9	109.4(2)
O1	Mo1	S3	104.3(4)	S4	Cu2	S9	83.4(2)
S1	Mo1	S3	150.0(2)	S	Cu3	S8	115.4(2)
S1a	Mo1	S3	79.84(15)	S	Cu3	S5a	112.4(2)
S2	Mo1	S3	81.8(2)	S8	Cu3	S5a	113.0(2)
O2	Mo2	S7	109.8(4)	S	Cu3	S7a	117.1(2)
O2	Mo2	S9	103.8(4)	S8	Cu3	S7a	113.1(2)
S7	Mo2	S9	101.9(2)	S5a	Cu3	S7a	81.2(2)
O2	Mo2	S6	102.9(4)	Sa	S	Cu1	109.7(2)
S7	Mo2	S6	145.3(2)	Sa	S	Cu2	108.4(2)
S9	Mo2	S6	80.6(2)	Cu1	S	Cu2	107.8(2)
O2	Mo2	S5	103.8(4)	Sa	S	Cu3	108.12(12)
S7	Mo2	S5	79.5(2)	Cu1	S	Cu3	110.7(2)
S9	Mo2	S5	150.0(2)	Cu2	S	Cu3	112.1(2)
S6	Mo2	S5	82.0(2)	Mo1	S1	Mo1a	75.77(13)
O3	Mo3	S7	104.1(4)	Mo1	S1	Cu1a	120.6(2)
O3	Mo3	S9	108.7(4)	Mo1a	S1	Cu1a	82.21(14)
S7	Mo3	S9	102.1(2)	Cu2	S2	Mo1	99.7(2)
O3	Mo3	S8	104.7(4)	Cu1	S3	Mo1	80.37(14)
S7	Mo3	S8	79.2(2)	Cu2	S4	Mo3	80.12(14)
S9	Mo3	S8	145.0(2)	Cu3a	S5	Mo2	79.88(14)
O3	Mo3	S4	103.3(4)	Cu1a	S6	Mo2	101.6(2)
S7	Mo3	S4	149.7(2)	Mo3	S7	Mo2	75.62(14)
S9	Mo3	S4	81.2(2)	Mo3	S7	Cu3a	119.2(2)
S8	Mo3	S4	81.5(2)	Mo2	S7	Cu3a	81.84(14)
S	Cu1	S6a	116.5(2)	Cu3	S8	Mo3	102.1(2)
S	Cu1	S3	112.8(2)	Mo2	S9	Mo3	75.36(14)
S6a	Cu1	S3	112.9(2)	Mo2	S9	Cu2	121.6(2)
S	Cu1	S1a	117.0(2)	Mo3	S9	Cu2	82.25(14)
S6a	Cu1	S1a	111.2(2)				

[a] a: $(-y, -x, {}^{1}/_{2} - z)$.

described. Selected bond distances and angles of **1** are collectedin Tables 4 and 5, and the ORTEP drawing of the anion is shown in Figure 1. From the configuration of the twelve metal atoms and all the S atoms, the anion can be described as a cage with an S_2^{2-} at the center. The cage has two puckered $Cu_3S_6C_6$ 15-membered rings, and each is composed of three Cu atoms combining three $^{-}SC_2H_4S^{-}$ units. The anion has a pseudo-3-fold axis exactly along the S−Sa bond and approximately perpendicular to the two 15-membered rings.

Each Mo atom displays tetragonal-pyramid (TPY) coordination geometry, with two S atoms of $^{-}SC_2H_4S^{-}$ (S_{edt}), two S atoms of binuclear molybdenum (S_{br}), and one terminal oxygen atom. The oxygen atom occupies the axial position of each TPY and the four remaining sulfido atoms are equatorial. The Mo atom is chelated by one $^{-}SC_2H_4S^{-}$ forming a five-membered ring. The average Mo−Mo bond distance is 2.888(2) Å, which is slightly longer than the reported Mo−Mo distance of $[Et_4N]_2[Mo_2S_4edt_2]$ (2.863 Å).[14] Each Cu atom is coordinated by four S atoms to give a distorted tetrahedral geometry [81.1(2)−120.0(2)•]. The S_2^{2-} ion assembled in the center of the cage with Cu−S bonds having approximate sp^3 geometry. Each S atom of the S_2^{2-} was bound with three Cu atoms, respectively. The average Cu−(μ_6−S_2) bond distance is 2.271(4) Å, which is within the reported range of Cu−S bond distances (2.2−2.4 Å). To our knowledge, this type of cluster containing μ_6−S_2 ligand is the first example of molybdenum−copper (or tungsten−copper) clusters.

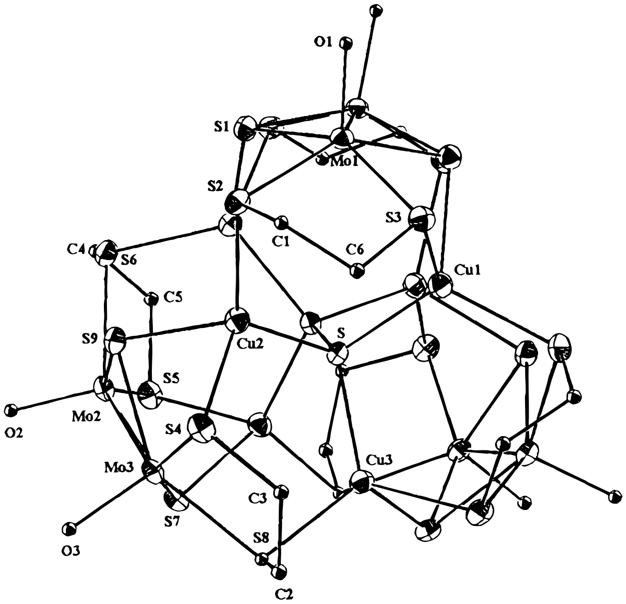

Figure 1. ORTEP drawing of the anion **1** (thermal ellipsoids at 20% probability level).

Comparing compound **1** with $[Mo_6Cu_6S_6(\mu_6\text{-}S)O_6(S_2)_6]^{2-}$,[9] the two compounds also are the cages containing six Mo atoms and six Cu atoms. However, there is an S^{2-} ion at the center of the latter cage and bond to six Cu atoms. The latter cage has two puckered Cu_3S_6 nine-membered rings, and the Mo atom is coordinated by an η^2-S_2 ligand.

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