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Heterobimetallic Clusters of Copper(I) with Trithiotungstate and Trithiomolybdate. Synthesis and Characterization of the Octanuclear Clusters $[Et_4N]_4[M_4Cu_4S_{12}O_4]$ (M = Mo, W) and the Dodecanuclear Clusters $[M_4Cu_4S_{12}O_4(CuTMEN)_4]$ (M = Mo, W; TMEN = *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)

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Synthetic methods for $[Et_4N]_4[W_4Cu_4S_{12}O_4]$ (**1**), $[Et_4N]_4[Mo_4Cu_4S_{12}O_4]$ (**2**), $[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**3**), and $[Mo_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**4**) are described. $[Et_4N]_2[MS_4]$, $[Et_4N]_2[MS_2O_2]$, $Cu(NO_3)_2\cdot 3H_2O$, and KBH_4 (or Et_4NBH_4) were used as starting materials for the synthesis of **1** and **2**. Compounds **3** and **4** were produced by reaction of $[Et_4N]_2[WOS_3]$, $Cu(NO_3)_2\cdot 3H_2O$, and TMEN and by reaction of $[Me_4N]_2[MO_2O_2S_8]$, $Cu(NO_3)_2\cdot 3H_2O$, and TMEN, respectively. Crystal structures of compounds **1**−**4** were determined. Compounds **1** and **2** crystallized in the monoclinic space group $C2/c$ with $a = 14.264(5)$ Å, $b = 32.833(8)$ Å, $c = 14.480(3)$ Å, $\beta = 118.66(2)°$, $V = 5950.8(5)$ Å^3, and $Z = 4$ for **1** and $a = 14.288(5)$ Å, $b = 32.937(10)$ Å, $c = 14.490(3)$ Å, $\beta = 118.75(2)°$, $V = 5978.4(7)$ Å^3, and $Z = 4$ for **2**. Compounds **3** and **4** crystallized in the trigonal space group $P3_221$ with $a = 13.836(6)$ Å, $c = 29.81(1)$ Å, $V = 4942(4)$ Å^3, and $Z = 3$ for **3** and $a = 13.756(9)$ Å, $c = 29.80(2)$ Å, $V = 4885(6)$ Å^3, and $Z = 3$ for **4**. The cluster cores have approximate C_{2v} symmetry. The anions of **1** and **2** may be viewed as consisting of two butterfly-type $[CuMOS_3Cu]$ fragments bridged by two $[MOS_3]^{2-}$ groups. Eight metal atoms in the anions are arranged in an approximate square configuration, with a $Cu_4M_4S_{12}$ ring structure. Compounds **3** and **4** can be considered to consist of one $[M_4Cu_4S_{12}O_4]^{4-}$ (the anions of **1** and **2**) unit capped by $Cu(TMEN)^+$ groups on each M atom; the $Cu(TMEN)^+$ groups extend alternately up and down around the Cu_4M_4 square. The electronic spectra of the compounds are dominated by the internal transitions of the $[MOS_3]^{2-}$ moiety. ^{95}Mo NMR spectral data are investigated and compared with those of other compounds.

Introduction

Heterometallic cluster compounds containing Cu(I), especially $[MoS_4]^{2-}/Cu^+$ and $[WS_4]^{2-}/Cu^+$ complexes,[1] have attracted much attention.[2] Apart from the possible relevance to the Mo−Cu biological antagonism,[1a,3a] such complexes also show potential application as materials with nonlinear physical properties.[3b] M−Cu−S complexes with different structure configurations have been reported, such as $[(PPh_3)_2CuS_2MS_2Cu(PPh_3)]$[4] (linear), $[MCu_3S_4Cl]$[5] (cubane-like), $[M_2Cu_4S_6O_2]^{4-}$[6] (cage), $[MS_4(CuL)_4]^{2-}$[7] (chain) (L = Br, SCN), $[(H_2O)_9Mo_3S_4CuCuS_4Mo_3(H_2O)_9]^{8+}$[8] (double-cubane-like), $[(CuCl)_5Cl_2MS_4]^{4-}$[9] (double-cubane-like), $[MCu_3S_4Cl_3]^{2-}$,[10] $[M_2Cu_5S_8(S_2CNMe_2)_3]^{2-}$,[11] and $[Bu_4N]_4[Cu_{12}Mo_8S_{32}]$[12] (M = Mo, W). Our recent contributions to the M−Cu−S system include the imcomplete cubane-like $[Et_4N][M_2CuS_4(PPh_3)(SCH_2CH_2S)_2]$,[13] the cubane-like clusters $\{M_3CuS_4\}$[14] and $[M_2Cu_2S_4(PPh_3)_2(SCH_2CH_2S)_2]$,[15] the butterfly-type complexes $[Et_4N][(PPh_3)_2AgS_3MOCu(CN)]$,[16] the double-cubane-like $[Cu_6S_6Me_2(SCMe_3)_2(O)_2(PPh_3)_4]$,[17] the ($\mu_6$-S)-containing cluster $[Et_4N]_2[(\mu_6\text{-}S)Cu_6S_6(S_2)_6Mo_6O_6]$,[18] etc. Herein, we report the synthesis and characterization of the octanuclear clusters $[Et_4N]_4[M_4Cu_4S_{12}O_4]$ and the dodecanuclear clusters $[M_4Cu_4S_{12}O_4(CuTMEN)_4]$, which contain $[MOS_3]^{2-}$ units acting as bi- and tridentate ligands, respectively (M = Mo, W; TMEN = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).

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(1) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem.* **1981**, *93*, 957; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934. (b) Wu, X-T.; Chen, P.-C.; Du, S.-W.; Zhu, N.-Y.; Lu, J.-X. *J. Cluster Sci.* **1994**, *5*, 265.

(2) (a) Holloway, C. E.; Melnik, M. *Rev. Inorg. Chem.* **1993**, *13*, 233. (b) Scattergood, C. D.; Bonney, P. G.; Slater, S. M.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1987**, 1749. (c) Müller, A.; Schimanski, J.; Bögge, H. *Z. Anorg. Allg. Chem.* **1987**, *544*, 107.

(3) (a) Mills, C. F. *Chem. Br.* **1979**, *15*, 212; *Philos. Trans. R. Soc. London* **1979**, *B288*, 51. (b) Shi, S.; Ji, W.; Lang, J.-P.; Xin, X.-Q. *J. Phys. Chem.* **1994**, *98*, 3570.

(4) Müller, A.; Bögge, H.; Tölle, H. G.; Joster, R.; Schimanski, U.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 654.

(5) Müller, A.; Bögge, H.; Schimanski, U. *J. Chem. Soc., Chem. Commun.* **1980**, 91.

(6) Doherty, R.; Hubbard, C. R.; Mighell, A. D.; Siedle, A. R.; Stewart, J. *Inorg. Chem.* **1979**, *18*, 2991.

(7) (a) Manoli, J. M.; Potvin, C.; Secheresse, F.; Marzak, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1557. (b) Nicholson, J. R.; Flood, A. C.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1179.

(8) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313.

(9) Secheresse, F.; Manoli, J. M.; Potvin, C.; Marzak, S. *J. Chem. Soc., Dalton Trans.* **1988**, 3055.

(10) Potvin, C.; Manoli, J. M.; Salis, M.; Secheresse, F. *Inorg. Chim. Acta* **1984**, *83*, L19.

(11) Lei, X.-J.; Huang, Z.-Y.; Liu, Q.-T.; Hong, M.-C.; Liu, H.-Q. *Inorg. Chem.* **1989**, *28*, 4302.

(12) Li, J.-G.; Xin, X.-Q.; Zhou, Z.-Y.; Yu, K.-B. *J. Chem. Soc., Chem. Commun.* **1991**, 249.

(13) Zhu, N.-Y.; Zheng, Y.-F.; Wu, X.-T. *Inorg. Chem.* **1990**, *29*, 2705.

(14) (a) Wu, X.-T.; Lu, S.-F.; Zhu, N.-Y.; Wu, Q.-J.; Lu, J.-X. *Inorg. Chim. Acta* **1987**, *133*, 39. (b) Wu, X.-T.; Zhang, H.-Q.; Zheng, Y.-F.; Lu, J.-X. *J. Mol. Struct.* **1989**, *197*, 33. (c) Zhang, H.-Q.; Zheng, Y.-F.; Wu, X.-T.; Lu, J.-X. *Inorg. Chim. Acta* **1989**, *156*, 277.

(15) Zhu, N.-Y.; Zheng, Y.-F.; Wu, X.-T. *J. Chem. Soc., Chem. Commun.* **1990**, 780.

(16) Du, S.-W.; Zhu, N.-Y.; Chen, P.-C.; Wu, X.-T.; Lu, J.-X. *J. Chem. Soc., Dalton Trans.* **1992**, 339.

(17) Du, S.-W.; Zhu, N.-Y.; Chen, P.-C.; Wu, X.-T. *Angew. Chem., Int. Ed. Engl.* **1992**, *8*, 31.

(18) Wu, X.-T.; Wang, B.; Zheng, Y.-F.; Lu, J.-X. *Jiegou Huaxue (Chin. J. Struct. Chem.)* **1988**, *71*, 47.

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Experimental Section

All experiments were carried out in the air. $[Et_4N]_2[MS_4]$ and $[Et_4N]_2[MO_2S_2]$ (M = Mo, W), $[Et_4N]_2[WOS_3]$, and $[Me_4N]_2[Mo_2O_2S_8]$ were obtained by published procedures. Other chemicals were used as purchased. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer using KBr pellets. Electronic spectra were obtained on a Shimadzu UV-3000 spectrophotometer in DMF solution between 600 and 200 nm. ^{95}Mo NMR spectra were recorded on a Varian Unity-500 spectrometer in DMSO solution. Elemental analyses were performed by the Elemental Analysis Laboratories in our institute.

$[Et_4N]_4[W_4Cu_4S_{12}O_4]$ (1). To a solution of $Cu(NO_3)_2·3H_2O$ (0.242 g, 1 mmol in 5 mL of DMF) was added KBH_4 (0.053 g, 1 mmol) with stirring. After 15 min, a solution of $[Et_4N]_2[WS_4]$ (0.286 g, 0.5 mmol in 15 mL of CH_3CN) was added to the dark suspension, and the mixture was stirred for 25 min. A solution of $[Et_4N]_2[WS_2O_2]$ (0.540 g, 1 mmol in 5 mL of CH_3CN) was then added, the reaction mixture was stirred for another 20 min, and then the orange precipitate was removed by filtration. The orange filtrate was allowed to stand at ambient temperature in the air for 2 days; the resulting yellow precipitate was removed by filtration. After an additional 3 days, 0.085 g of orange crystals was obtained. Anal. Calcd (found): C, 20.10 (19.62); H, 4.46 (4.12); N, 3.07 (2.86). IR (KBr pellet, cm^{-1}): W$-\mu_2$-S and W$-\mu_3$-S, 488 (w), 452.7 (vs), and 435.9 (shoulder); W$-$O, 902.6 (vs).

$[Et_4N]_4[Mo_4Cu_4S_{12}O_4]$ (2). A procedure similar to that used for the synthesis of the corresponding tungsten complex (**1**) was employed. To a solution of $Cu(NO_3)_2·3H_2O$ (0.242 g, 1 mmol in 10 mL of CH_3CN) was added Et_4NBH_4 (0.145 g, 1 mmol) with stirring. After 15 min, to the dark suspension was added a solution of $[Et_4N]_2[MoS_4]$ (0.242 g, 0.5 mmol in 10 mL of CH_3CN), and the mixture was stirred for 25 min. A solution of $[Et_4N]_2[MoO_2S_2]$ (0.452 g, 1 mmol in 5 mL of CH_3CN) was then added, the reaction mixture was stirred for 25 min, and the dark-red precipitate was filtered off. The dark-red filtrate was allowed to stand for 3 days at ambient temperature in the air, resulting in 0.07 g of dark-red crystals. Anal. Calcd (found): C, 24.33 (23.91); H, 4.65 (5.02); N, 3.60 (3.48). IR (KBr pellet, cm^{-1}): Mo$-\mu_2$-S and Mo$-\mu_3$-S, 497.6 (w), 462.9 (vs), and 434.0 (shoulder); Mo$-$O, 883.4 (vs).

$[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ (3). To a solution of $[Et_4N]_2[WOS_3]$ (0.278 g, 0.5 mmol in 5 mL of CH_3CN and 10 mL of CH_2Cl_2) was added a solution of $Cu(NO_3)_2·3H_2O$ (0.242 g, 1 mmol) and TMEN (0.30 mL, 2 mmol) in 10 mL of CH_3CN; a small amount of precipitate formed and was filtered off. The orange-red filtrate was allowed to stand at ambient temperature in the air for 1 day, resulting in the formation of 0.085 g of red crystals. Anal. Calcd (found): C, 14.09 (13.36); H, 3.06 (2.99); N, 5.22 (5.20). IR (KBr pellet, cm^{-1}): W$-\mu_3$-S, 435 (vs); W$-$O, 932 (vs).

$[Mo_4Cu_4S_{12}O_4(CuTMEN)_4]$ (4). To a solution of $[Me_4N]_2$-$[Mo_2O_2S_8]$ (0.314 g, 0.5 mmol in 15 mL of CH_3CN) was added a solution of $Cu(NO_3)_2·3H_2O$ (0.121 g, 0.5 mmol) and TMEN (0.15 mL, 1 mmol) in 10 mL of CH_3CN. This mixture was stirred for 5 min, and then filtered. The dark filtrate was allowed to stand for several days at ambient temperature in the air, and 0.041 g of dark-red crystals was produced. Anal. Calcd (found): C, 16.28 (15.96); H, 3.47 (3.57); N, 6.14 (6.21). IR (KBr pellet, cm^{-1}): Mo$-\mu_3$-S, 444 (vs); Mo$-$O, 916 (vs).

Crystal Structure Determination. Crystals of **1**$-$**4** were selected and mounted on glass fibers for single-crystal X-ray diffraction experiments. The crystallographic and machine data are given in Table 1, Table 2, and the supplementary Table S1. Diffraction data were collected on a CAD-4 κ-geometry diffractometer for **1** and **2** and on a RIGAKU AFC-5R diffractometer for **3** and **4** by use of Mo Kα radiation. Cell constants and orientation matrixes were obtained from least-squares by setting angles of 25 reflections for **1** and **2** and of 20 reflections for **3** and **4** in the range $12° < 2\theta < 50°$. Intensities were corrected for polarization and Lorentz factors and for absorption by using empirical scan data and DIFABS.

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

	1	**2**
formula	$N_4C_{32}H_{80}O_4S_{12}$-Cu_4W_4	$N_4C_{32}H_{80}O_4S_{12}$-Cu_4Mo_4
mol wt	1959.35	1607.71
a, Å	14.264(5)	14.288(5)
b, Å	32.833(8)	32.937(10)
c, Å	14.480(3)	14.490(3)
β, deg	118.66(2)	118.75(2)
V, Å^3	5950.8(5)	5978.4(7)
space group	*C*2/*c*	*C*2/*c*
Z	4	4
T, K	296	296
λ(Mo Kα), Å	0.710 73	0.710 73
crystal dimens, mm	0.32 × 0.32 × 0.25	0.22 × 0.18 × 0.13
μ, cm^{-1}	97.1	26.3
d_{calcd}, g/cm^3	2.19	1.79
no. of unique data	5331	5372
no. of obs data ($I > 3\sigma(I)$)	2839	2067
no. of variables refined	139	129
residuals: *R*, R_w^{a}	0.073, 0.089	0.089, 0.111
GOF	1.73	2.25
max shift in final cycle	0.08	0.09

^{a} $w = [\sigma^2(F_o^2) + (0.020F_o)^2 + 1.0]^{-1}$.

Table 2. Crystallographic Data and Refinement Details for the Structures of **3** and **4**

	3	**4**
formula	$N_8C_{24}H_{64}O_4S_{12}$-Cu_8W_4	$N_8C_{24}H_{64}O_4S_{12}$-Cu_8Mo_4
mol wt	2157.31	1805.67
a, Å	13.836(6)	13.756(9)
c, Å	29.81(1)	29.80(2)
V, Å^3	4942(4)	4885 (6)
space group	$P3_221$	$P3_221$
Z	3	3
T, k	296	296
λ(Mo Kα), Å	0.710 69	0.710 69
crystal dimens, mm	0.42 × 0.23 × 0.14	0.50 × 0.32 × 0.11
μ, cm^{-1}	100.33	36.92
d_{calcd}, g/cm^3	2.17	1.84
no. of unique data	3323	3282
no. of obs data ($I > 3\sigma(I)$)	1035	1324
no. of variables refined	151	151
residuals: *R*, R_w^{a}	0.055, 0.064	0.062, 0.075
GOF	1.32	1.62
max shift in final cycle	0.45	0.29

^{a} $w = 4F_o^2/\sigma^2(F_o^2)$.

The structures were solved by direct methods using MITHRIL,[19] and the positions of four heavy atoms were obtained from *E* maps. The remaining non-hydrogen atoms were located from difference Fourier maps. No attempt was made to locate hydrogen atoms for each structural determination. For **1** and **2**, the cations were all disordered and the structures were refined using a rigid model, in which the positions of carbon atoms changed with those of the corresponding nitrogen atoms, the populations of the disordered carbon atoms were fixed at 0.5, and the temperature factors of some carbon atoms were fixed according to *B*(atom 1) = 1.2*B*(atom 2), where atom 2 is bound to atom 1 (If atom 1 belongs to CH_2 groups, atom 2 is namely the corresponding nitrogen atom.) The refinement of structures of **1** and **2** was performed by full-matrix least-squares techniques using the SDP program package. For **3** and **4**, the structures were refined by use of the TEXSAN program package, origins were automatically selected by the program, and other enantiomorphs were checked. All calculations were carried out on a VAX-785 computer. Atomic scattering factors were taken from ref 20. Coordinates of cluster atoms for **1**$-$**4** are listed in Tables 3 and 4 and supplementary Tables S3 and S4. Coordinates of noncluster atoms for **1** and **2** are listed in supplementary Tables S2 and S3.

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(19) Gilmore, C. J. *MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*; University of Glasgow: Glasgow, Scotland, 1983.

(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, Tables 2.2a, 2.3.1.

Table 3. Atomic Coordinates for $[W_4Cu_4S_{12}O_4]^{4-}$ (**1**)

atom	*x*	*y*	*z*
W1	0.33616(7)	0.13133(3)	−0.09814(7)
W2	0.23750(7)	0.12555(4)	−0.51404(7)
Cu1	0.2897(2)	0.1286(1)	−0.3055(2)
Cu2	0.5497(2)	0.1298(1)	−0.0410(2)
S1	0.4129(5)	0.0899(2)	−0.1651(5)
S2	0.4601(5)	0.1696(3)	0.0239(5)
S3	0.2154(5)	0.1687(3)	−0.2262(5)
S4	0.3574(5)	0.1679(2)	−0.3936(5)
S5	0.3166(5)	0.0895(3)	−0.5838(5)
S6	0.1676(5)	0.0867(3)	−0.4399(5)
O1	0.273(1)	0.1006(5)	−0.044(1)
O2	0.136(1)	0.1534(7)	−0.613(1)

Table 4. Atomic Coordinates for $[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**3**)

atom	*x*	*y*	*z*
W1	0.3191(2)	0.0974(2)	0.28852(8)
W2	0.1315(3)	−0.3156(2)	0.20804(8)
Cu1	0.2374(7)	−0.1047(7)	0.2460(2)
Cu2	0.3838(8)	0.1962(6)	0.2053(2)
Cu3	0.5167(8)	0.1079(7)	0.2949(3)
Cu4	−0.0543(8)	−0.3087(7)	0.2096(3)
S1	0.216(2)	0.048(2)	0.2262(5)
S2	0.349(1)	−0.045(2)	0.3098(5)
S3	0.487(1)	0.244(1)	0.2719(5)
S4	0.301(1)	−0.175(1)	0.1893(5)
S5	0.068(2)	−0.260(2)	0.2672(5)
S6	0.020(1)	−0.349(1)	0.1497(5)
O1	0.247(3)	0.133(3)	0.332(1)
O2	0.141(4)	−0.444(4)	0.223(1)
N1	0.626(7)	0.157(7)	0.353(2)
N2	0.652(8)	0.087(8)	0.271(3)
N3	−0.219(5)	−0.459(5)	0.228(2)
N4	−0.150(6)	−0.228(6)	0.204(2)
C11	0.698(8)	0.103(7)	0.347(3)
C12	0.556(7)	0.111(7)	0.387(3)
C13	0.68(1)	0.28(1)	0.359(4)
C21	0.737(6)	0.121(6)	0.303(2)
C22	0.583(8)	−0.046(9)	0.266(3)
C23	0.661(8)	0.103(8)	0.226(3)
C31	−0.29(1)	−0.41(1)	0.239(4)
C32	−0.207(8)	−0.492(9)	0.275(3)
C33	−0.248(6)	−0.563(6)	0.201(2)
C41	−0.27(1)	−0.33(1)	0.204(4)
C42	−0.092(9)	−0.117(9)	0.238(3)
C43	−0.15(1)	−0.186(9)	0.154(4)

Results and Discussion

Syntheses of Octanuclear Clusters 1 and 2. $[Et_4N]_2[MS_4]$ and $[Et_4N]_2[MO_2S_2]$ were used as starting reaction materials, and Cu^+ cations were introduced through the reduction of $Cu(NO_3)_2{\cdot}3H_2O$ by KBH_4 or Et_4NBH_4. According to the sequence of addition of reaction materials, the syntheses of **1** and **2** possibly derive from an initially formed $[MS_4]^{2-}/Cu^+$ cluster and the $[MO_2S_2]^{2-}$ anion; however, this initial M−Cu cluster compound has not yet been characterized in our laboratory. The cluster anion of **1** and **2** can be considered to consist of two butterfly-type $[CuOMS_3Cu]$ fragments bridged by two bidentate $[MOS_3]^{2-}$ groups. The two cluster compounds are only slightly soluble in DMF.

Syntheses of Dodecanuclear Clusters 3 and 4. $[Et_4N]_2[WOS_3]$ and $[Me_4N]_2[Mo_2O_2S_8]$ were used respectively as starting materials for the syntheses of **3** and **4**. Structural determinations show that, in the molecules, the Cu cations are all in the 1+ oxidation state. These Cu^+ cations can be considered to derive from the reduction of $Cu(NO_3)_2{\cdot}3H_2O$ by $[WOS_3]^{2-}$ (or $[Mo_2O_2S_8]^{2-}$).[21] It was not expected that the structure of the octanuclear clusters (**1** and **2**) and that of the dodecanuclear clusters (**3** and **4**) would be closely related. It was thought that compounds **3** and **4** might, in principle, be synthesized from componds **1** and **2** by using the unit-construction method.[13,15,16,22] However, because of the poor solubility of **1** and **2**, this route was not successful. Compounds **3** and **4** are slightly soluble in CH_2Cl_2 and DMF.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) in $[Et_4N]_4[W_4Cu_4S_{12}O_4]$ (**1**)[a]

W1−Cu1	2.748(3)	W2−S6	2.191(6)
W1−Cu2	2.747(3)	W2−O2	1.73(1)
W1−S1	2.237(5)	Cu1−S1	2.325(6)
W1−S2	2.198(6)	Cu1−S3	2.312(7)
W1−S3	2.202(6)	Cu1−S4	2.326(6)
W1−O1	1.76(1)	Cu1−S6	2.339(6)
W2−Cu1	2.744(3)	Cu2−S1	2.322(6)
W2−Cu2*	2.747(3)	Cu2−S2	2.318(6)
W2−S4	2.245(7)	Cu2−S4*	2.327(6)
W2−S5	2.187(6)	Cu2−S5*	2.313(6)
Cu1−W1−Cu2	88.88(8)	S3−Cu1−S6	114.4(3)
S1−W1−S2	108.9(2)	S4−Cu1−S6	102.1(2)
S1−W1−S3	108.8(3)	W1−Cu2−W2*	178.0(1)
S1−W1−O1	107.6(5)	S1−Cu2−S2	102.1(2)
S2−W1−S3	111.1(3)	S1−Cu2−S4*	114.8(2)
S2−W1−O1	110.9(5)	S1−Cu2−S5*	110.7(3)
S3−W1−O1	109.5(5)	S2−Cu2−S4*	113.2(2)
Cu1−W2−Cu2*	90.01(8)	S2−Cu2−S5*	114.5(3)
S4−W2−S5	108.9(2)	S4*−Cu2−S5*	102.0(2)
S4−W2−S6	109.7(3)	W1−S1−Cu1	74.0(2)
S4−W2−O2	109.8(6)	W1−S1−Cu2	74.1(2)
S5−W2−S6	111.6(3)	Cu1−S1−Cu2	111.8(3)
S5−W2−O2	108.6(6)	W1−S2−Cu2	74.9(2)
S6−W2−O2	108.2(6)	W1−S3−Cu1	75.0(2)
W1−Cu1−W2	178.4(2)	W2−S4−Cu1	73.8(2)
S1−Cu1−S3	102.2(2)	W2−S4−Cu2*	73.8(2)
S1−Cu1−S4	116.3(2)	Cu1−S4−Cu2*	113.1(3)
S1−Cu1−S6	110.8(2)	W2−S5−Cu2*	75.3(2)
S3−Cu1−S4	111.5(2)	W2−S6−Cu1	74.5(2)

[a] Starred atoms are symmetry-translated by C_2.

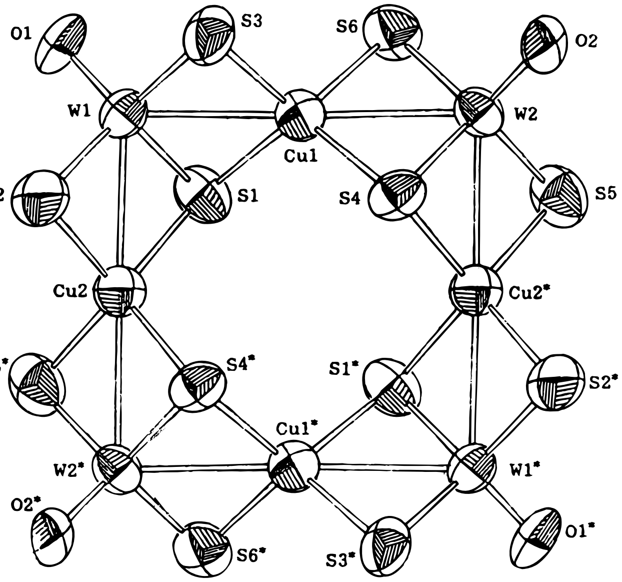

Figure 1. ORTEP drawing of the anion of **1** (thermal ellipsoids at 50% probability level).

Structure of the Octanuclear Cluster $[Et_4N]_4[W_4Cu_4S_{12}O_4]$ (1). Cluster **1** is isomorphous with the corresponding molybdenum cluster **2**. Selected bond distances and angles of **1** are collected in Table 5, and the structure of the anion is shown in Figure 1. The molecule is constrained to exhibit C_2 symmetry,

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(21) Clarke, N. J.; Laurie, S. H. *Inorg. Chim. Acta* **1982**, *66*, L35.

(22) Wu, X.-T.; Lu, J.-X. *Jiegou Huaxue (Chin. J. Struct. Chem.)* **1989**, *8*, 399.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) in $[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**3**)[a]

W1−O1	1.85(4)	Cu1−S2	2.33(2)
W1−S1	2.23(2)	Cu1−S4	2.33(2)
W1−S2	2.29(2)	Cu1−S5	2.34(2)
W1−S3	2.24(2)	Cu2−S1	2.29(2)
W1−Cu1	2.747(9)	Cu2−S3	2.34(2)
W1−Cu2	2.758(8)	Cu2−S4*	2.33(2)
W1−Cu3	2.67(1)	Cu2−S6*	2.32(2)
W2−O2	1.89(5)	Cu3−N1	2.17(7)
W2−S4	2.24(2)	Cu3−N2	2.15(9)
W2−S5	2.27(2)	Cu3−S2	2.27(2)
W2−S6	2.22(2)	Cu3−S3	2.23(2)
W2−Cu1	2.768(9)	Cu4−N3	2.26(6)
W2−Cu2*	2.781(8)	Cu4−N4	2.13(7)
W2−Cu4	2.62(1)	Cu4−S5	2.26(2)
Cu1−S1	2.35(2)	Cu4−S6	2.26(2)

O1−W1−S1	109(1)	W1−Cu2−W2*	173.6(3)
O1−W1−S2	113(1)	N1−Cu3−N2	78(3)
O1−W1−S3	111(1)	N1−Cu3−S2	111(2)
S1−W1−S2	109.2(7)	N1−Cu3−S3	112(2)
S1−W1−S3	108.0(6)	N2−Cu3−S2	120(3)
S2−W1−S3	106.7(6)	N2−Cu3−S3	123(2)
Cu1−W1−Cu2	87.4(2)	S2−Cu3−S3	108.0(9)
Cu1−W1−Cu3	88.7(3)	N3−Cu4−N4	84(3)
Cu2−W1−Cu3	88.1(3)	N3−Cu4−S5	110(2)
O2−W2−S4	110(1)	N3−Cu4−S6	110(2)
O2−W2−S5	111(1)	N4−Cu4−S5	118(2)
O2−W2−S6	111(1)	N4−Cu4−S6	123(2)
S4−W2−S5	108.3(7)	S5−Cu4−S6	108.1(8)
S4−W2−S6	107.6(6)	W1−S1−Cu1	73.7(6)
S5−W2−S6	109.3(6)	W1−S1−Cu2	75.1(6)
Cu1−W2−Cu2*	83.1(2)	Cu1−S1−Cu2	110(1)
Cu1−W2−Cu4	88.1(3)	W1−S2−Cu1	73.1(6)
Cu2*−W2−Cu4	89.0(3)	W1−S2−Cu3	71.8(7)
S1−Cu1−S2	104.1(8)	Cu1−S2−Cu3	111.1(8)
S1−Cu1−S4	115.9(7)	W1−S3−Cu2	74.0(6)
S1−Cu1−S5	111.8(8)	W1−S3−Cu3	73.4(6)
S2−Cu1−S4	115.0(8)	Cu2−S3−Cu3	111.6(7)
S2−Cu1−S5	106.8(7)	W2−S4−Cu1	74.6(6)
S4−Cu1−S5	103.1(7)	W2−S4−Cu2*	75.0(6)
W1−Cu1−W2	173.2(3)	Cu1−S4−Cu2*	104.6(7)
S1−Cu2−S3	102.9(7)	W2−S5−Cu1	73.7(6)
S1−Cu2−S4*	118.3(7)	W2−S5−Cu4	70.7(5)
S1−Cu2−S6*	112.4(8)	Cu1−S5−Cu4	108.9(7)
S3−Cu2−S4*	114.1(7)	W2−S6−Cu2*	75.6(6)
S3−Cu2−S6*	107.4(6)	W2−S6−Cu4	71.5(5)
S4*−Cu2−S6*	101.6(6)	Cu2*−S6−Cu4	111.4(7)

[a] Starred atoms are symmetry-translated by C_2.

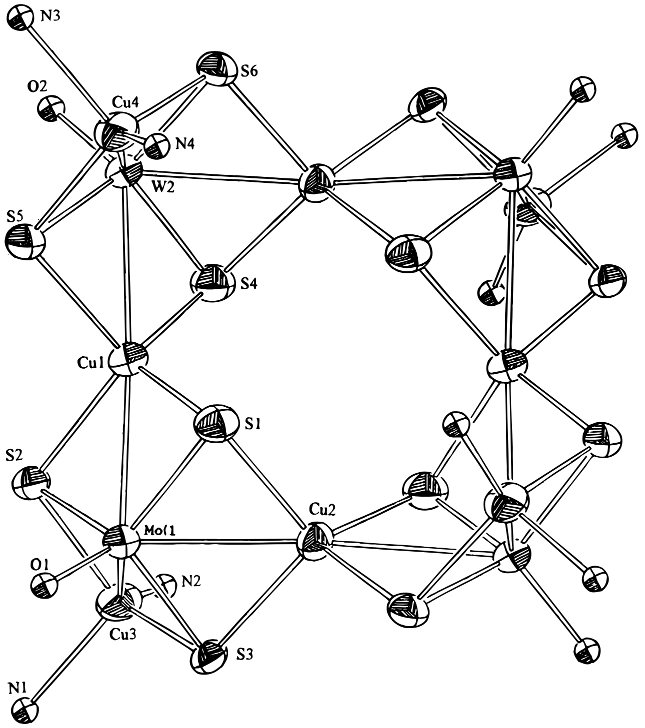

Figure 2. ORTEP drawing of **3** (thermal ellipsoids at 30% probability level). C atoms are omitted for clarity.

but the anion has approximate C_{2v} symmetry, with two mirror planes overlapping plane 1 (W1, S1, O1, W1*, S1*, O1*) and plane 2 (W2, S4, O2, W2*, S4*, O2*), respectively—the dihedral angle is 89.55 ± 0.09°. Furthermore, the dihedral angles between the mirror planes (plane 1 and plane 2) and the basal planes (plane 3 (W1, W2, Cu1, Cu2) and plane 4 (W1*, W2*, Cu1*, Cu2*)) are also near 90°. The angle between plane 3 and plane 4 is 175.52 ± 0.05°. Each W atom has tetrahedral coordination [107.6(5)−111.6(3)°], with one μ_3-S atom, two μ_2-S atoms, and one terminal oxygen atom. Each Cu atom is coordinated by two μ_2-S atoms and two μ_3-S atoms to give a distorted tetrahedral geometry [102.0(2)−116.3(2)°]. The average W−Cu bond distance is 2.747 Å, which lies in the reported range of W−Cu distances (2.621−2.784 Å). The configuration of eight metal atoms can be described as approximately square, in which each side containing a copper atom and two neighboring tungsten atoms is nearly linear [178.0(1)−178.4(2)°] and in which the angles about tungsten atoms bonding two copper atoms vary from 88.88(8) to 90.01(8)°. These metal atoms together with sulfur atoms form a ring structure that is rare in cluster chemistry. It is noted that there exist eight μ_2-S atoms and four μ_3-S atoms in the anion. According to our past experiments, μ_2-S atoms are still quite reactive, that is to say, the eight μ_2-S atoms can in principle react further with metal atoms to form a larger cluster. This type of cluster, containing only sulfur atoms from $[MO_nS_{4-n}]^{2-}$ units as ligands, is rare in the M−Cu−S system. Only two other clusters of this kind have been previously reported ($[Bu_4N]_4[Cu_{12}Mo_8S_{32}]$[12] and $[Cu_2S_4W]$[23].

Structure of the Dodecanuclear Cluster $[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ (3). Clusters **3** and **4** are isomorphous. Selected interatomic distances and angles of **3** are collected in Table 6, the structure is shown in Figure 2, and the packing diagram of the unit cell is shown in Figure 3. The molecule is crystallographically required to exhibit C_2 symmetry. Excluding C atoms, the rest of the molecule has approximate C_{2v} symmetry, with two mirror planes overlapping the S1, O1, W1, Cu3, N1, N2, S1*, O1*, W1*, Cu3*, N1*, N2* and S4, O2, W2, Cu4, N3, N4, S4*, O2*, W2*, Cu4*, N3*, N4* planes, respectively—the dihedral angle is 90.13 ± 0.02°. Each W atom has slightly distorted tetrahedral coordination [106.7(6)−113(1)°], with one terminal oxygen atom and three μ_3-S atoms. The Cu1 and Cu2 atoms are each coordinated by four μ_3-S atoms to give a distorted tetrahedral geometry [101.6(6)−118.3(7)°]. The Cu3 and Cu4 atoms both display highly distorted tetrahedral coordination, with two nitrogen atoms of TMEN and two μ_3-S atoms. For the Cu3 and Cu4 atoms, the average N−Cu−N angle of 81° is much smaller than the average S−Cu−S angle of 108.1°. Because of this fact, the average W−Cu length of 2.64 Å for the Cu3 and Cu4 atoms is shorter than that of 2.764 Å for the Cu1 and Cu2 atoms. The same effect is observed for the Cu−(μ_3-S) lengths (average values of 2.26 Å vs 2.33 Å for Cu3 and Cu4 vs Cu1 and Cu2, respectively). The Cu−W−Cu angles lie in the range 83.1(2)−89.0(3)°, close to those previously reported for other related clusters.[12] The molecule can be considered to consist of one $[W_4Cu_4S_{12}O_4]^{4-}$ (the anion of **1**) unit and four $Cu(TMEN)^+$ groups. These $Cu(TMEN)^+$ groups are bound to eight μ_2-S atoms of $[W_4Cu_4S_{12}O_4]^{4-}$ as

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(23) Pruss, E. A.; Snyder, B. S.; Stacy, A. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 256.

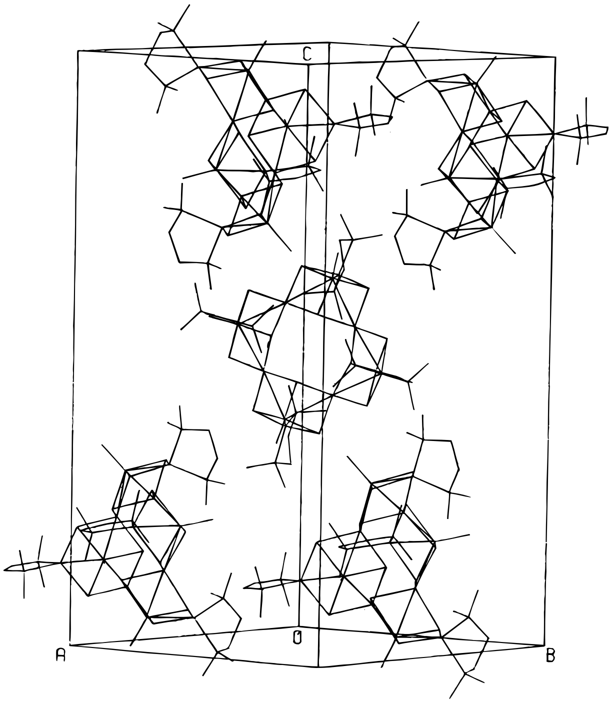

Figure 3. Packing diagram of the unit cell of **3**.

capping units on W atoms. As shown in Figure 2, two diagonally related Cu(TMEN)$^+$ groups are above and the other two Cu(TMEN)$^+$ groups are below the plane containing W1, W2, Cu1, and Cu2. As shown in Figure 3, there exist three different orientations for the molecules in the unit cell, along the A, B, and A + B axes, respectively.

The Cu atoms bonding to two nitrogen atoms of TMEN display highly distorted tetrahedral coordination. In **3**, the angles about the Cu3 atom are 78(3)° [N1−Cu3−N2], 111(2)° [N1−Cu3−S2], 112(2)° [N1−Cu3−S3], 120(3)° [N2−Cu3−S2], 123(2)°, [N2−Cu3−S3], and 108.0(9)° [S2−Cu3−S3]; the Cu4 atom displays bond angles similar to those of the Cu3 atom. This distorted tetrahedral coordination is similar to that in $WS_4(Cu(phen))_2$,[24] which also contains bidentate nitrogen ligands (1,10-phenanthroline).

Electronic Spectra. Data for the electronic spectra of the four title compounds are given in Table 7. Except for the absorptions in the range 334−420 nm, these spectra exhibit absorption bands similar to those of the corresponding $[MOS_3]^{2-}$ moieties. Thus, the principal feature can be attributed to the charge-transfer transitions within the $[MOS_3]^{2-}$ moiety. As Cu(TMEN)$^+$ groups are bound to $[M_4Cu_4S_{12}O_4]^{4-}$ units, the longest wavelength absorptions are scarcely shifted, but absorption bands at 348 nm for **1** and 420 nm for **2** disappear in the spectra of the corresponding dodecanuclear clusters **3** and **4**.

Table 7. Electronic Spectral Data Obtained in DMF

complex	λ, nm ($10^{-3}\epsilon$, dm^3 mol^{-1} cm^{-1})	ref
$[WOS_3]^{2-}$	375, 334, 270	25
$[Et_4N]_4[W_4Cu_4S_{12}O_4]$ (**1**)	380 (9.9), 348 (9.5), 270 (28)	this work
$[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**3**)	385 (24), 285 (61)	this work
$[MoOS_3]^{2-}$	465, 392, 313, 260	25
$[Et_4N]_4[Mo_4Cu_4S_{12}O_4]$ (**2**)	450 (11), 420 (10), 312 (27), 268 (23)	this work
$[Mo_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**4**)	450 (11), 320 (28), 265 (27)	this work

Table 8. ^{95}Mo NMR Spectral Data

complex	solvent	δ(Mo)[a]	ref
$[MoOS_3]^{2-}$	MeCN	1587 (<10)	27
$[Et_4N]_2[(NCCu)MoOS_3]$	MeCN	1199 (25)	27
$[Et_4N]_4[Mo_4Cu_4S_{12}O_4]$ (**2**)	DMSO	999 (78)	this work
$[Mo_4Cu_4S_{12}O_4(CuTMEN)_4]$ (**4**)	DMSO	679 (300)	this work

[a] Relative to external 2 M Na_2MoO_4 in D_2O, effective pH 11; line widths in hertz in parentheses.

^{95}Mo NMR Spectra. Compounds **2** and **4** were examined by ^{95}Mo NMR (Table 8). All resonances are shielded relative to $[MoOS_3]^{2-}$, and the ^{95}Mo chemical shift decreases by 200−400 ppm upon addition of each Cu^I cation to the $[MoOS_3]^{2-}$ core. This result agrees with that reported in ref 26. Only a single resonance peak occurs in ^{95}Mo NMR spectra for both **2** and **4**, and it does not shift in position during the recording of these spectra, suggesting that these two compounds are stable in DMSO solution (^{1}H spectral data for **4** in DMSO-d_6 solution also show that this compound is stable in DMSO solution).

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Supporting Information Available: Complete listings of crystallographic data, atomic positional parameters and their estimated standard deviations, bond distances and angles, and anisotropic displacement parameters (18 pages). Ordering information is given on any current masthead page.

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(24) Potvin, C.; Manoli, J. M. *Inorg. Chim. Acta* **1987**, *134*, 9.

(25) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934.

(26) Minelli, M.; Enemark, J. H.; Nicholson, J. R.; Garner, C. D. *Inorg. Chem.* **1984**, *23*, 4384.

(27) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519.