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Synthesis and Characterization of $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$: A Polynuclear Molybdenum−Copper Cluster Containing a Central Tetrahedral MoS_4 Encapsulated by Octahedral Cu_6 and Tetrahedral Cu_4 Arrays

Daxu Wu, Maochun Hong,* Rong Cao, and Hanqin Liu

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

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Introduction

Thiometalates $[MS_4]^{2-}$ (M = Mo, W) act as multidentate ligands to react with a wide variety of metal ions or neutral molecules to form various types of complexes, particularly with CuL (L = Cl, Br, I, R_2dtc, etc.), which led to a large number of complexes by successive addition across six edges of a MS_4 tetrahedron, such as $[MS_4CuL]^{2-}$,[1] $[MS_4(CuL)_2]^{2-}$,[2] $[MS_4(CuL)_3]^{2-}$,[3] $[MS_4(CuL)_4]^{2-}$,[4] $[MS_4(CuL)_5]^{2-}$,[5] $[MS_4(CuL)_6L_3]^{5-}$.[6] Up to now, $[MS_4(CuL)_6L_3]^{5-}$ is deemed the ultimate step of the addition of CuL to thiomolybdate. As a part of our interest in M−Cu−S system, we have successively isolated and characterized a series of compounds $[MS_4(CuR_2dtc)_3]^{2-}$,[3a,3b] $[M_2Cu_5S_8(R_2dtc)_3]^{2-}$,[7] and $[M_2Cu_5S_6E_2(R_2dtc)_3]^{2-}$ (M = Mo, W; E = S, O).[8] In this note we report the synthesis and structural characterization of $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$, a novel polynuclear Mo−Cu cluster consisting of a tetrahedral MoS_4 core encapsulated by octahedral Cu_6 and tetrahedral Cu_4 arrays of Cu(I) atoms and representing a further addition of CuCl to $[MoS_4Cu_6Cl_8]^{4-}$.

Experimental Section

$(NH_4)_2[MoS_4]$ was prepared according to literature methods.[9] Et_4NCl and CuCl were purchased from Beijing Hongxin Huagong Chang..

Table 1. Crystallographic Data for $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$

formula	$C_{32}H_{80}N_4MoCu_{10}S_4Cl_{12}$	Z	8
Fw	1806.05	d_{calc}, g cm^{-3}	1.93
space gruop	*Fddd*	T, K	296
a, Å	24.017(7)	μ, cm^{-1}	42.52
b, Å	43.146(15)	λ, Å (Mo Kα)	0.710 69
c, Å	12.011(7)	R^a	0.086
V, Å^3	12 446.2	$R_w{}^b$	0.085

[a] $R = \Sigma(|F_o| - |F_c|/\Sigma|F_o|$. [b] $R_w = \Sigma(w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)^{1/2}$.

Table 2. Atomic Coordinates and Thermal Parameters for $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$

atom	x	y	z	B (Å^2)
Mo	0.5000(0)	0.0000(0)	0.5000(0)	2.22(8)
Cu(1)	0.0000(0)	0.0000(0)	0.2262(4)	3.8(1)
Cu(2)	0.0000(0)	0.0628(1)	0.0000(0)	3.8(1)
Cu(3)	0.1123(2)	0.0000(0)	0.0000(0)	3.7(1)
Cu(4)	0.1569(2)	0.2004(1)	0.4353(4)	5.7(1)
Cl(1)	0.1904(2)	0.2211(1)	0.5986(5)	6.5(1)
Cl(2)	0.1920(2)	0.1541(1)	0.3634(5)	6.0(1)
Cl(3)	0.0754(2)	0.2187(2)	0.3542(7)	8.3(2)
S	0.4468(3)	0.0301(2)	0.3919(6)	2.1(1)
N(1)	0.2500(0)	0.0568(9)	0.2500(0)	3.7(9)
N(2)	0.2500(0)	0.1251(7)	0.7500(0)	2.5(7)
C(1)	0.215(2)	0.041(1)	0.344(4)	14(2)
C(2)	0.164(1)	0.264(9)	0.291(3)	8(1)
C(3)	0.301(4)	0.072(3)	0.305(9)	7(1)
C(4)	0.335(2)	0.046(1)	0.364(3)	7(1)
C(5)	0.001(2)	0.107(1)	0.399(5)	13(2)
C(6)	0.055(2)	0.0835(8)	0.385(4)	7(1)
C(7)	0.204(3)	0.110(1)	0.727(5)	8(1)
C(8)	0.202(2)	0.0847(9)	0.623(4)	7(1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$

Mo−Cu(1)	2.717(5)	Cu(4)−Cl(1)	2.302(7)
Mo−Cu(2)	2.711(6)	Cu(4)−Cl(2)	2.335(7)
Mo−Cu(3)	2.697(5)	Cu(4)−Cl(3)	2.324(8)
Mo−S	2.238(7)	Cu(1)−S	2.309(8)
Cu(1)−Cl(1)	2.401(6)	Cu(2)−S	2.303(8)
Cu(2)−Cl(2)	2.417(7)	Cu(3)−S	2.323(7)
Cu(3)−Cl(3)	2.372(7)		

Cu(1)−Mo−Cu(1′)	180.01(7)	Cl(2)−Cu(2)−S″	111.2(2)
Cu(1)−Mo−Cu(2)	90.01(3)	S−Cu(2)−S″	104.5(3)
Cu(1)−Mo−Cu(3)	90.01(2)	Cl(3)−Cu(3)−Cl(3′)	101.8(3)
Cu(2)−Mo−Cu(2′)	180.01(2)	Cl(3)−Cu(3)−S′	111.3(2)
Cu(2)−Mo−Cu(3)	90.01(2)	Cl(2)−Cu(2)−S″	114.2(3)
Cu(3)−Mo−Cu(3′)	180.01(3)	S′−Cu−S″	104.6(3)
S−Mo−S′	108.9(2)	Cl(1)−Cu(4)−Cl(2)	121.6(3)
S−Mo−S″	110.4(2)	Cl(1)−Cu(4)−Cl(3)	121.2(4)
S−Mo−S‡	109.1(3)	Cl(2)−Cu(4)−Cl(3)	116.2(3)
Cl(1)−Cu(1)−Cl(1′)	104.5(3)	Cu(1)−Cl(1)−Cu(4)	83.6(2)
Cl(1)−Cu(1)−S	114.5(2)	Cu(2)−Cl(2)−Cu(4)	84.9(2)
Cl(1)−Cu(1)−S′	109.8(2)	Cu(3)−Cl(3)−Cu(4)	83.3(2)
S−Cu(1)−S′	104.2(3)	Mo−S−Cu(1)	73.4(2)
Cl(2)−Cu(2)−Cl(2′)	107.5(3)	Mo−S−Cu(2)	73.3(2)
Cl(2)−Cu(2)−S	111.3(2)	Mo−S−Cu(3)	72.5(2)

DMSO and acac solvents were dried before use. Elemental analyses were performed by the Analytical Chemistry Group of this institute.

Preparation of $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$. $(NH_4)_2[MoS_4]$ (0.51 g, 2 mmol), Et_4NCl (1.32 g, 8 mmol), and CuCl (2.0 g, 20 mmol) were dissolved in 50 mL of acac/DMSO (v/v = 1:4). After the reaction mixture was stirred for 24 h at room temperature, the deep red solution was filtered. The dark-red crystalline product of the title compound was obtained from the filtrate left in air at ambient temperature for weeks. The product was filtered and washed with H_2O and acetone, affording 1.65 g of the title compound (46%). IR (KBr) (cm^{-1}): Et_4N^+,

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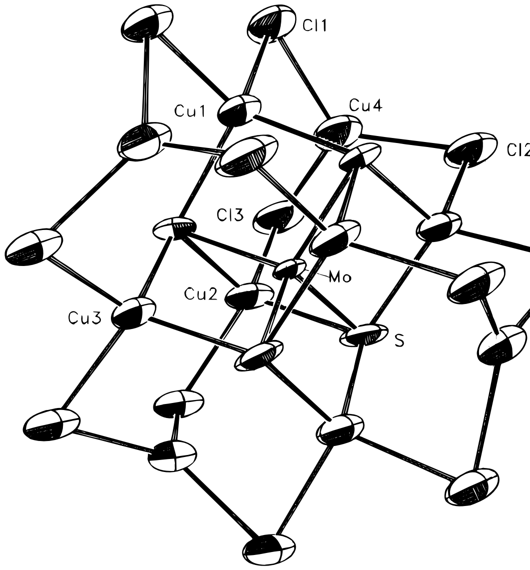

Figure 1. Perspective view of the anion structure of $[MoS_4Cu_{10}Cl_{12}]^{4-}$.

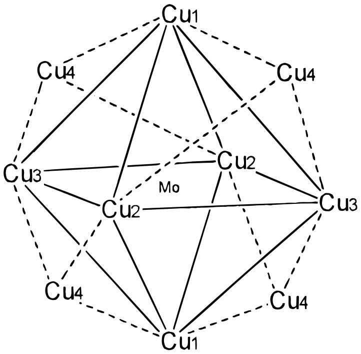

Figure 2. Schematic view of the $MoCu_{10}$ core formed by a central Mo, an octahedral Cu_6, and a tetrahedral Cu_4.

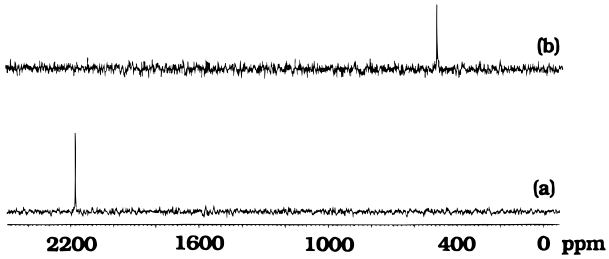

Figure 3. ^{95}Mo NMR spectra of (a) MoS_4^{2-} (2175 ppm) and (b) $[MoCu_{10}S_4Cl_{12}]^{4-}$ (505 ppm) in DMSO (Na_2MoO_4 as standard).

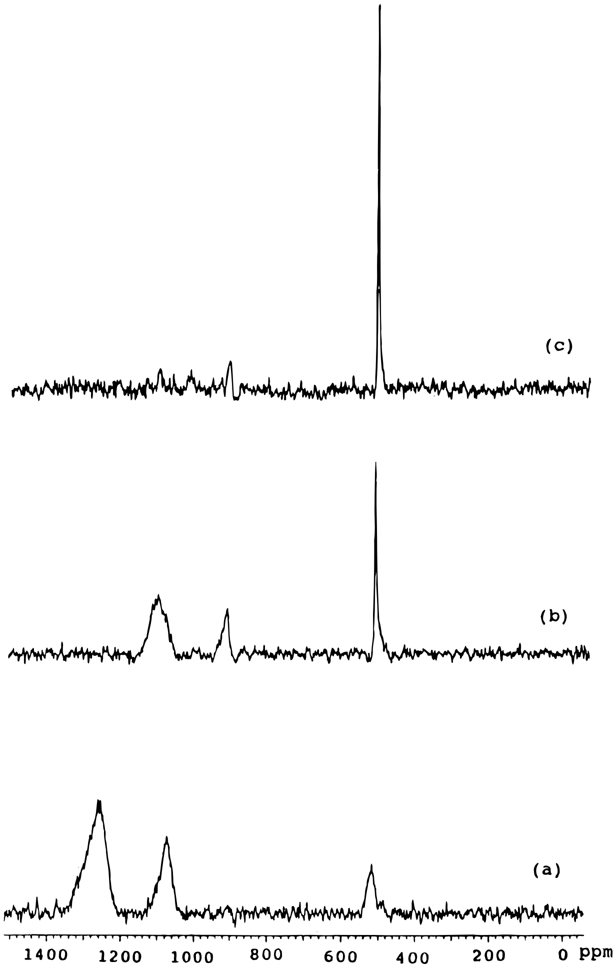

Figure 4. Dynamic ^{95}Mo NMR spectra for the reaction of MoS_4^{2-} and CuCl in DMSO/acac: (a) MoS_4^{2-} and CuCl in a ratio of 1:10 (1261, 1073, and 516 ppm); (b) mixture a + acac after 0.5 h (1104, 914, and 514 ppm); (c) mixture a + acac after 12 h (513 ppm) (Na_2MoO_4 as standard).

3000 (s), 1460 (s), 1191 (s), 800 (s); MoS_4, 434 (s). ^{95}Mo NMR (DMSO) (ppm): 507. Anal. Calcd for $C_{32}H_{80}N_4MoCu_{10}S_4Cl_{12}$: C, 21.26; H, 4.43; N, 3.10. Found: C, 21.48; H, 4.20; N, 3.26.

Instrumentation. ^{95}Mo NMR spectra were recorded on a Varian Unity-500 spectrometer. DMSO was used as solvent and Na_2MoO_4 as standard. IR spectra were measured on a Digilab 20E/D spectrophotometer.

Structure Determination. Suitable crystals for X-ray crystallographic examination were recrystallized from DMSO/THF. Determination of cell constants and data collection were carried out at room temperature on a Rigaku AFC5R four-circle diffractometer with Mo Kα radiation in the range $2 < 2\Theta < 46°$. A total of 3003 reflections were collected. Intensity data (1009 reflections with $I > 3\sigma(I)$) used for structure determination and refinement were corrected for empirical absorption (ψ-scan) and Lorentz−polarization effects. All calculations were performed on a VAX 11/785 computer with SDP program package. The structure was solved by direct methods. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to convergence. The crystallographic data are listed in Table 1, and the atomic coordinates and thermal parameters are given in Table 2 The selected bond distances and angles are in Table 3.

Results and Discussion

The reaction of $(NH_4)_2[MoS_4]$, Et_4NCl and CuCl in acac/DMSO gives rise to $(Et_4N)_4[MoS_4Cu_{10}Cl_{12}]$.

$$(NH_4)_2MoS_4 + 4Et_4NCl + 10CuCl \rightleftharpoons (Et_4N)_4[MoS_4Cu_{10}Cl_{12}] + 2NH_4Cl$$

Compared with other Mo−Cu−S complexes, the solvent and ratio of starting materials play important roles in the Mo−Cu−S reaction system, for instance, a ratio of MoS_4^{2-}: CuCl = 1:3 in CH_3CN affords $[MoS_4Cu_3Cl_3]^{2-}$ and $[MoS_4Cu_6Cl_9]^{5-}$, respectively,[3,6] while a ratio of 1:4 in $(CH_3)_2CO$ or CH_2Cl_2 gives $[MoS_4Cu_4Cl_4]^{2-}$.[4] For our reaction, a ratio of 1:10 in acac/DMSO yields the title compound.

The structure of anion $[MoS_4Cu_{10}Cl_{12}]^{4-}$, as shown in Figure 1, possesses a crystallographic D_2 and pseudo-T_d symmetry. The inner core is formed of a central MoS_4 tetrahedron encapsulated by six copper atoms across the edges of an S_4 tetrahedron, quite similar to that of the $[MoS_4Cu_6Cl_9]^{5-}$ anion.[6] The central MoS_4 retains the ideal geometry of free thiomolybdate, and the six copper atoms form a regular octahedral array. Then further addition of the other four copper atoms to $[MoS_4Cu_6]$ in a tetrahedral array by Cu−Cl−Cu bonding from four of the eight Cu_3 faces of the Cu_6 octahedron led to the title compound. The six copper atoms in the octahedral array are each in a slightly distorted tetrahedral environment formed by two sulfur atoms from MoS_4 and two bridge chlorides, while four copper atoms of the tetrahedral array are each in a triangular environment formed by three chlorine atoms. It also can been described that the four copper atoms in Cu_4 array are added from the directions of four faces of S_4 tetrahedron, while the six copper atoms of Cu_6 array are bound across the six edges of the S_4 tetrahedron. A drawing of $MoCu_{10}$ is shown in Figure 2.

The four Mo−S distances in the title compound are equal to 2.238(7) Å, which is slightly longer than the average value of 2.177(6) Å in $(Et_4N)_2MoS_4$.[10] S−Mo−S angles, ranging from 108.9(2) to 110.4(2)° with an average value of 109.4(2)°, are compatible to that of 109.47(37)° for $(Et_4N)MoS_4$. The average angles of S−Cu−S and S−Cu−Cl are 104.5(3) and 112.1(3)°, respectively. There are two sets of Cl−Cu−Cl angles: one is Cl−Cu(1,2,3)−Cl, ranging from 101.5(3) to 107.5(3)° with an average value of 104.5(3)°; the other is Cl−Cu(4)−Cl with an average value of 119.3(3)°. The IR spectrum shows that four identical ν_{Mo-S} stretching modes at 434 cm^{-1}, smaller than that (472 cm^{-1}) of $(NH_4)MoS_4$,[11] indicating that the regular atomic arrangement on the periphery of the cluster does not result in lowering of symmetry of the MoS_4 unit and that Mo−S bonds are weakened by bonding copper atoms.

The ^{95}Mo NMR technique was used to monitor the reaction process of MoS_4^{2-} and CuCl in DMSO. The anion $[MoS_4CuCl_{12}]^{4-}$ and starting material MoS_4^{2-} have resonance peaks at 507 and 2175 ppm, respectively (Figure 3). The resonance peak at 2175 ppm disappeared and three other peaks at 1261, 1073, and 516 ppm were observed after MoS_4^{2-} was mixed with CuCl in 10-fold excess (Figure 4a). By addition of acac, the first two, induced by $[MoS_4Cu_3Cl_3]^{2-}$ and $[MoS_4Cu_4Cl_4]^{2-}$ species,[12] gradually disappeared, while the third one, assigned to $[MoS_4Cu_{10}C_{12}]^{4-}$, heightened with time (Figure 4b), and finally only resonance peak at 513 ppm was observed (Figure 4c).

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Supporting Information Available: Tables listing crystallographic data, positional and thermal parameters, and significant bond distances and angles for $[MoS_4Cu_{10}Cl_{12}]^{4-}$ (5 pages). Ordering information is given on any current masthead page.

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