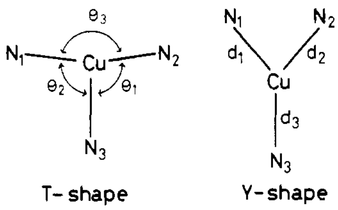

Figure 4. T- and Y-shaped complexes.

Solution and Refinement of the Structure. The positions of the copper atoms were obtained via direct methods using the MULTAN program. Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions, but their parameters were not refined. Finally two cycles of refinement led to convergence at $R = \sum[|F_o| - |F_c|]/\sum|F_o| = 0.0507$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_c|^2]^{1/2} = 0.0561$, $w = [\sigma^2(F) + (0.02F)^2]$, $S = 1.57$, and $\Delta e = 0.35$ e Å^{-3} for **1**, and the largest shift/esd at final cycle was 0.86. The fractional positional parameters for non-hydrogen atoms for **1** are given in Table II, and selected bond distances and angles are listed in Table III.

Results and Discussion

The overall structure of $[Cu(dmp)(CH_3CN)]ClO_4$ consists of two units, a $[Cu(dmp)(CH_3CN)]^+$ cation and uncoordinated ClO_4^- anion, as shown in Figure 1. The copper(I) complex is three-coordinate and has an approximately Y-shaped planar geometry. This is the second case of a three-coordinate Y-shaped copper(I) complex. The angles around copper, N(1)-Cu-N(2) = 82.9 (2)°, N(1)-Cu-N(3) = 139.0(3)°, and N(2)-Cu-N(3) = 137.7 (3)°, sum to 359.6 (3) Å, since the copper atoms lies 0.065 (1) Å from the plane defined by the three nitrogen atoms. The angle of 84.4 (3)° is much smaller than 120°, whereas two other angles, 139.0 (3) and 137.7 (4)°, are larger than 120°. Such a stereochemistry is unusual for copper(I) since trigonal planar is the preferred geometry of three-coordinate d^{10} metal complexes, and this must represent a compromise between ideality and the limits of stretch of the dmp ligand. Y-Shaped coordination probably offers rather little stabilization of copper compared with the regular sp^3 trigonal hybridization.

To our knowledge there is only one report of an acetonitrile for the three-coordinate copper(I) complex,[5b] where a Cu-N(CH_3CN) distance of 1.92 (2) Å is found. The present complex has a short Cu-N(CH_3CN) distance of 1.852 (7) Å. This is also remarkably short compared with the Cu-N(CH_3CN) distances (1.94-2.002 (3) Å) for four-coordinate copper(I) complexes[7] and (1.91 (5)-2.322 (4) Å) for five-coordinate copper(II) complexes.[8] The Cu-N(CH_3CN) distance is furthermore shorter than the those (1.890 (8)-2.295 (7) Å) reported for $[CuN_3]^+$ type complexes,[5,9] and the shorter end of the range (1.847 (17)-2.006 (22) Å) for the two-coordinate copper(I) complexes of $[CuN_2]^+$ type.[10] Thus, a short middle bond distance in a Y-shaped copper(I) structure is noteworthy. On the other hand, the other two Cu-N(dmp) distances of 2.015 (6) and 2.039 (7) Å are longer than the middle bond distance and can be compared with the range (1.890 (8)-2.295 (7) Å) for $[CuN_3]^+$ type complexes.[5,9] The structure of the hexafluorophosphate derivative $[Cu(dmp)(CH_3CN)]PF_6$ is essentially the same as that of the perchlorate derivative as shown in Figure 2.

It has been found for T-shaped copper(I) complexes that the middle bond distance is longer than the two terminal bond distances.[5,6] Figure 3 shows a plot of the difference in angles, $\Delta\theta$, against that in bond distances, Δd, in the three-coordinate copper(I) complexes with nitrogen donor atoms so far reported, where $\Delta\theta = (\theta_1 + \theta_2)/2 - \theta_3$ and $\Delta d = (d_1 + d_2)/2 - d_3$ (Figure 4). The positive value of $\Delta\theta$ increases as a copper(I) varies from regular trigonal-planar geometry to Y-shaped geometry, whereas the negative value increases as the copper(I) varies from the regular trigonal-planar geometry to T-shaped geometry. A good correlation between Δd and $\Delta\theta$ in Figure 3 demonstrates that the metal-donor atom distances depend on the bond angles around the copper in three-coordinate copper(I) complexes. For example, the middle bond distance, d_3, lengthens as the angle opposite the bond, θ_3, approaches 180° from 120° and shortens as θ_3 approaches 0° from 120°. A similar correlation can be expected for the series Y- and T-shaped copper(I) complexes with other donor atom sets[6] such as N_2O and N_2S.

Thus, the unusual bond angles in the three-coordinate copper(I) complexes with low symmetry such as Y- and T-shaped geometries are compensated for by regulating their bond distances.

Registry No. 1, 123148-39-0; 2, 123148-40-3; tetrakis(acetonitrile)-copper(I) perchlorate, 14057-91-1; tetrakis(acetonitrile)copper(I) hexafluorophosphate, 64443-05-6.

Supplementary Material Available: For $[Cu(dmp)(CH_3CN)]ClO_4$ and $[Cu(dmp)(CH_3CN)]PF_6$, tables of atomic parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and valence angles, and torsion angles (7 pages); tables of observed and calculated structure factors for $[Cu(dmp)(CH_3CN)]ClO_4$ and $[Cu(dmp)(CH_3CN)]PF_6$ (7 pages). Ordering information is given on any current masthead page.

---

(7) Csoeregh, I.; Kierkegaard, P.; Norrestam, R. *Acta Crystallogr.* **1975**, *B31*, 314. Gould, R. O.; Lavery, A. J.; Schroeder, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1492. Churchill, M. R.; Missert, J. R. *Inorg. Chem.* **1981**, *20*, 619. Lane, R. H.; Pantaleo, N. S.; Farr, J. K.; Coney, W. M.; Newton, M. G. *J. Am. Chem. Soc.* **1978**, *100*, 610. Willett, R. D.; Rundle, R. E. *J. Chem. Phys.* **1964**, *40*, 838.

(8) McKee, V.; Smith, J. *J. Chem. Soc., Chem. Commun.* **1983**, 1463. Bertrand, J. A.; Smith, J. H.; VanDerveer, D. G. *Inorg. Chem.* **1977**, *16*, 1477. Duffin, B. *Acta Crystallogr.* **1968**, *B24*, 396.

(9) (a) Gagnê, R. R.; Kreh, R. P.; Dodge, J. A.; Marsh, R. E.; McCool, M. *Inorg. Chem.* **1982**, *21*, 254. (b) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711.

(10) Englhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc. Dalton Trans.* 1985, 117. Munakata, M.; Kitagawa, S.; Shimono, H.; Masuda, H. *Inorg. Chim. Acta* **1989**, *158*, 217. Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013. Hendriks, H. M. J.; Birker, P. J. M. W. L.; van Rijin, J.; Verschoor, G. C.; Reedijk, J. *Ibid.* **1982**, *104*, 3607.

Contribution from the Fuzhou Laboratory of Structural
Chemistry and Fujian Institute of Research on the
Structure of Matter, Academia Sinica, Fuzhou,
Fujian, 350002 China

A Novel Polynuclear Mo-Cu Cluster from Tetrathiomolybdate: Preparation and Structure of $(Et_4N)_2[Mo_2Cu_5S_8(S_2CNMe_2)_3]\cdot 2H_2O$

Xinjian Lei, Zhiying Huang, Qiutian Liu, Maochun Hong, and Hanqin Liu*

Received September 29, 1988

Tetrathiomolybdate is a fundamental unit of some molybdoenzymes and exists in many biological systems.[1,2] It reacts with copper compounds to form various types of Mo-Cu-S complexes, such as $[MoS_4CuL]^{2-}$,[3] $[MoS_4(CuL)_2]^{2-}$,[3,4] $[MoS_4(CuL)_3]^{2-}$,[4,5]

---

(1) Coughlan, M. P., Ed. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon Press: New York, 1980.

(2) Spiro, T. G., Ed. *Molybdenum Enzymes*; Wiley: New York, 1985.

(3) (a) Acott, S. R.; Garner, C. D.; Nicholson, J. R.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1983**, 713. (b) Clark, R. J. H.; Joss, S.; Zvagulis, M.; Garner, C. D.; Nicholson, J. R. *J. Chem. Soc., Dalton Trans.* **1986**, 1595. (c) Sarkar, S.; Mishra, S. B. S. *Coord. Chem. Rev.* **1984**, *59*, 239. (d) Gheller, S. F.; Hambley, T. W.; Rodgers, J. R.; Brownlee, R. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Inorg. Chem.* **1984**, *23*, 2519. (e) Müller, A.; Dartmann, M.; Romer, C.; Legg, W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1060.

0020-1669/89/1328-4302$01.50/0

Table I. Crystallographic Data for $(Et_4N)_2[Mo_2Cu_5S_8(S_2CNMe_2)_3]\cdot 2H_2O$

chem formula: $Mo_2Cu_5S_{14}O_2N_5C_{25}H_{62}$
fw = 1423.28
a = 23.493 (6) Å
b = 17.353 (4) Å
c = 12.810 (4) Å
V = 5222.3 Å^3
Z = 4

space group: *Pnma* (No. 62)
T = 293 K
λ = 0.71073 Å
ρ_{calcd} = 1.810 g/cm^3
μ(Mo Kα) = 30.283 cm^{-1}
R(F_o) = 0.0535
$R_w(F_o)$ = 0.0743

Table II. Atomic Coordinates and Thermal Parameters for $(Et_4N)_2[Mo_2Cu_5S_8(S_2CNMe_2)_3]\cdot 2H_2O$

atom	x	y	z	B_{eq},[a] Å^2
Mo(1)	0.4880 (1)	0.2500 (0)	0.3179 (1)	2.86 (3)
Mo(2)	0.2624 (1)	0.2500 (0)	0.3494 (1)	2.58 (3)
Cu(1)	0.4432 (1)	0.1493 (1)	0.1877 (1)	3.70 (3)
Cu(2)	0.3403 (1)	0.1416 (1)	0.2922 (1)	3.68 (3)
Cu(3)	0.3126 (1)	0.2500 (0)	0.5360 (2)	4.06 (6)
S(1)	0.5632 (4)	0.2500 (0)	0.3809 (8)	10.5 (3)
S(2)	0.4962 (2)	0.2500 (0)	0.1399 (4)	3.7 (1)
S(3)	0.4392 (1)	0.1450 (2)	0.3631 (3)	3.51 (7)
S(4)	0.1732 (3)	0.2500 (0)	0.3240 (5)	5.7 (1)
S(5)	0.3148 (2)	0.2500 (0)	0.2003 (3)	3.4 (1)
S(6)	0.2861 (2)	0.1455 (2)	0.4417 (2)	3.36 (7)
S(11)	0.4223 (2)	0.0592 (2)	0.0744 (3)	4.85 (9)
S(12)	0.3342 (2)	0.0177 (2)	0.2376 (3)	4.28 (8)
S(21)	0.3971 (2)	0.2500 (0)	0.6353 (4)	4.9 (1)
S(22)	0.2819 (3)	0.2500 (0)	0.7171 (4)	5.0 (1)
N(1)	0.3765 (5)	−0.0768 (6)	0.0987 (9)	4.7 (3)
N(2)	0.3729 (8)	0.2500 (0)	0.840 (1)	6.3 (5)
N(3)	0.1339 (4)	0.0221 (6)	0.1507 (8)	4.4 (3)
C(11)	0.3782 (5)	−0.0049 (7)	0.1368 (9)	3.1 (3)
C(12)	0.4174 (7)	−0.1055 (9)	0.016 (1)	6.3 (4)
C(13)	0.3349 (7)	−0.1327 (8)	0.138 (1)	6.1 (4)
C(21)	0.3534 (9)	0.2500 (0)	0.740 (2)	4.4 (5)
C(22)	0.434 (1)	0.2500 (0)	0.860 (2)	8.5 (8)
C(23)	0.337 (1)	0.2500 (0)	0.931 (2)	8.2 (8)
C(31)	0.1129 (6)	−0.0068 (9)	0.044 (1)	5.3 (4)
C(32)	0.1707 (6)	−0.0428 (9)	0.195 (1)	5.4 (4)
C(33)	0.0843 (7)	0.044 (1)	0.223 (1)	7.7 (5)
C(34)	0.1675 (8)	0.0978 (9)	0.140 (1)	7.9 (5)
C(35)	0.0760 (6)	0.052 (1)	−0.017 (1)	5.9 (4)
C(36)	0.1909 (6)	−0.032 (1)	0.313 (1)	6.5 (4)
C(37)	0.0459 (7)	−0.026 (1)	0.250 (1)	8.9 (6)
C(38)	0.2163 (8)	0.090 (1)	0.057 (1)	9.4 (6)
O(1)	0.1368 (7)	0.2500 (0)	−0.105 (1)	6.9 (4)*
O(2)	0.448 (1)	0.811 (1)	0.283 (2)	8.3 (6)*

[a] Asterisks denote atoms refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as $B_{eq} = {}^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. The multiplicity of O(2) is 0.5.

and $[MoS_4(CuL)_4]^{2-}$.[6] The bidentate ligand dialkyldithiocarbamate (R_2dtc) coordinates well with many transition metals. Liu et al. have synthesized a series of single $[MoFe_3S_4]$ "cubanes" containing R_2dtc in both terminal and bridging modes.[7] We have also been interested in the Mo–Cu–dtc systems, and the series of compounds $[MS_4Cu_3(R_2dtc)_3]^{2-}$ (M = Mo, W; R_2 = Et_2, C_5H_{10}),[8] $[M_2Cu_5S_8(Me_2dtc)_3]^{2-}$ (M = Mo, W),[9] and $[M_2Cu_5S_6O_2(Et_2dtc)_3]^{2-}$ (M = Mo, W)[9] have been synthesized in this laboratory. Here we report the novel cluster compound $[Et_4N]_2[Mo_2Cu_5S_8(Me_2dtc)_3]\cdot 2H_2O$ consisting of two defective cubanes, $MoCu_2S_4$ and $MoCu_3S_4$, joined together by two R_2dtc bridges and two weak Cu–S bonds.

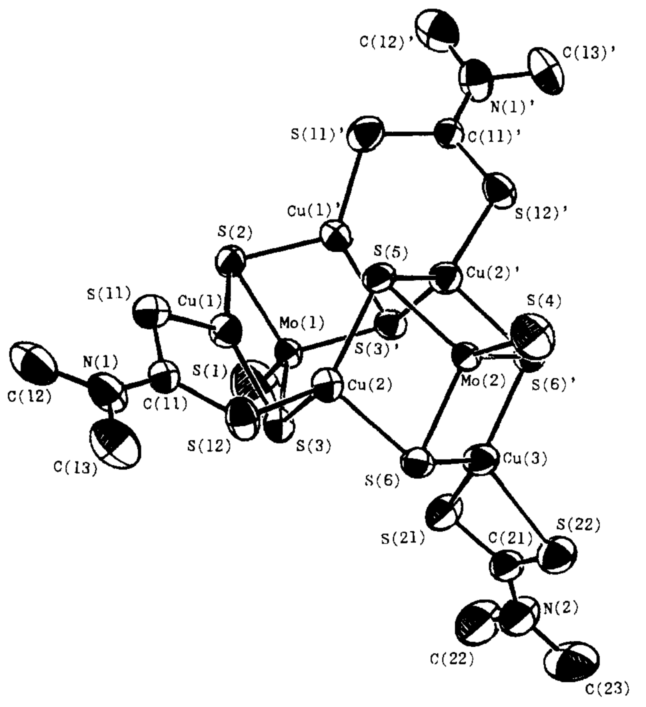

Figure 1. Perspective view of the anion $[Mo_2Cu_5S_8(S_2CNMe_2)_3]^{2-}$.

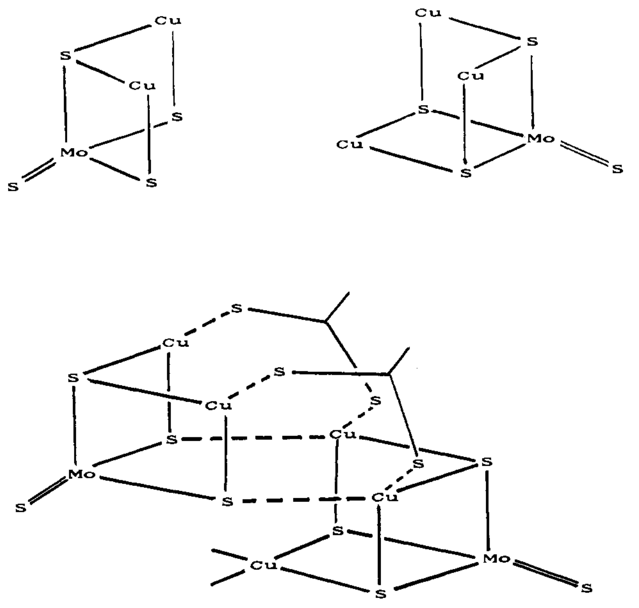

Figure 2. Schematic view of the $Mo_2Cu_5S_8$ core formed by two defective "cubane" units.

Experimental Section

All operations were carried out under a pure dinitrogen atmosphere. Me_2dtcNa and $[Et_4N]_2MoS_4$ were synthesized according to literature methods.[10] CuCl was purchased from Beijing Hongxin Huagong Chang. Solvents were dried, distilled, and degassed before use.

Preparation of $[Et_4N]_2[Mo_2Cu_5S_8(S_2CNMe_2)_3]\cdot 2H_2O$. A mixture of 1.5 g (15 mmol) of CuCl, 2.1 g (15 mmol) of NaS_2CNMe_2, and 2.4 g (5 mmol) of $[Et_4N]_2MoS_4$ was dissolved in 80 mL of DMF and stirred at room temperature. The rose red solution gradually turned dark. After it was stirred for 24 h, the solution was filtered and 50 mL of Et_2O was added to the filtrate. When this filtrate stood for several days, a red precipitate separated. This was filtered, and 30 mL of THF was added to induce further crystallization. A violet-black crystalline solid was

---

(4) (a) Jin, X.; Tang, K.; Tong, L.; Tang, Y. *Ziran Zazhi* **1984**, *7*, 314. (b) Müller, A.; Bogge, H.; Schimanski, U. *Inorg. Chim. Acta* **1983**, *69*, 5.

(5) (a) Müller, A.; Schimanski, U.; Schimanski, J. *Inorg. Chim. Acta* **1983**, *76*, L245. (b) Potvin, C.; Manoli, J. M.; Solis, M.; Secheresse, F. *Inorg. Chim. Acta* **1984**, *83*, L19.

(6) Nicholson, J. R.; Flood, A. C.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1179.

(7) (a) Liu, Q. T.; Huang, L. R.; Kang, B. S.; Yang, Y.; Lu, J. X. *Huaxue Xuebao* **1987**, *45*, 133 and references within. (b) Liu, Q. T.; Huang, L. R.; Liu, H. Q.; Lei, X. J.; Kang, B. S.; Lu, J. X. Submitted for publication in *Inorg. Chem.*

(8) (a) Lei, Xinjian; Liu, Qiutian; Liu, Hanqin. *Jiegou Huaxue* **1988**, *7*, 99. (b) Huang, Z. Y.; Lei, X. J.; Kang, B. S.; Liu, J. N.; Liu, Q. T.; Hong, M. C.; Liu, H. Q. To be submitted for publication.

(9) Liu, H. Q.; Cao, R.; Lei, X. J. Work in progress.

(10) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.

Table III. Selected Atomic Distances (Å) for the Anion $[Mo_2Cu_5S_8(S_2CNMe_2)]^{2-}$

Mo(1)–Cu(1)	2.636 (1)	Mo(2)–Cu(3)	2.664 (2)
Mo(2)–Cu(2)	2.725 (1)	Cu(1)–Cu(2)	2.765 (2)
Cu(1)–Cu(1)′	3.495 (1)	Cu(2)–Cu(3)	3.703 (2)
Cu(2)–Cu(2)′	3.762 (1)		
Mo(1)–S(1)	1.942 (7)	Mo(2)–S(4)	2.123 (4)
Mo(1)–S(2)	2.289 (4)	Mo(2)–S(5)	2.273 (3)
Mo(1)–S(3)	2.229 (2)	Mo(2)–S(6)	2.235 (2)
Cu(1)–S(2)	2.231 (2)	Cu(2)–S(12)	2.265 (3)
Cu(1)–S(3)	2.251 (3)	Cu(2)–S(3)	2.495 (3)
Cu(1)–S(11)	2.189 (3)	Cu(3)–S(6)	2.266 (3)
Cu(2)–S(5)	2.300 (2)	Cu(3)–S(21)	2.360 (4)
Cu(2)–S(6)	2.301 (3)	Cu(3)–S(22)	2.430 (4)

Table IV. Selected Bond Angles (deg) for the Anion $[Mo_2Cu_5S_8(S_2CNMe_2)_3]^{2-}$

S(1)–Mo(1)–S(2)	109.7 (3)	S(4)–Mo(2)–S(5)	114.0 (2)
S(1)–Mo(1)–S(3)	111.2 (1)	S(4)–Mo(2)–S(6)	109.1 (1)
S(2)–Mo(1)–S(3)	107.6 (1)	S(5)–Mo(2)–S(6)	108.1 (1)
S(3)–Mo(1)–S(3)′	109.6 (1)	S(6)–Mo(2)–S(6)′	108.5 (1)
S(2)–Cu(1)–S(3)	108.8 (1)	S(5)–Cu(2)–S(12)	127.0 (1)
S(2)–Cu(1)–S(11)	120.2 (1)	S(6)–Cu(2)–S(12)	104.5 (2)
S(3)–Cu(1)–S(11)	129.0 (1)	S(6)–Cu(3)–S(21)	121.3 (1)
S(3)–Cu(2)–S(5)	114.2 (2)	S(6)–Cu(3)–S(22)	115.3 (1)
S(3)–Cu(2)–S(6)	102.3 (1)	S(6)–Cu(3)–S(6)′	106.3 (1)
S(3)–Cu(2)–S(12)	101.3 (1)	S(21)–Cu(3)–S(22)	74.6 (1)
S(5)–Cu(2)–S(6)	105.0 (2)		
Mo(1)–S(2)–Cu(1)	71.3 (1)	Mo(2)–S(5)–Cu(2)	73.2 (1)
Cu(1)–S(2)–Cu(1)	103.1 (1)	Cu(2)–S(5)–Cu(2)	109.8 (2)
Mo(1)–S(3)–Cu(1)	72.1 (1)	Mo(2)–S(6)–Cu(2)	73.8 (1)
Mo(1)–S(3)–Cu(2)	113.8 (1)	Mo(2)–S(6)–Cu(3)	72.6 (1)
Cu(1)–S(3)–Cu(2)	71.1 (1)	Cu(2)–S(6)–Cu(3)	108.3 (1)
Cu(1)–S(11)–C(11)	106.8 (3)	Cu(3)–S(21)–C(21)	85.0 (5)
Cu(2)–S(12)–C(11)	114.5 (3)	Cu(3)–S(22)–C(21)	82.5 (5)

found and collected. This was washed with 1:4 (v/v) DMF–THF and dried in vacuo to afford 1.5 g (35%) of product. The IR spectrum (KBr) shows a characteristic Mo═S_t absorption at 513 cm^{-1} and Mo–S_b absorptions at 455, 444, and 422 cm^{-1}. Anal. calcd for $C_{25}H_{62}Cu_5Mo_2N_5O_2S_{14}$: C, 21.10; H, 4.40; Cu, 22.32; Mo, 13.48; N, 4.92; S, 31.54. Found: C, 20.62; H, 4.93; Cu, 21.62; Mo, 13.25; N, 4.93; S, 30.54. Elemental analyses were performed by the Analytical Chemistry Group of this institute.

Instrumentation. Proton NMR spectra were recorded on a Varian FT-80A spectrometer. DMSO-d_6 was used as solvent and TMS as internal standard with positive values given to downfield shifts. IR spectra were recorded on a Digilab-20E/D spectrophotometer.

Structure Determination. Diffraction data for the title compound were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The single crystal of the title compound was kept from air by a coating of epoxy resin. An empirical absorption correction (ψ scan) was applied. After data reduction (including correction for Lorentz and polarization effects), the remaining unique reflections with $I > 3\sigma(I)$ were used for the subsequent structure solution and refinement. Calculations were performed on a VAX 11/785 computer with the SDP program package. All metal atoms were located from an E map. A Fourier map phased by the metal atoms contained most of the remaining non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms except oxygen atoms led to convergence. Crystallographic data appear in Table I, and the atomic coordinates and thermal parameters are listed in Table II.

Results and Discussion

Since there are four formula units per unit cell and eight general positions, each $[Mo_2Cu_5S_8(S_2CNMe_2)_3]^{2-}$ anion is situated about a crystallographic mirror plane: atoms Mo(1), Mo(2), Cu(3), S(1), S(2), S(4), and S(5) are located on the mirror plane. The structure of the anion is depicted in Figure 1. Another view is shown in Figure 2. The $Mo_2Cu_5S_8$ framework consists of the two cubane-like units $[SMoS_3Cu_2]$ (I) and $[SMoS_3Cu_3]$ (II). These two units are similar to the cores in the compounds $[OMoS_3(CuPPh_3)Cu(PPh_3)_2]$ and $[OMoS_3(CuCl)_3]^{2-}$, respectively.[5] They are linked through two weak Cu–S bonds (Cu(2)–S(3) and Cu(2)′–S(3)′ = 2.495 (3) Å), and the two sets of copper atoms Cu(1)–Cu(2) and Cu(1)′–Cu(2)′ are connected by bridging Me_2dtc ligands. Tables III and IV list the main atomic distances and main bond angles, respectively.

Structure analysis shows that each of the two molybdenum atoms is in an S_4 tetrahedral center. The average bond angle of S–Mo–S for both units is 109.7 (20)°. However, the values of Mo–S distances vary, with the terminal Mo–S bond as the shortest, i.e. 1.942 (7) and 2.123 (4) Å in units I and II, respectively. From a structural point of view, there are three kinds of Cu atoms in this molecule: (a) atoms Cu(1) and Cu(1)′ are essentially in the center of the trigonal planes of S(2), S(3), S(11) and S(2), S(3)′, S(11)′, respectively; (b) atoms Cu(2) and Cu(2)′ are each in a slightly distorted tetrahedral environment; (c) atom Cu(3) is in the center of a highly distorted tetrahedron of atoms S(6), S(6)′, S(21), and S(22) with an angle S(21)–Cu(3)–S(22) of 74.6 (1)°, which is a normal chelate angle for $M(R_2dtc)$. Each of the six bridging sulfur atoms is triply connected. The three Me_2dtc ligands are of two types: two of these are bridging ligands connecting two copper atoms, Cu(1)–Cu(2) and Cu(1)′–Cu(2)′; the third is a terminal ligand chelating to atom Cu(3).

The title compound is diamagnetic from the magnetic susceptibility measurement. The ^1H NMR signal of CH_3– in Me_2dtc exhibits no paramagnetic broadening. The chemical shifts of $-N(CH_3)_2$ in all three Me_2dtc ligands are 3.5 ppm in DMSO-d_6 at room temperature.

The fact that the IR spectrum of the title compound is more complicated than that of $[MoS_4Cu_3(R_2dtc)_3]^{2-}$[8] in the region of 400–500 cm^{-1} is an indication of several different Mo–S_b absorptions. The absorption at 513 cm^{-1} is a characteristic stretching of the terminal Mo═S_t bond.

Acknowledgment. This work was supported by a National Natural Science Foundation Grant and by a Provincial Science Fund of Fujian.

Supplementary Material Available: A listing of the crystallographic data, full listings of atomic distances and bond angles, a listing of anisotropic thermal parameters, a view of the packing scheme in the unit cell, and an IR spectrum (6 pages); a listing of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry,
Lanzhou University, Lanzhou Gansu, PRC,
and Northwestern University, Evanston, Illinois 60208

Kinetics and Mechanism of Carbon Monoxide Substitution of Osmium Pentacarbonyl

Jian-Kun Shen,[†] Yi-Ci Gao,[†] Qi-Zhen Shi,[*,†] and Fred Basolo[*,‡]

Received February 24, 1989

Although osmium pentacarbonyl has been known[1] for more than four decades, no kinetic data have been reported on its rate of carbon monoxide substitution. With reference to early observations[2] that for a given transition-metal triad the organometallic complexes of the second-row metals are the most substitution labile, it is of interest to compare the rates of CO substitutions of the carbonyls $M(CO)_5$ (M = Fe, Ru, Os). Kinetic data are available for the rate of CO exchange of $Fe(CO)_5$,[3] for CO

[†] Lanzhou University.

[‡] Northwestern University.