Inorganica Chimica Acta, *169* (1990) 25–29

Heteronuclear W(Mo)–Cu–S Complexes of Dialkyldithiocarbamate. Syntheses of $(Et_4N)_2[MCu_3S_4(dtcR_2)_3]$ and Structures of $(Et_4N)_2[MCu_3S_4(dtcC_5H_{10})_3]\cdot DMF$ (M = W or Mo)

ZHIYING HUANG, XINJIAN LEI, BEISHENG KANG*, JIANGNAN LIU, QIUTIAN LIU, MAOCHUN HONG
and HANQIN LIU

Fuzhou Laboratory of Structural Chemistry and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002 (China)

(Received May 18, 1989)

Abstract

Compounds $(Et_4N)_2[MCu_3S_4(dtcR_2)_3]$ (M = W (1) or Mo (2); $R_2 = C_5H_{10}$ (a), Et_2 (b) or C_4H_8 (c) were synthesized by the reaction of $(Et_4N)_2MS_4$ and CuCl in the presence of $NadtcR_2$ in DMF. The crystal and molecular structures of 1a·DMF and 2a·DMF were determined from X-ray diffraction data. The compounds are isomorphous and crystallize in the triclinic space group $P\bar{1}$ with unit cell parameters for 1a(2a)·DMF: $a = 12.047(0)$ (12.053(2)), $b = 17.620(3)$ (17.650(5)), $c = 14.514(1)$ (14.533(4)) Å; $\alpha = 100.83(9)$ (100.43(3)), $\beta = 115.41(3)$ (115.47(2)), $\gamma = 79.49(8)$ (79.78(2))°; $V = 2715.9$ (2727.8) Å^3, $Z = 2$ (2), and $D_x = 1.611$ (1.497) g/cm^3. The final R values converged to 0.048 and 0.067 for M = W and Mo respectively.

The four metal atoms MCu_3 are coplanar with the central tetrahedron of MS_4 preserved. Each Cu(I) ion is coordinated to two inorganic S atoms from MS_4 and two organic S atoms from one $dtcC_5H_{10}$ ligand in a distorted tetrahedral geometry. Infrared spectra showed two stretching vibrations at 430–442 cm^{-1} for μ_3-S–M and 455–463 cm^{-1} for μ_2-S–M. The compounds are diamagnetic and show reversible one-electron oxidation–reduction at $E_{1/2} = 0.55$ V (2a).

Introduction

Transition-metal compounds have become an interesting series of complexes for their relevance to biological systems. It is well known, for example, that the Mo–Cu antagonism in nature results in copper deficiency of ruminants grazing on molybdenum-rich pastures owing to the formation of Cu–Mo protein [1, 2]. Di-, tri-, and tetranuclear mixed metal M–Cu–S clusters (M = Mo, W) have been studied extensively with the $[MS_4]$ core skeleton preserved [3–5]. However, the ligands involved in the aforementioned complexes are monodentate with either S, N, P or As as the chelating atom. It would be of interest to know what the molecular structures and physical and chemical properties of the resultant M–Cu–S complexes would be if bidentate ligands were employed.

In an extensive study of Mo–Fe–S cluster compounds with dialkyldithiocarbamate ligands ($dtcR_2$), a series of compounds $[MFe_3S_4(dtcR_2)_5]^{n-}$ (3) (M = Mo [6–9], $R_2 = Me_2$, Et_2, C_4H_8, C_5H_{10}; M = W [10], R = Et; $n = 0, 1$) with the cubane-like $[MFe_3S_4]$ core unit have been obtained. When CuCl was used instead of $FeCl_2$, cluster compounds with similar anion formulation $[MCu_3S_4(dtcR_2)_3]^{2-}$ (M = W (1) or Mo (2); $R_2 = C_5H_{10}$ (a), Et_2 (b) or C_4H_8 (c)) but with the planar $[MCu_3]$ arrangement were isolated as $[Et_4N]^+$ salts.

Interestingly enough, if Me_2dtc was employed in the preparation reaction, heptanuclear cluster compounds $(Et_4N)_2[M_2Cu_5S_8(dtcMe_2)_3]$ (M = Mo or W) were formed, one of which has been reported elsewhere [11]. In this paper studies on isomorphous compounds $(Et_4N)_2[MCu_3S_4(dtcC_5H_{10})_3]$ (M = W (1a); M = Mo (2a) [12] are reported.

Experimental

All operations were performed under an atmosphere of dinitrogen. A Schlenk type apparatus was used throughout the reactions. All solvents used were dried with molecular sieves and distilled over appropriate drying agents under nitrogen. DMF was distilled under reduced pressure.

Reagents Et_4NBr and anhydrous CuCl are commercially available. Compounds $(NH_4)_2MS_4$ [13], $(Et_4N)_2MS_4$ [14] and sodium dialkyldithiocarbamate [15] (NaS_2NCR_2, $R_2 = C_5H_{10}$, Et_2, C_4H_8) were obtained by literature methods. To the vigorously stirred solution of R_2NH (0.5 mol) and NaOH (0.5 mol) in 60 ml of H_2O an equal amount of CS_2 was added dropwise while maintaining the temperature at

---

*Author to whom correspondence should be addressed.

0020-1693/90/$3.50

5 °C. During this period snow-white flakes of the product $NadtcR_2$ began to appear and the duration of the reaction depended upon the substituent R of the dialkylamines used. All $NadtcR_2$ ligands have a characteristic C–N absorption at 1490–1550 cm^{-1}. Infrared spectra were obtained on a Perkin-Elmer 577 spectrophotometer. UV–Vis spectra were recorded on a Shimazu UV-300 spectrophotometer in 1 cm quartz cells. ^1H NMR spectra were recorded in the Fourier Transform mode on a Varian FT-80A spectrometer with TMS as internal standard. Cyclic voltammetry was performed in a trielectrode cell with SCE reference electrode, Pt plate working electrode with surface area of 0.12 cm^2 and Pt auxiliary electrode of a coil of 2.6 cm in diameter. The supporting electrolyte was Bu_4NBF_4 (0.1 M) and the sample was dissolved in CH_2Cl_2 solution (2–3 × 10^{-3} M). The scan rate was 100 mV/s.

Preparation of $(Et_4N)_2[WCu_3S_4(dtcC_5H_{10})_3]$ (1a)

A solution of 0.70 g (1.2 mmol) of $(Et_4N)WS_4$ and 0.50 g (5 mmol) of CuCl was stirred in 40 ml of DMF overnight at room temperature. The color of the solution changed from orange–yellow to orange–red and a small amount of orange–red precipitate appeared. Solid $NaS_2CNC_5H_{10}$ (1.46 g, 7.9 mmol) was added at this stage and the reaction solution turned immediately dark reddish and the precipitates dissolved within a few hours. Stirring was continued for 24 h and THF was added to precipitate the inorganic salts. The solution was filtered after several such operations and the filtrate was kept at 5 °C for a week to give large red crystals of **1a**. ν (KBr): 430, 455 (W–S), 1465 (C–N) cm^{-1}.

Compounds $(Et_4N)_2[WCu_3S_4(dtcR_2)_3]$ where $R_2 = Et_2$ (**1b**) and C_4H_8 (**1c**) were similarly synthesized and their IR spectra compared with **1a** indicating the presence of the same WCu_3S_4 core unit.

Preparation of $(Et_4N)_2[MoCu_3S_4(dtcC_5H_{10})_3]$ (2a)

A mixture of 1.5 g (15 mmol) of CuCl, 2.4 g (5 mmol) of $(Et_4N)_2MoS_4$ and 5.5 g (30 mmol) of $NadtcC_5H_{10}$ in 60 ml of DMF was stirred at room temperature for 25 h. The dark purplish filtrate obtained was mixed with an equal amount of benzene and allowed to stand at room temperature for separation of inorganic salts. After filtration of the inorganic salts, the filtrate was again mixed with 20 ml of benzene and stored at 4 °C to ensure crystallization of dark crystals of **2a** which were often contaminated with a small amount of red precipitate. Crystals suitable for X-ray diffraction studies and IR spectroscopy were manually selected. ν (KBr): 463, 442 (Mo–S), 1470 (C–N) cm^{-1}.

Preparation of $(Et_4N)_2[MoCu_3S_4(dtcEt_2)_3]$ (2b)

A mixture of 1.5 g (15 mmol) of CuCl, 2.4 g (5 mmol) of $(Et_4N)_2MoS_4$ and 5.1 g (30 mmol) of $NadtcEt_2$ in 60 ml of DMF was reacted at room temperature for 24 h. The dark purple solution was filtered and to the filtrate was added an equal amount of Et_2O. Large quantities of product separated as purplish black crystals after several days at 4 °C. The compound **2b** was filtered and washed with DMF/Et_2O (vol./vol. = 1/2) and dried *in vacuo*. A further crop of **2b** was obtained when the filtrate and wash were again mixed with 20 ml of Et_2O. The yield was 65%. *Anal.* Calc. for $C_{31}H_{70}N_5S_{10}Cu_3Mo$: C, 33.27; H, 6.26; N, 6.26; S, 28.67; Cu, 17.05; Mo, 8.47%. Found: C, 32.65; H, 5.89; N, 6.86; S, 28.14; Cu, 17.90; Mo, 7.80%. ν (KBr): 463, 436 (Mo–S), 1470 (C–N) cm^{-1}.

$(Et_4N)_2[MoCu_3S_4(dtcC_4H_8)_3]$ (2c) was similarly prepared. The infrared spectrum indicated the compound to have the same core structure but with a small amount of impurities.

Intensity Data Collection and Solution and Refinement of Structures

Dark red (M = W) or purplish black (M = Mo) air sensitive single crystals of the compounds **1a**·DMF and **2a**·DMF were obtained directly from the reaction solution and coated with epoxy resin. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The parameters utilized in intensity collection and refinement are summarized in Table 1 together with the crystal data. Calculations

TABLE 1. Summary of crystal data, intensity collection and structure refinement parameters for compounds $(Et_4N)_2$-$[MCu_3S_4(dtcC_5H_{10})_3]$·DMF

Data	Compound	
	1a·DMF	**2a**·DMF
Formula	$C_{37}H_{77}N_6OS_{10}Cu_3W$	$C_{37}H_{77}N_6OS_{10}Cu_3Mo$
M_r	1317.2	1229.3
a (Å)	12.047(0)	12.053(2)
b (Å)	17.620(3)	17.650(5)
c (Å)	14.514(1)	14.533(4)
Crystal system	triclinic	triclinic
α (°)	100.83(9)	100.43(3)
β (°)	115.41(3)	115.47(2)
γ (°)	79.49(8)	79.78(2)
V (Å^3)	2715.9	2727.8
Z	2	2
D_x (g/cm^3)	1.611	1.497
Space group	$P\bar{1}$	$P\bar{1}$
Unique data ($I > 3\sigma(I)$)	5063	4251
R	0.048	0.067
R_w	0.063	0.085
$F(000)$	1340	1322

TABLE 2. Atomic coordinates and thermal parameters for anion $[WCu_3S_4(dtcC_5H_{10})_3]^{2-}$

Atom	x	y	z	B_{eq} ($Å^2$)[a]
W	0.18370(3)	0.22053(2)	0.46591(3)	2.29(1)
Cu(1)	−0.0213(1)	0.2538(1)	0.5018(1)	4.00(4)
Cu(2)	0.0304(1)	0.1620(1)	0.2819(1)	4.18(4)
Cu(3)	0.2934(1)	0.2802(1)	0.6622(1)	4.05(4)
S(1)	0.0479(2)	0.1380(2)	0.4346(2)	3.24(7)
S(2)	0.1218(2)	0.3346(2)	0.5363(2)	3.30(7)
S(3)	0.1878(2)	0.2338(2)	0.3205(2)	3.72(7)
S(4)	0.3677(2)	0.1771(2)	0.5742(2)	3.56(7)
S(5)	−0.2420(2)	0.2903(2)	0.4089(2)	3.65(7)
S(6)	−0.1079(2)	0.2610(2)	0.6223(2)	4.11(8)
S(7)	−0.1755(3)	0.2220(2)	0.1611(2)	4.39(9)
S(8)	−0.0389(3)	0.0703(2)	0.1407(2)	4.57(9)
S(9)	0.4052(3)	0.3609(2)	0.8038(2)	4.16(8)
S(10)	0.2907(3)	0.2338(2)	0.8161(2)	5.95(9)
N(1)	−0.3537(7)	0.2945(6)	0.5328(6)	4.3(3)
N(2)	−0.2392(9)	0.1245(6)	−0.0109(7)	5.1(3)
N(3)	0.4339(8)	0.3207(6)	0.9806(7)	5.0(3)
C(11)	−0.2471(9)	0.2833(6)	0.5209(8)	3.5(3)
C(12)	−0.4748(9)	0.3112(8)	0.4481(9)	4.9(4)
C(13)	−0.528(1)	0.3934(8)	0.473(1)	6.0(4)
C(14)	−0.538(1)	0.4047(9)	0.575(1)	6.6(4)
C(15)	−0.412(1)	0.3833(8)	0.6589(9)	6.5(4)
C(16)	−0.360(1)	0.2978(8)	0.6344(9)	5.5(4)
C(21)	−0.1573(9)	0.1399(6)	0.0860(7)	3.4(3)
C(22)	−0.233(1)	0.0488(8)	−0.0761(9)	5.9(4)
C(23)	−0.216(1)	0.0651(9)	−0.170(1)	7.0(5)
C(24)	−0.324(1)	0.125(1)	−0.2297(9)	7.9(5)
C(25)	−0.325(1)	0.1998(8)	−0.1565(9)	7.4(4)
C(26)	−0.342(1)	0.1830(8)	−0.0653(9)	5.8(4)
C(31)	0.3824(9)	0.3051(7)	0.8778(8)	3.9(3)
C(32)	0.516(1)	0.3834(8)	1.0376(9)	5.8(4)
C(33)	0.476(2)	0.4328(9)	1.114(1)	8.2(5)
C(34)	0.465(1)	0.3839(9)	1.189(1)	7.2(5)
C(35)	0.385(1)	0.3214(9)	1.129(1)	7.6(5)
C(36)	0.429(1)	0.2709(8)	1.0509(9)	7.6(4)

[a] Values of B_{eq} are the isotropic equivalent thermal parameters defined as: $B_{eq} = (4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab\cos\gamma B_{1,2} + ac\cos\beta B_{1,3} + bc\cos\alpha B_{2,3}]$.

were performed on a VAX-11/785 computer with the SDP program package.

The intensity data collected were corrected for LP factors and empirical absorptions. The structures were solved by the heavy atom method and difference Fourier techniques to locate all non-hydrogen atoms. The structures were then refined by full-matrix least-squares procedures with anisotropic temperature factors for the anion and isotropic thermal parameters for the cations. The final factors of convergence are also listed in Table 1. Table 2 lists the atomic coordinates and displacement thermal parameters for the anion of **2a**.

Results and Discussion

Whether through stepwise addition (eqn. (1)) or the one-pot reaction (eqn. (2)) of starting materials, the tetranuclear compound **1a** or **2a** was obtained as the only isolable product.

$$(Et_4N)_2WS_4 + 3CuCl \xrightarrow{DMF} (Et_4N)_2[WCu_3S_4Cl_3] \xrightarrow{NadtcC_5H_{10}} \underset{\mathbf{1a}}{(Et_4N)_2[WCu_3S_4(dtcC_5H_{10})_3]} \qquad (1)$$

$$(Et_4N)_2MoS_4 + 3CuCl + 3NaS_2CNC_5H_{10} \xrightarrow{DMF} \underset{\mathbf{2a}}{(Et_4N)_2[MoCu_3S_4(dtcC_5H_{10})_3]} \qquad (2)$$

Compounds $[MCu_3S_4L_3Cl]$ with a planar MCu_3 arrangement have been reported [16] where L is the monodentate ligand $AsPh_3$ or PPh_3 with the atom Cu in trigonal geometry. Compounds **1a** and **2a** are the first $[MCu_3S_4L_3]^{2-}$ compounds in which L is a dithiocarbamate group coordinated bidentally to the Cu atom resulting in a distorted tetrahedral environment for copper due to the small bite angle of the group $dtcR_2$ (*vide infra*).

Selected bond distances and bond angles for anions of compounds **1a** and **2a** are listed in Tables 3 and 4, respectively. Only the structure of the anion of **1a** is depicted in Fig. 1 as the two compounds are isomorphous. In the anion $[MCu_3S_4(dtcC_5H_{10})_3]^{2-}$, the tetrahedral arrangement of MS_4 is essentially retained with slight distortion and lengthening of the M–S bonds due to coordination to the group $CudtcC_5H_{10}$. The four S atoms in MS_4 are of two types: two μ_2-S bridging atoms Cu and M and two μ_3-S bridging two Cu atoms to M. The difference between atoms μ_2-S and μ_3-S is also shown by IR absorptions. The weaker (μ_3-S)–M bonds have lower frequencies at 430 (**1a**) or 442 (**2a**) cm^{-1} and the stronger (μ_2-S)–M bonds absorb 20–25 cm^{-1} upfield at 455 (**1a**) or 463 (**2a**) cm^{-1} while both are lower than that in $(NH_4)_2MS_4$ (Mo–S, 472 cm^{-1} [3]; W–S, 460 cm^{-1} [14]). The MCu_3S_4 core is composed of three edge sharing planar MS_2Cu rhombs with the dihedral angle ranging from 65.6–67.6° while the four metal atoms lie in a plane and the four S atoms are either above or below it. There is an open site at (μ_2-S)–M–(μ_2-S) with an angle between 110.7–111.0° which is the larger S–M–S angle and should allow insertion of a fifth metal atom of appropriate size. We have thus obtained a pentanuclear compound with a $[WCu_4S_4]$ core by reaction of **1a** with CuCl [17].

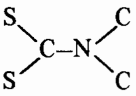
TABLE 3. Selected atomic distances (Å) for anion $[MCu_3S_4(dtcC_5H_{10})_3]^{2-}$

Atomic distance (Å)	M = W	M = Mo
M–Cu(1)	2.679(1)	2.671(1)
M–Cu(2)	2.652(1)	2.645(1)
M–Cu(3)	2.668(1)	2.663(1)
M–S(1)	2.232(4)	2.242(2)
M–S(2)	2.230(3)	2.239(2)
M–S(3)	2.188(3)	2.189(2)
M–S(4)	2.193(2)	2.178(2)
Cu(1)–S(1)	2.267(3)	2.256(3)
Cu(1)–S(2)	2.266(3)	2.253(1)
Cu(1)–S(5)	2.436(3)	2.446(2)
Cu(1)–S(6)	2.367(4)	2.367(2)
Cu(2)–S(1)	2.247(4)	2.251(2)
Cu(2)–S(3)	2.283(4)	2.266(2)
Cu(2)–S(7)	2.520(3)	2.528(3)
Cu(2)–S(8)	2.300(4)	2.288(3)
Cu(3)–S(2)	2.285(3)	2.281(2)
Cu(3)–S(4)	2.290(3)	2.278(3)
Cu(3)–S(9)	2.299(3)	2.289(3)
Cu(3)–S(10)	2.533(5)	2.560(3)
C(11)–S(5)	1.68(1)	1.676(10)
C(11)–S(6)	1.730(9)	1.767(9)
C(11)–N(1)	1.34(2)	1.409(8)
C(21)–S(7)	1.68(2)	1.721(8)
C(21)–S(8)	1.71(1)	1.692(8)
C(21)–N(2)	1.34(1)	1.35(1)
C(31)–S(9)	1.72(1)	1.663(9)
C(31)–S(10)	1.68(2)	1.707(9)
C(31)–N(3)	1.34(1)	1.37(2)

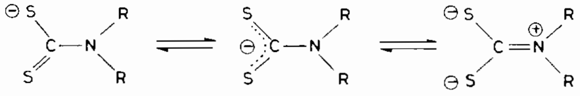
TABLE 4. Selected bond angles (°) for anion $[MCu_3S_4(dtcC_5H_{10})_3]^{2-}$

Bond angle (°)	M = W	M = Mo
S(1)–M–S(2)	108.1(1)	107.6(1)
S(1)–M–S(3)	108.8(2)	108.7(1)
S(2)–M–S(4)	108.9(1)	108.8(1)
S(3)–M–S(4)	110.7(1)	111.0(1)
S(1)–Cu(1)–S(2)	105.7(1)	106.6(1)
S(2)–Cu(1)–S(5)	122.5(1)	121.7(1)
S(5)–Cu(1)–S(6)	74.6(2)	74.4(1)
S(1)–Cu(2)–S(3)	105.1(2)	105.7(2)
S(3)–Cu(2)–S(7)	112.8(1)	112.0(1)
S(7)–Cu(2)–S(8)	74.2(2)	74.2(2)
S(2)–Cu(3)–S(4)	103.7(2)	104.0(2)
S(2)–Cu(3)–S(9)	118.1(1)	119.0(1)
S(4)–Cu(3)–S(10)	108.4(1)	107.5(1)
S(9)–Cu(3)–S(10)	73.8(1)	73.2(1)
M–S(1)–Cu(1)	73.2(1)	73.0(1)
M–S(1)–Cu(2)	72.6(1)	72.1(1)
M–S(2)–Cu(1)	73.2(1)	73.0(1)
M–S(2)–Cu(3)	72.4(1)	72.2(1)
M–S(3)–Cu(2)	72.7(1)	72.8(1)
M–S(4)–Cu(3)	73.0(1)	73.4(1)
Cu(1)–S(5)–C(11)	83.5(3)	83.5(3)
Cu(1)–S(6)–C(11)	84.6(4)	84.6(4)
Cu(2)–S(7)–C(21)	80.2(4)	80.2(4)
Cu(2)–S(8)–C(21)	86.6(3)	86.6(3)
Cu(3)–S(9)–C(31)	87.7(3)	87.7(3)
Cu(3)–S(10)–C(31)	81.0(5)	81.0(5)
S(5)–C(11)–S(6)	117.3(7)	120.6(4)
S(5)–C(11)–N(1)	122.3(7)	119.5(7)
S(6)–C(11)–N(1)	120.5(9)	119.9(7)
S(7)–C(21)–S(8)	118.1(5)	117.0(6)
S(7)–C(21)–N(2)	122.0(7)	123.4(6)
S(8)–C(21)–N(2)	119.5(7)	119.6(6)
S(9)–C(31)–S(10)	117.4(6)	118.6(7)
S(9)–C(31)–N(3)	119.9(8)	119.8(6)
S(10)–C(31)–N(3)	122.7(8)	121.1(7)

As the coordination of Cu in both **1a** and **2a** is composed of two inorganic S_b atoms from MS_4 with an average bite angle of 109.1° and two S atoms from $dtcR_2$ with an average bite angle of 74.2° in the four-membered chelating ring, the tetrahedral polyhedron is severely distorted. The planarity of the group



in the dithiocarbamate ligand is clearly shown by calculations of least-squares planes. In addition, the two Cu–S_t bonds differ by 0.22 Å for the ligands chelated to Cu(2) and Cu(3) which are linked to M by both μ_2- and μ_3-S_b atoms but only by 0.08 Å for that chelated to Cu(1) which is linked by two μ_3-S_b atoms. As a result, the coordination environment of atoms Cu(2) and Cu(3) is different from that for atom Cu(1). Consequently, it is believed that in the equilibrium



I II III

the former ligation may have more of structure **I** while the latter more of structure **II** or **III**.

^1H NMR data indicate the diamagnetic character of the compounds, δ ppm: 4.07 (α-H), 1.56 (β and γ-H) for **1a** and 4.04 (α-H), 1.55 (β, γ-H) for **2a** and do not shift very much from those for the free ligand $dtcC_5H_{10}^-(D_2O)$: 4.32 and 1.63 ppm, respectively.

Cyclic voltammetric measurements for **2a** in CH_2Cl_2 in the range of 0.0–1.0 V gave one pair of reversible oxidation–reduction waves, $E_{1/2} = 0.55$ V, $i_{pa}/i_{pc} = 1$.

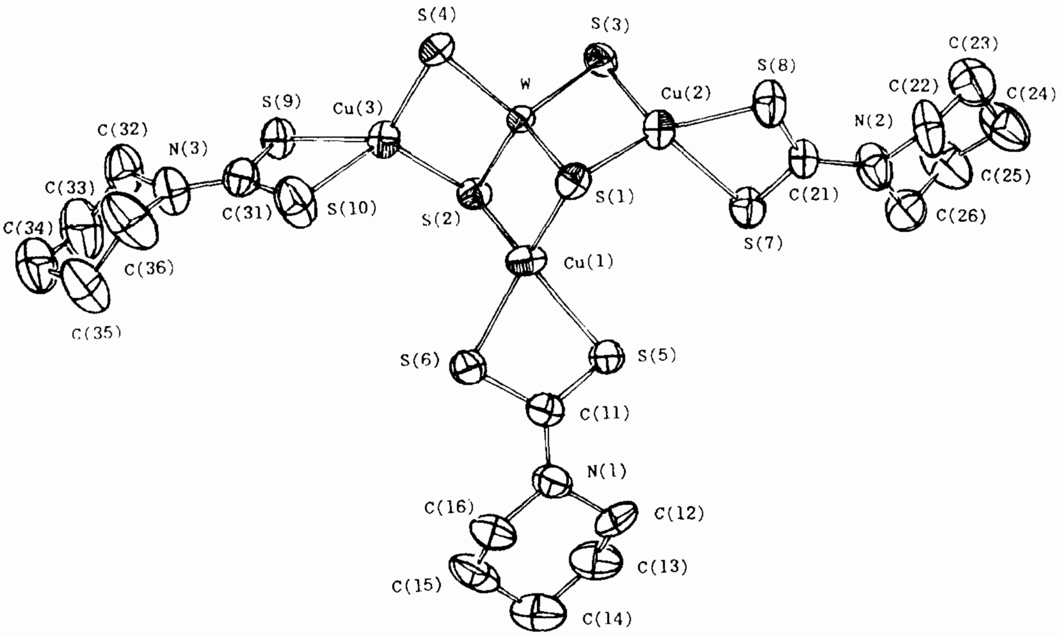


Fig. 1. ORTEP projection of the anion $[WCu_3S_4(S_2CNC_5H_{10})_3]^{2-}$.

Supplementary Material

Listings of positional parameters and temperature factors, of complete bond lengths and angles as well as of least-squares planes of compound **1a**·DMF are available from the authors on request.

Acknowledgements

Financial support from the Chinese National Science Foundation, the Science Funds of Chinese Academy of Sciences and of Fujian Province are greatly appreciated. We also thank Mr Huang Liangren for helpful discussions.

References

1 C. F. Mills, *Philos. Trans. R. Soc. London, Ser. B, 288* (1979) 51.

2 C. F. Mills, T. T. El-Gallad and I. Bremmer, *J. Inorg. Biochem., 14* (1981) 189.

3 A. Müller, *Angew. Chem., Int. Ed. Engl., 20* (1981) 934.

4 E. J. Underwood, *Trace Elements in Human and Animal Nutrition*, Academic Press, New York, 1977.

5 A. Müller, W. Hellman, J. Scheneider and U. Schimanski, *Inorg. Chim. Acta, 65* (1982) L41.

6 Q. T. Liu, L. R. Huang, B. S. Kang, C. W. Liu, L. L. Wang and J. X. Lu, *Acta Chim. Sinica, 44* (1986) 343; (1986) 107 (in English).

7 Q. T. Liu, L. R. Huang, B. S. Kang, Y. Yang and J. X. Lu, *Kexue Tongbao*, (1986) 904; *32* (1987) 898 (in English); *Acta Chim. Sinica, 45* (1987) 133.

8 Q. T. Liu, L. R. Huang, Y. Yang and J. X. Lu, *Acta Chim. Sinica, 46* (1988) 1.

9 Q. T. Liu, B. S. Kang, C. N. Cheng, L. R. Huang, J. H. Cai, B. T. Zhuang and J. X. Lu, *Scientia Sinica, B* (1988) 920.

10 X. J. Lei, Z. Y. Huang, M. C. Hong, Q. T. Liu and H. Q. Liu, *Jiegou Huaxue, 8* (1989) 152.

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

12 X. J. Lei, Q. T. Liu and H. Q. Liu, *Jiegou Huaxue, 7* (1987) 99.

13 G. Kruss, *Justus Liebigs Ann. Chem., 225* (1984) 29.

14 J. W. McDonald, G. D. Friesen, L. D. Rosenheim and W. E. Newton, *Inorg. Chim. Acta, 72* (1983) 205.

15 G. D. Thorn, *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam, 1962, p. 43.

16 S. Sarkar and S. B. S. Miskra, *Coord. Chem. Rev., 59* (1984) 239, and refs. therein.

17 J. N. Liu, unpublished results.