The synthesis and characterization of a novel cubane-like cluster $[(CH_3CH_2)_4N]_4[\{W_2Cu_2S_4\}(SCN)_8]$

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Abstract

A new synthetic procedure of the $[(CH_3CH_2)_4N]_2[W_2S_4(S_4)_2]$ compound under mild conditions is described and a novel heterometallic cubane-like cluster $[(CH_3CH_2)_4N]_4[\{W_2Cu_2S_4\}(SCN)_8]$ has been synthesized by reaction of $[(CH_3CH_2)_4N]_2[W_2S_4(S_4)_2]$ with CuCl and KSCN. $W_2Cu_2S_{12}N_{12}C_{40}H_{80}$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with cell parameters $a=19.88(1)$, $b=13.765(6)$, $c=25.85(1)$ Å, $\beta=109.45(4)°$, $V=6669(6)$ Å^3; $Z=4$; $D_{calc}=1.60$ g cm^{-3}; $\mu=45.42$ cm^{-1}; $T=296$ K; $M_r=1608.66$. Final $R=0.057$ for 4295 observed reflections with $I>3\sigma(I)$ and 453 variables. The unit cell contains four discrete high negative anions and sixteen discrete cations. The discrete anion comprises one cubane-like cluster core $\{W_2Cu_2S_4\}^{4+}$, six SCN^- ligands attached to two W atoms and two SCN^- ligands attached to two Cu atoms. The bond length of the W–W bond and the two W–Cu bonds are 2.845(2) and av. 2.781(3) Å, respectively. The W_2S_4 moiety of $\{W_2S_4(S_4)_2\}^{2-}$ remains in the product, except the W=S double bond lengths elongate slightly to av. 2.226(6) Å.

Introduction

The research on the synthetic analogues of the redox sites of iron–sulfur proteins has attracted many scientists to study the homometallic cubane-like $M_4(\mu_3\text{-}S)_4$ core clusters [1]. Meanwhile a number of heterometallic cubane-like clusters $M_2M'_2S_4$ [2] and $M_3M'S_4$ [3] has been reported by various synthetic methods. It has been established that the unit construction method [4] is a more convenient method to obtain clusters by use of reactive fragments as building blocks. Using the unit construction method, we have successfully synthesized cluster compounds with cores $[M_3CuS_4]$ (M = Mo [5], W [6]), $[M_2M'S_4]$ [7] (M = Mo, or W; M' = Cu, or Ag), $[M_2Cu_2S_4]$ [8] and $[MCu_3S_3X]$ [9] (M = Mo, X = Br, M = W, X = Cl).

The Mo(W)–Cu–S complexes have been widely studied [10] in relation to biochemical Mo/Cu antagonism, and they show rich structural varieties. Most M/Cu/S compounds have been synthesized using MS_4^{2-} (M = Mo, or W) as a starting material, but in recent years many new starting materials such as $[(S_n)ME(S)_2ME(S_n)]^{2-}$ [11] and $\{M_3S_4\}[S_2P(OCH_2CH_3)_2]_4 \cdot H_2O$ (M = Mo [5], or W [6]; E = O, or S; $n=2$ or 4) in which the oxide state of M is lower than 6 have been employed by our group using the synthetic method of unit construction reaction. Another new member of the cubane-like cluster family with $[W_2Cu_2S_4]^{4+}$ core is reported herein using the dinuclear tungsten complex $[(CH_3CH_2)_4N]_2[W_2S_4(S_4)_2]$ as a starting material.

The dinuclear tungsten complex [12] has been synthesized under restricted conditions at a relatively high temperature. Herein a convenient procedure to obtain the complex at a relatively low temperature in the open air will be described.

Experimental

IR spectra were recorded with a Perkin-Elmer 577 spectrophotometer, using KBr pellets. all reactants and solvents purchased were above the CP grade.

Synthesis

$[(CH_3CH_2)_4N]_2W_2S_4(S_4)_2$

A total of 60 ml DMF was added to a mixture of $(NH_4)_2WS_4$ (4.0 g, 11.5 mmol) and S (1.48 g, 46.2 mmol) at room temperature in the open air, the resulting suspension solution was stirred for 1.5 h

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to form a clear solution. Then $NH_2NH_2 \cdot 2HCl$ (1.0 g, 7.53 mmol) was added and stirring was continued for 2 h; the colour of the solution did not change. $(CH_3CH_2)_4NBr$ (4.0 g, 19.0 mmol) was added and stirring continued for another 1 h, then the solution was filtered. The filtrate was layered with 160 ml isopropanol and allowed to stand at 3–5 °C for several weeks. Yield 2.8 g (48%) of red–orange crystals. *Anal.* Calc. for $[(CH_3CH_2)_4N]_2W_2S_4(S_4)_2$: W, 36.30; S, 37.98; C, 18.97; H, 3.98; N, 2.77. Found: W, 35.48; S, 36.79; C, 20.05; H, 3.67; N, 3.18%. IR: 2950(w), 1475(s), 1450(s), 1435(s), 1390(m), 1368(m), 1184(m), 1172(s), 1000(s), 785(s), 512(vs), 495(sh), 460(w), 430–410(m, wide), 380(w), 350–320(m, wide), 295(m). The elemental analysis and IR spectra show that the product is the same as the reported $[(CH_3CH_2)_4N]_2W_2S_4(S_4)_2$ compound [12].

Title compound

To a 15 ml solution of $[(CH_3CH_2)_4N]_2W_2S_4(S_4)_2$ (0.20 g, 0.20 mmol), CuCl (0.06 g, 0.60 mmol) was added and the mixture was stirred for 5 min at room temperature in open air. Then KSCN (0.06 g, 0.60 mmol) was added and stirring continued for 5 h. After filtration, the filtrate was layered with isopropanol. A week later, 0.2 g of a black crystalline precipitate was obtained. Analytical pure crystals (0.15 g) were obtained by recrystallization of the mixture with $CH_3CN/(CH_3)_2CHOH$ (yield 45%). *Anal.* Calc. for $[(CH_3CH_2)_4N]_4[\{W_2Cu_2S_4\}(SCN)_8]$: W, 22.87; Cu, 7.9; S, 23.93; C, 29.88; H, 5.00; N, 10.45. Found: W, 22.66; Cu, 9.22; S, 24.65; C, 31.07; H, 5.03; N, 10.99%. IR: 3100–2800(w, wide), 2075(vs, wide), 1490–1430(s, wide), 1390(m), 1368(w), 1184(m), 1170(s), 1000(s), 945(w, wide), 784(s), 480(w), 475–450(w, wide), 430(m), 416(sh), 370(w, wide).

Crystal data and structure determination

A crystal with dimensions 0.50×0.20×0.10 mm was mounted in random orientation on a glass fibre. Some experimental conditions are reported in Table 1. Data were collected on a RIGAKU AFC5R diffractometer using Mo Kα radiation at c. 296 K. Cell constants were obtained by least-squares analysis on 20 diffraction maxima (the search limits of 2θ: 12.0–55.0°). Scan speed varied on the basis of SEARCH intensity, and a total of 12 657 (including 12 281 unique) reflections was collected; $R_{int} = 9.8\%$. Three standard reflections were measured periodically, no random deviations indicating crystal and electronic stability. Intensity was defined as $C - 1/2(t_c/t_b)(b_1 + b_2)$, where C = total number of counts, t_c = time spent counting peak intensity, t_b = time spent counting one side of the background, b_1 = high-angle background counts and b_2 = low-angle background counts; the intensity error $\sigma(F^2) = (C + 1/4(t_c/t_b)^2(b_1 + b_2) + (pI)^2)^{1/2}$, where I is the intensity and p is the factor that downweights strong reflections, taken to be 0.05. The data were corrected for Lorentz and polarization factors and for absorption using empirical scan data and DIFABS. Linear decay correction was applied. A total of 4295 reflections with $I \geqslant 3\sigma(I)$ was considered observed, and all were used in the refinement.

TABLE 1. Crystallographic data for $[(CH_3CH_2)_4N]_4\{W_2Cu_2S_4\}(SCN)_8$

Chemical formula	$W_2Cu_2S_{12}N_{12}C_{40}H_{80}$
Formula weight	1608.66
Crystal colour	dark red
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameters	
a (Å)	19.88(1)
b (Å)	13.765(6)
c (Å)	25.85(1)
β (°)	109.45(4)
V (Å^3)	6669(6)
Z	4
μ (cm^{-1})	45.42
$F(000)$	3208
$2\theta_{max}$ (°)	50.0
D_{calc} (g cm^{-3})	1.60
Temperature (K)	296
Diffractometer	Rigaku AFC5R
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Solution method	direct methods
Correction	Lp, ψ, DIFABS
No. variables	453
Residuals: R, R_w	0.057, 0.066
Goodness of fit: S	1.22
No. unique data	12281
No. observations with $I > 3(\sigma(I))$	4295
Max. shift $(\Delta/\sigma)_{max}$ in final cycle	0.15
Largest/smallest peaks in final difference map (e Å^{-3})	0.87/−0.99
Scan type	ω
Max. scan speed (° min^{-1})	16
Scan width	0.84° + 0.35° tan cθ

The structure was solved by direct methods using MITHRIL [13]; the W and Cu atoms were located in the E map. Most non-hydrogen atoms were located in the succeeding DIRDIF [14] program and some non-hydrogen atoms were located in the succeeding difference Fourier syntheses. The structure was refined by the full-matrix least-squares technique with anisotropic thermal parameters for all W, Cu, S atoms and the C, N atoms of the SCN$^-$ ligands, and isotropic thermal parameters for all atoms of the four $(CH_3CH_2)_4N^+$ cations (453 variables in all). Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.057$, $R_w = [\Sigma(|F_o| -$

$|F_c|)^2/\Sigma wF_o^2]^{1/2}=0.066$ and $S=[\Sigma w(|F_o|-|F_c|)^2/(N_o-N)]^{1/2}=1.22$, $w=1/\sigma^2(F_o)$. $(\Delta/\sigma)_{max}=0.15$; in the final difference electron density synthesis highest and lowest peaks were 0.87 and -0.99 e Å^{-3} which were in the vicinity of the W atom. All calculations were performed on a VAX 785 computer using the TEXSAN [15] program package.

The atomic coordinates and thermal parameters are listed in Table 2; the important bond lengths and bond angles are given in Tables 3 and 4, respectively.

Results and discussion

As reported [12], heating ammonium tetrathiotungstate and elemental sulfur in DMF followed by the addition of NEt_4Br and recrystallization from acetonitrile affords red crystalline $(NEt_4)_2W_2S_4(S_4)_2$ in high yield. In our procedure, the condition of heating is replaced by the addition of $NH_2NH_2\cdot HCl$, and the reaction occurs in the open air. That is the addition of $NH_2NH_2\cdot HCl$ may prompt the dimerization of WS_4^{2-} to $W_2S_{12}^{2-}$ even at low temperature. As a matter of fact, the internal redox reaction is reduced by HCl acid.

The complex containing the $\{M_2S_4\}^{2+}$ core has been proved to be a good starting material, in which the core may be added by one or two metal atoms to form incomplete cubane-like [7] or cubane-like [8] clusters. In the reaction of $W_2S_{12}^{2-}$, CuCl and KSCN, the W_2S_4 core of the dinuclear tungsten complex, $W_2S_{12}^{2-}$, was connected by two Cu atoms and then the S_4 group and Cl^- ligands were replaced by SCN^- ligands. Then, the cubane-like cluster was formed with a high negative charge.

The crystal structure of the cubane-like cluster consists of an independent cubane-like core anion, $\{W_2Cu_2S_4\}(SCN)_8^{4-}$, and four tetraethylammonium counterions. One of the four Et_4N^+ is disordered. The ORTEP drawing of the anion with four negative charges is shown in Fig. 1. The idealized symmetry of the anion belongs to C_{2v}. The cubane-like cluster, $[Et_4N]_4W_2Cu_2S_4(SCN)_8$, is the first example which has an independent anion in the Mo(W)/Cu/S cubane-like cluster family.

The anion contains a cubane-like core $\{W_2Cu_2S_4\}^{4+}$, which has been found in the neutral cluster [8b] $\{W_2Cu_2S_4\}(SCH_2CH_2S)_2(PPh_3)_2$. But there are some differences between them. In the anion, each W is coordinated by three μ_3-sulfido atoms and three nitrogen atoms from SCN ligands, in which the six atoms maintain the octahedral geometry. The four equatorial atoms of N(11), N(13), S(2), S(1) (or N(21), N(22), S(1), S(2)) are planar within 0.009 Å (0.048 Å), and the two atoms of S(3)

TABLE 2. Atomic coordinates and equivalent isotropic thermal parameters for $[Et_4N]_4\{W_2Cu_2S_4\}(SCN)_8$

Atom	x	y	z	B_{eq}[a]
W(1)	0.20416(5)	0.33749(7)	0.55484(4)	3.54(4)
W(2)	0.26241(5)	0.24194(7)	0.65772(4)	3.82(4)
Cu(1)	0.1932(2)	0.4192(2)	0.6501(1)	5.7(2)
Cu(2)	0.1136(2)	0.2416(2)	0.5953(1)	6.0(2)
S(1)	0.2945(3)	0.3955(4)	0.6332(2)	3.9(3)
S(2)	0.1987(3)	0.1708(4)	0.5725(2)	4.1(3)
S(3)	0.1040(3)	0.4011(4)	0.5622(3)	4.7(3)
S(4)	0.1785(4)	0.2728(5)	0.6940(3)	5.6(3)
S(11)	0.2619(4)	0.6276(5)	0.4689(3)	6.0(3)
S(12)	0.3932(5)	0.3076(7)	0.4754(4)	9.3(5)
S(13)	0.0732(5)	0.1973(7)	0.3788(3)	9.9(5)
S(21)	0.2723(4)	−0.0753(5)	0.7452(3)	5.9(3)
S(22)	0.4678(5)	0.3193(6)	0.8156(3)	8.9(4)
S(23)	0.4486(4)	0.0795(8)	0.6058(4)	10.6(6)
S(31)	0.1353(5)	0.6744(6)	0.7447(3)	7.8(4)
S(41)	−0.0985(4)	0.1402(8)	0.6108(4)	10.1(5)
N(11)	0.220(1)	0.468(1)	0.5186(8)	5(1)
N(12)	0.291(1)	0.304(1)	0.5262(7)	4.5(9)
N(13)	0.147(1)	0.295(1)	0.4748(7)	5(1)
N(21)	0.265(1)	0.098(1)	0.6909(7)	5(1)
N(22)	0.343(1)	0.270(2)	0.7322(9)	6(1)
N(23)	0.352(1)	0.184(1)	0.6384(8)	5(1)
N(31)	0.174(1)	0.526(1)	0.6898(8)	5(1)
N(41)	0.028(1)	0.186(2)	0.5919(9)	6(1)
C(11)	0.237(1)	0.533(2)	0.4980(9)	4(1)
C(12)	0.333(1)	0.307(2)	0.505(1)	4(1)
C(13)	0.116(1)	0.258(2)	0.4345(9)	5(1)
C(21)	0.271(1)	0.028(2)	0.715(1)	5(1)
C(22)	0.395(1)	0.288(2)	0.766(1)	5(1)
C(23)	0.394(1)	0.139(2)	0.625(1)	6(1)
C(31)	0.158(1)	0.590(2)	0.712(1)	5(1)
C(41)	−0.025(1)	0.166(2)	0.599(1)	5(1)
N(1)	0.831(1)	0.198(1)	0.4221(8)	5.2(4)*
N(2)	0.493(1)	−0.025(1)	0.8603(8)	5.8(5)*
N(3)	0.927(1)	0.020(1)	0.1941(7)	4.8(4)*
N(4)	0.307(1)	0.006(2)	0.387(1)	7.4(6)*
C(111)	0.779(1)	0.154(2)	0.448(1)	5.9(6)*
C(112)	0.724(1)	0.086(2)	0.411(1)	7.1(7)*
C(121)	0.789(1)	0.253(2)	0.369(1)	5.1(5)*
C(122)	0.736(1)	0.328(2)	0.377(1)	6.8(6)*
C(131)	0.878(1)	0.272(2)	0.465(1)	5.7(6)*
C(132)	0.933(1)	0.322(2)	0.447(1)	7.0(7)*
C(141)	0.873(1)	0.121(2)	0.403(1)	6.3(6)*
C(142)	0.927(2)	0.067(2)	0.452(1)	7.6(7)*
C(211)	0.472(1)	0.037(2)	0.809(1)	5.3(6)*
C(212)	0.532(1)	0.047(2)	0.783(1)	6.7(7)*
C(221)	0.422(1)	−0.021(2)	0.877(1)	7.4(7)*
C(222)	0.432(2)	−0.082(2)	0.929(1)	10(1)*
C(231)	0.512(1)	−0.130(2)	0.851(1)	6.1(6)*
C(232)	0.455(2)	−0.187(2)	0.808(1)	8.4(8)*
C(241)	0.559(1)	0.016(2)	0.907(1)	5.6(6)*
C(242)	0.547(1)	0.121(2)	0.920(1)	6.2(6)*
C(311)	0.960(1)	−0.025(2)	0.150(1)	7.2(7)*
C(312)	0.943(2)	0.036(2)	0.099(1)	7.9(8)*
C(321)	0.846(2)	0.030(2)	0.170(1)	7.8(8)*
C(322)	0.810(2)	−0.074(3)	0.155(1)	12(1)*
C(331)	0.953(2)	0.128(2)	0.208(1)	7.4(7)*
C(332)	1.037(2)	0.125(2)	0.234(1)	9(1)*
C(341)	0.949(1)	−0.050(2)	0.244(1)	7.2(7)*
C(342)	0.925(2)	−0.013(2)	0.291(1)	9.4(9)*
C(411)	0.337(4)	0.058(6)	0.442(3)	11(2)**
C(412)	0.265(2)	0.067(2)	0.464(1)	8.3(8)*
C(421)	0.230(3)	0.068(4)	0.336(2)	6(1)**

(*continued*)

TABLE 2. (*continued*)

Atom	x	y	z	B_{eq}^{a}
C(422)	0.252(3)	0.148(4)	0.335(2)	15(1)*
C(431)	0.361(3)	0.016(5)	0.361(3)	9(2)**
C(432)	0.346(2)	−0.046(2)	0.308(1)	9.4(9)*
C(441)	0.268(5)	−0.097(7)	0.374(4)	13(3)**
C(442)	0.320(4)	−0.162(6)	0.409(3)	11(2)**
C(451)	0.249(3)	−0.008(4)	0.415(2)	8(2)**
C(461)	0.309(4)	0.104(6)	0.367(3)	11(2)**
C(471)	0.302(6)	−0.100(8)	0.348(4)	16(3)**
C(481)	0.389(3)	−0.015(5)	0.436(2)	8(2)**
C(482)	0.392(5)	−0.130(6)	0.458(3)	14(3)**

$^a B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j B_{ij} a_i \cdot a_j$. Starred atoms were refined isotropically, meanwhile double-starred atoms were disordered and the multiplicity was fixed at 0.5.

TABLE 3. Selected bond lengths (Å)

W(1)–W(2)	2.845(2)	Cu(2)–S(2)	2.197(6)
W(1)–Cu(1)	2.781(3)	Cu(2)–S(3)	2.340(7)
W(1)–Cu(2)	2.708(3)	Cu(2)–S(4)	2.482(7)
W(2)–Cu(1)	2.776(3)	Cu(2)–N(41)	1.85(2)
W(2)–Cu(2)	2.860(4)	S(11)–C(11)	1.65(2)
W(1)–S(1)	2.355(6)	S(12)–C(12)	1.61(2)
W(1)–S(2)	2.350(6)	S(13)–C(13)	1.64(3)
W(1)–S(3)	2.241(6)	S(21)–C(21)	1.61(3)
W(1)–N(11)	2.10(2)	S(22)–C(22)	1.64(3)
W(1)–N(12)	2.14(2)	S(23)–C(23)	1.58(3)
W(1)–N(13)	2.08(2)	S(31)–C(31)	1.58(3)
W(2)–S(1)	2.355(6)	S(41)–C(41)	1.63(2)
W(2)–S(2)	2.358(6)	N(11)–C(11)	1.15(2)
W(2)–S(4)	2.210(7)	N(12)–C(12)	1.15(2)
W(2)–N(21)	2.15(2)	N(13)–C(13)	1.14(3)
W(2)–N(22)	2.09(2)	N(21)–C(21)	1.14(3)
W(2)–N(23)	2.15(2)	N(22)–C(22)	1.13(3)
Cu(1)–S(1)	2.222(6)	N(23)–C(23)	1.18(3)
Cu(1)–S(3)	2.384(7)	N(31)–C(31)	1.16(3)
Cu(1)–S(4)	2.377(7)	N(41)–C(41)	1.15(3)
Cu(1)–N(31)	1.90(2)		

TABLE 4. Selected bond angles (°)

W(1)–W(1)–Cu(2)	59.12(8)	N(21)–W(2)–S(1)	163.6(5)
W(2)–W(1)–Cu(2)	61.94(9)	N(21)–W(2)–S(2)	85.7(5)
Cu(1)–W(1)–Cu(2)	66.2(1)	N(21)–W(2)–S(4)	86.2(5)
W(1)–W(2)–Cu(1)	59.30(8)	N(21)–W(2)–N(22)	83.7(8)
W(1)–W(2)–Cu(2)	56.69(8)	N(21)–W(2)–N(23)	80.5(7)
Cu(1)–W(2)–Cu(2)	64.3(1)	N(22)–W(2)–S(1)	83.7(6)
W(1)–Cu(1)–W(2)	61.58(7)	N(22)–W(2)–S(2)	161.0(6)
W(1)–Cu(2)–W(2)	61.38(7)	N(22)–W(2)–S(4)	91.7(6)
S(1)–W(1)–S(2)	103.6(2)	N(22)–W(2)–N(23)	81.0(8)
S(1)–W(1)–S(3)	103.8(2)	N(23)–W(2)–S(1)	87.2(5)
S(2)–W(1)–S(3)	105.4(2)	N(23)–W(2)–S(2)	81.8(5)
N(11)–W(1)–S(1)	84.8(5)	N(23)–W(2)–S(4)	165.4(5)
N(11)–W(1)–S(2)	161.3(5)	S(1)–Cu(1)–S(3)	103.5(2)
N(11)–W(1)–S(3)	88.4(5)	S(1)–Cu(1)–S(4)	103.5(3)
N(11)–W(1)–N(12)	76.7(7)	S(3)–Cu(1)–S(4)	101.2(2)
N(11)–W(1)–N(13)	84.8(7)	N(31)–Cu(1)–S(1)	125.1(6)
N(12)–W(1)–S(1)	84.1(5)	N(31)–Cu(1)–S(3)	112.1(6)
N(12)–W(1)–S(2)	87.4(5)	N(31)–Cu(1)–S(4)	108.7(6)
N(12)–W(1)–S(3)	162.5(5)	S(2)–Cu(2)–S(3)	107.1(2)
N(12)–W(1)–N(13)	80.4(7)	S(2)–Cu(2)–S(4)	99.8(2)
N(13)–W(1)–S(1)	163.0(5)	S(3)–Cu(2)–S(4)	99.5(2)
N(13)–W(1)–S(2)	82.8(6)	N(41)–Cu(2)–S(2)	125.9(7)
N(13)–W(1)–S(3)	89.3(6)	N(41)–Cu(2)–S(3)	114.1(7)
S(1)–W(2)–S(2)	103.4(2)	N(41)–Cu(2)–S(4)	106.1(7)
S(1)–W(2)–S(4)	104.6(2)	W(1)–S(1)–W(2)	74.3(2)
S(2)–W(2)–S(4)	103.3(2)	Cu(1)–S(1)–W(1)	74.8(2)
Cu(1)–S(1)–W(2)	74.6(2)	W(1)–S(2)–W(2)	74.3(2)
Cu(2)–S(2)–W(1)	73.0(2)	Cu(2)–S(2)–W(2)	77.7(2)
W(1)–S(3)–Cu(1)	73.9(2)	W(1)–S(3)–Cu(2)	72.4(2)
Cu(1)–S(3)–Cu(2)	78.8(2)	W(2)–S(4)–Cu(1)	74.4(2)
W(2)–S(4)–Cu(2)	74.9(2)	Cu(1)–S(4)–Cu(2)	76.2(2)
C(11)–N(11)–W(1)	170(2)	C(12)–N(12)–W(1)	164(2)
C(13)–N(13)–W(1)	170(2)	C(21)–N(21)–W(2)	171(2)
C(22)–N(22)–W(2)	165(2)	C(23)–N(23)–W(2)	169(2)
C(31)–N(31)–Cu(1)	176(2)	C(41)–N(41)–Cu(2)	165(2)
N(11)–C(11)–S(11)	179(2)	N(12)–C(12)–S(12)	179(2)
N(13)–C(13)–S(13)	176(2)	N(21)–C(21)–S(21)	175(3)
N(22)–C(22)–S(22)	176(2)	N(23)–C(23)–S(23)	178(3)
N(31)–C(31)–S(31)	177(2)	N(41)–C(41)–S(41)	178(2)

and N(12) (or S(4) and N(23)) are near to the axis. Each Cu is tetrahedrally coordinated by three bridging μ_3-sulfido atoms and one N atom from the ligand of SCN. All the eight SCN$^-$ ligands are nearly linear coordinated to the metal atoms by the N side.

The cubane-like core of the anion has some distortion, because the dihedral angle of the two planes of W(1)/S(1)/S(2) and W(2)/S(1)/S(2) is 154.7(3)°; and that of Cu(1)/Cu(2)/S(3) and Cu(1)/Cu(2)/S(4) is 159.1(4)°. The two bonds of W(1)–S(3) and W(2)–S(4) are 2.241(6) and 2.210(7), respectively, which are much shorter than the other W–S bonds. According to the unit construction, the S(3) and S(4) atoms are the terminal sulfido atoms in the dinuclear tungsten complex. That is to say that the characteristic structural feature of the $\{W_2S_4\}^{2+}$ core remains in the product of the unit construction reaction. Meanwhile the two Cu(1)–S(1) 2.222(6) Å and Cu(2)–S(2) 2.197(6) Å bonds, which are approximately parallel to the two short W–S bonds, are also much shorter than the other Cu–S bonds. Therefore the cubane-like core is compressed along the two-fold axis. This type of distortion has also been observed in the same core cluster [8] of $\{W_2Cu_2S_4\}(SCH_2CH_2S)_2(PPh_3)_2$, although the coordination of the W atom (belongs to the tetrahedral-pyramidal geometry) and the charge of the cluster are different.

Further research on the reaction of the dinuclear tungsten complex with other metal complexes will be continued, and this will display a rich chemistry.

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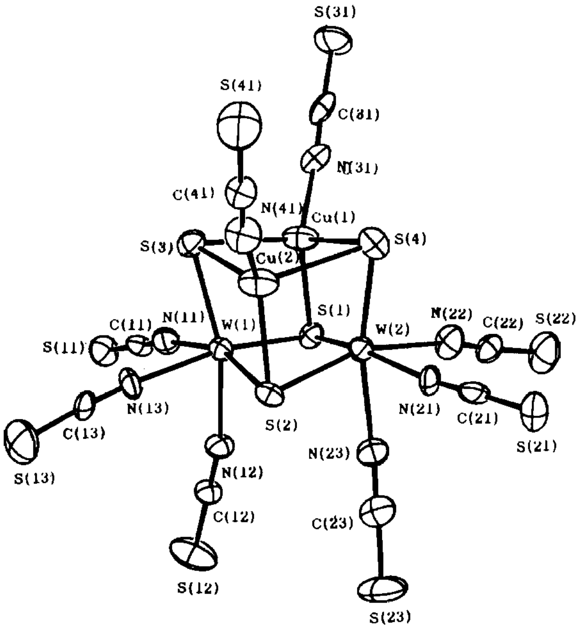

Fig. 1. The configuration of the anion of $W_2Cu_2S_4(NCS)_8^{4-}$.

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