Notes

Heterobimetallic Clusters derived from $[MS_4]^{2-}$ (M = Mo or W): Synthesis and Structural Characterization of $[NMe_4]_4[(CuCl)_5Cl_2WS_4]$, a Double Cubane-like Complex†

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Reaction of $[NMe_4]_2[MS_4]$ (M = Mo or W) with CuCl (1:3.5) in CH_3CN produces a hexanuclear complex anion $[(CuCl)_5Cl_2MS_4]^{4-}$. Crystals of $[NMe_4]_4[(CuCl)_5Cl_2WS_4]$ are monoclinic, space group *C2/c* with cell dimensions a = 21.610(4), b = 9.340(2), c = 19.570(5), β = 92.84(2)°, and Z = 4. Least-squares refinement based on 2 708 reflections with $I \geqslant 3\sigma(I)$ converged at R = 0.032. The anion has crystallographically imposed C_2 symmetry. The crystal structure determination shows that five of the six edges of the $[WS_4]^{2-}$ tetrahedron are co-ordinated by CuCl units forming an open double cubane-like structure; the cubic geometry is achieved by chlorine atoms.

Thiometalate anions like $[WS_4]^{2-}$ and $[MoS_4]^{2-}$ can be used for the preparation of new polynuclear transition-metal compounds.[1] These discrete anions have been shown to function as versatile multidentate chelates to a wide variety of metal ions[2] including the soft acid Cu^+. Concerning copper(I), this versatility is illustrated by a set of structurally characterized complexes prepared from Cu(CN)[3] and CuCl.[4–8] We describe here the preparation, properties, and *X*-ray structure analysis of $[NMe_4]_4[(CuCl)_5Cl_2WS_4]$, a new contribution to the study of discrete copper tetrathiometalate clusters.

Experimental

All manipulations were carried out in air. Chemicals were used as purchased. Elemental analyses were performed by the Service Central d'Analyses du CNRS. Infrared spectra (KBr and polyethylene pellets) were recorded on a Perkin-Elmer 580 B spectrophotometer. Electronic spectra were obtained on a Kontron 810 spectrophotometer in dimethylformamide (dmf) solution between 600 and 200 nm.

Preparation of $[NMe_4]_4[(CuCl)_5Cl_2WS_4]$ (**1**).—A suspension of $[NMe_4]_2[WS_4]$ (0.460 g, 1 mmol) and CuCl (0.350 g, 3.5 mmol) in CH_3CN (100 cm^3) was stirred for 1 h at room temperature. The red precipitate which formed was removed by filtration and identified as $Cu_2[WS_4]$. The resultant filtrate was allowed to stand at ambient temperature for 2 d whereupon orange well-shaped crystals of (**1**) formed which were filtered off and washed with Et_2O (20 cm^3) (Found: C, 16.55; H, 4.10; Cl, 21.25; Cu, 26.70; N, 4.80; S, 11.00; W, 15.65. Calc. for $C_{16}H_{48}Cl_7Cu_5N_4S_4W$: C, 16.35; H, 4.10; Cl, 21.15; Cu, 27.00; N, 4.75; S, 10.90; W, 15.70%). Complex (**1**) is soluble in dmf and slightly soluble in CH_3CN. Crystals of (**1**) prepared as described proved suitable for *X*-ray crystallographic studies.

Preparation of Analogous Molybdenum Compound.—The previous preparation was repeated with Mo but the reaction mixture was filtered after 1 h and the solution reduced to *ca.* 50 cm^3. Within 1 h at room temperature a mixture of dark-red hexagonal-shaped crystals, (**2**), and a microcrystalline violet powder deposited. Complex (**2**) was not clearly identified even though analytical results were obtained from various attempts (*viz.* Cl, 24.10; Cu, 29.45; Mo, 18.05; S, 11.25%). The products thus obtained were separated by filtration and the resultant filtrate yielded after 1 d a small amount of violet plate-like crystals, (**3**), together with a violet powder. Attempts at recrystallization from various solvents were unsuccessful. The crystals (**2**) or (**3**) were separated by hand and characterized by *X*-ray diffraction methods.

Crystal-structure Determination.—*Crystal data. For* (**1**). $C_{16}H_{48}Cl_7Cu_5N_4S_4W$, M = 1 174.5, monoclinic, space group *C2/c*, a = 21.610(4), b = 9.340(2), c = 19.570(5) Å, β = 92.84(2)°, U = 3 945 $Å^3$, Z = 4, D_c = 1.98 g cm^{-3}, $F(000)$ = 2 295.5, and μ(Mo-K_α) = 60.2 cm^{-1}.

For (**2**). Hexagonal system, space group $P6_322$, a = 11.522(5), c = 20.561(8) Å, and U = 2 363 $Å^3$. Thus far we have been unable to solve the crystal structure of (**2**) due to disorder in the crystal lattice.

For (**3**). Crystals of fair diffraction quality were not obtained; however oscillation and Weissenberg photographs indicated a monoclinic system with a = 21.7, b = 9.5, c = 19.6 Å, and β = 93.0°. On the basis of similar cell parameters and identical space group with those of (**1**), the formula $[NMe_4]_4[(CuCl)_5Cl_2MoS_4]$ can be assumed for (**3**).

Data collection and processing. For (**1**). Intensity data were collected on an Enraf-Nonius CAD4 automatic diffractometer using graphite-monochromated Mo-K_α radiation, a θ–2θ scan technique, and variable scan speeds. A unique quadrant of data $3 < 2\theta < 50°$ ($\pm h$, $+k$, $+l$) was collected. The data were corrected for background and for Lorentz polarization effects. An empirical absorption based on an azimuthal scan

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Final positional parameters for $[NMe_4]_4[(CuCl)_5Cl_2WS_4]$, with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
W	0.0	0.229 97(5)	$\frac{1}{4}$
Cu(1)	0.0	−0.054 4(2)	$\frac{1}{4}$
Cu(2)	0.115 07(5)	0.194 8(1)	0.302 02(6)
Cu(3)	0.071 10(5)	0.197 4(1)	0.142 11(6)
S(1)	0.025 60(9)	0.087 7(2)	0.340 8(1)
S(2)	0.080 5(1)	0.368 3(2)	0.227 0(1)
Cl(1)	0.0	−0.284 5(4)	$\frac{1}{4}$
Cl(2)	0.197 7(1)	0.211 5(3)	0.369 7(1)
Cl(3)	0.100 5(1)	0.249 1(3)	0.038 8(1)
Cl(4)	0.135 9(1)	0.002 6(3)	0.199 7(1)
N(1)	0.408 9(3)	0.784 5(9)	0.962 2(4)
C(1)	0.428 1(5)	0.876(1)	1.023 8(5)
C(2)	0.451 6(6)	0.817(2)	0.904 8(6)
C(3)	0.414 5(6)	0.628(1)	0.980 9(6)
C(4)	0.342 8(5)	0.820(2)	0.939 4(7)
N(2)	0.299 3(3)	0.785 9(9)	0.650 5(4)
C(5)	0.275 8(7)	0.896(2)	0.601 9(8)
C(6)	0.292 7(9)	0.834(2)	0.720 6(8)
C(7)	0.363 4(6)	0.745(2)	0.646 4(7)
C(8)	0.261(1)	0.665(2)	0.644(2)

Table 2. Selected bond lengths (Å) and angles (°) for $[NMe_4]_4$-$[(CuCl)_5Cl_2WS_4]$, with estimated standard deviations in parentheses; primes denote atoms generated by the binary axis

W–S(1)	2.265(2)	W–S(2)	2.231(2)
Cu(1)–Cl(1)	2.149(4)	Cu(1) ··· Cl(4)	3.188(2)
Cu(2)–Cl(2)	2.176(3)	Cu(2)–Cl(4)	2.743(3)
Cu(3)–Cl(3)	2.202(3)	Cu(3)–Cl(4)	2.526(3)
Cu(1)–S(1)	2.264(2)	Cu(2)–S(1)	2.336(2)
W ··· Cu(1)	2.656(2)	Cu(2)–S(2)	2.288(3)
W ··· Cu(2)	2.660(1)	Cu(3)–S(1′)	2.366(2)
W ··· Cu(3)	2.689(1)	Cu(3)–S(2)	2.305(3)
S(1)–W–S(2)	109.62(8)	S(1)–W–S(2′)	110.11(8)
S(1)–W–S(1′)	108.2(1)	S(2)–W–S(2′)	109.2(1)
Cu(1) ··· W ··· Cu(2)	82.90(3)	Cu(1) ··· W ··· Cu(3)	83.50(2)
Cu(2) ··· W ··· Cu(3)	74.15(3)	Cu(2) ··· W ··· Cu(3′)	104.19(3)
Cu(2) ··· W ··· Cu(2′)	165.80(6)	Cu(3) ··· W ··· Cu(3′)	167.00(5)
Cl(1)–Cu(1)–S(1)	125.89(6)	S(1)–Cu(1)–S(1′)	108.2(1)
S(1)–Cu(2)–S(2)	105.23(9)	S(2)–Cu(3)–S(1′)	104.18(9)
Cl(2)–Cu(2)–S(1)	120.0(1)	Cl(3)–Cu(3)–S(1′)	121.46(9)
Cl(2)–Cu(2)–S(2)	124.9(1)	Cl(3)–Cu(3)–S(2)	119.3(1)
Cl(2)–Cu(2)–Cl(4)	109.4(1)	Cl(3)–Cu(3)–Cl(4)	112.9(1)
S(1)–Cu(2)–Cl(4)	97.20(8)	S(1)–Cu(3)–Cl(4)	95.68(9)
S(2)–Cu(2)–Cl(4)	93.14(9)	S(2)–Cu(3)–Cl(4)	98.65(8)
Cl(1)–Cu(1) ··· W	180.00	Cl(4)–Cu(2) ··· W	89.17(6)
Cl(2)–Cu(2) ··· W	161.37(9)	Cl(4)–Cu(3) ··· W	93.26(7)
Cl(3)–Cu(3) ··· W	153.85(9)		
W–S(1)–Cu(1)	71.81(7)	Cu(1)–S(1)–Cu(2)	99.79(8)
W–S(1)–Cu(2)	70.62(7)	Cu(1)–S(1)–Cu(3′)	100.46(8)
W–S(1)–Cu(3′)	70.97(6)	Cu(2)–S(1)–Cu(3′)	127.7(1)
W–S(2)–Cu(2)	72.12(7)	Cu(2)–S(2)–Cu(3)	89.20(9)
W–S(2)–Cu(3)	72.70(7)	Cu(3)–Cl(4)–Cu(2)	75.36(7)

measurement was applied.[9] There was no evidence of crystal decay from standard reflections monitored every hour of exposure. A total of 3 458 unique reflections were measured, of which 2 708 were considered observed [$I \geqslant 3\sigma(I)$].

Structural analysis and refinement. For (**1**). The position of one unique tungsten atom was located from a Patterson map and the remaining non-hydrogen atoms from Fourier-difference maps. One of the two crystallographically independent $[NMe_4]^+$ cations had high thermal parameters probably as a result of disorder which was not solved. Hydrogen-atom contributions were omitted. All atoms were refined anisotropically. The final R value was 0.032. Complex neutral-atom scattering factors were employed [10] and all computations were performed on the GOULD concept 32/87 computer at the Université Pierre et Marie Curie using SHELX 76.[11] Atomic co-ordinates are given in Table 1, selected geometrical parameters in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

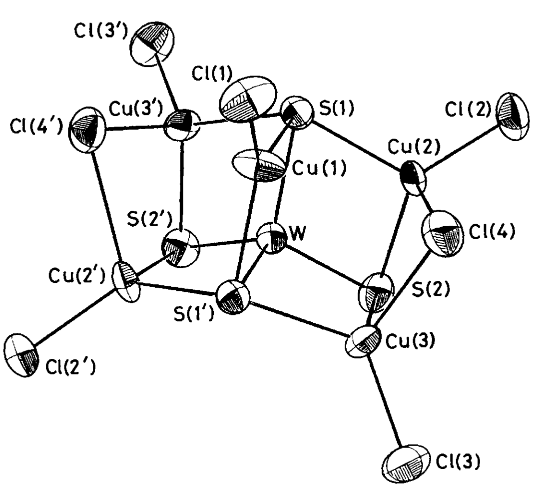

Figure. Perspective view of the $[(CuCl)_5Cl_2WS_4]^{4-}$ anion, showing the atom labelling. Half of the anion (primed atoms) is generated through a binary axis passing through the W, Cu(1), and Cl(1) atoms

Results and Discussion

A perspective view of the heteronuclear anion is shown in the Figure. *X*-Ray structure analysis reveals the existence of a 12-atom cage that contains a crystallographic C_2 axis. The tungsten atom and a CuCl unit lie on the binary axis generating an architecture comparable to distorted cubane-type clusters joined by a common face [W, Cu(1), Cl(1), S(1), S(1′)]. The co-ordination geometry about tungsten is nearly tetrahedral. Five CuCl units are bound to the WS_4 core [Cu–S 2.264(2)—2.366(2) Å]. Each CuCl unit is attached to one edge of the WS_4 tetrahedron leaving the sixth edge unco-ordinated and forming a distorted double cube with two vacant positions. The cubic geometry is achieved by chlorine [Cl(4)] atoms co-ordinated to the framework *via* two copper atoms [Cu(2) and Cu(3)]. The three independent copper atoms are not equivalent, Cu(1) is crystallographically strictly trigonal planar, while Cu(2) and Cu(3) adopt strongly distorted tetrahedral geometries with large Cu–Cl distances [Cu(2)–Cl(4) 2.743(3) and Cu(3)–Cl(4) 2.526(3) Å] as already reported in similar cubane structures.[12] Of interest is the bridging behaviour of the μ_4-S(1) sulphur atom, quite unusual in such complexes, with angles ranging from 70.62(7)° [W–S(1)–Cu(2)] to 127.7(1)° [Cu(2)–S(1)–Cu(3′)]. Another interesting feature is the configuration of the five copper atoms; the Cu_5 unit is a rectangular basal plane pyramid with the W atom located at the centre of the basal plane [deviation of W from the plane Cu(2), Cu(3), Cu(2′), Cu(3′) = 0.31 Å]. The W···Cu distances [2.656(2)—2.689(1) Å] are slightly longer than observed in copper–tungsten–sulphur clusters. Dihedral angles between the W,Cu(1), Cl(1), S(1), S(1′) and the W, Cu(1), Cl(1), Cl(4), Cl(4′), S(2), S(2′) planes are close to 90°. All atoms of (**1**) appear to be rather symmetrically distributed with respect to these mean planes. The tetra-anion approximates to C_{2v} symmetry. Furthermore the dihedral angles between these planes and the basal plane containing the four copper atoms are also close to 90°.

The complex anion shows strong similarities to the hexanuclear trianion $[(CuCl)_5Cl_2ReS_4]^{3-}$ already reported.[13] Reaction of (**1**) with five equivalents of NH_4SCN in CH_3CN gives a red product analysed as $[NMe_4]_2[\{Cu(NCS)\}_4WS_4]$.[14] Reaction of (**1**) with an excess of PPh_4Cl in dmf gives the known complex $[PPh_4]_2[(CuCl)_3WS_4]$.[5]

In the i.r. spectrum of (**1**) bands at 450s and 420m cm^{-1} are assigned to the bridged WS_4 group. The peak position observed at 434 nm on the electronic spectrum in dmf (attributed to the charge-transfer transition of the WS_4 moiety) is red shifted by 34 nm as expected when additional CuCl units are bound to the central WS_4 core.[6]

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