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LETTER

Synthesis and characterisation of $(NMe_4)_5[MoS_4(CuCl)_6Cl_3]$: the ultimate step of the addition of CuCl to thiomolybdate

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It is well known that thiometallates $[MS_4]^{2-}$ bind as multidentate ligands to a wide variety of metal ions and neutral molecules [1]. Among the latter, CuCl led to a large number of compounds by successive addition across the six edges of the MS_4 (M = Mo, W) tetrahedron. $[MS_4(CuCl)_2]^{2-}$ [2], $[MS_4(CuCl)_3]^{2-}$ [3], $[MS_4(CuCl)_4]^{2-}$ [4] and $[MS_4(CuCl)_5Cl_2]^{4-}$ [5] have been structurally characterized. Three copper atoms were added to $[ReS_4]^-$ [6] and $[VS_4]^{3-}$ [7], and five copper atoms to $[ReS_4]^-$ [8]. We report here the synthesis and structural characterisation of $(NMe_4)_5[MoS_4(CuCl)_6Cl_3]$ representing the ultimate step of the addition of CuCl to thiomolybdate.

Experimental

All manipulations were carried out in air. Elemental analyses were performed by the Service Central d'Analyses du CNRS, Solaize. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 580B spectrophotometer and electronic spectra on a Kontron 820 spectrophotometer (dmf solutions).

Preparation of $(NMe_4)_5[MoS_4(CuCl)_6Cl_3]$

The title compound was obtained by reacting $(NMe_4)_2[MoS_4]$ (0.372 g, 1 mmol) suspended in 100 ml of acetonitrile with CuCl (0.300 g, 3 mmol). The reaction mixture was stirred for 1 h at room temperature and then filtered. After standing several days at room temperature black hexagonal crystals deposited. *Anal.* Calc. for $C_{20}H_{60}Cl_9Cu_6MoN_5S_4$: C, 18.55; H, 4.65; Cl, 24.65; Cu, 29.45; Mo, 7.40; N, 5.40; S, 9.90. Found: C, 18.10; H, 4.75; Cl, 24.10; Cu, 29.45; Mo, 8.00; N, 5.10; S, 11.30%. Crystals suitable for X-ray determinations were obtained directly from the preparation.

Crystal structure determination

Crystal data, data collection procedure and refinement of the structure are given in Table 1. Data were corrected for LP factors and a set of 888 reflections was used in the calculations [9]. *E* Statistics and systematic extinctions were consistent with the non-centrosymmetric space group $Cmc2_1$. Direct methods yielded the positions of the Mo and Cu atoms. The remaining atoms were located from successive difference Fourier maps. Mo, Cu and Cl parameters were refined anisotropically, the others isotropically, to $R = 0.0458$ and $R_w = 0.0531$. The final difference map showed no residual peak greater than 1.0 e Å^{-3} in the Cu(1) region. Fractional atomic coordinates are given in Table 2, and selected bond distances and angles in Table 3. See also 'Supplementary material'.

TABLE 1. Summary of crystallographic data

Formula	$C_{20}H_{60}Cl_9Cu_6MoN_5S_4$
Molecular weight	1295.2
Crystal system	orthorhombic
Space group	$Cmc2_1$
a (Å)	19.945(3)
b (Å)	11.513(1)
c (Å)	20.541(7)
V (Å^3)	4717(2)
Z	4
ρ (calc.) (g cm^{-3})	1.82
$F(000)$	2592
Diffractometer	Enraf-Nonius CAD4
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
μ (Mo Kα) (cm^{-1})	36.2
Scan type	$\theta/2\theta$
Scan range	$0.80 + 0.345$ tgθ
θ limits (°)	1–23
Octants collected	$+h, +k, +l$
No. data collected	1825
No. unique reflections	1754
No. reflections used	888
Criteria	$(F_o)^2 > 3\sigma(F_o^2)$
R (%)	4.58
R_w (%)	5.31
Absorption corrections	Difabs
No. parameters	158
Weighting scheme	Chebyshev
Using parameters	4.79; −1.76; 3.82
Secondary extinction	yes

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0020-1693/92/$5.00

TABLE 2. Atomic coordinates for $(NMe_4)_5[MoS_4Cu_6Cl_9]$

Atom	*x*	*y*	*z*
Mo(1)	0.0000	0.0002(3)	0.1228(2)
S(1)	0.0000	0.0005(8)	0.2323(3)
S(2)	0.0000	−0.1853(7)	0.0866(4)
S(3)	0.0930(2)	0.0936(5)	0.0867(2)
Cu(1)	−0.1052(1)	−0.1047(2)	0.0642(2)
Cu(2)	0.0000	0.2106(3)	0.0646(3)
Cu(3)	0.0000	−0.1876(4)	0.1962(2)
Cu(4)	0.0936(2)	0.0935(4)	0.1965(2)
Cl(1)	−0.1643(3)	−0.1649(7)	−0.0199(3)
Cl(2)	0.0000	0.3283(9)	−0.0187(5)
Cl(3)	0.0000	−0.3355(8)	0.2619(5)
Cl(4)	0.1680(3)	0.1682(7)	0.2612(3)
Cl(5)	−0.1556(3)	−0.1549(5)	0.1720(3)
Cl(6)	0.0000	0.3105(7)	0.1715(4)
N(1)	0.3313(8)	0.330(1)	0.376(1)
C(11)	0.324(2)	0.323(3)	0.446(1)
C(12)	0.397(1)	0.392(2)	0.364(1)
C(13)	0.332(1)	0.213(3)	0.349(1)
C(14)	0.273(2)	0.397(3)	0.349(1)
N(2)	−0.3341(5)	0.002(1)	0.1229(7)
C(21)	−0.399(1)	0.047(3)	0.101(1)
C(22)	−0.273(2)	0.073(3)	0.103(1)
C(23)	−0.327(2)	−0.127(3)	0.103(1)
C(24)	−0.334(2)	−0.000(4)	0.196(2)
N(3)	0.0000	0.337(2)	0.375(1)
C(31)	0.064(2)	0.396(3)	0.349(1)
C(32)	0.0000	0.209(3)	0.361(2)
C(33)	0.0000	0.352(4)	0.446(2)

TABLE 3. Selected interatomic distances and angles for $(NMe_4)_5[MoS_4Cu_6Cl_9]$

Mo(1)–S(1)	2.249(8)	Mo(1)–S(3)	2.269(5)
Mo(1)–S(2)	2.262(8)		
S(1)–Cu(3)	2.29(1)	S(3)–Cu(1)	2.342(6)
S(1)–Cu(4)	2.275(6)	S(3)–Cu(2)	2.336(6)
S(2)–Cu(1)	2.339(4)	S(3)–Cu(4)	2.255(6)
S(2)–Cu(3)	2.252(9)		
Cu(1)–Cl(1)	2.204(7)	Cu(2)–Cl(2)	2.18(1)
Cu(1)–Cl(5)	2.500(7)	Cu(2)–Cl(6)	2.48(1)
Cu(3)–Cl(3)	2.17(1)	Cu(4)–Cl(4)	2.169(7)
Mo(1)...Cu(1)	2.703(3)	Mo(1)...Cu(3)	2.636(6)
Mo(1)...Cu(2)	2.700(5)	Mo(1)...Cu(4)	2.633(4)
Cu(1)...Cu(1)′	4.195(5)	Cu(1)...Cu(2)	4.192(2)
Cu(1)...Cu(3)	3.558(5)	Cu(1)...Cu(4)	3.555(4)
Cu(2)...Cu(4)	3.555(6)	Cu(3)...Cu(4)	3.737(5)
Cu(4)...Cu(4)′	3.736(6)		
S(2)–Mo(1)–S(1)	109.3(4)	S(3)–Mo(1)–S(2)	109.9(2)
S(3)–Mo(1)–S(1)	109.0(2)	S(3)–Mo(1)–S(3)	109.7(3)
Cu(3)–S(1)–Mo(1)	71.0(3)	Cu(1)–S(2)–Mo(1)	71.9(2)
Cu(4)–S(1)–Mo(1)	71.2(2)	Cu(3)–S(2)–Mo(1)	71.5(3)
Cu(1)–S(3)–Mo(1)	71.8(2)		
Cu(4)–S(3)–Mo(1)	71.2(2)		
Cu(4)–S(1)–Cu(3)	109.9(3)	Cu(1)–S(2)–Cu(1)	127.5(4)
Cu(4)–S(1)–Cu(4)	110.4(4)	Cu(3)–S(2)–Cu(1)	101.6(2)
Cu(2)–S(3)–Cu(1)	127.3(2)		
Cu(4)–S(3)–Cu(1)	101.3(3)		
Cu(4)–S(3)–Cu(2)	101.5(3)		

Results and discussion

The structure of $(NMe_4)_5[MoS_4(CuCl)_6Cl_3]$ is shown in Fig. 1 with the labelling scheme. The anionic aggregate is formed of a central MoS_4 tetrahedron encapsulated by a distorted octahedron of copper atoms. The MoS_4 core has retained the ideal geometry of free thiomolybdate with similar S–W–S angles, 109.0(2)–109.9(2)°, and Mo–S bond lengths ranging from 2.249(8) to 2.269(5) Å. Each copper atom is bound across an edge of the MoS_4 tetrahedron giving to each sulfur atom a μ_4-S coordination. The six copper atoms form a distorted octahedron; the local idealised symmetry is lowered to C_{3v}. The σ_v mirror containing the Cl(3), Cu(3), S(1), S(2), Mo, Cu(2), Cl(2) and Cl(6) atoms is also the crystallographic mirror plane. Table 3 illustrates the distortion of the Cu_6 octahedron: the 12 edges of the octahedron can be separated into three sets of different Cu···Cu distances. In the Cu(1) Cu(1)′ Cu(2) face the Cu···Cu separations are quite similar, 4.195(5)–4.192(2) Å, each Cu atom being linked to two chlorine atoms as shown in Fig. 2. These distances are different from the Cu···Cu distances in the corresponding parallel Cu(3) Cu(4) Cu(4)′ face, 3.736(6)–3.737(5) Å, in which each copper atom is bound to only one chlorine. The faces containing copper

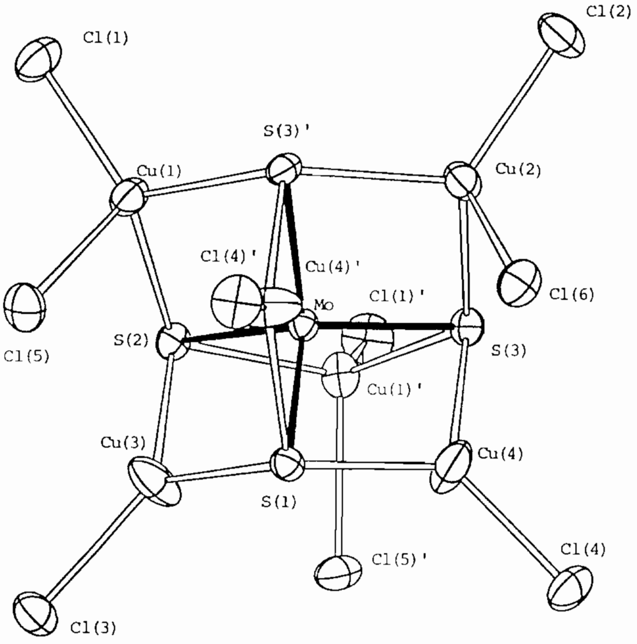

Fig. 1. Structure of $[MoS_4(CuCl)_6Cl_3]^{5-}$ (30% ellipsoids). Half of the anion (primed atoms) is generated through the mirror plane passing through Cl(3), Cu(3), S(1), S(2), Mo, Cu(2), Cl(2) and Cl(6).

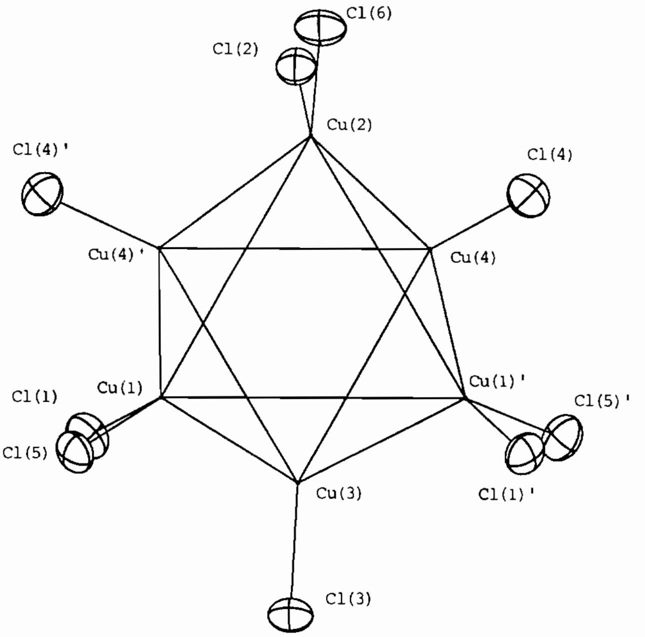

Fig. 2. Copper octahedron arrangement with the distribution of terminal chorine atoms. The MoS_4 tetrahedron is omitted for clarity.

atoms bound alternately to one and two chlorine atoms, e.g. Cu(2), Cu(4), Cu(1)′, see Fig. 2, are distorted. The Mo atom remains located on the C_3 axis passing through the centers of these faces.

The three trigonal Cu(3), Cu(4) and Cu(4)′ atoms are bound to only one terminal chloro ligand through a short Cu–Cl distance, av. 2.17(1) Å. Cu(1), Cu(2) and Cu(1)′ in a tetrahedral geometry are bound to two chlorines through a comparable short distance, av. 2.19(1) Å, and a longer bond, av. 2.49(1) Å.

The Cl(5) and Cl(6) atoms involved in these long Cu–Cl bonds do not serve as bridging ligands with Cu(3) and Cu(4), respectively, because the shortest Cl(5)–Cu(3) or Cl(6)–Cu(4) contact of 3.15 Å precludes any μ_2-Cl bridge, as observed for $[MoS_4(CuCl)_5Cl_2]^{4-}$ [5] and $[ReS_4(CuCl)_5Cl_2]^{3-}$ [8].

The Cu–S distances reflect the mode of coordination of the copper atoms, av. 2.268(15) Å for trigonal geometry, av. 2.339(2) Å for a tetragonal environment. These values are very similar to those reported for $[MoS_4(CuCl)_5Cl_2]^{4-}$ [5]. Owing to the distortion of the Cu octahedron, the Mo···Cu distances are slightly different, av. 2.634(1) Å for Cu(3), Cu(4) and 2.700(1) for Cu(1), Cu(2), respectively.

Since a nearly perfect *Td* symmetry is observed for the MoS_4 core, only one ν(M–S) frequency is observed in the IR spectrum, located at 435 cm^{-1} with a shoulder at 455 cm^{-1}. Electronic spectra show the expected S → Mo charge transfer shifted to 512 nm ($\epsilon = 3340$ $l\ mol^{-1}\ cm^{-1}$) with a shoulder at 372 nm.

Supplementary material

Thermal parameters and remaining bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

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