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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
Disorder in main residue
R factor = 0.022
wR factor = 0.056
Data-to-parameter ratio = 23.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

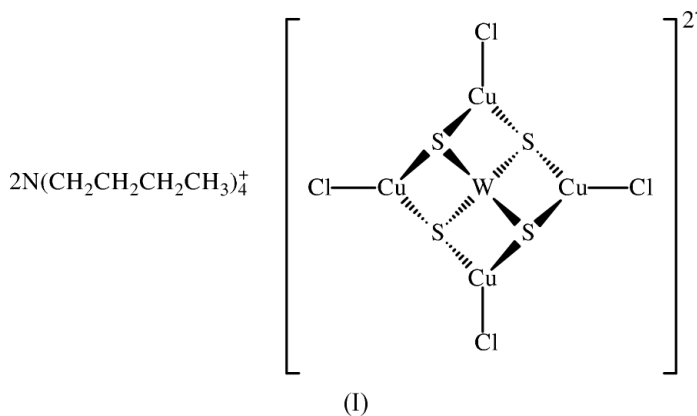
Bis(tetra-*n*-butylammonium) tetrakis[chloro-(μ_3 -sulfido)copper(I)]tungstate(VI): a second polymorph

The title compound, $(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{WS}_4(\text{CuCl})_4]$, has been obtained in a second polymorphic form. The anion, in which four of the six $\text{S} \cdots \text{S}$ edges of the central WS_4 tetrahedron are bridged by CuCl neutral molecular units to give a planar pentanuclear WCu_4 framework, is disordered on a crystallographic fourfold rotation axis, requiring equal occupancy of two sets of four positions for the S atoms. Copper has distorted trigonal planar coordination, involving two μ_3 -S atoms and a terminal Cl atom. The two independent cations lie on positions of symmetry $\bar{4}$.

Received 22 November 2004
Accepted 23 November 2004
Online 27 November 2004

Comment

We recently reported the structure of a second tetragonal polymorph of $(\text{N}^t\text{Bu}_4)_2[\text{MoS}_4(\text{CuCl})_4]$ in space group $P4/n$ (Brooks *et al.*, 2004); the first polymorph, in space group $I\bar{4}$, had very similar cell parameters (Sécheresse *et al.*, 1991). The title tungsten analogue, (I), was also prepared as a precursor for the synthesis of complexes with the WS_4Cu_4 core and a range of terminal ligands (Hossaini Sadr *et al.*, 2004) and it is found to be isostructural with the second polymorph of the molybdenum complex. There are no significant differences between the two structures, and a full discussion was given in the previous report.



Sécheresse *et al.* (1991) reported that the compound was isostructural with the molybdenum analogue in its body-centred tetragonal form, though only the cell parameters and space group are given and the Cambridge Structural Database entry (refcode SORLIU; Version 5.25; Allen, 2002) contains no atomic coordinates or other information indicating that the crystal structure has been fully determined. Two other salts of the same anion have been reported: in the tetraphenylphosphonium salt (Clegg *et al.*, 1987), the anion forms dimers through pairs of chloro bridges between Cu atoms, and in the tetra-*n*-propylammonium salt (Sécheresse *et al.*, 1991), further

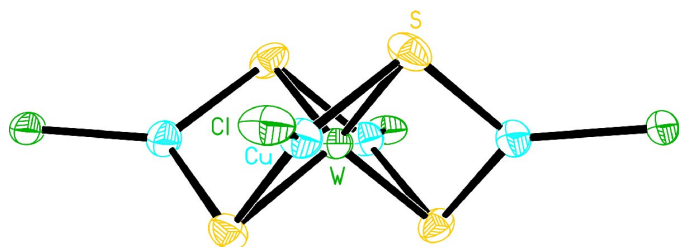


Figure 1

The structure of the anion, with atom labels for the asymmetric unit and 50% probability displacement ellipsoids. Only one component of the disorder is shown for the S atoms.

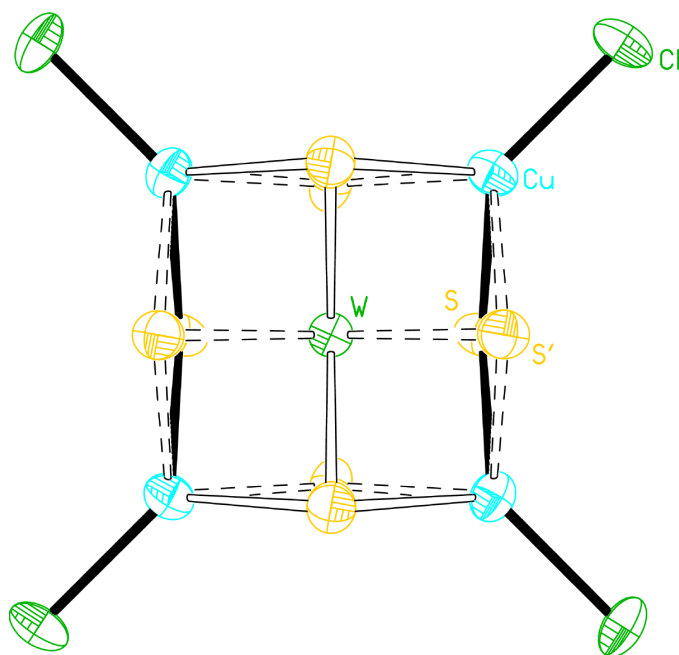


Figure 2

The anion with both disorder components, viewed along the crystallographic fourfold rotation axis. The second disorder component is shown with dashed ellipsoids and bonds; four of the W-S bonds are obscured by the four that are visible.

bridges are formed, linking the anions into a polymeric chain. A combination of terminal and bridging halogen atoms has been found in some other $[MS_4(CuX)_n]^{2-}$ complexes (Nicholson *et al.*, 1983), and the interplay is clearly subtle.

Experimental

A mixture of $(NH_4)_2[WS_4]$ (0.35 g, 1.0 mmol), solid $(NBu_4)Br$ (0.65 g, 2.0 mmol) and $CuCl$ (0.40 g, 4.0 mmol) in dry acetone (120 ml) was stirred vigorously in air at ambient temperature for 14 h. The resulting solution was filtered and the filtrate was concentrated to about 20 ml. The product was precipitated from the solution by addition of diethyl ether (4×25 ml) and removal of the supernatant solution each time. The orange-red precipitate was washed with diethyl ether (3×20 ml) and dried *in vacuo*. A saturated acetone solution of the complex was rendered slightly turbid by addition of *n*-pentane and air-stable orange crystals suitable for X-ray diffraction were collected after 48 h. The crystals were washed with diethyl ether several times. IR (KBr, cm^{-1}): (W-S) 441 (*s*).

Crystal data

$(C_{16}H_{36}N)_2[WCu_4Cl_4S_4]$
 $M_r = 1192.97$
 Tetragonal, $P4/n$
 $a = 13.3652$ (5) Å
 $c = 13.668$ (2) Å
 $V = 2441.5$ (4) Å³
 $Z = 2$
 $D_x = 1.623$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 54 reflections
 $\theta = 2.5$ – 25.0°
 $\mu = 4.47$ mm⁻¹
 $T = 150$ (2) K
 Plate, purple
 $0.44 \times 0.38 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)
 $T_{min} = 0.147$, $T_{max} = 0.637$
 42475 measured reflections
 2804 independent reflections

2441 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.047$
 $\theta_{max} = 27.5^\circ$
 $h = -17 \rightarrow 17$
 $k = -17 \rightarrow 17$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.056$
 $S = 1.11$
 2804 reflections
 119 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 2.9221P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.33$ e Å⁻³
 $\Delta\rho_{min} = -0.59$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

W-S	2.2435 (13)	Cu-S ⁱ	2.2296 (14)
W-S'	2.2555 (13)	Cu-S'	2.2882 (13)
Cu-Cl	2.1586 (7)	Cu-S' ⁱ	2.2961 (13)
Cu-S	2.2302 (13)		
S-W-S ⁱⁱ	109.61 (8)	S ⁱ -Cu-S'	107.96 (5)
S-W-S ⁱⁱⁱ	108.63 (5)	S-Cu-S' ⁱ	107.89 (5)
S-W-S' ⁱ	108.86 (5)	W-S-Cu	72.34 (4)
S'-W-S ⁱⁱ	112.23 (7)	W-S-Cu ⁱⁱⁱ	72.35 (4)
Cl-Cu-S	124.08 (4)	Cu-S-Cu ⁱⁱⁱ	113.64 (6)
Cl-Cu-S ⁱ	124.19 (4)	W-S'-Cu	71.05 (4)
Cl-Cu-S'	127.81 (4)	W-S'-Cu ⁱⁱⁱ	70.91 (4)
Cl-Cu-S' ⁱ	128.00 (4)	Cu-S'-Cu ⁱⁱⁱ	109.02 (6)
N1-C1-C2-C3	-174.12 (19)	N2-C5-C6-C7	-173.2 (2)
C1-C2-C3-C4	-172.5 (2)	C5-C6-C7-C8	74.5 (3)

Symmetry codes: (i) $\frac{1}{2} - y, x, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (iii) $y, \frac{1}{2} - x, z$.

The space group $P4/n$ was determined unambiguously from the systematic absences and confirmed by successful refinement; there is pseudo-body-centring, reflections with $h + k + l = 2n + 1$ having an average intensity approximately half that for reflections with $h + k + l = 2n$. Atom W lies on a crystallographic fourfold rotation axis (4 or C_4), while the two N atoms lie at improper fourfold rotation sites ($\bar{4}$ or S_4); thus, the asymmetric unit of the structure consists of one-quarter of the anion and two separate quarters of cations. The coordinates of the isostructural molybdenum complex were taken as starting parameters for refinement. As in the previous structure, the S atoms are disordered equally over two independent sets of equivalent positions, generating eight positions around the central W atom; each anion contains two S atoms from one set (S) and two from the other (S'). H atoms were placed geometrically (C-H = 0.98–0.99 Å) and refined with a riding model; $U_{iso}(H)$ values were constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. The final difference map contains one peak greater than 1 e Å⁻³, which lies 0.88 Å from the W atom.

Data collection: COLLECT (Nonius, 1998); cell refinement: EvalCCD (Duisenberg *et al.*, 2003); data reduction: EvalCCD;

program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

We thank the EPSRC (UK) and the Research Office of Azarbaijan University for financial support.

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