

Tetraethylammonium [1-methylimidazole-2(3H)-thione]copper(I)-di- μ -sulfido-dioxotungstate(VI)Azizolla Beheshti,^a Neil R. Brooks,^b William Clegg^{b*} and Rahman Khorrmdin^a^aDepartment of Chemistry, Faculty of Science, Shahid Chamran University, Ahvaz, Iran, and ^bSchool of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.064$ Å
 R factor = 0.092
 wR factor = 0.233
Data-to-parameter ratio = 17.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title complex, tetraethylammonium [1-methylimidazole-2(3H)-thione-2 κ S]dioxo-1 κ^2 O-di- μ -sulfido-1:2 κ^4 -S:S-copper(I)tungstate(VI), $(\text{C}_8\text{H}_{20}\text{N})[\text{WCuO}_2\text{S}_2(\text{Hmimt})]$, where Hmimt is 1-methylimidazole-2(3H)-thione ($\text{C}_4\text{H}_6\text{N}_2\text{S}$), the W and Cu atoms have tetrahedral and trigonal planar coordination, respectively. Two sulfide ligands bridge the two metal centres; tungsten is additionally coordinated by two terminal oxo ligands and copper by the exocyclic S atom of Hmimt. The bridged W...Cu distance is 2.670 (3) Å. Anions are linked into chains by N—H...O hydrogen bonds between Hmimt and oxo ligands.

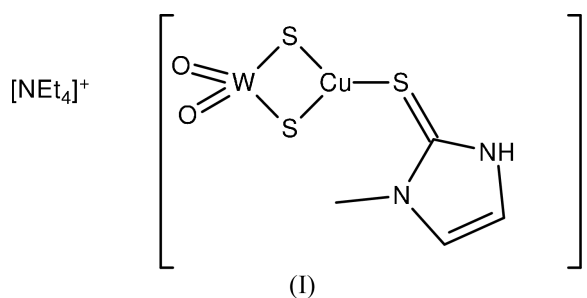
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Comment

Monovalent coinage metals are typical soft acids and their chemistry is largely based upon coordination by soft bases, such as sulfur donor ligands. Among the sulfur-containing ligands, heterocyclic thiones are of particular interest. Complexes of these ligands with transition metals are of interest in bioinorganic chemistry, because of the search for simple model compounds for metal proteins (Raper, 1996; Akrivos, 2001). In view of this, Cu^{I} (Dai *et al.*, 2004; Aslanidis *et al.*, 2004; Cox *et al.*, 1999), Ag^{I} (Isab *et al.*, 2002; Casas *et al.*, 1996) and Au^{I} (Ahmad, 2004; Isab & Hussain, 1985, 1986) complexes with thiones have been widely studied in recent years. We report here the synthesis and characterization of a copper(I) complex with Hmimt [1-methylimidazole-2(3H)-thione] and $[\text{WO}_2\text{S}_2]^{2-}$ as a sulfur-donor ligands. The anion of the title compound, (I), is only the second example of copper coordination by the $[\text{WO}_2\text{S}_2]^{2-}$ metalloligand to be verified by X-ray crystallography (Beheshti *et al.*, 2001) and only the third example for any metal, the other being a palladium complex (Long *et al.*, 1999).



A view of the structure is shown in Fig. 1 and selected geometric parameters are given in Table 1. The asymmetric unit consists of an $(\text{Et}_4\text{N})^+$ cation and an

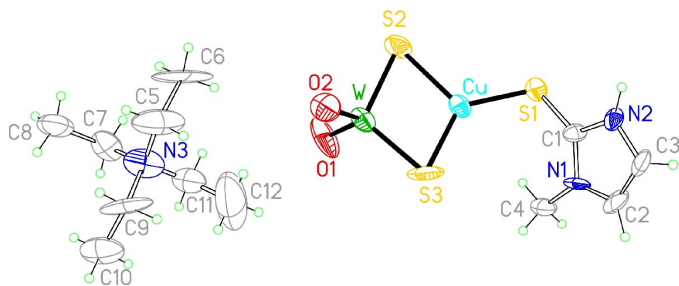


Figure 1
The molecular structure, with atom labels and 50% probability ellipsoids for non-H atoms.

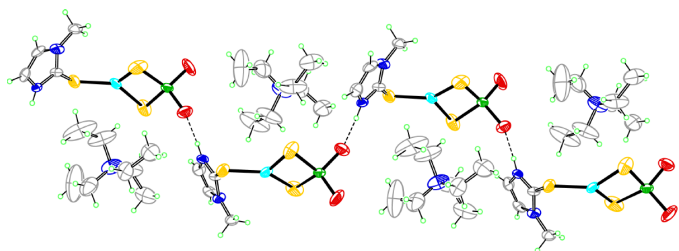


Figure 2
The chain of anions generated by N—H...O hydrogen bonding (shown as dashed lines).

$[\text{O}_2\text{WS}_2\text{Cu}(\text{Hmimt})]^-$ anion. The geometry of the cation is unexceptional. The Cu atom, with trigonal–planar geometry, is coordinated by the exocyclic S atom of an Hmimt ligand and by two S atoms of the dithiotungstate group, similar to the arrangement in $(\text{PPh}_4)[\text{O}_2\text{WS}_2\text{Cu}(\text{PPh}_3)] \cdot \text{Me}_2\text{CO}$ (Beheshti *et al.*, 2001), where triphenylphosphine replaces the Hmimt ligand. In the $[\text{O}_2\text{WS}_2\text{Cu}(\text{Hmimt})]^-$ anion, the three Cu–S bonds are slightly shorter than those in other compounds in which copper(I) is coordinated by three S atoms in a trigonal array involving bridging thiolates, including the clusters $(\text{Et}_4\text{N})[\text{Cu}_5(\text{SBu})_6]$ (2.260–2.290 Å; Bowmaker *et al.*, 1984) and $(\text{Me}_4\text{N})_2[\text{Cu}_4(\text{SPh})_6] \cdot \text{EtOH}$ (2.263–2.346 Å; Dance *et al.*, 1983). The Cu–S1 bond is significantly shorter than Cu–S bonds (2.202–2.401 Å) in complexes in which copper(I) is coordinated in a trigonal array by a thiotungstate as a bidentate ligand. This observation can be rationalized as a delocalization of charge from Cu^{I} to W^{VI} when a π -donor ligand such as Hmimt and a π -acceptor ligand such as $[\text{WO}_2\text{S}_2]^{2-}$ are bonded to a Cu^{I} atom. By the same reasoning, the Cu–S3 bond is shorter than that observed in $(\text{PPh}_4)[\text{O}_2\text{WS}_2\text{Cu}(\text{PPh}_3)] \cdot \text{Me}_2\text{CO}$ (average 2.239 Å), in which copper(I) is coordinated by PPh_3 as a π -acceptor ligand (Beheshti *et al.*, 2001).

The Cu1–S1–C1 angle is essentially the same as those obtained for the terminal Hmimt ligand in $[\text{Cu}(\text{Hmim})_3](\text{NO}_3)$ (average 107.3°; Atkinson *et al.*, 1985). The bending at the thione S atom introduces an asymmetry in the anion which is also apparent in the dimensions of the WS_2CuS core. In particular, the S3–Cu–S1 angle on the same side of the anion as the Hmimt ligand is significantly greater than the other two bond angles at the Cu atom. This deviation from ideal

trigonal–planar angles of 120° is attributed to steric effects and the bonding requirements of the Hmimt ligand.

The C2–C3 bond length in the Hmimt ligand is clearly consistent with a localized double bond and the thione C=S bond is weakened and lengthened on coordination relative to that of the uncoordinated Hmimt molecule (1.676 Å; Raper *et al.*, 1983), due to a reduction in the π -bond character of the thione linkage accompanying metal–thione coordination. The ^1H NMR signals of Hmimt are shifted downfield from those for the uncoordinated molecule, indicating that the ligand remains attached to Cu in solution in dimethyl sulfoxide. The ^{13}C NMR signals, compared with their positions in the spectrum of the uncomplexed ligand, support the coordination through S, leading to a weakening of the C=S bond and some partial double bond character for C–N (Popovic *et al.*, 2000; Bierbach *et al.*, 1998).

Tungsten has only slightly distorted tetrahedral coordination. The double sulfide bridges generate a short $\text{W} \cdots \text{Cu}$ distance of 2.670 (3) Å, which is not interpreted as a significant direct metal–metal bond.

The NH group of Hmimt forms a hydrogen bond with an oxo ligand attached to tungsten in a neighbouring anion, with an $\text{N} \cdots \text{O}$ distance of 2.70 (3) Å and an $\text{N}–\text{H} \cdots \text{O}$ angle of 177°. Repetition of this hydrogen bond by a screw axis generates a chain of anions along the *b* axis (Fig. 2). The tautomeric form of Hmimt is also confirmed by characteristic bands in the FT–IR spectrum, with an N–H but no S–H stretching vibration, and by the presence of a ^1H NMR signal for H bonded to N. There are no other significant interactions among the components apart from normal coulombic and van der Waals forces; the packing is shown in Fig. 3.

The FT–IR spectrum of the complex exhibits strong features at 902 and 837 cm^{-1} characteristic of the symmetric and asymmetric stretching vibrations of the $\text{W}=\text{O}$ bonds in the coordinated $[\text{WO}_2\text{S}_2]^{2-}$ anion, respectively. The band at 437 cm^{-1} is assigned to the bridging W–S bonds.

Experimental

$(\text{NH}_4)_2[\text{WO}_2\text{S}_2]$ (0.316 g, 1.0 mmol) was dissolved in dimethylformamide (5 ml) and solid $(\text{Et}_4\text{N})\text{Br}$ (0.441 g, 2.1 mmol) was added. The mixture was stirred at room temperature for 5 min. CuCl (0.1 g, 1.01 mmol) was added and the mixture was stirred for another 5 min and then filtered. 2-Propanol (10 ml) and diethyl ether (20 ml) were added to the filtrate. After stirring for 5 min, the precipitate was collected by filtration. It was washed with 2-propanol (3 ml) and diethyl ether (5 ml) and dried *in vacuo* to give a hygroscopic orange powder of $(\text{Et}_4\text{N})[\text{O}_2\text{WS}_2\text{CuCl}]$ (yield 59%). $(\text{Et}_4\text{N})_2[\text{O}_2\text{WS}_2\text{CuCl}]$ (0.128 g, 0.2 mmol) was dissolved in acetonitrile (5 ml). Hmimt (0.049 g, 0.43 mmol) was added and the mixture was stirred at room temperature for 30 min and then filtered. Dry diethyl ether was added to the filtrate until a cloudiness persisted throughout the solution. Upon leaving the solution to stand in a sealed flask at 278 K overnight, pale-orange crystals of $(\text{Et}_4\text{N})[\text{O}_2\text{WS}_2\text{Cu}(\text{Hmimt})]$ were obtained. ^1H NMR ($\text{DMSO}-d_6$): δ 12.62 (s, NH), 7.23 (s, CH), 7.06 (s, CH), 3.53 (s, NCH_3), together with characteristic signals for the cation; ^{13}C NMR ($\text{DMSO}-d_6$): δ 155.64 (C1), 121.87 (C3), 116.34 (C2), 34.96 (NCH_3), and cation signals, using the numbering scheme of Fig. 1.

Crystal data

(C₈H₂₀N)[WCuO₂S₂(C₄H₆N₂S)]
M_r = 587.93
 Orthorhombic, *P*₂₁₂₁
a = 7.1985 (5) Å
b = 16.3720 (14) Å
c = 17.244 (2) Å
V = 2032.3 (3) Å³
Z = 4
D_x = 1.922 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 17595 reflections
 $\theta = 2.5\text{--}26.0^\circ$
 $\mu = 7.02\text{ mm}^{-1}$
T = 150 (2) K
 Block, pale orange
 0.34 × 0.16 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1997)
T_{min} = 0.190, *T_{max}* = 0.570
 17533 measured reflections
 3557 independent reflections

3369 reflections with *I* > 2σ(*I*)
R_{int} = 0.035
 $\theta_{\text{max}} = 25.0^\circ$
h = -8 → 6
k = -19 → 19
l = -20 → 20

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.092
wR (*F*²) = 0.233
S = 1.24
 3557 reflections
 201 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 149.3501P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.043
 $\Delta\rho_{\text{max}} = 3.68\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.79\text{ e \AA}^{-3}$
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.0029 (6)
 Absolute structure: Flack (1983),
 1506 Friedel pairs
 Flack parameter = 0.35 (5)

Table 1

Selected geometric parameters (Å, °).

W—S2	2.288 (7)	S1—C1	1.75 (3)
W—S3	2.228 (10)	N1—C1	1.37 (3)
W—O1	1.77 (2)	N1—C2	1.36 (4)
W—O2	1.75 (2)	N1—C4	1.40 (3)
Cu—S1	2.189 (7)	N2—C1	1.34 (3)
Cu—S2	2.340 (9)	N2—C3	1.37 (4)
Cu—S3	2.168 (9)	C2—C3	1.33 (4)
S2—W—S3	107.0 (3)	W—S3—Cu	74.8 (3)
S2—W—O1	107.8 (12)	C1—N1—C2	106 (2)
S2—W—O2	106.3 (8)	C1—N1—C4	121 (2)
S3—W—O1	114.2 (13)	C2—N1—C4	132 (2)
S3—W—O2	112.2 (9)	C1—N2—C3	109 (2)
O1—W—O2	108.9 (12)	S1—C1—N1	130 (2)
S1—Cu—S2	121.7 (3)	S1—C1—N2	122 (2)
S1—Cu—S3	130.9 (4)	N1—C1—N2	108 (2)
S2—Cu—S3	107.2 (4)	N1—C2—C3	110 (3)
Cu—S1—C1	106.5 (10)	N2—C3—C2	106 (3)
W—S2—Cu	70.4 (2)		
S2—Cu—S1—C1	157.1 (9)	Cu—S1—C1—N1	65 (3)
S3—Cu—S1—C1	-18.0 (11)	Cu—S1—C1—N2	-121 (2)

H atoms were positioned geometrically and refined with a riding model, and with *U*_{iso} values constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom. Large and highly anisotropic displacement ellipsoids for the atoms of the cation indicate probable disorder, but no simple disorder model could be resolved; refinement was assisted by restraints on geometry and displacement parameters, and the overall precision of the structure is relatively low as a result. The cation and anion are both achiral, but the compound crystallizes in a non-centrosymmetric space group; the refined Flack (1983) parameter of 0.35 (5) indicates partial inversion twinning of the structure. The maximum and minimum final difference electron density features both lie almost 1 Å from the W atom.

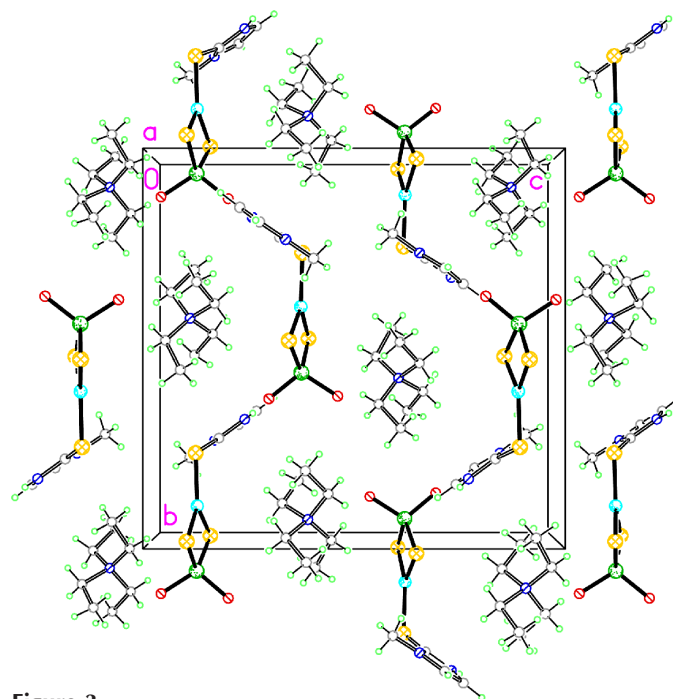


Figure 3

The crystal packing, viewed down the *a* axis.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EvalCCD* (Duisenberg *et al.*, 2003); data reduction: *EvalCCD*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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