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N—H···S and N—H···O hydrogen bonding in tetra-*n*-butylammonium (imidazolidine-2-thione-2κS)dioxo-1$\kappa^2 O$-di-μ-sulfido-1:2$\kappa^4 S$:S-copper(I)tungstate(VI)

Azizolla Beheshti,[a]* William Clegg,[b]* Sophie H. Dale[b] and Ahmad Solimankhani[a]

[a]Department of Chemistry, Faculty of Science, Shahid Chamran University, Ahvaz, Iran, and [b]School of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England

Correspondence e-mail:
beheshti_a@hotmail.com, w.clegg@ncl.ac.uk

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In the title complex, $(C_{16}H_{36}N)[WCuO_2S_2(C_3H_6N_2S)]$, 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 imidazolidine-2-thione. There is an intramolecular N—H···S hydrogen bond in the anion, and anions are linked into chains by N—H···O intermolecular hydrogen bonds. The more loosely held cation is disordered.

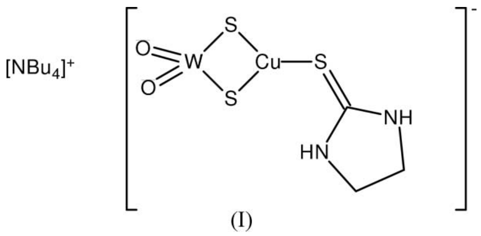
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.033
wR factor = 0.073
Data-to-parameter ratio = 16.4

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

Comment

The formation of hydrogen bonds, including intramolecular N—H···S hydrogen bonds, in many biological macromolecules such as azurin and rubredoxin, has been confirmed by X-ray crystallography, vibrational and NMR spectroscopic studies (Houseman *et al.*, 1992; Adman, 1991; Backes *et al.*, 1991; Blake *et al.*, 1992; Watenpaugh *et al.*, 1979; Tsukihara *et al.*, 1981; Adman *et al.*, 1975; Baker, 1988). We present here a copper(I) complex, (I), with two kinds of hydrogen bonds, namely intramolecular N—H···S and intermolecular N—H···O.



(I)

The structure of the bimetallic anion is shown in Fig. 1 and selected geometric parameters are given in Table 1. The disordered cation is geometrically unexceptional. In the $[O_2WS_2Cu(Imt)]^-$ anion (Imt is imidazolidine-2-thione), the coordination environments of tungsten(VI) and copper(I) are slightly distorted tetrahedral and rather more strongly

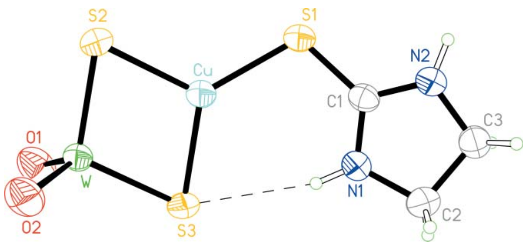


Figure 1
The structure of the anion with atom labels and 50% probability displacement ellipsoids for non-H atoms. The intramolecular hydrogen bond is shown as a dashed line.

distorted trigonal planar, respectively. The angular deviations around the Cu atom may be attributed to steric effects and the constraints of the WS_2Cu four-membered ring. Copper is coordinated by two bridging S and a terminal, monodentate S-donating Imt ligand. The bridging angles at S are the smallest angles in the complex and are only slightly larger than the value required for regular edge-sharing tetrahedra (70.5°; Summerville & Hoffman, 1976). Narrowing of the bridging angle is inevitably accompanied by a reduction in the W$\cdots$Cu separation distance, which is not, however, considered as indicating a direct metal-metal bond. The Cu—S1 distance and Cu—S—C angle are typical of terminal monodentate S-donating thiones attached to trigonal planar Cu(I) (Beheshti *et al.*, 2004). In common with other thione complexes, a slight lengthening of the S—C distance occurs, relative to that of the C═S bond length in the free Imt ligand, due to a reduction in the π-bond character of the thione linkage accompanying metal-thione coordination. The Cu—S2 and Cu—S3 distances are in the range [2.168 (9)–2.340 (9) Å] reported for $(Et_4N)[WO_2S_2Cu(Hmimt)]$, where Hmimt is the closely related ligand 1-methylimidazole-2(3*H*)-thione (Beheshti *et al.*, 2004).

Although there are many crystallographically characterized examples of complexes in which Cu^I is bonded across S$\cdots$S edges of $[WS_4]^{2-}$ and $[OWS_3]^{2-}$ tetrahedra, the title complex appears to be only the third case for $[O_2WS_2]^{2-}$, the others being the closely related Cu(Hmimt) complex mentioned above (Beheshti *et al.*, 2004) and a $CuPPh_3$ complex (Beheshti *et al.*, 2001).

The striking feature of the structure of the anion is the orientation of the thione ligand; this brings one NH group of the heterocyclic ligand into a position close to one bridging sulfur atom of the WO_2S_2 group, with the formation of an intramolecular N—H$\cdots$S hydrogen bond (Fig.1 and Table 2). In addition to the intramolecular N—H$\cdots$S hydrogen bond, the second NH group of Imt forms an intermolecular hydrogen bond with an oxo ligand attached to tungsten in a neighbouring anion (Fig. 2 and Table 2). This hydrogen bond generates a chain of anions. Such hydrogen bonds have been found to play important roles in regulating the properties of metal-sulfur proteins as well as their model complexes (Houseman *et al.*, 1992; Sun *et al.*, 1993).

In the solid state, infrared spectroscopy may also be used to probe the mode of coordination of Imt and $[WO_2S_2]^{2-}$ ligands. Uncoordinated Imt exhibits N—H stretching and C═S bands at 3200 and 510 cm^{-1}, respectively. The corresponding N—H and C═S vibration bands were observed at 3308 and 500 cm^{-1} for the complex. The shifts of ν(N—H) (108 cm^{-1} upwards) and ν(C═S) (10 cm^{-1} downwards) and the absence of a ν(S—H) band at 2500 cm^{-1} clearly indicate that the Imt ligand is coordinated only *via* the thione sulfur in the complex. The W═O stretching frequencies of the $[WO_2S_2]^{2-}$ ligand in the complex (918 and 867 cm^{-1}) are shifted to higher values than for the free $[WO_2S_2]^{2-}$ anion (850 and 795 cm^{-1} in the ammonium salt; McDonald *et al.*, 1983); this indicates that the $[WO_2S_2]^{2-}$ ligand is coordinated through its sulfur atoms. The band at 437 cm^{-1} is assigned to the bridging W—S bonds. Thus, the infrared spectroscopic results are consistent with the X-ray structural analysis.

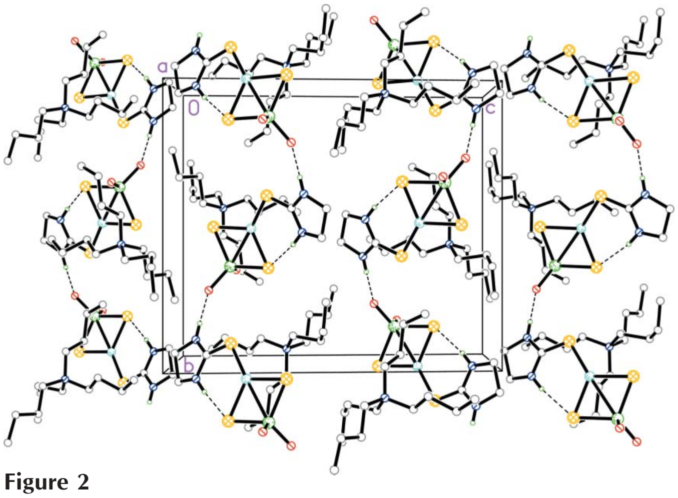


Figure 2
A section of the packing, viewed along the *a* axis. Hydrogen bonds are shown as dashed lines, and other H atoms have been omitted, together with minor disorder components.

Experimental

$(NH_4)_2[WO_2S_2]$ (0.316 g, 1.0 mmol) was dissolved in acetone (40 ml) and solid $(n\text{-}Bu_4N)Br$ (0.676 g, 2.1 mmol) was added. The mixture was stirred at room temperature for 5 min. CuCl (0.099 g, 1 mmol) was added and the mixture was stirred for 1 h. Imt (0.112 g, 1.1 mmol) was added and the mixture was stirred at room temperature for 4 h and then filtered. The filtrate was evaporated under vacuum. The oily residue was dissolved in dichloromethane (25 ml) and the solution filtered to remove any insoluble material. The filtrate was evaporated to dryness under vacuum. The residue was washed with distilled water (2 × 2 ml), 2-propanol (2 × 2 ml) and diethyl ether (2 × 5 ml) and dried *in vacuo* to give a pale-brown powder. The yield at this stage was 0.43 g (46%). Crystals were obtained by diffusing diethyl ether into a saturated solution in acetone. On leaving the solution to stand in a refrigerator overnight, air-stable orange crystals were deposited, which are soluble in common organic solvents. ^1H NMR (DMSO-d_6, 300 K): δ 8.38 (*s*, N—H), 3.68 (*s*, CH_2); ^{13}C NMR (DMSO-d_6, 300 K): δ 180.23 (C1), 45.41 (C2 and C3) (using the atom numbering of Fig. 1). In the ^1H NMR spectrum of the complex, the ligand signals are shifted down-field from their positions in the spectrum of the free ligand (N—H,7.94 and CH_2 3.505 p.p.m.), but in the ^{13}C NMR spectrum of the complex, the C═S signal is shifted up-field from its position in the spectrum of the free ligand (183.35 p.p.m.), due to the reduction of the C═S bond order upon coordination and a shift of electron density producing partial double bond character in the C—N bond. These observations indicate that, in DMSO-d_6, the ligand remains coordinated to the metal.

Crystal data

$(C_{16}H_{36}N)[WCuO_2S_2(C_3H_6N_2S)]$
$M_r = 688.13$
Monoclinic, $P2_1/c$
$a = 10.6925$ (16) Å
$b = 14.875$ (2) Å
$c = 17.2342$ (8) Å
$\beta = 94.742$ (7)°
$V = 2731.7$ (6) Å^3
$Z = 4$

$D_x = 1.673$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 227 reflections
$\theta = 2.5$–27.5°
$\mu = 5.23$ mm^{-1}
$T = 150$ (2) K
Block, orange
0.77 × 0.43 × 0.31 mm

m1510 Beheshti *et al.* • $(C_{16}H_{36}N)[WCuO_2S_2(C_3H_6N_2S)]$ *Acta Cryst.* (2005). E**61**, m1509–m1511

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 2001)
$T_{\min} = 0.100$, $T_{\max} = 0.239$
28801 measured reflections
6215 independent reflections
4881 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -19 \rightarrow 18$
$l = -22 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.074$
$S = 1.07$
6215 reflections
378 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0159P)^2 + 6.5317P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.029$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.96$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.00053 (11)

Table 1
Selected geometric parameters (Å, °).

W—Cu	2.6755 (6)	Cu—S3	2.2459 (14)
W—O1	1.731 (4)	S1—C1	1.711 (5)
W—O2	1.750 (3)	C1—N1	1.338 (6)
W—S2	2.2652 (13)	C1—N2	1.326 (6)
W—S3	2.2670 (13)	N1—C2	1.471 (6)
Cu—S1	2.2047 (13)	C2—C3	1.543 (7)
Cu—S2	2.2385 (14)	C3—N2	1.453 (6)
O1—W—O2	109.42 (18)	S1—C1—N1	126.8 (4)
O1—W—S2	109.53 (14)	S1—C1—N2	123.3 (3)
O1—W—S3	109.63 (15)	N1—C1—N2	109.9 (4)
O2—W—S2	110.36 (13)	C1—N1—C2	111.5 (4)
O2—W—S3	111.47 (13)	N1—C2—C3	101.2 (4)
S2—W—S3	106.37 (5)	C2—C3—N2	102.5 (4)
S1—Cu—S2	123.40 (5)	C1—N2—C3	112.0 (4)
S1—Cu—S3	128.57 (5)	W—S2—Cu	72.89 (4)
S2—Cu—S3	108.02 (5)	W—S3—Cu	72.72 (4)
Cu—S1—C1	106.99 (16)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S3	0.87 (1)	2.66 (2)	3.490 (4)	160 (5)
N2—H2···O2$^{\rm i}$	0.87 (1)	1.87 (1)	2.729 (5)	174 (5)

Symmetry code: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

The cation is disordered. Most C atoms could be resolved into two components with sensible connectivities. Separate occupancy factors were refined for the components of each *n*-butyl group, giving values of 0.747 (9), 0.660 (12), 0.690 (9) and 0.817 (10) for the major sites; similarity restraints were applied to the displacement parameters and bond lengths. The remaining C atoms may also be disordered, to a smaller extent, but this could not be resolved. H atoms bonded to N were located in a difference map and refined with a restrained N—H distance of 0.87 (2) Å, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm N})$. Other H atoms were positioned geometrically and refined with a riding model, with C—H = 0.95–0.99 Å, and with $U_{\rm iso}({\rm H}) = 1.2$ (1.5 for methyl groups) times $U_{\rm eq}({\rm C})$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); 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.

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Acta Cryst. (2005). E**61**, m1509–m1511 Beheshti *et al.* • $(C_{16}H_{36}N)[WCuO_2S_2(C_3H_6N_2S)]$ **m1511**