Polysulfonylamines. CLXXI. [Di(methanesulfonyl)amido-κN]-bis(2-picoline-κN)copper(I)[1]

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The title compound, $[Cu(C_2H_6NO_4S_2)(C_6H_7N)_2]$, consists of monomeric molecules in which the Cu atom displays planar but irregular coordination by three N-atom donors; Cu—N = 2.1054 (12) (amide N), 1.9514 (12) and 1.9589 (12) Å, and N—Cu—N = 141.24 (5), 111.54 (5) and 107.20 (5)°. Intramolecular Cu···O contacts are observed. The packing involves (interconnected) layer formation via C—H···O interactions in two directions, three hydrogen bonds combining to form layers parallel to (101) and five to form layers parallel to (10$\bar{2}$).

Comment

We are interested in the synthesis and structure of complexes of the coinage metals with nitrogen ligands. We have been able to show that amine complexes of gold(I) are much more stable than normally assumed on the basis of hard/soft incompatibility, and that they can be stabilized further by using disulfonylamides $(RSO_2)_2N^-$, especially di(methanesulfonyl)-amide ($R = CH_3$; henceforth DMS), as counter-ions (Ahrens et al., 2000, and references therein). Amine complexes of silver(I) disulfonylamides are easier to prepare (Zerbe & Jones, 2004) because the silver salts are available as stable starting materials, whereas homoleptic gold(I) disulfonyl-amides are not known. The disulfonylamides can coordinate to silver(I), but rarely to gold(I), which has little tendency to increase its coordination number beyond two.

We now wished to extend our studies to complexes of copper(I). The starting material, copper(I) DMS, is available (Linoh, 1989) but is of limited stability. Nevertheless, an initial synthesis and structure determination, that of the title compound, (I), proved successful. The molecule of (I) is shown in Fig. 1.

The Cu centre of (I) exhibits planar three-coordination by two picoline (2-methylpyridine) N atoms and the N atom of the amide (r.m.s. deviation of four atoms = 0.007 Å), but the coordination is far from regular, with the Cu—N_{amide} bond

being 0.15 Å longer than the Cu—$N_{picoline}$ bonds. Consistent with this, the angle opposite Cu—N_{amide} is (by far) the largest (Table 1).
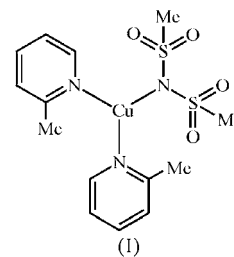
The dimensions of the picoline ligands may be regarded as normal. The ring angles at the N atom are slightly less than the ideal value of 120° (Table 1).

All three ligands are essentially perpendicular to the CuN_3 plane, with interplanar angles of 85.37 (5)° from the first picoline molecule, 78.34 (5)° from the second and 80.34 (3)° from the SNS plane of the amide.

A search of the Cambridge Structural Database (Version 5.25; Allen, 2002) showed that there are few examples of monomeric copper(I) complexes with three monodentate nitrogen ligands. Habiyakare et al. (1992) presented the structures of seven $[CuL_3]^+$ complexes (L are various methylpyridines). In each case, the coordination geometry was planar but with considerable variation in angles, ranging from almost regular (all three angles 120°) to irregular (106–141°). Particularly wide angles tended to be associated with ligands that were approximately coplanar with the CuN_3 plane, and with weak axial contacts from the Cu centres to the counter-anions. The Cu—N bond lengths are clustered around 2.00 Å, but with a range of 1.962 (4)–2.10 (1) Å; the C—N—C angles showed a slight tendency to be less than 120°, with an average value of 118.6°, but again with appreciable scatter (115.9–124.9°). Näther & Beck (2004) have recently presented the structure of the neutral molecule chlorodipiperidine-copper(I), which is also trigonal planar at Cu, with a wide N—Cu—N angle of 135.37 (7)°.

The DMS group in (I) displays the usual conformation, with approximate C_2 symmetry, whereby the local twofold axis is the bisector of the S—N—S angle. As a measure of the
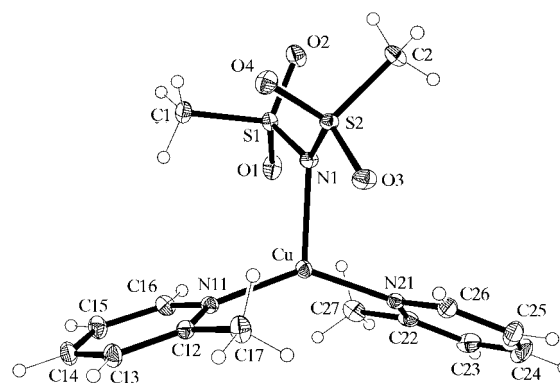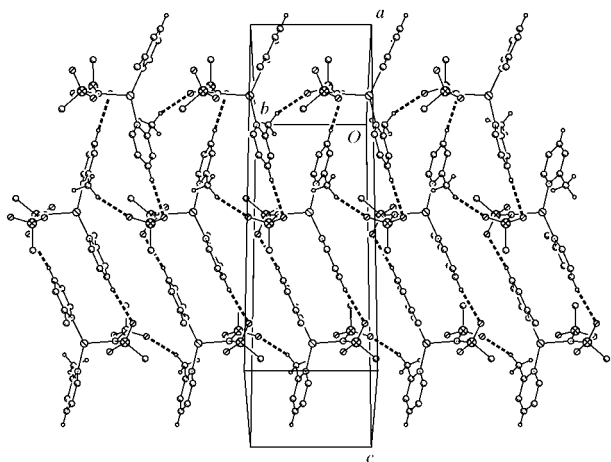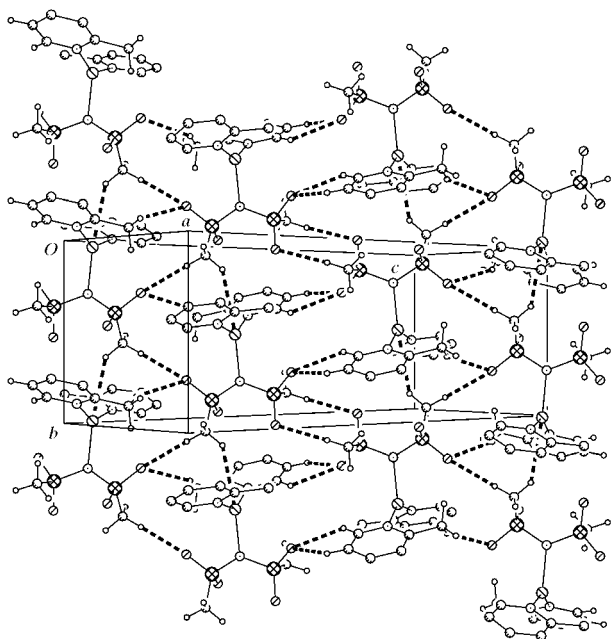

Figure 1
The molecule of (I) in the crystal, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

metal-organic compounds

Figure 2
The layer formation in (I), viewed perpendicular to (101). Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonds have been omitted.

Figure 3
The layer formation in (I), viewed perpendicular to (10$\bar{2}$). Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonds have been omitted.

deviation from ideal symmetry, we use the average absolute difference $\Delta\tau_{SN}$ between equivalent torsion angles about the S—N bonds; here, the value is 3.8°. A further general feature is the presence of two antiperiplanar S—N—S—O$_{ap}$ groupings that together form a W-shaped sequence of five atoms. The two O$_{ap}$ atoms, which as usual form the narrower O—S—N angles (as in the essentially 'free' DMS anion in its 1-aza-4-azoniabicyclo[2.2.2]octane salt; Henschel *et al.*, 1997), are involved in short intramolecular contacts to the Cu atom, with Cu···O1 = 3.0545 (12) Å and Cu···O3 = 3.0360 (11) Å.

In a long series of publications, we have established that the O atoms of the DMS group are versatile hydrogen-bond acceptors (*e.g.* Wijaya *et al.*, 2004, and references therein).

However, the current structure contains no classical hydrogen-bond donors. In such cases, 'weak' hydrogen bonds of the form C—H···O (Desiraju & Steiner, 1999) would be expected and are indeed observed (Table 2). In the following discussion, the numbering refers to the order in Table 2.

The complete hydrogen-bonding pattern in (I) is three-dimensional and complex, but may be analysed in terms of layer formation in two directions. Hydrogen bonds 1–3, including one from each *para* H atom of the picoline ligands, combine to form layers parallel to (101) (Fig. 2). The remaining hydrogen bonds 4–8, of which 4 and 5 form a bifurcated (C—H···)$_2$O unit, and 7 and 8 represent hydrogen bonds between DMS units (as we have commonly observed, *e.g.* Wijaya *et al.*, 2004), combine to form layers parallel to (10$\bar{2}$) (Fig. 3). The final interaction in Table 2 is included as a reminder that metal atoms may also fulfil the criteria for hydrogen-bond acceptors.

Experimental

Copper(I) di(methanesulfonyl)amide, prepared according to the method of Linoh (1989), was dissolved in excess 2-picoline and the solution overlayered with diethyl ether. Despite considerable decomposition, a few colourless crystals of (I) formed. Clearly, the method needs thorough optimization before it can be used as a reliable synthetic procedure.

Crystal data

$[(C_2H_6NO_4S_2)Cu(C_6H_7N)_2]$	$D_x = 1.570$ Mg m^{-3}
$M_r = 421.99$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 7138
$a = 10.2353$ (6) Å	reflections
$b = 7.7684$ (4) Å	$\theta = 2$–30.5°
$c = 23.0287$ (14) Å	$\mu = 1.48$ mm^{-1}
$\beta = 102.780$ (4)°	$T = 133$ (2) K
$V = 1785.69$ (18) Å^3	Block, colourless
$Z = 4$	$0.39 \times 0.25 \times 0.17$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	5215 independent reflections
	4267 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.030$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	$\theta_{max} = 30.0$°
	$h = -14 \rightarrow 14$
$T_{min} = 0.625$, $T_{max} = 0.746$	$k = -10 \rightarrow 10$
35 736 measured reflections	$l = -31 \rightarrow 32$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$
$wR(F^2) = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.002$
5215 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
221 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1	2.1054 (12)	Cu—N21	1.9589 (12)
Cu—N11	1.9514 (12)		
N11—Cu—N21	141.24 (5)	O2—S1—N1	112.29 (6)
N11—Cu—N1	111.54 (5)	O4—S2—N1	112.68 (6)
N21—Cu—N1	107.20 (5)	C16—N11—C12	117.93 (12)
O1—S1—N1	104.63 (7)	C26—N21—C22	118.86 (13)
O3—S2—N1	104.96 (6)		
S2—N1—S1—O1	173.13 (8)	S1—N1—S2—O3	176.71 (8)

Table 2
Hydrogen-bonding and short-contact geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
C24—H24···O1$^{\mathrm{i}}$	0.95	2.58	3.531 (2)	176
C27—H27A···O2$^{\mathrm{ii}}$	0.98	2.43	3.371 (2)	161
C14—H14···O4$^{\mathrm{iii}}$	0.95	2.64	3.5863 (19)	174
C15—H15···O1$^{\mathrm{iv}}$	0.95	2.64	3.1930 (18)	118
C16—H16···O1$^{\mathrm{iv}}$	0.95	2.47	3.1278 (17)	126
C17—H17A···O3$^{\mathrm{v}}$	0.98	2.62	3.4563 (19)	143
C1—H1C···O2$^{\mathrm{vi}}$	0.98	2.55	3.4560 (18)	154
C2—H2A···O3$^{\mathrm{vii}}$	0.98	2.41	3.3908 (18)	177
C2—H2B···Cu$^{\mathrm{viii}}$	0.98	2.94	3.7529 (17)	141

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $x, 1+y, z$; (iii) $2-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vi) $1-x, -y, 1-z$; (vii) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (viii) $x, y-1, z$.

Methyl H atoms were clearly identified in difference syntheses, idealized and refined as rigid groups allowed to rotate but not tip. Other H atoms were included using a riding model. C—H bond lengths were fixed at 0.98 (methyl) or 0.95 Å (aromatic), and methyl H—C—H angles at 109.5°. $U_{\mathrm{iso}}(\mathrm{H})$ values were fixed at $1.2U_{\mathrm{eq}}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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