Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Diisothiocyanato[di(2-pyridyl)methanediol]copper(II) bis(dimethyl sulfoxide), [Cu(NCS)$_2$(dpydiol)]·2DMSO

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Received 10 May 2001
Accepted 23 May 2001
Online 15 June 2001

Key indicators

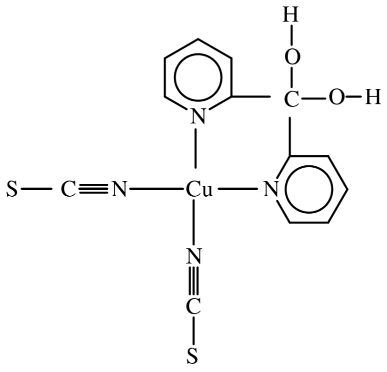
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.057
wR factor = 0.152
Data-to-parameter ratio = 11.3

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

The crystal and molecular structure of green [Cu(NCS)$_2$(C$_{11}$H$_{10}$N$_2$O$_2$)]·2(CH$_3$)$_2$SO, which forms a distinct dimer in the crystalline state, was determined. The stereochemistry of the monomer is a distorted five-coordinate square pyramidal arrangement of four N atoms and a displaced fifth ligand position occupied by an oxygen of a hydroxy group of the gem-diol ligand. Two of the nitrogen ligands are N-bonded thiocyanates and the other two N atoms are furnished by the di(2-pyridyl)methanediol ligand. The copper to nitrogen distances are 1.935 (4), 1.942 (4) Å for the two thiocyanates and 2.025 (3), 2.032 (3) Å for the di(2-pyridyl)methanediol ligand. The copper to oxygen distance is 2.475 (3) Å and the copper to sulfur distance in the dimer is 3.1394 (17) Å.

Comment

The isolation of the normally labile hydrate of a ketone by complexing a ketone containing ligand with a transition metal has been demonstrated by several different authors (Parker *et al.*, 2000; Deveson *et al.*, 1996; Wang *et al.*, 1986; Sommerer *et al.*, 1993; Papadopoulos *et al.*, 1996; Tangoulis *et al.*, 1997; Breeze et al., 1996; Yang *et al.*, 1998). The title compound, [Cu(NCS)$_2$(dpydiol)].2(CH$_3$)$_2$SO, (I), where dpydiol = di(2-pyridyl)methanediol, contains one gem-diol ligand with the two hydroxy groups each hydrogen bonded to a solvent dimethylsulfoxide molecule. The two hydroxy groups on a gem-diol ligand have a strong tendency to hydrogen bond to the solvent and one of the hydroxy groups has an O atom occupying a fifth ligand position. The thiocyanate complex with only one gem-diol ligand is uniquely different because the sixth ligand position about the copper atom is occupied by a sulfur atom from a neighboring molecule, which produces a distinct dimer in the crystalline state.



(I)

DOI: 101107/S1600536801008534

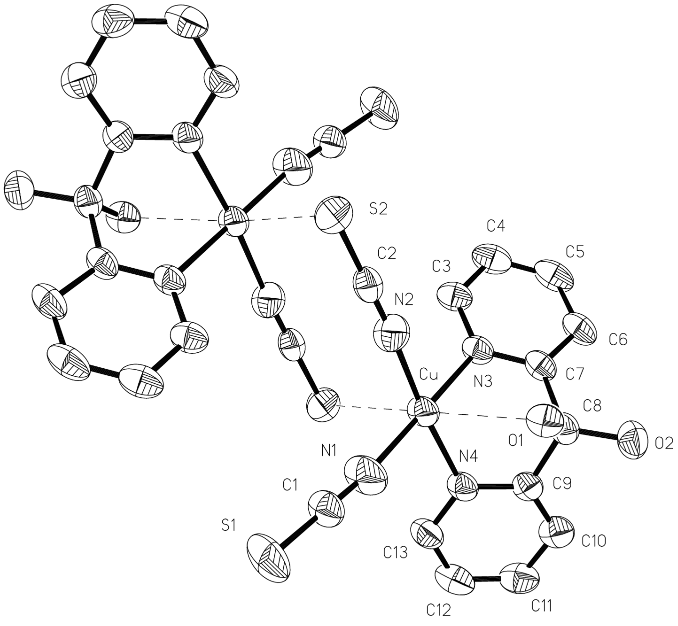


Figure 1
Displacement ellipsoid (50% probability) plot of [Cu(NCS)$_2$(dpydiol)] showing the atom-numbering scheme. H atoms have been omitted.

A drawing of the structure with displacement ellipsoids and the atom labeling scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 1.

The X-ray structure of the complex (Fig. 1) contains a copper atom positioned at the center of a distorted octahedron. The N atoms from the di(2-pyridyl)methanediol ligand and the two thiocyanate ions surround the copper atom in a square planar arrangement. The thiocyanate ligand distances and angles are: Cu—N1, Cu—N2, 1.935 (4) Å, 1.942 (4) Å, and N1—Cu—N2 angle of 91.77 (17)°. The di(2-pyridyl)-methanediol ligand distances and angles are: Cu—N3, Cu—N4, 2.032 (3) Å, 2.025 (3) Å, and N3—Cu—N4 87.43 (13)°. The fifth ligand position is occupied by an O atom of the di(2-pyridyl)methanediol ligand and with a Cu—O1 distance of 2.475 (3) Å with O1—Cu—N1 and O1—Cu—N2 angles of 110.15 (16) and 100.91 (13)° respectively. These results are very close to the observed distances in [Cu(dpydiol)$_2$]Br$_2$.4H$_2$O which had a Cu—O distance of 2.464 (3) Å for the two di(2-pyridyl)methanediol ligands (Parker *et al.*, 2000).

Two diisothiocyanato copper(II) complexes, [Cu(NCS)$_2$(bipy)] and [Cu(NCS)$_2$(phen)] where bipy is 2,2′-bipyridine and phen is 1,10-phenanthroline, crystallize as infinite linear polymers (Breneman & Parker, 1993; Parker *et al.*, 1994). The ability of the ketone ligand to hydrate and then bond to the central copper as the fifth ligand gives the preferred crystalline state in the case of [Cu(NCS)$_2$(dpydiol)]. The resulting Cu—O bond distance of 2.475 (3) Å is shorter than what would be expected if an infinite polymer rather than a dimer with a Cu—S bond distance of 3.1394 (17) Å were formed.

Experimental

A 15 ml solution of di-2-pyridyl ketone (0.737 g, 4.0 mmol) dissolved in ethanol was added to a 15 ml solution of Cu(NO$_3$)$_2$.3 H$_2$O (0.483 g, 2.0 mmol) in water. Mixing of these two solutions produced an exothermic reaction and a brilliant purple solution. A 15 ml solution of NH$_4$NCS (0.304 g, 4.0 mmol) in water was slowly added with continuous stirring to the purple solution. The reaction with ammonium thiocyanate produced a blue–purple solution which contained a dark green precipitate. The green solid was filtered and air-dried. This green solid was dissolved in dimethylsulfoxide and allowed to crystallize by solvent evaporation for several days. A single crop of bright green crystals was obtained for the X-ray structure determination.

Crystal data

$C_{17}H_{16}CuN_4O_4S_4$
$M_r = 532.12$
Triclinic, $P\overline{1}$
$a = 9.317$ (4) Å
$b = 10.713$ (5) Å
$c = 12.797$ (6) Å
$\alpha = 104.99$ (2)°
$\beta = 93.03$ (3)°
$\gamma = 103.46$ (2)°
$V = 1191$ (1) Å^3
$Z = 2$
$D_x = 1.484$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20.0$–22.9°
$\mu = 1.30$ mm^{-1}
$T = 295$ K
Prism, green
0.50 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair,1990)
$T_{\min} = 0.613$, $T_{\max} = 0.677$
3354 measured reflections
3185 independent reflections
3090 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 23.1$°
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 14$
1 standard reflection frequency: 167 min intensity decay: 3.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.152$
$S = 1.07$
3185 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1156P)^2 + 0.9807]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.01$ e Å^{-3}
$\Delta\rho_{\min} = -0.88$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—N1	1.935 (4)	Cu—N3	2.032 (3)
Cu—N2	1.942 (4)	Cu—O1	2.477 (3)
Cu—N4	2.025 (3)		
N1—Cu—N2	91.77 (17)	N4—Cu—N3	87.43 (13)
N1—Cu—N4	91.24 (16)	O1—Cu—N1	110.0 (1)
N2—Cu—N4	174.98 (14)	O1—Cu—N2	100.9 (1)
N1—Cu—N3	177.36 (16)	O1—Cu—N3	71.7 (1)
N2—Cu—N3	89.71 (15)	O1—Cu—N4	74.3 (1)

H atoms were set to ride on respective C atoms. Ideal positions were determined with C—H bond lengths = 0.96 Å, O—H bond lengths = 0.85 Å and $U_{\rm iso} = 0.08$ Å^2 The S atom on one of the DMSO molecules is disordered with two refined occupancy factors of 0.776 and 0.224 for S4 and S5. H atoms were omitted on this disordered DMSO and S5 was refined isotropically.

Data collection: *CAD*-4 *Manual* (Schagen *et al.* 1989); cell refinement: *CAD*-4 *Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXTL*/*PC* (Siemens, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997);

molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

The financial support for this study by the Northwest Institute for Advanced Studies at Eastern Washington University is gratefully acknowledged.

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