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Bis[μ-(di-2-pyridyl ketone thiosemicarbazonato-N^1,N'',S:N')]bis[(isothiocyanato-N)copper(II)] Bis(dimethylformamide) Solvate

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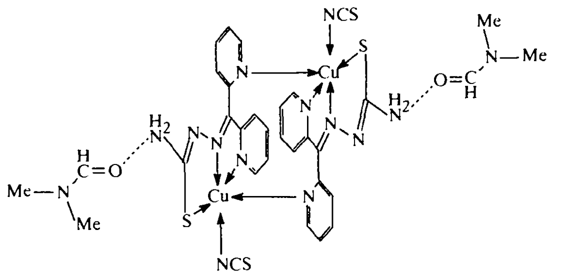
Abstract

In the title compound, $[Cu_2(NCS)_2(C_{12}H_{10}N_5S)_2].2C_3H_7NO$, derived from the tetradentate ligand di-2-pyridyl ketone thiosemicarbazone, the coordination geometry about each Cu^{II} atom is distorted square pyramidal, with one pyridine N atom, the S atom and the imino N atom from the thiosemicarbazone ligand, together with the N atom from an isothiocyanato ligand, in the basal plane; a pyridyl N atom of an adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

Comment

Thiosemicarbazones belong to a large group of thiourea derivatives, the biological activities of which are a function of the parent aldehyde or ketone (Podhye & Kauffman, 1985; Liberta & West, 1992). A number of thiosemicarbazones and their copper and iron compounds have also been found to be active in cell destruction, as well as in the inhibition of DNA synthesis (West *et al.*, 1993; Liu *et al.*, 1995). We report here the crystal structure of a new copper(II) thiosemicarbazone complex, (I).



(I)

The title complex (Fig. 1) has a dimeric structure. The coordination geometry about the copper(II) ion is square pyramidal. The pyridine N4 atom, the imino N3 atom and the thiosemicarbazone S1 atom, together with the thiocyano N6 atom, comprise the basal plane, whereas the apical position is occupied by the pyridine N5($-x$, $1-y$, $-z$) atom of the symmetry-related half of the dimer. The basal plane shows appreciable tetrahedral distortion (mean deviation from the plane 0.15 Å), which deforms the square-pyramidal coordination polyhedron towards trigonal-bipyramidal geometry. The bond lengths in the basal plane agree well with those generally found in copper(II) complexes containing thiosemicarbazone derivatives acting as mononegative tridentate ligands (Farrarri *et al.*, 1989; Garcia-Tojal *et al.*, 1994).

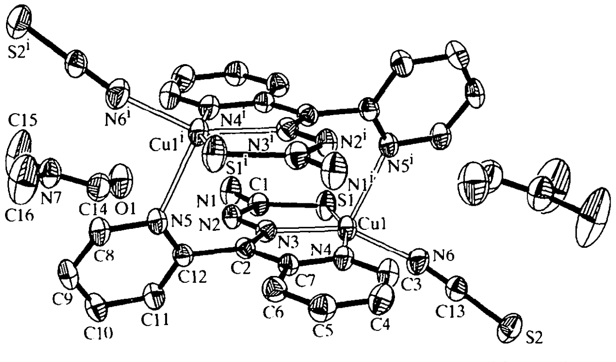


Fig. 1. View of the title compound. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $-x$, $1-y$, $-z$.]

While the thiosemicarbazone moiety in the 'free' ligand has an *E* configuration about both C2—N3 and C1—N2 (Duan *et al.*, 1996), the copper(II) complex has the *E* configuration about C2—N3, but a *Z* configuration about C1—N2, with the donors placed on the same

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side. The data in Table 1 show that all the bond distances in the side chain are intermediate between formal single and double bonds, pointing to extensive electron delocalization over the entire moiety.

The conformation of the title complex is stabilized by favourable π–π interactions between the planar chelate rings of symmetry-related ligands in the dimeric molecule. The overlap occurs between the chelate ring defined by atoms Cu1, N3, C2, C7 and N4 (mean deviation from best plane 0.0038 Å), and its counterpart ring, and between the basal pyridine ring defined by atoms N4, C3, C4, C5, C6 and C7 (mean deviation from the best plane 0.0039 Å), and the *N*,*S*-chelate ring defined by atoms Cu1, S1, C1, N2 and N3 (mean deviation from the best plane 0.023 Å). The centre-to-centre distance is 3.35 (2) Å for the first pair of rings and 3.63 (2) Å for the second.

Hydrogen bonding occurs between N1 and the O atom of a dimethylformamide solvent molecule [N1···O1 2.894 (7) Å and N1—H1*A*···O1 174.1 (3)°], and between N1 and the S atom of a thiocyanato ligand [N1···S2($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) 3.490 (3) Å and N1—H1*B*···S2($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) 160.8 (3)°], resulting in a two-dimensional network parallel to $(10\bar{1})$.

Experimental

The title compound was synthesized by refluxing a methanol solution of (di-2-pyridyl ketone thiosemicarbazonato)copper(II) chloride dimethylformamide solvate (0.4 g) and potassium thiocyanide (0.37 g, 5 mmol) for 4 h. The resulting dark-green crystalline solid was isolated and dried under vacuum. Good quality crystals were obtained by evaporating a methanol solution of the compound in air.

Crystal data

$[Cu_2(NCS)_2(C_{12}H_{10}N_5S)_2]$.-
  $2C_3H_7NO$
$M_r = 902.07$
Monoclinic
$P2_1/n$
$a = 8.340\ (2)$ Å
$b = 11.600\ (2)$ Å
$c = 20.898\ (3)$ Å
$\beta = 101.27\ (3)°$
$V = 1982.8\ (7)$ Å^3
$Z = 2$
$D_x = 1.511$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 240
  reflections
$\theta = 1.0$–$27.6°$
$\mu = 1.333$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.36 × 0.32 × 0.18 mm
Dark blue

Data collection

Rigaku RAXIS IIC image-
  plate (IP) diffractometer
Oscillation IP scans
Absorption correction:
  multi-scan (*ABSCOR*;
  Higashi, 1995)
  $T_{min} = 0.56$, $T_{max} = 0.84$
6725 measured reflections

3719 independent reflections
3016 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 26.74°$
$h = 0 \rightarrow 10$
$k = -14 \rightarrow 14$
$l = -26 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.121$
$S = 1.118$
3717 reflections
244 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.304$ e Å^{-3}
$\Delta\rho_{min} = -0.502$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—N6	1.970 (2)	S1—C1	1.737 (3)
Cu1—N3	1.985 (2)	N1—C1	1.330 (4)
Cu1—N4	2.038 (2)	N2—C1	1.328 (3)
Cu1—S1	2.2708 (9)	N2—N3	1.347 (3)
Cu1—N5'	2.361 (2)	N3—C2	1.306 (3)
N6—Cu1—N3	152.66 (10)	N4—Cu1—S1	163.16 (7)
N6—Cu1—N4	94.31 (10)	N6—Cu1—N5'	92.22 (10)
N3—Cu1—N4	80.35 (9)	N3—Cu1—N5'	114.47 (8)
N6—Cu1—S1	97.79 (9)	N4—Cu1—N5'	90.45 (9)
N3—Cu1—S1	83.54 (7)	S1—Cu1—N5'	100.69 (6)

Symmetry code: (i) $-x$, $1-y$, $-z$.

Data were collected on a Rigaku RAXIS IIC image-plate diffractometer using Mo $K\alpha$ radiation from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{max} = 55.2°$; 60 oscillation frames in the range 0–180°, exposure 8 min per frame). Absorption corrections were made using the *ABSCOR* program based on Fourier-coefficient fitting to the intensities of symmetry-equivalent reflections (Tanner & Krause, 1994; Krause & Phillips, 1992; Higashi, 1995). All the non-H atoms were refined anisotropically. All H atoms were placed in calculated positions (C—H 0.96 Å), assigned fixed isotropic displacement parameters [$1.2U_{eq}$(parent atom)] and allowed to ride.

Data collection: *BIOTEX* (Krause & Phillips, 1992). Cell refinement: *BIOTEX*. Data reduction: *BIOTEX*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1117). Services for accessing these data are described at the back of the journal.

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Bis[μ-(di-2-pyridyl ketone thiosemicarbazonato-N^1,N'',S:N')]bis[(acetato-O)copper(II)] Dimethanol Solvate

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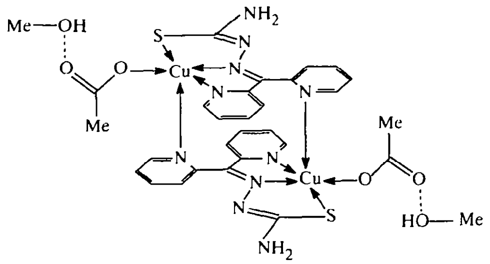
Abstract

In the title compound, $[Cu_2(C_2H_3O_2)_2(C_{12}H_{10}N_5S)_2].2CH_4O$, the coordination geometry about each Cu^{II} atom is distorted square pyramidal, with one pyridine N atom, the S atom and the imino N atom from the thiosemicarbazone ligand, together with one O atom from acetate, in the basal plane; a pyridyl N atom of an adjacent moiety occupies the apical position, serving as a bridge to form a centrosymmetric dimeric structure.

Comment

Thiosemicarbazones belong to a large group of thiourea derivatives, the biological activities of which are a function of the parent aldehyde or ketone (Podhye & Kauffman, 1985; Liberta & West, 1992). It has been postulated that many N-heterocyclic carbaldehyde thiosemicarbazones act as tridentate N_2S ligands which bond to iron or copper in the synthesis of precursors of DNA (West *et al.*, 1993; Liu *et al.*, 1995). The solution chemistry and crystal structure of pyridine-2-carbaldehyde thiosemicarbazone (HL') (Biyuskin *et al.*, 1987), the active precursor complex [CuL'(OAc)] (Bell & Theocharis, 1987), as well as many other N-heterocyclic carbaldehyde thiosemicarbazones (Brown & Agrawal, 1977, 1978*a*,*b*) and their metal complexes, have been studied (Farrarri *et al.*, 1989; Garcia-Tojal *et al.*, 1994). We report here the crystal structure of a new acetate-coordinated copper(II) thiosemicarbazone complex, (I), derived from di-2-pyridyl ketone.



(I)

The title complex (Fig. 1) has a dimeric structure. The coordination geometry about each copper(II) ion is square pyramidal. The pyridine N4 atom, the imino N3 atom and the thiosemicarbazone S1 atom, together with the acetate O1 atom, comprise the basal plane, while the apical position is occupied by the pyridine N5($\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$) atom of the symmetry-related half of the dimer. The basal plane shows appreciable tetrahedral distortion (mean deviation from the plane 0.16 Å), which deforms the square-pyramidal coordi-

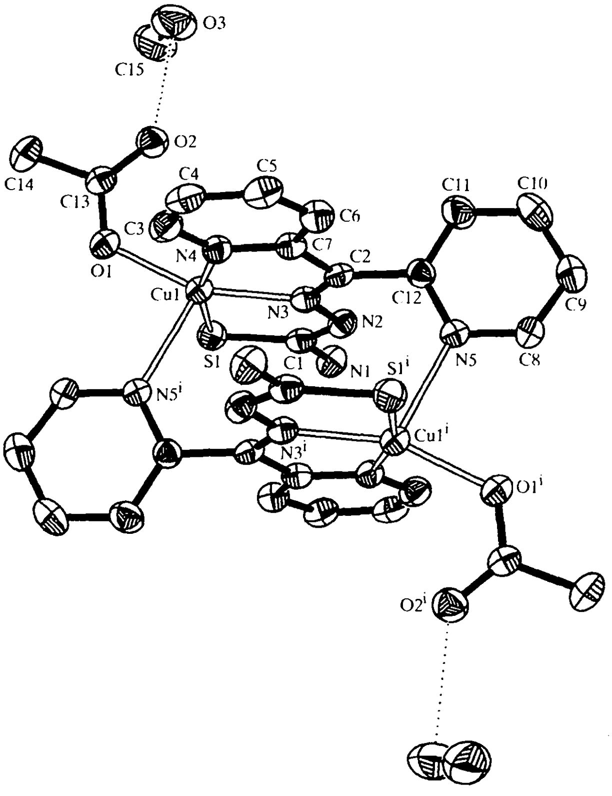


Fig. 1. View of the title compound. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$.]