

Bis(μ -phenyl 2-pyridyl ketone N^4,N^4 -butane-1,4-diylthiosemicarbazonato)-bis[chlorocopper(II)]

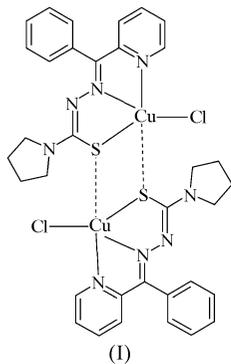
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The title compound, $[\text{Cu}_2(\text{C}_{17}\text{H}_{17}\text{N}_4\text{S})_2\text{Cl}_2]$, exhibits a dimeric structure related by a centre of symmetry. The monomers are linked to each other by the longest Cu—S apical distance observed to date among Cu^{II} square-pyramidal complexes of N^4 -substituted thiosemicarbazones. Each Cu^{II} atom deviates from the coordination square plane, which contains the pyridyl and imine N atoms, the thiolate S atom and the Cl^- anion, towards the S atom of the adjacent monomer. The dimers pack in a zigzag manner through the crystal.

Comment

Recently, there has been considerable interest in the coordination chemistry of thiosemicarbazones, mainly due to their interesting physicochemical and biological properties (Sreekanth *et al.*, 2003, 2005; John *et al.*, 2002, 2004; Philip *et al.*, 2004; Joseph *et al.*, 2004). Thiosemicarbazones act as chelating ligands with the copper(II) ion by bonding through the thione S and hydrazine N atoms, and hence these types of compounds



can coordinate *in vivo* to the metal ion. Because of such coordination, the thiosemicarbazone moiety undergoes a steric reorientation that could favour its biological activity. As

far as the present study is concerned, there are only a few reports in the literature on the crystal structures of metal complexes of similar compounds (Rebolledo *et al.*, 2003; Demertzi *et al.*, 1999; Liu *et al.*, 1999). Recently, we reported the crystal structures of the uncomplexed ligand, namely 2-benzoylpyridine N^4,N^4 -(butane-1,4-diyl)thiosemicarbazone (HBpypTsc), and its Fe^{III} complex (Sreekanth & Kurup, 2004). Crystal structures of some Cu^{II} complexes (Sreekanth & Kurup, 2003) and one Au^{III} complex (Sreekanth *et al.*, 2004) of the same thiosemicarbazone have also been reported. However, the present crystal structure of the title compound, (I) or CuBpypTscCl , is the first report where the copper(II) complexes ‘dimerize’ around an inversion centre *via* a long Cu—S contact.

Compound (I) crystallizes with one independent molecule in the unit cell (Fig. 1). The thiosemicarbazone loses a H atom from its tautomeric thiol form and acts as a tridentate ligand, coordinating to the Cu^{II} atom through the pyridyl N, azomethine N and thiolate S atom. The thiosemicarbazone moiety in the free ligand (Sreekanth & Kurup, 2004) shows *Z* configurations about both the C1—N2 and N3—C13 bonds, whereas in the present Cu^{II} complex it exists in an *E* conformation about the C1—N2 bond and a *Z* configuration about the N3—C13 bond; this suggests that a possible rotation about the azomethine double bond occurs during coordination.

A novel aspect of the molecular structure of (I) is that, in the crystal lattice, two inversion-symmetry-related monomers are arranged so that each S atom of the monomeric part is at the apical position of the square-pyramidal structure of the other part, with $\text{Cu—S}^{\text{i}} = 3.0627(4) \text{ \AA}$ [symmetry code: (i) $-x, 2 - y, -z$]. Such square-pyramidal structures occur through bridging by either the thiolate or the coordinating halide anion for Cu^{II} complexes of thiosemicarbazones. This unique feature

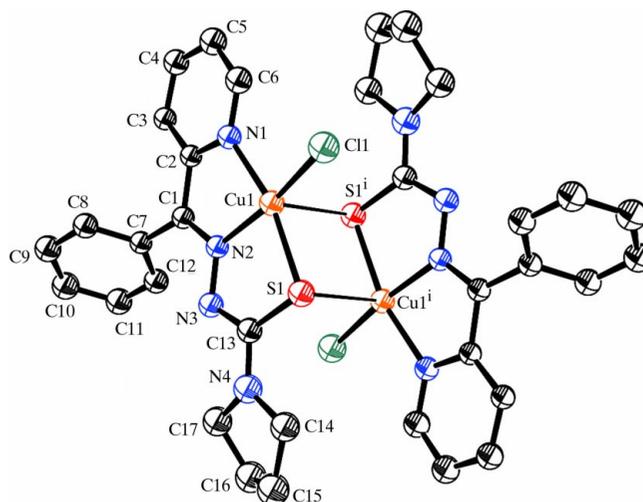


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. Only the atoms in the asymmetric unit and inversion-symmetry-related atoms Cu1^{i} and S1^{i} are labelled [symmetry code: (i) $-x, 2 - y, -z$].

is not observed in the bromo analogue, CuBpypTscBr (Sreekanth & Kurup, 2003), where the S atom is positioned 6.084 Å from the Cu^{II} centre of the adjacent molecule in the unit cell. The present compound contains the longest apical Cu—S distance reported to date for square-pyramidal Cu^{II} complexes of *N*⁴-substituted thiosemicarbazones. In a Cu^{II} complex of *S*-methylisothiosemicarbazone (Kravtsov *et al.*, 1993), the Cu—S apical distance between adjacent molecules is also long, at 3.126 Å, longer than the Cu—Sⁱ value in (I). In addition, where the square-pyramidal geometry exists through the bridging of adjacent molecules, the in-plane Cu—S (2.924 Å; Joseph *et al.*, 2004), Cu—Cl (2.777 Å; Sreekanth & Kurup, 2003) and Cu—Cl (2.779 Å; Dallavalle *et al.*, 2002) distances are shorter compared with the corresponding distances in (I).

The copper(II) ion of (I) lies 0.1299 (1) Å out of the square plane described by atoms N1, N2, S1 and Cl1, towards the apical S atom. The two coordinated N atoms have Cu—N bond distances differing by 0.051 (1) Å. The thiosemicarbazone moiety comprising atoms C1, N2, N3, C13, S1 and N4 retains its planarity even after coordination, as evidenced by the maximum out-of-plane deviation of 0.0110 (2) Å for N2. Ring-puckering analyses (Cremer & Pople, 1975) reveal that the pyrrolidine ring comprising atoms N4, C14, C15, C16 and C17 exists in an envelope conformation, with C16 as the flap atom.

The C13—S1 bond lengthens by 0.065 (2) Å upon coordination to the Cu^{II} atom. The free ligand exists as the thione tautomer and coordinates to the Cu^{II} atom in the deprotonated thiolate form, thus rendering a single-bond character for the C—S bond. Similarly, coordination of the azomethine N atom to the central Cu^{II} atom results in a redistribution of the electron density along the thiosemicarbazone chain, giving rise to changes in the bond distances along the moiety compared with those of the uncoordinated thiosemicarbazone. For instance, the azomethine bond distance increases by 0.010 (3) Å, while the N2—N3 and N3—C13 bond distances decrease by 0.011 (2) and 0.020 (3) Å, respectively, in (I) compared with the free ligand. Comparisons with CuBpypTscSH and CuBpypTscBr show that the metal–ligand bond lengths (Table 1) do not show any regular trends among the related structures.

The unit cell contains two centrosymmetric dimer molecules packed in a zigzag manner in the crystal lattice. One intermolecular contact (entry 2 in Table 2) is observed. A C6—H6···Cl1 intramolecular hydrogen-bonding interaction (Table 2) leads to the formation of a five-membered ring in the molecule.

Experimental

The ligand HBpypTsc was prepared by adapting the procedure of Scovill (1991). A solution of HBpypTsc (1 mmol) in chloroform (5 ml) was then refluxed with a solution of copper chloride (1 mmol) in methanol (5 ml) for 15 min. The resulting solution was cooled and allowed to stand for 2 d whereupon light-blue single crystals of (I) were isolated. Elemental analysis found (calculated): C 49.86 (49.20), H 4.27 (4.13), N 23.95% (23.63%).

Crystal data

[Cu₂(C₁₇H₁₇N₄S)₂Cl₂]
M_r = 816.8
 Monoclinic, *P*₂₁/*n*
a = 11.1069 (18) Å
b = 8.2919 (14) Å
c = 18.642 (3) Å
 β = 98.061 (3)°
V = 1699.9 (5) Å³
Z = 2

D_x = 1.596 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 564 reflections
 θ = 2.0–26.9°
 μ = 1.57 mm⁻¹
T = 293 (2) K
 Rectangular, light blue
 0.35 × 0.30 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.583, *T_{max}* = 0.624
 12 249 measured reflections

3680 independent reflections
 2911 reflections with *I* > 2σ(*I*)
R_{int} = 0.024
 θ_{max} = 26.9°
h = -14 → 14
k = -10 → 9
l = -21 → 23

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.031
wR (*F*²) = 0.080
S = 1.04
 3392 reflections
 281 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.4986P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.006$
 $\Delta\rho_{\text{max}} = 0.37 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.9756 (17)	S1—C13	1.746 (2)
Cu1—N1	2.0268 (18)	N2—C1	1.305 (3)
Cu1—Cl1	2.2396 (7)	N2—N3	1.355 (2)
Cu1—S1	2.2550 (7)	N3—C13	1.340 (3)
Cu1—S1 ⁱ	3.0627 (4)		
N2—Cu1—N1	80.48 (7)	N2—Cu1—S1	84.73 (5)
N2—Cu1—Cl1	169.58 (5)	N1—Cu1—S1	164.98 (5)
Cl1—Cu1—S1	97.27 (3)	Cl1—Cu1—S1 ⁱ	102.92 (3)
S1—Cu1—S1 ⁱ	88.59 (3)	C1—N2—N3	119.52 (17)
N1—Cu1—Cl1	96.84 (5)		

Symmetry code: (i) $-x, 2 - y, -z$.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C6—H6···Cl1	0.92 (2)	2.71 (3)	3.348 (3)	128 (2)
C3—H3···N3 ⁱⁱ	0.93	2.74	3.631 (3)	160

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

The H atom attached to atom C3 was fixed geometrically, while the other H atoms were located from a difference Fourier map and refined isotropically. The C—H distances are in the range 0.88 (3)–1.01 (3) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1101). Services for accessing these data are described at the back of the journal.

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