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Bis[*N*-phenyl(dicyclohexylthiophosphinoyl)thiomethanamido-*S*,*S*′]-copper(II)

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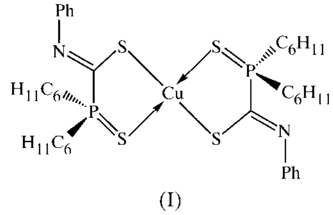
The ligands in [Cu($C_{19}H_{27}NPS_2$)$_2$] adopt an *S*,*S*′-chelation mode leading to an S_4 donor set which defines a square-planar geometry about the Cu atom, which lies on an inversion centre.

Comment

Phosphine ligands of the type R_2PC(S)N(H)R' (R, R' = alkyl, aryl) are known to adopt a variety of coordination modes involving one or more of the P, S and N donor atoms (Siasios & Tiekink, 1996*a*). Oxidation of the P centre, leading to ligands of the general formula R_2P(Y)C(S)N(H)R' (Y = O, S or Se), gives rise to different coordination possibilities. Anti-arthritic activity has been displayed by gold complexes of the phosphine ligands (Whitehouse *et al.*, 1998) and in this context, Cu complexes of these species have been investigated. The crystal structure of one of these, (I), is reported herein.



(I)

The molecular structure is shown in Fig. 1 and selected geometric parameters are collected in Table 1. The Cu atom is located on a centre of symmetry and exists in a distorted square-planar coordination geometry defined by an S_4 donor set. The greatest deviation from ideal geometry is manifested in the chelate angle of 95.85 (4)°. The [Cy_2P(S)C(S)=NPh]$^-$ monoanion (Cy is cyclohexyl) coordinates *via* the thioamide-S1 and phosphinoyl-S2 atoms, forming a five-membered Cu—S—C—P—S ring. There is significant puckering in the ring as seen in the Cu—S2—P1—C1 and S1—C1—P1—S2 torsion angles of −23.2 (1) and 23.8 (2)°, respectively. This feature of the structure may be traced to the tetrahedral requirements of the P atom. The Cu—S1 distance of 2.274 (1) Å is shorter than the Cu—S2 distance of 2.307 (1) Å, consistent with significant thiolate character in the former bond. This conclusion is supported by comparing relevant geometric parameters in the complex with those in uncoordinated [Cy_2P(S)C(S)N(H)Ph] (Siasios & Tiekink, 1994). Thus, the respective S1—C1 and C1—N1 distances in the complex of 1.726 (3) and 1.272 (4) Å are significantly longer and shorter than 1.624 (2) and 1.317 (3) Å, as found in the uncoordinated ligand. In contrast, the P1—C1 distances are equal within experimental error, *i.e.* 1.834 (3) *cf.* 1.846 (3) Å. Nevertheless, the P1=S2 distance of 1.999 (1) Å is elongated compared with 1.9495 (9) Å in the free ligand. The lack of planarity in the five-membered ring, mentioned above, precludes extensive delocalization of π-electron density over these atoms.

The shortest non-H intermolecular contact of 3.614 (6) Å occurs between C17 and C18^{i} [symmetry code: (i) $-x, -1-y, -1-z$]. These arise from the partial overlap of two phenyl rings; however, there is no evidence for extensive π-stacking in the lattice. There are no close intermolecular interactions involving the Cu centres that might be expected for complexes of this type. An examination of the crystal structure reveals that symmetry-related cyclohexyl groups occupy positions above and below the Cu coordination plane preventing close associations.

The *S*,*S*′-chelation mode of the ligand found in the present structure has two precedents in the literature, namely in octahedral [Mn{Ph_2P(S)C(S)=NPh}(CO)$_4$] (Antoniadis *et al.*, 1982) and square-planar [Ni{Ph_2P(S)C(S)=NPh}$_2$] (Siasios & Tiekink, 1996*b*). In contrast, an *S*,*N*-chelation mode is found in the structure of [CpMn{Ph_2P(S)C(S)=NPh}(CO)$_2$] (Ambrosius *et al.*, 1984). Similar –Cu—S—C—P—S– five-membered rings as seen in the title structure have been observed in the structures of {[(PhSCH$_2$)$_3$P=S]CuX}$_2$ (X = Cl and Br) and {[(PhSCH$_2$)$_3$P=S](CuI)$_2$}$_2$ (Fuchs *et al.*, 1997), but these involve sp^3 rather than sp^2 C atoms. Finally, square-planar CuS$_4$ geometries are known in related dithiocarbamate,

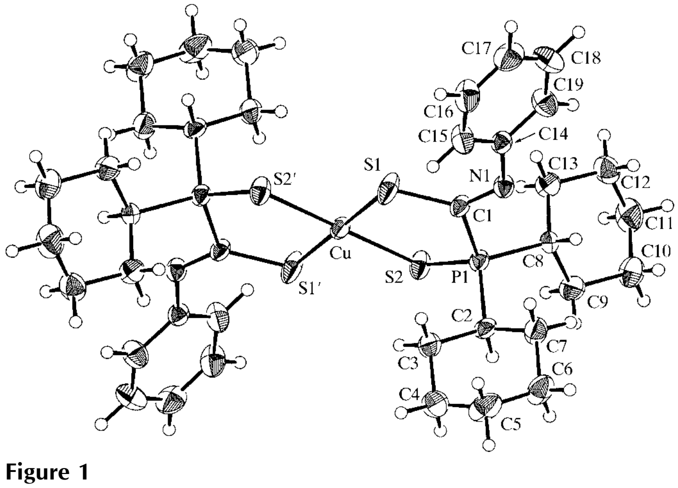


Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 35% probability level (Johnson, 1976).

i.e. Cu($S_2CNR'_2$)$_2$ (*e.g.* Einstein & Field, 1974; Manotti Lanfredi *et al.*, 1996), and dithiophosphate, *e.g.* {Cu[S_2P(O-*o*-tolyl)$_2$]$_2$} (Yordanov *et al.*, 1983), structures.

Experimental

The title complex was prepared by reacting a twofold molar excess of [Cy_2P(S)C(S)N(H)Ph] (Siasios & Tiekink, 1994) with $CuSO_4\cdot5H_2O$ in an ethanol/dichloromethane mixture (1/1). The brown precipitate that was isolated was recrystallized by the slow evaporation of a dichloromethane solution of the complex at 295 K.

Crystal data

[Cu($C_{19}H_{27}NPS_2$)$_2$]
M_r = 792.60
Triclinic, $P\overline{1}$
a = 8.430 (1) Å
b = 10.305 (3) Å
c = 12.380 (2) Å
α = 89.90 (2)°
β = 82.31 (1)°
γ = 68.62 (1)°
V = 991.1 (3) Å^3

Z = 1
D_x = 1.328 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11.1–12.3°
μ = 0.871 mm^{-1}
T = 293 K
Prismatic, brown
0.40 × 0.20 × 0.10 mm

Data collection

AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.709, $T_{\rm max}$ = 0.917
6080 measured reflections
5779 independent reflections
3059 reflections with $I > 2.00\sigma(I)$

$R_{\rm int}$ = 0.028
$\theta_{\rm max}$ = 30°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: 0.27%

Refinement

Refinement on F
R = 0.044
wR = 0.031
S = 1.750
3059 reflections
214 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o) + 0.003|F_o|^2]$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.37 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.35 e Å^{-3}

All C—H distances were constrained to be 0.95 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

Table 1
Selected geometric parameters (Å, °).

Cu—S1	2.274 (1)	P1—C2	1.823 (4)
Cu—S2	2.307 (1)	P1—C8	1.820 (3)
S1—C1	1.726 (3)	N1—C1	1.272 (4)
S2—P1	1.999 (1)	N1—C14	1.412 (4)
P1—C1	1.834 (3)		
S1—Cu—S2	95.85 (4)	C1—P1—C2	107.6 (2)
S1—Cu—S2$^{\rm i}$	84.15 (4)	C1—P1—C8	107.6 (2)
Cu—S1—C1	109.0 (1)	C2—P1—C8	108.8 (2)
Cu—S2—P1	102.47 (5)	C1—N1—C14	123.9 (3)
S2—P1—C1	110.2 (1)	S1—C1—P1	117.1 (2)
S2—P1—C2	111.3 (1)	S1—C1—N1	131.0 (3)
S2—P1—C8	111.1 (1)	P1—C1—N1	111.9 (2)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1299). Services for accessing these data are described at the back of the journal.

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