

## (Benzoxazole-2-thiolato-S)(benzoxazole-2-thione-S)bis(triphenylphosphine)copper(I)

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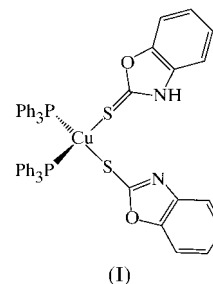
The Cu atom in [Cu(C<sub>7</sub>H<sub>4</sub>NOS)(C<sub>7</sub>H<sub>5</sub>NOS)(C<sub>18</sub>H<sub>15</sub>P)<sub>2</sub>] is tetrahedrally coordinated by a P<sub>2</sub>S<sub>2</sub> donor set. One S atom is derived from neutral benzoxazole-2-thione and the other from the deprotonated form of the ligand. The two sulfur ligands are connected *via* an N—H...N interaction, leading to the formation of an eight-membered ring.

### Comment

Metal–phosphine complexes are ubiquitous in coordination chemistry owing to their wide variety of applications, such as in catalysis, biological chemistry and simply as stabilizing ligands. In a biological context, the mononuclear gold complex (1-thio-β-D-glucopyranose-2,3,4,6-tetraacetato-S)(triethylphosphine)gold(I), auranofin, is used in the treatment of rheumatoid arthritis (Sadler & Sue, 1994). Subsequently, other phosphine–gold(I) thiolates have been tested for antiarthritic activity (Whitehouse *et al.*, 1998), as well as for cytotoxicity (Webster *et al.*, 1996). Research in this field has been directed towards coupling phosphine–gold(I) centres with thiol ligands that have biological activity in their own right (Cookson *et al.*, 1994). The thiol benzoxazole-2-thione, LH, is a precursor to compounds that are known to possess antifungicidal activity. Recently, some organotin derivatives were evaluated for their trypanocidal activity, *i.e.* activity against the parasite that causes sleeping sickness (Susperregui *et al.*, 1998). In this report, the structure of a phosphine–Cu<sup>I</sup> complex is reported containing this thiol, (I).

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are listed in Table 1. The Cu atom exists within a P<sub>2</sub>S<sub>2</sub> donor set defined by two phosphine P atoms and two S atoms. One S atom is derived from a deprotonated ligand whilst the other is from the neutral form, so that the Cu atom is in the +1 oxidation state. The overall coordination geometry is distorted tetrahedral, with the widest angle at Cu involving the two bulky phosphine ligands. The Cu–P distances are experimentally equivalent, but a disparity

exists in the Cu–S distances; the Cu–S1 distance of 2.376 (1) Å is shorter than the corresponding Cu–S2 distance of 2.467 (1) Å. This difference indicates that different forms of the ligand exist, *i.e.* *L* and *LH*, with the ligand containing S1 functioning as a thiolate. Further support for this assignment is



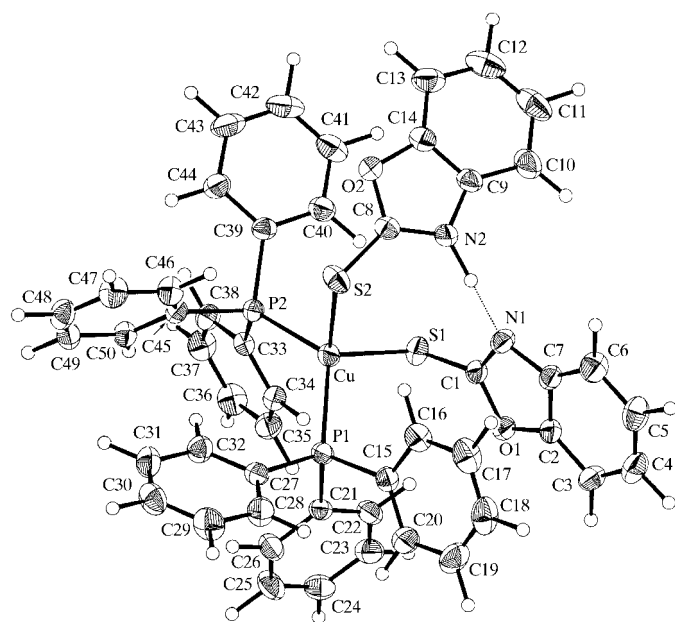
found in the magnitude of the associated C–S distances, with C1–S1 of 1.701 (2) Å being significantly longer than C8–S2 of 1.672 (3) Å. The C8–S2 distance in the complex is, as expected, longer than the comparable distance of 1.643 (3) Å in the structure of *LH* (Groth, 1973). The H2 atom, *i.e.* bound to N2, was located from a difference map (see *Experimental*), suggesting ordering of this atom. Further, this is consistent with the ligand containing the S2 atom functioning primarily as a thione and thus it should be formulated as *LH*.

The H2 atom participates in an interesting intramolecular interaction in that it forms a close contact with the N1 atom, as shown in Fig. 1. While both ligands are effectively planar, that containing the S1 atom has a mean deviation of 0.015 Å and the *LH* ligand, *i.e.* with formally *sp*<sup>3</sup> N, is less planar with a mean deviation of 0.035 Å. The *L* and *LH* ligands are disposed so as to be almost orthogonal to each other, so that the dihedral angle between their respective least-squares planes is 67.9°. The respective N2–H2, H2...N1 and N2...N1 distances are 0.95, 1.78 and 2.662 (3) Å, and the angle subtended at H2 is 154°. This mode of intramolecular association between *L* and *LH* leads to the formation of an eight-membered ring. Other intramolecular interactions serve to stabilize the molecular structure. Thus, there are face-to-face π...π interactions between *L* and the C15–C20 aromatic ring although, owing to the mismatch in sizes, the overlap is such as to place the five-membered ring of *L* in closer proximity to the adjacent aromatic ring. The distance between the centroid of the five-membered ring and that of C15–C20 is 3.80 Å (dihedral angle 14.6°). A comparable separation of 4.27 Å is noted between the five-membered ring of *LH* and C39–C44; dihedral angle 4.1°. Furthermore, intramolecular S...H (S1...H40 2.78 Å and S2...H46 2.82 Å) and O1...H (O1...H22 2.48 Å) contacts are also observed, precluding their participation in intermolecular interactions (see below). An analogous association between the N atoms of *L* and *LH*, as described above, has been reported previously.

In the structure of [(Ph<sub>3</sub>P)<sub>2</sub>CuL<sub>2</sub>][Li(thf)<sub>2</sub>].0.5THF, the [Li(thf)<sub>2</sub>]<sup>+</sup> cation substitutes for the H<sup>+</sup> in (Ph<sub>3</sub>P)<sub>2</sub>Cu(*L*)(*LH*) (Beswick *et al.*, 1996). In this structure, both molecules comprising the asymmetric unit have crystallographically imposed twofold symmetry, indicating that within each independent molecule the two Cu–S distances are equal. This

equivalence indicates that both ligands are deprotonated, in contrast with the structure reported herein. Indeed, the structure of (I) represents the first authenticated example of coordinating LH. However, other structures containing L are known.

Monodentate S-coordination is found in  $[(\text{Ph}_3\text{P})_2\text{CuL}_2]\cdot[\text{Li}(\text{thf})_2]\cdot 0.5\text{THF}$  (Beswick *et al.*, 1996),  $\text{Ph}_3\text{PAuL}$  (Muir *et al.*, 1989) and  $[\text{AuL}_2]^-$  (Vicente *et al.*, 1994). Monodentate N-coordination has been reported in the structure of  $[(\text{L})\text{Li}(\text{HMPA})_2]\cdot\text{H}_2\text{NC}_6\text{H}_4\text{OH}$  (Armstrong *et al.*, 1992) and S,N-chelation has been observed in  $[\text{Bu}_2\text{SnL}_2]$  (Susperregui *et al.*, 1998). Finally, a tridentate mode of coordination, utilizing monodentate N and bidentate bridging S, has been found in the structure of  $[(\text{Ph}_3\text{P})\text{CuL}]_4$  (Beswick *et al.*, 1996).



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

The primary intermolecular interactions stabilizing the lattice are of the type  $\text{C}-\text{H}\cdots\pi$ , as all electronegative atoms besides the O2 atom, which forms only a weak contact of 2.86 Å to H5(1 - x, -1 - y, -z), participate in intramolecular interactions. The major  $\text{C}-\text{H}\cdots\pi$  contacts occur between phenyl-bound H23 to the ring centroid of the six-membered ring of L ( $\text{H}\cdots$ ring centroid distance: 2.56 Å;  $\text{C}-\text{H}\cdots$ ring centroid angle: 153°; symmetry operation: -x, -y, -z), phenyl-bound H17 and the six-membered ring of LH (2.65 Å and 153°; symmetry operation: 1 - x, -1 - y, -z), and H11 of LH and phenyl C33-C38 (2.70 Å and 148°; symmetry operation: -x, -1 - y, -z). These combine to link a total of four complex molecules in a relatively strong embrace and other  $\text{C}-\text{H}\cdots\pi$  interactions provide additional stabilization to the structure.

## Experimental

Crystals of  $(\text{Ph}_3\text{P})_2\text{Cu}(\text{L})(\text{LH})$  were isolated from the reaction mixture  $[\text{CH}_2\text{Cl}_2/\text{EtOH}$  (1/1); 293 K] containing equimolar quantities of  $(\text{Ph}_3\text{P})_3\text{CuCl}$ , LH and KOH. Single crystals were obtained from the slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of the product.

### Crystal data

$[\text{Cu}(\text{C}_7\text{H}_4\text{NOS})(\text{C}_7\text{H}_5\text{-NOS})(\text{C}_{18}\text{H}_{15}\text{P})_2]$	$Z = 2$
$M_r = 889.48$	$D_x = 1.367 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.499$ (2) Å	Cell parameters from 25 reflections
$b = 13.173$ (2) Å	$\theta = 11.0\text{--}12.4^\circ$
$c = 14.615$ (3) Å	$\mu = 0.719 \text{ mm}^{-1}$
$\alpha = 85.16$ (2)°	$T = 293 \text{ K}$
$\beta = 79.05$ (2)°	Prismatic, colourless
$\gamma = 66.15$ (2)°	$0.35 \times 0.30 \times 0.10 \text{ mm}$
$V = 2160.6$ (8) Å <sup>3</sup>	

### Data collection

Rigaku AFC-7R diffractometer	$h = -17 \rightarrow 17$
$\omega$ -2 $\theta$ scans	$k = -18 \rightarrow 18$
13070 measured reflections	$l = 0 \rightarrow 20$
12612 independent reflections	3 standard reflections
7586 reflections with $I > 3\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.018$	intensity decay: 0.04%
$\theta_{\text{max}} = 30^\circ$	

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R = 0.038$	$w = 1/[\sigma^2(F_o) + 0.002 F_o ^2]$
$wR = 0.026$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.990$	$\Delta\rho_{\text{max}} = 0.28 \text{ e \AA}^{-3}$
7586 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
532 parameters	

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

Cu—S1	2.376 (1)	O1—C2	1.382 (3)
Cu—S2	2.467 (1)	O2—C8	1.368 (3)
Cu—P1	2.3026 (8)	O2—C14	1.391 (3)
Cu—P2	2.3006 (8)	N1—C1	1.309 (3)
S1—C1	1.701 (2)	N1—C7	1.395 (3)
S2—C8	1.672 (3)	N2—C8	1.316 (3)
O1—C1	1.385 (3)	N2—C9	1.385 (3)
S1—Cu—S2	110.27 (4)	C8—O2—C14	106.7 (2)
S1—Cu—P1	107.12 (3)	C1—N1—C7	106.6 (2)
S1—Cu—P2	104.47 (3)	C8—N2—C9	109.3 (2)
S2—Cu—P1	111.63 (3)	S1—C1—O1	118.8 (2)
S2—Cu—P2	99.91 (3)	S1—C1—N1	128.6 (2)
P1—Cu—P2	122.90 (3)	O1—C1—N1	112.6 (2)
Cu—S1—C1	105.46 (9)	S2—C8—O2	121.6 (2)
Cu—S2—C8	104.90 (9)	S2—C8—N2	129.1 (2)
C1—O1—C2	104.7 (2)	O2—C8—N2	109.3 (2)

The H atom on the N2 atom was located from a difference map, refined to confirm the assignment and subsequently fixed at a distance of 0.95 Å in the final cycles of the refinement. All C—H distances were fixed at 1.08 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1995); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN for Windows*; software used to prepare material for publication: *TEXSAN for Windows*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1301). Services for accessing these data are described at the back of the journal.

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