inferred that this second H_2O may contract the lattice in the case of the Me_2Sn compound by hydrogen bonding, while a similar contraction is prevented by the more voluminous R groups in (II) and $Ph_2SnL(H_2O)$.

In (II) a short intermolecular distance O(4)···O(5) $(\bar{y}, -\frac{1}{2}+x, \frac{1}{2}+z)$ of 2·707 (7) Å exists, indicating hydrogen bridging between the dimeric units.

The Sn—N distance in (I) and in (II) is significantly shorter than in the polymeric $Ph_2SnL(H_2O)$ [2·338 (3) Å; Gielen *et al.*, 1987], which has a very similar environment around Sn. In other comparable R_2Sn compounds the Sn—N distance has also been found to be slightly larger (see Gielen *et al.*, 1987). The distance Sn—O(5) is distinctly longer than in $Ph_2Sn(H_2O)L$ [2·271 (3) Å; Gielen *et al.*, 1987] and in $[Bu_3Sn(OH_2)_2]^+$ [2·326 (5) and 2·295 (4) Å; Davies, Goddard, Hursthouse & Walker, 1986] but significantly shorter than in $Me_3SnO_2CCH_2NMe_2.H_2O$ (2·386 Å; Jurkschat, Tzschach, Zschunke, Grand & Albrand, 1987).

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Structure of Bis(*μ*-pyridine-2-thione-*μ*-*S*)-bis[iodo(pyridine-2-thione-*S*)copper(I)]

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Abstract. $[Cu(C_5H_5NS)_2I]_2$, $M_r = 825{\cdot}55$, monoclinic, $C2/c$, $a = 13{\cdot}139\ (2)$, $b = 9{\cdot}888\ (1)$, $c = 20{\cdot}405\ (4)$ Å, $\beta = 94{\cdot}92\ (1)^\circ$, $V = 2641{\cdot}1\ (7)$ Å^3, $Z = 4$, $D_m = 2{\cdot}065$, $D_x = 2{\cdot}076$ Mg m^{-3}, m.p. 323 K, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}321$ mm^{-1}, $F(000) = 1583{\cdot}9$, $T = 296\ (2)$ K. Final R value 0·0235 for 1767 observed reflections with $F_o \geq 3{\cdot}0\sigma(F_o)$. The structure consists of dimers, $[Cu(C_5H_5NS)_2I]_2$, each having a twofold symmetry axis and a $(CuIS_2)_2$ core in *cis* conformation stabilized by two strong intramolecular I···H—N hydrogen bonds. Each Cu atom has a distorted tetrahedral coordination with one terminal and two bridging S atoms and a terminal I atom. The two tetrahedra are joined along the S(2)···S(2′) edge. The Cu···Cu separation is 3·139 Å.

Introduction. Complexes of copper with pyridine-2-thione (py2SH) have been known for some time and continue to be investigated (Raper, 1985). Recently the structures of copper halide complexes $[Cu(py2SH)_3]_2X_2$, (X = Cl, Br), consisting of centrosymmetric dimers (Stergioudis, Kokkou, Rentzeperis & Karagiannidis, 1987), have been reported. Since the stereochemistry of Cu^I with soft ligands is very flexible, it was deemed worthwhile to carry out also the X-ray

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Table 1. *Positional and equivalent isotropic thermal parameters* (× 10^4) *of the non-*H *atoms in DPTCI*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
I	1176·3 (3)	1143·2 (3)	942·1 (2)	452
Cu	652·3 (6)	2805·5 (6)	1890·5 (3)	541
S(1)	692 (1)	5085 (1)	1768·3 (6)	541
S(2)	−1245 (1)	2316 (1)	2027·6 (6)	445
N(1)	1177 (3)	4634 (5)	546 (2)	428
N(2)	−1333 (3)	−252 (4)	2426 (2)	472
C(11)	951 (4)	5557 (5)	1000 (2)	388
C(13)	1395 (4)	4936 (6)	−74 (3)	529
C(14)	1388 (5)	6239 (7)	−272 (3)	569
C(15)	1153 (5)	7231 (6)	168 (3)	556
C(16)	938 (4)	6909 (5)	784 (3)	486
C(21)	−1340 (3)	609 (5)	1913 (2)	380
C(23)	−1364 (5)	−1608 (6)	2370 (3)	594
C(24)	−1401 (5)	−2207 (7)	1783 (3)	610
C(25)	−1420 (5)	−1379 (7)	1244 (3)	613
C(26)	−1393 (5)	−20 (7)	1297 (3)	537

crystal structure determination of the title compound (DPTCI hereafter).

Experimental. To a 30 ml suspension of CuI (0·38 g, 2 mmol) in chloroform was added an excess of pyridine-2-thione (0·67 g, 6 mmol) dissolved in ethanol (100 ml). The mixture was heated under reflux with stirring for 6 h and then filtered. The orange-yellow filtrate was allowed to stand at room temperature for a few days and the resulting orange crystals were found to be suitable for X-ray structure investigation.

Crystal dimensions 0·2 × 0·1 × 0·4 mm, density measured by flotation in 1,2-dibromoethane/ethanol; Syntex $P2_1$ diffractometer, θ–2θ scan, $2\theta \leq 47{\cdot}0°$, scan speed variable between 2·0 and 20·0° min^{-1}, scan range 1·9° (2θ) plus α_1–α_2 separation, background counting 0·5 of scan time. Cell parameters from 15 independent reflections with $19 < 2\theta < 26°$. Data collected/unique/$R_{int}(F)$, 2573/1971/0·0071. Range of *hkl*: 0→14, −10→0, −22→22. Three reflections monitored periodically showed < 3·0% intensity fluctuation, Lp and numerical absorption correction ($T_{max}/T_{min} = 0{\cdot}6375/0{\cdot}3546$) applied. The positions of Cu, I and S(1) were deduced from an E map, a difference Fourier synthesis revealed the positions of all the other non-hydrogen atoms. Refinement, based on F, by full-matrix least-squares minimization of $\sum w\Delta^2$ with *SHELX76* (Sheldrick, 1976). H atoms initially located from ΔF maps, positions and isotropic temperature factors subsequently refined by least squares. Non-H atoms anisotropic. Unit weights. Number of refined parameters 185. $S = 2{\cdot}72$ for observed reflections. Four reflections, showing strong extinction effects, were given zero weight during final refinement cycles. $wR = 0{\cdot}0256$ for observed data. $R/wR = 0{\cdot}0280/0{\cdot}0411$ for all data. $\Delta\rho_{max}/\Delta\rho_{min} = 0{\cdot}539/-0{\cdot}491$ e Å^{-3}, $\Delta/\sigma_{max} = 0{\cdot}166$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic parameters of the non-H atoms are given in Table 1,* and bond distances and angles in Fig. 1. Fig. 2 is an *ORTEP* (Johnson, 1976) drawing. The asymmetric unit consists of the (pyridine-2-thione)$_2$CuI group but this is connected with its rotation equivalent to form a dimer, with a $(\mathrm{CuIS_2})_2$ core. Each Cu of the core has a distorted tetrahedral coordination to one terminal (S1) and two bridging (S2, S2′) sulfur atoms and a terminal I atom. The two tetrahedra are joined along the S(2)···S(2′) edge and a crystallographic twofold axis is perpendicular to this edge (Fig. 2).

In the present structure the halide has been accepted into the Cu coordination sphere. This is testimony to the similarity of the 'softness' of the acid (Cu$^+$) and the base (I$^-$). In the analogous compounds $[\mathrm{Cu(py2SH)_3}]_2X_2$ (X = Cl, Br) (Stergioudis *et al.*, 1987), which were prepared by the reaction of Cu$^{\mathrm{II}}$ halide with excess py2SH and which also are dimeric, the halides being 'harder' are not coordinated to Cu.

As expected, the terminal Cu—S(1) distance of 2·268 (1) Å is shorter than the two bridging Cu—S distances of 2·328 (1) and 2·577 (2) Å. The reason for the large asymmetry in the two bridging Cu—S

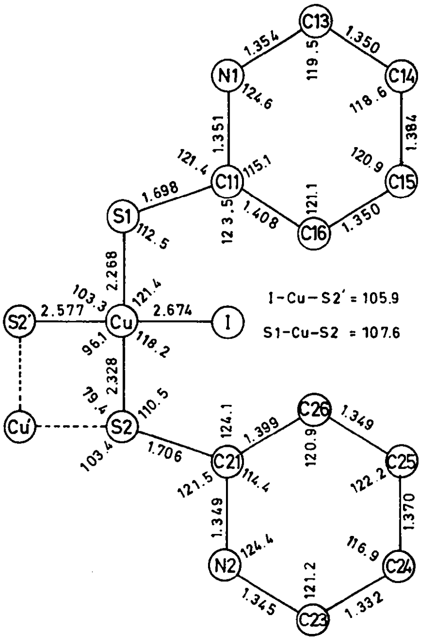

Fig. 1. Bond distances (Å) and angles (°) in DPTCI. (E.s.d.'s involving Cu are 0·001–0·002 Å for distances and 0·1° for angles; those involving S atoms: 0·005 Å, 0·2°; all others: 0·006–0·009 Å, 0·4–0·6°.)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles with e.s.d.'s have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51364 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances is not obvious although it has been observed before in similar complexes, as in the case of chlorobis(1-methylimidazoline-2-thione)copper(I) (Creighton *et al.*, 1985) and chlorobis(6-mercaptopurine)copper(I) (Shoemaker, Singh & Hodgson, 1976). The Cu—S distances are significantly longer than corresponding bonds in monomeric complexes with trigonal coordination around the Cu atom [*e.g.* chlorobis(1-ethyl-1,3-imidazolidine-2-thione)copper(I) (Battaglia, Bonamartini Corradi, Devillanova & Verani, 1979), chlorobis(*N,N*-dimethylimidazolidine-2-thione)copper(I) (Devillanova, Verani, Battaglia & Bonamartini Corradi, 1980) and chlorobis(tetrahydro-1*H*-pyrimidine-2-thione)copper(I) (Bret, Castan, Jugie, Dubourg & Roques, 1983)]. The Cu—I bond length [2·674 (1) Å] is within the range of values (2·622–2·785 Å) previously reported for Cu^I complexes (Dyason, Engelhardt, Healy & White, 1986; Rath, Holt & Tanimura, 1986). The Cu···Cu separation of 3·139 Å is too long to be considered a Cu···Cu interaction (Mehrotra & Hoffmann, 1978).

Angles Cu—S—C [103·4 (2) and 112·5 (2)°] at the thione S atoms are in the range previously observed for coordinated py2SH molecules. Although the geometry of the core Cu_2S_2 is very similar to that found in the complexes $[Cu(py2SH)_3]_2X_2$ (X = Cl, Br) in this complex the S—Cu—S and the Cu—S—Cu angles [103·3 (1) and 76·7 (1)°] deviate from the ideal values (109·5 and 70·5°) for a symmetrical tetrahedral dimer, consistent with the elongation of the bridging Cu—S bond (Summerville & Hoffmann, 1976).

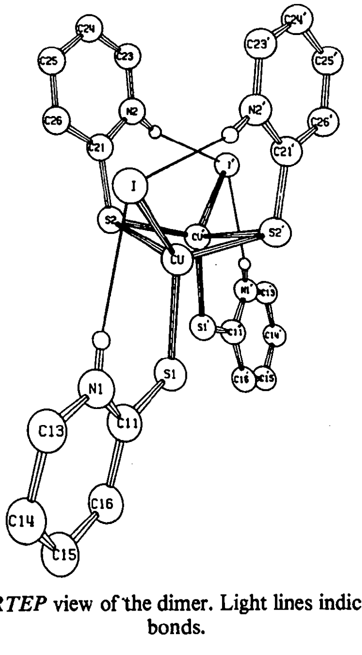

Fig. 2. An *ORTEP* view of the dimer. Light lines indicate hydrogen bonds.

Unexpectedly, the conformation of the core is *cis*, but this arrangement affords two strong intramolecular I···H—N hydrogen bonds [I···N(1) = 3·546 (1) Å, ∠I···H(1)—N(1) = 168 (1)°; I···N(2) = 3·594 (1) Å, ∠I···H(2)—N(2) = 167 (1)°] (Fig. 2), which stabilize this conformation. These hydrogen bonds must be the main reason for the essentially parallel arrangement of the four pyridine rings around the core (no angle between any two of these rings differs from 180° by more than 17°).

The Cu_2S_2 core has a hinge angle [angle between the planes defined by CuS(2)S(2′) and Cu′S(2)S(2′) (Fig. 2)] of 34·5° while in the analogous complex chlorobis(1-methylimidazoline-2-thione)copper(I) (Creighton *et al.*, 1985) the hinge angle is 0° (planar core). Mehrotra & Hoffmann (1978) have concluded that there is no large electronic effect influencing this angle which is primarily determined by steric and crystal packing forces.

A comparison of the IR spectra of the ligand and its copper complex shows that the NH stretch vibration does not shift to significantly lower frequencies, indicating absence of Cu—N bonds. The existence of the band at 3160 cm^{-1} and the absence of one at 2500 cm^{-1} is in agreement with the N-protonated form of the ligand in the complex.

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