Copper Co-ordination to Thioether Ligands.[1] Chemical, Spectroscopic, and Crystallographic Studies on Copper(I) Complexes of 2-(3,3-Dimethyl-2-thiabutyl)pyridine and the 2-(3,3-Dimethyl-2-thiabutyl)pyridinium Cation

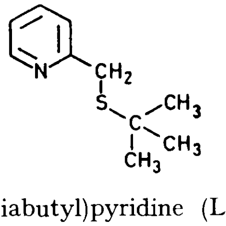
By **Eric W. Ainscough, Edward N. Baker,* Andrew M. Brodie,** and **Nigel G. Larsen,** Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North, New Zealand
Kevin L. Brown, Chemistry Division, DSIR, Petone, New Zealand

The ligand 2-(3,3-dimethyl-2-thiabutyl)pyridine (L) and its protonated cation, 2-(3,3-dimethyl-2-thiabutyl)-pyridinium ion (LH^+), have been used to prepare the copper(I) complexes $[CuL_nBr]$ (n = 1 or 2) and $[Cu(LH)X_2]$ (X = Cl or Br). Electronic and i.r. spectroscopic data for these complexes are presented, and the chemical relationships between them discussed. The crystal and molecular structures of $[CuL_2Br]$ and $[\{Cu(LH)Br_2\}_2]$ have been determined by single-crystal *X*-ray diffraction techniques, from diffractometer data. Crystals of $[CuL_2Br]$ are monoclinic, space group $P2_1/n$, with a = 16.927(3), b = 8.867(1), c = 15.371(2) Å, β = 100.61(1)°, and Z = 4. Crystals of $[\{Cu(LH)Br_2\}_2]$ are also monoclinic, space group $P2_1/n$, with a = 15.700(3), b = 9.038(3), c = 9.926(2) Å, β = 98.66(1)°, and Z = 2. After full-matrix least-squares refinement final R values are 0.066 (for 2 032 observed reflections) and 0.047 (for 1 538 observed reflections) respectively. The complex $[CuL_2Br]$ is monomeric, the distorted tetrahedral geometry round the copper atom being completed by a bromide ion [Cu–Br 2.424(2) Å], the pyridyl nitrogen and thioether sulphur of a bidentate ligand L [Cu–N 2.109(9), Cu–S 2.357(3) Å], and the thioether sulphur of a unidentate ligand L [Cu–S 2.310(3) Å]. The complex $[\{Cu(LH)Br_2\}_2]$ exists as a centrosymmetric dimer with the distorted tetrahedral copper(I) centres dibromo-bridged [Cu–Br 2.597(1) Å]. The two remaining co-ordination positions round each copper are occupied by a terminal bromide ion [Cu–Br 2.363(1) Å] and the thioether sulphur [Cu–S 2.276(2) Å] of an LH^+ cation.

INTEREST in the interaction of thioether ligands with copper,[2-7] both as Cu^I and Cu^{II}, has been intensified by the observation that the thioether sidechain of methionine is a ligand for copper in the blue copper proteins, azurin[8] and plastocyanin.[9] The expectation (now confirmed) that the other copper ligands in these proteins would include histidyl nitrogen atoms has led us to further explore the interaction of copper with ligands containing both thioether sulphur and heterocyclic nitrogen-donor atoms.

The studies of Hodgson and co-workers on the copper(II) complexes of 2-aminomethylpyridine,[10] 2-(2-aminoethyl)pyridine,[11-14] and their mono- and di-alkyl *N*-substituted derivatives[11,15,16] have shown that even with such simple bidentate ligand systems a variety of Cu^{II} co-ordination geometries can occur. Thus the bulkiness of the co-ordinated amino-group of 2-(2-dimethylaminoethyl)pyridine apparently influences the adoption of a pseudotetrahedral co-ordination geometry in the complex dichloro[2-(2-dimethylaminoethyl)pyridine]-copper(II).[16]

We envisaged that similar effects might be observed with 2-alkylthioalkylpyridine ligands, by the use of bulky thioether substituents, and have therefore investigated the copper(I) and copper(II) complexes of


L

2-(3,3-dimethyl-2-thiabutyl)pyridine (L). The copper(II) complexes will be reported later; here we describe the characterisation of copper(I) complexes of L.

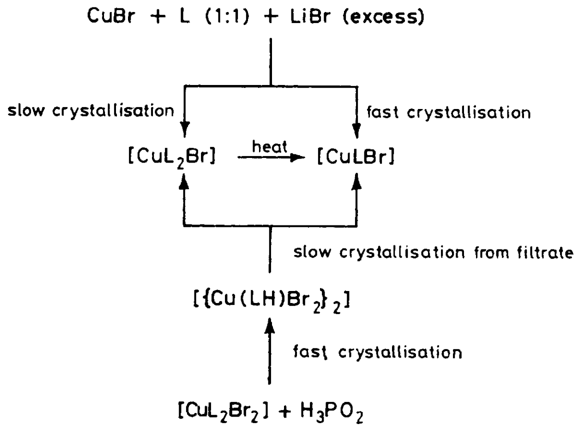
In these studies, we have observed that three distinct types of copper(I) complex are formed, each type dependent on small variations in the preparative procedures. Complexes of the type [CuLBr], $[CuL_2Br]$, and in the presence of the protic reducing agent hypophosphorous acid (H_3PO_2), $[\{Cu(LH)X_2\}_2]$ (X = Cl or Br) have been characterised. In this paper we outline the chemical relationships between these species and report the molecular structures of $[CuL_2Br]$ and the yellow dimer $[\{Cu(LH)Br_2\}_2]$.

RESULTS AND DISCUSSION

Synthesis of [CuLBr], $[CuL_2Br]$, *and* $[\{Cu(LH)X_2\}_2]$ (X = Cl *or* Br).—The complex [CuLBr] is prepared from CuBr and the ligand L (1 : 1) in absolute ethanol (containing excess of LiBr) by removing the solvent *in vacuo* to induce rapid precipitation. On the other hand, if a concentrated solution is allowed to stand, allowing slow crystal formation, $[CuL_2Br]$ is formed. On heating, crystals of $[CuL_2Br]$ gradually turn opaque and then melt sharply at 135 °C, the melting point of the mono(ligand) complex [CuLBr].

An alternative method for preparing copper(I) complexes of thioether ligands is to reduce copper(II) species with a few drops of hypophosphorous acid, H_3PO_2.[2] *In situ* reductions of the copper(II) complexes $[CuL_2Cl_2]$ and $[CuL_2Br_2]$ (preparations to be published), in ethanol, however, not only reduce Cu^{II} to Cu^I, but also result in the protonation of the pyridyl nitrogen of the ligand L. This unusual reaction is similar to that observed when the mixed nitrogen–phosphorus ligand [2-(diphenylphosphino)ethyl]diethylamine is treated with $CuCl_2$; a copper(I) complex is obtained and the amine function is protonated.[17] In the present case, yellow dimeric complexes $[\{Cu(LH)X_2\}_2]$ (X = Cl or Br) can be isolated.

Although the chloro-complex slowly oxidises in the presence of atmospheric oxygen, and must be stored *in vacuo*, the bromo-complex is stable. The relationships between the three types of copper(I) complex are illustrated in the Scheme.



SCHEME L = 2-(3,3-Dimethyl-2-thiabutyl)pyridine, reactions carried out in ethanol

The Structure of Bromo[2-(3,3-*dimethyl*-2-*thiabutyl*)-*pyridine*-N,S][2-(3,3-*dimethyl*-2-*thiabutyl*)*pyridine*-S]-*copper*(I), [CuL$_2$Br].—In this discrete monomeric species one ligand L is chelated, while the other is unidentate and bound only *via* the sulphur atom (see Figure 1). The distorted tetrahedral inner co-ordination sphere of the copper atom (dihedral angle ω = 88.5°) thus consists of a terminal bromine [Cu–Br 2.424(2) Å], the thioether sulphur and pyridyl nitrogen of the chelated ligand [Cu–S 2.357(3), Cu–N 2.109(9) Å], and the thioether sulphur of the unidentate ligand [Cu–S 2.310(3) Å]. The pyridyl nitrogen of the latter does not participate in any inter- or intra-molecular bonding interactions. There are no intermolecular contacts of less than 3.5 Å. Bond distances and angles are listed in Table 1, and the numbering of the molecule is shown in Figure 1.

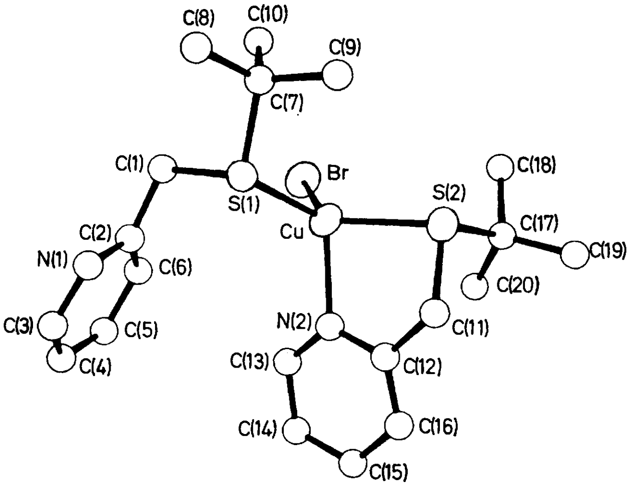


FIGURE 1 Structure of [CuL$_2$Br] showing the atom labelling

A comparison of metal–ligand bond lengths with those in analogous structures suggests that the chelated ligand L is bound less strongly than unidentate ligands. The Cu–N bond, 2.109(9) Å, is significantly longer than the corresponding Cu–N bonds in the copper(I) complexes of bipyridine[18] [2.01(2) Å], pyridine[19] [2.05(1) Å], and substituted pyridine ligands[5,20-22] (2.00—2.04 Å). It corresponds closely to the predicted Cu^{I}–N single-bond length of 2.09 Å (taking the covalent bond radii of Cu^{I} and N as 1.35 Å and 0.74 Å respectively[23]). Likewise the Cu–S bond to the thioether sulphur of the chelated ligand is slightly longer than usual. At 2.357(3) Å it is at the upper limit of the range of Cu^{I}–S bond lengths found in other thioether complexes,[3,5,6,24,25] *viz.* 2.25—2.35 Å, and it is significantly longer than the Cu^{I}–S bond to the unidentate ligand L [2.310(3) Å].

TABLE 1

Bond lengths (Å) and angles (°) for [CuL$_2$Br] with estimated standard deviations in parentheses

(*a*) Bond lengths

Cu–Br	2.424(2)	C(6)–C(2)	1.39(1)
Cu–S(1)	2.310(3)	C(7)–C(8)	1.53(1)
Cu–S(2)	2.357(3)	C(7)–C(9)	1.52(1)
Cu–N(2)	2.109(9)	C(7)–C(10)	1.55(1)
S(1)–C(1)	1.83(1)	C(11)–C(12)	1.52(1)
S(1)–C(7)	1.85(1)	C(12)–N(2)	1.34(1)
S(2)–C(11)	1.83(1)	N(2)–C(13)	1.32(1)
S(2)–C(17)	1.86(1)	C(13)–C(14)	1.40(2)
C(1)–C(2)	1.54(1)	C(14)–C(15)	1.38(2)
C(2)–N(1)	1.33(1)	C(15)–C(16)	1.40(2)
N(1)–C(3)	1.32(1)	C(16)–C(12)	1.36(1)
C(3)–C(4)	1.34(2)	C(17)–C(18)	1.54(1)
C(4)–C(5)	1.37(2)	C(17)–C(19)	1.53(2)
C(5)–C(6)	1.39(2)	C(17)–C(20)	1.56(2)

C–H bonds range from 0.82 Å to 1.15 Å (mean 0.98 Å).

(*b*) Bond angles *

Br–Cu–S(1)	109.0(1)	S(1)–C(7)–C(9)	106.7(8)
Br–Cu–S(2)	120.7(1)	S(1)–C(7)–C(10)	108.3(8)
Br–Cu–N(2)	113.0(2)	C(8)–C(7)–C(9)	111(1)
S(1)–Cu–S(2)	115.1(1)	C(8)–C(7)–C(10)	111(1)
S(1)–Cu–N(2)	111.6(2)	C(9)–C(7)–C(10)	111(1)
S(2)–Cu–N(2)	85.4(3)	S(2)–C(11)–C(12)	113.3(8
Cu–S(1)–C(1)	105.6(4)	C(11)–C(12)–N(2)	117(1)
Cu–S(1)–C(7)	111.3(3)	C(11)–C(12)–C(16)	120(1)
C(1)–S(1)–C(7)	100.1(5)	N(2)–C(12)–C(16)	123(1)
Cu–S(2)–C(11)	93.3(4)	C(12)–N(2)–Cu	117.4(
Cu–S(2)–C(17)	113.4(4)	C(12)–N(2)–C(13)	117(1)
C(11)–S(2)–C(17)	105.0(5)	C(12)–N(2)–Cu	124.7(
S(1)–C(1)–C(2)	108.7(8)	N(2)–C(13)–C(14)	124(1)
C(1)–C(2)–N(1)	119(1)	C(13)–C(14)–C(15)	117(1)
C(1)–C(2)–C(6)	121(1)	C(14)–C(15)–C(16)	119(1)
N(1)–C(2)–C(6)	120(1)	C(15)–C(16)–C(12)	119(1)
C(2)–N(1)–C(3)	120(1)	S(2)–C(17)–C(18)	103.0(8)
N(1)–C(3)–C(4)	124(1)	S(2)–C(17)–C(19)	109.7(9)
C(3)–C(4)–C(5)	118(1)	S(2)–C(17)–C(20)	110.9(8)
C(4)–C(5)–C(6)	119(1)	C(18)–C(17)–C(19)	113(1)
C(5)–C(6)–C(2)	119(1)	C(18)–C(17)–C(20)	111(1)
S(1)–C(7)–C(8)	108.3(8)	C(19)–C(17)–C(20)	109(1)

* Bond angles at the carbon atoms, involving hydrogen atoms, all have approximately tetrahedral values.

The above observations suggest that the relatively rigid nature of the chelate ring [Cu, N(2), C(12), and C(11) are necessarily coplanar] leads to less effective overlap with the orbitals of the tetrahedrally co-ordinated copper atom, at the same time resulting in stronger bonding by the other (unidentate) ligands. The chelate-bite angle is only 85.4(3)°, compared with 92—96° for a more flexible five-membered chelate ring such as 3,6-dithiaoctane,[3,24] and the ideal tetrahedral angle of 109.5°. Likewise, the intra-chelate ring angle Cu–S(2)–C(11) is unusually small [93.3(4)°], much less than the more-nearly tetrahedral angles (105.4—114.1°) seen around the sulphur atoms of the unidentate ligands in this complex and in $[\{Cu(LH)Br_2\}_2]$ (see below).

Other bond lengths and angles (Table 1) are as expected. The Cu–Br bond [2.424(2) Å] is shorter than the range of values (2.45—2.55 Å) usually observed for Cu–Br bonds in tetrahedral copper(I) complexes.[26-28] These all refer to bridging bromine atoms, however, and the only terminal Cu–Br bond we are aware of in a four-co-ordinate copper(I) complex is that in $[\{Cu(LH)Br_2\}_2]$ (see below), *viz.* 2.363(1) Å. Bond distances and angles within the ligands L are normal, and the pyridyl rings are planar. The puckered nature of the five-membered chelate ring is shown by the deviation [0.743(3) Å] of the sulphur atom, S(2), from the least-squares plane through the coplanar Cu, N(2), C(12), and C(11) atoms.

*The Structure of Di-μ-bromo-bis{bromo[2-(3,3-dimethyl-2-thiabutyl)pyridinium-*S]*copper*(I)}, $[\{Cu(LH)Br_2\}_2]$.—The two distorted tetrahedral copper(I) centres of this centrosymmetric dimer are bridged by two bromide ions, with the two remaining co-ordination positions of each copper(I) ion being occupied by a terminal bromide ion and a sulphur-bound 2-(3,3-dimethyl-2-thiabutyl)-pyridinium cation (Figure 2). The complex, which could be written as $LH^+(CuBr_2^-)_2LH^+$, is thus one of a small number of inorganic zwitterions (see, for example, refs. 29 and 30). Bond distances and angles are listed in Table 2, and the numbering of the atoms is shown in Figure 2.

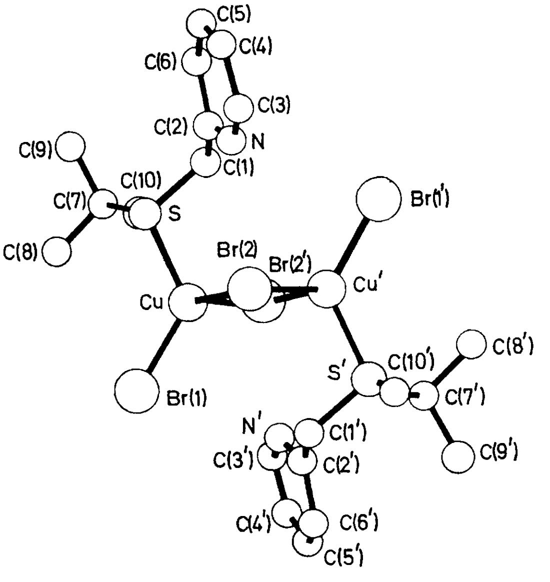


FIGURE 2 Structure of $[\{Cu(LH)Br_2\}_2]$ showing the atom labelling

TABLE 2

Bond lengths (Å) and angles (°) for $[\{Cu(LH)Br_2\}_2]$ * with estimated standard deviations in parentheses

(*a*) Bond lengths

Cu–Br(1)	2.363(1)	N–C(3)	1.32(1)
Cu–Br(2)	2.573(1)	C(3)–C(4)	1.35(1)
Cu–Br(2′)	2.621(1)	C(4)–C(5)	1.39(1)
Cu–S	2.276(2)	C(5)–C(6)	1.36(1)
S–C(1)	1.840(8)	C(6)–C(2)	1.38(1)
S–C(7)	1.844(7)	C(7)–C(8)	1.54(1)
C(1)–C(2)	1.47(1)	C(7)–C(9)	1.53(1)
C(2)–N	1.33(1)	C(7)–C(10)	1.51(1)

C–H bond lengths vary from 0.83 Å to 1.13 Å (mean 0.96 Å). The bond N–H(2) is 0.87(1) Å.

(*b*) Bond angles

Cu–Br(2)–Cu′	75.5(1)	N–C(2)–C(6)	117.1(7)
Br(2)–Cu–Br(2′)	104.5(1)	C(2)–N–C(3)	124.0(7)
Br(2)–Cu–Br(1)	109.3(1)	N–C(3)–C(4)	120.4(8)
Br(2)–Cu–S	106.5(1)	C(3)–C(4)–C(5)	117.8(8)
Br(1)–Cu–Br(2′)	110.9(1)	C(4)–C(5)–C(6)	120.3(8)
Br(1)–Cu–S	126.2(1)	C(5)–C(6)–C(2)	120.3(8)
S–Cu–Br(2′)	97.2(1)	S–C(7)–C(8)	102.2(5)
Cu–S–C(1)	106.3(3)	S–C(7)–C(9)	108.8(6)
Cu–S–C(7)	114.1(2)	S–C(7)–C(10)	111.8(6)
C(1)–S–C(7)	104.2(4)	C(8)–C(7)–C(9)	110.0(7)
S–C(1)–C(2)	109.8(5)	C(8)–C(7)–C(10)	110.8(7)
C(1)–C(2)–N	117.7(6)	C(9)–C(7)–C(10)	112.7(7)
C(1)–C(2)–C(6)	125.2(7)		

(*c*) Other distances and angles of interest

Cu · · · Cu′	3.182(1) Å
N · · · Br(2′)	3.300(5) Å
N–H(2) · · · Br(2′)	161.8(8)°

* The two halves of the dimer are related by a crystallographic centre of symmetry. Primed atoms refer to the centrically related atoms at (−*x*, −*y*, 1 − *z*).

A notable feature of the structure is the close approach (3.30 Å) between the protonated pyridyl nitrogen of the LH^+ ligand and a bridging bromine atom. It is significantly shorter than the expected N · · · Br van der Waals separation (3.45 Å) and the angle N–H · · · Br (161.8°) indicates that the geometry is ideal for an N–H · · · Br hydrogen bond. Similar interactions have been observed previously, albeit with less favourable geometry.[31-33]

The two bridging Cu–Br bonds [2.621(1) and 2.573(1) Å] are fairly long, at the upper limit of the normal range for such bonds (2.45—2.55 Å).[26-28] The other two bond distances to the copper atom are correspondingly short, the terminal Cu–Br bond 2.363(1) Å and the Cu–S (thioether) bond 2.276(2) Å. The latter compares with the observed range of 2.25 to 2.35 Å (mean 2.31 Å) for Cu–S bonds in other thioether complexes[3,5,6,24,25] and is more than 0.1 Å shorter than the predicted Cu^I–S single bond length of 2.39 Å (based on a covalent bond radius of 1.04 Å for sulphur[23]). The angles at the sulphur atom [104.2(4) to 114.1(2)°] are approximately tetrahedral. Those around the Cu atoms deviate considerably from ideal tetrahedral angles, ranging from 97.2(1) to 126.2(1)°.

The geometry of the dibromo-bridge closely parallels that of other such bridges linking tetrahedral Cu^I centres. There is a direct relationship between the angle Br(2)–Cu–Br(2′), the angle Cu–Br(2)–Cu′, and the Cu · · · Cu′ separation. The values observed here

[104.5(1)°, 75.5(1)°, and 3.182(1) Å] are closely similar to those in the structure of the triethylphosphine–copper(I) bromide tetramer [26] [101.25(3)°, 77.48(4)°, and 3.184(2) Å]. As the angle at the copper atoms increases, the angles at the bridging bromine atoms decrease, and the Cu · · · Cu separation decreases, as in the structure of the methylacrylonitrile–copper(I) bromide tetramer [28] [Br–Cu–Br′ 106.2(1)—108.2(1)°, Cu–Br–Cu′ 73.43(5)° and 72.77(9)°, Cu · · · Cu 2.993(2) Å]. Despite the short Cu · · · Cu separations there is good evidence that no Cu–Cu bonding interaction occurs in such complexes.[26]

Thioether Bonding to Copper.—Two features of Cu^I–S (thioether) bonding are worthy of comment. Firstly, although the length of such bonds varies considerably, depending on whether the thioether ligand is chelated or not, on the flexibility of any chelate ring, and on the strength of other bonds to the copper atom, in *all* copper(I)–thioether complexes, the Cu–S bonds are consistently shorter than the predicted Cu^I–S single-bond length (2.39 Å). The shortening ranges from *ca.* 0.1 Å as in [$\{Cu(LH)Br_2\}_2$], where the sulphur ligand is unidentate and two other ligands (the bridging bromines) are less strongly bound, to *ca.* 0.03 Å for the chelated sulphur ligand in [CuL_2Br]. Other thioether ligands, such as the more flexible chelates, 2,5-dithiahexane and 3,6-dithiaoctane, lie in between, the average shortening being about 0.08 Å. We believe that these crystallographic data provide further evidence supporting the view that a partial π component is a feature of Cu^I–S (thioether) bonds. Similar conclusions have been reached for Cu^I–S bonds in disulphide complexes.[21]

Secondly, the flexibility of the thioether sulphur atom clearly makes it a very suitable ligand for metals in proteins, where the co-ordination geometry is mediated by the constraints imposed by the protein structure. Thus even in small copper complexes thioether ligands display a wide range of metal–sulphur bond lengths, the angles at the sulphur atoms can vary widely (93—120°), and the sulphur atoms may act as unidentate or bridging ligands.[24]

Physicochemical Study of the Copper(I) *Complexes.*—Infrared evidence for the protonation of the pyridyl nitrogen in the complexes [$\{Cu(LH)X_2\}_2$] (X = Cl or Br) is provided by the appearance of broad nitrogen–hydrogen absorptions in the 2 400—3 000 cm^{-1} range. The ν(N–H) values (2 630 cm^{-1} for [$\{Cu(LH)Cl_2\}_2$] and 2 850 cm^{-1} for [$\{Cu(LH)Br_2\}_2$]) are characteristic of pyridinium salts [34] and may be compared with the value of *ca.* 2 500 cm^{-1} for the free hydrobromide [LH]Br. The anion dependence of the frequencies (*i.e.* Cl < Br) for the complexes is in line with the *X*-ray structural evidence for N–H · · · X hydrogen bonding, the smaller Cl^- ion being expected to form the strongest hydrogen bond. Similar anion dependency of ν(N–H) frequencies has been observed previously for pyridinium salts,[34] complexes of phosphine–pyridinium ligands,[35,36] and [$Co(NH_3)_6]X_3$ complexes.[37] For the free ligand L, the highest pyridine ring absorption occurs at 1 593 cm^{-1} and in the [$\{Cu(LH)X_2\}_2$] complexes at 1 618 (X = Cl) and 1 616 cm^{-1} (X = Br). The upward shift is typical of pyridyl compounds bearing a positive charge on the nitrogen [34,35] and as expected,[35] is greater than observed for [CuLBr] (1 595 cm^{-1}) and other metal(II) complexes of L.[38] In the far-i.r. region, ν(Cu–X) absorptions can be tentatively assigned as follows: [$\{Cu(LH)Cl_2\}_2$] 231 (terminal) and 204 cm^{-1} (bridging); [$\{Cu(LH)Br_2\}_2$] 182 (terminal) and 132 cm^{-1} (bridging). For [CuLBr] a band at 182 cm^{-1} can be assigned to ν(Cu–Br), but in view of the wide range of frequencies observed for copper–bromine vibrations,[39] it is not possible to decide whether the bromine is terminal or bridging.

The yellow colour of the [$\{Cu(LH)X_2\}_2$] complexes is unusual for compounds containing Cu^I bound to a thioether, and arises from the tailing into the visible of a broad electronic absorption band [shoulder *ca.* 420 nm (reflectance) for X = Cl and Br; 435 nm (CH_2Cl_2) for X = Cl]. The fact that the band maximum is independent of the anion suggests that it could be tentatively assigned to a sulphur–copper type charge-transfer absorption which has been red-shifted as a result of the strong Cu–S π interaction. It is of interest to note that for a variety of clusters containing copper(I)–thiolate sulphur bonds, the intense band in the 400—500 nm range has been assigned to a $S\rightarrow Cu^I$ transition.[40] In donor solvents, such as methanol and nitromethane, the yellow colour of the [$\{Cu(LH)X_2\}_2$] complexes disappears immediately and the band at *ca.* 420 nm is no longer observed. In these solutions the Λ values (calculated per monomer unit, Experimental section) are in the range expected for 1 : 1 electrolytes.[41] Such behaviour can be explained in terms of dissociation induced by solvation [equation (1)] and is typical of inorganic

$$[\{Cu(LH)X_2\}_2] \rightleftharpoons 2[CuX_2]^- + 2LH^+ \qquad (1)$$

zwitterions,[30] although the dissociation is not normally as rapid. This explanation is supported by the isolation of [$AsPh_4$][$CuCl_2$] from a methanol solution of [$\{Cu(LH)Cl_2\}_2$] and [$AsPh_4$]Cl.

EXPERIMENTAL

Infrared spectra were recorded on a Beckman IR 20 spectrophotometer (250—4 000 cm^{-1}) and a Grubb-Parsons Cube mark II Interferometer (40—400 cm^{-1}). Electronic spectra were obtained using a Shimadzu MPS-5000 spectrophotometer and conductivities (at *ca.* 10^{-3} mol dm^{-3}) were measured at room temperature using a Philips PR9500 conductivity meter and PW9510 cell. Microanalyses were by Professor A. D. Campbell, University of Otago. All solvents were dried according to established procedures. The reagents, 2-methylpyridyl chloride hydrochloride and t-butyl thiol, were purchased from Aldrich Chemical Co.

Synthesis of 2-(3,3-*Dimethyl*-2-*thiabutyl*)*pyridine.*—This was prepared following a modification of the literature method for 2-(2-thiapropyl)pyridine.[42] To a cooled solution of sodium (9.20 g, 0.4 mol) dissolved in ethanol (300 cm^3) was added 2-methylpyridyl chloride hydrochloride (32.81 g, 0.2 mol) and t-butyl thiol (18.04 g, 0.2 mol). The mixture was refluxed under dinitrogen for 30 min and then allowed to stand overnight, after which the precipitated NaCl was removed by filtration. Addition of water caused the separation of an oil, which was extracted into diethyl ether. The ether extract was dried (anhydrous Mg[SO$_4$]) and the solvent removed (rotary evaporator) before distilling the product *in vacuo* (12 mmHg, 128—130 °C).* Yield 27.56 g (76%) (Found: C, 66.3; H, 8.4; N, 7.5; S, 17.1. $C_{10}H_{15}NS$ requires C, 66.25; H, 8.3; N, 7.7; S, 17.7%).

Preparation of the Complexes.—[CuLBr]. The ligand L (0.182 g, 1 mmol) was added to a filtered ethanol solution of copper(I) bromide (0.143 g, 1 mmol) and excess of lithium bromide. The resulting solution was concentrated (rotary evaporator), cooled to 0 °C, and rapid crystallization induced by scratching with a glass rod. The white crystals of the product were filtered off, washed with ethanol, and dried *in vacuo*, m.p. 135—136 °C. Yield 0.243 g (75%) (Found: C, 37.2; H, 4.6; Br, 24.7; N, 4.55. $C_{10}H_{15}BrCuNS$ requires C, 37.0; H, 4.7; Br, 24.6; N, 4.3%), Λ 31 (in nitromethane); 35 S cm^2 mol^{-1} (in methanol).

[CuL$_2$Br]. If in the above preparation the solution was allowed to stand at 0 °C for 2 days white crystals were deposited in low yield. These were identified as [CuL$_2$Br] from the single-crystal *X*-ray structural analysis (see below), m.p. 135 °C (see text).

[{Cu(LH)Cl$_2$}$_2$]. To copper(II) chloride dihydrate (0.170 g, 1 mmol) dissolved in ethanol was added the ligand L (0.363 g, 2 mmol) in the same solvent. The dark green solution was warmed and hypophosphorous acid added dropwise until a yellow colour resulted. After the solution was reduced in volume to 5 cm^3, cooling to 0 °C afforded yellow crystals of the product, which were filtered off, washed with ethanol, and dried *in vacuo*, m.p. 123—125 °C. Yield 0.245 g (77%) (Found: C, 37.9; H, 5.2; Cl, 22.45; N, 4.3. $C_{10}H_{16}Cl_2CuNS$ requires C, 37.9; H, 5.1; Cl, 22.4; N, 4.4%), Λ (per monomer) 92 (in nitromethane); 115 S cm^2 mol^{-1} (in methanol). The complex is slowly oxidised in air but stable when stored *in vacuo*.

[{Cu(LH)Br$_2$}$_2$]. This was prepared from copper(II) bromide (0.223 g, 1 mmol) following the above method, m.p. 138—140 °C (Found: C, 29.95; H, 4.2; N, 3.3. $C_{10}H_{16}Br_2CuNS$ requires C, 29.6; H, 4.0; N, 3.45%), Λ (per monomer) 84 (in nitromethane); 123 S cm^2 mol^{-1} (in methanol).

Reaction of Tetraphenylarsonium Chloride with [{Cu(LH)Cl$_2$}$_2$].—To a freshly prepared warm methanol solution of [{Cu(LH)Cl$_2$}$_2$] (0.179 g, 0.28 mmol) was added [AsPh$_4$]Cl (0.237 g, 0.57 mmol) and two drops of H_3PO_2. Reduction of the solvent volume *in vacuo* yielded a mixture of yellow crystals of [{Cu(LH)Cl$_2$}$_2$], and white crystals, identified as [AsPh$_4$][CuCl$_2$], m.p. 179—180 °C (lit.,[43] 176—178 °C) (Found: C, 55.7; H, 3.85; Cl, 14.2. $C_{24}H_{20}AsCl_2Cu$ requires C, 55.7; H, 3.9; Cl, 13.7%).

Crystallography.—(a) *Bromo*[2-(3,3-*dimethyl*-2-*thiabutyl*)-*pyridine*-N,S][2-(3,3-*dimethyl*-2-*thiabutyl*)*pyridine*-S]*copper*-(I), [CuL$_2$Br]. The space group and cell dimensions of the crystals, prepared as above, were determined by oscillation, Weissenberg, and precession photography. More accurate cell dimensions were determined from the least-squares analysis [44] of the positions of 12 general reflections on a four-circle *X*-ray diffractometer.

Crystal data. $C_{20}H_{30}BrCuN_2S_2$, $M = 506.03$, Monoclinic, $a = 16.927(3)$, $b = 8.867(1)$, $c = 15.371(2)$ Å, $\beta = 100.61(1)°$, $U = 2\,268$ Å^3, $F(000) = 1\,040$, $D_m = 1.48$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.482$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$Å, μ(Mo-K_α) = 45.7 cm^{-1}, space group $P2_1/n$ from systematic absences.

Data collection and reduction. A crystal fragment (dimensions *ca.* 0.02 × 0.02 × 0.02 cm) was used for data collection on a computer-controlled Hilger and Watts four-circle diffractometer. The orientation of the crystal was defined by a least-squares treatment [44] of the positions of 12 general reflections. A θ—2θ scan, consisting of 80 steps of 0.01° through each reflection, with a count of 1 s at each step and a background count of 20 s at the beginning and end of each scan, was used, up to $\theta = 26°$. Three standard reflections, monitored after every 100 measurements, showed no systematic intensity changes. Equivalent reflections were merged to give 2 032 reflections for which $I > 2\sigma(I)$. Lorentz and polarisation corrections were made, but no absorption corrections.

Structure determination. Bromine and copper atom positions were deduced from a three-dimensional Patterson map, and the remaining 24 non-hydrogen atoms located in two subsequent electron-density maps. The structure was refined using the full-matrix least-squares program CUCLS (a local version of ORFLS,[45] adapted by the University of Canterbury for a Burroughs B6700 computer). The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o{}^2/[\sigma(F_o)^2]^2$. Using isotropic temperature factors, the conventional R factor was reduced to 0.093 after five cycles. Two further cycles, with anisotropic temperature factors for bromine, copper, and sulphur atoms, saw the refinement converge with $R = 0.072$. A difference map revealed the positions of all hydrogen atoms, which were then included in subsequent structure-factor calculations (but not refined). Isotropic B values were taken as 1.2 times those of the atoms to which the hydrogens were attached. After a further two cycles with anisotropic temperature factors for all non-hydrogen atoms refinement had converged with $R = 0.066$ and $R' = 0.072$. Final atomic co-ordinates are listed in Table 3. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 23042 (21 pp.).†

(b) *Di*-μ-*bromo*-*bis*{*bromo*[2-(3,3-*dimethyl*-2-*thiabutyl*)-*pyridinium*-S]*copper*(I)}, [{Cu(LH)Br$_2$}$_2$]. The crystals were pale yellow plates. Preliminary photography confirmed the space group as $P2_1/n$ and accurate cell dimensions were determined from least-squares analysis [44] of the positions of 12 general reflections on a four-circle *X*-ray diffractometer.

Crystal data. $C_{20}H_{32}Br_4Cu_2N_2S_2$, $M = 811.31$, Monoclinic, $a = 15.700(3)$, $b = 9.038(3)$, $c = 9.926(2)$ Å, $\beta = 98.66(1)°$, $U = 1\,392.5$ Å^3, $F(000) = 788$, $D_m = 1.92$ g cm^{-3} (flotation), $Z = 2$, $D_c = 1.93$ g cm^{-3}, Cu-K_α radiation, $\lambda = 1.541\,8$ Å, μ(Cu-K_α) = 95.30 cm^{-1}, space group $P2_1/n$ from systematic absences.

Data collection and reduction. A crystal of approximate dimensions 0.25 × 0.20 × 0.05 mm was mounted on a Hilger and Watts automated diffractometer. The crystal orientation was refined by a least-squares treatment [44] of the setting angles of 12 reflections. Intensities were measured with a θ—2θ scan with 80 steps of 0.01° (counting 1 s per step and 20 s background on each side of each scan). The intensities of three reflections well separated in reciprocal space were monitored throughout the data collection and showed only random fluctuations (±2%) in the mean values. All reflections in the reciprocal space octant with $\theta < 57°$

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 3

Final atomic co-ordinates for $[CuL_2Br]$ with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	0.760 3(1)	0.450 4(2)	0.026 0(1)
Br	0.791 1(1)	0.239 3(1)	−0.062 3(1)
S(1)	0.724 6(2)	0.359 9(3)	0.154 2(2)
S(2)	0.682 6(2)	0.654 5(4)	−0.040 5(2)
N(1)	0.882 8(6)	0.281(1)	0.309 7(7)
N(2)	0.854 8(6)	0.608(1)	0.053 3(5)
C(1)	0.783 8(7)	0.188(1)	0.181 9(7)
C(2)	0.869 6(7)	0.233(1)	0.225 9(7)
C(3)	0.957 0(8)	0.307(2)	0.351 3(9)
C(4)	1.021 8(9)	0.296(2)	0.313(1)
C(5)	1.010 4(7)	0.253(2)	0.225(1)
C(6)	0.933 2(8)	0.221(1)	0.181 0(8)
C(7)	0.622 2(6)	0.279(1)	0.132 2(7)
C(8)	0.601 9(8)	0.225(2)	0.220 3(8)
C(9)	0.565 9(7)	0.404(2)	0.092(1)
C(10)	0.620 8(8)	0.146(2)	0.065 8(8)
C(11)	0.747 4(7)	0.795(1)	0.024 3(7)
C(12)	0.836 0(7)	0.754(1)	0.039 3(8)
C(13)	0.931 7(7)	0.573(1)	0.072 5(7)
C(14)	0.994 6(8)	0.677(2)	0.079 1(8)
C(15)	0.973 8(8)	0.827(2)	0.064 8(8)
C(16)	0.892 2(8)	0.865(1)	0.043 1(7)
C(17)	0.693 1(8)	0.689(1)	−0.157 0(7)
C(18)	0.644 1(8)	0.558(2)	−0.207 5(8)
C(19)	0.659 4(8)	0.844(2)	−0.186 7(8)
C(20)	0.783 1(8)	0.681(2)	−0.167 0(8)
H(1a)	0.755	0.125	0.225
H(1b)	0.800	0.130	0.125
H(3)	0.960	0.350	0.405
H(4)	1.078	0.317	0.355
H(5)	1.045	0.244	0.180
H(6)	0.930	0.190	0.120
H(8a)	0.640	0.140	0.245
H(8b)	0.540	0.190	0.196
H(8c)	0.610	0.250	0.280
H(9a)	0.502	0.385	0.090
H(9b)	0.570	0.460	0.140
H(9c)	0.590	0.450	0.030
H(10a)	0.610	0.225	0.025
H(10b)	0.660	0.071	0.078
H(10c)	0.555	0.140	0.065
H(11a)	0.735	0.893	−0.008
H(11b)	0.730	0.820	0.080
H(13)	0.960	0.470	0.075
H(14)	1.045	0.674	0.085
H(15)	1.015	0.910	0.070
H(16)	0.860	0.960	0.040
H(18a)	0.645	0.585	−0.265
H(18b)	0.597	0.607	−0.200
H(18c)	0.670	0.472	−0.195
H(19a)	0.695	0.917	−0.152
H(19b)	0.613	0.870	−0.163
H(19c)	0.660	0.870	−0.245
H(20a)	0.775	0.670	−0.235
H(20b)	0.800	0.570	−0.147
H(20c)	0.815	0.760	−0.137

were measured. Of the 2 097 reflections measured, 1 538 for which $I > 3\sigma(I)$ were used in the subsequent analysis. Data were corrected for absorption analytically,[46] the corrections ranging from 1.603 to 3.281.

Structure determination. The structure was solved by direct methods [47] and refined by full-matrix least-squares methods using SHELX-76.[48] The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$ where the weight $w = 1/(\sigma_F)^2$. A difference-Fourier synthesis revealed the positions of all hydrogen atoms. The non-hydrogen atoms were refined with anisotropic temperature parameters, while hydrogen-atom positions only were refined ($U_H = 0.07$ Å^2). At convergence (all shifts < estimated standard deviation), $R = 0.047$ and $R' = 0.048$. A weighting analysis confirmed the validity of the weighting scheme. A final difference-Fourier synthesis showed no peaks of chemical significance (all peaks <0.5 e Å^{-3}). Final atomic co-ordinates are listed in Table 4. Observed and calculated structure factors and anisotropic thermal parameters are in SUP 23042.

TABLE 4

Final atomic co-ordinates for $[\{Cu(LH)Br_2\}_2]$ * with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	0.048 0(1)	0.147 2(2)	0.465 7(1)
Br(1)	0.198 9(1)	0.180 5(1)	0.509 9(1)
Br(2)	0.012 9(1)	−0.079 4(1)	0.310 4(1)
S	−0.051 4(1)	0.323 3(2)	0.389 7(1)
C(1)	−0.155 5(5)	0.227 0(10)	0.351 4(9)
C(2)	−0.214 4(4)	0.280 1(8)	0.443 2(7)
N	−0.198 5(4)	0.238 6(8)	0.573 2(6)
C(3)	−0.244 0(6)	0.282 5(11)	0.667 5(9)
C(4)	−0.313 7(6)	0.369 6(10)	0.634 0(10)
C(5)	−0.334 7(6)	0.412 2(11)	0.498 4(10)
C(6)	−0.286 1(5)	0.363 3(9)	0.404 6(9)
C(7)	−0.036 0(5)	0.408 1(8)	0.226 1(8)
C(8)	0.056 1(6)	0.470 9(12)	0.258 8(9)
C(9)	−0.100 5(6)	0.533 9(11)	0.194 0(11)
C(10)	−0.041 7(6)	0.295 0(11)	0.113 2(9)
H(1a)	−0.172(6)	0.253(12)	0.279(10)
H(1b)	−0.138(6)	0.127(11)	0.373(9)
H(2)	−0.157(6)	0.180(11)	0.610(10)
H(3)	−0.235(6)	0.255(11)	0.754(11)
H(4)	−0.351(6)	0.381(10)	0.711(9)
H(5)	−0.381(6)	0.474(10)	0.470(9)
H(6)	−0.295(6)	0.384(10)	0.311(10)
H(8a)	0.070(6)	0.055(11)	0.326(10)
H(8b)	0.103(6)	0.376(10)	0.276(9)
H(8c)	0.072(5)	0.508(10)	0.174(10)
H(9a)	−0.166(6)	0.485(10)	0.178(8)
H(9b)	−0.087(6)	0.604(10)	0.271(10)
H(9c)	−0.100(6)	0.582(11)	0.122(10)
H(10a)	−0.018(6)	0.338(10)	0.030(10)
H(10b)	−0.001(6)	0.208(11)	0.141(10)
H(10c)	−0.098(6)	0.264(11)	0.094(9)

* Atoms in the other half of the centrosymmetric dimer are related by the transformation $(-x, -y, 1 - z)$.

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