# Copper Co-ordination to Thioether Ligands.[1] Spectroscopic Studies of Dimeric Copper(II) Complexes of 2-(3,3-Dimethyl-2-thiabutyl)pyridine and the Crystal Structure of Di-μ-bromo-bis{bromo[2-(3,3-dimethyl-2-thiabutyl)pyridine-*NS*]copper(II)}

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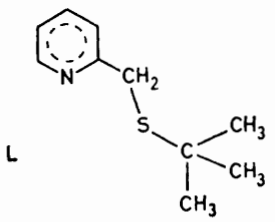
Dimeric complexes of the type $[(CuLX_2)_2]$ [X = Cl or Br, L = 2-(3,3-dimethyl-2-thiabutyl)pyridine] have been prepared and characterised by electronic, electron spin resonance, and far-i.r. spectroscopy. The structure of $[(CuLBr_2)_2]$ has been determined by single-crystal *X*-ray diffraction techniques, from diffractometer data. Crystals are Triclinic, space group $P\bar{1}$, with $a$ = 9.040(1), $b$ = 13.100(2), $c$ = 15.455(2) Å, $\alpha$ = 120.26(1), $\beta$ = 92.80(1), $\gamma$ = 111.31(1)°, and $Z$ = 2. After full-matrix least-squares refinement, the final $R$ value was 0.079 for 3 070 observed data. The complex consists of discrete, non-centrosymmetric, dibromo-bridged dimers. The co-ordination geometry of each copper(II) centre is distorted square pyramidal. A chelated ligand L [mean Cu–S = 2.352(6), Cu–N = 2.06(2) Å] and two bromide ions [mean Cu–Br = 2.372(3) and 2.415(3) Å] form the tetrahedrally distorted basal plane of each square pyramid, with a longer [mean 2.902(4) Å] apical Cu–Br bridging bond. The tetrahedral distortions are attributed to steric effects.

THE confirmation, by *X*-ray structural analyses, of the co-ordination of cysteine thiolate and methionine thioether sulphur to copper in the 'blue' copper proteins plastocyanin [2] and azurin [3] has further stimulated studies on low molecular weight copper–sulphur complexes. Such studies are complementary to work on the proteins themselves, since they offer the chance to explore the effects of many variations of ligands and co-ordination geometries, as well as giving bond length data which are much more precise than those generally available from crystallographic studies of proteins.

As part of our continuing interest in thioether complexes of copper,[1,4-6] we have investigated the interaction of the *SN*-chelating ligand 2-(3,3-dimethyl-2-thiabutyl)pyridine (L) with this metal. We anticipated




L

that the bulkiness of the t-butyl substituent on the thioether sulphur might lead to copper(II) co-ordination geometries distorted from the usual planar or tetragonal states [noting that in both plastocyanin and azurin the copper(II) atom has a distorted tetrahedral geometry].

The present work is therefore aimed at (i) investigating the behaviour and structures of copper complexes of the ligand L, both in solution and in the solid state, (ii) examining the effects of any geometrical distortions on the $Cu^{II}$–S and $Cu^{II}$–N bonds, and (iii) comparing complexes of $Cu^{I}$ and $Cu^{II}$ with the same ligand, L.

Crystallographic and spectroscopic properties of copper(I) of complexes L have already been reported;[1] here we present results on the corresponding copper(II) complexes, $[(CuLX_2)_2]$ (X = Cl or Br).

## RESULTS AND DISCUSSION

*Preparation and Characterisation.*—The complexes $[(CuLX_2)_2]$ (X = Cl or Br) were prepared as air-stable crystalline solids by the reaction of the ligand L with the appropriate copper halide in ethanol. Molecular weight measurements in chloroform and acetone indicate a dimeric structure in these solvents [X = Cl, $M_r$ 662 ($CHCl_3$), 662 (acetone), $M_r$ (calc.) 631; X = Br, $M_r$ 785 ($CHCl_3$), 799 (acetone), $M_r$ (calc.) 809]. These results are supported by the solid-state structure of the bromo-complex (see below).

The molar conductivities, which are given in the Experimental section, show the complexes to be essentially non-electrolytes in nitromethane, but in methanol the values ($\Lambda$ *ca.* 70 S cm$^2$ mol$^{-1}$ per monomer) are close to the range expected [7] for 1 : 1 electrolytes ($\Lambda$ 100—130 S cm$^2$ mol$^{-1}$). Spectroscopic evidence, presented below, confirms the extensive solvation in methanol, with the formation of the $[Cu(HOMe)_6]^{2+}$ ion.

*The Crystal Structure of Di-μ-bromo-bis{bromo[2-(3,3-dimethyl-2-thiabutyl)pyridine]copper(II)}, $[(CuLBr_2)_2]$.*—The title compound crystallises as discrete, non-centrosymmetric, dibromo-bridged dimers (Figure 1). Each copper(II) centre has a distorted square-pyramidal co-ordination geometry, with the severely distorted 'basal plane' consisting of the thioether sulphur and pyridyl nitrogen atoms of a chelated ligand L, and two bromide ions. The apex of each pyramid is formed by a long bond to one of the basal bromide ions of the other copper(II) centre. The t-butyl thioether substituents appear to block the approach of any potential sixth ligand towards each copper atom. Bond lengths and angles within the dimer are listed in Table 1, and details of planes through groups of atoms are in Table 2. There are no dimer–dimer approaches less than 3.5 Å.

The distortions in the two square pyramids are reflected in the bond angles and mean plane calculations.

The L–Cu–L angles involving basal ligands *trans* to one another range from 142.1 to 171.0°, while the angles L(basal)–Cu–L(apical) which are ideally 90° (or slightly greater where the metal lies above the basal plane) range from 82.6 to 103.4° for Cu(1) and 83.9 to 125.3° for Cu(1a). The four basal ligands are in each case far from coplanar. The atoms N(1), S(1), Br(1), and Br(2) are displaced by 0.3—0.4 Å above or below their mean

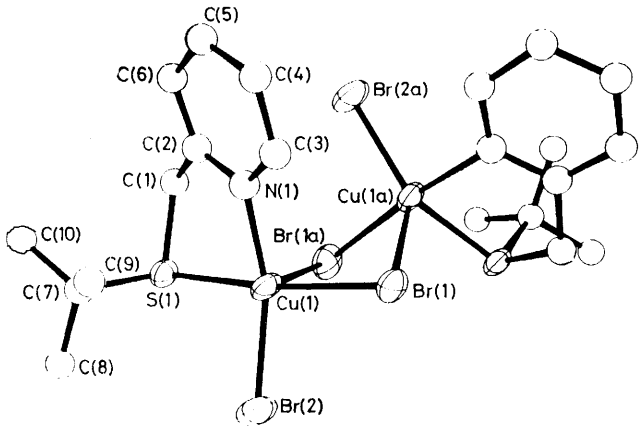



FIGURE 1 The structure of $[(CuLBr_2)_2]$, showing the numbering system used. Atom labels are shown for one half of the dimer only; atoms in the other half are labelled X(*n*a)

plane, and N(1a), S(1a), Br(1a), and Br(2a) by 0.4—0.5 Å. These distortions take the form of a twist in each basal plane towards a more tetrahedral geometry, the extent of this twist being seen in the dihedral angles * $\omega_1 = 28.9$ and $\omega_2 = 38.8°$ (*cf.* 0° for square-planar geometry and 90° for tetrahedral).

Spectroscopic data (see below) show that the distorted copper co-ordination geometry persists in solution. The reasons for it, as in many other tetrahedrally distorted copper(II) complexes, appear to be steric, arising from the need to minimise non-bonded contacts within each half of the dimer, at the same time stabilising the molecule by bringing both halves together. Thus the twisting of the Cu(1),N(1),S(1) and Cu(1),Br(1),Br(2) planes, in opposite senses, eases the contact between Br(1) and C(3), although the distance is still somewhat short at 3.30 Å (*cf.* normal van der Waals separation of *ca.* 3.7 Å). A similar effect is seen in the other half of the dimer, where the twist is such as to ease the contact between Br(2a) and C(3a). This contact, which would be *ca.* 3.0 Å if the basal atoms were coplanar, is increased to 3.26 Å by the tetrahedral distortion. At the same time, in each half of the dimer the twist has the effect of bringing the bridging bromine atom closer to the opposing copper atom.

The Cu–S bond lengths, 2.353(5) and 2.351(6) Å, are within the range (2.30—2.41 Å, mean *ca.* 2.34 Å) normally found for equatorial $Cu^{II}$–S(thioether) bonds.[5,8-14] Assuming the covalent radius of sulphur to be 1.04 Å [15] and the in-plane radius of $Cu^{II}$ about 1.30 Å,[16] these

* $\omega_1$ Is defined by the planes through Cu(1),S(1),N(1) and Cu(1),Br(1),Br(2) and $\omega_2$ by the planes through Cu(1a),S(1a),-N(1a) and Cu(1a),Br(1a),Br(2a).

TABLE 1

Selected bond lengths (Å) and angles (°) *

| | | | |
|---|---|---|---|
| Cu(1)–Br(1) | 2.412(3) | Cu(1a)–Br(1a) | 2.417(3) |
| Cu(1)–Br(2) | 2.356(3) | Cu(1a)–Br(2a) | 2.388(3) |
| Cu(1)–Br(1a) | 2.965(4) | Cu(1a)–Br(1) | 2.839(4) |
| Cu(1)–S(1) | 2.353(5) | Cu(1a)–S(1a) | 2.351(6) |
| Cu(1)–N(1) | 2.04(2) | Cu(1a)–N(1a) | 2.08(2) |
| S(1)–C(1) | 1.84(2) | S(1a)–C(1a) | 1.81(2) |
| S(1)–C(7) | 1.90(2) | S(1a)–C(7a) | 1.84(2) |
| N(1)–C(2) | 1.37(2) | N(1a)–C(2a) | 1.36(3) |
| C(1)–C(2) | 1.48(3) | C(1a)–C(2a) | 1.51(3) |
| Br(1)–Cu(1)–Br(2) | 93.9(1) | Br(1a)–Cu(1a)–Br(2a) | 92.7(1) |
| Br(1)–Cu(1)–S(1) | 166.5(2) | Br(1a)–Cu(1a)–S(1a) | 92.3(2) |
| Br(1)–Cu(1)–N(1) | 93.1(5) | Br(1a)–Cu(1a)–N(1a) | 171.0(5) |
| Br(1)–Cu(1)–Br(1a) | 84.8(1) | Br(1a)–Cu(1a)–Br(1) | 87.5(1) |
| Br(2)–Cu(1)–S(1) | 93.5(2) | Br(2a)–Cu(1a)–S(1a) | 142.1(2) |
| Br(2)–Cu(1)–N(1) | 153.9(5) | Br(2a)–Cu(1a)–N(1a) | 94.6(5) |
| Br(2)–Cu(1)–Br(1a) | 103.4(1) | Br(2a)–Cu(1a)–Br(1) | 125.3(1) |
| S(1)–Cu(1)–N(1) | 85.1(5) | S(1a)–Cu(1a)–N(1a) | 85.3(5) |
| S(1)–Cu(1)–Br(1a) | 82.6(2) | S(1a)–Cu(1a)–Br(1) | 92.4(2) |
| N(1)–Cu(1)–Br(1a) | 102.3(5) | N(1a)–Cu(1a)–Br(1) | 83.9(5) |
| Cu(1)–Br(1)–Cu(1a) | 85.9(1) | Cu(1)–Br(1a)–Cu(1a) | 83.0(1) |
| Cu(1)–S(1)–C(1) | 91.9(7) | Cu(1a)–S(1a)–C(1a) | 95.4(7) |
| Cu(1)–S(1)–C(7) | 109.7(7) | Cu(1a)–S(1a)–C(7a) | 106.9(7) |
| C(1)–S(1)–C(7) | 106.8(9) | Cu(1a)–S(1a)–C(7a) | 104(1) |
| Cu(1)–N(1)–C(2) | 117(1) | Cu(1a)–N(1a)–C(2a) | 117(1) |
| Cu(1)–N(1)–C(3) | 122(1) | Cu(1a)–N(1a)–C(3a) | 120(2) |
| C(2)–N(1)–C(3) | 120(2) | C(2a)–N(1a)–C(3a) | 122(2) |
| S(1)–C(1)–C(2) | 112(1) | S(1a)–C(1a)–C(2a) | 113(2) |
| C(1)–C(2)–N(1) | 117(2) | C(1a)–C(2a)–N(1a) | 119(2) |
| C(1)–C(2)–C(6) | 121(2) | C(1a)–C(2a)–C(6a) | 120(2) |
| N(1)–C(2)–C(6) | 122(2) | N(1a)–C(2a)–C(6a) | 120(2) |

* Bond lengths and angles are listed for the copper co-ordination sphere and for chelate ring atoms; other bond lengths and angles have been deposited. Standard deviations are in parentheses.

must represent essentially single bonds (calculated value 2.34 Å). Thus, as in a similarly distorted complex whose structure has been reported,[13] the tetrahedral distortions seen here do not affect the Cu–S bond lengths.

TABLE 2

Least-squares planes through groups of atoms *

Plane (i) Br(1), Br(2), N(1), S(1)

$-0.3836X - 0.7707Y - 0.5089Z + 8.4320 = 0$

[Br(1) −0.35, Br(2) 0.32, N(1) 0.42, S(1) −0.39, Cu(1) −0.11, Br(1a) −3.07]

Plane (ii) Br(1a), Br(2a), N(2), S(2)

$-0.1179X - 0.8940Y - 0.4323Z + 10.8696 = 0$

[Br(1a) 0.40, Br(2a) −0.43, N(2) 0.50, S(2) −0.48, Cu(1a) 0.31, Br(1) 3.02]

Plane (iii) Cu(1), Br(1), Br(2)

$-0.5632X - 0.6917Y - 0.4521Z + 8.3277 = 0$

[N(1) 0.87, S(1) −0.46, Br(1a) −2.88]

Plane (iv) Cu(1), N(1), S(1)

$-0.0930X - 0.8299Y - 0.5501Z + 8.2009 = 0$

[Br(1) −0.56, Br(2) 1.03, Br(1a) −2.86]

Plane (v) Cu(1a), Br(1a), Br(2a)

$-0.2934X - 0.7205Y - 0.6283Z + 11.9320 = 0$

[N(1a) 0.19, S(1a) −1.43, Br(1) 2.32]

Plane (vi) Cu(1a), N(1a), S(1a)

$0.1568X - 0.9658Y - 0.2066Z + 8.0053 = 0$

[Br(1a) 0.36, Br(2a) −1.47, Br(1) 2.82]

Dihedral angles (°) between planes: (iii)—(iv) 28.9, (v)—(vi) 38.8.

* Distances of atoms from the planes (Å) are given in square brackets. $X,Y,Z$, are orthogonalised co-ordinates related to the fractional co-ordinates $x/a$, $y/b$, $z/c$ as follows: $X = 9.040(x/a) - 4.760(y/b) - 0.756(z/c)$; $Y = 12.204(y/b) - 8.654(z/c)$; $Z = 12.783(z/c)$.

The Cu–N bonds, 2.04(2) and 2.08(2) Å, appear slightly longer than in other copper(II) complexes of substituted pyridyl ligands [14,17-20] (2.00—2.06, mean *ca.* 2.02 Å), but the difference is barely statistically significant.

Some variation can be seen in the equatorial Cu–Br bond lengths; the terminal Cu–Br bonds, 2.356(3) and 2.388(3) Å, are shorter than those to the bridging bromine atoms, 2.412(3) and 2.417(3) Å. A similar effect, and similar bond lengths, are found in other copper(II) dibromo-bridged dimers, such as bis[dibromo(*NN*-dimethylethylenediamine)copper(II)].[21] In the latter complex the terminal Cu–Br bond is 2.401(1) Å and the bond to the bridging bromine, 2.463(2) Å. Similarly, the axial Cu–Br bridging bonds, 2.965(4) and 2.839(4) Å, the angles subtended at the bridging bromide ions, 85.9(1) and 83.0(1)°, and the Cu···Cu separation [3.591(4) Å] are all normal for this type of tetragonal pyramidal dimer. Other distances and angles in the ligands are as expected, although the constraints of the five-membered chelate ring result in rather small internal angles at the sulphur atoms [Cu–S–C(1) = 91.9(7) and 95.4(7)°].

Comparison of this complex with the analogous copper(I) complex, $[CuL_2Br]$,[1] shows that the Cu–S and Cu–N bond lengths are closely similar in the two structures. Thus the Cu–S bonds average 2.352(6) Å for the $Cu^{II}$ case, and 2.333(3) Å for $Cu^{I}$, while the Cu–N bonds have mean values of 2.06(2) Å for $Cu^{II}$ and 2.11(1) Å for $Cu^{I}$. Similar observations have been made for other $Cu^{I}/Cu^{II}$ pairs of complexes,[5,14] and it is clear that neither changes of oxidation state nor geometrical distortions *require* changes in copper–ligand bond lengths, for ligands of these types.

*Spectroscopic Studies.*—Spectroscopic data for the complexes $[(CuLX_2)_2]$ (X = Cl or Br) are generally consistent with the crystal structure. In the far-i.r., bands at 296 and 282 $cm^{-1}$ (X = Cl) and 244 and 227 $cm^{-1}$ (X = Br) can be assigned to essentially Cu–X stretching frequencies for equatorial bonds. The ν(Cu–Br) : ν(Cu–Cl) ratio is 0.81 : 1, which is in the expected range (0.74—0.84).[22] Similar assignments have been made for $[\{Cu(2Me\text{-}py)_2X_2\}_2]$ [23] (2Me-py = 2-methylpyridine) and $[\{Cu(Me_2NCH_2CH_2NH_2)X_2\}_2]$,[24] which also have halogen-bridged dimeric structures.[21,25]

Electronic spectra (see Table 3) suggest the structure seen in the solid state persists in solution, in solvents of low donor capacity. For example, the solid-state reflectance spectra are similar to spectra of solutions in $CH_2Cl_2$. The low-energy ligand-field band, centred at 850 nm, is characteristic of the distorted tetragonal pyramidal geometry found for $[(CuLBr_2)_2]$ in the solid state. A similar low-energy (800 nm) ligand-field band [26] is exhibited by the complex $[\{Cu(BuSCH_2CH_2SBu)Cl_2\}_2]$, which also has a tetrahedrally distorted pyramidal dimeric structure.[13] Other dimeric complexes with more regular tetragonal–pyramidal geometries around the copper atom, *e.g.* $[\{Cu(2Me\text{-}py)_2X_2\}_2]$ [25] and $[\{Cu(Me_2NCH_2CH_2NH_2)X_2\}_2]$,[21] show the bands at higher energies.[24,27] Tentative assignments for ligand-to-metal charge-transfer (l.m.c.t.) absorptions are consistent with previous work on related complexes.[4,26]

TABLE 3

Electronic spectral data for the complexes

| Complex | Absorption maxima [a]/nm: Solid | $CH_2Cl_2$ | MeOH | Glycerol–MeOH (20 : 80) [b] | Assignment |
|---|---|---|---|---|---|
| $[(CuLCl_2)_2]$ | | 292 (5 450) | | | Cl(apical)→Cu |
| | 372 | 367 (3 000) | 357 (1 180) | 367 (1 300) | Cl→Cu |
| | 433 | 447 (1 130) | | | σ(S)→Cu |
| | 850 [c] | 820 (310) [c] | 850 (145) [c] | 762 (335) | *d–d* |
| | | | | 1 025 (355) | *d–d* |
| $[(CuLBr_2)_2]$ | | 320 (sh) (3 830) | 309 (2 060) | | Br(apical)→Cu |
| | 370 (sh) | 352 (5 100) | 358 (1 280) | 369 | Br→Cu |
| | 420 | 415 (sh) (2 560) | | 390 (sh) | σ(S)→Cu + Br→Cu |
| | 560 | 582 (630) | | | Br→Cu |
| | 840 [c] | 870 (390) [c] | 850 (265) [c] | 785 | *d–d* |
| | | | | 1 010 | *d–d* |

Absorption coefficients (ε/$dm^3$ $mol^{-1}$ $cm^{-1}$) are given in parentheses. [b] At 90 K. [c] Asymmetric maximum tailing into near-i.r.

TABLE 4

E.s.r. data for the complexes [a]

| Complex | Solvent | $g_{\|}$ | $10^4A_{\|}$/$cm^{-1}$ | $g_{\perp}$ |
|---|---|---|---|---|
| $[(CuLCl_2)_2]$ | *b* | 2.227 | 135 | 2 065 |
| | *c* | 2.279 | 144 | |
| | | 2.430 [d] | 126 | |
| | *e* | 2.270 | 143 | |
| | | 2.425 [d] | 122 | |
| $[(CuLBr_2)_2]$ | *b* | 2.108 [f] | | |
| | *c* | 2.161 | 151 | |
| | | 2.430 [d] | 126 | |
| | *e* | 2.288 | 150 | |
| | | 2.425 [d] | 122 | |

[a] At 77 K. [b] Nitromethane solution. [c] In MeOH. [d] Assigned to $[Cu(HOMe)_6]^{2+}$ ion. [e] In glycerol–MeOH (20 : 80). [f] Isotropic value.

E.s.r. data for the complexes $[(CuLX_2)_2]$ in frozen solution (Table 4) also highlight the relationship between solid-state and solution behaviour. In nitromethane, the e.s.r. parameters for the chloro-complex fit the criteria recently suggested by Bencini *et al.*[28] for distorted square-pyramidal geometries, namely that the low-field region approximates tetragonal $Cu^{II}$ spectra, but $A_{\|}$ is lower than the normal value of 150 × $10^{-4}$ —

$200 \times 10^{-4}$ cm$^{-1}$, while the high-field region is more spread out.

In methanol, however, solvolysis and dissociation of the $[(CuLX_2)_2]$ complexes apparently occurs. This is shown by the conductivity results and by the disappearance of the σ(S)→Cu and X→Cu l.m.c.t. bands in the 400—600 nm region of the electronic spectrum. The e.s.r. spectra, however, allow the identification of the $[Cu(HOMe)_6]^{2+}$ ion. The e.s.r. spectra of $[(CuLX_2)_2]$ complexes in frozen methanol show at least two species to be present (Table 4 and Figure 2), one of which has

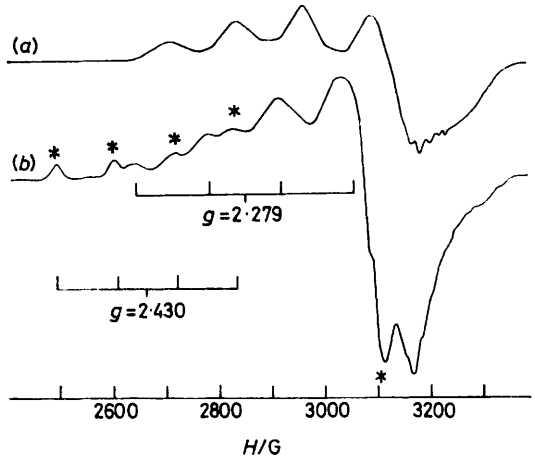



FIGURE 2 Frozen-solution (77 K) e.s.r. spectra for $[(CuLCl_2)_2]$: (*a*) in nitromethane, (*b*) in methanol. Peaks marked (*) are assigned to the ion $[Cu(HOMe)_6]^{2+}$

parameters identical to those observed for a dilute solution of copper(II) chloride in methanol. Moreover, dilution of the sample causes an enhancement of the $[Cu(HOMe)_6]^{2+}$ e.s.r. signal relative to the other peaks. The spectrum of the other species is similar but not identical to that obtained for $[CuL_2X][BF_4]$ in the same solvent,[29] suggesting the presence of a five-co-ordinate species. Support for this conclusion comes from the low-temperature electronic spectra recorded in glycerol–methanol (20 : 80) (Table 3). In the ligand-field region of the spectrum two well resolved bands which closely resemble those of $[CuL_2X][BF_4]$ [29] are observed.

*Conclusions.*—In the complexes examined here {$[(CuLBr_2)_2]$ and, by analogy, $[(CuLCl_2)_2]$}, the tetrahedral distortions in the copper equatorial ' plane ' arise from steric interactions involving the *ortho*-carbon atom of the pyridyl ring, C(3). The t-butyl substituent on the thioether sulphur atom does not make any obvious contribution to the distortions, although it may restrict the copper co-ordination number to five, by blocking the approach of any sixth ligand. Further tetrahedral distortions should be achieved by substitution at the *ortho*-carbon, C(3), while retaining the t-butyl groups. As far as copper–thioether interactions are concerned it is clear from these and other thioether complexes of copper(I) and copper(II) [1,5,6,8-14] that such interactions are remarkably flexible. Bond lengths vary widely (2.28—2.61 Å) as do the angles at the sulphur atoms (92—120°), and sulphur ligands may be monodentate or bridging. Geometrical and oxidation-state changes are thus easily accommodated, features which make methionine thioether sulphur an ideal inner co-ordination sphere ligand in biological systems such as copper proteins, where varying active-site geometries and ' site-structure rigidity ' [30] may be encountered.

## EXPERIMENTAL

Electronic spectra were recorded on a Shimadzu MPS-5000 spectrophotometer. Standard Shimadzu acrylic cuvettes (2 mm) were used to obtain spectra at *ca.* 90 K (liquid air temperature). Electron spin resonance spectra were measured at 77 K on a Varian E 104A instrument, spectral *g* values being calibrated with a diphenylpicrylhydrazyl standard. Infrared spectra were obtained on a Beckman IR 20 spectrophotometer (250—4 000 cm$^{-1}$) and a Grubb-Parsons Cube Mark II Interferometer (40—400 cm$^{-1}$). Conductivities (at *ca.* $10^{-3}$ mol dm$^{-3}$) were measured at room temperature with a Philips PR9500 conductivity meter and PW9510 cell. Molecular weights were determined using a Hitachi–Perkin-Elmer 115 molecular weight osmometer. Microanalyses were by Professor A. D. Campbell, University of Otago. All solvents were purified according to established procedures. The synthesis of the ligand 2-(3,3-dimethyl-2-thiabutyl)pyridine has been described previously.[1]

*Preparation of the Complexes.*—$[(CuLCl_2)_2]$. To copper(II) chloride dihydrate (0.340 g, 2 mmol) dissolved in ethanol was added the ligand (L) (0.363 g, 2 mmol) dissolved in the same solvent. Concentration of the solution, using a rotary evaporator, yielded dark green crystals which were filtered off, washed with ethanol, and dried *in vacuo*, m.p. 128—130 °C. Yield, 0.418 g (66%) (Found: C, 38.2; H, 4.8; N, 4.15. $C_{10}H_{15}Cl_2CuNS$ requires C, 38.0; H, 4.8; N, 4.4%). Λ (per monomer) 67 (in methanol), 4 S cm$^2$ mol$^{-1}$ (in nitromethane).

$[(CuLBr_2)_2]$. Following the above method, but using copper(II) bromide in excess and keeping solvent volumes to a minimum, afforded the product as black crystals, m.p. 108—110 °C. Yield, similar to above (Found: C, 29.8; H, 3.85; Br, 39.3; N, 3.4. $C_{10}H_{15}Br_2CuNS$ requires C, 29.7; H, 3.7; Br, 39.5; N, 3.5%). Λ (per monomer) 74 (in methanol), 10 S cm$^2$ mol$^{-1}$ (in nitromethane).

*Crystallography.*—Preliminary unit-cell dimensions were determined from oscillation, Weissenberg, and precession photographs, and more accurate cell dimensions from the least-squares analysis [31] of the positions of 12 general reflections on a four-circle *X*-ray diffractometer.

*Crystal data.* $C_{20}H_{30}Br_4Cu_2N_2S_2$, $M = 809.3$, Triclinic, $a = 9.040(1)$, $b = 13.100(2)$, $c = 15.455(2)$ Å, $\alpha = 120.26(1)$, $\beta = 92.80(1)$, $\gamma = 111.31(1)°$, $U = 1\,411$ Å$^3$, $F(000) = 786$, $D_m = 1.90$ g cm$^{-3}$ (by flotation), $Z = 2$, $D_c = 1.905$ g cm$^{-3}$, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 77.2 cm$^{-1}$, space group $P\bar{1}$.

*Data collection and reduction.* Data were collected on a computer-controlled Hilger and Watts four-circle diffractometer, from a crystal with dimensions *ca.* 0.03 × 0.01 × 0.02 cm, mounted about its *a* axis. The orientation of the crystal was defined by a least-squares treatment [31] of the positions of 12 general reflections. A θ—2θ scan, consisting of 30 steps of 0.02° through each reflection, with a count of 1.5 s at each step and a background count of 9 s at the beginning and end of each scan, was used. Standard

reflections, monitored after every 100 measurements, showed no systematic intensity changes. Reflections $hkl$, $\bar{h}kl$, $\bar{h}\bar{k}l$, and $h\bar{k}l$ were measured, up to $\theta = 26°$. Equivalent reflections were merged to give 3 070 reflections for which $I_{hkl} > 2\sigma(I_{hkl})$. Lorentz and polarisation corrections were applied to the data, but no absorption corrections were made.

*Structure determination.* The positions of two copper and four bromine atoms, consistent with a dimeric structure, were deduced from a Patterson vector map. An electron–density map, calculated in space group $P1$, then revealed the positions of the copper and bromine atoms of the other dimer in the unit cell. These were clearly centrically related to the first, and all further calculations were done assuming space group $P\bar{1}$. The remainder of the structure was determined from a further electron–density map, and refined by full-matrix least-squares refinement.[32] The quantity minimised was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/[\sigma(F_o)^2]^2$. Three cycles of refinement with isotropic temperature factors reduced $R$ to 0.174, and four further cycles, in which anisotropic thermal parameters were given to copper, bromine, and sulphur atoms, saw the refinement converge with $R = 0.079$. A weighting analysis confirmed the validity of the weighting scheme. Final atomic co-ordinates are listed in Table 5. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 23108 (18 pp.).*

TABLE 5

Fractional atomic co-ordinates with estimated standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| Cu(1) | 0.820 2(3) | 0.789 8(3) | 0.629 1(2) |
| Br(1) | 0.766 1(3) | 0.856 0(2) | 0.796 0(2) |
| Br(2) | 0.955 6(4) | 0.671 3(3) | 0.639 7(2) |
| S(1) | 0.904 4(6) | 0.779 2(6) | 0.484 3(4) |
| N(1) | 0.625(2) | 0.805(2) | 0.574(1) |
| C(1) | 0.803(2) | 0.877(2) | 0.482(2) |
| C(2) | 0.640(3) | 0.839(2) | 0.503(2) |
| C(3) | 0.482(3) | 0.775(2) | 0.599(2) |
| C(4) | 0.348(3) | 0.781(3) | 0.556(2) |
| C(5) | 0.364(3) | 0.817(3) | 0.483(2) |
| C(6) | 0.508(3) | 0.841(2) | 0.453(2) |
| C(7) | 0.783(3) | 0.605(2) | 0.363(2) |
| C(8) | 0.906(3) | 0.546(3) | 0.349(2) |
| C(9) | 0.617(3) | 0.527(2) | 0.376(2) |
| C(10) | 0.748(3) | 0.615(2) | 0.269(2) |
| Cu(1a) | 0.892 9(3) | 1.114 4(3) | 0.838 8(2) |
| Br(1a) | 1.088 2(3) | 1.064 8(2) | 0.743 3(2) |
| Br(2a) | 0.792 3(3) | 1.172 8(3) | 0.732 9(2) |
| S(1a) | 1.079 4(7) | 1.207 1(6) | 0.999 1(4) |
| N(1a) | 0.720(2) | 1.132(2) | 0.922(1) |
| C(1a) | 0.921(3) | 1.163(2) | 1.058(2) |
| C(2a) | 0.763(3) | 1.162(2) | 1.021(2) |
| C(3a) | 0.577(3) | 1.117(2) | 0.881(2) |
| C(4a) | 0.462(3) | 1.137(2) | 0.941(2) |
| C(5a) | 0.507(3) | 1.170(2) | 1.044(2) |
| C(6a) | 0.656(3) | 1.181(2) | 1.083(2) |
| C(7a) | 1.165(3) | 1.388(2) | 1.069(2) |
| C(8a) | 1.272(4) | 1.452(3) | 1.184(2) |
| C(9a) | 1.284(4) | 1.425(3) | 1.008(2) |
| C(10a) | 1.034(3) | 1.438(3) | 1.079(2) |

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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