Sulphur Ligand–Metal Complexes. Part 16.[1] Copper Complexes of Thioethers and the Single-crystal *X*-Ray Structure of the Polymeric Mixed-valence Complex, Penta-μ-chloro-tris-μ-tetrahydrothiophene-tetracopper(I,II)†

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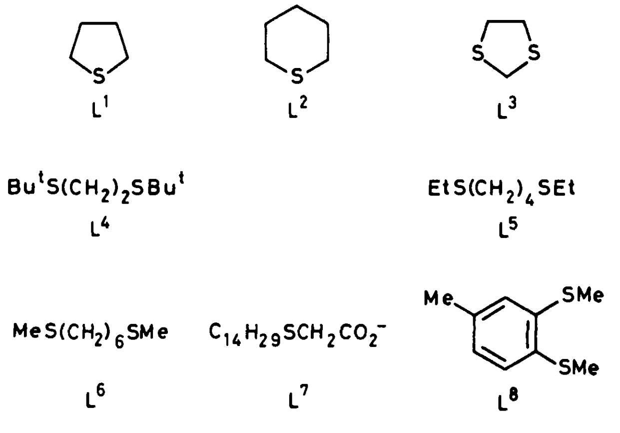
The interaction of the cyclic, thioether ligand, L^1 (tetrahydrothiophene), with $CuCl_2{\cdot}2H_2O$ in acetone yields the polymeric, mixed-valence complex $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$, the crystal and molecular structure of which has been determined by *X*-ray diffraction techniques. Crystals of the complex are monoclinic, space group $P2_1/n$, with a = 12.2288(6), b = 13.0277(7), c =14.0605(7) Å, β = 95.815(4)°, and Z = 4. The structure was solved by direct methods and Fourier-difference techniques, and refined by block-diagonal least squares to R = 0.029 for 2 770 observed intensities. The structure is polymeric with μ-Cl or μ-L^1 linkages between Cu atoms giving rise to three different ring systems, *viz*. $[Cu(\mu\text{-}Cl)]_2$ and $[Cu(\mu\text{-}L^1)]_3$ fused to $[Cu(\mu\text{-}L^1)\{Cu(\mu\text{-}Cl)\}_2]$. The copper atoms designated as Cu^{II} are bound to four chlorine atoms to give a geometry intermediate between tetrahedral and square planar, and those designated as Cu^I have distorted tetrahedral S_2Cl_2 donor sets. This complex, if left in its mother-liquor, forms the oxidised thioether ligand complex $[\{Cu(L^1O)Cl_2\}_n]$ (L^1O = tetrahydrothiophene 1-oxide). Other cyclic thioethers, L^2 (thiacyclohexane) and L^3 (1,3-dithiacyclopentane), form either copper(I) or copper(II) complexes: [CuLX] (L = L^1 or L^3, X = Cl or Br; L = L^2, X = Cl), $[(CuCl)_3L^1{}_2]$, $[CuL^3{}_2]ClO_4{\cdot}2H_2O$, and $[CuL^3Cl_2]$. The bidentate thioethers L^4 (2,2,7,7-tetramethyl-3,6-dithiaoctane), L^5 (3,8-dithiadecane), L^6 (2,9-dithiadecane), and L^8 [3,4-di(methylthio)toluene] yield the complexes: [CuLX] (L = L^4, X = Cl or Br), $[(CuX)_2L]$ (L = L^4 or L^5; X = Cl, Br, or I), $[CuL_2]BF_4$ (L = L^4 or L^5), $[(CuCl_2)_2L^4]$, $[CuL^4(NO_3)_2]{\cdot}H_2O$, $[(CuX)_3L^6{}_2]$ (X = Cl, Br oı I), and $[CuL^8Cl_2]$. The ligand L^7 (tetradecylthioacetate ion) forms the copper(II) complex $[CuL^7{}_2]{\cdot}2H_2O$. These complexes have been characterised by a variety of spectroscopic techniques and, where possible, structures are proposed.

The presence of Cu–S thioether bonding in the blue copper proteins plastocyanin[2] and azurin[3,4] has resulted in many attempts to prepare small molecule analogues of the active copper site.[5–9] This type of research has been at the expense of a systematic study of the reactions between copper and thioethers. Previously[10] we reported a study of the interaction of copper with the bidentate thioethers 2,5-dithiahexane and 3,6-dithiaoctane. In this paper we extend these studies to include the uni- and bi-dentate thioethers L^1—L^8 and discuss the nature of the copper complexes formed.

Sigel *et al.*[11] have reported that for tetrahydrothiophene (L^1) log $K_{CuL^1}^{Cu^{2+}}$ is 0.02 in 50% aqueous ethanol, indicating weak co-ordination of the unidentate thioether ligand to copper(II). This ligand has been used to develop a new method for removing sulphur compounds from hydrocarbon oils by extraction with an excess of $CuBr_2$ in aqueous solution, but the nature of the complexes so formed was not certain.[12] We find that L^1 does react with copper(II) chloride to give $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$, which represents a new structural type for a mixed-valence copper complex. Its reactivity towards oxygen, to produce a tetrahydrothiophene 1-oxide (L^1O) complex, is also discussed.



The other cyclic thioethers, thiacyclohexane (L^2) and 1,3-dithiacyclopentane (L^3), have been studied for comparison with L^1 and the bidentates. We have also extended our earlier studies[10] to dithioethers with longer chains, *i.e.* 3,8-dithiadecane (L^5) and 2,9-dithiadecane (L^6), and the more sterically bulky 2,2,7,7-tetramethyl-3,6-dithiaoctane (L^4). Other variations include the incorporation of double-bond character in the backbone chain, as in 3,4-di(methylthio)toluene (L^8), and the replacement of one thioether group by carboxylate, as in the tetradecylthioacetate ion (L^7). For the bidentate O,S ligands, such as tetrahydrothiophene-2-carboxylate and ethylthio-

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† *Supplementary data available* (No. SUP 56070, 6 pp.): H-atom co-ordinates, thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical data and melting points for the complexes

	Analyses (%)[a]			
Complex	C	H	X[b]	M.p. (θ_c/°C)
$[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$	20.75(20.7)	3.6 (3.5)	25.6 (25.5)[c]	120
$[CuL^1Cl]$	26.0 (25.7)	5.0 (4.3)	20.1 (19.0)	124[d]
$[CuL^1Br]$	20.2 (20.7)	4.2 (3.6)	31.7 (34.5)	84[d]
$[(CuCl)_3L^1{}_2]$	20.2 (20.3)	3.6 (3.4)	23.0 (22.5)	75[d]
$[CuL^2Cl]$	29.7 (29.85)	5.0 (5.0)	17.9 (17.6)	144—150
$[CuL^3Cl_2]$	15.0 (15.0)	2.7 (2.5)	29.6 (29.5)	134—136
$[CuL^3Cl]$	17.5 (17.6)	2.9 (2.9)	17.7 (17.3)	
$[CuL^3Br]$	14.8 (14.4)	2.7 (2.4)	34.1 (32.0)	
$[CuL^3{}_2]ClO_4{\cdot}2H_2O$[e]	17.6 (17.5)	3.8 (3.6)		
$[(CuCl_2)_2L^4]$	25.15(25.3)	4.8 (4.7)	30.35(29.8)	115—120[d]
$[CuL^4(NO_3)_2]{\cdot}H_2O$	29.9 (30.2)	6.0 (6.1)		108—110
$[(CuCl)_2L^4]$	30.0 (29.7)	5.45(5.5)	17.9 (17.6)	205—209
$[CuL^4Cl]$	39.3 (39.4)	7.3 (7.2)	11.6 (11.6)	>200[d]
$[(CuBr)_2L^4]$	25.0 (24.3)	4.7 (4.5)	32.6 (32.4)	180[d]
$[CuL^4Br]$	34.4 (34.3)	6.35(6.3)		110[d]
$[CuL^4{}_2]BF_4$	42.7 (42.7)	7.65(7.9)	23.1 (22.8)[f]	
$[(CuI)_2L^4]$	22.0 (20.5)	4.2 (3.8)	44.9 (43.2)	177[d]
$[(CuCl)_2L^5]$	26.3 (25.5)	5.1 (4.8)	18.7 (18.8)	130—132
$[(CuBr)_2L^5]$	21.4 (20.7)	4.0 (3.9)	31.4 (34.4)	130—133
$[(CuI)_2L^5]$	18.7 (17.2)	3.5 (3.2)	44.9 (45.4)	154—160
$[CuL^5{}_2]BF_4$	36.9 (37.9)	6.9 (7.2)		82—92
$[(CuCl)_3L^6{}_2]$	30.5 (29.4)	5.2 (5.5)	15.95(16.3)	94—95
$[(CuBr)_3L^6{}_2]$	24.7 (24.4)	4.85(4.6)	30.1 (30.5)	101—102
$[(CuI)_3L^6{}_2]$	21.1 (20.7)	4.2 (3.9)	39.9 (41.0)	126—128
$[CuL^7{}_2]{\cdot}2H_2O$	56.6 (57.0)	9.7 (9.9)		
$[CuL^8Cl_2]$	34.1 (33.9)	3.6 (3.8)	22.6 (22.2)	180—182

[a] Calculated values given in parentheses. [b] Halogen figures unless otherwise stated. [c] Cu 36.4, (36.5) %. [d] Decomposed. [e] A dehydrated form was also observed. [f] S analysis.

acetate, log $K_{CuL}{}^{Cu^{2+}}$ values are 4.31 and 3.92 respectively,[13] the oxygen atom causing an increased stability as compared to the unidentate, L^1. Thus it would be expected that L^7 should have a similar stability constant which would allow the isolation of a copper(II) complex.

Experimental

Electronic spectra were recorded on a Shimadzu MPS-5000 spectrophotometer. Infrared spectra were obtained on a Unicam SP3-300 spectrophotometer and a Grubb-Parsons Cube Mark II interferometer (40—400 cm^{-1}). Proton n.m.r. spectra were recorded on a JEOL JNM-C-60 HL spectrometer. Electron spin resonance spectra were measured at 77 K on a Varian E-104A instrument, spectral g values being calibrated with a diphenylpicrylhydrazyl (dpph) standard. Conductivities were measured at room temperature with a Philips PR 9500 conductivity meter and PW 9510 cell. Magnetic moments were measured by the Faraday method. Microanalyses were by Professor A. D. Campbell, University of Otago. Analytical data are summarised in Table 1.

The thioethers L^1 and L^2 were obtained from the Aldrich Chemical Co., while L^4, L^5, and L^6 were purchased from K and K Laboratories and L^7 from Evans Chemetics. The ligands L^3 and L^8 were synthesised following published methods.[14,15]

Preparation of the Copper Complexes.—$[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$. To a filtered solution of copper(II) chloride dihydrate (3.39 g, 0.02 mol) dissolved in acetone (200 cm^3) was added dropwise the ligand L^1 (1 cm^3, 0.02 mol). After about 50 min black-green crystals of the product were filtered off and washed with acetone. The yield was 13—17%. A similar reaction with L^2 resulted only in the isolation of $[CuL^2Cl]$.

Oxidation of $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$ *to* $[\{Cu(L^1O)Cl_2\}_n]$. If the black-green product obtained above was not collected as outlined but left to stand in the acetone solution for 20 h, an orange product was obtained which was filtered off and washed with acetone (Found: C, 20.5; H, 3.5; Cl, 29.7. Calc. for $C_4H_8Cl_2CuOS$: C, 20.15; H, 3.4; Cl, 29.7%). This compound was first prepared by Meek *et al.*[16]

Reaction of dimethyl, diethyl, or benzyl methyl sulphide with $CuCl_2{\cdot}2H_2O$. The compound $CuCl_2{\cdot}2H_2O$ (2 mmol) and the appropriate sulphide (2 mmol) were dissolved in acetone (15 cm^3) and left to stand for 1—2 d. The orange products which formed were washed with acetone and diethyl ether. Yields 13—20%. As for $[\{Cu(L^1O)Cl_2\}_n]$, all the compounds showed a new i.r. band in the 940—920 cm^{-1} range, assignable to $\nu(S=O)$, and hence are formulated as $[Cu(LO)Cl_2]$ (LO = the mono-oxidised sulphide ligand) although none was obtained analytically pure (*e.g.* Found: C, 21.1; H, 4.6; Cl, 28.4. $C_4H_{10}Cl_2CuOS$ requires C, 20.0; H, 4.2; Cl, 29.5%).

$[CuL^1X]$ (X = Cl *or* Br). To $CuCl_2{\cdot}2H_2O$ or $CuBr_2$ (0.50 mmol) dissolved in methanol (15 cm^3) was added the ligand L^1 (0.50 mmol) dropwise. After 1 week for X = Cl and 24 h for X = Br, white crystals were isolated, washed with methanol and then diethyl ether, and dried *in vacuo*. Yields *ca.* 60%.

$[(CuCl)_3L^1{}_2]$. To $CuCl_2{\cdot}2H_2O$ (340 mg, 2 mmol) dissolved in methanol (30 cm^3) was added L^1 (350 mg, 4 mmol) dropwise. The reducing agent H_3PO_2 (five drops) was added and the resulting colourless crystals were washed with methanol and diethyl ether and dried under vacuum. Yield 73%.

$[CuL^3Cl_2]$, $[(CuCl_2)_2L^4]$, *and* $[CuL^8Cl_2]$. The ligand L^3 (2 mmol), L^4 (1 mmol), or L^8 (2 mmol) was added dropwise to $CuCl_2{\cdot}2H_2O$ (2 mmol) dissolved in acetone (15—20 cm^3). The resulting brown (L^3 and L^8) or dark green (L^4) precipitates were filtered off and washed with acetone and diethyl ether. Yields were about 25%.

Table 2. Final atomic co-ordinates for $[\{Cu^{I}_3Cu^{II}L^1_3Cl_5\}_n]$ with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu(1)	0.503 00(4)	0.207 14(5)	0.770 64(4)	C(11)	0.656 9(4)	−0.005 1(4)	0.977 9(4)
Cu(2)	0.732 32(5)	0.413 58(5)	1.183 45(5)	C(12)	0.712 3(6)	−0.068 8(6)	0.910 7(6)
Cu(3)	0.813 37(5)	0.127 68(5)	1.165 83(5)	C(13)	0.826 2(6)	−0.046 4(6)	0.914 7(7)
Cu(4)	0.674 14(5)	0.255 46(5)	0.948 55(4)	C(14)	0.853 2(4)	0.061 5(5)	0.937 9(4)
S(1)	0.746 47(9)	0.105 52(9)	1.009 03(8)	C(21)	0.640 5(4)	0.509 2(4)	0.957 9(4)
S(2)	0.725 52(9)	0.407 97(9)	1.018 60(8)	C(22)	0.711 1(6)	0.565 7(7)	0.896 0(6)
S(3)	0.695 51(9)	0.242 90(9)	1.224 60(8)	C(23)	0.817 9(6)	0.529 0(7)	0.898 9(6)
Cl(1)	0.479 91(9)	0.240 42(10)	0.925 30(8)	C(24)	0.850 6(4)	0.452 9(4)	0.971 7(4)
Cl(2)	0.407 15(11)	0.056 75(10)	0.762 52(10)	C(31)	0.548 9(4)	0.219 4(4)	1.191 0(4)
Cl(3)	0.460 60(9)	0.253 22(10)	0.619 17(8)	C(32)	0.496 2(5)	0.222 5(7)	1.283 2(5)
Cl(4)	0.682 35(10)	0.255 49(11)	0.780 70(8)	C(33)	0.568 3(6)	0.227 5(9)	1.362 8(5)
Cl(5)	0.903 25(10)	0.012 93(10)	1.263 06(10)	C(34)	0.685 1(5)	0.232 8(5)	1.351 9(4)

$[CuL^3X]$ (X = Cl or Br). To $CuCl_2{\cdot}2H_2O$ or $CuBr_2$ (2 mmol) in methanol (20 cm^3) was added the ligand L^3 (2 mmol). A few drops of H_3PO_2 were added to effect the reduction. The white precipitate was collected and washed with ethanol and diethyl ether.

$[CuL^3_2]ClO_4{\cdot}2H_2O$. To $Cu(ClO_4)_2{\cdot}6H_2O$ (1 mmol) dissolved in acetone (15 cm^3) was added the ligand L^3 (4 mmol). After 3 d white crystals were collected and washed with acetone and diethyl ether.

$[CuL^4(NO_3)_2]{\cdot}H_2O$. To $Cu(NO_3)_2{\cdot}3H_2O$ (480 mg, 2 mmol), which had been crushed to a fine powder, was added excess of L^4. After standing overnight, the resulting green crystals were washed with diethyl ether. Yield 35%.

$[(CuX)_2L^4]$ (X = Cl, Br, *or* I). These were prepared by similar methods of which the following is typical. To $CuCl_2{\cdot}2H_2O$ (340 mg, 2 mmol) dissolved in methanol (30 cm^3) was added dropwise the ligand L^4 (412 mg, 2 mmol). The solution was reduced with about ten drops of H_3PO_2 and after 1 h the resulting white crystals were filtered off, washed with methanol and diethyl ether, and dried under vacuum. For X = I, excess of $LiI{\cdot}H_2O$, dissolved in acetone, was added to the $CuCl_2{\cdot}2H_2O + L^4 +$ methanol solution. Yields *ca.* 60%.

$[CuL^4X]$ (X = Cl *or* Br). These were prepared by similar methods of which the following is typical. To $CuCl_2{\cdot}2H_2O$ (85 mg, 0.50 mmol) dissolved in ethanol (20 cm^3) was added the ligand L^4 (103 mg, 0.50 mmol) dropwise. The solution was reduced with four drops of H_3PO_2 and left to stand for 24 h. The product was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. For X = Br the solvent was methanol.

$[CuL^4_2]BF_4$. To $Cu(BF_4)_2{\cdot}6H_2O$ (500 mg, 2 mmol) dissolved in triethyl orthoformate was added L^4 (830 mg, 4 mmol) dropwise. After 45 min white crystals were filtered off, washed with diethyl ether, and vacuum dried. Yield 45%.

$[(CuX)_2L^5]$ (X = Cl, Br, *or* I). A typical preparation is given. To $CuCl_2{\cdot}2H_2O$ (340 mg, 2 mmol) dissolved in methanol (30 cm^3) was added ligand L^5 (350 mg, 2 mmol). The solution was reduced with H_3PO_2 and the resulting white precipitate was washed with methanol then diethyl ether and dried under vacuum. Yield 90%. The iodo-complex was obtained in 59% yield when excess of $LiI{\cdot}H_2O$ replaced H_3PO_2 in the above procedure.

$[CuL^5_2]BF_4$. To $Cu(BF_4)_2{\cdot}6H_2O$ (500 mg, 2 mmol) dissolved in triethyl orthoformate (20 cm^3) was added the ligand L^5 (700 mg, 4 mmol) dropwise. The solution was reduced with H_3PO_2 (five drops). A colourless oil precipitated which crystallised when cooled to 0 °C. The crystals were washed with diethyl ether. Yield 31%.

$[(CuX)_3L^6_2]$(X = Cl, Br, *or* I). A typical preparation is described. To $CuCl_2{\cdot}2H_2O$ (510 mg, 3 mmol) dissolved in methanol (30 cm^3) was added the ligand L^6 (360 mg, 2 mmol) dropwise. The solution was reduced with H_3PO_2 (five drops) and the resulting colourless crystals were washed with methanol and diethyl ether and dried under vacuum. Yield 77%. In the preparation of the bromide a dark oil immediately precipitated and after about 2 weeks in the presence of a few drops of H_3PO_2 white crystals were obtained. The iodo-complex was prepared by adding excess of $LiI{\cdot}H_2O$ to a methanol solution containing $CuCl_2{\cdot}2H_2O$ (340 mg, 2 mmol) and L^6 (240 mg, 1.3 mmol). A black oil precipitated and this was slowly reduced over a 2-week period. A few drops of H_3PO_2 were added to ensure complete reduction. The white crystals were worked up in the same way as for the chloro-complex.

$[CuL^7_2]{\cdot}2H_2O$. To a suspension of NaL^7 in ethanol (25 cm^3) [prepared from Na (0.046 g, 2 mmol) and L^7 (0.576 g, 2 mmol)] was added $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) in ethanol. After stirring for several minutes the dark green solution was filtered and allowed to stand. The light green product was washed with ethanol and diethyl ether. Yield 65%.

Crystallography.—The complex $[\{Cu^{I}_3Cu^{II}L^1_3Cl_5\}_n]$ was obtained as dark green capped needles from acetone. The space group was determined from precession photographs and the final cell dimensions were obtained from a least-squares analysis of 65 general reflections with $44 < 2\theta < 50°$ on a four-circle *X*-ray diffractometer.

Crystal data. $C_{12}H_{24}Cl_5Cu_4S_3$, $M = 696$, monoclinic, $a = 12.2288(6)$, $b = 13.0277(7)$, $c = 14.0605(7)$ Å, $\beta = 95.815(4)°$, $U = 2228.5$ Å^3, $F(000) = 1\,380$, $Z = 4$, $D_c = 2.07$ g cm^{-3}, Mo-K_α radiation, $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å, $\mu(\text{Mo-}K_\alpha) = 46.5$ cm^{-1}, space group $P2_1/n$ from systematic absences.

Data collection and reduction. Intensity data were collected on a modified Picker four-circle diffractometer at 20 °C, using graphite-monochromatized Mo-K_α radiation to $2\theta_{max.}$ of 50° with the θ—2θ scan technique, and a scan speed of 4° min^{-1} in 2θ. The crystal dimensions were 0.31 × 0.26 × 0.17 mm, and the data were subjected to line-profile analysis.[17] Three standard reflections, chosen from different regions of reciprocal space, were monitored after every 100 measurements; no significant intensity changes were noted, with mean deviations of ±0.8% over the collection. A total of 4 127 reflections (*hkl*; −*h*, *kl*) were measured and corrected for absorption (by Gaussian integration).[18] Lorentz and polarisation factors[19] were applied, and symmetry-equivalent reflections averaged giving a total of 2 770 independent reflections [$I > 3\,\sigma(I)$] as determined from counting statistics.[18]

Structure determination. The structure was solved by direct methods[20] and subsequent Fourier difference analyses. It was refined by block-diagonal least-squares methods,[18] minimising the quantity $\Sigma w(\Delta F)^2$, where $\Delta F = |F_o| - |F_c|$ and the weighting

Table 3. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for the complex $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$; primed atoms are related to those in Table 2 by symmetry operations (see Figure)

Cu(1)–Cl(1)	2.263(1)	Cu(2)–Cl(2′)	2.340(1)	S(1)–C(11)	1.836(5)	S(2)–C(21)	1.835(5)
Cu(1)–Cl(2)	2.280(1)	Cu(2)–Cl(5′′′′)	2.290(1)	S(1)–C(14)	1.816(5)	S(2)–C(24)	1.823(5)
Cu(1)–Cl(3)	2.223(1)	Cu(2)–S(2)	2.312(1)	S(3)–C(31)	1.834(5)	S(3)–C(34)	1.812(5)
Cu(1)–Cl(4)	2.273(1)	Cu(2)–S(3)	2.352(1)	C(11)–C(12)	1.473(9)	C(12)–C(13)	1.418(10)
Cu(3)–Cl(3′)	2.514(1)	Cu(4)–Cl(1)	2.373(1)	C(13)–C(14)	1.473(10)	C(21)–C(22)	1.482(9)
Cu(3)–Cl(5)	2.238(1)	Cu(4)–Cl(4)	2.372(1)	C(22)–C(23)	1.388(10)	C(23)–C(24)	1.451(9)
Cu(3)–S(1)	2.291(1)	Cu(4)–S(1)	2.273(1)	C(31)–C(32)	1.506(8)	C(32)–C(33)	1.354(10)
Cu(3)–S(3)	2.292(1)	Cu(4)–S(2)	2.277(1)	C(33)–C(34)	1.454(9)		
Cl(1)–Cu(1)–Cl(2)	95.69(5)	Cl(1)–Cu(1)–Cl(3)	146.02(5)	Cu(3)–S(1)–C(14)	111.3(2)	Cu(4)–S(1)–C(11)	112.6(2)
Cl(1)–Cu(1)–Cl(4)	95.78(5)	Cl(2)–Cu(1)–Cl(3)	96.62(5)	Cu(4)–S(1)–C(14)	109.9(2)	C(11)–S(1)–C(14)	93.8(3)
Cl(2)–Cu(1)–Cl(4)	136.83(6)	Cl(3)–Cu(1)–Cl(4)	95.59(5)	Cu(2)–S(2)–Cu(4)	116.20(6)	Cu(2)–S(2)–C(21)	113.9(2)
S(2)–Cu(2)–S(3)	103.20(5)	S(2)–Cu(2)–Cl(2′)	114.83(5)	Cu(2)–S(2)–C(24)	114.0(2)	Cu(4)–S(2)–C(21)	107.9(2)
S(2)–Cu(2)–Cl(5′′′′)	113.17(5)	S(3)–Cu(2)–Cl(2′)	103.16(5)	Cu(4)–S(2)–C(24)	109.2(2)	C(21)–S(2)–C(24)	93.3(3)
S(3)–Cu(2)–Cl(5′′′′)	106.89(5)	Cl(2′)–Cu(2)–Cl(5′′′′)	114.06(5)	Cu(2)–S(3)–Cu(3)	112.79(5)	Cu(2)–S(3)–C(31)	107.5(2)
S(1)–Cu(3)–S(3)	104.67(5)	S(1)–Cu(3)–Cl(3′)	91.26(5)	Cu(2)–S(3)–C(34)	110.2(2)	Cu(3)–S(3)–C(31)	115.6(2)
S(1)–Cu(3)–Cl(5)	127.53(6)	S(3)–Cu(3)–Cl(3′)	100.54(5)	Cu(3)–S(3)–C(34)	114.7(2)	C(31)–S(3)–C(34)	94.5(3)
S(3)–Cu(3)–Cl(5)	120.34(6)	Cl(3′)–Cu(3)–Cl(5)	104.56(5)	S(1)–C(11)–C(12)	107.1(4)	C(11)–C(12)–C(13)	111.9(6)
S(1)–Cu(4)–S(2)	120.53(5)	S(1)–Cu(4)–Cl(1)	109.07(5)	C(12)–C(13)–C(14)	113.7(6)	S(1)–C(14)–C(13)	105.4(4)
S(1)–Cu(4)–Cl(4)	108.55(5)	S(2)–Cu(4)–Cl(1)	111.10(5)	S(2)–C(21)–C(22)	107.1(4)	C(21)–C(22)–C(23)	114.5(5)
S(2)–Cu(4)–Cl(4)	113.11(5)	Cl(1)–Cu(4)–Cl(4)	90.32(4)	C(22)–C(23)–C(24)	116.5(6)	S(2)–C(24)–C(23)	107.1(4)
Cu(1)–Cl(1)–Cu(4)	85.85(4)	Cu(1)–Cl(2)–Cu(2′′′)	108.79(5)	S(3)–C(31)–C(32)	105.4(4)	C(31)–C(32)–C(33)	114.5(5)
Cu(1)–Cl(3)–Cu(3′′′)	91.17(5)	Cu(1)–Cl(4)–Cu(4)	85.64(4)	C(32)–C(33)–C(34)	118.6(5)	S(3)–C(34)–C(33)	106.0(4)
Cu(3)–Cl(5)–Cu(2′′)	104.55(5)	Cu(3)–S(1)–C(11)	118.3(2)				
Cu(3)–S(1)–Cu(4)	109.82(5)						

Table 4. Dihedral angles (°) around the copper atoms in the complex $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$

Atoms defining planes	Copper atom	Dihedral angle
Cl(1),Cu(1),Cl(4) and Cl(2),Cu(1),Cl(3)	Cu(1)	53
S(2),Cu(2),S(3) and Cl(5),Cu(2),Cl(2′)	Cu(2)	88
S(1),Cu(3),S(3) and Cl(3′),Cu(3),Cl(5)	Cu(3)	84
Cl(1),Cu(4),Cl(4) and S(1),Cu(4),S(2)	Cu(4)	91

$w = 1/[\sigma(F_o)^2 + 0.0005\,F_o{}^2)]$. All non-hydrogen atoms were refined with anisotropic thermal parameters; all but ten of the hydrogen atoms were refined isotropically. The latter atoms were refined with fixed isotropic thermal parameters equal to 1.1 times that of the carbon atom to which they were bonded. The secondary extinction parameter was refined; at convergence R was 0.029, R' 0.039. The subsequent difference electron-density map showed no features of significance and average values of the minimised function showed little dependence on $|F_o|$ or on $\lambda^{-1}\sin\theta$.

Final atomic co-ordinates are listed in Table 2 and bond lengths and angles in Table 3. The numbering system for the non-hydrogen atoms is shown in the Figure, hydrogen atoms being numbered according to their bonded carbon atoms.

Results and Discussion

Most of the compounds reported in Table 1 were obtained by conventional methods described in the Experimental section. Of particular interest is the reaction between L^1 and $CuCl_2\cdot2H_2O$ in cold acetone. This produced a green solution from which black-green crystals were isolated. By obtaining a full set of analytical data we formulated it as the mixed-valence compound $Cu^I{}_3Cu^{II}L^1{}_3Cl_5$, and this was confirmed by the crystal structure. To our knowledge this is the second thioether mixed-valence compound, the first being $[Cu^I{}_2Cu^{II}\{MeS(CH_2)_2SMe\}_6][ClO_4]_4$.[21] Recently, 4-methylthiazole (mtz) was shown to react with $CuCl_2$ to form the mixed-valence complex $[Cu^ICu^{II}(mtz)_4Cl_3]$, however in this case the thioether sulphurs are not co-ordinated to the copper.[22]

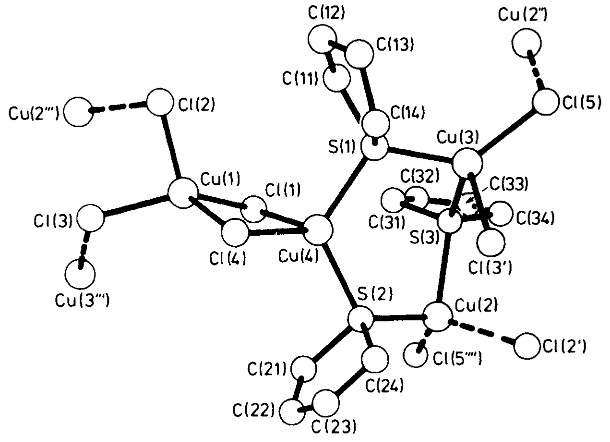

Figure. Structure of the polymeric complex $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$, showing the atom numbering scheme. The copper atoms labelled Cu(1) are designated as Cu^{II} and those labelled Cu(2), Cu(3), and Cu(4) as Cu^I. Atoms with superscripts are symmetry generated by the following operations: (′) $x + 0.5, 0.5 - y, z + 0.5$; (″) $1.5 - x, y - 0.5, 2.5 - z$; (‴) $x - 0.5, 0.5 - y, z\ 0.5$; (⁗) $1.5 - x, y + 0.5, 2.5 - z$

Crystal Structure of $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$.—The structure determination shows that the complex is polymeric (see Figure) with each copper atom being linked to another by bridging chlorine atoms or tetrahydrothiophene (L^1) ligands. The resulting structure contains three different ring systems. The first is a four-membered ring, formed by Cl(1) and Cl(4) linking Cu(1) and Cu(4). The copper atom Cu(4) then forms part of the second ring which is six-membered, and of the type $(Cu–S)_3$, *i.e.* Cu(4)–S(1)–Cu(3)–S(3)–Cu(2)–S(2). Finally this latter ring is fused to another ring, Cu(2)–S(3)–Cu(3)–Cl(3′)–Cu(1′)–Cl(2′), which is also six-membered. These rings form chains, each of which is cross-linked to others *via* Cl(5) atoms.

The structure contains two distinct types of copper atoms.

Table 5. Electronic and e.s.r. spectral data for the complexes

	Electronic[a]		Frozen solution[b] e.s.r.			Powder e.s.r.		
Compound	$\lambda_{max.}$/nm	Assignment	$g_{\parallel}$	$10^4 A_{\parallel}$/cm^{-1}	$g_{\perp}$	g_1	g_2	g_3
$[\{Cu^{I}_3Cu^{II}L^1_3Cl_5\}_n]$	465	Cl→Cu				2.052	2.170	2.254
	850, 1 080	*d–d*						
$[CuL^3Cl_2]$	440	S→Cu	2.425	138	2.098[c]	2.032	2.070	2.181
	665, 825(sh)	*d–d*	2.365	149	*ca.* 2.098[d]			
$[(CuCl_2)_2L^4]$	465(sh)	S→Cu	2.425	138	2.098[c]	2.092(g_{iso})		
	825	*d–d*	2.372	150	*ca.* 2.098[d]			
$[CuL^7_2]\cdot 2H_2O$	370	S→Cu				2.079	2.142	2.332
	775	*d–d*						
$[CuL^8Cl_2]$	500	S→Cu	2.425	138	2.098[c]		2.072	2.149
	825	*d–d*	2.335	152	*ca.* 2.098[d]			

[a] Reflectance spectra, sh = shoulder. [b] In acetone. [c] Major species, due to uncomplexed $CuCl_2$ in acetone. [d] Minor species.

The first, Cu(1), is bound to four chlorine atoms and can be assigned an oxidation number of +2, since magnetic susceptibility results, presented below, show there is only one Cu^{2+} ion per $Cu_4L^1_3Cl_5$ formula unit. Moreover the geometry around Cu(1) is intermediate between square planar and tetrahedral, and similar to that found around the Cu^{2+} ion in $[PPh_4]_2[Cu_2Cl_6]$.[23] The dihedral angle between the planes defined by Cu(1),Cl(1),Cl(4) and Cu(1),Cl(2),Cl(3) is 53°, which can be compared with 50° for the dihedral angle in the $[Cu_2Cl_6]^{2-}$ ion referred to above. The Cu(1)–Cl bond lengths range from 2.223(1) to 2.280(1) Å. These distances fall between the bridged (mean 2.306 Å) and the terminal Cu–Cl distances (mean 2.189 Å) found in the $[Cu_2Cl_6]^{2-}$ dimer.[23]

The remaining three copper atoms, Cu(2), Cu(3), and Cu(4), are characterised by CuS_2Cl_2 donor sets and together form the second type of copper with oxidation number +1. The geometries around these copper atoms can be described as distorted tetrahedral and the dihedral angles are all close to 90° (Table 4). The Cu–S distances range from 2.273(1) to 2.352(1) Å compared to 2.315—2.337 Å found for Cu^{I}–S bonds in complexes where the thioether ligands are bridging; however as far as we are aware, only two such complexes are known, *viz.* $[\{Cu(MeSCH_2CH_2SMe)Cl\}_n]$[24] and $[\{(CuI)_4(Et_2S)_3\}_n]$.[25] Characterised terminal Cu^{I}–S(thioether) bonds are much more numerous and cover a wider range of distances (2.25—2.72 Å).[7,21,26,27] Both the shortest and the longest Cu^{I}–Cl bond in the complex [2.238(1) and 2.514(1) Å respectively] are associated with Cu(3), suggesting some sort of compensatory effect. It is noted that in the Cu(1)(μ-Cl)$_2$Cu(4) ring, the longer Cu–Cl bonds (mean 2.372 Å) involve the Cu^{I} atom, Cu(4), whereas the shorter Cu–Cl bonds (mean 2.268 Å) are linked to the Cu^{II} atom, Cu(1). In contrast, while the mixed-valence complex $[Cu^{I}Cu^{II}(mtz)_4Cl_3]$ also contains a Cu^{I}(μ-Cl)$_2$Cu^{II} ring, the copper(II) centre has a five-co-ordinate, distorted tetragonal pyramidal geometry.[22] The result is a long apical Cu^{II}–Cl bond of 2.613(1) Å and a shorter basal Cu^{II} – Cl bond of 2.340(1) Å, bridging to the Cu^{I}. This asymmetry is reflected in the Cu^{I}–(μ-Cl) distances which are 2.340(2) and 2.662(2) Å respectively. Finally the Cu^{I}–Cu^{II} separation, *i.e.* the Cu(1)–Cu(4) distance, in the present compound is 3.158(1) Å which may be compared with that of 3.244(1) Å found in $[Cu^{I}Cu^{II}(mtz)_4Cl_3]$.

Physicochemical Studies and Reactivity of $[\{Cu^{I}_3Cu^{II}L^1_3Cl_5\}_n]$.—The variation in bulk magnetic susceptibility of a polycrystalline sample was measured over the temperature range 93—298 K. It obeyed the Curie–Weiss law with no perceptible deviation down to 93 K. The small value for θ(−2.4 K) is consistent with a structure having non-interacting copper(II) and copper(I) sites. The room-temperature magnetic moment of 1.95 μ_B per formula unit is in the range typically found for isolated copper(II) ions,[28] and demonstrates that of the four copper ions only one is copper(II).

The powder e.s.r. spectrum of $[\{Cu^{I}_3Cu^{II}L^1_3Cl_5\}_n]$ is rhombic in character, exhibiting three *g* values (g_x, g_y, and g_z) clearly resolved (Table 5). The linewidth for the high-field *g* is narrow. The spectrum is consistent with the distorted tetrahedral geometry[29] about the copper(II) atoms as found from the crystal structure.

The electronic reflectance spectrum for the compound shows *d-d* bands at 850 and 1 090 nm, in line with the pseudo-tetrahedral $CuCl_4$ structure,[30] while the absorption at 465 nm is assigned to a Cl–Cu^{II} charge transfer.[31] A search for an intervalence charge-transfer absorption was unsuccessful. This is consistent with strictly localised valence (Class I behaviour) at the copper(I) and copper(II) centres.[32,33]

In the solid state, at low temperatures (*ca.* 0 °C), the compound is stable, but at room temperature, after several months, some reduction is observed. It is either insoluble in organic solvents or breakdown occurs, and recovery of the unchanged compound is impossible. In aqueous solution, splitting of the complex into its component copper(I) and copper(II) moieties is observed according to equation (1). This

$$\frac{1}{n}[\{Cu^{I}_3Cu^{II}L^1_3Cl_5\}_n] \xrightarrow{H_2O} 3[CuL^1Cl] + CuCl_2\,(aq) \quad (1)$$

reaction provided a method for the analysis of Cu^{II} (by iodine titration with $Na_2S_2O_3$) and Cu^{I} (gravimetrically, by weighing the complex $[CuL^1Cl]$). The copper determinations were important to verify the formula for the complex. Similar splitting by solvents has been observed with the mixed-valence complexes $[Cu^{I}_2Cu^{II}\{MeS(CH_2)_2SMe\}_6]X_4$ (X = ClO_4 or BF_4)[21] and $[Cu^{I}Cu^{II}_2(O_2CMe)_5\{P(OEt)_3\}_2]$.[33]

If the black-green mixed-valence compound was left to stand in its acetone mother-liquor for 20 h an orange product was isolated. This showed a new band in the i.r. spectrum at about 920 cm^{-1}, which was assigned as a ν(S=O) stretch of a copper-complexed sulphoxide ligand. The compound was verified by microanalyses to be $[Cu(L^1O)Cl_2]$ (L^1O = tetrahydrothiophene 1-oxide), which Meek *et al.*[16] first prepared from $CuCl_2$ and L^1O. A single-crystal *X*-ray structure[34] shows the complex to contain linear chains of copper(II) ions with three bridging ligands (two chlorines and one oxygen) between each pair of copper ions. The copper geometry is severely distorted from octahedral with four short copper–ligand bonds (three chlorines and one oxygen) and two long copper–ligand bonds (one chlorine and one oxygen). The reflectance spectrum shows a Cl→Cu^{II} charge-transfer band at about 400 nm and a broad *d–d* absorption at 850 nm, which is similar to that of many square pyramidal complexes of Cu^{II}, indicating the long Cu–O interaction to be very weak.

This mild oxidation to the sulphoxide does not occur in the solid state or in ethanol, but only in the acetone mother-liquor. Sunlight is not required to activate the reaction as it does in the conversion of $[RuBr_3(NO)(Et_2S)_2]$ into $[\{RuBr_3(NO)(Et_2SO)\}_2]$.[35] The copper ion may have an influence similar to that found in the oxidation of phosphines in metal complexes. This oxygen activation by copper also occurs when other thioethers, *e.g.* R_2S (R = Me or Et) or benzyl methyl sulphide, react with $CuCl_2 \cdot 2H_2O$ in acetone over 1 or 2 d. Similar orange compounds to the above sulphoxide are formed, with varying degrees of purity (see Experimental section).

In view of the report[12] on the extraction of L^1 using $CuBr_2$, we have briefly investigated the reaction of these two species in an attempt to obtain a bromo-analogue of $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$. Reaction of $CuBr_2$ with neat L^1 yields a dark red-purple solution [$\lambda_{max.}$ 430(sh) and 528 nm] from which an unstable solid can be isolated (g_{iso} = 2.11). The exact nature of the coloured species is uncertain but its reduction to Cu^I readily occurs in the presence of acetone or water.

Physicochemical Studies on Copper(II) *Complexes with Ligands* L^2—L^8.—The interaction of ligands L^5 and L^6 with $CuCl_2 \cdot 2H_2O$ in acetone produced yellow-brown oils of thioether complexes that could not be solidified, while L^4 gave $[(CuCl_2)_2L^4]$ in low yields. This is in contrast with ligands L = 2,5-dithiahexane and 3,6-dithiaoctane which gave the complexes $[CuLCl_2]$.[10] The i.r. spectrum of $[(CuCl_2)_2L^4]$ was similar to that for $[Cr_2(CO)_{10}L^4]$ where L^4 has been shown to exhibit a bridging co-ordination mode.[36] The structure of $[CuLCl_2]$ (L = 3,6-dithiaoctane) consists of an alternately bridged and an alternately spaced linear-chain compound, in which the copper(II) ions are six-co-ordinate.[37] (Two chloride ligands and two sulphur atoms from the bidentate thioether constitute the equatorial plane, with a sulphur atom and chloride ion from adjacent monomeric units loosely bound in the two axial positions.) In contrast $[\{Cu(Bu^nSCH_2CH_2SBu^n)Cl_2\}_2]$ is a dichloro-bridged dimer with five-co-ordinate copper(II) ions bound by a bidentate thioether ligand and three Cl^- ions.[38] Presumably, with L^4, the sterically hindering tertiary butyl groups do not allow any of the above structures to exist, instead only one ligand is associated with two copper ions and a structure where the ligand and the chloro-groups are bridging seems preferred. I.r. bands at 300 and 306 cm^{-1} can be assigned to a combination of ν(Cu–Cl) and ν(Cu–S) stretches. For $[CuL^4(NO_3)_2] \cdot H_2O$, the i.r. spectrum in the region 1 600—400 cm^{-1} is more complicated than for $[(CuCl_2)_2L^4]$ but is similar to $[CuL^4{}_2]BF_4$ where L^4 is probably chelating. In addition, bands at 1 285 and 1 018 cm^{-1} are consistent with covalently bound nitrate ions. The electronic reflectance spectrum shows a band at 370 nm, assignable to S→Cu^{II} charge transfer by analogy with other copper(II) thioether complexes.[8,39] The *d–d* absorption band at 710 nm is in line with a tetragonal structure. Both complexes are essentially non-electrolytes in nitromethane and show normal magnetic moments at room temperature: $[(CuCl_2)_2L^4]$, 1.80 μ_B per Cu; $[CuL^4(NO_3)_2] \cdot H_2O$, 1.78 μ_B.

The introduction of another thioether sulphur atom into the five-membered ring of L^1 results in ligand L^3. Accordingly, the nature of the chloro-complexes changes and $[CuL^3Cl_2]$ was isolated. Unlike $[\{Cu^I{}_3Cu^{II}L^1{}_3Cl_5\}_n]$, a S→$Cu^{II}$ charge-transfer band is found at 440 nm (Table 5). It is of interest to note that L^2, which is the six-membered analogue of L^1, does not form an isolable copper(II) nor a mixed-valence complex. Only a copper(I) complex, $[CuL^2Cl]$, was obtained.

Placing π character in the backbone of the chelate ring of 2,5-dithiahexane (dth) gives a ligand like L^8. It, too, gave a complex of the type $[CuL^8Cl_2]$ with a normal magnetic moment of 1.84 μ_B. While it shows a similar *d–d* band energy to $[Cu(dth)Cl_2]$, its S→Cu^{II} charge-transfer band is at lower energy.

The e.s.r. data for the above copper(II) complexes are presented in Table 5. The powder spectra are consistent with tetragonal structures, however in acetone solution, extensive solvolysis occurs to give uncomplexed $CuCl_2$ as the major species and thioether complexes as minor species. The latter's signals increased in intensity upon the addition of excess of ligand. Electronic spectra in acetone solution also indicated the presence of solvated $CuCl_2$.

When the thioether ligand contains an additional binding site like a carboxylate group the stability constant increases,[11] for example such interactions may be important in the function of biotin[11,13,40] and α-lipoic acid. (The latter contains a 1,2-dithiolane ring and forms weaker complexes than the thiolane ring of biotin.) The interaction of the tetradecylthioacetate ion, L^7, with copper(II) results in the formation of a pale green complex, $[CuL^7{}_2] \cdot 2H_2O$. The electronic reflectance spectrum shows a broad *d–d* band at 775 nm and a band at 370 nm can only be assigned to a S→Cu^{II} charge-transfer absorption thus proving the presence of such an interaction. The magnetic moment of 1.87 μ_B at room temperature is normal. The powder e.s.r. spectrum displays three peaks corresponding to powder *g* values for g_x, g_y, and g_z showing the complex has rhombic character, and a tetragonal structure where the thioether atoms are *trans* to each other in the equatorial plane seems preferable. The carboxylate groups may also be *trans* and evidence of their co-ordination is obtained from the i.r. spectrum where the antisymmetric $\nu(CO_2^-)$ stretching band is shifted to lower frequency at 1 590 cm^{-1} (*cf.* 1 680 cm^{-1} for the free ligand). This complex is a weak Lewis base as it can be recrystallised unchanged from pyridine. In a recent study it was shown that when the substituent attached to the thioether sulphur atom is replaced by methyl or ethyl groups, then pyridine adducts are obtained.[41] The large tetradecyl groups may hinder close approach of the pyridine.

Physicochemical Studies on Copper(I) *Complexes of Ligands* L^1—L^6.—The range of thioethers available has allowed a comprehensive study of the type of copper(I) complexes formed, and factors such as chain length, bulkiness of the substituent group attached to sulphur, nature of halide used, the ratio of reactants, and rate of crystallisation influence the obtained stoicheiometries of the complexes (see Table 1) and control the structures.

We previously reported that 2,5-dithiahexane (dth) forms complexes of the type [Cu(dth)X] (X = Cl, Br, or I) while 3,6-dithiaoctane (dto) forms the complexes $[(CuX)_2(dto)]$ (X = Cl or Br).[10] The crystal structure of $[\{Cu(dth)Cl\}_n]$[24] shows it to be polymeric with terminal chloro-groups and chelating and bridging dth ligands attached to copper(I), to give it a distorted-tetrahedral geometry. We inferred that dto was bridging in its complexes. With ligand L^4, complexes with both of the stoicheiometries observed above are encountered, *viz.* $[CuL^4X]$ (X = Cl or Br) and $[(CuX)_2L^4]$ (X = Cl, Br, or I). For $[CuL^4Cl]$ and $[(CuCl)_2L^4]$, ν(Cu–Cl) bands at 190 cm^{-1} for the former and at 198 and 210 cm^{-1} for the latter are suggestive of bridging chloro-groups, as opposed to the terminal ones in $[\{Cu(dth)Cl\}_n]$ [ν(Cu–Cl) at 271 cm^{-1}] and bridging in $[(CuCl)_2(dto)]$ [ν(Cu–Cl) 218 and 181 cm^{-1}].[10] Bands at 142 and 168 cm^{-1} in the i.r. spectrum of $[(CuBr)_2L^4]$ are also consistent with bridging ν(Cu–Br) absorptions. Whilst the actual co-ordination modes of L^4 in these compounds must remain in doubt until *X*-ray structures are available, we assume it may be bridging in $[(CuCl)_2L^4]$ because the i.r. spectrum is similar to that of $[Cr_2(CO)_{10}L^4]$ where the bridging L^4 mode is established.[36] Hence $[(CuCl)_2L^4]$ may have a polymeric structure involving bridging chloride and L^4 ligands, giving a tetrahedral geometry about copper(I), or it may have a dimeric structure similar to that of $[\{(CuCl)_2(dppm)\}_2]$ [dppm = bis(diphenylphosphino)methane].[42] However, this chloro-derivative was not isomorphous with the bromo- or iodo-analogues, and hence L^4 in these latter systems may be bridging and chelating. For $[CuL^4{}_2]BF_4$, which is a 1:1 electrolyte in acetone, we assume L^4 may be chelating. The proton n.m.r. spectrum of $[CuL^4{}_2]BF_4$, in $CDCl_3$, showed the CH_3 protons to have moved downfield by 0.13 p.p.m. and the $S(CH_2)_2S$ protons by 0.41 p.p.m. on complexation. Finally, $[CuL^4Cl]$ and $[CuL^4Br]$ do not have similar *X*-ray powder diffraction patterns and we suggest, from i.r. data, that L^4 in the former complex is bridging while in the latter it may be chelating. Increasing the L^4 backbone chain length by two methylene groups gives ligand L^5, which in the complex $[CuL^5{}_2]BF_4$ (which is a 1:1 electrolyte in acetone) is chelating, whereas it is bridging in $[Cr_2(CO)_{10}L^5]$.[36] The proton n.m.r. spectrum of $[CuL^5{}_2]BF_4$, in $CDCl_3$, showed the CH_3 protons to have moved 0.16 p.p.m. downfield, the SCH_2CH_2 0.23 p.p.m., and the CH_2SCH_2 0.31 p.p.m., when compared with the free ligand. Of the halogeno-species only one type, *i.e.* $[(CuX)_2L^5]$ (X = Cl, Br, or I), was isolated. Bands at 167 and 195 cm^{-1} in the i.r. spectrum of $[(CuCl)_2L^5]$ are consistent with bridging ν(Cu–Cl) absorptions, however it is not clear what the co-ordination modes of L^5 are, but presumably some similarity with the series $[(CuX)_2L^4]$ (X = Cl, Br, or I) exists.

Increasing the backbone chain length by an extra two methylene groups to give ligand L^6 results in a change of the stoicheiometry of the halogeno-complexes to $[(CuX)_3L^6{}_2]$. The *X*-ray powder patterns for $[(CuX)_3L^6{}_2]$ (X = Cl or Br) were comparable, as were their i.r. spectra. In the far-i.r. spectra bands at 166(sh), 194, and 200 cm^{-1} are assignable to bridging chloro-groups attached to copper. The iodo-analogue was not isomorphous with the other halogeno-complexes and its i.r. spectrum was similar to $[Cr_2(CO)_{10}L^6]$ indicating a bridging mode of co-ordination for L^6.[36] The simplest structure based on a 3:2 stoicheiometry for $[(CuI)_3L^6{}_2]$ is shown by $[\{(CuI)_3(dppm)_2\}_3]$ where both iodide and dppm ligands are bridging in a trimeric structure.[43] The chloro- and bromo-analogues presumably have a different co-ordination mode for L^6.

The cyclic ligand L^1 also forms a complex based on a 3:2 stoicheiometry, *viz.* $[(CuCl)_3L^1{}_2]$. Bands at 194 and 202 cm^{-1} in the i.r. spectrum are assigned to ν(Cu–Cl) bands. In addition L^1 forms the 1:1 complexes $[CuL^1X]$ (X = Cl or Br) with ν(Cu–X) at 188, 194, and 200 cm^{-1} (X = Cl) and 125, 132, and 142 cm^{-1} (X = Br). In all these complexes it thus appears that the halogen groups are bridging and we assume L^1 is also. The other cyclic ligands, L^2 and L^3, form the similarly formulated compounds $[CuL^2Cl]$ and $[CuL^3X]$ (X = Cl or Br), as well as $[CuL^3{}_2]ClO_4 \cdot 2H_2O$.

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