Sulphur Ligand Metal Complexes. Part 6.[1] Copper Complexes of 2,5-Dithiahexane and 3,6-Dithiaoctane

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The dithioethers 2,4-dithiahexane (dth) and 3,6-dithiaoctane (dto) form the following complexes, some of which have been previously reported, with Cu^{II} and Cu^{I}: $Cu(BF_4)_2L_2$ and CuX_2L (L = dth or dto, X = Cl or Br); $[CuL_2]X$ (L = dth or dto, X = BF_4; L = dth, X = ClO_4); CuXL (L = dth, X = Cl, Br, or I; L = dto, X = I or SCN); and $(CuCl)_2L$ (L = dto, X = Cl or Br). The complexes have been characterized by a variety of physicochemical techniques and where possible structures are proposed. The nature of the copper–sulphur bond is discussed and it is concluded that thioethers do not form appreciable π bonds with Cu^{II}. The chelated thioether ligand is readily displaced, *e.g.* from $CuCl_2L$ (L = dth or dto) and CuCl(dth), by a variety of ligands (*e.g.* pyridine, pyrrolidine, 2,2'-bipyridyl, ethylenediamine, PPh_3, PMe_3S, and $Na[S_2PMe_2]\cdot 2H_2O$). With PPh_3 and CuCl(dth) the adduct CuCl(PPh_3)(dth) is formed.

CURRENT interest in complexes containing metal–sulphur bonds (especially copper–sulphur bonds) lies in their use as simple bonding models for biological molecules. For example (+)-biotin and the methionine residue of proteins and enzymes incorporate thioether groups which are potential metal binding sites,[2] and the blue copper redox proteins are thought to contain copper bound to one cysteinyl sulphur atom.[3-5] The copper(II) complex of *N*-methylthioformylhydroxamic acid has been found in the culture broth of *Pseudomanas fluorescens* [6] and is presumably an antibiotic, and the copper(II) complex of 3-ethoxy-2-oxobutyraldehyde bis(thiosemicarbazone) [7,8]

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has been shown to have activity against a variety of tumours in animals. Although in 1957 Nyholm and his co-workers[9] concluded, from studies on nickel(II) complexes, that dialkyl sulphides are reluctant to form π bonds with transition metals, it is generally assumed that sulphur in such SR_2 ligands has suitable vacant *d* orbitals which can participate in d_π–d_π bonding, especially with later transition elements or transition elements in low oxidation states. Recently[1] we presented electronic spectral evidence, supported by an *X*-ray structure, which indicated that although alkyl sulphides exhibit a π acidity this is not as great as that of related phosphine ligands bound to zero-valent Group 6 metal carbonyls.

In this paper we report a more comprehensive study of the interaction of two dithioethers, *viz.* 2,5-dithiahexane, $MeS[CH_2]_2SMe$ (dth), and 3,6-dithiaoctane, $EtS[CH_2]_2SEt$ (dto), with copper in an attempt to gain further chemical and physical information about the nature of the copper–sulphur interaction than has been obtained in the previous studies where $CuCl_2(dth)$,[10,11] CuX(dth) (X = Cl or Br),[11] $CuCl_2(dto)$,[12] and $Cu(BF_4)_2(dth)_2$[10] were first reported. Improved methods for the preparation of some of the copper(I) complexes are given as well as the use of the complexes as precursors for other copper derivatives. Few dto complexes with other metal ions have been reported previously;[13,14] however, dth has been shown to complex with a variety of metal ions, either as a chelate[9,13–15] or as a bridging ligand.[15–17]

RESULTS AND DISCUSSION

Preparation and Characterization of the Copper(II) *Complexes*.—The complexes were prepared by reaction of the dth or dto ligand with the appropriate metal salt in acetone or methanol. For $CuBr_2(dto)$, dto was used as solvent, and for $Cu(BF_4)_2(dto)_2$ it was necessary to carry out the reaction in the presence of the dehydrating agent triethyl orthoformate. Once isolated, the complexes were generally stable in the absence of moisture, although in most common organic solvents they were reduced to colourless copper(I) derivatives. **CAUTION.** Attempted isolation of the previously reported[10] complex $Cu(ClO_4)_2(dth)_2$ resulted in a violent explosion.

As dto is oxidized in air a limited study of complexes containing 1,2-bis(ethylsulphinyl)ethane (bese) was made mainly to determine from i.r. studies whether these complexes [$CuCl_2(bese)$, $Cu(NO_3)_2(bese)$, and $CuX_2(bese)$ ($X = BF_4^-$ or PF_6^-)] contaminated similar dto complexes during their preparations. No contamination occurred and preparative details are given in the Experimental section. Strong ν(S=O) bands at 1 019 and 1 047 cm^{-1} in the free ligand shifted to 900 and 950 cm^{-1} in the complexes. This is consistent with bonding through the oxygen atom as found for similar complexes containing 1,2-bis(methylsulphinyl)ethane.[18]

X-Ray powder photographs show the complexes $CuX_2(dto)$ (X = Cl or Br) to be isomorphous as are $CuX_2(dth)$ (X = Cl or Br). The i.r. spectra of all the copper(II) complexes indicate the ligand to be chelating rather than bridging. The i.r. spectra of dth complexes have been well documented previously.[13,19,20] In particular, the presence of a strong band in the 825—855 cm^{-1} region assignable to a CH_2 rocking mode confirms the chelating function of the ligand. For dto complexes only limited data are available;[13] however, similar criteria seem to apply. Moreover the spectra are similar to that of $[Cu(dto)_2][BF_4]$ which has recently been shown by a single-crystal *X*-ray analysis in this laboratory to contain chelated dto ligands.[21] As for the related ethylenediamine complex, $Cu(BF_4)_2(en)_2$,[22] the i.r. spectra of $Cu(BF_4)_2L_2$ (L = dth or dto) gives evidence of semi-co-ordination of the $[BF_4]^-$ anion. For L = dth the ν_3 band of the $[BF_4]^-$ ion was broad and centred at *ca.* 1 050 cm^{-1}, while ν_1 occurred at 760 cm^{-1} and ν_4 at 520 cm^{-1}. Similarly for L = dto ν_1 was at 763 cm^{-1}, ν_3 at 1 050 cm^{-1}, and ν_4 at 522 cm^{-1}. For the complexes CuX_2L (L = dth or dto, X = Cl or Br) the ν(Cu–S) and ν(Cu–X) stretching frequencies would be expected to occur at similar positions; however, tentative assignments have been made for the ν(Cu–X) modes (Table 2). The ν(Cu–Cl) bands appeared at *ca.* 300 cm^{-1} and ν(Cu–Br) at *ca.* 250 cm^{-1}. The assignment for $CuCl_2(dth)$ is in agreement with that of Flint and Goodgame.[10] The Cu–X modes fall in the range expected for tetragonally distorted octahedral complexes. Lever and Mantovani[23] assigned bands to ν(Cu–X) for a range of related CuX_2L complexes (L = chelating amine, X = Cl or Br) which are considered to have distorted octahedral structures. For example, $CuCl_2L$ (L = antisymmetric *NN*-dimethylethylenediamine) shows ν(Cu–Cl) at 302 cm^{-1} while the analogous bromide shows ν(Cu–Br) at 233 cm^{-1}. For $CuCl_2(py)_2$ (py = pyridine), which is known to be polymeric distorted octahedral,[24] one of the ν(Cu–Cl) bands appears at 287 cm^{-1},[25–27] and one of the ν(Cu–Br) bands of the isostructural bromide[28] occurs at 256 cm^{-1}.[25–27]

The electronic-reflectance spectral data for the complexes confirm the distorted octahedral nature of the

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complexes. The halide complexes CuX_2L (L = dth or dto, X = Cl or Br) all showed a broad band assignable to *d–d* absorptions at *ca.* 12 500 cm^{-1} (Table 2), and the spectra of $Cu(BF_4)_2L_2$ (L = dth or dto) showed a broad *d–d* band in the 18 000—18 500 cm^{-1} region (Table 2). This latter band is solvent dependent. The *d–d* bands for the sulphide complexes appear at lower energies than for the related complexes of chelating amines. For instance the $Cu(BF_4)_2L_2$ amine complexes show bands in the range 18 650—19 000 cm^{-1} whereas the halides CuX_2L absorb in the 13 500—16 900 cm^{-1} region.[29] These results, and the fact that the $[BF_4]^-$ anion is semi-co-ordinated in the $Cu(BF_4)_2L_2$ sulphide complexes, provides evidence that the contribution from the related amine and sulphide ligands to the total charge accumulation on the central copper(II) ion is not significantly different. Thus the chelating thioether ligands are functioning essentially as σ donors and their π-bonding ability when bound to the copper(II) ion must be minimal. This conclusion has been confirmed by a single-crystal *X*-ray analysis in this laboratory [21] on one of the complexes $Cu(BF_4)_2(dth)_2$. The complex has a strongly tetragonally distorted environment about the metal atom with a square-planar arrangement of four sulphur atoms (from the chelated dth ligands) around the copper atom with a fluorine from each of the $[BF_4]^-$ groups weakly co-ordinated in the axial positions. The mean Cu–F distance of 2.579 ± 0.005 Å is only slightly greater than that (2.56 ± 0.01 Å) found in the related ethylenediamine complex $Cu(BF_4)_2(en)_2$.[30] Moreover the mean Cu–S bond length of 2.317 Å may be compared to the value of 2.34 Å calculated for

TABLE 1

Analytical, m.p., conductivity, and i.r. data for the complexes

Complex	Found [a](%) C	H	X	M.p. (θ_c/°C)	Λ [b] S cm^3	ν(Cu–X) [c] cm^{-1}
$Cu(BF_4)_2(dth)_2$	20.6 (19.9)	4.0 (4.2)	26.3 (26.6) [d]	*e*	197 [f]	
$CuCl_2(dth)$ [g]	18.7 (19.0)	3.9 (3.9)	27.7 (27.9)	125	5	308
$CuBr_2(dth)$ [g]	14.0 (13.9)	3.0 (2.9)	47.3 (46.2)	130—131	20	256
$Cu(BF_4)_2(dto)_2$	26.9 (26.8)	5.3 (5.25)		*e*	*e*	
$CuCl_2(dto)$ [h]	25.4 (25.3)	5.05 (5.0)	26.5 (24.9)	124—126	11 [f]	312, 302
$CuBr_2(dto)$ [h]	19.4 (19.3)	3.6 (3.8)	43.0 (42.8)	129—131	19 [f]	256, 243
$Cu(BF_4)_2(bese)$	24.3 (24.0)	5.7 (4.7)		*e*	*e*	
$Cu(PF_6)_2(bese)_2$	22.0 (22.45)	4.1 (4.4)		190—195 (decomp.)	*e*	
$Cu(NO_3)_2(bese)$	19.9 (19.4)	4.0 (3.8)	7.3 (7.6) [i]	184—185	*e*	
$CuCl_2(bese)$	23.25 (22.75)	4.6 (4.5)	22.0 (22.4)	174—176	*e*	
$Cu(BF_4)(dth)_2$	25.8 (24.3)	5.3 (5.1)	31.9 (32.5) [d]	155—156	30,[f] 30 [j]	
$Cu(ClO_4)(dth)_2$	24.4 (23.6)	5.1 (4.9)	29.6 (30.1) [d]	*e*	102 [k]	
CuCl(dth)	22.2 (21.7)	4.9 (4.6)	16.4 (16.0)	143	17 [j]	271
CuBr(dth) [l]	18.8 (18.1)	3.9 (3.8)	30.15 (30.1)	128—130	14 [j]	169, 152
CuI(dth) [l]	15.3 (15.2)	3.5 (3.2)		133 (decomp.)	*e*	139
$Cu(BF_4)(dto)_2$	32.0 (32.0)	6.3 (6.3)	28.0 (28.4) [d]	85—86	31 [j]	
$(CuCl)_2(dto)$	20.3 (20.7)	4.4 (4.05)	21.1 (20.4)	128—129	135 [m]	218, 181
$(CuBr)_2(dto)$	16.4 (16.5)	3.5 (3.2)	37.1 (36.6)	85—86	30 [j]	152, 145 (sh)
CuI(dto)	21.0 (21.15)	4.4 (4.1)	18.2 (18.8) [d]	125 (decomp.)	66 [m]	159 (sh), 155
Cu(dto)(SCN)	31.2 (30.9)	5.55 (5.2)	5.05 (5.15) [i]	125—126	54 [m]	
$CuCl(PPh_3)(dth)$	54.6 (54.65)	5.3 (5.2)	8.5 (7.3)	192—197 (decomp.)	20 [k]	246

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm^{-3} solutions. [c] As Nujol mulls. [d] S. [e] Not recorded. [f] In nitromethane. [g,h,l] Isomorphous pairs. [i] N. [j] In dimethyl sulphoxide. [k] In acetone. [m] In acetonitrile.

TABLE 2

Electronic spectral data (cm^{-1}) for the copper(II) complexes [a]

Complex	*d–d*	Charge transfer		State
$Cu(BF_4)_2(dth)_2$	18 500		22 500	*b*
	16 130 (35)		25 700 (465)	*c*
	15 748 (35)		26 170 (240)	*d*
	18 018		23 148	*e*
$Cu(BF_4)_2(dto)_2$	18 000		22 300	*b*
$CuCl_2(dth)$ [f]	12 350		22 100	*b*
	12 980 (230)			*c*
$CuCl_2(dto)$ [g]	12 500		22 500	*b*
	13 150 (285)			*c*
$CuBr_2(dth)$	12 500	18 300	21 800	*b*
	13 422 (410), 15 625 (380)	18 800 (500)		*c*
$CuBr_2(dto)$	12 700	18 700	23 500	*b*
	13 330 (290), 15 384 (280)	18 600 (400)		*c*

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] Solid, diluted with MgO. [c] In $MeNO_2$. [d] In MeCN. [e] In Me_2CO. [f] *M* (in $MeNO_2$) 279 (calc. 257). [g] *M* (in $MeNO_2$) 266 (calc. 285).

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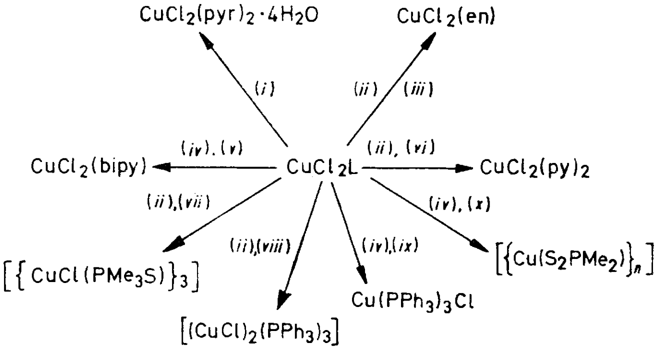
a single Cu–S bond in a tetragonal complex.[21] Interestingly, the complex $Cu(ClO_4)_2L$ (L = 1,4,8,11-tetrathiacyclotetradecane) has a similar geometry and Cu–S bond lengths and exhibits a band at 17 540 cm^{-1} (ε 1 900 dm^3 mol^{-1} cm^{-1}, obtained from stability constants) which has been assigned as a S $\longrightarrow$ Cu charge transfer and so mimics the redox protein azurin.[31]

Examination of the reflectance spectra also allows the assignment of ligand to metal charge-transfer transitions. In particular a band at *ca.* 23 000 cm^{-1} in all the complexes is assigned to a S $\longrightarrow$ Cu charge transfer. Such transitions have been identified in the range 23 000—25 000 cm^{-1} for a variety of copper(II) complexes *e.g.* substituted thiourea complexes of copper(II) perchlorate,[32] bis(diethyldithiocarbamato)copper(II),[33] bis(di-isopropyldithiocarbamato)copper(II),[34] and tertiary phosphine sulphide complexes of copper(II) chloride.[35] Complexes with the less polarizable amine ligands, $Cu(BF_4)_2L_2$, show N $\longrightarrow$ Cu charge-transfer bands at *ca.* 40 000 cm^{-1}.[36] The extra band at *ca.* 19 000 cm^{-1} in $CuBr_2L$ (L = dth or dto) may be a S $\longrightarrow$ Cu charge-transfer band,[37] although a Br $\longrightarrow$ Cu charge transfer cannot be discounted.

The instability of the complexes in solution prevented a detailed study; however, it was possible to obtain limited data in nitromethane. All of the halogeno-complexes CuX_2L (L = dth or dto) were essentially non-electrolytes in this solvent (Table 1), whereas the $Cu(BF_4)_2L_2$ complexes were 2 : 1 electrolytes. Molecular-weight data on $CuCl_2L$ showed the complexes to be monomeric in nitromethane, the polymeric structures presumably being cleaved by solvent molecules although the species must still be solvated as the spectra were still typical of Cu^{II} in a distorted octahedral environment. The high intensity of the *d–d* bands in nitromethane solution is presumably related to 'intensity stealing' from the nearby S $\longrightarrow$ Cu charge-transfer bands.

Reactivity of the Copper(II) *Complexes.*—Weakly bound dto and dth were easily displaced from the complexes by a variety of ligands (L), *e.g.* pyridine, pyrrolidine, ethylenediamine, and 2,2′-bipyridyl to form the complexes $CuCl_2L_2$ or $CuCl_2L$ (see Scheme 1). Reducing ligands such as PMe_3S, PPh_3, and $Na[S_2PMe_2]\cdot 2H_2O$ also displaced the thioethers under mild conditions and copper(I) derivatives were formed (Scheme 1). The dth and dto copper(II) complexes are therefore convenient precursors for a variety of copper complexes. That thioethers form labile complexes has been suggested to be important in some metal–enzyme reactions as it would allow a rapid rearrangement of the complexes necessary for the enzyme to act as a catalyst.[2]

Preparation and Characterization of the Copper(I) *Complexes.*—The complexes of formula CuX(dth) (X = Cl or Br) were more conveniently prepared than previously reported [11,38] by the addition of hypophosphorous acid to a methanol solution of the appropriate copper(II) complex, while CuI(dth) was prepared for the first time by the addition of LiI to a solution of the copper(II) chloride complex. The complex CuI(dto) was prepared in a similar way, while Cu(dto)(SCN) was obtained by the addition of K[SCN] to an acetone solution of copper(II) nitrate and dto. Interestingly, no complexes of formulae CuX(dto) (X = Cl or Br) could be isolated using reaction conditions similar to those for CuX(dth) (X = Cl or Br); instead only complexes of the type $(CuX)_2(dto)$ were found. A similar situation has been observed previously in complexes of copper(I) halides with the unidentate sulphides SMe_2 and SEt_2.[39] Whereas $CuBr(SMe_2)$ was isolated, the complex containing SEt_2 was of different stoicheiometry, *e.g.* $(CuBr)_4(SEt_2)_3$, even though the reaction conditions were similar. There appears to be a delicate balance of factors which controls the structure of copper(I) complexes. Other new complexes $[CuL_2][BF_4]$ (L = dth or dto) and $[Cu(dth)_2][ClO_4]$ were obtained by the reduction of the appropriate copper(II) derivative with hypophosphorous acid. The dth complexes gave low carbon and hydrogen analyses using the normal analytical cycle but good results were obtained by cooling the samples prior to the commencement of the combustion cycle (Table 1). This may account for the low analyses reported earlier by Braterman and Wilson.[38] All the complexes are stable in the absence of moisture at room temperature. The complexes did not produce parent molecular ions in the mass spectrograph, instead only parent ligand ions were formed. No suitable solvent was found for the determination of molecular weights. Conductivity measurements show the $[CuL_2]$-



SCHEME 1

(*i*) Excess of pyrrolidine (pyr); (*ii*) L = dth or dto; (*iii*) en; (*iv*) L = dto; (*v*) bipy; (*vi*) excess of py; (*vii*) PMe_3S; (*viii*) 2 PPh_3; (*ix*) 4 PPh_3; (*x*) $Na[S_2PMe_2]\cdot 2H_2O$

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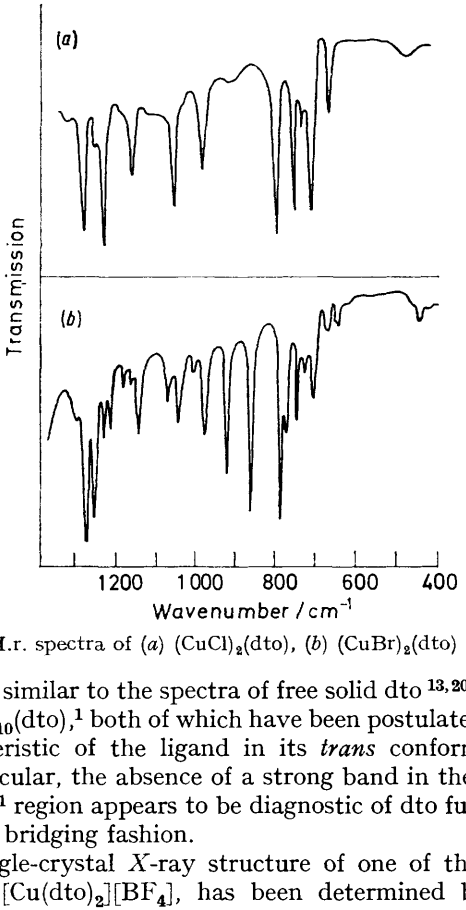
[BF_4] complexes to be 1 : 1 electrolytes and the halide complexes to be essentially non-electrolytes but showing some dissociation. *X*-Ray powder photographs show only one pair of complexes to be isomorphous, *viz.* CuX(dth) (X = Br and I).

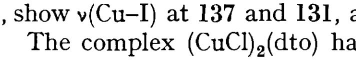
From criteria discussed earlier it is concluded that the i.r. spectral data (600—1 600 cm^{-1}) show all the copper(I) complexes of dth and dto (with one exception) to contain chelated ligands. However, $(CuCl)_2$(dto) exhibited a comparatively simple i.r. spectrum (Figure) which is similar to the spectra of free solid dto [13,20] and of $Cr_2(CO)_{10}$(dto),[1] both of which have been postulated to be characteristic of the ligand in its *trans* conformation. In particular, the absence of a strong band in the 800—900 cm^{-1} region appears to be diagnostic of dto functioning in a bridging fashion.



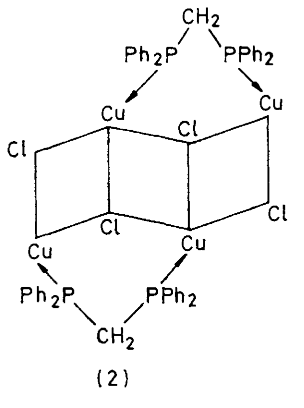
I.r. spectra of (*a*) $(CuCl)_2$(dto), (*b*) $(CuBr)_2$(dto)

A single-crystal *X*-ray structure of one of the complexes, $[Cu(dto)_2][BF_4]$, has been determined by this laboratory.[21] It shows a distorted tetrahedral arrangement of the sulphur ligands about copper, the dto ligands being chelated, and an average Cu–S bond length of 2.307 Å (*cf.* the theoretical value for a single Cu–S of 2.39 Å) consistent with a π-bonding component from *d* orbitals of the copper to *d* orbitals of sulphur. The complexes $[Cu(dth)_2]X$ (X = BF_4 or ClO_4) presumably have similar structures. For the halide complexes the far-i.r. data point to a greater complexity of structural types. The metal–halogen frequencies (Table 1), which generally can be readily identified as strong absorptions, do serve to give certain information concerning the environment of the halogen atom. For instance CuCl(dth) showed a ν(Cu–Cl) band at 271 cm^{-1} indicative of a terminal Cu–Cl bond as bridging ν(Cu–Cl) frequencies are expected to be lower (below 240 cm^{-1}).[35,40,*] Furthermore the complexes $[\{CuCl(PMe_3S)\}_3]$ and $CuCl(SPh_2PCH_2PPh_2S)\cdot Me_2CO$, which contain three-co-ordinate Cu^I, have ν(Cu–Cl) at 275 [41] and 274 cm^{-1} (ref. 35) respectively. This evidence, together with the fact that CuCl(dth) forms a simple adduct $CuCl(PPh_3)$(dth) (see below), suggests that the complex has three-co-ordinate trigonal-planar geometry.

Two strong bands for CuBr(dth) at 169 and 152 cm^{-1} assigned as ν(Cu–Br) indicate that the bromines are bridging. Although there is a lack of structural data, bands at 164 and 92 cm^{-1} for $[\{CuBr(TeR_2)_2\}_2]$ (R = *p*-tolyl) have been assigned by McWhinnie and Rattanaphani [42] to bridging Br–Cu stretches. The simplest structure for CuBr(dth) would be that of a tetrahedral dimer, (1). The isomorphous iodide CuI(dth) showed a band at 139 cm^{-1} which has been tentatively assigned to ν(Cu–I). The complexes $[\{Cu(AsEt_3)I\}_4]$ [43] and $[(CuI)_4(SEt_2)_3]$,[39] which contain bridging iodine atoms in a $(CuI)_4$ core, show ν(Cu–I) at 137 and 131, and 121 cm^{-1} respectively. The complex $(CuCl)_2$(dto) has two broad bands at 218 and 181 cm^{-1} due to ν(Cu–Cl) stretches and is consistent with halogen bridging. As already established, dto is bridged in this complex and a probable structure is one similar to that of $[\{(CuCl)_2(dppm)\}_2]$[dppm = bis(diphenylphosphino)methane] which has been shown to be based on the ' step ' structure [44,45] (2) and where the bridging dppm group is



(1) S⌒S = dth



(2)

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[*] *Note added in proof.* A single crystal *X*-ray structure has just been performed on CuCl(dth) in this laboratory. It exists as a dimer containing terminal chloro-groups but with each dth chelating and bridging giving both Cu atoms a distorted tetrahedral geometry.

[40] B. W. Cook, R. G. J. Miller, and P. F. Todd, *J. Organometallic Chem.*, 1969, **19**, 421.

[41] E. W. Ainscough, G. A. Bowmaker, A. M. Brodie, and R. Whiting, *Austral. J. Chem.*, 1975, **28**, 1431.

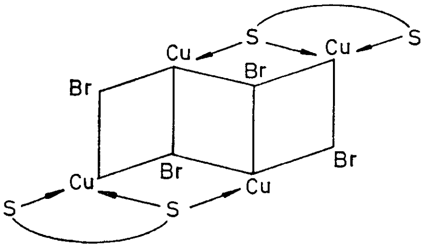
[42] W. R. McWhinnie and V. Rattanaphani, *Inorg. Chim. Acta*, 1974, **9**, 153.

[43] R. J. Knappstein, M.Sc. Thesis, University of Auckland, 1974.

[44] G. Nardin and L. Randaccio, *Acta Cryst.*, 1974, **B30**, 1377.

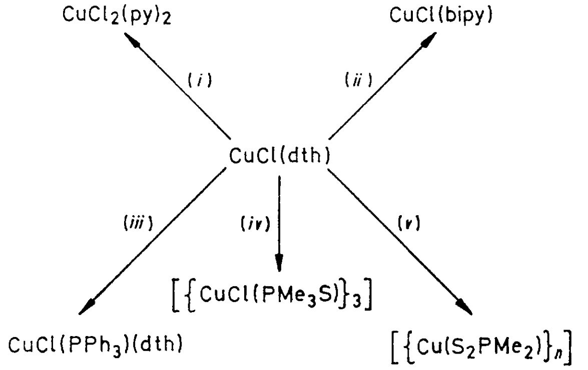
[45] A. Camus, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1975, **12**, 23.

replaced by dto. A polymeric step structure is also possible. The complex $(CuBr)_2(dto)$ has two bands at 152 and 145 cm^{-1} assignable to ν(Cu–Br) and as before this was interpreted as being due to bridging bromides. A step-structure involving chelating dto, as well as donor sulphur atoms bridging two copper atoms, as occurs in $[(CuI)_4(SEt_2)_3]$,[39] is shown in (3). Even though a single-crystal *X*-ray analysis would ultimately be required to solve the structure of both these complexes, the proposed geometries do serve to illustrate their complexity and in the case of sulphur ligands this problem is compounded by sulphur being able to co-ordinate to one or more copper atoms. For CuI(dto) a strong split band at 157 cm^{-1} was assigned as ν(Cu–I) consistent with a terminal iodide and hence a trigonal-planar arrangement of ligands about copper is suggested. For $CuI\{Te(C_6H_4Me\text{-}p)_2\}$ a band at 163 cm^{-1} was assigned[42] to a terminal ν(Cu–I). Strong bands in the Raman spectrum at 2 102 and 776 cm^{-1} for Cu(dto)(SCN), which are assigned to ν(CN) and ν(CS) respectively, are consistent with bridging thiocyanate groups.[46] The simplest structure would be a tetrahedral dimer as was proposed for CuBr(dth), (1); $[\{Cu(NCS)(PMePh_2)\}_2]$ [47] contains this structural unit.



(3) S⌒S = dto

Reactivity of the Copper(I) *Complexes*.—Even though the structure of $[Cu(dto)_2][BF_4]$ indicates that the Cu–S bond contains some π character, the chelating ligands are readily displaced under mild conditions by a variety of ligands, *e.g.* 2,2′-bipyridyl, PMe_3S, and $Na[S_2PMe_2]\cdot 2H_2O$, to produce known copper(I) derivatives (Scheme 2). However, when CuCl(dth) and PPh_3 were allowed to react in a 1 : 1 molar ratio in methanol (with a little warming) displacement of dth did not occur, instead the adduct $CuCl(PPh_3)(dth)$ was isolated. The i.r. spectrum showed that dth was chelating and a strong band at 246 cm^{-1} was assigned as a terminal ν(Cu–Cl). From a single-crystal *X*-ray analysis, the complex $[\{CuCl(SMe_2PPMe_2S)\}_2]$ [48] contains terminal chloro-groups each copper having a tetrahedral arrangement of ligands, and this complex, we have found, has a similar absorption at 257 cm^{-1}. Hydrogen-1 n.m.r. spectroscopy confirmed the presence of both dth and PPh_3. The adduct is therefore suggested to be a tetrahedral monomeric complex; ν(Cu–Cl) is lowered from 271 cm^{-1} in CuCl(dth) (being potentially three-co-ordinate) to 246 cm^{-1} in the four-co-ordinate adduct. Morgan[11] first reported that when CuCl(dth) was dissolved in pyridine a coloured solution appeared. We have isolated the known copper(II) complex $[\{CuCl_2(py)_2\}_n]$ from this reaction after the addition of chloride ions.



SCHEME 2 (*i*) py and LiCl; (*ii*) bipy; (*iii*) PPh_3; (*iv*) PMe_3S; (*v*) $Na[S_2PMe_2]\cdot 2H_2O$

EXPERIMENTAL

Infrared spectra were recorded using a Beckman IR20 spectrophotometer (250—4 000 cm^{-1}) and a Grubb-Parsons Cube MkII interferometer (40—300 cm^{-1}). N.m.r. spectra were obtained on a JEOL JNM-C-60 HL spectrometer and electronic spectra on a Shimadzu MPS 5000 spectrophotometer. Raman spectra were obtained using an RCA LD 2 140 argon-ion laser with a Spex 1401 double monochrometer. Conductivity measurements were made at 25 °C using Philips PR 9500 and PW 9510 conductivity meter and cell. *X*-Ray powder photographs were obtained using a Philips PW 1011 and PW 1352 generator and recording unit. Microanalyses were by Professor A. D. Campbell, University of Otago. Analytical and m.p. data are summarized in Table 1.

All the solvents were dried according to established procedures. The sulphide ligands were used as purchased while 1,2-bis(ethylsulphinyl)ethane (bese) was prepared following the method described for 1,2-bis(methylsulphinyl)ethane by Bell and Bennett.[49] No attempt was made to separate the *racemic* mixture.

The Complexes.—CuX_2L (L = dth *or* dto, X = Cl; L = dth, X = Br. These were prepared by similar methods of which the following is typical. Copper(II) chloride dihydrate (0.852 g, 5.0 mmol) was dissolved in acetone and dto (0.752 g, 5.0 mmol) was added to form a dark green precipitate, which was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 90%. For L = dth and X = Br ethanol was used as solvent.

$CuBr_2(dto)$. To finely ground $CuBr_2$ (0.223 g, 1.0 mmol) was added excess of dto (5.0 mmol). This mixture was left to react for 15 min. The dark brown product was filtered to remove the excess of dto, washed with diethyl ether, and dried *in vacuo*, yield 95%.

$Cu(BF_4)_2(dto)_2$. Copper(II) tetrafluoroborate hexahydrate (0.173 g, 0.5 mmol) was dissolved in triethyl orthoformate and heated under reflux until the solution changed from blue to green. The solution was then allowed to cool. The ligand dto (0.150 g, 1.0 mmol) was added slowly and a

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[46] L. C. Nathan, *J. Chem. Educ.*, 1974, **51**, 285.

[47] A. P. Gaughan, R. F. Zido, and Z. Dori, *Inorg. Chim. Acta*, 1970, **4**, 640.

[48] F. A. Cotton, B. A. Frenz, D. L. Hunter, and Z. C. Mester, *Inorg. Chim. Acta*, 1974, **11**, 111.

[49] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1927, 1798.

brown precipitate formed. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 60%. This complex is not stable and completely decomposed in 3 weeks. The analogous dth complex was prepared according to the method of Flint and Goodgame.[10]

$CuCl_2$(bese). The salt $CuCl_2·2H_2O$ (0.170 g, 1.0 mmol) was dissolved in ethanol and 2,2-dimethoxypropane (dmp) (5 cm^3) added. The ligand base (0.182 g, 1.0 mmol) was added as an ethanol solution. The resulting solution was heated until a yellow colour appeared and an extra 15 cm^3 of dmp were added. More heat was applied until a yellow-green precipitate appeared. The precipitate was filtered off, washed with dmp, and dried *in vacuo*, yield 5%.

$Cu(BF_4)_2(bese)_2$. The salt $Cu[BF_4]_2·6H_2O$ (0.348 g, 1.0 mmol) was dissolved in dmp and heated until the solution changed colour from blue to green. To this solution was added bese (0.364 g, 2.0 mmol) in acetone containing ethanol (2—3 cm^3). The resulting solution was heated until a blue precipitate appeared. The solution was allowed to cool, before the precipitate was filtered off, washed with dmp, and dried *in vacuo*, yield 11%.

$Cu(NO_3)_2$(bese). This complex was prepared in a manner similar to that described above but using $Cu[NO_3]_2·3H_2O$ dissolved in triethyl orthoformate, yield 23%.

$Cu(PF_6)_2(bese)_2$. The salt $Cu[BF_4]_2·6H_2O$ (0.174 g, 0.5 mmol) was dissolved in acetone and an equal amount of dmp added. A second solution containing bese (0.182 g, 1.0 mmol) dissolved in acetone with ethanol (3 cm^3) was added to the first solution. To the resulting solution was added $[NH_4][PF_6]$ (0.165 g, 1.0 mmol) as an acetone solution. The solution was heated until a blue precipitate appeared, which was filtered off, washed with hot acetone, and dried *in vacuo*, yield 14%.

$CuXL_2$ (L = dth *or* dto, X = BF_4; L = dth, X = ClO_4). These complexes were prepared by similar methods of which the following is typical. The salt $Cu[BF_4]_2·6H_2O$ (0.172 g, 0.5 mmol) was dissolved in methanol and dto (0.150 g, 1.0 mmol) was added slowly to give a dark green solution. Hypophosphorous acid was added dropwise until the solution became colourless. On the addition of diethyl ether a cloudy solution resulted which was left to stand. The white crystals which formed overnight were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 21%. For L = dth, gentle heating was required after the addition of H_3PO_2 to effect the reduction.

CuX(dth) *and* $(CuX)_2$(dto) (X = Cl or Br). These complexes were prepared by similar methods of which the following is typical. The salt $CuCl_2·2H_2O$ (0.170 g, 1.0 mmol) was dissolved in methanol and dth (0.150 g, 1.0 mmol) was added to give a dark green solution. While stirring and heating, H_3PO_2 was added dropwise until the solution became colourless. The solution was allowed to stand overnight to yield the white crystalline product, which was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 92%.

CuIL (L = dth *or* dto). Typically, these complexes were prepared as follows.

The salt $CuCl_2·2H_2O$ (0.255 g, 1.5 mmol) was dissolved in methanol and dth (0.183 g, 1.5 mmol) was added to give a dark green solution. To this solution was added a methanol solution of $LiI·H_2O$ (0.455 g, 3.0 mmol) to produce a cream precipitate. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 78%.

Cu(dto)(SCN). The salt $Cu[NO_3]_2·3H_2O$ (0.242 g, 1.0 mmol) was dissolved in acetone and dto (0.150 g, 1.0 mmol) was added to give a dark green solution. Potassium thiocyanate (0.195 g, 2.0 mmol) was slowly added as an acetone solution to give a dark red solution and a white precipitate of $K[NO_3]$. The white precipitate was filtered off, and the red filtrate was treated with a few drops of H_3PO_2 until the solution became colourless and was then left to stand. White crystals precipitated and these were filtered off after 15 min, washed with diethyl ether, and dried *in vacuo*, yield 79%.

Reactivity Studies.—The displacement reactions were carried out under similar conditions and are typified by the following examples. Products were characterized by elemental analysis and m.p.s and by a comparison of their i.r. and electronic spectra with those of authentic samples.

Reaction of $CuCl_2$(dto) *with pyridine*. The complex (0.142 g, 0.5 mmol) was dissolved in methanol and a two-fold excess (0.08 g) of pyridine was added slowly to give a teal-blue precipitate. The precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 99%.

Reaction of $CuCl_2$(dto) *with* PPh_3. The complex (0.071 g, 0.25 mmol) was dissolved in methanol and PPh_3 (0.262 g, 1.0 mmol) was added slowly as a solution in ethanol–methanol (1 : 1). A clear solution resulted which on standing overnight yielded white crystals of $CuCl(PPh_3)_3$. These were filtered off, washed with diethyl ether, and dried *in vacuo*, yield 70%. A similar reaction using 0.5 mmol of PPh_3 yielded the complex $[(CuCl)_2(PPh_3)_3]$.

The complex $CuCl(PPh_3)$(dth).—Finely ground CuCl(dth) (0.110 g, 0.5 mmol) was suspended in methanol and PPh_3 (0.131 g, 0.5 mmol) was added as a warm solution in methanol–ethanol (1 : 1). The mixture was warmed gently until the majority of the suspended material had dissolved, was filtered, and then allowed to cool. A white crystalline product formed which was filtered off, washed with diethyl ether, and dried *in vacuo*, yield 51%. N.m.r. (τ) in $CDCl_3$: 7.89(CH_3), 7.27 (CH_2), and 2.65 (Ph), with the expected intensity.

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