Sulphur Ligand Metal Complexes.
Part 15. [1]. Sulphur–Nitrogen Donor Ligand Complexes of Copper

ERIC W. AINSCOUGH*, ANDREW M. BRODIE* and NIGEL G. LARSEN+

Department of Chemistry, Biochemistry and Biophysics, Massey University, Palmerston North, New Zealand

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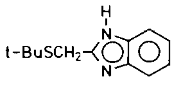
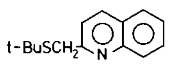
The interaction of the following nitrogen–sulphur donor ligands with copper has been investigated: 2-(3,3-dimethyl-2-thiabutyl)benzimidazole (L^1)*, 2-(3,3-dimethyl-2-thiabutyl)quinoline* (L^2)*, 2-ethylthioethylamine* (L^3)*, 2-(2-thiabutyl)pyridine* (L^4)*, 2-(2-pentafluorophenyl-2-thiaethyl)pyridine* (L^5)*, 2-methylthio-2-imidazoline* (L^6)*, and 2-methylthiobenzimidazole* (L^7)*. The copper(II) complexes* $CuLX_2$ ($L = L^1$, L^2, L^3 *or* L^4, $X = Cl$ *or* Br), $CuL_2X_2{\cdot}H_2O$ ($L = L^1$, $X = ClO_4$; $L = L^7$, $X = BF_4$), CuL_2X_2 ($L = L^3$, L^5 *or* L^7, $X = Cl$ *or* Br; $L = L^3$ *or* L^4, $X = BF_4$; $L = L^3$, $X = ClO_4$; $L = L^7$, $X = NO_3$), $[CuL_2X]BF_4$ ($L = L^3$, $X = Cl$; $L = L^4$, $X = Br$), $CuL^3_2(SO_4)$, $CuL^6_4X_2$ ($X = Cl$, Br *or* BF_4) *and the copper(I) complexes* CuL^2Br, $Cu(L^2H)Br_2$ *and* $CuL^2_2(ClO_4)$ *have been isolated and structures proposed on the basis of conductivity, infrared, electronic and e.s.r. spectral measurements. The study shows that the use of sterically bulky thioether ligands can induce Cu(II) to adopt a pseudo-tetrahedral coordination as in the complexes* $CuLX_2$ ($L = L^1$ *or* L^2, $X = Cl$ *or* Br)*. In the ligands* L^5, L^6 *and* L^7*, the thioether sulphur does not coordinate strongly to Cu(II) if at all. E.s.r. data indicate that the Cu(II) complexes undergo extensive solvation and dissociation in methanol.*

Introduction

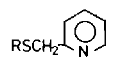
Our studies [2, 3] and those of others [4–12], have shown that copper–thioether interactions are remarkably flexible. Bond lengths vary widely (2.28–2.61 Å), as do the angles at the sulphur atoms (92–120°), and sulphur ligands may be monodentate or bridging. These are features which make methionine thioether sulphur an ideal ligand in the blue copper proteins, plastocyanin [13] and azurin [14], as geometrical and oxidation state changes can be easily accommodated during redox processes. In order to explore the flexibility of thioether ligands further, we have studied the copper complexes of the sulphur–nitrogen donor ligands, L^1–L^7, shown below. The complexes these ligands form with copper(II) halides emphasize their different bonding characteristics. For instance, spectroscopic evidence indicates


L^1

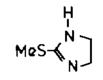

L^2

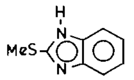
$EtSCH_2CH_2NH_2$

L^3


L^4 R = Et

L^5 R = C_6F_5


L^6


L^7

that the complexes $CuLX_2$ ($L = L^1$ or L^2, $X = Cl$ or Br) are pseudo-tetrahedral, whereas the less sterically bulky ligands, L^3 and L^4, do not give rise to this geometrical type. In the $CuL^5_2X_2$ ($X = Cl$ or Br) complexes, the presence of the electron withdrawing pentafluorophenyl substituent on the thioether sulphur, reduces its donor properties so that the ligand acts as a nitrogen donor only. Similarly, the thioether sulphur does not interact with copper, in the complexes $CuL^6_4X_2$ ($X = Cl$ or Br) and $CuL^7_2X_2$ ($X = Cl$ or Br), but this is presumably related mainly to steric factors. Also included in this report are a variety of other copper(II) L^1–L^7 ligand complexes, where the anion is ClO_4^-, BF_4^-, SO_4^{2-} or NO_3^-, and some copper(I) L^2 ligand complexes. Structures are proposed on the basis of physicochemical studies.

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*Authors to whom correspondence should be addressed.

+Present address: Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007, U.S.A.

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Experimental

Electronic spectra were recorded on a Shimadzu MPS-5000 spectrophotometer. Infrared spectra were obtained on a Beckman IR 20 spectrophotometer (250–4000 cm^{-1}) and a Grubb-Parsons Cube Mark II Interferometer (40–400 cm^{-1}). Electron spin resonance spectra were measured at 77 K on a Varian E 104A instrument, spectral g values being calibrated with a DPPH standard. Conductivities were measured at room temperature with a Philips PR9500 conductivity meter and PW9510 cell. Microanalyses were by Professor A. D. Campbell, University of Otago. All solvents were purified according to established procedures.

The ligands

2-(3,3-Dimethyl-2-thiabutyl)benzimidazole (L^1) was prepared from 2-chloromethylbenzimidazole (Aldrich Chemical Co.) and t-butylthiolate, following a method similar to that described for 2-(3,3-dimethyl-2-thiabutyl)-pyridine [2], and recrystallized from ethanol, m.p. 189–93 °C(dec). 2-(3,3-Dimethyl-2-thiabutyl)quinoline (L^2) was similarly prepared from 2-chloromethylquinoline hydrochloride (Aldrich Chemical Co.), and recrystallized from ethanol at −78 °C, m.p. 51–7 °C. The ligand L^2 decomposes over a period of one month and hence should be freshly prepared. The L^2 complexes are similarly unstable. 2-Ethylthioethylamine (L^3) and 2-methylthio-2-imidazoline (L^6) were purchased as their hydrochloride (L^3) and hydroiodide (L^6) salts, from B.D.H. Chemicals Ltd. and Aldrich Chemical Co. respectively. Neutralization of the salts with aqueous 2 *M* NaOH, followed by diethylether extraction, yielded the free ligands. 2-(2-Thiabutyl)pyridine (L^4) and 2-(2-pentafluorophenyl-2-thiaethyl)pyridine (L^5) were prepared from 2-picolylchloride hydrochloride (Aldrich Chemical Co.) and the appropriate thiolate, as for L^1. The ligands L^3–L^5 were all freshly distilled under reduced pressure before use, L^6 was recrystallized from diethylether and 2-methylthiobenzimidazole (L^7) was used as purchased (Aldrich Chemical Co.).

Preparation of the Copper(II) Complexes

These were generally obtained by similar methods using the appropriate copper salt and ligand in the desired molar ratios. The following is a typical preparation.

To copper(II) chloride dihydrate (0.241 g, 1.4 mmol), dissolved in the minimum volume of ethanol, was added the ligand L^1 (0.312 g, 1.4 mmol) dissolved in the same solvent. Crystals of the product, which formed on standing at room temperature, were filtered off, washed with ethanol, diethylether, and dried *in vacuo*. Yield 0.449 g (89%).

If crystallization of the complex did not occur after *ca.* 30 min, the solution was concentrated using a rotary evaporator, cooled and diethylether added. In the case of $CuL^1_2(ClO_4)_2 \cdot H_2O$ and $CuL^7_4(BF_4)_2 \cdot$-H_2O, the reactants were dissolved in acetone. For the complexes CuL^3X_2 (X = Cl or Br), it was necessary to use excess copper halide, and for $CuL^3_2X_2$ (X = Cl or Br), to add the copper salt to excess ligand. For the L^6 ligand complexes, the small quantity of a gelatinous precipitate which formed initially on mixing the reactants, was removed by filtration, before leaving the solutions to stand at 4 °C.

[CuL$_2$X]BF$_4$ (L = L^3, X = Cl; L = L^4, X = Br)

To copper(II) tetrafluoroborate hexahydrate (0.345 g, 1.0 mmol), dissolved in ethanol containing the ligand L^3 (0.201 g, 2.0 mmol), was added LiCl (0.040 g, 0.9 mmol), dissolved in an ethanol–acetone mixture. The total volume at this stage was 60 cm^3, in order to avoid precipitation of $CuL^3_2(BF)_4)_2$ and $CuL^3_nCl_2$ (n = 1 or 2). The solution was concentrated, using a rotary evaporator, cooled, and rapid crystallization induced by scratching with a glass rod. The crude complex, $[CuL^3_2Cl]BF_4$, was recrystallized from the minimum volume of ethanol. Yield 0.104 g (26%). $[CuL^4_2Br]BF_4$ was similarly prepared by warming LiBr and $CuL^4_2(BF_4)_2$ in acetone.

Preparation of the Copper(I) Complexes

CuL^{2}Br

The ligand L^2 (0.231 g, 1.0 mmol) was slowly added to a filtered ethanol solution of copper(I) bromide (0.143 g, 1.0 mmol) containing excess LiBr. On standing, crystals of the product formed which were washed with ethanol and dried *in vacuo*. Yield 0.194 g (52%).

Cu(L^{2}H)Br$_2$

To CuL^2Br_2 (0.454 g, 1 mmol), suspended in warm methanol, was added hypophosphorous acid (5 drops). After the copper(II) complex dissolved, the product precipitated out. Yield 0.094 g (25%).

CuL$^2_2$(ClO$_4$)

To copper(II) perchlorate hexahydrate (0.370 g, 1.0 mmol) in ethanol, was added the ligand L^2 (0.462 g, 1.0 mmol). The resulting green solution was filtered, concentrated using a rotary evaporator, and cooled to give a brown oil, which solidified on scratching with a glass rod. Recrystallization was achieved from ethanol.

Results and Discussion

Copper(II) Complexes

The copper(II) complexes were prepared by the reaction of the ligands L^1–L^7 with the appropriate metal salt, generally in ethanol. Details are given in the Experimental Section and analytical data, colours and melting points of the complexes are listed in Table I. Except in the case of the ligands L^3 and L^6, the resulting metal–ligand stoichiometries of the isolated complexes were independent of reactant metal–ligand ratios.

The complexes $CuLX_2$ ($L = L^1$ or L^2, $X = Cl$ or Br)

These complexes are essentially non-electrolytes in acetone or nitromethane (Table II) and exhibit spectral properties consistent with a pseudo-tetrahedral arrangement of the ligands about the Cu(II). In particular the observation of d–d bands in the near i.r. region (Table III) is characteristic of this geometry [15–19]. The spectra are similar to those reported for complexes where a $CuCl_2N_2$ pseudo-tetrahedral donor set has been confirmed by X-ray crystallography. For example, the solid state spectrum of Cu[2-(2-dimethylaminoethyl)pyridine]Cl_2 has d–d bands at 800 and 1030 nm [20]. In the i.r. (Table II) bands assignable to essentially Cu–X stretching frequencies appear in the regions expected for terminal Cu–X bonds [21, 22]. E.s.r. parameters, obtained from frozen solutions, are also given in Table II. The values of the hyperfine coupling constant, $A_{/\!/}$, of around $140–150 \times 10^{-4}$ cm^{-1} are not as low as has often been found for distorted tetrahedral complexes of copper(II) ($<130 \times 10^{-4}$ cm^{-1}) [23–28]. It has been suggested that the ratio $g_{/\!/}/A_{/\!/}$ is a convenient guide to estimating the degree of distortion towards a tetrahedral geometry in four coordinate copper(II) complexes [29]. For square planar complexes, the ratio lies between the range 105 to 135 cm, while larger values (*ca.* 200 cm) are expected when a tetrahedral distortion is introduced into the chromophore. For example, the value for Cu[2-(2-dimethylaminoethyl)pyridine]Cl_2 is 236 cm [30]. The lower $g_{/\!/}/A_{/\!/}$ ratios found for the present

TABLE I. Colours, Analytical Data, and Melting Points, for the Complexes.

Complex	Colour	Analyses^a (%)				M.p. (°C)
		C	H	N	X	
CuL^1Cl_2	orange	40.7(40.6)	4.8(4.55)	7.8(7.9)	19.7(20.0)	140
CuL^1Br_2	brown	32.75(32.5)	3.8(3.6)	6.4(6.3)	35.6(36.0)	180–4
$CuL^1_2(ClO_4)_2 \cdot H_2O$	brown	40.0(40.0)	4.8(4.75)	7.5(7.8)	9.2(9.8)	130–3
CuL^2Cl_2	brown	46.0(46.0)	4.6(4.7)	4.0(3.8)	19.1(19.4)	110–2
CuL^2Br_2	black	37.1(37.0)	3.7(3.8)	3.35(3.1)	35.4(35.15)	99–101
CuL^2Br	yellow	44.6(44.9)	4.4(4.6)	3.9(3.7)		198–200
$Cu(L^2H)Br_2$	gold	36.9(36.9)	4.0(3.7)	3.1(3.2)		98–9
$CuL^2_2(ClO_4)$	orange	53.4(53.75)	5.7(5.5)	4.5(4.5)		^{b}
CuL^3Cl_2	blue	20.3(20.05)	4.8(4.6)		29.25(29.6)	122–3
CuL^3Br_2	green	14.4(14.6)	3.5(3.4)	4.3(4.3)		109–11
$CuL^3_2Cl_2$	blue green	28.0(27.9)	6.7(6.4)	8.0(8.1)		114–6
$CuL^3_2Br_2$	green	22.4(22.15)	5.2(5.1)	6.2(6.5)		115–8
$CuL^3_2(ClO_4)_2$	purple	20.6(20.8)	4.9(4.8)		15.1(15.3)	^{b}
$CuL^3_2(BF_4)_2$	purple	21.6(21.5)	5.2(4.95)	6.3(6.3)		175–7
$CuL^3_2(SO_4)$	blue green	26.3(26.7)	6.1(6.2)	7.3(7.8)		178–80
$[CuL^3_2Cl]BF_4$	blue	23.7(24.25)	5.5(5.6)	6.8(7.1)		114–6
CuL^4Cl_2	lime green	33.5(33.4)	3.9(3.85)	5.2(4.9)	24.8(24.7)	154–7
CuL^4Br_2	brown	25.4(25.55)	2.9(2.9)	3.8(3.7)		139–41
$CuL^4_2(BF_4)_2$	green	35.2(35.3)	4.1(4.1)	5.15(5.1)		211–4
$[CuL^4_2Br]BF_4$	green	35.6(35.8)	4.4(4.1)	5.0(5.2)		120–5
$CuL^5_2Cl_2$	blue	40.7(40.2)	1.9(1.7)	3.9(3.9)		104–6
$CuL^5_2Br_2$	olive green	35.8(35.8)	1.6(1.5)	3.5(3.5)		99–101
$CuL^6_4Cl_2$	blue	32.5(32.1)	5.6(5.4)	18.7(18.7)		114–6
$CuL^6_4Br_2$	black	28.3(27.9)	5.1(4.7)	16.5(16.3)		101–3
$CuL^6_4(BF_4)_2$	black	27.2(27.4)	4.8(4.6)	15.5(16.0)		119–21
$CuL^7_2Cl_2$	brown	41.6(41.5)	3.6(3.5)	11.9(12.1)	15.4(15.3)	219–22
$CuL^7_2Br_2$	black	35.4(34.8)	3.3(2.9)		28.4(29.0)	205–7
$CuL^7_2(NO_3)_2$	pale green	37.5(37.2)	3.2(3.1)	15.7(16.3)		208–12
$CuL^7_4(BF_4)_2 \cdot H_2O$	brown	42.25(42.1)	3.8(3.8)	11.85(12.3)		^{b}

^{a}Calculated values are given in parentheses. ^{b}Not recorded.

TABLE II. Conductivities, E.s.r., and I.r. Spectral Data for the Complexes.

Complex	Λ^{a} (S cm^2 mol^{-1})		E.s.r. parameters^{b}				ν(M–X)^{c} (cm^{-1})
	$MeNO_2$	Other	$g_{/\!/}$	10^4 $A_{/\!/}$ (cm^{-1})	$g_{\perp}$	State	
CuL^1Cl_2		14^{d}	2.268	153	2.127	d	280
CuL^1Br_2		16^{d}					232
$CuL^1_2(ClO_4)_2 \cdot H_2O$		163^{d}	2.202	164	2.067	g	
CuL^2Cl_2	8	64^{e}	2.412	143	2.108	d	268
CuL^2Br_2	11	75^{e}	2.412	135	2.116	d	230
$CuL^2_2(ClO_4)$	81	27^{f}					
CuL^3Cl_2	13		2.430^{j} 2.372	126 133		e	285,254
CuL^3Br_2			2.430^{j} 2.270	126 146		e	226
$CuL^3_2Cl_2$	21	109^{e}	2.202	175	2.095	h	189,182(sh)^{m}
$CuL^3_2Br_2$	39	116^{e}					163
$CuL^3_2(ClO_4)_2$	127		2.169	154	2.061	d	
$CuL^3_2(BF_4)_2$	150						
$[CuL^3_2Cl]BF_4$	76	136^{e}	2.169	142	2.073^{k}	g	187
CuL^4Cl_2	11	2^{f}	2.214	156	2.101	g	287
CuL^4Br_2	14	3^{f}					
$CuL^4_2(BF_4)_2$	166	37^{f}	2.245	164	2.130	d	
$[CuL^4_2Br]BF_4$	86						
$CuL^5_2Cl_2$	12		2.234	162	2.074	h	
$CuL^5_2Br_2$	13						
$CuL^6_4Cl_2$	64	20^{d}	2.246	186	2.071	g	
$CuL^6_4Br_2$	90	36^{d}	2.234	188	2.067	g	
$CuL^6_4(BF_4)_2$	177	51^{f}	2.251	187^{l}	2.029	d	
$CuL^7_2Cl_2$			2.218(g_1)		2.054(g_2) 2.030(g_3)	i	282
$CuL^7_2Br_2$			2.180		2.060	i	217
$CuL^7_2(NO_3)_2$	29	4^{d}					
$CuL^7_4(BF_4)_2 \cdot H_2O$	146		2.257	188	2.057	d	

[a] For 10^{-3} mol l^{-1} solutions. Values expected for 1:1 electrolytes: 75–95 ($MeNO_2$), 100–140 (acetone), 80–115 (MeOH), and 20–30 ($PhNO_2$). [b] At 77 K. [c] As Nujol mulls; sh = shoulder. [d] In acetone. [e] In MeOH. [f] In $PhNO_2$. [g] In $MeNO_2$. [h] In CH_2Cl_2. [i] Solid. [j] Assigned to $Cu(MeOH)_6^{2+}$ ion. [k] $A_{\perp}$ 92 × 10^{-4} cm^{-1}. [l] A_N 16 gauss. [m] Shoulder due to solid state or isotopic effects.

complexes (CuL^1Cl_2 148, CuL^2Cl_2 169, and CuL^2Br_2 179 cm) would suggest that in solution they are best described as having a flattened tetrahedral geometry. The e.s.r. spectrum of CuL^1Br_2 in nitromethane is poorly resolved, but two species appear to be present and in acetone an extra band at 640 nm (ϵ = 380 l mol^{-1} cm^{-1}), not seen in the solid state electronic spectrum appears, suggestive of square planar or tetragonal copper(II). The coexistence of two distinct chromophores, one tetrahedral and one tetragonal, has been postulated previously for the complex dibromobis(dehydrodithizone)copper(II) [31]. Assignments of ligand to metal charge transfer (LMCT) absorptions (Table III) are consistent with other work [3, 32], however it has been recently pointed out that π(N) → Cu bands ($\epsilon \sim 2000$ l mol^{-1} cm^{-1}) for tetrahedral imidazole type Cu(II) complexes can occur near 400 nm [33]. Since this is in the expected region for σ(S) → Cu LMCT absorptions the assignments in Table III must be regarded as tentative until further studies are carried out.

It is of interest to compare the present complexes $CuLX_2$ ($L = L^1$ or L^2, X = Cl or Br) with those prepared by Livingstone *et al.* in an earlier study, using 8-methylthioquinoline [34] and 2-methyl-8-methylthioquinoline [35]. Only with the latter ligand were pseudo-tetrahedral, $CuLX_2$ complexes

TABLE III. Electronic Spectral Data for the Complexes.

Complex	Absorption maxima (nm)^a			Assignment
	Solid	CH_2Cl_2	Me_2CO	
CuL^1Cl_2	420		453(730)	σ(S) → Cu
	850		930(170)^b	d–d
	1150(sh)			d–d
CuL^1Br_2			435(1840)	σ(S) → Cu + Br → Cu
	540		580(542)	Br → Cu
			650(sh)(380)	d–d
	850		980(312)	d–d
	1300		1250(sh)(190)	d–d
$CuL^1_2(ClO_4)_2\cdot H_2O$	410			π(N) → Cu
	480(sh)			σ(S) → Cu
	790(sh)			d–d
CuL^2Cl_2	395(sh)	395(2190)		Cl → Cu
	410(sh)	435(sh)(1450)		σ(S) → Cu
	540			π(S) → Cu
	850	800(sh)(165)		d–d
	1200	1075(201)		d–d
CuL^2Br_2		362(sh)(3880)		Br → Cu
	495	450(sh)(2130)		σ(S) → Cu + Br → Cu
	615	592(564)		Br → Cu
	850	770(269)		d–d
	1460	1150(298)		d–d
CuL^3Cl_2	360^b			σ(S) → Cu + Cl → Cu
	770^b			d–d
CuL^3Br_2	455			Br → Cu
	790^b			d–d
$CuL^3_2Cl_2$	370			σ(S) → Cu
	688	750(238)		d–d
	1120(sh)			d–d
$CuL^3_2Br_2$	405^b	360(sh)^c		σ(S) → Cu
	647	750^b		d–d
	850(sh)			d–d
$CuL^3_2(ClO_4)_2$	355	345^c		σ(S) → Cu
	385(sh)			σ(S) → Cu
	537^b	560		d–d
$CuL^3_2(BF_4)_2$	360	341^c		σ(S) → Cu
	390(sh)			σ(S) → Cu
	535^b	560		d–d
$[CuL^3_2Cl]BF_4$	385	350(3348)		σ(S) → Cu
	680	720(262)^b		d–d
	812			d–d
CuL^4Cl_2	355(sh)	354(2900)		Cl → Cu
	416	433(1400)		σ(S) → Cu
	790^b	770(175)^b		d–d
CuL^4Br_2	350(sh)	348(5100)		Br → Cu
	415(sh)	420(sh)(2290)		σ(S) → Cu + Br → Cu
	520	553(700)		Br → Cu
	780^b	750(370)^b		d–d
$CuL^4_2(BF_4)_2$	412	372(6100)		σ(S) → Cu
	602	625(350)		d–d

(Continued overleaf)

TABLE III *(continued)*

Complex	Absorption maxima (nm)[a]			Assignment
	Solid	CH_2Cl_2	Me_2CO	
$[CuL^4_2Br]BF_4$	390	360(4450)		Br → Cu
		405(sh)(2330)		σ(S) → Cu + Br → Cu
	785	800(590)		d–d
	925(sh)	925(sh)(490)		d–d
$CuL^5_2Cl_2$	355(sh)			Cl → Cu
		437(sh)(290)		π(N) → Cu ?
	740	790(110)		d–d
$CuL^5_2Br_2$	366			Br → Cu
	435(sh)			Br → Cu
	705			d–d
$CuL^6_4Cl_2$	367	418	427(1055)	π(N) → Cu
	675	850	825(150)	d–d
$CuL^6_4Br_2$	380(sh)		415(sh)[c]	π(N) → Cu + Br → Cu
	475		450(sh)	Br → Cu
	770		820	d–d
$CuL^6_4(BF_4)_2$	492			σ(S) → Cu
	830		665(78)	d–d
$CuL^7_2Cl_2$	500(sh)			d–d
	620			d–d
	750(sh)			d–d
$CuL^7_2Br_2$	418			Br → Cu
	515(sh)			d–d
	640(sh)			d–d
	720(sh)			d–d
$CuL^7_2(NO_3)_2$	435(sh)			π(N) → Cu
	705		680(90)	d–d
$CuL^7_4(BF_4)_2 \cdot H_2O$	385			π(N) → Cu
	555(sh)		540	d–d

[a] Absorption coefficients (ϵ/l mol^{-1} cm^{-1}) are given in parentheses; sh = shoulder. [b] Asymmetric maximum. [c] Insufficiently soluble to record ϵ.

obtained, and this was explained in terms of steric repulsion between the hydrogen atoms of the 2-methyl groups and the halogen ligands impeding square planar coordination. In the present work, use of the sterically bulky L^1 and L^2 ligands has achieved the same result.

The complex $CuL^1_2(ClO_4)_2 \cdot H_2O$

Attempts to prepare a copper(II) perchlorate complex with the ligand L^2 were unsuccessful, but with L^1 a brown solid, $CuL^1_2(ClO_4)_2 \cdot H_2O$ was obtained. Overall, the spectral data (Tables II and III) point to this complex being five coordinate with a water molecule in the fifth position. A distorted square pyramidal geometry is likely since the e.s.r. spectrum is not of the 'reversed type' expected for a trigonal bipyramidal environment about the copper(II) [36–38]. An N_2S_2O coordination sphere, where S is a thioether is not uncommon for Cu(II). For example [Cu{1,8-bis(2-pyridyl)-3,6-dithiaoctane}ClO_4]ClO_4 is square pyramidal [12] and [Cu{2-pyridylmethylbis(2-ethylthioethyl)amine}SO_4] is distorted trigonal bipyramidal [39].

The complexes $CuL^3_2X_2$ ($X = ClO_4$, BF_4, Cl or Br), $[CuL^3_2Cl]BF_4$ and CuL^3X_2 (X = Cl or Br)

Some time ago Uhlig *et al.* prepared a series of copper complexes with the ligand $MeSCH_2CH_2NH_2$, which is the methyl substituted analogue of L^3, however no spectroscopic data were reported [40]. Subsequently the X-ray structure of $Cu(MeSCH_2CH_2NH_2)_2(ClO_4)_2$ was determined, and showed the copper(II) to have a tetragonal coordination with a *trans*- CuN_2S_2 unit and weakly coordinated ClO_4^- ions [8]. The electronic spectrum of the complex was reported in a separate paper [32]. The similarity of the electronic spectra of the complexes $CuL^3_2X_2$ ($X = ClO_4$ or BF_4) (Table III) and the above complex would suggest that the L^3 ligand complexes also have the same structure as the methyl analogue. Infrared spectral data support weak anion coordination [41, 42] with the ν_3 modes of the ClO_4^- and BF_4^- ions both showing a slight splitting. (For $CuL_2^3(ClO_4)_2$-$\nu_3(ClO_4^-)$ 1097, 1052 cm^{-1}, and for $CuL_2^3(BF_4)_2$-$\nu_3(BF_4^-)$ 1052, 1020 cm^{-1}.) As for all the L^3 complexes, the ν(N–H) absorptions show significant shifts (50–100 cm^{-1}) to lower wavenumbers from the free ligand values, thus confirming nitrogen coordination.

The bis ligand complexes $CuL_2^3X_2$ (X = Cl or Br) also appear to have a tetragonal geometry with the halogens bound *trans* to each other. The ligand field maxima (Table III) are red shifted in relation to the spectra of the complexes $CuL_2^3X_2$ (X = ClO_4 or BF_4) and a low energy shoulder appears; factors which are consistent with the complexes having a *trans* tetragonal structure where the anions occupy the axial coordination positions [43, 44]. This conclusion is supported by the far i.r. data, since no bands assignable to ν(Cu–X) are seen above 200 cm^{-1} (Table II). In general ν(Cu–X) frequencies will be found below 200 cm^{-1} if the Cu–X bonds are axial [21, 43]. Furthermore, the absence of bands near 500 nm in the visible spectrum of $CuL_2^3Br_2$, assignable to Br → Cu LMCT [32] also indicates the Cu–Br bonds are probably axial, rather than equatorial. The e.s.r. spectrum (Table II) of $CuL_2^3Cl_2$, in CH_2Cl_2 solution, is of axial character, the $A_{/\!/}$ parameter having a typical tetragonal value of 175×10^{-4} cm^{-1}.

The complex $[CuL_2^3Cl]BF_4$ also appears to have a tetragonal like structure in the solid state, with an axial Cu–Cl bond (ν(Cu–Cl) at 187 cm^{-1}) and weak BF_4^- ion coordination ($\nu_3(BF_4^-)$ split with bands at 1100 and 1030 cm^{-1}) [41]. In nitromethane $[CuL_2^3Cl]BF_4$ is a 1:1 electrolyte (Table II) and the e.s.r. spectrum (Table II) is indicative of a geometry intermediate beween square pyramidal and trigonal bipyramidal. The low field region approximates tetragonal copper(II), but with $A_{/\!/}$ lower than the normal tetragonal value of $150–200 \times 10^{-4}$ cm^{-1}, while the high field region is more spread out [36].

The low solubility of the mono ligand complexes CuL^3X_2 (X = Cl or Br) would tend to favour a polymeric structure (with tetragonal copper(II) as in Cu(en)X_2 (en = $H_2NCH_2CH_2NH_2$, X = Cl or Br) [45, 46]) rather than a dimeric one (with square pyramidal copper(II) as in $[CuLBr_2]_2$ (L = 2-(3,3-dimethyl-2-thiabutyl)pyridine) [3]). From spectral data alone, it is difficult to distinguish these geometries. It is clear that in methanol solution the complexes break down as the major species seen in the e.s.r. spectrum has $g_{/\!/}$ 2.430 and $A_{/\!/}$ 126×10^{-4} cm^{-1}, values characteristic of the $Cu(MeOH)_6^{2+}$ ion [3].

Tentative assignments for ligand to metal charge transfer absorptions (Table III) are consistent with previous work on related complexes [3, 32]. In all cases an intense band assignable to σ(S) → Cu LMCT is observed in the region expected (380–450 nm) for complexes containing equatorial Cu–S (thioether) bonds (Cu–S distance ~ 2.3 Å). For a structurally related series CuL_2X_2 (where L is an N–S (thioether) ligand and X = ClO_4 or BF_4) the wavelength of the σ(S) → Cu band reflects the nature of the nitrogen donor ligand. For the complexes CuL_2X_2 (L = L^3 or $MeSCH_2CH_2NH_2$ [32]) the nitrogen donor is an aliphatic amine and the band is ⩽ 390 nm but for the complexes CuL_2X_2 (L = L^4 or 2-(3,3-dimethyl-2-thiabutyl)pyridine [1]) the nitrogen donor is a 2-substituted pyridine and the band occurs in the 410–435 nm region (solid state spectra). The energy of the σ(S) → Cu LMCT band is dependent on the basicity of the nitrogen coligand, the more basic aliphatic nitrogen donor increasing the electron build up on the copper ion and hence the charge transfer band increases in energy. Similar trends have been observed for π(O) → Cu LMCT absorptions in a series of copper(II) phenoxide complexes [47].

The complexes $CuL_2^4BF_4)_2$, CuL^4X_2 (X = Cl or Br), $[CuL_2^4Br]BF_4$ and $CuL_2^5X_2$ (X = Cl or Br)

Earlier studies by Livingstone *et al.* on the copper complexes of 2-(2-thiapropyl)pyridine, which is the methyl substituted analogue of L^4, indicated that it behaved as an S–N chelate [48], and recently we studied 2-(3,3-dimethyl-2-thiabutyl)pyridine, which is the t-butyl analogue [1, 3]. An X-ray structure on the complex $[CuLBr_2]_2$ (L = 2-(3,3-dimethyl-2-thiabutyl)pyridine), confirmed copper(II)–thioether coordination [3]. Spectroscopic data on the L^4 ligand complexes indicate that their structures are similar to the t-butyl substituted thioether analogues *viz.* $CuL_2^4(BF_4)_2$ tetragonal with weak BF_4^- coordination ($\nu_3(BF_4^-)$ 1095, 1036, 986 cm^{-1}), $[CuL_2^4Br]BF_4$ square pyramidal with noncoordinated BF_4^- ions ($\nu_3(BF_4^-)$ unsplit at 1055 cm^{-1}), and CuL^4X_2 (X = Cl or Br) dimeric square pyramidal with halogen bridges. With the ligand L^5 it was of interest to see whether or not the pentafluorophenyl substituted thioether sulphur was coordinated to copper(II). Previous studies with L^5 showed that the sulphur coordinates to soft metal centres, as in $WL^5(CO)_4$ [49] and ML^5Cl_2 (M = Pd or Pt) [50], however it does not appear to coordinate strongly to Cu(II). Equatorial thioether–copper(II) bonds result in a prominent (ϵ ~ 1000 l mol^{-1} cm^{-1}) σ(S) → Cu charge transfer band near 400 nm [3, 32] such as exhibited by the L^4 ligand complexes (Table III) but not by $CuL_2^5X_2$ (X = Cl or Br). The observation of d–d bands at wavelengths longer than 700 nm (Table III) suggests the complexes may be five coordinate dimers formed by halogen bridges linking CuN_2X_2 units together, as found in the complexes [Cu(2-methylpyridine)$_2X_2$]$_2$ (X = Cl or Br) for example [51, 52]. A monomeric structure, with weak axial Cu–S bonding cannot be completely ruled out, as this would be difficult to detect spectroscopically [53] but a polymeric structure with six coordinate Cu as in Cu(pyridine)$_2$X$_2$ (X = Cl or Br) is unlikely, since the substitution of pyridine at the two position tends to block coordination of halogen ligands at the sixth copper binding site [51, 52, 54].

The complexes $CuL^6_4X_2$ (X = BF_4, Cl or Br), $CuL^7_4(BF_4)_2 \cdot H_2O$ and $CuL^7_2X_2$ (X = Cl, Br or NO_3)

With L^6 (2-methylthio-2-imidazoline), the tetrakis ligand complexes $CuL^6_4X_2$ (X = Cl, Br or BF$_4$) were isolated, whereas with L^7 (2-methylthiobenzimidazole) only the tetrafluoroborate complex $CuL^7_4(BF_4)_2 \cdot H_2O$ was of this type, the others all being bis complexes *viz.* $CuL^7_2X_2$ (X = Cl, Br or NO$_3$). With benzimidazole itself all the complexes isolated by Goodgame and Haines had the formula CuL_4X_2 (L = benzimidazole, X = Cl, Br, NO$_3$ or ClO$_4$) [44], however imidazole and other substituted imidazoles give both 1:2 and 1:4 complexes with Cu(II) [55, 56]. In the i.r. the ν(N–H) stretching frequency moves to higher wave numbers (3300–3200 cm^{-1}) when compared with the free ligand value (*ca.* 3100 cm^{-1} in nujol). This is taken as evidence for the expected [55] coordination of the pyridine nitrogen, rather than the pyrrole nitrogen for all the complexes. In general, this is supported by the absence of strong electronic spectral bands, near 400 nm, assignable to σ(S) → Cu LMCT (Table III). Copper(II) complexes of substituted imidazole ligands are expected to exhibit weak ($\epsilon \sim 200$ l mol^{-1} cm^{-1}) π(N) → Cu LMCT bands near 400 nm, however these can be readily detected in reflectance spectra. σ(N) → Cu MLCT are more intense and normally occur at higher energies in the u.v. region [53]. For the L^6 and L^7 ligand complexes tentative assignments for LMCT bands, consistent with earlier studies [3, 32, 53] are given in Table III.

Spectroscopic data indicate the complexes $CuL^6_4X_2$ (X = Cl or Br) have tetragonal CuN_4X_2 ligand sets, with the d–d bands being similar to those observed for CuL_4X_2 (L = 1,2-dimethylimidazole) complexes [56]. The anion coordination must be weak, as the complexes show appreciable conductivities in nitromethane and nitrobenzene (Table II) indicating partial dissociation. However the observation of an electronic spectral band at 475 nm for $CuL^7_2Br_2$, (not seen for $CuL^7_2Cl_2$) assignable to a Br → Cu LMCT band suggests that at least one Cu–Br must be shorter (*ca.* 2.4 Å) than expected for an axial Cu–Br bond [32]. The complex Cu(imidazole)$_4$I$_2$ has Cu–I distances differing by 0.44 Å [57]. The $CuL^7_2X_2$ (X = Cl or Br) complexes are insoluble in common solvents and hence polymeric distorted octahedral structures are favoured. $CuL^7_2(NO_3)_2$ is a nonelectrolyte in acetone and in the i.r., the observed nitrate bands at 1295 (ν_5) and 1029 cm^{-1} (ν_2) confirm anion coordination [58]. The room temperature magnetic moments, μ_{eff}, for these complexes ($CuL^7_2Cl_2$ 1.87, $CuL^7_2Br_2$ 1.72, and $CuL^7_2(NO_3)_2$ 1.85 B.M.) are normal for copper(II) [59].

With the tetrafluoroborate salts $CuL^6_4(BF_4)_2$ and $CuL^7_4(BF_4)_2 \cdot H_2O$ an interesting difference in ligand coordination behaviour is seen. For $CuL^7_4(BF_4)_2 \cdot H_2O$, in the i.r. the ν_3 band of the BF_4^- ion shows features (1095(sh), 1065, 1012(sh) cm^{-1}) expected for weak coordination, and the observation of a broad d–d band at 555 nm, in the solid state, is similar to that observed for Cu(benzimidazole)$_4$(ClO$_4$)$_2$ (526 and 646(sh) nm) [44]. A tetragonal coordination with a CuN$_4$ unit in the xy plane is therefore likely. In solution the complex is a 1:2 electrolyte but the d–d band is not significantly shifted. In contrast, for $CuL^6_4(BF_4)_2$ in the solid state, i.r. evidence shows the BF_4^- is not coordinated (ν_3 unsplit) and the d–d band is at considerably lower energies (830 nm). Moreover a new band is seen at 490 nm which can be assigned to σ(S) → Cu LMCT. In solution, this latter band is no longer apparent and the d–d band undergoes a blue shift to 665 nm, a value consistent with a $CuN_4(solvent)_2^{2+}$ species being present. It therefore appears that while a Cu–S bond (*ca.* 2.3 Å in length [53]) exists in the solid state, it is no longer present in solution. In a separate experiment, copper(II) chloride was added to L^6 in CDCl$_3$ to give a Cu(II) concentration of 8.9×10^{-4} mol l^{-1}, and the proton n.m.r. spectrum recorded. The S–CH$_3$ proton resonance of the free ligand did not shift and no broadening of the signal could be detected, although the N–H proton resonance moved upfield and the CH$_2$ methylene proton resonance broadened. These results are consistent with the Cu(II) ions interacting with the amine nitrogen but not the thioether sulphur. For the thioether ligand, n-BuSCH$_2$CH$_2$SBu-n in CDCl$_3$, the addition of CuCl$_2$ caused selective broadening of the signals due to the methylene hydrogens adjacent to the S donors, as thioether coordination occurred [32]. The e.s.r. spectra (Table II), in particular the values of the parameters $g_{/\!/}$ and $A_{/\!/}$, of all the L^6 ligand complexes, are normal for copper(II) complexes containing CuN$_4$ chromophores. If sulphur donors were binding in equatorial positions, lower values would be expected [29], comparable to those exhibited by $CuL^1_2(ClO_4)_2 \cdot H_2O$, which has a CuS$_2N_2$ donor set in the xy plane. For $CuL^6_4(BF_4)_2$, nine N superhyperfine lines are observed on the lowest field copper hyperfine line, with the intensity pattern expected for four equivalent nitrogens. A similar superhyperfine structure has also been seen for Cu(1,2-dimethylimidazole)$_4$Cl$_2$ in an ethylene glycol/H$_2$O glass [56].

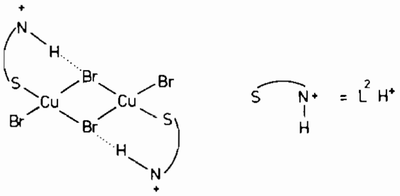
The Solvation and Dissociation of the Cu(II) Complexes in Methanol

It has been pointed out that coordination complexes tend to be subject to solvation and dissociation when dissolved in methanol [60]. Not surprisingly therefore, the mono ligand CuL^3X_2 and $CuL^5_2X_2$ halide complexes in this study all show appreciable conductivity values in methanol and electronic spectral bands undergo considerable changes as compared to solid state spectra. The e.s.r. spectra in frozen methanol show at least two species are present, one of which can be identified as the $Cu(MeOH)_6{}^{2+}$ ion, since it has parameters identical to those observed for a dilute solution of copper(II) chloride dissolved in methanol. ($g_{/\!/}$ 2.430, $A_{/\!/}$ 126×10^{-4} cm^{-1}) [3]. Moreover, dilution of the samples causes an enhancement of the $Cu(MeOH)_6{}^{2+}$ e.s.r. signal relative to the other peaks. The e.s.r. spectra of the bis ligand complexes generally show two species present also, but since neither correspond to the $Cu(MeOH)_6{}^{2+}$ ion, solvation is not as complete with the higher ligand to copper(II) ratio. Representative results for CuL^3X_2 (X = Cl and Br) are given in Table II.

Copper(I) Complexes

The complexes CuL^2Br, $CuL^2_2(ClO_4)$ and $Cu(L^2H)Br_2$

The interaction of L^2 with copper(II) perchlorate causes reduction of the metal, only a copper(I) complex $CuL^2_2(ClO_4)$ being isolated, in contrast to the results found for the other N–S donor ligands (*e.g.* L^3, L^4, and 2-(3,3-dimethyl-2-thiabutyl)pyridine [3]) where copper(II) complexes were obtained. This is presumably a function of the steric requirements of L^2 which forces the metal into a tetrahedral coordination thus facilitating its reduction to copper(I). The complex CuL^2Br was prepared from copper(I) bromide, however if L^2 was reacted with copper(II) bromide in the presence of the protic reducing agent, H_3PO_2, a copper(I) complex, formulated as $Cu(L^2H)Br_2$ was obtained. This complex is another example of a small number of inorganic zwitterions [61, 62] and probably has a dimeric structure, as found by X-ray analysis for the analogous 2-(3,3-dimethyl-2-thiabutyl)pyridine complex [2]. It therefore should be written as $L^2H^+(CuBr_2{}^-)_2L^2H^+$, with the ligand being protonated on the pyridyl nitrogen, and bound to Cu(I) via the thioether sulphur only.



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