The Interaction of 1-Methylimidazoline-2(3*H*)-thione with Copper(II) Salts†

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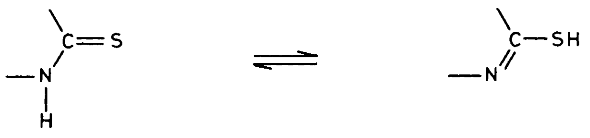
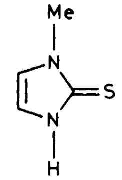
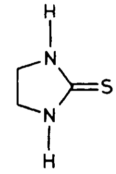
The interaction of 1-methylimidazoline-2(3*H*)-thione (HL^1) with the appropriate copper(II) species in ethanol solution directly produces the blue mixed-valence complexes, $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4]X_2\cdot yH_2O$ (X = O_2CMe or OH, *y* = 2; X = ClO_4 or PF_6, *y* = 0). With $CuCl_2\cdot 2H_2O$ the product is dependent on the HL^1 : Cu molar ratio. If HL^1 was in excess, e.s.r. spectroscopy indicated the formation of a '$Cu^{II}S_4$' species, *viz.* $[Cu(HL^1)_4]^{2+}$, in solution. At a 3:1 (HL^1 : Cu) molar ratio (Cu^{II} added to HL^1) the known copper(I) complex, $[Cu_2(HL^1)_4Cl_2]$ is obtained. However, using a 1.5:1 (HL^1:Cu) molar ratio, and with HL^1 added to Cu^{II}, the product is a mixed-valence complex formulated as $[Cu_2(HL^1)_2Cl_3]$. These compounds, and others obtained with imidazolidine-2-thione (HL^2) and 4,5-diphenylimidazoline-2(3*H*)-thione (HL^3), have been characterized by spectroscopic techniques. In nitromethane solution HL^1 reacts in the presence of copper to yield the chelate N-donor ligand, bis(1-methylimidazol-2-yl) sulphide (L^4) in the dimeric complex $[Cu_2(L^4)_2Cl_4]$.

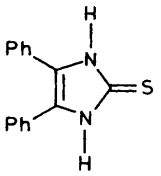
Over the past decade considerable interest has been generated in heterocyclic thioamide ligands.[1] An important feature of such ligands is the 'thione' (*a*) to 'thiol' (*b*) tautomerism. Structural evidence indicates that the thione form (*a*) generally dominates in the solid but in solution, especially just prior to complexation, the tautomeric equilibria can be modified by the nature of the metal salt, the presence of base, or the nature of the solvent. Hence a potentially rich co-ordination chemistry is available. For example, 1-methylimidazoline-2(3*H*)-thione (HL^1) reacts with the appropriate mono- or di-valent copper salts in ethanol to give copper(I) complexes, *viz.* $[Cu_2(HL^1)_4Cl_2]$,[2] $[Cu_2(HL^1)_5]SO_4\cdot 3H_2O$,[3] and $[Cu(HL^1)_3]NO_3$,[4] in which the ligand is in the thione form. By contrast, the reaction of $[Cu(MeCN)_4]ClO_4$ and $[Cu_2(O_2CMe)_4(H_2O)_2]$ with HL^1 in a 1:1 MeCN–MeOH solution, gives an unusual stoicheiometry in the mixed-valence complex $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4][BPh_4]_2\cdot 4MeCN$.[5] This cluster complex contains the anionic ligand L^1 linked to both the Cu^I and Cu^{II} atoms by copper–thiolate bonds.

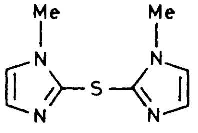

(*a*) (*b*)

In this paper we investigate more fully the interaction of 1-methylimidazoline-2(3*H*)-thione (HL^1) with copper(II) salts, considering the effects the reaction conditions have on the products obtained. In view of the interest in complexes containing copper(II)–thiolate bonds as small-molecule mimics for the 'blue' copper protein metal site,[6] we have examined the conditions required for the formation of the L^1 mixed-valence cluster. We also briefly report on attempts to obtain similar Cu–S interactions using the related heterocyclic thioamides imidazolidine-2-thione (HL^2) and 4,5-diphenylimidazoline-2(3*H*)-thione (HL^3). On transferring to nitromethane as solvent for the $CuCl_2$–HL^1 system, we show that the HL^1 molecule no longer remains intact, but instead the elements of 'H_2S' are lost and the chelate N-donor ligand, bis(1-methylimidazol-2-yl) sulphide (L^4), is formed bound to copper(II) in the complex $[Cu_2(L^4)_2Cl_4]$. This parallels behaviour recently reported[7] in methanol solvent.‡


HL^1


HL^2


HL^3


L^4

Experimental

Electronic spectra were recorded on a Shimidazu MPS-5000 spectrophotometer. Electron spin resonance spectra were measured at 110 K on a Varian E-104A instrument fitted with a Varian E-257 temperature control unit. Spectral *g* values were calibrated with a diphenylpicrylhydrazyl standard. Infrared spectra were obtained on a Pye Unicam SP3-300 instrument. The ligands HL^1, HL^2, and HL^3 were obtained from the Aldrich Chemical Co. and the complex $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4][BPh_4]_2\cdot 4MeCN$ was prepared following the literature method.[5] Microanalyses were by Professor A. D. Campbell, University of Otago and are listed in the Table.

Preparation of the Copper Complexes.—$[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4]X_2\cdot yH_2O$ (X = ClO_4 or PF_6, *y* = 0; X = O_2CMe, *y* = 2). These complexes were all prepared by similar methods, of which the following is typical. To a filtered solution of copper

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† *Non-S.I. units employed:* B.M. = 9.274×10^{-24} J T^{-1}.

‡ We thank a referee for bringing this paper to our attention.

Table. Analytical and electronic spectral data for the complexes

Complex	Analyses (%)[a] C	H	N	$\lambda_{max.}$(nm)[b]
$[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][O_2CMe]_2\cdot 2H_2O$[c]	26.6	3.5	14.2	625 (sh) (2 800), 698 (3 125)[d]
	(26.6)	(3.3)	(14.2)	
$[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][ClO_4]_2$	24.9	2.9	14.1	437 (sh) (1 070), 625 (sh) (3 500), 693 (3 910)[d]
	(24.1)	(2.85)	(14.1)	
$[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][PF_6]_2$	24.1	2.9	13.6	433 (sh) (1 050), 625 (sh) (3 300), 695 (3 680)[d]
	(23.2)	(2.75)	(13.55)	
$[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][OH]_2\cdot 2H_2O$	25.9	3.0	14.9	630, 750 (sh)[e]
	(25.9)	(3.2)	(15.1)	
$[Cu^ICu^{II}(HL^1)_2Cl_3]$	21.45	2.7	12.1[f]	425 (sh), 837[e]
	(20.8)	(2.6)	(12.2)	
$[Cu(L^2)(OH)]$	20.0	3.2	15.7	570[e]
	(19.8)	(3.3)	(15.4)	
$[Cu(L^3)Cl]$	51.4	4.1	7.5[g]	620[e]
	(51.4)	(3.3)	(8.0)	
$[Cu_2(L^4)Cl_4]$	28.7	3.1	16.8[h]	384, 770[e]
	(29.2)	(3.1)	(17.05)	

[a] Calculated values are given in parentheses. [b] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] $\mu_{eff.}$ 1.80 B.M. per Cu^{II}. [d] In $MeNO_2$. [e] As Nujol mull. [f] Cl Found 23.0 (Calc. 23.0%). [g] Cl Found 10.2 (Calc. 10.1%). [h] Cl Found 22.2 (Calc. 21.6%).

acetate hydrate (0.60 g, 3 mmol) in ethanol (30 cm^3) was added slowly an ethanolic solution (15 cm^3) of HL^1 (0.68 g, 6 mmol). To the resulting deep blue solution was added dropwise NH_4PF_6 (0.49 g, 3 mmol) dissolved in ethanol (20 cm^3). After cooling in an ice-bath for 0.5 h the blue solid was filtered off and washed with ethanol and dried under vacuum. For X = O_2CMe, the above procedure was repeated but without the addition of NH_4PF_6. The deep blue solution was placed in an ice-bath for 2 h. For X = ClO_4, the ligand HL^1 (0.68 g, 6 mmol) was added to a solution of sodium (0.14 g, 6 mmol) in ethanol (20 cm^3) before being added to $Cu(ClO_4)_2\cdot 6H_2O$ in ethanol. Yields 30—70%.

$[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][OH]_2\cdot 2H_2O$. To a 1% aqueous ethanol solution of HL^1 (25 cm^3) was added 14 drops of concentrated NH_4OH or n-butylamine. This solution was added dropwise to $CuSO_4\cdot 5H_2O$ in water (20 cm^3). The resulting blue-black precipitate was collected, washed with water, and dried under vacuum. Yield 0.09 g (22%).

$[Cu^ICu^{II}(HL^1)_2Cl_3]$. A solution of HL^1 (1.67 g, 15 mmol) in ethanol (150 cm^3) was added to $CuCl_2\cdot 2H_2O$ (1.73 g, 10 mmol) in ethanol (100 cm^3). The yellow-green precipitate was washed with $CHCl_3$ and ethanol prior to vacuum drying. Yield 1.25 g (55%). When $CuCl_2\cdot 2H_2O$ (0.02 g, 0.10 mmol) in ethanol (2 cm^3) was added to HL^1 (0.20 g, 1.75 mmol) in ethanol (20 cm^3) a bright green solution was obtained. The e.s.r. spectrum was recorded immediately (see Results and Discussion section).

$[Cu(L^2)(OH)]$. A solution of HL^2 (0.41 g, 4 mmol) in water (50 cm^3) containing 28 drops of concentrated NH_4OH was added slowly to $CuSO_4\cdot 5H_2O$ (0.50 g, 2 mmol) in water (30 cm^3). The very fine purple precipitate produced was collected and washed with water. Yield 0.10 g (30%).

$[Cu(L^3)Cl]$. The salt $CuCl_2\cdot 2H_2O$ (0.68 g, 2 mmol) in ethanol (20 cm^3) was added dropwise to HL^3 (1.00 g, 4 mmol) in ethanol (350 cm^3). An intense yellow solution resulted which on standing for 2 h produced a flocculent blue precipitate which was collected and washed with ethanol.

$[Cu_2(L^4)_2Cl_4]$. To 0.37 g (1 mmol) of $CuCl_2\cdot 2H_2O$ in ethanol (5 cm^3) was added 0.23 g (2 mmol) of HL^1 dissolved in nitromethane (30 cm^3). The solution immediately became dark brown but on standing turned green and after 3 d green crystals were deposited. These were recrystallized from nitromethane and dried under vacuum. An identical product was also obtained by dissolving $[Cu^ICu^{II}(HL^1)_2Cl_3]$ in nitromethane and allowing the solution to stand for 1 week. Yield 50%.

Results and Discussion

Ethanol Solvent.—Dobry-Duclaux *et al.*[8] first reported the interaction of 1-methylimidazoline-2(3*H*)-thione (HL^1) with copper salts and formulated the products as $[\{Cu^{II}(L^1)_2\}_2]$ and $[Cu^{II}(Cu^IL^1)_5(L^1)][ClO_4]$, although only the latter complex was isolated. We have reinvestigated the reaction of HL^1 with copper(II) salts in ethanol or aqueous ethanol solvent systems. Using copper(II) acetate dihydrate in a 1:2 molar ratio with HL^1, a dark blue precipitate, formulated on the basis of analytical and spectroscopic data (Table) as $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][O_2CMe]_2\cdot 2H_2O$, was obtained. The close similarity of the e.s.r. and electronic spectral properties of this compound to those of the structurally characterized mixed-valence cluster $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4][BPh_4]_2\cdot 4MeCN$[5] is supportive of the presence of a common complex cation, $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(\text{solvent})_4]^{2+}$. In the presence of copper(II), with anions such as $[PF_6]^-$ and $[ClO_4]^-$, the same mixed-valence cluster dication is formed and the product obtained under basic conditions is similarly formulated as $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4]_2[OH]_2\cdot 2H_2O$.

The electronic spectra for these complexes are given in the Table. The intense absorptions in the visible can be assigned to charge transfer transitions from the nitrogen and sulphur atoms of the anionic L^1 ligand to the copper(II) centres, and in this respect they mimic the spectra of the 'blue' copper proteins.[9,10] For the $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4]^{2+}$ cation the assignments are $\pi(N)\rightarrow Cu^{II}$, 420; $\sigma(S)\rightarrow Cu^{II}$, 635; and $\pi(S)\rightarrow Cu^{II}$, 880 nm (MeCN solvent). The spectra of the other complexes are not always as well resolved as the structurally characterized complex but all are dominated by the intense $\sigma(S)\rightarrow Cu^{II}$ absorption in the 600—700 nm region. The resonance-Raman spectrum was obtained for solid $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4][BPh_4]_2\cdot 4MeCN$ using 647.1 nm excitation (*i.e.* within the electronic absorption envelope). Resonance-enhanced Raman peaks are observed at 151, 201, 316, 440, and 507 cm^{-1}. Assignments are difficult, especially in view of recent papers on 'blue' copper proteins,[10,11] however the bands at 316 cm^{-1} and 440 cm^{-1} are in the range where ν(Cu–N) and ν(Cu–S)

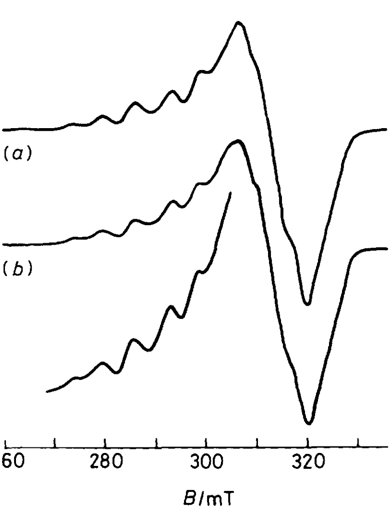

Figure 1. Frozen solution e.s.r. spectra (in nitromethane) of (*a*) $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4][BPh_4]_2 \cdot 4MeCN$ and (*b*) $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(H_2O)_4][ClO_4]_2$

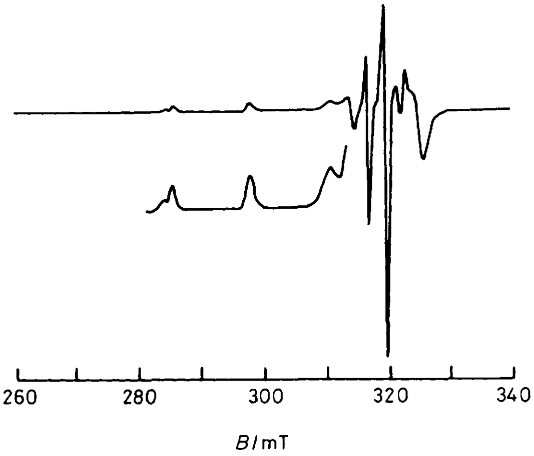

Figure 2. Frozen solution e.s.r. spectrum (in ethanol) of the proposed $[Cu(HL^1)_4]^{2+}$ species

stretches have been assigned in other copper(II)–thiolate compounds.[12]

The e.s.r. spectra, although virtually identical to that observed for the $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(MeCN)_4]^{2+}$ cation cannot be as simply interpreted.[5] A re-examination of the spectrum of the latter complex, recorded as a frozen solution in nitromethane, shows five hyperfine lines in the $g_\parallel$ region with an average splitting of 61 mT (Figure 1) indicative of weak dipolar interactions between the copper(II) centres. Such interactions have been observed in dinuclear copper(II) complexes[13] and dimers.[14] From studies on molecular metal oxides containing Cu^{II} it has been suggested that 10 Å is the upper limit for the distance over which identifiable electronic effects may be transmitted.[15] On ageing, the blue nitromethane solutions turn green and a second e.s.r.-detectable species is observed ($g_\parallel \approx 2.27$, $|A_\parallel| \approx 180 \times 10^{-4}$ cm^{-1}) consistent with Cu^{II} in a nitrogen-donor ligand environment, suggesting reaction of the thiolate form of L^1 to L^4 (see below).

The present study points to a remarkable stability for the $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(solvent)_4]^{2+}$ cation. Although Agnus *et al.*[5] prepared the structurally characterized cluster from a Cu^I–Cu^{II}–HL^1 system, we have shown that addition of a copper(I) reactant is not necessary. In fact, the e.s.r. spectrum reported by Dobry-Duclaux *et al.*[8] on the so called '$[\{Cu^{II}(L^1)_2\}_2]$' complex [obtained in solution from copper(II) acetate and HL^1] corresponds to that of the mixed-valence cluster and the mixed-valence complex isolated by them should be similarly reformulated. Furthermore, we also found that the colourless copper(I) complex, $[Cu_2(HL^1)_4Cl_2]$,[2] when dissolved in water produced a blue solution with the same spectral properties, thus reinforcing the observation that the tendency to form the $[Cu^I_{10}Cu^{II}_2(L^1)_{12}(solvent)_4]^{2+}$ cation, from either Cu^I or Cu^{II} salts and HL^1, is high in the presence of both base (*e.g.* water) and oxygen.

In an attempt to probe further the interaction of HL^1 with copper salts its reaction with $CuCl_2 \cdot 2H_2O$ in ethanol was examined. The actual reaction product obtained depended on the ligand to copper ratio used. For instance, if the ligand was in a large excess an intense green solution was initially observed. The e.s.r. spectrum generated from a frozen sample (Figure 2) indicates the formation of an unstable $[Cu(HL^1)_4]^{2+}$ species with co-ordination of the thione sulphur to Cu^{II}. The observed parameters ($g_\parallel = 2.126$, $|A_\parallel| = 126 \times 10^{-4}$ cm^{-1}, and $g_\perp = 2.023$) are similar to $[CuL_4]^{2+}$ thiourea species (*e.g.* for L = *N*,*N*-dimethyl-*N*′-p-tolylthiourea, $g_\parallel = 2.126$, $|A_\parallel| = 125 \times 10^{-4}$ cm^{-1}, and $g_\perp = 2.031$)[16] and the spectral profile also corresponds to an 'S_4' donor set bound to Cu^{II}.[17] Furthermore, the position of the point arising from the $g_\parallel$ – $|A_\parallel|$ parameters on the 'S_4' delineator on a Blumberg–Peisach plot implies a distortion of $[Cu(HL^1)_4]^{2+}$ towards tetrahedral.[17,18] When the copper is added to HL^1 in a 1 : 3 ($Cu : HL^1$) molar ratio the known copper(I) complex $[Cu_2(HL^1)_4Cl_2]$ was isolated. However, if instead HL^1 is added to the Cu^{II} solution in a 1.5:1 (HL^1:Cu) molar ratio a yellow-green compound, formulated as $[Cu^ICu^{II}(HL^1)_2Cl_3]$ precipitated. The presence of the neutral HL^1 ligand is inferred from the ν(N–H) absorption at 3 100 cm^{-1} and other characteristic thioamide bands in the i.r. spectrum. The magnetic moment of 1.85 B.M. per copper(II) ion at room temperature and the electronic spectrum (425 nm $N \rightarrow Cu^{II}$ or $Cl \rightarrow Cu^{II}$, and 837 nm *d–d*) support the formulation.

Other heterocyclic ligands which have been reported to form mixed-valence complexes with copper have been characterized by *X*-ray crystallography, *viz.* $[Cu^ICu^{II}(mtz)_4Cl_3]$ (mtz = 4-methylthiazole)[19] and $[\{Cu^I_3Cu^{II}(tht)_3Cl_5\}_n]$ (tht = tetrahydrothiophene).[20] Attempts to obtain crystals of $[Cu^ICu^{II}(HL^1)_2Cl_3]$ were unsuccessful as ligand reaction took place (see below). Finally it is noted that from a potentiometric study in aqueous solution, Lenarcik and Wisniewski[21] postulated that the green complex obtained when the metal:ligand molar ratio is greater than 1:1 contains both HL^1 and L^1 bound to copper(II). This is another possible type of product.

In general, especially in ethanol solution, heterocyclic thioamides reduce copper(II) salts to copper(I)[1] although there are exceptions as reported in this study (with HL^1) and elsewhere (with 2-thiazolidinethione)[22] where the copper(II) state has been stabilized. We also find that complexes containing copper(II) can be isolated under certain conditions (see Experimental section for details) with the heterocyclic thiones, HL^2 and HL^3. The complexes have been tentatively formulated as $[Cu^{II}(L^2)(OH)]$ and $[Cu^{II}(L^3)Cl]$ on the basis of analytical and spectroscopic results. Magnetic and spectral data* point to the presence of copper(II) but the low solubility and magnetic moments suggest the complexes are polymeric.

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* For $[Cu^{II}(L^2)(OH)]$ $\mu_{eff.}$ 0.70 B.M.; e.s.r. (aqueous acetone) $g_\parallel$ 2.244, $|A_\parallel|$ 157 × 10^{-4} cm^{-1}, $g_\perp$ 2.097; $\lambda_{max.}$(Nujol) 570 nm. For $[Cu^{II}(L^3)Cl]$ $\mu_{eff.}$ 1.10 B.M.; e.s.r. (solid) g_{iso} 2.063; $\lambda_{max.}$(Nujol) 620 nm.

For $[Cu^{II}(L^2)(OH)]$, a band at 3 345 cm^{-1} in the i.r. spectrum may be assigned to a ν(O–H) stretch of a bridging hydroxy group and the bands arising from the L^2 ligand are similar to those observed for $[Os_3H(CO)_9(L^2)]$ where L^2 is chelating and bridging.[23]

Nitromethane Solvent.—The reaction of HL^1 with $CuCl_2 \cdot 2H_2O$ in nitromethane yielded green crystals. The i.r. spectrum revealed the absence of the ν(N–H) absorption and other bands characteristic of the thioamide chromophore.[24] Other spectral data showed the presence of copper(II) [$\lambda_{max.}$(Nujol) 770 nm (*d–d* band); e.s.r. (nitromethane) $g_{\parallel}$ 2.258, $|A_{\parallel}|$ 172 × 10^{-4} cm^{-1}, $g_{\perp}$ 2.062]. Elemental analyses indicated the loss of sulphur. The same product was obtained from the attempted recrystallization of $[Cu^{I}Cu^{II}(HL^1)_2Cl_3]$ from nitromethane. A single-crystal *X*-ray analysis[25] shows that the complex is $[Cu_2(L^4)_2Cl_4]$ containing the monosulphide of 1-methylimidazoline-2(3*H*)-thione (HL^1), *viz.* bis(1-methylimidazol-2-yl) sulphide (L^4), and is the same as the compound which crystallizes after 6 weeks from the reaction of $CuCl_2 \cdot 2H_2O$ and HL^1 in methanol.[7] The complex consists of a centrosymmetric dichloro-bridged dimer. Each copper atom has a distorted tetragonal-pyramidal geometry, with two chlorine atoms and two nitrogen atoms, from the chelating L^4 ligand in the base and the bridging chlorine at the apex.[7,25]

Mechanistically, L^4 may be formed by the copper(II) oxidation of HL^1 to its disulphide which then loses sulphur. The complex $[Cu_2(L^4)_2Cl_4]$ would arise from the subsequent oxidation of Cu^I. The observation that $[Cu_2(L^4)_2Cl_4]$ forms much more rapidly in nitromethane than methanol (3 d *cf.* 6 weeks) is of interest. We have also observed copper-promoted formation of monosulphides for the thione, benzothiazoline-2-thione, and its 6-ethoxy derivative in pyridine as solvent.[26] These results are in contrast to the reaction of copper(II) salts with thiazolidine-2-thione in nitromethane where we obtained complexes of the ligand 3-(2-thiazolin-2-yl)thiazolidine-2-thione.[27] Further reactivity studies involving other copper salts and different solvents are underway.

Acknowledgements

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