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Asymmetric copper complexes of stable mono-*tert*-butyl monobenzyl dithioether N_2S_2 ligands †

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Attempts to form copper complexes of new N_2S_2 compounds, in which one sulfur donor is a thiolate and the other a thioether, have been made by protecting the potential thiolate through *tert*-butylation and benzylating the other. Whereas earlier work with symmetrical bis(*tert*-butylated thioethers) had shown that de-*tert*-butylation occurs upon co-ordination to copper, to yield the bis(thiolate) complex, this proves not to be the case with these asymmetric compounds. Thus, complexation of *N*-[2-(benzylsulfanyl)benzyl]-*N'*-[2-(*tert*-butylsulfanyl)benzylidene]ethane-1,2-diamine, L^1, and *N*-[2-(benzylsulfanyl)benzyl]-*N'*-{[2-(*tert*-butylsulfanyl)benzyl]ethane-1,2-diamine, L^2, leads to stable copper(I) complexes and in the case of L^1 a stable copper(II) complex as well. The copper(I) perchlorate complexes of L^1 and L^2 have been characterised by X-ray crystallography and both complex cations are found to have distorted-tetrahedral structures [CuN_2–CuS_2 dihedral angles of 74.05(9) and 73.5(2)°, respectively] in which the *tert*-butyl group is retained. The 2-cyanoethyl group has also been investigated as a protecting group for the thiolate moiety in *N*-[(2-benzylsulfanyl)benzyl]-*N'*-[2-(2-cyanoethylsulfanyl)benzylidene]-*N'*-methylethane-1,2-diamine, L^3, which forms a stable complex with copper(II) but not with copper(I). Decyanoethylation of $[CuL^3]^{2+}$ could not be induced.

The binding site for the copper ion in all of the blue copper electron-transport proteins that have been structurally characterised is formed from the convergence of two unsaturated nitrogen atoms, arising from histidine residues, a thiolate sulfur, arising from a cysteine residue and, with the exception of stellacyanin, a thioether sulfur arising from a methionine residue.[1–3] This combination of donor atoms, in the fixed spatial relationship enforced by the structure of the protein, imparts a combination of electronically related properties (intense absorption band near 600 nm, high reduction potential, small hyperfine splitting constant) to the copper ion, which has yet to be simulated using ligands of low molecular weight. One of the difficulties associated with simulating this environment around a copper ion, to facilitate studies of its effect on the metal, stems from the ease with which thiolates undergo oxidative dimerisation to form disulfides, when not spatially isolated. To some extent this has been overcome by the use of sterically hindered thiolates,[4–7] but more commonly aromatic thiols have been used to model cysteine co-ordination owing to the lower tendency that they show towards oxidation, than cysteine itself, or aliphatic thiols in general.[8–11] Nonetheless aromatic thiols when used in this way have commonly, though not always, been protected by *tert*-butylation,[12–20] as a way of pre-empting oxidation during ligand synthesis. This technique appears well suited to this type of work since de-*tert*-butylation commonly occurs upon co-ordination to metal ions of high Lewis acidity such as Ni^{2+}, Cu^{2+}, Zn^{2+} and even Cu^+, forming the desired metal–thiolate bond. The *tert*-butyl group is believed to be lost as isobutene and in reluctant cases this can be encouraged by using refluxing 2-methoxyethanol (b.p. 125 °C) as solvent.[12]

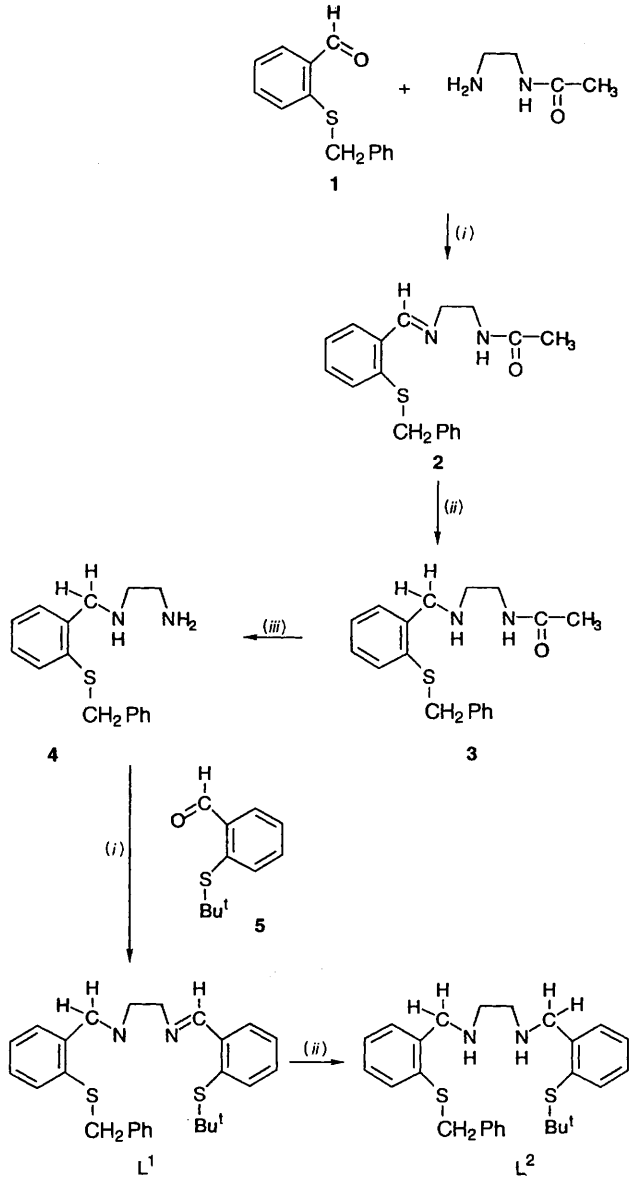
In all reported cases where *tert*-butylation has been used as a technique for thiol protection prior to co-ordination it has ultimately led to the formation of symmetrical ligands the complexes of which contain two thiolate moieties. No case of the use of the *tert*-butyl function as a protecting group in the production of a single metal–thiolate interaction within a complex appears to have been recorded. This is surprising in view of the apparent generality of this protection–deprotection method and the fact that such an approach could lead directly to models for the metal-ion binding site in blue copper proteins. Accordingly, it became the objective of this piece of work to explore the feasibility of using this pathway to synthesise N_2S_2 compounds having both thioether and thiolate sulfur donors. The reaction scheme by which this was to be achieved is shown as Scheme 1. Interestingly, however, the final objective of forming copper complexes with both thiolate and thioether donors was not realised owing to the reluctance of L^1 and L^2 (or L^3, Scheme 2) to undergo de-*tert*-butylation (or decyanoethylation) upon co-ordination to copper(II) or any of the other metal ions mentioned above. We feel that it is of importance to record the progress that we did make with this investigation, however, to demonstrate that it cannot be assumed that de-*tert*-butylation will always accompany co-ordination to copper or zinc and, moreover, that stable *tert*-butyl thioether complexes of copper(I) can be isolated and characterised.

Results and Discussion

Ligand syntheses

Compound **4**, which is the thioether comprising half of L^2, was synthesised by standard techniques using the route shown in Scheme 1. Owing to the tendency of the imine group in **2** to hydrolyse under milder conditions than those necessary to hydrolyse the acetyl protecting group, it was necessary to reduce this prior to deacetylation. This was unfortunate as it prevented the study of asymmetric compounds involving two unsaturated nitrogens atoms (which occur at the blue copper site), however it still permitted the opportunity to examine the chemistry at the sulfur sites in the presence of one or no imino-groups. Condensation of **4** with 2-*tert*-butylsulfanylbenzaldehyde **5** proceeded cleanly giving the protected thiolate L^1, which could then be easily reduced to the more hydrolytically stable diamine L^2 when required.

† *Non-SI units employed:* eV ≈ 1.60 × 10^{-19} J, mmHg ≈ 133 Pa, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.



Scheme 1 (*i*) EtOH; (*ii*) $NaBH_4$; (*iii*) (*a*) HCl, (*b*) NaOH

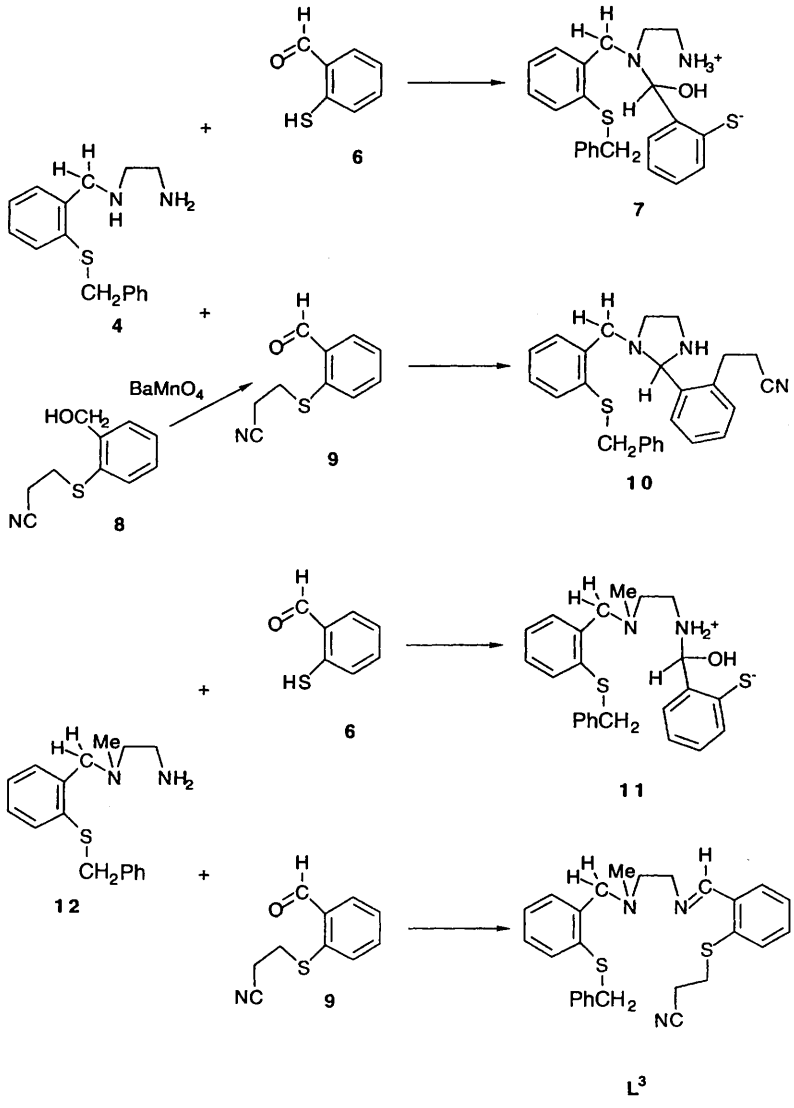
The ease of condensation of compound **4** with 2-*tert*-butylsulfanylbenzaldehyde warrants comment, since analogous reactions performed using 2-sulfanylbenzaldehyde **6**, prepared from 2,2′-dithiodibenzaldehyde, or 2-(2-cyanoethylsulfanyl)-benzaldehyde **9** (Scheme 2), prepared from 2-cyanoethyl-sulfanylbenzenemethanol **8**, did not lead to the analogous imine. Instead these aldehydes gave products which appeared to arise from attack by the secondary amine at the carbonyl group giving rise to a stable hemiaminal **7** in the first case and to the aminal **10** in the second. When the secondary amine was methylated, giving compound **12**, to block hemiaminal or aminal formation involving that nitrogen atom, reaction with **9** gave the desired imine L^3, but with 2-sulfanylbenzaldehyde a stable hemiaminal **11**, apparently from nucleophilic attack by the primary amine, still formed. Although in this instance spontaneous dehydration to the imine would be expected it could not be induced, even under the most stringent of conditions, such as treatment with phosphorus pentaoxide. These reactions are summarised in Scheme 2. The aminal and hemiaminals were never completely purified, but their presence as the dominant reaction product was inferred from ^1H and ^{13}C NMR spectroscopy. Thus, **7** shows a non-exchangeable one-proton resonance in the ^1H spectrum at δ 5.4 which correlates with a methine carbon resonance at δ 62.0 in the ^{13}C spectrum [attached proton test (APT), heteronuclear correlation (HETCOR)] consistent with a hemiaminal group.[21] Monitoring of the ^1H NMR spectrum during the formation of **10** shows the development of a resonance at δ 4.8, consistent with hemiaminal formation, which is gradually replaced over 24 h by a resonance at δ 4.0 consistent with the aminal structure.[21,22] Compound **11** showed a non-exchangeable one-proton resonance in the ^1H spectrum at δ 5.6 correlating with a carbon resonance at δ 62.1 again suggesting hemiaminal formation, although in this compound it must, of necessity, involve the primary amine, which makes it difficult to understand why subsequent dehydration to the imine does not occur. This is also a possible structure for compound **7** although that shown seems more likely, on the grounds that it is incapable of dehydration.

Complexation of the asymmetrically protected N_2S_2 compounds

When a refluxing ethanolic solution of L^1 was treated with $[Cu(MeCN)_4]ClO_4$, under anhydrous and anaerobic conditions for 2 h, a yellow solid was obtained which, after recrystallisation from methanol, gave bright orange crystals. The ^1H NMR spectrum recorded in $(CD_3)_2CO$ showed clearly the presence of the imine, aromatic and *tert*-butyl protons which, along with the ^{13}C NMR spectrum, indicated that the compound had not spontaneously de-*tert*-butylated. Subsequently, X-ray diffraction analysis (see below) confirmed this and that the isolated complex was $[CuL^1]ClO_4$. When the synthesis was repeated under similar conditions in refluxing 2-methoxyethanol an identical product was obtained, albeit in lower yield, indicating that copper(I) is incapable of inducing cleavage of the sulfur–carbon (*tert*-butyl) bond even at the higher temperature, where the entropically favoured liberation of isobutene might be expected to occur more readily. Reaction of L^1 with copper(II) in the form of $[Cu(dmso)_2Br_2]$ (dmso = dimethyl sulfoxide) in anhydrous ethanol at 0 °C led to the isolation, in high yield, of the green complex $[CuL^1]Br_2$. Again de-*tert*-butylation did not occur and attempts to encourage this by use of higher reaction temperatures led only to partial hydrolysis of the imino bond, which was also noted when hydrated copper(II) or zinc(II) salts were used in the synthesis.

Since the instability of L^1 towards hydrolysis was hindering the investigation of sulfur–carbon bond cleavage it was reduced to the amine L^2 using $NaBH_4$ in ethanol. Reaction of L^2 with $[Cu(MeCN)_4]ClO_4$ in refluxing ethanol under anaerobic and anhydrous conditions afforded pale yellow crystals of $[CuL^2]ClO_4$, which were characterised by ^{13}C NMR spectroscopy, microanalysis and X-ray crystallography. All of these techniques indicated quite clearly that, again, de-*tert*-butylation does not occur under these conditions. Reaction with a variety of different copper(II) salts under both anhydrous and hydrous conditions and at temperatures ranging from 0 to 125 °C failed to give any characterisable copper(II) product.

In contrast to L^1 and L^2, the cyanoethylated compound L^3 failed to form an isolable copper(I) species. Reaction of L^3 with $[Cu(MeCN)_4]ClO_4$, in a similar manner to that described above, initially gave an orange solution which could not be prevented from rapidly turning green, suggesting oxidation to copper(II), even though rigorously anhydrous and anaerobic conditions were maintained. The copper(II) complex was isolated in analytically pure form from the reaction of $[Cu(dmso)_2Br_2]$ with L^3 at 0 °C in ethanol. The bright green solid showed bands in the infrared spectrum (Nujol) consistent with the retention of both the imine and nitrile moieties. The band due to the nitrile at 2245 cm^{-1} was only slightly shifted from its position for free L^3 (2243 cm^{-1}) suggesting that it was not co-ordinated. Conductivity measurements in both ethanol and nitromethane indicated that the complex was a non-electrolyte, and by implication that both bromide ions are co-ordinated in these solvents. These observations support $[CuL^3Br_2]$ as the best formulation for this product. Attempts



Scheme 2

to decyanoethylate the complex, by using the previously reported method of heating it in dimethylformamide in the presence of K_2CO_3,[23] were unproductive, resulting only in decomposition.

Structures of $[CuL^1]ClO_4$ and $[CuL^2]ClO_4$

The orange crystals of $[CuL^1]ClO_4$ were suitable for the collection of X-ray diffraction data. Analysis revealed the structure of the $[CuL^1]^+$ cation to be as shown in Fig. 1. The geometry about the copper(I) ion is that of a distorted tetrahedron with the dihedral angle between the planes defined by the copper atom and the two nitrogen atoms and that defined by the copper atom and the two sulfur atoms being 74.05(9)°. This indicates that the co-ordination geometry of the ligand about the copper(I) ion is much closer to being that of a regular tetrahedron than that of the dibenzyl diimine $[CuL^4]^+$ determined previously,[24] where the dihedral angle is 60.0(1)°. This is understandable in terms of saturation of one imine bond removing the requirement that this function has to maintain coplanarity with the aromatic ring (and hence extend the π conjugation). This tendency is not fully realised in $[CuL^1]^+$, however, as the dihedral angle N(2)–C(17)–C(18)–C(23) is −29.5(6)° indicating that a twist away from coplanarity arises upon metal co-ordination. The dihedral angle N(1)–C(14)–C(13)–C(8) is −73.5(5)° and this demonstrates the lack of any such geometrical constraint associated with the amine. The Cu–S bond lengths are typical for copper(I)–thioether

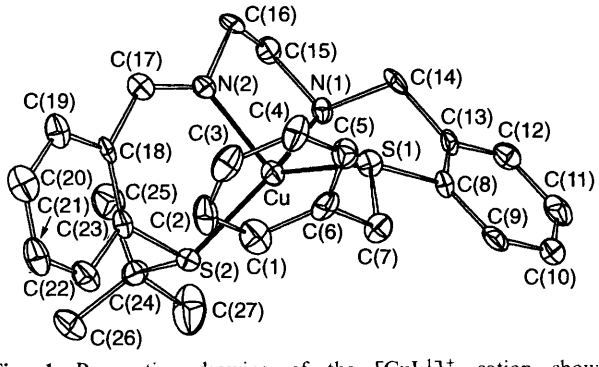
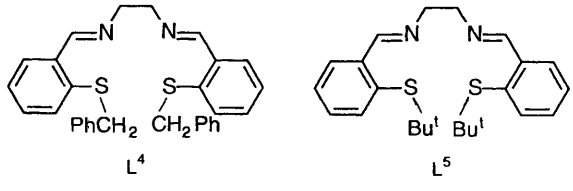


Fig. 1 Perspective drawing of the $[CuL^1]^+$ cation showing displacement ellipsoids of the non-hydrogen atoms at the 50% probability level



interactions, but differ slightly in that the sulfur atom with the benzyl substituent is at a greater distance from the copper(I) ion

[2.299(1) Å] than is the sulfur atom carrying the *tert*-butyl substituent [2.219(1) Å]. This may be due to the increased steric bulk associated with the aromatic ring over that of the *tert*-butyl group. The copper–amino nitrogen bond length is 2.090(3) Å, slightly longer than the copper–imino nitrogen bond, 2.034(3) Å, which is to be expected on the grounds of the stronger soft–soft interaction that exists between copper(I) and imino-nitrogen. Other important bond lengths and angles appear in Table 2.

Recrystallisation of $[CuL^2]ClO_4$ from dry methanol afforded pale lemon yellow crystals suitable for X-ray diffraction. The asymmetric cation has a distorted-tetrahedral geometry as depicted in Fig. 2. The dihedral angle between the planes defined by the copper atom and the two nitrogen atoms and by the copper atom and the two sulfur donors is 73.5(2)°. This is not significantly different to that in $[CuL^1]^+$ which possesses the added geometrical constraint of the conjugated imine system. This value must represent the limit to which this 6-5-6 chelating ring system can approach tetrahedral co-ordination as a consequence of the relatively small bite of the 1,2-diaminoethane moiety. The dihedral angle C(8)–C(13)–C(14)–N(1) is −72.9(9)° in $[CuL^2]^+$, similar to the same angle in $[CuL^1]^+$, but N(2)–C(17)–C(18)–C(23) [−70.2(9)°] is much larger than that in $[CuL^1]^+$ [−29.5(6)°] indicative of the rotational freedom now available in this bond. The Cu–S bond lengths are similar to those on $[CuL^1]^+$ with again the benzylthioether–copper bond being slightly longer than the *tert*-butylthioether–copper bond [2.305(2) and 2.220(2) Å respectively]. The Cu–N(2) bond is longer in this complex [2.107(6) Å] than in $[CuL^1]^+$ [2.034(3) Å] due to the decrease in strength of the interaction that occurs between copper(I) and nitrogen when changing from imine to amine. Other important bond lengths and angles are given in Table 2.

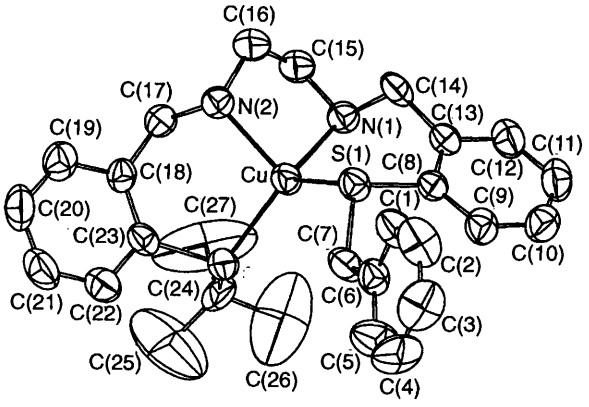


Fig. 2 Perspective drawing of the $[CuL^2]^+$ cation showing displacement ellipsoids of the non-hydrogen atoms at the 50% probability level

Electrochemical and spectral properties

Both $[CuL^1]ClO_4$ and $[CuL^2]ClO_4$ were subjected to cyclic voltammetry in nitromethane at a scan rate of 25 mV s^{-1}. In each case quasi-reversible one-electron transfer behaviour was observed. The two complexes show similar $E_{\frac{1}{2}}$ values of 0.31 and 0.34 V *vs.* saturated calomel electrode (SCE), respectively, similar to that shown by the dibenzyl diimine, $[CuL^4]ClO_4$ (0.28 V).[24] The anodic-to-cathodic peak-potential separations are 0.13 and 0.17 V. The ratio of anodic-to-cathodic peak currents is very close to unity in both cases. For further comparison the di-*tert*-butyl diimine $[CuL^5]ClO_4$ was also synthesised.[25] Under the same conditions it too showed quasi-reversible behaviour with $E_{\frac{1}{2}} = 0.38$ V and an interpeak separation of 0.23 V. Thus it appears from the enhanced $E_{\frac{1}{2}}$ value that the shortening of the copper(I)–thioether bonds, noted in the solid-state structures above, when a *tert*-butyl group replaces a benzyl group, is paralleled by an enhanced thermodynamic stability of the copper(I) species.

Table 1 Crystal data and refinement summary[a] for $[CuL^1]ClO_4$ and $[CuL^2]ClO_4$

	$[CuL^1]ClO_4$	$[CuL^2]ClO_4$
Empirical formula	$C_{27}H_{32}ClCuN_2O_4S_2$	$C_{27}H_{34}ClCuN_2O_4S_2$
M	611.6	613.6
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	11.402(2)	15.934(7)
b/Å	18.183(4)	10.267(6)
c/Å	13.253(3)	9.543(3)
α/°	—	107.62(3)
β/°	90.69(1)	96.48(3)
γ/°	—	101.56(1)
U/Å^3	2747(1)	1432(1)
D_m/g cm^{-3}	1.44(2)[b]	1.41(2)[b]
Z	4	2
D_c/g cm^{-3}	1.479	1.423
F(000)	1272	640
T/K	163(2)	293(2)
μ/cm^{-1}	10.7	10.4
Transmission coefficients	0.67–0.87	0.77–0.92
θ_{max}/°	22.5	25
h,k,l ranges	±12, 0–19, 0–14	±18, ±12, 0–11
No. reflections sampled	3601	5280
No. reflections measured	3601	3998
No. used in refinement	3601	3741
No. parameters refined	335	334
R	0.057	0.071
R'	0.182	0.098
Goodness of fit	5.03(6)	3.19(4)
Final shift/error (maximum, average)	0.20,[c] 0.02	0.04, 0.02
Extinction coefficient	0.008(1)	—
$\Delta\rho_{min}$, $\Delta\rho_{max}$/e Å^{-3}	−0.61, 0.71	−0.78, 1.11

[a] Details in common: Mo-Kα radiation (λ 0.710 73 Å); refinement on F^2; $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] By flotation in a 1,2-dibromoethane–hexane mixture. [c] U_{12} of C(25).

Table 2 Selected bond lengths (Å) and angles (°)

$[CuL^1]ClO_4$							
Cu–S(1)	2.299(1)	C(12)–C(13)	1.392(6)	C(23)–C(18)	1.406(6)	C(4)–C(3)	1.366(7)
Cu–S(2)	2.219(1)	C(12)–C(11)	1.386(6)	C(23)–C(22)	1.396(6)	C(3)–C(2)	1.388(7)
Cu–N(1)	2.090(3)	C(5)–C(4)	1.385(6)	N(2)–C(17)	1.253(5)	C(22)–C(21)	1.380(6)
Cu–N(2)	2.034(3)	C(5)–C(6)	1.394(6)	N(2)–C(16)	1.472(5)	C(20)–C(21)	1.385(6)
S(1)–C(8)	1.785(4)	C(8)–C(13)	1.391(6)	C(17)–C(18)	1.492(5)	C(20)–C(19)	1.391(6)
S(1)–C(7)	1.813(4)	C(8)–C(9)	1.388(6)	C(18)–C(19)	1.392(6)	C(25)–C(24)	1.497(6)
S(2)–C(23)	1.792(4)	C(10)–C(9)	1.378(6)	C(14)–C(13)	1.516(6)	C(24)–C(26)	1.528(6)
S(2)–C(24)	1.855(4)	C(10)–C(11)	1.406(6)	C(1)–C(6)	1.393(6)	C(24)–C(27)	1.524(6)
N(1)–C(14)	1.493(5)	C(15)–C(16)	1.521(5)	C(1)–C(2)	1.414(7)		
N(1)–C(15)	1.497(5)	C(7)–C(6)	1.507(6)				
S(1)–Cu–S(2)	124.12(5)	S(1)–C(8)–C(13)	116.3(3)	S(2)–C(23)–C(18)	126.3(3)	C(18)–C(19)–C(20)	121.3(4)
S(1)–Cu–N(1)	95.24(9)	S(1)–C(8)–C(9)	123.0(3)	S(2)–C(23)–C(22)	114.9(3)	C(1)–C(6)–C(5)	118.5(4)
S(1)–Cu–N(2)	109.3(1)	C(13)–C(8)–C(9)	120.7(4)	C(18)–C(23)–C(22)	118.7(4)	C(1)–C(6)–C(7)	120.6(4)
S(2)–Cu–N(1)	136.08(9)	C(9)–C(10)–C(11)	119.9(4)	Cu–N(2)–C(17)	128.3(3)	C(5)–C(6)–C(7)	120.9(4)
S(2)–Cu–N(2)	96.9(1)	N(1)–C(15)–C(16)	111.9(3)	Cu–N(2)–C(16)	109.4(2)	S(2)–C(24)–C(25)	111.1(3)
N(1)–Cu–N(2)	86.0(1)	C(14)–C(13)–C(12)	118.9(3)	C(17)–N(2)–C(16)	121.3(3)	S(2)–C(24)–C(26)	108.1(3)
Cu–S(1)–C(8)	99.8(1)	C(14)–C(13)–C(8)	122.2(4)	N(2)–C(17)–C(18)	124.2(3)	S(2)–C(24)–C(27)	104.3(3)
Cu–S(1)–C(7)	119.7(1)	C(12)–C(13)–C(8)	119.0(4)	C(23)–C(18)–C(17)	126.2(3)	C(25)–C(24)–C(26)	111.3(3)
C(8)–S(1)–C(7)	104.8(2)	S(1)–C(7)–C(6)	107.7(3)	C(23)–C(18)–C(19)	119.0(4)	C(25)–C(24)–C(27)	111.1(4)
Cu–S(2)–C(23)	102.9(1)	C(8)–C(9)–C(10)	120.2(4)	C(17)–C(18)–C(19)	114.8(3)	C(26)–C(24)–C(27)	110.7(3)
Cu–S(2)–C(24)	114.9(1)	C(5)–C(4)–C(3)	121.0(4)	N(1)–C(14)–C(13)	111.8(3)	C(12)–C(11)–C(10)	119.4(4)
C(23)–S(2)–C(24)	104.8(2)	C(4)–C(3)–C(2)	120.2(4)	C(6)–C(1)–C(2)	120.5(4)	N(2)–C(16)–C(15)	109.0(3)
Cu–N(1)–C(14)	112.2(2)	C(23)–C(22)–C(21)	121.6(4)	C(13)–C(12)–C(11)	120.8(4)	C(1)–C(2)–C(3)	119.2(4)
Cu–N(1)–C(15)	104.7(2)	C(21)–C(20)–C(19)	119.5(4)	C(4)–C(5)–C(6)	120.6(4)		
C(14)–N(1)–C(15)	111.3(3)	C(22)–C(21)–C(20)	119.7(4)				
$[CuL^2]ClO_4$							
Cu–S(1)	2.305(2)	C(8)–C(9)	1.38(1)	N(2)–C(16)	1.483(8)	C(18)–C(23)	1.40(1)
Cu–S(2)	2.220(2)	C(8)–C(13)	1.412(8)	N(2)–C(17)	1.467(9)	C(19)–C(20)	1.38(1)
Cu–N(1)	2.068(5)	C(9)–C(10)	1.37(1)	C(1)–C(2)	1.39(1)	C(20)–C(21)	1.35(1)
Cu–N(2)	2.107(6)	C(10)–C(11)	1.36(1)	C(1)–C(6)	1.37(1)	C(21)–C(22)	1.38(1)
S(1)–C(7)	1.802(7)	C(11)–C(12)	1.38(1)	C(2)–C(3)	1.38(1)	C(22)–C(23)	1.38(1)
S(1)–C(8)	1.771(7)	C(12)–C(13)	1.40(1)	C(3)–C(4)	1.39(2)	C(24)–C(25)	1.47(2)
S(2)–C(23)	1.773(8)	C(13)–C(14)	1.50(1)	C(4)–C(5)	1.37(1)	C(24)–C(26)	1.42(2)
S(2)–C(24)	1.81(1)	C(15)–C(16)	1.53(1)	C(5)–C(6)	1.37(1)	C(24)–C(27)	1.44(1)
N(1)–C(14)	1.47(1)	C(17)–C(18)	1.511(9)	C(6)–C(7)	1.519(9)		
N(1)–C(15)	1.476(9)	C(18)–C(19)	1.38(1)				
S(1)–Cu–S(2)	116.89(8)	C(9)–C(8)–C(13)	120.4(7)	Cu–N(2)–C(16)	104.8(4)	C(18)–C(19)–C(20)	122.4(8)
S(1)–Cu–N(1)	97.5(2)	C(8)–C(9)–C(10)	119.9(6)	Cu–N(2)–C(17)	108.0(5)	C(19)–C(20)–C(21)	118.5(9)
S(1)–Cu–N(2)	113.2(2)	C(9)–C(10)–C(11)	121.3(7)	C(16)–N(2)–C(17)	111.7(4)	C(20)–C(21)–C(22)	120.7(8)
S(2)–Cu–N(1)	135.5(2)	C(10)–C(11)–C(12)	119.5(8)	C(2)–C(1)–C(6)	120.9(7)	C(21)–C(22)–C(23)	121.2(8)
S(2)–Cu–N(2)	102.8(2)	C(11)–C(12)–C(13)	121.7(6)	C(1)–C(2)–C(3)	119(1)	S(2)–C(23)–C(18)	124.2(5)
N(1)–Cu–N(2)	87.1(2)	C(8)–C(13)–C(12)	117.2(6)	C(2)–C(3)–C(4)	119.4(7)	S(2)–C(23)–C(22)	116.7(6)
Cu–S(1)–C(7)	107.1(3)	C(8)–C(13)–C(14)	123.0(6)	C(3)–C(4)–C(5)	119.8(8)	C(18)–C(23)–C(22)	118.8(7)
Cu–S(1)–C(8)	102.8(2)	C(12)–C(13)–C(14)	119.7(6)	C(4)–C(5)–C(6)	121.3(9)	S(2)–C(24)–C(25)	110.5(7)
C(7)–S(1)–C(8)	103.4(4)	N(1)–C(14)–C(13)	113.1(6)	C(1)–C(6)–C(5)	119.1(6)	S(2)–C(24)–C(26)	108.0(8)
Cu–S(2)–C(23)	104.8(3)	N(1)–C(15)–C(16)	111.1(5)	C(1)–C(6)–C(7)	122.8(7)	S(2)–C(24)–C(27)	115.1(9)
Cu–S(2)–C(24)	117.7(3)	N(2)–C(16)–C(15)	110.4(6)	C(5)–C(6)–C(7)	118.0(8)	C(25)–C(24)–C(26)	110(1)
C(23)–S(2)–C(24)	106.5(4)	N(2)–C(17)–C(18)	112.9(5)	S(1)–C(7)–C(6)	118.1(6)	C(25)–C(24)–C(27)	107(1)
Cu–N(1)–C(14)	111.1(3)	C(17)–C(18)–C(19)	117.9(7)	S(1)–C(8)–C(9)	122.2(5)	C(26)–C(24)–C(27)	107(1)
Cu–N(1)–C(15)	103.9(4)	C(17)–C(18)–C(23)	123.8(7)	S(1)–C(8)–C(13)	117.3(5)		
C(14)–N(1)–C(15)	111.7(6)	C(19)–C(18)–C(23)	118.3(6)				

The electronic spectra of $[CuL^1]ClO_4$ and $[CuL^2]ClO_4$ differ in that the latter complex lacks the $\pi \longrightarrow \pi^*$ bands associated with the imino group of the former. Thus, the latter complex shows just two bands at 211 (ε 34 100) and 233 nm (13 450 $dm^3\ mol^{-1}\ cm^{-1}$) which may be attributed to the $\pi \longrightarrow \pi^*$ transitions of the aromatic rings. The former complex, on the other hand, shows four bands at 210, 224, 246 and 294 nm (41 600, 21 200, 12 800 and 3300 $dm^3\ mol^{-1}\ cm^{-1}$) where the first two are most likely the $\pi \longrightarrow \pi^*$ bands of the aromatic rings and the second the $\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$ bands, respectively, both associated with the imino group. It is of interest that no absorption bands which could clearly be identified as metal–ligand charge transfer were identified from these two complexes. This is in contrast to the situation with $[CuL^4]ClO_4$ where two such bands are seen at 341 and 407 nm (2300 and 990 $dm^3\ mol^{-1}\ cm^{-1}$)[26] and also the di-*tert*-butyl analogue $[CuL^5]ClO_4$ where they are seen at 354 and 416 nm (2200 and 1200 $dm^3\ mol^{-1}\ cm^{-1}$).[25]

Experimental

Melting points were recorded using a Reichert hot-stage apparatus and, along with boiling points, are uncorrected. Elemental analyses were performed by the Australian Microanalytical Service or the Chemical and Micro Analytical Service Ltd. The ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 75.462 MHz, ^1H NMR spectra on either a Varian Gemini 300 spectrometer operating at 300.075 MHz or a Hitachi R-1200 60 MHz spectrometer. Chemical shifts are quoted on the δ scale relative to tetramethylsilane as internal standard. Molar conductivities were measured with a Philips PW9504 conductivity bridge on

10^{-3} mol dm^{-3} solutions at 293 K and correlated with different electrolyte types using the data reviewed by Geary.[27] Electronic spectra were recorded using a Hewlett-Packard 8452A diode-array spectrophotometer. Gaussian resolution of the electronic spectra was performed using the GRAMS/386, Version 1.05A, deconvolution program.[28] Infrared spectra were recorded as Nujol mulls on a Bio-Rad FTS-40A spectrophotometer, mass spectra on a Kratos M25RF spectrometer operating at an ionising voltage of 70 eV. Selected fragment ions are reported as their mass to charge ratio (m/z) followed by their relative intensities as compared to the base fragment.

Magnetic susceptibility measurements were recorded using the Gouy method on a Sherwood Scientific magnetic susceptibility balance at ambient temperature. Cyclic voltammetry was conducted in a three-electrode cell having a glassy carbon working electrode, platinum-wire counter electrode, and an $Ag–AgClO_4$ reference electrode, on 10^{-3} mol dm^{-3} degassed solutions of complexes with 10^{-1} mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte. A BAS 100B electrochemical analyser was the controlling unit. The $E_{\frac{1}{2}}$ values were normalised to the saturated calomel electrode *via* the ferrocene–ferrocenium couple (+0.154 V *vs.* SCE) according to the method of Gagné *et al.*[29]

Solvents were dried and purified according to standard methods.[30] 2-*tert*-Butylsulfanylbenzaldehyde **5**,[31] 2-sulfanylbenzenemethanol,[32] barium manganate,[33] tetrakis(acetonitrile)copper(I) perchlorate[34] and $[Cu(dmso)_2Br_2]$[35] were prepared according to published procedures.

Preparations

2-(Benzylsulfanyl)benzaldehyde 1. This compound was prepared as described previously.[24] As the ^{13}C NMR spectrum had not previously been reported it is presented here. ^{13}C NMR ($CDCl_3$): δ 191.5 (C=O), 141.1, 136.2, 134.8, 134.0, 131.6, 130.0, 129.0 (2C), 128.7 (2C), 127.6, 126.2 (aromatic C) and 39.0 (SCH_2).

***N*-Acetyl-*N'*-[2-(benzylsulfanyl)benzylidene]ethane-1,2-diamine 2.** *N*-Acetylethane-1,2-diamine (Aldrich) and compound **1** (equimolar amounts) were allowed to stir overnight in absolute ethanol at room temperature. Removal of the solvent afforded the imine quantitatively, as a yellow oil, which was used without further purification in the formation of **3**.

***N*-Acetyl-*N'*-[2-(benzylsulfanyl)benzyl]ethane-1,2-diamine 3.** To a solution of the imine **2** (14.25 g, 45.64 mmol) in absolute ethanol (100 cm^3) was added $NaBH_4$ (2.59 g, 1.5 molar equivalents) and the resulting solution refluxed for 3.5 h. Ethanol was removed by evaporation and the residue dissolved in water (50 cm^3) and dichloromethane (40 cm^3). The organic extract was separated and the aqueous layer washed with dichloromethane (3 × 40 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated yielding 13.76 g (96%) of a golden-yellow oil. The compound could be used without further purification. Attempts to purify it by distillation resulted in decomposition, however a small portion was purified by Chromatotron separation using 4% methanol in dichloromethane as eluent. The compound was recovered as an oil (Found: C, 68.4; H, 7.40; N, 9.55. $C_{18}H_{22}N_2OS$ requires C, 68.75; H, 7.05; N, 8.90%). NMR ($CDCl_3$): ^1H, δ 7.40–7.10 (m, 9 H, aromatic H), 6.28 (br s, 1 H, NH amide), 4.10 (s, 2 H, SCH_2), 3.74 (s, 2 H, aryl CH_2N), 3.25 (m, 2 H, CH_2N amide), 2.65 (t, 2 H, CH_2N amine), 1.87 (s, 3 H, CH_3) and 1.65 (br, 1 H, NH amine); ^{13}C, δ 170.2 (C=O), 139.8, 137.2, 135.8, 130.1, 129.6, 128.9 (2C), 128.6 (2C), 128.0, 127.4, 126.5 (aromatic C), 51.8 (aryl CH_2N), 47.6 (CH_2N amine), 39.2 (SCH_2), 38.9 (CH_2N amide) and 23.2 (CH_3). m/z 314 (M^+, 4%).

***N*-[2-(Benzylsulfanyl)benzyl]ethane-1,2-diamine 4.** A solution of compound **3** (15.40 g, 49.0 mmol) in absolute ethanol (70 cm^3) and concentrated hydrochloric acid (20 cm^3) was refluxed overnight. On cooling to room temperature the dihydrochloride salt separated as a white solid. This was collected by vacuum filtration, washed with a little cold ethanol and dried at the pump. The yield of crude product was 11.89 g (70%). It was recrystallised from absolute ethanol as a white powder (hygroscopic), m.p. 193–197 °C. Microanalysis results suggest the salt is a hemihydrate (Found: C, 54.6; H, 6.6; N, 7.6. $C_{16}H_{22}Cl_2N_2S·0.5H_2O$ requires C, 54.2; H, 6.5; N, 7.9%).

The free amine was obtained as follows. A solution of the dihydrochloride salt (3.36 g, 9.75 mmol) in water (100 cm^3) was made strongly basic by the addition of concentrated NaOH solution. The resulting milky solution was extracted with dichloromethane (3 × 50 cm^3) and the combined organic extracts were dried ($MgSO_4$). After filtration and evaporation a pale yellow oil was obtained, 2.55 g (96%). It was purified by distillation at reduced pressure, b.p. 145–150 °C (0.1 mmHg). Owing to its hygroscopic nature microanalyses were not satisfactory although the product appeared pure according to NMR spectroscopy. NMR ($CDCl_3$): ^1H, δ 7.39–7.13 (m, 9 H, aromatic H), 4.09 (s, 2 H, SCH_2), 3.78 (s, 2 H, aryl CH_2N), 2.75 (t, 2 H, CH_2NH_2), 2.60 (t, 2 H, CH_2NH) and 1.44 (s, 3 H, NH, NH_2); ^{13}C, δ 140.6, 137.5, 135.3, 130.5, 129.4, 128.9 (2C), 128.5 (2C), 127.7, 127.3, 126.6 (aromatic C), 52.0 (CH_2NH), 51.8 (aryl CH_2N), 41.8 (CH_2NH_2) and 39.4 (SCH_2). m/z 272 (M^+, 6%).

***N*-[2-(Benzylsulfanyl)benzyl]-*N'*-[2-(*tert*-butylsulfanyl)-benzylidene]ethane-1,2-diamine L¹.** Solutions of compound **4** (0.92 g, 3.4 mmol) in absolute ethanol (10 cm^3) and 2-(*tert*-butylsulfanyl)benzaldehyde **5** (0.65 g, 3.4 mmol) in absolute ethanol (10 cm^3) were mixed and stirred overnight at room temperature. The solution was evaporated to dryness leaving a yellow oil, which was used without purification. ^1H NMR ($CDCl_3$) of the crude material: δ 9.13 (imine). m/z 448 (M^+, 2%).

***N*-[2-(Benzylsulfanyl)benzyl]-*N'*-[2-(*tert*-butylsulfanyl)-benzyl]ethane-1,2-diamine L².** To a solution of crude L^1 (2.68 g, 6.0 mmol) in absolute ethanol (100 cm^3) was added $NaBH_4$ (0.34 g, 1.5 molar equivalents) and the resulting solution refluxed for 4 h. It was then evaporated to dryness and the residue shaken with dichloromethane (70 cm^3) and water (50 cm^3). The organic layer was separated and the aqueous phase washed with dichloromethane (2 × 50 cm^3). The combined organic extracts were dried ($MgSO_4$), filtered and evaporated leaving a pale yellow oil, 2.64 g (98%). The crude compound was sufficiently pure for metal-complexation reactions. NMR ($CDCl_3$): ^1H, δ 7.57–7.12 (m, 13 H, aromatic H), 4.06 (s, 2 H, SCH_2), 4.01 (s, 2 H, $Bu^tSC_6H_4CH_2$), 3.78 (s, 2 H, $PhCH_2SC_6H_4CH_2$), 2.68 (s, 4 H, CH_2CH_2), 1.67 (br, 2 H, NH) and 1.28 (s, 9 H, CH_3); ^{13}C, δ 145.5, 140.6, 138.7, 137.3, 135.1, 131.8, 130.3, 129.4, 129.2, 128.9, 128.7 (2C), 128.4 (2C), 127.4, 127.1, 126.7, 126.4 (aromatic C), 52.3 ($Bu^tSC_6H_4CH_2$), 51.6 ($PhCH_2SC_6H_4CH_2$), 48.7, 48.5 (CH_2CH_2), 47.1 (quaternary C), 39.2 (SCH_2) and 31.1 (CH_3). The compound could also be isolated from the reaction mixture by precipitation of the dihydrochloride salt. After the reduction period the solution was cooled and dilute hydrochloric acid (4 mol dm^{-3}) was added until no more precipitate formed. After cooling in a refrigerator for several hours, the solid was collected by vacuum filtration and recrystallised from 80% aqueous ethanol as a fine white powder, m.p. 217–219 °C (Found: C, 61.7; H, 7.05; N, 5.20. $C_{27}H_{36}Cl_2N_2S_2$ requires C, 61.95; H, 6.90; N, 5.35%).

2,2'-Dithiodibenzaldehyde. This compound was prepared *via* a modified literature procedure.[36] Barium manganate powder (13.5 g) was suspended in a solution of 2-sulfanylbenzenemethanol (2.24 g, 16.0 mmol) in dichloromethane (50 cm^3) and the resulting mixture refluxed gently for 40 h. After cooling,

the solution was filtered through a Celite pad. Filtrate and washings were evaporated leaving a pale yellow solid, 1.91 g (87%). Recrystallisation from 95% ethanol gave pale yellow needles, m.p. 148–151 °C (lit.,[36] 145 °C). NMR ($CDCl_3$): ^1H, δ 10.22 (s, 2 H, CH=O) and 7.90–7.35 (m, 8 H, aromatic H); ^{13}C, δ 191.8 (C=O), 140.1, 134.7, 134.3, 133.9, 126.8 and 126.4 (aromatic C).

When the literature procedure was employed, *i.e.* using activated MnO_2 oxidant, incompletely oxidised product was obtained. This was determined to be 2,2′-dithiodibenzenemethanol. NMR ($CDCl_3$–CD_3OD): ^1H, δ 7.55–7.21 (m, 8 H, aromatic H), 4.75 (s, 4 H, CH_2) and 4.73 (s, 2 H, OH); ^{13}C, δ 140.5, 134.0, 129.7, 127.4, 127.3, 127.0 (aromatic C) and 61.2 (CH_2).

2-Sulfanylbenzaldehyde 6. This compound was prepared conveniently from 2,2′-dithiodibenzaldehyde according to the published procedure.[36] The purified product was obtained by distillation at reduced pressure thus avoiding the lengthy chromatography reported. Typical yield 90%; b.p. 95–100 °C (0.1 mmHg). NMR ($CDCl_3$): ^1H, δ 10.15 (s, 1 H, CH=O), 7.80–7.10 (m, 4 H, aromatic H) and 5.50 (s, 1 H, SH); ^{13}C, δ 192.6 (C=O), 138.0, 135.9, 133.3, 131.5, 131.0 and 124.8 (aromatic C).

2-(2-Cyanoethylsulfanyl)benzenemethanol 8. 2-Sulfanylbenzenemethanol (4.78 g, 34.1 mmol) was dissolved in dry benzene (25 cm^3) under nitrogen and ethanolic sodium hydroxide solution (2 cm^3, 1 mol dm^{-3}) was added. The mixture was cooled to 0 °C and acrylonitrile (1.81 g, 1 molar equivalent) added dropwise with stirring. When the addition was complete the solution was allowed to warm gradually to room temperature overnight. After diluting with hydrochloric acid (1 cm^3, 4 mol dm^{-3}) and water (20 cm^3), the benzene layer was separated and aqueous phase washed with ether (2 × 25 cm^3). The combined organic extracts were washed with NaCl solution (2 × 15 cm^3), dried ($MgSO_4$) and evaporated leaving a yellow oil, 6.12 g (93%). The pure product was obtained by distillation; b.p. 145–150 °C (0.1 mmHg) (Found: C, 62.1; H, 5.85; N, 7.25. $C_{10}H_{11}NOS$ requires C, 62.15; H, 5.75; N, 7.25%). NMR ($CDCl_3$): ^1H, δ 7.60–7.15 (m, 4 H, aromatic H), 4.80 (s, 2 H, aryl CH_2), 3.11 (t, 2 H, SCH_2), 2.57 (t, 2 H, CH_2CN) and 2.50 (s, 1 H, OH); ^{13}C, δ 142.7, 132.2, 131.6, 128.9, 128.5, 128.3 (aromatic C), 118.2 (CN), 63.2 (aryl CH_2), 30.4 (SCH_2) and 18.2 (CH_2CN). *m/z* 193 (M^+, 22%).

2-(2-Cyanoethylsulfanyl)benzaldehyde 9. A solution of compound **8** (2.72 g, 14.1 mmol) in dichloromethane (100 cm^3) was stirred with $BaMnO_4$ powder (8.2 g, three-fold excess by mass) for 20 h. The solution was filtered with the aid of Celite and the filtrate evaporated leaving a pale orange solid, 2.36 g (88%). The material was purified by recrystallisation from benzene–cyclohexane (1:1 v/v), m.p. 70–71 °C (Found: C, 62.75; H, 4.75; N, 7.35. $C_{10}H_9NOS$ requires C, 62.8; H, 4.75; N, 7.35%). NMR ($CDCl_3$): ^1H, δ 10.31 (s, 1 H, CH=O), 7.85–7.30 (m, 4 H, aromatic H), 3.20 (t, 2 H, SCH_2) and 2.66 (t, CH_2CN); ^{13}C, δ 191.4 (C=O), 138.3, 134.8, 134.4, 132.5, 129.3, 126.9 (aromatic C), 117.9 (CN), 29.1 (SCH_2) and 17.8 (CH_2CN). *m/z* 191 (M^+, 83) and 137 ($M^+ - CH_2$=CHCN, 100%).

When methanol was used as the recrystallising solvent problems often arose due to the formation of the dimethyl acetal adduct; b.p. 90 °C (0.05 mmHg). NMR ($CDCl_3$): ^1H, δ 8.00–7.20 (m, 4 H, aromatic H), 5.77 (s, 1 H, CH), 3.40 (s, 6 H, CH_3), 3.15 (t, 2 H, SCH_2) and 2.55 (t, 2 H, CH_2CN); ^{13}C, δ 139.8, 132.3, 132.2, 129.3, 127.8, 127.5 (aromatic C), 118.1 (CN), 101.5 (CH), 53.7 (2C, CH_3), 30.5 (SCH_2) and 18.1 (CH_2CN). *m/z* 237 (M^+, 10), 206 ($M^+ - OCH_3$, 90) and 183 ($M^+ - CH_2$=CHCN, 100%). The aldehyde could readily be recovered from the acetal by treating with dilute hydrochloric acid solution (3 mol dm^{-3}) and recrystallising the resulting solid from benzene–cyclohexane as described.

***N*-Acetyl-*N*′-[2-(benzylsulfanyl)benzyl]-*N*′-methylethane-1,2-diamine.** To a solution of compound **3** (2.57 g, 8.17 mmol) in dry dichloromethane (50 cm^3) was added solid K_2CO_3 (1.36 g, 1.2 molar equivalents) followed by methyl iodide (3.48 g, 3 equivalents) and the solution allowed to stir at room temperature overnight. The solution was filtered, dried ($MgSO_4$) and evaporated leaving a thick yellow oil, 3.21 g. The product was used for the production of **12** without purification, however purification by column chromatography, using 5% MeOH in CH_2Cl_2 as eluent, gave a white solid which was recrystallised from pentane, m.p. 74–75 °C (Found: C, 69.65; H, 7.40; N, 8.45. $C_{19}H_{24}N_2OS$ requires C, 69.45; H, 7.35; N, 8.55%). NMR ($CDCl_3$): ^1H, δ 7.45–7.10 (m, 9 H, aromatic H), 6.45 (br, 1 H, NH), 4.16 (s, 2 H, SCH_2), 3.52 (s, 2 H, aryl CH_2N), 3.25 (m, 2 H, CH_2N amide), 2.45 (m, 2 H, CH_2N), 2.11 (s, 3 H, $COCH_3$) and 1.73 (s, 3 H, NCH_3); ^{13}C, δ 170.4 (C=O), 137.7, 137.6, 136.8, 130.5, 129.0 (2C), 128.7 (2C), 128.2, 127.8, 127.5, 125.4 (aromatic C), 61.4 (aryl CH_2N), 55.2 (CH_2N), 40.5 (NCH_3), 38.6 (SCH_2), 36.5 (CH_2N amide) and 23.0 ($COCH_3$). *m/z* 328 (M^+, 8%).

***N*-[2-(Benzylsulfanyl)benzyl]-*N*-methylethane-1,2-diamine 12.** A solution of the above compound (2.8 g, 8.5 mmol) in ethanol (25 cm^3) and concentrated HCl solution (8 cm^3) was refluxed for 5 h. The volume was reduced then diluted with water (20 cm^3). The solution was made basic by the addition of solid K_2CO_3 then extracted with dichloromethane (4 × 20 cm^3). The combined organic extracts were washed with water (20 cm^3), dried ($MgSO_4$) and evaporated leaving a yellow oil, 1.94 g (80%). The oil was purified by distillation, b.p. 150 °C (0.1 mmHg). NMR ($CDCl_3$): ^1H, δ 7.50–7.10 (m, 9 H, aromatic H), 4.10 (s, 2 H, SCH_2), 3.51 (s, 2 H, aryl CH_2N), 2.75 (t, 2 H, CH_2NH_2), 2.42 (t, 2 H, CH_2N), 2.14 (s, 3 H, CH_3) and 1.33 (s, 2 H, NH_2); ^{13}C, δ 139.0, 137.5, 137.0, 130.0, 129.2, 128.9 (2 C), 128.5 (2C), 127.6, 127.2, 125.7 (aromatic C), 60.7 (aryl CH_2N), 60.3 (CH_2N), 41.9 (CH_3), 39.6 (CH_2NH_2) and 38.9 (SCH_2). *m/z* 286 (M^+, 5%).

***N*-[2-(Benzylsulfanyl)benzyl]-*N*′-[2-(2-cyanoethylsulfanyl)-benzylidene]-*N*′-methylethane-1,2-diamine L[3].** Solutions of compound **12** (0.196 g, 0.68 mmol) in absolute ethanol (20 cm^3) and **9** (0.131 g, 0.68 mmol) in absolute ethanol (10 cm^3) were mixed and stirred overnight at room temperature. The solution was evaporated to dryness leaving a yellow oil. The crude compound was sufficiently pure for metal-complexation reactions. NMR ($CDCl_3$): ^1H, δ 8.85 (s, 1 H, CH=N), 7.95–7.90 (m, 1 H, aromatic H), 7.50–7.10 (m, 12 H, aromatic H), 4.05 (s, 2 H, SCH_2 aryl), 3.80 (t, 2 H, CH_2N imine), 3.62 (s, 2 H, aryl CH_2N), 2.98 (t, 2 H, SCH_2CH_2), 2.76 (m, 2 H, CH_2N amine), 2.44 (t, 2 H, CH_2CN), 2.27 (s, 3 H, CH_3) and 1.90 (br, 1 H, NH); ^{13}C, δ 160.1 (C=N), 139.1, 137.9, 137.5, 136.6, 133.5, 133.4, 130.9, 129.9, 129.6, 129.0 (2C), 128.7, 128.6, 128.5 (2C), 127.5, 127.1, 126.0 (aromatic C), 117.9 (CN), 60.2 (aryl CH_2N), 59.6 (CH_2N imine), 57.8 (CH_2N amine), 42.4 (CH_3), 39.1 (SCH_2 aryl), 31.2 (SCH_2CH_2) and 18.0 (CH_2CN).

{*N*-[2-(Benzylsulfanyl)benzyl]-*N*′-[2-(*tert*-butylsulfanyl)-benzylidene]ethane-1,2-diamine-*S*,*S*′,*N*,*N*′}copper(I) perchlorate, [CuL^1]ClO_4. CAUTION: perchlorate salts of metal complexes are potentially explosive. Although we have had no incidents with this or the following perchlorate salts suitable precautions should be taken.

To a solution of L^1 (1.97 g, 4.4 mmol) in dry deoxygenated ethanol (20 cm^3) was added a solution of $[Cu(MeCN)_4]ClO_4$ (1.44 g, 4.4 mmol) in dry deoxygenated ethanol (20 cm^3) under nitrogen. The resulting mixture was refluxed for 2 h, cooled, and the yellow precipitate filtered off under nitrogen and dried under vacuum. The complex was recrystallised from dry methanol under nitrogen; yield 2.24 g (83%), m.p. 168–172 °C (decomp.). The pure product is air stable when in the solid state

(Found: C, 53.2; H, 5.4; N, 4.7. $C_{27}H_{32}ClCuN_2O_4S_2$ requires C, 53.0; H, 5.3; N, 4.6%). ^{13}C NMR [$(CD_3)_2CO$]: δ 163.3 (C=N), 141.5, 139.4, 138.3, 135.7, 135.6, 133.6, 132.9, 132.4, 132.2, 131.8, 130.7, 130.1, 130.0 (2C), 129.2 (2C), 128.6, 125.7 (aromatic C), 57.9, 54.0, 53.5, 53.3, 53.2 (C) and 42.8 (3C, CH_3). $\Lambda_M(MeNO_2)$: 88 Ω^{-1} cm^2 mol^{-1} (1:1). Electronic spectrum (EtOH): λ_{max}/nm 212 (ε/dm^3 mol^{-1} cm^{-1} 59 000) and 290 (3500) (sh); (Gaussian resolution) 210 (41 600), 224 (21 200), 246 (12 800) and 294 (3300).

{*N*-[2-(Benzylsulfanyl)benzyl]-*N'*-[2-(*tert*-butylsulfanyl)-benzylidene]ethane-1,2-diamine-*S*,*S'*,*N*,*N'*}dibromo copper(II), [CuL^1Br_2]. To a cooled (0 °C) solution of L^1 (0.607 g, 1.35 mmol) in dry deoxygenated ethanol (10 cm^3), under nitrogen, was added a solution of [$Cu(dmso)_2Br_2$] (0.514 g, 1.35 mmol) in dry ethanol (15 cm^3). The resulting dark green solution was stirred at 0 °C for 30 min. The bright green precipitate was collected, washed with dry ethanol (10 cm^3) and ether (10 cm^3), then dried under vacuum. The yield of bright green solid was 0.71 g (78%), m.p. 128–130 °C (Found: C, 48.25; H, 4.80; N, 4.05. $C_{27}H_{32}Br_2CuN_2S_2$ requires C, 48.25; H, 4.80; N, 4.15%). $\Lambda_M(MeNO_2)$ 21 (non-electrolyte); (EtOH) 29 Ω^{-1} cm^2 mol^{-1} (< 1:1). Magnetic moment: μ_{eff} = 1.82 μ_B. Visible spectrum (EtOH): λ_{max}/nm 644 (ε/dm^3 mol^{-1} cm^{-1} 220). IR (Nujol): 3150 (ν_{NH}), 1650 cm^{-1} ($\nu_{C=N}$).

{*N*-[2-(Benzylsulfanyl)benzyl]-*N'*-[2-(*tert*-butylsulfanyl)-benzyl]ethane-1,2-diamine-*S*,*S'*,*N*,*N'*}copper(I) perchlorate, [CuL^2]ClO_4. To a solution of L^2 (0.70 g, 1.56 mmol) in dry deoxygenated ethanol (10 cm^3), under nitrogen, was added a solution of [$Cu(MeCN)_4$]ClO_4 (0.51 g, 1.56 mmol) in dry ethanol (30 cm^3). The resulting mixture was refluxed briefly to ensure dissolution of reactants, then allowed to cool to 0 °C. The off-white solid was collected by vacuum filtration under nitrogen and recrystallised from dry methanol to give pale yellow crystals; yield 0.69 g (72%), m.p. 188–190 °C (Found: C, 52.95; H, 5.65; N, 4.50. $C_{27}H_{34}ClCuN_2O_4S_2$ requires C, 52.85; H, 5.55; N, 4.55%). ^{13}C NMR (CD_3CN): δ 141.3, 138.9, 137.6, 135.3, 132.7, 131.9, 131.8, 130.6, 130.3, 129.1, 128.8 (3C), 128.4, 128.3 (2C), 128.0, 127.5 (aromatic C), 53.0, 52.2, 50.7, 46.8, 40.3, 31.0, and 29.3. $\Lambda_M(MeNO_2)$: 81 Ω^{-1} cm^2 mol^{-1} (1:1). Electronic spectrum (EtOH): λ_{max}/nm 215 (ε/dm^3 mol^{-1} cm^{-1} 46 000); (Gaussian resolution) 211 (34 100) and 233 (13 450).

{*N*-[2-(Benzylsulfanyl)benzyl]-*N'*-[2-(2-cyanoethylsulfanyl)-benzylidene]-*N'*-methylethane-1,2-diamine-*S*,*S'*,*N*,*N'*}dibromo-copper(II), [CuL^3Br_2]. To a cooled (0 °C) solution of L^3 (0.492 g, 1.07 mmol) in dry deoxygenated ethanol (10 cm^3), under nitrogen, was added a solution of [$Cu(dmso)_2Br_2$] (0.406 g, 1.07 mmol) in dry ethanol (20 cm^3). The solution was stirred at 0 °C for 30 min then the green precipitate was collected by vacuum filtration. The solid was recrystallised by suspending in ether and dissolving by dropwise addition of methanol. Cooling at −20 °C for 24 h yielded a bright green powder; 0.149 g (20%), m.p. 99–101 °C (Found: C, 47.35; H, 4.40; N, 6.25. $C_{27}H_{29}Br_2CuN_3S_2$ requires C, 47.45; H, 4.30; N, 6.15%). $\Lambda_M(MeNO_2)$ 32 (non-electrolyte); (EtOH) 29 Ω^{-1} cm^2 mol^{-1} (< 1:1). Visible spectrum (EtOH): λ_{max}/nm 662 (ε/dm^3 mol^{-1} cm^{-1} 240). IR (Nujol): 2245 ($\nu_{C\equiv N}$), 1639 cm^{-1} ($\nu_{C=N}$).

Crystallography

Computer programs of the XTAL system[37] were used in the structure determinations and refinements. The program CRYLSQ[38] was used for least-squares refinements with neutral scattering factors for all atoms. Crystal data, unit-cell dimensions and a refinement summary are given in Table 1.

[CuL^1]ClO_4. Data collected on a Siemens P4 diffractometer were corrected for absorption. The structure was solved by a combination of Patterson and Fourier methods. The non-hydrogen atomic coordinates and anisotropic thermal parameters were refined by full-matrix least squares minimising the function $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = 1/\sigma^2(F_o^2)$ and values of $\sigma^2(F_o^2)$ were obtained from counting statistics. All reflection data were used in the refinement. The positions of the hydrogen atoms, except for those associated with the carbon atoms of the *tert*-butyl group which were calculated, were located in difference maps. The hydrogen atoms were given arbitrary isotropic thermal parameters and not refined. An extinction parameter was refined.[39]

[CuL^2]ClO_4. Absorption corrections were applied using the method of Gaussian quadrature (8 × 8 × 8 grid). Of the 5280 reflections recorded on a Nonius CAD-4 diffractometer 3998 were regarded as observed, $I > 3\sigma(I)$.

The position of the copper atom was located in a Patterson vector map and all other non-hydrogen atoms were located in subsequent electron-density maps. The non-hydrogen atom coordinates and anisotropic thermal parameters were refined as above. Hydrogen atoms were placed in calculated positions with arbitrarily assigned isotropic thermal parameters. The hydrogen-atom positions were not refined but were recalculated later in the refinement. The *tert*-butyl and benzyl groups undergo large thermal motion bordering on disorder.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/105.

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