

Synthesis and crystal structures of some bis-benzimidazoles, -benzothiazoles and -benzoxazoles by an alternative route: their complexation with copper(II) salts†

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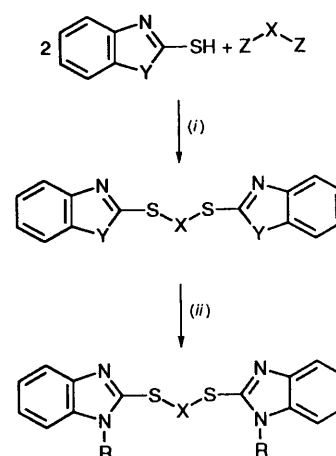
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A novel and convenient synthetic route towards new bis-benzimidazoles, -benzothiazoles and -benzoxazoles from readily available starting materials has been established. These compounds have thioethers at the 2 position of the heterocycle and the resultant carbon–thioether linkage is stable under the conditions of synthesis. The crystal structures of bis(benzoxazol-2-ylsulfanyl)methane, bis(benzothiazol-2-ylsulfanyl)methane and 1,8-bis(benzothiazol-2-ylsulfanyl)-3,6-dioxaoctane have been determined. Differences in the packings of the first two are attributed to the greater number of S...S interactions of the second. Two of the new series have been complexed with copper(II) salts. The bis(benzoxazole) series showed no tendency to complex copper(II). The unusual crystal structure of the copper(II) complex with 1,8-bis(benzimidazol-2-ylsulfanyl)-3,6-dioxaoctane has been determined, indicating a four-co-ordinate copper(II) atom in a distorted square-planar environment. The two bis(benzimidazole) moieties act as bidentate ligands with nitrogen donors. The thioether donors of the chain, although apparently ordered around the copper, are too distant to be regarded as donors but probably influence the spectroscopic properties of the copper site and are described as quasi-co-ordinated. Relevant spectroscopic and analytical details of the new compounds and their complexes are given.

Our interest in compounds that will transport^{1,2} and complex metals^{3,4} and which contain nitrogen heterocycles with possible nitrogen, oxygen and sulfur donor atoms has led us to synthesise a number of bis-benzimidazoles, -benzothiazoles and -benzoxazoles (see Scheme 1 and Table 1). Traditionally these have been synthesised *via* condensation of the relevant O-substituted aniline with a carboxylic acid, nitrile or ester in acidic media^{5,6} or by direct fusion⁷ of the reactants. Only the use of polyphosphoric acid is common to the formation of all three classes;⁸ however such reactions are susceptible to decarboxylation at the high temperatures often required. We report here a common and more convenient preparative route (Scheme 1) to all three classes of compound, and the crystal structures of bis(benzoxazol-2-ylsulfanyl)methane (L¹), bis(benzothiazol-2-ylsulfanyl)methane (L⁴) and 1,8-bis(benzothiazol-2-ylsulfanyl)-3,6-dioxaoctane (L⁶), together with that of a copper(II) complex of 1,8-bis(benzimidazol-2-ylsulfanyl)-3,6-dioxaoctane (L¹⁰).

The copper and zinc co-ordination chemistry of bis(benzimidazole) compounds has been extensively studied because of their potential as low-molecular-weight mimics/models of the active sites in many metalloproteins.^{9,10} Such studies have revealed much about the co-ordination geometry and donor properties of these compounds towards zinc(II), copper(I) and copper(II). Bis(benzothiazole) compounds are also of interest as potential mimics for metalloproteins¹¹ and more recently bleomycin.¹² The benzoxazoles have been studied as potential models for calcimycin,¹³ but their complexation behaviour towards transition metals is somewhat limited. Since the sulfur and oxygen atoms of the heterocyclic ring as well as the nitrogens are potential co-ordination sites, our intention was to explore whether the sulfur atom of the thiazole ring and the oxygen atom of the oxazole ring altered the co-ordination behaviour towards copper(II). Since the copper(II) ion has the



Scheme 1 General synthetic scheme for compounds L¹–L¹¹. (i) (a) NEtPr'₂, (b) tetrahydrofuran (thf), reflux, 17 h; (ii) (Y = NH) (a) 80% suspension of NaH in oil, (b) alkyl halide or toluene-*p*-sulfonate, gentle reflux, 48 h

least stringent requirements for high symmetry as opposed to other first-row transition metals, it was regarded as ideal to check each compound for its potential in metal chelation.

Experimental

Reagents and solvents used were of commercially available reagent-grade quality. Tetrahydrofuran was distilled over calcium hydride and used immediately. **CAUTION:** shock sensitivity of the perchlorate complexes synthesised has not been observed, but care should be taken to prevent explosion. Proton NMR spectra were run on a Bruker WP200 spectrometer. Elemental analysis was performed on a Carlo Erba 1106 Elemental Analyser. Fast atom bombardment and

† Non-SI unit employed: cal = 4.184 J.

Table 1 Compounds synthesised and respective yields

Compound	X	Y	Z	Yield (%)
L ¹	CH ₂	O	Cl	84
L ²	(CH ₂) ₂ O(CH ₂) ₂	O	Cl	76
L ³	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	O	I	77
L ⁴	CH ₂	S	Cl	79
L ⁵	(CH ₂) ₂ O(CH ₂) ₂	S	Cl	78
L ⁶	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	S	I	73
L ^{7a}	(CH ₂) ₂ N(R)(CH ₂) ₂	S	OR	52
L ⁸	CH ₂	NH	Cl	61
L ⁹	(CH ₂) ₂ O(CH ₂) ₂	NH	Cl	58
L ¹⁰	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	NH	I	54
L ^{11b}	(CH ₂) ₂ O(CH ₂) ₂ O(CH ₂) ₂	NH	I	68

^a R = O₂SC₆H₄Me-*p*. ^b R = (CH₂)₃Me.

electron-impact mass spectra were obtained on a Kratos MS80 RF spectrometer, UV/VIS solution spectra in methanol (and in one instance by solid-state reflectance) with a Perkin-Elmer 550S instrument, fingerprint IR spectra (from KBr discs) on a Nicolet 20 PC-IR spectrometer and ESR spectra at X-band frequency on a Bruker 200D spectrometer.

Compounds L¹,¹⁴ L⁴ (ref. 15) and L⁸ (ref. 15) have been prepared previously *via* a different synthetic route.

Synthesis of compounds

L³. To a stirred solution of freshly distilled tetrahydrofuran (60 cm³) containing 2-sulfanylbenzoxazole (4.55 g, 0.03 mol) was added ethyldiisopropylamine (4.52 g, 0.035 mol) in slight excess. The solution was refluxed gently for 30 min, then 1,2-bis(2-iodoethoxy)ethane (5.02 g, 0.014 mol) was added dropwise and the mixture refluxed gently for 17 h. The mixture was cooled and the resultant solid material filtered off to leave a yellow solution which was concentrated *in vacuo* to yield a pale yellow oil. The oil was dissolved in chloroform and washed with saturated NaCl (3 × 20 cm³) and distilled water (3 × 20 cm³). The organic extracts were dried over anhydrous magnesium sulfate, filtered and reduced to a pale yellow oil *in vacuo*. The oil was treated with hot ethanol and charcoal, and the clean ethanolic filtrate left to stand at -20 °C for 48 h; then a small amount of water was added, which resulted in a white precipitate. After 48 h the precipitate was filtered off at the pump, washed with water, and air dried to leave a fine white powder. Compounds L¹–L⁶ were prepared similarly using similar concentrations; yields are in Table 1.

L⁷. This compound was synthesised in a similar manner to that above using *N*-toluene-*p*-sulfonylbis[2-(toluene-*p*-sulfonyloxy)ethyl]amine¹⁶ instead of the dihalide component. The final product was separated by flash chromatography [eluent, light petroleum (b.p. 60–80 °C)–ethyl acetate (5:1)] and crystallised to give a white solid.

L⁸–L¹⁰. The bis(benzimidazole) derivatives were prepared in a similar manner; however, on removal of the thf, the crude oil was treated three times with ethanol–charcoal and water (due to the insolubility of benzimidazoles in chloroform) to obtain a pure solid product.

L¹¹. This compound was prepared according to the literature method.¹ The final product was purified using flash chromatography [eluent, light petroleum–ethyl acetate (1:1.5)] to leave a pale yellow oil.

Elemental analyses and ¹H NMR data for the compounds are presented in Tables 2 and 3 respectively. Infrared spectra compared well with those in the literature.¹⁵

Synthesis of copper(II) complexes

All copper(II) complexes were prepared by equimolar addition of compound L (0.50 mmol) to the corresponding copper(II) salt in methanol (25 cm³). The benzimidazoles immediately gave a green solution on addition of the copper(II) salt. The methanolic solution was heated for 30 min and allowed to cool gradually to room temperature. Slow evaporation of the solution yielded dark green crystalline/powdered materials after several days. The bis(benzothiazoles) were complexed in the same manner and heated for a minimum of 1 h. There seemed no apparent colour change during this time. The solution was reduced in volume whilst hot until the first sign of precipitation. It was then allowed to cool gradually to room temperature. Dark green powders were obtained after slow evaporation of the methanol. The benzoxazoles failed to complex even when forcing conditions were employed such as longer reflux times and the addition of triethyl orthoformate.

Elemental analyses for these complexes are given in Table 4. Attempts to characterise the metal–ligand co-ordination by FAB mass spectroscopy were unsuccessful, showing only signals for the ligands.

X-Ray crystallography

Crystal data for compounds L¹, L⁴ and L⁶ and for the copper(II) perchlorate complex of L¹⁰ are given in Table 6, together with other information on the structure determinations.

Measurements for L¹ and L⁶ were made on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Cell parameters were refined from 2θ values of selected reflections measured at ±ω to minimise systematic errors. Intensities were measured with ω–θ scans and an on-line profile-fitting procedure.¹⁷ Absorption corrections were not required, but a correction was made for the observed 4% decay in intensity of regularly monitored standard reflections for L⁶.

Measurements for L⁴ and the copper complex were made on a Siemens SMART CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation. Cell parameters were refined from the spot positions and setting angles of selected strong reflections for L⁴, and from the observed ω angles of strong reflections taken from the complete data set for the complex. Semiempirical absorption corrections were applied, based on the high degree of redundancy and symmetry equivalence in the data sets.

The structures were solved by direct methods (heavy-atom methods for the copper complex) and refined by full-matrix least squares on F², with weighting w⁻¹ = σ²(F_o²) + (aP)² + (bP), where P = (2F_c² + F_o²)/3. An isotropic extinction parameter x was refined, whereby F_c is multiplied by (1 + 0.001 x F_c²λ³/sin 2θ)⁻¹. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included with a riding model for positions and isotropic displacement parameters. Disorder was resolved and modelled in three parts of the structure of the complex. Each of the oxygen atoms in the two L¹⁰ ligands was disordered over two positions, with site occupancy factors 0.55:0.45, 0.45:0.55, 0.62:0.38 and 0.85:0.15 respectively. Both perchlorate anions were disordered, and each was refined as two interpenetrating tetrahedra with the chlorine site in common; site occupancy factors were 0.55:0.45 and 0.50:0.50. Diffuse electron-density regions for the solvent molecules were interpreted as two fully occupied but disordered sites, and restraints were applied to C–O bond lengths and anisotropic displacement parameters.

The residuals are defined as wR2 = [Σw(F_o² – F_c²)²/Σw(F_o²)²]^{1/2} for all data, conventional R1 = Σ||F_o – |F_c||/Σ|F_o| for reflections having F_o² > 2σ(F_o²). The goodness of fit was calculated on F² for all data. Programs were standard Stoe DIF4 and Siemens SMART control software, Siemens

Table 2 Elemental analysis data for compounds L¹–L¹¹

Compound	Appearance	M.p./°C	Analysis ^a (%)			Mass spectrum, <i>m/z</i>
			C	H	N	
L ¹	White solid	129 ^b				
L ²	White solid	78	58.2 (58.1)	3.8 (4.3)	7.3 (7.5)	372 (<i>M</i> ⁺) ^c
L ³	White solid	65	57.9 (57.7)	4.8 (4.9)	6.6 (6.7)	417 (<i>M</i> + H ⁺) ^d
L ⁴	Pale yellow solid	100 ^e	52.3 (52.0)	2.9 (2.9)	8.1 (8.1)	346 (<i>M</i> ⁺) ^c
L ⁵	Pale yellow solid	68	53.3 (53.4)	6.6 (6.9)	3.6 (4.0)	404 (<i>M</i> ⁺) ^c
L ⁶	Pale yellow solid	76	53.7 (53.6)	4.6 (4.5)	6.1 (6.3)	449 (<i>M</i> + H ⁺) ^d
L ⁷	White solid	126	53.8 (53.9)	3.9 (4.2)	7.4 (7.5)	558 (<i>M</i> + H ⁺) ^d
L ⁸	White solid	219 ^f	57.7 (57.7)	3.3 (3.9)	17.4 (18.0)	313 (<i>M</i> + H ⁺) ^d
L ⁹	White solid	235	58.4 (58.4)	4.8 (4.9)	14.7 (15.1)	370 (<i>M</i> ⁺) ^c
L ¹⁰	White solid	165	56.8 (58.0)	4.7 (5.4)	12.6 (13.5)	414 (<i>M</i> ⁺) ^c
L ¹¹	Pale yellow oil	Oil ^g	62.7 (63.9)	7.6 (7.3)	10.4 (10.6)	527 (<i>M</i> ⁺) ^c

^a Calculated values in parentheses. ^b Lit.,¹⁴ 126 °C. ^c Electron-impact mass spectrometry. ^d Fast atom bombardment mass spectrometry. ^e Lit.,¹⁵ 96 °C. ^f Lit.,¹⁵ 212 °C. ^g Oil analysed at Zeneca Specialties.

Table 3 Proton NMR data for compounds L¹–L¹¹

Compound	δ	
	Aromatics	X
L ¹	7.67–7.58 (2 H, m) 7.55–7.3 (2 H, m) 7.37–7.20 (4 H, m)	5.16 (2 H, s)
L ²	7.58–7.52 (2 H, m) 7.44–7.37 (2 H, m) 7.30–7.16 (4 H, m)	3.93–3.87 (4 H, t) 3.53–3.47 (4 H, t)
L ³	7.61–7.52 (2 H, m) 7.46–7.37 (2 H, m) 7.30–7.16 (4 H, m)	3.89–3.83 (4 H, t) 3.52–3.46 (4 H, t) 3.66 (4 H, s)
L ⁴	7.92–7.87 (2 H, m) 7.78–7.73 (2 H, m) 7.47–7.24 (4 H, m)	5.32 (2 H, s)
L ⁵	7.84–7.79 (2 H, m) 7.74–7.19 (2 H, m) 7.42–7.22 (4 H, m)	3.93–3.86 (4 H, t) 3.60–3.53 (4 H, t)
L ⁶	7.85–7.81 (2 H, m) 7.74–7.70 (2 H, m) 7.42–7.22 (4 H, m)	3.89–3.83 (4 H, t) 3.58–3.52 (4 H, t) 3.67 (4 H, s)
L ^{7*}	7.71–7.67 (2 H, m) 7.66–7.56 (4 H, m) 7.26–7.10 (6 H, m)	3.71–3.55 (8 H, m)

* δ 2.29 (3 H, s, *p*-MeC₆H₄SO₂).

SAINT for integration of area-detector frames, SHELXTL,¹⁸ and local programs. Refined atomic coordinates are given in Tables 7–10.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

The bis-benzimidazoles, -benzothiazoles and -benzoxazoles can be prepared easily and in good yields with dihalides or di-toluene-*p*-sulfonates, avoiding the problems outlined earlier and those of having to synthesise multidonor dicarboxylic acids. Increasing the bridge chain length does not affect the yields appreciably, which is often a problem associated with the

Phillips condensation reaction. As a result of using dihalides and di-toluene-*p*-sulfonates more flexibility is possible when considering complementary donor atoms for favourable metal co-ordination. The use of 2-sulfanyl starting materials leaves a sulfur atom in the 2 position. The strength of the C–S bond formed at the 2 position has been examined by alkylating the bis(benzimidazoles) at the secondary nitrogen with an alkyl halide. The resulting product has been isolated and characterised showing the bond is able to withstand the conditions employed. As a result this type of alkylated ligand may be incorporated into transport systems.¹ As ligands, the benzothiazoles usually co-ordinate through the (less basic) nitrogen and not the sulfur, and they lack the feature of prototropy which makes imidazoles so versatile in biology. Benzoxazoles are even less known, although a benzoxazole unit provides a nitrogen-donor group in calcimycin.

The structure of compound L¹ is shown in Fig. 1. It crystallises as extremely long thin needles. The structure has parallel aromatic rings which are spaced 4.247 Å apart, further than customary for π – π interactions. Owing to the layered packing arrangement (Fig. 2), attempts to intercalate other materials between the molecules are being explored.

The analogous bis(benzothiazole) L⁴ shown in Fig. 3 shows a strikingly different packing. There are two independent molecules in the asymmetric unit, which are linked together by S...S interactions [S(1)...S(8) 3.537(2), S(1)...S(7) 3.536(2), S(2)...S(7) 3.725(2) Å] to form a loose dimer of parallel molecules. These are then arranged in a herringbone packing arrangement, shown in Fig. 4.

The crystal structure of bis(benzothiazole) L⁶ is shown in Fig. 5. It is a spectacularly long thin molecule, with SCCO torsion angles *gauche* ($\pm 56.4^\circ$) but the OCCO angle is *anti* (180.0°). Recent¹⁹ *ab initio* calculations on the prototypes 1,2-dimethoxyethane and 2-methoxyethyl methyl sulfide, subsequently expanded with molecular mechanics and molecular dynamics simulations of single molecules in the gas phase, suggest the intrinsic preference of the OCCO unit for an *anti* torsion over *gauche* by 1.4 kcal mol^{–1} while for SCCO it is only 0.8 kcal mol^{–1}. The S...S links between adjacent thiazole and chain sulfurs create chains of molecules extended along the *b* axis, as shown in Fig. 6 [S(1)...S(2'') and S(2)...S(1'')]

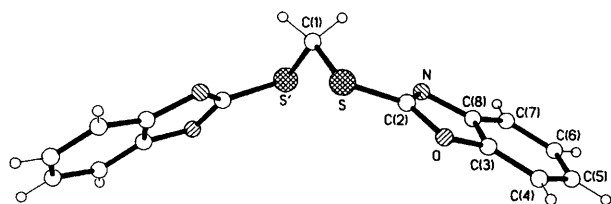


Fig. 1 Molecular structure of compound L^1 with atom labelling. Symmetry operation for primed atoms: $1 - x, y, \frac{1}{2} - z$

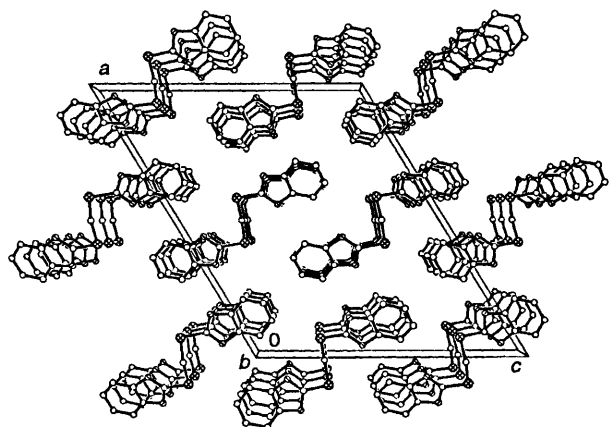


Fig. 2 Crystal packing of compound L^1 viewed along the short b axis, showing the parallel stacking

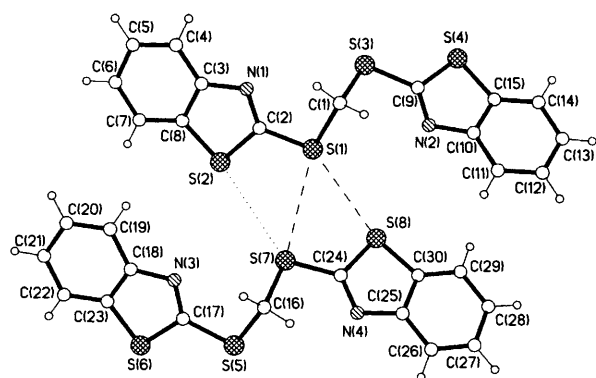


Fig. 3 Molecular structure of compound L^4 with atom labelling and the intermolecular $S \cdots S$ interactions between the two crystallographically independent molecules

3.580(2), $S(2) \cdots S(2'')$ 3.712(3) Å, where the double prime denotes the symmetry operation $1 - x, 1 - y, -z$.

The complexation of these compounds was intended to give us some basic information about their co-ordinating ability. That the benzimidazoles L^8 – L^{10} complexed with copper salts was readily indicated by an immediate colour change upon mixing the two. The benzothiazoles were eventually made to complex under forcing conditions; this problem has also been noted by Thompson *et al.*¹¹ The benzoxazoles simply failed to co-ordinate. The trend of complexation between the three series may be explained in terms of the relative basicities. Recent work by Elguero and co-workers²⁰ on the pK_a values of these types of heterocycle shows that benzimidazole > benzothiazole > benzoxazole with $pK_a(HB^+)$ for the parent free base in the order $5.56 > 1.2 > -0.13$. Analytical figures suggest that all complexes were of a 1:1 nature with respect to ligand and metal except in the case of the copper perchlorate complex of L^{10} which had two ligands per copper.

The crystal structure of the copper perchlorate complex of $[CuL^{10}_2]^{2+}$ is shown in Figs. 7 and 8. The copper(II) is held in

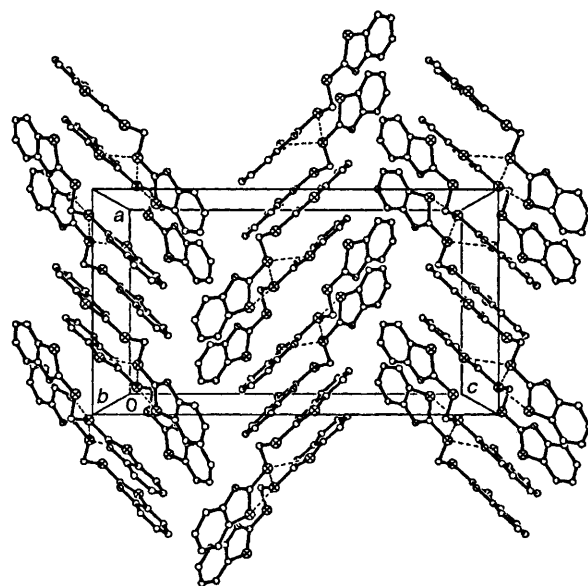


Fig. 4 Section through the crystal packing of compound L^4 showing the herringbone arrangement of the pairs of molecules

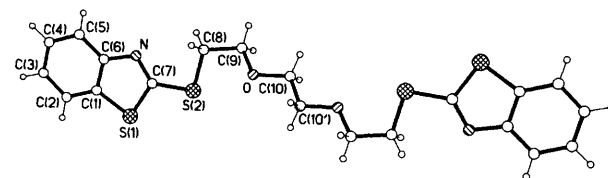


Fig. 5 Molecular structure of compound L^6 with atom labelling. Symmetry operation for primed atoms: $1 - x, 2 - y, -z$

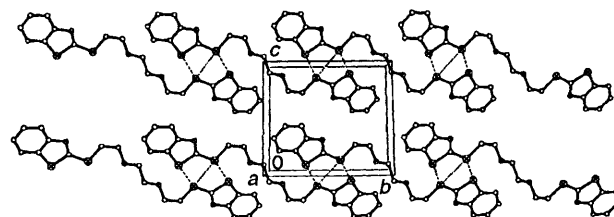


Fig. 6 Section through the crystal packing of compound L^6 showing the chains of molecules linked by $S \cdots S$ interactions

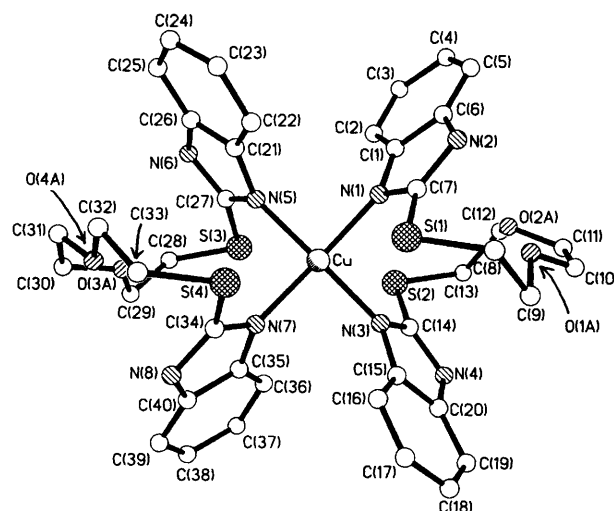


Fig. 7 Structure of the $[CuL^{10}_2]^{2+}$ cation with atom labelling. Only one component for each disordered oxygen atom is shown

distorted square-planar geometry. The two bis(benzimidazole) moieties act as bidentate ligands with equivalent Cu–N

Table 4 Elemental analysis data for copper(II) complexes of L¹–L¹⁰

Reagents ^a	Product	Appearance	M.p./°C	Analysis (%) ^b		
				C	H	N
L ⁴ + CuCl ₂ ·2H ₂ O	L ⁴ ·CuCl ₂	Dark green	205	37.5 (37.5)	2.0 (2.1)	6.1 (5.8)
L ⁵ + CuCl ₂ ·2H ₂ O	L ⁵ ·CuCl ₂ ·H ₂ O	Dark green	230	38.9 (38.8)	3.2 (3.3)	5.0 (5.0)
L ⁶ + CuCl ₂ ·2H ₂ O	L ⁶ ·CuCl ₂	Dark green	210	41.7 (41.3)	3.2 (3.5)	4.7 (4.8)
L ⁸ + CuCl ₂ ·2H ₂ O	L ⁸ ·CuCl ₂	Green	209	40.2 (40.3)	2.9 (2.7)	12.5 (12.5)
L ⁹ + CuCl ₂ ·2H ₂ O	L ⁹ ·CuCl ₂ ·H ₂ O	Green	219	41.2 (41.3)	3.9 (3.9)	10.8 (10.7)
L ¹⁰ + CuCl ₂ ·2H ₂ O	L ¹⁰ ·CuCl ₂ ·H ₂ O	Green	200	42.0 (42.4)	4.5 (4.3)	10.0 (9.9)
L ⁹ + Cu(ClO ₄) ₂ ·6H ₂ O	L ⁹ ·Cu(ClO ₄) ₂ ·H ₂ O·0.5MeOH	Dark green	183	34.0 (33.3)	3.3 (3.3)	8.4 (8.4)
L ¹⁰ + Cu(ClO ₄) ₂ ·6H ₂ O	2L ¹⁰ ·Cu(ClO ₄) ₂ ·2H ₂ O·MeOH	Dark green	226	42.3 (42.5)	3.9 (4.5)	9.7 (9.7)

^a L¹–L³ gave no complexation with CuCl₂·2H₂O. ^b Calculated values in parentheses.**Table 5** The UV/VIS data for compounds L¹–L¹⁰ and their copper(II) complexes in methanol and in the solid state

Compound	$\lambda_{\max}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
L ¹	210 (18 900), 248 (19 500), 278 (22 600), 286 (24 300)
L ²	212 (15 900), 250 (25 570), 278 (25 300), 286 (23 700)
L ³	212 (13 550), 250 (20 800), 278 (19 900), 286 (18 150)
L ⁴	226 (33 900), 282 (22 450), 290 (21 950), 302 (20 200)
L ⁴ + CuCl ₂	228 (31 000), 282 (22 010), 290 (21 300), 300 (19 760), 750 (55)
L ⁵	230 (21 450), 280 (19 300), 290 (17 700), 300 (14 050)
L ⁵ + CuCl ₂	228 (23 200), 280 (18 550), 288 (16 890), 300 (13 340), 755 (41)
L ⁶	228 (23 600), 280 (16 700), 290 (15 500), 300 (11 900)
L ⁶ + CuCl ₂	228 (26 490), 280 (21 460), 290 (14 490), 300 (11 100), 760 (40)
L ⁸	216 (11 050), 226 (12 400), 248 (13 750), 304 (22 850)
L ⁸ + CuCl ₂	214 (10 080), 224 (17 720), 250 (12 283), 292 (14 490), 750 (60)
L ⁹	226 (14 200), 252 (10 100), 286 (20 350), 292 (21 900)
L ⁹ + CuCl ₂	224 (15 980), 250 (11 920), 284 (20 700), 290 (19 960), 365 (580), 764 (65)
L ⁹ + Cu(ClO ₄) ₂	220 (19 610), 250 (10 780), 284 (18 230), 290 (17 090), 362 (612), 565 (180), 715 (70)
L ¹⁰	228 (14 130), 250 (14 700), 284 (21 050), 290 (20 000)
L ¹⁰ + CuCl ₂	224 (14 610), 250 (12 020), 286 (19 670), 290 (19 200), 360 (580), 755 (63)
L ¹⁰ + Cu(ClO ₄) ₂	222 (11 595), 248 (8260), 284 (14 920), 290 (14 050), 360 (642), 565 (143), * 705 (59)*

* Solid-state reflectance visible spectrum indicated 555 nm and a broad feature at *ca.* 705 nm.**Table 6** Crystallographic data for compounds L¹, L⁴, L⁶ and [CuL¹⁰]₂²⁺

	L ¹	L ⁴	L ⁶	[CuL ¹⁰] ₂ [ClO ₄] ₂ ·3MeOH
Formula	C ₁₅ H ₁₀ N ₂ O ₂ S ₂	C ₁₅ H ₁₀ N ₂ S ₄	C ₂₀ H ₂₀ N ₂ O ₂ S ₄	C ₄₃ H ₅₆ Cl ₂ CuN ₈ O ₁₅ S ₄
<i>M</i>	314.4	346.5	448.6	1187.6
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	21.359(8)	12.542(3)	10.709(7)	49.020(4)
<i>b</i> /Å	4.2467(13)	21.408(5)	10.450(7)	14.5384(11)
<i>c</i> /Å	18.119(5)	22.170(5)	9.575(7)	15.7845(12)
β /°	121.04(2)		105.22(9)	91.864(2)
<i>U</i> /Å ³	1408.2(8)	5953(2)	1033.9(12)	11 243(2)
<i>Z</i>	4	16	2	8
<i>D</i> _c /g cm ^{−3}	1.483	1.547	1.441	1.403
μ/mm^{-1}	0.38	0.63	0.48	0.70
<i>F</i> (000)	648	2848	468	4936
<i>T</i> /K	293	160	160	160
Crystal size/mm	0.72 × 0.38 × 0.20	0.55 × 0.38 × 0.08	0.60 × 0.44 × 0.27	0.78 × 0.50 × 0.20
$\theta_{\max}$ /°	25.0	25.6	22.5	25.7
Maximum indices <i>hkl</i>	24, 5, 21	15, 25, 26	11, 11, 10	59, 17, 19
Reflections measured	2070	24 381	3093	23 785
Unique reflections	1216	5157	1354	9383
<i>R</i> _{int}	0.0113	0.0754	0.0170	0.0470
Transmission		0.701–0.800		0.642–0.806
Extinction coefficient <i>x</i>	0.0127(10)	0.000 46(9)	0	0.000 34(6)
Weighting parameters <i>a</i> , <i>b</i>	0.0359, 0.9527	0.0304, 9.6691	0, 0.4138	0.0828, 43.4398
No. refined parameters	97	380	127	800
<i>wR</i> 2 (all data)	0.0763	0.1224	0.0768	0.1888
<i>R</i> 1 ('observed' data)	0.0282 (1135)	0.0565 (4148)	0.0286 (1226)	0.0656 (7994)
Goodness of fit	1.057	1.222	1.055	1.121
Maximum, minimum electron density/e Å ^{−3}	0.187, −0.171	0.337, −0.344	0.246, −0.210	0.733, −0.596

distances. The geometry of the CuL¹⁰₂ complex (Fig. 8) is unusual because of the nature of the ligand, which in addition to providing two rigid benzimidazole units has the adjacent chain sulfurs at the 2 position of the molecule fixed while the polyether chain connecting them has no constraints and is

found to be disordered. The co-ordinating tertiary nitrogens are at an average distance from the copper of 1.990 Å, but form a very flat tetrahedron about it; this is at 0.003 Å and the nitrogens are at ±0.34 Å from the CuN₄ mean plane. The sulfurs are at essentially equivalent (3.348–3.436 Å) distances from the copper,

with which they also form an approximate plane (Fig. 8) (rectangular array) with deviations of ± 0.44 Å for the sulfurs. The distances are too long for a conventional interaction, being beyond the long-distance interactions sometimes noted (*e.g.* copper–methionine sulfur)²¹ for copper proteins, where the Cu...S distance may modulate the rate of electron transfer. For each of the Cu–N interactions there is one Cu–N–C angle inclined towards the copper (123.5–126.0°), the adjacent angle being slightly larger (128.6–130.6°) indicative of tilting of the sulfur towards the copper ion. We would like to describe the sulfurs as quasi-co-ordinated. These four sulfurs are in a position to complete with the four nitrogen donor atoms a skewed square antiprism around the copper, one pair of nitrogen and one pair of sulfur donor atoms from each ligand

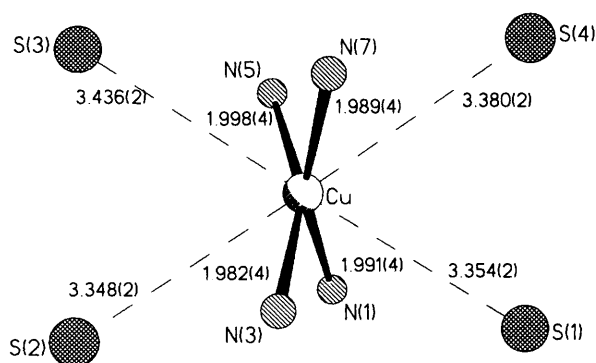


Fig. 8 Environment of the copper(II) ion with Cu–N and Cu...S distances. The view is perpendicular to that of Fig. 7

Table 7 Atomic coordinates ($\times 10^4$) for compound **L**¹

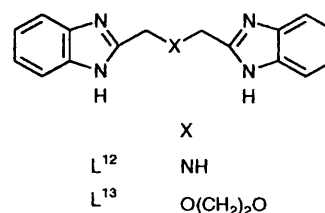
Atom	x	y	z
C(1)	5000	–1600(6)	2500
S	4173.9(2)	618.7(11)	2142.7(2)
C(2)	4017.4(8)	1779(4)	1141.1(9)
O	3403.0(6)	3571(3)	672.8(7)
N	4403.6(7)	1234(3)	798.0(8)
C(3)	3407.0(8)	4206(4)	–77.4(10)
C(4)	2905.5(10)	5918(4)	–783.9(12)
C(5)	3053.6(11)	6153(5)	–1438.5(12)
C(6)	3661.8(11)	4745(5)	–1381.8(12)
C(7)	4158.7(10)	3036(5)	–667.7(11)
C(8)	4018.2(8)	2782(4)	–3.8(9)

Table 8 Atomic coordinates ($\times 10^4$) for compound **L**⁴

Atom	x	y	z	Atom	x	y	z
S(1)	8 039.3(9)	1 019.2(5)	4 233.3(5)	S(5)	10 595.6(9)	–1 620.2(5)	4 165.6(5)
S(2)	10 267.7(9)	1 020.0(5)	3 744.9(5)	S(6)	12 758.8(9)	–1 508.7(5)	3 594.6(5)
S(3)	6 659.4(9)	2 166.8(5)	4 471.5(5)	S(7)	9 233.8(9)	–468.2(5)	4 390.1(5)
S(4)	5 093.1(9)	2 340.8(5)	5 487.9(5)	S(8)	7 730.1(9)	–106.9(5)	5 387.6(5)
N(1)	8 826(2)	1 816.2(14)	3 392.8(14)	N(3)	11 208(3)	–733(2)	3 367.9(14)
N(2)	5 615(3)	1 246(2)	5 063.7(14)	N(4)	7 993(3)	–1 259.8(14)	5 037.7(14)
C(1)	6 899(3)	1 476(2)	4 024(2)	C(16)	9 383(3)	–1 205(2)	4 004(2)
C(2)	8 989(3)	1 352(2)	3 752(2)	C(17)	11 457(3)	–1 223(2)	3 679(2)
C(3)	9 753(3)	1 951(2)	3 070(2)	C(18)	12 081(3)	–539(2)	3 028(2)
C(4)	9 867(3)	2 424(2)	2 644(2)	C(19)	12 091(3)	–21(2)	2 646(2)
C(5)	10 842(4)	2 512(2)	2 368(2)	C(20)	13 011(4)	116(2)	2 331(2)
C(6)	11 711(4)	2 134(2)	2 512(2)	C(21)	13 921(4)	–254(2)	2 391(2)
C(7)	11 622(3)	1 655(2)	2 927(2)	C(22)	13 933(3)	–767(2)	2 767(2)
C(8)	10 630(3)	1 567(2)	3 206(2)	C(23)	13 007(3)	–905(2)	3 090(2)
C(9)	5 794(3)	1 838(2)	5 010(2)	C(24)	8 301(3)	–692(2)	4 938(2)
C(10)	4 858(3)	1 143(2)	5 518(2)	C(25)	7 240(3)	–1 269(2)	5 504(2)
C(11)	4 466(3)	561(2)	5 690(2)	C(26)	6 746(3)	–1 805(2)	5 727(2)
C(12)	3 711(3)	535(2)	6 142(2)	C(27)	6 020(3)	–1 745(2)	6 191(2)
C(13)	3 328(3)	1 073(2)	6 418(2)	C(28)	5 793(3)	–1 161(2)	6 444(2)
C(14)	3 698(3)	1 651(2)	6 250(2)	C(29)	6 270(3)	–623(2)	6 225(2)
C(15)	4 478(3)	1 685(2)	5 799(2)	C(30)	7 002(3)	–684(2)	5 757(2)

being above and below the copper. The ether oxygen donor atoms are well removed from the co-ordination sphere and the N–C–S section of the heterocycle is asymmetric bidentate. Disorder in the polyether chain does not extend to the sulfurs which must have a weak impact on the copper and certainly shield it from the approach of other reagents, while preserving the possibility of electron transfer at the copper. The perchlorate anions are non-co-ordinating and are disordered in the unit cell, as are molecules of methanol solvent.

This new kind of ligation is unique. A bis(benzimidazole) structure of the same stoichiometry $[\text{CuL}^{12}_2]^{2+}$ previously reported by Berends and Stephan²² has the copper in an octahedral environment with all six nitrogen donors from the two ligands co-ordinated. The two aliphatic nitrogens are situated at apical sites of the co-ordination sphere. The necessity for two bis(benzimidazoles) to surround the copper in our complex could therefore be argued. Since aza donors are favoured over ether donors and the thioether donors at the 2 position of the molecule are sterically hindered to an extent that they are beyond the typical thioether bond length so a second bis(benzimidazole) moiety arranges itself to satisfy the copper's co-ordination requirements. In another related structure²³ $[\text{CuL}^{13}\text{Br}_2]$ a bis(benzimidazole) **L**¹³ forces a square-planar copper array with two nitrogen and two bromide ligands in the square plane; however, the two oxygens in the linking chain are inclined towards the copper in a very unusual polyhedron. This is the closest comparison in the literature with the present structure, since the oxygens are at a distance from the copper of 2.74 Å somewhat beyond the expected van der Waals separation. In the present structure the sulfurs are in a preferential co-ordination orientation (even though they are situated beyond the expected sulfur–copper bond van der Waals distance) because of their proximity to the nitrogen. In the structure shown for the complex $[\text{CuL}^{10}_2]^{2+}$ the co-ordination sphere of the copper is completely blocked by the ligand N_4S_4 donor set. This device is promising for the design of biomimetic ligands in



which the 2-sulfanylbenzimidazole unit provides the donor and the linking chain may be modified, *e.g.* to provide a cavity for other entities as desired.

UV/VIS spectra

Electronic spectra in the UV and visible regions are shown in Table 5 for the compounds and their copper(II) complexes in methanolic solutions. The expected bands for the heteroatomic compounds were found in the UV region, shifted to longer

wavelengths for the benzimidazole series L^8-L^{10} by the presence of the sulfur substituent at the 2 position. Ligand-to-metal charge-transfer bands (l.m.c.t.) at $27.8 \times 10^3 \text{ cm}^{-1}$ (ϵ ca. $580\text{--}640 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) were observed for the copper complexes of L^8-L^{10} at lower energy than for analogous complexes examined previously.^{4,24–27} The analogous chloride complexes $[\text{CuL}]^{2+}$ had ligand-field bands at $(13.3\text{--}13.1) \times 10^3 \text{ cm}^{-1}$ (ϵ ca. 60–65), while the perchlorates (for L^9 and L^{10}) showed two bands [17.7×10^3 and $(14.2\text{--}14.0) \times 10^3 \text{ cm}^{-1}$] in solution. The sample of the $[\text{CuL}^{10}_2][\text{ClO}_4]_2$ complex used for UV/VIS spectroscopy was from the same crop of crystals as that used for the crystallographic determination. In the solid-state reflectance spectrum (visible region) two bands appeared (18.0×10^3 and $14.2 \times 10^3 \text{ cm}^{-1}$). The spectra for this complex are consistent in the solid state and solution, and correspond to the tetrahedrally distorted square-planar geometry observed in the crystal; the spectra of the chloride complexes indicate a different geometry, perhaps with chloride co-ordinated to the copper.* In the single ligand complex a chloride or solvent molecule could approach the copper and the bands at $(13.1\text{--}13.2) \times 10^3 \text{ cm}^{-1}$ are consistent with a distorted-octahedral structure. The spectra of benzothiazoles $L^4\text{--}L^6$ changed little on co-ordination to copper(II) (minor changes in λ and ϵ). There was no clear shoulder in the near-UV region

Table 9 Atomic coordinates ($\times 10^4$) for compound L^6

Atom	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	8 125(2)	2 440(2)	2 120(2)
C(2)	8 554(2)	1 178(2)	2 148(2)
C(3)	9 601(2)	834(2)	3 258(3)
C(4)	10 217(2)	1 710(2)	4 307(2)
C(5)	9 787(2)	2 957(2)	4 301(2)
C(6)	8 709(2)	3 320(2)	3 200(2)
S(1)	6 884.6(5)	3 190.6(5)	839.1(6)
C(7)	7 226(2)	4 602(2)	1 875(2)
N	8 163(2)	4 544(2)	3 049(2)
S(2)	6 301.0(5)	5 949.8(5)	1 226.0(5)
C(8)	7 077(2)	7 108(2)	2 593(2)
C(9)	6 226(2)	8 275(2)	2 443(2)
O	5 994.7(13)	8 754.5(13)	1 009.3(14)
C(10)	5 093(2)	9 783(2)	765(2)

* A referee suggested that halide bridging may be present.

Table 10 Atomic coordinates ($\times 10^4$) for $[\text{CuL}^{10}_2][\text{ClO}_4]_2 \cdot 3\text{MeOH}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cu	1 202.91(10)	2 452.8(3)	4 866.4(3)	O(3B)	265(6)	2 016(21)	5 708(18)
N(1)	1 361.4(7)	3 250(2)	3 982(2)	C(30)	178(2)	2 352(6)	6 458(6)
C(1)	1 293.0(9)	3 339(3)	3 121(3)	C(31)	250(2)	3 329(6)	6 586(5)
C(2)	1 089.7(10)	2 931(3)	2 618(3)	O(4A)	510.3(12)	3 440(3)	6 865(4)
C(3)	1 080.2(12)	3 140(3)	1 769(3)	O(4B)	468(6)	3 649(20)	6 242(16)
C(4)	1 268.2(12)	3 734(4)	1 416(3)	C(32)	607(2)	4 354(4)	6 941(5)
C(5)	1 469.2(12)	4 147(4)	1 901(3)	C(33)	882.4(14)	4 270(4)	7 324(4)
C(6)	1 475.5(10)	3 944(3)	2 762(3)	S(4)	1 127.0(3)	3 717.7(8)	6 639.7(8)
N(2)	1 649.8(8)	4 249(3)	3 419(3)	C(34)	1 032.5(11)	2 564(3)	6 644(3)
C(7)	1 573.9(9)	3 806(3)	4 128(3)	N(7)	1 088.5(8)	2 022(2)	5 997(2)
S(1)	1 702.6(3)	4 009.9(9)	5 148.2(8)	C(35)	1 023.5(10)	1 129(3)	6 252(3)
C(8)	2 066.8(11)	4 139(4)	4 987(4)	C(36)	1 042.3(10)	290(3)	5 829(3)
C(9)	2 206.7(11)	3 247(5)	4 820(4)	C(37)	951.7(12)	−481(3)	6 254(4)
O(1A)	2 082.8(14)	3 051(5)	3 959(5)	C(38)	845.3(13)	−424(4)	7 054(4)
O(1B)	2 098(2)	2 547(7)	4 299(6)	C(39)	823.2(12)	399(4)	7 476(3)
C(10)	2 229.7(13)	2 491(5)	3 509(4)	C(40)	920.0(11)	1 166(3)	7 061(3)
C(11)	2 084.3(13)	2 001(6)	2 826(5)	N(8)	933.7(10)	2 087(3)	7 308(2)
O(2A)	1 809(2)	2 032(7)	2 789(6)	Cl(1)	618.1(3)	1 863.9(8)	9 452.7(8)
O(2B)	1 888(2)	1 447(6)	3 013(4)	O(5)	568.7(10)	2 404(3)	8 713(2)
C(12)	1 694.7(13)	1 262(6)	2 296(4)	O(6A)	584(2)	2 370(10)	10 169(6)
C(13)	1 563.4(13)	437(4)	2 684(4)	O(7A)	460(3)	1 120(7)	9 425(7)
S(2)	1 338.4(3)	730.4(9)	3 536.7(8)	O(8A)	903(2)	1 640(11)	9 410(7)
C(14)	1 563.4(10)	943(3)	4 382(3)	O(6B)	715(5)	2 373(13)	10 179(14)
N(3)	1 518.3(8)	1 601(3)	4 943(2)	O(7B)	341(3)	1 564(11)	9 725(11)
C(15)	1 712.8(10)	1 473(3)	5 602(3)	O(8B)	756(3)	1 016(7)	9 358(7)
C(16)	1 759.8(11)	1 941(3)	6 364(3)	Cl(2)	2 172.2(3)	5 817.0(13)	2 694.0(13)
C(17)	1 973.8(12)	1 646(4)	6 884(4)	O(9A)	2 242(4)	6 194(13)	1 986(13)
C(18)	2 140.6(12)	914(4)	6 659(4)	O(10A)	1 913(3)	6 017(10)	3 060(12)
C(19)	2 098.6(11)	444(4)	5 908(4)	O(11A)	2 369(4)	6 017(22)	3 394(13)
C(20)	1 880.0(10)	732(3)	5 392(3)	O(12A)	2 170(4)	4 831(14)	2 630(22)
N(4)	1 779.3(9)	407(3)	4 620(3)	O(9B)	2 348(4)	5 705(16)	1 958(14)
N(5)	832.0(7)	2 938(2)	4 551(2)	O(10B)	1 907(2)	5 984(9)	2 304(11)
C(21)	743.7(9)	3 855(3)	4 496(3)	O(11B)	2 287(3)	6 606(9)	3 111(10)
C(22)	884.5(10)	4 675(3)	4 642(3)	O(12B)	2 190(4)	5 049(14)	3 102(14)
C(23)	734.1(11)	5 485(3)	4 573(3)	O(1M)	151.1(8)	−2 530(3)	6 246(3)
C(24)	453.9(11)	5 477(3)	4 363(4)	C(1MA)	308(3)	−3 096(12)	6 804(9)
C(25)	314.4(11)	4 668(3)	4 205(3)	C(1MB)	245(5)	−1 930(21)	6 975(13)
C(26)	466.3(9)	3 865(3)	4 268(3)	O(2M)	2 043(2)	−1 085(5)	4 041(5)
N(6)	388.8(8)	2 954(3)	4 159(2)	C(2MA)	2 356(4)	−1 025(15)	3 988(11)
C(27)	612.5(9)	2 437(3)	4 349(3)	C(2MB)	1 762(5)	−1 494(15)	4 038(16)
S(3)	626.2(3)	1 241.0(8)	4 270.2(8)	O(3M)	1 642(9)	7 121(30)	3 931(18)
C(28)	303.3(11)	893(4)	4 722(4)	C(3M)	1 369(10)	7 491(34)	3 950(19)
C(29)	292.4(13)	1 031(4)	5 652(5)	O(4M)	2 018(12)	7 234(19)	4 683(27)
O(3A)	347(4)	1 958(13)	5 882(12)	C(4M)	2 058(12)	6 713(23)	5 497(27)

consistent with l.m.c.t. absorption although careful analysis of the first-order derivative spectra distinguished a broad envelope at ca. 350–400 nm for L^5 – $CuCl_2$. For each of the L^4 – L^6 complexes the ligand-field band was at $13.3 \times 10^3 \text{ cm}^{-1}$ (ϵ ca. $40\text{--}55 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), consistent with distorted-octahedral geometry.

ESR Spectra

The spectrum for the copper(II) perchlorate complex of L^{10} in methanol showed hyperfine coupling on both $g_{\perp}$ and $g_{\parallel}$, though the latter is not well resolved: $g_{\perp} = 2.05$, $g_{\parallel} = 2.18$, $A_{\perp} = 13 \times 10^{-4} \text{ cm}^{-1}$ and $A_{\parallel} = 101 \times 10^{-4} \text{ cm}^{-1}$. These values are consistent with the approximately square-planar structure found in the solid state or with a distorted-tetragonal structure with one or two molecules of co-ordinated methanol.²⁷ There are some interesting comparisons in the literature. The anhydrous complex $[Cu(en)_2(NO_3)_2]$ (en = ethane-1,2-diamine) has a tetragonally distorted octahedral structure²⁸ with elongated axial Cu–O bonds and in aqueous solution^{29,30} its ESR parameters were $g_{\perp} = 2.04$ and $g_{\parallel} = 2.2$. Similar values were obtained for the bis(bidentate) almost planar structure³¹ of $[CuL_2]$ (L = salicylaldehyde oximate) with $g_{\perp} = 2.06$ and $g_{\parallel} = 2.22$ in solution.³² However, while the A values for the latter were $A_{\parallel} = 144 \times 10^{-4}$ and $A_{\perp} = 14.6 \times 10^{-4} \text{ cm}^{-1}$, consistent with our results, the A and B values quoted^{29,30} for the solution ESR spectra of $[Cu(en)_2]^{2+}$ were considerably larger. In comparing values of A it should be remembered that these may represent hyperfine contributions from either copper or nitrogen or both.

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