Metal-directed Syntheses of Dithiadiazacyclotetradecane Macrocycles with Pendant Alcohol and Nitro or Carboxylate Groups involving Macrocycle Ring Expansion†

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Copper(II)-directed condensation of 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine with nitroethane or diethyl malonate and formaldehyde yielded (*anti*-6-methyl-6-nitro-1,11-dithia-4,8-diazacyclotetradecan-13-ol)copper(II) and (diethyl 13-hydroxy-1,11-dithia-4,8-diazacyclotetradecane-6,6-dicarboxylate)copper(II) respectively in good yields. The latter was readily converted by decarboxylation and hydrolysis in aqueous base to the copper(II) complex of *anti*-13-hydroxy-1,11-dithia-4,8-diazacyclotetradecane-6-carboxylic acid from which the free ligand can be obtained by zinc–acid reduction of the copper ion, whereas the former can be converted by zinc–acid reduction directly to the hydrochloride salt of the free *anti*-6-amino-6-methyl-1,11-dithia-4,8-diazacyclotetradecan-13-ol ligand. The condensations should yield a thirteen-membered macrocycle with a pendant hydroxymethyl group fused to a macrocyclic ring carbon, but the molecules undergo a Wagner–Meerwein or alternate carbon skeleton rearrangement to yield the fourteen-membered macrocycle with a pendant alcohol group. The pendant alcohol can act as an axial donor group, as illustrated in the crystal structure analyses of (*anti*-6-methyl-6-nitro-1,11-dithia-4,8-diazacyclotetradecan-13-ol)copper(II) and (*anti*-13-hydroxy-1,11-dithia-4,8-diazacyclotetradecane-6-carboxylato)copper(II) as perchlorate salts. The former complex crystallizes in the monoclinic $P2_1/c$ space group, $a = 8.703(2)$, $b = 18.699(2)$, $c = 13.293(2)$ Å, $\beta = 105.15(1)°$ and the latter in the monoclinic $P2_1/n$ space group, $a = 7.450(1)$, $b = 15.325(2)$, $c = 16.772(1)$ Å, $\beta = 98.38(1)°$. In both complexes the alcohol is disposed *anti* to the nitro or carboxylate group. In the former, the copper ion lies in a distorted-octahedral environment of two sulfur donors (Cu–S_{av} 2.333 Å), two nitrogen donors (Cu–N_{av} 2.016 Å), the pendant alcohol donor [Cu–O 2.365(3) Å] and a perchlorate anion [Cu–O 2.544(3) Å], whereas in the latter a dimer with each copper in a very distorted octahedral environment exists where each carboxylate bridges to the alternate copper ion [Cu–O 2.293(3) Å] and the alcohol is weakly bound [Cu–O 2.520(3) Å] in addition to the macrocycle heteroatoms (Cu–N_{av} 2.035, Cu–S_{av} 2.353 Å).

The metal-directed syntheses of a range of pendant-arm macromonocyclic polyamines and polyamino acids formed using formaldehyde and the carbon acids nitroethane and diethyl malonate respectively have been examined, particularly with copper(II) as the templating metal ion.[1,2] These reactions lead to ring closing at pairs of *cis*-disposed primary amines, resulting in molecules with C-pendant nitro or *gem* diester groups. The former can be readily reduced to a pendant primary amine group, and the latter readily decarboxylated and hydrolysed to an acid group. These pendant NH_2 and CO_2H groups bound directly to a carbon in the macrocyclic ring can both act as pendant donors to metal ions.[1-3] The metal-directed cyclization chemistry described above occurs with multidentate ligands with terminal primary amine donors essentially independent of the type of internal donors, as exemplified by the identical chemistry resulting for reaction of the copper(II) complex of both $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ and $NH_2(CH_2)_2S(CH_2)_3S(CH_2)_2NH_2$.[4,5] However, examples of this type of chemistry with mixed-donor systems have been relatively few, despite the general interest shown in mixed N,S donor macrocycles.[6-13]

It has been shown recently that the OH group attached directly to a macrocyclic ring carbon in a like manner to amine and carboxylate groups also exhibits the potential to act as a pendant donor.[14] However, aliphatic alcohols are not sufficiently strong carbon acids to permit analogous condensation chemistry to that pursued with nitroalkanes and dialkyl malonates, but can be introduced *via* precursor acyclic ligands prepared separately and containing an alcohol group attached directly to a carbon atom. We have recently reported a copper(II)-directed condensation reaction of L^1 with formaldehyde and either diethyl malonate or nitroethane, where condensation occurs readily in high yield to form L^4 and L^2 (and L^3 following reduction) respectively,[14] but this remains the only example of a system with a pendant alcohol group prepared by this type of condensation chemistry. In this report, we have extended the chemistry to employ a precursor L^6 with a longer pendant CH_2OH arm attached to a carbon of the chain. On macrocyclization, a dissymmetric thirteen-membered ring macrocycle is expected to form (yielding L^7 and L^9) rather than the symmetric fourteen-membered ring macrocycles actually obtained (L^2 and L^4). However, a Wagner–Meerwein or alternate carbon skeleton rearrangement[15] occurs readily concomitant with the condensation reaction, yielding fourteen-membered ring macrocycles. Evidence of axial interaction of the pendant groups with the metal ion and of the stereoselective formation of the isomers of *anti* configuration (L^2, L^5) rather than those of *syn* configuration in the reactions is established by X-ray crystal structure analyses of the copper(II) complexes of L^2 and L^5.

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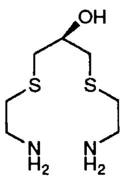
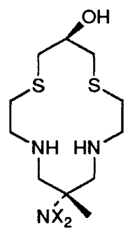
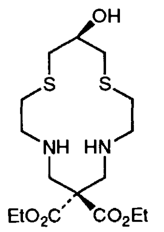
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



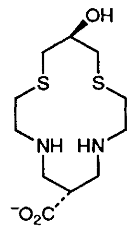
L^1



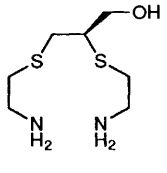
X
L^2 O
L^3 H



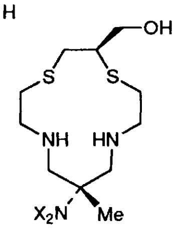
L^4



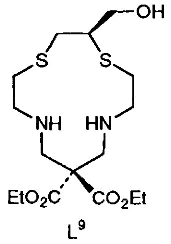
L^5



L^6



X
L^7 O
L^8 H



L^9

Experimental

*Syntheses.—4-Hydroxymethyl-*3,6-*dithiaoctane*-1,8-*diamine*. The new ligand 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine (L^6) was prepared in > 90% yield by the same method as reported for L^1,[14,16] except that 2,3-dibromopropan-1-ol was employed instead of 1,3-dibromopropan-2-ol in the reaction with the sodium salt of 2-aminoethane-1-thiol, with the product characterized spectroscopically. The proton decoupled ^{13}C NMR spectrum in D_2O showed signals at δ 36.3, 38.1, 40.3, 40.9, 42.0 (× 2) and 70.2 (L^1 exhibits signals at δ 36.2, 38.0, 40.9 and 70.1).

(4-*Hydroxymethyl*-3,6-*dithiaoctane*-1,8-*diamine*)*copper*(II) *perchlorate* $[CuL^6][ClO_4]_2$. A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.5 g, 4.0 mmol) in water (300 cm^3) and 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine (0.8 g, 3.7 mmol) in methanol (50 cm^3) were mixed, the pH adjusted to 7.0 with 2.5 mol dm^{-3} NaOH (*ca.* 1 cm^3) and the suspension stirred for 1 h, filtered through Kieselguhr, the purple filtrate diluted to *ca.* 2 dm^3 with water and loaded onto a column (5 × 15 cm) of SP Sephadex C-25 resin (Na^+-form). After washing with water, the column was eluted with 0.25 mol dm^{-3} $NaClO_4$ (pH 6) solution, yielding a single band. The eluate was rotary evaporated to *ca.* 50 cm^3, then the solution set aside. Crystals of the product formed readily, incorporating $NaClO_4$ (presence of sodium ion determined), and were collected and air dried (0.60 g, 25%), with further product crystallizing only very slowly (Found: C, 14.4; H, 2.8; N, 4.65. Calc. for $C_7H_{18}Cl_2CuN_2O_9S_2{\cdot}NaClO_4$: C, 14.1; H, 3.05; N, 4.7%). Electronic spectrum (in water): λ_{max} 570 (ε 233), 322 (2800) and 234 nm (1610 dm^3 mol^{-1} cm^{-1}). Cyclic voltammetry (0.1 mol dm^{-3} aqueous $NaClO_4$, glassy carbon, 100 mV s^{-1} scan rate): $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ −0.20 V *vs.* Ag–AgCl (Δ*E* 73 mV).

(anti-6-*Methyl*-6-*nitro*-1,11-*dithia*-4,8-*diazacyclotetradecan*-13-*ol*)*copper*(II) *perchlorate*, $[CuL^2][ClO_4]_2$. A suspension of 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine (1.2 g, 5.55 mmol) in ethanol (50 cm^3) and $Cu(ClO_4)_2{\cdot}6H_2O$ (2.1 g, 5.5 mmol) in water (200 cm^3) was adjusted to pH 10 with NaOH solution (2.5 mol dm^{-3}) and was warmed to *ca.* 50 °C and stirred for 30 min, then filtered through Kieselguhr. The purple filtrate was heated to *ca.* 60 °C, and nitroethane (1.05 g, 13.4 mmol) and an excess of formaldehyde (3 cm^3, 38% aq.) were added. The resultant mixture was stirred and heated overnight, cooled to room temperature and filtered through Kieselguhr to remove some brown sludge. The filtrate was diluted to 3 dm^3 with water and loaded onto a column (4.5 × 21 cm) of SP Sephadex C-25 cation-exchange resin. After washing with water, it was eluted with 0.25 mol dm^{-3} $NaClO_4$ (pH 3) to give a single band which was collected and rotary evaporated to *ca.* 0.2 dm^3. Purple crystals of the product formed on several weeks of standing, and were collected and air dried (0.2 g, 6%); further solid was isolated only after extended standing (Found: C, 23.2; H, 4.35; N, 7.4. Calc. for $C_{11}H_{23}Cl_2CuN_3O_{11}S_2$: C, 23.1; H, 4.05; N, 7.35%). Electronic spectrum (in water): λ_{max} 559 (ε 238), 332 (6200) and 252 nm (2700 dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr disc): $\nu(NO_2)$ 1549 and 1347 cm^{-1}. Cyclic voltammetry (0.1 mol dm^{-3} aqueous $NaClO_4$, glassy carbon, 100 mV s^{-1} scan rate): $E_{\frac{1}{2}}$ $(Cu^{II}–Cu^{I})$ −0.37 V (Δ*E* 82 mV), E_{pc} (NO_2 reduction) −1.08 V (irreversible) *vs.* Ag–AgCl.

(*Diethyl* 13-*hydroxy*-1,11-*dithia*-4,8-*diazacyclotetradecane*-6,6-*dicarboxylate*)*copper*(II) *perchlorate hydrate* (2/5), $[CuL^4][ClO_4]_2{\cdot}2.5H_2O$. A mixture of 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine (1.26 g, 6.0 mmol) in ethanol (50 cm^3) and $Cu(ClO_4)_2{\cdot}6H_2O$ (2.3 g, 6.05 mmol) in water (200 cm^3) was adjusted to pH 9.2 with NaOH solution (2.5 mol dm^{-3}), stirred for 30 min, then filtered through Kieselguhr. The filtrate was heated to *ca.* 60 °C and stirred, and diethyl malonate (1.05 g, 6.6 mmol) and an excess of formaldehyde (4 cm^3, 38% aq.) were added. The resultant solution was heated and stirred overnight, cooled to room temperature and filtered through Kieselguhr to remove some dark brown sludge. The filtrate was diluted with water (2 dm^3), loaded onto a column (4.5 × 21.5 cm) of SP Sephadex C-25 cation-exchange resin, washed with water, then eluted with 0.25 mol dm^{-3} $NaClO_4$ (pH 6) to give two bands. The first major band was collected, rotary evaporated to *ca.* 50 cm^3 and set aside to crystallize. Small purple needles of product formed on standing for several weeks, and were collected, washed and air dried (0.16 g, 4%), with further crops collected only on further extended standing (Found: C, 27.1; H, 4.5; N, 4.0. Calc. for $C_{16}H_{30}Cl_2CuN_2O_{13}S_2{\cdot}2.5H_2O$: C, 27.35; H, 5.0; N, 4.0%). Electronic spectrum (in water): λ_{max} 558 (ε 254), 332 (6870) and 254 (2670 dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr disc): $\nu(CO_2R)$ 1731 cm^{-1}. Cyclic voltammetry (0.1 mol dm^{-3} aqueous $NaClO_4$, glassy carbon, 100 mV s^{-1} scan rate): $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ −0.34 V (Δ*E* 58 mV) *vs.* Ag–AgCl. The second minor band (< 10% size of first band) was collected, but did not yield a solid due to the small amount present; similar to the major band in colour, it was presumably a partially hydrolysed (monoester) product.

(anti-13-*Hydroxy*-1,11-*dithia*-4,8-*diazacyclotetradecane*-6-*carboxylato*)*copper*(II) *perchlorate dihydrate*, $[CuL^5][ClO_4]{\cdot}2H_2O$. A solution of $[CuL^4][ClO_4]_2$ was prepared as described above starting with 4-hydroxymethyl-3,6-dithiaoctane-1,8-diamine (5.44 g, 26.1 mmol). Instead of chromatography to isolate the diester, the pH of the filtered solution was adjusted to 10.1 with NaOH (*ca.* 5 cm^3 of a 2.5 mol dm^{-3} solution), then refluxed overnight. The cooled solution was diluted to 3 dm^3, loaded onto a column (5 × 30 cm) of SP Sephadex C-25 cation-exchange resin, washed with water and eluted with 0.2 mol dm^{-3} $NaClO_4$ (pH 7) to yield two bands. The first major band was collected and rotary evaporated to *ca.* 400 cm^3 and set aside to crystallize. After several weeks, some purple crystals were collected and air dried (0.5 g, 4%), with further product being recovered only on extended standing (Found: C, 26.75; H, 5.3; N, 5.4. Calc. for $C_{11}H_{21}ClCuN_2O_7S_2{\cdot}2H_2O$: C, 26.8; H, 5.1; N, 5.7%). Electronic spectrum (in water): λ_{max} 554 (ε 295), 330 (8000) and 248 nm (2980 dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr disc): 1580 cm^{-1} $\nu(CO_2^-)$. Cyclic voltammetry (0.1 mol dm^{-3} aqueous $NaClO_4$, glassy carbon, 100 mV s^{-1} scan rate): $E_{\frac{1}{2}}(Cu^{II}–Cu^{I})$ −0.46 V (Δ*E* 80 mV) *vs.* Ag–AgCl. The minor band (< 10% size of major band) was collected and concentrated, but did not yield a solid. However, being spectroscopically similar to the first, it may possibly be the complex of the minor *syn* geometric isomer.

anti-13-*Hydroxy*-1,11-*dithia*-4,8-*diazacyclotetradecane*-6-*carboxylic acid hydrochloride* $HL^5{\cdot}2HCl$. The major band eluted from the Sephadex column in the reaction immediately above

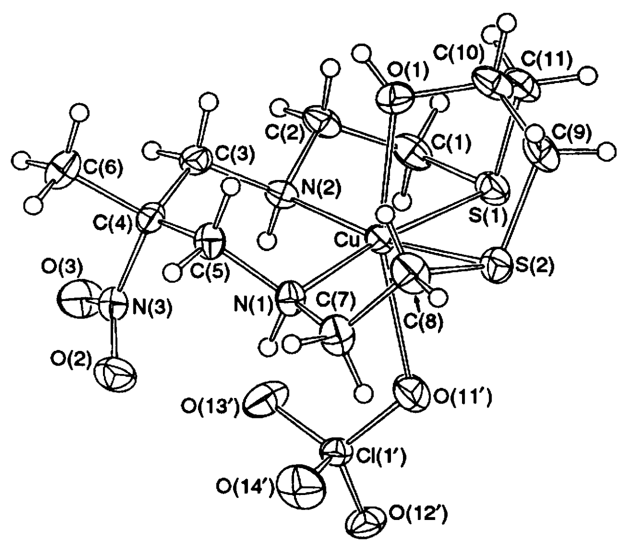


Fig. 1 View of the $[CuL^2]^{2+}$ cation, showing atom numbering

Table 1 Atomic coordinates (× 10^4) for non-hydrogen atoms in $[CuL^2][ClO_4]_2$ **1**

Atom	*x*	*y*	*z*
Cu	6 567(1)	3 164(1)	1 252(1)
S(1)	8 452(1)	3 152(1)	318(1)
S(2)	6 502(1)	1 902(1)	1 142(1)
N(1)	4 745(3)	3 115(1)	1 908(2)
N(2)	6 974(3)	4 225(1)	1 535(2)
N(3)	3 880(3)	4 641(2)	2 163(2)
O(1)	8 678(3)	2 813(2)	2 682(2)
O(2)	2 616(3)	4 318(2)	1 941(2)
O(3)	4 028(4)	5 243(1)	1 869(3)
C(1)	8 837(4)	4 105(2)	439(3)
C(2)	8 602(4)	4 407(2)	1 439(3)
C(3)	6 826(4)	4 494(2)	2 551(3)
C(4)	5 347(4)	4 280(2)	2 880(2)
C(5)	5 055(4)	3 483(2)	2 927(3)
C(6)	5 446(5)	4 606(2)	3 957(3)
C(7)	4 167(5)	2 370(2)	1 939(3)
C(8)	5 500(5)	1 842(2)	2 200(4)
C(9)	8 564(5)	1 699(2)	1 808(4)
C(10)	9 564(4)	2 356(2)	2 174(3)
C(11)	10 076(4)	2 763(2)	1 315(3)
Cl(1)	3 240(1)	1 289(1)	4 334(1)
O(11)	4 585(3)	1 754(2)	4 469(2)
O(12)	2 496(3)	1 193(1)	3 254(2)
O(13)	3 764(4)	618(2)	4 817(2)
O(14)	2 149(4)	1 600(2)	4 844(3)
Cl(2)	8 825(1)	8 909(1)	376(1)
O(21)	8 038(5)	8 931(2)	−688(3)
O(22)	8 821(5)	9 580(2)	850(3)
O(23)	10 408(4)	8 663(2)	476(3)
O(24)	8 098(8)	8 398(3)	904(5)

(repeated based on 3.5 g of L^6) was collected and rotary evaporated to *ca.* 0.5 dm^3. It was reduced by the addition of 3 mol dm^{-3} HCl and excess zinc dust. Following filtration, the clear solution was diluted to *ca.* 4 dm^3 with water, loaded onto a column (3.5 × 22 cm) of Dowex 50 W × 2 cation-exchange resin (H^+-form), washed with 0.5 dm^3 of water and 0.1 dm^3 of 1 mol dm ^{3} HCl to remove zinc ion, and then rapidly eluted with 5 mol dm^{-3} HCl. The eluate was evaporated to dryness to yield a white powder (0.6 g). IR spectrum (KBr disc): ν(OH) 3400 and ν(CO_2H) 1721 cm^{-1}. NMR (D_2O): ^1H, δ 2.9–3.3 and 3.5–3.8 (m, 18 H); ^{13}C, δ 29.8 (× 2), 38.2, 39.2 (× 2), 46.1 (× 2), 47.5 (× 2), 70.2 and 174.0.

Table 2 Atomic coordinates (× 10^4) for non-hydrogen atoms in $[CuL^5][ClO_4]\cdot 2H_2O$ **2**

Atom	*x*	*y*	*z*
Cu	444(1)	8 225(1)	5 142(1)
S(1)	2 608(2)	7 355(1)	4 602(1)
S(2)	1 890(2)	7 710(1)	6 382(1)
N(1)	−1 493(5)	8 725(2)	5 752(2)
N(2)	−819(5)	8 405(2)	3 995(2)
O(1)	−1 059(5)	6 755(2)	5 184(2)
O(2)	−2 029(4)	10 528(2)	5 048(2)
O(3)	−2 012(5)	10 296(2)	3 754(2)
C(1)	1 846(9)	6 268(3)	4 841(4)
C(2)	530(8)	6 250(3)	5 452(3)
C(3)	1 320(9)	6 546(3)	6 286(3)
C(4)	242(7)	8 110(4)	6 992(3)
C(5)	−1 600(7)	8 219(3)	6 495(3)
C(6)	−3 331(6)	8 867(3)	5 319(3)
C(7)	−3 391(6)	9 210(3)	4 471(3)
C(8)	−2 814(7)	8 541(3)	3 894(3)
C(9)	−2 402(6)	10 087(3)	4 425(3)
C(10)	−382(8)	7 701(3)	3 455(3)
C(11)	1 640(8)	7 523(4)	3 555(3)
Cl(1)	−1 633(2)	10 499(1)	7 893(1)
O(11)	−316(9)	10 393(4)	7 403(4)
O(12)	−1 857(10)	9 728(4)	8 294(5)
O(13)	−3 270(9)	10 809(6)	7 527(6)
O(14)	−998(14)	11 184(7)	8 391(7)
O(W1)	2 005(7)	9 229(4)	9 035(3)
O(W2)	1 132(7)	·4 478(3)	7 224(3)

anti-6-*Amino*-6-*methyl*-1,11-*dithia*-4,8-*diazacyclotetradecan*-13-*ol hydrochloride*, $L^3\cdot 3HCl$. The band eluted from the Sephadex column in the reaction yielding $[CuL^2]^{2+}$ (repeated based on 1.7 g of L^6) was collected and rotary evaporated to *ca.* 0.5 dm^3. It was reduced by the addition of 3 mol dm^{-3} HCl and excess zinc dust. Following filtration, the clear solution was diluted to *ca.* 4 dm^3 with water, loaded onto a column (4 × 26.5 cm) of Dowex 50 W × 2 cation-exchange resin (H^+-form), washed with 0.5 dm^3 of water and 1 dm^3 of 1 mol dm^{-3} HCl to remove zinc ions, and then eluted with 5 mol dm^{-3} HCl. The eluate was collected and rotary evaporated to dryness to yield a white powder (0.7 g). IR spectrum (KBr disc): ν(OH) 3400, ν(NH_2^+, NH_3^+) 1620, 1445 cm^{-1}. NMR: ^1H (D_2O/D^+), δ 1.7 (s, 3 H, CH_3), 2.7–3.1, 3.3–3.6 (m, 17 H) and 5.6 (1 H, OH); ^{13}C (D_2O), 19.4, 27.9 (× 2), 36.2 (× 2), 45.5 (× 2), 50.7 (× 2), 53.2 and 68.8.

Physical Methods.—Electronic spectra of compounds (in water) were recorded on a Hitachi 150–20 spectrophotometer, whereas IR spectra of compounds (as KBr discs) were recorded on a Bio-Rad FT7 Fourier-transform spectrometer. Cyclic voltammetry in nitrogen-purged aqueous 0.1 mol dm^{-3} $NaClO_4$ employed a BAS CV27 electrochemical controller with a glassy carbon working electrode, Ag–AgCl reference electrode and platinum wire auxiliary electrode. NMR spectra were recorded (D_2O solutions) using a JEOL FX-90Q spectrometer and sodium 3-trimethylsilylpropionate as an internal reference.

X-Ray Crystal Structure Analysis.—For diffractometry the crystals were mounted on a glass fibre with cyanoacrylate resin. Lattice parameters at 294 K were determined by least-square fits to the setting parameters of 25 independent reflections, measured and refined on an AFC-7 four-circle diffractometer employing graphite-monochromated Cu-Kα radiation. Intensity data were collected in the range $1 < \theta < 60°$. Data reduction and application of Lorentz, polarization, absorption (analytical) and decomposition corrections were carried out using the TEXSAN system.[17] For $[CuL^2][ClO_4]_2$ **1**, 3100 reflections were collected in the range $0 < h < 9$, $0 < k < 21$, $-14 < l < 14$ of which all 3100 remained after merging of equivalents; for $[CuL^5][ClO_4]\cdot 2H_2O$ **2**, 2814 reflections in the range $0 < h < 8$, $0 < k < 17$, $-18 < l < 18$ were collected

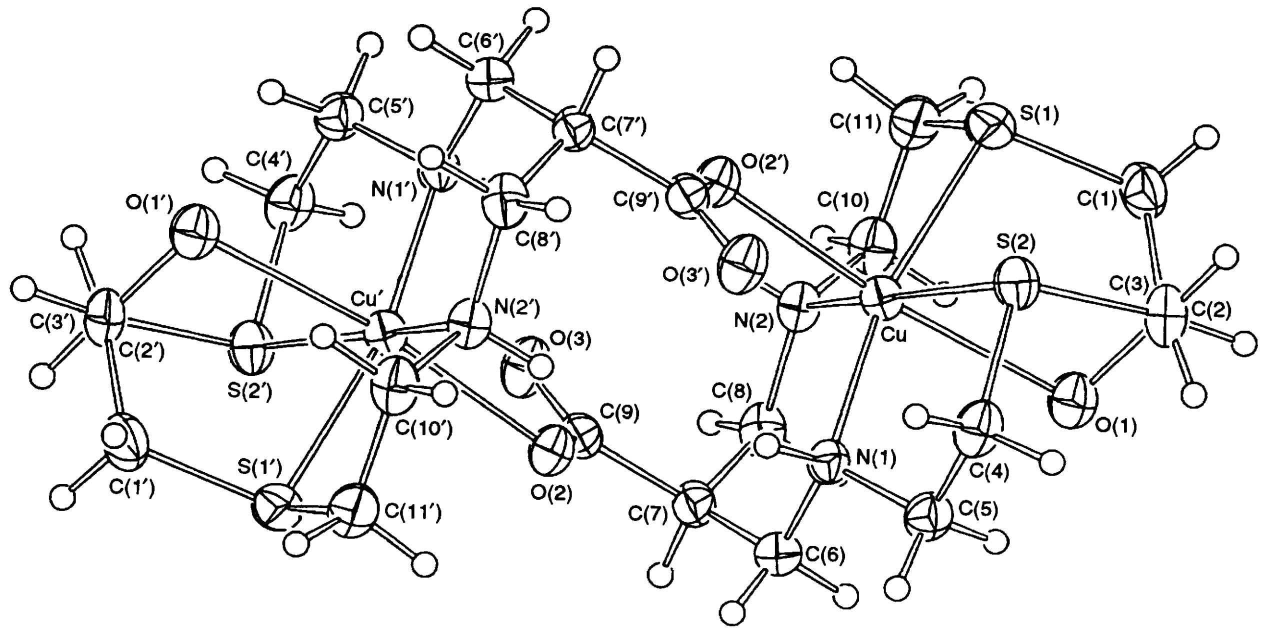


Fig. 2 View of the $[CuL^5]^+$ cation dimer, showing atom numbering

and refined. The structures were solved by direct methods using the computer program SHELXS 86[18] and extended by difference Fourier methods using the SHELXL 93[19] program. Full-matrix least-squares refinement on F^2 was employed.

Hydrogen atoms were placed at geometrically calculated sites according to the recommended specifications of the SHELXL 93 program and refined with isotropic displacement of parameters. All other atoms were refined anisotropically. Residuals on $|F|$ and $|F|^2$ respectively at convergence were $R1 = 0.040$, $wR2 = 0.1437$ for **1** and $R1 = 0.052$, $wR2 = 0.1395$ for **2** $\{R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ with a final weight $= 1/[\sigma^2(F_o)^2 + (0.1000P)^2]$ for **1** and a final weight $= 1/[\sigma^2(F_o)^2 + (0.3018P)^2 + 41.8P]$ for **2**$\}$ where $P = [(\text{max.}\ (F_o^2, 0) + 2F_c^2)/3]$. The weighted R-index based on F_o^2 ($wR2$) is, for compelling statistical reasons, much higher than the conventional R-index based on F_o with a threshold of say $F_o > 3\sigma(F_o)$. For comparison with structures refined against F the latter is therefore provided as well (as $R1$). Despite the fact that $wR2$ and not $R1$ is the quantity minimised, $R1$ has the advantage that it is relatively insensitive to the weighting scheme, and so is more difficult to manipulate. Neutral atom scattering factors were employed.[20] Plots were drawn with ORTEP.[21] Drawings of the cations of **1** and **2** are shown in Figs. 1 and 2 with (atom numbering scheme), atomic coordinates in Tables 1 and 2, and bond lengths and angles in Tables 3 and 4.

Crystal data. $[CuL^2][ClO_4]_2$ **1**, $C_{11}H_{23}Cl_2CuN_3O_{11}S_2$, $M = 571.88$, monoclinic, space group $P2_1/c$, $a = 8.703(2)$, $b = 18.699(2)$, $c = 13.293(2)$ Å, $\beta = 105.15(1)°$, $U = 2088.1(6)$ Å^3, D_c $(Z = 4) = 1.819$ g cm^{-3}, $F(000)$ 1172. Monochromated Cu-Kα radiation, $\lambda = 1.540\,50$ Å, $\mu_{Cu} = 6.275$ mm^{-1}. Specimen $0.20 \times 0.25 \times 0.12$ mm. $A^*_{min,max}$ 1.862, 3.356; residual extrema $+0.64$, -0.53 e Å^{-3}.

$[CuL^5][ClO_4]\cdot 2H_2O$, $C_{11}H_{24}ClCuN_2O_9S_2$ **2**, $M = 487.40$, monoclinic, space group $P2_1/n$, $a = 7.450(1)$, $b = 15.325(2)$, $c = 16.772(1)$ Å, $\beta = 98.38(1)°$, $U = 1894.4(4)$ Å^3, D_c $(Z = 4) = 1.709$ g cm^{-3}, $F(000) = 1000$. Monochromated Cu-Kα radiation, $\lambda = 1.540\,50$ Å, $\mu_{Cu} = 5.434$ mm^{-1}. Specimen $0.15 \times 0.18 \times 0.22$ mm. $A^*_{min,max}$ 1.869, 3.106; residual extrema $+0.89$, -0.38 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Condensation reactions employing formaldehyde and nitroethane or diethyl malonate with the copper(II) complex of L^6 proceed readily to yield acid-stable macrocyclic products, and parallel chemistry recently described with L^1 where similar cyclic products are obtained.[14] Reactions forming acid-stable dithiadiaza macrocycles proceeded in reasonable yield with either carbon acid, even when stoichiometric amounts of the carbon acid were employed. Evidently, the condensation chemistry forming thirteen- to sixteen-membered macrocycles studied in detail for reactions of N_4 donor molecules[2] transfers readily to mixed S_2N_2 donor analogues, with the presence of a pair of *cis*-disposed primary amine groups being the primary requirement for condensation. The pair of 'spectator' donors remote from the site of ring formation have only a secondary effect on reactivity, and the implication is that the nature of these donors may be varied at will provided the precursor complex is sufficiently stable to accommodate the reaction conditions.

However, the anticipated dithiadiaza macrocycles L^7–L^9 with both a thirteen-membered ring and a CH_2OH pendant group do not form. The products isolated from both types of condensation reactions were spectroscopically similar to the recently described complex of L^4, and this was not anticipated if a different ring size was produced. Structural studies, described in detail below, and NMR spectroscopy of the free ligands, confirm that the products of these reactions are fourteen-membered macrocycles L^2–L^5, carrying an OH pendant group. Rearrangement of the $SCH_2CH(CH_2OH)S$ five-membered chelate ring to a six-membered $SCH_2CH(OH)CH_2S$ chelate ring has occurred, apparently concomitant with the condensation chemistry. This carbon skeleton rearrangement to yield the fourteen-membered macrocycle with a pendant alcohol group may involve a Wagner–Meerwein rearrangement[15] in which the alcohol group is transferred to the copper ion as an hydroxyl anion following C–O bond cleavage, leaving a carbon cation which undergoes rearrangement and subsequent attack by hydroxide. An alternate scheme involving C–S bond cleavage is illustrated below. A driving force for this rearrangement may be the strong preference by the metal ion for a fourteen- rather than a thirteen-membered macrocycle ring.

The macrocycles L^2–L^5 produced in this study carry two

Table 3 Bond lengths (Å) and angles (°) for the $[CuL^2]^{2+}$ ion

Cu–N(1)	1.999(3)	Cu–N(2)	2.032(3)
Cu–S(1)	2.3027(11)	Cu–S(2)	2.3635(11)
Cu–O(1)	2.365(3)	Cu–O(11′)	2.544(3)
S(1)–C(1)	1.812(4)	S(1)–C(11)	1.818(4)
S(2)–C(9)	1.822(4)	S(2)–C(8)	1.842(4)
N(1)–C(5)	1.482(4)	N(1)–C(7)	1.485(4)
N(2)–C(3)	1.481(4)	N(2)–C(2)	1.496(4)
N(3)–O(3)	1.209(4)	N(3)–O(2)	1.222(4)
N(3)–C(4)	1.537(4)	O(1)–C(10)	1.434(5)
C(1)–C(2)	1.503(5)	C(3)–C(4)	1.517(5)
C(4)–C(5)	1.516(5)	C(4)–C(6)	1.536(4)
C(7)–C(8)	1.494(6)	C(9)–C(10)	1.510(6)
C(10)–C(11)	1.533(6)		
N(1)–Cu–N(2)	94.84(10)	N(1)–Cu–S(1)	172.76(9)
N(2)–Cu–S(1)	89.66(8)	N(1)–Cu–S(2)	88.43(7)
N(2)–Cu–S(2)	170.29(8)	S(1)–Cu–S(2)	88.05(4)
N(1)–Cu–O(1)	100.05(11)	N(2)–Cu–O(1)	93.51(10)
S(1)–Cu–O(1)	85.30(7)	S(2)–Cu–O(1)	76.90(7)
N(1)–Cu–O(11′)	89.26(11)	N(2)–Cu–O(11′)	99.00(10)
S(1)–Cu–O(11′)	84.42(8)	S(2)–Cu–O(11′)	90.17(8)
O(1)–Cu–O(11′)	163.74(10)	C(1)–S(1)–C(11)	103.8(2)
C(1)–S(1)–Cu	94.82(12)	C(11)–S(1)–Cu	97.95(13)
C(9)–S(2)–C(8)	102.6(2)	C(9)–S(2)–Cu	99.98(14)
C(8)–S(2)–Cu	91.25(12)	C(5)–N(1)–C(7)	113.0(3)
C(5)–N(1)–Cu	113.7(2)	C(7)–N(1)–Cu	111.6(2)
C(3)–N(2)–C(2)	108.2(3)	C(3)–N(2)–Cu	116.7(2)
C(2)–N(2)–Cu	109.3(2)	O(3)–N(3)–O(2)	123.2(3)
O(3)–N(3)–C(4)	117.9(3)	O(2)–N(3)–C(4)	118.9(3)
C(10)–O(1)–Cu	100.8(2)	C(2)–C(1)–S(1)	112.5(2)
N(2)–C(2)–C(1)	110.0(3)	N(2)–C(3)–C(4)	117.1(3)
C(3)–C(4)–C(5)	115.9(3)	C(3)–C(4)–N(3)	109.6(3)
C(5)–C(4)–N(3)	109.7(3)	C(3)–C(4)–C(6)	108.4(3)
C(5)–C(4)–C(6)	108.7(3)	N(3)–C(4)–C(6)	103.8(3)
N(1)–C(5)–C(4)	114.2(3)	N(1)–C(7)–C(8)	112.2(3)
C(7)–C(8)–S(2)	106.0(3)	C(10)–C(9)–S(2)	113.5(3)
O(1)–C(10)–C(9)	107.5(3)	O(1)–C(10)–C(11)	110.7(3)
C(9)–C(10)–C(11)	114.8(4)	C(10)–C(11)–S(1)	114.8(3)

Primed atoms are related to their unprimed equivalents by x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$.

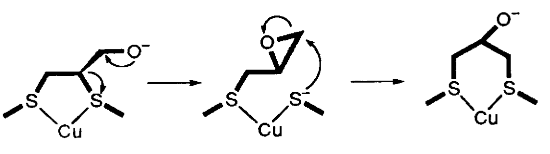


Table 4 Bond lengths (Å) and angles (°) for the $[CuL^5]^+$ ion dimer

Cu–N(2)	2.034(4)	Cu–N(1)	2.036(4)
Cu–O(2′)	2.293(3)	Cu–S(2)	2.3355(13)
Cu–S(1)	2.3715(14)	Cu–O(1)	2.520(3)
Cu–Cu′	5.4943(14)	S(1)–C(11)	1.817(6)
S(1)–C(1)	1.823(6)	S(2)–C(4)	1.815(5)
S(2)–C(3)	1.835(5)	N(1)–C(6)	1.469(6)
N(1)–C(5)	1.480(6)	N(2)–C(10)	1.474(6)
N(2)–C(8)	1.486(6)	O(1)–C(2)	1.432(6)
O(2)–C(9)	1.242(6)	O(2)–Cu′	2.293(3)
O(3)–C(9)	1.244(6)	C(1)–C(2)	1.518(8)
C(2)–C(3)	1.506(8)	C(4)–C(5)	1.508(8)
C(6)–C(7)	1.512(7)	C(7)–C(8)	1.514(7)
C(7)–C(9)	1.540(6)	C(9)–C(9′)	3.820(9)
C(10)–C(11)	1.516(8)		
N(2)–Cu–N(1)	99.2(2)	N(2)–Cu–O(2′)	86.09(14)
N(1)–Cu–O(2′)	99.97(14)	N(2)–Cu–S(2)	167.98(11)
N(1)–Cu–S(2)	87.06(11)	O(2′)–Cu–S(2)	103.02(9)
N(2)–Cu–S(1)	87.78(12)	N(1)–Cu–S(1)	167.08(11)
O(2′)–Cu–S(1)	91.31(9)	S(2)–Cu–S(1)	84.24(5)
N(2)–Cu–O(1)	90.08(14)	N(1)–Cu–O(1)	88.40(14)
O(2′)–Cu–O(1)	171.25(12)	S(2)–Cu–O(1)	79.79(9)
S(1)–Cu–O(1)	80.67(9)	N(2)–Cu–Cu′	75.54(11)
N(1)–Cu–Cu′	65.51(10)	O(2′)–Cu–Cu′	38.77(9)
S(2)–Cu–Cu′	116.47(4)	S(1)–Cu–Cu′	127.13(4)
O(1)–Cu–Cu′	147.03(9)	C(11)–S(1)–C(1)	104.5(3)
C(11)–S(1)–Cu	95.3(2)	C(1)–S(1)–Cu	100.3(2)
C(4)–S(2)–C(3)	102.2(3)	C(4)–S(2)–Cu	97.2(2)
C(3)–S(2)–Cu	100.3(2)	C(6)–N(1)–C(5)	109.5(4)
C(6)–N(1)–Cu	119.1(3)	C(5)–N(1)–Cu	110.8(3)
C(10)–N(2)–C(8)	109.9(4)	C(10)–N(2)–Cu	111.6(3)
C(8)–N(2)–Cu	116.4(3)	C(2)–O(1)–Cu	98.2(3)
C(9)–O(2)–Cu′	113.1(3)	C(2)–C(1)–S(1)	114.7(4)
O(1)–C(2)–C(3)	108.7(4)	O(1)–C(2)–C(1)	111.3(4)
C(3)–C(2)–C(1)	114.7(5)	C(2)–C(3)–S(2)	115.4(4)
C(5)–C(4)–S(2)	111.2(3)	N(1)–C(5)–C(4)	111.6(4)
N(1)–C(6)–C(7)	114.4(4)	C(6)–C(7)–C(8)	113.2(4)
C(6)–C(7)–C(9)	113.7(4)	C(8)–C(7)–C(9)	112.1(4)
N(2)–C(8)–C(7)	113.3(4)	O(2)–C(9)–O(3)	124.6(4)
O(2)–C(9)–C(7)	118.9(4)	O(3)–C(9)–C(7)	116.5(4)
O(2)–C(9)–C(9′)	62.3(2)	O(3)–C(9)–C(9′)	98.6(3)
C(7)–C(9)–C(9′)	109.5(3)	N(2)–C(10)–C(11)	111.6(4)
C(10)–C(11)–S(1)	112.4(3)		

Primed atoms are related to their unprimed equivalents by $-x$, $-y + 2$, $-z + 1$.

pendant substituents, located on opposite 'ends' of the macrocyclic ring, and can exist (except in the case of L^4) as two non-interconvertible geometric isomers, designated as *syn* (OH and NX_2 or CO_2H groups on the same side of the macrocyclic plane) or *anti* (groups on opposite sides of the macrocyclic plane). If the pendant alcohol group is involved in axial interaction with the copper ion in solution during the condensation reaction, it may direct the chemistry towards formation of the *anti* isomer. This would arise, for example, if the nitro group in the partly constructed macrocycle [then part of an intermediate $NHCH_2CH(Me)(NO_2)$ arm] interacts axially with the copper, and necessarily on the opposite side of the molecule to the bound alcohol group, steering cyclization towards stereoselective or even stereospecific production of the *anti* isomer. Chromatography indicates a single isomer in this case, predicted to be the *anti* isomer; the product has been examined by X-ray crystallography, described below. In the case of the formation of the complex of the diester L^4, there is necessarily a single product with both *gem* substituents identical, but selective hydrolysis and binding of one carboxylate in the *anti* disposition with subsequent decarboxylation of the unbound group would lead to predominantly the *anti* isomer of L^5. It has been suggested that decarboxylation proceeds from the *gem* acid ester and not the diester, so this proposal involving carboxylate binding has some validity. Further, copper(II) has been shown to catalyse intramolecular ester hydrolysis somewhat *via* weak complexation of a pendant ester group,[22] promoting *gem* acid ester formation. These predictions are supported by the observation of predominantly one isomer.

In the present examples, the L^6 precursor, but not its macrocyclic products, contain a chiral carbon at the site where the hydroxymethyl pendant attaches to the ring. We have not attempted to resolve the precursor acyclic ligand, but did attempt resolution of the $[CuL^6]^{2+}$ complex by chromatography on a Sephadex column employing a chiral eluant (tartaric acid), without success. The cyclic complexes are kinetically stable, since macrocyclisation leads to products which dissociate only extremely slowly compared with open-chain analogues, and their kinetic stability is as indicative of macrocyclization as are the characteristic physical properties of the nitro or ester functional groups introduced. The copper(II) complex of the diester L^4 undergoes ester hydrolysis and decarboxylation only slowly in aqueous base, yielding the monoacid anion macrocyclic complex. This behaviour is also observed for a range of analogues, with a monoester actually being isolated in some cases where hydrolysis has been performed in alcoholic base which permits re-esterification; that re-esterification is involved has been demonstrated by introduction of a methyl group in place of an original ethyl group in the monoester.[23] Both nitro-pendant and ester- or acid-pendant macrocycles exhibit characteristic IR vibrations arising from the presence of the nitro, ester or acid groups, with the former also being readily identified by an irreversible multielectron reduction wave in voltammetry. The copper ion is readily removed from the macrocycles by reduction with zinc in aqueous acid, as exemplified by the isolation of the hydrochloride salt of the free ligands L^3 and L^5, characterised by IR and NMR spectroscopy. In the case of the nitro-pendant macrocycle, reduction to the pendant amine is also achieved. Macrocyclization was confirmed for the complexes of L^2 and L^5 by X-ray crystal structure analyses.

The $[CuL^2]^{2+}$ ion contains a fourteen-membered macrocycle with pairs of *cis*-disposed secondary amine and thioether donors bound to the copper ion in a distorted plane in addition to bonds to an axial pendant alcohol group and a weakly co-ordinated perchlorate [Cu–$OClO_3$ 2.544(3) Å], generating an overall distorted-octahedral geometry. The six-membered chelate ring in $[CuL^2]^{2+}$ carrying the nitro pendant adopts the preferred chair conformation with the nitro substituent displaced well away from the metal centre, and located on the opposite side of the macrocyclic ring to the alcohol substituent in an *anti* configuration. The $[CuL^5]^+$ ion consists of the same basic fourteen-membered N_2S_2 macrocycle, but carries pendant alcohol and carboxylate groups in an *anti* disposition. In this case the copper also lies in a distorted-octahedral environment involving the macrocycle heteroatoms, the pendant alcohol and a pendant carboxylate group bridging from an adjacent complex ion, the whole assembly thus consisting of a dimer linked by two bridging carboxylates. The Cu–OH bond in this structure is long [2.520(3) Å] compared with the Cu–OH distance [2.365(3) Å] in $[CuL^2]^+$. Fitting of a least-squares plane to the copper, nitrogen and sulfur atoms can be performed with a root mean square deviation of fitted atoms of 0.130 Å in the case of $[CuL^2]^{2+}$ and 0.075 Å for $[CuL^5]^+$. The copper is not displaced towards the alcohol group in the case of the $[CuL^2]^{2+}$ complex, but is part of the slightly distorted-square plane, since the root mean square of donor atoms in the absence of the copper (0.145) is not changed much. For the $[CuL^5]^+$ complex dimer, however, the root mean square of donor atoms alone falls significantly to 0.006, with the copper displaced towards the other copper atom from the donor plane by 0.188(2) Å. The secondary nitrogen donors adopt (*R*,*S*) stereochemistry in each complex with the five-membered chelate rings in relatively undistorted skew conformations. Although a strong Cu–OH bond is seen to the pendant alcohol in one axial site for $[CuL^2]^{2+}$, there is no close approach to the other axial site. However, for the $[CuL^5]^+$ cation, a carboxylate completes the distorted-octahedral co-ordination sphere with a Cu–OCO distance of 2.293(3) Å.

The Cu–N distances for $[CuL^2]^{2+}$ [1.999(3), 2.032(3) Å] are slightly shorter than those in for $[CuL^5]^+$ [2.034(4), 2.036(4) Å], and Cu–S distances for $[CuL^2]^{2+}$ [2.3027(11), 2.3635(11) Å] are also shorter than for $[CuL^5]^+$ [2.3355(13), 2.3715(14) Å], the general expansion of the co-ordination sphere being presumably particularly associated with the variation in pendant alcohol bond length with structure. The close approach of the alcohol group in the former structure [2.365(3) Å] compared with the latter [2.520(3) Å] is associated with decreased Cu–S–C angles [99.98(14), 97.95(13)° for L^2 *vs.* 100.3(2), 100.3(2)° for L^5] and C–C–O angles [107.5(3), 110.7(3)° for L^2 *vs.* 108.7(4), 111.3(4)° for L^5]; these angles are compressed as the pendant approaches closer to the copper.

The Cu–N distances in the present structures are similar to those in $[CuL^4]^{2+}$ (average 2.035 Å)[14] but longer than in the analogue of L^2 without the pendant alcohol group (average 2.024 Å).[5] The Cu–S distances here are also similar to those in $[CuL^4]^{2+}$ (average 2.338 Å)[14] but noticeably longer than in the structure of the unsubstituted analogue (average 2.295 Å).[5] This is presumably tied to involvement of the two thioether donors and the pendant alcohol in the case of the L^2, L^4 and L^5 complexes in reasonably rigid facial co-ordination, with consequent effects on the metal–donor distances. The Cu–S and Cu–N distances are still similar to distances in pure sulfur-donor (2.30 Å)[24] and nitrogen-donor (2.005 Å)[4] macrocycles.

The dimer formed for the copper(II) complex of L^5 arises from the six-membered chelate ring carrying each carboxylate pendant adopting a chair conformation with the co-ordinated secondary nitrogen atoms in (*R*,*S*) configurations which forbid close approach of the carboxylate ion to its parent metal ion, but directs it as an equatorial pendant towards the adjacent copper ion. A twelve-membered ring including the two metal ions and the two carboxylate groups results, with the Cu $\cdots$ Cu separation 5.4953(14) Å. The copper atoms are displaced from the mean CuN_2S_2 plane towards the carboxylate. The two carboxylate planes are approximately parallel to each other (Fig. 2), with planes separated by 3.82 Å. The overall dimer is a relatively rigid molecule in the solid state, but there is no strong evidence for its persistence as a primary species in aqueous solution.

The CuN_2S_2 macrocycles show physical properties intermediate between those of CuN_4 and CuS_4 macrocycles, as exemplified by the d–d electronic transition maximum which shifts from near 19 600 cm^{-1} (CuN_4) to 18 700 cm^{-1} (CuN_2S_2) to 17 500 cm^{-1} (CuS_4). A transition near 30 000 cm^{-1} in all thioether complexes can be assigned to metal–thioether charge transfer by analogy with earlier studies.[12,25] The copper(II) complexes of L^1–L^5 and analogues reported earlier all exhibit Cu^{II}–Cu^{I} couples in the range −0.15 to −0.46 V *vs.* Ag–AgCl, showing some variation with size and substituents. A general positive shift in the Cu^{II}–Cu^{I} couple for CuN_2S_2 systems of *ca.* 250 mV compared with analogous CuN_4 systems can be related to the greater π-acceptor ability of sulfur donors and their capacity to stabilise Cu^I,[12] this stabilisation being also influenced by the inherently larger ring in the CuN_2S_2 *vs.* CuN_4 systems which is more appropriate for accommodating the larger Cu^I ion. The electronic influence of the substituents can be exemplified by the –OH pendant causing an average shift in $E_{\frac{1}{2}}$ of 35 mV compared with rings without this substituent. Likewise, changing from a NO_2 and Me substituent pair to a CO_2^- and H pair causes an average shift in $E_{\frac{1}{2}}$ of *ca.* 90 mV. Electronic influences of substituents have been examined in detail for complexes of macrobicyclic ligands.[26] The presence of the nitro pendants is clearly defined by stepwise or concerted multielectron reductions near −1 V, but ester or acid groups at best yield an ill-defined one-electron wave near −1.5 V.

The validity of the cyclization reactions well established for polyamine systems[1,2] but previously examined only for limited examples of mixed-donor systems has been confirmed in this study as generally applicable for synthesis of *cis*-N_2S_2 macrocyclic systems. Moreover, examples with two pendant groups attached directly to the ring yet capable of co-ordination have been introduced, yielding mixed-donor ligands capable of pseudo-encapsulation[3] of metal ions demanding six-co-ordination. Axial co-ordination of pendants in the solid state to copper(II) suggests that this mode of co-ordination will extend to other metal ions. Potentially, *syn* and *anti* isomers of the above two may exist, but co-ordination of the alcohol group during cyclization may be responsible for directing the stereochemistry dominantly to the *anti* isomers reported here.

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