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Inter- and intra-molecular pathways in polyamine synthesis from diamines†

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Received 19th October 2000, Accepted 18th December 2000
First published as an Advance Article on the web 12th February 2001

Characterisation, largely through crystal structure determinations of their metal complexes, of the polyamine products of several reactions between (in all but one case) polyalcohol benzenesulfonates and 1,2- and 1,3-diamines, confirmed that intramolecular reaction pathways are important only in the 1,2-diamine reactions. Even under conditions where the amine reactants are in large excess, however, it is possible to obtain products resulting from alkylation of a diamine by more than one molecule of sulfonate (or, in one case, of a bromochloroalkane). In metal ion complexes formed by the new ligands there are examples of only partial coordination of the N-donor sites, giving species which might be suitable for further, selective functionalisation at the unbound centres. Conversion of the complexes into macrocyclic derivatives also suited to further functionalisation is straightforward.

Introduction

The structural variety of polyamines and the stability of their complexes is reflected in a remarkable coordination chemistry.[1] It is this, paradoxically, which provides the impetus for further investigation of their syntheses and their applications. The biological activity of the proton complexes of many polyamines is well known[2] and the synthesis of rigidified analogues of naturally occurring polyamines is of potential therapeutic significance.[3] We have sought to prepare new polyamines which, in particular, might be used to provide functionalised macro(poly)cyclic species suitable, amongst other things, for immobilisation on solid supports. The syntheses are based predominantly upon the reactions of various diamines with polyol arylsulfonates (Fig. 1) and the product distributions reflect differing degrees of competition between inter- and intra-molecular pathways, as has been established in related earlier work.[4–8] In the present publication we provide basic characterisation of several amine families differing with respect to donor atom separation, denticity and chirality, largely through structural characterisation of metal complexes of the new amines.

Experimental

Analytical and spectroscopic instrumentation

Nuclear magnetic resonance spectra were acquired, usually in D_2O solvent, using Varian Gemini 200 (^1H at 200 MHz and ^{13}C at 50.3 MHz) or Bruker ARX 500 (^1H at 500.13 MHz and ^{13}C at 125.8 MHz) spectrometers. Chemical shifts are expressed in ppm relative to an internal standard of acetone, taken as being δ 2.22 for ^1H and δ 30.89 for ^{13}C spectra (relative to TMS). Elemental microanalyses were carried out by the Chemistry Centre of Western Australia, the Australian National University Microanalytical Service, and Kosin University Microanalytical Service. All samples were thoroughly dried under vacuum (0.1 mmHg) at 50 °C for 4 hours prior to their analysis. Ion exchange chromatography was performed under gravity flow using H^+ form Dowex 50W × 2 (200–400 mesh) or Na^+ form SP Sephadex C25 (200–400 mesh) cation exchange resins. All eluate evaporations were performed at reduced pressure (≈ 20 mmHg) using a Büchi rotary evaporator and a water aspirator. The Schlenk technique using high purity argon or nitrogen was employed wherever it was necessary to exclude oxygen from preparative mixtures. UV-visible absorption spectra (200–800 nm) were recorded on a Hewlett-Packard 8452A Diode Array or a Hitachi 3200 spectrophotometer. Circular dichroism (CD) spectra were recorded using a JASCO J-200 Automatic Spectropolarimeter.

Preparative chemistry

Glycerol (1,2,3-propanetriol), neopentyl glycol (2,2-dimethylpropane-1,3-diol), pentaerythritol (2,2-bis(hydroxymethyl)-propane-1,3-diol), 1-bromo-3-chloro-2-methylpropane, ethane-1,2-diamine, propane-1,3-diamine, (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine and benzenesulfonyl chloride were purchased from Aldrich and used as received. The alcohols were all converted into their benzene sulfonates (benzenesulfonyl esters) by literature procedures.[9,10] All organic solvents were distilled prior to use.

With one exception (see below) polyamine formation reactions were all conducted by the common procedure of reaction

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† Electronic supplementary information (ESI) available: unit-cell contents for compounds **1**, **5**, **6**, **8** and **12**. See http://www.rsc.org/suppdata/dt/b0/b008452m/

DOI: 10.1039/b008452m

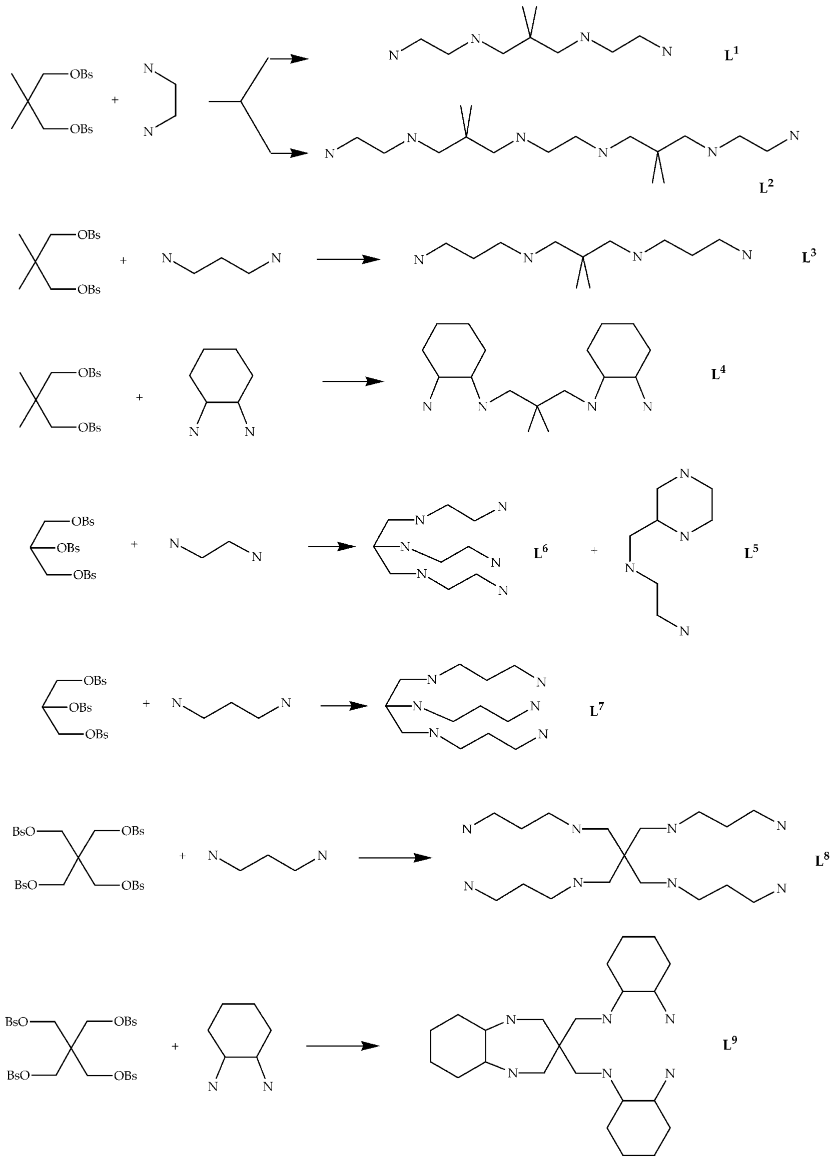


Fig. 1 Reaction pathways observed in some reactions of poly(benzenesulfonates) (benzenesulfonate = Bs) and one related material with diamines.

under nitrogen of a given polyalcohol poly(benzenesulfonate) with a large excess (twentyfold molar ratio) of a given diamine at the boiling point of the diamine, no solvent being added. After cooling the reaction mixture, sufficient methanolic KOH to neutralise the theoretical stoichiometric amount of acid released was added and, after cooling again, any precipitated potassium benzenesulfonate was filtered out and washed with diethyl ether. The filtrate mixture was then distilled under reduced pressure to remove as much as possible of the excess of diamine (along with the methanol and ether). Initially, following a procedure described in earlier literature,[8] the residue was then treated with Co^{II} under oxidising conditions to give a mixture of cobalt(III) complexes which was subjected to cation exchange chromatography to achieve species separation. Although this generally worked well to separate cleanly the reaction products, the existence of isomeric forms of the complexes of a given ligand occasionally led to a chromatographic separation of much greater complexity than was necessary for this purpose alone. As the ligands could in general be far more easily removed from the copper(II) than their cobalt(III) complexes, in later studies the product mixtures were separated through cation exchange chromatography of their copper(II) complexes. The "free" ligands were then isolated by treatment of the complexes with an excess of HCl and precipitation of their hydrochlorides by addition of ethanol. In achronological order, the particular systems (Fig. 1) investigated were as follows.

(i) Neopentyl glycol bis(benzenesulfonate) and ethane-1,2-diamine. The crude amine mixture obtained from 4.8 g of the sulfonate was added to a solution of $CuSO_4{\cdot}5H_2O$ (3.2 g) in water (200 mL) and the deep blue solution formed absorbed on a column of Na^+ form SP Sephadex C25 cation exchange resin. Elution with 0.3 mol L^{-1} sodium chloride revealed six components. F1, a minor component, contained only ethane-1,2-diamine as the amine ligand and was discarded. The violet F2 was visually the major component and the complex in it was obtained by evaporating the eluate to dryness and extracting with ethanol to leave NaCl behind. Two further cycles of evaporation and extraction of the residue with ethanol gave a product (3.7 g) practically free of NaCl. F3 and F4 were trace components and, because their green colour suggested they were not amine complexes, both were discarded. The violet, slowly eluting F5 and F6 were also present in small quantities but treatment of their eluates as described for F2 provided 60 mg (F5) and 280 mg (F6). The hydrochlorides of the ligands present in F2 (**L**^{1}), F5 and F6 (both **L**^{2}) were isolated by dissolving the complexes in an excess of 0.5 mol L^{-1} HCl, adsorbing the solution formed on H^+ form Dowex 50W × 2 cation exchange resin, removing Cu^{II} by elution with 1 mol L^{-1} HCl, the protonated ligands by elution with 3 mol L^{-1} HCl, evaporation of the latter eluates to dryness under vacuum, and crystallisation of the residues by trituration with ethanol. Vapour diffusion of ethanol into solutions of ligand $\mathbf{L}^2$ in dilute HCl was used to produce crystals of **5** suitable for the X-ray work. ^{1}H NMR spectra (D_2O solvent): F2 ligand ($\mathbf{L}^1$), δ 1.23 (s, CH_3, 6H), 3.21 (s, CH_2, 4H) and 3.48 (br s, CH_2, 8H); F5 and F6 ligands (of $\mathbf{L}^2$), 1.23 (s, CH_3, 12H), 3.22 (s, CH_2, 8H), 3.49 (br s, CH_2, 8H) and 3.61 (s, CH_2, 4H). The complex present in F2 was precipitated by addition of $NaClO_4$ to its concentrated aqueous solution and cooling at 4 °C for 12 h and then recrystallised similarly. Found C, 23.8; H, 5.2; N, 12.4. $[Cu(\mathbf{L}^1)][ClO_4]_2 = [Cu(C_9H_{24}N_4)][ClO_4]_2$ **1** requires C, 23.98; H, 5.37; N, 12.43%. As shown by a crystal structure determination (see ahead), precipitation of the complex in the presence of high concentrations of chloride resulted in deposition of a chloride perchlorate, **4**.

(ii) 1-Bromo-3-chloro-2-methylpropane and ethane-1,2-diamine. The commercial availability of this mixed-halide alkylating agent was exploited for comparison with a closely related tosylate as used above. A mixture of 1-bromo-3-chloro-2-methylpropane (4.3 g) and ethane-1,2-diamine (30 g) was heated under N_2 at 120 °C for 72 h. After neutralisation with NaOH and removal of NaCl/NaBr, the product mixture was treated in exactly the same way as those obtained from the benzenesulfonates. Chromatography of the copper(II) complexes (SP Sephadex/0.3 mol L^{-1} NaCl) revealed three components, the first eluted being simply $[Cu(en)_2]^{2+}$(trace), the second $[Cu(\mathbf{L}^{1'})]^{2+}$ and the third $[Cu(\mathbf{L}^{2'})]^{2+}$. The eluate containing $[Cu(\mathbf{L}^{1'})]^{2+}$ was evaporated to dryness, the complex freed from NaCl by extraction into ethanol (giving, on evaporation, 8.0 g of crude $[Cu(\mathbf{L}^{1'})]Cl_2$) and then crystallised from its concentrated aqueous solution by addition of $NaClO_4$ and cooling to ≈4 °C. Found C, 21.6; H, 5.3; N, 12.7. $[Cu(\mathbf{L}^{1'})][ClO_4]_2 = [Cu(C_8H_{22}N_4)][ClO_4]_2$ **2**, **3** requires C, 22.00; H, 5.08; N, 12.83%. $\mathbf{L}^{1'}$ was isolated as its hydrochloride from the complex as described above for $\mathbf{L}^1$. NMR spectra (0.5 mol L^{-1} DCl): ^{1}H δ 1.22 (d, J 9 Hz, CH_3, 3H), 2.49 (br m, CH, 1H), 3.16 (m), 3.31 (m) (CH_2 of 3-carbon link, 4H) and 3.50 (br m, $NHCH_2CH_2NH_2$, 8H); ^{13}C δ 16.7 (CH_3), 30.9 (CH), 37.6, 47.1, 53.1 (CH_2). Similar treatments of the third eluate gave the crude copper(II) chloride complex of $\mathbf{L}^{2'}$ (2.9 g) and subsequently the ligand hydrochloride. NMR spectra (0.5 mol L^{-1} DCl): ^{1}H δ 1.22 (d, J 12 Hz, CH_3, 6H), 2.52 (br m, CH, 2H), 3.18 (m), 3.32 (m) (CH_2 of 3-carbon link, 8H) and 3.50 (m, "external" NCH_2CH_2N, 8H) and 3.59 (br s, "internal" NCH_2CH_2N, 4H); ^{13}C δ 16.1 (CH_3), 30.4 (CH), 36.9, 45.3, 46.4, 52.5, 52.6 (CH_2).

(iii) Neopentyl glycol bis(benzenesulfonate) and propane-1,3-diamine. Chromatography as above of the copper(II) complexes of the reaction products from 7.7 g of sulfonate revealed four blue components. The first eluted was by far the dominant species and provided 5.6 g of solid after removal of NaCl. The second band was a simple propane-1,3-diamine complex, and the third and fourth very slowly eluted bands contained such small amounts of complex that they could not be further characterised. ^{1}H NMR spectrum (D_2O solvent): F1 ligand ($\mathbf{L}^3$), δ 1.17 (s, CH_3, 6H); 2.05, 2.09, 2.13, 2.15, 2.17, 2.21 (m, CH_2, 4H); 3.04, 3.08, 3.12, 3.18, 3.22 (m, δ 3.12 peak strongest, CH_2, 12H). Addition of $NaClO_4$ to a concentrated aqueous solution of F1 gave a blue, crystalline precipitate which was then converted back (anion exchange resin) into the chloride: Found C, 34.0; H, 8.8; N, 14.5. $[Cu(\mathbf{L}^3)]Cl_2\cdot 2H_2O = [Cu(C_{11}H_{28}N_4)]Cl_2\cdot 2H_2O$ requires C, 34.15; H, 8.34; N, 14.48%. Some of this purified chloride was reprecipitated with perchlorate to give crystals suitable for a structure determination, showing that material to be a chloride perchlorate, $[Cu_4(\mathbf{L}^3)_4Cl_2(OH_2)_2][ClO_4]_6$ **6**. Dissolution of the chloride (0.5 g) in 1 mol L^{-1} HCl (50 mL) gave a pale blue solution which was diluted with water (450 mL) and passed through H^+ form Dowex 50W × 2. Free Cu^{II} was removed by elution with 0.5 mol L^{-1} HBr, then the protonated ligand was eluted with 3 mol L^{-1} HBr. The eluate was taken to near dryness under vacuum and the ligand hydrobromide precipitated as a white powder by the addition of ethanol. Found C, 18.7; H, 5.8; N, 7.7. $[H_4\mathbf{L}^3]Br_4\cdot HBr\cdot 5H_2O = C_{11}H_{43}Br_5N_4O_5$ requires C, 18.58; H, 6.10; N, 7.98%.

(iv) Neopentyl glycol bis(benzenesulfonate) and (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine. Chromatography as above of the copper(II) complexes of the product revealed six blue species but the first was present in quantities too small for it to be characterised and the second and fourth proved to be just complexes of (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine. The third band contained far more material (4.14 g from 3.85 g of sulfonate) than either of the fifth and sixth fractions, though sufficient material was present in these for it to be possible to isolate the ligands present and show the two to have identical ^{1}H NMR spectra. ^{1}H NMR spectra (D_2O solvent): F3 ligand ($\mathbf{L}^4$), δ 1.22 (s, CH_3, 6H); 1.3–2.4 (ill resolved multiplets, cyclohexyl CH_2, 16H); 3.15, 3.37 (q, neopentyl CH_2, 4H, J_{AB} 12 Hz); 3.42–3.64 (m, cyclohexyl CH, 4H); F5, F6 ligands, 0.98–2.40 (ill resolved multiplets with an intense singlet at 1.22); 3.00–3.60 (overlapping multiplets). For microanalysis, the copper(II) complex of $\mathbf{L}^4$ present in F3 was precipitated by addition of $NaClO_4$ to its concentrated solution in water. Found C, 35.2; H, 6.5; N, 9.5. $[Cu(\mathbf{L}^4)][ClO_4]_2\cdot H_2O = [Cu(C_{17}H_{36}N_4)][ClO_4]_2\cdot H_2O$ requires C, 35.39; H, 6.64; N, 9.71%.

(v) Glycerol tris(benzenesulfonate) and ethane-1,2-diamine. The orange-brown colour of the crude amine mixture obtained here appeared to be associated with poor yields of simple polyamine products and the presence of seemingly large quantities of dark brown to black materials in the cobalt(III) complexes mixture which adhered very strongly to cation exchange resins and which we have not succeeded in characterising. The crude amine mixture obtained from 10.3 g of glycerol tris(benzenesulfonate) after 48 h reaction under N_2 with boiling ethane-1,2-diamine was dissolved in methanol (100 mL) containing glacial acetic acid (1 mL) and $CoSO_4\cdot 7H_2O$ (5.7 g), and air drawn through the solution for 3 h. The resulting brown solution was acidified with concentrated HCl (10 mL) and evaporated to near dryness on a steam bath. The residue was dissolved in water (100 mL) and the solution absorbed on a column of H^+ form Dowex 50W × 2 cation exchange resin to give a dark brown band at the head of the column. Elution with 2 mol L^{-1} HCl rapidly removed a large quantity of Co^{II}, followed by trace amounts of purple and green materials which were possibly just bis(ethane-1,2-diamine)cobalt(III) species and not further characterised. Continued elution removed a broad yellow band which, after evaporation to dryness under vacuum, was rechromatographed on SP Sephadex C-25 cation exchange resin using 0.1 mol L^{-1} trisodium citrate as eluent. This provided four components, from which the complex cations present were isolated by absorption of the eluate fractions on H^+ form Dowex 50W × 2, re-elution with HCl and evaporation of these eluates to dryness under vacuum. Yields: F1(red), 0.33 g; F2(orange), 0.16 g; F3(yellow), 0.06 g and F4(yellow), 0.28 g (ethanol-washed residues, vacuum dried). F3 was identified as $[Co(en)_3]Cl_3$ on the basis of its ^{1}H and ^{13}C NMR spectra, and discarded. All the other fractions showed very complicated ^{1}H NMR spectra with strongly overlapped multiplets in the region $\delta \approx 2$–3.5 but the ^{13}C spectra were all well resolved and reflected the lack of any symmetry in the three molecules. ^{13}C NMR: F1, δ 40.57, 42.35, 43.98, 44.02, 44.75, 44.82, 51.08, 54.54 and 58.40 (CH); F2, 44.65, 44.96, 46.01, 47.40, 52.45, 53.21, 55.17, 60.27 (CH) and 62.89; F4, 40.81, 44.90, 46.35, 46.69, 46.82, 51.31, 51.50, 56.32 and 61.97 (CH) (all CH_2 resonances except where indicated). Found C, 24.3; H, 6.5; N, 18.9.

$[Co(\mathbf{L}^5)(en)Cl]Cl_2{\cdot}HCl{\cdot}H_2O = [Co(C_7H_{18}N_4)(C_2H_8N_2)Cl]Cl_2{\cdot}HCl{\cdot}H_2O$ **7** requires C, 24.67; H, 7.13; N, 19.18%. Crystals of F1 suitable for X-ray diffraction studies were grown by vapour diffusion of ethanol into a solution of the complex in dilute HCl. The hexamine nature of the ligand, $\mathbf{L}^6$, in F4 was inferred from the conversion of F4 into a cage complex, structural characterisation of which is reported elsewhere.[11]

(vi) Glycerol tris(benzenesulfonate) and propane-1,3-diamine. Reaction of the sulfonate (10.3 g) with propane-1,3-diamine (30 g) at reflux over 48 h again produced, after removal of as much as possible of the excess of diamine by vacuum distillation, a viscous, brownish oil which was then converted into its cobalt(III) complexes as above. The mixture was directly adsorbed onto Na^+ form SP Sephadex C25 resin and the various species present eluted using 0.1 mol L^{-1} trisodium citrate. Co^{II} was first removed, followed by a bis(propane-1,3-diamine)cobalt(III) species, then a major band of a red-orange complex. This third eluate fraction was resorbed on Dowex 50W × 2 and the complex present isolated by elution with 5 mol L^{-1} HCl and evaporation of the eluate to dryness under vacuum. The deliquescent residue was converted into the chloride perchlorate by passage of its aqueous solution through a column of perchlorate form Dowex 1 anion exchange resin, to provide an air stable red-orange powder (2.8 g), the cobalt(III) complex of $\mathbf{L}^7$. Visible spectrum in 1 mol L^{-1} HCl: λ_{max} 481 nm, ε_{max} 103 M^{-1} cm^{-1}. δ ^{13}C (in 1 mol L^{-1} DCl): 23.62, 26.78, 28.22, 39.04, 39.80, 40.89, 47.99, 49.21, 51.91, 55.18, 55.66 and 64.93 (CH). Found C, 26.1; H, 5.9; N, 14.5. $[Co(\mathbf{L}^7)]Cl[ClO_4]_2 = [Co(C_{12}H_{32}N_6)]Cl(ClO_4)_2$ requires C, 26.03; H, 5.82; N, 15.18%.

(vii) Pentaerythritol tetrakis(benzenesulfonate) and propane-1,3-diamine. A remarkably large number of components (at least 12) was observed on chromatography of the cobalt(III) complexes of the polyamine product mixture but it was apparent that this was at least partly a consequence of aquation reactions of the initial complexes which occurred at a rate similar to that of the chromatographic separation. By reduction of the isolated cobalt(III) species with $NaBH_4$ under acidic conditions to release the attached ligands, it was found that essentially only one product ligand was present along with some unchanged propane-1,3-diamine. Fortunately, complexes of the diamine eluted from Dowex 50W × 2/HCl as two bands immediately following a cobalt(II) band and well separated from slower-moving components, so that, although the various cobalt(III) species were not identified, chromatography of the complexes was useful for ligand purification. Thus, all eluate fractions subsequent to the first three were combined and evaporated to dryness under vacuum. The residue was dissolved in water and an excess of $NaBH_4$, followed by enough concentrated HCl to make its concentration in the mixture ≈1 mol L^{-1}, was added to reduce Co^{III} to Co^{II} (indicated by vigorous effervescence and the deposition of a black precipitate which slowly redissolved to give a pinkish solution). This solution was absorbed on a column of Dowex 50W × 2 cation exchange resin, free Co^{II} eluted with 0.5 mol L^{-1} HCl and the colourless protonated polyamine eluted with 5 mol L^{-1} HCl. The second eluate was taken to near dryness, then triturated with ethanol to give a white, crystalline solid. From 7.0 g of the tetrakis(benzenesulfonate), 4.8 g of the hydrochloride of $\mathbf{L}^8$ were thereby obtained. Crystals of the product suitable for X-ray diffraction studies were grown by vapour diffusion of ethanol into a concentrated aqueous solution. Analysis of the dried solid corresponded to a considerably lower degree of hydration than that deduced from the crystal structure (see ahead, **8**). Found C, 29.6; H, 8.6; N, 15.6. $\mathbf{L}^8{\cdot}8HCl{\cdot}2H_2O = C_{17}H_{44}N_8{\cdot}8HCl{\cdot}2H_2O$ requires C, 29.67; H, 8.20; N, 16.27%. To prepare the copper(II) complex of $\mathbf{L}^8$, the hydrochloride (0.35 g), Li_2CO_3 (0.07 g) and $CuCO_3$ (0.12 g) were slurried with water (5 mL). After the initial effervescence had subsided, the mixture was heated on a steam bath for 5 minutes to give a deep blue solution. This was filtered, diluted with ethanol (15 mL) and then with acetone (50 mL). Deep blue microcrystals rapidly deposited and were collected and washed with acetone and ether. Yield: 0.20 g. Crystals of **9** suitable for X-ray crystallography were obtained by slow evaporation of an aqueous solution, the nitrate **10** being obtained *via* anion exchange.

(viii) Pentaerythritol tetrakis(benzenesulfonate) and (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine. Reaction of 2.8 g of the sulfonate led ultimately to a green solution of cobalt(III) complexes which was absorbed on a column of Dowex 50W × 2 cation exchange resin. Elution with HCl solutions of concentrations increasing from 0.2 to 4 mol L^{-1} revealed six components. The first eluted was Co^{II}, while the second, third and sixth species were bis- and tris-cyclohexanediamine complexes of Co^{III} (as revealed by isolation of the "free" ligand after BH_4^- reduction in acid). The fourth and major green component provided a green powder (1.1 g) on evaporation of its eluate to dryness. The trace of material in the fifth, purple band off the column was not identified. To obtain crystals of the fourth fraction suitable for X-ray diffraction, it was recrystallised from dilute HCl by vapour diffusion of ethanol. Found C, 38.0; H, 7.9; N, 11.6. $[Co(H_2\mathbf{L}^9)Cl_2]Cl_3{\cdot}4.5H_2O = [Co(C_{23}H_{46}N_6)Cl_2]Cl{\cdot}2HCl{\cdot}4{\cdot}5H_2O$ **11** requires C, 37.80; H, 8.00; N, 11.67%. Visible spectrum (in 1 mol L^{-1} HCl): λ_{max} 615 nm, $\varepsilon = 47.9$ M^{-1} cm^{-1}. Circular dichroism: 630, $\Delta\varepsilon = +1.43$; 563, $\Delta\varepsilon = -0.17$; 450, $\Delta\varepsilon = +0.55$; 391 nm, $\Delta\varepsilon = -0.25$ M^{-1} cm^{-1}.

Macrocycle formation reactions based on the well established template reaction of a linear tetramine complex with nitroethane and formaldehyde[1b,12,13] were investigated for the copper(II) complexes of $\mathbf{L}^1$ and $\mathbf{L}^{1'}$.

(ix) The copper(II) complex of 6,6,13-trimethyl-13-nitro-1,4,8,11-tetraazacyclotetradecane, $\mathbf{L}^{10}$. Nitroethane (0.85 g), triethylamine (2.5 g) and aqueous formaldehyde (37%, 8 mL) were added to a solution of $[Cu(\mathbf{L}^1)]Cl_2$ (4.1 g) in methanol (50 mL) and the mixture was heated and stirred at 50 °C for 5 h. After evaporation to dryness and redissolution of the product mixture in water, chromatography (SP Sephadex/0.3 mol L^{-1} NaCl) provided separation of two components, the purple leading band being reactant and the trailing reddish purple band the desired macrocyclic product. Its eluate was taken to dryness and the complex isolated as its chloride (3.2 g) by extraction into ethanol and evaporation of this extract. Crystals suitable for structure determinations were obtained from this crude chloride both by addition of $NaPF_6$ to its concentrated aqueous solution (and extended storage at ≈4 °C, resulting in the chloride hexafluorophosphate **12**) and by conversion into the nitrate **13** *via* anion exchange followed by precipitation from water by vapour diffusion of ethanol. Found C, 28.8; H, 5.7; N, 12.7. $[Cu(\mathbf{L}^{10})]Cl[PF_6]{\cdot}1.5H_2O = [Cu(C_{13}H_{29}N_5O_2)]Cl[PF_6]{\cdot}1.5H_2O$ requires C, 28.31; H, 5.82; N, 12.68%. Found, C, 31.8; H, 6.1; N, 20.0; $[Cu(C_{13}H_{29}N_5O_2)][NO_3]_2{\cdot}H_2O$ requires C, 31.67; H, 6.34; N, 19.89%.

(x) The copper(II) complex of 6,13-dimethyl-6-nitro-1,4,8,11-tetraazacyclotetradecane, $\mathbf{L}^{11}$. Substituting $[Cu(\mathbf{L}^{1'})]Cl_2$ (3.3 g) for the reactant in preparation (ix), essentially identical observations were made, though the product ultimately obtained by recrystallisation (ethanol plus ether) of what was presumed to be the crude chloride actually proved to be a tetrachlorocuprate, $[Cu(\mathbf{L}^{11})][CuCl_4]$ **14** (6.1 g). Found C, 26.1; H, 5.8; N, 12.2. $[Cu(\mathbf{L}^{11})][CuCl_4]{\cdot}0.5H_2O = [Cu(C_{12}H_{27}N_5O_2)][CuCl_4]{\cdot}0.5H_2O$ requires C, 26.15; H, 5.12; N, 12.70%.

Structure determinations

At the University of Western Australia diffraction data were acquired in a number of modes, at the specified temperature, all instruments being equipped with monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å. Using a single counter instrument in 2θ–θ scan mode, N unique reflections were measured within the specified $2\theta_{max}$ limit, N_o with $I > 3\sigma(I)$ being considered 'observed', Gaussian absorption corrections being applied (structures **7**–**11**). Data were also measured using a Bruker AXS CCD instrument (structures **1**, **2**, **4**–**6**, **12**, **13**) ($2\theta_{max} = 58°$), $N_{t(otal)}$ reflections within a full sphere being merged to N unique, R_{int} as specified after 'empirical'/multiscan absorption correction within the proprietary/preprocessing software, the 'observed' criterion applicable being $F > 4\sigma(F)$. Anisotropic thermal parameter forms were refined in a full matrix context for non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w (statistical weights) on $|F|$ are quoted at convergence. Neutral atom complex scattering factors were employed within the Xtal 3.4 program system.[14] Refinement in almost all determinations was seriously impeded by disorder/'thermal motion'/site occupancy problems and ambiguities. Straightforward refinements are noted as such! Pertinent results are given in the Figures and Tables below; individual variations in procedure/difficulties/idiosyncrasies are cited as 'variata'. For the room temperature determinations, 20% displacement ellipsoids are shown, for the low temperature, 50%. Hydrogen atoms, where shown, have arbitrary radii of 0.1 Å. Two structure determinations (**3**, **14**) at Pukyong National University were performed (by BJK) at room temperature using four-circle diffractometer data (Mo-Kα radiation), with data collection, cell refinement and data reduction based on STOE proprietary software, while the structure solution was obtained with SHELXS 97[15] and the structure refinement performed with SHELXL 97.[15]

$Cu(L^1)(ClO_4)_2 = [Cu(L^1)(O{\cdot}ClO_2{\cdot}O)]_{(\infty|\infty)}ClO_4$ 1. $C_9H_{24}Cl_2CuN_4O_8$, $M = 450.8$. CCD instrument, T *ca.* 153 K. Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 13.791(1)$, $b = 9.1815(8)$, $c = 27.573(2)$ Å, $\beta = 90.524(2)°$, $V = 3491$ Å^3, D_c $(Z = 8) = 1.71_5$ g cm^{-3}, $\mu_{Mo} = 16.0$ cm^{-1}, specimen $0.45 \times 0.40 \times 0.36$ mm, 'T'$_{min,max} = 0.51, 0.75$, $N_t = 51632$, $N = 13588$ ($R_{int} = 0.036$), $N_o = 10597$, $R = 0.049$, $R_w = 0.059$, $|\Delta\rho_{max}| = 1.6(1)$ e Å^{-3}.

Variata. (x, y, z, U_{iso}) were refined for all hydrogen atoms. Anionic perchlorate oxygen atoms (O(42–44)) were modelled as a pair of rotationally disordered components about Cl–O(41), site occupancies 0.5; perchlorate 1 within the polymer was modelled with the coordinated oxygen atoms O(11,12) ordered, albeit with elongated displacement envelopes, while the remaining ClO_2 component was disordered over two sets of sites, occupancies 0.5. $2\theta_{max}$ was 68°. Since there is, not infrequently, interest in the temperature-dependent behaviour of copper(II) structures, we note that in this particular case a preliminary determination was undertaken at room temperature (T *ca.* 300 K) (wherein the perchlorate disorder was not resolved). Cu–N (room, low temperature) did not differ significantly at the 3σ level; Cu–O differed rather more but, even so, by no more than 0.02 Å. Data for the room temperature determination are deposited. (Cell dimensions *etc.*: $a = 13.887(1)$, $b = 9.2532(9)$, $c = 27.778(3)$ Å, $\beta = 90.634(2)°$, $V = 3569$ Å^3, R, $R_w = 0.052$, 0.069 for $N_t = 40411$, $N = 8745$ ($R_{int} = 0.023$), $N_o = 6577$ ($2\theta_{max} = 58°$), $|\Delta\rho_{max}| = 0.88(3)$ e Å^{-3}).

$[Cu(L^{1'})(OClO_3)_2]$ 2. $C_8H_{22}Cl_2CuN_4O_8$, $M = 436.7$. CCD instrument, T *ca.* 153 K. Monoclinic, space group $P2_1$ (C^2_2, no. 4), $a = 8.368(1)$, $b = 24.884(4)$, $c = 8.508(1)$ Å, $\beta = 114.917(3)°$, $V = 1607$ Å^3, D_c $(Z = 4) = 1.80_5$ g cm^{-3}, $\mu_{Mo} = 17.4$ cm^{-1}, specimen $0.12 \times 0.10 \times 0.06$ mm, 'T'$_{min,max} = 0.74, 0.89$, $N_t = 16230$, $N = 4227$ ($R_{int} = 0.047$), $N_o = 3150$, $R = 0.042$, $R_w = 0.041$, $|\Delta\rho_{max}| = 0.6(1)$ e Å^{-3}.

Variata. An initial refinement of x_{abs} with 'Friedel pair' data preserved distinct gave a value of *ca.* 0.5. Accordingly, the data were merged.

$[Cu(L^{1'})(O{\cdot}ClO_2{\cdot}O)]_{(\infty|\infty)}ClO_4$ 3. $C_8H_{22}Cl_2CuN_4O_8$, $M = 436.7$. STOE instrument, T *ca.* 293 K. Monoclinic, space group $P2_1/n$ (C^5_{2h}, no. 14 (variant)), $a = 9.567(2)$, $b = 13.745(3)$, $c = 12.562(3)$ Å, $\beta = 91.26(3)°$, $V = 1652$ Å^3, D_c $(Z = 4) = 1.75_6$ g cm^{-3}, $\mu_{Mo} = 16.9$ cm^{-1}, specimen $0.30 \times 0.30 \times 0.20$ mm, 'T'$_{min,max} = 0.59, 0.81$, $N = 3780$, $N_o = 2774$, $R = 0.058$, $R_w = 0.14$, $|\Delta\rho_{max}| = 0.5$ e Å^{-3}.

Variata. The bridging perchlorate was modelled as disordered over two sites of equal occupancy.

$[Cu(L^1)Cl]ClO_4$ 4. $C_9H_{24}Cl_2CuN_4O_4$, $M = 386.8$. CCD instrument, T *ca.* 300 K. Orthorhombic, space group $Pnma$ (D^{16}_{2h}, no. 62), $a = 11.246(1)$, $b = 9.373(2)$, $c = 15.291(2)$ Å, $V = 1612$ Å^3, D_c $(Z = 4) = 1.59_4$ g cm^{-3}, $\mu_{Mo} = 17.0$ cm^{-1}, specimen $0.40 \times 0.20 \times 0.18$ mm; 'T'$_{min,max} = 0.75, 0.91$, $N_t = 19214$, $N = 2235$ ($R_{int} = 0.022$), $N_o = 1847$, $R = 0.031$, $R_w = 0.040$; $|\Delta\rho_{max}| = 0.44$ e Å^{-3}.

Variata. $(x, y, z, U_{iso})_H$ were refined throughout; the perchlorate was modelled with O(22,23) disordered, site occupancies 0.72(1) and complements.

$[H_6L^2]Cl_6.2H_2O$ 5. $[(H_3N(CH_2)_2NH_2CH_2C(Me_2)CH_2NH_2CH_2)_2]Cl_6{\cdot}2H_2O \equiv C_{16}H_{50}Cl_6N_6O_2$, $M = 571.3$. CCD instrument, T *ca.* 153 K. Monoclinic, space group $P2_1/c$, $a = 7.0501(8)$, $b = 18.946(2)$, $c = 11.005(1)$ Å, $\beta = 105.383(1)°$, $V = 1417$ Å^3, D_c $(Z = 2) = 1.33_9$ g cm^{-3}, $\mu_{Mo} = 6.3$ cm^{-1}, specimen $0.45 \times 0.35 \times 0.30$ mm, 'T'$_{min,max} = 0.65, 0.96$, N_t (CCD data) $= 15638$, $N = 3519$ ($R_{int} = 0.028$), $N_o = 3181$, $R = 0.026$, $R_w = 0.037$, $|\Delta\rho_{max}| = 0.47$ e Å^{-3}.

Variata. Refinement was straightforward, all hydrogen atoms refining in (x, y, z, U_{iso}).

$[\{Cu(L^3)(OH_2)\}_2Cl][\{Cu(L^3)\}_2Cl][ClO_4]_6$ 6. $C_{44}H_{116}Cl_8Cu_4N_{16}O_{26}$, $M = 1823.3$. CCD instrument, T *ca.* 300 K. Monoclinic, space group $C2/c$ (C^6_{2h}, no. 15), $a = 42.632(3)$, $b = 9.9729(8)$, $c = 18.659(1)$ Å, $\beta = 101.365(1)°$, $V = 7778$ Å^3, D_c $(Z = 4) = 1.55_7$ g cm^{-3}, $\mu_{Mo} = 14.3$ cm^{-1}, specimen $0.40 \times 0.25 \times 0.20$ mm, 'T'$_{min,max} = 0.70, 0.91$, $N_t = 34329$, $N = 9754$ ($R_{int} = 0.035$), $N_o = 5964$, $R = 0.043$, $R_w = 0.047$, $|\Delta\rho_{max}| = 0.65$ e Å^{-3}.

Variata. (x, y, z, U_{iso}) were refined for all hydrogen atoms except those associated with the water molecule which were not located. Perchlorates 4,5 were modelled as rotationally disordered about Cl(n)–O(n1), O(n2–4) having site occupancies refining to 0.79(1), 0.81(1) and complements respectively. (These values are so similar that the disorder may be concerted.) Three quarters of a sphere of data were measured.

$[Co(HL^5)(en)Cl]Cl_3{\cdot}H_2O$ 7. $C_9H_{29}Cl_4CoN_6O$, $M = 438.1$. Single-counter instrument, T *ca.* 295 K. Triclinic, space group $P\bar{1}$ (C^1_i, no. 2), $a = 11.265(4)$, $b = 10.177(2)$, $c = 8.382(2)$ Å, $\alpha = 97.91(2)$, $\beta = 97.51(3)$, $\gamma = 107.01(2)°$, $V = 895$ Å^3, D_c $(Z = 2) = 1.62_5$ g cm^{-3}, $\mu_{Mo} = 15.6$ cm^{-1}, specimen $0.48 \times 0.26 \times 0.41$ mm, $T_{min,max} = 0.52, 0.69$, $2\theta_{max} = 65°$, $N = 6056$, $N_o = 5347$, $R = 0.031$, $R_w = 0.041$, $|\Delta\rho_{max}| = 1.25$ e Å^{-3}.

Variata. Refinement was straightforward, all hydrogen atoms refining in (x, y, z, U_{iso}).

$[H_8L^8]Cl_8{\cdot}7.5H_2O$ 8. $C_{17}H_{67}Cl_8N_8O_{7.5}$, $M = 787.4$. Single counter instrument, T *ca.* 295 K. Monoclinic, space group $C2/c$, $a = 21.636(6)$, $b = 17.446(5)$, $c = 10.360(4)$ Å, $\beta = 94.82(3)°$, $V = 3897$ Å^3, D_c $(Z = 4) = 1.34_2$ g cm^{-3}, $\mu_{Mo} = 6.2$ cm^{-1}, specimen $0.32 \times 0.55 \times 0.65$ mm, $T_{min,max} = 0.77, 0.83$, N(hemisphere) $= 9154$, $N = 4439$ ($R_{int} = 0.033$), $N_o = 3142$, $R = 0.057$, $R_w = 0.060$, $|\Delta\rho_{max}| = 0.69$ e Å^{-3}.

Variata. $(x, y, z, U_{iso})_H$ were refined for the ligand; hydrogen atoms were located in difference maps for O(1–3) and included in the refinement with constrained parameters. Other residues O(4–6) were modelled as oxygen atoms only, occupancy 0.5, 0.25, 0.25, 'Cl(5)' also having occupancy 0.5 (caveat: *cf.* O), with high 'thermal motion' evident among Cl(4,5), O(1–4).

$[(CuCl)_2L^8]Cl_2{\cdot}2H_2O$ 9. $C_{17}H_{48}Cl_4Cu_2N_8O_2$, $M = 665.5$. Single counter instrument, T *ca.* 295 K. Triclinic, space group $P\bar{1}$, $a = 12.531(4)$, $b = 12.271(2)$, $c = 10.075(2)$ Å, $\alpha = 99.22(1)$, $\beta = 112.61(2)$, $\gamma = 90.64(2)°$, $V = 1407$ Å^3, D_c $(Z = 2) = 1.57_1$ g cm^{-3}, $\mu_{Mo} = 19.2$ cm^{-1}, specimen $0.65 \times 0.75 \times 0.48$ mm, $T_{min,max} = 0.25$, 0.47, $2\theta_{max} = 56°$, $N = 6779$; $N_o = 5569$, $R = 0.047$, $R_w = 0.052$, $|\Delta\rho_{max}| = 0.91$ e Å^{-3}.

Variata. $(x, y, z, U_{iso})_H$ were refined throughout except for the water molecules for which they were not located.

$[(CuONO_2)_2L^8][NO_3]_2{\cdot}3H_2O$ 10. $C_{17}H_{50}Cu_2N_{12}O_{15}$, $M = 789.8$. Single counter instrument, T *ca.* 295 K. Orthorhombic, space group $Pbca$ (D_{2h}^{15}, no. 61), $a = 22.843(9)$, $b = 18.422(6)$, $c = 15.489(5)$ Å, $V = 6518$ Å^3, D_c $(Z = 8) = 1.60_9$ g cm^{-3}, $\mu_{Mo} = 13.9$ cm^{-1}, specimen $0.95 \times 0.35 \times 0.23$ mm, $T_{min,max} = 0.53$, 0.68, $2\theta_{max} = 50°$, N(hemisphere) = 9636, $N = 5735$ ($R_{int} = 0.082$), $N_o = 3810$, $R = 0.049$, $R_w = 0.061$, $|\Delta\rho_{max}| = 0.79$ e Å^{-3}.

Variata. $(x, y, z, U_{iso})_H$ were refined throughout the ligand; hydrogen atoms were located for water molecule 1 only and constrained. O(3) was modelled as disordered over a pair of sites, occupancies set at 0.5 after trial refinement. The projection of the Figure does not show the elongation of the ellipsoid of C(45), suggestive of conformational disorder in that ring, resulting in associated torsion angle anomalies.

$[Co(H_2L^9)Cl_2]Cl_3{\cdot}{\approx}4.5H_2O$ 11. $C_{23}H_{57}CoCl_5N_6O_{4.5}$, $M = 438.1$. Single counter instrument, T *ca.* 295 K. Orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), $a = 17.339(7)$, $b = 15.529(4)$, $c = 12.625(4)$ Å, $V = 3399$ Å^3, D_c $(Z = 4) = 1.41_8$ g cm^{-3}, $\mu_{Mo} = 9.4$ cm^{-1}, specimen $0.42 \times 0.32 \times 0.75$ mm, $T_{min,max} = 0.68$, 0.75, $2\theta_{max} = 60°$, $N = 5459$, $N_o = 4124$, $R = 0.046$, $R_w = 0.048$ (preferred hand), $|\Delta\rho_{max}| = 0.7$ e Å^{-3}.

Variata. Site occupancy of O(5) was constrained to 0.5 after trial refinement. Hydrogen atoms were not located for O(3–5), the remainder being included with parameters constrained at estimates.

$[Cu(L^{10})Cl(OH_2)]PF_6{\cdot}0.5H_2O$ 12. $C_{13}H_{32}ClCuF_6N_5O_{3.5}P$, $M = 558.4$. CCD instrument, T *ca.* 153 K. Monoclinic, space group $P2_1/n$, $a = 6.5904(8)$, $b = 17.471(2)$, $c = 19.014(2)$ Å, $\beta = 96.038(2)°$, $V = 2177$ Å^3, D_c $(Z = 4) = 1.70_3$ g cm^{-3}, $\mu_{Mo} = 12.8$ cm^{-1}, specimen $0.15 \times 0.10 \times 0.06$ mm, 'T'$_{min,max} = 0.76$, 0.93, $N_t = 21705$, $N = 5523$ ($R_{int} = 0.055$), $N_o = 3592$, $R = 0.051$, $R_w = 0.056$, $|\Delta\rho_{max}| = 0.73(9)$ e Å^{-3}.

Variata. The hexafluorophosphate was disordered, resolved residues for F(2) – F(6) being modelled as pairs of components, site occupancies set at 0.5 after trial refinement. Hydrogen atoms were not resolved in association with a further residue, modelled as half a water molecule oxygen, nor with the coordinated water molecule oxygen.

$[Cu(L^{10})(ONO_2)_2]{\cdot}H_2O$ 13. $C_{13}H_{31}CuN_7O_9$, $M = 493.0$. CCD instrument, T *ca.* 153 K. Monoclinic, space group $C2/c$, $a = 19.018(3)$, $b = 9.015(2)$, $c = 12.256(2)$ Å, $\beta = 97.504(2)°$, $V = 2083$ Å^3, D_c $(Z = 4) = 1.57_2$ g cm^{-3}, $\mu_{Mo} = 11.1$ cm^{-1}, specimen $0.45 \times 0.40 \times 0.05$ mm, 'T'$_{min,max} = 0.60$, 0.86, $N_t = 9784$, $N = 2559$ ($R_{int} = 0.029$), $N_o = 2227$, $R = 0.038$, $R_w = 0.042$, $|\Delta\rho_{max}| = 0.65$ e Å^{-3}.

Variata. Modelling in space group $C2/c$ entails disorder of the molecule, and the lattice water, about inversion centres, manifest in half-weighting of the nitro and methyl-12 moieties, hydrogen atoms in association with the latter not being resolved. Other hydrogens were refined in $(x, y, z, U_{iso})_H$.

$[Cu(L^{11})][CuCl_4]$ 14. $C_{12}H_{27}Cl_4Cu_2N_5O_2$, $M = 542.3$. STOE instrument, T *ca.* 298 K. Monoclinic, space group Cc (C_s^4, no. 9), $a = 17.439(4)$, $b = 8.037(2)$, $c = 15.946(3)$ Å, $V = 2063$ Å^3, D_c $(Z = 4) = 1.74_6$ g cm^{-3}, $\mu_{Mo} = 26.0$ cm^{-1}, specimen $0.50 \times 0.30 \times 0.20$ mm, 'T'$_{min,max} = 0.62$, 0.74, $2\theta_{max} = 55°$, $N = 2383$, $N_o = 2383$, $R = 0.039$, $R_w = 0.095$ (preferred hand), $|\Delta\rho_{max}| = 0.5$ e Å^{-3}.

CCDC reference number 186/2308.

See http://www.rsc.org/suppdata/dt/b0/b008452m/ for crystallographic files in .cif format.

Results and discussion

1 Polyamines derived from propane-1,3-diamine

Although propane-1,3-diamine units are commonly found as constituents of polyamines and macrocycles,[1,16] and linear polyamines in particular have often been synthesized by reactions similar to those of the present work,[17] little information is available on direct comparison of 1,2- and 1,3-diamines with respect to the competition between intra- and intermolecular pathways in reactions with electrophilic polyol derivatives. As reaction of two sulfonate ester groups of the same molecule with a diamine must result in the formation of a larger ring from a 1,3- than from a 1,2-diamine, it might be expected that intramolecular processes in the present systems would be less prominent for 1,3- than for 1,2-diamines.[18] Indeed, we have observed no evidence of cyclic products from propane-1,3-diamine, meaning that the reaction products were relatively simple to characterise and it is for this reason that we have chosen to describe first their syntheses.

Reaction between the bis(benzenesulfonate) of neopentyl glycol and propane-1,3-diamine gave essentially a single product, $\mathbf{L}^3$ (Fig. 1). Trace amounts of at least two other species were observed as their copper(II) complexes but, on the basis of results obtained for the ethane-1,2-diamine products (see ahead), we assume that these were likely to have been derived from a reaction pathway in which the initial steps are consecutive reactions of propane-1,3-diamine with two molecules of sulfonate. (While in all present reactions a large excess of diamine was always used, it may be noted that the solutions were actually moderately concentrated in polysulfonate.) The ^{1}H nuclear magnetic resonance spectrum of the bulk product is completely consistent with a reaction in which amino groups of two independent diamine molecules displace the sulfonate groups of a single diol derivative molecule (Fig. 1). That the product is a quadridentate amine of the "333-tet" type[1a,19] was confirmed by the remarkable structure determined for its copper(II) complex, **6**, $[Cu_4(\mathbf{L}^3)_4Cl_2(OH_2)_2][ClO_4]_6$ (Fig. 2). The solid contains a pair of binuclear cations with $(\mathbf{L}^3)$Cu units bridged in both by chloride entities, each disposed on a crystallographic symmetry element, one a twofold axis, the other an inversion centre. Cu(2)–Cl(2)–Cu(2) is thus (obligate) linear and Cu(1)–Cl(1)–Cu(1) bent (162.49(6)°). Cu(2) is five-coordinate but Cu(1) six-coordinate due to the approach of a residue modelled as a water molecule oxygen (Cu(1)–O(01) 2.986(5) Å), having little other apparent impact on the geometry about the Cu (Tables 1(c), 2). Ligands of the 333-tet type are known to be relatively unsuited to chelation of a single transition metal ion because of the steric problems associated with the adoption of the favoured chair conformation by all three fused six-membered chelate rings,[1a,19] though $[Cu(333\text{-}tet)(ClO_4)]ClO_4$ [3,3,3-tet = N,N'-bis(3-aminopropyl)-1,3-diamine] does contain the chair–chair–chair form in the crystal,[20] presumably because the N_4 donor atom array is able to distort well away from planarity. A similar conclusion may apply in the present system, since all four tetramine entities are bound in the chair–chair–chair mode but again in association with marked deviations of the N_4 units from planarity.

Unlike the sulfonate of neopentyl glycol (and those of related polyols such as pentaerythritol and 1,1,1-tris(hydroxymethyl)ethane), the trisulfonate of glycerol can undergo base-catalysed elimination as an alternative to nucleophilic substitution and we assume this is the reason for the relatively poor yields of substitution products in the reactions we have studied of this sulfonate. Nonetheless, it is possible in the case of reaction with

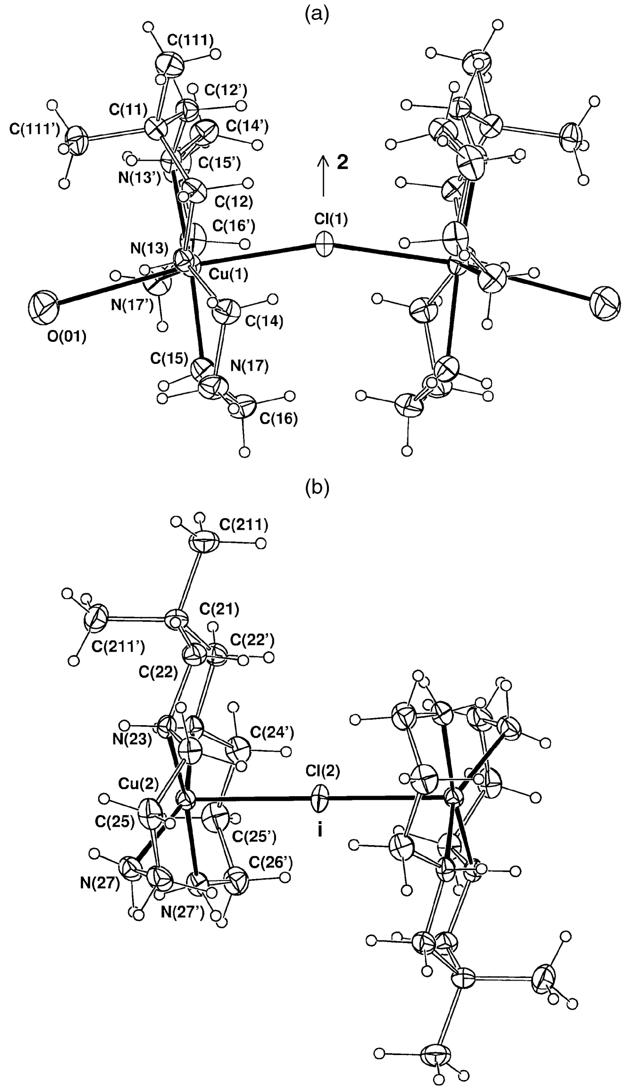


Fig. 2 (a),(b) Projections of the two cations of $[\{Cu(\mathbf{L}^3)(OH_2)\}_2Cl][\{Cu(\mathbf{L}^3)\}_2Cl][ClO_4]_6$, **6**, cation 1 lying on a crystallographic *2* axis, and 2 about an inversion centre. A figure showing the unit cell contents, projected down *b*, is deposited as Electronic Supplementary Material (ESI).

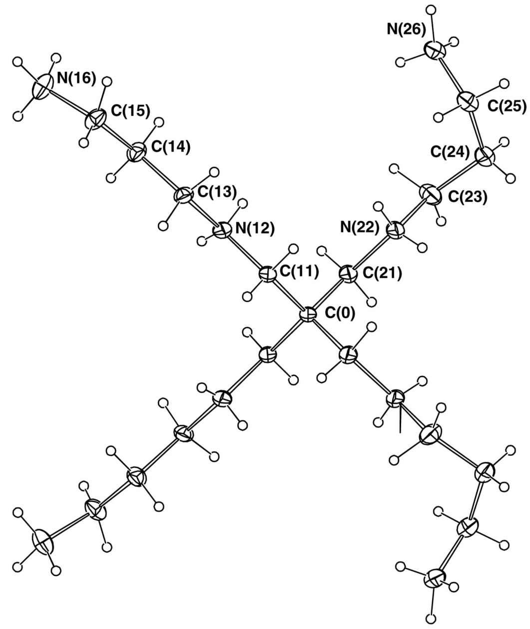


Fig. 3 The $[H_8\mathbf{L}^8]^{8+}$ cation, in the octachloride salt, **8**, projected normal to the crystallographic *2* axis which lies horizontal in the page. A figure showing the unit cell contents, projected down *c*, is deposited as ESI.

propane-1,3-diamine to isolate a hexamine species, $\mathbf{L}^7$ (Fig. 1), in acceptable yield, with no evidence being obtained for the presence of other substitution products. The cobalt(III) complex of this hexamine has the pinkish yellow colour typical of tris(1,3-diamine) complexes (and distinguishing them from yellow tris(1,2-diamine species) but there is evidence from its ^{13}C nuclear magnetic resonance spectrum that it may exist in two diastereomeric forms, unlike the complex of the analogous hexamine ("stn") derived from reaction of 1,1,1-tris(hydroxymethyl)ethane derivatives.[4,21] Efforts to obtain crystals of the material suitable for a structure determination were unsuccessful.

Analysis of the products of the reaction of the tetrakis(benzenesulfonate) of pentaerythritol with propane-1,3-diamine by formation and chromatography of their cobalt(III) complexes proved unfortunate because of the (unsurprising) lability[21,22] of these complexes, although the chromatography was still seemingly useful in enabling separation of simple propane-1,3-diamine complexes from others. As first demonstrated by a crystal structure determination of the hydrochloride of the "free" ligand **8**, once again a single polyamine, an octamine $\mathbf{L}^8$ derived by substitution involving four independent diamine units (Fig. 1), was the only significant product. Ready isolation of the fully protonated octamine is consistent with the minimum separation of at least three methylene units between every basic site,[23] though the crystal structure (Fig. 3) shows an extended array which is presumably partly determined by repulsions between the charge centres. One half of the formula unit comprises the asymmetric unit of the structure, the cation disposed with the central quaternary carbon atom lying on a crystallographic *2* axis. Torsion angles in the branches, outwards from C(1)–N(2) are 177.7(3), −178.3(3), 177.4(3), −169.6(3) (branch 1) and 179.9(3), −172.1(3), −66.9(6), −67.3(6)° (branch 2), predominantly *trans*, so that the cation is sprawling rather than compact. Despite the high charge, one of the anions is ill defined, as is a substantial water complement, these moieties being disordered/partly occupied. Hydrogen bonding is extensive but again dominated by a few short contacts, most especially anion-protonated amine group (specified by N···Cl (< 3.5 Å) rather than H···Cl distances in view of the relatively imprecise hydrogen locations here): Cl(1)···N(12,22,26), N(26)($1\frac{1}{2} - x$, $1\frac{1}{2} - y$, $1 - z$) 3.058(4), 3.195(4), 3.187(5) (quasi-tridentate) 3.267(4); Cl(2)···N(22), N(16)(x, $1 - y$, $z - \frac{1}{2}$), ($1\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$), N(26) ($1\frac{1}{2} - x$, $1\frac{1}{2} - y$, $1 - z$) 3.385(4), 3.368(5), 3.129(5), 3.320(4); Cl(3)···N(16)(x, $1 - y$, $z - \frac{1}{2}$), N(26)($1\frac{1}{2} - x$, $1\frac{1}{2} - y$, $1 - z$) 3.186(5), 3.129(4) Å. Cl(4), disposed on a crystallographic *2* axis, is surrounded by water molecules: Cl(4)···O(01)($1 - x$, $1 - y$, $1 - z$) (x, $2 - y$, $\frac{1}{2} + z$), O(02)(x, y, z), ($1 - x$, y, $1\frac{1}{2} - z$) 2.996(5) (× 2), 2.908(5) (× 2), as is the half-occupied 'Cl(5)', Cl(5)···O(04), O(05)($1 - x$, y, $1\frac{1}{2} - z$), ($1 - x$, $1 - y$, $1 - z$), O(06) ($1 - x$, y, $1\frac{1}{2} - z$) 3.06(1), 3.17(2), 2.82(2), 2.64(2), the latter also contacting N(12) (x, y, z) ($1 - x$, $1 - y$, $1 - z$) 3.059(6), 3.106(7) Å. O···O, N contacts also are found (< 3 Å): O(01)···O(01) ($1 - x$, y, $\frac{1}{2} - z$), O(02)($1 - x$, y, $\frac{1}{2} - z$) 3.010(7), 2.726(7), N(22) 2.826(6); O(02)···O(03) ($1 - x$, y, $\frac{1}{2} - z$) 2.731(8); O(03)···O(04), N(16) (x, $1 - y$, $\frac{1}{2} + z$) 2.700(9), 2.893(8); O(04)···O(05) (x, y, z) ($1 - x$, y, $1\frac{1}{2} - z$) 2.246(2) Å.

In complexes of $\mathbf{L}^8$ with both copper(II) chloride, **9**, and nitrate, **10**, the ligand functions as a binucleating species, binding two five-coordinate CuN_4X ($X = Cl$ or NO_3) units in which the geometry may be considered intermediate between square-pyramidal and trigonal bipyramidal. Although in both species the mean CuN_4 planes are close to coplanar, there is an interesting difference between the two in that unidentate nitrate ligands bind on the same side ("*cis*") while chloride ligands

Table 1 Copper atom environments (distances in Å, angles in °) of $\mathrm{N_4Cu(X)(Y)}$ entities in complexes of $\mathbf{L}^1$ and $\mathbf{L}^3$

(a) $[\mathrm{Cu}(\mathbf{L}^1)(\mathrm{OClO_2O})]_{(\infty|\infty)}\mathrm{ClO_4}$ **1**, $[\mathrm{Cu}(\mathbf{L}^{1'})(\mathrm{OClO_3})_2]$ **2** and $[\mathrm{Cu}(\mathbf{L}^{1'})(\mathrm{OClO_2O})]_{(\infty|\infty)}\mathrm{ClO_4}$ **3**. Values are for molecules 1 and 2 of **2**, 'cations' 1 and 2 of **1**, and **3**

Atom	*r*	N(*n*6)	N(*n*3′)	N(*n*6′)	O(*n*1)[a]	O(*n* ± 1 2)
N(*n*3)	2.045(5), 1.991(6)	84.4(2), 85.9(2)	93.0(2), 93.9(2)	179.0(2), 179.0(2)	88.3(2), 89.9(2)	94.9(2), 90.3(2)
	2.011(2), 2.020(2)	85.54(9), 85.36(9)	93.25(9), 93.60(8)	179.1(1), 175.9(1)	96.8(1), 98.58(8)	84.13(8), 82.12(8)
	2.010(4)	84.9(2)	94.4(2)	177.9(2)	101.2(8)	93.3(8)
N(*n*6)	2.016(5), 2.031(5)		176.4(3), 177.6(2)	96.4(2), 95.0(2)	93.0(2), 92.8(2)	87.4(2), 86.4(2)
	2.011(2), 2.007(3)		176.26(9), 178.10(9)	95.4(1), 95.9(1)	98.82(9), 92.52(9)	82.58(8), 84.41(9)
	2.003(5)		178.7(2)	95.4(2)	100.2(6)	73.0(8)
N(*n*3′)	2.024(4), 2.018(5)			86.2(2), 85.2(2)	89.5(2), 89.6(2)	90.3(2), 91.2(2)
	2.018(2), 2.009(2)			85.83(9), 85.3(1)	84.82(9), 86.06(8)	93.78(7), 97.03(8)
	2.007(4)			85.2(2)	78.8(6)	108.2(8)
N(*n*6′)	1.978(5), 2.024(5)				91.2(2), 90.5(2)	85.6(2), 89.4(2)
	2.014(2), 2.012(3)				83.0(1),85.3(1)	96.05(9), 94.1(2)
	2.009(5)				76.7(5)	88.9(8)
O(*n*1)	2.540(6), 2.518(6)					176.8(2), 179.2(2)
	2.572(3), 2.551(2)					178.37(8), 176.79(8)
	2.69(2)					164(1)
O(*n*1′)	2.517(6), 2.556(6)					
	2.577(2), 2.591(2)					
	2.50(2)					

(b) $[\mathrm{Cu}(\mathbf{L}^1)\mathrm{Cl}]\mathrm{ClO_4}$ **4**. Primed atoms are generated by the mirror plane through the copper atom; Cl(1*) is generated by $(x - \frac{1}{2}, 1\frac{1}{2} - y, \frac{1}{2} - z)$[b]

Atom	*r*	N(3)	N(6)	Cl(1*)	N(3′)	N(6′)
Cl(1)	2.6885(7)	92.55(5)	94.62(7)	171.14(2)	81.40(5)	91.33(7)
N(3)	2.013(1)		85.27(7)	(81.40(5))	93.11(6)	172.71(8)
N(6)	2.023(2)			(91.33(7))	(172.71(8))	95.45(8)
Cl(1*)	2.908(7)					(94.62(7))

(c) $[\{\mathrm{Cu}(\mathbf{L}^3)(\mathrm{OH_2})\}_2\mathrm{Cl}][\{\mathrm{Cu}(\mathbf{L}^3)\}_2\mathrm{Cl}][\mathrm{ClO_4}]_6$ **6**. Values for cation $n = 2$ are given *italicised* below those for cation $n = 1$[c]

Atom	*r*	N(*n*3)	N(*n*7)	N(*n*3′)	N(*n*7′)	Cl(*n*)
O(01)	2.986(5)	74.3(1)	80.8(2)	97.2(1)	82.9(2)	165.31(9)
N(*n*3)	2.065(3)		92.3(2)	95.6(1)	157.2(2)	93.26(9)
	2.063(3)		*85.7(1)*	*96.0(1)*	*170.2(1)*	*91.06(8)*
N(*n*7)	2.019(4)			171.1(1)	84.9(2)	92.2(1)
	2.057(4)			*153.0(1)*	*84.6(2)*	*112.4(1)*
N(*n*3′)	2.067(3)				86.2(2)	91.6(1)
	2.060(3)				*93.2(1)*	*94.49(8)*
N(*n*7′)	2.064(4)					109.5(1)
	2.036(4)					*91.4(1)*
Cl(*n*)	2.5808(5)					
	2.5887(4)					

[a] For Cu(2) of structure **1** read O(21) $(1 + x, y, z)$. Angles subtended by the pairs of heavy atoms at O(11), O(12) are 122.6(5)/124.0(5), 127.4(5)/128.3(4) and at O(21,22) are 131.7(1), 129.5(1)°. The entry for **3** corresponds to the array with the shorter pair of Cu–O distances, O(12′), O(14′) $(\frac{1}{2} - x, \frac{1}{2} + y, 1\frac{1}{2} - z) \equiv$ O(*n*1), O(*n* ± 1 2). For the other perchlorate component, Cu···O(13), O(14) $(\frac{1}{2} - x, \frac{1}{2} + y, 1\frac{1}{2} - z)$ are 3.00(1), 2.755(8) Å. [b] Cu lies 0.127(1) Å out of the (exact) $\mathrm{N_4}$ plane; Cl–Cu–Cl* is 167.95(3)°. [c] Cl(2) lies on a crystallographic inversion centre, Cl(1) at twofold axis; Cu(1)–Cl(1)–Cu(1′) is 162.49(6)°. Atom deviations from the $\mathrm{N_4}$ 'planes' (χ^2 4837, 10266) are (N(3,3′,7,7′)Cu) −0.100(4), 0.116(4), 0.224(6), −0.264(6), 0.224(1) (Cu(1)), −0.162(4), 0.155(4), 0.318(4), 0.270(5), −0.241(1) Å (Cu(2)).

Table 2 Ligand torsion angles (°) for structures **1** ('cations' 1,2), **2** (molecules 1,2), **3**, **4** and **6** ('cations' 1,2)[a]

Atoms	**1**	**2**	**3**	**4**	**6**
C(2′)–C(1)–C(2)–N(3)	−66.0(5), −66.3(5)	−69.5(8), −67.2(8)	−69.2(7)	−65.9(2)	−69.9(5), −70.4(4)
C(2)–C(1)–C(2′)–N(3′)	66.4(5), 66.6(5)	67.0(8), 71.3(8)	70.2(7)	—	72.8(4), 70.1(4)
C(1)–C(2)–N(3)–C(4)	−179.34(4), −179.6(3)	−177.6(6), 179.9(6)	179.4(5)	−178.3(2)	−179.9(4), 180.0(3)
C(1)–C(2′)–N(3′)–C(4′)	176.8(4), 179.6(3)	−179.9(6), 175.0(6)	179.9(6)	—	178.4(3), 178.0(3)
C(1)–C(2)–N(3)–Cu	56.9(4), 56.2(4)	59.9(7), 55.6(8)	54.9(6)	57.6(2)	46.7(5), 51.2(4)
C(1)–C(2′)–N(3′)–Cu	−57.9(4), −56.3(4)	−55.8(7), −61.5(7)	−56.7(7)	—	−52.5(4), −50.1(4)
C(2)–N(3)–C(4)–C(5)	−172.1(4), −170.73(3)	−171.2(6), −172.2(6)	−174.7(5)	−175.1(2)	170.8(4), 163.9(4)
C(2′)–N(3′)–C(4′)–C(5′)	168.1(4), 173.8(4)	171.1(6), 167.1(6)	174.9(5)	—	−163.9(4), −171.1(4)
Cu–N(3)–C(4)–C(5)	−42.7(4), −40.5(4)	−43.5(7), −42.0(7)	−44.5(5)	−44.9(2)	−54.9(4), −64.9(4)
Cu–N(3′)–C(4′)–C(5′)	37.6(4), 44.0(4)	40.8(7), 39.0(7)	45.4(5)	—	64.4(5), 56.1(4)
N(3)–C(4)–C(5)–N(6)	55.0(5), 54.9(5)	56.0(8), 53.3(8)	56.1(6)	55.3(2)	72.0(6), 63.3(5)
N(3′)–C(4′)–C(5′)–N(6′)	−52.6(5), −53.7(5)	−54.6(8), −53.9(8)	−56.8(7)	—	−66.1(4), −75.8(5)
C(4)–C(5)–C,N(6)–Cu,N(7)	−39.4(5), −41.8(4)	−39.9(7), −37.5(7)	−39.4(6)	−37.0(2)	−67.7(7), −64.3(5)
C(4′)–C(5′)–C,N(6′)–Cu,N(7′)	40.6(4), 36.6(5)	40.6(7), 41.6(7)	38.6(6)	—	64.8(6), 66.8(5)

[a] For compound **6**, C(5)–C(6)–N(7)–Cu are 53.3(6), 69.6(3) with primed counterparts −67.3(5), −45.8(5)°.

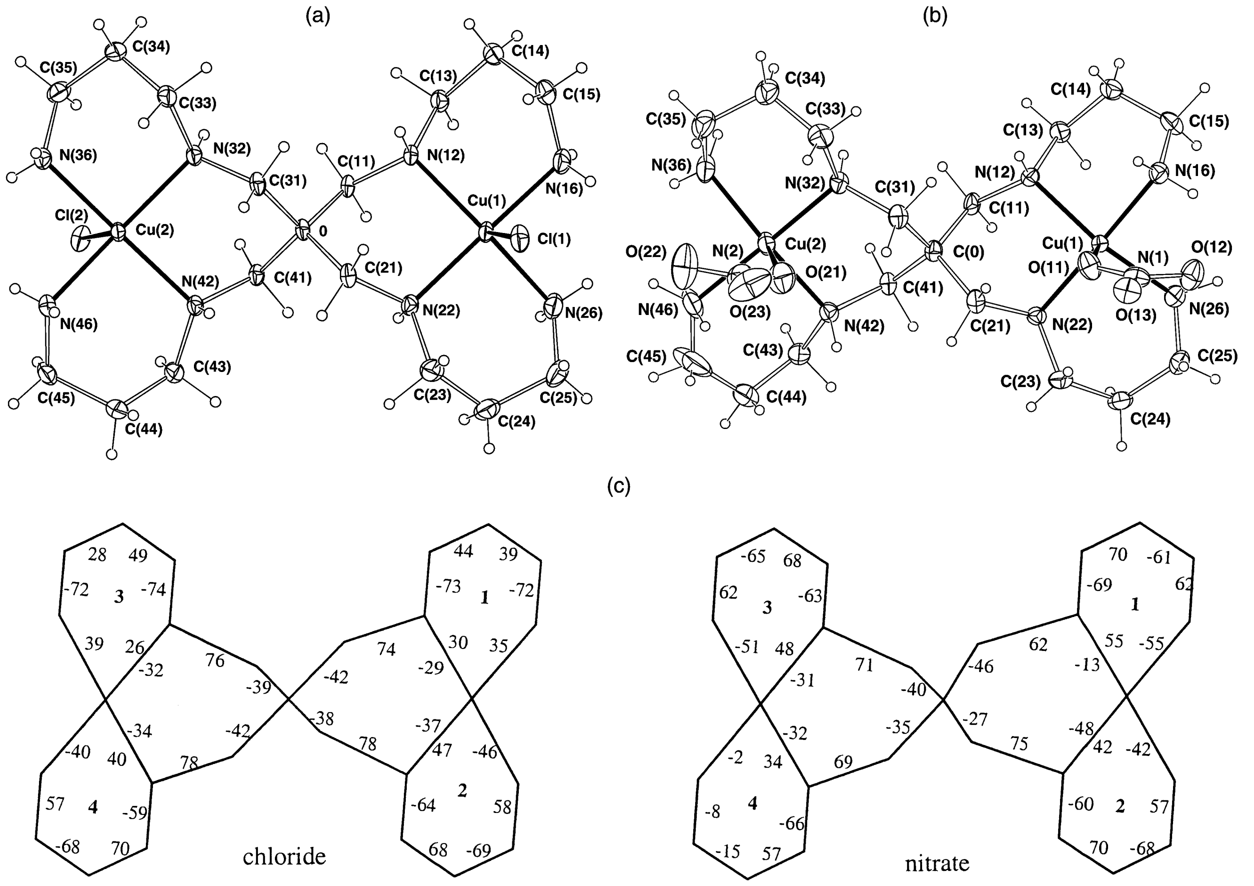


Fig. 4 Projections of the cations of $[(CuX)_2\mathbf{L}^8]X_2{\cdot}nH_2O$ (a) **9**, X = Cl, $n = 2$, and (b) **10**, X = NO_3, $n = 3$ normal to the moiety 'plane'. (c) Schematic diagram of the intra-ring torsion angles as descriptors of ring conformations for the two complexes (s.u.'s typically 0.3, 0.6 °).

Table 3 Selected cation geometries (distances in Å, angles in °) of $[(CuX)_2\mathbf{L}^8]^{2+}$ (X = Cl **9** or ONO_2 **10**). Values for the nitrate are given in *italics* below those for the chloride. Segments 1/2 and 3/4 pertain to the environs of Cu(1) and Cu(2) respectively

	Segment 1/2 (n = 1 or 2)		Segment 3/4 (n = 3 or 4)
Cu(1)–X(1)	2.685(1) *2.371(4)*	Cu(2)–X(2)	2.700(1) *2.506(5)*
Cu(1)–N(n2)	2.086(4), 2.028(3) *2.068(4), 2.020(5)*	Cu(2)–N(n2)	2.076(3), 2.054(4) *2.032(4), 2.048(4)*
Cu(1)–N(n6)	1.994(3), 2.035(6) *1.980(5), 2.014(6)*	Cu(2)–N(n6)	2.023(5), 2.025(3) *2.016(6), 1.987(7)*
X(1)–Cu(1)–N(n2)	111.19(9), 93.21(9) *107.7(2), 85.4(2)*	X(2)–Cu(2)–N(n2)	108.28(8), 93.03(9) *81.8(2), 91.9(2)*
X(1)–Cu(1)–N(n6)	88.1(1), 98.2(1) *87.0(2), 106.4(2)*	X(2)–Cu(2)–N(n6)	87.2(1), 91.8(1) *111.3(2), 90.3(2)*
N(n2)–Cu(1)–N(n6)	90.3(2), 90.0(2) *90.0(2), 93.5(2)*	N(n2)–Cu(2)–N(n6)	90.0(1), 91.7(2) *89.9(2), 91.4(3)*
N(n2)–Cu(1)–N(n'6)	150.5(2), 178.2(2) *145.9(2), 172.2(2)*	N(n2)–Cu(1)–N(n'6)	159.8(1), 179.5(1) *171.4(3), 156.8(2)*
N(12)–Cu(1)–N(22)	90.4(1) *90.5(2)*	N(32)–Cu(2)–N(42)	89.5(1) *92.4(2)*
N(16)–Cu(1)–N(26)	88.6(2) *90.4(2)*	N(36)–Cu(2)–N(46)	88.7(2) *89.6(3)*
C(n1)–N(n2)–C(n3)	108.1(3), 109.8(3) *107.6(4), 109.7(5)*	C(n1)–N(n2)–C(n3)	108.9(3), 110.1(3) *108.5(4), 108.0(4)*
Cu(1)–N(n2)–C(n3)	109.8(3), 114.7(3) *106.8(3), 114.2(4)*	Cu(1)–N(n2)–C(n3)	110.1(2), 116.2(3) *112.7(4), 111.8(4)*
Cu(1)–N(n2)–C(n1)	110.5(2), 110.5(2) *115.2(3), 110.2(4)*	Cu(2)–N(n2)–C(n1)	110.9(2), 110.4(3) *112.8(3), 112.0(3)*
Cu(1)–N(n6)–C(n5)	115.4(3), 118.9(4) *116.9(4), 117.6(5)*	Cu(2)–N(n6)–C(n5)	113.5(3), 119.5(3) *117.7(5), 128.3(9)*

bind on opposite sides ("*trans*") (Fig. 4) of the average plane, concomitant with differences in associated chelate ring torsion angles. Thus, in the chloride, the rings fused through the *spiro*-carbon atom derived from pentaerythritol adopt the skew-boat conformation, as does one "terminal" chelate ring about each copper. In the nitrate the two terminal rings on one Cu may be considered to be in chair conformations, while one is chair and the other skew-boat on the other Cu. Despite such differences, N–Cu–N bond angles are regular and very close to 90°, although there is a greater disparity of Cu–N distances for the terminal skew-boat than for the terminal chair chelate rings (Table 3). The range of Cu–N distances is, however, similar to that in various "unconstrained" $[Cu(NH_3)_4]^{2+}$ derivatives[1a] and in $[Cu(333\text{-}tet)][ClO_4]_2$.[20] In the latter, as noted above, the three rings all adopt essentially chair conformations but the Cu^{II} is also six-coordinate *via* perchlorate coordination and it is not immediately apparent what factors may principally determine these conformational differences. Magnetic suceptibility measurements (4–300 K) on both the chloride and nitrate of the copper(II) complex of $\mathbf{L}^8$ show Curie–Weiss behaviour and indicate negligible interaction between the copper centres, though the acetate, presently of unknown structure, is more strongly antiferromagnetic.

2 Polyamines derived from 1,2-diamines

(a) Ethane-1,2-diamine. The reaction of the bis(benzenesulfonate) of neopentyl glycol with ethane-1,2-diamine is analogous to a large number of reactions which have been used to produce open-chain quadridentate amines and appears, as in these earlier studies,[17,19] to give essentially just such a product, $\mathbf{L}^1$ (Fig. 1) of the "232-tet" type.[1a,19] The ^1H nuclear magnetic resonance spectrum of the major reaction product is completely consistent with this structure and the assignment is confirmed by crystal structure determinations of the copper(II) complex as its perchlorate, **1**, and chloride perchlorate, **4**. In contrast to the analogous complex of 232-tet itself [*N*,*N*′-bis(2-aminoethyl)propane-1,3-diamine],[20] the perchlorate does not crystallise as isolated $[Cu(L)(ClO_4)_2]$ units but as a coordination polymer, $[Cu\mathbf{L}^1(OClO_2O)]_{(\infty|\infty)}ClO_4$, (Fig. 5a; Tables 1 and 2), two formula units comprising the asymmetric unit of the structure. CuN_4 units, much closer to planar than in the complexes of $\mathbf{L}^3$ and $\mathbf{L}^8$ described above, are linked by O(disordered ClO_2)O perchlorate bridges in their fifth and sixth *trans*-co-ordination sites, the two moieties of the asymmetric unit alternating in the undulating polymer which is generated by the unit *a* translation, the asymmetric unit spanning that dimension of the unit cell. The chloride perchlorate, $[Cu\mathbf{L}^1Cl]ClO_4$ (Fig. 5b; Tables 1 and 2), has a structure which may be superficially regarded as made up of mononuclear cations and perchlorate counter ions, but in fact has the chloride moieties bridging, less symmetrically, successive $Cu\mathbf{L}^1$ units stacked up *a* in a manner similar to that found in the perchlorate; in both structures successive $\mathbf{L}^1$ ligands are turned end-for-end about the (undulating) polymer axis. Here, one half of the formula unit makes up the asymmetric unit of the structure, the polymer lying in a crystallographic mirror plane which bisects it and the (disordered) perchlorate counter ion. As for 232-tet, the quadridentate ligand is bound in both cases in its "meso", *R*,*S* form, with the central chelate ring in its chair form and the flanking five-membered chelate rings in mirror-image *gauche* conformations. As elsewhere,[20] this seems compatible with near planarity of the CuN_4 unit.

Importantly, the very minor additional reaction product detected was not the diazepam possibly formed by intramolecular substitution following the first displacement of a sulfonate group by an ethane-1,2-diamine nitrogen but a hexamine, $\mathbf{L}^2$ (Fig. 1), seemingly produced by initial dialkylation of the diamine with two molecules of disulfonate, followed by independent nucleophilic substitution of the remaining sulfonate groups by another two molecules of diamine. The spacing of the basic sites in this molecule by C_3 units appears to be sufficient to allow ready isolation of the hexahydrochloride (*viz.* the fully protonated form). A low-temperature, single-crystal X-ray study of the hexahydrochloride dihydrate, **5**, in which all hydrogen atoms were successfully located and refined, and all nitrogen atoms definitively established as such by refinement, confirmed the ligand structure (Fig. 6). The substance crystallises with one half of the formula unit comprising the asymmetric unit, an ionic complex, with all nitrogen atoms fully protonated, the centre of the central $(H_2)C–C(H_2)$ bond being disposed on a crystallographic inversion centre, so that one half of the cation, three counter ions and one water molecule are crystallographically independent. Torsion angles in the independent half of the cation string, from the central C–C bond outwards, are: 180(−), 173.6(1), 164.0(1), −79.0(1), 177.1(1), 180.0(1), 174.7(1), −86.3(1)°, a mixture of *trans* and *gauche* dispositions. Again, the hydrogen bonding is seemingly dominated by a limited number of short interactions: anion–protonated amine and water, Cl(1)···H(3bB), N(3b) 2.28(2), 3.128(1),

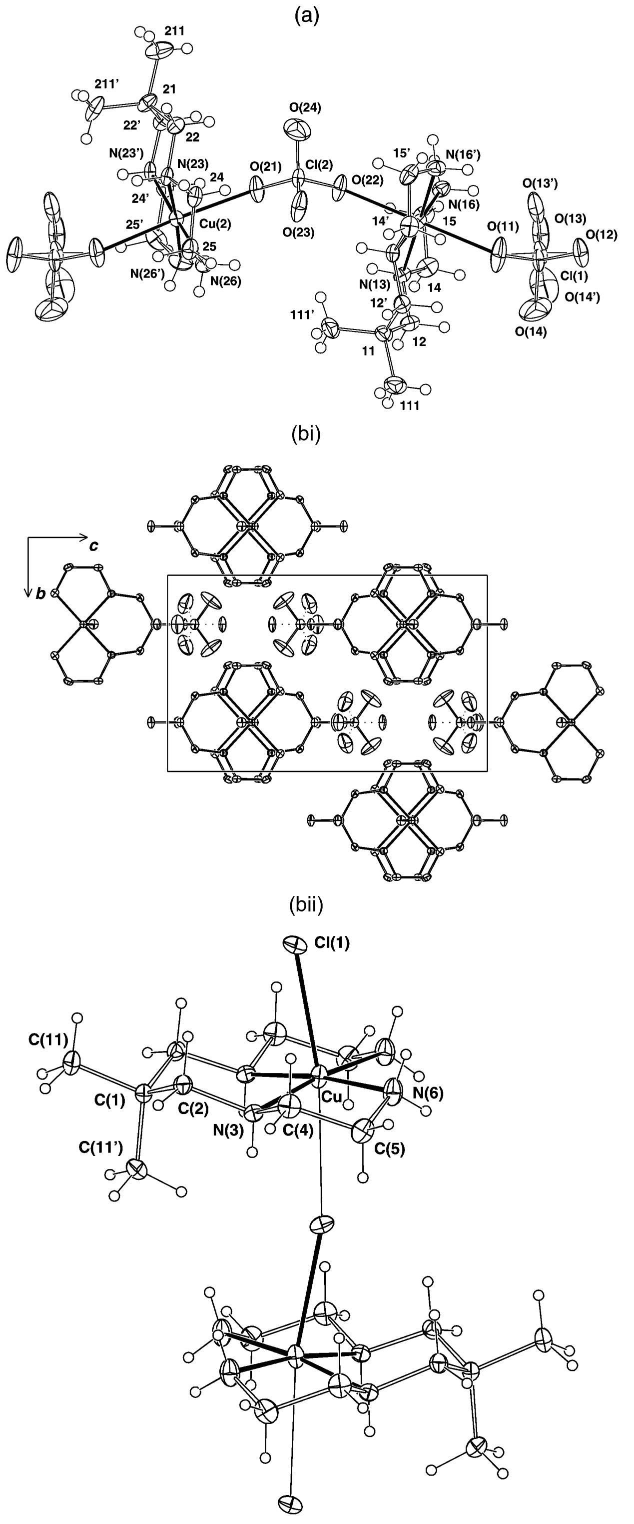


Fig. 5 (a) Section of the polymeric cation of $[Cu\mathbf{L}^1(OClO_2O)]_{(\infty|\infty)}ClO_4$, **1**; *a* lies horizontal in the page. A figure showing the unit cell contents, projected down *b*, is deposited as ESI. (b) (i) The unit cell contents $[Cu\mathbf{L}^1Cl]ClO_4$, **4**, projected down *a*, showing the columnar stacking of the cations and associated perchlorates up that axis. (ii) A side-on view of a cation stack, *a* lying vertically in the page.

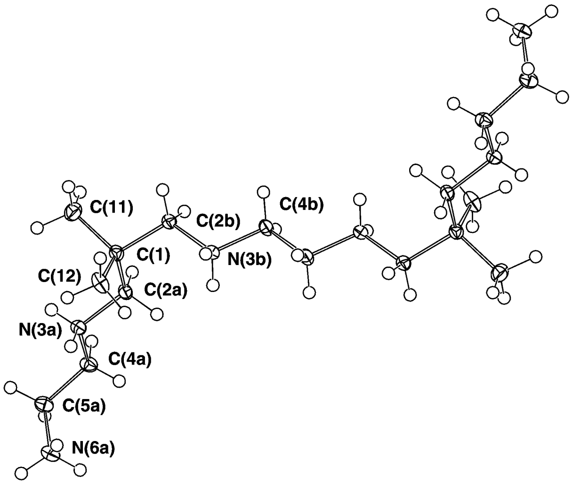


Fig. 6 Projection of the centrosymmetric $[H_6L^6]^{6+}$ cation in compound **5**. A figure showing the unit cell contents of $[H_6L^6]Cl_6{\cdot}2H_2O$, **5**, down *a*, and indicating short hydrogen-bonded contacts is deposited as ESI.

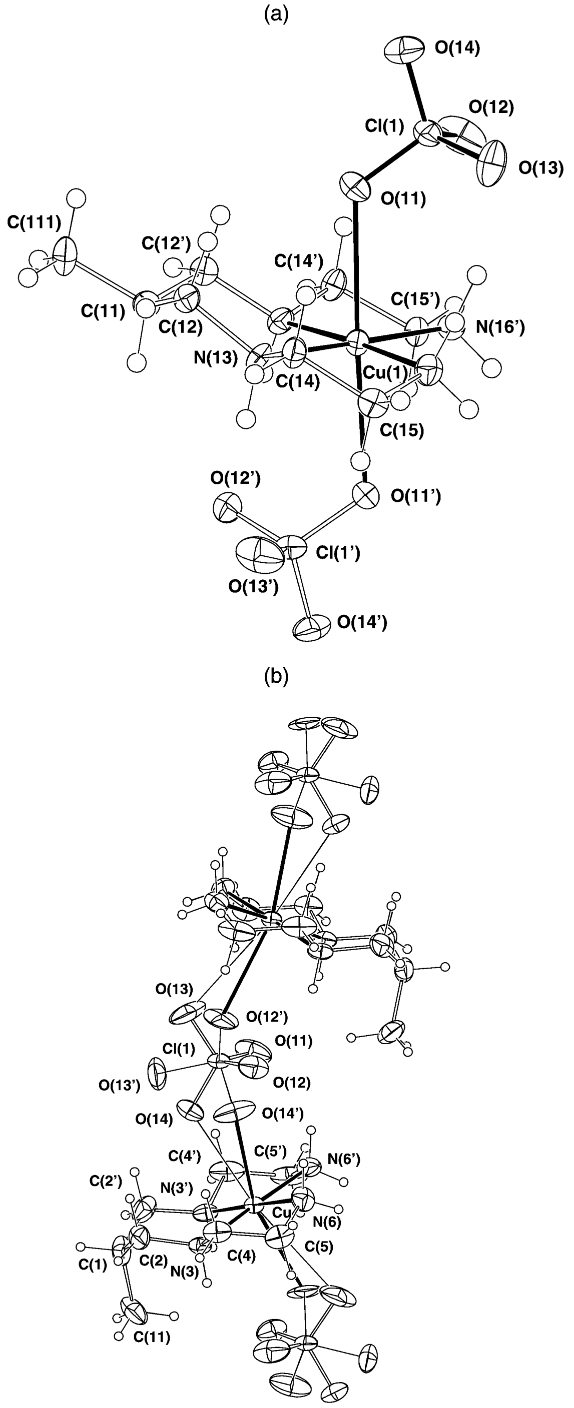


Fig. 7 (a) A single molecule (molecule 1) of $[Cu(\mathbf{L}^{1'})(OClO_3)_2]$, **2** (molecule 2 is similar). (b) Projection of the polymeric cation of $[Cu(\mathbf{L}^{1'})(OClO_2O)]^{+}{}_{(\infty|\infty)}$, **3**, showing the modelling of the perchlorate in terms of components rotationally disordered about Cl–O(1), entailing coordination *via* O(13,14) or O(12′,14′).

Cl(1)···H(01A), O(01) 2.33(2), 3.128(1); Cl(2)···H(3aA), N(3a) ($x - 1$, y, $z - 1$) 2.38(1), 3.105(1); Cl(2)···H(6aA), N(6a) ($x - 1$, $\frac{1}{2} - y$, $z - \frac{1}{2}$) 2.37(2), 3.186(1); Cl(3)···H(3bA), N(3b) 2.23(2), 3.086(1); and water-protonated amine, O(01)···H(6aC), N(6a) 2.09(2), 2.863(1) Å.

While there are close parallels in the properties of ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ and $\mathbf{L}^{1'}$ and $\mathbf{L}^{2'}$, there are also some significant differences, associated significantly with the prochiral nature of the central carbon atom of the propyl units in $\mathbf{L}^{1'}$ and $\mathbf{L}^{2'}$. Seemingly, the complex $(Cu\mathbf{L}^{1'})(ClO_4)_2$ can adopt two solid state structures of comparable energy, since samples drawn on different occasions from crystalline masses produced by supposedly identical procedures contain isomeric species, differing notably in that structure **2** has the methyl substituent on the central six-membered (chair) chelate ring in an equatorial orientation, whereas in structure **3** it is axial (Fig. 7). Given that interconversion of these two species would require not only inversion of all three chelate rings in the complex but also inversion of the two, "inner" coordinated nitrogen atoms, it seems unlikely that this difference could be associated with the different temperatures for the two structure determinations (especially given the minor effects of temperature seen in two structure determinations of $[Cu(\mathbf{L}^{1'})(OClO_2O)]_{(\infty|\infty)}ClO_4)$ and thus we ascribe it to chance selection of different crystals from similar syntheses. Structure **2** is very closely similar to that of Cu(232-tet)$(ClO_4)_2$,[20] in that it contains "molecular" $[Cu(\mathbf{L}^{1'})(OClO_3)_2]$ units, whereas structure **3** is based upon polymeric $[Cu(\mathbf{L}^{1'})(OClO_2O)]_n$ strands very similar to those in the complex of $\mathbf{L}^1$ (structure **1**). A short amine–perchlorate oxygen hydrogen bond is found in the molecular structure, linking the two independent molecules of the asymmetric unit: O(13)···H(26a) ($2 - x$, $y - \frac{1}{2}$, $2 - z$) 2.1_4 Å (est.). In the polymeric array the perchlorate is modelled in terms of weak coordination *via* two pairs of oxygen atoms, disordered by rotation about an undisordered Cl–O bond. In the structure of the nickel(II) complex of another derivative of 232-tet[24] an axially oriented methyl substituent is found on the central atom of an approximately chair-form 6-membered chelate ring and, interestingly, this central atom is a tertiary nitrogen which is presumably free to undergo inversion, so that here at least it appears that the axial orientation must be thermodynamically preferred. While much structural evidence indicates that equatorial orientations are favoured for single substituents on six-membered rings,[1a,25] axial orientations are known even in simple (bidentate) systems[26] and calculations indicate that the energy differences may not be large,[27] so that subtle solid state effects may tip the balance. In linear and macrocyclic quadridentate ligand complexes with similarly sized methyl and nitro group substituents on the central carbon of propyl links, stereoselective coordination with both axial and equatorial methyl group orientations is well established[13,28,29] and this is further discussed ahead in relation to the macrocyclic ligand complex structures **12**–**14**.

The structure of hexamine ligand $\mathbf{L}^{2'}$, though established on the basis of spectroscopic evidence only, shows that, as also indicated by earlier work,[8] the product distribution may be markedly dependent on whether sulfonate or halide groups are displaced by the amine. The yield of $\mathbf{L}^{2'}$ relative to that of the tetramine ($\mathbf{L}^{1'}$) greatly exceeds that of its analogue $\mathbf{L}^2$, though it is conceivable that this reflects simply the high reactivity of the bromo substituent leading to reaction during the initial stage of

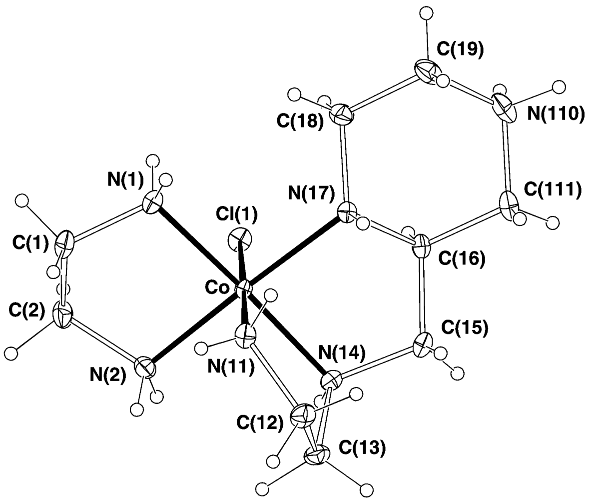


Fig. 8 Projection of the $[Co(H\mathbf{L}^5)(en)Cl]^{3+}$ cation in complex **7**.

Table 4 Selected geometries of $[Co(H\mathbf{L}^5)(en)Cl]Cl_3{\cdot}H_2O$ **7**. The cobalt environment. r/Å is the metal–ligand atom distance; other entries are the angles (°) subtended by the relevant atoms at the head of the row and column

Atom	*r*	N(1)	N(2)	N(11)	N(14)	N(17)
Cl(1)	2.2651(8)	88.84(6)	87.29(6)	177.93(4)	93.90(5)	90.75(5)
N(1)	1.958(2)		85.83(7)	92.08(7)	176.67(7)	96.71(6)
N(2)	1.967(1)			90.93(8)	92.39(6)	176.76(7)
N(11)	1.961(2)				85.12(7)	90.98(7)
N(14)	1.959(1)					85.16(6)
N(17)	1.989(1)					

Also: Co–N–C at N(1,2,11) are 110.4(1), 109.1(1), 112.0(1); Co–N(14)–C(13,15) are 108.1(1), 111.1(1), and Co–N(17)–C(16,18) are 106.37(8), 121.2(1)°. Torsion angles in the bonds around the C_4N_2 ring beginning with the C(16)–N(17) bond are 59.3(2), −58.0(2), 56.6(3), −55.2(3), 54.8(2), −57.4(2)°, around the five-membered C_2N_2Co rings, beginning with N(1)–C(1), N(11)–C(12) and N(14)–C(15) are −34.5(2), 46.9(3), −37.5(2), 14.9(2), 11.1(2); −19.4(2), 41.3(2), −44.7(2), 27.5(1), −4.5(1); and −22.5(2), 45.7(2), −47.1(2), 28.4(1), −3.5(1)°.

mixing the reagents, when in fact the diamine was gradually added to the dihalide. Although the ^{1}H and ^{13}C NMR spectra indicate that $\mathbf{L}^{2'}$ is a single species, it is not obvious why there should be a marked preference for one possible isomer over another (*R**,*R** or *R**,*S**) and we presume that either the spectral differences are extremely small or that isolation of the ligand by formation of the copper(II) complex may have led to fractionation.

The reaction of the tris(benzenesulfonate) of glycerol with ethane-1,2-diamine does not seem to be an efficient pathway to polyamine formation. Nevertheless, nucleophilic substitution can be detected and it is clear that in this system intramolecular reaction following the initial or second step of substitution is at least as important as further intermolecular reaction. Full characterisation of the reaction products ($\mathbf{L}^5$ and $\mathbf{L}^6$; Fig. 1) was complicated by the apparent presence of diastereomers of the cobalt(III) complex of the hexamine product component and only the more abundant of these two isomers (the fourth fraction of the chromatographic separation of the cobalt(III) complexes of the product mixture) has been unambiguously identified as the hexamine $\mathbf{L}^6$ by a structure determination of its cage derivative which will be reported elsewhere.[11] The structure of the complex cation containing $\mathbf{L}^5$ (and ethane-1,2-diamine, presumably arising from its use in large excess in the synthesis) found in the first fraction of the chromatographic separation and crystallised as its trichloride monohydrate, **7**, is shown in Fig. 8. The determination is precise, to the extent of refining all hydrogen atom parameters and establishing nitrogen (*versus* carbon) atom locations definitively. Monoprotonated $\mathbf{L}^5$ coordinates in this complex as a *fac*-N_3-tridentate ligand, with, among the various remaining possible modes of co-ordination of the remaining ligands, the chloride anion coordinating *trans* to the acyclic peripheral nitrogen. The metal atom environment is summarised in Table 4; the C_4N_2 six-membered ring is a relatively unperturbed ‘chair’, while the two fused chelate rings are envelopes, C(12,15) as ‘flaps’ unsymmetrically disposed distal and adjacent to the ‘central’ nitrogen, N(14). The ethane-1,2-diamine has quasi-*2* symmetry about the line through N(2) and the midpoint of the N(1)–C(1) bond. Bond lengths and angles about the metal hold no surprises; hydrogen bonding is dominated by a relatively few quite short contacts, notably between the halide counter ions and the protonated amine Cl(2)···H(110a), N(110a) (x, $y - 1$, z) 2.16(2), 3.098(2), Cl(3)···H(110b), N(110b) 2.24(4), 3.200(2) Å, and the other coordinated amine groups of the cation, Cl(4)···H(1bN), N(1) ($1 - x$, $2 - y$, $2 - z$) 2.30(2), 3.160(2), Cl(4)···H(17), N(17) 2.37(2), 3.198(2), and, more distantly, the water molecule, Cl(2)···H(01b), O(01) (x, $1 + y$, $z - 1$) 2.56(4), 3.118(3) Å. The water molecule oxygen is also hydrogen-bonded by one of the en amine moieties: O(01)···H(11a), N(11) 2.19(3), 2.915(3) Å.

Formation of the piperazine derivative $\mathbf{L}^5$ must be the result of an intramolecular reaction, though there is at present no evidence as to whether such a step follows one or two intermolecular substitutions (or both). Note that this red complex, $[Co(H\mathbf{L}^5)(en)Cl]Cl_3{\cdot}H_2O$, is clearly different in colour to the yellow second and fourth chromatographic fractions, so that although it is presumably possible for isomers of it to be present, it is for this reason that the second is presumed to be a diastereomer of the fourth and not the first (although if $\mathbf{L}^5$ binds as a quadridentate species along with en, then of course this argument would be invalid). In all, there is a complete lack of symmetry as shown by the detection of nine resonances in the ^{13}C nuclear magnetic resonance spectrum of each. For present purposes, it suffices to recognise that cyclic and open chain amines are produced in similar amounts. Owing to the overall inefficiency of the reaction, the analogous synthesis with the less readily accessible diamine (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine was not investigated.

(b) (1*R*),(2*R*)-*trans*-Cyclohexane-1,2-diamine. The reaction of the bis(benzenesulfonate) of neopentyl glycol with (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine appeared closely to parallel that with ethane-1,2-diamine in giving a dominant product showing a ^{1}H nuclear magnetic resonance spectrum fully consistent with it being an open chain tetramine produced by displacement of both sulfonates by separate diamine molecules (Fig. 1). The scale of the synthesis with the cyclohexanediamine was such that other trace components observed as their copper(II) complexes could not fully be characterised and it is assumed that they may be analogous to the hexamine species detected in the ethane-1,2-diamine system (and that the use of a sulfonate reactant has minimised their production). Given that the configuration of (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine fixes its chelate rings in a λ conformation, a square planar array of the four N donor atoms of $\mathbf{L}^4$ would require that, unlike the unsubstituted 232-tet ligand complex (where the outer rings are enantiomeric), the central six-membered chelate ring should adopt a chiral, λ, skew-boat conformation, as is observed in the cobalt(III) complex **10** of the related ligand $\mathbf{L}^9$ (see below). Unfortunately, attempts to confirm both the nature of $\mathbf{L}^4$ and this predicted conformation by determination of the crystal structure of $[Cu(\mathbf{L}^4)][ClO_4]_2$ were unsuccessful due to the unsatisfactory nature of the crystals.

Although the reactions of various derivatives of pentaerythritol with ethane-1,2-diamine appear to differ to some degree depending on the exact nature of the leaving group,[4–8] the product distributions all reflect significant competition of

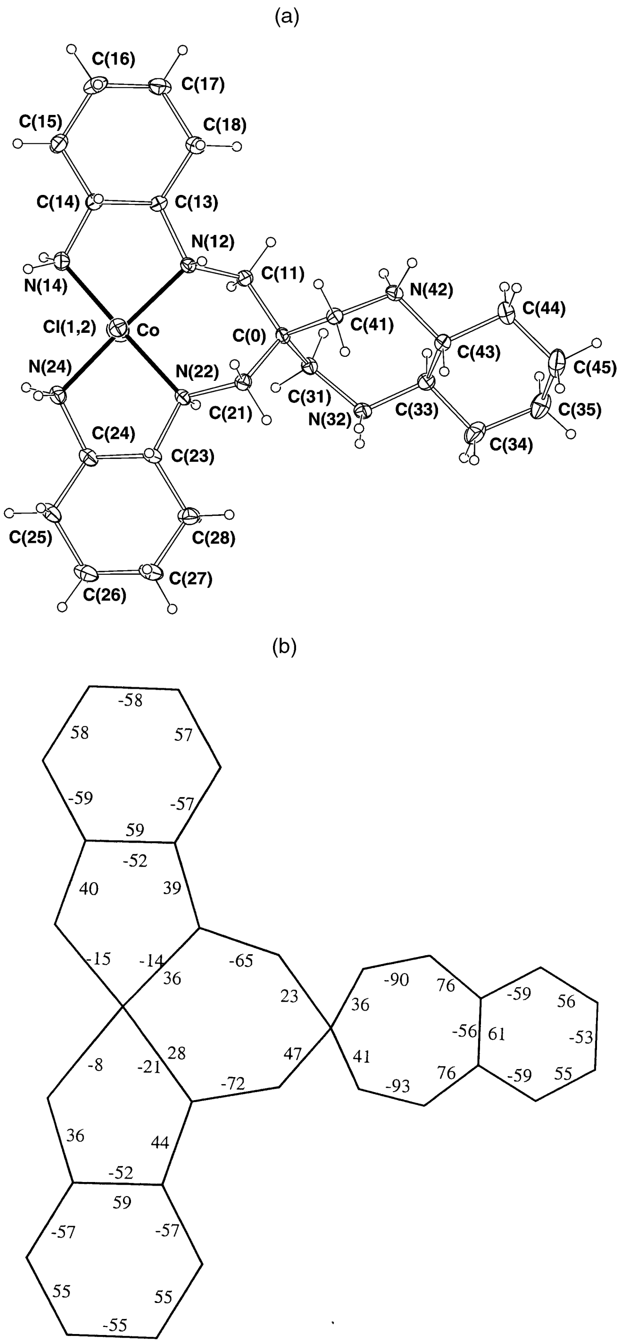


Fig. 9 (a) Projection of the *trans*-$[Co(H_2L^9)Cl_2]^{3+}$ cation in **11**, down the Cl–Co–Cl line. (b) Torsion angles (to nearest degree) within the rings (s.u.'s are typically 0.5°).

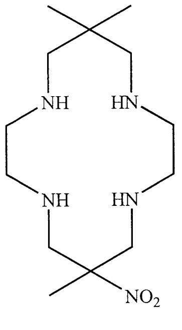
intramolecular with intermolecular pathways, leading to both hexamine and octamine species in these reactions. (1*R*),(2*R*)-*trans*-Cyclohexane-1,2-diamine is somewhat restricted in its conformational mobility compared to that of ethane-1,2-diamine and this may be the reason that its reaction with the tetrakis(benzenesulfonate) of pentaerythritol gives but a single product, both spectroscopic and analytical measurements indicating it to be the hexamine $\mathbf{L}^9$ (Fig. 1). Determination of the crystal structure of the cobalt(III) complex **11** (Fig. 9; Table 5) shows that the ligand is indeed the species formed by displacement of two sulfonate groups by one diamine unit to give a seven-membered ring and the other two sulfonate groups by independent diamine units. The *trans*-CoN_4Cl_2 environment of the metal is as expected from the green colour of the complex and dimensions of this inner unit are generally rather similar to those in the previously characterised[8] analogue derived from ethane-1,2-diamine, though the fixed chirality of the cyclohexane moieties imposes rather different conformations upon the whole molecule, so that the six-membered chelate ring is δ-skew-boat and the inner coordinated nitrogen atom configurations are *S*,*S*, rather than chair and *R*,*S* as in the analogue. There appears to be no significant systematic difference between the distances from the metal to the inner (N(*n*2)) and outer (N(*n*4)) nitrogens (Table 5). In the present case the asymmetric unit of the structure is the full formula unit, devoid of crystallographic symmetry, though the chiral cation has quasi-*2* symmetry. The complex crystallises in orthorhombic space group $P2_12_12_1$, so that the individual crystal is enantiomerically pure. The coordinated chloride ions are approached by water molecules, Cl(1)···O(01) 3.392(4); Cl(2)···O(05) 3.37(1) Å, the others by protonated amine groups and water molecules, Cl(3)···N(32), N(42) $(x-\frac{1}{2}, \frac{1}{2}-y, 1-z)$, O(01) $(x-\frac{1}{2}, \frac{1}{2}-y, 1-z)$, O(05) 3.076(4), 3.190(4), 3.274(4), 2.73(2) (O(05) being refined with site occupancy 0.5), Cl(4)···O(02) $(1\frac{1}{2}-x, \bar{y}, z-\frac{1}{2})$, O(03), O(4) $(\frac{1}{2}+x, \frac{1}{2}-y, 1-z)$ 3.063(4), 3.201(5), 3.075(5), Cl(5)···N(32), O(01) $(1\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$, O(03) $(x-\frac{1}{2}, \frac{1}{2}-y, 1-z)$, O(04) 3.134(4), 3.348(4), 3.371(5), 3.172(5) Å, with water–water contacts O(01)···O(04) $(1\frac{1}{2}-x, 1-y, z-\frac{1}{2})$ 3.102(6), O(02)···O(03) 2.681(6) Å, in an extended hydrogen-bonding array.

Table 5 The metal environment (distances in Å, angles in °) of $[Co(H_2L^9)Cl_2]Cl_3\cdot4.5H_2O$ **11**

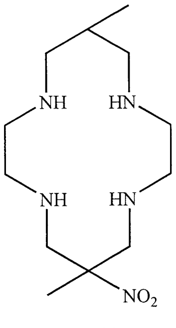
Atom	*r*	Cl(2)	N(12)	N(14)	N(22)	N(24)
Cl(1)	2.261(1)	176.64(6)	88.8(1)	89.8(1)	93.8(1)	87.9(1)
Cl(2)	2.249(2)		93.3(1)	87.7(1)	88.7(1)	90.1(1)
N(12)	1.986(4)			87.0(2)	91.8(2)	176.1(2)
N(14)	1.941(4)				176.1(2)	95.1(2)
N(22)	1.953(4)					86.3(2)
N(24)	1.947(4)					

3 Template formation of functionalised tetraazamacrocycles

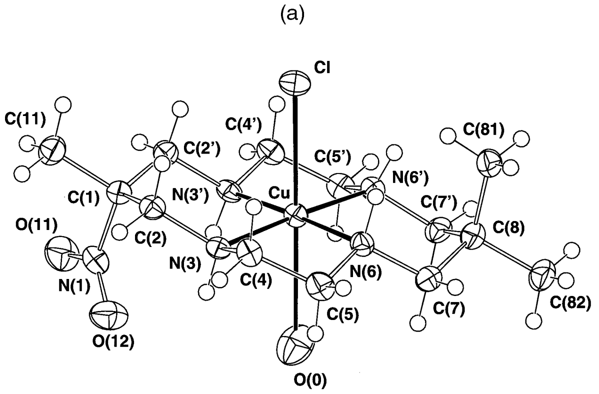
Reactions between metal complexes of linear polyamines, formaldehyde and nitroethane[12] are well established as highly stereoselective pathways to functionalised azamacrocycles[1b,13,30] and appear to work smoothly in the case of copper(II) complexes of $\mathbf{L}^1$ (**12**, **13**) and $\mathbf{L}^{1'}$ (**14**). Here, the product, $\mathbf{L}^{11}$, derived from $\mathbf{L}^{1'}$ appears to be a single diastereomer, with both methyl substituents equatorial in the tetrachlorocuprate of its copper(II) complex, **14**, the NO_2(axial)/CH_3(eq) configuration also being found for the single asymmetric carbon atom in both the chloride/hexafluorophosphate, **12**, and nitrate, **13**, of the copper(II) complex of the macrocycle, $\mathbf{L}^{10}$, derived from $\mathbf{L}^1$ (Fig. 10). The basic macrocycle in each of **12**–**14**, disposed about the Cu atom as $[(\mathbf{L}^{10,11})Cu]$, takes the same and familiar form usually seen in the bound parent macrocycle "cyclam",[31] of symmetry quasi *2*/*m*, in each of the three complexes, with similar geometrical and conformational parameters (Table 6). The species **12** and **13** differ only in the axial substituents on Cu, being Cl and H_2O in **12** and $2ONO_2$ in **13**; in the latter one half of the formula unit comprises the asymmetric unit of the structure as modelled in space group *C2*/*c*, the copper atom lying on a crystallographic inversion centre, entailing modelling of the nitro group as disordered over the two possible equivalent axial sites at either end of the symmetrical ligand framework. Significant differences are found in the environmental parameters of the metal relative to those of **9** and **10**, as might be expected contingent upon the change from five-coordination found with the open chain quadridentate ligands. In **12** the cations stack up the short axis *a*, with hydrogen bonds between the chloro and aqua ligands of successive molecules (Cl···O(0) (*x* − 1, *y*, *z*) 3.085(4) Å), a not uncommon occurrence with a recent parallel in a similar array.[32] The $[PF_6]^-$ anions and lattice water molecules lie in tunnels between the stacks.



L^{10}



L^{11}



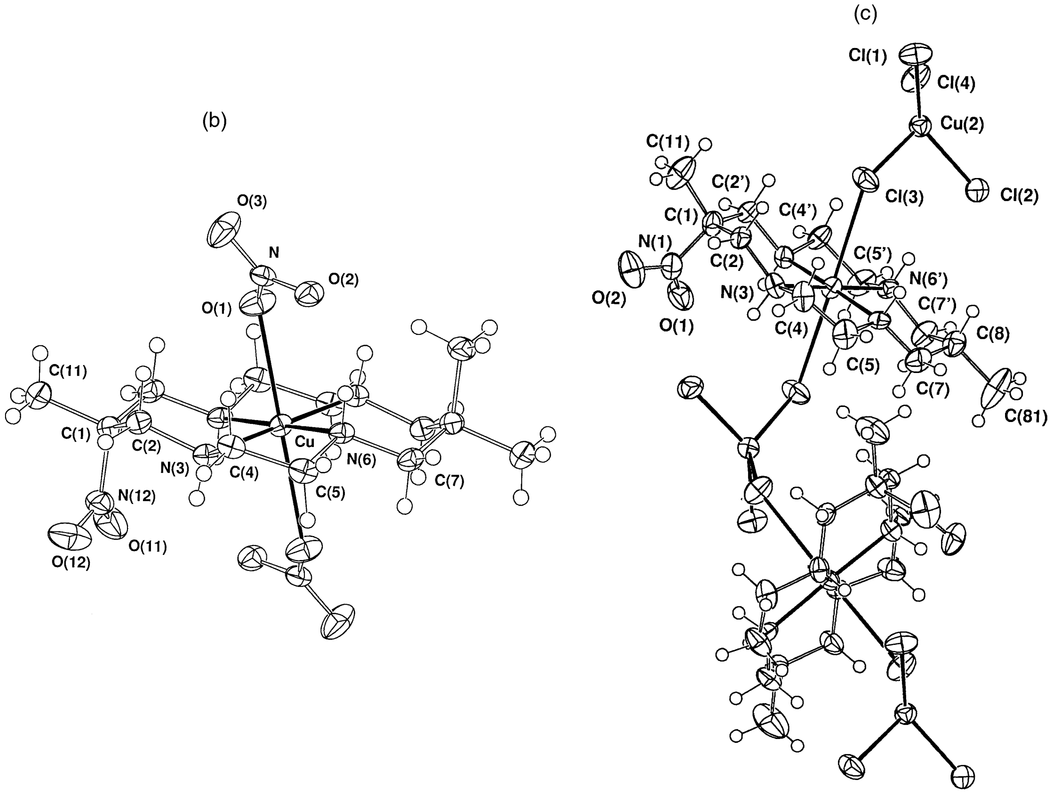


Fig. 10 Projections of: (a) The $[Cu(L^{10})Cl(OH_2)]^+$ cation of **12**; (b) the centrosymmetric $[Cu(L^{10})(ONO_2)_2]^+$ cation of **13** (the nitro group is scrambled with its inversion-related methyl counterpart; one isolated complex unit is shown) and (c) the asymmetric unit of complex **14** in its one-dimensional polymeric stack. A figure of the unit cell contents of **12**, projected down *a*, showing the stacking of cations up that axis, is deposited as ESI.

The precipitation of **14** as a tetrachlorocuprate species is somewhat puzzling in regard to the origin of the $[CuCl_4]^{2-}$ entity. This may mean that it is incorrect to consider the macrocycle formation reaction as occurring stereospecifically, and that another isomer is formed which does not strongly bind to Cu^{II}, ultimately releasing it to provide the counter anion in the isolated solid. The phenomenon has been observed before, however, in crystallisation of a closely similar compound[30b] after purification and may simply be a reflection of the low solubility of the isolated material and halide ion assisted removal of Cu^{II} from the macrocycle. Unlike this related species derived from a 13-membered ring macrocycle, which is dimeric, **14** is in fact polymeric, with the $[CuCl_4]^{2-}$ unit bridging $[(L^{11})Cu]^{2+}$ entities and forming chains similar to the perchlorate bridged entities found in **1**, **3** and many related species.[20,30] The geometry of the anion, as is not uncommon, is greatly distorted from the tetrahedral norm, subject to serious squashing down one of the tetrahedral $\bar{4}$ axes, and with two of the Cu–Cl distances slightly lengthened, presumably in consequence of their interactions with the cations.

Conclusion

Both the present observations and those already in the literature indicate that the formation of polyamines by reaction of polyalkylating agents with diamines reaches a critical point at the change from 1,2- to 1,3-diamines. All reactions of 1,3-diamines studied to date result in what might be considered the simplest outcome in that intermolecular reactions appear to be completely dominant and thus the products are exclusively open-chain species. It is interesting that this seems to be true even when it is possible to form rings of a size which appears to be favoured when formed in an inverse reaction involving a 1,2-diamine. Thus, the reactions of pentaerythritol derivatives with both ethane-1,2-diamine[5,8] and (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine result in significant or exclusive (in the latter case) formation of polyamines containing a seven-membered ring unit produced by intramolecular reaction, yet seven-membered ring-containing species have not been detected in the products of reaction of glycerol tris(benzenesulfonate) with propane-1,3-diamine. Clearly, purely statistical factors may have some influence here, as may differences in proton

Table 6 Selected geometries of structures **12**, **13** and **14**

(a) The metal environment (distances/Å; angles/°); in **12**, X, X′ are Cl, $O(H_2)$, in **13**, ONO_2 (× 2, symmetry related),[a] in **14** Cl(3), Cl(4), (x, 2 − y, $\frac{1}{2}$ − z)

Atom	r	N(6)	N(3′)	N(6′)	X	X′
N(3)	2.021(3)	86.1(1)	93.1(1)	176.2(1)	94.27(9)	84.5(1)
	2.020(2)	86.54(6)	93.46(6)	180(−)	90.98(6)	89.02(6)
	2.02(1)	86.5(4)	93.5(4)	179.2(5)	90.9(3)	89.0(3)
N(6)	2.019(3)		177.5(1)	94.5(1)	90.2(1)	89.2(1)
	2.008(2)		(180(−))	(93.46(6))	90.82(6)	89.18(6)
	2.02(1)		178.6(5)	93.6(4)	91.8(3)	89.7(3)
N(3′)	2.021(3)			86.1(1)	92.1(1)	88.4(1)
	(2.008(2))			(86.54(6))	(89.02(6))	(90.98(6))
	2.000(9)			86.5(3)	89.6(3)	88.8(3)
N(6′)	2.011(3)				89.5(1)	91.8(1)
	(2.020(2))				(89.18(6))	(90.82(6)
	1.996(9)				88.3(2)	91.8(2)
X	2.693(1)					178.70(9)
	2.532(1)					180(−)
	2.920(4)					178.4(2)
X′	2.622(4)					
	(2.532(1))					
	2.874(4)					

(b) Torsion angles; where there are two values in each entry, they are for the unprimed and primed segments

Atoms	Parameter	Atoms	Parameter
C(2′)–C(1)–C(2)–N(3)	−57.8(5), 63.1(5)	C(7′)–C(8)–C(7)–N(6)	−67.9(4), 66.9(5)
	−64.3(2)		−63.4(2)
	−59(1), 65(1)		−65(1), 65(1)
C(1)–C(2)–N(3)–C(4)	174.1(3), 177.2(3)	C(5)–N(6)–C(7)–C(8)	−178.9(3), −178.6(3)
	179.1(2)		179.3(2)
	178.1(1), −174(1)		−178(1), −173(1)
C(2)–N(3)–C(4)–C(5)	−172.9(3), 168.2(3)	C(4)–C(5)–N(6)–C(7)	−170.4(3), 173.1(3)
	−170.7(2)		−171.7(2)
	−166(1), 172(1)		−170(1), 174(1)
N(3)–C(4)–C(5)–N(6)	55.9(4), −55.8(4)		
	55.7(2)		
	50(1), −59(1)		
Cu–N(3)–C(2)–C(1)	51.1(4), −60.6(4)	Cu–N(6)–C(5)–C(4)	−39.4(4), 42.0(4)
	56.2(2)		−40.7(2)
	54(1), −53(1)		−36(1), 44(1)
Cu–N(3)–C(4)–C(5)	−43.3(4), 40.7(4)	Cu–N(6)–C(7)–C(8)	55.9(4), −53.5(4)
	−41.4(2)		54.7(2)
	−36(1), 44(1)		53(1), −57(1)

[a] For N(3′,6′), X′ read inversion related N(6,3), X. In **14**, for the $[CuCl_4]^{2-}$ anion: Cu(2)–Cl (1,2,3,4), 2.233(3), 2.250(3), 2.274(5), 2.267(5) Å; Cl(1)–Cu(2)–Cl(2,3,4) 140.7(1), 96.0(2), 96.4(1); Cl(2)–Cu(2)–Cl(3,4) 97.3(1), 98.2(2); Cl(3)–Cu(2)–Cl(4), 137.7(1)°. Cu(1)–Cl(3)–Cu(2) is 126.3(1); Cu(2)–Cl(4)–Cu(1) (x, 2 − y, z − $\frac{1}{2}$) is 125.6(1)°.

distributions over the nitrogen centres of reaction intermediates, which may themselves differ (aziridines *vs*. azetidines, for example), and very small energy differences between reaction pathways can, of course, give rise to seemingly dramatically different product distributions. Observations based solely on preparative procedures cannot, however, be attributed the weight that might be given to a full investigation of rates and rate laws for these reactions and have value only for a very restricted range of conditions.

The ligand syntheses investigated herein were intended to provide polyamines suitable for extended syntheses of new and functionalised macro(poly)cycles, as well as, in the case of species derived from (1*R*),(2*R*)-*trans*-cyclohexane-1,2-diamine, for use as chiral ligands in complexes potentially of value as asymmetric catalysts.[33] We will report our investigations of these and other prospects in later publications.

Acknowledgements

We gratefully acknowledge partial support of this work by the Australian Research Council and by grants (to Y. K.) from Kosin University. We thank Annegret Hall for magnetic measurements.

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