Polyamine Synthesis and Co-ordination: Structural Characterisation of Cobalt(III) Complexes from an Octadentate Ligand Preparation *

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The nature of the two principal products of the reaction between pentaerythritol [2,2-bis(hydroxymethyl)propane-1,3-diol] tetrabenzenesulfonate and ethane-1,2-diamine (en) has been confirmed by crystal-structure determinations on their cobalt(III) complexes, the less abundant species, 5,5-bis(4-amino-2-azabutyl)-3,7-diazanonane-1,9-diamine, L^1, being characterised in its bis(quadridentate) form in a green, tetrachloro, binuclear complex, and the more abundant 6,6-bis(4-amino-2-azabutyl)-1,4-diazacycloheptane, L^2, in a form where the ring nitrogen atoms are unco-ordinated, as a green, mononuclear *trans* dichlorotetramine complex. Compounds L^1 and L^2 have also been characterised in various forms produced when these dichloro complexes are treated with en. In green [*trans*-$Cl_2CoL^1CoCl_2$-*trans*]Cl_2·$4H_2O$ **1**, the binuclear cation has quasi-2 symmetry about the central carbon atom of the ligand which embraces the two cobalt atoms each bound equatorially by four N atoms; Co–Cl(*trans*) 2.234(8)–2.251(7) and Co–N 1.92(2)–1.99(2) Å. In one isomer of the mixed-ligand complexes of L^1 and en, structurally characterised both as the chloride [(en)CoL^1Co(en)]Cl_6· ≈ $7H_2O$ **2a**, and as the nitrate [(en)CoL^1Co(en)][NO_3]$_6$·$6H_2O$ **2b**, the cation also has approximate 2 symmetry, broken significantly only by differing conformations of the two en ligands in **2a**; Co–N 1.957(7)–1.986(4) Å. Another product of the reaction of **1** with en was the known mononuclear, orange complex [Co(H_2L^1)]Cl_5· ≈ $2.3H_2O$ **3**, where the ligand is disposed about the cobalt in a half cage, with the fourth diprotonated arm pendant from the cap; Co–N at the open end 1.97_7 Å (mean) nearer the cap 1.96_4 Å, the difference being significant. In green *trans*-[$CoCl_2$(H_2L^2)]Cl_3· ≈ $3.45H_2O$ **4**, the bicyclic ligand co-ordinates the cobalt equatorially through four N atoms; Co–Cl(*trans*) 2.259(1) and 2.263(1) Å, and Co–N (pairwise) 1.946(2), 1.948(3) Å for the 'inner' nitrogens and 1.960(2), 1.971(2) Å for the outer/terminal nitrogens. One of the immediate products of the reaction of en with **4** was [Co(en)(H_2L^2)]Cl_5· ≈ 0.6EtOH **5**. In this cation the cobalt is co-ordinated by the en and both arms of ligand L^2, the seven-membered ring nitrogen atoms being unco-ordinated and protonated after isolation from acidic solution; Co–N 1.95(1)–1.986(5) Å. One of the products of more extended reaction between en and **4** was red [Co(en)(H_2L^2)]Cl_5·$3H_2O$ **6**, in which the ligand is diprotonated on the two nitrogen atoms of one of the 'arms'; it co-ordinates through both nitrogen atoms of the seven-membered ring, *cis* in the co-ordination sphere [Co–N 1.986(4) and 2.012(4) Å], the two nitrogen atoms of the other ligand arm occupying a further *cis* pair of sites [Co–N 1.966(4) and 1.972(4) Å], with the *cis* pair of Co–N(en) distances being 1.975(4) and 1.981(4) Å.

Polyamine synthesis by reaction of a simple amine with a polyfunctional alkylating agent is a commonly adopted procedure, despite the problems associated with the formation of product mixtures which are difficult to separate and purify by methods such as distillation.[1] Formation of metal complexes is often a successful and mild method for separation,[1–4] and in the case of the octamine L^1 (Scheme 1) has been used to obtain the pure ligand from the product mixture in a single-step process[3] as well as to characterise at least two polyamines in addition to L^1 in their pure forms.[4] As part of a project concerned with the formation of polymers incorporating polyamines as metal binding sites, we have been interested in the properties of complexes of L^1 and other polyamines which may be coproducts of its synthesis. By treating the ligand product mixture from the conventional synthesis with an excess of Co^{II} under oxidising conditions, we obtained, as previously observed by others,[3,5] two green dichlorocobalt(III) complexes which have now been shown by crystal structure determinations to be particular isomers of the complexes of L^1 and L^2.

Polyamine synthesis is also commonly conducted within the co-ordination sphere of a metal by means of 'template reactions',[6] and the complexes of L^1 and L^2 are of further interest as precursors to mixed-amine complexes which may be subjected to, for example, reactions of the type used in 'cage' amine syntheses[7] in order to provide functionalised macrocycles.[8] We report in addition, therefore, the structures of four complexes obtained by reactions of the *trans*-dichlorocobalt(III) complexes of L^1 and L^2 with ethane-1,2-diamine.

Experimental

Instrumentation.—Electronic spectra were measured with a Hewlett-Packard 8452A diode-array spectrophotometer, ^1H and ^{13}C NMR spectra on a Bruker AM300 spectrometer. The

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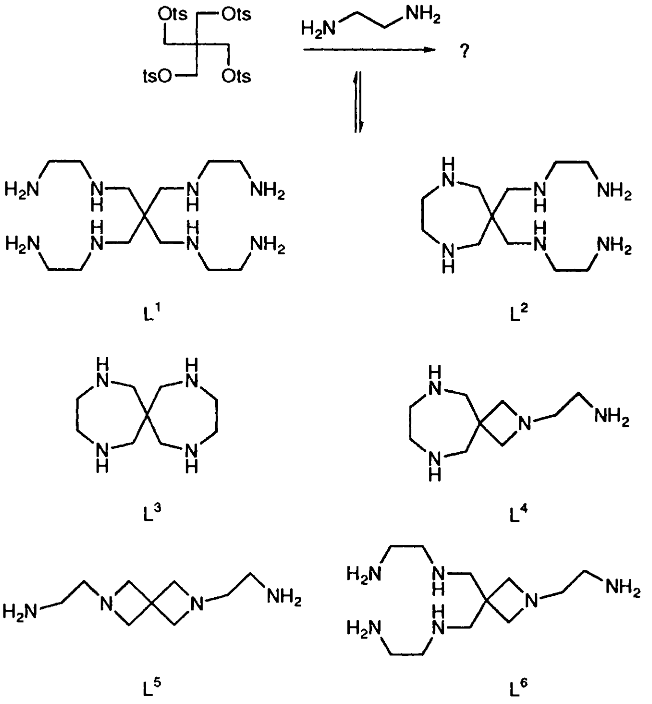
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 Possible products of the reaction of one molecule of pentaerythritol tetrabenzenesulfonate with ethane-1,2-diamine. ts = p-$MeC_6H_4SO_2$

carbon-13 resonances were identified using distortionless enchancements of polarisation transfer (DEPT) editing. Microanalyses were performed using a LECO CHN932 instrument at the Chemistry Centre of Western Australia.

Synthesis.—Dichlorotetraminecobalt(III) *species*. The tetrabenzenesulfonate of pentaerythritol [2,2-bis(hydroxymethyl)-propane-1,3-diol] was treated with ethane-1,2-diamine under established conditions[1] to provide a viscous oil of mixed polyamines. This crude mixture (32.4 g) was dissolved in methanol (200 cm^3) and partly neutralised by the addition of concentrated HCl (10 cm^3). It was then mixed with a solution of $CoBr_2{\cdot}6H_2O$ (70 g) in methanol (500 cm^3) and aerated for 3 h under ambient conditions. Concentrated HCl (300 cm^3) was added and this final mixture evaporated by heating on a steam-bath until a crust of green crystals began to form. The mixture was cooled to room temperature and the precipitate filtered off. This green solid was dissolved in dilute HCl (0.5 mol dm^{-3}, 1 l) and the solution passed onto a column of Dowex 50WX2 cation-exchange resin (H$^+$ form, 50 × 7 cm). The column was washed with 0.1 mol dm^{-3} HCl (1 l) to remove the fast-moving pink cobalt(II) species, then eluted with 2 mol dm^{-3} HCl to separate four bands. After the first two, green bands had been removed, the concentration of HCl eluent was increased to 3 mol dm^{-3} to remove more rapidly two trailing yellow bands. These yellow materials constituted approximately 3% of the total yield and appeared to be complicated mixtures which we have not further characterised. Their NMR spectra were consistent with the possibility that they resulted from the reaction of more than 1 mol of the benzenesulfonate with ethanediamine.

The eluates from the green bands were evaporated to dryness under vacuum to give green residues which were washed with acetone and dried in vacuum. Yields: band 1 (faster eluting), complex **1**, 7.5 g; band 2, complex **4**, 20.7 g. Both complexes were recrystallised from the minimum volume of 1 mol dm^{-3} HCl by the addition of acetone. Crystals suitable for X-ray diffraction measurements were grown by slow evaporation of HCl solutions of the complexes. Complex **1** (Found: C, 22.6; H, 6.1; Cl, 28.2, N, 15.8. $C_{13}H_{36}Cl_6Co_2N_8{\cdot}4H_2O$ requires C, 22.10; H, 6.25; Cl, 30.10; N, 15.85%): visible spectrum in 1 mol dm^{-3} HCl (λ_{max}/nm, log ε_{max}) 622, 1.85; ^{1}H NMR in dilute D_2SO_4, δ 2.50 (br, 2 H, CH_2), 3.05 (sh), 2.8 (br, 20 H, CH_2), 5.43 (br, 4 H, NH_2), 5.58 (br, 4 H, NH_2), 6.30 (br, 2 H, NH), and 6.69 (br, 2 H, NH); ^{13}C NMR in dilute D_2SO_4, δ 42.80, 50.75, 54.69, 55.57, 55.71 (all CH_2), 45.37 (quaternary C). Complex **4** (Found: C, 25.0; H, 6.3; Cl, 31.3; N, 15.9. $C_{11}H_{28}Cl_3CoN_6{\cdot}2HCl{\cdot}3.5H_2O$ requires C, 24.20; H, 6.85; Cl, 32.50; N, 15.40%): visible spectrum in 1 mol dm^{-3} HCl (λ_{max}/nm, log ε_{max}) 620, 1.57; ^{1}H NMR in dilute D_2SO_4, δ 2.81, 2.85, 2.9–3.1 (m, 12 H, CH_2 of ligand arms), 3.54, 3.74, 3.78 (m, 8 H, CH_2 of pendant seven-membered ring), 5.43, 5.56, 6.34 (br, 6 H, NH on co-ordinated nitrogen); ^{13}C NMR in dilute D_2SO_4, δ 42.63, 45.14, 45.32, 48.80, 52.13, 52.97, 55.46 (all CH_2), 42.13 (quaternary C).

Hexaminecobalt(III) *species*. (*a*) *From the binuclear cobalt*(III) *reactant*. Ethane-1,2-diamine (0.15 g) was added to a solution of complex **1** (0.71 g) in methanol (50 cm^3) and the mixture heated at reflux for 10 min. The colour changed rapidly from green through purple to red and some yellow precipitate formed during the period at reflux. The final mixture was acidified with concentrated HCl and evaporated to dryness under vacuum. The yellow residue was dissolved in water and absorbed on a column of SP Sephadex C25 resin (Na$^+$ form). Elution with phosphate buffer (pH 7, [Na$^+$] = 0.3 mol dm^{-3}) removed first a trace of purplish material in two bands (F1, which was discarded), followed by a readily removed yellow species (F2) shown from its ^{1}H and ^{13}C NMR spectra to be $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine), and then three yellow-orange complexes (F3, F4, F5) in well separated bands. A minor yellow-orange band (F6) remained virtually unmoved by this treatment but was subsequently eluted with 2 mol dm^{-3} NaCl. The effluents for these last four complexes were absorbed on Dowex 50WX2 resin (H$^+$ form) and the separate complexes recovered by elution with 3 mol dm^{-3} HCl and evaporation of the eluates to dryness under vacuum. Species F3 was ultimately shown (in fact, by its crystal structure determination as compound **3**) to be the known[3] complex $[CoL^1]Cl_3{\cdot}2HCl{\cdot}2H_2O$; F4 proved to be identical with a component which was actually first obtained as the apparent major species by fractional crystallisation of the crude product mixture. The ^{13}C NMR spectra provided the most convenient way of distinguishing the various products (^{1}H spectra showed exceedingly complicated patterns of overlapping multiplets), and were the basis for identifying F4 with the earlier-isolated material (and probably with F6, see Discussion). In the search for crystals suitable for crystallographic studies, all components were initially crystallised as chlorides by vapour diffusion of ethanol into their solutions in dilute HCl. Thus, F3 provided compound **3** and F4 compound **2a** (Found: C, 23.0; H, 9.0; N, 19.1. $C_{17}H_{52}Cl_6Co_2N_{12}{\cdot}7H_2O$ requires C, 23.15; H, 7.55; N, 19.05%). A portion of F4 was also recrystallised twice by vapour diffusion of ethanol into its solution in dilute HNO_3, thereby providing compound **2b** (Found: C, 19.8; H, 5.9; N, 24.7. $C_{17}H_{52}Co_2N_{18}O_{18}{\cdot}6H_2O$ requires C, 19.95; H, 6.30; N, 24.65%). Crystallisation of F5 from EtOH–HCl gave a voluminous precipitate which appeared to occlude solvent, though it was still readily collected by filtration (Found: C, 22.7; H, 7.7; N, 18.9. $C_{17}H_{52}Cl_6Co_2N_{12}{\cdot}8H_2O$ requires C, 22.70; H, 7.60; N, 18.70%).

(*b*) *From the mononuclear cobalt*(III) *reactant*. Ethane-1,2-diamine (1.32 g) was added to a suspension of complex **4** (5.46 g) in methanol (100 cm^3), and the mixture heated at reflux for 15 min. (The initially insoluble **4** dissolved readily once it had been deprotonated by the added ethane-1,2-diamine.) After cooling, the orange solution, containing some yellow precipitate, was acidified by the addition of concentrated HCl (5 cm^3) and evaporated to dryness under vacuum. The yellow residue was subjected to chromatography on SP Sephadex as described in preparation (*a*). Here, a trace of yellow material (seemingly purely organic) was eluted first and was closely followed by two very minor purple bands [seemingly bis(ethane-1,2-diamine)cobalt(III) complexes]; all three of these rapidly eluted species were discarded. A minor yellow band (F4) of $[Co(en)_3]^{3+}$ was eluted next, just ahead of a major orange band (F5) followed by another three minor yellow-orange bands (F6, F7, F8). In an earlier experiment involving a longer period of heating at reflux (60 min) for the initial reaction, the product mixture was subjected to chromatography on SP Sephadex with 0.2 mol dm^{-3} K_2SO_4 as eluent and a band of red material (F9) was observed as a minor product trailing a major band which proved to be a mixture of yellow-orange species, subsequently separated as above. After recovery *via* Dowex 50WX2 as chloride salts, the various complexes were crystallised from water by vapour diffusion of ethanol into the solutions. The first (major) orange band (F5) from the phosphate eluent chromatography was thus the source of complex **5** and the minor red band (F9) from the sulfate elution the source of complex **6**. (Found for F5: C, 26.2; H, 8.9; N, 19.1. $C_{13}H_{36}Cl_3CoN_8{\cdot}2HCl{\cdot}3H_2O$ requires C, 26.15; H, 7.45; N, 18.80. Found for F6: C, 26.5; H, 7.3; N, 19.2. $C_{13}H_{36}Cl_3CoN_8{\cdot}2HCl{\cdot}2H_2O$ requires C, 27.00; H, 7.30; N, 19.35. Found for F7: C, 26.5; H, 9.9; N, 18.8. $C_{13}H_{36}Cl_3CoN_8{\cdot}2HCl{\cdot}3H_2O$ requires C, 26.15; H, 7.45; N, 18.80. Found for F8: C, 27.2; H, 7.4; N, 19.1. $C_{13}H_{36}Cl_3CoN_8{\cdot}2HCl{\cdot}2H_2O$ requires C, 27.00; H, 7.30; N, 19.35. Found for F9 (**6**): C, 24.0; H, 9.1; N, 17.9. $C_{13}H_{36}Cl_3CoN_8{\cdot}2HCl{\cdot}5H_2O$ requires C, 24.70; H, 7.65; N, 17.70%). Note that, for some reason which is presently not understood, hydrogen analyses on these compounds were erratic and typically high. Crystals of **5** and **6** suitable for crystallographic measurements were grown by vapour diffusion of ethanol into their solutions in dilute HCl.

Structure Determinations.—Unique room-temperature diffractometer data sets ($T \approx 295$ K, 2θ–θ scan mode, monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) measured on capillary-mounted specimens yielded N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms (but see below); where feasible, $(x, y, z, U_{iso})_H$ were constrained at estimated values. Difference-map artefacts assigned as water molecule oxygen atoms were constrained at unit site occupancy after initial refinement of that parameter (but see below). Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being assigned. Neutral atom complex scattering factors were employed, computation using the XTAL 3.2 program system[9] implemented by S. R. Hall. Pertinent results are given in the Figures and Tables.

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

Crystal/refinement data. Complex **1**, $[trans\text{-}Cl_2CoL^1CoCl_2\text{-}trans]Cl_2{\cdot}4H_2O$, $C_{13}H_{36}Cl_6Co_2N_8{\cdot}4H_2O$, $M = 707.1$, monoclinic, space group $P2_1$ (C_2^2, no. 4), $a = 15.523(5)$, $b = 14.030(4)$, $c = 6.502(5)$ Å, $\beta = 100.96(5)°$, $U = 1390$ Å^3, D_c ($Z = 2$) = 1.69 g cm^{-3}, $F(000) = 732$, $\mu_{Mo} = 18.1$ cm^{-1}, specimen 0.06 × 0.08 × 0.31 mm, $A^*_{min,max} = 1.10, 1.17$, $2\theta_{max} = 50°$, $N = 2554$, $N_o = 1744$, $R = 0.082$, $R' = 0.096$ (alternative chirality: 0.083, 0.097).

Abnormal features/variations in procedure. A small, weakly diffracting, badly formed specimen yielded a weak data set only capable of supporting a refinement of less-than-optimum precision. Anisotropic thermal parameters were refined for Co, Cl only; water molecule hydrogen atoms were not located.

Complex **2a**, $[(en)CoL^1Co(en)]Cl_6{\cdot} \approx 7H_2O$, $C_{17}H_{52}Cl_6Co_2N_{12}{\cdot} \approx 7H_2O$, $M \approx 881.4$, orthorhombic, space group $Pbcn$ (D_{2h}^{14}, no. 60), $a = 19.13(2)$, $b = 15.211(8)$, $c = 25.535(5)$ Å, $U = 7431$ Å^3, D_c ($Z = 8$) = 1.58 g cm^{-3}, $F(000) \approx 3712$, $\mu_{Mo} = 13.8$ cm^{-1}, specimen 0.24 × 0.18 × 0.38 mm, $A^*_{min,max} = 1.24, 1.28$, $2\theta_{max} = 50°$, $N = 6535$, $N_o = 3261$, $R = 0.054$, $R' = 0.053$.

The complex cations are interspersed with sheets of diffuse and disorganised residues, presumed to comprise chloride ions and water molecules of crystallisation. Five of the six chloride ions were confidently assigned and refined with populations indicative of full site occupancy. Refinement of the remaining components and their site occupancies suggested the tentative assignment of residues Cl(6), Cl(6′) as chloride ions of half weight at which value their population was constrained. Other residues O(1)–O(4) were assigned as fully weighted water molecule oxygen atoms, no associated hydrogen atoms being assigned, while O(5)–O(12) were ultimately assigned as half-weighted water molecule oxygen atoms. Ligand hydrogen atoms were included constrained in (x, y, z, U_{iso}). Atom C(1) of the ligand (disordered) was modelled as a pair of half-weighted components with isotropic thermal parameters.

Complex **2b**, $[(en)CoL^1Co(en)][NO_3]_6{\cdot}6H_2O$, $C_{17}H_{64}Co_2N_{18}O_{24}$, $M = 1022.7$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 14.985(5)$, $b = 16.210(3)$, $c = 16.811(2)$ Å, $\beta = 98.46(2)°$, $U = 4039$ Å^3, D_c ($Z = 4$) = 1.68 g cm^{-3}, $F(000) = 2512$, $\mu_{Mo} = 9.3$ cm^{-1}, specimen 0.07 × 0.23 × 0.23 mm, $A^*_{min,max} = 1.07, 1.23$, $2\theta_{max} = 55°$, $N = 8099$, $N_o = 4396$, $R = 0.049$, $R' = 0.049$.

Hydrogen atoms were located in difference maps for all water molecule oxygens except O(5), O(6), for which thermal motion was high; site occupancies for all artefacts modelled as water molecule oxygens were constrained at unity after trial refinement.

Complex **3**, $[Co(H_2L^1)]Cl_5{\cdot} \approx 2.3H_2O$, $C_{13}H_{38}Cl_5Co_2N_8{\cdot} \approx 2.3H_2O$, $M \approx 583.2$, monoclinic, space group $P2_1/c$, $a = 18.119(3)$, $b = 11.434(6)$, $c = 12.73(1)$ Å, $\beta = 104.24(4)°$, $U = 2555$ Å^3, D_c ($Z = 4$) ≈ 1.52 g cm^{-3}, $F(000) \approx 1022$, μ_{Mo} 12.2 cm^{-1}, specimen 0.48 × 0.32 × 0.38 mm, $A^*_{min,max} = 1.31, 1.83$, $2\theta_{max} = 50°$, $N = 4483$, $N_o = 3929$, $R = 0.031$, $R' = 0.039$.

The values of $(x, y, z, U_{iso})_H$ were refined except in association with O(03), for which they were not located; site occupancy of O(03) refined to 0.302(9).

Complex **4**, $trans\text{-}[CoCl_2(H_2L^2)]Cl_3{\cdot} \approx 3.45H_2O$, $C_{11}H_{30}Cl_5CoN_6{\cdot} \approx 3.45H_2O$, $M \approx 544.8$, triclinic, space group $P\bar{1}$, (no. 2), $a = 15.377(6)$, $b = 9.735(2)$, $c = 8.066(6)$ Å, $\alpha = 100.70(3)$, $\beta = 99.67(4)$, $\gamma = 98.40(2)°$, $U = 1150$ Å^3, D_c ($Z = 2$) = 1.57 g cm^{-3}, $F(000) \approx 569$, $\mu_{Mo} = 13.5$ cm^{-1}, specimen 0.57 × 0.14 × 0.43 mm, $A^*_{min,max} = 1.17, 1.59$, $2\theta_{max} = 60°$, $N = 6700$, $N_o = 5205$, $R = 0.039$, $R' = 0.044$.

The site occupancy of 'water molecule' O(4) refined to 0.45(1); hydrogen atoms were not located. All other hydrogen atoms in the structure were located and refined in (x, y, z, U_{iso}).

Complex **5**,* $[Co(en)(H_2L^2)]Cl_5{\cdot} \approx 0.6EtOH$, $C_{13}H_{38}Cl_5CoN_8{\cdot} \approx 0.6EtOH$, $M \approx 570.3$, monoclinic, space group $P2_1/c$, $a = 12.111(6)$, $b = 15.33(1)$, $c = 15.21(1)$ Å, $\beta = 118.67(5)°$, $U = 2478$ Å^3, D_c ($Z = 4$) = 1.53 g cm^{-3}; $F(000) \approx 1198.4$, $\mu_{Mo} = 12.5$ cm^{-1}, specimen 0.27 × 0.22 × 0.43 mm, $A^*_{min,max} = 1.25, 1.31$, $2\theta_{max} = 50°$, $N = 4118$, $N_o = 2985$, $R = 0.057$, $R' = 0.064$.

All hydrogen atoms except those associated with the solvent were located in difference maps and refined in (x, y, z, U_{iso}).

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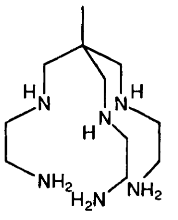
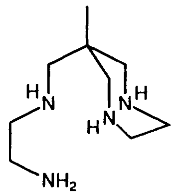
* *Note added at proof:* Since the submission of this paper the isomorphous compound $[Co(en)(H_2L^2)]Cl_3[NO_3]_2{\cdot}H_2O$ has been crystallized from aqueous nitrate solution and its structure determined with superior precision [$C_{13}H_{40}Cl_4CoN_9O_4$, $M = 587.3$, $a = 11.945(2)$, $b = 15.231(3)$, $c = 15.444(4)$ Å, $\beta = 119.0(5)°$, $U = 2456$ Å^3, $D_c = 1.59$ g cm^{-3} $F(000) = 1232$, $\mu_{Mo} = 11.7$ cm^{-1}, specimen 0.11 × 0.34 × 0.11 mm, $A^*_{min,max} = 1.23, 1.32$, $2\theta_{max} = 50°$, $N = 4295$, $N_o = 3256$, $R = 0.041$, $R' = 0.050$]. Hydrogen atoms constrained in estimated (x, y, z, U_{iso}). Core geometries exhibit a number of significant albeit minor differences *vis-à-vis* complex **5**. Full details are deposited at the Cambridge Crystallographic Data Centre.



L^7



L^8

Difference-map artefacts were modelled as an ethanol molecule of solvent, population refining to 0.62(1).

Complex **6**, $[Co(en)(H_2L^2)]Cl_5{\cdot}3H_2O$, $C_{13}H_{38}Cl_5CoN_8{\cdot}3H_2O$, $M = 596.8$, triclinic, space group $P\bar{1}$, $a = 13.608(6)$, $b = 12.426(3)$, $c = 8.979(2)$ Å, $\alpha = 105.19(2)$, $\beta = 99.28(3)$, $\gamma = 111.56(2)°$, $U = 1306$ Å^3, D_c $(Z = 2) = 1.52$ g cm^{-3}, $F(000) = 628$, $\mu_{Mo} = 12.0$ cm^{-1}, specimen $0.23 \times 0.08 \times 0.43$ mm, $A^*_{min,max} = 1.10, 1.26$, $2\theta_{max} = 50°$, $N = 4590$, $N_o = 3420$, $R = 0.040$, $R' = 0.043$.

All hydrogen atoms were located in difference maps, those associated with the cation being refined in (x, y, z, U_{iso}), and the remainder constrained. Difference-map artefacts were assigned as water molecule oxygen atoms; their populations when refined did not deviate significantly from unity and they were set to that value. Atom Cl(5) was modelled as disordered over two sites, populations refining to $x = 0.86(1)$ and $1 - x$.

Table 1 Carbon-13 NMR data for complexes derived by reactions of **1** and **4** with ethane-1,2-diamine. All resonances correspond to methylene carbons other than those marked * which correspond to the quaternary carbon. Solvent: 0.1 mol dm^{-3} DCl

Complexes derived from binuclear **1**	δ
F3 = **3**	57.13, 57.02, 51.21, 51.10, 50.96, 46.52, 44.78*, 43.11, 35.55
F4 = **2**	55.92, 54.90, 54.62, 52.36, 45.03, 44.83, 43.63*, 43.58
F5	56.87, 56.38, 56.02, 55.92, 55.84, 55.69, 55.08, 54.91, 54.74, 54.63, 54.47, 54.07, 52.94, 52.61, 52.40, 52.05, 51.16, 50.94, 50.26, 49.52, 46.49, 46.11, 45.06, 44.70, 44.50, 44.30, 44.23, 43.62, 43.48, 43.33, 43.08, 42.82, 42.02*, 41.53
F6	55.87, 54.86, 54.59, 52.37, 44.85, 44.67, 44.57, 43.59* 43.44, 43.33
Complexes derived from mononuclear **4**[a]	
F5 = **5**	55.99, 54.03, 53.12, 52.92, 52.77, 52.03, 45.39, 45.12, 44.89, 44.77, 43.42, 43.37, 41.02*
F6	63.37, 60.78, 56.92, 55.84, 54.00, 53.27, 53.11, 52.78, 52.13, 52.01, 50.92, 46.47, 45.38, 44.90, 44.61, 44.51, 43.51, 43.24, 43.06, 42.95, 40.9*, 36.03*, 35.49, 34.20
F7[b]	56.84, 55.87, 54.87, 54.59, 52.82, 52.38, 51.12, 46.45, 44.86, 44.56, 43.33, 42.94
F8	56.87, 55.88, 54.85, 54.60, 54.00, 53.10, 52.76, 52.34, 52.00, 51.12, 49.50, 46.46, 45.36, 44.86, 44.57, 43.45, 43.32, 40.96*, 35.47
F9 = **6**	59.63, 55.98, 55.65, 55.55, 54.19, 51.83, 50.90, 49.95, 46.46, 45.60, 44.95, 44.83, 43.71, 40.14*, 39.60*, 36.07, 35.47

[a] The chemical shifts in the spectra of these complexes are dependent upon the acid concentration and 0.1 mol l^{-1} DCl was a completely arbitrary choice for a common solvent. [b] For all preparations of this complex the spectra of the total chromatographic residue showed weak resonances attributable to contamination with traces of F6.

Discussion

Ligand Synthesis and Separation.—Reaction of excess of ethane-1,2-diamine with the tetrabenzenesulfonate (or similar derivative, such as the bromide) of pentaerythritol can in principle give rise to six products (Scheme 1) incorporating one pentaerythritol moiety. In the case of the related reaction between ethane-1,2-diamine and the tritosylate[1] or tribromide[10,11] of 1,1,1-tris(hydroxymethyl)ethane, it is known from a crystal structure determination[12] that the desired open-chain sexidentate ligand L^7 is accompanied in the product by the cyclic quadridentate amine L^8. Thus, seven-membered ring formation in a reaction intermediate is obviously competitive with further intermolecular reaction with ethane-1,2-diamine. We have also observed[13] that when mild reaction conditions (temperatures below 100 °C) are used in the reaction between ethane-1,2-diamine and the tosylate of a long-chain analogue of $CH_3C(CH_2OH)_3$ the product reaction mixture contains an amine which forms a green *trans*-$[CoN_4Cl_2]^+$ species and which may therefore be an analogue of L^4 and contain a four-membered ring. Such azetidine species may undergo reaction with ethane-1,2-diamine under more forcing conditions[14] and hence may not appear in reaction mixtures produced under 'standard' conditions. Thus, the number of compounds possibly present in pentaerythritol reaction products may be as small as three (L^1, L^2 and L^3). In any case, the ligand found to be present in the structurally characterised complexes **4**–**6** described herein and constituting the major reaction product is the species L^2, containing a seven-membered ring as seen in the L^7 side-product. This material has been previously detected and isolated[3,4] but not structurally characterised. The other significant product, presently characterised in complexes **1**–**3**, is L^1. The relative amounts of L^1 and L^2 found in the present work are quite different to those observed by others[4] (though together they represent the overwhelming bulk of the product in all instances, only a product derived from reaction of two pentaerythritol moieties having previously been observed[4] to accompany L^1 and L^2 in significant amounts), and this is perhaps indicative that the cyclic species L^2 may also undergo a ring-opening reaction with ethane-1,2-diamine to give L^1. Alternatively, if the activation energies for intra- and intermolecular tosylate displacement by ethanediamine nitrogen are significantly different, it may be that we have inadvertently failed to duplicate the reaction-temperature control used by others.

Complex-ion Formation and Isomerism.—The ligands L^1 and L^2 would be expected to be far superior complexing agents to L^3,[15] an expectation which is consistent with the isolation presently of just the complexes of these compounds in significant yields from the preparative mixture. The isomeric forms of these complexes are, however, not so readily predicted, especially since the simple 'parent' compound 3,7-diazanonane-1,9-diamine (L^9) is known to form cobalt(III) complexes differing with respect to both the configuration around cobalt and about the secondary nitrogen donor atoms.[15–17] There is a precedent for bimetallic complexes of L^1 [in its essentially bis(square-planar) form] in that all known structures[18,19] have revealed a form centrosymmetric with respect to at least the polyamine ligand, *i.e.* with a ligand conformation in each half corresponding to the achiral R^*,S^* (and presumably δ-chair-λ)[20] form found in the *trans*-dichlorocobalt(III) complex of 3,7-diazanonane-1,9-diamine, but in general few guidelines exist to predict reliably the isomers which might be expected to predominate in the present systems. Spectroscopic methods are frequently particularly useful in the characterisation of cobalt(III) stereoisomerism[15] but although ^1H and ^{13}C NMR spectra for the isolated dichloro complexes **1** and **4**, for example, indicate that they have relatively high symmetry, they are not fully definitive of the structures, even given that the green colours indicate that there is a *trans*-

Table 2 Cobalt atom environments: *r* is the cobalt–ligand atom distance (Å); other entries are the angles (°) subtended at the metal by the relevant ligand atoms at the head of the row and column

(*a*) $[\textit{trans}\text{-Cl}_2\text{CoL}^1\text{CoCl}_2\text{-}\textit{trans}]^{2+}$ **1**[a]

(*i*)

Co(1)	*r*	Cl(2)	N(12)	N(15)	N(22)	N(25)
Cl(1)	2.251(7)	179.2(3)	90.0(5)	90.9(6)	86.6(6)	89.5(6)
Cl(2)	2.243(7)		90.8(5)	88.9(6)	93.6(6)	89.8(6)
N(12)	1.98(2)			88.7(7)	93.7(7)	178.9(8)
N(15)	1.97(2)				176.5(7)	92.2(8)
N(22)	1.94(2)					85.4(8)
N(25)	1.92(2)					

(*ii*)

Co(1′)	*r*	Cl(2′)	N(12′)	N(15′)	N(22′)	N(25′)
Cl(1′)	2.240(7)	178.5(3)	89.8(5)	89.7(7)	88.2(6)	89.6(6)
Cl(2′)	2.234(8)		91.3(5)	89.3(7)	92.8(6)	89.3(6)
N(12′)	1.97(2)			87.4(8)	94.2(8)	178.5(8)
N(15′)	1.92(2)				177.4(8)	91.2(8)
N(22′)	1.99(2)					87.2(8)
N(25′)	1.94(2)					

(*b*) $[(\text{en})\text{CoL}^1\text{Co}(\text{en})]^{6+}$ **2a** and **2b**[b]

(*i*) **2a** (the chloride)

Co(1)	*r*	N(15)	N(22)	N(25)	N(1)	N(2)
N(12)	1.972(5)	86.2(2)	88.3(2)	94.1(2)	175.8(3)	93.6(2)
N(15)	1.957(7)		172.0(3)	89.5(3)	90.9(3)	90.8(3)
N(22)	1.974(6)			85.2(3)	94.9(3)	95.2(3)
N(25)	1.968(7)				88.8(2)	172.3(2)
N(1)	1.976(6)					83.5(2)
N(2)	1.972(6)					

Co(1′)	*r*	N(15′)	N(22′)	N(25′)	N(1′)	N(2′)
N(12′)	1.973(5)	86.2(2)	90.1(2)	94.8(2)	174.4(3)	92.4(2)
N(15′)	1.970(6)		173.6(3)	89.6(3)	89.7(2)	91.5(3)
N(22′)	1.979(6)			85.5(3)	94.3(3)	93.8(3)
N(25′)	1.962(7)				89.0(3)	172.7(2)
N(1′)	1.969(6)					83.8(3)
N(2′)	1.960(6)					

(*ii*) **2b** (the nitrate)

Co(1)	*r*	N(15)	N(22)	N(25)	N(1)	N(2)
N(12)	1.971(4)	85.9(2)	88.6(2)	94.6(2)	176.0(2)	93.3(2)
N(15)	1.963(5)		172.0(3)	89.6(2)	91.3(2)	91.1(2)
N(22)	1.979(4)			85.1(2)	94.5(2)	95.0(8)
N(25)	1.961(4)				88.2(2)	172.1(2)
N(1)	1.975(4)					84.0(2)
N(2)	1.984(4)					

Co(1′)	*r*	N(15′)	N(22′)	N(25′)	N(1′)	N(2′)
N(12′)	1.986(4)	86.5(2)	89.4(2)	94.5(2)	176.2(2)	92.8(2)
N(15′)	1.967(5)		172.8(2)	89.1(2)	91.9(2)	92.1(3)
N(22′)	1.963(4)			85.4(2)	92.6(2)	94.0(2)
N(25′)	1.967(4)				88.8(2)	172.6(2)
N(1′)	1.973(4)					83.9(2)
N(2′)	1.966(4)					

(*c*) $[\text{Co}(\text{H}_2\text{L}^1)]^{5+}$ **3**

	r	N(15)	N(22)	N(25)	N(32)	N(35)
N(12)	1.964(2)	85.6(1)	91.1(1)	92.8(1)	90.6(1)	175.5(1)
N(15)	1.978(2)		175.4(1)	90.9(1)	93.4(1)	91.3(1)
N(22)	1.966(3)			86.0(1)	89.8(1)	92.2(1)
N(25)	1.978(2)				174.7(1)	90.6(1)
N(32)	1.962(2)					86.3(1)
N(35)	1.975(2)					

(*d*) $\textit{trans}\text{-}[\text{CoCl}_2(\text{H}_2\text{L}^2)]^{3+}$ **4**

	r	Cl(2)	N(12)	N(15)	N(22)	N(25)
Cl(1)	2.263(1)	178.60(4)	89.77(6)	90.33(8)	89.54(7)	89.33(7)
Cl(2)	2.259(1)		90.98(6)	88.55(8)	91.57(7)	89.89(7)
N(12)	1.960(2)			85.9(1)	95.09(9)	178.3(1)
N(15)	1.948(3)				179.0(1)	92.8(1)
N(22)	1.971(2)					86.3(1)
N(25)	1.946(2)					

(*e*) $[\text{Co}(\text{en})(\text{H}_2\text{L}^2)]^{5+}$ **5**

	r	N(15)	N(22)	N(25)	N(1)	N(2)
N(12)	1.959(7)	85.8(3)	89.6(3)	92.9(3)	176.0(2)	94.0(3)
N(15)	1.980(6)		173.5(3)	90.6(3)	90.6(3)	90.8(3)
N(22)	1.986(5)			85.0(2)	94.1(3)	94.2(2)
N(25)	1.966(6)				88.9(3)	173.0(3)
N(1)	1.95(1)					84.3(4)
N(2)	1.975(7)					

Table 2 (*continued*)

(*f*) $[Co(en)(H_2L^2)]^{5+}$ **6**

	r	N(15)	N(32)	N(35)	N(1)	N(2)
N(12)	1.966(4)	84.6(2)	93.0(2)	98.0(2)	166.8(1)	86.3(2)
N(15)	1.972(4)		170.4(2)	94.8(2)	88.4(2)	93.6(2)
N(32)	1.986(4)			76.3(2)	95.7(2)	95.6(2)
N(35)	2.012(4)				93.7(2)	170.9(2)
N(1)	1.975(4)					83.0(2)
N(2)	1.981(4)					

(*g*) Full ligand geometry for **3**, as a precise example of a half-cage

	n			
	1	2	3	4
C(0)–C(*n*1)	1.528(4)	1.534(4)	1.529(4)	1.542(3)
C(*n*1)–N(*n*2)	1.493(3)	1.490(3)	1.494(3)	1.486(3)
N(*n*2)–C(*n*3)	1.493(4)	1.489(4)	1.499(4)	1.498(3)
C(*n*3)–C(*n*4)	1.508(4)	1.504(4)	1.503(4)	1.503(4)
C(*n*4)–N(*n*5)	1.486(4)	1.481(4)	1.498(4)	1.483(4)
C(*n*+1,1)–C(0)–C(*n*1)	111.2(2)	110.5(2)	110.7(2)	109.7(2)
C(*n*+2,1)–C(0)–C(*n*1)	111.3(2)	103.2(2)		
C(0)–C(*n*1)–N(*n*2)	112.9(2)	113.2(2)	112.5(2)	115.2(2)
C(*n*1)–N(*n*2)–C(*n*3)	112.3(2)	112.9(2)	112.5(2)	113.3(2)
C(*n*1)–N(*n*2)–Co	117.9(2)	117.8(2)	118.3(2)	
C(*n*3)–N(*n*2)–Co	107.9(2)	108.0(2)	107.8(2)	
N(*n*2)–C(*n*3)–C(*n*4)	106.6(2)	106.9(2)	107.3(2)	110.7(2)
C(*n*3)–C(*n*4)–N(*n*5)	106.8(2)	107.6(2)	107.5(2)	110.1(2)
C(*n*4)–N(*n*5)–Co	109.5(2)	108.6(2)	109.3(2)	

[a] The corresponding environments of the two cobalt atoms are related by approximate, non-crystallographic 2 symmetry. [b] As in compound **1** the two cobalt environments are related by approximate 2 symmetry (but see Table 3 and text).

CoN_4Cl_2 distribution of the donor atoms,[16] and crystallographic studies have been essential anchor points in the present work.

Full consideration of the stereochemistry of octahedral cobalt(III) complexes incorporating L^1 and L^2 is exceedingly complicated. Not only are various configurations at secondary nitrogen and around cobalt possible but these may also occur within different constitutional isomers. Familiar restrictions[21] do apply in that the size of the carbon chains linking the nitrogen-donor atoms restricts any adjacent pair of nitrogens to *cis* positions on the metal co-ordination octahedron, and the configuration of a co-ordinated secondary nitrogen atom is only variable, for a given arrangement of the other donor atoms, when that atom is central in a meridional array with two others (or possibly when it is part of a large, flexible chelate ring involving one unco-ordinated nitrogen donor). Even if for L^1 consideration is limited to its possible binuclear complexes with four nitrogen atoms bonded to each of two octahedral metal ions with unidentate ligands completing the co-ordination spheres, each half of the complex may adopt *trans-R*,R**, *trans-R*,S**, *cis*-β-*R*,R**, *cis*-β-*R*,S** or *cis*-α-*R*,R** configurations,[21] so that, taking enantiomer pairs as single species, there are 35 forms which may occur. If the system is simplified by taking an obligate *cis*-spanning ligand such as ethane-1,2-diamine to complete the metal-ion co-ordination spheres, 12 forms remain. The possible set of mononuclear complexes formed by L^2 is markedly the simpler only if the possibility of forming species containing constitutionally isomeric quadridentate forms of the ligand is ignored. If only the acyclic N-donor atoms are bound along with a bidentate ethane-1,2-diamine, for example, then only three forms, *cis*-β-*R*,R**, *cis*-β-*R*,S** and *cis*-α-*R*,R**, would be expected. In fact our preparative work indicates that this is not the case, though we have not found conditions where forms involving binding to the nitrogen-donor atoms of the diazepam ring are actually dominant in the mixture of complexes present.

The compounds L^1 and L^2 contain 13 (12 secondary, one quaternary) and 11 (10 secondary, one quaternary) carbon atoms, respectively, and these numbers define the maximum numbers of signals to be anticipated in the ^{13}C NMR spectra of their complexes (aside from signals due to coligands). The presence of fewer signals implies some element of symmetry in the complex-ion structure, and the observations of six resonances for complex **1** and eight for **4** are consistent with the centre of symmetry and (effective) vertical plane of symmetry, respectively, revealed by the crystal-structure determinations (see below), assuming two signals in **1** are accidentally isochronous. For many of the other complexes presently isolated, however, the spectra (see below) indicate a lack of molecular symmetry and/or the presence of a mixture of diastereomers. The presence of diastereomers we attribute to the fact that the chromatographic separations of the products of the reactions of **1** and **4** with ethanediamine were carried out using phosphate buffers of a pH close to 7, conditions which would allow rapid NH exchange and 'planar' inversion at N in hexamine cobalt(III) species,[22] so that isomers differing only with respect to secondary nitrogen configurations would not be separated. The use of phosphate media also occasionally led to artefacts in that some of the complexes formed relatively insoluble phosphate salts which tended partially to precipitate when elution was commenced and material was concentrated at the head of the column, so leading to 'double bands' of the one species. We consider, in fact, that F6 from complex **1** may actually be the same as F4 for this reason, though there are some slight differences in their NMR spectra. Despite these problems, phosphate buffers proved superior separators in the present systems to any other eluents investigated.

Chemical shift values for the peaks observed in the ^{13}C NMR spectra of all the hexamine species presently studied are given in Table 1. The spectra were recorded in a common, dilute acid solvent in order to avoid confusing differences initially encountered in some cases because of varying extents of protonation of pendant arms incorporating amino groups. This in itself caused some difficulties because the spectrum obtained for the complex F3 derived from **1** then differed from that in the literature[3] for $[Co(H_2L^1)]^{5+}$ **3** (with which F3 was finally identified), and even in 0.1 mol dm^{-3} DCl amino-group proton exchange took place and gave rise to shifts in the ^{13}C resonances of adjacent carbons.[23] Thus, the data given in Table 1 for F3 are not consistent with the effective C_3 symmetry expected for the molecule in solution [and neither are the data for neutral D_2O solution, in which resonances were observed at δ 56.8, 51.3, 51.0, 46.5, 43.0, 42.9 and 35.7 (CH_2) and 44.8 (quaternary)] and the only explanation we have for this, aside from restricted rotation of the pendant arm, is the presence of an equilibrium mixture of deuteriated and protonated forms. It may be that in several other cases peaks separated by only ≈0.1 ppm are of the same origin[23] and hence it is difficult unambiguously to assign the symmetry of the present complexes, at least those which contain pendant arms, on the

Table 3 Ligand torsion angles (°); 'equivalent' values are laid out in parallel and where two values are given they are for unprimed and primed sections respectively

(*a*) $[trans\text{-}Cl_2CoL^1CoCl_2\text{-}trans]^{2+}$

C(21)–C(0)–C(11)–N(12)	66(2), 63(2)	C(11)–C(0)–C(21)–N(22)	−62(2), −61(2)
C(0)–C(11)–N(12)–C(13)	175(2), 178(2)	C(0)–C(21)–N(22)–C(23)	179(2), 174(2)
C(0)–C(11)–N(12)–Co	−62(2), −56(3)	C(0)–C(21)–N(22)–Co	53(2), 50(3)
C(11)–N(12)–C(13)–C(14)	171(2), 173(2)	C(21)–N(22)–C(23)–C(24)	−176(2), −175(2)
Co–N(12)–C(13)–C(14)	41(2), 41(2)	Co–N(22)–C(23)–C(24)	−43(2), −43(2)
N(12)–C(13)–C(14)–C(15)	−55(2), −50(3)	N(22)–C(23)–C(24)–N(25)	53(2), 51(3)
C(13)–C(14)–N(15)–Co	40(2), 37(2)	C(23)–C(24)–N(25)–Co	−39(2), −35(2)

(*b*) $[(en)CoL^1Co(en)]^{6+}$ **2a** and **2b**; values for **2b** are given below those for **2a**

N(1)–C(1)*–C(2)–N(2)	−29(2), −48.7(8) −45.2(6), −50.4(6)	Co–N(2)–C(2)–C(1)*	8(1), 34.1(7) 26.4(6), 42.6(5)
C(0)–C(11)–N(12)–C(13)	168.4(6), 171.4(6) 171.0(4), 175.4(4)	C(0)–C(21)–N(22)–C(23)	−83.1(8), −82.8(8) −80.7(6), −78.5(6)
C(11)–N(12)–C(13)–C(14)	165.2(6), 171.4(6) 166.3(4), 169.6(4)	C(21)–N(22)–C(23)–C(24)	167.9(6), 162.3(6) 169.3(4), 168.0(4)
Co–N(1)–C(1)*–C(2)	36(1), 42.1(7) 43.8(5), 36.2(5)	C(23)–C(24)–N(25)–Co	43.4(7), 44.0(7) 43.7(5), 43.4(5)
C(12)–C(13)–C(14)–N(15)	−52.9(8), −52.4(8) −52.1(6), −53.0(6)	N(22)–C(23)–C(24)–N(25)	−48.4(8), −45.6(8) −49.6(5), −48.8(5)
C(13)–C(14)–N(15)–Co	45.2(7), 39.3(7) 44.1(6), 40.6(5)		

(*c*) $[Co(H_2L^1)]^{5+}$ **3**

	n			
	1	2	3	4
C(41)–C(0)–C(*n*1)–N(*n*2)	−174.6(2)	−169.7(2)	−165.7(2)	—
C(0)–C(*n*1)–N(*n*2)–C(*n*3)	109.1(3)	110.8(3)	109.4(2)	−168.5(2)
C(0)–C(*n*1)–N(*n*2)–Co	−17.2(3)	−16.2(3)	−17.3(3)	—
C(*n*1)–N(*n*2)–C(*n*3)–C(*n*4)	175.7(2)	−173.8(2)	−175.0(2)	−64.9(3)
Co–N(*n*2)–C(*n*3)–C(*n*4)	−44.1(2)	−41.7(3)	−42.8(3)	—
N(*n*2)–C(*n*3)–C(*n*4)–N(*n*5)	52.5(3)	52.1(3)	50.6(3)	−174.6(2)
C(*n*3)–C(*n*4)–N(*n*5)–Co	−36.3(3)	−37.4(3)	−34.5(3)	—
C(*n*1)–C(0)–C(41)–N(42)	68.1(3)	−173.4(2)	−55.2(3)	—

(*d*) $trans\text{-}[CoCl_2(H_2L^2)]^{3+}$ **4**

C(21)–C(0)–C(11)–N(12)	−63.4(2)	C(11)–C(0)–C(21)–N(22)	65.1(3)
C(0)–C(11)–N(12)–C(13)	178.0(2)	C(0)–C(21)–N(22)–C(23)	−179.3(2)
C(0)–C(11)–N(12)–Co	52.2(2)	C(0)–C(21)–N(22)–Co	−54.4(2)
C(11)–N(12)–C(13)–C(14)	−175.9(2)	C(21)–N(22)–C(23)–C(24)	172.6(2)
Co–N(12)–C(13)–C(14)	−43.2(2)	Co–N(22)–C(23)–C(24)	41.4(2)
N(12)–C(13)–C(14)–N(15)	51.5(3)	N(22)–C(23)–C(24)–N(25)	−47.5(3)
C(13)–C(14)–N(15)–Co	−35.8(3)	C(23)–C(24)–N(25)–Co	31.0(2)
C(0)–C(31)–N(32)–C(33)	86.8(3)	C(0)–C(36)–N(35)–C(34)	88.0(3)
C(31)–N(32)–C(33)–C(34)	−73.7(3)	C(36)–N(35)–C(34)–C(33)	−75.5(3)
N(32)–C(33)–C(34)–N(35)	57.4(3)		

(*e*) $[Co(en)(H_2L^2)]^{5+}$ **5**

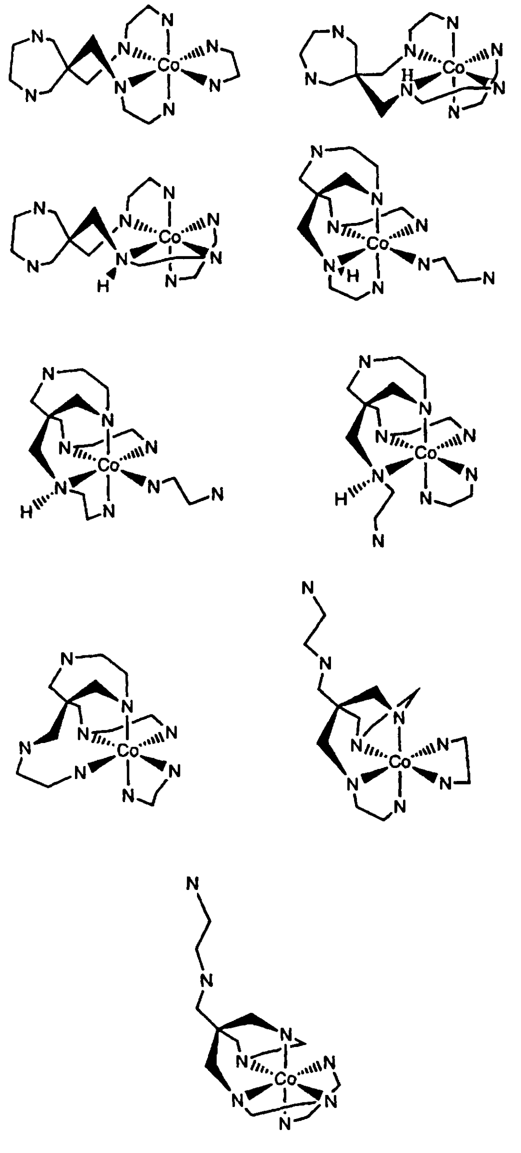
C(21)–C(0)–C(11)–N(12)	57.0(8)	C(11)–C(0)–C(21)–N(22)	−53.7(8)
C(0)–C(11)–N(12)–C(13)	172.4(7)	C(0)–C(21)–N(22)–C(23)	−78.6(7)
C(0)–C(11)–N(12)–Co	−62.1(8)	C(0)–C(21)–N(22)–Co	53.1(8)
C(11)–N(12)–C(13)–C(14)	170.6(7)	C(21)–N(22)–C(23)–C(24)	164.5(6)
Co–N(12)–C(13)–C(14)	38.2(7)	Co–N(22)–C(23)–C(24)	27.8(8)
N(12)–C(13)–C(14)–N(15)	−52.8(8)	N(22)–C(23)–C(24)–N(25)	−47.9(9)
C(13)–C(14)–N(15)–Co	42.1(7)	C(23)–C(24)–N(25)–Co	46.4(8)
C(0)–C(31)–N(32)–C(33)	−92.8(9)	C(0)–C(36)–N(35)–C(34)	−88.8(7)
C(31)–N(32)–C(33)–C(34)	75.3(8)	C(36)–N(35)–C(34)–C(33)	75.5(9)
N(32)–C(33)–C(34)–N(35)	−56.2(9)		
Co–N(1)–C(1)–C(2)	44.6(7)	Co–N(2)–C(2)–C(1)	32.2(7)
N(1)–C(1)–C(2)–N(2)	−49.4(7)		

Table 3 (*continued*)

(*f*) $[Co(en)(H_2L^2)]^{5+}$ **6**

C(0)–C(11)–N(12)–C(13)	151.4(4)	C(0)–C(21)–N(22)–C(23)	179.5(5)
C(11)–N(12)–C(13)–C(14)	−95.8(5)	C(21)–N(22)–C(23)–C(24)	167.7(5)
N(12)–C(13)–C(14)–N(15)	−50.7(5)	N(22)–C(23)–C(24)–N(25)	83.8(7)
C(13)–C(14)–N(15)–Co	39.6(4)		
C(0)–C(11)–N(12)–Co	21.6(6)		
Co–N(12)–C(13)–C(14)	39.2(5)		
C(0)–C(31)–N(32)–C(33)	−84.3(4)	C(0)–C(36)–N(35)–C(34)	99.0(4)
C(0)–C(31)–N(32)–Co	37.2(4)	C(0)–C(36)–N(35)–Co	−18.0(5)
C(31)–N(32)–C(33)–C(34)	95.4(5)	C(36)–N(35)–C(34)–C(33)	−75.2(5)
Co–N(32)–C(33)–C(34)	−28.5(5)	Co–N(35)–C(34)–C(33)	49.0(4)
N(32)–C(33)–C(34)–N(35)	−13.6(6)		
Co–N(1)–C(1)–C(2)	45.0(5)	Co–N(2)–C(2)–C(1)	34.7(4)
N(1)–C(1)–C(2)–N(2)	−50.6(4)		

* In the unprimed half of complex **2a**, for the second disordered component, C(1″): Co–N(1)–C(1″)–C(2), Co–N(2)–C(2)–C(1″), N(1)–C(1″)–C(2)–N(2) are −28(1), −30(1), 37(1)°.



Scheme 2 Some of the possible modes of co-ordination of L^2 and ethane-1,2-diamine in mononuclear, octahedral cobalt(III) complexes. Hydrogen atoms are not shown except where necessary to clarify the nature of the isomeric form

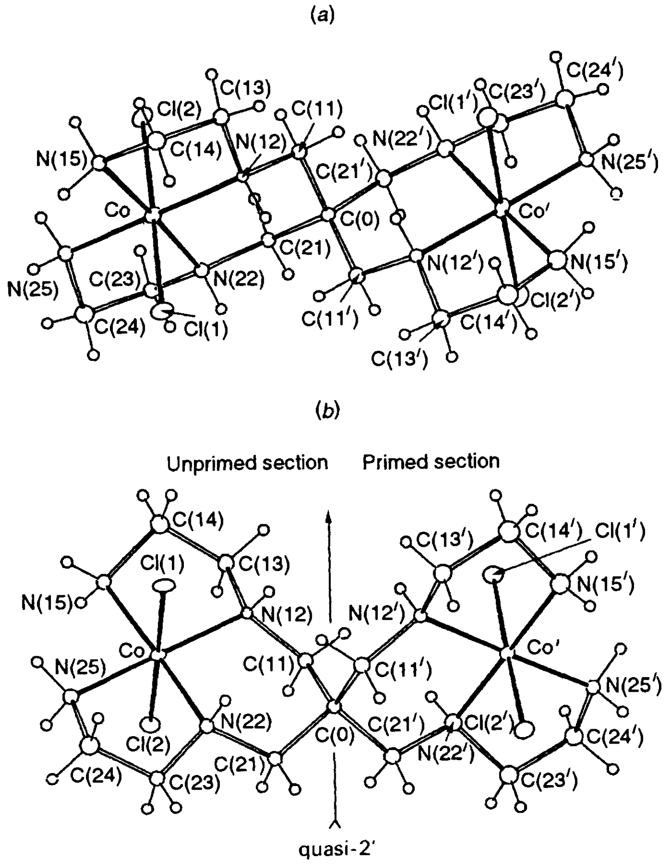


Fig. 1 The $[trans\text{-}Cl_2CoL^1CoCl_2\text{-}trans]^{2+}$ cation of complex **1** projected (*a*) down and (*b*) normal to the quasi-2 axis. In all figures 20% thermal envelopes are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å

basis of their nuclear magnetic resonance spectra. Nonetheless, for binuclear complexes derived from the binuclear complex **1**, F4, F5 and F6, pendant arms incorporating amino groups should be absent and the spectra more certainly interpretable, and indeed that of F4 is consistent with the symmetrical structure for the cation revealed in the structures of both **2a** and **2b** (see below). The simplest interpretation of the ^{13}C NMR spectrum of the residue from F5 is that it contains a mixture of two (presumably diastereomeric) unsymmetrical species. The spectrum of F6 shows only very slight differences from that of F4 and it may be that F6 is in fact an unsymmetrical diastereomer of F4 (related by inversion about one chiral nitrogen) that initially precipitates on the chromatography column but ultimately isomerises to largely F4 when finally forced into solution.

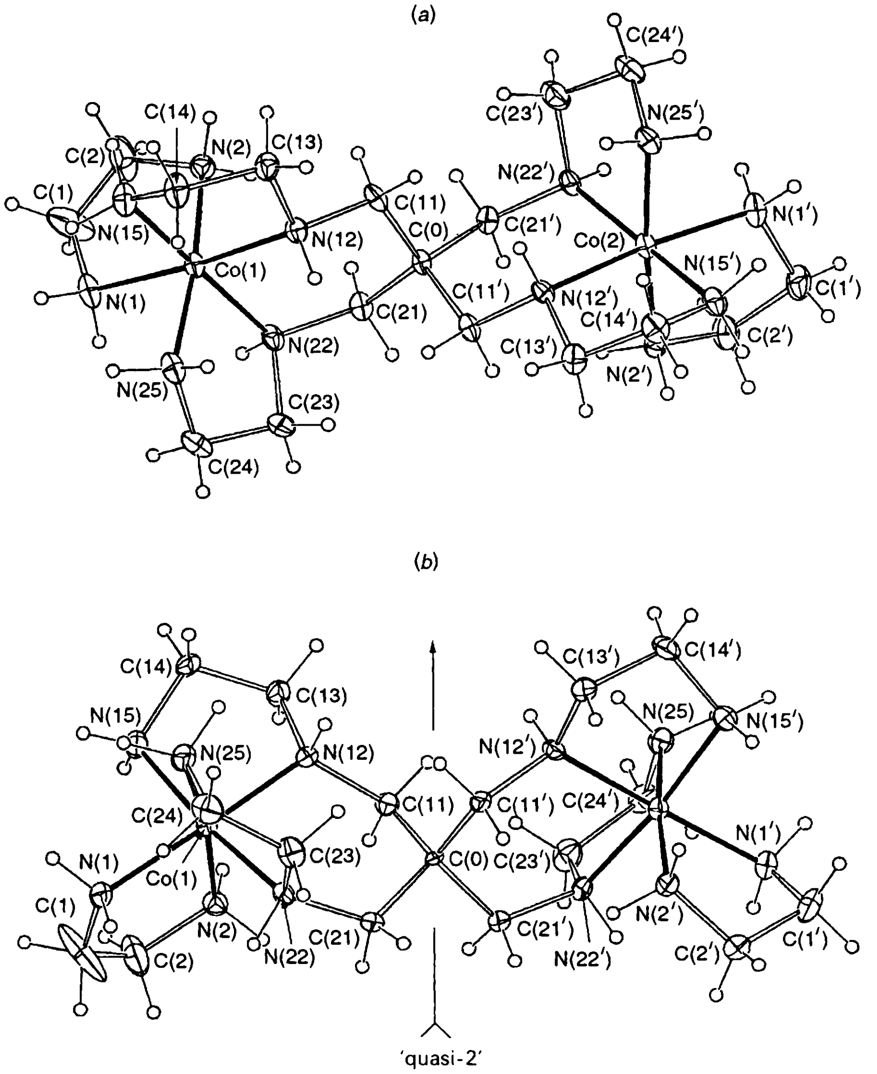


Fig. 2 The $[(en)CoL^1Co(en)]^{6+}$ cation of complex **2a** (*a*) down and (*b*) normal to the quasi-2 axis

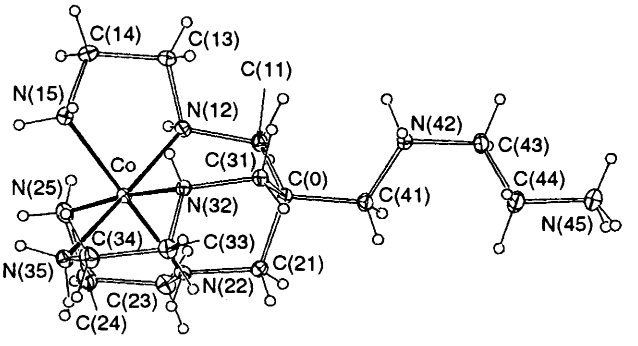


Fig. 3 The $[Co(H_2L^1)]^{5+}$ cation of complex **3**

The results in Table 1 show, subject to the qualifications above, that the reaction of complex **4** with ethanediamine produces only unsymmetrical species and that at least three of these are present as diastereomer mixtures. Some of the structures possible for this complex ion system are shown in Scheme 2, and it is obviously the case that their number can exceed that observed. In the case of complex **5** it is noteworthy that although good crystals are easily obtained, they actually form from a solution which appears to contain a greater amount of a diastereomeric form. The isolated solid (quaternary carbon resonance at δ 39.60) can be observed to equilibrate with this other form in neutral but not acidic solution, consistent with the supposition that the interconversion results from inversion about a co-ordinated asymmetric nitrogen. Since many of the possible structures for mixed complexes of L^2 and ethanediamine with Co^{III} are of C_1 symmetry and hence not readily distinguished spectroscopically, it is obvious why crystal structure determinations are so important to full characterisation of the complexes actually isolated.

Structure Determinations.—Although one of the determinations, complex **1**, is of less than desirable precision in consequence of a difficult specimen, all the present room-temperature single-crystal X-ray studies serve firmly to establish the nature of the complexes concerned, being consistent with their formulation, as above, as two species containing binuclear cations, $[trans\text{-}Cl_2CoL^1CoCl_2\text{-}trans]Cl_2{\cdot}4H_2O$ **1** (Fig. 1) and $[\beta\text{-}cis(R^*,R^*)\text{-}(en)CoL^1Co(en)\text{-}(S^*,S^*)cis\text{-}\beta]\text{-}Cl_6{\cdot} \approx 7H_2O$ and $\text{-}[NO_3]_6{\cdot}4H_2O$ **2a** and **2b** (Fig. 2), and four mononuclear species, $[Co(H_2L^1)]Cl_5{\cdot} \approx 2.3H_2O$ **3** (Fig. 3), $trans\text{-}[CoCl_2(H_2L^2)]Cl_3{\cdot} \approx 3.45H_2O$ **4** (Fig. 4), plus two constitutional isomers of $[Co(en)(H_2L^2)]Cl_5$ as ethanol and water solvates [≈0.6EtOH **5** (Fig. 5) and $3H_2O$ **6** (Fig. 6)]. In each case a single formula unit comprises the asymmetric unit of the structure; the binuclear complex **1** crystallizes in a chiral lattice, monoclinic space group $P2_1$, and the bulk sample is presumably an equiproportional mixture of crystals of both hands. Selected bond lengths and angles are given in Table 2, ligand torsion angles in Table 3 and atomic coordinates in Tables 4–9.

The binuclear array of complex **1** has been described before

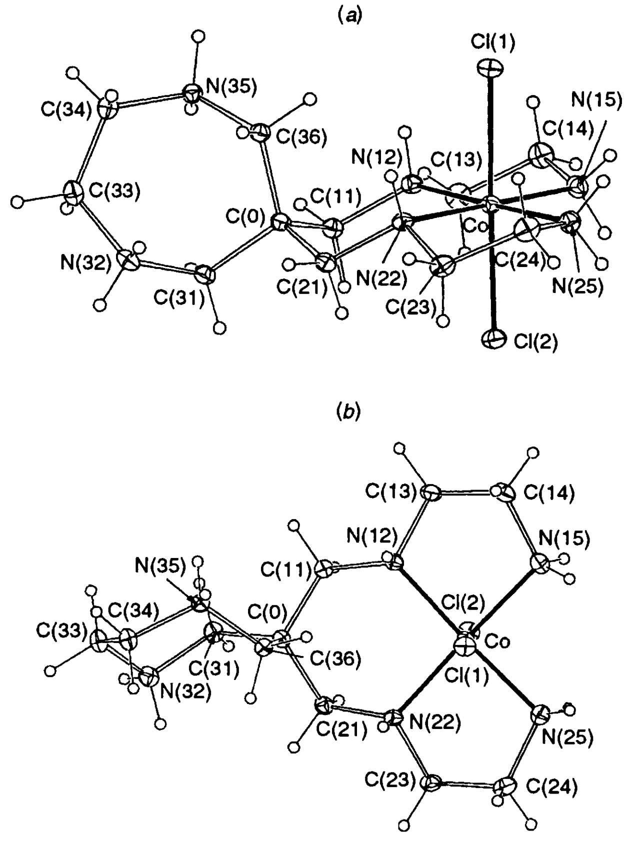


Fig. 4 The *trans*-$[CoCl_2(H_2L^2)]^{3+}$ cation of complex **4** projected (*a*) normal to and (*b*) down the ClCoCl line

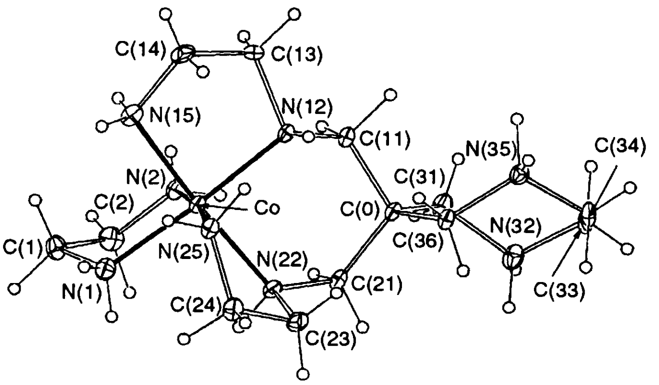


Fig. 5 The $[Co(en)(H_2L^2)]^{5+}$ cation of complex **5**

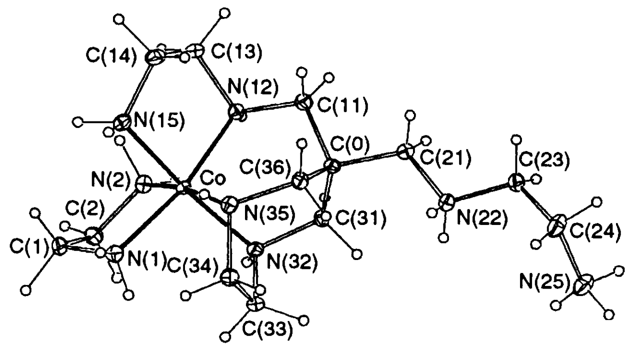


Fig. 6 The $[Co(en)(H_2L^2)]^{5+}$ cation of complex **6**

Table 4 Non-hydrogen positional parameters for [*trans*-$Cl_2CoL^1CoCl_2$-*trans*]$Cl_2 \cdot 4H_2O$ **1**

Atom	*x*	*y*	*z*
Co	0.9757(2)	0.5*	0.7254(5)
Cl(1)	0.9793(4)	0.3974(5)	0.993(1)
Cl(2)	0.9742(4)	0.6024(5)	0.460(1)
Cl(0)	0.7418(5)	0.2892(5)	0.750(1)
C(0)	0.779(1)	0.605(1)	0.766(3)
C(11)	0.787(1)	0.545(2)	0.571(3)
N(12)	0.851(1)	0.467(1)	0.619(3)
C(13)	0.850(1)	0.405(2)	0.431(4)
C(14)	0.926(2)	0.338(2)	0.480(4)
N(15)	1.010(1)	0.398(1)	0.548(3)
C(21)	0.866(1)	0.659(2)	0.843(3)
N(22)	0.948(1)	0.597(1)	0.913(3)
C(23)	1.024(1)	0.655(2)	0.978(3)
C(24)	1.101(2)	0.593(2)	1.028(4)
N(25)	1.096(1)	0.533(1)	0.834(3)
O(1)	0.679(1)	0.970(2)	0.453(3)
O(2)	0.778(1)	0.135(2)	0.418(3)
Co′	0.5637(2)	0.5711(3)	0.7620(5)
Cl(1′)	0.5399(4)	0.4757(5)	0.481(1)
Cl(2′)	0.5837(4)	0.6660(5)	1.043(1)
Cl(0′)	0.7947(5)	0.8277(5)	1.243(1)
C(11′)	0.755(1)	0.549(2)	0.940(3)
N(12′)	0.670(1)	0.497(1)	0.878(3)
C(13′)	0.651(2)	0.439(2)	1.060(4)
C(14′)	0.558(2)	0.402(2)	0.987(4)
N(15′)	0.499(1)	0.484(2)	0.905(3)
C(21′)	0.714(1)	0.687(2)	0.686(4)
N(22′)	0.626(1)	0.660(1)	0.603(3)
C(23′)	0.566(2)	0.743(2)	0.550(4)
C(24′)	0.475(2)	0.709(2)	0.481(4)
N(25′)	0.458(1)	0.641(1)	0.648(3)
O(1′)	0.667(2)	0.143(2)	1.030(4)
O(2′)	0.679(2)	0.954(2)	0.882(4)

* Defines origin.

for a [*trans*-$Cl_2ML^1MCl_2$-*trans*] species for the neutral nickel(II) complex; torsion angles for that array are similar in sign and magnitude to those of the present compound, as also are those for the array devoid of chlorine atoms, containing square-planar nickel(II);[19] in the latter ⟨Ni–N⟩ is 1.9_3 Å, comparable with the present, while in the system with two chlorine atoms *trans* in an octahedral array ⟨Ni–N⟩ is 2.0_8 Å,[19] so that these values span the present ones. In all of these systems the torsions are also similar to those found in the mononuclear symmetry, being of opposed sign in the two strands about each metal atom. Thus, both halves of the complex can be considered as *trans*-(R^*,S^*)-$[CoL^9Cl_2]^+$ units. Of some interest is the fact that, despite its relative imprecision, ⟨Co–Cl⟩ in the binuclear complex, 2.2_4 Å, is significantly less than the value of 2.2_6 Å in the mononuclear species, though this is presumably only a consequence of the sensitivity of this bond length to variations in the rest of the co-ordination sphere of the cation (see below).

In complexes **2a** and **2b** we have a common cation $[(en)CoL^1Co(en)]^{6+}$, with the ligand embracing two metal atoms as in other known examples but, for the first time, doing so in the context of the other two sites of the six-co-ordinate environment being obligate *cis* rather than *trans*. Despite this, the angular environments about the metals seem relatively unstrained, all *trans* angles being greater than 172 °; the Co–N bond lengths also are closely clustered around values typical of 'unstrained' hexaammine or tris(ethane-1,2-diamine)cobalt(III) species,[24] ⟨Co–N⟩ being 1.96_9 Å within the range 1.958(7)–1.979(6) Å (*i.e.* 0.02 Å). The array has quasi-2 symmetry, but a significant, if minor, perturbation is that found in the torsions of the en rings which differ; the thermal envelope of C(1) (Fig. 2) is abnormally elongated in (as far as the cation is concerned) an otherwise well behaved refinement, suggesting that the unprimed en ring may be incipiently or actually disordered between two conformations as in the final model. The five-membered chelate rings are all half-chairs, while the six-membered rings are 'chairs'. In the two halves of the centrosymmetric complex ion the quadridentate ligand unit can

Table 5 Non-hydrogen positional parameters for [(en)CoL^{1}Co(en)]-Cl$_6$· ≈ 7H$_2$O **2a** and -[NO$_3$]$_6$·4H$_2$O **2b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Complex **2a**							
Co(1)	0.692 29(6)	0.409 68(6)	0.317 26(4)	N(12′)	0.826 6(3)	0.365 9(3)	0.505 8(2)
Cl(1)	0.696 8(1)	0.236 6(1)	0.524 69(8)	C(13′)	0.883 5(4)	0.299 5(5)	0.511 0(3)
Cl(2)	0.549 1(1)	0.100 5(1)	0.432 18(8)	C(14′)	0.886 1(4)	0.269 7(5)	0.566 7(3)
Cl(3)	0.677 2(1)	0.703 9(1)	0.377 59(9)	N(15′)	0.890 8(3)	0.350 5(4)	0.599 2(2)
C(0)	0.768 8(4)	0.465 9(4)	0.438 4(2)	C(21′)	0.762 8(4)	0.542 0(5)	0.479 2(3)
C(11)	0.701 7(4)	0.414 4(4)	0.434 1(3)	N(22′)	0.761 3(3)	0.522 2(4)	0.536 3(2)
N(12)	0.697 0(3)	0.354 7(4)	0.387 1(2)	C(23′)	0.689 3(4)	0.497 9(6)	0.553 4(3)
C(13)	0.636 1(4)	0.294 8(5)	0.393 0(3)	C(24′)	0.692 5(4)	0.451 4(5)	0.605 6(3)
C(14)	0.621 7(5)	0.253 8(5)	0.340 3(3)	N(25′)	0.748 9(3)	0.386 7(4)	0.602 4(2)
N(15)	0.615 4(4)	0.328 2(4)	0.303 1(2)	N(1′)	0.843 4(3)	0.514 5(4)	0.631 4(2)
C(21)	0.784 4(4)	0.519 0(5)	0.388 2(3)	C(1′)	0.914 5(5)	0.551 3(6)	0.632 6(3)
N(22)	0.776 8(3)	0.477 6(4)	0.335 6(2)	C(2′)	0.929 6(4)	0.580 1(5)	0.577 6(3)
C(23)	0.841 8(4)	0.425 8(5)	0.321 7(3)	N(2′)	0.911 0(3)	0.506 8(4)	0.542 1(2)
C(24)	0.824 7(4)	0.370 7(5)	0.274 6(3)	O(1)	0.5	0.046(2)	0.25
N(25)	0.757 8(4)	0.325 7(4)	0.285 2(2)	O(2)	0.458 5(6)	0.694 5(9)	0.474 6(6)
N(1)	0.680 1(3)	0.465 1(4)	0.247 9(2)	O(3)	0.391 6(8)	0.721 0(7)	0.322 3(5)
C(1)*	0.613 9(9)	0.507(1)	0.244 2(7)	O(4)	0.522 8(6)	0.763 4(9)	0.357 0(7)
C(1″)*	0.637 0(8)	0.550(1)	0.254 2(6)	O(5)*	0.5	0.798(3)	0.25
C(2)	0.595 1(6)	0.547 3(7)	0.294 7(3)	O(6)*	0.5	0.873(2)	0.25
N(2)	0.625 7(3)	0.501 0(4)	0.339 9(2)	O(7)*	0.516(1)	0.483(2)	0.443(1)
Co(1′)	0.830 03(5)	0.441 46(7)	0.568 54(4)	O(8)*	0.544(2)	0.573(2)	0.483(2)
Cl(1′)	0.304 8(1)	0.109 9(1)	0.266 42(8)	O(9)*	0.483(2)	0.674(2)	0.398(1)
Cl(2′)	0.261 6(2)	0.324 0(2)	0.341 81(9)	O(10)*	0.500 1(7)	0.447 6(9)	0.423 2(5)
Cl(3′)*	0.476 3(4)	0.427 4(5)	0.367 0(4)	O(11)*	0.416(1)	0.264(1)	0.302 1(6)
Cl(3″)*	0.457 3(4)	0.368 6(8)	0.318 6(3)	O(12)*	0.449(1)	0.176(2)	0.284 3(6)
C(11′)	0.830 9(4)	0.405 8(4)	0.452 5(2)				
(*b*) Complex **2b**							
Co(1)	0.665 05(5)	0.836 16(4)	0.821 81(4)	N(01)	0.401 3(4)	0.600 1(3)	0.579 9(3)
C(0)	0.446 3(4)	0.869 8(3)	0.716 9(3)	O(11)	0.404 1(3)	0.675 5(2)	0.568 7(2)
C(11)	0.516 0(3)	0.816 2(3)	0.683 0(3)	O(12)	0.467 5(4)	0.558 2(3)	0.575 0(3)
N(12)	0.580 6(3)	0.771 8(2)	0.744 8(2)	O(13)	0.333 1(4)	0.568 9(4)	0.599 4(4)
C(13)	0.634 5(4)	0.711 7(3)	0.702 3(3)	N(02)	0.452 7(3)	0.886 1(3)	0.326 5(3)
C(14)	0.712 2(4)	0.684 0(3)	0.761 9(3)	O(21)	0.481 9(3)	0.830 8(3)	0.373 6(3)
N(15)	0.757 8(3)	0.758 5(3)	0.797 4(2)	O(22)	0.413 4(3)	0.946 9(2)	0.349 5(2)
C(21)	0.491 1(3)	0.930 9(3)	0.782 6(3)	O(23)	0.457 4(5)	0.878 5(3)	0.254 4(3)
N(22)	0.561 1(3)	0.900 7(2)	0.847 9(2)	N(03)	0.253 5(4)	0.533 4(4)	0.387 8(3)
C(23)	0.520 5(4)	0.859 1(3)	0.913 3(3)	O(31)	0.289 6(4)	0.495 7(3)	0.337 7(3)
C(24)	0.595 2(4)	0.817 4(3)	0.967 3(3)	O(32)	0.226 7(6)	0.497 2(5)	0.441 6(4)
N(25)	0.647 3(3)	0.768 7(3)	0.915 0(2)	O(33)	0.244 9(5)	0.608 3(4)	0.381 2(3)
N(1)	0.755 6(3)	0.900 5(3)	0.893 5(3)	N(04)	0.697 3(3)	0.586 5(3)	0.024 4(3)
C(1)	0.817 8(4)	0.940 9(4)	0.844 7(3)	O(41)	0.667 9(3)	0.579 1(3)	−0.049 8(2)
C(2)	0.761 9(4)	0.976 1(4)	0.771 6(3)	O(42)	0.749 5(3)	0.534 7(3)	0.057 8(3)
N(2)	0.694 5(3)	0.913 6(3)	0.738 0(2)	O(43)	0.673 7(3)	0.646 8(2)	0.061 3(2)
Co(1′)	0.228 35(5)	0.843 96(4)	0.606 48(4)	N(05)	0.089 5(4)	0.285 4(3)	0.032 6(3)
C(11′)	0.374 2(3)	0.817 6(3)	0.748 2(3)	O(51)	0.161 8(3)	0.320 8(3)	0.047 6(3)
N(12′)	0.307 2(3)	0.775 6(2)	0.685 9(2)	O(52)	0.026 8(3)	0.314 8(3)	−0.014 5(3)
C(13′)	0.247 7(4)	0.722 7(3)	0.727 8(3)	O(53)	0.078 8(3)	0.218 7(3)	0.068 8(3)
C(14′)	0.170 9(4)	0.694 0(3)	0.666 0(3)	N(06)	0.051 9(4)	0.844 2(4)	0.333 2(3)
N(15′)	0.130 0(3)	0.769 0(3)	0.624 3(2)	O(61)	−0.010 8(4)	0.833 4(4)	0.277 3(3)
C(21′)	0.402 8(3)	0.932 8(3)	0.653 2(3)	O(62)	0.097 1(4)	0.785 1(4)	0.362 3(3)
N(22′)	0.334 7(3)	0.906 4(2)	0.585 5(2)	O(63)	0.066 9(5)	0.915 1(4)	0.357 7(3)
C(23′)	0.376 3(4)	0.865 3(3)	0.520 1(3)	O(1)	0.029 9(3)	0.654 0(3)	0.246 2(3)
C(24′)	0.303 3(4)	0.824 9(3)	0.463 2(3)	O(2)	0.095 1(4)	0.644 4(4)	0.482 9(3)
N(25′)	0.248 6(3)	0.776 6(3)	0.513 4(3)	O(3)	0.853 5(3)	0.684 8(3)	0.165 8(3)
C(1′)	0.096 2(4)	0.972 4(3)	0.578 8(3)	O(4)	0.017 8(5)	0.500 7(4)	0.300 1(4)
N(1′)	0.145 4(3)	0.913 9(3)	0.533 2(2)	O(5)	0.804 6(5)	0.669 9(4)	0.566 3(4)
N(2′)	0.199 5(3)	0.921 0(3)	0.689 4(2)	O(6)	0.028 4(7)	0.435 4(7)	0.442 5(6)
C(2′)	0.160 5(4)	0.998 2(3)	0.650 5(3)				

* Site occupancy factor = 0.5.

be described as having the *cis*-β configuration where the two asymmetric nitrogen-donor centres are of the same absolute configuration but of course are of opposite configuration in the two halves. This particular material can also be rather readily crystallised in a pure form from the synthesis reaction product mixture but it is only one of at least three species present in comparable amounts.

The cation of complex **3** is the known[3,5] cage-precursor species [Co(H$_2$L^1)]$^{5+}$, in which the fourth arm of the ligand pendant from the cap is fully protonated. This complex has not previously been structurally characterised though, in the form where the pendant arm is singly protonated, the cage derived from it has.[5] The present determination is quite precise and we give the full ligand geometry as archetypical, the *trans* disposition of C(41)–N(42) to branch 2 [about C(0)–C(41)] seemingly having no significant, non-trivial effect on the

Table 6 Non-hydrogen positional parameters for $[Co(H_2L^1)]Cl_5 \cdot \approx 2.3H_2O$ **3**

Atom	*x*	*y*	*z*
Co	0.835 44(2)	0.539 63(3)	0.205 04(3)
Cl(1)	0.606 59(4)	0.128 56(6)	−0.027 93(6)
Cl(2)	0.525 02(4)	0.373 85(6)	0.106 51(6)
Cl(3)	0.935 49(4)	0.745 23(6)	−0.009 49(6)
Cl(4)	0.671 49(4)	0.776 33(7)	−0.176 25(6)
Cl(5)	0.886 07(5)	0.177 62(7)	0.252 47(8)
C(0)	0.714 7(1)	0.470 5(2)	0.000 6(2)
C(11)	0.727 6(1)	0.365 9(2)	0.077 7(2)
N(12)	0.775 0(1)	0.395 1(2)	0.188 1(2)
C(13)	0.729 7(2)	0.395 8(3)	0.271 4(2)
C(14)	0.782 8(2)	0.435 5(3)	0.376 0(2)
N(15)	0.817 7(1)	0.546 9(2)	0.352 2(2)
C(21)	0.787 8(1)	0.502 8(2)	−0.033 1(2)
N(22)	0.854 8(1)	0.519 0(2)	0.060 8(2)
C(23)	0.913 0(1)	0.425 3(3)	0.068 7(2)
C(24)	0.972 2(1)	0.445 2(3)	0.172 9(2)
N(25)	0.932 3(1)	0.454 8(2)	0.261 0(2)
C(31)	0.684 5(1)	0.576 1(2)	0.050 9(2)
N(32)	0.743 9(1)	0.630 8(2)	0.139 9(2)
C(33)	0.769 1(2)	0.747 8(2)	0.108 6(2)
C(34)	0.833 3(2)	0.788 4(2)	0.200 2(2)
N(35)	0.889 9(1)	0.690 7(2)	0.226 7(2)
C(41)	0.659 3(1)	0.436 3(3)	−0.107 6(2)
N(42)	0.579 7(1)	0.413 2(2)	−0.101 6(2)
C(43)	0.532 0(2)	0.357 6(3)	−0.202 1(2)
C(44)	0.522 0(2)	0.439 2(3)	−0.297 2(2)
N(45)	0.468 8(1)	0.387 6(2)	−0.393 5(2)
O(01)	0.948 7(2)	0.067 0(2)	0.059 3(3)
O(02)	0.728 7(2)	0.466 7(3)	−0.322 1(3)
O(03)*	0.590 3(7)	0.839(1)	0.111 8(8)

* Site occupancy factor = 0.302(9).

Table 7 Non-hydrogen positional parameters for *trans*-$[CoCl_2(H_2L^2)]Cl_3 \cdot \approx 3.45H_2O$ **4**

Atom	*x*	*y*	*z*
Co	0.152 22(2)	0.755 07(3)	0.876 47(4)
Cl(1)	0.172 19(4)	0.917 60(7)	1.126 18(7)
Cl(2)	0.130 57(4)	0.588 88(6)	0.630 21(7)
Cl(3)	0.435 57(4)	0.990 69(7)	0.192 57(7)
Cl(4)	0.110 78(5)	0.250 35(8)	0.835 7(1)
Cl(5)	0.552 15(7)	0.608 07(9)	0.785 9(1)
C(0)	0.287 7(2)	0.960 3(2)	0.690 1(3)
C(11)	0.320 0(2)	0.830 1(3)	0.746 1(3)
N(12)	0.282 3(1)	0.787 1(2)	0.889 8(3)
C(13)	0.315 0(2)	0.657 9(3)	0.929 6(4)
C(14)	0.268 6(2)	0.615 4(3)	1.066 2(4)
N(15)	0.171 4(2)	0.607 4(2)	1.004 6(3)
C(21)	0.186 2(2)	0.930 1(3)	0.619 3(3)
N(22)	0.130 7(1)	0.904 1(2)	0.747 3(3)
C(23)	0.033 4(2)	0.874 0(3)	0.665 9(3)
C(24)	−0.018 3(2)	0.829 8(3)	0.794 4(4)
N(25)	0.023 6(1)	0.721 8(3)	0.869 7(3)
C(31)	0.334 2(2)	0.975 6(3)	0.538 4(3)
N(32)	0.344 2(2)	1.117 1(2)	0.491 1(3)
C(33)	0.427 6(2)	1.218 9(3)	0.591 1(4)
C(34)	0.423 3(2)	1.278 1(3)	0.775 1(3)
N(35)	0.405 7(1)	1.168 4(2)	0.878 3(3)
C(36)	0.310 7(2)	1.092 8(3)	0.838 0(3)
O(1)	0.051 0(2)	0.593 6(3)	0.244 7(3)
O(2)	0.219 0(2)	0.287 7(4)	0.537 3(4)
O(3)	0.360 6(2)	0.539 2(4)	0.495 6(5)
O(4)*	0.250 8(8)	0.298(1)	0.221(1)

* Site occupancy factor = 0.45(1).

Table 8 Non-hydrogen positional parameters for $[Co(en)(H_2L^2)]Cl_5 \cdot \approx 0.6EtOH$ **5**

Atom	*x*	*y*	*z*
Co	0.591 40(8)	0.618 82(5)	0.275 83(6)
Cl(1)	0.722 6(2)	0.797 3(1)	0.134 1(1)
Cl(2)	0.755 0(2)	0.515 3(1)	−0.066 4(1)
Cl(3)	0.583 3(2)	0.318 5(1)	0.180 7(1)
Cl(4)	0.814 5(2)	0.483 9(2)	0.557 4(1)
Cl(5)	0.931 9(2)	0.251 7(2)	0.362 4(2)
C(0)	0.818 5(6)	0.522 0(4)	0.227 3(5)
C(11)	0.682 1(6)	0.536 6(4)	0.144 4(5)
N(12)	0.619 1(5)	0.612 4(4)	0.159 3(4)
C(13)	0.494 7(6)	0.624 8(5)	0.066 5(5)
C(14)	0.423 6(8)	0.692 3(5)	0.090 1(6)
N(15)	0.422 2(6)	0.664 0(5)	0.181 3(5)
C(21)	0.825 4(6)	0.512 9(5)	0.330 4(5)
N(22)	0.768 7(5)	0.582 9(4)	0.363 4(4)
C(23)	0.851 4(7)	0.663 1(5)	0.401 9(6)
C(24)	0.774 6(7)	0.737 5(5)	0.406 3(6)
N(25)	0.657 2(6)	0.738 5(4)	0.308 4(4)
C(31)	0.852 6(7)	0.432 0(5)	0.202 6(6)
N(32)	0.993 0(6)	0.412 5(4)	0.249 3(5)
C(33)	1.045 1(9)	0.435 9(6)	0.182 0(7)
C(34)	1.061 3(7)	0.531 5(6)	0.177 5(7)
N(35)	0.943 3(6)	0.584 7(4)	0.146 5(5)
C(36)	0.905 5(7)	0.595 0(4)	0.225 7(6)
N(1)	0.551 4(7)	0.624 3(5)	0.385 6(5)
C(1)	0.454 5(8)	0.556 4(6)	0.369 1(6)
C(2)	0.495 1(8)	0.476 2(5)	0.339 3(6)
N(2)	0.524 6(7)	0.498 8(4)	0.258 6(5)
O(01)*	1.111(2)	0.746(2)	0.354(2)
C(01)*	1.107(2)	0.755(2)	0.428(2)
C(02)*	1.188(4)	0.698(3)	0.517(3)

* Site occupancy factor = 0.62(1).

Table 9 Non-hydrogen positional parameters for $[Co(en)(H_2L^2)]Cl_5 \cdot 3H_2O$ **6**

Atom	*x*	*y*	*z*
Co	0.640 78(4)	0.305 39(5)	0.804 92(7)
Cl(1)	0.886 0(1)	0.172 5(1)	0.743 8(2)
Cl(2)	0.632 26(9)	0.056 9(1)	0.354 2(1)
Cl(3)	0.464 1(1)	0.551 6(1)	0.826 4(1)
Cl(4)	1.103 94(9)	0.645 3(1)	0.720 4(2)
Cl(5)[a]	0.796 8(1)	0.841 4(2)	1.190 0(4)
Cl(5′)[b]	0.765(2)	0.855(1)	1.083(4)
C(0)	0.740 2(3)	0.475 9(4)	0.623 0(5)
C(11)	0.634 1(4)	0.369 4(4)	0.506 9(6)
N(12)	0.593 6(3)	0.269 7(3)	0.571 6(4)
C(13)	0.470 5(3)	0.198 7(4)	0.509 6(6)
C(14)	0.423 6(4)	0.251 9(5)	0.632 5(6)
N(15)	0.483 1(3)	0.255 6(4)	0.788 9(5)
C(21)	0.786 0(4)	0.554 3(4)	0.522 5(6)
N(22)	0.885 5(3)	0.672 7(4)	0.608 3(5)
C(23)	0.921 0(4)	0.737 9(5)	0.496 2(7)
C(24)	1.005 3(4)	0.868 7(5)	0.581 0(8)
N(25)	1.120 0(3)	0.883 5(4)	0.628 1(7)
C(31)	0.819 4(4)	0.422 3(4)	0.679 4(5)
N(32)	0.799 8(3)	0.381 6(3)	0.817 9(4)
C(33)	0.859 0(4)	0.488 7(4)	0.973 2(6)
C(34)	0.779 2(4)	0.541 7(4)	1.022 2(5)
N(35)	0.681 4(3)	0.487 6(3)	0.878 8(4)
C(36)	0.711 0(4)	0.549 4(4)	0.759 5(6)
N(1)	0.663 9(3)	0.301 0(4)	1.025 8(4)
C(1)	0.617 1(4)	0.171 2(4)	1.020 9(6)
C(2)	0.654 2(4)	0.104 0(5)	0.894 2(6)
N(2)	0.625 8(3)	0.133 8(3)	0.748 6(5)
O(01)	0.788 0(3)	0.854 5(4)	0.700 3(5)
O(02)	0.961 6(4)	0.825 3(4)	0.944 5(5)
O(03)	0.640 5(4)	0.818 4(4)	0.881 5(6)

[a] Site occupancy factor = 0.86(1). [b] Site occupancy factor = 1 − 0.86(1).

geometry associated with branch 2 *vis-à-vis* branches 1 and 3. As might be expected, significant differences are found in the angular parameters of branch 4 *vis-à-vis* the remainder. About the metal atom, bond lengths Co–N(*n*2) are significantly shorter than Co–N(*n*5) (means 1.96_4 and 1.97_7 Å, respectively); angles N(*n*2)–Co–N(*n*′2) enclosed by the cap (mean $90._5$°), perhaps surprisingly, do not differ non-trivially from N(*n*5)–Co–N(*n*′5) (mean $90._9$°). These bond length and angle characteristics are in fact closely similar to those of the related cage complex[5] and to those of other half-cage species.[24] The 'twist' angle of the quasi-3 symmetry is 55(1)°, *cf.* the parent $[Co(en)_3]^{3+}$, 54(1)°.[24] As is usual in such complexes, we find, amongst the copious hydrogen bonds involving the anions (the strongest being associated with the protonated pendant arm), that three anions are 'chelated' by the amine hydrogen atoms in the interligand space around the equator of the co-ordination sphere [Cl(3) ··· N(22,35) 3.205(3), 3.366(4); Cl(4) ··· N(15,32) $(x, \frac{3}{2} - y, z - \frac{1}{2})$ 3.281(3); Cl(5) ··· N(12,25) 3.177(2), 3.273(3) Å].

The hydration of the mononuclear complex **4**, established from the refinement of site occupancies, is made up of three 'normal', fully occupied lattice sites, with associated hydrogen atom locations being established and refined, and a fourth of partial occupancy, with high thermal motion a possible foil for disorder, and without location of associated hydrogen atoms. In both **1** and **4** the metal atom is bound equatorially by the $C[CH_2NH(CH_2)_2NH_2]_2$ quadridentate moiety, formally equivalent to L^9. In this more precise determination we note that ⟨Co–Cl⟩ 2.260 Å, is very similar to those found in *trans*-$[CoCl_2(chxn)(NH_2R)_2]^+$ (chxn = cyclohexane-1,2-diamine) (2.263 Å),[25] *trans*-(*R**,*R**)-$[CoCl_2L^{10}]^+$ (L^{10} = 4,7-diazadecane-1,10-diamine) [2.255(8) Å],[26] and *trans*-$[CoCl_2L^{11}]^+$ (L^{11} = *N*,*N*′-dimethyl-3,7-diazanonane-1,9-diamine) [2.250(2) Å],[27] though a little longer than found in the more symmetrical *trans*-$[CoCl_2(en)_2]^+$ cation (2.23 Å).[28] Such variations are, however, within the range of Co–Cl bond lengths found as a function of the rest of the co-ordination environment.[29,30] Of more interest is the observation that in this complex a systematic difference is resolvable between Co–N(secondary) [1.960(2), 1.971(2) Å] and Co–N(primary) [1.948(3), 1.946(2) Å], possibly associated with the angular distortions in the equatorial plane, the different basicities of the nitrogen atoms, or hydrogen-bonding interactions found between the terminal amine groups and successive O(1) water oxygen atoms. Consideration of Fig. 4 and the torsion angles of Table 3 shows that the cobalt environment and its immediate ring system are a good approximation to *m* symmetry [*m* through C(0) and $CoCl_2$], while the peripheral ring, in 'chair' conformation, also approximates *m* symmetry, this time about a plane approximately normal to the $CoCl_2$ 'line'. As noted above, the *R**,*S** configuration for the inner, asymmetric N donors must be associated with this ligand conformation. Ring conformations[31] of both the half-chair five-membered chelate rings and the central, chair, six-membered ring in the immediate cobalt environment are similar to those found in the $[CuL^9]^{2+}$ array.[18]

The complexes **5** and **6** provide a contrast with **4** in that although they contain ligand L^2, and do so in its diprotonated form [all associated hydrogen atoms being locatable and refinable in (x, y, z, U_{iso})], they contain cations with a CoN_6 rather than a *trans*-Cl_2CoN_4 environment, the N_6 set being made up of a pair of *cis*-Co–N(en) bonds, a pair of *cis*-Co–N bonds drawn from one pendant arm of the ligand, and a pair of *cis*-Co–N bonds arising from co-ordination either of the nitrogen-donor atoms of the other pendant arm or of the seven-membered ring of the ligand. Thus, complex **5** is, at least as far as the ionic species are concerned, a constitutional isomer of **6**, the cation of which is also $[Co(en)(H_2L^2)]^{5+}$, but differing from that of **6** by virtue of a change in role of the potentially co-ordinating entities of ligand L^2. The two nitrogen atoms of the seven-membered ring are protonated and the two arms of the ligand embrace the metal atom in a necessarily different mode (*cis*-β-*R**,*R**) to that found in complex **4**, since the co-ordination of the other two ligating atoms of the en must be necessarily *cis*. Accordingly, the two arms of the ligand have lost their symmetrical relationship of complex **4**, although the diazepam ring conformation is similar. The five-membered chelate rings of both the bi- and quadri-dentate ligand moieties are all in essentially half-chair conformations. The cobalt environment appears less strained in **5** than in **6**: *e.g.*, the *trans* angles in **5** are greater than 173.0(3)°, whereas in **6** all are less than this value, while ⟨Co–N⟩ in **5** is 1.96_9, *cf.* 1.98_2 Å in **6**. Diminished restraints in **5** may be the reason for its equilibration in neutral (but not in acidic) solutions with a diastereoisomer which we assume differs only in the configuration about the 'planar' secondary nitrogen donor N(12). In fact, **5** appears to be the minor component of the equilibrium mixture but its tabular crystals are very easily separated mechanically from the fine needles formed by the major component and it was for this reason that it was the species structurally characterised.

The array of complex **6** is of interest from a number of points of view. First, it establishes that the two nitrogen atoms at the 1 and 4 positions of a seven-membered ring can be placed so as to co-ordinate to a central metal atom without undue strain, to the extent that these diazepam nitrogens may possibly be bound in preference to donors within an open-chain arm. In the only other case of co-ordination of a diazacycloheptane unit to Co^{III} all other donor atoms are also bound.[12] Certainly where ring nitrogen atoms are tertiary, there is evidence that their binding to metal ions is weaker than that of open-chain nitrogen donors.[32] The other pendant arm is diprotonated, interestingly, in preference to simple protonation of the ring system in unco-ordinated mode as in **4**; that example, however, was in the context of the last pair of ligands (which were unidentate) being *trans*, whereas here, with en co-ordinated, they must be *cis*. It is difficult, however, to draw any conclusions regarding the thermodynamic differences between the two modes of co-ordination of diprotonated L^2 seen in the complexes **5** and **6**. It would appear that **6** is in fact generated from **5** by slow reaction in boiling methanol in the presence of free ethanediamine, since at short reaction times (≈5 min) between **4** and ethane-1,2-diamine **5** is by far the dominant product, with **6** undetectable, and even after 1 h **6** is still very much a minor component. The constraint of the ring system in **6** appears to be primarily responsible for the small 'bite' angle [76.3(2)°] between N(32) and N(35), *cf.* that for the en ligand [N(1)–Co–N(2) 83.0(2)°], where the ethylene bridge can adopt a *gauche*, half-chair configuration; the latter value is similar to that between N(12) and N(15) [84.6(2)°] where the ring is similarly less constrained in conformation, and a half-chair. The six-membered metallacycle is a 'boat'. The distances Co–N(32,35) are, concomitantly, the longest in the co-ordination sphere, while Co–N(*n*5) are consistently longer than Co–N(*n*2). The seven-membered base ring is a chair (Fig. 6).

Conclusion

Our objective in treating the complexes **1** and **4** with ethane-1,2-diamine was to produce species incorporating a facial array of primary amino groups, one necessarily derived from the bidentate ligand, which could be subjected to a 'capping' reaction as involved in the formation of 'cage' and other multidentate ligand complexes,[7,8] and so link the two ligands in the metal co-ordination sphere into new pendant-arm macrocycles. In fact, the readily isolated complexes **2** and **5** are of the appropriate structure and we are currently investigating their behaviour. The ligand reorganisation accompanying the formation of complex **6** provides a system where facial triimine formation would be impossible, though where other pathways to intramolecular ligand linkage may be exploited and where, of course, reactions may be conducted on the pendant amino groups.

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