Quinquedentate Co-ordination of Amino-substituted Tetraazacycloalkanes to Cobalt(III). Part 1. Complexes of Macrocycles of Differing Ring Size, and Crystal Structures of *cis* Isomers†

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The pendant-arm macrocycles 12-methyl-1,4,7,10-tetraazacyclotridecan-12-amine (L^{13}), 6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine (L^{14}) and 10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine (L^{15}) react readily in water with cobalt(II) ion and air, followed by aqueous hydrochloric acid addition and equilibration with activated charcoal, to yield almost exclusively *cis*-$[Co(L^n)Cl]^{2+}$ complexes (n = 13, 14 or 15). A *trans* isomer is detected in addition to the *cis* only in the case of L^{14}, and then to only *ca.* 2% of total complexes. With 3-methyl-1,5,9,13-tetraazacyclohexadecan-3-amine (L^{16}) a *trans* isomer is the sole product, however. The three *cis* complexes were crystallized readily as perchlorate or tetrachlorocobaltate salts: $[Co(L^{13})Cl][CoCl_4]\cdot0.25MeOH$, triclinic, space group $P\bar{1}$, a = 15.682(8), b = 14.864(2), c = 8.938(4) Å, α = 96.32(4), β = 97.34(6), γ = 102.59(2)°; $[Co(L^{14})Cl][ClO_4]_2$, monoclinic, space group $P2_1/c$, a = 9.856(4), b = 17.36(2), c = 12.08(1) Å, β = 98.95(5)°; and $[Co(L^{15})Cl][ClO_4]_2\cdot H_2O$, orthorhombic, space group $Pn2_1a$, a = 16.708(4), b = 13.343(3), c = 9.886(1) Å. Single crystal X-ray structure determinations were refined to residuals of 0.050, 0.051 and 0.037 for 4848, 3035 and 1549 'observed' reflections respectively. In all cases the pendant primary amine and two adjacent secondary amines necessarily occupy an octahedral face, with the chloro ligand *cis* to the primary amine, and secondary amines adopt *RRSS* stereochemistries. There is an increase in average Co–N distances with macrocycle size (1.94_8, 1.95_4, 1.98_1 Å for L^{13}, L^{14} and L^{15} respectively), although the Co–N(pendant primary amine) distance is relatively invariant [range 1.955(4)–1.962(5) Å]. The Co–Cl distance, however, is minimized for L^{14} [2.245(2), 2.236(2), 2.273(2) Å for L^{13}, L^{14} and L^{15} respectively]. This latter trend is reflected in the comparative rate constants for stereoretentive base hydrolysis (k_{OH} 4300, 76, 6700 dm^3 mol^{-1} s^{-1} respectively), suggesting a ground-state influence on the reaction rate.

Polyamines which act as quinquedentate ligands to traditional inert metal ions such as cobalt(III), chromium(III) and rhodium(III) have been the subject of extensive studies. Cobalt(III) complexes have been reported with simple linear molecules such as penten (L^1 = 1,11-diamino-3,6,9-triazaundecane),[1] branched-chain species such as trenen [L^2 = 1,8-diamino-3-(2-aminoethyl)-3,6-diazaoctane],[2] and macrocyclic ligands such as 1,4,7,10,13-pentaazacyclopentadecane (L^3).[3] Recently, we reported cobalt(III) complexes of a new type of quinquedentate branched-chain ligand, 1,5,9-triamino-5-methyl-3,7-diazanonanane (L^4), which contains a $NHCH_2CMe(NH_2)CH_2NH$ component in the chain capable of co-ordinating only to the face of an octahedron, and exhibiting relatively short Co–N bond distances.[4] The latter ligand exhibits geometry analogous to the pendant-arm macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^5), which is known to co-ordinate as a sexi-, quinque- or quadri-dentate ligand to cobalt(III).[5] The prospect of deliberately developing quinquedentate ligands based on a macromonocycle with a single pendant arm rather than the double pendants in L^5 was readily identified and pursued.

Reaction of linear tetraamines $H_2N(CH_2)_nNH(CH_2)_mNH(CH_2)_nNH_2$ (n, m = 2 or 3) as the copper(II) complexes in basic solution with nitroethane and formaldehyde produces macromonocyclic complexes with a pendant nitro group, characterized by crystal structure analyses.[6] Reduction with zinc in aqueous acid yields the analogous macrocycles L^{13}, L^{14}, L^{15} and L^{16}, each with a pendant primary amino group. When co-ordinated as quinquedentate ligands, *cis* or *trans* geometries are inherently available. These ligands may be seen as analogues of L^4, but with the primary amines of the main chain in the latter ligand linked by a methylene chain to form a macrocycle ring. In this and the following paper details of the co-ordination of the new potentially quinquedentate ligands to cobalt(III) are presented. Syntheses, spectroscopic properties, preliminary base-hydrolysis rates, and X-ray crystal-structure analyses of the *cis* isomers are reported herein. Structural studies of the *trans* isomers, as well as molecular mechanics calculations and the detailed base-hydrolyses kinetics of the series of complexes appear in the following paper.[7]

Experimental

Syntheses.—The complexes (12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane)-, (6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane)-, (10-methyl-10-nitro-1,4,8,12-tetraazacyclo-

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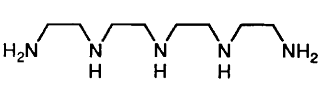
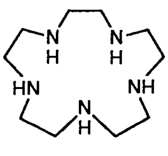
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



L^{1}



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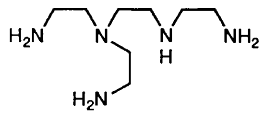
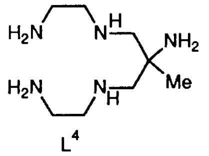
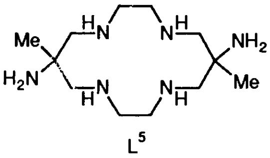


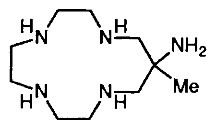
L^{2}



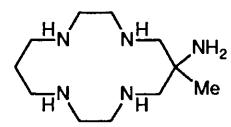
L^{4}



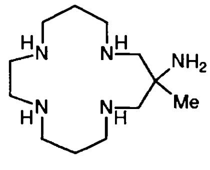
L^{5}



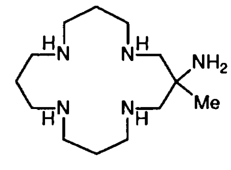
L^{13}



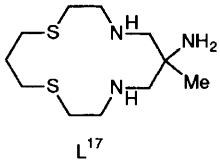
L^{14}



L^{15}



L^{16}



L^{17}

pentadecane)- and (3-methyl-3-nitro-1,5,9,13-tetraazacyclohexadecane)-copper(II) perchlorate were prepared as previously described.[6,8–10] The pentahydrochloride salts of the free ligands 12-methyl-1,4,7,10-tetraazacyclotridecan-12-amine (L^{13}), 6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine (L^{14}), 10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine (L^{15}) and 3-methyl-1,5,9,13-tetraazacyclohexadecan-3-amine (L^{16}) were all prepared by a variation of the method previously described for L^{15}.[11] Equal amounts of aqueous solutions of the copper(II) complex of the precursor nitromacrocycle and 3 mol dm^{-3} HCl were added dropwise at equal rates to a constantly stirring excess of zinc dust on a heater-stirrer adjusted to maintain the reaction mixture at *ca.* 50 °C. Any significant concentration of unreduced complex was avoided in this way, assisted by further addition of zinc dust during the reaction if necessary. The final colourless solution was filtered to remove reduced copper and excess of zinc dust, diluted at least six-fold with water, and loaded onto a column (20 × 4 cm) of Dowex 50WX2 cation-exchange resin. The column was washed with 1 mol dm^{-3} HCl to remove zinc(II) ion, and when testing the eluate with hydroxide ion showed the absence of zinc ion, elution of the protonated ligand was achieved with 3–4 mol dm^{-3} HCl. The presence of the ligand in eluted fractions was monitored by the addition of aqueous copper ion and hydroxide ion to an aliquot, which in the presence of ligand produced a purple complex in solution which did not decolourize on addition of acid. The eluate was taken to dryness in a rotary evaporator, twice stirred with ethanol and taken to dryness, and finally stirred with diethyl ether and taken to dryness to yield a free-flowing white powder in each case. The purity of the hydrochloride salt was checked by ^{1}H and ^{13}C NMR spectroscopy, microanalysis and by the absence of a characteristic C=O resonance in the infrared spectrum known to exist for the by-product observed in the previous method of reduction.[11]

cis-*Chloro*(12-*methyl*-1,4,7,10-*tetraazacyclotridecan*-12-*amine*)*cobalt*(III) *perchlorate chloride*, [Co(L^{13})Cl][ClO$_4$]Cl. Reaction was carried out on a 2 mmol scale. An aqueous solution (100 cm^3) of L^{13}·5HCl and CoCl$_2$·6H$_2$O (1:1.1 molar ratio) was adjusted to pH 7 by the addition of 2.5 mol dm^{-3} aqueous NaOH. The resultant solution was aerated for *ca.* 2 h, then concentrated HCl (*ca.* 15 cm^3) was added with constant stirring. Activated charcoal (*ca.* 1 g) was added and the solution was left stirring for 12 h to permit hydrolysis of the brown peroxo intermediate, anation and equilibration of possible isomers. Finally the resultant red solution was filtered, diluted to *ca.* 1 dm^3, and loaded onto a 25 × 2 cm column of Dowex 50WX2 cation-exchange resin (H$^+$ form). After washing with 0.5–1.0 mol dm^{-3} HCl in order to remove unreacted cobalt(II) ion (present in slight excess in the reaction mixture), elution of the single band of the cobalt(III) cation was completed with 2–3 mol dm^{-3} HCl. Concentration of the eluate on a rotary evaporator to a small volume (*ca.* 10–20 cm^3) and addition of a small volume (*ca.* 3–5 cm^3) of 3 mol dm^{-3} HClO$_4$ yielded good-quality crystals of the product on standing for several days. These were collected, washed with ethanol, and air dried (yield 60%); further crops were obtained on standing the filtrate for extended periods (Found: C, 26.9; H, 6.1; N, 15.6. Calc. for C$_{10}$H$_{25}$Cl$_3$CoN$_5$O$_4$: C, 27.0; H, 5.7; N, 15.75%). Electronic spectrum (in water): λ_{max} 519 (ε 120), 459 (140) and 357 nm (140 dm^3 mol^{-1} cm^{-1}). NMR (D$_2$O): ^{1}H, δ 1.34 (s, 3 H) and 2.6–3.6 (m, 16 H); ^{13}C, δ 20.3, 49.45, 51.55, 52.5, 53.55, 54.4, 57.3 (×2), 62.4 and 67.8.

cis-*Chloro*(12-*methyl*-1,4,7,10-*tetraazacyclotridecan*-12-*amine*)*cobalt*(III) *tetrachlorocobaltate*(II), [Co(L^{13})Cl][CoCl$_4$]. This salt was prepared in a similar manner to the perchlorate salt above, except that a three-fold molar excess of cobalt(II) chloride was employed, and equilibration with charcoal was not employed. Chromatography on Dowex resin again identified a single product. The product crystallized readily in the presence of excess of cobalt(II) ion from a methanol and aqueous hydrochloric acid mixture as the tetrachlorocobaltate salt in a form suitable for X-ray structure determination.

cis- *and* trans-*Chloro*(6-*methyl*-1,4,8,11-*tetraazacyclotetradecan*-6-*amine*)*cobalt*(III) *perchlorate hemihydrate*, [Co(L^{14})Cl][ClO$_4$]$_2$·0.5H$_2$O. This complex was prepared in the manner described for the perchlorate salt of L^{13}. However, elution readily separated two bands, each collected and isolated as described above. *trans* Isomer: the first minor band yielded purple crystals on standing (yield < *ca.* 1%) (Found: C, 25.0; H, 5.2; N, 13.1. Calc. for C$_{11}$H$_{28}$Cl$_3$CoN$_5$O$_{8.5}$: C, 24.85; H, 5.3; N, 13.15%). Electronic spectrum (in water): λ_{max} 550 (ε 79), 450 (26) and 360 nm (87 dm^3 mol^{-1} cm^{-1}). NMR (D$_2$O): ^{1}H, δ 1.35 (s, 3 H) and 2.5–3.5 (m, 16 H); ^{13}C, δ 14.75, 23.3, 44.3, 49.8, 50.6, 57.3 and 63.6. *cis* Isomer: the second major band yielded red-purple crystals on standing (yield 45%) (Found: C, 25.2; H, 5.2; N, 13.0. Calc. for C$_{11}$H$_{28}$Cl$_3$CoN$_5$O$_{8.5}$: C, 24.85; H, 5.3; N, 13.15%). Electronic spectrum (in water): λ_{max} 525 (ε 92), 470 (94) and 365 nm (128 dm^3 mol^{-1} cm^{-1}). NMR (D$_2$O): ^{1}H, δ 1.35 (s, 3 H) and 2.4–3.4 (m, 16 H); ^{13}C, δ 19.8, 26.3, 48.4, 50.5, 52.3, 52.6, 55.4, 56.2, 57.2, 60.5 and 67.7.

cis-*Chloro*(10-*methyl*-1,4,8,12-*tetraazacyclopentadecan*-10-*amine*)*cobalt*(III) *perchlorate hemihydrate*, [Co(L^{15})Cl][ClO$_4$]$_2$·0.5H$_2$O. This complex was prepared in the manner described for the perchlorate salt of L^{13}, with chromatography separating a single band, from which crystals of X-ray quality were isolated (yield 40%); further complex separated on extended standing (Found: C, 26.5; H, 5.7; N, 12.8. Calc. for $C_{12}H_{30}Cl_3CoN_5O_{8.5}$: C, 26.4; H, 5.55; N, 12.85%). Electronic spectrum (in water): λ_{max} 540 (ε 125), 480 (sh, 87) and 368 nm (175 $dm^3 mol^{-1} cm^{-1}$). NMR (D_2O): ^1H, δ 1.36 (s, 3 H) and 2.2–3.4 (m, 16 H); ^{13}C, δ 18.4, 20.1, 23.3, 43.85, 45.1, 49.0, 51.8, 52.0, 53.95, 56.5, 58.4 and 61.8.

trans-*Chloro*(3-*methyl*-1,5,9,13-*tetraazacyclohexadecan*-3-*amine*)*cobalt*(III) *chloride perchlorate*, $[Co(L^{16})Cl][ClO_4]Cl$. Synthesis was performed as described for the perchlorate salt of L^{13}, with chromatography permitting isolation of a single major band. In some attempts at this synthesis additional minor bands were obtained, but were not reproducible in amount. They proved from spectroscopic characterization to arise from minor amounts of macrocyclic cleavage products.[11] The single band of the product yielded purple crystals on concentration and standing (yield *ca.* 20%); further product was obtained on extended standing (Found: C, 32.8; H, 6.8; N, 14.6. Calc. for $C_{13}H_{32}Cl_3CoN_5O_4$: C, 32.7; H, 6.4; N, 14.3%). Electronic spectrum (in water): λ_{max} 560 (ε 93) and 390 nm (121 $dm^3 mol^{-1} cm^{-1}$). NMR (D_2O): ^1H, δ 1.47 (s, 3 H) and 2.1–3.4 (m, 16 H); ^{13}C, δ 18.6, 22.0, 25.7 (× 2), 48.15, 52.0, 53.65, 59.45 and 67.4.

Physical Methods.—Electronic spectra of aqueous solutions were recorded using Hitachi 220A or 150–20 spectrophotometers, IR spectra using a Bio-Rad FTS-7 FT-IR spectrometer, with complexes dispersed in KBr discs, and ^1H and ^{13}C nuclear magnetic resonance spectra in D_2O using a JEOL FX90-Q spectrometer. Chemical shifts are cited *versus* tetramethylsilane, although sodium 3-trimethylsilylpropionate and dioxane were employed as internal standards for ^1H and ^{13}C NMR spectra respectively. Elemental microanalyses were performed by the Australian National University Microanalytical Service.

Structure Determinations.—Unique data sets were measured at *ca.* 295 K within the limit $2\theta_{max} = 50°$ using an Enraf-Nonius CAD-4 diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.7106_9$ Å; conventional 2θ–θ scan mode). N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values. Conventional residuals R, R' on $|F|$ at convergence are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed:[12] computation used the XTAL 3.0 program system[13] implemented by S. R. Hall. Pertinent results are given in Fig. 1 and Tables 1–4.

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

Crystal data. *cis*-$[Co(L^{13})Cl][CoCl_4]\cdot0.25MeOH = C_{10}H_{25}Cl_5Co_5N_5\cdot0.25MeOH$, $M = 518.5$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 15.682(8)$, $b = 14.864(2)$, $c = 8.938(4)$ Å, $\alpha = 96.32(4)$, $\beta = 97.34(6)$, $\gamma = 102.59(2)°$, $U = 1996$ Å^3, $D_c = 1.73$ g cm^{-3} ($Z = 4$), $F(000) = 1054$, $\mu_{Mo} = 22.2$ cm^{-1}. Specimen: 0.08 × 0.20 × 0.36 mm; $A^*_{min,max} = 1.17, 1.49$. $N = 6768$, $N_o = 4848$; $R = 0.050$, $R' = 0.059$.

cis-$[Co(L^{14})Cl][ClO_4]_2 = C_{11}H_{27}Cl_3CoN_5O_8$, $M = 522.7$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 9.856(4)$, $b = 17.36(2)$, $c = 12.08(1)$ Å, $\beta = 98.95(5)°$, $U = 2043$ Å^3, $D_c = 1.70$ g cm^{-3} ($Z = 4$), $F(000) = 984$, $\mu_{Mo} = 12.0$ cm^{-1}. Specimen: 0.45 × 0.58 × 0.60 mm; $A^*_{min,max} = 1.46, 1.63$. $N = 3574$, $N_o = 3035$; $R = 0.051$, $R' = 0.066$.

cis-$[Co(L^{15})Cl][ClO_4]_2\cdot H_2O = C_{12}H_{31}Cl_3CoN_5O_9$, $M = 554.7$, orthorhombic, space group $Pn2_1a$ (C_{2v}^9, no. 33), $a = 16.708(4)$, $b = 13.343(3)$, $c = 9.886(1)$ Å, $U = 2204$ Å^3, $D_c = 1.67$ g cm^{-3} ($Z = 4$), $F(000) = 1152$, $\mu_{Mo} = 11.2$ cm^{-1}. Specimen: 0.30 × 0.24 × 0.33 mm; $A^*_{min,max} = 1.21, 1.30$. $N = 1751$, $N_o = 1549$; $R = 0.037$, $R' = 0.042$ (preferred chirality).

Abnormal features. For *cis*-$[Co(L^{13})Cl][CoCl_4]$, difference-map artefacts located close to a centre of symmetry were modelled, after population refinement, as half-weighted components of a disordered methanol solvate species. No associated hydrogen atoms were located in difference maps. For *cis*-$[Co(L^{15})Cl][ClO_4]_2$ a difference-map artefact was included, after initial population refinement, as a fully populated oxygen atom, presumably a monohydrate. Associated hydrogen atoms were not located in difference maps. Perchlorate and tetrachlorocobaltate thermal motions are high and adversely affect the precision of the studies; thermal vibrational amplitudes are also high in the hydrocarbon strings of the macrocycles.

Results and Discussion

The series of saturated tetraazamacrocycles L^{13}–L^{16}, each with a single pendant primary amine attached directly to the ring as part of a common $NHCH_2CHMe(NH_2)CH_2NH$ unit, are obtained readily as hydrochloride salts following direct reduction of their nitro-substituted precursors with zinc in aqueous acid. The series are all potentially quinquedentate ligands, with various numbers of five- and six-membered chelate rings formed following co-ordination. From L^{13} to L^{16} the system changes chelate ring-size patterns for the co-ordinated macrocycle component from [5556] to [5656] to [6665] to [6666], while in each case the pendant primary amine co-ordination leads to a boat conformation for the 'cap' unit and two additional five-membered chelate rings. Syntheses of pentaaminechlorocobalt(III) complexes involving equilibration over activated charcoal isolated essentially a single geometric isomer in each case, with the *cis* geometry dominant for L^{13}, L^{14} and L^{15}, and a 'changeover' to *trans* geometry observed for L^{16}.

The less preferred isomer is detected only with L^{14}, and in that case the *trans* isomer is present to only approximately 2% in the equilibrated mixture. Previously, the related 14-membered macrocyclic ligand L^5 has been bound in a sexi-, quinque- and tetra-dentate manner to cobalt(III), with the *trans* geometry observed in the quinquedentate co-ordination mode,[5] surprisingly at variance with the result in this case. However, products in that study were not true thermodynamic products, since any attempts at equilibration can lead to conversion into the sexidentate complex with necessarily *trans* geometry.[5] Further, deliberate synthesis and characterization of *cis* isomers of L^5 has now been pursued.[14] Detection and characterization of both isomers of L^{14} in a ratio of *ca.* 2:98 for *trans*:*cis* indicates a preference for the *cis* isomer by *ca.* 10 kJ mol^{-1}. For the acyclic analogue L^4 the *trans* geometry is favoured in $[Co(L^4)Cl]^{2+}$, although a *cis* isomer was observed following halide substitution by thiocyanate.[4]

The *cis* isomers of the complexes $[Co(L^{13})Cl]^{2+}$, $[Co(L^{14})Cl]^{2+}$ and $[Co(L^{15})Cl]^{2+}$ were subjected to single-crystal X-ray structure analyses. Non-hydrogen atomic coordinates for the structures appear in Tables 1–3. Bond lengths and angles for the cobalt environments are compared in Table 4, and ligand torsion angles are compared in Table 5. Although the precision of the determinations is adversely affected by large thermal vibrational amplitudes (see above), some tentative conclusions may be proposed concerning trends in the cation parameters. The two cations (presented with opposite chiralities) present in the case of L^{13} do not differ greatly (Tables 4 and 5). The Co–N distances are variable with each compound (Table 4), but the average Co–N distance does increase with ring size from 1.94_8 (L^{13}) to 1.95_4 (L^{14}) to 1.98_1 Å (L^{15}). Notably, the Co–N(1) (pendant amine) distance is relatively constant, between 1.955(4) and 1.962(5) Å for all cases (including the 16-membered complex, which has *trans* geometry);[7] this constancy, despite the variable macrocycle size, is maintained at the cost of other distortions in the facial capping unit, for example N(3a)–

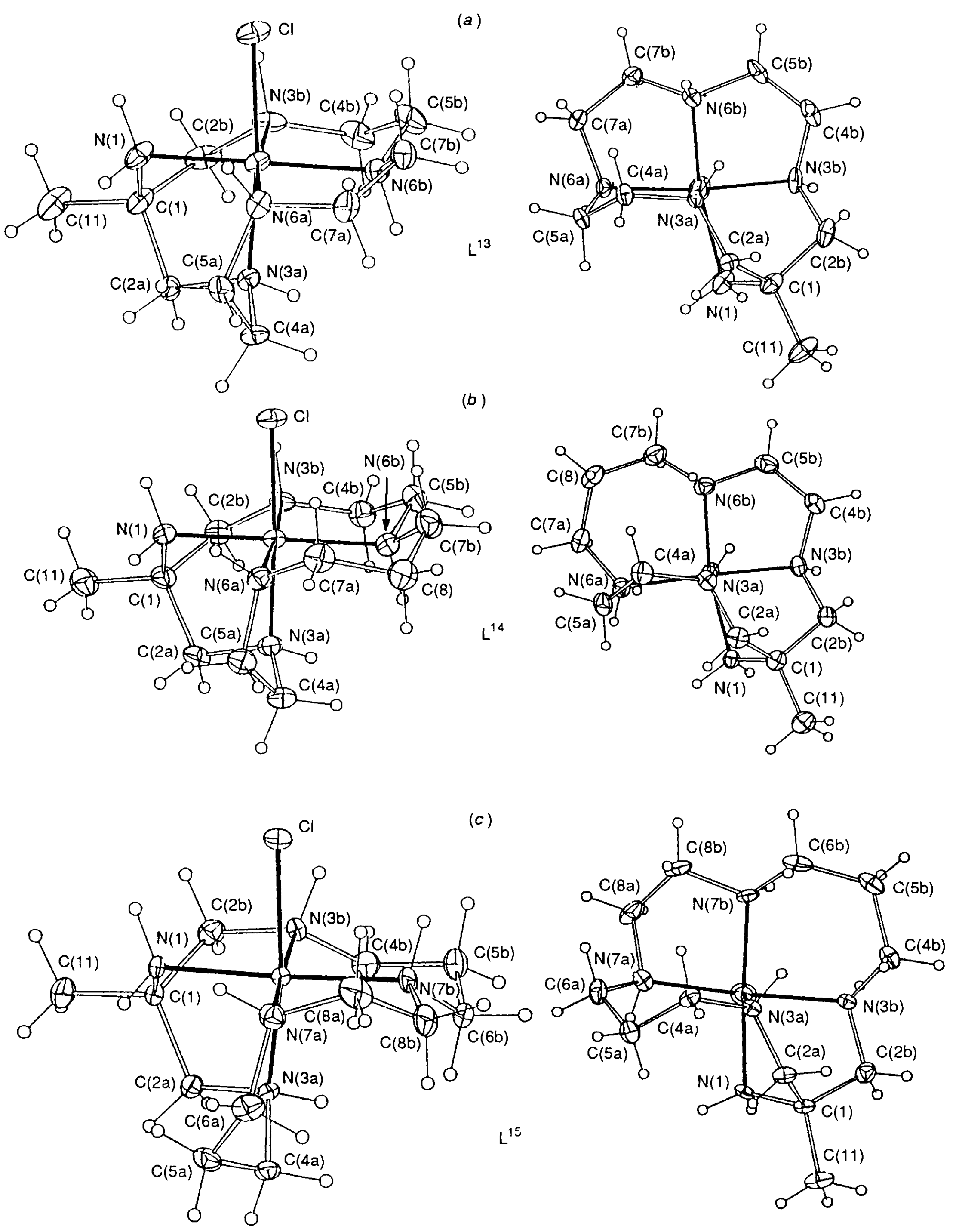


Fig. 1 Projections of the cations (*a*) $[Co(L^{13})Cl]^{2+}$, (*b*) $[Co(L^{14})Cl]^{2+}$ and (*c*) $[Co(L^{15})Cl]^{2+}$ (20% thermal ellipsoids are shown for the non-hydrogen atoms whereas hydrogen atoms have arbitrary radii of 0.1 Å)

Co–N(3b) angles diminish consistently with increasing ring size [92.3(3), 91.0(2), 86.7(2), 79.5(3)° from 13- through to 16-membered[7] ring].

Examination of Table 4 shows some distortion of the CoN_5O octahedron, with the N(1)–Co–N(6b) axis being deformed toward a line joining the atoms N(3a) and N(3b). Distortion is similar for L^{13} and L^{14} [169.2(3), 167.4(2)° respectively] but is much relieved for the larger L^{15} [176.6(3)°]. Tied to this distortion is the observation that the N–Co–N angles in the five-membered rings formed by co-ordination of the pendant amines are all close to 84°. There is considerable strain in the angles C(2a)–N(3a)–C(4a) and C(2b)–N(3b)–C(4b), both being as high as 118(1)° for L^{13} and L^{14}, but falling to near 111(1)° for L^{15}. It can be seen that this is consequent upon co-ordination of the pendant primary amines which 'pull' the C(2a) and C(2b) atoms toward the metal centre and hence open the angles at the adjacent co-ordinated secondary amines. There is less strain in the other five-membered chelate rings, with angles [*e.g.* N(3a)–C(4a)–C(5a) and C(4a)–C(5a)–N(6a)] close to 109°. The angle formed at the pendant primary amine, C(1)–N(1)–Co [100.3(5), 101.4(3) and 100.6(9)° for L^{13}, L^{14} and L^{15} in turn], is quite small compared with an ideal tetrahedral geometry. To relieve this strain either the axial Co–N bond must be shortened or the N(3a)–Co–N(3b) angle contracted even more. Bond compression requires more energy than bond angle deformation, and intraligand non-bonded interactions may

Table 1 Non-hydrogen positional coordinates for $[Co(L^{13})Cl][CoCl_4]\cdot 0.25MeOH$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cation 1				Cation 2			
Co(1)	0.926 63(7)	0.293 70(7)	0.331 9(1)	Co(1′)	0.405 25(7)	0.175 01(7)	0.700 6(1)
Cl(1)	1.042 9(1)	0.354 7(2)	0.515 8(2)	Cl(1′)	0.380 9(1)	0.019 2(1)	0.680 8(2)
C(1)	0.862 4(6)	0.415 2(5)	0.180 5(9)	C(1′)	0.278 6(5)	0.247 2(6)	0.804 2(9)
C(11)	0.833 4(7)	0.504 1(6)	0.151(1)	C(11′)	0.186 1(6)	0.255 9(7)	0.826(1)
N(1)	0.890 6(5)	0.412 2(4)	0.344 7(7)	N(1′)	0.277 2(4)	0.163 2(5)	0.689 8(7)
C(2a)	0.786 3(5)	0.331 1(5)	0.136 2(9)	C(2a′)	0.324 8(6)	0.327 3(6)	0.730(1)
N(3a)	0.818 0(4)	0.249 0(4)	0.183 3(6)	N(3a′)	0.412 2(4)	0.310 0(4)	0.701 2(7)
C(4a)	0.751 5(5)	0.184 6(5)	0.252 8(9)	C(4a′)	0.435 3(6)	0.337 0(5)	0.550 6(9)
C(5a)	0.768 0(5)	0.211 9(6)	0.423 5(9)	C(5a′)	0.400 7(5)	0.252 1(6)	0.430 6(9)
N(6a)	0.864 0(4)	0.226 5(4)	0.475 1(6)	N(6a′)	0.425 2(4)	0.170 9(4)	0.487 9(7)
C(7a)	0.891 3(6)	0.136 2(6)	0.486(1)	C(7a′)	0.520 0(5)	0.170 3(6)	0.480 4(9)
C(2b)	0.941 2(6)	0.405 1(6)	0.099 8(9)	C(2b′)	0.333 1(6)	0.236 2(6)	0.953 2(9)
N(3b)	0.992 7(4)	0.347 9(5)	0.183 0(7)	N(3b′)	0.400 9(4)	0.185 1(4)	0.916 6(7)
C(4b)	1.020 0(6)	0.272 4(7)	0.092(1)	C(4b′)	0.492 4(5)	0.220 4(6)	0.997 1(9)
C(5b)	1.042 7(6)	0.207 2(7)	0.200(1)	C(5b′)	0.550 7(5)	0.173 6(6)	0.906 6(9)
N(6b)	0.965 0(4)	0.181 3(4)	0.280 4(7)	N(6b′)	0.531 2(4)	0.194 7(4)	0.750 4(7)
C(7b)	0.974 9(6)	0.136 1(6)	0.416 2(9)	C(7b′)	0.563 5(5)	0.144 4(6)	0.626 7(9)
Anions							
Co(3)	0.728 57(7)	0.476 35(7)	0.675 6(1)	Co(4)	0.774 61(6)	0.010 51(6)	−0.152 1(1)
Cl(31)	0.746 8(2)	0.629 0(2)	0.742 6(3)	Cl(41)	0.626 8(1)	−0.037 8(2)	−0.155 3(2)
Cl(32)	0.662 3(2)	0.424 4(2)	0.430 7(3)	Cl(42)	0.815 8(2)	−0.071 0(2)	−0.345 0(2)
Cl(33)	0.638 2(2)	0.406 8(2)	0.834 8(3)	Cl(43)	0.842 0(2)	−0.011 0(2)	0.079 2(2)
Cl(34)	0.858 9(2)	0.433 3(2)	0.709 5(3)	Cl(44)	0.805 2(2)	0.165 8(1)	−0.169 2(2)
Solvent							
C*	0.470(2)	0.454(2)	0.024(4)	O*	0.485(1)	0.434(1)	0.185(2)

* Population = 0.5.

Table 2 Non-hydrogen positional coordinates for $[Co(L^{14})Cl][ClO_4]_2$

Atom	*x*	*y*	*z*
Co	0.794 66(6)	0.445 46(3)	0.809 68(4)
Cl	0.816 7(1)	0.540 0(7)	0.936 7(1)
C(1)	1.007 4(5)	0.347 9(3)	0.817 7(4)
N(1)	0.993 7(4)	0.433 6(2)	0.822 9(3)
C(11)	1.153 3(6)	0.320 8(3)	0.828 0(5)
C(2a)	0.925 5(5)	0.328 0(3)	0.703 8(4)
N(3a)	0.787 4(4)	0.365 2(2)	0.695 1(3)
C(4a)	0.735 7(6)	0.401 1(3)	0.584 2(4)
C(5a)	0.794 0(6)	0.480 4(3)	0.582 4(4)
N(6a)	0.780 4(4)	0.521 2(2)	0.688 3(3)
C(7a)	0.664 9(6)	0.578 8(3)	0.679 9(4)
C(8)	0.524 2(6)	0.542 8(4)	0.681 6(5)
C(2b)	0.937 8(5)	0.317 8(3)	0.914 4(4)
N(3b)	0.820 2(4)	0.368 7(2)	0.927 6(3)
C(4b)	0.686 8(5)	0.331 9(3)	0.936 8(4)
C(5b)	0.581 1(5)	0.394 3(3)	0.916 9(4)
N(6b)	0.596 9(4)	0.434 5(2)	0.810 6(3)
C(7b)	0.510 1(6)	0.505 8(4)	0.792 3(5)
Cl(1)	1.138 5(1)	0.605 72(7)	0.721 1(1)
O(11)	1.235 9(4)	0.657 9(2)	0.694 0(4)
O(12)	1.149 5(6)	0.531 8(3)	0.677 2(4)
O(13)	1.152(1)	0.597 1(5)	0.829 9(5)
O(14)	1.016 1(6)	0.633 4(4)	0.687(1)
Cl(2)	0.415 1(1)	0.283 45(8)	0.603 0(1)
O(21)	0.450 5(5)	0.275 8(3)	0.495 9(4)
O(22)	0.379 6(6)	0.362 4(3)	0.616 2(4)
O(23)	0.306 5(6)	0.235 0(3)	0.617 9(5)
O(24)	0.531 5(6)	0.268 8(4)	0.683 9(5)

Table 3 Non-hydrogen positional coordinates for $[Co(L^{15})Cl][ClO_4]_2\cdot H_2O$

Atom	*x*	*y*	*z*
Co	0.412 60(5)	0.000 00*	0.814 97(9)
Cl	0.540 9(1)	0.054 9(2)	0.833 7(2)
C(1)	0.375 1(4)	−0.101 7(6)	1.037 7(7)
C(11)	0.363 6(6)	−0.124 4(8)	1.189 0(9)
N(1)	0.404 4(3)	0.000 8(6)	1.013 0(5)
C(2a)	0.295 9(4)	−0.107 0(6)	0.963 1(8)
N(3a)	0.303 7(3)	−0.058 2(5)	0.828 1(6)
C(4a)	0.233 3(4)	0.007 1(7)	0.797 7(7)
C(5a)	0.238 7(4)	0.106 5(7)	0.869 6(8)
C(6a)	0.294 5(5)	0.177 4(6)	0.796 4(9)
N(7a)	0.379 6(4)	0.142 7(5)	0.784 2(7)
C(8a)	0.413 5(6)	0.170 8(8)	0.651(1)
C(2b)	0.438 1(5)	−0.169 2(6)	0.977 2(9)
N(3b)	0.453 3(3)	−0.138 7(4)	0.835 7(6)
C(4b)	0.427 2(5)	−0.217 8(6)	0.740 3(9)
C(5b)	0.440 8(5)	−0.188 5(8)	0.592(1)
C(6b)	0.397 8(5)	−0.095 9(9)	0.546 5(9)
N(7b)	0.425 9(3)	−0.006 8(6)	0.616 8(6)
C(8b)	0.394 3(6)	0.087 1(9)	0.558(1)
Cl(1)	0.161 2(1)	−0.263 4(2)	0.685 0(2)
O(11)	0.104 1(3)	−0.266 3(5)	0.578 8(7)
O(12)	0.231 4(3)	−0.215 0(6)	0.639 0(6)
O(13)	0.180 0(4)	−0.364 4(5)	0.720 6(7)
O(14)	0.128 0(4)	−0.212 0(6)	0.797 9(7)
Cl(2)	0.088 9(1)	−0.018 7(2)	1.192 2(3)
O(21)	0.039 2(6)	0.033 9(7)	1.274(1)
O(22)	0.073 7(7)	−0.023(2)	1.066(1)
O(23)	0164 3(4)	0.009(2)	1.208(1)
O(24)	0.077(1)	−0.112(1)	1.239(2)
O	0.198 1(4)	0.119 9(6)	0.465 0(7)

* Defines origin.

dominate both of these factors.[15] In this case it is apparent that deformation of the C(1)–N(1)–Co angles shared to some degree by a reduction of the *cis* N(3a)–Co–N(3b) angles results in the smallest increase in strain energy, although this is tied to slightly 'contracted' co-ordination spheres compared with 'usual' systems at least for the smaller ring sizes.

The sexidentate cobalt(III) complex of L^5 has a 'cap' geometry similar to that observed in this series of complexes, except that the two 'caps' in that molecule lie in a *trans* disposition.[5] The very short Co–N distances in that molecule [1.946(2) Å for the pendant amine, average 1.937(2) Å for the secondary amines] are reflected in extreme physical properties, such as a very negative redox potential and a shift in electronic maxima to high energy. Distances in the 14-membered macrocycle analogue L^{14} in this case are longer [1.955(4) Å for the pendant amine, average 1.953(4) Å for the secondary amines], presumably because the steric demands of a molecule with a single 'cap' are reduced, but still shorter than typical distances for *cis* and *trans* cobalt(III) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) [1.986(7)–2.016(6) Å][16,17] and from average distances in $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine) of 1.964(7) Å.[5] The apparently 'compressed' geometry in $[Co(L^5)]^{3+}$ is a consequence of a sterically efficient ligand; clearly, the same 'compression' observed here in the single-pendant analogue arises in the same manner. The smaller ring ligand L^{13} [Co–N(pendant) 1.963(7), average Co–N (secondary) 1.944(6) Å] also exhibits shorter bonds, whereas with the larger ring L^{15} distances [Co–N(pendant) 1.962(5), average Co–N(secondary) 1.986(14) Å] are, except for the pendant, more comparable with other polyaminecobalt(III) complexes. Although it does not exhibit a *cis* geometry, it is notable that Co–N distances for the macrocycle nitrogens are even longer with the 16-membered macrocycle, whereas the pendant amine distance is similar.[7]

Table 4 Cobalt environments (distances in Å, angles in °) for $[Co(L^n)Cl]^{2+}$ (n = 13, 14 or 15)

	n = 13	13′	14	15
Co–Cl	2.244(2)	2.246(2)	2.236(2)	2.273(2)
Co–N(1)	1.959(7)	1.966(7)	1.955(4)	1.962(5)
Co–N(3a)	1.961(5)	1.986(6)	1.957(4)	1.982(6)
Co–N(6a)	1.943(6)	1.963(6)	1.958(4)	2.005(7)
Co–N(3b)	1.929(7)	1.931(6)	1.938(4)	1.982(6)
Co–N(6b)	1.925(7)	1.918(6)	1.960(4)	1.974(6)
Cl–Co–N(1)	90.9(2)	88.9(2)	91.9(1)	89.0(2)
Cl–Co–N(3a)	173.7(2)	172.8(2)	175.9(1)	170.6(2)
Cl–Co–N(6a)	90.5(2)	90.7(2)	90.5(1)	88.0(2)
Cl–Co–N(3b)	90.2(2)	91.3(2)	90.7(1)	88.2(2)
Cl–Co–N(6b)	94.0(2)	94.0(2)	93.3(1)	89.4(2)
N(1)–Co–N(3a)	83.9(3)	85.1(3)	84.7(2)	82.7(2)
N(1)–Co–N(6a)	104.2(3)	104.6(3)	94.9(2)	97.3(3)
N(1)–Co–N(3b)	82.1(3)	82.1(3)	81.6(2)	85.8(3)
N(1)–Co–N(6b)	169.1(3)	169.4(3)	167.4(2)	176.6(3)
N(3a)–Co–N(6a)	87.3(2)	86.9(3)	87.6(2)	97.4(3)
N(3a)–Co–N(3b)	92.7(3)	91.9(3)	91.0(2)	86.7(2)
N(3a)–Co–N(6b)	91.7(3)	92.6(3)	90.5(2)	98.6(3)
N(6a)–Co–N(3b)	173.6(3)	173.0(2)	176.3(2)	175.1(3)
N(6a)–Co–N(6b)	85.5(3)	85.6(3)	96.5(2)	85.6(3)
N(3b)–Co–N(6b)	88.1(3)	87.6(3)	86.8(2)	91.2(3)

When n = 15, for N(6a) or N(6b) read N(7a) or N(7b)

For complexes crystallized from equilibrated solutions, in all three *cis* structures with 13-, 14- and 15-membered rings, and also in the 14- and 16-membered ring structures which are *trans*,[7] the secondary nitrogens adopt *RRSS* stereochemistries. From earlier studies with folded and flat cyclam alone[18] these configurations are known to be some of the most stable. Binding of the $NHCH_2CMe(NH_2)CH_2NH$ unit to an octahedral face can occur with only *RS* stereochemistry for the two secondary nitrogens involved for *trans* and only *SS*(*RR*) for the *cis* geometry respectively, limiting possible overall nitrogen configurations in each case. Although configurations other than *RRSS* have been observed with folded substituted cyclams, for example the 13-amino-13-methyl-1,4,8,11-tetraazacyclotetradecane-6-carboxylic acid has been isolated as a chloropentaaminecobalt(III) ion with *RRRR* stereochemistry at the secondary nitrogens,[19] these have arisen from solutions which have not been equilibrated (usually because equilibration leads to sexi- rather than quinque-dentate co-ordination), and the isolated compounds may not represent the thermodynamically favoured isomer.

It is notable that co-ordination of 6-methyl-1,11-dithia-4,8-diazacyclotetradecan-6-amine (L^{17}), the dithioether analogue of L^{14}, has been defined around cobalt(III) with a parallel quinquedentate *cis* geometry,[20] and with acetate ion in the sixth co-ordination site. Despite the inherently longer Co–S distances, the Co–N distances in the $NHCH_2CMe(NH_2)CH_2NH$ cap are essentially the same in the thioether and polyaza molecules {Co–N(1) 1.946(7) [1.955(4) for pentaamine]; Co–N(3a) 1.937(7) [1.957(4)]; Co–N(3b) 1.950(7) [1.938(4)] Å}. The N(1)–Co–S angle [167.9(3)°] is very similar to N(1)–Co–N(6b) [167.4(2)°], identifying comparable distortion of the octahedron upon co-ordination of the pendant amine. Structurally the azathioether and aza macrocycles are very similar; replacement of the two secondary amines of *RR* configuration by thioether donor occurs with effective retention of the stereochemistry, and the major difference lies only in the geometry of the $S(NH)(CH_2)_3S(NH)$ chelate ring which varies from a chair (aza macrocycle) to a skew boat (azathioether macrocycle),[20] possibly an influence of the longer Co–S bonds. Electronic spectroscopy of the tetragonally distorted molecules is not particularly revealing due to splitting under the

Table 5 Ligand torsion angles (°) for $[Co(L^n)Cl]^{2+}$ (n = 13, 14 or 15). Where two values are found in each entry, they are for sections a and b

	n = 13	13′	14	15
Co–N(1)–C(1)–C(2)	62.5(7), −55.2(6)	−62.8(6), 55.4(6)	60.0(4), −57.2(3)	−60.3(7), 58.7(6)
N(1)–C(1)–C(2)–N(3)	−52.9(8), 30.3(7)	55.7(7), −30.4(8)	−50.9(5), 34.3(4)	43(1), −53(1)
C(1)–C(2)–N(3)–Co	17.4(7), 10.2(7)	−20.6(7), −10.4(7)	17.0(4), 5.0(4)	−4(2), 19(1)
C(1)–C(2)–N(3)–C(4)	138.4(6), 133.9(7)	−140.9(6), −134.4(7)	138.4(4), 131.8(4)	−136(1), −114(1)
C(2)–N(3)–C(4)–C(5)	−92.4(7), −161.7(6)	91.2(8), 163.7(7)	−84.5(5), −164.6(4)	79(1), 179.1(9)
Co–N(3)–C(4)–C(5)	28.7(8), −37.4(7)	−28.2(8), 38.7(7)	37.4(5), −37.5(4)	−47.7(8), 53.5(9)
N(3)–C(4)–C(5)–N,C(6)	−46.6(9), 52.7(8)	46.8(9), −54.7(8)	−46.0(6), 51.5(5)	79(1), −60(1)
C(4)–C(5)–N,C(6)–C,N(7)	−79.4(8), −166.2(6)	77.8(8), 168.1(6)	−102.2(5), −171.2(4)	−61(1), 65(1)
C(4)–C(5)–N(6)–Co	42.1(7), −42.6(7)	−42.6(7), 44.5(6)	32.0(5), −40.9(5)	
C(5)–C(6)–N(7)–Co				16(1), −61.8(9)
C(5)–C(6)–N(7)–C(8)				142(1), 170.4(7)
C(5)–N(6)–C(7)–C(8)			79.3(6), −177.5(4)	
C(6)–N(7)–C(8)–C(8)				89(2), 169.4(7)
Co–N(6)–C(7)–C(8)			−50.7(5), 58.1(5)	
Co–N(7)–C(8)–C(8)				46.5(9), 36.4(9)
N(6)–C(7)–C(7)–N(6)	−39.5(7)	41.6(8)		
N(6)–C(7)–C(8)–C(7)			66.9(6), −69.7(6)	
N(7)–C(8)–C(8)–N(7)				−55(1)
Co–N(6)–C(7)–C(7)	14.6(7), 47.0(6)	−16.8(7), −48.0(7)		
C(5)–N(6)–C(7)–C(7)	135.1(7), 169.6(6)	−136.1(7), −171.1(6)		

Table 6 Comparative physical properties of pentaaminechlorocobalt(III) complexes

Complex[a]	Electronic spectrum λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	Average bond length/Å		Base-hydrolysis rate constant k_{OH}^{298}/dm^3 mol^{-1} s^{-1}	Ref.
		Co–N	Co–Cl		
$[Co(NH_3)_5Cl]^{2+}$	534 (50), 364 (47)	1.973	2.286	1.6	21
χ-[Co(en)(dien)Cl]$^{2+}$	518 (86), 488 (84), 366 (88)	1.960	2.268	3 000	22
π-[Co(en)(dien)Cl]$^{2+}$	525 (67), 475 (44), 361 (71)	1.968	2.249	27	22
αβ-[Co(L^2)Cl]$^{2+}$	525 (99), 480 (101), 360 (107)	1.97	2.271	3 500	1
cis-[Co(L^4)Cl]$^{2+}$	518 (87), 450 (51), 357 (100)	1.943	2.261	2.4	4
cis-[Co(L^{13})Cl]$^{2+}$	519 (120), 459 (140), 357 (140)	1.948	2.245	4 300	*b*
cis-[Co(L^{14})Cl]$^{2+}$	525 (92), 470 (94), 365 (128)	1.954	2.236	76	*b*
trans-[Co(L^{14})Cl]$^{2+}$	550 (79), 450 (26), 360 (87)	1.961	2.244	9 100	*b*,7
cis-[Co(L^{15})Cl]$^{2+}$	540 (125), 480(sh) (87), 368 (175)	1.975	2.273	6 700	*b*
trans-[Co(L^{16})Cl]$^{2+}$	560 (93), 390 (121)	2.010	2.222	11 100	*b*,7

[a] dien = Diethylenetriamine = 3-azapentane-1,5-diamine. [b] This work.

$^1A_{1g} \longrightarrow {}^1T_{1g}$ envelope, although the higher-energy transition to the $^1T_{2g}$ level which is not split shows a shift in maximum to higher energy which correlates very modestly with Co–N distance, being at higher energy for L^{13} and L^{14} complexes than for L^{15}. A comparison of some physical data for selected pentaaminechlorocobalt(III) complexes appears in Table 6. It is notable from these data that relatively short Co–N distances are associated with complexes with the $HNCH_2CMe(NH_2)$-CH_2NH 'cap' bound to an octahedral face of cobalt(III). This is even true for the pentaaminechloro complex of the acyclic L^4 ligand.[4]

Base-hydrolysis rate constants determined at 25 °C for the series of complexes are also included in Table 6. For pentaaminechlorocobalt(III) ions it was observed earlier[4] that hydrolysis of the L^4 complex was slow in comparison with other systems,[1,2,4,21,22] and it was proposed that this may arise from the relatively short Co–Cl bond. This implied that ground-state control of hydrolysis is important. Comparison of quite disparate ligand systems is not exceptionally reliable, since k_{OH} is sensitive to the nature and disposition of polyamine ligands,[23] but the current series of related compounds offer a more telling test of this concept. It is apparent that the trend in k_{OH} with macrocycle ring size for the structurally related series of *cis* isomers [4300 (L^{13}), 76 (L^{14}), 6700 (L^{15}) dm^3 mol^{-1} s^{-1}] follows the trend in Co–Cl bond length [2.245(2) (L^{13}), 2.236(2) (L^{14}), 2.273(2) Å (L^{15})], with the shortest Co–Cl distance being tied to the slowest base-hydrolysis rate constant. This suggests a strong influence of the ground state on the reaction. More detailed analysis of the hydrolysis kinetics is included in the following paper.[7] Base hydrolysis of [Co(L^{17})Cl]$^{2+}$, the thioether analogue of [Co(L^{14})Cl]$^{2+}$, occurs [k_{OH} 1080 dm^3 mol^{-1} cm^{-1} at 25 °C] approximately fifteen-fold faster than that observed for the L^{14} complex, an effect attributed to the influence of the thioether donors.[20]

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