# Quinquedentate Co-ordination of Amino-substituted Tetraazacycloalkanes to Cobalt(III). Part 3.† Synthesis of an Unsymmetric Ligand and Crystal Structure of its cis-Chlorocobalt(III) Complex‡

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The unsymmetric pendant-arm macrocycle 9-methyl-9-nitro-1,4,7,11-tetraazacyclotetradecane ($L^1$) was prepared by a copper(II)-directed condensation of 3,6-diazanonane-1,9-diamine with nitroethane and formaldehyde. Reduction of the copper(II) complex of $L^1$ with zinc in aqueous acid produced the new potentially quinquedentate polyamine 9-methyl-1,4,7,11-tetraazacyclotetradecan-9-amine ($L^2$). Reaction of $L^2$ in water with cobalt(II) ion and air, followed by aqueous hydrochloric acid and equilibration with activated charcoal, yielded exclusively cis-$[CoL^2(Cl)][ClO_4]_2$, which crystallized in the monoclinic space group $P2_1/c$, with $a = 12.745(5)$, $b = 11.438(5)$, $c = 14.414(8)$ and $\beta = 104.80(3)°$. 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. The average Co–N distance is $1.96_0$ Å, and the Co–Cl distance is 2.252(1) Å. Stereoretentive base hydrolysis ($k_{OH}$ 9100 dm³ mol⁻¹ s⁻¹) and other structural and physical properties are compared with those of the symmetric analogue 6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine.

Recently, we reported cobalt(III) complexes of a new type of quinquedentate branched-chain ligand, 1,5,9-triamino-5-methyl-3,7-diazanonane, which contains a $-NHCH_2C(CH_3)-(NH_2)CH_2NH-$ component in the chain capable of co-ordinating only to the face of an octahedron.[1] Related quinquedentate ligands based on a macromonocycle with a single pendant arm were developed later. Reaction of linear tetraamines $H_2N-(CH_2)_nNH(CH_2)_mNH(CH_2)_nNH_2$ ($n = m = 2$; $n = 2$, $m = 3$; $n = 3$, $m = 2$; or $n = m = 3$) as the copper(II) complexes in basic solution with nitroethane and formaldehyde produces macromonocyclic complexes with a pendant nitro group.[2,3] Reduction with zinc in aqueous acid yields analogous macrocycles, now with a pendant primary amino group.[4] All examples reported to date have some symmetry, and it was of interest to investigate an unsymmetrical analogue. We now report copper(II)-directed syntheses based on $H_2N(CH_2)_2NH(CH_2)_2NH-(CH_2)_3NH_2$, which leads to the unsymmetrically substituted tetraazacyclotetradecane ($L^1$, as the nitro pendant, and $L^2$ as the amine pendant), and comparison with the symmetric analogues ($L^3$ and $L^4$).[3,4] Details of the co-ordination of the new potentially quinquedentate ligand $L^2$ to cobalt(III) are presented. Synthesis, spectroscopic properties, base hydrolysis, and an X-ray crystal structure analysis of the cis-$[CoL^2(Cl)]-[ClO_4]_2$ isomer is reported herein.

## Experimental

Syntheses.—Preparations of (6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane)copper(II) perchlorate and chloro(6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine)cobalt(III) perchlorate have been described previously.[3,4]

L¹  X = O
L²  X = H

L³  X = O
L⁴  X = H
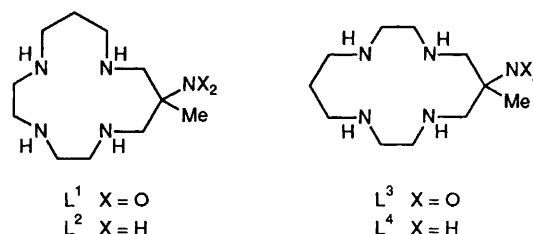
3,6-Diazanonane-1,9-diamine.—Essentially the previously described method was employed.[5] 3-Azapentane-1,5-diamine (0.3 mol) and $CH_2=CHCN$ (0.2 mol) were dissolved and refluxed in toluene overnight, then concentrated to an oil. Reduction was achieved by slow addition (2 h) of a dry ethanolic solution (40 cm³) of the crude nitrile to sodium (15 g) in toluene (60 cm³), followed by slow addition of ethanol (20 cm³) and methanol (20 cm³). After standing, the solution was treated with concentrated HCl (60 cm³), filtered, and the solution taken to dryness. After treatment with concentrated NaOH in excess the solvent was removed, the residue extracted with hot toluene, the solvent removed again, and the product collected following distillation under vacuum [b.p. 140–145 °C, 9 mmHg (ca. 1200 Pa)]. ¹³C NMR ($D_2O$): δ 32.8, 39.9, 41.2, 47.8, 48.9 (× 2) and 52.0.

(9-Methyl-9-nitro-1,4,7,11-tetraazacyclotetradecane)-copper(II) perchlorate, $[CuL^1][ClO_4]_2$. The copper(II) complex of 3,6-diazanonane-1,9-diamine was prepared by addition of an equimolar amount of copper(II) perchlorate (6.9 g) dissolved in methanol to a methanolic solution of the free ligand (3 g), and precipitated by addition of diethyl ether. The collected complex was redissolved in methanol (300 cm³), and nitroethane (1.5 g), formaldehyde (6 cm³, 38% aqueous) and triethylamine (2 cm³) were added. Following heating and stirring for ca. 2 h, the solution was diluted with distilled water and loaded onto a column of SP-Sephadex C-25 (Na⁺ form) resin. Elution with

0.2 mol dm$^{-3}$ NaClO$_4$ removed one major acid-stable band, as well as a band corresponding to starting material. The former was concentrated by rotary evaporation, and yielded (*ca.* 50%) a blue-purple solid on standing (Found: C, 25.3; H, 4.8; N, 13.3. Calc. for C$_{11}$H$_{25}$Cl$_2$CuN$_5$O$_{10}$: C, 25.3; H, 4.8; N, 13.4%). Electronic spectrum (water): $\lambda_{max}$ 554 nm ($\varepsilon$ 166 dm$^3$ mol$^{-1}$ cm$^{-1}$). $E_{\frac{1}{2}}$ $-0.78$ (Cu$^{II}$–Cu$^I$, irreversible) and $-1.10$ V (–NO$_2$, irreversible) (*vs.* Ag–AgCl).

9-*Methyl*-1,4,7,11-*tetraazacyclotetradecan*-9-*amine penta-hydrochloride*, L$^2$·5HCl. The pentahydrochloride salt of the free ligand L$^2$ was prepared by a variation[4] of the method previously described[6] for analogues. The purity of the hydrochloride salt was checked by $^1$H and $^{13}$C NMR spectroscopy, and by the absence of a characteristic C=O resonance in the infrared spectrum known to exist for the by-product observed in the earlier method of reduction.[6]

cis-*Chloro*-(9-*methyl*-1,4,7,11-*tetraazacyclotetradecan*-9-*amine*)*cobalt*(III) *perchlorate*, cis-[CoL$^2$(Cl)][ClO$_4$]$_2$. Reaction was carried out on a 2 mmol scale. An aqueous solution (100 cm$^3$) of L$^2$·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 to stir for 12 h. Finally the resultant red solution was filtered, diluted to *ca.* 1 cm$^3$, 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 two bands (a 2+ and a 3+ complex) was completed with 2–3 mol dm$^{-3}$ HCl. Concentration of the eluates on a rotary evaporator to a small volume (*ca.* 10–20 cm$^3$) gave two solutions which were spectroscopically identical, consistent with anation of an aqua complex to produce a chloro complex in the case of the 3+ band, 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 40%); further crops were obtained on standing the filtrate for extended periods (Found: C, 25.5; H, 5.3; N, 13.4. Calc. for C$_{11}$H$_{27}$Cl$_3$CoN$_5$O$_8$: C, 25.3; H, 5.2; N, 13.4%). Electronic spectrum (in water): $\lambda_{max}$ 530 ($\varepsilon$ 92), 455 (sh, 20) and 362 nm (98 dm$^3$ mol$^{-1}$ cm$^{-1}$). NMR (D$_2$O): $^1$H, $\delta$ 1.39 (s, 3 H) and 2.4–3.5 (m, 16 H); $^{13}$C, $\delta$ 21.9, 31.1, 52.9, 55.3, 57.2 (× 2), 58.6, 60.2, 64.7, 65.9 and 67.4.

*Physical Methods.*—Electronic spectra of aqueous solutions were recorded using an Hitachi 150-20 spectrophotometer, IR spectra using a Bio-Rad FTS-7 FT-IR spectrometer with complexes dispersed in KBr discs and $^1$H and $^{13}$C nuclear magnetic resonance spectra, with chemical shifts cited *versus* tetramethylsilane, in D$_2$O using a JEOL FX90-Q spectrometer. Elemental microanalyses were performed by the Australian National University Microanalytical Service. Kinetics of base hydrolysis were determined using buffers as previously described.[4]

*Structure Determination of* [CoL$^2$(Cl)][ClO$_4$]$_2$.—A unique data set was measured at *ca.* 295 K to $2\theta_{max} = 50°$ [Syntex P2$_1$ diffractometer, monochromatic Mo-K$\alpha$ radiation ($\lambda = 0.7107_3$ Å), $2\theta$–$\theta$ scan mode]. 3605 Independent reflections were obtained, 2903 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction, and after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U_{iso})$ were refined for all hydrogen atoms. Conventional residuals $R,R'$ on $|F|$ were 0.032, 0.037 [statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]. Neutral atom complex scattering factors were employed;[7] computation used the XTAL 3.0 program system[8] implemented by S. R. Hall. Pertinent results are given in Fig. 1 and Tables 1–3.

*Crystal data.* C$_{11}$H$_{27}$Cl$_3$CoN$_5$O$_8$, $M = 522.6$, monoclinic, space group $P2_1/c$ ($C^5_{2h}$, no. 14), $a = 12.745(5)$, $b = 11.438(5)$, $c = 14.414(8)$ Å, $\beta = 104.80(3)°$, $U = 2032$ Å$^3$, $D_c = 1.71$ g cm$^{-3}$ ($Z = 4$), $F(000) = 1080$, $\mu_{Mo} = 12.1$ cm$^{-1}$. Specimen: 0.44 × 0.28 × 0.42 mm; $A^*_{min,max} = 1.24, 1.58$. $N = 3605$, $N_o = 2903$.

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

## Results and Discussion

Reaction of the tetraaminecopper(II) ion with formaldehyde and nitroethane in methanolic base proceeds readily to yield the macrocycle L$^1$ with a new –NHCH$_2$CH(CH$_3$)(NO$_2$)CH$_2$NH– unit completing the cycle, and possessing a [3322] methylene pattern between the secondary amine groups as distinct from the [3232] pattern in the symmetric analogue L$^3$ previously reported.[3] The nitro group is clearly defined by an irreversible electrochemical reduction near $-1$ V and by strong infrared absorbances near 1550 and 1350 cm$^{-1}$, similar to those of previous examples.[2,3] However, the L$^1$ complex is spectroscopically distinct from the L$^3$ relative, with an electronic maximum at lower energy [554 (L$^1$), 510 nm (L$^3$)] and larger absorption coefficient ($\varepsilon$ 166, 77 dm$^3$ mol$^{-1}$ cm$^{-1}$ for L$^1$,L$^3$ respectively). The [CuL$^1$]$^{2+}$ complex is more comparable with the 13-membered macrocycle 12-methyl-1,4,7,10-tetraazacyclo-tridecan-12-amine (L$^5$),[9] which displays a [3222] methylene pattern (maximum at 530 nm, $\varepsilon$ 166 dm$^3$ mol$^{-1}$ cm$^{-1}$), suggesting that the pairs of adjacent five- and six-membered chelate rings in [CuL$^1$]$^{2+}$ lead to distortions which influence the ligand-field strength of the macrocycle. Despite the spectroscopic difference, the copper(II,I) reduction potential is very similar for both the L$^1$ and L$^3$ complexes ($-0.78$ and $-0.76$ V respectively), and essentially irreversible.

The pendant amine macrocycle L$^2$ is obtained readily as the hydrochloride salt following direct reduction of its nitro-substituted precursor with zinc in aqueous acid. Synthesis with this potentially quinquedentate ligand of a pentaaminechloro-cobalt(III) complex involving equilibration over activated charcoal was readily achieved, and a single *cis* geometric isomer was isolated. The *cis* geometry dominates for L$^4$ also,[4] although in that case a small amount (*ca.* 1%) of the *trans* isomer was detected. Previously, the related 14-membered macrocyclic ligand 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-di-amine (L$^6$) has been bound in a sexi, quinque- and tetra-dentate manner to cobalt(III), and both *cis* and *trans* geometries were observed in the quinquedentate co-ordination mode,[10,11] although the products in that study were not true thermo-dynamic products, since any attempts at equilibration can lead to conversion into the sexidentate complex with necessarily *trans* geometry.

The *cis* isomer of the complex [CoL$^2$(Cl)]$^{2+}$ was subjected to a single-crystal X-ray structure analysis (Fig. 1). Non-hydrogen atomic coordinates for the structure appear in Table 1. Bond lengths and angles for the cobalt environments are compared for the complexes of L$^2$ and L$^4$ (ref. 4) in Table 2 and ligand torsion angles are compared in Table 3. The Co–N distances are variable in each compound (Table 2), but the averages vary little for the two 14-membered rings [1.96$_0$ (L$^2$), 1.95$_4$ Å (L$^4$)]; however they differ appreciably from those found in 13- or 15-membered analogues [1.94$_8$ (L$^5$), 1.98$_1$ Å (L$^7$)]$^4$ (L$^7$ = 10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine). Notably, the Co–N(1) (pendant amine) distance is relatively constant, between 1.955 and 1.960 Å, for all cases; the constancy despite the variable macrocycle size is maintained at the cost of other distortions in the facial capping unit.[4] In the capping unit the N(3a)–Co–N(3b) angles are relatively consistent for L$^2$,L$^4$ (89.7, 91.0° respectively). The quite compressed angle formed at the pendant primary amine, C(1)–N(1)–Co [101.4(2)°, 101.4(3)° for L$^2$,L$^4$ respectively], is identical in the two cases. The secondary
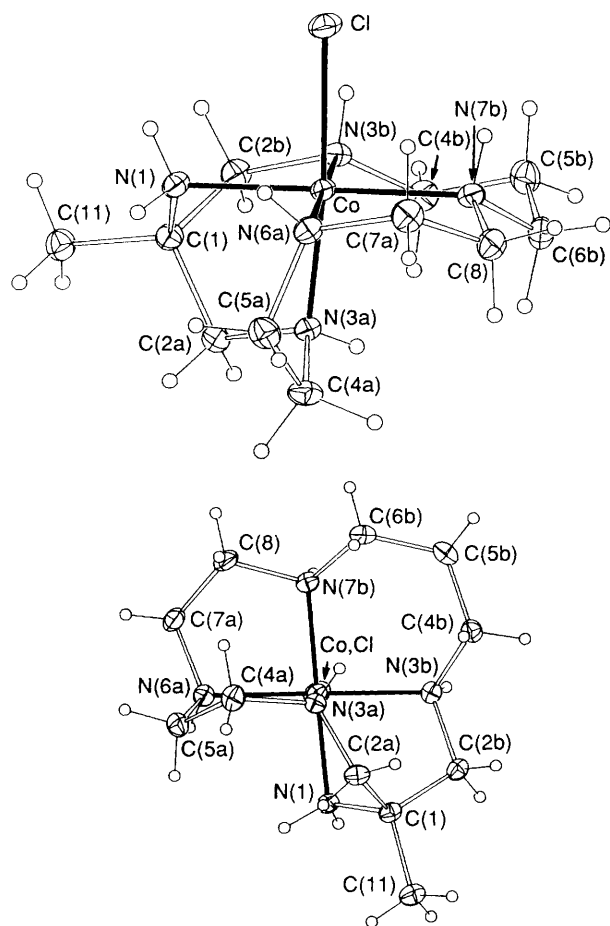
**Fig. 1** Projections of the cation $[CoL^2(Cl)]^{2+}$; 20% thermal ellipsoids are shown for the non-hydrogen atoms, whereas hydrogen atoms have arbitrary radii of 0.1 Å

**Table 1** Non-hydrogen positional coordinates for $[CoL^2(Cl)][ClO_4]_2$

| Atom | $x$ | $y$ | $z$ |
|------|-----|-----|-----|
| Co | 0.210 49(3) | 0.476 69(4) | 0.662 44(3) |
| Cl | 0.081 13(6) | 0.356 74(7) | 0.577 44(6) |
| C(1) | 0.167 4(2) | 0.704 0(3) | 0.626 6(2) |
| N(1) | 0.170 7(2) | 0.599 6(2) | 0.565 6(2) |
| C(11) | 0.137 7(4) | 0.817 2(3) | 0.570 5(3) |
| C(2a) | 0.281 7(3) | 0.709 8(3) | 0.693 1(3) |
| N(3a) | 0.320 5(2) | 0.588 8(2) | 0.725 4(2) |
| C(4a) | 0.428 8(3) | 0.556 1(3) | 0.708 7(3) |
| C(5a) | 0.411 7(3) | 0.490 1(3) | 0.615 5(3) |
| N(6a) | 0.319 4(2) | 0.406 6(2) | 0.605 7(2) |
| C(7a) | 0.347 6(3) | 0.288 9(3) | 0.648 8(3) |
| C(8) | 0.350 3(3) | 0.294 7(4) | 0.753 0(3) |
| C(2b) | 0.082 4(3) | 0.672 9(3) | 0.679 3(3) |
| N(3b) | 0.104 7(2) | 0.553 3(2) | 0.722 2(2) |
| C(4b) | 0.125 7(3) | 0.555 7(3) | 0.828 2(2) |
| C(5b) | 0.148 4(3) | 0.435 9(4) | 0.872 3(3) |
| C(6b) | 0.254 4(3) | 0.382 7(3) | 0.863 4(2) |
| N(7b) | 0.250 1(2) | 0.355 4(2) | 0.762 0(2) |
| Cl(1) | 0.200 90(6) | 0.473 73(7) | 0.310 42(6) |
| O(11) | 0.127 8(2) | 0.567 7(3) | 0.310 0(3) |
| O(12) | 0.241 2(4) | 0.431 2(5) | 0.400 2(2) |
| O(13) | 0.144 9(3) | 0.383 9(3) | 0.251 8(3) |
| O(14) | 0.286 5(3) | 0.509 7(3) | 0.274 0(4) |
| Cl(2) | 0.428 39(7) | 0.697 53(8) | 0.991 83(6) |
| O(21) | 0.448 0(2) | 0.630 4(3) | 0.914 9(2) |
| O(22) | 0.419 3(2) | 0.624 2(3) | 1.068 6(2) |
| O(23) | 0.329 0(2) | 0.762 2(3) | 0.956 9(2) |
| O(24) | 0.514 8(2) | 0.778 0(2) | 1.024 8(2) |

**Table 2** Cobalt environments (distances in Å, angles in °) for $[CoL^n(Cl)]^{2+}$ ($n$ = 2 or 4)

| Ligand[a] | $L^2$ | $L^{4\,b}$ |
|-----------|-------|-----------|
| Co–Cl | 2.252(1) | 2.236(2) |
| Co–N(1) | 1.955(3) | 1.955(4) |
| Co–N(3a) | 1.946(3) | 1.957(4) |
| Co–N(6a) | 1.954(3) | 1.958(4) |
| Co–N(3b) | 1.980(3) | 1.938(4) |
| Co–N(7b),N(6b) | 1.967(3) | 1.960(4) |
| | | |
| Cl–Co–N(1) | 91.70(9) | 91.9(1) |
| Cl–Co–N(3a) | 174.82(9) | 175.9(1) |
| Cl–Co–N(6a) | 91.26(8) | 90.5(1) |
| Cl–Co–N(3b) | 91.19(8) | 90.7(1) |
| Cl–Co–N(7b),N(6a) | 89.03(8) | 93.3(1) |
| N(1)–Co–N(3a) | 83.3(1) | 84.7(2) |
| N(1)–Co–N(6a) | 94.5(1) | 94.9(2) |
| N(1)–Co–N(3b) | 84.9(1) | 81.6(2) |
| N(1)–Co–N(7b),N(6b) | 178.8(1) | 167.4(2) |
| N(3a)–Co–N(6a) | 87.8(1) | 87.6(2) |
| N(3a)–Co–N(3b) | 89.7(1) | 91.0(2) |
| N(3a)–Co–N(7b),N(6b) | 96.0(1) | 90.5(2) |
| N(6a)–Co–N(3b) | 177.5(1) | 176.3(2) |
| N(6a)–Co–N(7b),N(6b) | 86.5(1) | 96.5(2) |
| N(3b)–Co–N(7b),N(6b) | 94.1(1) | 86.8(2) |

[a] Atom N(7b) in $L^2$ is equivalent in location to N(6b) in $L^4$; other donor atoms have identical locations and numbering about the metal ion in each structure. [b] Ref. 4.

nitrogens in the $L^2$ complex adopt *RRSS* stereochemistries, like $L^4$ and other related complexes.[4]

Examination of Table 2 shows some distortion of the $CoN_6$ octahedron, with the N(1)–Co–N(6b),N(7b) axis being deformed toward a line joining the atoms N(3a) and N(3b) only for $L^4$ (angles being 178.8 and 167.4° for $L^2$ and $L^4$ respectively). The N–Co–N angles in the five-membered rings formed by co-ordination of the pendant amines are close to 84° in each complex, but other angles in $L^2$ approximate more closely a right angle than those for $L^4$, presumably a result of the different dispositions of five- and six-membered chelates in the two complexes. Considerable strain in the angle C(2a)–N(3a)–C(4a) (114.9°) in the $L^2$ complex is diminished in C(2b)–N(3b)–C(4b) (111.9°), the greater flexibility of the six-membered chelate ring which incorporates C(4b) presumably being responsible. For the $L^4$ complex both angles are similar (near 115°), and both C(4a) and C(4b) in that case are part of five-membered chelate rings. This deformation is a direct result of co-ordination of the pendant primary amines which 'pulls' the C(2a) and C(2b) atoms toward the metal centre and hence opens 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° in both $L^2$ and $L^4$ complexes. 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 occurs, since this presumably results in the smallest increase in strain energy. This is tied to slightly 'contracted' co-ordination spheres compared with 'usual' systems {distances for cobalt(III) complexes of 1,4,8,11-tetraazacyclotetradecane are 1.986(7)–2.016(6) Å,[12,13] and the average distance in [Co(en)$_3$]$^{3+}$ (en = ethane-1,2-diamine) is 1.964(7) Å[10]}, the slightly greater contraction being seen with the more distorted $L^4$ complex. Notably, the Co–Cl bond in the $L^2$ complex [2.252(1) Å] is appreciably longer than the distance in the $L^4$ complex [2.236(2) Å], and the origin of this difference is not clear given the modest differences in Co–N distances.

A comparison of some physical data for the $L^2$ and $L^4$ pentaaminechlorocobalt(III) complexes appears in Table 4. Electronic spectroscopy of the tetragonally distorted molecules is complicated due to splitting under the $^1A_{1g} \longrightarrow {}^1T_{1g}$ envelope, although all transitions are shifted slightly to higher

**Table 3** Ligand torsion angles (°) for $[CoL^n(Cl)]^{2+}$ ($n$ = 2 or 4). Where two values are found in each entry they are for sections a and b

| Atoms | $L^2$ | $L^4$ * |
|---|---|---|
| Co–N(1)–C(1)–C(2) | 58.6(3), −59.3(2) | 60.0(4), −57.2(3) |
| N(1)–C(1)–C(2)–N(3) | −40.6(4), 49.0(3) | −50.9(5), 34.3(4) |
| C(1)–C(2)–N(3)–Co | 3.1(4), −14.3(3) | 17.0(4), 5.0(4) |
| C(1)–C(2)–N(3)–C(4) | 126.8(3), 118.9(3) | 138.4(4), 126.8(4) |
| C(2)–N(3)–C(4)–C(5) | −95.5(4), −179.9(3) | −84.5(5), −164.6(4) |
| Co–N(3)–C(4)–C(5) | 27.6(4), −52.8(4) | 37.4(5), −37.5(4) |
| N(3)–C(4)–C(5)–N(6) | −40.9(4), 67.7(4) | −46.0(6), 51.5(5) |
| C(4)–C(5)–N,C(6)–C,N(7) | −88.0(4), −67.6(4) | −102.2(5), −171.2(4) |
| C(4)–C(5)–N(6)–Co | 34.9(3) | 32.0(5), −40.9(5) |
| C(5)–C(6)–N(7)–Co | | 54.0(4) |
| C(5)–C(6)–N(7)–C(8) | | −175.6(3) |
| C(5)–N(6)–C(7)–C(8) | 84.7(4) | 79.3(6), −177.5(4) |
| C(6)–N(7)–C(8)–C(7) | | −170.5(3) |
| Co–N(6)–C(7)–C(8) | −38.3(3) | −50.7(5), 58.1(5) |
| Co–N(7)–C(8)–C(7) | | −34.5(3) |
| N(6)–C(7)–C(8)–N,C(7) | 47.7(4) | 66.9(6), −69.7(6) |

* Ref. 4.

**Table 4** Comparative physical properties of $cis$-$CoN_5Cl^{2+}$ complexes with 14-membered macrocyclic rings

| | $cis$-$[CoL^2(Cl)]^{2+}$ | $cis$-$[CoL^4(Cl)]^{2+}$ |
|---|---|---|
| Electronic spectrum | 530 (92), | 525 (87), |
| $[\lambda_{max}/nm\ (\varepsilon/dm^3\ mol^{-1}\ cm^{-1})]$ | 455 (sh, 20), | 450 (51), |
| | 362 (98) | 357 (100) |
| Average Co–N distance/Å | 1.960 | 1.954 |
| Co–Cl distance/Å | 2.252(1) | 2.236(2) |
| Base hydrolysis data | | |
| $k_{OH}^{298}/dm^3\ mol^{-1}\ s^{-1}$ | 9100 | 76 |
| $\Delta H^{\ddagger}/kJ\ mol^{-1}$ | 60 ± 4 | 75 ± 3 |
| $\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1}$ | 35 ± 12 | 42 ± 10 |

energy for $L^4$ compared with $L^2$, and perhaps relate to the slightly more compressed co-ordination sphere in the former complex. Base-hydrolysis rate constants determined at 25 °C for the complexes (Table 4) show the $L^2$ complex hydrolyses 120-fold faster than the $L^4$ complex. Although the Co–N distances are very similar in each complex, the distinctly longer Co–Cl distance in the former presumably defines the difference, with a lower enthalpy of activation the major contributor to the faster rate constant (Table 4). This implies that ground-state control of hydrolysis is important. Previously, we have found that $k_{OH}$ follows variations in the Co–Cl bond length for a series of related complexes,[4] and the current result fits well with that observation.

## Acknowledgements

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