Quinquedentate Co-ordination of Amino-substituted Tetraazacycloalkanes to Cobalt(III). Part 2.[1] Crystal Structures of *trans* Isomers, Molecular Mechanics Calculations and Base-hydrolysis Kinetics†

Trevor W. Hambley,[a] **Geoffrey A. Lawrance,***[,b] **Manuel Martinez,**[c] **Brian W. Skelton**[d] **and Allan H. White**[d]
[a] *School of Chemistry, The University of Sydney, New South Wales 2006, Australia*
[b] *Department of Chemistry, The University of Newcastle, Callaghan 2308, Australia*
[c] *Departament de Quimica Inorganica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[d] *Department of Chemistry, The University of Western Australia, Nedlands 6009, Australia*

Chlorocobalt(III) complexes of 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}), 10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine (L^{15}) and 3-methyl-1,5,9,13-tetraazacyclohexadecan-3-amine (L^{16}) were isolated as *trans* isomers only for L^{16} and the minor isomer of L^{14}. Of the two *trans* complexes, $[Co(L^{14})Cl][ClO_4]_2$ crystallized in the monoclinic space group $P2_1/c$, $a = 9.107(3)$, $b = 16.448(4)$, $c = 13.898(5)$ Å and $\beta = 99.16(3)°$, and $[Co(L^{16})Cl]Cl[ClO_4]$ crystallized in the same space group, $a = 16.868(9)$, $b = 7.531(5)$, $c = 20.51(2)$ Å and $\beta = 126.61(5)°$. Single-crystal X-ray structure determinations were refined to residuals of 0.056 and 0.071 for 2711 and 2314 'observed' reflections respectively. In both cases the pendant primary amine and two adjacent secondary amines necessarily occupy an octahedral face, with the chloro ligand *trans* to the primary amine. Average macrocycle Co–N distances vary with ring size (1.96_1, 2.01_0 Å for L^{14} and L^{16} respectively), as does the Co–Cl distance [2.244(2), 2.222(3) Å respectively], yet the Co–N(pendant) distance is constant within experimental error for both structures [1.961(4), 1.956(8) Å respectively]. Molecular mechanics calculations have been employed to predict the isomer preferences in all cases, and define the *cis* isomer of the L^{14} complex as more stable than the *trans* isomer by 4.4 kJ mol^{-1} (corresponding to a predicted *cis*:*trans* ratio of 86:14), reasonably consistent with the experimental ratio of *ca.* 98:2. For the *trans* isomers, base hydrolyses are rapid (k_{OH} 9100 and 11 100 dm^3 mol^{-1} s^{-1} for L^{14} and L^{16} respectively), and not particularly sensitive to clear differences in Co–Cl distance. For the *cis* isomers the Co–Cl distances are minimized for L^{14} (2.24_5, 2.23_6, 2.27_3 Å for L^{13}, L^{14} and L^{15} respectively), and this trend is reflected well in the comparative rate constants for base hydrolysis (k_{OH} 4300, 76 and 6700 dm^3 mol^{-1} s^{-1} respectively). Variations in rate constants are tied to variations in the activation enthalpy, but not the activation entropy. Factors influencing base-hydrolysis rate constants for the series are discussed, and the significance of ground-state effects on hydrolysis rate is examined.

A wide variety of potentially quinquedentate amine ligands, including macrocyclic species, have been bound to cobalt(III).[2,3] Recently reported branched-chain ligands which contain a $NHCH_2CMe(NH_2)CH_2NH$ component which can co-ordinate only to the face of an octahedron include 1,5,9-triamino-5-methyl-3,7-diazanonanane (L^1)[4] and the pendant-arm macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecan-6,13-diamine (L^2).[5] A related saturated C-pendant macrocycle which has recently been reported is 5-(aminomethyl)-2,5,10,-12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L^3).[6] The analogous C-pendant macrocycles, 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}), each contain a single pendant primary amino group, which avoids sexidentate co-ordination met upon equilibration of complexes of L^2.[4] In this and the preceding paper,[1] details of the co-ordination of the new potentially quinquedentate ligands L^{13}–L^{16} to cobalt(III) are presented. Co-ordination as quinquedentate ligands to other octahedral metal ions has also been defined.[7] The crystal structure analyses of *trans* isomers are reported herein, as well as a comprehensive molecular mechanics analysis and full details of the base-hydrolysis kinetics of the series of complexes.

Experimental

Syntheses.—Syntheses of the chlorocobalt(III) complexes of ligands L^{13} to L^{16} are described in the preceding paper.[1]

Reaction Kinetics.—Base-hydrolysis kinetics were followed at a range of temperatures in a thermostatted (±0.1 °C) cell holder of an Hitachi 220A spectrophotometer connected to a refrigerated controlled-temperature circulating bath. Buffers of concentration 0.01–0.02 mol dm^{-3} and total ionic strength 0.1 mol dm^{-3} ($NaClO_4$) were employed. The pH range 7.6–9.9 was covered with the buffers tris(hydroxymethyl)amine, borate and carbonate. First-order rate constants for reactions followed spectrophotometrically at a wavelength in the range 480–510 nm and employing at least a ten-fold excess of buffer were obtained from absorbance *vs.* time data by conventional non-linear least-squares computational methods. No effect of varying the buffer concentration on rate constants was

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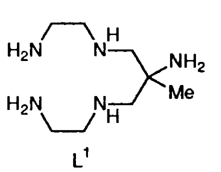
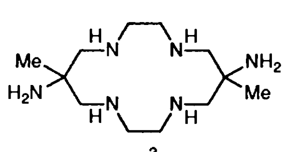
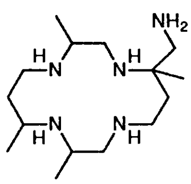
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



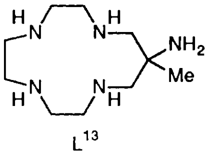
L^{1}



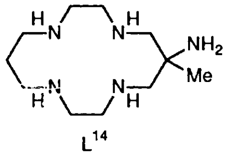
L^{2}



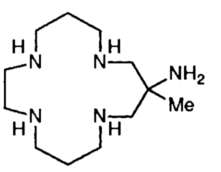
L^{3}



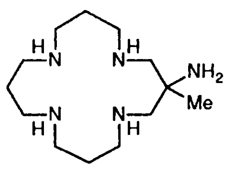
L^{13}



L^{14}



L^{15}



L^{16}

observed. Activation parameters were calculated from rate constants determined at least at three temperatures (5, 15, 25, 35 °C employed) over a range of no less than 20 °C by standard computational methods. For the sake of brevity, routine pH- and temperature-dependent rate constants are not reproduced, with only the rate constant at 25 °C and activation parameters appearing herein for each complex.

Structure Determinations.—General details are given in the preceding paper.[1] 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. *trans*-[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 = 9.107(3), b = 16.448(4), c = 13.898(5) Å, β = 99.16(3)°, U = 2055 Å^3, D_c = 1.69 g cm^{-3} (Z = 4), $F(000)$ = 1080, μ_{Mo} = 11.9 cm^{-1}. Specimen: 0.30 × 0.22 × 0.37 mm; $A^*_{min,max}$ = 1.28, 1.39. N = 3581, N_o = 2711; R = 0.056, R' = 0.065.

trans-[Co(L^{16})Cl]Cl[ClO$_4$] = $C_{13}H_{31}Cl_3CoN_5O_4$, M = 486.7, monoclinic, space group $P2_1/c$, a = 16.868(9), b = 7.531(5), c = 20.51(2) Å, β = 126.61(5)°, U = 2092 Å^3, D_c = 1.55 g cm^{-3} (Z = 4), $F(000)$ = 1016, μ_{Mo} = 11.7 cm^{-1}. Specimen: 0.20 × 0.62 × 0.04 mm; $A^*_{min,max}$ = 1.10, 1.57. N = 3661, N_o = 2314; R = 0.071, R' = 0.076.

Abnormal features. As reported in the previous paper,[1] macrocycle and anion thermal motion is very high, possibly encompassing some disorder, leading to higher than desirable residuals; in the case of [Co(L^{16})Cl]Cl[ClO$_4$], this situation was compounded by the unhelpful crystal habit (a fragile plate) resulting in generally weak data. In spite of this the model otherwise refined meaningfully.

Molecular Mechanics.—The strain energy was calculated using a force field described elsewhere.[8] Starting coordinates were taken from the crystal structure where possible, or adapted from structural data for an analogue where the appropriate isomer had not been characterized structurally, and minimization of the strain energy was achieved using a locally developed program.[9]

Results and Discussion

The series of chlorocobalt(III) complexes of the related ligands L^{13} to L^{16} displays two geometries, with the chloro ligand either *cis* or *trans* to the pendant primary amine and the macrocycle either folded or planar respectively. Both isomers were detected following equilibration only with L^{14}.[1] The two *trans* isomers isolated in the series have been characterized by X-ray crystal-structure analyses, details of the cobalt environment and the ligand torsional angles being collected in Tables 3 and 4 respectively. Whereas the secondary nitrogen–cobalt distances vary with ring size, the Co–N(1) distance is the same within experimental error, a trend already noted and discussed for the *cis* isomers.[1] Distortions of the octahedron are more marked for the smaller ring, with the Cl–Co–N(1) angle reduced to 170.0(1)° for L^{14} but relaxed to 174.1(2)° for L^{16}. This indicates that the six- (L^{16}) *versus* five-membered (L^{14}) macrocycle chelate rings, commencing at N(3a) and N(3b) adjacent to the ring with the co-ordinated pendant, have different influences on the 'pitch' of the 'cap' unit, variations in which show up clearly in ligand torsional angle variations in that region (Table 4). Views of the two cations appear in Fig. 1.

There are very few structures of pentaminechlorocobalt(III) ions which feature a saturated tetraamine macrocycle with a C-pendant primary amine as the fifth donor of the quinquedentate ligand. The most pertinent is the substituted cyclam L^{3}, which has a CH_2NH_2 arm extending from a carbon adjacent to a nitrogen of a six-membered chelate ring.[4] This leads to a similar, though less-symmetrical, arrangement to that observed with L^{14}; in the latter the primary amine is attached directly to the central carbon of a six-membered ring, leading to equivalent-size chelate rings involving the pendant primary amine and adjacent secondary amines in each case. For [Co(L^{3})Cl]$^{2+}$ the Cl–Co–N(*trans*) angle is 170.9°, very similar to that observed with the substituted cyclam L^{14}, indicating significant distortions in the former ligand also. However, the Co–N-(pendant) distance [1.974(3) Å] appears slightly longer in the L^{3} complex with the more flexible pendant chain than in the L^{14} complex [1.961(4) Å]. The range of Co–N distances is greater in the L^{3} structure,[4] with the average (1.98_3 Å) somewhat longer than in the L^{14} complex (1.96_1 Å). The Co–Cl distance in L^{3} [2.264(1) Å] is longer than in L^{14} [2.244(2) Å] by about the same amount as the average variation in Co–N distances, defining a generally more expanded co-ordination sphere in the former molecule, indicative of the ligand in the latter being more sterically efficient.

It is interesting that the average Co–N distance and the Co–Cl distance are possibly slightly longer in the *trans* isomer of the L^{14} complex compared with the *cis* isomer[1] (Table 7). The slightly expanded co-ordination sphere in the less-favoured isomer (average Co–L 2.00_8 *versus* 2.00_1 Å) is consistent with less steric strain in the *cis* geometry and the experimental observation of the *cis* isomer being favoured following equilibration. Molecular mechanics calculations for the two isomers of the complex of L^{14} predict an energy difference between the two isomers of 4.4 kJ mol^{-1} (corresponding to *cis*:*trans* of 86:14), reasonably consistent with the substantial preference for the *cis* isomer found experimentally following equilibration with charcoal. Similar calculations with the other members of the series of complexes of L^{13}–L^{16} have been performed, with minimized energies and predicted isomer distributions for the series appearing in Table 5. It is notable that the *cis* isomer is predicted to be the more stable in each case, with the difference decreasing from L^{13} to L^{14} to L^{15}. The most surprising result is that for L^{16}, which suggests the *trans* isomer is very much less stable than the *cis*, at odds with the trend up to that size and with the experimental observations. In all cases for which crystal structures have been determined, the energy-minimized

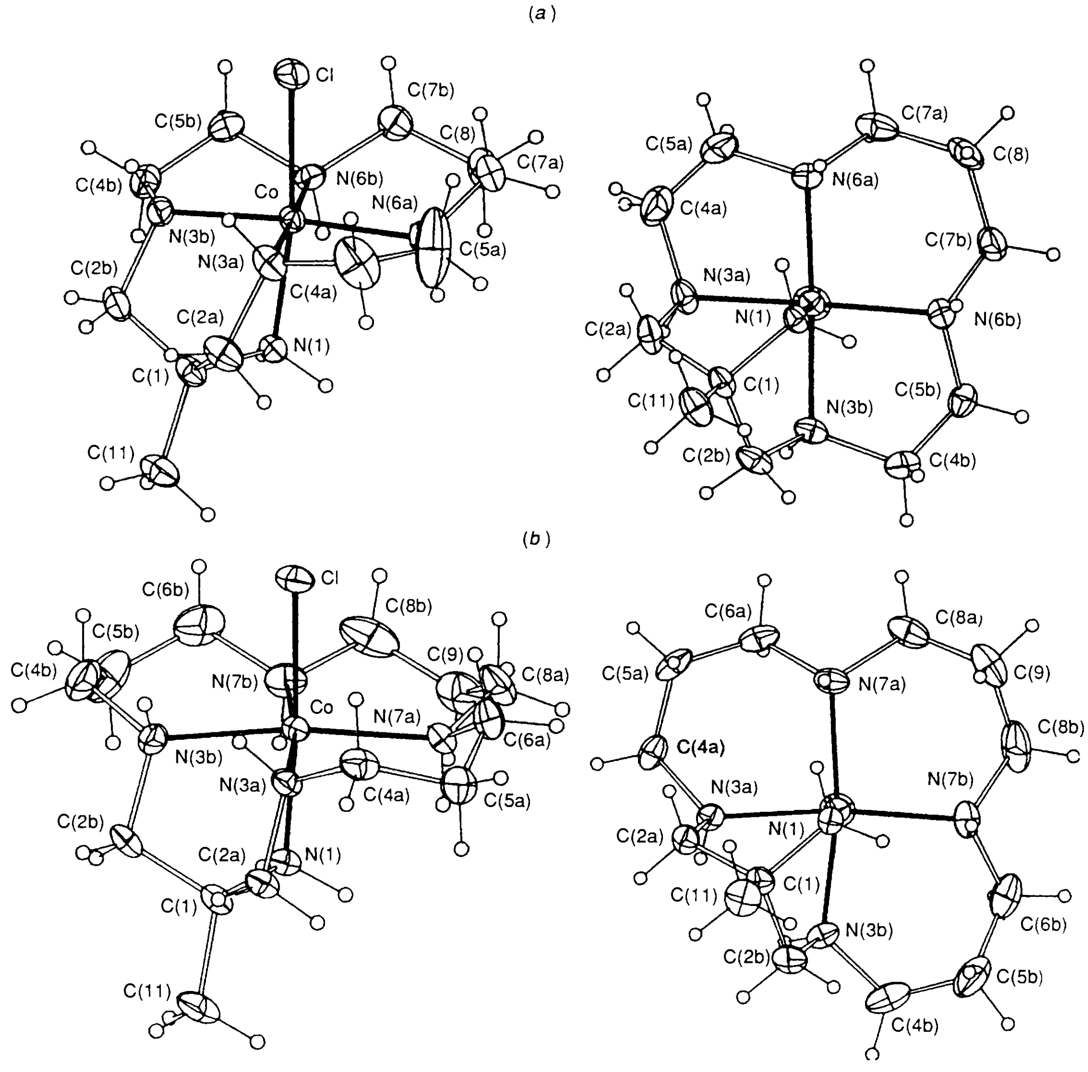


Fig. 1 Views of the molecular cations $[Co(L^n)Cl]^{2+}$: (*a*) $n = 14$, (*b*) $n = 16$

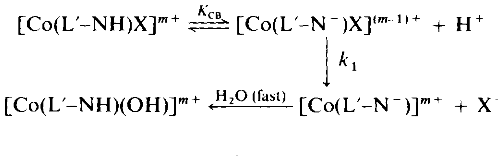
geometries are in very good agreement with these geometries. Metal–ligand bond lengths and most notably trends in these bond lengths are also very well reproduced by the models (Table 6). Average Co–N bond lengths increase monotonically with ligand size, but the Co–Cl bond lengths follow a non-linear pattern for the *cis* isomers, although a monotonic increase is predicted for the *trans* isomers. However, the fact that molecular mechanics calculations reproduce the variations for the *cis* isomers indicates that steric interactions are responsible.

The obvious discontinuity for L^{16} deserves some comment. Minimized energies increase substantially from L^{14} to L^{15}, and again from L^{15} to L^{16}, indicative of large increases in strain for the larger rings when co-ordinated in either geometry. The involvement of the cap unit, which determinedly retains an essentially constant Co–N(1) distance throughout the series while other distances vary substantially, may present peculiar steric influences which are over(or under) estimated in calculations for the most strained molecules. Deviations between experiment and prediction are most obvious with L^{15} and particularly L^{16}, and imply some subtleties not accommodated by the model. It is notable that there is an effective relative compression along the axis perpendicular to the macrocycle plane for the *trans* isomers. As the size of the ring increases the Co–N(secondary) distances increase whereas Co–N(1) remains essentially constant and short while the Co–Cl distance contracts. A similar contraction for the amine donor *trans* to the primary amine in the *cis* isomers would require compensation throughout the macrocycle, and perhaps an overall higher-energy system. This 'directed' compression may offer stability not accommodated in the model.

Base hydrolysis of the $[Co(L^n)Cl]^{2+}$ complexes showed a single process involving replacement of the co-ordinated chloride ion, characterized by the simple rate equation (1).

$$k_{obs} = k_{OH}[OH^-] \qquad (1)$$

Pentaaminehalogenocobalt(III) ion kinetics have been extensively studied, and there is general acceptance that they follow the well established S_N1_{CB} (conjugate base) mechanism for hydrolysis of cobalt(III) amine complexes in aqueous base (Scheme 1).[10,11] Although the rate equation for this mechanism


$$\begin{array}{ccc} [Co(L'\text{-}NH)X]^{m+} & \overset{K_{CB}}{\rightleftharpoons} & [Co(L'\text{-}N^-)X]^{(m-1)+} + H^+ \\ & & \downarrow k_1 \\ [Co(L'\text{-}NH)(OH)]^{m+} & \xleftarrow{H_2O\,(fast)} & [Co(L'\text{-}N^-)]^{m+} + X^- \end{array}$$

Scheme 1

is of the form (2), by assuming an amido species reactive with

$$k_{obs} = k_1K_{CB}[OH^-]/(1 + K_{CB}[OH^-]) \qquad (2)$$

Table 1 Non-hydrogen atom coordinates for *trans*-[Co(L^{14})Cl]-[ClO_4]$_2$

Atom	*x*	*y*	*z*
Co	0.754 43(8)	0.447 05(4)	0.697 48(5)
Cl	0.717 0(2)	0.528 0(1)	0.565 9(1)
C(1)	0.649 5(7)	0.435 5(3)	0.867 1(4)
C(11)	0.630 2(8)	0.401 8(4)	0.965 7(5)
N(1)	0.759 2(5)	0.387 3(3)	0.820 0(3)
C(2a)	0.714 8(8)	0.520 5(4)	0.874 8(5)
N(3a)	0.759 0(6)	0.543 3(3)	0.780 4(4)
C(4a)	0.906(1)	0.582 6(5)	0.788 5(7)
C(5a)	1.010(1)	0.540 0(6)	0.752(1)
N(6a)	0.971 0(5)	0.458 9(3)	0.714 5(4)
C(7a)	1.047 2(7)	0.437 6(5)	0.631 3(5)
C(8)	1.012 1(8)	0.353 2(6)	0.596 6(5)
C(2b)	0.505 7(7)	0.432 0(4)	0.795 7(5)
N(3b)	0.538 9(5)	0.434 7(3)	0.692 4(4)
C(4b)	0.486 1(7)	0.361 6(4)	0.634 7(5)
C(5b)	0.588 3(7)	0.344 0(4)	0.564 0(4)
N(6b)	0.743 3(5)	0.348 7(3)	0.615 7(3)
C(7b)	0.852 0(8)	0.340 7(4)	0.547 2(5)
Cl(1)	0.622 2(2)	0.163 63(9)	0.772 1(1)
O(11)	0.652 7(5)	0.088 5(2)	0.821 5(3)
O(12)	0.618(1)	0.226 9(3)	0.835 8(4)
O(13)	0.489(1)	0.161 4(5)	0.713 5(7)
O(14)	0.727 5(9)	0.183 9(4)	0.716 6(7)
Cl(2)	1.145 4(2)	0.324 4(1)	0.920 7(1)
O(21)	1.036 9(8)	0.366 3(6)	0.960 7(6)
O(22)	1.247 4(8)	0.293 9(5)	0.992 8(6)
O(23)	1.208(1)	0.380 5(8)	0.875 2(8)
O(24)	1.066(1)	0.272 9(6)	0.858 9(7)

Table 2 Non-hydrogen atom coordinates for *trans*-[Co(L^{16})Cl]-Cl(ClO_4]

Atom	*x*	*y*	*z*
Co	0.769 58(7)	0.764 8(2)	0.729 36(6)
Cl	0.866 5(2)	0.569 5(3)	0.726 9(1)
C(1)	0.587 0(6)	0.803(1)	0.687 7(5)
N(1)	0.675 2(4)	0.916 3(9)	0.729 1(4)
C(11)	0.500 2(7)	0.899(2)	0.679 5(6)
C(2a)	0.563 5(6)	0.765(1)	0.606 0(5)
N(3a)	0.652 2(5)	0.691 7(9)	0.619 0(4)
C(4a)	0.648 8(7)	0.703(1)	0.544 2(5)
C(5a)	0.677 8(8)	0.883(2)	0.534 6(6)
C(6a)	0.783 3(8)	0.926(1)	0.601 4(6)
N(7a)	0.802 7(5)	0.964(1)	0.681 2(5)
C(8a)	0.901 4(8)	1.047(2)	0.731 9(8)
C(9)	0.936 2(8)	1.091(2)	0.816 1(9)
C(2b)	0.617 5(6)	0.638(1)	0.739 2(6)
N(3b)	0.712 4(5)	0.575 4(9)	0.759 1(4)
C(4b)	0.771 4(9)	0.475(2)	0.837 2(7)
C(5b)	0.834(1)	0.590(2)	0.906 8(7)
C(6b)	0.914 8(9)	0.679(2)	0.908 9(7)
N(7b)	0.878 9(5)	0.823(1)	0.847 9(4)
C(8b)	0.963 0(7)	0.926(2)	0.866 8(7)
Cl(1)	0.758 2(2)	1.063 2(4)	0.945 9(2)
O(11)	0.814 3(8)	1.092(1)	0.914 1(5)
O(12)	0.750 3(8)	1.222(1)	0.974 2(5)
O(13)	0.811 6(6)	0.935(1)	1.007 8(5)
O(14)	0.669 1(7)	0.989(2)	0.884 9(6)
Cl(2)	0.622 2(2)	1.267 7(3)	0.625 8(1)

Table 3 Cobalt environments (distances in Å, angles in °) for *trans*-[Co(L^n)Cl]$^{2+}$, $n = 14$ or 16

	$n = 14$	16
Co–Cl	2.244(2)	2.222(3)
Co–N(1)	1.961(4)	1.956(8)
Co–N(3a)	1.954(5)	2.000(6)
Co–N(6a)	1.958(5)	2.046(9)
Co–N(3b)	1.964(5)	2.010(9)
Co–N(6b)	1.971(5)	2.039(7)
Cl–Co–N(1)	170.0(1)	174.1(2)
Cl–Co–N(3a)	89.2(2)	92.1(3)
Cl–Co–N(6a)	93.3(2)	93.2(3)
Cl–Co–N(3b)	90.6(1)	91.7(2)
Cl–Co–N(6b)	91.7(1)	90.9(3)
N(1)–Co–N(3a)	84.2(2)	84.5(3)
N(1)–Co–N(6a)	93.6(2)	91.6(4)
N(1)–Co–N(3b)	82.1(2)	83.0(3)
N(1)–Co–N(6b)	94.7(2)	91.9(3)
N(3a)–Co–N(6a)	85.5(2)	91.5(3)
N(3a)–Co–N(3b)	91.9(2)	79.5(3)
N(3a)–Co–N(6b)	177.9(2)	171.8(4)
N(6a)–Co–N(3b)	175.2(2)	169.9(2)
N(6a)–Co–N(6b)	96.3(2)	96.0(3)
N(3b)–Co–N(6b)	86.3(2)	92.7(3)

For N(6), read N(7) in L^{16}.

respect to reprotonation or substitution, it reduces to the form (1) when $K_{CB} \ll 1$, with $k_{OH} = k_1 K_{CB}$. Where there are several non-equivalent sites for deprotonation available, several sets of K_{CB} (alternatively expressed in terms of k_f/k_b deprotonation/protonation rate constants) and k_1 may contribute to the overall observed rate, although one deprotonation site may dominate the reaction. Qualitative NMR experiments indicated that at least some amine proton exchange was significantly faster than chloride hydrolysis in the present complexes, and rate-determining deprotonation is not commonly observed,[10] making k_1 the rate-determining step. Base-hydrolysis rate constants determined at 25 °C and activation parameters for the series of L^{13} to L^{16} complexes including both *cis* and *trans* isomers are included in Table 7, along with data for L^3.

For pentaaminechlorocobalt(III) ions it was observed earlier that hydrolysis of the L^1 complex was slow in comparison with other systems,[2] and it has been proposed that this may arise from the relatively short Co–Cl bond, shorter bonds requiring more energy to stretch to a given distance. Comparisons between quite disparate ligand systems are not exceptionally reliable, since k_{OH} values are sensitive to the nature and disposition of polyamine ligands.[10] Whether a more compact ground state may be important in determining hydrolysis rates can be examined for the [Co(L^n)Cl]$^{2+}$ series of closely related complexes, which offer a more telling test of this concept. Examination of Table 7 shows that, for the three related *cis* isomers, there is a correlation between base-hydrolysis rate constant and structure; 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}] correlates with the trend in Co–Cl bond length [2.245(2) (L^{13}), 2.236(2) (L^{14}), 2.273(2) (L^{15})],[1] with the shortest distance corresponding to the lowest rate constant. This suggests a strong influence of the ground state on the hydrolysis reaction. It is apparent at the same time that average Co–N distance increases monotonically with increasing ring size, and that the overall average Co–L distance (*i.e.* averaging all bond lengths) also increases uniformly. Thus there is some justification in asserting, in this closely related series, that the shorter Co–Cl distance leads to the slower hydrolysis rate, *i.e.* there is dominant ground-state control of hydrolysis. Similar relationships between leaving-group bond distance in the ground state and hydrolysis rate have been invoked previously for pentaaminehalogeno-cobalt(III) and -chromium(III) compounds with unidentate amine ligands.[12] Perhaps the most valid comparison with simple systems in this case is with the pentakis(methylamine)cobalt(III) system, which has, at least, secondary amines in the co-ordination sphere.[13,14] The data of Table 7 indicate that the co-ordination spheres of at least L^{13} and L^{14} complexes are considerably contracted relative to this unidentate methylamine complex, indicative of the sterically efficient ligands dealt with here, and yet base-hydrolysis rates are larger or not

Table 4 Ligand torsion angles (°) for *trans*-$[Co(L^n)Cl]^{2+}$, n = 14 or 16. Where two values are given in each entry, they are for sections a and b

	n = 14	16
Co–N(1)–C(1)–C(2)	−59.1(4), 58.4(5)	−59.0(6), 60.0(9)
N(1)–C(1)–C(2)–N(3)	47.3(6), −36.4(6)	54.0(9), −48(1)
C(1)–C(2)–N(3)–Co	−12.2(6), −2.8(6)	−22(1), 12.2(8)
C(1)–C(2)–N(3)–C(4)	−135.6(6), 119.5(5)	−161.8(7), 152.7(8)
C(2)–N(3)–C(4)–C(5)	114(1), −147.5(5)	81.6(9), −88(2)
Co–N(3)–C(4)–C(5)	−10(1), −26(6)	−52(1), 46(2)
N(3)–C(4)–C(5)–N,C(6)	−4(1), 46.8(6)	65(1), −66(2)
C(4)–C(5)–N,C(6)–C,N(7)	147(1), −173.7(5)	−73(1), 73(2)
C(4)–C(5)–N(6)–Co	15(1), −44.4(5)	
C(5)–C(6)–N(7)–Co		59(1), −54(2)
C(5)–C(6)–N(7)–C(8)		−165.6(9), 167(1)
C(5)–N(6)–C(7)–C(8)	177.4(6), 174.6(6)	
Co–N(6)–C(7)–C(8)	−55.3(7), 51.6(7)	
C(6)–N(7)–C(8)–C(9)		−178.7(9), −172(1)
Co–N(7)–C(8)–C(9)		−45(1), 49(2)
N(6)–C(7)–C(8)–C(7)	69.0(8), −67.6(8)	
N(7)–C(8)–C(9)–C(8)		72(1), −74(2)

Table 5 Minimized energies and predicted isomer distributions for $[Co(L^n)Cl]^{2+}$ (n = 13–16)

	U_{tot}/kJ mol^{-1}		
Ligand	*trans*	*cis*	*trans*:*cis*
L^{13}	147.9	137.8	2:98
L^{14}	148.5	144.1	14:86
L^{15}	178.5	177.3	38:62
L^{16}	222.6	209.8	0.4:99.6

Table 6 Comparison of bond lengths (Å) from energy-minimized structures and crystal structures

Ligand	Bond		*trans*	*cis*
L^{13}	Co–Cl	calc.	2.249	2.251
		X-ray	—	2.245(2)
	Co–N(av.)	calc.	1.957	1.960
		X-ray	—	1.94_8
L^{14}	Co–Cl	calc.	2.244	2.242
		X-ray	2.244(2)	2.236(2)
	Co–N(av.)	calc.	1.976	1.967
		X-ray	1.96_1	1.95_4
L^{15}	Co–Cl	calc.	2.236	2.277
		X-ray	—	2.273(2)
	Co–N(av.)	calc.	1.983	1.977
		X-ray	—	1.97_5
L^{16}	Co–Cl	calc.	2.221	2.274
		X-ray	2.222(3)	—
	Co–N(av.)	calc.	2.013	1.992
		X-ray	2.01_0	—

markedly smaller for the quinquedentates, an effect related to the availability of secondary nitrogen sites for deprotonation and multidentate ligand geometry influences on conjugate base formation discussed later. The base-hydrolysis rate of $[Co(L^{14S})Cl]^{2+}$ (k_{OH} 1080 dm^3 mol^{-1} cm^{-1} at 25 °C), the dithioether analogue of $[Co(L^{14})Cl]^{2+}$ (L^{14S} = 6-methyl-1,-11-dithia-4,8-diazacyclotetradecan-6-amine), is approximately fifteen-fold faster than that observed for the L^{14} complex, an effect attributed to the influence of the thioether donors.[15]

Examination of activation parameters determined for the three *cis* complexes shows that the activation enthalpy varies in a parallel manner with both Co–Cl bond length and hydrolysis rate constant, whereas the activation entropy is relatively constant. If bond breaking precedes bond making, and if one assumes the same degree of dissociation of the M–Cl bond in the activated state, then more energy will be required to stretch to a given distance for molecules with shorter M–Cl distances in the ground state. Since the compounds are structurally very similar, it is not unreasonable to expect the entropy changes involved in forming the activated state (which will include significant changes in solvent electrostriction) to be relatively similar, and for the energy requirements for stretching the bond, defined in the activation enthalpy, to be a more dominant variable.

For the *trans* complexes it is comparison of L^{14} and L^3 which we expect is most telling, since these at least have the same 14-membered parent macrocycle framework. The longer Co–Cl bond in the latter is associated with the faster base hydrolysis rate, although the difference of a factor of only 3 is not compelling. The variation in the base-hydrolysis rate constant from *trans*-L^{14} to -L^{16} is not great either, and the modest increase for L^{16} is not consistent with a dominant ground-state influence, since the Co–Cl bond is substantially shorter in the L^{16} complex. It must be noted, however, that the overall average Co–L distance is substantially greater for the L^{16} complex compared with the L^{14} complex, perhaps influencing lability, and that only more flexible six-membered chelate rings exist in the macrocyclic part of L^{16}. Flexibility and its influence on the ease of adjusting geometry to a five-co-ordinate activated state may be important, but is difficult to define meaningfully. Probably consideration of the Co–Cl distance alone as a controller of reaction rate is too simplistic. Like the series of *cis* complexes, it is noted again that the variation in activation enthalpy is the dominant effect on activation parameters.

The *cis* isomer of L^{14} exhibits base hydrolysis some 120 times slower than does the *trans* isomer, the variation arising largely from a greater activation enthalpy. Since the Co–N and Co–Cl distances in the two isomers are slightly but not greatly different, it seems unlikely that ground-state influences define the difference totally. It has been suggested by Henderson and Tobe[16] that a molecule which possesses a 'flat' nitrogen (*i.e.* one that is at the centre of a group of three *meridionally* disposed donors) *cis* to the leaving group will be very much more labile towards base hydrolysis than those in which the nitrogen in question is 'bent' (*i.e.* the centre of three *facially* disposed donors). Examination of the structures of the two isomers shows that of the secondary nitrogens in the *cis* isomer only one [N(6b) in L^{13}, L^{14}; N(7b) in L^{15}] is centred in a *mer* group of secondary donors, whereas the *trans* isomer has all centred in *mer* groups of secondary donors. A 'flat' nitrogen will permit better p_π–d_π overlap in the formation of the five-co-ordinate intermediate, and if one assigns the acceleration for the *trans* isomer to this effect then the variation is defined in this case by the activated and not the ground state. Although both isomers possess 'flat' nitrogens, the site of deprotonation may not be unique (with only *mer* sites leading to a relatively highly 'active' intermediate, deprotonation at *fac* sites may not contribute appreciably to hydrolysis) leading to an averaged acceleration in the case of the

Table 7 Comparative kinetic and structural data for $[Co(L^n)Cl]^{2+}$ compounds

				Bond distance/Å		
L^n	k_{OH}/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	Av. Co–N	Co–Cl	Av. Co–L
L^{13}(*cis*)	4 300 ± 100	67 ± 4	47 ± 15	1.94_8	2.245	1.99_8
L^{14}(*cis*)	76 ± 6	75 ± 4	42 ± 13	1.95_4	2.236	2.00_1
L^{15}(*cis*)	6 700 ± 100	58 ± 3	30 ± 10	1.97_5	2.273	2.02_5
L^{14}(*trans*)	9 100 ± 600	61 ± 4	33 ± 14	1.96_1	2.244	2.00_8
L^3(*trans*)	22 000	—	—	1.98_3	2.264	2.03_0
L^{16}(*trans*)	11 100 ± 500	34 ± 3	31 ± 8	2.01_0	2.222	2.04_5
$(NH_2Me)_5$	1 800	78	72	1.98_8	2.283	2.03_7
Average error				(0.005)	(0.002)	

trans isomer compared with the *cis* isomer. These observations indicate immediately that attempts to compare structurally disparate systems are not particularly relevant, since both ground- and activated-state contributions to the rate processes across a disparate series will become confused. The concept of a 'flat' nitrogen as used here is not strictly a structural one, but it may be useful to reflect on the structural aspects alone. Since, upon deprotonation, the nitrogen may adopt a flat geometry, perhaps the protonated forms which better approach a planar geometry may be more prone to rapid deprotonation. The ground-state 'planarity' can be defined by the sum of the angles around the nitrogen (Σ), which is 360° for an ideal planar and 328.2° for an ideal tetrahedral geometry. The Σ values around N(6b) [with summed estimated standard deviation (e.s.d.) in parentheses] in *cis* isomers of L^{13} and L^{14} or N(7b) in L^{15} are 334.7(16), 336.7(10) and 338.9(28)° respectively, whereas the value in the *trans* isomer of L^{14} is 335.3(16)°. Comparable angles around N(6a) or N(7a) are 330.4(16), 341.3(10), 339.8(28) and 338.8(16)° in turn. Although all are non-ideal, there is really no obvious relationship between the angles at a site and the potential lability or rate constant, and we believe it would be unreasonable to expect this to be the case in view of the multiplicity of factors influencing structure and reaction rate.

Other requirements for high lability put forward by Henderson and Tobe[16] include a requirement that the plane of the amide group in the activated state should be able to lie perpendicular to the trigonal plane of the cobalt, that there should be five-membered rings on either side of this group to hold it in position, and that there should be unidentate ligands or a six-membered chelate occupying the remaining equatorial sites in the intermediate to minimize strain. In the present series, variations in chelate ring size alone will introduce effects according to these concepts, which will add to ground-state influences. Although the pendant-arm macrocyclic complex $[Co(L^4)Cl]^{2+}$ [L^4 = *N,N'*-bis(2-aminoethyl)-1,4,7-triazacyclononane] is one example of a system which does not fit well with these 'rules' for rapid base hydrolysis,[17] suggesting that subtle influences cannot be accounted for by general concepts, it is true that a great majority of systems obey the concepts. The present series appears to fit modestly well with the rules of Henderson and Tobe,[16] once allowance is made for the influence of short Co–Cl distances.

Nevertheless, it is clear that there are conflicting outcomes even for this closely structurally related series. There is some evidence to suggest that the rate of base hydrolysis is tied in a straightforward way to the metal-leaving group distance in the ground state, at least for the *cis* isomers, which have a possibly unique site for deprotonation leading to a viable intermediate, and satisfy most of the rules proposed for lability.[16] Under these circumstances there are less opportunities for ground-state influences to be disguised by other contributions, with unusually short bond lengths leading to relatively slow hydrolysis. The available *trans* isomers present a less clear picture, with the relative constancy of base-hydrolysis rates notable, despite significant variation in Co–Cl distances. Whereas the *cis* isomers, upon loss of the chloride, can conveniently relax into an intermediate trigonal-bipyramidal geometry with the anticipated site of deprotonation perpendicular to the trigonal plane and *trans* to the pendant primary amine, it is less clear that the *trans* isomer can conveniently adopt a trigonal-bipyramidal geometry and may even prefer a square-based pyramidal intermediate. The insensitivity of the hydrolysis rate in the case of the *trans* isomers to structural changes in the ligand framework may be in some way tied to this prospect, although with a limited amount of data for comparison extended analysis is not warranted. Continuing studies on relationships between hydrolysis behaviour and structure in a series of closely related complexes may lead to a more effective analysis of the factors influencing kinetic processes, and permit a more finite definition of mechanisms.

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