Chlorocobalt(III) and Chlorochromium(III) Complexes of a New Chiral Quinquedentate Polyamine based on *RR-trans*-Cyclohexane-1,2-diamine†

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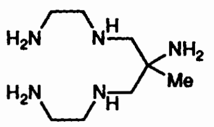
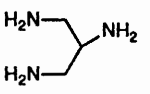
The potentially quinquedentate ligand *RR,RR*-1,3-bis(2′-aminocyclohexylamino)-2-methylpropan-2-amine (L^3) readily forms both chloropentaaminecobalt(III) and chloropentaaminechromium(III) complex cations. The [Co(L^3)Cl]Cl[ClO$_4$]·2H$_2$O compound crystallized in the orthorhombic space group $P2_12_12_1$, a = 10.414(2), b = 12.789(3), c = 18.869(4) Å, with the co-ordinated chloride in a *trans* disposition relative to the central primary amine in the ligand, the two pairs of nitrogen donors from the cyclohexane-1,2-diamine residues being coplanar with the cobalt ion. The –NH–CH$_2$–C(CH$_3$)(NH$_2$)–CH$_2$–NH– core of the ligand necessarily occupies an octahedral face. Metal–nitrogen distances (Co–N 1.944–1.971 Å) are slightly longer than in the 5-methyl-3,7-diazanonane-1,5,9-triamine analogue although still relatively short for cobalt(III)–amine bonds, whereas Co–Cl (2.241 Å) is also short. Chiroptical properties of the complexes are reported. Base hydrolysis reactions of the chloro–cobalt(III) and –chromium(III) complexes both exhibit two steps, assigned to chloride hydrolysis and *trans–cis* isomerization reactions.

Amidst a range of polyamines which can act as quinquedentate ligands to inert octahedral metal ions, we have recently reported aspects of the cobalt(III) co-ordination chemistry with 5-methyl-3,7-diazanonane-1,5,9-triamine (L^1).[1] This ligand was based on the linear 2,3,2-tet (3,7-diazanonane-1,9-diamine) polyamine with an additional primary amine and a methyl group attached to the central carbon atom of the chain. The central part of the ligand is structurally analogous to propane-1,2,3-triamine (L^2), a molecule which can bind as a tridentate ligand only to an octahedral face.[2] Following co-ordination of the 'core' of L^1 to an octahedral face, two geometric isomers are possible depending on whether the primary amine donors of the two (2-aminoethyl) arms bind in the same plane as the two secondary amine donors and the metal ion (leading to an isomer in which the central primary amine and the sixth unidentate site are in a *trans* disposition) or whether only one of the arms binds in that plane (producing a *cis* disposition of the central primary amine and the sixth site).

During synthesis of stereogenic macrocyclic polyamines, we have been able to prepare an analogue of L^1 based on *RR-trans*-cyclohexane-1,2-diamine rather than ethane-1,2-diamine.[3] This molecule, *RR,RR*-1,3-bis(2′-aminocyclohexylamino)-2-methylpropan-2-amine (L^3), has a skeleton identical to that of L^1, but contains relatively rigid cyclohexane rings fused to the skeleton. These rings introduce rigidity, steric bulk and stereogenicity to the molecule. Apart from the *RR,RR* isomer (L^3) reported here, two closely related *meso* forms (*r-meso*, L^4 and *s-meso*, L^5)‡ are inherently available, but are not obtained in any reasonable yield by the synthetic route employed. Further, an analogue based on *cis*-cyclohexane-1,2-diamine was not obtained.[3] The ligand L^3, however, is readily prepared in high yield, and hence the co-ordination chemistry reported herein is mainly devoted to this ligand. Chloropentaamine–cobalt(III) and –chromium(III) complexes of L^3 are examined herein.


L^1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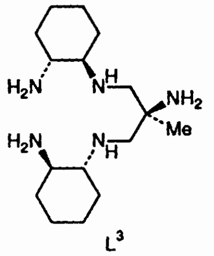
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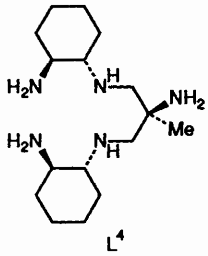
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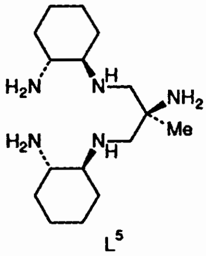
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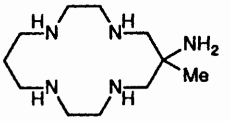
L^6

Experimental

Syntheses.—RR,RR-1,3-*Bis*(2′-*aminocyclohexylamino*)-2-*methylpropan*-2-*amine Hydrochloride*, L^3·5HCl, was prepared

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ The *RR,RR* isomer has four stereogenic carbon centres based on the two cyclohexane-1,2-diamine fragments, but the central tertiary carbon (with the primary amine and methyl substituents in addition to the two *RR*-2′-aminocyclohexylamine substituents) is non-stereogenic. However, when both an *RR*- and an *SS*-2′-aminocyclohexylamine substituent are present, the central tertiary carbon is formally pseudoasymmetric. We have assigned *r* or *s* stereochemistry to this centre based on the rule of pseudo-asymmetric centres which assigns a precedence for the *RR*- over the *SS*-arm. Consequently, the '*meso*' form of the ligand exists in two forms, *RRrSS* and *SSsRR*, differing in the stereochemistry of the central tertiary carbon, and labelled trivially as *r-meso* (L^4) and *s-meso* (L^5) herein.

by zinc–acid reduction of the copper(II) complex of the 2-nitro analogue as described elsewhere,[3] the chemistry being based on techniques reported previously.[4]

[RR,RR-1,3-*Bis*(2′-*aminocyclohexylamino*)-2-*methylpropan*-2-*amine*]*chlorocobalt*(III) *perchlorate hydrate*, $[Co(L^3)Cl][ClO_4]_2{\cdot}H_2O$. A solution of $L^3{\cdot}5HCl$ (2 g) in water (100 cm^3) was mixed with an excess of $CoCl_2{\cdot}6H_2O$ (1.2 g) and hydrogen peroxide (2 cm^3, 32% w/w) was added with stirring. The pH was raised to *ca*. 9 with NaOH solution and the solution was stirred for 1 h, then the pH was lowered to *ca*. 1 with concentrated HCl, and the solution was heated at 50 °C for 30 min. The filtrate was diluted 10-fold with water, sorbed onto a column (40 × 4 cm) of Dowex 50W × 2 cation exchange resin, washed with water and 1 mol dm^{-3} HCl to remove excess of cobalt(II) ion, then eluted with 3 mol dm^{-3} HCl to give a broad orange band. This band was collected, rotary evaporated to a small volume (*ca*. 10 cm^3), and set aside to crystallize after the addition of $HClO_4$ (3 cm^3, 5 mol dm^{-3}). Small red crystals formed on standing, and were collected, washed with ethanol and air dried (1.5 g, 60%). The filtrate yielded further crops on standing for extended periods (Found: C, 31.8; H, 6.3; N, 11.8. Calc. for $C_{16}H_{37}Cl_3CoN_5O_9$: C, 31.6; H, 6.1; N, 11.5%). Electronic spectrum (in water): λ_{max} 524 (ε 61), 455 (sh) (39) and 358 nm (92 $dm^3\ mol^{-1}\ cm^{-1}$). NMR (D_2O): ^1H, δ 1.3 (s, 3 H) and 3.0–4.5 (m, 24 H); ^{13}C, δ 19.8, 24.4 (×4), 28.3, 30.4, 33.9, 34.0, 54.3, 56.6, 59.3, 61.0, 65.8, 67.5 and 72.6. Crystals of X-ray quality were obtained as a mixed chloride perchlorate dihydrate salt by slow crystallization from a *ca*. 2 mol dm^{-3} HCl solution.

[RR,RR-1,3-*Bis*(2′-*aminocyclohexylamino*)-2-*methylpropan*-2-*amine*]*chlorochromium*(III) *perchlorate trihydrate*, $[Cr(L^3)Cl][ClO_4]_2{\cdot}3H_2O$. A suspension of $L^3{\cdot}5HCl$ (1 g) in ethanol (80 cm^3) was treated with triethylamine (1.5 cm^3) and a slight molar excess of anhydrous $CrCl_3$ (0.4 g) added with constant stirring. The red-purple solution was stirred at room temperature for 15 h, diluted to 1 dm^3 with 0.2 mol dm^{-3} aqueous HCl, and filtered through Kieselguhr to remove a small amount of green solid. The solution was sorbed onto a column (17 × 3 cm) of Dowex 50W × 2 (H^+ form) cation exchange resin, washed with water and 1 mol dm^{-3} HCl, then eluted with 3 mol dm^{-3} HCl to give a broad orange band. Two bands were collected, the first red-purple and the second red-orange, and both were rotary evaporated to a small volume. During this process, the electronic spectrum of the second band changed to be identical with that of the first, suggesting, along with the order of elution, that the second was an aqua species anated by chloride during work-up. Both bands were recombined, diluted to 2 dm^3 with water, resorbed onto the Dowex column, and rechromatographed, yielding a single red-purple band. After being concentrated to *ca*. 5 cm^3, the solution was set aside to crystallize after the addition of $HClO_4$ (3 cm^3, 3 mol dm^{-3}). Red crystals formed on standing for *ca*. 3 weeks, and were collected, washed with ethanol and air dried (0.6 g, 50%). The filtrate yielded further crops on standing for extended periods (Found: C, 30.1; H, 6.5; N, 10.8. Calc. for $C_{16}H_{41}Cl_3CrN_5O_{11}$: C, 30.3; H, 6.3; N, 10.8%). Electronic spectrum (in water): λ_{max} 540 (sh) (ε 85), 489 (113), 371 (122) and 225 (sh) nm (9420 $dm^3\ mol^{-1}\ cm^{-1}$). IR spectrum (KBr disc); 3230, 1630, 1395, 995 (NH), 2942, 2863 (CH), 1120 and 625 (ClO_4^-) cm^{-1}.

Physical Methods.—Electronic spectra were recorded using an Hitachi 150–20 spectrophotometer, IR spectra of compounds dispersed in KBr discs on a BioRad FT-IR 7 spectrometer. Circular dichroism spectra were measured as aqueous solutions using a Roussel-Jouan dichrograph. The NMR spectra were recorded using a JEOL FX90Q Fourier transform spectrometer with sodium trimethylsilylpropionate and 1,4-dioxane as internal standards for ^1H and ^{13}C respectively, but with shifts cited *versus* tetramethylsilane.

Reaction Kinetics.—An Applied Photophysics DX-17 stopped-flow spectrofluorimeter was employed for base hydrolysis kinetics, with reaction followed at a number of wavelengths between 350 and 550 nm. Sodium hydroxide concentrations in the range 0.025–0.3 mol dm^{-3} were employed, with the total ionic strength maintained at 0.5 mol dm^{-3} with $NaClO_4$, and complex concentrations no greater than 0.002 mol dm^{-3}. Temperature was controlled (±0.1 °C) with a thermostatted circulating refrigerated water-bath. Kinetic analysis employed the suite of programs provided with the instrument, including global analysis software developed for the machine in this laboratory. Data reported are the average of multiple independent sets (typically seven) collected under each condition of base concentration and temperature employed in the study, with deviation of observed rates between independent runs always less than 10%. Data were analysed successfully in terms of a single or two sequential reactions.

Structure Determination.—*Crystal data*. $[Co(L^3)Cl]Cl[ClO_4]{\cdot}2H_2O$, *M* 562.82, orthorhombic, space group $P2_12_12_1$, $a = 10.414(2)$, $b = 12.789(3)$, $c = 18.869(4)$ Å, $U = 2513$ Å^3, D_c ($Z = 4$) = 1.487 g cm^{-3}, μ(Mo-Kα) = 9.85 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å, $F(000) = 1184$. Specimen: red, 0.22 × 0.22 × 0.26 mm. $A^*_{min,max}$ 0.774, 0.853. $N = 2805$, $N_o = 2585$, range of *hkl* 0–13, 0–16, 0–23, merging $R = 0.01$, $R = 0.027$, $R' = 0.030$, residue extrema +0.3, −0.2 e Å^{-3}.

Cell constants at 21 °C were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4F four-circle diffractometer employing graphite-monochromated Mo-Kα radiation. Intensity data were collected in the range $1 < \theta < 26.5°$ using an ω–2θ scan mode. The scan widths and horizontal counter apertures employed were (1.00 + 0.35 tan θ)° and (2.70 + 1.05 tan θ) mm. Independent reflections with $I > 2.5\,\sigma(I)$ were considered observed and used for solution of structures. Data reduction and application of Lorentz, polarization and absorption corrections were carried out using the Enraf-Nonius Structure Determination Package.[5] The structure was solved by heavy-atom methods using SHELX 76[6] and the solution was extended by Fourier difference methods. Hydrogen atoms were included at calculated sites (C–H, N–H 0.97 Å) with isotropic thermal parameters and all other atoms with the exception of minor contributors to the disordered perchlorate atoms were refined anisotropically. Full-matrix least-squares refinement of an overall scale factor and positional and thermal parameters converged (all shifts < 0.06σ). Residues on |*F*| at convergence are conventional *R*, *R*′, $w = g/(\sigma^2 F_o + kF_o^2)$ where *g*, *k* are 1.19, 2.9 × 10^{-4}. Scattering factors and anomalous dispersion terms used for Co were taken from ref. 7 and all others used were those supplied in SHELX 76.[6] Plots were drawn using ORTEP,[8] with the atom numbering scheme given in Fig. 1. Non-hydrogen atom coordinates, bond lengths and bond angles are listed in Tables 1 and 2. Absolute configuration was not determined in the structure solution, since the absolute configuration of the precursor cyclohexane-1,2-diamine isomer employed for synthesis of the ligands herein has been fully established previously, and was employed as defined.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Molecular Mechanics Calculations.—The molecular mechanics calculations were carried out using methods described elsewhere.[9,10] The force-field parameters have also been reported previously with the exception of those for the chloro ligand. The force constant used for the Co–Cl bond length was that reported by Snow[11] and non-bonded interactions were calculated with a van der Waals radius of 1.95 Å and a relative permittivity of 0.190. The MOMEC 87 program was used for all calculations.[12]

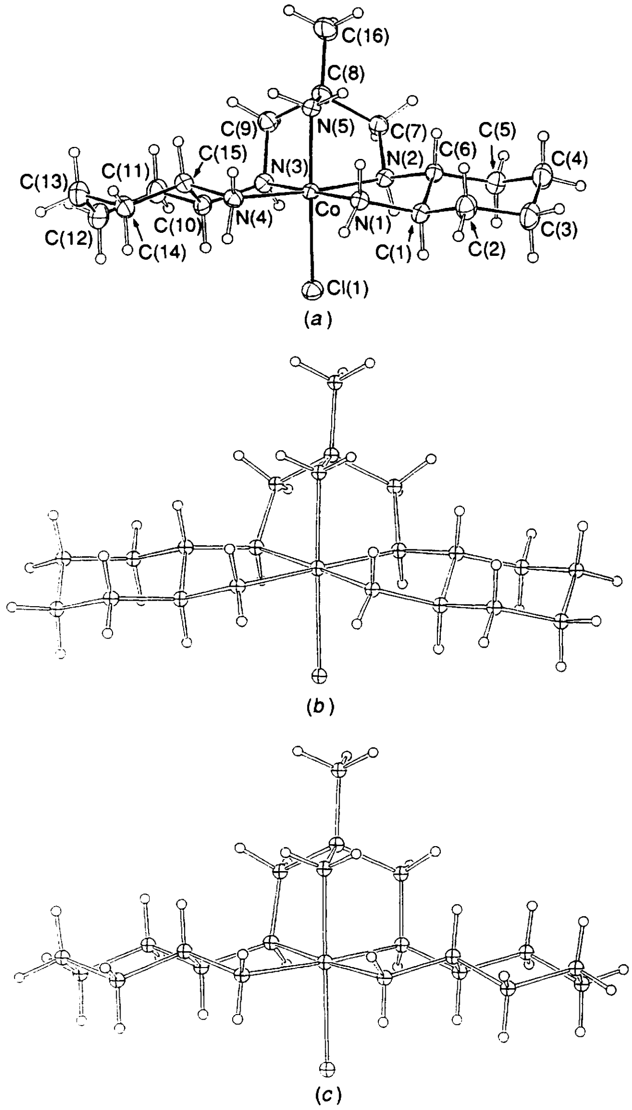

Fig. 1 Views of (*a*) the cation *RR*,*RR*-*trans*-$[Co(L^3)Cl]^{2+}$ showing atom numbering; (*b*) and (*c*); related *r-meso* (L^4) and *s-meso* (L^5) isomers, respectively, generated by molecular mechanics

Table 1 Non-hydrogen atom coordinates (× 10^4) for $[Co(L^3)Cl]Cl[ClO_4]\cdot 2H_2O$*

Atom	*x*	*y*	*z*
Co	7 378.2(4)	7 871.6(3)	9 180.8(2)
Cl(1)	5 976.6(8)	7 450.4(7)	10 035.7(5)
N(1)	8 331(3)	6 592(2)	9 412(1)
N(2)	6 523(3)	7 035(2)	8 441(1)
N(3)	6 381(3)	9 122(2)	8 926(1)
N(4)	8 283(3)	8 786(2)	9 850(1)
N(5)	8 469(3)	8 250(2)	8 385(1)
C(1)	7 610(3)	5 691(2)	9 123(2)
C(2)	8 383(4)	4 677(3)	9 108(2)
C(3)	7 612(5)	3 806(3)	8 744(2)
C(4)	7 148(5)	4 135(3)	8 012(2)
C(5)	6 378(4)	5 147(3)	8 037(2)
C(6)	7 181(3)	6 000(2)	8 388(2)
C(7)	6 581(3)	7 629(3)	7 764(2)
C(8)	7 491(4)	8 572(3)	7 849(2)
C(9)	6 795(4)	9 483(3)	8 206(2)
C(10)	6 524(3)	9 905(3)	9 502(2)
C(11)	6 045(4)	11 010(3)	9 342(2)
C(12)	6 270(5)	11 708(3)	9 979(3)
C(13)	7 677(5)	11 711(3)	10 198(2)
C(14)	8 168(5)	10 605(3)	10 354(2)
C(15)	7 922(3)	9 897(3)	9 719(2)
C(16)	8 092(5)	8 893(3)	7 149(2)
Cl(2)	8 398(1)	8 336(1)	1 649(1)
Cl(3)	9 055(1)	5 738(1)	6 277(1)
O(1)	7 769(4)	5 909(3)	6 496(3)
O(2)	9 806(9)	6 574(7)	6 464(6)
O(3)	9 477(9)	4 824(8)	6 568(6)
O(4)	9 093(6)	5 641(7)	5 523(3)
O(2′)	9 953(22)	5 383(19)	6 857(12)
O(3′)	9 179(17)	4 947(15)	5 812(11)
O(4′)	9 754(20)	6 630(16)	6 097(11)
O(5)	6 369(3)	3 866(3)	5 999(2)
O(6)	5 381(3)	8 340(3)	1 916(3)

* Primes indicate minor contributors to a disordered perchlorate anion. Occupancies: O(2)–O(4) 0.76(1), O(2′)–O(4′) 0.24.

Results and Discussion

Reaction of L^3 with $Co^{2+}(aq)$ and subsequent oxidation, or directly with $CrCl_3$, yielded complexes with 1 : 1 metal : ligand ratios which, from aqueous hydrochloric acid, produced in each case apparently a single MN_5Cl isomer. This is indicated by chromatographic behaviour and also from the isolation of only one crystal form from solution in each case for all batches obtained. The free *RR*,*RR*-L^3 ligand lacks elements of symmetry, and the ^{13}C NMR spectrum of the cobalt(III) complex isolated is consequently not particularly indicative of a *trans* or *cis* isomer. For the *cis* isomer of the analogue L^1 found in the nitratopentaamine complex, eight lines were observed in the ^{13}C NMR spectrum, all carbons being inequivalent.[1] By contrast, the *trans* isomer of the chloropentaamine complex of L^1 was readily identified because it yielded only five resonances due to a mirror plane bisecting the metal, tertiary carbon and methyl carbon atoms; this plane is absent in this isomer for L^3. Infrared spectroscopy of the *cis* isomer in the case of L^1 exhibited splitting in the H–N–H bending vibration region into two peaks separated by 26 cm^{-1}.[1] The observance of single peaks in this region for both the cobalt(III) and chromium(III) complexes of L^3 suggests that the *trans* geometry may apply in both cases.

Again, electronic spectroscopy is not particularly helpful, since whether the chloride is *trans* to a primary or secondary amine, the basic MN_5Cl chromophore is preserved and the distinction is too subtle to effect successful identification. Both the cobalt(III) and chromium(III) complexes exhibit some splitting of the lowest energy absorption envelope, consistent with usual expectations for the MN_5Cl chromophore in both cases, but the electronic spectra are not unusual. Maxima for the chlorocobalt(III) complex of L^1 [518, 450 (sh), 357 nm][1] are at higher energy than those of L^3 [524, 455 (sh), 358 nm], but this effect may be related to the slightly more 'compressed' chromophore in the former. The asymmetry of the ligand imposes chirality on the complex, and circular dichoism spectra of the chloro–cobalt(III) and –chromium(III) complexes were recorded in aqueous solution (Fig. 2).

Circular dichroism spectra of the cobalt(III) and chromium(III) complexes are very similar despite the d^6 and d^3 configurations respectively, both showing a small positive Cotton effect at low energy and a dominant positive Cotton effect at higher energy under the lower energy absorption envelope. As a result of the low symmetry of the complexes, the formal $^1T_{1g} \longleftarrow {}^1A_{1g}(O_h)$ (cobalt) and $^4T_{2g} \longleftarrow {}^4A_{2g}(O_h)$ (chromium) transition are split into (at least for C_{4v} symmetry) transitions to ^1E and $^1A_2$ levels (cobalt) and to ^4E and $^4A_2$ levels (chromium), with the E levels possibly subject to further minor splitting. The spectrum for the cobalt(III) complex, with maxima at 596 (Δε −0.125), 512 (+0.595), 385 (+0.086) and 344 nm (−0.082 $dm^3\ mol^{-1}\ cm^{-1}$) is very similar to that observed for *trans*-$[Co(RR\text{-}chxn)_2(NH_3)_2]^{3+}$ (chxn = cyclohexane-1,2-diamine)[13] which exhibits maxima at 530 (Δε −0.070), 465 (+0.670) and 370 nm (−0.020 $dm^3\ mol^{-1}\ cm^{-1}$), except that the transitions under the first absorption envelope at least are shifted to lower energy as

Table 2 Bond lengths (Å) and angles (°) for the cation $[Co(L^3)Cl]^{2+}$

Cl(1)–Co	2.241(1)	N(1)–Co	1.963(3)
N(2)–Co	1.971(3)	N(3)–Co	1.967(3)
N(4)–Co	1.961(3)	N(5)–Co	1.944(3)
C(1)–N(1)	1.479(4)	C(6)–N(2)	1.494(4)
C(7)–N(2)	1.488(4)	C(9)–N(3)	1.498(4)
C(10)–N(3)	1.484(4)	C(15)–N(4)	1.491(4)
C(8)–N(5)	1.493(4)	C(2)–C(1)	1.526(4)
C(6)–C(1)	1.510(4)	C(3)–C(2)	1.535(5)
C(4)–C(3)	1.522(6)	C(5)–C(4)	1.524(5)
C(6)–C(5)	1.525(4)	C(8)–C(7)	1.541(5)
C(9)–C(8)	1.529(5)	C(16)–C(8)	1.519(5)
C(11)–C(10)	1.528(5)	C(15)–C(10)	1.512(5)
C(12)–C(11)	1.516(6)	C(13)–C(12)	1.522(7)
C(14)–C(13)	1.533(6)	C(15)–C(14)	1.523(5)
O(1)–Cl(3)	1.418(4)	O(2)–Cl(3)	1.370(7)
O(3)–Cl(3)	1.364(6)	O(4)–Cl(3)	1.429(5)
O(2′)–Cl(3)	1.510(22)	O(3′)–Cl(3)	1.346(16)
O(4′)–Cl(3)	1.395(21)		

N(1)–Co–Cl(1)	88.2(1)	N(2)–Co–Cl(1)	94.9(1)
N(2)–Co–N(1)	86.2(1)	N(3)–Co–Cl(1)	91.6(1)
N(3)–Co–N(1)	177.8(1)	N(3)–Co–N(2)	91.7(1)
N(4)–Co–Cl(1)	89.6(1)	N(4)–Co–N(1)	96.4(1)
N(4)–Co–N(2)	174.9(1)	N(4)–Co–N(3)	85.8(1)
N(5)–Co–Cl(1)	175.1(1)	N(5)–Co–N(1)	94.8(1)
N(5)–Co–N(2)	81.5(1)	N(5)–Co–N(3)	85.3(1)
N(5)–Co–N(4)	93.9(1)	C(1)–N(1)–Co	108.1(2)
C(6)–N(2)–Co	108.8(2)	C(7)–N(2)–Co	108.2(2)
C(7)–N(2)–C(6)	112.1(2)	C(9)–N(3)–Co	108.6(2)
C(10)–N(3)–Co	108.5(2)	C(10)–N(3)–C(9)	115.2(3)
C(15)–N(4)–Co	109.9(2)	C(8)–N(5)–Co	101.1(2)
C(2)–C(1)–N(1)	113.7(3)	C(6)–C(1)–N(1)	106.6(2)
C(6)–C(1)–C(2)	111.2(3)	C(3)–C(2)–C(1)	110.4(3)
C(4)–C(3)–C(2)	111.9(3)	C(5)–C(4)–C(3)	111.9(3)
C(6)–C(5)–C(4)	109.4(3)	C(1)–C(6)–N(2)	107.8(3)
C(5)–C(6)–N(2)	114.3(3)	C(5)–C(6)–C(1)	112.0(3)
C(8)–C(7)–N(2)	109.6(2)	C(7)–C(8)–N(5)	105.9(2)
C(9)–C(8)–N(5)	103.6(3)	C(9)–C(8)–C(7)	110.6(3)
C(16)–C(8)–N(5)	112.5(3)	C(16)–C(8)–C(7)	112.0(3)
C(16)–C(8)–C(9)	111.9(3)	C(8)–C(9)–N(3)	107.5(3)
C(11)–C(10)–N(3)	116.5(3)	C(15)–C(10)–N(3)	106.9(3)
C(15)–C(10)–C(11)	112.0(3)	C(12)–C(11)–C(10)	109.8(3)
C(13)–C(12)–C(11)	111.4(4)	C(14)–C(13)–C(12)	111.7(4)
C(15)–C(14)–C(13)	110.0(3)	C(10)–C(15)–N(4)	107.1(3)
C(14)–C(15)–N(4)	113.2(3)	C(14)–C(15)–C(10)	111.8(3)
O(2)–Cl(3)–O(1)	110.2(5)	O(3)–Cl(3)–O(1)	108.6(4)
O(3)–Cl(3)–O(2)	112.4(6)	O(4)–Cl(3)–O(1)	109.3(3)
O(4)–Cl(3)–O(2)	107.9(5)	O(4)–Cl(3)–O(3)	108.5(5)
O(3′)–Cl(3)–O(2′)	100(1)	O(4′)–Cl(3)–O(2′)	95(1)
O(4′)–Cl(3)–O(3′)	113(1)		

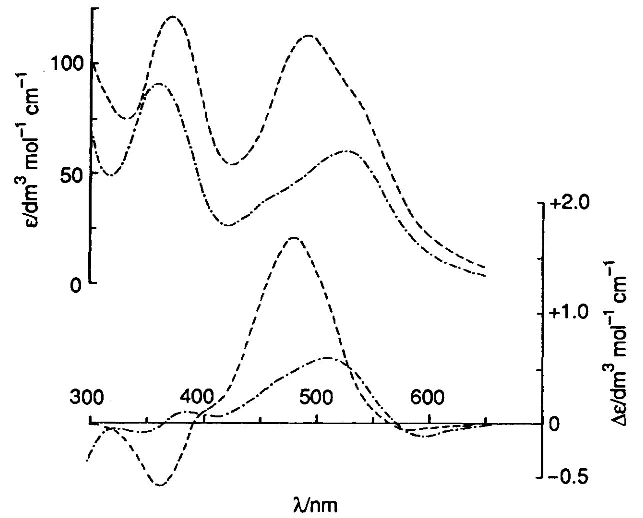

Fig. 2 Electronic (upper traces) and circular dichroism (lower traces) spectra of *RR,RR-trans*-$[Co(L^3)Cl]^{2+}$ (–••–) and *RR,RR-trans*-$[Cr(L^3)Cl]^{2+}$ (– – – – –)

a result of the different chromophore, consistent with the same chirality applying in each case. The rotational strengths are similar in each case, not surprising given the equivalent number, type, relative spatial location of stereogenic centres, and preferred chelate ring conformations involving the cyclohexane-1,2-diamine units in each. For *trans*-$[Co(R\text{-}pn)_2(NH_3)_2]^{2+}$ (pn = propane-1,2-diamine) with only two stereogenic centres, a similar pattern is observed [maxima at 518 ($\Delta\varepsilon$ −0.125), 463 (+0.580) and 358 nm (−0.050 $dm^3\ mol^{-1}\ cm^{-1}$)],[14] but the rotational strength is reduced only slightly. What is surprising is that the separation and relative size of the two transitions under the lowest energy absorption envelope are very similar for both *trans*-$[Co(RR\text{-}chxn)_2(NH_3)_2]^{3+}$ and $[Co(L^3)Cl]^{2+}$, since the CoN_6 chromophore in the former complex has been suggested to lead to a small splitting of the ^1E and $^1A_2$ components of less than 200 cm^{-1},[15] whereas the CoN_5Cl chromophore in the latter is expected to exhibit substantially greater splitting, as indicated by the asymmetry in the electronic maximum in this case (Fig. 2). However, since the observed spectra are the result of combination of transitions of opposite signs, the outcome may be coincidental, particularly if the Cotton effect of one component is dominant. The lower energy and lower rotational strength transition has been conventionally assigned to the transition to the ^1E level.[13–16] For the chromium(III) analogue, no comparisons with simple systems can be made, but structurally analogous complexes producing similar Cotton effects is consistent with the concept of sector rules in defining circular dichroism spectra,[17] whereas the size of Cotton effects, which are modelled on the symmetric chromophore in a chiral environment, can clearly vary with the chromophore.

To confirm the geometry of the cobalt(III) complex, a crystal structure analysis was performed. The structure consists of the complex cation, a perchlorate anion disordered by rotation about one of the Cl–O bonds, a chloride anion and two water molecules. The structural analysis confirms that two *RR-trans*-cyclohexane-1,2-diamine residues are incorporated into the quinquedentate ligand, and that the central primary amine is *trans* to the unidentate chloro ligand (Fig. 1). Nevertheless, the molecular cation possesses no internal symmetry. This is because the secondary amine groups have opposite chiralities but each is adjacent to a tertiary carbon atom with *R* chirality. The cyclohexane rings adopt chair conformations and the adjacent five-membered chelate rings skew conformations. As with previous structures of this type,[1,18,19] there is evidence of considerable strain in the co-ordinated ligand. Most notable are the nominally tetrahedral angles Co–N(5)–C(8) and N(5)–C(8)–C(9) which are 101.1(2) and 103.6(3)° respectively, and are associated with co-ordination of the primary amine of the $-NH-CH_2-C(Me)(NH_2)-CH_2-NH-$ 'capping' group.

The average Co–N bond length is 1.961 Å. While this is shorter than bonds in compounds such as $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5Cl]^{2+}$, both of which are 1.973 Å,[20,21] it is longer than the bonds observed in related structures. In $[Co(L^1)Cl]^{2+}$, for example, the average bond length is 1.943 Å.[1] Notably, the Co–N distance [1.944(3) Å] from the primary amine of the 'capping' group in $[Co(L^3)Cl]^{2+}$ is significantly shorter than the other distances, and equates with the distance observed in $[Co(L^1)Cl]^{2+}$ of 1.944(2) Å whereas other Co–N comparisons between the structures differ by around 0.025 Å. Lengthening of this bond would necessarily involve significant angle distortions as a consequence of the rigid pair of five-membered chelate rings resulting from co-ordination, and presumably this is best relieved by a close approach to the metal ion. Notably, in $[Co(L^2)_2]^{3+}$,[2] the central amine of the facially co-ordinated tridentate ligand exhibits a similar short bond [1.942(2) Å] whereas the less constrained terminal amine bonds are notably

Table 3 Observed base hydrolysis rate constants (s^{-1}) for $[M(L^n)Cl]^{2+}$ (n = 1 or 3) complex ions

		$[Co(L^1)Cl]^{2+}$	$[Co(L^3)Cl]^{2+}$		$[Cr(L^3)Cl]^{2+}$	
$[OH^-]$/mol dm^{-3}	T/°C	k_{obs}	k_{obs1}	k_{obs2}	k_{obs1}	k_{obs2}
0.025	25.0	0.028	0.593	0.043	0.240	0.038
0.050	25.0	0.058	1.105	0.080	0.415	0.081
0.100	18.0	—	0.732	0.072	0.600	0.110
	25.0	0.119	2.32	0.143	0.940	0.158
	32.0	0.358	5.99	0.415	1.55	0.255
	39.0	1.18	16.6	1.39	2.13	0.327
	45.0	3.56	—	—	—	—
0.20	25.0	0.224	4.81	0.295	1.75	0.273
0.30	25.0	0.326	5.91	0.425	2.92	0.44

longer [1.961(2) and 1.964(2) Å]. The most likely explanation for the bond lengths generally being slightly longer in the present structure compared with that of the L^1 analogue is that incorporation of the cyclohexane rings introduces additional strain into the structure, the rigid cyclohexane ring effectively fixing the bite angle for the two attached nitrogen donors. The Co–Cl bond length of 2.241(1) Å is clearly shorter than those in $[Co(L^1)Cl]^{2+}$, 2.261(1) Å,[1] and $[Co(NH_3)_5Cl]^{2+}$, 2.286(2) Å,[21] and it is not immediately clear why this bond is decreasing as the steric bulk of the molecule is increasing.

Molecular mechanics calculations were carried out in order to determine whether bond length differences between $[Co(L^1)Cl]^{2+}$ and $[Co(L^3)Cl]^{2+}$ have a steric origin, and to compare the geometries of the $[Co(L^3)Cl]^{2+}$ and the hypothetical $[Co(L^4$ [or $L^5])Cl]^{2+}$ complexes. The calculations produce L^1 and L^3 geometries which agree reasonably well with the crystal structure geometries. However, molecular mechanics modelling of the two structures $[Co(L^1)Cl]^{2+}$ and $[Co(L^3)Cl]^{2+}$ predicts almost identical Co–N bond lengths, 1.959 and 1.962 Å respectively, and almost identical Co–Cl bond lengths. Thus, the small but significant differences in the bond lengths observed in the crystal structures of $[Co(L^1)Cl]^{2+}$ and $[Co(L^3)Cl]^{2+}$ do not appear to be steric in origin. The minimized total strain energies for $[Co(L^3)Cl]^{2+}$ (160.0 kJ mol^{-1}), $[Co(L^4)Cl]^{2+}$ (166.4 kJ mol^{-1}) and $[Co(L^5)Cl]^{2+}$ (164.5 kJ mol^{-1}) (structures as defined in Fig. 1) show that, at least for the conformations considered, the former is the most stable and could be expected to form under all circumstances. However, the differences in energies are small. It is notable that $[Co(L^4)Cl]^{2+}$ appears to be the one with a geometry well disposed towards formation of the doubly capped ligand, fitting with experimental observations where the double capped macrocycle is formed essentially to the exclusion of the half capped compound during the condensation reaction employing racemic cyclohexane-1,2-diamine, whereas reaction with either the *RR* or *SS* diamine produces both acyclic and cyclic species, the acycle being the dominant product.[3]

Base hydrolysis reactions of both the chloro–cobalt(III) and –chromium(III) complexes of L^3 exhibit two steps. Despite assignment problems inherent in the low symmetry of the precursor, the ^{13}C NMR spectra of the acid-quenched intermediate and final product in the case of the cobalt(III) complex differ substantially in pattern, suggesting that the second step involves an isomerization reaction which follows the base-catalysed chloride hydrolysis. Alternatively, the second step could involve dissociation of the central primary amine, but we see no evidence of facile reversible binding of this amine in this or other cobalt(III) analogues. Reversible dissociation and binding of such a 'capping' group has definitely been established, however, in the chromium(III) complex of 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine.[22] The analogue $[Co(L^1)Cl]^{2+}$ displays only a single rate process assigned to chloride hydrolysis, with NMR spectroscopy in that case supporting configurational integrity in the reaction.

Kinetic data for the reactions of the complexes in strong base (0.025–0.3 mol dm^{-3} hydroxide ion) are collected in Table 3. Both processes observed exhibited simple first-order dependence on hydroxide ion concentration for each complex. Pentaamine halogeno–cobalt(III) and –chromium(III) ion kinetics in basic solution have been extensively studied,[23,24] and a major reaction is halide hydrolysis which in these complexes has been established to generally follow a S_N1_{CB} (conjugate base) mechanism, as outlined elsewhere.[19] A number of cobalt(III) complexes of pendant-arm macrocycles with an identical 'capping' unit on one octahedral face to that operating in the present complexes (*e.g.* 6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine, L^6) have been examined in detail recently, and hydrolysis in those systems was related to the variation in Co–Cl bond, shorter bonds requiring more energy to stretch to a given distance in a dominantly dissociative mechanism.[19] Hydrolysis in $[Co(L^3)Cl]^{2+}$ is much slower than in those cases, and some 800-fold slower than in $[Co(NH_2Me)_5Cl]^{2+}$.[25] The generally less compressed co-ordination sphere in $[Co(L^3)Cl]^{2+}$ compared with $[Co(L^1)Cl]^{2+}$ is associated with a slower hydrolysis in the latter (*ca.* 20-fold slower), although the more compressed overall co-ordination sphere in the latter is offset by a slightly longer Co–Cl bond than observed in the former complex, suggesting that ground state Co–Cl distance is not the only parameter influencing the outcome. Activation enthalpy increases with decreasing hydrolysis rate constant, but activation entropy also increases, but is large and positive for both above complexes (Table 4). This latter effect is commonly observed for base hydrolysis of chloropentaaminecobalt(III) ions, since a significant positive contribution from changes in solvent electrostriction in forming the activated state operates. The second process in the case of the $[Co(L^3)Cl]^{2+}$ ion also exhibits a large positive activation entropy, which is appropriate for a dissociative-based isomerization reaction where significant changes in solvent electrostriction in forming the transition state may also apply.

The significantly slower hydrolysis rates in the quinquedentate acyclic complexes compared with cyclic analogues with the same disposition of leaving group and 'capping' primary amine group is notable. The activation enthalpy is diminished and the activation entropy notably less positive in the cyclic analogues. The two types of complexes both satisfy the majority of the rules proposed for lability in base hydrolysis proposed by Henderson and Tobe,[26] except the number of secondary amine donors is reduced in the acyclic systems. The presence of the additional chelate ring in the macrocycle linking the two terminal primary amine sites in the acyclic ligands does not lead to a marked change in the N–Co–N angle involving those donors. The angle does not vary significantly from 96.5° (L^1)[1] and 96.4° (L^3) to 96.7° (L^6),[19] suggesting that there is no marked difference in strain as a result of introducing the additional chelate ring and thus cyclizing the ligand, although k_{OH}(macrocycle)/k_{OH}(acycle) is *ca.* 4000. There is a prospect that the difference may relate to

Table 4 Comparative kinetic and structural data for $[M(L^n)Cl]^{2+}$ compounds

					Bond distance*/Å		
M	L^n	k_{OH}^{298}/dm^3 mol^{-1} s^{-1}	$\Delta H‡$/kJ mol^{-1}	$\Delta S‡$/J K^{-1} mol^{-1}	Co–N	Co–Cl	Co–L
Co	L^1	1.1 (±0.04)	131 (±4)	+177 (±11)	1.94_3	2.261	1.99_6
Co	L^3	22.6 (±1.4)	109 (±2)	+128 (±6)	1.96_7	2.242	2.01_3
		1.47 (±0.10)	105 (±7)	+93 (±19)			
Co	L^6	9100	61	+33	1.96_1	2.244	2.00_8
Co	$(NH_2Me)_5$	1800	78	+72	1.98_8	2.283	2.03_7
Cr	L^3	9.2 (±0.5)	44 (±2)	−98 (±5)			
		1.50 (±0.08)	38 (±3)	−130 (±7)			
Cr	$(NH_2Me)_5$	0.42	103	+85			

* Co–L is the average of all bond distances, Co–N the average of all amine bond distances.

the ability of the more flexible acycles to adopt a trigonal-bipyramidal intermediate, with significant structural change in forming the transition state, whereas the macrocycle is less able to adopt this geometry and operates *via* a square-based pyramidal intermediate[1] which would involve less rearrangement in attaining the transition state and subsequently a lower activation enthalpy and activation entropy.

Surprisingly, the two reactions for the $[Cr(L^3)Cl]^{2+}$ ion exhibit negative rather than positive activation entropy values. The possibility of chromium proceeding *via* an associative mechanism even in base hydrolysis reactions has been proposed recently.[27] The distinctly different activation entropies from cobalt(III) to chromium(III) may be interpreted as further support for this proposition. The second step in the case of the chromium complex exhibits similar activation parameters to the first, suggesting a similar associative process as one would expect, and the prospect of either dissociation of a secondary amine arm or isomerization as in the cobalt analogue may be considered. Why the complexes of L^3 exhibit a second process whereas this is not seen with L^1 is not obvious either, although it is known that L^1 can form both *cis* and *trans* cobalt(III) complexes,[1] the outcome apparently depending on the donor in the sixth site. One presumes that the geometric isomer found in the precursor does not represent the thermodynamically stable form under the reaction conditions in the case of L^3. Since only small energy differences direct isomer preference, the origins of such effects are subtle. It is interesting that the complexes are not impeded in their rearrangement chemistry by the large cyclohexane rings; intuitively, one may have suspected the quinquedentate L^1 based on ethane-1,2-diamine would have been more likely to exhibit geometric rearrangement than the one (L^3) based on cyclohexane-1,2-diamine.

Acknowledgements

Support of this work by the Australian Research Council is gratefully acknowledged. Measurements of the circular dichroism spectra were performed by Dr. L. R. Gahan (University of Queensland), to whom we extend our gratitude.

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Received 24*th December* 1992; *Paper* 2/06857E