Chlorometal(III) Complexes of a New Chiral Quinquedentate Polyamino Acid based on (*SS*)-*trans*-Cyclohexane-1,2-diamine†

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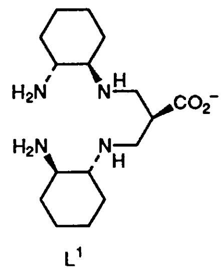
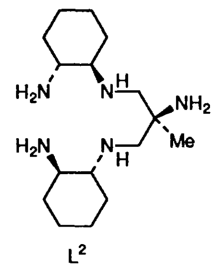
The potentially quinquedentate ligand (*SS,SS*)-3-(2-aminocyclohexylamino)-2-(2-aminocyclohexylaminomethyl)propionic acid (HL^1), prepared *via* a metal-directed condensation reaction, readily formed a (carboxylatotetraamine)chlorocobalt(III) complex cation as well as the rhodium(III) and chromium(III) analogues. The compound *SS,SS*-$[CoL^1(Cl)][ClO_4]\cdot 0.75HClO_4\cdot 2H_2O$ crystallizes in the orthorhombic space group $P2_12_12_1$, $a = 7.825(2)$, $b = 16.566(6)$, $c = 19.737(11)$ Å, and the crystal structure determined by X-ray diffraction methods refined to a residual of 0.066 for 1475 independent observed reflections. The co-ordinated chloride has a *trans* disposition relative to the carboxylate group of the ligand, the two pairs of nitrogen donors from the cyclohexane-1,2-diamine residues being coplanar with the cobalt ion. The $NHCH_2CH(CO_2^-)CH_2NH$ core of the ligand necessarily occupies an octahedral face. Metal–nitrogen distances [Co–N 1.920(11)–1.982(11) Å] are slightly longer than in the 3-(2-aminoethylamino)-2-(2-aminoethylaminomethyl)propionic acid analogue although the metal–oxygen distance [1.916(10) Å] is comparable to that in the analogue, as is the Co–Cl distance [2.223(4) Å]. Comparisons of structures and kinetics of base hydrolysis with related systems are drawn.

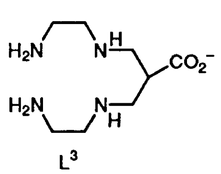
This work concerns the synthesis of a new potentially quinquedentate polyamino acid ligand (*SS,SS*)-3-(2-aminocyclohexylamino)-2-(2-aminocyclohexylaminomethyl)propionic acid (HL^1) and its co-ordination to the inert octahedral cobalt(III), rhodium(III) and chromium(III) metal ions. Recently, we reported some related work on chlorometal(III) complexes of a new quinquedentate polyamine ligand (*RR,RR*)-1,3-bis(2-aminocyclohexylamino)-2-methylpropan-2-amine (L^2).[1] Both these ligands evolve from condensation reactions employing (*RR*)- or (*SS*)-*trans*-cyclohexane-1,2-diamine, formaldehyde and the carbon acids diethyl malonate (for L^1) or nitromethane (for L^2) around a copper(II) template. Where ethane-1,2-diamine is employed in place of the chiral diamine in this and the former study, the analogues 3-(2-aminoethylamino)-2-(2-aminoethylaminomethyl)propionic acid (HL^3)[2] and 5-methyl-3,7-diazanonane-1,5,9-triamine (L^4)[3] can be prepared. All four ligands are based on a linear 3,7-diazanonane-1,9-diamine polyamine framework with additional substitution including a donor on the central carbon of the chain. The 'core' three donors of the potentially quinquedentate ligands can bind only to an octahedral face and, following co-ordination of this 'core', two geometric isomers are possible depending on whether the primary amine donors of the two arms bind in the same plane as that of the two secondary amine donors and the metal ion (leading to a *trans* disposition for the central donor group and the sixth unidentate site) or whether only one of the arms binds in that plane (producing a *cis* disposition of the central donor group and the sixth site). The co-ordination of the central primary amine in L^2 or L^4 in an enforced 'boat' conformation leads to considerable strain in the system, apparently relieved somewhat when that primary amine is replaced by a carboxylate group as a result of introducing less-strained six- rather than five-membered chelate rings.



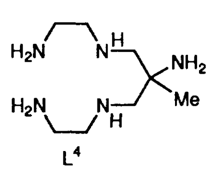
L^1



L^2



L^3



L^4

The relatively rigid cyclohexane rings fused to the skeletons in L^1 and L^2 introduce rigidity, steric bulk and stereogenicity to the molecule.‡ We have chosen to concentrate on polydentate ligands derived from (*RR*)- or (*SS*)-*trans*-cyclohexane-1,2-diamine, although two closely related *meso* forms (*r-meso* and *s-meso*) are inherently available, as are in principle compounds based on *cis*-cyclohexane-1,2-diamine (possible stereoisomers are discussed more fully in an earlier paper[1]). The current paper completes a study of co-ordination of the four related ligands L^1–L^4 to inert octahedral complexes, during which the crystal structures of the chlorocobalt(III) complexes of all four have been determined, and that of the complex of L^1 is reported herein.

Experimental

Syntheses.—*trans*-Cyclohexane-1,2-diamine (*RR*- or *SS*-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ The drawings of L^1 and L^2 are for the *RR,RR* isomer.

chxn) was resolved as described previously,[4] the optically pure forms isolated and *SS*-chxn used as the hydrochloride salt.

[*Methyl* (SS,SS)-3-(2-*aminocyclohexylamino*)-2-(2-*aminocyclohexylaminomethyl*)*propionate*]*copper*(II) *perchlorate sesquihydrate*, $[\mathrm{CuL}^5][\mathrm{ClO}_4]_2\cdot1.5\mathrm{H_2O}$. A solution of *SS*-chxn·2HCl (19 g, 101 mmol) and copper(II) perchlorate hexahydrate (18.8 g, 50 mmol) in water (400 cm^3) was warmed to *ca.* 50 °C, triethylamine (14 cm^3) and diethyl malonate (7.8 cm^3, 51 mmol) added with stirring, and the suspension taken to reflux. A solution of formaldehyde (8 cm^3, 37% w/w) in methanol (40 cm^3) was added dropwise. Reflux was continued overnight, the suspension dissolving during this period to a red-purple solution. The reaction mixture was evaporated to a small volume, and the sticky solid which precipitated was collected and dried in a vacuum desiccator (19.6 g). A sample of this intermediate (1 g) in methanol (200 cm^3), was treated with triethylamine (1 cm^3) and water (2 cm^3) and refluxed overnight. After cooling to room temperature, the solution was diluted to *ca.* 1.5 dm^3 with water, sorbed onto a column (16 × 3.5 cm) of SP Sephadex C-25 cation-exchange resin (Na^+ form), washed with water, then eluted with 0.2 mol dm^{-3} sodium perchlorate to give a major band and a minor band which did not crystallize. The major band was collected, rotary evaporated to a small volume (*ca.* 20 cm^3), and set aside to crystallize. Small purple crystals formed very slowly on standing, and were collected, washed with ethanol and air dried (0.5 g, 40%) (Found: C, 32.9; H, 6.0; N, 9.3. Calc. for $\mathrm{C_{17}H_{34}Cl_2CuN_4O_{10}\cdot1.5H_2O}$: C, 33.1; H, 6.0; N, 9.1%). Electronic spectrum (in water): $\lambda_{\max}$ 530 (102) and 253 nm (ε 7260 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$). Cyclic voltammetry (water, glassy C, 100 mV s^{-1} scan): E_p −0.65 V (irreversible). IR spectrum (KBr disc): 2931m, 2858w ($\mathrm{CH_2}$), 1720m ($\mathrm{CO_2Me}$), 1629s ($\mathrm{NH_2}$), 1115vs, 623s cm^{-1} ($\mathrm{ClO_4}^-$).

(SS,SS)-3-(2-*Aminocyclohexylamino*)-2-(2-*aminocyclohexylaminomethyl*)*propionic acid hydrochloride*, $\mathrm{HL}^1\cdot4\mathrm{HCl}$. The intermediate in the above reaction (18.8 g) in methanol (800 cm^3) with triethylamine (18 cm^3) and water (40 cm^3) was refluxed overnight, cooled, diluted to *ca.* 10 dm^3 with water and loaded onto a column (24 × 5 cm) of SP Sephadex C-25 resin. Elution as above yielded 600 cm^3 of the major product. This solution and 3 mol dm^{-3} HCl were added dropwise to a constantly stirring excess of zinc powder (25 g). The resultant solution was then heated to *ca.* 50 °C and stirred until colourless, cooled to room temperature, then filtered to remove the excess of zinc powder and copper metal. This solution was diluted to *ca.* 10 dm^3 with water, loaded onto a column of Dowex 50Wx2 (H^+ form) cation-exchange resin, washed with water and 2 mol dm^{-3} HCl to remove zinc ion, then eluted with 5 mol dm^{-3} HCl. The latter eluate was collected, rotary evaporated to dryness, twice washed with ethanol (15 cm^3) and taken to dryness again to yield a white powder (8 g, 58%) (Found: C, 39.1; H, 8.5; N, 10.7. Calc. for $\mathrm{C_{16}H_{36}Cl_4N_4O_2\cdot0.5EtOH\cdot2H_2O}$: C, 39.4; H, 8.4; N, 10.8%). NMR ($\mathrm{D_2O}$): ^{1}H, δ 1.3–2.0 (m, 16 H), 2.1–2.4 (m, 6 H) and 3.3–3.7 (m, 9 H); ^{13}C, δ 25.3 (×2), 25.4 (×2), 28.95, 29.1, 32.2 (×2), 40.9, 46.3, 47.9, 53.7 (×2), 61.8, 62.7 and 177.2. IR spectrum (KBr disc): 1716m ($\mathrm{CO_2H}$), 2950vs (br), 2020m (br), 1615s and 1520m cm^{-1} ($\mathrm{NH_2}^+$, $\mathrm{NH_3}^+$).

[(SS,SS)-3-(2-*Aminocyclohexylamino*)-2-(2-*aminocyclohexylaminomethyl*)*propionato*]*chlorocobalt*(III) *chloride pentahydrate*, $[\mathrm{CoL}^1(\mathrm{Cl})]\mathrm{Cl}\cdot5\mathrm{H_2O}$. To a solution of $\mathrm{HL}^1\cdot4\mathrm{HCl}$ (1 g, 2.2 mmol) in water (80 cm^3) was added $\mathrm{CoCl_2\cdot6H_2O}$ (0.57 g, 2.4 mmol), the pH was adjusted to *ca.* 7 with 2.5 mol dm^{-3} NaOH, 30% $\mathrm{H_2O_2}$ (1.5 cm^3) was added and the solution was stirred vigorously for 4 h. The solution was adjusted to pH *ca.* 1 with 5 mol dm^{-3} HCl, activated charcoal (1 g) was added, and the mixture was stirred at *ca.* 60 °C overnight. The resultant cherry-red solution was filtered through Kieselguhr to remove solids, diluted to 1 dm^3 with water, and sorbed onto a column (21 × 3.5 cm) of Dowex 50Wx2 (H^+ form) cation-exchange resin. After washing with water and 1 mol dm^{-3} HCl to remove unreacted cobalt(II), elution with 4 mol dm^{-3} HCl gave a single red band. The eluate from the column was evaporated to dryness and dried in a desiccator (0.64 g, 60%) (Found: C, 36.0; H, 7.5; N, 10.45. Calc. for $\mathrm{C_{16}H_{31}Cl_2CoN_4O_2\cdot5H_2O}$: C, 36.1; H, 7.8; N, 10.5%). Electronic spectrum (in water): $\lambda_{\max}$ 560 (sh) (59), 510 (83), 370 (81) and 240 nm (ε 14 050 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$). NMR ($\mathrm{D_2O}$): ^{1}H, δ 1.1–1.9 (m, 16 H) and 2.0–3.3 (m, 15 H); ^{13}C, δ 26.4 (×2), 26.8 (×2), 31.55, 32.1, 35.2, 35.9, 49.5, 50.6, 55.0, 61.4, 62.2, 73.0, 74.0 and 183.7. IR spectrum (KBr disc): 3200, 1615, 1405, 1020 (NH), 2939, 2861, (CH), 1650, 1450 cm^{-1} ($\mathrm{CO_2}^-$). Alternatively, after being concentrated to *ca.* 15 cm^3, the solution was set aside to crystallize after the addition of $\mathrm{HClO_4}$ (3 cm^3, 3 mol dm^{-3}). X-Ray-quality red crystals of the perchlorate salt with $0.75\mathrm{HClO_4\cdot2H_2O}$ of crystallization formed in low yield on standing for *ca.* 20 weeks, and were collected, washed with ethanol and air dried.

[(SS,SS)-3-(2-*Aminocyclohexylamino*)-2-(2-*aminocyclohexylaminomethyl*)*propionato*]*chlorochromium*(III) *perchlorate hydrogen perchlorate tetrahydrate*, $[\mathrm{CrL}^1(\mathrm{Cl})][\mathrm{ClO}_4]\cdot\mathrm{HClO_4}\cdot4\mathrm{H_2O}$. A solution of $\mathrm{HL}^1\cdot4\mathrm{HCl}$ (1 g, 2.2 mmol) and triethylamine (1.5 cm^3) in ethanol (80 cm^3) was stirred constantly, and anhydrous $\mathrm{CrCl_3}$ (0.4 g, 2.5 mmol) was added. The resultant red-purple solution was stirred overnight, filtered through Kieselguhr to remove some green solid, diluted to 1 dm^3 with 0.2 mol dm^{-3} HCl, loaded onto a column (21 × 3.5 cm) of Dowex 50Wx2 cation-exchange resin, washed with water and 1 mol dm^{-3} HCl, and eluted with 5 mol dm^{-3} HCl. Two bands were isolated. The second red-orange band changed in spectrum to be identical to the first red-purple band on rotary evaporation, consistent with chloride anation of an aqua species. The concentrated bands were combined, diluted to 1 dm^3, sorbed onto the Dowex column and rechromatographed, yielding a single band. After concentration to *ca.* 15 cm^3, 3 mol dm^{-3} $\mathrm{HClO_4}$ (3 cm^3) was added, and the red-purple product crystallized on standing (Found: C, 28.65; H, 5.7; N, 7.8. Calc. for $\mathrm{C_{16}H_{32}Cl_3CrN_4O_{10}\cdot4H_2O}$: C, 28.65; H, 6.0; N, 8.3%). Electronic spectrum (in water): $\lambda_{\max}$ 492 (75), 381 (57) and 210 nm (ε 13 400 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$). IR spectrum (KBr disc): 3200, 3090, 1615, 1585, 1405, 1020 (NH), 2939, 2866 (CH), 1615, 1450 ($\mathrm{CO_2}^-$), 1115, 626 cm^{-1} ($\mathrm{ClO_4}^-$).

[(SS,SS)-3-(2-*Aminocyclohexylamino*)-2-(2-*aminocyclohexylaminomethyl*)*propionato*]*chlororhodium*(III) *perchlorate hydrogen perchlorate dihydrate*, $[\mathrm{RhL}^1(\mathrm{Cl})][\mathrm{ClO}_4]\cdot\mathrm{HClO_4}\cdot2\mathrm{H_2O}$. A solution of $\mathrm{HL}^1\cdot4\mathrm{HCl}$ (0.55 g) in hot water (150 cm^3) was adjusted to pH *ca.* 7 with NaOH, and mixed with a hot solution of $\mathrm{RhCl_3\cdot3H_2O}$ (0.26 g) in water (150 cm^3). The resultant initially orange solution was refluxed and stirred overnight. The yellow solution was cooled to room temperature, diluted to 1 dm^3 with 0.1 mol dm^{-3} HCl, filtered through Kieselguhr to remove some yellow solid, loaded onto a column (13 × 4 cm) of Dowex 50Wx2 (H^+ form) cation-exchange resin, washed with 1 mol dm^{-3} HCl and a single yellow band eluted with 5 mol dm^{-3} HCl. This was evaporated to dryness to yield a yellow powder of the chloride salt (0.56 g, 50%). Alternatively, the solution was evaporated to 20 cm^3, 3 mol dm^{-3} $\mathrm{HClO_4}$ (3 cm^3) was added, and the small yellow crystals of the perchlorate which separated on standing for several days were collected, washed with alcohol and air dried (Found: C, 28.3; H, 5.5; N, 7.7. Calc. for $\mathrm{C_{16}H_{32}Cl_3N_4O_{10}Rh\cdot2H_2O}$: C, 28.0; H, 5.4; N, 8.1%. Electronic spectrum (in water): $\lambda_{\max}$ 360 (sh) (300) and 257 nm (ε 1940 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$). NMR ($\mathrm{D_2O}$): ^{13}C, δ 22.3 (×3), 23.5, 26.0, 26.2, 29.1 (×2), 36.7, 42.6, 44.7, 50.5, 51.0, 57.6, 59.3 and 178. IR spectrum (KBr disc): 3225, 1615, 1400 (NH), 2934, 2861 (CH), 1640, 1455 ($\mathrm{CO_2}^-$), 1120, 625 cm^{-1} ($\mathrm{ClO_4}^-$).

Physical Methods.—Electronic spectra were recorded using an Hitachi 150-20 spectrophotometer, IR spectra of compounds dispersed in KBr discs on a Bio-Rad FT-IR 7 spectrometer, and NMR spectra using a JEOL FX90Q FT spectrometer using sodium trimethylsilylpropionate as an internal standard, but with shifts cited *versus* tetramethylsilane. Base hydrolysis reaction kinetics was studied on an Applied Photophysics DX-17 stopped-flow spectrofluorimeter as described earlier.[1]

Structure Determination.—Crystal data. $[CoL^1(Cl)][ClO_4]\cdot 0.75HClO_4\cdot 2H_2O$, $M = 552.66$, orthorhombic, space group $P2_12_12_1$, $a = 7.825(2)$, $b = 16.566(6)$, $c = 19.737(11)$ Å, $U = 2559(2)$ Å^3, D_c ($Z = 4$) = 1.435 g cm^{-3}, μ(Mo-Kα) = 10.53 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å, $F(000) = 1158$. Specimen: red, 0.30 × 0.09 × 0.20 mm, $N = 2588$, $N_o = 1475$, h 0–13, k 0–16, l 0–23. Merging $R = 0.01$, $R = 0.066$, $R' = 0.071$, residual extrema +0.6 and −0.4 e Å^{-3}.

Lattice parameters 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 $1 < \theta < 25.0°$ using an ω-scan mode. The scan widths and horizontal counter apertures employed were $(1.55 + 0.35 \tan \theta)°$ and $(2.70 + 0.40 \tan \theta)$ mm. Data reduction and application of Lorentz, polarization and absorption corrections were carried out using the Enraf-Nonius Structure Determination Package.[5] Independent reflections with $I > 2.5\sigma(I)$ were considered observed and used in calculations. The structure was solved by direct methods using SHELXS 86[6] and the solution was extended by Fourier difference methods. Hydrogen atoms were refined with isotropic thermal parameters and all other atoms were refined anisotropically. A partially occupied perchlorate anion (of a formal $HClO_4$ molecule but with the proton located elsewhere in the structure, as described later in the Discussion) was refined with a group occupancy factor; this converged to 0.75(2). Full-matrix least-squares refinement of an overall scale factor and positional and thermal parameters converged (all shifts $< 0.07\sigma$). Residuals on $|F|$ at convergence are conventional R, R', $w = g/(\sigma^2 F_o + kF_o^2)$ where g and k are 1.06 and 3.8×10^{-3}. 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] A plot was drawn using ORTEP,[8] and the atom numbering scheme is given in Fig. 1. Non-hydrogen atom coordinates, bond lengths and angles are listed in Tables 1 and 2. The absolute configuration (*SS,SS*) was confirmed by refining the alternative configuration ($R = 0.069$), although the absolute configuration of the precursor cyclohexane-1,2-diamine isomer employed for synthesis of the ligands herein has been fully established previously.

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 HL^1 with Co^{2+}(aq) and subsequent oxidation, or directly with $CrCl_3$ or $RhCl_3$, yielded apparently a single MN_5Cl isomer. This is indicated by the chromatographic behaviour and spectroscopy of the isolated solids. The free *SS,SS*-L^1 ligand lacks elements of symmetry, and the *trans* or *cis* isomer is not readily assigned from the ^{13}C NMR spectrum of the cobalt(III) complex. By contrast, for the cobalt(III) complex of the analogue L^3, the ^{13}C NMR spectrum is indicative of the isomer owing to a mirror plane bisecting the metal in the *trans* isomer.[2] Infrared spectroscopy provides some indication of the symmetry of the complex cation, since splitting in the H–N–H bending vibration region into two peaks for the *cis* isomer in the case of analogues is contrasted by a single peak in this region for the *trans* geometry.[2,3] Applying this in the present case supports a common *trans* geometry for the cobalt(III) and rhodium(III) complexes, but a *cis* geometry for the chromium(III) complex isolated. A tendency for the complexes to crystallize with a perchloric acid molecule of crystallization suggests that protonation of the pendant carboxylate and substitution in the co-ordination sphere by a water molecule is possible, but there was no evidence from infrared spectroscopy of the isolated solids for dominantly a CO_2H rather than a co-ordinated CO_2^- group. The presence of only a weak band or in some cases no band at 1720 cm^{-1} in the infrared spectrum in the region expected for a CO_2H group, in addition to the much stronger bands near 1630 and 1450 cm^{-1} associated with the CO_2^- group, defines this. Neither is there any evidence from electronic spectroscopy of facile carboxylate 'lid-on lid-off' reactions in solution. The way in which a perchloric acid molecule of crystallization is incorporated into the structure of the complexes without formal carboxylate dissociation occurring is clarified in the crystal structure analysis below.

Electronic spectroscopy is of some use in assigning geometry,

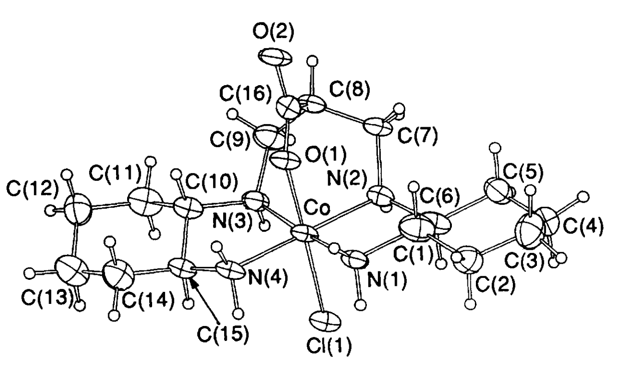

Fig. 1 The cation *SS,SS-trans*-$[CoL^1(Cl)]^+$ showing the atom numbering

Table 1 Non-hydrogen atom coordinates (×10^4) for $[CoL^1(Cl)][ClO_4]\cdot 0.75HClO_4\cdot 2H_2O$

Atom	*x*	*y*	*z*
Co	9 336(2)	6 010(1)	2 300(1)
Cl(1)	7 125(4)	5 372(2)	2 763(2)
N(1)	8 952(12)	6 940(7)	2 860(6)
N(2)	10 792(14)	5 578(7)	3 037(6)
C(1)	10 161(21)	6 934(10)	3 435(9)
C(2)	9 622(22)	7 469(9)	4 023(8)
C(3)	10 778(30)	7 392(11)	4 610(8)
C(4)	11 131(24)	6 538(11)	4 800(9)
C(5)	11 646(20)	6 027(11)	4 246(7)
C(6)	10 397(18)	6 089(9)	3 648(8)
C(7)	12 635(16)	5 496(10)	2 838(8)
C(8)	12 861(17)	5 431(9)	2 091(8)
C(9)	11 694(19)	4 817(10)	1 740(10)
N(3)	9 883(13)	5 087(7)	1 725(6)
N(4)	7 886(14)	6 388(7)	1 566(6)
C(10)	9 282(19)	5 301(7)	1 005(7)
C(11)	9 169(24)	4 566(8)	557(8)
C(12)	8 551(25)	4 812(12)	−154(9)
C(13)	6 879(23)	5 309(12)	−84(10)
C(14)	7 058(23)	6 032(10)	391(8)
C(15)	7 632(17)	5 733(8)	1 073(8)
O(1)	11 169(11)	6 598(6)	1 887(5)
O(2)	13 851(12)	6 627(8)	1 529(6)
C(16)	12 616(21)	6 240(12)	1 811(8)
Cl(2)	14 697(6)	8 177(4)	3 105(3)
O(3)	15 015(29)	8 798(12)	3 590(8)
O(4)	15 800(23)	8 369(12)	2 555(9)
O(5)	12 972(22)	8 295(14)	2 894(14)
O(6)	14 969(18)	7 438(11)	3 378(10)
Cl(3)*	7 487(14)	8 506(6)	496(8)
O(7)*	8 983(31)	7 932(13)	706(14)
O(8)*	7 765(32)	9 062(20)	−59(12)
O(9)*	6 771(66)	8 822(23)	1 075(15)
O(10)*	6 179(43)	8 019(16)	172(28)
O(11)	9 742(20)	8 634(8)	1 930(11)
O(12)	8 264(22)	6 896(12)	8 714(11)

* Occupancy 0.75.

Table 2 Bond lengths (Å) and angles (°) for the cation $[CoL^1(Cl)]^+$

Cl(1)–Co	2.223(4)	C(9)–C(8)	1.532(20)	N(1)–Co	1.920(11)	C(8)–C(7)	1.488(22)
N(2)–Co	1.982(11)	N(3)–C(9)	1.486(17)	N(3)–Co	1.951(12)	C(16)–C(8)	1.461(22)
N(4)–Co	1.943(12)	C(15)–N(4)	1.471(17)	O(1)–Co	1.916(10)	C(10)–N(3)	1.539(18)
C(1)–N(1)	1.477(20)	C(15)–C(10)	1.483(19)	C(6)–N(2)	1.505(19)	C(11)–C(10)	1.508(18)
C(7)–N(2)	1.502(17)	C(13)–C(12)	1.552(23)	C(2)–C(1)	1.520(21)	C(12)–C(11)	1.504(22)
C(6)–C(1)	1.474(22)	C(15)–C(14)	1.503(21)	C(3)–C(2)	1.476(23)	C(14)–C(13)	1.529(23)
C(4)–C(3)	1.490(23)	C(16)–O(2)	1.287(19)	C(5)–C(4)	1.439(21)	C(16)–O(1)	1.287(19)
C(6)–C(5)	1.536(19)						
N(1)–Co–Cl(1)	91.3(3)	N(2)–Co–Cl(1)	88.5(4)	C(1)–C(6)–N(2)	109(2)	C(5)–C(6)–N(2)	116(1)
N(2)–Co–N(1)	87.5(5)	N(3)–Co–Cl(1)	92.1(4)	C(5)–C(6)–C(1)	111(2)	C(8)–C(7)–N(2)	112(1)
N(3)–Co–N(1)	176.2(4)	N(3)–Co–N(2)	91.0(5)	C(9)–C(8)–C(7)	115(2)	C(16)–C(8)–C(7)	107(2)
N(4)–Co–Cl(1)	90.3(4)	N(4)–Co–N(1)	94.6(5)	C(16)–C(8)–C(9)	111(1)	N(3)–C(9)–C(8)	112(1)
N(4)–Co–N(2)	177.6(5)	N(4)–Co–N(3)	87.0(5)	C(9)–N(3)–Co	115(1)	C(10)–N(3)–Co	106.9(8)
O(1)–Co–Cl(1)	177.3(3)	O(1)–Co–N(1)	87.4(4)	C(10)–N(3)–C(9)	112(2)	C(15)–N(4)–Co	109.6(8)
O(1)–Co–N(2)	93.8(5)	O(1)–Co–N(3)	89.2(5)	C(11)–C(10)–N(3)	112(1)	C(15)–C(10)–N(3)	107(1)
O(1)–Co–N(4)	87.5(5)	C(1)–N(1)–Co	109.7(9)	C(15)–C(10)–C(11)	113(2)	C(12)–C(11)–C(10)	109(1)
C(6)–N(2)–Co	105.5(8)	C(7)–N(2)–Co	113.1(9)	C(13)–C(12)–C(11)	108(2)	C(14)–C(13)–C(12)	113(2)
C(7)–N(2)–C(6)	117(1)	C(2)–C(1)–N(1)	113(2)	C(15)–C(14)–C(13)	108(2)	C(10)–C(15)–N(4)	107(1)
C(6)–C(1)–N(1)	107(1)	C(6)–C(1)–C(2)	111(2)	C(14)–C(15)–N(4)	113(1)	C(14)–C(15)–C(10)	109(2)
C(3)–C(2)–C(1)	112(2)	C(4)–C(3)–C(2)	113(2)	C(16)–O(1)–Co	118(1)	O(1)–C(16)–C(8)	119(2)
C(5)–C(4)–C(3)	114(2)	C(6)–C(5)–C(4)	111(2)	O(2)–C(16)–C(8)	121(2)	O(2)–C(16)–O(1)	118(2)

since the basic MN_4OCl chromophore exhibits a unique O–Co–Cl axis in the case of the *trans* isomer. As a result of lower symmetry, the formal ${}^1T_{1g} \longleftarrow {}^1A_{1g}(O_h)$ (cobalt) and ${}^4T_{2g} \longleftarrow {}^4A_{2g}$ (chromium) transition will be 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 splitting greater for *trans* than *cis* geometry. Splitting of the lower-energy transition in the case of cobalt(III) into transitions at 560 and 510 nm contrasts with no observable splitting in the case of the chromium(III) complex, suggesting (within the constraints of comparing different systems) differing geometries. The cobalt(III) spectrum is more consistent with the *trans* geometry assigned from infrared spectroscopy, and likewise the spectrum of the chromium(III) complex is more appropriate for the *cis* geometry. Examination of geometric isomers of a range of quinquedentate polyamine macrocycles earlier indicated a preference for the *cis* geometry with the larger chromium(III) ion compared with the cobalt(III) ion for the same ligand,[9] and variation in the preferred isomer with metal ion is in no way unprecedented.

To confirm the geometry of the cobalt(III) complex, and to permit comparisons with other compounds, a crystal structure analysis was performed. The structure consists of the unipositive complex cation, a perchlorate anion, two water molecules and a partially occupied [75(2)%] perchlorate which is presumably part of a perchloric acid molecule of crystallization. (It is notable that the chromium and rhodium complexes also crystallize with perchloric acid of crystallization.) There are a number of weak hydrogen bonds between the amine donor groups, the water molecules and the perchlorate anions. However, there is also one very strong hydrogen bond between a water molecule and the non-co-ordinated O atom of the carboxylate group [O(2)···O(12) 2.535 Å]. Hydrogen bonds as strong as this are generally observed when highly acidic groups are present, and it is therefore likely that the proton of the perchloric acid of crystallization resides between these O atoms. In this context, it is notable that the C–O(2) bond is unusually long for a non-co-ordinated carbonyl group, and in fact the C–O(1) and C–O(2) distances are the same within the error of the determination. This may be consistent with partial protonation, and one could conjecture about the existence of an equilibrium between the co-ordinated species $Co{-}^-O{-}C(R){=}OH^+$ and $Co{-}O{=}C(R){-}OH$.

The structural analysis confirms that two (*SS*)-*trans*-cyclohexane-1,2-diamine residues are incorporated into the quinquedentate ligand, and that the carboxylate group is *trans* to the unidentate chloro ligand (Fig. 1), the known absolute configuration of the cation being confirmed by refining the alternative configuration. The molecular cation has no symmetry elements, in common with the L^2 analogue. This is because the secondary amine groups have opposite chiralities but each is adjacent to a tertiary carbon atom with *S* chirality. The cyclohexane rings adopt chair conformations and the adjacent five-membered chelate rings skew conformations. As with the previously reported structure of L^3,[2] there is evidently less strain in the co-ordinated ligand than is the case in the amine-capped analogues L^2 and L^4.[1,3] This is because the central donor of the $NHCH_2CH(CO_2^-)CH_2NH$ unit involves the formation of six- rather than the five-membered chelate rings found in the alternative $NHCH_2C(Me)(NH_2)CH_2NH$ 'capping' unit.

Bond lengths to the cobalt atom in $[CoL^1(Cl)]^+$ are fairly normal, except that those to the N(amine) atoms are slightly shorter than in less-strained molecules [average 1.95(1) Å compared with typically 1.97 Å for polyamine complexes] but are typical of 'capped ligands' of this type. It is notable that the average Co–N distance in the analogous complex of L^3 [1.946(3) Å] is the same within experimental error,[2] despite the presence of the fused cyclohexane rings in the present case. By contrast, bond lengths were found to be generally slightly longer in the structure of the chlorocobalt(III) complex of L^2 compared with that of L^4,[1,3] and it is presumed that this relates to the inherently more compact structure desired in that case as a result of the presence of an amine 'cap' rather than a carboxylate 'cap'. Since the rigid cyclohexane ring effectively fixes the bite angle for the two attached nitrogen donors, this will operate against an overall 'shrinking' of the co-ordination sphere, but is coincidentally appropriate for $[CoL^1(Cl)]^+$. The Co–Cl bond length of 2.223(4) Å is clearly shorter than that in $[CoL^3(Cl)]^+$ of 2.255(1) Å despite the increasing steric bulk of the molecule, but this is possibly offset by what appears to be a longer *trans* Co–O distance of 1.916(10) Å in $[CoL^1(Cl)]^+$ compared with 1.901(2) Å in $[CoL^3(Cl)]^+$.[2]

Halogenoamine-cobalt(III) and -chromium(III) ion kinetics in basic solution has been extensively studied,[10,11] and a major reaction is halide hydrolysis which generally follows a S_N1_{CB} (conjugate base) mechanism, as outlined elsewhere.[9] The chloro-cobalt(III), -chromium(III) and -rhodium(III) complexes of L^1 exhibit a hydrolysis process in 0.025–0.3 mol dm^{-3}

aqueous base which is first order in $[OH^-]$ and can be ascribed to base hydrolysis of the chloride ion. At 25 °C, observed second-order rate constants are 51 (Co), 2.7 (Cr) and 0.16 $dm^3\ mol^{-1}\ s^{-1}$ (Rh). The processes are complicated by additional reactions presumably resulting from isomerization reactions similar to those reported for complexes of L^2.[1] The analogue $[CoL^3(Cl)]^+$ exhibits a second-order rate constant for chloride hydrolysis of 200 $dm^3\ mol^{-1}\ s^{-1}$, and NMR spectra of that simpler system also clearly indicate isomerization to a 40:60 equilibrium mixture of the *cis* and *trans* isomers. Reaction rates are influenced by two major considerations. A labilizing effect of the *trans* carboxylate group may be anticipated, and presumably largely accounts for the 80-fold faster rate in the case of $[CoL^3(Cl)]^+$ compared with $[CoL^4(Cl)]^{2+}$.[2,3] Another important factor influencing hydrolysis rates in these systems is the variation in Co–Cl bond distance, shorter bonds in the ground state requiring more energy to stretch to a given distance in the intermediate of a dominantly dissociative mechanism.[9] Notably, the Co–Cl distances in $[CoL^3(Cl)]^+$ [2.255(1) Å] and $[CoL^4(Cl)]^{2+}$ [2.261(1) Å] are very similar,[2,3] permitting the *trans* effect to dominate. Distances in the $[CoL^1(Cl)]^+$ [2.223(4) Å] and $[CoL^2(Cl)]^{2+}$ [2.241(1) Å][1] ions differ by a significantly greater amount, allowing for a strong contribution from ground-state distance influences which would oppose the *trans* effect for the L^1 complex, accounting for the similar rates for $[CoL^1(Cl)]^+$ (51 $dm^3\ mol^{-1}\ s^{-1}$) and $[CoL^2(Cl)]^{2+}$ (23 $dm^3\ mol^{-1}\ s^{-1}$). Chloride hydrolysis of the chromium(III) complex of L^1 is only approximately 20-fold slower than that of the cobalt(III) complex, whereas that of the rhodium(III) complex is over 300-fold slower, similar to general trends for inert octahedral halogenometal(III) systems with these metal ions.[10,11]

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