Quinquedentate Co-ordination of Amino-substituted Tetraazacycloalkanes to Chromium(III)†

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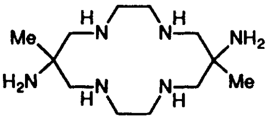
The pendant-arm macrocycles 12-methyl-1,4,7,10-tetraazacyclotridecane-12-amine (L^3), 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine (L^4) and 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine (L^5) react readily in methanol with chromium(II) ion, followed by dilution with aqueous hydrochloric acid and chromatography, to yield *cis*- and or *trans*-$[Cr(L^n)Cl]^{2+}$ complexes (n = 3, 4 or 5). The two *trans* complexes were crystallized readily as perchlorate salts: $[Cr(L^4)Cl][ClO_4]_2{\cdot}H_2O$, monoclinic, space group $P2_1/c$, a = 11.015(4), b = 13.549(4), c = 17.238(3) Å, β = 125.20(3)°; $[Cr(L^5)Cl][ClO_4]_2$, triclinic, space group $P\bar{1}$, a = 13.270(3), b = 9.445(3), c = 9.396(3) Å, α = 100.04(2), β = 96.14(2), γ = 107.15(2)°. Single-crystal X-ray structure determinations were refined to residuals of 0.030 and 0.052 for 2946 and 3211 'observed' reflections respectively. In each case the pendant primary amine and two adjacent secondary amines necessarily occupy an octahedral face, with the chloro ligand *trans* to the primary amine, and secondary amines adopting *RRSS* stereochemistries. There is an increase in average Cr–N distances with macrocycle size (2.06_9, 2.07_9 Å for the L^4 and L^5 complexes respectively), although the Cr–N (pendant primary amine) distance is invariant [2.077(3) Å in each case]. The Cr–Cl distance is smaller for L^4 [2.297(1) Å] than for L^5 [2.306(1) Å]. The second-order rate constants for base hydrolysis are k_{OH} 1.4×10^5, 2.6×10^7, 0.7, and 8.2 $dm^3\ mol^{-1}\ s^{-1}$ for *cis*-L^3, *cis*- and *trans*-L^4, and *trans*-L^5 respectively, with markedly greater values for the *cis* isomers arising largely from lower activation enthalpies, and a greater value for the longer Cr–Cl bond length in the two *trans* isomers.

Quinquedentate polyamine ligands bound to traditional inert metal ions such as cobalt(III), chromium(III) and rhodium(III) have been the subject of a range of studies.[1] We have recently been investigating the co-ordination chemistry of a new type of quinquedentate ligand, consisting of a saturated macrocycle with four nitrogen or mixed nitrogen–thioether donors and with an additional primary amine pendant to the ring, containing a $NHCH_2CMe(NH_2)CH_2NH$ unit which must co-ordinate to an octahedral face.[2–4] These ligands exhibit a 'cap' geometry for the pendant group analogous to that found in the macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1) which has two pendant arms, and which is known to co-ordinate as a sexi- or quinque-dentate ligand to chromium(III).[5] In the present cases the single 'cap' permits quinquedentate co-ordination at most. Acyclic polyamines such as 5-methyl-3,7-diazanonane-1,5,9-triamine (L^2) also produce the same type of 'cap' binding to octahedral metal ions.[6] In this paper, we report some co-ordination chemistry of ligands L^3–L^5 with chromium(III).‡ Syntheses, spectroscopic properties, and base hydrolysis rates of *cis* and *trans* isomers are presented, and X-ray crystal structure analyses of *trans* isomers are also recorded.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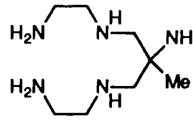
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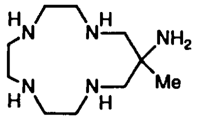
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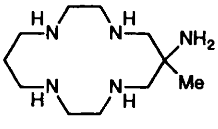
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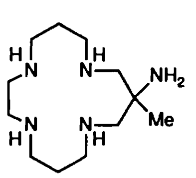
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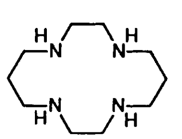
L^6

Experimental

Syntheses.—The complexes (12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane)-, (6-methyl-6-nitro-1,4,8,11-tetraazacyclotetradecane)- and (10-methyl-10-nitro-1,4,8,12-tetraazacyclopentadecane)-copper(II) perchlorate were prepared as previously described.[7–9] The pentahydrochloride salts of the free ligands L^3–L^5 were all prepared by reduction of the nitro groups and the copper ion in the above complexes using a variation of the method previously described for L^5.[2,10]

cis-Chloro(12-*methyl*-1,4,7,10-*tetraazacyclotridecane*-12-*amine*)*chromium*(III) *perchlorate*, $[Cr(L^3)Cl][ClO_4]_2$. Reaction was carried out on a 4 mmol scale. The salt $L^3{\cdot}5HCl$ was

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

‡ L^3 = 12-methyl-1,4,7,10-tetraazacyclotridecane-12-amine; L^4 = 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine; L^5 = 10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine.

suspended in ethanol (150 cm^3) and triethylamine (2.0 cm^3) was added. To the resultant solution, anhydrous chromium(II) chloride was added with constant stirring. The red-purple solution was stirred for 2 h, diluted to 2 dm^3 with 0.2 mol dm^{-3} aqueous HCl, and filtered. The solution was loaded onto a column (25 × 2 cm) of Dowex 50Wx2 (H$^+$ form) cation-exchange resin, washed with 1 mol dm^{-3} aqueous HCl to remove any chromium(II) ion, and eluted with 2–3 mol dm^{-3} aqueous HCl. Two bands were isolated, corresponding to 2+ (purple) and 3+ (red-orange) charged complexes. Upon rotary evaporation to concentrate the bands, the second band changed in colour and electronic spectrum to be identical with the first, consistent with chloride anation of an initial aqua species. Both bands were combined, diluted, resorbed on the Dowex column, and rechromatographed, yielding a single band. After concentration to *ca.* 5 cm^3, 3 mol dm^{-3} $HClO_4$ (*ca.* 2 cm^3) was added, and the purple product crystallized on standing (Found: C, 24.0; H, 5.2; N, 13.8. Calc. for $C_{10}H_{25}Cl_3CrN_5O_8$: C, 23.9; H, 5.0; N, 13.9%). Electronic spectrum (in 1 mol dm^{-3} aqueous HCl): λ_{max} 533 (118) and 395 nm (ε 71 dm^3 mol^{-1} cm^{-1}).

cis- *and* trans-*Chloro*(6-*methyl*-1,4,8,11-*tetraazacyclotetradecane*-6-*amine*)*chromium*(III) *perchlorate*, $[Cr(L^4)Cl][ClO_4]_2$. These complexes were prepared in the manner described for the perchlorate salt of L^3. However, elution readily separated several bands, each collected and isolated as described above. The first relatively fast-moving band was removed with 1 mol dm^{-3} HCl, and yielded a pink solid on crystallization. The electronic spectrum of this minor product, its reactivity in aqueous base, and microanalysis suggested a tetraaminedichlorochromium(III) species with a dangling and protonated amine, probably of *trans* geometry (Found: C, 23.9; H, 4.8; N, 12.8. Calc. for $C_{11}H_{28}Cl_4CrN_5O_8$: C, 23.9; H, 5.1; N, 12.7%). Electronic spectrum (in 1 mol dm^{-3} aqueous HCl): λ_{max} 510 (46), 420 (sh, 32) and 363 nm (ε 76 dm^3 mol^{-1} cm^{-1}). Detailed study of this product was not pursued.

cis *Isomer*. The first broad major band was removed with 2–3 mol dm^{-3} HCl and the major fraction yielded purple crystals on concentration, acidification ($HClO_4$) and standing (yield *ca.* 20%) (Found: C, 24.6; H, 5.5; N, 13.4. Calc. for $C_{11}H_{27}Cl_3CrN_5O_8$: C, 24.9; H, 5.3; N, 13.6%). Electronic spectrum (in 1 mol dm^{-3} HCl): λ_{max} 535 (94), 480 (sh, 28) and 405 nm (ε 90 dm^3 mol^{-1} cm^{-1}).

trans *Isomer*. Upon further standing of the filtrate from the above crystallization, a mixture of well formed purple and red crystals formed and were collected. The good-quality red crystals were readily separated from the residue of the other isomer (yield 15%), and analysed as a dihydrate (Found: C, 24.65; H, 5.45; N, 12.7. Calc. for $C_{11}H_{27}Cl_3CrN_5O_8 \cdot 2H_2O$: C, 24.75; H, 5.45; N, 13.1%). Electronic spectrum (in water): λ_{max} 520 (63), 430 (30) and 365 nm (ε 91 dm^3 mol^{-1} cm^{-1}).

A further band which eluted more slowly from the column yielded a non-crystalline solid with very broad absorbances in the electronic spectrum, indicative of a mixture. By analogy with the behaviour of the L^3 system, this slow-moving 3+ band was assigned as the isomers of the pentaamineaqua complexes, which anate upon standing. Detailed work-up was not pursued.

trans-*Chloro*(10-*methyl*-1,4,8,12-*tetraazacyclopentadecane*-10-*amine*)*chromium*(III) *perchlorate*, $[Cr(L^5)Cl][ClO_4]_2$. This complex was prepared in the manner described for the perchlorate salt of L^3, with chromatography separating a single 2+ band from a single 3+ band, from each of which crystals were isolated following work-up as described for L^3 (yield 40%); more complex separated on prolonged standing. The first band yielded red crystals of a quality suitable for X-ray structure analysis (Found: C, 27.25; H, 5.7; N, 13.25. Calc. for $C_{12}H_{29}Cl_3CrN_5O_8$: C, 27.2; H, 5.5; N, 13.2%). Electronic spectrum (in water): λ_{max} 525 (67), 450 (43) and 375 nm (ε 111 dm^3 mol^{-1} cm^{-1}). The second band yielded red crystals of a pentaaminechloro compound on standing, as a result of chloride anation of the initial aqua complex, although in this case the complex crystallized as a mixed chloride–perchlorate salt (Found: C, 31.5; H, 6.9; N, 15.2. Calc. for $C_{12}H_{29}Cl_3CrN_5O_4$: C, 31.0; H, 6.3; N, 15.05%). Electronic spectrum (in water): λ_{max} 521 (60), 446 (35) and 371 nm (ε 98 dm^3 mol^{-1} cm^{-1}). Slight differences in both the electronic and infrared spectra may arise simply from the two species being different salts, but could indicate different N-based isomers. However, base-hydrolysis kinetics of the two forms were identical within experimental error, suggesting geometrically identical cations.

Physical Methods.—Electronic spectra of aqueous solutions were recorded using Hitachi 220A or 150-20 spectrophotometers, IR spectra using a Bio-Rad FTS-7 FT-IR spectrometer, with complexes dispersed in KBr discs. Elemental microanalyses were performed by the Australian National University Microanalytical Service.

Base-hydrolysis kinetics was followed at least at three temperatures over a range of ⩾20 °C in a thermostatted (±0.1 °C) cell holder of an Hitachi 220A spectrophotometer connected to a refrigerated controlled-temperature circulating bath. Buffers of concentration normally 0.02 mol dm^{-3} and total ionic strength 0.1 mol dm^{-3} ($NaClO_4$) were employed for study of the *cis* isomers, whereas for the *trans* isomers hydroxide ion solutions were employed. The pH range 4.0–7.4 used in the former cases was covered with the buffers succinate and phosphate. 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–time data by standard non-linear least-squares computational methods. For the sake of brevity, routine temperature and pH-dependent rate constants are not reproduced, with only the second-order rate constant at 25 °C and activation parameters appearing herein for each complex.

Structure Determinations.—Unique data sets were measured at *ca.* 295 K within the limit $2\theta_{max} = 50^\circ$ using an Enraf–Nonius CAD-4 four-circle diffractometer (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; conventional 2θ–θ scan mode). N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included, constrained at estimated values in $[Cr(L^5)Cl][ClO_4]_2$ but refined in $[Cr(L^4)Cl][ClO_4]_2 \cdot H_2O$. Conventional residuals R,R' on $|F|$ at convergence are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed:[11] computation used the XTAL 3.0 program system[12] implemented by S. R. Hall. Pertinent results are given in Fig. 1 and Tables 1–4.

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

Crystal data. *trans*-$[Cr(L^4)Cl][ClO_4]_2 \cdot H_2O$, $C_{11}H_{29}Cl_3CrN_5O_9$, $M = 533.7$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 11.015(4)$, $b = 13.549(4)$, $c = 17.238(3)$ Å, $\beta = 125.20(3)$, $U = 2102$ Å^3, $D_c = 1.69$ g cm^{-3} ($Z = 4$), $F(000) = 1108$, $\mu_{Mo} = 9.1$ cm^{-1}. Specimen: 0.88 × 0.70 × 0.09 mm; $A^*_{min,max} = 1.09, 1.60$. $N = 3708$, $N_o = 2946$; $R = 0.030$, $R' = 0.033$.

trans-$[Cr(L^5)Cl][ClO_4]_2$, $C_{12}H_{29}Cl_3CrN_5O_8$, $M = 529.8$, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 13.270(3)$, $b = 9.445(3)$, $c = 9.396(3)$ Å, $\alpha = 100.04(2)$, $\beta = 96.14(2)$, $\gamma = 107.15(2)$, $U = 1092$ Å^3, $D_c = 1.61$ g cm^{-3} ($Z = 2$), $F(000) = 550$, $\mu_{Mo} = 8.7$ cm^{-1}. Specimen: 0.26 × 0.23 × 0.50 mm; $A^*_{min,max} = 1.17, 1.27$. $N = 3839$, $N_o = 3211$; $R = 0.052$, $R' = 0.065$.

Abnormal features. There was high perchlorate thermal motion in the latter structure.

Results and Discussion

The saturated tetraazamacrocycles L^3–L^5, with a primary

Table 1 Non-hydrogen positional coordinates for $[Cr(L^4)Cl][ClO_4]_2\cdot H_2O$

Atom	*x*	*y*	*z*
Cr	0.191 62(4)	0.178 46(3)	0.215 89(3)
Cl	0.041 37(8)	0.044 79(5)	0.184 37(5)
C(1)	0.397 2(3)	0.286 4(2)	0.377 1(2)
N(1)	0.340 9(3)	0.295 2(2)	0.274 8(2)
C(11)	0.511 8(4)	0.365 9(3)	0.438 6(3)
C(2a)	0.259 8(4)	0.297 6(3)	0.378 1(2)
N(3a)	0.127 8(3)	0.249 7(2)	0.293 0(2)
C(4a)	0.007 7(3)	0.320 6(2)	0.227 7(2)
C(5a)	−0.083 9(3)	0.279 5(2)	0.128 7(2)
N(6a)	0.018 9(2)	0.255 3(2)	0.101 3(2)
C(7a)	−0.058 2(3)	0.205 8(2)	0.007 0(2)
C(8)	0.046 9(4)	0.174 7(2)	−0.017 8(2)
C(2b)	0.465 4(4)	0.183 9(3)	0.409 6(2)
N(3b)	0.377 3(3)	0.110 6(2)	0.332 3(2)
C(4b)	0.463 9(4)	0.063 7(3)	0.299 7(2)
C(5b)	0.361 4(4)	0.034 7(2)	0.196 9(2)
N(6b)	0.267 7(3)	0.120 4(2)	0.141 1(2)
C(7b)	0.153 3(4)	0.092 7(2)	0.041 0(2)
Cl(1)	0.187 69(9)	0.447 52(5)	−0.015 38(5)
O(11)	0.244 1(3)	0.384 4(2)	0.065 6(2)
O(12)	0.300 5(3)	0.468 3(2)	−0.028 6(2)
O(13)	0.140 4(3)	0.536 9(2)	0.002 2(2)
O(14)	0.065 8(3)	0.399 3(2)	−0.097 9(2)
Cl(2)	0.631 13(8)	0.262 04(6)	0.200 22(5)
O(21)	0.506 6(3)	0.204 5(2)	0.130 9(2)
O(22)	0.764 2(3)	0.206 3(2)	0.240 9(2)
O(23)	0.642 3(3)	0.348 8(2)	0.158 3(2)
O(24)	0.611 7(3)	0.288 0(2)	0.273 3(2)
O	0.239 4(4)	0.495 7(2)	0.214 5(3)

Table 2 Non-hydrogen positional coordinates for $[Cr(L^5)Cl][ClO_4]_2$

Atom	*x*	*y*	*z*
Cr	0.196 70(5)	0.647 56(7)	0.249 76(7)
Cl	0.026 72(9)	0.474 4(1)	0.202 7(1)
C(1)	0.385 0(4)	0.691 8(5)	0.132 6(5)
C(11)	0.500 1(4)	0.767 7(7)	0.115 1(6)
N(1)	0.354 8(3)	0.778 9(4)	0.262 3(4)
C(2a)	0.368 9(4)	0.535 4(6)	0.166 0(6)
N(3a)	0.256 3(3)	0.470 3(4)	0.184 3(4)
C(4a)	0.239 7(4)	0.347 8(5)	0.267 7(6)
C(5a)	0.273 0(5)	0.403 7(6)	0.430 7(6)
C(6a)	0.203 2(4)	0.485 2(6)	0.504 4(5)
N(7a)	0.219 1(3)	0.636 5(4)	0.468 6(4)
C(8a)	0.155 3(4)	0.719 7(6)	0.545 0(5)
C(2b)	0.304 6(4)	0.682 7(5)	−0.002 3(5)
N(3b)	0.201 2(3)	0.692 9(4)	0.039 5(4)
C(4b)	0.188 7(4)	0.839 6(5)	0.015 1(5)
C(5b)	0.107 9(4)	0.889 7(6)	0.090 5(6)
C(6b)	0.141 2(4)	0.945 1(5)	0.255 2(6)
N(7b)	0.131 7(3)	0.814 6(4)	0.326 9(4)
C(8b)	0.164 5(4)	0.861 0(6)	0.487 8(5)
Cl(1)	0.498 4(1)	0.796 3(1)	0.667 4(1)
O(11)	0.589 2(3)	0.895 9(4)	0.765 2(5)
O(12)	0.413 8(4)	0.852 3(7)	0.670 3(8)
O(13)	0.470 8(5)	0.657 7(5)	0.710 9(7)
O(14)	0.512 9(6)	0.771(1)	0.526 4(6)
Cl(2)	0.174 6(1)	0.216 0(2)	−0.217 4(1)
O(21)	0.098 9(3)	0.186 9(5)	−0.348 2(5)
O(22)	0.274 7(4)	0.294 3(9)	−0.240 6(7)
O(23)	0.145 5(5)	0.311 7(7)	−0.112 7(6)
O(24)	0.166 6(8)	0.085 6(8)	−0.179 2(8)

Table 3 Chromium environments (distances in Å, angles in °) for $[Cr(L^n)Cl]^{2+}$ ($n = 4$ or 5)

	L^4	L^5
Cr–Cl	2.297(1)	2.306(1)
Cr–N(1)	2.077(3)	2.077(3)
Cr–N(3a)	2.066(3)	2.081(4)
Cr–N(6a), N(7a)	2.067(2)	2.071(4)
Cr–N(3b)	2.080(2)	2.096(4)
Cr–N(6b), N(7b)	2.057(3)	2.072(4)
Cl–Cr–N(1)	167.30(9)	170.2(1)
Cl–Cr–N(3a)	93.14(8)	89.1(1)
Cl–Cr–N(6a), N(7a)	91.73(8)	93.0(1)
Cl–Cr–N(3b)	93.06(8)	97.74(9)
Cl–Cr–N(6b), N(7b)	92.77(8)	88.3(1)
N(1)–Cr–N(3a)	78.2(1)	82.7(1)
N(1)–Cr–N(6a), N(7a)	96.72(9)	92.9(1)
N(1)–Cr–N(3b)	78.70(9)	76.8(1)
N(1)–Cr–N(6b), N(7b)	96.0(1)	100.3(1)
N(3a)–Cr–N(6a), N(7a)	85.0(1)	93.3(2)
N(3a)–Cr–N(3b)	95.6(1)	88.5(2)
N(3a)–Cr–N(6b), N(7b)	174.1(1)	175.4(2)
N(6a), N(7a)–Cr–N(3b)	175.2(1)	169.2(1)
N(6a), N(7a)–Cr–N(6b), N(7b)	94.4(1)	83.1(2)
N(3b)–Cr–N(6b), N(7b)	84.6(1)	95.6(2)

amine attached directly to the tetraazacycloalkane ring as part of a common $NHCH_2CMe(NH_2)CH_2NH$ unit, are all potentially quinquedentate ligands. Chelate rings involving the tetraazacycloalkane formed following co-ordination of the macrocycle follow the size patterns [5556] to [5656] to [6665] for L^3, L^4 and L^5 in turn, while in each case the pendant primary amine co-ordination leads to a boat conformation for the 'cap' unit and two additional five-membered chelate rings. Syntheses of pentaaminechlorochromium(III) complexes resulted in the isolation of a single geometric isomer of *cis* geometry for L^3, both *cis* and *trans* isomers for L^4, and a single *trans* isomer for L^5, that is a 'change-over' from prefered *cis* to *trans* geometry was observed as the ring size increased. The *trans* isomers were defined by X-ray crystallography, whereas the *cis* isomers were assigned from their distinctly different spectra. Previously, the related 14-membered macrocyclic ligand L^1 has been isolated bound in a sexi- and quinque-dentate manner to chromium(III), with both the *cis* and *trans* geometries being observed in the quinquedentate co-ordination mode,[5] comparable with the result for L^4 reported here. Detection and characterization of isomers of L^4 in a *trans*:*cis* ratio close to *ca.* 1:1 indicates little preference for either isomer in this case, whereas the smaller or larger macrocycles lead exclusively to a single isomer.

We have also established the co-ordination chemistry with cobalt(III),[2] where again chloropentaaminecobalt(III) ions show a transition in preferred geometry with increasing macrocycle ring size, from preferentially *cis* for L^3–L^5 to *trans* for the sixteen-membered macrocycle 3-methyl-1,5,9,13-tetraazacyclohexadecane-3-amine. The 'change-over' occurs at a smaller macrocycle ring size for chromium(III) than with cobalt(III). Although the free-ion radii of chromium(III) and cobalt(III) are identical (63 pm), observed average M–L bond distances are consistently inherently longer for chromium(III),[13] and this will have a bearing on isomer preference, as the steric strain energy differs for the two geometries,[2] and is influenced by the M–L distance.

The *trans* isomers of $[Cr(L^4)Cl]^{2+}$ and $[Cr(L^5)Cl]^{2+}$ were subjected to single-crystal X-ray structure analyses. Non-hydrogen atomic coordinates for the structures appear in Tables 1 and 2. Bond lengths and angles for the chromium environments are compared in Table 3 and ligand torsion angles in Table 4. The Cr–N distances are variable in each compound (Table 3), but the average Cr–N distance does increase with ring size from 2.06$_9$ (L^4) to 2.07$_9$ Å (L^5). Notably, the Cr–N(1) (pendant amine) distance is constant [2.077(3) Å] in each structure; the constancy, despite the variable macrocycle size, is maintained at the cost of other distortions in the facial capping unit. For example, angle N(3a)–Cr–N(3b) diminishes with increasing ring size (95.6° for L^4, *cf.* 88.5° for L^5). The same trend occurs with the analogous cobalt(III) complexes, although

Table 4 Ligand torsion angles (°) for $[Cr(L^n)Cl]^{2+}$ (n = 4 or 5). Where two values are found in each entry, they are for sections a and b

	L^4	L^5
Cr–N(1)–C(1)–C(2)	−59.8(2), 58.9(3)	−60.1(3), 56.9(4)
N(1)–C(1)–C(2)–N(3)	36.7(3), −37.1(4)	58.3(4), −26.1(5)
C(1)–C(2)–N(3)–Cr	4.7(3), −3.5(4)	−25.5(4), −17.2(4)
C(1)–C(2)–N(3)–C(4)	−115.4(4), 117.4(4)	−159.2(4), 112.1(4)
C(2)–N(3)–C(4)–C(5)	154.4(4), −150.8(3)	78.0(6), −162.7(4)
Cr–N(3)–C(4)–C(5)	33.1(4), −29.0(3)	−50.8(6), −39.9(4)
N(3)–C(4)–C(5)–N(6), C(6)	−55.1(4), 51.1(5)	69.1(6), 72.0(5)
C(4)–C(5)–N(6), C(6)–C(7), N(7)	175.1(3), −173.8(4)	−71.4(5), −75.4(5)
C(4)–C(5)–N(6)–Cr	47.4(3), −46.2(4)	
C(5)–C(6)–N(7)–Cr		55.9(5), 49.1(5)
C(5)–C(6)–N(7)–C(8)		−177.4(4), 179.2(4)
C(5)–N(6)–C(7)–C(8)	−175.9(3), 175.6(4)	
Cr–N(6)–C(7)–C(8)	−54.6(4), 53.8(4)	
C(6)–N(7)–C(8)–C(8)		−172.5(4), −177.7(4)
Cr–N(7)–C(8)–C(8)		−40.6(4), −41.7(5)
N(6)–C(7)–C(8)–C(7)	68.2(4), −68.1(4)	
N(7)–C(8)–C(8)–N(7)		55.3(5)

distortions in those cases are greater as a consequence of the inherently shorter M–N distances.[2]

Examination of Table 3 and Fig. 1 shows clear distortion of the CrN_5Cl octahedron. The N(1)–Cr–Cl axis is deformed toward a line joining the atoms N(3a) and N(3b); distortion in L^4 [167.30(9)°] is relieved somewhat for the larger L^5 [170.2(1)°] but the N–Cr–N angles in the five-membered rings formed by co-ordination of the pendant amines are all near or even below 80°. Some strain appears also in the angles C(2a)–N(3a)–C(4a) and C(2b)–N(3b)–C(4b) for L^4 [113.6(2), 113.1(3)° respectively], but these fall on average for L^5 [113.4(4), 108.8(3)° respectively]. This is a direct result of co-ordination of the pendant primary amine, which 'pulls' the C(2a) and C(2b) atoms toward the metal centre and hence opens the angles at the adjacent co-ordinated secondary amines somewhat. There is less strain in other five-membered chelate rings which do not involve the 'cap', with angles [*e.g.* N(3a)–C(4a)–C(5a) and C(4a)–C(5a)–N(6a) in L^4] close to 109°. The angle formed at the pendant primary amines, C(1)–N(1)–Cr [100.9(2), 100.8(2)° for L^4 and L^5 in turn] is reduced from the ideal tetrahedral value, with relief only achieved by either shortening the axial Cr–N bond (which requires more energy than bond-angle deformation) or by the N(3a)–Cr–N(3b) angle contracting even more. Deformation of the C(1)–N(1)–Cr angles shared to some degree by a reduction of the *cis* N(3a)–Cr–N(3b) angles results in the smallest increase in strain energy, although this is tied to slightly 'contracted' co-ordination spheres compared with 'usual' systems at least for the smaller macrocyclic ring.

For the complexes crystallized, the secondary nitrogens adopt *RRSS* stereochemistries. From earlier studies with folded and flat 1,4,8,11-tetraazacyclotetradecane (L^6) alone,[13] these configurations are known to be some of the most stable. Binding of the $NHCH_2CMe(NH_2)CH_2NH$ unit to an octahedral face can occur with only *RS* stereochemistry for the two secondary nitrogen atoms involved for *trans* and only *SS*(*RR*) for the *cis* geometry respectively, limiting possible overall nitrogen configurations in each case.

The sexidentate chromium(III) complex of L^1 has a similar 'cap' geometry to that observed in this series of complexes, the two 'caps' in that molecule lying in a *trans* disposition.[5] The quite short Cr–N distances in that molecule (2.06_7 Å for the pendant amine, average 2.04_0 Å for the secondary amines) are reflected in extreme physical properties, such as a very negative redox potential and a shift in electronic maxima to high energy. Distances in the fourteen-membered macrocycle analogue L^4 in this case are longer (2.077 Å for the pendant amine, average 2.06_8 Å for the secondary amines), presumably because the steric demands of a molecule with a single 'cap' are reduced, but they are still slightly reduced relative to typical distances for chromium(III) complexes of L^6 (2.08_0–2.10_0 Å)[14,15] and from average distances in $[Cr(en)_3]^{3+}$ (en = ethane-1,2-diamine) of 2.07_5 Å.[16] The apparently 'compressed' geometry in $[Cr(L^1)]^{3+}$ is a consequence of a sterically efficient ligand;[5] clearly, the same 'compression' observed here in the single-pendant analogue arises in the same manner. The larger ring L^5 distances [Cr–N(pendant) 2.077(3), average Cr–N(secondary) 2.08_0 Å] are more comparable with other polyaminechromium(III) complexes. Precisely the same trends have been defined for the cobalt(III) chemistry.[2]

Electronic spectroscopy of the tetragonally distorted molecules is revealing, with significant splitting under the $^4A_{2g} \rightarrow {}^4T_{2g}$ envelope occurring for the *trans* isomers (maxima near 520 and 440 nm), but small or undetected splitting observed for the *cis* isomers. The higher-energy transition $^4A_{2g} \rightarrow {}^4T_{1g}$ is not split, but shows a shift in maxima to higher energy with diminution of the macrocycle ring size for both the *cis* and *trans* isomer pairs. A comparison of some physical data for selected pentaaminechlorochromium(III) complexes appears in Table 5.[17–24] It is notable from the data that Cr–N distances for complexes with the $HNCH_2CMe(NH_2)CH_2NH$ 'cap' bound to an octahedral face are not significantly longer than for the simple and unhindered pentaamine, yet Cr–Cl distances are contracted compared with the pentaamine.

Base-hydrolysis rate constants determined at 25 °C for the series of pentaaminechlorochromium(III) ions are also included in Table 5. Although comparisons of quite disparate ligand systems is not totally appropriate, since k_{OH} is sensitive to the nature and disposition of polyamine ligands,[25] the relatively low rate constants for the pendant-arm ligand series with slightly 'compressed' co-ordination spheres suggests some influence of the ground state on hydrolysis rates. It is apparent that k_{OH} varies with macrocycle ring size for the structurally related isomer pairs, and is consistent with the trend in Cr–Cl bond length for the two *trans* isomers [k_{OH} 0.7 $dm^3\ mol^{-1}\ s^{-1}$, Cr–Cl 2.297(1) Å (L^4); k_{OH} 8.2 $dm^3\ mol^{-1}\ s^{-1}$, Cr–Cl 2.306(1) Å (L^5)], with the shortest Cr–Cl distance being tied to the lowest base-hydrolysis rate constant. This suggests an influence of the ground state on the reaction, and parallels results from the more detailed study of the cobalt(III) series.[2]

The distinctly greater base-hydrolysis rates for the *cis* compared with the *trans* isomers is notable. For example, the *cis* isomer of L^4 is hydrolysed *ca.* 10^7-fold faster than the *trans* isomer. The faster rates of hydrolysis for the *cis* isomers arise largely in the activation enthalpy, when activation parameters for *cis*-L^3 and *cis*-L^4 are compared with *trans*-L^4 and *trans*-L^5 (Table 6). Positive activation entropies observed are consistent with the operation of a conjugate base mechanism,[25]

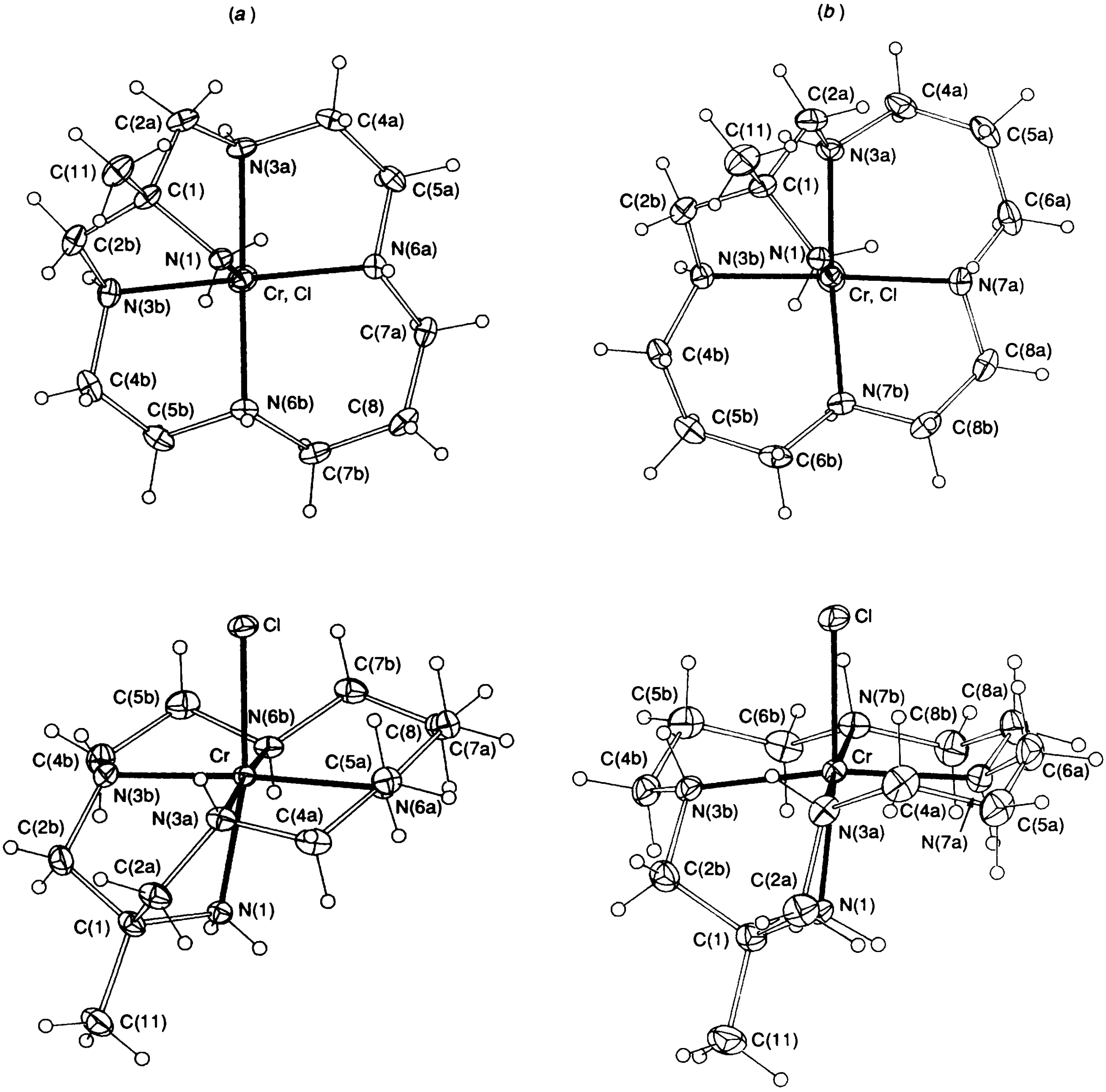

Fig. 1 Projections of the cations (*a*) $[Cr(L^4)Cl]^{2+}$ and (*b*) $[Cr(L^5)Cl]^{2+}$; 20% thermal ellipsoids are shown for the non-hydrogen atoms, whereas hydrogen atoms have arbitrary radii of 0.1 Å

Table 5 Comparative physical properties of (mainly) pentaaminechlorochromium(III) complexes

		Bond lengths/Å		Base hydrolysis		
Complex[a]	Electronic spectrum[b]	Cr–N	Cr–Cl	k_{OH}^{298}[c]	k_{OH}^{Co}/k_{OH}^{Cr}	Ref.
$[Cr(NH_3)_5Cl]^{2+}$	512 (36), 375 (39)	2.074	2.327	0.008	2×10^2	17–19
$[Cr(NH_2Me)_5Cl]^{2+}$	555 (63), 382 (65)			1.8	3.2×10^4	17, 20
fac-$[Cr(en)(dien)Cl]^{2+}$	514 (79), 373 (91)			0.076	1.2×10^2	21, 22
fac-$[Cr(tn)(dien)Cl]^{2+}$	526 (71), 375 (88)			0.080	1.4×10^3	21, 22
cis-$[Cr(L^3)Cl]^{2+}$	533 (118), 395 (71)			1.4×10^5	3.1×10^{-2}	*d*,2
cis-$[Cr(L^4)Cl]^{2+}$	535 (94), 480 (sh)(28), 405 (90)			2.6×10^7	2.8×10^{-6}	*d*,2
trans-$[Cr(L^4)Cl]^{2+}$	520 (63), 430 (30), 365 (91)	2.069	2.297	0.7	1.3×10^4	*d*,2
trans-$[Cr(L^5)Cl]^{2+}$	525 (67), 450 (43), 375 (111)	2.079	2.306	8.2	—	*d*
trans-$[Cr(L^6)Cl_2]^+$				1.7	4.7×10^4	23, 24
cis-$[Cr(L^6)Cl_2]^+$		2.08–2.10	2.33_0	12.0	2.3×10^5	14, 15, 23, 24

[a] dien = Diethylenetriamine, tn = trimethylenediamine. [b] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}). [c] Units dm^3 mol^{-1} s^{-1}. [d] This work.

Table 6 Activation parameters for base hydrolysis of chromium(III) complexes

Complex	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
cis-$[Cr(L^3)Cl]^{2+}$	57 ± 3	+40 ± 9
cis-$[Cr(L^4)Cl]^{2+}$	49 ± 4	+60 ± 12
trans-$[Cr(L^4)Cl]^{2+}$	96 ± 5	+80 ± 15
trans-$[Cr(L^5)Cl]^{2+}$	86 ± 4	+63 ± 13

and are reasonably constant for the series in the range 60 ± 20 J K^{-1} mol^{-1}, supporting a common reaction and gross mechanism.

Normally, base-hydrolysis rate constants for cobalt(III) systems are 10^2- to 10^5-fold greater than those for their chromium(III) analogues (see k_{OH}^{Co}/k_{OH}^{Cr} data in Table 5), and this is observed here for the *trans* isomers. The reverse behaviour for the two *cis* isomers in this case is notable, as no such cases have been reported before. The much greater observed second-order base-hydrolysis rate constant for the *cis* compared with the *trans* isomers may relate to steric influences favouring formation of a five-co-ordinate intermediate, or to changes in deprotonation/protonation rates in the conjugate base pre-equilibrium, assuming the favoured dissociative conjugate base mechanism applies.[25] Arguments supporting the operation of this mechanism for these complexes, at least for L^5, have been advanced elsewhere.[4] Although hexaamine and tris(ethane-1,2-diamine) complexes of cobalt(III) and chromium(III) have essentially identical amine proton-exchange rates, exchange in *trans*-L^6 chromium complexes is slower by up to 10^3-fold compared with the *cis* isomer and near 10^5-fold compared with the tris(ethane-1,2-diamine),[25] indicating that the ligand type and geometry influence these rates. If a secondary amine is the source of conjugate base formation, as is expected, it is possible that deprotonation in the *trans* isomers, where the macrocycle is 'flat', is significantly slower than in the folded *cis* isomers, with subsequent influence on the observed rate constants. More detailed analyses of base-hydrolysis kinetics will be necessary to elucidate this chemistry. At this stage, we have established the viability of binding these pendant-arm macrocycles as quinquedentate ligands to chromium(III), leaving a single site available for substitution chemistry.

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References

1 M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 1972, 1627; D. A. Buckingham, P. G. Marzilli and A. M. Sargeson, *Inorg. Chem.*, 1968, **8**, 1595; R. W. Hay, R. Bembi, W. J. Moodie and P. R. Norman, *J. Chem. Soc., Dalton Trans.*, 1982, 2131; P. S. Pallavicini, A. Perotti, A. Poggi, B. Seghi and L. Fabbrizzi, *J. Am. Chem. Soc.*, 1987, **109**, 5137; L. R. Gahan, G. A. Lawrance and A. M. Sargeson, *Aust. J. Chem.*, 1982, **35**, 1119; R. W. Hay, M. P. Pujari, B. Korybut-Daskiewicz, G. Ferguson and B. L. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1989, 85; *Coordination Chemistry of Macrocyclic Complexes*, ed. G. A. Melson, Plenum, New York, 1982.

2 G. A. Lawrance, T. M. Manning, M. Maeder, M. Martinez, M. A. O'Leary, W. C. Patalinghug, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, in the press; T. W. Hambley, G. A. Lawrance, M. Martinez, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, in the press.

3 G. A. Lawrance, M. Martinez, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1991, **44**, 113.

4 G. A. Lawrance, M. Martinez, B. W. Skelton, R. van Eldik and A. H. White, *Aust. J. Chem.*, in the press.

5 P. V. Bernhardt, P. Comba, N. F. Curtis, T. W. Hambley, G. A. Lawrance, M. Maeder and A. Siriwardena, *Inorg. Chem.*, 1990, **29**, 3208.

6 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1990, 235.

7 P. Comba, N. F. Curtis, G. A. Lawrance, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 497.

8 G. A. Lawrance, M. Rossignoli, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1987, **40**, 1441.

9 G. A. Lawrance and M. A. O'Leary, *Polyhedron*, 1987, **6**, 1291; P. Comba, N. F. Curtis, G. A. Lawrance, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 2145.

10 G. A. Lawrance, M. A. O'Leary, B. W. Skelton, F.-H. Woon and A. H. White, *Aust. J. Chem.*, 1988, **41**, 1533.

11 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

12 *The XTAL User's Manual – Version 3.0*, eds. S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland, 1991.

13 N. F. Curtis, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1982, pp. 219–344.

14 D. A. House and V. McKee, *Inorg. Chem.*, 1984, **23**, 4237.

15 E. Forsellini, T. Parasassi, G. Bombieri, M. L. Tobe and M. E. Sosa, *Acta Crystallogr., Sect. C*, 1986, **42**, 563.

16 A. Whuler, C. Brouty, P. Spinat and P. Herpin, *Acta Crystallogr., Sect. B*, 1975, **31**, 2069.

17 M. Parris and W. J. Wallace, *Can. J. Chem.*, 1969, **47**, 2257.

18 T. W. Hambley and P. A. Lay, *Inorg. Chem.*, 1986, **25**, 4553.

19 D. A. House, *Coord. Chem. Rev.*, 1977, **23**, 223.

20 D. A. Buckingham, B. A. Foxman and A. M. Sargeson, *Inorg. Chem.*, 1970, **9**, 1790.

21 B. S. Dawson and D. A. House, *Inorg. Chem.*, 1977, **16**, 1354.

22 C. S. Dong and D. A. House, *Inorg. Chim. Acta*, 1976, **19**, 23.

23 E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1781.

24 J. Lichtig and M. L. Tobe, *Inorg. Chem.*, 1978, **17**, 2442.

25 M. L. Tobe, *Adv. Inorg. Bioinorg. Mech.*, 1983, **2**, 1.

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