6,13-Diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane, L^7, a New, Potentially Sexidentate Polyamine Ligand. Variable Co-ordination to Cobalt(III) and Crystal Structure of the Complex $[Co(L^7)]Cl_2[ClO_4]$ †

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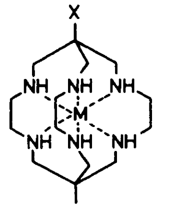
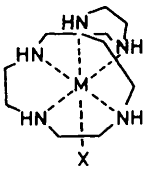
The facile synthesis of the hydrochloride salt of *anti*-6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane, a new type of potentially sexidentate ligand, is described. The ligand can act as a quadridentate macrocyclic ligand to cobalt(III) with both amine pendants unco-ordinated, or as a quinque- or sexi-dentate one with one or two amine pendants co-ordinated axially, respectively. All three types of cobalt(III) complexes have been prepared and characterized spectroscopically. The sexidentate form crystallizes in the space group $C2/c$, with a = 15.616(4), b = 7.497(1), c = 17.922 Å, β = 108.63(1)°, and Z = 4, and displays the shortest Co–N bond lengths reported for a precisely determined cobalt(III) hexa-amine structure. The macrocyclic Co–N distances are 1.937(2) Å whereas the pendant Co–N distances are similar at 1.946(2) Å. The short Co–N bond lengths are reflected in physical properties, with maxima in the electronic spectra shifted toward higher energy and the cobalt(III)–cobalt(II) redox couple shifted to a more negative potential compared with other CoN_6 analogues. The cobalt(III)–cobalt(II) self-exchange rate for the sexidentate complex, determined *via* a cross reaction with Zn^I, is estimated as ≈900 $dm^3 mol^{-1} s^{-1}$, *ca.* 100-fold faster than the value for $[Co(L^1)]^{3+}$ (L′ = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]-eicosane), and nearly 10^8-fold faster than the value for $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine).

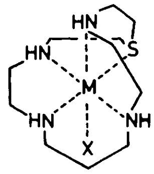
Much attention has been focused in recent years on multidentate and macrocyclic ligands which either partly or wholly encapsulate octahedral metal ions.[1–3] The family of 'sarcophagine' ligands (L^1; various X, Y substituents) can accommodate a metal ion in an octahedral environment inside the hexa-aza macrobicyclic ligand.[2,3] As well as exhibiting extraordinary resistance to hydrolysis in a range of metal-ion oxidation states, these compounds generally show extreme physical properties in comparison with analogues which contain only uni- or bi-dentate amine ligands. Macromonocycles may also 'wrap up' metal ions. Penta-aza- (L^2) and tetra-azathioether (L^3) ligands may act as quinquedentate ligands;[4,5] in an analogous fashion, the hexa-aza (L^4) ligand may completely surround the octahedral metal ion.[6] Optical and geometrical isomers have been reported for some of these compounds; one possible geometry of complexes of these ligands is shown in the diagrams.



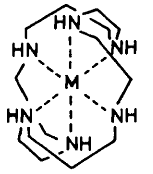
$[M(L^1)]^{n+}$



$[M(L^2)X]^{n+}$

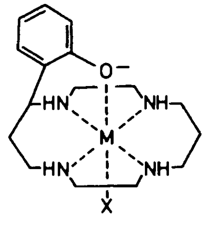


$[M(L^3)X]^{n+}$

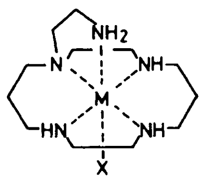


$[M(L^4)]^{n+}$

An alternative approach is to employ a macrocycle which may occupy the four equatorial sites of an octahedral metal ion and, *via* pendant co-ordinating functional groups, bind one or both of the axial positions. Recent examples of this include oxygen[7] and nitrogen[8] donors binding at the axial sites, and connected to the macrocycle at either a carbon or a nitrogen atom. Complexes of this type of ligand, $[M(L^5)]^{n+}$ and $[M(L^6)]^{n+}$, are illustrated.



$[M(L^5)X]^{n+}$



$[M(L^6)X]^{n+}$

Here we report the potentially six-co-ordinating macrocycle 6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L^7), synthesized *via* a metal-directed condensation around $[Cu(en)_2]^{2+}$ (en = ethane-1,2-diamine) involving nitroethane and formaldehyde,[9] and subsequent reduction. This new class of macrocycle has the pendant amine attached directly to the macrocycle framework; with this disubstituted example capable of acting as a sexidentate ligand. Variable co-ordination to cobalt(III), and, particularly, physical properties of the sexi-

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† (6,13-Diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane-$N^1N^4N^8N^{11}N'N''$)cobalt(III) dichloride perchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

dentate complex are reported. More details of the synthetic chemistry involving L^7 and cobalt(III) appear in a subsequent paper.[10,*]

Experimental

*Syntheses.—6,13-Diamino-6,13-dimethyl-*1,4,8,11-*tetra-azacyclotetradecane–hexahydrochloride dihydrate,* $[L^7]\cdot 6HCl\cdot 2H_2O$. A solution of (6,13-dimethyl-6,13-dinitro-1,4,8,11-tetra-azacyclotetradecane)copper(II) perchlorate[10] (18 g) was dissolved in hydrochloric acid (1 mol dm^{-3}, 400 cm^3) and an excess of granulated zinc added. The mixture was stirred and warmed at *ca.* 60 °C until no colour remained in solution (*ca.* 2 h). Gravity filtration was employed to remove copper metal and the excess of zinc. The filtrate was diluted to *ca.* 2 dm^3 and sorbed onto a column (10 × 3 cm) of Dowex 50Wx2 (H^+ form) cation-exchange resin. Washing with 1 mol dm^{-3} HCl removed zinc ion (identified by raising the pH of a sample of eluate to *ca.* 8 to precipitate the hydroxide). The macrocycle was removed with 3 mol dm^{-3} HCl [identified by neutralizing an aliquot of the eluate and adding Cu^{2+}(aq) to produce a bright purple, acid-stable solution]. The eluate was concentrated on a rotary evaporator until precipitation of the white product occurred. This solid was collected, and further concentration of the filtrate yielded a second crop. The hygroscopic macrocyclic amine salt was washed with ethanol and diethyl ether then dried under vacuum (14 g, 75%) (Found: C, 27.9; H, 7.9; N, 15.9. Calc. for $C_{12}H_{40}Cl_6N_6O_2$: C, 28.1; H, 7.9; N, 16.3%). N.m.r.: ^1H(NaOD), δ 1.07 (s, 6 H, $-CH_3$), 2.41 [s, 8 H, $-CH_2-$(cap)], and 2.66 [s, 8 H, $-CH_2-$(en)]; ^{13}C (D_2O, ^1H decoupled) δ 20.2, 47.5, 53.4, and 55.4 p.p.m.

(6,13-*Diamino*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *perchlorate.* $[Co(L^7)][ClO_4]_3$. To an aqueous solution of $Na_3[Co(CO_3)_3]$[11] (0.5 g in 100 cm^3) was added $L^7\cdot 6HCl$ (0.71 g). The resultant solution was then stirred at 50 °C for 90 min. The orange-red solution was diluted to 500 cm^3 with water and sorbed onto a column (15 × 3 cm) of SP Sephadex C-25 resin (Na^+ form). Washing with 0.2 mol dm^{-3} $NaClO_4$ removed some Co^{2+}(aq) as well as some five-co-ordinated complex (see below). The desired product was eluted with 0.5 mol dm^{-3} $NaClO_4$ and concentrated on a rotary evaporator until crystallization commenced. The mixture was allowed to stand at room temperature for several days, and then the yellow product was collected, washed with ethanol then diethyl ether, and dried under vacuum (0.25 g, 28%). The filtrate yielded further crops on standing for extended periods (Found: C, 23.7; H, 4.9; N, 13.4. Calc. for $C_{12}H_{30}Cl_3CoN_6O_{12}$: C, 23.4; H, 4.9; N, 13.6%). Electronic spectrum (in water): $\lambda_{max.}$ 447 (ε 73) and 328 nm (ε 76 dm^3 mol^{-1} cm^{-1}). N.m.r. (D_2O): ^1H, δ 1.35 (s, 6 H, $-CH_3$), 2.6—3.4 [q, 8 H, $-CH_2-$(cap)], and 2.9—3.6 [q, 8 H, $-CH_2-$(en)]; ^{13}C (^1H decoupled), δ 19.1, 53.8, 60.4, and 65.2 p.p.m.

(6-*Amino*-13-*ammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*chlorocobalt*(III) *chloride-diperchlorate monohydrate,* $[Co(HL^7)Cl]Cl[ClO_4]_2\cdot H_2O$. A solution of $CoCl_2\cdot 6H_2O$ (0.5 g) in methanol (80 cm^3) was added to a flask and the solution resulting from stirring a suspension of $L^7\cdot 6HCl$ (1.0 g) in methanol with triethylamine (*ca.* 2 cm^3) was added. The mixture was fitted with an air bubbler and aerated for 1 h. Concentrated HCl (3 cm^3) was added, the solution filtered, diluted to *ca.* 2 dm^3, and sorbed onto a column (15 × 3 cm) of Dowex 50Wx2 (H^+ form) cation-exchange resin. Washing with 1 mol dm^{-3} HCl removed unreacted Co^{2+}(aq) first. The red band of the product was eluted next using 3 mol dm^{-3} HCl. This was collected, evaporated to dryness, and recrystallized by dissolution in water (*ca.* 10 cm^3), followed by addition of 5 mol dm^{-3} $HClO_4$ (*ca.* 2 cm^3) and standing. The crimson crystals were collected, washed with ethanol and diethyl ether, and dried under vacuum (0.20 g, 20%). Further crops were collected after extended periods (Found: C, 23.8; H, 5.8; N, 13.8. Calc. for $C_{12}H_{33}Cl_4CoN_6O_9$: C, 23.8; H, 5.5; N, 13.8%). Electronic spectrum (in water): $\lambda_{max.}$ 518 (ε 81), 470 (ε 83), 347 (ε 170), and 233 nm (ε 9 300 dm^3 mol^{-1} cm^{-1}). N.m.r.: ^1H(D_2O–DCl), δ 1.37 [s, 3 H, $-CH_3$(free)], 1.45 [s, 3 H, $-CH_3$(bound)], 2.99 [s, 4 H, $-CH_2-$(cap, free)], 3.29 [d, 8 H, $-CH_2-$(en)], and 3.49 [s, 4 H, $-CH_2-$(cap, bound)]; ^{13}C (dimethyl sulphoxide, ^1H decoupled), δ 20.2, 26.2, 52.8, 54.9, 55.7, 56.6, 61.4, and 68.0 p.p.m.

trans-(6,13-*Diammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*dichlorocobalt*(III) *perchlorate–dihydrate,* $[Co(H_2L^7)Cl_2][ClO_4]_3\cdot 2H_2O$. In the synthesis described above, this compound elutes as a band following the red band of the CoN_5Cl species. Although contaminated by co-eluted CoN_6 species, evaporation to *ca.* 10 cm^3 followed by addition of $HClO_4$, then ethanol (*ca.* 100 cm^3) led to precipitation of the green product, selectively. This was collected, washed with ethanol and diethyl ether, and dried under vacuum (0.15 g, 15%) (Found: C, 19.8; H, 5.3; N, 11.1. Calc. for $C_{12}H_{36}Cl_5CoN_6O_{14}$: C, 19.8; H, 5.3; N, 11.5%). Electronic spectrum (in water): $\lambda_{max.}$ 620 (ε 140), 440 (sh), (ε 180), 378 (sh) (ε 250), and 233 nm (ε 10 400 dm^3 mol^{-1} cm^{-1}). N.m.r.: ^1H(D_2O), δ 1.56 (s, 6 H, $-CH_3$), 2.97 [s, 8 H, $-CH_2-$(en)], and 3.09 [s, 8 H, $-CH_2-$(cap)]; ^{13}C (D_2O–DCl, ^1H decoupled), δ 23.8, 53.9, 55.3, and 63.0 p.p.m.

Physical Methods.—Electronic spectra were recorded using an Hitachi 150-20 spectrophotometer. N.m.r. spectra were recorded using a JEOL FX90-Q FT n.m.r. spectrometer, using sodium trimethylsilylpropionate and dioxane as internal standards for ^1H and ^{13}C n.m.r., respectively; chemical shifts cited are given *versus* $SiMe_4$. Cyclic voltammetry was performed with a BAS model CV27 controller and a conventional three-electrode configuration with a glassy carbon working electrode, silver–silver chloride reference electrode and platinum counter electrode. Alternatively, polarography using a PAR model 303 static mercury drop electrode and an AMEL model 457 controller was employed. Argon or nitrogen was used as a purge gas and all solutions were 0.1 mol dm^{-3} in $NaClO_4$. Infrared spectra (KBr discs) employed a Nicolet MX-1 FT-IR spectrometer.

Pulse radiolysis experiments were performed with a van de Graaff electron accelerator which delivered electron pulses (3 μs) at *ca.* 1 MeV through the thin wall of a cell with a 1-cm optical path as previously described.[12] Dosimetry was performed with an aerated aqueous solution of potassium thiocyanate, employing a value of ε 7 600 dm^3 mol^{-1} cm^{-1} at 480 nm and $G(OH) = G[(CNS)_2] = 2.8$. Radiolytically initiated electron-transfer reactions were performed in triply distilled water at $[Co] < 10^{-3}$ mol dm^{-3} in the presence of 0.02 mol dm^{-3} $ZnSO_4$. Each single pulse yielded initially Zn^+, which decayed spontaneously and by a redox reaction with the cobalt(III) complex. Decay was monitored at 310 nm for various concentrations of cobalt(III).

Structure Determination.—Crystal data. $C_{12}H_{30}Cl_3CoN_6O_4$, $M = 487.7$, monoclinic, space group $C2/c$, $a = 15.616(4)$, $b = 7.497(1)$, $c = 17.922$ Å, $\beta = 108.63(1)°$, $U = 1\,988.1(1)$ Å^3, D_c $(Z = 4) = 1.629$ g cm^{-3}, $F(000) = 1\,016$, $\mu_{Mo} = 12.75$ cm^{-1}. Specimen: pale yellow needles, 0.31 × 0.14 × 0.08 cm. $A^*_{min.,max.} = 0.91, 0.78$. $N = 2\,007$, $N_o = 1\,526$, range of *hkl* 0 to 16, 0 to 8, −21 to 21, merging $R = 0.006$, $R = 0.029$, $R' =$

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[*] Ligand abbreviations: L^1 = 3,6,10,13,16,19-hexa-azabicyclo-[6.6.6]eicosane (for X = Y = H); L^2 = 1,4,7,10,13-penta-azacyclopentadecane; L^3 = 7-thia-1,4,10,13-tetra-azacyclopentadecane; L^4 = 1,4,7,11,14,17-hexa-azacycloeicosane; L^5 = 5-(2′-oxidophenyl)-1,4,8,11-tetra-azacyclotetradecane; L^6 = 1-(2′-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane.

Table 1. Positional co-ordinates for $[Co(L^7)]Cl_2[ClO_4]$

Atom	*x*	*y*	*z*
Co	0.0000	0.0000	0.0000
N(1)	0.119 1(1)	0.047 1(3)	−0.007 2(1)
N(2)	−0.021 9(1)	−0.160 1(3)	−0.089 4(1)
N(3)	−0.060 0(1)	0.177 8(3)	−0.078 8(1)
C(1)	0.187 4(2)	−0.024 7(4)	0.065 0(2)
C(2)	−0.140 8(2)	0.072 5(3)	−0.125 7(1)
C(3)	−0.099 4(2)	−0.088 0(4)	−0.154 8(2)
C(4)	−0.065 0(2)	−0.186 7(4)	−0.106 0(2)
C(5)	0.122 0(2)	−0.021 3(4)	−0.084 5(2)
C(6)	−0.204 8(2)	0.175 6(4)	−0.194 9(2)
Cl(1)	0.0000	0.584 9(1)	0.2500
O(1)	−0.065 2(4)	0.475 9(6)	0.265 8(4)
O(2)	−0.059 3(8)	0.616 0(12)	0.162 9(5)
O(3)	0.0000	0.782 4(21)	0.2500
O(4)	−0.029 3(8)	0.740 0(15)	0.211 9(7)
O(5)	−0.046 9(9)	0.514 0(15)	0.296 8(7)
O(6)	−0.094 2(14)	0.515 8(29)	0.220 7(16)
O(7)	−0.014 3(15)	0.581 2(26)	0.165 2(10)
O(8)	−0.096 7(12)	0.597 3(25)	0.174 3(11)
O(9)	−0.009 5(13)	0.768 7(31)	0.272 8(13)
Cl(2)	0.141 3(1)	0.544 9(1)	0.536 7(1)

Table 2. Bond distances (Å) and angles (°) for $[Co(L^7)]Cl_2[ClO_4]$

N(1)–Co	1.937(2)	N(2)–Co	1.936(2)
N(3)–Co	1.946(2)	C(1)–N(1)	1.485(3)
C(5)–N(1)	1.484(3)	C(3)–N(2)	1.488(3)
C(4)–N(2)	1.492(3)	C(2)–N(3)	1.497(3)
C(1)–C(2)	1.528(3)	C(3)–C(2)	1.531(4)
C(6)–C(2)	1.526(3)	C(5)–C(4)	1.503(4)
O(1)–Cl(1)	1.402(4)	O(2)–Cl(1)	1.551(8)
O(3)–Cl(1)	1.48(2)	O(4)–Cl(1)	1.35(1)
O(5)–Cl(1)	1.38(1)	O(6)–Cl(1)	1.48(2)
O(7)–Cl(1)	1.45(2)	O(8)–Cl(1)	1.67(2)
O(9)–Cl(1)	1.45(3)		
N(2)–Co–N(1)	88.8(1)	N(3)–Co–N(1)	94.5(1)
N(3)–Co–N(2)	85.0(1)	C(1)–N(1)–Co	108.4(2)
C(5)–N(1)–Co	108.3(2)	C(5)–N(1)–C(1)	116.9(2)
N(1)–Co–N(2)	91.2(1)	C(3)–N(2)–Co	107.8(1)
C(4)–N(2)–Co	108.2(1)	C(4)–N(2)–C(3)	117.2(2)
N(1)–Co–N(3)	85.5(1)	C(2)–N(3)–Co	99.6(1)
N(2)–Co–N(3)	95.0(1)	C(3)–C(2)–N(3)	103.4(2)
C(6)–C(2)–N(3)	113.7(2)	C(6)–C(2)–C(3)	111.3(2)
C(2)–C(3)–N(2)	110.3(2)	C(5)–C(4)–N(2)	110.0(2)
C(4)–C(5)–N(1)	109.2(2)		

0.043, residual extrema = 0.42, −0.25 e Å^{-3}. A unique data set was measured for $[Co(L^7)]Cl_2[ClO_4]$ (crystallized as the mixed salt from aqueous HCl–$NaClO_4$ solution) at 294 K. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer within the limit $2\theta_{max.} = 50°$, with monochromatic Mo-K_α radiation, λ = 0.710 69 Å, graphite monochromator, and operating in the ω—θ scan mode. 2 007 Independent reflections were obtained, 1 526 with $I > 2.5\sigma(I)$ being considered observed and used for solution of the structure. Data were reduced and Lorentz, polarization, and decomposition corrections were applied using a local data reduction program. The structure was solved by Patterson and Fourier synthesis techniques, and was refined by full-matrix least-squares analysis with SHELX 76.[13] Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included and constrained at estimated values. Residuals on $|F|$ at convergence are conventional $R = 0.029$, $R' = 0.043$, $w = g/(\sigma^2 F_o + kF_o^2)$ where g, k are 1.30, 4.0 × 10^{-4}. Scattering factors and anomalous dispersion corrections for Co were taken from the International Tables,[14] and for all others the values supplied in SHELX 76 were used. Absorption correction was by numerical integration.[15] Non-hydrogen atom co-ordinates are listed in Table 1. The atomic nomenclature is defined in the Figure, drawn with ORTEP.[16] Important non-hydrogen interatomic distances and angles are collected in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen-atom co-ordinates and anisotropic thermal parameters.

Molecular Mechanics.—The strain energy was calculated using a force field described elsewhere.[17] Starting co-ordinates were taken from the crystal structure and minimization of the strain energy was achieved using a locally developed program.[18]

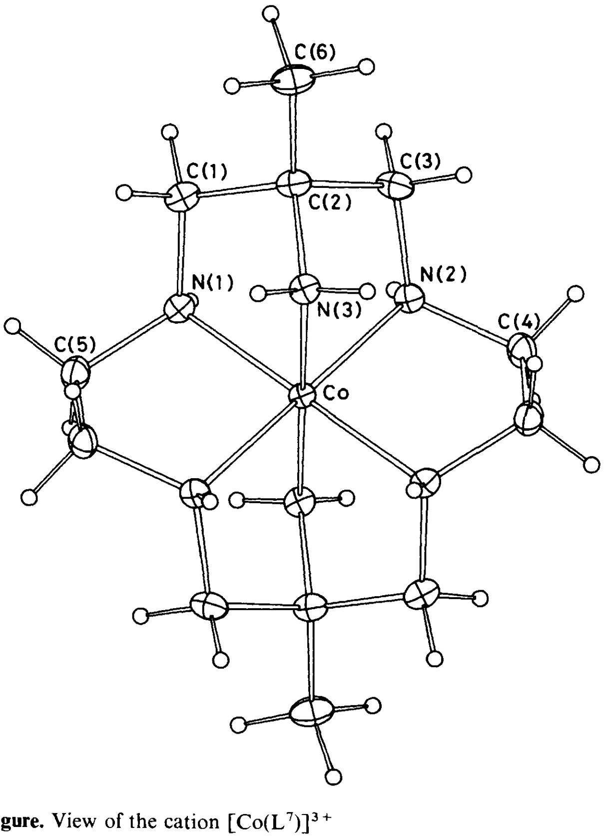


Figure. View of the cation $[Co(L^7)]^{3+}$

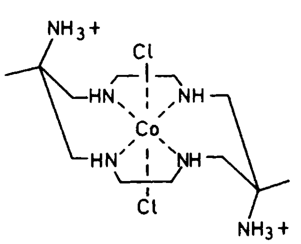
Results

Reactions of the macrocycle L^7 with either Co^{2+}(aq) and air, or with $[Co(CO_3)_3]^{3-}$, yielded products exclusively comprising the ligand co-ordinated to cobalt(III) in a 1:1 ratio with one of the three co-ordination modes illustrated below. Sensitivity of the reaction to choice of solvent was observed. Reactions performed in aqueous solution favoured $[Co(L^7)]^{3+}$ and $[Co(HL^7)Cl]^{3+}$, with little evidence of the green $[Co(H_2L^7)Cl_2]^{3+}$. When methanol was employed as solvent there was an approximately equal distribution of the three products. Essentially, all of the ligand was taken up by cobalt

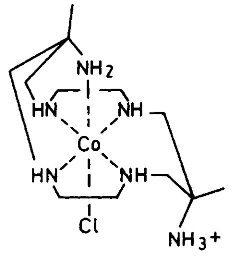
Table 3. Some comparative physical properties of hexa-aminecobalt(III) ions

Complex ion	Electronic spectrum, $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Redox potential, $E_{\frac{1}{2}}$/V *vs.* Ag–AgCl	Self-exchange rate, k_{ex}/dm^3 mol^{-1} s^{-1}	Co–N bond length/Å
$[Co(NH_3)_6]^{3+}$	475 (75), 339 (46)	−0.28[a]	≈10^{-6}[b]	1.961[c]
$[Co(en)_3]^{3+}$	468 (75), 340 (68)	−0.42[a]	3.4 × 10^{-5}[d]	1.964[e]
$[Co(L^1)]^{3+}$	471 (135), 343 (108)	−0.66[a]	2.2[f]	1.974[g]
$[Co(L^7)]^{3+}$	447 (73), 328 (76)	−0.79	≈900	1.937, 1.946

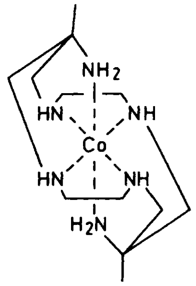
[a] Ref. 21. [b] A. Hammershøi, D. Gesolowitz, and H. Taube, *Inorg. Chem.*, 1984, **23**, 979. [c] B. N. Figgis, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1979, **32**, 417. [d] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 1961, **65**, 1892. [e] Cambridge Crystallographic Data Base files; average over 27 structures. [f] Ref. 2. [g] A. J. Balahura, G. Ferguson, B. L. Ruhl, and R. G. Wilkins, *Inorg. Chem.*, 1983, **22**, 3990.



$[Co(H_2L^7)Cl_2]^{3+}$

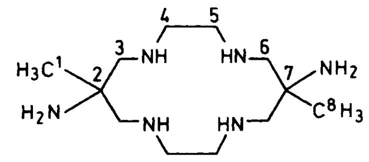


$[Co(HL^7)Cl]^{3+}$



$[Co(L^7)]^{3+}$

Table 4. Assignments of the ^{13}C n.m.r. spectra of L^7 and cobalt(III) complexes of L^7[a]



L^7·6HCl	$[Co(L^7)]^{3+}$	$[Co(HL^7)Cl]^{3+}$		$[Co(H_2L^7)Cl_2]^{3+}$
20.2 (1)	19.1 (1)	20.2 (1)	55.7 (6)	23.8 (1)
47.5 (4)	53.8 (4)	26.2 (8)[b]	56.6 (3)	53.9 (4)
53.4 (2)	60.4 (3)	52.8 (5)	61.4 (7)	55.3 (3)
55.4 (3)	65.2 (2)	54.9 (4)	68.0 (2)	63.0 (2)

[a] Chemical shifts (p.p.m. *versus* $SiMe_4$). Numbers in parentheses refer to the carbon assignment on the diagram; in all but one case 1, 2, 3, and 4 are equivalent to 8, 7, 6, and 5 respectively. [b] Adjacent to the co-ordinated nitrogen.

but, due to the relatively high solubilities of the complexes, crystallization was slow and incomplete, affecting the yields of isolated products.

The electronic spectrum of each complex defined a $Co^{III}N_{6-n}Cl_n$ (n = 0, 1, or 2) chromophore. The spectrum of the green $[Co(H_2L^7)Cl_2]^{3+}$ ion displayed the characteristic splitting of the $^1T_{1g}$ excited state to a $^1A_{2g}$ and ^1E_g state under the influence of the tetragonally distorted ligand field. This pronounced splitting is indicative of a *trans* geometry, with the two low-energy maxima (620, 440 nm) similar in position to those of the analogous complex of the unsubstituted parent macrocycle, cyclam (1,4,8,11-tetra-azacyclotetradecane) (625, 420 nm).[19] A smaller splitting is observed for the $^1A_{2g}$ and ^1E_g components in the $[Co(HL^7)Cl]^{3+}$ complex, as expected. The pseudo-octahedral $[Co(L^7)]^{3+}$ ion displays symmetric absorption envelopes for the two $^1T_{1g} \longleftarrow {}^1A_{1g}$ and $^1T_{2g} \longleftarrow {}^1A_{1g}$ transitions. However, the transitions occur at higher energy compared with other CoN_6^{3+} species, and with lower molar absorption coefficients than reported for macrobicyclic hexa-amines (Table 3).

N.m.r. spectra gave conclusive evidence for the geometries of the three cobalt complexes. As might be expected, the two molecules of D_{2h} symmetry, *i.e.* $[Co(L^7)]^{3+}$ and *trans*-$[Co(H_2L^7)Cl_2]^{3+}$, yielded only four different ^{13}C resonances, comprising two sets of four and two sets of two equivalent carbons. There exist two possible geometric isomers of $[Co(HL^7)Cl]^{3+}$. One would have the cyclam ring in the equatorial plane of the metal with one pendant primary amine group co-ordinated in an axial position. This arrangement possesses a σ_v symmetry element and thus should only exhibit eight different ^{13}C resonances, there being four pairs of equivalent carbons. This was in fact observed in the ^{13}C n.m.r. spectrum with slight broadening of peaks indicating conformational inequivalences. If the structure comprised the cyclam ring in a *cis* configuration then all twelve carbon atoms would be magnetically inequivalent. Assignments of the resonances were made by comparisons between the complexed forms as well as the free ligand (Table 4).

The structure of $[Co(L^7)]Cl_2[ClO_4]$ consists of the complex cation at a centre of symmetry, a disordered perchlorate anion on a two-fold axis, and a chloride anion at a general site. There are hydrogen bonds between amine hydrogen atoms and both perchlorate oxygen atoms and the chloride anions. The crystal-structure analysis confirms that the ligand is six-co-ordinate; four co-ordination sites come from the cyclam 'core' and the other two from the amine substituents. The geometry of the ligand is best described as being derived from the (A) or (*R*,*R*,*S*,*S*) isomer of *trans*-$[Ni(cyclam)]^{2+}$.[20] The equatorial plane is occupied by the four atoms from the cyclam core and the axial sites by the amine pendants.

The six-membered chelate rings, which adopt chair conformations, are folded back in order to enable co-ordination of the amine substituents. The torsion angles Co(1)–N(1)–C(1)–C(2), 12.0, and Co(1)–N(2)–C(3)–C(2), 6.5°, show that these rings have nearly ideal boat conformations. The five-membered chelate rings in the equatorial plane adopt a slightly flattened-skew conformation [N(1)–C(5)–C(4)–N(2), 43.6°] and those two involving the equatorial nitrogen atoms adopt marginally more puckered skew conformations [N(*1*)–C(1)–C(2)–N(2), 48.1, N(2)–C(3)–C(2)–N(3), 44.1°]. The boat and flattened-skew conformations indicate significant strain in the ligand and this is also shown in a number of the bond angles, most notably in the nominally tetrahedral angles Co(*1*)–N(3)–C(2), which is close to 99.6(1)°, and C(1)–N(1)–C(5) and C(3)–N(2)–C(4), which are opened to 116.9(2) and 117.2(2)° respectively. High degrees of strain are often reflected in the metal–ligand bond lengths, but in the present structure the Co–N bonds are unusually short. The distances of 1.937(2), 1.936(2), and 1.946(2) Å for Co(1)–N(1), Co(1)–N(2), and Co(1)–N(3) respectively are, we believe, the shortest, precisely determined distances for hexa-aminecobalt(III) complexes. Bond lengths and angles are given in Table 2.

Voltammetry identified one-electron cobalt(III)–cobalt(II) redox couples for all three complexes. The voltammograms of $[Co(H_2L^7)Cl_2]^{3+}$ and $[Co(HL^7)Cl]^{3+}$ displayed irreversible cathodic waves at −0.03 and −0.29 V (*versus* Ag–AgCl) respectively, with the irreversible behaviour possibly related to rapid chloride dissociation in the reduced form. A reversible couple was observed for $[Co(L^7)]^{3+}$, centred at −0.79 V (ΔE 60 mV, scan rate 100 mV s^{-1}). This couple is found at a more negative potential than for other hexa-amine analogues (Table 3).[21]

The electron-transfer cross reaction between $[Co(L^7)]^{3+}$ and Zn^I was measured by monitoring the disappearance of Zn^I at 310 nm in the presence of various concentrations of Co^{III}. The $[Co^{III}]$ was always in excess, the Zn^I being formed *in situ via* reaction of Zn^{II} with the aquated electron in a single pulse. The electron-transfer rate constant obtained was $(2.1 \pm 0.2) \times 10^8$ $dm^3\ mol^{-1}\ s^{-1}$. This rate was used to estimate the self-exchange rate for Co^{III}–Co^{II} *via* the Marcus–Hush theory,[22,23] for which the cross reaction rate is given by equation (1), where k_{11} and

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}} \qquad (1)$$

k_{22} are the self-exchange electron-transfer rate constants for, in this case, $[Co(L^7)]^{3+/2+}$ and $Zn^{2+/1+}$ respectively; K_{12} is the equilibrium constant and f_{12} is a frequency factor (which can be set at unity for first approximations). If one has comparable data for a similar compound reacting with Zn^I, then k_{22} can be eliminated and an expression for the self-exchange rate constant for the first compound can be obtained [equation (2)],

$$k_{11}{}^{A} = [k_{11}{}^{B}(k_{12}{}^{A})^2K_{12}{}^{B}]/[(k_{12}{}^{B})^2K_{12}{}^{A}] \qquad (2)$$

and substituting for K_{12} using equation (3),

$$K_{12}{}^{A,B} = \exp\,[nF/RT(E^{\ominus}(A,B) - E^{\ominus}(Zn^{2+/1+}))] \qquad (3)$$

one obtains, at 25 °C, equation (4).

$$k_{11}{}^{A} = k_{11}{}^{B}[(k_{12}{}^{A})^2/(k_{12}{}^{B})^2] \\ \exp\{38.94[E^{\ominus}(B) - E^{\ominus}(A)]\} \qquad (4)$$

For the hexa-amine $[Co(L^1)]^{3+}$, k_{11} = 2.2 $dm^3\ mol^{-1}\ s^{-1}$,[2] $E^{\ominus}$ = −0.43 V,[21] and for the cross reaction with Zn^I, k_{12} = 1.1×10^8 $dm^3\ mol^{-1}\ s^{-1}$.[24] Substituting these values and the values $E^{\ominus}$ = −0.55 V, k_{12} = 2.1×10^8 $dm^3\ mol^{-1}\ s^{-1}$ for $[Co(L^7)]^{3+}$ into equation (4) yields a value for the self-exchange electron-transfer rate constant for the latter of $(9 \pm 2) \times 10^2$ $dm^3\ mol^{-1}\ s^{-1}$. This relatively fast rate is at least 100-fold faster than the rate for $[Co(L^1)]^{3+}$, and approaches that reported for mixed-donor N,S-macrobicyclic cobalt(III) complexes.[25]

Discussion

The ligand L^7 effectively consists of a fourteen-membered cyclam macrocycle with primary amines attached to the central carbons of the $(-CH_2-)_3$ components of the molecule, disposed on opposite sides of the macrocycle ring. These 'pendants' are able to act as axial donors to octahedral metal ions, as described in this work and elsewhere;[26] it appears that L^7 may act as a six-co-ordinate ligand to all or most inert octahedral metal ions. The $[Co(H_2L^7)Cl_2]^{3+}$ and $[Co(HL^7)Cl]^{3+}$ ions are stable in acidic conditions but convert into $[Co(L^7)]^{3+}$ in neutral or basic solution. The reverse reactions of these processes were not observed in acidic solution; $[Co(L^7)]^{3+}$ is inert to heating in strong aqueous acid for many hours. The kinetics of these processes is being pursued independently. The high symmetry of the $[Co(L^7)]^{3+}$ ion precludes the existence of metal-based optical isomers, and examination of molecular models reveals that the asymmetric nitrogen donors in the equatorial plane of the molecule may assume only one configuration (*RRSS*), ruling out the existence of any N-based diastereoisomers.

The ligand L^7 represents a new type of multidentate amine ligand. The pendant donors are not attached to the macrocycle by a carbon chain, as in L^6 for example, but are directly attached to the macrocycle ring itself, and make use of the flexibility of these rings to dispose themselves for co-ordination. The six-membered chelate rings must fold over to permit co-ordination of the amine in the axial site. Because of the form of attachment, elongation of the axial bonds is not permitted without substantial distortion from octahedral geometry, since axial elongation must occur with concomitant movement 'sideways' as a result of direct attachment to the macrocycle ring. This may account for the absence of six-co-ordination to Cu^{II},[27] even though this metal ion can be effectively encapsulated by the L^1 macrobicycle.[28] It is only with the larger and more flexible macrocycles that some axial interaction, albeit weak, can be seen in crystal structures of nitro precursors of analogues of L^7.[29]

Determination of the *X*-ray crystal structure of $[Co(L^7)]^{3+}$ has defined unusually short Co–N bonds. The Co–N(1),N(2),N(3) distances of 1.937, 1.936, and 1.946 Å can be compared with the average Co–N distance in $[Co(en)_3]^{3+}$ of 1.964(7) Å (Cambridge Crystallographic Data Base files; average over 27 structures). In *cis* and *trans* cyclam complexes of cobalt(III), Co–N distances vary from 1.986(7) to 2.016(6) Å,[30] whereas in complexes of L^1 analogues distances exceed 1.98 Å.[4] It appears that the bonds are compressed in order to minimize the strain involved in co-ordination of the axial nitrogen atoms. The C–C and C–N bonds do not appear to reflect the strain (Table 2). Contrarily, the Ni–N bond lengths in $[Ni(L^7)]^{2+}$ are closer to 'normal', but distortions are greater.

In order to investigate whether the unusually short Co–N bond lengths are a consequence of the ligand geometry we have applied the technique of molecular mechanics to $[Co(L^7)]^{3+}$. The strain-energy minimized and crystal-structure geometries are compared in Table 5. In general there is good agreement between the two, and in particular the highly deformed angles are well reproduced. The predicted Co–N bond lengths are slightly longer than the crystal-structure values, but are also unusually short, confirming that the ligand is responsible for the unusual distances. It has been shown elsewhere[17] that the preference of the ligand L^7 for a 'compressed' geometry makes reduction to Co^{II}, with concomitant increase in the Co–N bond length, difficult and that this contributes to the unusually negative reduction potential.

Physical properties do in general reflect the short Co–N distances (Table 3). The short bonds result in a large ligand-field perturbation of the *d*-orbitals on Co^{III}, seen in a high energy ${}^1T_{1g} \longleftarrow {}^1A_{1g}$ and ${}^1T_{2g} \longleftarrow {}^1A_{1g}$ transition. A correlation between $\lambda_{max.}$ and Co–N bond lengths has been noted previously,[31] and the present data conform to that correlation.

For $[Co(L^7)]^{3+}$, the cobalt(III)–cobalt(II) redox couple is reversible on the voltammetric time-scale, and more negative than for other hexa-amines (Table 3).[21] Although inappropriate

Table 5. Comparisons of selected bond lengths (Å) and bond angles (°) determined from the X-ray structure (observed) and from molecular mechanics calculations (calculated) for $[Co(L^7)]^{3+}$

N(1)–Co	1.937(2)	1.948
N(2)–Co	1.936(2)	1.948
N(3)–Co	1.946(2)	1.956
N(2)–Co–N(1)	88.8(1)	90.4
N(3)–Co–N(1)	94.5(1)	92.7
N(3)–Co–N(2)	85.0(1)	87.3
N(1)–Co–N(2)	91.2(1)	89.7
N(1)–Co–N(3)	85.5(1)	87.3
N(2)–Co–N(3)	95.0(1)	92.7
C(1)–N(1)–Co	108.4(2)	105.9
C(5)–N(1)–Co	108.3(2)	106.8
C(5)–N(1)–C(1)	116.9(2)	116.6
C(3)–N(2)–Co	107.8(1)	105.9
C(4)–N(2)–Co	108.2(1)	106.8
C(4)–N(2)–C(3)	117.2(2)	116.6
C(2)–N(3)–Co	99.6(1)	97.5
C(3)–C(2)–N(3)	103.4(2)	105.3
C(6)–C(2)–N(3)	113.7(2)	111.9
C(6)–C(2)–C(3)	111.3(2)	110.9
C(6)–C(2)–C(1)	110.7(2)	110.9
C(3)–C(2)–C(1)	113.8(2)	112.4
C(1)–C(2)–N(3)	103.6(2)	105.3
N(1)–C(1)–C(2)	109.0(2)	110.0
C(2)–C(3)–N(2)	110.3(2)	110.1
C(5)–C(4)–N(2)	110.0(2)	109.9
C(4)–C(5)–N(1)	109.2(2)	109.9

for study of electron-transfer kinetics with conventional reducing agents as a consequence of this, we were able to obtain and follow a reaction with Zn$^{\mathrm{I}}$, a powerful one-electron reducing agent.[32] The estimated self-exchange rate for $[Co(L^7)]^{3+/2+}$ of 900 dm^3 mol^{-1} s^{-1} is consistent with molecular mechanics calculations of bond-length relaxations from cobalt(III) to cobalt(II),[17] which predict an average change of only 0.152 Å for $[Co(L^7)]^{3+/2+}$ compared with 0.196 and 0.205 Å for the $(en)_3$ and (L^1) analogues, respectively. We have been unable to isolate and crystallize the cobalt(II) compound for structural study, to confirm these predictions. Despite the smaller than usual relaxation, a slow self-exchange rate constant was anticipated.

This anomaly has been noted previously in macrobicyclic hexa-amines, where self-exchange rate constants are rapid. Inner-sphere electron transfer may be ruled out since there are no potentially bridging groups on the ligand and also no possibility of d-orbital overlap on the nitrogen donors in the transition state, as has been suggested to occur on sulphur in mixed N,S-donor macrobicyclic cobalt(III) complexes for which exceptionally fast self-exchange electron-transfer rate constants have been reported.[25] In the absence of structural data on the cobalt(II) complex of L^7, extended discussion seems unwarranted; however, it is clear that the present compound exhibits apparently anomalous self-exchange electron-transfer behaviour analogous to that well established for macrobicyclic hexa-amines $[Co(L^1)]^{n+}$.

All three complexes isolated in this study contain the cyclam residue in a *trans* geometry. The absence of any *cis*-based isomers involving Co$^{\mathrm{III}}$ and L^7 is not surprising. The vast majority of cobalt(III) complexes containing cyclam and substituted cyclams adopt a *trans* geometry with all four donors in the one plane. *cis*-Based cyclam complexes do exist, but special conditions appear to be needed to synthesize them in preference to the *trans* analogues.[33] There appears to be a *cis* isomer formed in the related rhodium(III) chemistry.[34] Under appropriate circumstances, most products seem to be able to be converted into the stable hexa-amine. Thus the molecule L^7 (also referred to as diammac) represents a new type of six-coordinate polyamine ligand.

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References

1 G. A. Melson (ed.), 'Coordination Chemistry of Macrocyclic Complexes,' Plenum, New York, 1982; J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, 'Inclusion Compounds,' Harcourt Brace Jovanovich, New York, 1983, vol. 2.

2 A. M. Sargeson, *Chem. Brit.*, 1979, **15**, 23; *Pure Appl. Chem.*, 1984, **56**, 1603.

3 R. J. Geue, T. W. Hambley, J. M. Harrowfield, A. M. Sargeson, and M. R. Snow, *J. Am. Chem. Soc.*, 1984, **106**, 5478; I. I. Creaser, R. J. Geue, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, and M. R. Snow, *ibid.*, 1982, **104**, 6016; H. A. Boucher, G. A. Lawrance, P. A. Lay, A. M. Sargeson, A. M. Bond, D. F. Sangster, and J. C. Sullivan, *ibid.*, 1983, **105**, 4652.

4 R. W. Hay, R. Bembi, W. T. Moodie, and P. R. Norman, *J. Chem. Soc., Dalton Trans.*, 1982, 2131.

5 M. Komada, T. Koike, H. Hoshiga, R. Machida, and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1984, 673.

6 D. J. Royer, G. J. Grant, D. G. van Derveer, and M. J. Castillo, *Inorg. Chem.*, 1982, **21**, 1902.

7 E. Kimura, S. Joke, T. Koike, and M. Komada, *J. Am. Chem. Soc.*, 1987, **109**, 5529.

8 P. S. Pallavicini, A. Perotti, A. Poggi, B. Seghi, and L. Fabrizzi, *J. Am. Chem. Soc.*, 1987, **109**, 5139.

9 P. Comba, N. F. Curtis, G. A. Lawrance, A. M. Sargeson, B. W. Skelton, and A. H. White, *Inorg. Chem.*, 1986, **25**, 4260.

10 N. F. Curtis and A. Siriwardena, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

11 H. F. Bauer and W. C. Drinkard, *Inorg. Synth.*, 1966, **8**, 202.

12 H. A. Boucher, A. M. Sargeson, D. F. Sangster, and J. C. Sullivan, *Inorg. Chem.*, 1981, **20**, 3719.

13 G. M. Sheldrick, SHELX 76, A Program for X-Ray Crystal Structure Determination, University of Cambridge, 1976.

14 D. T. Cromer and J. T. Waber, 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

15 P. Coppens, L. Leisorwitz, and D. Rabinovich, *Acta Crystallogr.*, 1965, **18**, 1035.

16 C. K. Johnson, ORTEP, A Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory, Tennessee, U.S.A., 1965.

17 T. W. Hambley, *Inorg. Chem.*, 1988, **27**, 2496.

18 T. W. Hambley, MOMEC 87, A Program for Strain-Energy Minimization, University of Sydney, Australia, 1987.

19 B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102, 1109.

20 T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1986, 565.

21 A. M. Bond, G. A. Lawrance, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 2010.

22 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966, 979; *ibid.*, 1965, **43**, 677; *Annu. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Phys. Chem.*, 1963, **67**, 853.

23 N. S. Hush, *Trans. Faraday Soc.*, 1961, **57**, 557.

24 G. A. Lawrance, E. Miles, and A. M. Sargeson, unpublished work.

25 R. V. Dubs, L. R. Gahan, and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 2523.

26 N. F. Curtis, G. J. Gainsford, T. W. Hambley, G. A. Lawrance, K. R. Morgan, and A. Siriwardena, *J. Chem. Soc., Chem. Commun.*, 1987, 295.

27 G. A. Lawrance, B. W. Skelton, A. H. White, and P. Comba, *Aust. J. Chem.*, 1986, **39**, 1101.

28 L. L. Martin, Doctoral Dissertation, The Australian National University, 1988.

29 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.

30 R. J. Restivo, G. Ferguson, R. W. Hay, and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1978, 1131; T. F. Lai and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1562.

31 U. Sakaguchi, K. Tomioka, and H. Yoneda, *Chem. Lett.*, 1984, 1425.

32 G. A. Lawrance and D. F. Sangster, *J. Chem. Soc., Dalton Trans.*, 1987, 1425.

33 C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1968, 1549.

34 P. V. Bernhardt and G. A. Lawrance, unpublished work.

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