Synthesis of a New Potentially Sexidentate Pendant-arm Macrocyclic Polyamino Acid and Co-ordination to Cobalt(III)†

Trevor W. Hambley,[a] Geoffrey A. Lawrance,*[,b] Marcel Maeder[b] and Eric N. Wilkes[b]
[a] *School of Chemistry, The University of Sydney, New South Wales 2006, Australia*
[b] *Department of Chemistry, The University of Newcastle, Callaghan 2308, Australia*

From reaction of bis(ethane-1,2-diamine)copper(II) with formaldehyde and diethyl malonate then formaldehyde and nitroethane in turn the pendant-arm macrocyclic complex ion (hydrogen 13-methyl-13-nitro-1,4,8,11-tetraazacyclotetradecane-6-carboxylate)copper(II) was prepared. Reduction with zinc in aqueous acid yields the free pendant-arm β-polyamino acid macrocycle hydrogen 13-amino-13-methyl-1,4,8,11-tetraazacyclotetradecane-6-carboxylate (L^3) as the hydrochloride salt. Co-ordination to cobalt(III) was achieved following reaction with cobalt(II) ion and air, yielding the chloro(hydrogen 13-amino-13-methyl-1,4,8,11-tetraazacyclotetradecane-6-carboxylate)cobalt(III) ion, as well as its aqua analogue. The chlorocobalt(III) complex crystallized as the perchlorate salt in the space group *Pbca*, $a = 10.256(4)$, $b = 12.689(5)$, $c = 33.08(2)$ Å, $Z = 8$, with the co-ordinated chloride in a *cis* disposition relative to the pendant amine, the four secondary amines co-ordinated in a folded geometry with uncommon *RRRR* stereochemistry, and the pendant carboxylic acid group not co-ordinated. Equilibration of the reaction mixture from this synthesis at pH 8 over activated carbon yielded almost exclusively the complex with the ligand bound as a sexidentate ligand where the pendant amine and carboxylate groups occupy *trans* sites. This complex crystallized as the perchlorate salt in the space group $P2_1/n$ with $a = 10.939(2)$, $b = 13.355(2)$, $c = 14.596(2)$ Å, $\beta = 102.17(1)°$ and $Z = 4$. Metal–donor distances [Co–O 1.899(2), Co–N(pendant) 1.956(2), average Co–N(secondary) 1.95_1 Å] are at the short end of the range for saturated polydentate amino acid ligands, presumably influenced by the sterically efficient ligand.

The synthesis of pendant-arm macrocyclic ligands, and their interaction with metal ions, has attracted a great deal of attention recently.[1–4] For molecules based on largely polyazamacrocycles two distinct types can be identified, those involving pendants branched from the nitrogens and those branched from a carbon in the macrocyclic framework. Inherently, because of the relative ease of alkylation of amines, the former group have been more extensively studied, with a wide range of pendant arms carrying additional potential donors introduced.[2] Conversion of the secondary into tertiary amines is a natural consequence of this chemistry, which can introduce steric problems when co-ordinating these ligands. Branching the chain from a carbon in the ring should produce sterically more efficient ligands, yet the synthetic chemistry in such cases can be more demanding.

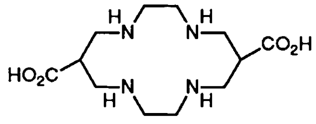
Nevertheless, a limited range of molecules have been prepared, employing some well planned chemistry. Metal-directed condensation of 2,6-diacetylpyridine and 3,6-bis(2-aminoethyl)-3,6-diazaoctane-1,8-diamine produces a macrocycle with five heteroatoms in the ring and two 2-aminoethyl pendant arms.[5] A range of diaminediamide macrocycles with a 2-ethylpyridine pendant attached to a methylene of the macrocycle between the two amide groups have been prepared by condensation between linear tetraamines and a substituted malonic acid diester.[6] Reaction of an N-protected imidazole-substituted acrylate with a linear tri-, tetra- or penta-amine produces, following diborane reduction and deprotection, a macrocycle with a pendant imidazole attached directly to a carbon adjacent to a secondary amine of the macrocycle ring.[7,8] Michael addition of a tetraamine to coumarin, and subsequent diborane reduction of the amide group, generates a phenol-appended macrocycle where again the pendant is adjacent to a secondary amine.[9] A pentaazacycloalkane with a C-pendant 4-aminobutane unit has also been reported recently, prepared by a conventional organic route.[10]

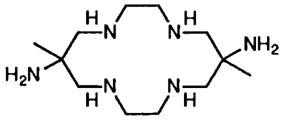
An alternative approach to C-based pendant-arm macrocycles has involved reactions of co-ordinated ligands. We have explored extensively chemistry involving formaldehyde and nitroethane, which builds new $-NHCH_2C(CH_3)(NO_2)CH_2-NH-$ links between *cis*-disposed primary amines.[1,11–14] Related chemistry has established that a co-ordinated imine can react in base with nitroethane to yield a $-NHCH(CH_2NO_2)CH_2-$ unit.[15,16] In both cases, facile reduction to the primary amines with zinc and aqueous acid yields molecules with C-pendant primary amines. Binding of such pendants to a range of metal ions has been well defined.[1]

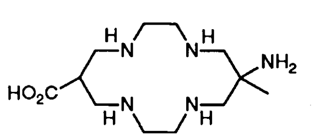
Other carbon acids may be substituted and treated in the same way as nitroethane. We defined some time ago a role for diethyl malonate, leading to C-pendant ethoxycarbonyl groups,[17] and have recently been investigating the conversion of these groups into simple pendant carboxylates.[18] From bis(ethane-1,2-diamine)copper(II) as precursor, routes to both the acyclic pendant hydrogen 3,7-diazanonane-1,9-diamine-5-carboxylate and the cyclic dihydrogen 1,4,8,11-tetraazacyclotetradecane-6,13-dicarboxylate (L^1) have been pursued.[18–20] The latter ligand offers two pendant carboxylates in place of the two pendant amines in the analogue 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^2), but has been prepared only in very low yield.[18,20] Since the acyclic ligand methyl 3,7-diazanonane-1,9-diamine-5-carboxylate can be prepared by a copper(II)-directed reaction in relatively high yield,[19] and the chemistry with nitroethane and formaldehyde is known to proceed readily in high yield,[11] we have now examined proceeding *via* the copper(II) complex of this acyclic ligand to

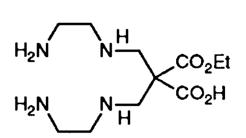
---

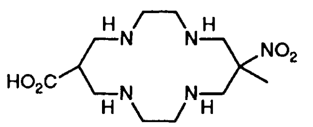
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

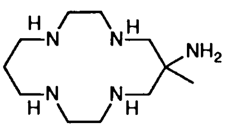

L^1


L^2


L^3


L^4


L^5


L^6

prepare the potentially sexidentate ligand hydrogen 13-amino-13-methyl-1,4,8,11-tetraazacyclotetradecane-6-carboxylate (L^3). This ligand possesses both a pendant amine and a pendant carboxylate group. The chemistry leading to this new polyamino acid, and its co-ordination chemistry with cobalt(III), is described herein.

Experimental

Syntheses.—Bis(ethane-1,2-diamine)copper(II) perchlorate was prepared by careful addition of ethane-1,2-diamine to a methanolic solution of copper(II) perchlorate hexahydrate in a 2:1 molar ratio. Precipitation was completed by addition of diethyl ether, and the complex was collected and dried in a vacuum desiccator.

{*Ethyl hydrogen bis*[(*2-aminoethyl*)*aminomethyl*]*malonate*}-*copper*(II) *Perchlorate*, [CuL^4][ClO$_4$]$_2$.—This was prepared essentially as described.[19] To a suspension of bis(ethane-1,2-diamine)copper(II) perchlorate (5 g) in methanol (200 cm^3) was added diethyl malonate (2 cm^3) and triethylamine (2 cm^3). A solution of formaldehyde (2 cm^3, 38% aqueous) in methanol (20 cm^3) was added dropwise over 1 h to the refluxing suspension. Reflux was continued for 4 h. On cooling, the purple product precipitated and was collected, washed with ethanol and air dried (3.2 g, 46%) (Found: C, 24.3; H, 4.8; N, 10.6. Calc. for $C_{11}H_{24}Cl_2CuN_4O_{12}$: C, 24.5; H, 4.5; N, 10.4%). Electronic spectrum (in water): λ_{max} 531 (ε 75) and 241 nm (ε 7560 dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr disc): $\nu(CO_2R)$ 1730 and 1795 cm^{-1}.

(*Hydrogen* 13-*methyl*-13-*nitro*-1,4,8,11-*tetraazacyclotetradecane*-6-*carboxylate*)*copper*(II) *Perchlorate Monohydrate*, [CuL^5][ClO$_4$]$_2$·H$_2$O.—A solution of [CuL^4][ClO$_4$]$_2$ (4 g) in methanol (600 cm^3), triethylamine (4 cm^3) and water (20 cm^3) was stirred at 60 °C for 4 h. After dilution to 2 dm^3 with water, the solution was sorbed onto a column of SP Sephadex C25 (Na$^+$ form) resin (20 × 5 cm). A single band was eluted with 0.2 mol dm^{-3} NaClO$_4$ solution, collected and concentrated to 30 cm^3 on a rotary evaporator. This solution of the pendant methoxycarbonyl form of [CuL^4][ClO$_4$]$_2$ was then diluted to 200 cm^3 with methanol. To it was added formaldehyde (4 cm^3, 38% aqueous), triethylamine (6 cm^3) and nitroethane (4 cm^3). The solution was stirred at 60 °C for 4 h and then at room temperature for 8 h. Some 0.5 g of a purple precipitate was collected, washed with ethanol and air dried. To the remaining solution, formaldehyde (2 cm^3, 38% aqueous) and nitroethane (2 cm^3) were added and the solution stirred at 60 °C for 2 h. After this period 1.1 g of a purple precipitate were collected, washed with ethanol and air dried. Comparison of the infrared spectra of the two precipitates showed them to be identical. The precipitate was recrystallized from aqueous solution treated with perchloric acid (Found: C, 24.9; H, 4.5; N, 11.6. Calc. for $C_{12}H_{27}Cl_2CuN_5O_{13}$: C, 24.7; H, 4.7; N, 12.0%). Electronic spectrum (in water): λ_{max} 512 (ε 79), 252 (ε 7770) and 193 nm (ε 6180 dm^3 mol^{-1} cm^{-1}). IR spectrum (KBr disc): $\nu(CO_2R)$ 1737, 1716, $\nu(NO_2)$ 1552, 1343 cm^{-1}. Voltammetry (hanging mercury drop electrode, in water): $E_{\frac{1}{2}}$ −0.46 V, ΔE 330 mV.

Hydrogen 13-*Amino*-13-*methyl*-1,4,8,11-*tetraazacyclotetradecane*-6-*carboxylate Pentahydrochloride Tetrahydrate*, L^3·5HCl·4H$_2$O.—The complex [CuL^5][ClO$_4$]$_2$·H$_2$O (4 g) was dissolved in water (100 cm^3). This solution and hydrochloric acid (3 mol dm^{-3}, 100 cm^3) were added dropwise from separate dropping funnels over 1 h to zinc powder (6 g) while stirring. The solution was stirred for 0.5 h at 60 °C and then filtered to remove copper and any remaining zinc. The solution was diluted to 2 dm^3 with water and sorbed onto a column of Dowex 50W × 2 (H$^+$ form) resin (4 × 15 cm). The column was washed with 1 mol dm^{-3} HCl until no further evidence of zinc(II) ion elution (*i.e.* formation of zinc hydroxide on addition of base) was present, and then the product was eluted with 3 mol dm^{-3} HCl (elution of the required macrocycle being indicated by the formation of an acid-stable species on addition of base and Cu^{2+} to a small sample of the eluent). The product was taken to dryness on a rotary evaporator, washed with ethanol then diethyl ether and dried in a vacuum desiccator (1.5 g) (Found: C, 27.7; H, 7.1; N, 13.3. Calc. for $C_{12}H_{40}Cl_5N_5O_6$: C, 27.3; H, 7.6; N, 13.3%). NMR (D$_2$O): ^{1}H, δ 1.60 (s, 3 H) and 2.8–3.8 (m, 17 H); ^{13}C, δ 20.8, 41.9, 47.3, 47.8, 50.6, 54.1, 55.6 and 175.

cis-*Cobalt*(III) *Complexes of* L^3.—The compound L^3·5HCl·4H$_2$O (1.5 g) and cobalt(II) chloride hexahydrate (0.89 g, 20% excess) were dissolved in water (100 cm^3) (pink solution). The pH was adjusted to 9 with aqueous sodium hydroxide (2.5 mol dm^{-3}), then air was bubbled through the solution for 75 min. The brown solution was re-acidified by addition of hydrochloric acid (40 cm^3, 10 mol dm^{-3}) and stirred at 80 °C for 36 h. The red solution was diluted to 1 dm^3 with water and sorbed onto a column of Dowex 50W × 2 (H$^+$ form) resin (4 × 10 cm), washed with 0.5 mol dm^{-3} hydrochloric acid and eluted with 3 mol dm^{-3} hydrochloric acid, resulting in two bands, separated and crystallized in turn as follows.

cis-*Chloro*(*hydrogen* 13-*amino*-13-*methyl*-1,4,8,11-*tetraazacyclotetradecane*-6-*carboxylate*)*cobalt*(III) *perchlorate monohydrate*, [CoL^3(Cl)][ClO$_4$]$_2$·H$_2$O. This red-pink solution was collected first, reduced in volume and left to crystallize after the addition of a small amount of perchloric acid. On standing red crystals formed, which were collected, washed with isopropyl alcohol and air dried (yield *ca.* 60%) (Found: C, 24.8; H, 4.6; N, 11.9. Calc. for $C_{12}H_{29}Cl_3CoN_5O_{11}$: C, 24.8; H, 5.0; N, 11.9%). Electronic spectrum (in water): λ_{max} 524 (ε 86), 477 (ε 83) and 365 nm (ε 114 dm^3 mol^{-1} cm^{-1}). NMR (D$_2$O): ^{1}H, δ 1.33 (s, 3 H) and 2.3–3.5 (m, 17 H); ^{13}C, δ 19.5, 49.0, 52.7, 53.3, 53.4, 53.8, 54.3, 56.7, 60.1 and 169. IR spectrum (KBr disc): $\nu(CO_2R)$ 1718, $\nu(NH_2)$ 1605 cm^{-1}. Voltammetry (as above): $E_{\frac{1}{2}}$ −0.46 V, ΔE 63 mV.

cis-*Aqua*(*hydrogen* 13-*amino*-13-*methyl*-1,4,8,11-*tetraazacyclotetradecane*-6-*carboxylate*)*cobalt*(III) *perchlorate*, [CoL^3(H$_2$O)][ClO$_4$]$_3$. This orange band was collected second and treated as above. On standing orange-red crystals formed (yield *ca.* 40%) (Found: C, 22.0; H, 4.5; N, 11.3. Calc. for $C_{12}H_{29}Cl_3CoN_5O_{15}$: C, 22.2; H, 4.5; N, 10.8%). Electronic spectrum (in water): λ_{max} 530(sh) (ε 68), 474 (ε 95) and 358 nm (ε 106 dm^3 mol^{-1} cm^{-1}). NMR (D$_2$O): ^{13}C, δ 17.6, 33.6, 46.8, 50.2, 51.3, 53.6, 55.3, 59.8, 66.0 and 174. IR spectrum (KBr disc): $\nu(CO_2R)$ 1717, $\nu(NH_2)$ 1600 cm^{-1}. Voltammetry (as above): $E_{\frac{1}{2}}$ −0.48 V, ΔE 63 mV.

trans-(13-*Amino*-13-*methyl*-1,4,8,11-*tetraazacyclotetradecane*-6-*carboxylato*)*cobalt*(III) *Perchlorate Monohydrate*, $[Co(L^3 - H)][ClO_4]_2{\cdot}H_2O$.—The compound $L^3{\cdot}5HCl{\cdot}4H_2O$ (2.1 g) and cobalt(II) chloride hexahydrate (1.05 g, 10% excess) were dissolved in water (200 cm^3) (pink solution). The pH was adjusted to 7.5 with aqueous sodium hydroxide (2.5 mol dm^{-3}), then air was bubbled through the solution for 2 h. The brown solution was re-acidified by addition of hydrochloric acid (60 cm^3, 10 mol dm^{-3}) and stirred at 80 °C for 2 h and then unheated for 48 h. The solution pH was adjusted to 8 with aqueous sodium hydroxide (2.5 mol dm^{-3}) and then the red solution was heated with activated charcoal for 5 h. The solution was filtered, diluted to 1 dm^3 with water and sorbed onto a column of Dowex 50W × 2 (H^+ form) resin (4 × 10 cm). A dilute red-pink band spread across the column during loading. It was eluted with 1 mol dm^{-3} HCl resulting in a small volume of the pink solution, to which was added a small amount of sodium perchlorate. On standing a small amount of red crystalline solid formed (< 10% of total cobalt). Insufficient was available to make a full characterization, but spectroscopic studies suggest it was the *trans* chloropentaamine [electronic spectrum (in water): λ_{max} 522 (ε 63), 444 (ε 43) and 354 nm (ε 99 dm^3 mol^{-1} cm^{-1})]. The dominant orange band also eluted slowly with 1 mol dm^{-3} HCl. The solution was reduced in volume on a rotary evaporator, and a small amount of sodium perchlorate was added and the solution left to crystallize. On standing, orange crystals formed (*ca.* 90% of total cobalt). These were collected, washed with ethyl alcohol and diethyl ether and air dried. X-Ray studies confirmed it as the sexidentate complex (Found: C, 26.2; H, 5.2; N, 12.5. Calc. for $C_{12}H_{28}Cl_2CoN_5O_{11}$: C, 26.2; H, 5.1; N, 12.7%). Electronic spectrum (in water): λ_{max} 481 (ε 87) and 339 nm (ε 92 dm^3 mol^{-1} cm^{-1}). NMR (D_2O): ^1H, δ 1.29 (s, 3 H) and 2.7–3.8 (m, 17 H); ^{13}C, δ 18.3, 45.3, 47.6, 52.7, 58.1, 66.2 and 184.9. IR spectrum (KBr disc): $\nu(CO_2^-)$ 1627, 1400 cm^{-1}. Voltammetry (as above): $E_{\frac{1}{2}}$ −0.42 V, Δ*E* 80 mV.

Physical Methods.—Electronic spectra were recorded in aqueous solution using an Hitachi 150-20 spectrophotometer, IR spectra on complexes dispersed in KBr discs using a Bio-Rad FTS-7 Fourier-transform spectrometer. Electrochemical measurements were performed with a AMEL model 473 controller linked to an EG&G PAR model 303A static mercury drop electrode. A conventional three-electrode system, with Ag–AgCl reference electrode, platinum counter electrode and nitrogen purge gas, was employed, with 0.1 mol dm^{-3} $NaClO_4$ as an electrolyte. Proton and ^{13}C NMR spectra were recorded on a JEOL FX90Q Fourier-transform spectrometer in D_2O solutions with sodium 3-trimethylsilylpropionate and dioxane as internal standards, although shifts are cited *versus* tetramethylsilane.

Structure Determination.—*Crystal data*. $[CoL^3(Cl)][ClO_4]_2$ **1**, $C_{12}H_{27}Cl_3CoN_5O_{10}$, M = 566.66, orthorhombic, space group *Pbca*, a = 10.256(4), b = 12.689(5), c = 33.08(2) Å, U = 4305 Å^3, $D_c(Z = 8)$ = 1.749 g cm^{-3}, $F(000)$ = 2336, μ(Mo-Kα) = 12.30 cm^{-1}. $A_{min,max}$ 1.13, 1.21, range of *hkl* 0–12, 0–15, 0–39, R = 0.050, R' = 0.052, $w = 2.90/(\sigma^2 F_o + 0.000\,231 F_o^2)$, residual extrema +0.6, −0.6 e Å^{-3}.

$[Co(L^3 - H)][ClO_4]_2{\cdot}H_2O$ **2**, $C_{12}H_{28}Cl_2CoN_5O_{11}$, M = 548.22, monoclinic, space group $P2_1/n$, a = 10.939(2), b = 13.355(2), c = 14.596(2) Å, β = 102.17(1)°, U = 2084.4 Å^3, $D_c(Z = 4)$ = 1.747 g cm^{-3}, $F(000)$ = 1136, μ(Mo-Kα) = 11.42 cm^{-1}. $A_{min,max}$ 1.22, 1.37, range of *hkl* −13 to 13, 0–15, 0–17, R = 0.033, R' = 0.039, $w = 2.71/(\sigma^2 F_o + 0.000\,143 F_o^2)$, residual extrema +0.6, −0.5 e Å^{-3}.

Lattice parameters at 21 °C were determined by least-squares fits to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4F four-circle diffractometer employing graphite-monochromated Mo-Kα radiation (0.7107 Å) and operating in the ω (for **1**) or ω–2θ (for **2**) scan modes.

Data were reduced and Lorentz, polarization and absorption corrections were applied using the Enraf-Nonius Structure Determination Package.[21] Of the 4158 and 3998 independent non-zero reflections collected for compounds **1** and **2** respectively, 2073 and 3206 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations. The structures were solved by direct and heavy-atom methods respectively, using SHELX 76[22] and the solutions were extended by Fourier difference methods. Hydrogen atoms were included at calculated sites (C–H, N–H 0.97 Å) with group isotropic thermal parameters for **1** and were refined with isotropic thermal parameters for **2**. All other atoms with the exception of minor contributors to disordered species (one perchlorate anion in **1**) were refined anisotropically. Scattering factors and anomalous dispersion terms used for Co were taken from ref. 23 and all others used were those supplied in SHELX 76. All calculations were carried out using SHELX 76, and plots were drawn using ORTEP.[24] The atom numbering schemes are given in Fig. 1. Final atomic coordinates, bond lengths and angles are listed in Tables 1–6.

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

Results and Discussion

Reactions of the macrocycle L^3 with Co^{2+}(aq) and air yielded products exclusively comprising the ligand co-ordinated to cobalt(III) in a 1:1 ratio, in one of three co-ordination modes. No complex with the macrocycle co-ordinated as a tetradentate ligand, involving apparently co-ordination of the secondary amines alone, was detected. The detected products isolated exhibited quinque- or sexi-dentate co-ordination. Of the two geometries with quinquedentate co-ordination one had the five amines co-ordinated in an unusual *cis* configuration in which the co-ordinated chloride ion is *trans* to a secondary amine rather than to the primary pendant amine. In this geometry, the secondary amine hydrogens adopt an *RRRR* rather than the more common *RRSS* configuration.[25] This isomer is thought to be a kinetic product, with the other geometries, where either a chloride ion or the carboxylate pendant is bound *trans* to the primary amine pendant, favoured after equilibration over charcoal at near neutral pH. Spectroscopic and electrochemical studies suggest that the *cis* isomer isomerises slowly to the *trans* form in neutral solution. In the *trans* configuration the secondary amines are necessarily in the more stable *RRSS* configuration, consistent with results found for the similar pendant-arm sexidentate ligand 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^2).[26]

The chloropentaamine complex with *RRRR* nitrogen configuration was defined by an X-ray crystal structure analysis, which showed that the secondary amines N(2), N(3) and N(4) of the macrocycle lie in a plane with the pendant amine N(5), whereas one secondary amine, N(1), lies out of this plane. The nitrogens N(5), N(1) and N(4), which form an octahedral face, are joined by two five-membered chelate rings centred on N(1) in a distorted 'butterfly' arrangement, akin to a *fac*-dien {*e.g.* as in the $[Co(dien)(P_3O_{10})]$ complex[27] (dien = 3-azapentane-1,5-diamine)}. The Co–N distances in the structure are variable, ranging from 1.940(6) Å for Co–N(2) to 1.975(5) Å for both Co–N(3) and Co–N(4). The Co–Cl distance of 2.266(2) Å is not significantly different from that of 2.261(1) Å in the structure of $[CoL^7(Cl)]^{2+}$ (L^7 = 5-methyl-3,7-diazanonane-1,5,9-triamine) where the primary 'cap' amine of the acyclic ligand was located *trans* rather than *cis* to the chloride ion,[28] but significantly longer than distances of 2.224(2) Å in *trans*-$[CoL^6(Cl)]^{2+}$ and 2.236(2) Å in *cis*-$[CoL^6(Cl)]^{2+}$ [29,30] analogues (L^6 = 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine) which have the identical macrocycle except for the absence of the unco-ordinated pendant carboxylate. What is different in the latter *cis* complex is that the amine adopts the more favourable *RRSS*

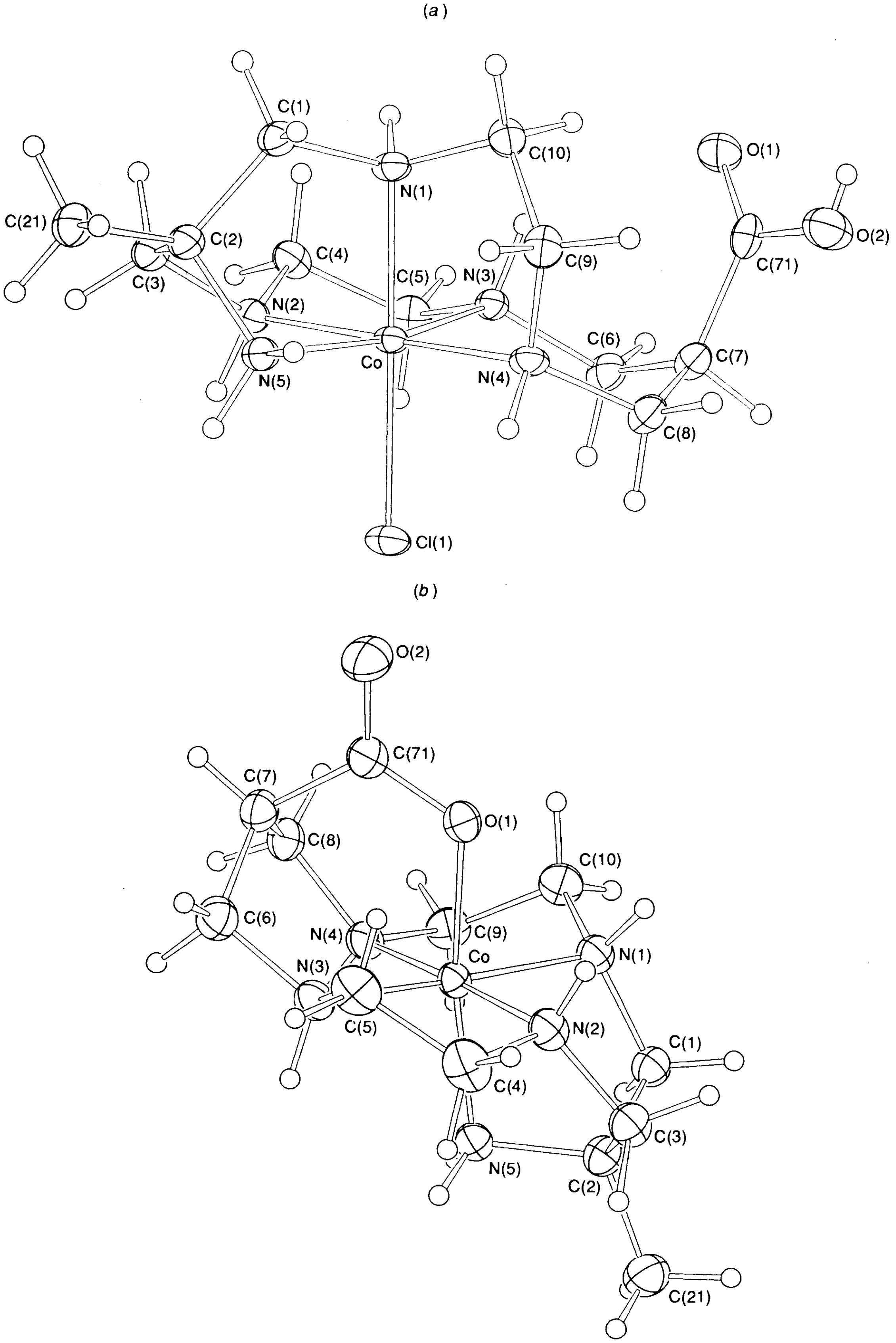


Fig. 1 View of the cations (*a*) $[CoL^3(Cl)]^{2+}$ and (*b*) $[Co(L^3 - H)]^{2+}$, with numbering schemes

compared with the *RRRR* geometry in this case. The octahedron is less distorted in the former case, and the average Co–N distance (1.95_4 Å) is shorter than in the present example (1.96_4 Å).

Examination of Table 4 shows the distortion of the CoN_5Cl octahedron, with the N(5)–Co–N(3) axis being deformed towards a line joining atoms N(1) and N(2); the angle of 167.3(2)° is essentially the same as that observed (167.4°) in the

Table 1 Positional parameters (× 10^4) for $[CoL^3(Cl)][ClO_4]_2$

Atom	*x*	*y*	*z*
Co	1708(1)	2088(1)	1203(1)
N(1)	738(5)	3341(4)	1375(2)
N(2)	1182(5)	2306(4)	646(2)
N(3)	3242(5)	2973(4)	1080(2)
N(4)	2143(5)	1864(4)	1778(2)
N(5)	3(5)	1379(4)	1226(2)
O(1)	4170(5)	4536(4)	1716(2)
O(2)	4317(7)	3682(5)	2302(2)
C(1)	−685(7)	3137(5)	1317(2)
C(2)	−847(7)	2206(5)	1034(2)
C(3)	−276(7)	2426(6)	619(2)
C(4)	1967(7)	3163(5)	465(2)
C(5)	3328(7)	3030(6)	626(2)
C(6)	4519(7)	2689(6)	1263(2)
C(7)	4464(7)	2650(5)	1719(2)
C(8)	3561(7)	1800(6)	1894(2)
C(9)	1332(7)	2591(6)	2025(2)
C(10)	1107(7)	3604(6)	1796(2)
C(21)	−2284(7)	1887(6)	1012(2)
C(71)	4307(7)	3731(6)	1902(2)
Cl(1)	2748(2)	581(1)	1026(1)
Cl(2)	2440(2)	410(2)	2906(1)
O(3)	3199(8)	1310(6)	2970(2)
O(4)	1429(10)	563(7)	2642(3)
O(5)	3167(14)	−46(11)	2552(4)
O(6)	2532(32)	−171(20)	3232(5)
O(5′)	2854(18)	−621(14)	2979(8)
O(6′)	1347(13)	498(12)	3236(5)
Cl(3)	1770(3)	527(2)	−346(1)
O(7)	835(10)	296(7)	−634(3)
O(8)	1509(10)	1533(6)	−191(2)
O(9)	1686(10)	−240(9)	−61(3)
O(10)	3013(10)	442(8)	−515(3)

Primes indicate disordered species. Occupancies: O(5)–O(6) 0.53(2), O(5′)–O(6′) 0.47(2).

Table 2 Positional parameters (× 10^4) for $[Co(L^3 - H)][ClO_4]_2 \cdot H_2O$

Atom	*x*	*y*	*z*
Co	4101(1)	6174(1)	1304(1)
N(2)	2886(2)	6162(2)	116(2)
O(1)	4772(2)	4934(1)	1003(1)
N(3)	2887(2)	5427(2)	1849(2)
N(5)	3402(2)	7509(2)	1399(2)
O(2)	5174(2)	3353(1)	1372(2)
N(4)	5306(2)	6280(2)	2492(2)
N(1)	5297(2)	6853(2)	703(2)
C(1)	4853(3)	7892(2)	454(2)
C(2)	3463(3)	7933(2)	460(2)
C(3)	2710(3)	7205(2)	—255(2)
C(4)	1710(3)	5699(3)	280(2)
C(5)	2049(3)	4920(3)	1038(2)
C(6)	3449(3)	4717(2)	2603(2)
C(7)	4799(3)	4455(2)	2579(2)
C(8)	5705(3)	5300(2)	2953(2)
C(9)	6375(3)	6916(2)	2334(2)
C(10)	6536(3)	6760(2)	1347(2)
C(21)	2952(3)	8988(2)	304(2)
C(71)	4927(2)	4198(2)	1594(2)
OW(2)	1400(3)	7052(2)	2428(3)
Cl(1)	3830(1)	7035(1)	4646(1)
Cl(2)	812(1)	5071(1)	7584(1)
O(11)	798(3)	2396(2)	1171(2)
O(12)	623(5)	2585(3)	−418(3)
O(13)	2447(3)	2155(4)	465(3)
O(14)	814(6)	1044(3)	248(3)
O(21)	1937(2)	5606(2)	7980(2)
O(22)	−242(2)	5731(2)	7492(2)
O(23)	875(3)	4676(2)	6703(2)
O(24)	678(2)	4291(2)	8218(2)

Table 3 Bond lengths (Å) for $[CoL^3(Cl)][ClO_4]_2$

N(1)–Co	1.960(5)	N(2)–Co	1.940(6)
N(3)–Co	1.975(5)	N(4)–Co	1.975(5)
N(5)–Co	1.968(5)	Cl(1)–Co	2.266(2)
C(1)–N(1)	1.495(9)	C(10)–N(1)	1.481(8)
C(3)–N(2)	1.506(8)	C(4)–N(2)	1.480(8)
C(5)–N(3)	1.505(8)	C(6)–N(3)	1.486(8)
C(8)–N(4)	1.506(9)	C(9)–N(4)	1.488(8)
C(2)–N(5)	1.505(8)	C(71)–O(1)	1.200(8)
C(71)–O(2)	1.325(9)	C(2)–C(1)	1.516(9)
C(3)–C(2)	1.518(9)	C(21)–C(2)	1.530(9)
C(5)–C(4)	1.504(10)	C(7)–C(6)	1.511(9)
C(8)–C(7)	1.535(9)	C(71)–C(7)	1.508(10)
C(10)–C(9)	1.511(10)	O(3)–Cl(2)	1.397(7)
O(4)–Cl(2)	1.370(8)	O(5)–Cl(2)	1.506(12)
O(6)–Cl(2)	1.311(16)	O(5′)–Cl(2)	1.398(17)
O(6′)–Cl(2)	1.568(14)	O(7)–Cl(3)	1.381(8)
O(8)–Cl(3)	1.401(7)	O(9)–Cl(3)	1.359(8)
O(10)–Cl(3)	1.397(9)		

cyclic analogue *cis*-$[(CoL^6(Cl)]^{2+}$,[30] indicating a primary influence of the common co-ordinated pendant. Tied to this distortion is the observation that the N–Co–N angles in the five-membered rings formed on co-ordinating the pendant amine are small at 81.7(2) and 84.7(2)°. Co-ordination of the pendant primary amine effectively 'pulls' the C(3) and C(1) atoms towards the metal centre and hence opens the angles at the adjacent co-ordinated secondary amines; this is shown in substantial strain in the angle C(3)–N(2)–C(4) (116.3°), although the C(1)–N(1)–C(10) angle (114.1°) is less strained (unlike the observation in the analogue), and angles around N(3) and N(4) are close to normal, defining less strain in other five-membered chelate rings. The C(2)–N(5)–Co angle formed at the pendant primary amine of 100.4° is substantially smaller than other C–N–Co angles (range 108.3–118.7°); some others, *e.g.* C(6)–N(3)–Co and C(8)–N(4)–Co, are significantly greater to match an expanded N(3)–Co–N(4) angle. It is notable that the longest bond lengths are those of Co–N(4) and Co–N(3) [both 1.975(5) Å] whereas in the unsubstituted analogue these distances are similar to others at 1.959(4) Å. There is for the CoN_4 plane a minor tetrahedral distortion from square planarity (*ca.* ±0.03 Å), with the cobalt also displaced by 0.06 Å from the plane towards the chloride ligand. Whether the distortions in the present structure are defined by the *RRRR* geometry compared with the *RRSS* geometry in the analogue, or whether there is some steric influence of the unco-ordinated carboxylate group (which is absent in the analogous structure), is difficult to define, although both may contribute.

Co-ordination of the ligand in a sexidentate manner necessarily involves binding of the pendant amine and carboxylate groups in *trans* dispositions, where the secondary amines adopt *RRSS* stereochemistry. The co-ordinated carboxylate is planar to within 0.003 Å, but the Co atom lies 0.33 Å out of this plane. The average Co–N bond length is slightly shorter than that in the quinquedentate analogue **1** (1.95_2 compared with 1.96_3 Å); however, it is not obvious whether this is the result of the constraints of the additional co-ordination or the different geometrical arrangement. The six-membered chelate rings of the 14-membered macrocycle which encircles the metal ion are folded back into nearly ideal boat conformations to permit co-ordination of the primary amine and the carboxylate. The equatorial five-membered chelate rings are slightly flattened skew confirmations, and those involving the axial pendant nitrogen adopt slightly more puckered skew conformations. Significant strain in the ligand is indicated by the boat and flattened skew conformations, most notable in the nominal tetrahedral angles Co–N(5)–C(2), which has fallen to 100.8°,

Table 4 Bond angles (°) for $[CoL^3(Cl)][ClO_4]_2$

N(2)–Co–N(1)	91.1(2)	N(3)–Co–N(1)	90.1(2)
N(3)–Co–N(2)	86.9(2)	N(4)–Co–N(1)	87.3(2)
N(4)–Co–N(2)	176.9(2)	N(4)–Co–N(3)	95.8(2)
N(5)–Co–N(1)	84.7(2)	N(5)–Co–N(2)	81.7(2)
N(5)–Co–N(3)	167.3(2)	N(5)–Co–N(4)	95.6(2)
Cl(1)–Co–N(1)	176.7(2)	Cl(1)–Co–N(2)	90.3(2)
Cl(1)–Co–N(3)	93.0(2)	Cl(1)–Co–N(4)	91.2(2)
Cl(1)–Co–N(5)	92.5(2)	C(1)–N(1)–Co	108.6(4)
C(10)–N(1)–Co	109.0(4)	C(10)–N(1)–C(1)	114.1(5)
C(3)–N(2)–Co	110.2(4)	C(4)–N(2)–Co	109.7(4)
C(4)–N(2)–C(3)	116.3(5)	C(5)–N(3)–Co	106.2(4)
C(6)–N(3)–Co	118.7(4)	C(6)–N(3)–C(5)	111.4(5)
C(8)–N(4)–Co	118.1(4)	C(9)–N(4)–Co	108.3(4)
C(9)–N(4)–C(8)	115.7(6)	C(2)–N(5)–Co	100.4(4)
C(2)–C(1)–N(1)	108.7(5)	C(1)–C(2)–N(5)	102.7(5)
C(3)–C(2)–N(5)	106.6(5)	C(3)–C(2)–C(1)	111.8(6)
C(21)–C(2)–N(5)	113.3(6)	C(21)–C(2)–C(1)	110.0(6)
C(21)–C(2)–C(3)	112.1(6)	C(2)–C(3)–N(2)	108.2(6)
C(5)–C(4)–N(2)	106.3(5)	C(4)–C(5)–N(3)	107.7(6)
C(7)–C(6)–N(3)	112.4(6)	C(8)–C(7)–C(6)	115.0(6)
C(71)–C(7)–C(6)	112.0(6)	C(71)–C(7)–C(8)	115.1(6)
C(7)–C(8)–N(4)	116.6(6)	C(10)–C(9)–N(4)	109.7(5)
C(9)–C(10)–N(1)	108.6(5)	O(2)–C(71)–O(1)	123.5(7)
C(7)–C(71)–O(1)	125.6(6)	C(7)–C(71)–O(2)	110.9(6)
O(4)–Cl(2)–O(3)	113.7(5)	O(5)–Cl(2)–O(3)	99.0(6)
O(5)–Cl(2)–O(4)	86.2(8)	O(6)–Cl(2)–O(3)	107.2(9)
O(6)–Cl(2)–O(4)	131(2)	O(6)–Cl(2)–O(5)	112(2)
O(8)–Cl(3)–O(7)	108.3(5)	O(9)–Cl(3)–O(7)	106.3(7)
O(9)–Cl(3)–O(8)	112.7(6)	O(10)–Cl(3)–O(7)	110.0(7)
O(10)–Cl(3)–O(8)	113.0(5)	O(10)–Cl(3)–O(9)	106.2(7)

Table 5 Bond lengths (Å) for $[Co(L^3 - H)][(ClO_4]_2{\cdot}H_2O$

N(2)–Co	1.950(2)	O(1)–Co	1.899(2)
N(3)–Co	1.959(2)	N(5)–Co	1.956(2)
N(4)–Co	1.949(2)	N(1)–Co	1.946(2)
C(3)–N(2)	1.492(4)	C(4)–N(2)	1.491(4)
C(71)–O(1)	1.295(3)	C(5)–N(3)	1.499(4)
C(6)–N(3)	1.484(4)	C(2)–N(5)	1.496(4)
C(71)–O(2)	1.220(3)	C(8)–N(4)	1.494(3)
C(9)–N(4)	1.502(4)	C(1)–N(1)	1.489(3)
C(10)–N(1)	1.483(3)	C(2)–C(1)	1.524(4)
C(3)–C(2)	1.534(4)	C(21)–C(2)	1.515(4)
C(5)–C(4)	1.507(5)	C(7)–C(6)	1.525(4)
C(8)–C(7)	1.525(4)	C(71)–C(7)	1.514(4)
C(10)–C(9)	1.503(4)	O(21)–Cl(2)	1.435(2)
O(22)–Cl(2)	1.435(2)	O(23)–Cl(2)	1.406(3)
O(24)–Cl(2)	1.421(3)		

Table 6 Bond angles (°) for $[Co(L^3 - H)][ClO_4]_2{\cdot}H_2O$

O(1)–Co–N(2)	90.6(1)	N(3)–Co–N(2)	87.9(1)
N(3)–Co–O(1)	88.8(1)	N(5)–Co–N(2)	82.3(1)
N(5)–Co–O(1)	170.5(1)	N(5)–Co–N(3)	97.3(1)
N(4)–Co–N(2)	176.3(1)	N(4)–Co–O(1)	92.7(1)
N(4)–Co–N(3)	93.7(1)	N(4)–Co–N(5)	94.2(1)
N(1)–Co–N(2)	90.0(1)	N(1)–Co–O(1)	88.5(1)
N(1)–Co–N(3)	176.5(1)	N(1)–Co–N(5)	85.2(1)
N(1)–Co–N(4)	88.5(1)	C(3)–N(2)–Co	109.1(2)
C(4)–N(2)–Co	108.1(2)	C(4)–N(2)–C(3)	113.3(2)
C(71)–O(1)–Co	120.7(2)	C(5)–N(3)–Co	105.3(2)
C(6)–N(3)–Co	114.6(2)	C(6)–N(3)–C(5)	112.7(2)
C(2)–N(5)–Co	100.8(2)	C(8)–N(4)–Co	114.6(2)
C(9)–N(4)–Co	107.9(2)	C(9)–N(4)–C(8)	113.6(2)
C(1)–N(1)–Co	109.2(2)	C(10)–N(1)–Co	106.7(2)
C(10)–N(1)–C(1)	116.1(2)	C(2)–C(1)–N(1)	107.8(2)
C(1)–C(2)–N(5)	103.3(2)	C(3)–C(2)–N(5)	105.2(2)
C(3)–C(2)–C(1)	111.4(2)	C(21)–C(2)–N(5)	113.8(2)
C(21)–C(2)–C(1)	111.7(2)	C(21)–C(2)–C(3)	111.0(2)
C(2)–C(3)–N(2)	109.5(2)	C(5)–C(4)–N(2)	108.5(2)
C(4)–C(5)–N(3)	106.4(3)	C(7)–C(6)–N(3)	112.5(2)
C(8)–C(7)–C(6)	112.4(2)	C(71)–C(7)–C(6)	110.9(2)
C(71)–C(7)–C(8)	108.9(2)	C(7)–C(8)–N(4)	112.4(2)
C(10)–C(9)–N(4)	108.7(2)	C(9)–C(10)–N(1)	108.6(2)
O(2)–C(71)–O(1)	122.1(3)	C(7)–C(71)–O(1)	115.8(2)
C(7)–C(71)–O(2)	122.1(2)	O(22)–Cl(2)–O(21)	109.7(1)
O(23)–Cl(2)–O(21)	110.6(2)	O(23)–Cl(2)–O(22)	109.7(1)
O(24)–Cl(2)–O(21)	107.5(1)	O(24)–Cl(2)–O(22)	108.7(1)
O(24)–Cl(2)–O(23)	110.6(2)		

and C(3)–N(2)–C(4) and C(1)–N(1)–C(10) (opened out to 113.3, 116.1° respectively). The six-membered skew-boat rings formed by co-ordination of the carboxylate O(1) exhibit less strain, with Co–O(1)–C(71) close to ideal (120.7°) and other angles in the rings much closer to tetrahedral [*e.g.* C(71)–C(7)–C(8) 108.9, N(4)–C(8)–C(7) 112.4°] than observed in the rings formed by co-ordination of the amine pendant. Evidently, the six-membered rings formed by the carboxylate introduce smaller steric effects than the five-membered rings formed by the primary amine. This is confirmed by the angles O(1)–Co–N(4) and O(1)–Co–N(3) (92.7, 88.8°) being less distorted than the N(5)–Co–N(2) and N(5)–Co–N(1) angles (82.3, 85.2°) at the other 'cap' of the molecule. All of the distances Co–N(5), Co–N(1) and Co–N(2) (1.956, 1.946, 1.950 Å), which involve the octahedral face formed by the co-ordination of the pendant amine, are slightly shorter than 'usual' Co–N distances {*e.g.* compare with Co–N 1.964(7) Å in $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine)}, but the Co–N distances for the face formed at the carboxylate 'cap' are also short [Co–N(3) 1.959, Co–N(4) 1.949 Å], although the Co–O distance [1.899(2) Å] is similar to or at most at the short end of the range of those in amino acid complexes.[31] Thus, overall, there is a modest 'compression' of the co-ordination sphere despite the evident angle strain introduced by sexidentate co-ordination.

Both structures exhibit some significant non-bonded interactions involving hydrogen bonding between amine hydrogens and (where relevant) co-ordinated chloride, carboxylate, perchlorate and water oxygens. The NH ··· Y distances fall within the range 2.0–2.7 Å (tabulated in the Supplementary material), and may contribute to stabilization of the observed structures. For example, the N(3)–HN(3) ··· O(1) distance of 2.30 Å represents a possible intramolecular hydrogen bond in the quinquedentate structure which may contribute to stabilization of the uncommon *RRRR* geometry observed.

The structure of L^3 as a sexidentate ligand can be compared with that of the analogue L^2, which has two primary amine pendants. Both ligands are based on the fourteen-membered cyclam macrocycle with pendant groups attached to the central carbon of the $-(CH_2)_3-$ links of the molecule. In principle, two geometric isomers may exist in each case, depending on whether the two co-ordinating pendants are on opposite (*anti*) or the same (*syn*) sides of the macrocycle plane. For the hexaamine L^2 the *anti* isomer predominates, although the minor *syn* isomer has recently been isolated.[32] We have found, from NMR spectroscopy of all fractions from isolation of the free ligand L^3, no evidence for a *syn* isomer, the *anti* isomer being the only one formed. This may be a result of the synthetic method, since the carboxylate in the acyclic intermediate may adopt a geometry where it binds weakly in an axial site, thus directing the condensation chemistry with nitroethane and formaldehyde to occur effectively on the 'opposite' side of the molecule, leading exclusively to the *anti* isomer. The same type of directing ability by an acyclic nitro-substituted intermediate has been proposed to account for the dominance of the *anti* isomer in the synthesis which produces L^2,[32] although in that case the much weaker interaction of the nitro group permits some *syn* isomer to form. The L^1 ligand, with two pendant carboxylates, has been prepared recently in only low yield, and no evidence for a *syn* isomer has been forthcoming in that system either.[20] Further, structural characterization of sexidentate co-ordination to cobalt(III) has not been reported for this latter ligand to date.

All of L^1, L^2 and L^3 are capable of acting as sexidentate ligands, with both pendants co-ordinated in *trans* axial sites. Folded geometries of any of the macrocycles do not permit all six potential donors to co-ordinate, as observed in the $[CoL^3(Cl)]^{2+}$ complex already discussed above.

All of the ligands L^1, L^2 and L^3 represent sterically efficient potentially sexidentate ligands where the pendant groups are attached at carbons of the macrocyclic ring rather than at the nitrogen heteroatoms. As one progresses from sexidentate complexation of L^2 to L^3 to L^1 the chromophore changes from CoN_6 to CoN_5O to *trans*-CoN_4O_2, and, apart from changes in donor, the strained five-membered rings introduced by co-ordination of the pendant primary amine are successively replaced by less strained six-membered rings formed by co-ordination of the pendant carboxylates. Since donors axial to the macrocycle ring are changing, it is most reasonable to define the outcome of this transition on the metal-ion environment by examining the structures rather than comparing spectroscopic parameters. At least for L^2 and L^3 this is possible. Differences in the two 'caps' of L^3 have been discussed, but it is notable that one apparent consequence of the introduction of the carboxylate group in L^3 is a 'swelling' of the general co-ordination sphere relative to L^2. The average distances for the secondary nitrogen donors in L^3 [1.951(2) Å] and L^2 [1.937(2) Å][26] are not equivalent, and even the primary amine cap exhibits a longer distance in L^3 [1.956(2) Å] compared with L^2 [1.946(2) Å].[26] The consequence of introduction of a carboxylate pendant in place of an amine pendant is a diminution in strain, with angles less distorted and metal–donor distances less compressed, although cobalt–donor distances are still comparatively short. One may anticipate, for L^1, even longer distances, approaching more closely those in *cis* and *trans* isomers of unsubstituted 1,4,8,11-tetraazacyclotetradecane [1.986(7) to 2.016(6) Å].[33]

In the $[Co(L^3 - H)]^{2+}$ complex ion, physical properties do reflect the short cobalt–donor distances. The $^1T_{1g} \longleftarrow {}^1A_{1g}$ and $^1T_{2g} \longleftarrow {}^1A_{1g}$ transitions are at slightly higher energy than for CoN_5O^{2+} chromophores generally {*e.g.* 481 and 339 *versus* 487 and 345 nm for $[Co(en)_2(gly)]^{2+}$ (gly = glycine)}.[34] The cobalt(III)–cobalt(II) redox couple ($E_{\frac{1}{2}}$ −0.42 V *vs.* Ag–AgCl) is quasi-reversible on the voltammetric time-scale, and more negative than for other acetatopentaamine ions [*e.g.* $E_{\frac{1}{2}}$ −0.32 V for acetatopentaamminecobalt(III)].[35] The size of $\Delta E_{\frac{1}{2}}$ for $[Co(L^n)^{m+} - Co(NH_3)_5X^{m+}]$ varies from −0.10 ($n = 3$, X = acetate) to −0.51 V ($n = 2$, X = ammonia); likewise, $\Delta(\nu)$ for the low-energy electronic transition varies from 260 for the acid to 1320 cm^{-1} for the amine. This is consistent with the less 'compressed' environment in L^3 compared with L^2. Although L^3 is a sterically efficient ligand, it introduces less 'compression' than the hexaamine L^2. The generality of this observation is currently being examined with a range of metal ions.

Acknowledgements

Support of this work by the Australian Research Council is gratefully acknowledged.

References

1 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **93**, 297.

2 T. A. Kaden, *Top. Curr. Chem.*, 1984, **121**, 157.

3 R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875.

4 *Coordination Chemistry of Macrocyclic Complexes*, ed. G. A. Melson, Plenum, New York, 1982.

5 B. K. Wagnon and S. C. Jackels, *Inorg. Chem.*, 1989, **28**, 1923.

6 E. Kimura, T. Koike, R. Machida, R. Nagai and M. Kodama, *Inorg. Chem.*, 1984, **23**, 4181.

7 E. Kimura, M. Shionoya and Y. Iitaka, in *Current Topics in Macrocyclic Chemistry in Japan*, ed. E. Kimura, Hiroshima University School of Medicine, 1987, pp. 64–69.

8 E. Kimura, T. Koike, H. Nada and Y. Iitaka, *J. Chem. Soc., Chem. Commun.*, 1986, 1322.

9 E. Kimura, T. Koike and M. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1985, 385.

10 H. Fujioka, E. Kimura and M. Kodama, *Chem. Lett.*, 1982, 737.

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

12 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.

13 G. A. Lawrance, T. M. Manning, M. A. O'Leary, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1990, 2491.

14 G. A. Lawrance, M. Maeder, M. A. O'Leary and F.-H. Woon, *Polyhedron*, 1990, **9**, 2227.

15 B. Korybut-Daskiewicz, *J. Coord. Chem.*, 1988, **19**, 101.

16 R. W. Hay, M. P. Pujari, B. Korybut-Daskiewicz, G. Ferguson and B. L. Ruhl, *J. Chem. Soc., Dalton Trans.*, 1989, 85.

17 G. A. Lawrance and M. A. O'Leary, *Polyhedron*, 1987, **6**, 1291.

18 G. A. Lawrance, B. W. Skelton, A. H. White and E. N. Wilkes, *Aust. J. Chem.*, 1991, **44**, 113.

19 P. V. Bernhardt, G. A. Lawrance, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1990, **43**, 339.

20 L. Xin, N. F. Curtis and D. C. Weatherburn, *Transition Met. Chem.*, in the press.

21 Enraf-Nonius Structure Determination Package, Enraf-Nonius, Delft, 1985.

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

23 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

24 C. K. Johnson, ORTEP, A Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory, TN, 1965.

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

26 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1989, 1059.

27 G. P. Haight, jun., T. W. Hambley, P. Hendry, G. A. Lawrance and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1985, 488.

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

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

30 T. W. Hambley, G. A. Lawrance, M. Martinez, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, in the press.

31 T. W. Hambley, *Acta Crystallogr., Sect. B*, 1988, **44**, 601.

32 P. V. Bernhardt, P. Comba, T. W. Hambley, G. A. Lawrance and K. Varnagy, *J. Chem. Soc., Dalton Trans.*, 1991, 277.

33 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.

34 C. T. Lui and B. E. Douglas, *Inorg. Chem.*, 1964, **3**, 1356.

35 N. J. Curtis, G. A. Lawrance and A. M. Sargeson, *Aust. J. Chem.*, 1983, **36**, 1327.

Received 4*th November* 1991; *Paper* 1/05575E