Chapter Three

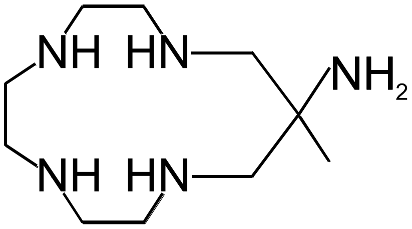
Tetraaminoacid Macrocycles: Coordination Chemistry

3.1 Introduction

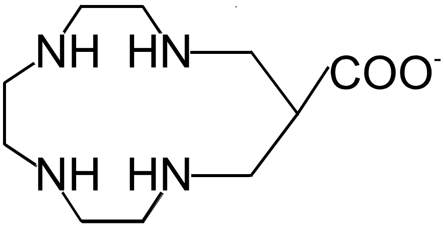
The coordination chemistry of tetraaza macrocycles bearing coordinating pendant(s) have received quite a large amount of study in recent years.[1] This has been, at least in part, because of the ability of the pendants to occupy vacant coordination sites once the metal has been secured within the centre of the macrocycle by the ring amines. Macrocycles with two or more pendants in suitable disposition have the ability to totally encapsulate many metal ions. Some ligands of this type will be discussed in the following chapters. Ligands of the type prepared in the previous chapter, that is bearing only one pendant, usually leave a 'vacant' coordination site on metal ions preferring six-coordination. This mode of coordination allows studies into the properties of the sixth coordination site, such as base hydrolysis studies of Co(III) complexes without the complicating interaction of multiple ligands, and the preparation of interesting coordination geometries such as polymers through pendants serving two coordination sites as bridging ligands.

For this study, the Co(III) and Ni(II) complexes of carboxylate-pendant ligands L6 and L8 were prepared and compared with those of their amine-pendant analogues L5 and L7. The Co(III) complex of L5 had been prepared previously[2], while the other complexes were prepared for this study. The pairs L5, L7 and L6, L8 differ in replacement of pendant amine and methyl groups in the former pair by a pendant carboxylate group and hydrogen in the latter pair. Quinquedentate ligands bound to cobalt(III) form an extensive group,[3,4] and reported examples are dominated by polyamine ligands, including linear, branched and cyclic examples. Macrocyclic tetraamines with a single additional amine pendant represent one group of ligands studied recently,[2,5,6,7] with both *cis* and *trans* arrangements of the pendant and the group occupying the sixth coordination site reported, although a preference towards *cis* coordination appears to exist from both experimental observations and molecular mechanics calculations.[7]

The introduction of a pendant which carries both a different donor group and is anionic clearly presents a different ligand field environment to that met with a neutral polyamine ligand, and this could influence the rate of ligand substitution in the sixth site. Previously, comparisons of amines/carboxylates have been limited and have required a combination of ligands, as exemplified in *trans*-$[Co(en)_2(OAc)Cl]^+$ versus trans-$[Co(en)_2(NH_3)Cl]^{2+}$. Closely related N_5/N_4O polydentate ligands which bind with all but the sixth site of the octahedron accommodated by the polydentate ligand have not been examined earlier. In this chapter, the syntheses and base hydrolysis reactions of



L1



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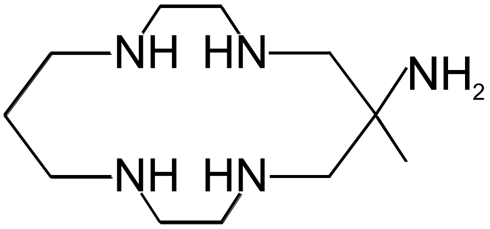

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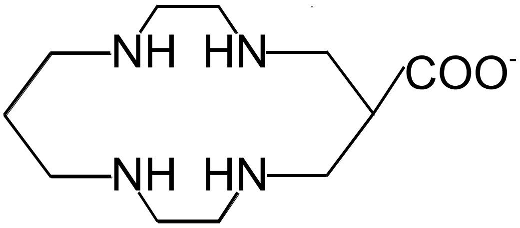

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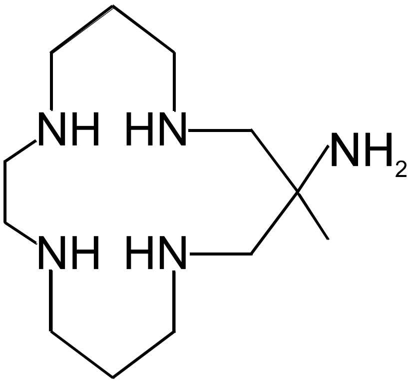

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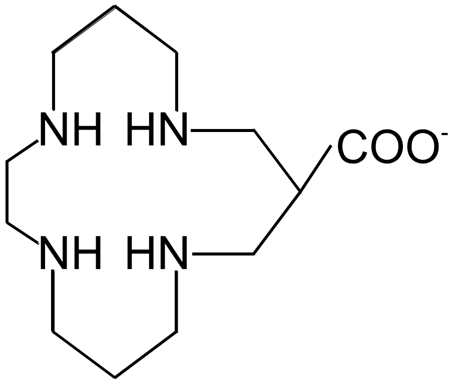

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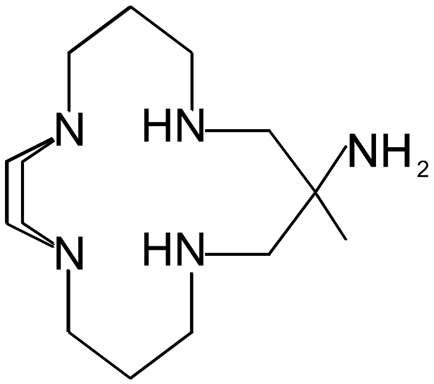

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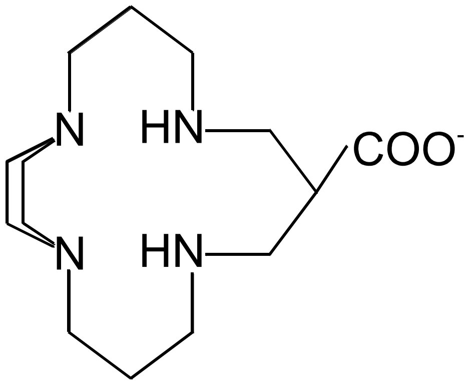

L8

chlorocobalt(III) complexes of two tetraazamacrocycles carrying pendant carboxylate groups is discussed, and are compared with analogues carrying a pendant amine group. The crystal structure analysis of the aquation product for one carboxylate pendant complex (L5) is also reported.

Co(III) is the definitive inert octahedral metal ion. The Ni(II) ion is, however, demonstrably more labile while still being able to achieve octahedral geometry in the high-spin d^8 configuration. Nickel(II) complexes of both O-donor (carboxylate) and N-donor (amine) as well as mixed N,O-donor (amino acid) ligands have been widely examined.[8] Structural forms in the solid state ranging from monomers and small clusters to one dimensional chains and even two dimensional lattices have been reported. Carboxylate donors are interesting because of their ability to offer two possible donor atoms which may act as a bridge between nickel(II) atoms, forming dimers, trimers or one dimensional polymers. Simple carboxylic acids such as succinic and adipic acids form polymeric octahedral complexes of the form $Ni(L\text{-}L)\cdot 2H_2O$.[9,10] Bulky monocarboxylic acids and Ni(II) form carboxylate bridged dimers; for example, $[Ni_2(\mu\text{-}Me_3CCO_2)_4L_2]$ where L = 2-Etpy, 2,4-Me_2py and 2,5-Me_2py (py=pyradine) have been reported.[11]

For mixed nitrogen oxygen donor sets, polymeric carboxylate bridged complexes of the form $[NiL_2]$ can be produced when L= $RC(ONH_2)COOH$ (R= H, Me, Pr, $PhCH_2$).[12] The EDTA analogue pydta forms a Ni_2L_2 dimer, but the carboxylates coordinate without bridging.[13] The tripodal ligand diethylenetriamine-N’-acetic acid (dtma) forms a 1:1 carboxylate bridged chain with nickel(II) where imidazole occupies the remaining octahedral site.[14] This is the only reported case of a tripodal ligand acting as both the bridging and terminal species.

In the case of carboxylate pendants the pendants may also act as a bridge between nickel centres. The structure of the Ni(II) complex of the 1,4,6,10-tetrazadodecane-*N,N’,N”,N’”*-tetraacetic acid (‘dota’) and spectroscopic data for the closely related 14-membered cyclam ring analogue ‘teta’ have been reported.[15] These coordinate with an N_4O_2 ligand system. However, the basket-like complex has the metal above the nitrogen plane and the oxygen donors *cis* to each other, restricting the ability of the carboxylate groups to act as a bridge. The ligands L6 and L8 (as well as L2 and L4) have the capacity to form bridges between metal centres. Interestingly, the possibility exists for a polymer to form in which each carboxylate bridges to the next in the chain. Structural characterisation of L6 (reported in this chapter) as the nickel(II) complex confirms the capacity of such carboxylate-pendant ligands to form bridges and promote formation of one dimensional chains. The amine pendants of L1, L3, L5 and L7 do not offer this capacity.

3.2 Experimental

3.2.1 Nickel Complexes

(10-Methyl-1,4,8,12-tetraazacyclopentadecane-10-amine)nickel(II) perchlorate, [Ni(L5)](ClO_4)$_2$

1 g of the ligand (L5·5HCl) was dissolved in 100 cm^3 of H_2O. To this was added 0.86 g of $Ni(ClO_4)_2 \cdot 6H_2O$. The pH of the solution was adjusted to ~8.5 by slow addition of NaOH (2.5 mol dm^{-3}, aqueous) with constant stirring. The solution was then left to stir overnight at ~ 50 °C, producing a purple solution. The solution was diluted to 2 dm^3 with water and sorbed onto a column of SP Sephadex C25 resin (Na^+ form, 20 x 3 cm) and then washed with 500 cm^3 of H_2O. Elution with 0.2 mol dm^{-3} $NaClO_4$ produced 2 poorly separated bands. The first (minor) yellow band failed to yield an acceptable solid. The second pink band was collected, reduced in volume to 50 cm^3 by rotary evaporation, during which purple solid formed. This was collected by vacuum filtration, washed with ethanol and ether and dried in a vacuum desiccator. The remaining solution was left to stand and 2 crops of crystalline solid were collected over the next week to give an almost quantitative yield. During this period the solution changed from purple/pink (mainly octahedral) to yellow/orange (mainly square planar species). However, all isolated solids were identical, as confirmed spectroscopically. (Found: C, 28.8; H, 5.8; N, 14.0. $C_{12}H_{29}N_5Cl_2NiO_8$ requires: C, 28.8; H, 5.9; N, 13.7%.) Electronic spectrum (water): λ_{max} 973 (ε 8), 810 (5), 772 (5), 529 (9), 341nm (13 dm^3 mol^{-1} cm^{-}

^{1}).Infrared spectrum (KBr disc) 1603 (-NH_2) cm^{-1}. $E_{1/2}$ ($Ni^{II/III}$) 0.52 V (ν. Ag/AgCl).

Aqua(7-methyl-1,5,9,13-tetraazabicyclo[1.1.2.2]heptadecane-7-amine)nickel(II) perchlorate, [Ni(L7)H_2O](ClO_4)$_2$

The ligand L7·5HCl (1 g) was dissolved in 100 cm^3 of H_2O. To this was added 0.81 g of $Ni(ClO_4)_2 \cdot 6H_2O$. The pH of the solution was adjusted to ~8.5 by slow addition of NaOH (2.5 mol dm^{-3}, aqueous) with constant stirring. The solution was then left to stir overnight at ~ 50 °C, producing a purple solution. The solution was diluted to 2 dm^3 with water and sorbed onto a column of SP Sephadex C25 resin (Na^+ form, 20 x 3 cm) and then washed with 500 cm^3 of H_2O. Elution with 0.2 mol dm^{-3} $NaClO_4$ produced only one band. The purple band was collected, reduced in volume to 50 cm^3 by rotary evaporation, during which purple solid formed. This was collected and dried as above. The remaining solution was left to stand and after 24 hours a second crop of crystalline solid was collected to give an almost quantitative yield. Infrared spectroscopy confirmed that both crops were identical. (Found: C, 30.6; H, 6.1; N, 12.5. $C_{14}H_{33}N_5Cl_2NiO_9$ requires : C, 30.9; H, 6.1; N, 12.9%.) Electronic spectrum (water): λ_{max} 1005 (ε 6), 825 (5), 776 (6), 633 (4), 535(7), 339 nm (9 dm^3 mol^{-1} cm^{-1}). Infrared spectrum (KBr disk): 1618 (NH_2) cm^{-1}. $E_{1/2}$ ($Ni^{II/III}$) 0.58 V (ν. Ag/AgCl).

(1,4,8,12-Tetraazacyclopentadecane-10-carboxylate)nickel(II) perchlorate dihydrate [Ni(L6)](ClO$_4$)·2H$_2$O

The ligand HL6·4HCl (1 g) was dissolved in 150 cm^3 of H_2O. To this was added 0.9 g of $Ni(ClO_4)_2 \cdot 6H_2O$. The pH of the solution was adjusted to ~8 by slow addition of NaOH (2.5 mol dm^{-3}, aqueous) with constant stirring. The solution was then left to stir for 18 hours at ~ 50 °C, producing a purple solution. The solution was diluted to 2 dm^3 with water and sorbed onto a column of SP Sephadex C25 resin (Na^+ form, 20 x 3 cm) and then washed with 500 cm^3 of H_2O. Elution with 0.2 mol dm^{-3} $NaClO_4$ produced a major purple/pink band. This was collected, reduced in volume to 30 cm^3 by a rotary evaporation and left to stand. After 3 days, clumps of purple crystals were collected. No further crops were isolated from the purple solution on standing. (Found: C, 32.1; H, 6.7; N, 12.4. $C_{12}H_{31}N_4ClNiO_8$ requires : C, 31.9; H, 6.5; N, 12.4%.) Electronic spectrum (water): λ_{max} 1057 (ε 4), 753 (4), 540 (8), 346 nm (14 dm^3 mol^{-1} cm^{-1}). Infrared spectrum (KBr disk): 1586s (COO$^-$) cm^{-1}. $E_{1/2}$ (Ni$^{II/III}$) 0.56 V (v. Ag/AgCl).

(1,5,9,13-Tetraazabicyclo[1.1.2.2]heptadecane-7-carboxylate)nickel(II) perchlorate [Ni(L8)](ClO$_4$)

The ligand L8·4HCl (1 g) was dissolved in 150 cm^3 of H_2O. To this was added 0.85 g of $Ni(ClO_4)_2 \cdot 6H_2O$. The pH of the solution was adjusted to ~8 by slow addition of NaOH (2.5 mol dm^{-3}, aqueous) with constant stirring. The solution was then left to stir for 12 hours at ~ 50 °C, producing a purple solution. The solution was diluted to 5 dm^3 with water and sorbed onto a column of SP

Sephadex C25 resin (Na^+ form, 20 x 3 cm) and then washed with 500 cm^3 of H_2O. Elution with 0.2 mol dm^{-3} $NaClO_4$ produced one major purple/pink band. This was collected, reduced in volume to 50 cm^3 by rotary evaporation during which purple solid formed. This was collected and dried in as above. The remaining solution was left to stand and three crops of crystalline solid were collected over the next week to give an almost quantitative yield. During this period, the solution changed from purple/pink to yellow/orange. However, infrared spectroscopy confirmed all crops were the same compound. (Found: C, 38.1; H, 6.3; N, 12.5. $C_{14}H_{27}N_4ClNiO_6$ requires : C, 38.1; H, 6.2; N, 12.7%.) Electronic spectrum (water): λ_{max} ~1100 (ε 7), 820 (7), 776 (9), 665 (8), 560 (13), 358 nm (24 dm^3 mol^{-1} cm^{-1}). Infrared spectrum (KBr disk): 1570s (COO^-) cm^{-1}. $E_{1/2}$ ($Ni^{II/III}$) 0.60 V (v. Ag/AgCl).

3.2.2 Cobalt Complexes

cis-Chloro(10-methyl-1,4,8,12-tetraazacyclopentadecane-10-amine)cobalt(III) perchlorate, [Co(L5)Cl](ClO$_4$)$_2$.

This complex was prepared essentially as described previously,[5] and isolated as a red-purple solid (Found: C, 26.5; H, 5.6; N, 12.8. $C_{12}H_{29}Cl_3CoN_5O_8.0.5H_2O$ requires C, 26.4; H, 5.6; N, 12.9%). Electronic spectrum (water): λ_{max} 540 (ε 125), 485 (sh, 90), 368 nm (175 dm^3 mol^{-1} cm^{-1}). NMR(D_2O): ^1H, δ 1.36 (s, 3H), 2.2 - 3.3 (m, 16H); ^{13}C, δ 18.5, 20.1, 23.3, 43.8, 45.1, 49.0, 51.8, 52.0, 54.0, 56.5, 58.4, 61.8 p.p.m.

cis-Chloro(1,4,8,12-tetraazacyclopentadecane-10-carboxylate)cobalt(III) Perchlorate, [Co(L6)Cl](ClO$_4$).

A solution containing (HL6)·4HCl·H_2O (1.5 g, 3.6 mmol) and $CoCl_2 \cdot 6H_2O$ (1.0 g, 4.2 mmol) in water (100 cm^3) was adjusted to pH 9 and aerated for 75 min. The brown solution was acidified with conc. HCl (20 cm^3) and stirred and heated at *ca* 70°C for several hours, diluted to 1 dm^3 and sorbed on a column containing Dowex 50Wx2 (H^+ form) cation exchange resin. After washing with water and 0.5 mol dm^{-3} HCl, the column was eluted with 3 mol dm^{-3} HCl, separating initially a major red and then a minor green band (*trans*-dichloro complex). The red band was reduced significantly in volume by rotary evaporation and left to crystallise after addition of a small amount of concentrated perchloric acid, yielding red crystals on standing for several weeks. These, crystallising with an additional molecule of perchloric acid as the trihydrate, were collected and air dried (Found: C, 23.7; H, 5.0; N, 8.8. $C_{12}H_{25}Cl_2CoN_4O_6 \cdot HClO_4 \cdot 3H_2O$ requires C, 23.8; H, 5.3; N, 9.2%). Electronic spectrum (water): λ_{max} 571 (ε 33), 478 (38), 370(sh) nm (80 dm^3 mol^{-1} cm^{-1}). NMR (D_2O): ^1H, δ 1.8 - 3.1 (m), 5.9 - 7.1 (m); ^{13}C, δ 25.5, 27.8, 46.8, 49.8, 51.0, 51.4, 51.8, 53.8, 55.4, 55.6, 59.2, 182.8 p.p.m. Crystals of base hydrolysed and reacidified (perchloric acid) aqua complex were crystallised on extended standing [λ_{max} 534 (ε 39), 380 nm (61 dm^3 mol^{-1} cm^{-1})], and characterised by an X-ray crystal structure analysis.

trans-Chloro(7-methyl-1,5,9,13-tetraazabicyclo[1.1.2.2]heptadecane-7-amine)cobalt(III) Chloride Perchlorate, [Co(L7)Cl]Cl(ClO$_4$).

This compound was prepared essentially as described previously,[16] and isolated as purple crystals (Found: C, 32.2; H, 6.7; N, 13.1. $C_{14}H_{31}Cl_3CoN_5O_4 \cdot 1.5H_2O$ requires C, 31.9; H, 6.9; N, 13.3%). Electronic spectrum (water): λ_{max} 576 (ε 48), 504 (49), 386 (66 dm^3 mol^{-1} cm^{-1}). NMR (D_2O): ^{1}H, δ 1.33 (s, 3H), 2.1 - 3.6 (m, 24H), 6.7 (s, br); ^{13}C, δ 20.8, 25.9, 54.1, 61.0, 61.9, 62.8, 64.7, 67.0 p.p.m.

trans-Chloro(1,5,9,13-tetraazabicyclo[1.1.2.2]heptadecane-7-carboxylate)cobalt(III) Perchlorate, [Co(L8)Cl](ClO$_4$).

This compound was prepared essentially as described for L6 above, yielding red crystals, crystallising like L6 with an additional molecule of perchloric acid as the dihydrate (Found: C, 27.6; H, 4.9; N, 8.7. $C_{14}H_{27}Cl_2CoN_4O_4 \cdot HClO_4 \cdot 2H_2O$ requires C, 27.5; H, 5.2; N, 9.1%). Electronic spectrum (water): λ_{max} 578 (ε 76), 388 (62 dm^3 mol^{-1} cm^{-1}). NMR (D_2O): ^{1}H, δ 2.0 - 3.5 (m, 24H), 8.3 (s, br); ^{13}C, δ 23.6, 44.2, 49.5, 52.7, 58.2, 58.5, 59.0, 181.2 p.p.m.

3.2.3 Physical Methods

Electronic spectra were recorded in aqueous solution using an Hitachi 220A spectrophotometer. IR spectra were recorded on complexes dispersed in KBr disc using a BioRad FTS-7 Fourier-transform spectrometer. Both ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded in D_2O using a JEOL

FX90Q or a Bruker Advance 300 spectrometer. Electrochemical measurements were performed with a BAS CV27 controller. A conventional three electrode system, with Ag-AgCl reference electrode, platinum counter electrode, a glassy carbon working electrode and nitrogen purge gas was employed, with $NaClO_4$ as an electrolyte. A scan rate of 100 mV s^{-1} was used for the reported results.

The kinetics of reactions with aqueous base (NaOH, 0.1 mol dm^{-3}) were studied using an Applied Photophysics DX17MV stopped-flow spectrometer at 25°C with ionic strength maintained at 0.1 mol dm^{-3} with $NaClO_4$. The disappearance of the chloro complex was followed at selected wavelengths in the visible region after equilibration of reactants at the chosen temperature for at last ten minutes prior to a kinetic run. Analysis of the absorbance-time curves was performed using a fitting program supplied with the stopped-flow; at least three determinations were performed under any particular set of conditions. Activation parameters were determined from measurements at four temperatures over a range of *ca* 20°C.

3.2.4 X-Ray Crystal Structure Determination

Crystal data.

$[Ni(L8)](ClO_4)$ Formula $C_{14}H_{27}N_4ClNiO_6$, M 441.56, monoclinic, space group $P2_1/a$, a = 10.807(8), b = 14.340(6), c = 11.789(3)Å, β = 96.49(9)°, U = 1815(2) $Å^3$, D_c = 1.616 g cm^{-3}, F(000) = 928 electrons, $\mu(CuK\alpha)$ = 56.05 cm^{-1}. $A_{min.,max.}$ 1.01, 1.60, range of *hkl* -0 to 12, 0 to 16, -13 to 13, R = 0.066, R' = 0.081, $w = 1/\sigma^2(F_0^2) + (0.1 \times P^2)$, where $P = (\max(F_0^2, 0) + 2 \times F_c^2)/3$, residual extrema

+0.78, -0.65 e $Å^{-3}$. (Data collected University of Sydney, School of Chemistry; solved University of Newcastle.)

$[Co(L5)(OH_2)](ClO_4)_2{\cdot}2H_2O$ Formula $C_{12}H_{31}CoN_4Cl_2O_{13}$, M 569.24. Monoclinic, space group $P2_{1/c}$, a = 9.581(2), b = 16.214(2), c = 14.350(2) Å, β = 94.66(1)°, U = 2221.9(5) $Å^3$. D_c (Z = 4) = 1.702 g cm^{-3}. F(000) = 1184. μ_{Mo} = 10.84 cm^{-1}; specimen: 0.40 by 0.25 by 0.18 mm; range of *hkl* 0 to 9, 0 to 21, -14 to 14; $Å^*_{min,max}$ 0.7571, 0.8378; residual extrema +0.55, -0.54 e$Å^{-3}$. N = 4245, N_o = 4114; R = 0.036, R_w 0.030. (Data collected and solved at the University of Sydney, School of Chemistry.)

Data for the nickel complex were measured at 294 K on an ACF-7 four circle diffractometer employing graphite monochromated CuKα radiation. Intensity data were collected in the range $1<\theta<60°$. Data reduction and application of the Lorentz, polarization, absorption and decomposition corrections were carried out using the teXsan system.[17] The structure was solved by direct methods, using SHELXS-86 [18] and the solutions were refined by least squares methods using SHELXL-93.[19] Hydrogen atoms were included at calculated sites (C-H, N-H 0.97 Å) with group isotropic thermal parameters. All other atoms were refined anisotropically. Scattering factors and anomalous dispersion terms used for Ni were taken from International Tables [20] and all others used were those supplied in SHELXL-93. Data for the cobalt complex was collected on an Enraf-Nonius CAD4 diffractometer employing graphite monochromated Mo-Kα radiation at 294 K to a maximum 2θ value of 50.0°. All calculations were performed using the teXsan crystallographic software package. The structure was solved using direct methods and expanded using Fourier techniques,[21] with full-matrix least-squares refinement. With the exception of the isotropically refined O8 and O9 sites of a disordered perchlorate counterion, all of the non-hydrogen atoms were refined anisotropically. The disordered perchlorate was refined with eight partially occupied oxygen sites. The perchlorate oxygen occupancies were refined and then rounded to the first decimal place. The hydrogen atoms bonded to O3 and O17 were located and fixed at convergence; otherwise, the hydrogens were located and refined isotropically. Neutral atom scattering factors were taken from International Tables,[22] whereas anomalous dispersion effects were included in the structure factor calculation. [23] All plots were drawn using ORTEP [24] or Schakal 92.[25]

3.3 Results and Discussion

3.3.1 Nickel(II) Complexes

The 15-membered ring macrocycles L5 and L6, as well as the reinforced analogues L7 and L8, readily form paramagnetic octahedral nickel(II) complexes in which the pendant amine or carboxylate occupies an axial site. Coordination of the carboxylate is defined by shifts in the infrared absorbance from ~1720 cm^{-1} (-COOH) in the free protonated ligand to below 1620 cm^{-1} ($-COO^-$) in the complex. By contrast, the 13-membered macrocycles L1 and L2 do not readily yield high-spin nickel(II) complexes, and show a tendency towards yellow square planar species with the pendant group dangling. It has been shown that the cavity of 13-membered macrocycles is too small to contain the high-spin Ni(II) ion, octahedral coordination only being achieved by the ligand taking on a *cis* configuration.[26] Even with inert cobalt(III), synthetic facility changes with macrocycle ring size in these mono-pendant macrocycles.[5,7] Coordination of the carboxylate pendant has been confirmed in the X-ray crystal structure of the nickel(II) complex of L8.

The UV/Vis spectra of the purple 'octahedral' complexes all show numerous maxima. In a uniform octahedral field one would only expect three transitions. For the nickel complex of H_2dota, which has a N_4O_2 (*cis* oxygens) chromophore, four transitions are reported both in diffuse reflectance and solution spectra. Square planar species are usually characterised by a single transition around 460 nm. The two highest energy transitions which appear near 340 and 540 nm are assigned to $A_{2g}\rightarrow T_{1g(P)}$ and $A_{2g}\rightarrow T_{1g(F)}$ transitions and these appear consistently for all octahedral complexes. However, above 600 nm there is significant variation in the number and relative size of peaks. Comparison of spectra between the amine pendant and acid pendant species (Table 3.1) show they are very similar, suggesting that L5- L8 adopt a similar geometry in solution and possibly in the solid form as well. In general, there is a weakening of the ligand field for the carboxylate pendant species compared with the amine pendant analogues, with the two high energy transitions shifted to somewhat lower energies. The ligand fields for the 'strapped' 15 membered macrocycles are also somewhat weaker than those for the ‘unstrapped’ analogues, presumably due to steric influences.

Table 3.1 Selected physical properties of the pendant-arm Ni(II) complexes.

Ligand	L5	L6	L7	L8
Pendant	$-NH_2$	$-COO^-$	$-NH_2$	$-COO_-$
Ring Size	[15]	[15]	[15s][a]	[15s][a]
Electronic Spectrum	[λ_{max}, nm (ε_{max}, dm^3 mol^{-1} cm^{-1})]			
	973(8)	1057(8)	1005(6)	1100(7)
	810(5)	804(5)	825(5)	820(7)
	772(5)	753(6)	776(6)	776(9)
	-	-	633(4)	665(8)
	559(9)	540(8)	535(7)	560(13)
	341(13)	346(14)	339(9)	358(24)
Ni $^{II/III}$ Redox Potential (V v. Ag/AgCl)				
	0.52	0.56	0.58	0.60
Characteristic IR Absorbance of Pendant (cm^{-1})				
	1603	1586	1618	1570

[a] S represents an additional $-CH_2-CH_2-$ strap.

Both the acid pendant octahedral complexes exhibit (COO^-) peaks in the infrared spectrum below 1590 cm^{-1}. This is consistent with bridging carboxylato groups,[27] and so it is assumed that L6 may exhibit a similar one-dimensional chain structure to that confirmed for L8 and described below. The amine pendant species L5 and L7 show peaks at 1603 and 1618 cm^{-1} respectively, consistent with a coordinated primary amine.

Very little variation was noted for the $E_{1/2}$ values (determined versus Ag/AgCl) of L5- L8 (0.52 to 0.6 V) for the Ni^{3+}/Ni^{2+} couple, although the values for the acid pendant complexes tend to be slightly more positive than they are for the amine pendant species. This is consistent with different electronic influences of the two pendant types, which parallel small differences observed in the visible spectroscopy. The observed $E_{1/2}$ values seem to be fairly consistent with that found by Kimura and co-workers for a cyclam analogue with a single pendant amine (0.56 V).[28] The complexes all exhibit quasireversible behaviour, consistent with stable Ni(III) species at least on a short timescale.

The complex $[Ni(L8)](ClO_4)$ crystallises in a form where the pendant carboxylate serves as a bridging group between pairs of nickel centres, a process which persists in a linear fashion throughout the crystal, leading to a one dimensional chain compound. Positional parameters for the X-ray structure solution appear in Table 3.2, with bond lengths and bond angles for the complex cation collected in Tables 3.3 and 3.4 respectively. The Ni atom is coordinated in a distorted octahedral environment with two oxygen donors, one from a carboxylate oxygen of the 'parent' pendant macrocycle and one from the carboxylate oxygen of an adjacent macrocycle, *trans* to each other in axial sites. The Ni lies slightly above (0.026 Å) the plane formed by the four secondary nitrogen donors, towards the 'parent' pendant. A view of the nickel environment together with atom numbering appears in Figure 3.1. There is a pronounced displacement of the Ni towards the secondary (N(2) and N(1))

Table 3.2 Positional parameters for [Ni(L8)]ClO_4

Atom	*x*	*y*	*z*
Ni	1521(1)	1829(1)	7498(1)
O(1)	3363(3)	2325(2)	7597(3)
O(2)	-443(3)	1483(2)	7230(3)
N(2)	1088(4)	2912(3)	8526(4)
N(1)	1177(4)	2634(3)	6034(3)
N(3)	1853(4)	771(4)	8745(5)
N(4)	2033(4)	567(4)	6698(6)
C(1)	1486(5)	3629(4)	6198(5)
C(2)	2400(4)	3818(3)	7270(5)
C(3)	1767(5)	3788(4)	8351(5)
C(4)	1176(10)	2670(7)	9828(7)
C(5)	832(10)	1683(7)	10066(7)
C(6)	1748(9)	973(7)	9920(8)
C(7)	3140(6)	432(5)	8549(9)
C(8)	3210(7)	292(5)	7289(10)
C(9)	1007(6)	1(4)	8286(8)
C(10)	1090(6)	-94(4)	6978(9)
C(11)	2052(10)	574(7)	5399(9)
C(12)	1275(10)	1290(8)	4806(7)
C(13)	1714(7)	2250(7)	5033(6)
C(14)	3516(4)	3170(3)	7366(4)
Cl	998(2)	6619(1)	7227(2)
O(11)	2251(8)	6238(7)	7443(7)
O(12)	347(9)	6278(10)	8049(8)
O(13)	557(8)	6277(11)	6180(7)
O(14)	1065(11)	7487(6)	7232(15)

Figure 3.1
View of the cation $[\mathrm{Ni(L8)}]^{+}$.
The oxygen from the adjoining linked molecule is included to show a complete coordination sphere. Anions and hydrogen atoms are omitted for clarity.

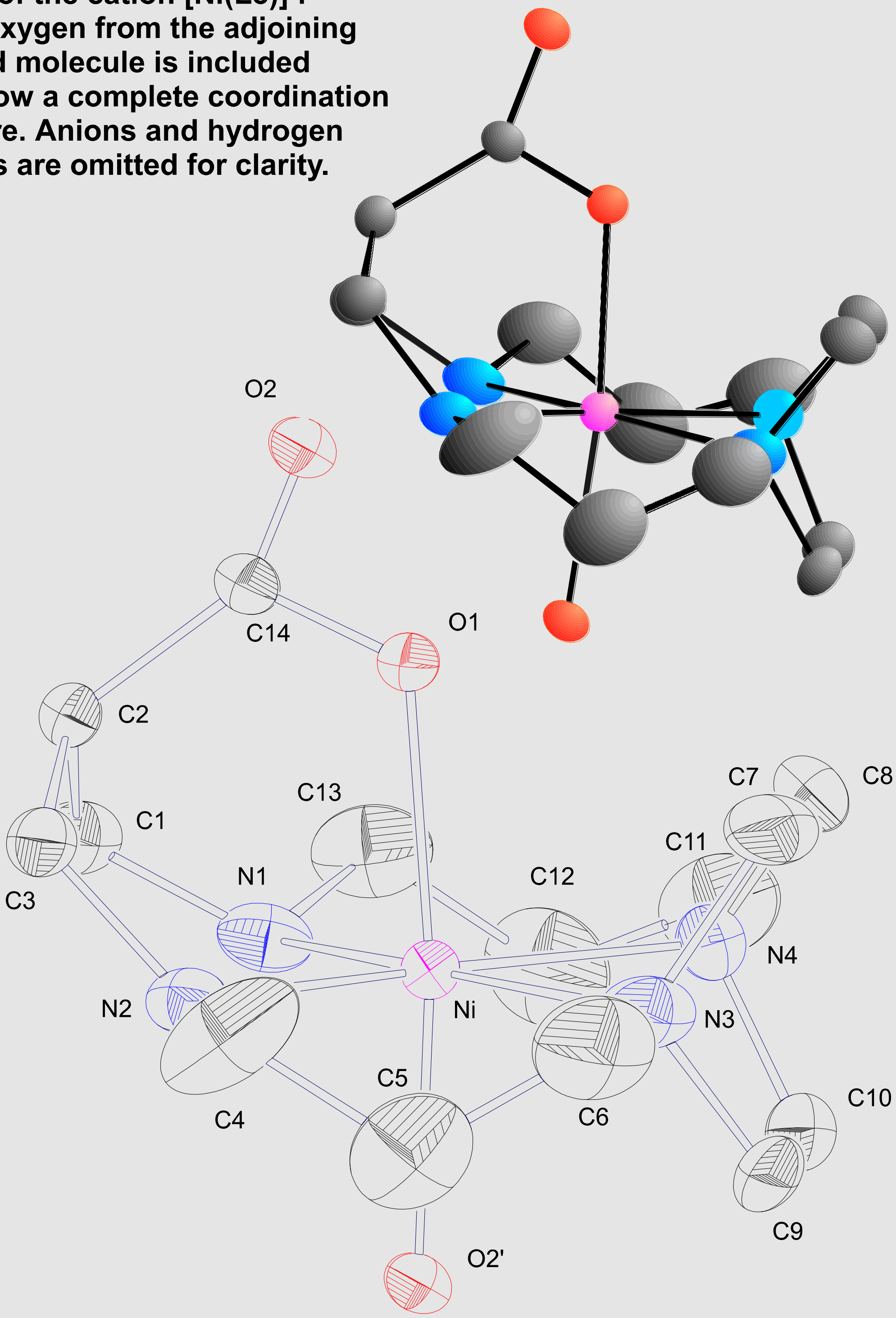

Table 3.3 Bond lengths [Å] for $[Ni(L8)]^+$

Ni-N(2)	2.057(4)	N(1)-C(1)	1.474(8)	C(2)-C(3)	1.513(8)
Ni-N(1)	2.074(4)	N(1)-C(13)	1.478(8)	C(2)-C(14)	1.517(6)
Ni-O(1)	2.104(3)	N(3)-C(6)	1.433(11)	C(4)-C(5)	1.498(13)
Ni-N(3)	2.114(5)	N(3)-C(9)	1.496(9)	C(5)-C(6)	1.443(13)
Ni-N(4)	2.142(5)	N(3)-C(7)	1.516(9)	C(7)-C(8)	1.509(13)
Ni-O(2)	2.168(3)	N(4)-C(8)	1.434(10)	C(9)-C(10)	1.562(12)
O(1)-C(14)	1.257(6)	N(4)-C(10)	1.456(8)	C(11)-C(12)	1.46(2)
N(2)-C(3)	1.481(7)	N(4)-C(11)	1.534(12)	C(12)-C(13)	1.471(14)
N(2)-C(4)	1.567(9)	C(1)-C(2)	1.538(8)		

nitrogens (on the same side as the pendant) with Ni-N bonds (2.057(4) and 2.074(4) Å) being considerably shorter than those for the tertiary (N(3) and N(4)) nitrogens (2.114(5) and 2.142(5) Å). A similar effect was seen for the Cu(II) complex of the same ligand, but to a smaller degree (2.037(4) vs 2.082(4) and 2.035(4) vs 2.062(4) Å) as referred to in Chapter 2. This effect probably arises as a result of differing steric demands of the tertiary and secondary amine donors in concert with the coordination of the carboxylate pendant which demands, together with the adjacent pair of secondary amines, reasonably ‘tight’ facial coordination. This is also reflected in the O-Ni-O bond angle (171.79(13)°) where distortion towards the pendant is still observed despite the displacement of the nickel towards N(1) and N(2). The Ni is also displaced slightly towards N(2) and N(3), resulting in a skewing of the 6

Table 3.4 Bond angles [deg] for [Ni(L8)]$^+$.

N(2)-Ni-N(1)	92.2(2)	C(3)-N(2)-Ni	114.2(3)	C(3)-C(2)-C(14)	110.5(4)
N(2)-Ni-O(1)	89.3(2)	C(4)-N(2)-Ni	114.7(5)	C(3)-C(2)-C(1)	112.2(4)
N(1)-Ni-O(1)	86.4(2)	C(1)-N(1)-C(13)	111.2(5)	C(14)-C(2)-C(1)	112.6(5)
N(2)-Ni-N(3)	99.4(2)	C(1)-N(1)-Ni	114.4(3)	N(2)-C(3)-C(2)	114.8(4)
N(1)-Ni-N(3)	167.9(2)	C(13)-N(1)-Ni	114.1(5)	C(5)-C(4)-N(2)	113.9(6)
O(1)-Ni-N(3)	96.8(2)	C(6)-N(3)-C(9)	112.8(6)	C(6)-C(5)-C(4)	117.2(8)
N(2)-Ni-N(4)	170.0(2)	C(6)-N(3)-C(7)	112.7(7)	N(3)-C(6)-C(5)	112.8(7)
N(1)-Ni-N(4)	97.7(2)	C(9)-N(3)-C(7)	104.0(6)	C(8)-C(7)-N(3)	110.0(6)
O(1)-Ni-N(4)	91.2(2)	C(6)-N(3)-Ni	120.1(5)	N(4)-C(8)-C(7)	107.6(6)
N(3)-Ni-N(4)	70.6(3)	C(9)-N(3)-Ni	103.3(4)	N(3)-C(9)-C(10)	108.7(5)
N(2)-Ni-O(2)	88.5(2)	C(7)-N(3)-Ni	102.1(4)	N(4)-C(10)-C(9)	106.7(6)
N(1)-Ni-O(2)	85.7(2)	C(8)-N(4)-C(10)	108.4(7)	C(12)-C(11)-N(4)	114.4(6)
O(1)-Ni-O(2)	171.79(13)	C(8)-N(4)-C(11)	112.1(7)	C(11)-C(12)-C(13)	114.6(8)
N(3)-Ni-O(2)	91.3(2)	C(10)-N(4)-C(11)	108.6(6)	C(12)-C(13)-N(1)	110.2(6)
N(4)-Ni-O(2)	92.3(2)	C(8)-N(4)-Ni	106.1(5)	O(1)-C(14)-O(2)$^{\#2}$	123.4(4)
C(14)-O(1)-Ni	117.4(3)	C(10)-N(4)-Ni	103.2(4)	O(1)-C(14)-C(2)	119.0(4)
C(14)$^{\#1}$-O(2)-Ni	140.1(3)	C(11)-N(4)-Ni	117.8(5)	O(2)$^{\#2}$-C(14)-C(2)	117.6(4)
C(3)-N(2)-C(4)	110.4(5)	N(1)-C(1)-C(2)	113.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z   #2 x+1/2,-y+1/2,z

membered chelate ring linking the pendant to the Ni away from an ideal boat conformation which is enforced by the coordination of the pendant. The Ni-N distances (2.057-2.142 Å) are all within parameters reported for other nickel amine complexes, if on the long side for N(3) and N(4). Appropriate comparisons include Ni(H$_2$dota) [2.177(6)-2.114(7)][15] and the amine pendant cyclam analogue, 6-amino-1,4,8,11-tetrazacyclotetradecane,[28] 2.052(7)-2.086(9) Å, which offer tertiary and secondary donors respectively.

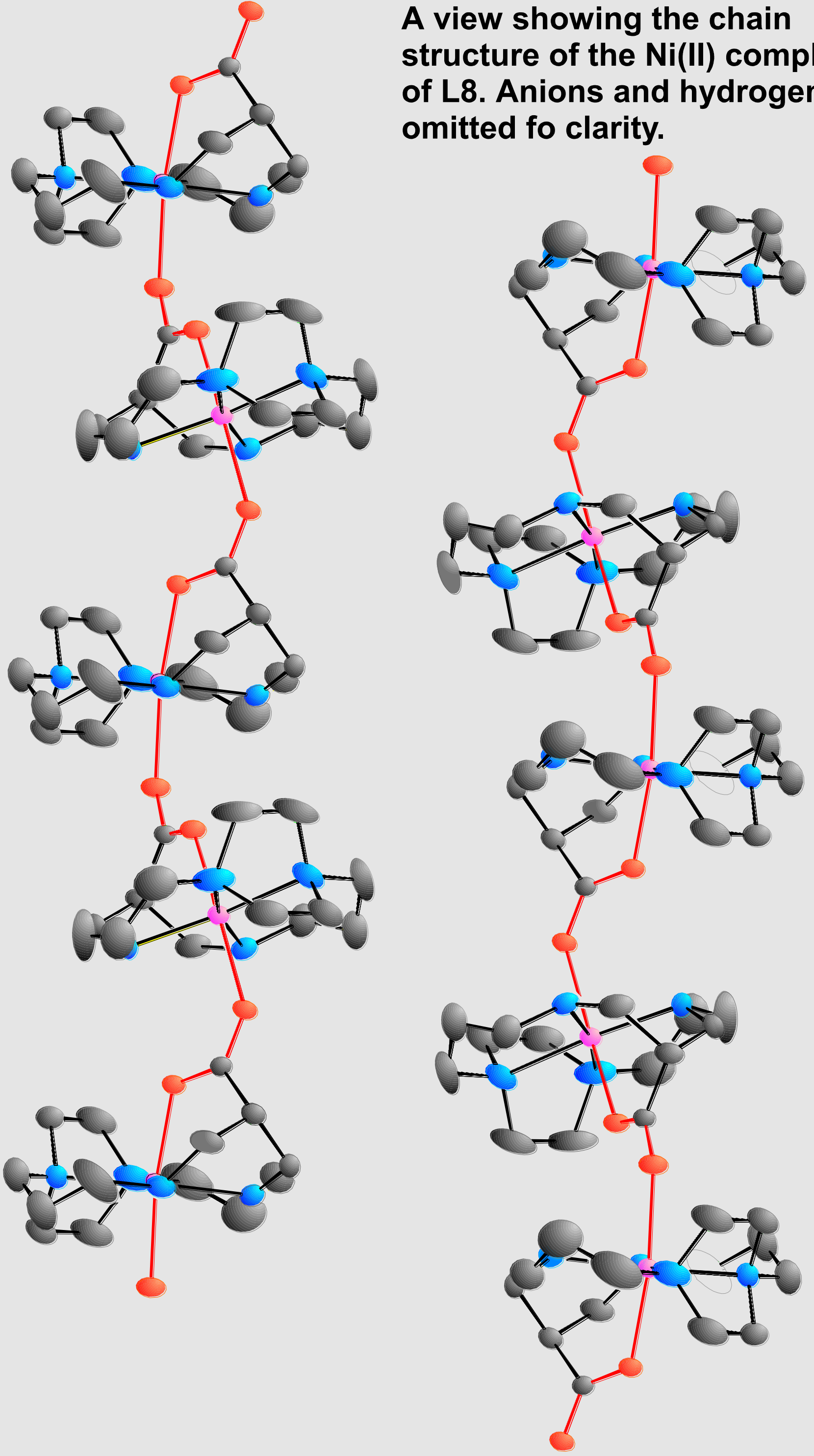

Figure 3.2
A view showing the chain structure of the Ni(II) complex of L8. Anions and hydrogens omitted fo clarity.

The two Ni-O distances (2.104(3) and 2.168(3) Å) differ substantially, with the shorter distance associated with the 'internal' bond and the larger with the bridging bond to the next nickel atom. The two carboxylate distances, C(14)-O(1) and C(14)-O(2), are identical.

The complex forms a one dimensional chain (see Figure 3.2) of the general formula $[Ni_x(L8)_x](ClO_4)_x$ with a two fold screw symmetry along *a* with bridging carboxylates in a *syn-anti* conformation.[29] The mean angle between nitrogen planes is 32.4°. The second oxygen on each carboxylate bonds to the vacant axial position of the complex directly above it, completing the octahedral donor set. The short primary Ni-O bond (2.104(3) Å) compared with that linking the two complexes (2.168(3) Å) is reflected in the infrared spectra where a second lower energy peak can be seen as a shoulder to the main COO^- peak. The Ni-O bond lengths are longer than those observed for other carboxylato bound species ($Na_2[Ni_2(2,6\text{-pydota})_2]$,[13] 2.010(4)-2.051(4); $[Ni(H_2dota)]$,[15] 2.025(6) Å). The bond lengths are more reminiscent of those found for bound water oxygens [28] (2.167(7) Å) or bound hydroxy oxygens ($[Ni(ahpdH)_2]$, 2.153(2)-2.141(2) Å).[30] The distances are, however, analogous with those found in the internally bridged dtma/imidazole complex (2.081(2) and 2.144(2) Å).[14] Whether this is a result of the bridging nature of the carboxylates, a mode of reducing the strain in the chelate ring formed by the coordination of the carboxylate, or a combination of these, is unclear. This structure appears to be the first one-dimensional chain structure where a C-pendant group attached directly to a macrocyclic ring acts as the bridging group.

3.3.2 Cobalt (III) Complexes

Syntheses of the cobalt(III) complexes of the pendant arm carboxylate macrocycles L6 and L8 proceed readily with a single isomer of the pentacoordinated ligand complex isolated following chromatography in each case. An additional green band isolated during chromatography in each reaction is consistent with the presence of some *trans*-dichlorocobalt(III) complex where the pendant is protonated and unbound. These are minor by-products in the reported syntheses, although they appear to form more readily than do analogous compounds when the amine pendant analogue (L5 or L7) is employed. The coordination of the carboxylate in the isolated complexes is supported by infrared spectroscopy, with the presence of a carboxylate anion indicated by a strong resonance at 1600 cm^{-1}, compared with 1730 cm^{-1} for complexes with protonated and unbound carboxylate groups, such as found in green *trans*-dichloro complexes. Shifts in the electronic maxima to lower energy, discussed below, also are indicative of the introduction of an O-donor into the coordination sphere. With the complex of L6, electronic spectroscopy suggests a *cis* disposition of the pendant carboxylate and chloride groups from the small separation of the ^1E and $^1A_2$ components of the $^1T_1$ transition, and this is confirmed by NMR spectroscopy, with all carbons being non-equivalent as expected for the necessarily folded macrocycle. The complex of the amine analogue L5 has been isolated only with *cis* stereochemistry,[5] and this geometry is suggested to be more stable in that case based on molecular mechanics examination.[7] The more rigid strapped macrocycles L7 and L8 were expected to prefer a geometry with all tertiary and secondary amines in the plane, thus avoiding unfavourable folding of the rigid macrocycle. This *trans* geometry (of the pendant and unidentate donor) is supported for the complex of L7 by the observation of a larger separation of the ^1E and $^1A_2$ components of the $^1T_1$ transition (maxima at 576 and 504 nm compared with 540 and 485(sh) nm in the analogue complex of L5 which adopts a *cis* geometry). The *trans* geometry was confirmed for the complexes of both L7 and L8 from ^{13}C NMR spectroscopy, with several pairs of carbons equivalent, as expected for the higher symmetry which involves a mirror plane through the tertiary carbon and the metal ion, bisecting the ligand (see Figure 3.3). The lower symmetry of the *cis* complexes was also observable in the amine region (5.5-7.5 ppm) of the ^1H NMR. While the *trans* isomer exhibited only one peak in this region the *cis* isomers showed four (see Figure 3.4), consistent with the secondary amine protons being in non-equivalent magnetic environments. However this effect is relatively short lived with the peaks disappearing in a matter of hours as the protons exchange. Thus, in this study, we are examining pairs of complexes with common *cis* (L5 and L6) or *trans* (L7 and L8) geometry in at least the chloro complexes.

The replacement of a pendant primary amine donor in a macrocyclic pentaamine ligand by a carboxylate donor has a number of consequences. Firstly, it introduces a different donor atom which, along with a chloride ion in

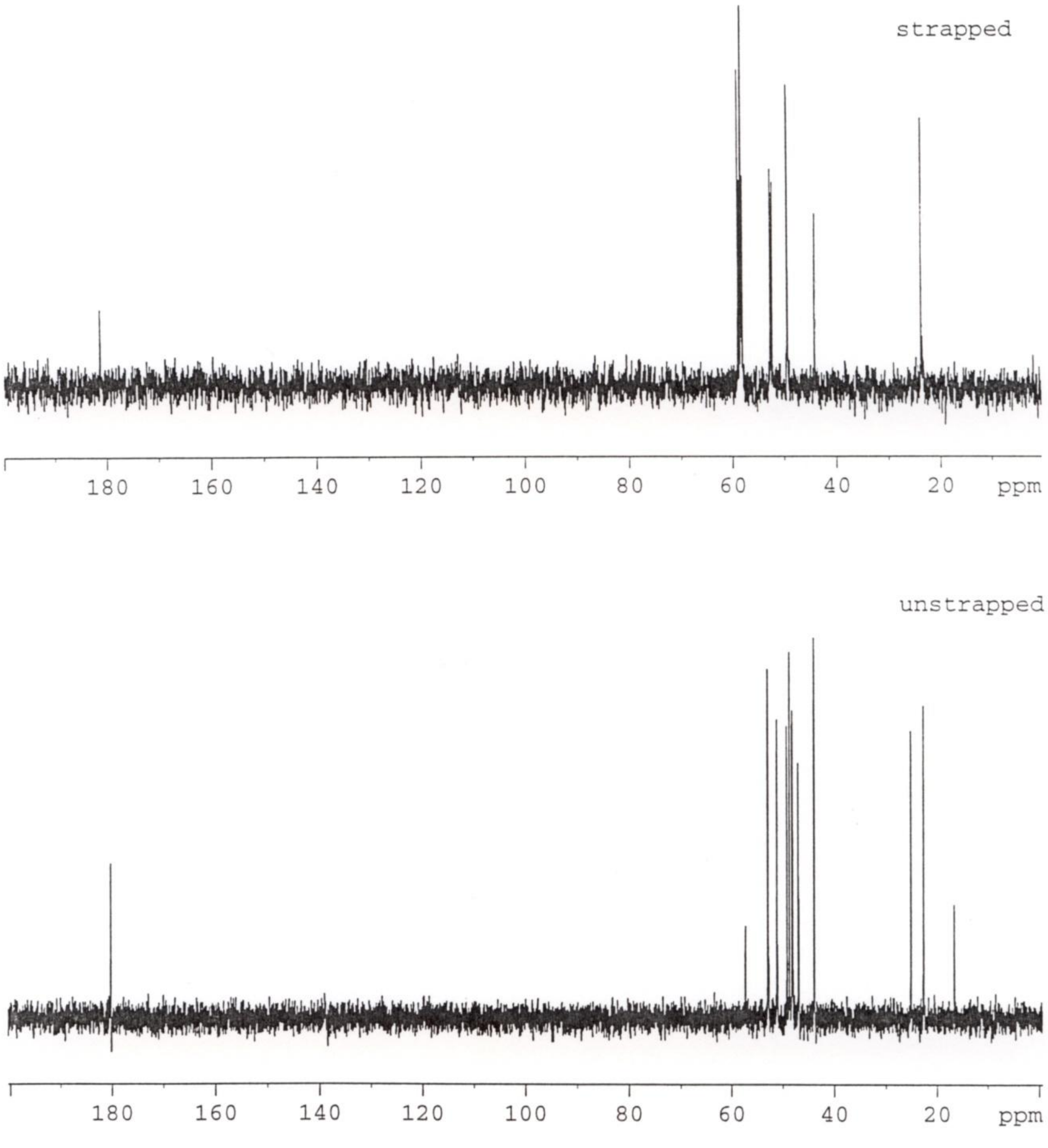

Figure 3.3. The ^{1}H decoupled ^{13}C NMR of the complexes *trans*-[Co(L8)Cl]$^+$ (upper) and *cis*-[Co(L6)Cl]$^+$ (lower); the number of carbon environments in each is consistent with the symmetry.

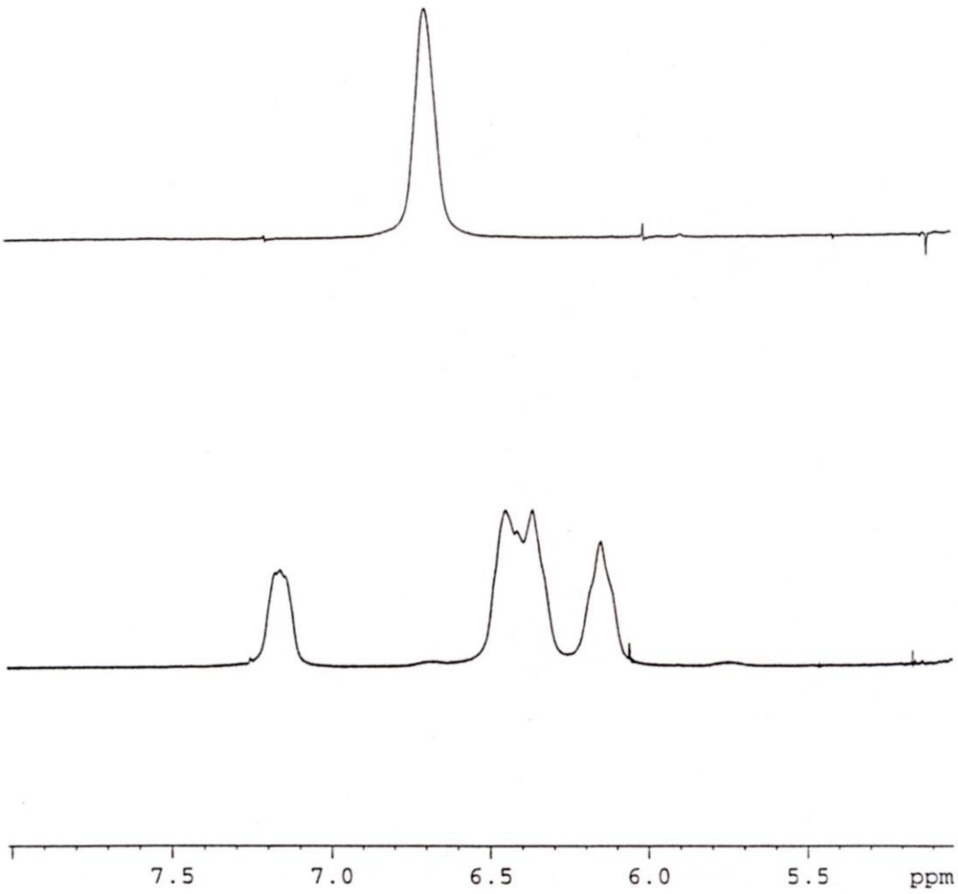

Figure 3.4. A portion of the ^1H NMR spectrum of the complexes *trans*-[Co(L8)Cl]$^+$ (upper) and *cis*-[Co(L5)Cl]$^{2+}$ (lower), showing the greater number of magnetic environments experienced by the secondary amine in the *cis* complex.

the sixth site, leads to three non-equivalent donor sets along each axis direction in the case of a *cis* isomer or one markedly unique axis (O and Cl donors versus N-only donors in other directions) in the case of a *trans* isomer. This is reflected in the electronic spectra, with [Co(L5)Cl]$^{2+}$ exhibiting maxima at 540, 480(sh) and 368 nm whereas [Co(L6)Cl]$^+$ has lower energy maxima at 571, 478 and 382 nm, for example. Likewise, the hydrolysis product [Co(L7)(OH$_2$)]$^{3+}$, with maxima at 526 and 368 nm, differs from [Co(L8)(OH$_2$)]$^{2+}$

where maxima are also shifted to lower energy (548, 376 nm). There are few appropriate polydentate systems with which to make a comparison, but the shifts anticipated should presumably reflect the effect seen on replacement of an ammine ligand in the hexaamminecobalt(III) ion by an acetate group, where the lower energy $^1A_{1g} \rightarrow {}^1T_{1g}(O_h)$ transition shifts from 475 nm to 502 nm and the higher energy $^1A_{1g} \rightarrow {}^1T_{2g}(O_h)$ transition shifts from 339 to 351 nm. Where a single low energy absorption envelope is observed or else when an average position is estimated in the polydentate systems, very similar shifts to these occur.

Further, the introduction of a charged carboxylate donor in place of a neutral primary amine donor clearly changes charge and electronic effects in the complex, which should influence the rate at which a leaving group departs. The presence of an anionic carboxylate donor either *cis* or *trans* to an anionic chloride leaving group should promote the departure of the like-charged group on simple electrostatic grounds. However, in base hydrolysis, a pre-equilibrium is involved prior to the formation of the five-coordinate intermediate in the accepted mechanism (eq. 1),[31] and replacement of the primary amine by the carboxylate both removes one possible site of deprotonation (leaving only secondary amines) and in addition may influence the pK_a of the remaining amine groups. Solvation electrostriction around the reactant ions will vary with overall charge, and influence both the ease with which a group departs and the stability of an intermediate. Moreover, the five-coordinate intermediate is believed to be stabilised by strong cobalt(III)-amide anion bonding, and there is a prospect that the presence of another negatively charged donor such as a carboxylate group may destabilise the intermediate by presenting an additional negative charge and associated electron density.

$$[\mathrm{M(LNH)X}] \Leftrightarrow \mathrm{H}^{+} + [\mathrm{M(LN^{-})X}] \xrightarrow{\text{slow}} \mathrm{X}^{-} + [\mathrm{M(LN^{-})}]^{\#}$$
$$\xrightarrow{\text{fast }(+\mathrm{OH_2})} [\mathrm{M(LNH)(OH)}] \qquad (1)$$

The hydrolysis reactions of the $\mathrm{Co(L)Cl}^{n+}$ complexes in aqueous base proceed with a single step observed in each case. The observed rate constants determined by stopped-flow methods (Table 3.5) show, for each complex, a simple first-order dependence on hydroxide ion concentration, common for reactions of this type. Temperature dependence studies yielded activation parameters typical of base hydrolysis reactions of chlorocobalt(III) complexes, with characteristically large positive activation entropies which have been interpreted previously[31] in terms of a dissociative mechanism (eq. 1). A summary of the results of the hydrolysis kinetics study appear in Table 3.6.

The range of effects which may result from replacement of an amine donor by a carboxylate donor suggests that the effect on the kinetics of reaction cannot be readily predicted. Experimental results (Table 3.6) shows that, with either a *cis* or *trans* precursor geometry, the base hydrolysis rate for the carboxylate pendant macrocycles are slightly slower (two- to four-fold) than is the case with their amine pendant analogues. The minor effect is reflected in a slightly higher activation enthalpy, although there is also an apparent increase in

Table 3.5 Observed rate constants for the base hydrolysis of the chlorocobalt(III) complexes.

$[OH^-]$ (mol dm^{-3})		$4.5x10^{-2}$	$9.0x10^{-2}$	0.18	
		$k_{obs}(s^{-1})^a$	$k_{obs}(s^{-1})^a$	$k_{obs}(s^{-1})^a$	k_{OH}(mol dm^{-3} s^{-1})^b
$L6H_{-1}$	13 °C	18(1)	34(1)	87(1)	354
	19 °C	40(1)	79(1)	205(1)	844
	25 °C	93(1)	196(2)	455(5)	1803
	31 °C	217(2)	402(5)	760(6)	2620
L7	13 °C	296(6)	340(8)	433(7)	1017
	18 °C	409(4)	499(5)	675(4)	1974
	25 °C	582(5)	744(4)	1047(9)	3433
	31 °C	683(4)	953(7)	1494(11)	6008
$L8H_{-1}$	13 °C	34(1)	38(1)	101(1)	526
	19 °C	56(1)	82(1)	204(1)	1141
	25 °C	112(1)	141(2)	401(2)	2248
	32 °C	240(2)	320(5)	720(6)	3682

(a) error in parentheses

(b) second order rate constant determined from fit of data cited at various base concentrations

activation entropy to compensate somewhat. Any *cis* or *trans* labilising effect of the carboxylate group on the like-charged chloride leaving group must be offset by other effects, most likely relating to stability of the putative five-coordinate intermediate which may be diminished slightly by the presence of charged donor groups. This may arise via direct electronic effects, or else by indirect effects related to a less tightly bound electrostricted solvation layer for the lower charged intermediate in the carboxylate complexes.

Table 3.6. Comparative base hydrolysis kinetics data for $[Co(L)Cl]^{n+}$ compounds.

L	k_{OH}^{298}, $dm^3\ mol^{-1}\ s^{-1}$	$\Delta H^{\neq}$, $kJ\ mol^{-1}$	$\Delta S^{\neq}$, $J\ K^{-1}\ mol^{-1}$
L5[a]	6,700 (± 100)	73 (± 3)	63 (±10)
L6	1,800 (± 60)	79 (± 3)	81 (± 9)
L7	3,450 (± 90)	67 (± 2)	47 (± 6)
L8	2,250 (± 80)	73 (± 3)	63 (± 9)

(a) data from reference (5)

It is notable that base hydrolysis rate constants for a range of *trans*-$[Co(cyclam)(X)Cl]^+$ ions ($X = N_3^-$, NCS^-, NO_2^-, CN^-) differ only by from 7-fold faster to 14-fold slower than that for *trans*-$[Co(cyclam)(NH_3)Cl]^{2+}$.[32,33,34] The substitution of a neutral amine by anionic groups in the *trans* site in this case thus also influences the base hydrolysis rate only modestly, as in the present study. Likewise, base hydrolysis rates for *trans*-$[Co(en)_2(CH_3COO)Cl]^+$ (10.8 $dm^3\ mol^{-1}\ s^{-1}$ at 25°C)[35] and *trans*-$[Co(en)_2(NH_3)Cl]^{2+}$ (75 $dm^3\ mol^{-1}\ s^{-1}$)[36] do not differ greatly. Small effects are by no means universal, however, and pairs with different spectator ligands where large variations exist can be found; the subtleties of hydrolysis reactions are clearly not yet understood.

Base hydrolysis reactions followed in aqueous base exhibit a single process in the stopped-flow time regime. The base hydrolysis reaction of the complex of L5 studied previously was reported to occur with retention of configuration;[2] spectroscopic evidence suggests retention also occurs with the complexes of L7 and L8 (>90%, based on NMR evidence). Retention of geometry with the strapped L7 and L8 ligands is consistent with the preference for the *trans* isomer resulting from the presence of the 'strap'. While we have isolated the aqua complex formed following hydrolysis of L6 as a *trans* isomer, NMR studies indicate that in the time frame of the base hydrolysis reaction the complex retains a *cis* geometry with only a very small amount of *trans* isomer forming (see Figure 3.5). However, over a longer time frame, geometric rearrangement (isomerisation) occurs to yield an equilibration mixture of *cis* and *trans* isomers, from which crystallised the isolated product.

The aquacobalt(III) complex cation of L6 displays a distorted octahedral geometry in the X-ray crystal structure analysis, with all four macrocycle secondary nitrogens bound in the plane of the cobalt and the pendant carboxylate occupying one axial site, *trans* to a coordinated water molecule (Figure 3.6). Positional parameters appear in Table 3.7, with bond lengths and

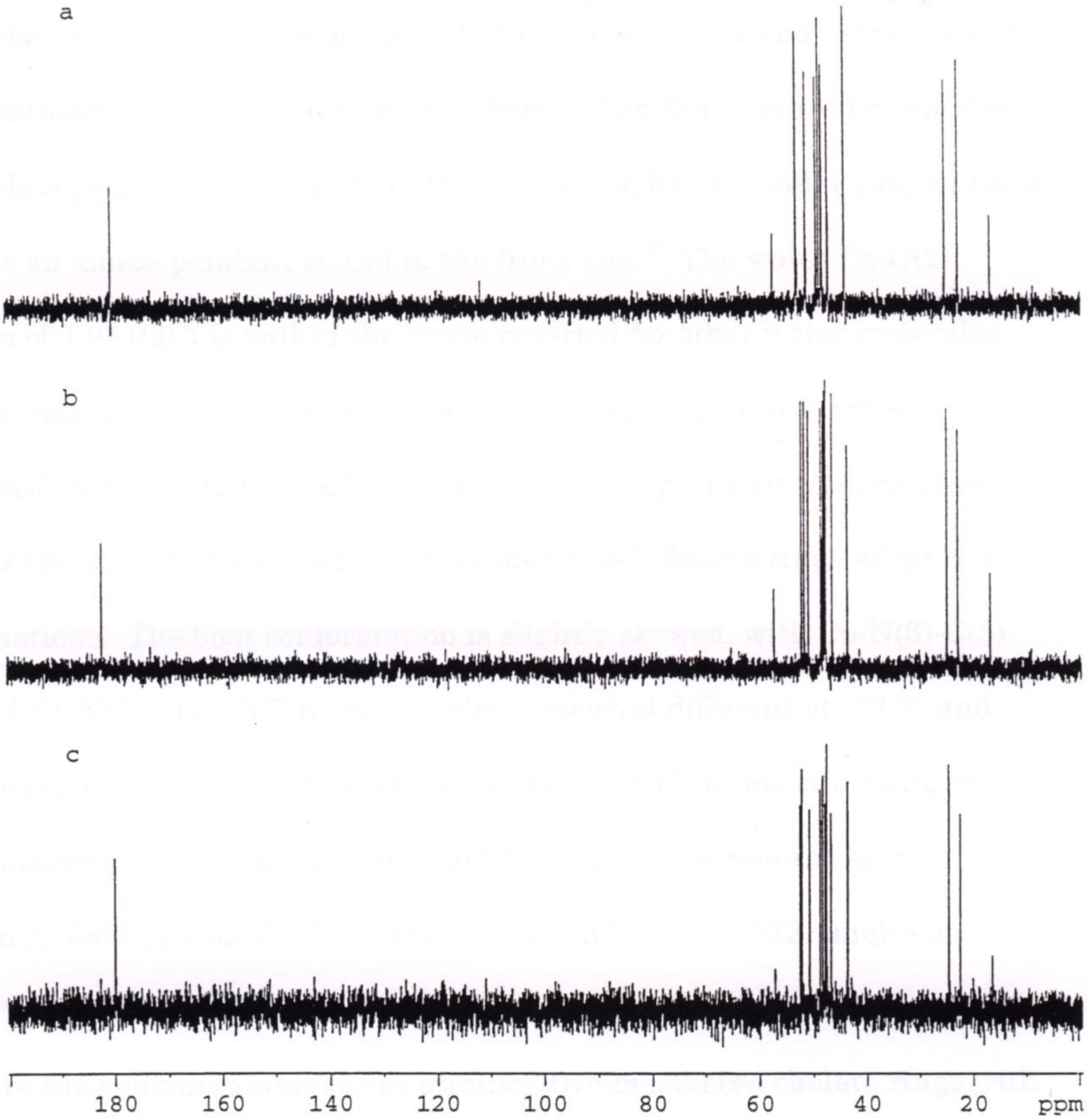

Figure 3.5. Three ^{13}C NMR spectra demonstrating the retention of geometry of *cis* form of the Co(III) complex of L6 during base hydrolysis. The first spectra (a) is the neutral solution of the complex. In the next (b) NaOD has been added and in the third the solution has been reacidified with DCl. The whole experiment was carried out in under an hour.

bond angles for the complex cation collected in Tables 3.8 and 3.9 respectively. The average Co-N distance of 1.990 Å is not significantly larger than that reported for L5 (1.986 Å),[5] despite the different pendant group. The carboxylate Co-O(1) distance of 1.882(2) Å is at the shorter end of the range for bound carboxylate groups, and slightly shorter than that reported in another carboxylate-pendant macrocycle (1.899(2) Å) which has a smaller ring and also contains an amine pendant bound in the *trans* site.[37] The water Co-O(2) distance of 1.934(2)Å is within the range reported for other water molecules bound to cobalt(III). The carboxylate group necessarily requires the six-membered chelate ring to which it is attached to adopt a boat conformation, whereas the other two unsubstituted six-membered chelate rings adopt chair conformations. The boat conformation is slightly skewed, with Co-N(3)-C(8)-C(7) and Co-N(2)-C(6)-C(7) torsion angles somewhat different at -33.9° and -26.4° respectively. The bound carboxylate oxygen O(1) forms two additional six-membered chelate rings via N(2) and N(3), the three donors being necessarily facially bound. The O(1)-Co-N(2) and O(1)-Co-N(3) angles of 86.9(1)° and 86.6(1)° are closer to ideal than what is observed in the analogue L5 where the pendant amine forms strained five-membered chelate rings with equivalent angles of 83.9(3)° and 82.1(3)°.[36] The Co-O(1)-C(12) angle of 121.2(2)° is nevertheless opened out from the normal tetrahedral angle, although angles around C(7) do not indicate any particular strain. The O(1)-Co-O(3) angle of 176.46(9)° arises because the unidentate water bond is slightly bent away from the side of the molecule with carboxylate group

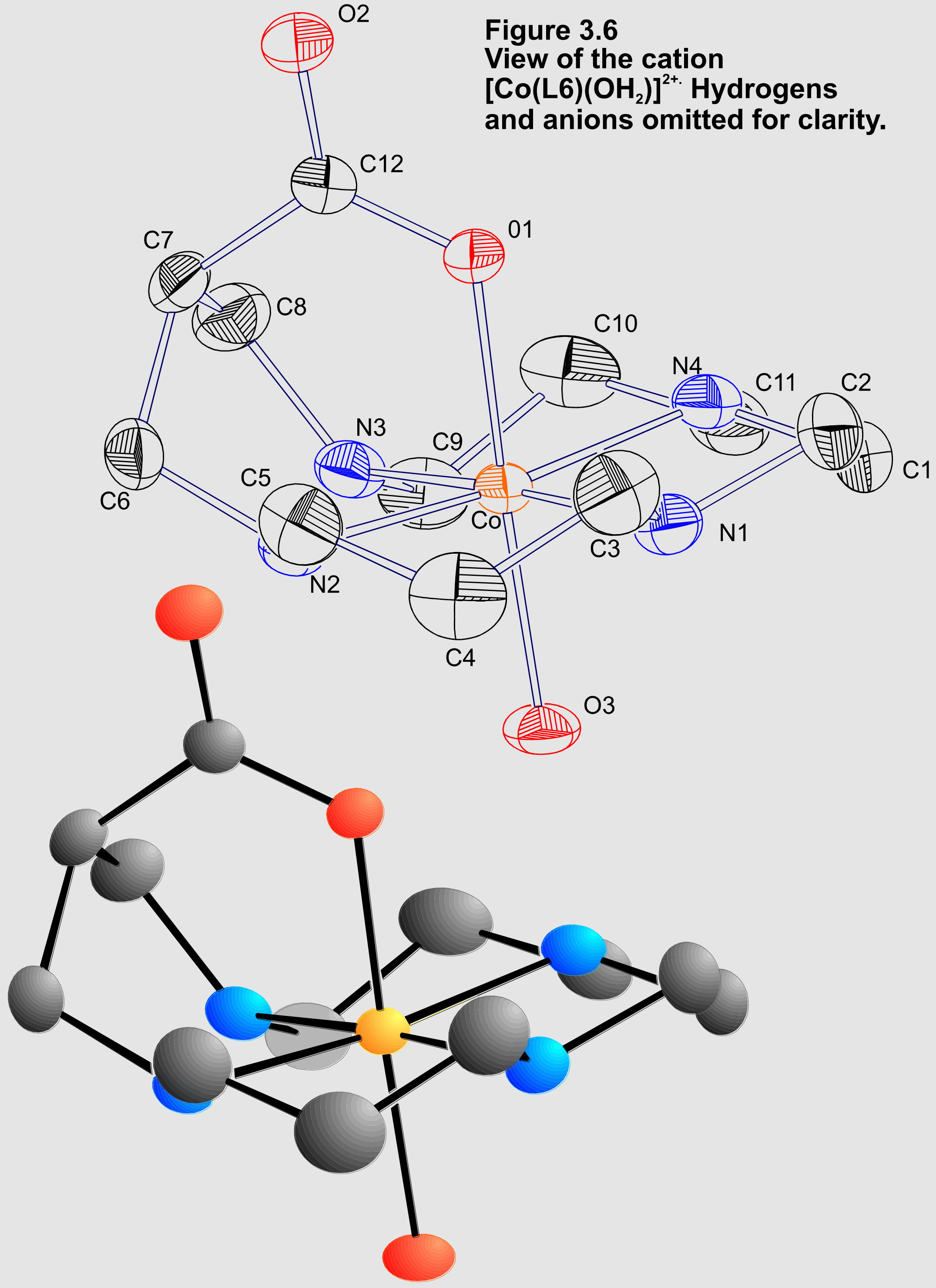

Figure 3.6
View of the cation
[Co(L6)(OH$_2$)]$^{2+}$. Hydrogens
and anions omitted for clarity.

necessarily requires the facial capping unit, as seen in Figure 3.6. The N(2)-Co-N(3) angle of 87.6 (1)° in the six-membered ring with the capping group is smaller than the equivalent angles for the unsubstituted six-membered

Table 3.7 Non-hydrogen Atom Coordinates and Parameters for $[Co(L6)(OH_2)](ClO_4)_2 \cdot 2H_2O$.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co(1)	0.44202(4)	0.77555(2)	0.17410(2)	O(16)	0.3987(4)	0.1048(2)	0.6184(2)
Cl(1)	0.75974(8)	0.43344(5)	0.07359(5)	O(17)	0.1270(3)	0.1403(2)	0.5658(3)
Cl(2)	0.1216(1)	0.13408(7)	0.11242(7)	N(1)	0.6346(3)	0.7311(2)	0.1737(2)
O(1)	0.4346(2)	0.7814(1)	0.0428(1)	N(2)	0.5017(3)	0.8952(2)	0.1752(2)
O(2)	0.3902(2)	0.8548(1)	-0.0858(1)	N(3)	0.2488(3)	0.8148(2)	0.1856(2)
O(3)	0.4618(2)	0.7678(1)	0.3091(1)	N(4)	0.3829(3)	0.6590(2)	0.1575(2)
O(4)	0.6393(3)	0.4611(2)	0.0154(2)	C(1)	0.5061(4)	0.6061(2)	0.1803(2)
O(5)	0.8765(3)	0.4809(2)	0.0547(2)	C(2)	0.6271(4)	0.6450(2)	0.1393(3)
O(6)	0.7844(3)	0.3486(2)	0.0555(2)	C(3)	0.7442(4)	0.7770(2)	0.1297(3)
O(7)	0.7290(3)	0.4432(1)	0.1687(1)	C(4)	0.7588(4)	0.8630(3)	0.1688(3)
O(8)	0.1247(6)	0.0879(3)	0.0296(4)	C(5)	0.6379(4)	0.9164(2)	0.1364(3)
O(9)	0.204(1)	0.1002(8)	0.0537(9)	C(6)	0.3920(4)	0.9505(2)	0.1278(2)
O(10)	0.2687(6)	0.1657(5)	0.1203(5)	C(7)	0.2982(3)	0.9040(2)	0.0542(2)
O(11)	0.153(1)	0.1830(9)	0.1816(6)	C(8)	0.1864(4)	0.8575(2)	0.1005(2)
O(12)	0.041(1)	0.1974(8)	0.0590(8)	C(9)	0.1462(4)	0.7588(2)	0.2262(2)
O(13)	0.017(1)	0.1872(7)	0.1075(6)	C(10)	0.1301(4)	0.6779(2)	0.1758(3)
O(14)	0.1121(7)	0.0779(4)	0.1868(4)	C(11)	0.2561(4)	0.6245(2)	0.1949(2)
O(15)	-0.008(2)	0.085(1)	0.123(1)	C(12)	0.3800(3)	0.8440(2)	-0.0018(2)

Table 3.8 Bond lengths for the cation $[Co(L6)(OH_2)]^{2+}$ (Å)

atom	distance	atom	distance
Co(1)- O(1)	1.882(2)	N(2)- H(1N)	0.75(3)
Co(1)- O(3)	1.934(2)	N(3)- C(8)	1.487(4)
Co(1)- N(1)	1.981(3)	N(3)- C(9)	1.491(4)
Co(1)- N(2)	2.022(3)	N(3)- H(3N)	0.78(3)
Co(1)- N(3)	1.977(3)	N(4)- C(1)	1.475(4)
Co(1)- N(4)	1.982(3)	N(4)- C(11)	1.477(4)
O(1)- C(12)	1.288(3)	N(4)- H(2N)	0.79(3)
O(2)- C(12)	1.231(3)	C(1)- C(2)	1.483(5)
N(1)- C(2)	1.481(4)	C(1)- H(1a)	0.93(3)
N(1)- C(3)	1.470(4)	C(1)- H(1b)	0.97(3)
N(1)- H(4N)	0.77(3)	C(2)- H(2a)	0.98(3)
N(2)- C(5)	1.499(4)	C(2)- H(2b)	0.94(3)
N(2)- C(6)	1.502(4)	C(3)- C(4)	1.506(5)

chelate rings of 94.9(1)° [N(1)-Co-N(2)] and 93.2(1)° [N(3)-Co-N(4)], presumably arising from the constraints of the rigid facial capping involving that ring; this closed angle is probably also responsible for the slight skewing of the boat discussed above. The two secondary amines of the facial capping unit necessarily adopt *RS* stereochemistry, whereas the two opposite secondary amines forming part of the standard skew five-membered chelate ring adopt *RR* stereochemistry. There are a number of hydrogen bonding interactions involving the coordinated water and secondary amine protons.

Table 3.9 Bond angles for the cation $[Co(L6)(OH_2)]^{2+}$(°)

atom	angle	atom	angle
O(1)- Co(1)- O(3)	176.46(9)	Co(1)- O(1)- C(12)	121.2(2)
O(1)- Co(1)- N(1)	88.57(9)	C(2)- N(1)- C(3)	110.5(3)
O(1)- Co(1)- N(2)	86.93(9)	Co(1)- N(2)- C(5)	118.2(2)
O(1)- Co(1)- N(3)	96.20(9)	Co(1)- N(2)- C(6)	112.5(2)
O(1)- Co(1)- N(4)	86.60(9)	C(5)- N(2)- C(6)	107.1(2)
O(3)- Co(1)- N(1)	87.9(1)	Co(1)- N(3)- C(8)	113.5(2)
O(3)- Co(1)- N(2)	92.87(9)	Co(1)- N(3)- C(9)	119.3(2)
O(3)- Co(1)- N(3)	87.33(9)	C(8)- N(3)- C(9)	111.7(3)
O(3)- Co(1)- N(4)	93.58(9)	Co(1)- N(4)- C(1)	108.2(2)
N(1)- Co(1)- N(2)	94.9(1)	Co(1)- N(4)- C(11)	123.6(2)
N(1)- Co(1)- N(3)	174.7(1)	C(1)- N(4)- C(11)	111.5(3)
N(1)- Co(1)- N(4)	84.8(1)	N(4)- C(1)- C(2)	107.6(3)
N(2)- Co(1)- N(3)	87.6(1)	N(1)- C(2)- C(1)	106.7(3)
N(2)- Co(1)- N(4)	173.5(1)	N(1)- C(3)- C(4)	110.9(3)
N(3)- Co(1)- N(4)	93.2(1)	C(3)- C(4)- C(5)	112.1(3)
O(8)- O(9)- O(10)	138(1)	N(2)- C(5)- C(4)	115.4(3)
O(9)- O(10)- O(11)	102.4(7)	N(2)- C(6)- C(7)	111.6(2)
O(10)- O(11)- O(13)	102.4(6)	C(6)- C(7)- C(8)	110.0(3)
O(10)- O(11)- O(14)	91.3(8)	C(6)- C(7)- C(12)	112.4(3)
O(13)- O(11)- O(14)	84.0(6)	C(8)- C(7)- C(12)	109.2(3)
Co(1)- N(1)- C(2)	108.9(2)	N(3)- C(8)- C(7)	110.0(3)
Co(1)- N(1)- C(3)	121.0(2)	N(3)- C(9)- C(10)	112.9(3)
O(1)- C(12)- O(2)	122.5(3)	C(9)- C(10)- C(11)	111.7(3)
O(1)- C(12)- C(7)	116.6(2)	N(4)- C(11)- C(10)	113.0(3)
O(2)- C(12)- C(7)	120.9(3)		

A capacity for the coordination of the pendant carboxylate group to metal ions in an octahedral geometry has been demonstrated by this study of nickel(II) and cobalt(III) complexes. This matches coordination of a pendant amine group in analogues. Although pendant groups are attached directly to a carbon of the macrocyclic ring, the ring to which they are attached is sufficiently flexible to permit the close approach and coordination in an axial site. Clearly, strain in the amine-pendant case is higher than in the carboxylate-pendant case, the former introducing addition 5-membered chelate rings and the latter only 6-membered chelate rings. Further, the pendant-carboxylate group has the capacity to act as a bridging ligand as displayed in the case of the nickel(II) system. The role of the pendant carboxylate group in macrocyclic ligands with two pendant groups will be explored in the following chapters.

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