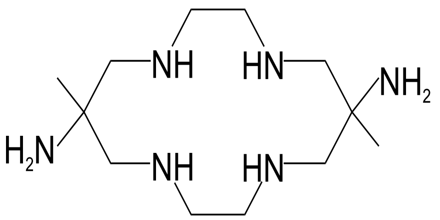
Chapter Five

Coordination Chemistry of Acammac and Diacmac

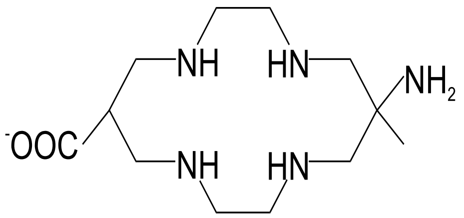
5.1 Introduction

The transition metal ion complexes of macrocycles with additional potentially coordinating pendants have been extensively studied in recent years.[1] One rationale for this interest has the been the potential of these ligands to totally encapsulate a small metal ion by binding the metal ion in the centre of usually four macrocyclic ring donors and using the pendant donors to coordinate to additional sites above and below the macrocyclic ring. The more studied type of pendant-arm macrocycle are those based on N-alkylation reactions of secondary amines in the macrocyclic ring. The less explored type have the pendant arm(s) attached to carbon atom(s) of the macrocyclic ring, which usually represents a greater synthetic challenge.

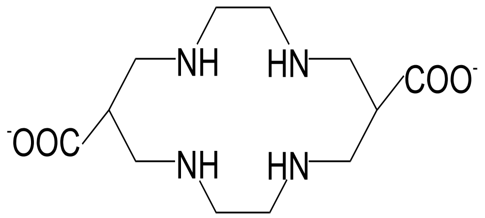
One facile route to the production of such C-pendant macrocycles is by the reaction of bis(ethane-1,2-diamine)copper(II) with formaldehyde and a carbon acid in the presence of base to form new propyl bridges between adjacent pairs of amines with pendants attached to each central bridge carbon, as discussed in earlier chapters. The nature of the pendants is dependant on the carbon acid used. Nitroethane produces pairs of methyl and nitro pendants whereas



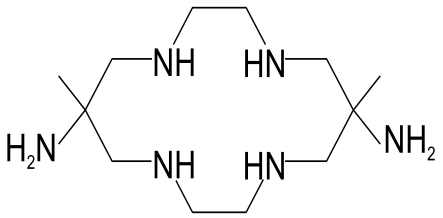
L1



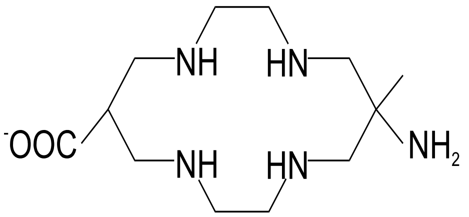
L2



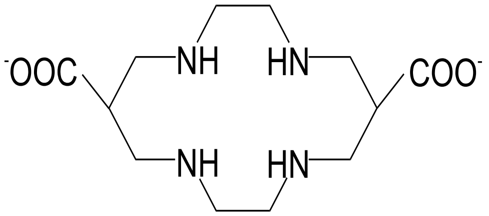
L3



L4



L5



L6

diethylmalonate (or dimethylmalonate) produces pairs of two ethyl ester (or methyl ester) pendants. Reduction or else decarboxylation and hydrolysis of these compounds leads to the formation of amine (L1, L4) or carboxylate (L3, L6) pendants respectively. The step-wise use of both carbon acids in stoichiometric amounts can lead to the production of a macrocycle with mixed pendants after reduction (L2, L5), as described in Chapter 4.

All three ligands, as *trans* isomers (L1-L3), can achieve pseudo encapsulation of at least an octahedral metal ion by trapping it between the four ring nitrogens of the cyclam-like macrocycle and then using the two pendants to occupy the other two available coordination sites. However, due to the albeit limited flexibility of the saturated macrocyclic ring and the possibility of unbound pendant donors, a number of other coordination geometries are possible. The macrocycle may take on a folded geometry (Figure 5.1), and such folded geometries cannot make use of all the donor atoms of the macrocycle, thus leaving some coordination sites on the metal free to be filled by other ligands. A number of examples exist in which only one or neither of the pendant donors are coordinated.[2] This may arise from the donor preference or preferred coordination geometry of the metal ion or else be a kinetically favoured product of the complexation reaction. Likewise, the *cis* isomers (L4-L6) may adopt a number of coordination geometries, including the case where all six donor groups are coordinated. The ability to adopt a range of coordination modes distinguish the pendant arm donor molecules from the macrocyclic 'cage' molecules such as sarcophagine (3,6,10,13,16,19-hexazabicyclo[6.6.6]eicosane) which effectively and usually irreversibly bind metal ions in an internal cavity employing all six donor groups.[3]

The metal complexes of L1 have been extensively studied,[4] showing the ability of the ligand to coordinate in a hexadentate, quiquedentate or tetradentate manner to a wide range of metal ions. In the majority of cases, L1 forms a conventional encapsulation complex with both pendants coordinated. The metal complexes of this ligand often display shorter bond lengths than found for other polyamine analogues, the ligand exerting a stronger ligand field. This encapsulation mode of coordination is also available to the dicarboxylate

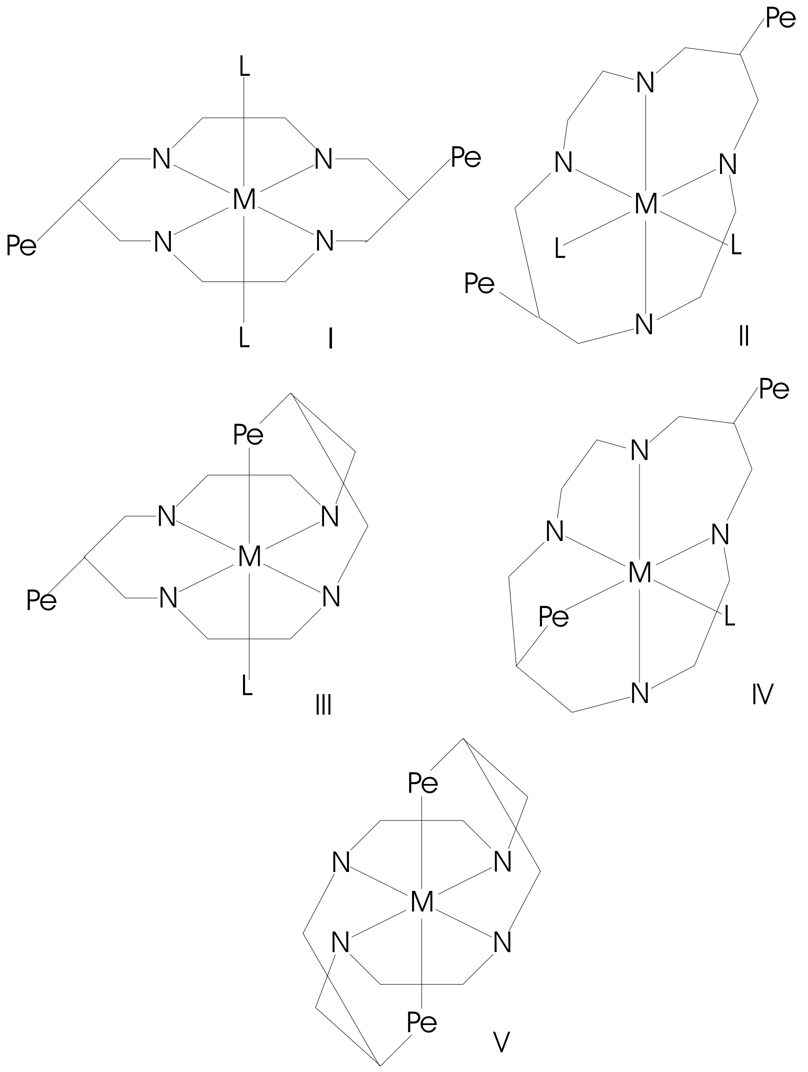


Figure 5.1

Possible tetradentate (I and II), quiquedentate (III and IV) and hexadentate (V) coordination of *trans* isomers of L1, L2 and L3 to an octahedral metal ion in which all ring nitrogens are coordinated. In the case of L2, additional isomers exist since the two pendant donors (Pe) are non-equivalent. (Secondary amines are represented by N in the above diagram.)

pendant molecule L3. To date, only complexes of Cu(II), Ni(II)[5] and Fe(III) [6] have been reported for L3, although the Co(III) and Ni(II) chemistry is explored herein. However, it is apparent that L3 exerts a weaker ligand field compared with L1. The intermediate ligand L2, with one amine and one carboxylate pendant, presents a potentially hexadentate coordination mode with a ligand field strength intermediate between L1 and L3.

It is possible for the two pendant donors to bind another metal ion other than the metal ion bound by the donors of the macrocyclic ring, thus effectively linking metal centres. The carboxylate pendant of related mono pendant-arm macrocyclic ligands have been shown to be able to bridge between the parent complex ion and another metal ion, as described with nickel(II) in Chapter 3. This behaviour has yet to be observed for L3,[5] or its amine analogues.

The *cis* isomers L4, L5 and L6 represent the minor and most soluble isomer in the *trans/cis* mixture of all the pendant arm macrocycles, and have proved difficult to isolate in a pure form. The presence of L4 was only firmly established years after the chemistry of L1 had been explored, and the separation of the two isomers has only been achieved by chromatography of the copper(II) complex of the mixture, a process complicated by the presence of N-based isomers of the complexes. This method is further complicated in the case of the pendant carboxylate ligands by protonation-deprotonation equilibria. Consequently, the coordination chemistry of the series of ligands has been focussed on the major and more accessible *trans* isomers.

Nevertheless, the condensation reactions are stereoselective and not stereospecific, and the presence of both isomers of each ligand has been clearly established during this study.

In this chapter, the synthesis and characterisation of the Cu(II), Co(III), Cr(III), Fe(III) and Rh(III) complexes of L2 are described and their properties are compared to those reported or determined for L1 and L3. Structures of two cobalt(III) complexes of L2 are described,[7] one in which the macrocyclic ring is folded with the pendant carboxylate uncoordinated, the other being the hexadentate product. The Co(III) and Ni(II) complexes of L3 have been prepared and are described herein. The Co(III) chemistry of L3 is similar to L1, the ligand forming a range of complexes including tetra- and hexadentate forms with the structure of the hexadentate form reported herein. The existance of *cis* isomers L5 and L6, to match the known L4, has been established in two x-ray crystal structures. The structure and characterisation of the Ni(II) complex of L5, the *cis* analogue of L2, and the Co(III) complex of L6, the *cis* analogue of L3, are described. The former compound crystallised preferentially, following reaction of a Ni(II) salt with a mixture of L2 and L5, as a dimer with two metal centres linked by two carboxylate bridges. The L6 complex was one of the products isolated by chromatography following preparation of the Co(III) complexes of a L3, L6 mixture. Consequently, full structural characterisation of all of the series L1-L6 has now been achieved.

5.2 Experimental

5.2.1 Cobalt (III) Complexes

Quiquedentate Cobalt(III) Complexes of Acammac (L2)

(L2).5HCl.4H_2O (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}), followed by bubbling air through the solution for 75 minutes. The brown solution was re-acidified by the addition of hydrochloric acid (40 cm^3, 10 mol dm^{-3}) and stirred at 80°C for 36 hours. The red solution was diluted to 1 dm^3 with water and sorbed onto a column of Dowex 50Wx2 (H^+ form) resin (4 x 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 crystallised in turn as:

cis-*(trans-6-Methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylic acid)chlorocobalt(III) perchlorate monohydrate, cis-[Co(HL2)Cl](ClO_4)$_2$.H_2O.* Red/pink in colour, this band was collected first, reduced in volume and left to crystallise after the addition of a small amount of perchloric acid. On standing, red crystals formed and were collected, washed with iso-propyl 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 (83) and 365 nm (114 dm^3 mol^{-1} cm^{-1}). NMR (D_2O): ^1H, δ 1.33 (s, 3H) 2.3 - 3.5 (m, 17H); ^{13}C, δ 19.5, 54.3, 53.8, 53.4, 53.3, 52.7, 49.0, 56.7, 60.1, 169.0 p.p.m. IR Spectrum (KBr disc): 1718 (-COOH), 1605 ($-NH_2$) cm^{-1}. Voltammetry: $E_{1/2}$(HMDE, H_2O) -0.46 V (ΔE 63 mV).

cis-*Aqua(trans-6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylic acid)cobalt(III) perchlorate monohydrate, cis-*$[Co(HL2)H_2O](ClO_4)_3$.
This orange band was collected second and treated as above. On standing, orange/red crystals formed (yield *ca* 40%) (Found C, 23.0; H, 4.5; N, 11.3. Calc. for $C_{12}H_{28}Cl_3CoN_5O_{14}$: C, 22.8; H, 4.3; N,11.1%). Electronic spectrum (in water): λ_{max} 530 sh (ε 68), 474 (95) and 358 nm (106 $dm^3\ mol^{-1}\ cm^{-1}$). NMR (D_2O): ^{13}C, δ 17.6, 55.3, 53.6, 51.3, 50.2, 46.8, 33.6, 59.8, 66.0, 174.0 p.p.m. IR Spectrum (KBr disc): 1717 (-COOH), 1600 ($-NH_2$) cm^{-1}. Voltammetry: $E_{1/2}$(HMDE, H_2O) -0.48 V (ΔE 63 mV).

Hexadentate Cobalt(III) Complex of Acammac (L2).

(trans-6-Methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylate)cobalt(III) perchlorate monohydrate, $[Co(L2)](ClO_4)_3.H_2O$.
(L2).5HCl.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}), followed by bubbling air through the solution for 2 hours. The brown solution was re-acidified by the addition of hydrochloric acid (60 cm^3, 10 mol dm^{-3}) and stirred at 80°C for 2 hours and then unheated for 48 hours. 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 hours. The solution was filtered, diluted to 1 dm^3

with water and sorbed onto a column of Dowex 50Wx2 (H^+ form) resin (4 x 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 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 characterisation, but spectroscopic studies suggest it was the *trans*-chloropentaamine [Electronic spectrum (in water): λ_{max} 522 (ε 63), 444 (43) and 354 (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 crystallise. On standing, orange crystals formed (*ca* 90% of total cobalt). These were collected, washed with alcohol and diethyl ether and air dried. X-ray studies confirmed it as the hexadentate complex (Found C, 26.2; H, 5.2; N, 12.5. Calc. for $C_{12}H_{27}Cl_2CoN_5O_{11}$: C, 26.2; H, 5.1; N,12.7%). Electronic spectrum (in water): λ_{max} 481 (ε 87), 339 nm (92 dm^3 mol^{-1} cm^{-1}). NMR (D_2O): ^1H, δ 1.29 (s, 3H) 2.7 - 3.8 (m, 17H); ^{13}C, δ 18.3, 52.7, 47.6, 45.3, 58.1, 66.2, 184.9 p.p.m. IR Spectrum (KBr disc): 1627 ($-COO^-$), cm^{-1}. Voltammetry: $E_{1/2}$(HMDE, H_2O) -0.42 V (ΔE 80 mV.)

Cobalt(III) Complexes of Diacmac (L3 and L6)

1,4,8,11-Tetraazacylotetradecene-6,13-dicarboxylic acid hydrochloride (0.5 g) was dissolved in water (100 cm^3) and the pH adjusted to ~ 8 using aqueous NaOH. To this was added $CoCl_2.6H_2O$ (0.3 g), with stirring. The solution initially changed to a yellow colour and then, with continued stirring, to a red brown colour. The solution was allowed to stir at room temp for 24 hours and then the pH of the solution was adjusted to ~2 with HCl. The solution was then left to stir for 3 days at room temperature, diluted to 3 dm^3 and loaded onto a column of Dowex 50Wx2 (H^+ form) resin (3 x 30 cm). The column was washed with 1 dm^3 of H_2O and then the products eluted with 1 mol dm^{-3} HCl. Four separate bands were observed. All bands were collected reduced in volume to ~5 cm^3 and left crystallise after the addition of a drop of $HClO_4$.

Band 1: Hexadentate complex of L3

(trans-1,4,8,11-Tetraazacylotetradecene-6,13-dicarboxylate)cobalt(III) perchlorate, [Co(L3)]ClO₄.

This orange pink band was evaporated to dryness, yielding a small amount of orange solid. Infrared studies showed a single absorbance in the $-COO^-$ region at 1613 cm^{-1}. NMR studies confirmed that this was the hexadentate *trans* complex with a single amine peak in the ^1H spectra and only four peaks in the ^{13}C spectrum suggesting very high symmetry in the molecule. (Found: C, 31.6; H, 5.6; N, 12.3%. Calc. for $C_{12}H_{24}Cl_3CoN_4O_4$: C, 31.8; H, 5.3; N, 12.3%). Electronic Spectrum (in water): λ_{max} 511 (ε 28), 343 (35) and 236 (sh) nm (90 dm^3 mol^{-1} cm^{-1}). IR Spectrum (KBr disc): 1613 (COO^-) cm^{-1}. Voltammetry: $E_{1/2}$(HMDE, H_2O) -0.62 V. NMR (D_2O): ^1H δ 2.5-3.7 (multiplet $-CH_2-$, -CH-) and δ 6.9 (singlet, -NH-); ^{13}C, δ 50.0, 50.7, 55.7 and 184.4 ppm.

Band 2:

This pink band evaporated to dryness leaving a small amount of green solid which characterisation showed to be the same as band 3. The solid was redissolved in water (50 cm^3) and filtered. The pH of the resulting pink solution (λ_{max} 563, 435 and 366 (sh) nm) was adjusted to ~11 and allowed to stir at 60 °C for 4 hours. The UV/Vis spectrum of the orange solution and the IR spectrum of the solid after the solution was taken to dryness showed it to be the same species as the solid isolated from band 1.

Band 3: trans-Dichloro complex of H_2L3

trans-*dichloro(trans-1,4,8,11-tetraazacylotetradecene-6,13-dicarboxylic acid)cobalt(III) chloride*, *$Co(H_2L3)Cl_2]Cl$.*

This band was collected, reduced in volume to ~ 20 cm^3 and left to stand. After 3 days a green solid had precipitated from the yellow green solution. This was collected, washed with ethanol and diethyl ether and air dried. (Found: C, 32.1; H, 5.2; N, 12.5. Calc. for $C_{12}H_{24}Cl_3CoN_4O_4$: C, 31.8; H, 5.3; N, 12.4%). Electronic Spectrum (in water): λ_{max} 615 (ε 134), 450 (200) and 360 nm (255 $dm^3\ mol^{-1}\ cm^{-1}$). IR Spectrum (KBr disc): 1730 cm^{-1} (COOH) NMR (D_2O): ^1H δ 2.8-3.5 (multiplet $-CH_2-$, -CH-) and δ 6.6 (singlet, -NH-); ^{13}C, δ 45.7, 50.7, 53.7 and 175.3.

Band 4: Quinquedentate complex of HL6

trans-*Aqua(cis-1,4,8,11-tetraazacylotetradecane-6-carboxylate-13-carboxylic acid)cobalt(III) perchlorate hydrate, $[Co(HL6)(OH_2)](ClO_4)_2$.*

After a week, red crystals had formed in the small volume of solution collected, following slow evaporation. These were collected and air dried. X-ray crystallography confirmed that this was the L6 isomer. NMR (D_2O): ^1H δ 2.4-3.7 (multiplet $-CH_2-$, -CH-) and δ 6.9, 7.1, 7.2 and 7.4 (singlets, -NH-), ^{13}C, δ 47.6, 48.1, 48.8, 50.1, 52.2, 53.8, 54.6, 55.7, 58.5, 179.5 and 182.3 ppm. Electronic Spectrum (H_2O): λ_{max} 546 (ε 70), 448 (50) and 357 nm (97 dm^3 mol^{-1} cm^{-1}). IR Spectrum (KBr disc): 1721 (-COOH), 1630 and 1590 cm^{-1} ($-COO^-$).

5.2.2 Copper(II) Complex

(6-Methyl-1,4,8,11-tetraazacyclotetradecane-6-amino-13-carboxylic acid)copper(II) perchlorate, $[Cu(HL2)](ClO_4)_2$

Both HL2.5HCl (2g) and $Cu(NO_3)_2.3H_2O$ (1g) were dissolved in water (100 cm^3). The pH of the solution was adjusted to ~ 8 with aqueous NaOH (2.5 mol dm^{-3}) and the solution allowed to stir at room temperature overnight. The solution was then diluted to 2 dm^3 with water and loaded onto a column of SP-Sephadex (C-25) cation exchange resin (3 x 25 cm). The column was then washed with 1 dm^3 of water. Elution with 0.3 mol dm^{-3} $NaClO_4$ resulted in two bands. Both bands proved to be stable in acidic solution and were thus identified as being macrocyclic products. Adjusting the pH of aliquots of the solutions to ~10 followed by readjustment to pH ~3 resulted in solutions with identical UV/Vis spectra. On this basis, the compounds were attributed to the protonated and deprotonated forms of the carboxylate pendant or else N-based isomers. Both solutions were reduced in volume to ~ 50 cm^3 and then left to stand. Within 24 hours, the first solution had precipitated a purple solid which was shown (IR spectrum: 1634 cm^{-1}, COO^-) to be the deprotonated form.[8] Within a week, the second solution had precipitated a pink solid which was shown (IR spectrum: 1706 cm^{-1}, COOH) to be the protonated form of the complex. The visible spectra, measured at pH ~10 and then pH ~3, showed identical λ_{max}, confirming that both products were of the same ligand in different protonation states. The protonated complex was characterised by microanalysis. (Found C, 26.8; H, 5.4; N, 12.7. $C_{12}H_{27}N_5O_{10}Cl_2Cu$ requires C, 26.9; H, 5.1; N, 13.1%). Electronic spectrum λ_{max} (H_2O, pH 7) 514 nm (ε 75 dm^3 mol^{-1} cm^{-1}) Voltammetry: $E_{1/2}$ (DME, H_2O) -0.64 V (vs Ag/AgCl).

5.2.3 Nickel(II) Complexes

Ni(II) complexes of acammac (L2 and L5)

(cis-6-Methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylate)nickel(II) perchlorate, [Ni(L5)](ClO_4).

1 g of the hydrochloride salt of the acammac ligand and 0.84 g of $Ni(ClO_4)_2.6H_2O$ were dissolved in 50 cm^3 of water. While stirring, the pH of the solution was adjusted to ~10 by the slow addition of aqueous NaOH (2.5 mol dm^{-3}). The solution was warmed to ~50° C and left to stir overnight. The solution was then filtered to remove any precipitated hydroxides, diluted to 5 dm^3 and loaded onto a Sephadex cation exchange column. Elution with 0.2 mol dm^{-3} $NaClO_4$ resolved three bands; the second (green) band, apparently $Ni^{2+}_{(aq)}$,

was discarded. The first and major band, purple in colour, was collected and reduced in volume to 20 cm^3 by rotary evaporation. After standing for 3 days, purple/pink crystals of a quality suitable for x-ray analysis were collected. Two further crops of crystals were collected, after which the solution had changed to an orange colour and no further crops were isolated. Infrared analysis confirmed that the later crops were the same as the original. X-ray crystallography showed this to be a Ni(II) complex of the *cis* isomer (L5) (Found C, 35.7; H, 5.5; N, 16.0. $C_{13}H_{24}N_5O_6ClNi$ requires C, 35.4; H, 5.5; N, 15.9%). Electronic spectrum λ_{max} (H_2O, pH 7) 932 (ε 4), 800 (3), 696 (3), 585 (3), 495(5), 327 nm (7 $dm^3\ mol^{-1}\ cm^{-1}$). IR spectrum: 1583 cm^{-1} ($-COO^-$, bridging). Voltammetry: $E_{1/2}$ (DME, H_2O) -1.36 V (vs Ag/AgCl).

The remaining yellow solution is consistent with a low spin complex of apparently L3; it did not crystallise on standing. It was taken to dryness and infrared studies confirmed the presence of an uncoordinated carboxylic acid (1716 cm^{-1}). The final band separated by chromatography was also yellow in colour and was thought to also be the low spin tetradentate complex. It was, however, in too small a yield to be isolated.

Ni(II) complexes of diacmac (L3 and L6)

(cis/trans-1,4,8,11-Tetraazacylotetradecene-6,13-dicarboxylic acid)nickel(II) chloride perchlorate hydrate, $[Ni(H_2(L3/L6)]Cl(ClO_4)_2.H_2O$

1,4,8,11-Tetraazacylotetradecane-6,13-dicarboxylic acid hydrochloride (0.5 g) was dissolved in water (80 cm^3) and to this solution was added an equimolar amount of $Ni(ClO_4)_2.6H_2O$, with stirring. The pH of the solution was adjusted to ~8.5 and the solution was left to stir at 60 °C for 18 hours, resulting in a pink solution. $NaClO_4$ (100 cm^3, 2 mol dm^{-3}) was added and the volume of the solution reduced to 50 cm^3, after which the solution had turned to a yellow colour. The solution was allowed to evaporate to dryness and then 1 cm^3 of 5 mol dm^{-3} HCl was added. The solution was left to sit for 4 hours and then the remaining yellow solid was collected. Analysis of the solid showed it to be the low spin perchlorate salt of the Ni(II) complex of the ligand with the carboxylates protonated and unbound. (Found: C, 24.8; H, 4.9; N, 9.5. Calc. for $C_{12}H_{28}Cl_2NiN_4O_{10}$: C, 24.7; H, 4.5; N, 9.6%). Electronic Spectrum (in water): λ_{max} 345 (ε 12) and 210 nm (48 dm^3 mol^{-1} cm^{-1}). IR Spectrum (KBr disc): 1731 (-COOH) cm^{-1}. A proportion of the solid was redissolved in a minimum amount of D_2O and placed in a sealed container after the addition of two drops of concentrated DCl. Overnight a mixture of purple and pink crystals formed and were separated physically. The IR spectra of the two samples differ. The pink crystals showed evidence of both coordinated (1605 cm^{-1}) and protonated, uncoordinated (1728 cm^{-1}) carboxylates, while the purple crystals showed two distinct absorbances (1723 and 1702 cm^{-1}). The purple solid predominated (*ca* 4:1 purple:pink). This closely approximates the free ligand ratio, and it is possible that the purple solid may be the complex of L3 while the pink is the complex of L6. Amounts of solid isolated were insufficient to pursue characterisation further.

5.2.4 Chromium(III) complex

(trans-6-Methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylate)chromium(III) perchlorate, $[Cr(L2)](ClO_4)_3$.

HL2.4HCl (2 g) was dissolved in methanol (400 cm^3) to which was added 5 equivalents of 1,4-diazabicycloctane (2.46 g). To this was slowly added a methanolic solution (0.54 g in 20 cm^3) of $CrCl_2$. The orange red solution was left to stir in air for twelve hours and then diluted to 1 dm^3 with water and loaded onto a column of Dowex 50Wx2 cation exchange resin. An orange-red band was eluted from the column with 3 mol dm^{-3} HCl leaving a green (presumably the *trans*-dichloro complex) and a red (presumably the chloro complex) band which were too small to warrant isolation. The eluted product was reduced in volume to 10 cm^3 and a small amount of perchloric acid (0.5 cm^3, 3 mol dm^{-3}) was added to facilitate crystallisation. After 5 weeks the solution had failed to crystallise and it was diluted to 200 cm^3 with water and the pH adjusted to ~ 7.5. This solution was left to stir for twelve hours, diluted to 1 dm^3 with water and loaded onto a SP-Sepadex C-25 column. An orange band was eluted with 0.3 mol dm^{-3} $NaClO_4$ with no other fractions apparent. The eluted product was reduced in volume to 20 cm^3 and left to crystallise. Within 2 days, orange crystals had formed and were collected and air dried. A further crop of crystals was isolated a week later and were shown by infrared spectroscopy to be the same as the first crop. (Found C, 27.8; H, 5.3; N, 13.2. $C_{12}H_{26}N_5O_{10}Cl_2Cr$ requires C, 27.6; H, 5.0; N, 13.4%). Electronic spectrum (in water): λ_{max} 517 (ε 48), 415 (32) and 365 nm (70 dm^3 mol^{-1} cm^{-1}). IR Spectrum

(KBr disc): 1622 (-COO$^-$) cm^{-1}. Voltammetry: $E_{1/2}$ (DME, H_2O) -0.44 V (vs Ag/AgCl).

5.2.5 Rhodium(III) Complex

trans-*Chloro(trans-6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylic acid)rhodium(III) perchlorate monohydrate,*

$[Rh(HL2)Cl].(ClO_4)_2.Cl.H_2O$

A solution of $RhCl_3.3H_2O$ (0.75 g in 150 cm^3 of water) was heated to 80 °C. To this was added dropwise a solution of HL2.5HCl (1.4 g in 80 cm^3 of water) which had been neutralised with 2.5 mol dm^{-3} aqueous NaOH. The reaction mixture was allowed to reflux for 24 hours before being diluted to 1 dm^3 and loaded onto a column of Dowex 50Wx2 cation exchange resin. The eluate was monitored spectrophotometrically at 300 nm, employing a flow-through spectrophotometer cell. Washing with 1 mol dm^{-3} HCl removed uncomplexed species, which were discarded. The product was eluted as a yellow band with 3 mol dm^{-3} HCl and concentrated on a rotary evaporator to ~ 20 cm^3, 3 cm^3 of perchloric acid (5 mol dm^{-3}) was added, and the solution was left to stand. After a week, yellow crystals formed which were collected and washed with ethanol and diethyl ether. Infrared spectral studies of the product showed the carboxylate arm to be protonated and uncoordinated. (Found C, 23.1; H, 4.5; N, 11.2. $C_{12}H_{29}N_5O_{11}Cl_3Rh$ requires C, 23.0; H, 4.6; N, 11.24%). Electronic spectrum (in water): λ_{max} 347 (sh) (ε 200), ~278(sh) (351) and 230 nm (363 dm^3 mol^{-1} cm^{-1}). IR Spectrum (KBr disc): 1611 (-COO$^-$), 1716 (-COOH) cm^{-1}. Voltammetry: $E_{1/2}$ (DME, H_2O) -1.16 V; E_{pc} (GCE, H_2O),-1.04 V (vs Ag/AgCl).

Further refluxing of the product in basic conditions (pH ~10) over extended periods (4 weeks) yielded no product with a coordinated carboxylate.

5.2.6 Iron(III) Complex

(trans-6-Methyl-1,4,8,11-tetraazacyclotetradecane-6-amine-13-carboxylate)iron(III) perchlorate trihydrate, $[Fe(L2)](ClO_4)_2.HClO_4.3H_2O$.

Both HL2.4HCl (1 g) and iron(II) perchlorate hexahydrate (0.88 g) were dissolved in water (25 cm^3) at ~ 80° C. To this was added 1.08 g of sodium acetate (6:1 ratio acetate:hydrochloride salt). After heating for several hours, the solution had darkened in colour and a brown orange solid had formed. Sodium perchlorate (2 g) was added to aid precipitation of the product and the solution was allowed to sit for 18 hours at room temperature. The brown orange solid was collected by filtration and washed with cold water. This product was then dissolved in a minimum amount of hot boiling water, filtered to remove precipitated iron oxide and crystallised by standing at room temperature. The resulting dull brown crystals tended to slowly decompose to the oxide, but infrared studies confirmed that they were the product with a coordinated carboxylate. (Found C, 21.3; H, 4.5; N, 9.9. $C_{12}H_{33}N_5O_{17}Cl_3Fe$ requires C, 21.2; H, 4.9; N, 10.3%). Electronic spectrum (in water): λ_{max} 681 (ε 16), 466 (85), ~402(124 sh), 339 (439) and 216 nm (1280 dm^3 mol^{-1} cm^{-1}). IR Spectrum (KBr disc): 1627 ($-COO^-$) cm^{-1}. Voltammetry: $E_{1/2}$ (DME, H_2O) -0.34 V; E_{pc} (GCE, H_2O) -0.45 V, E_{pa} -0.34 V; (vs Ag/AgCl).

5.2.7 Physical Methods

Electronic spectra were recorded in aqueous solution at neutral pH using an Hitachi 220A spectrophotometer. IR spectra were recorded on complexes dispersed in KBr discs 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 DPX 300 spectrometer. Electrochemical measurements (cyclic voltammograms) 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 0.1 mol dm^{-3} $NaClO_4$ as an electrolyte. A scan rate of 100 mV s^{-1} was used for the reported results. A limited number of polarographic studies employed a conventional Metrohm static mercury drop electrode and controller. Elemental microanalyses were performed by the Australian National University Microanalysis Service. Potentiometric titrations were carried out essentially as described previously[9] using a Metrohm 665 automated burette and an IBM clone computer fitted with a Fylde Scientific pH card connected to a Metrohm combined glass electrode. All measurements were fully automated under control of the IBM clone computer. Titrations were performed at 25.0 ± 0.1°C in constant ionic strength (I = 0.5, KCl) aqueous solutions under nitrogen. Solutions of ligand (6 x 10^{-4} mol dm^{-3}) alone and in the presence of 0.9 or 0.5 equivalents of metal ion were titrated with 83 increments (of 4 x 10^{-6} dm^3) of 0.4 mol dm^{-3} NaOH. Equilibrium constants were calculated from potentiometric data with a TURBO BASIC version of the program TITFIT.[9] For each system, each titration was repeated at least three times, with good reproducibility (*ca* ± 0.1 log units) in the determined constants.

5.2.7 X-Ray Crystal Structure Determinations

Crystal data

[Co(HL2)Cl]$(ClO_4)_2$. Formula $C_{12}H_{27}Cl_3CoN_5O_{10}$, 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 electrons, μ(MoKα) = 12.30 cm^{-1}. $A_{min.,max.}$ 1.13, 1.21, range of *hkl* 0 to 12, 0 to 15, 0 to 39, R = 0.050, R' = 0.052, w = $2.90/(\sigma^2 F_o + 0.000231 F_o^2)$, residual extrema +0.6, -0.6 e Å^{-3}.

[Co(L2)]$(ClO_4)_2.H_2O$. Formula $C_{12}H_{28}Cl_2CoN_5O_{11}$, 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 electrons, μ(MoKα) = 11.42 cm^{-1}. $A_{min.,max.}$ 1.22, 1.37, range of *hkl* -13 to 13, 0 to 15, 0 to 17, R = 0.033, R' = 0.039, $w = 2.71/(\sigma^2 F_o + 0.000143 F_o^2)$, residual extrema +0.6, -0.5 e Å^{-3}.

[Co(L3)](ClO_4). Formula $C_{12}H_{22}ClCoN_4O_8$, M = 444.71, monoclinic, space group $C2_c$, a = 16.258(7), b = 9.050(3), c = 15.413(6)Å, β = 133.29(3)°, U = 1650(1) Å^3, D_c (Z = 4) = 1.789 g cm^{-3}, F(000) = 920 electrons, μ(MoKα) = 11.42 cm^{-1}. $A_{min.,max.}$ 0.893, 0.825, range of *hkl* -19 to 14, 0 to 10, 0 to 18, R = 0.041, R' = 0.053, $w = 1/\sigma^2$, residual extrema +0.6, -0.5 e Å^{-3}.

$[Ni(L5)](ClO_4)$. Formula $C_{12}H_{26}N_5ClNiO_6$, M = 430.51, monoclinic, space group $P2_1/n$ a = 8.770(6), b = 8.276(5), c = 25.009(3)Å, β = 96.12(2)°, U = 1805(2) Å^3, D_c = 1.621 g cm^{-3} , F(000) = 920 electrons, μ(CuKα) = 56.05 cm^{-1}. $A_{min.,max.}$ 1.01, 1.60, range of hkl -0 to 9, 0 to 9, -28 to 27, R = 0.073, R' = 0.146, w = $1/(\sigma^2(F_0^2) + (0.1726 \text{ x } P)^2 + (0.64 \text{ x}P))$, where $P = (\max(F_o^2, 0) + 2 \text{ x } F_c^2)/3$, residual extrema +0.77, -0.68 e Å^{-3}.

$[Co(HL6)(OH_2)](ClO_4)Cl.H_2O$. Formula $C_{12}H_{27}N_4Cl_2CoO_{10}$, M = 517.21, monoclinic, space group $P2_1/c$ a = 9.694(4), b =16.135(1), c = 12.973(5)Å, β = 93.00(2)°, U = 2026.4(12) Å^3, D_c = 1.695 g cm^{-3} , F(000) = 1072 electrons; μ(CuKα) = 56.05 cm^{-1}. $A_{min.,max.}$ 1.01, 1.60, range of hkl -0 to 11, 0 to 19, -15 to 15, R = 0.037, R' = 0.045, w = $1/(\sigma^2(F_0^2) + (0.1726 \text{ x } P)^2 + (0.64 \text{ x}P))$, where $P = (\max(F_0^2, 0) + 2 \text{ x } F_c^2)/3$, residual extrema +0.673, -0.675 e Å^{-3}.

Data sets for $[Co(HL2)Cl](ClO_4)_2$, $[Co(L2)](ClO_4)_2.H_2O$, $[Co(L3)](ClO_4)$ and $[Ni(L5)](ClO_4)$ were collected by Dr Trevor Hambley at the University of Sydney. Lattice parameters at 21° C were determined by least-squares fits to the setting parameters of 25 independent reflections. Intensity data were collected in the range $1<\theta<60°$. For the Co(III) structures, data were measured on an Enraf-Nonius CAD4F four-circle diffractometer employing graphite monochromated MoKα radiation (0.7107 Å) . Data were reduced and Lorentz, polarization and absorption corrections were applied using the Enraf-Nonius Structure Determination Package.[10] For the Ni(II) structure, data was measured on an ACF-7 four circle diffractometer employing graphite monochromated CuKα radiation. Data reduction and application of the Lorentz, polarization, absorption and decomposition corrections were carried out using the teXsan system.[11]

The [Co(HL2)Cl]$(ClO_4)_2$ and [Co(L2)]$(ClO_4)_2.H_2O$ structures were solved at the University of Newcastle by direct methods and heavy atom methods respectively, using SHELX-76[12] and the solutions were extended by difference Fourier methods. Hydrogen atoms were included at calculated sites (C-H, N-H 0.97 Å) with group isotropic thermal parameters in [Co(HL2)Cl]$(ClO_4)_2$ and were refined with isotropic thermal parameters in [Co(L2)]$(ClO_4)_2.H_2O$. All other atoms with the exception of minor contributors to disordered species [one perchlorate anion in [Co(HL2)Cl]$(ClO_4)_2$] were refined anisotropically.

The [Co(L3)](ClO_4) structure was solved and refined by Dr Trevor Hambley at the University of Sydney using the teXsan system.[11]

The [Ni(L5)](ClO_4) structure was solved at the University of Newcastle by direct methods, using SHELXS-86 [13] and refined by difference Fourier methods using SHELXL-93 [14]. Hydrogen atoms were included at calculated sites (C-H, N-H 0.97 Å) with group isotropic thermal parameters. All other atoms with the exception of minor contributors to disordered species [one perchlorate anion] were refined anisotropically.

Data for $[Co(L6H)(OH_2)](ClO_4)Cl.H_2O$ was collected and the structure solved by Dr Paul Bernhardt at the University of Queensland. Lattice parameters at 25° C were determined by least-squares fits to the setting parameters of 25 independent reflections. Data were measured on an ACF-7 four circle diffractometer employing graphite monochromated CuKα radiation. Intensity data were collected in the range $1<\theta<60°$. Data were reduced and Lorentz, polarization and absorption corrections were applied using the Enraf-Nonius Structure Determination Package. The structure was solved by direct methods, using SHELXS-86 and the solutions were refined by difference Fourier methods using SHELXL-93. Hydrogen atoms were included at calculated sites (C-H, N-H 0.97 Å) with group isotropic thermal parameters. All other atoms with the exception of minor contributors to disordered species [one perchlorate anion] were refined anisotropically.

Scattering factors and anomalous dispersion terms used for Co and Ni were taken from International Tables,[15] and all others used were those supplied the structural determination package used. All plots were drawn using ORTEP [16] or Schakal 92.[17] Final atomic coordinates, bond lengths and bond angles are listed in the appropriate tables in the text.

5.3 Results and Discussion

5.3.1 Metal Complexes of *trans*-Acammac (L2)

The potentially hexadentate ligand L2 is an ‘intermediate’ between L1 (two primary amine pendants) and L3 (two carboxylate pendants), as it offers both a primary amine pendant and a carboxylate pendant to metal ions. All three ligands have a common cyclam (1,4,8,11-tetraazacyclotetradecane, L7) core. Possible modes of binding and geometries of octahedral complexes of trans isomers of the series appear in Figure 5.1, illustrating the potentially diverse coordination chemistry available.

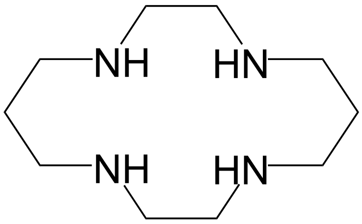
Copper(II)

The Jahn-Teller distorted copper(II) complexes of L2 and its close relatives L1 and L3 find the metal ion in the plane of the macrocycle but do not permit the close approach of pendant donors in the axial sites, effectively generating square planar complexes. The common coordination sphere of the series, effectively all with a common 14-membered macrocyclic core, leads to essentially identical absorption spectra, with maxima similar to that found for $Cu(cyclam)^{2+}$. A structural study of $[Cu(L1)]^{2+}$ with amines unprotonated but unbound and displaced well away from the axial sites reflect the limited role for pendants in square planar complexes.[18] However, with inert complex ions preferring octahedral coordination, the pendants come into play as important donor groups, as discussed below.

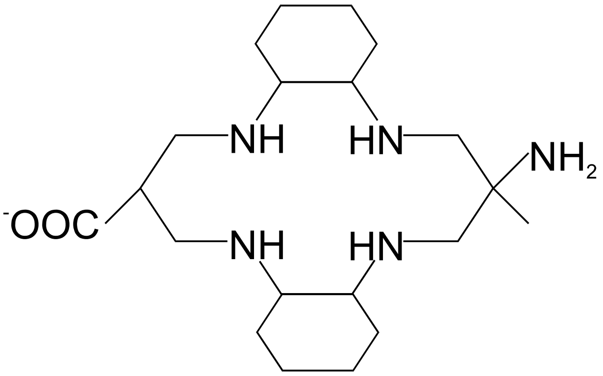
Attempts to separate the *trans-* and *cis-* isomers of acammac (L2 and L5) as their copper(II) complexes were hindered by both the formation of N-based isomers and the protonation/deprotonation chemistry of the carboxylate pendant. Chromatography of a neutral solution of the Cu(II) complex of the ligands on SP Sephadex C25 resin resulted in three bands; however, examination of the bands by electronic spectroscopy at various pH values suggested that they just varied in the protonation of the carboxylate and/or were mixtures of N-based isomers which could be readily interconverted. The copper(II) complexes of diammac (L1 and L4) were able to be separated into a number of bands consisting of different N-based isomers but a single geometric isomer of the ligand in each case using chromatography on strong-acid Dowex 50Wx2 resin.[19] However, chromatography on SP Sephadex C25 resin proved less successful, with bands composed of mixtures found.[19] Alternatively, the analogous macrocycles based on cyclohexane-1,2-diamine rather than 1,2-ethanediamine proved separable into *cis/trans* isomers on weak acid SP Sephadex C25 resin, but not on Dowex 50Wx2 resin. [20] Clearly, separation conditions are specific for each ligand, and it is not surprising that suitable conditions for separation could not be readily found. Currently, the use of HPLC to establish separation protocols for such isomer mixtures are under investigation, but as yet have not been extended to a preparative scale. The sensitivity in chromatographic behaviour with pH as a result of the presence of the free carboxylate group suggested that, to differentiate between and separate the *cis-* and *trans-* isomers, a less labile octahedral metal ion which could coordinate the carboxylate would be more effective as a medium for the separation. This has been established at least with diacmac, as described later.

Nickel(II)

Attempts to isolate an octahedral complex of L2 were not successful with the alternate low spin square planar form dominating. This was isolated as a yellow solid (λ_{max} 338 nm) for which the IR spectrum clearly showed the carboxylate to be protonated and hence unavailable for coordination. It appears that it may be possible to form a high spin form of the complex in solution, as can be seen from the development of a characteristic pink/purple colour in solution under basic conditions. However, only the low spin species forms as a solid from this solution. The closely similar ligand L8 forms an isolable and X-ray structurally characterised octahedral Ni(II) complex under analogous reaction conditions.[20] The only structural difference between this ligand and L2 is the presence of the cyclohexane rings on the ethyl bridges between adjacent secondary amines, which enhance the overall rigidity of the macrocycle, but as a consequence of their bulk and hydrophobic nature probably also affect competition for axial sites by solvent molecules. The ligand field strengths of L2 and L8 also differ;[20] since strong field macrocyclic ligands appear to promote square planar complex formation, the stronger field L2 would have a greater inherent tendency towards stabilising a square planar geometry than the weaker ligand field L8. Hexadentate coordination of L2 was, however, readily achieved with inert octahedral metal ions, as described below.



L7

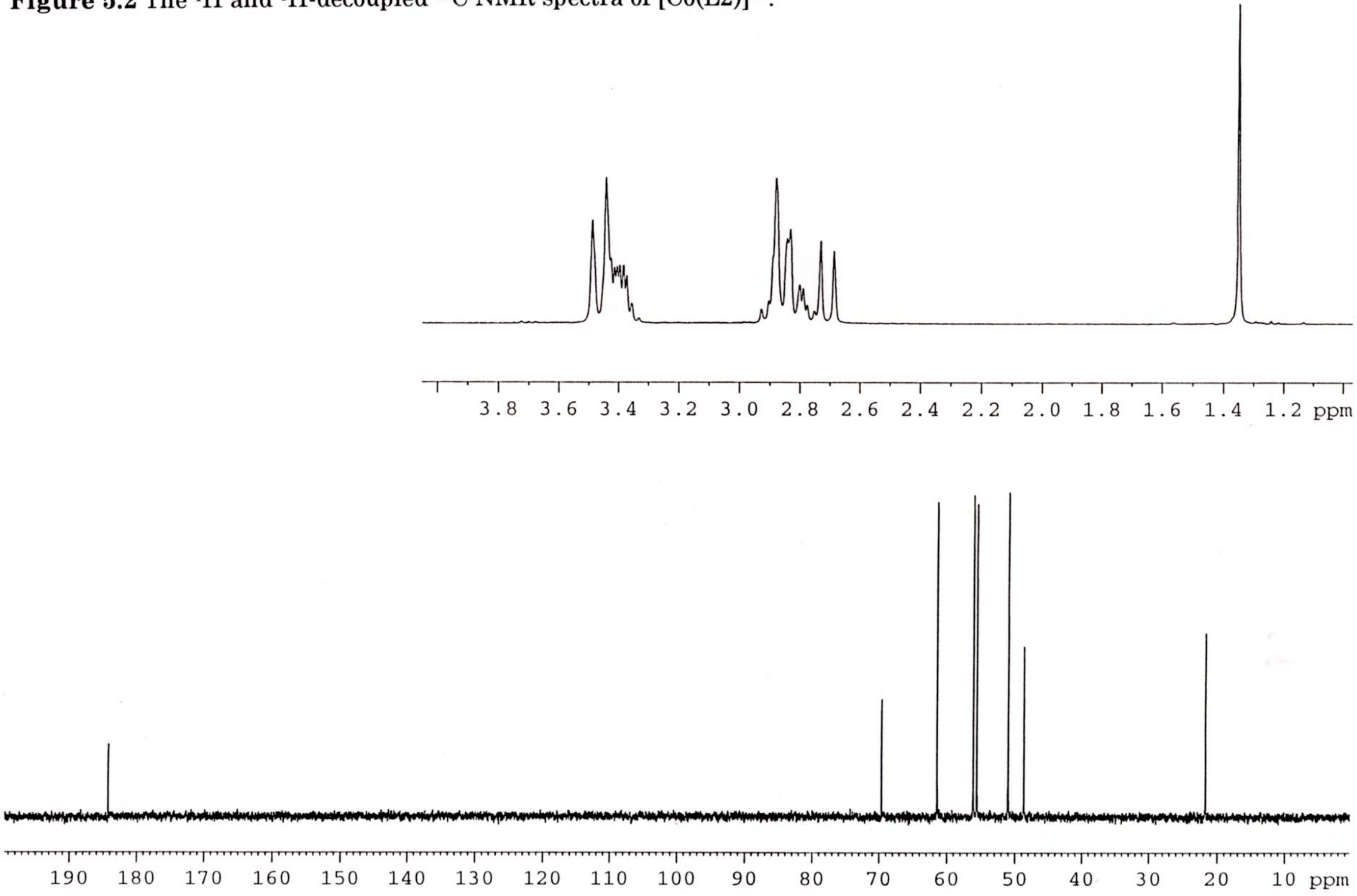


L8

Cobalt(III)

Reactions of the macrocycle L2 with $Co^{2+}_{(aq)}$ and air yielded products exclusively comprising the ligand coordinated to cobalt(III) in a 1:1 ratio, in one of three coordination modes. No complex with the macrocycle coordinated as a tetradentate ligand, involving apparently coordination of the secondary amines alone, was detected under the reaction conditions employed. The products isolated following chromatographic separation exhibited quiquedentate or hexadentate coordination. Of the two geometries with quinquedentate coordination of the ligand L2, one had the five amines coordinated in an unusual folded configuration in which the coordinated chloride ion is *trans* to a secondary amine rather than to the primary pendant amine (type IV, Figure 5.1). In this geometry, the secondary amine hydrogens adopts an *RRRR* configuration, rather than the *RRSS* configuration commonly met when the four secondary amines occupy the same plane (type III, Figure 5.1).[21] The two species are easily differentiated by their NMR spectra, with the complex with folded geometry showing experimentally 10 independent signals in the ^{1}H-decoupled ^{13}C NMR spectrum. This is consistent with non-equivalent carbon enviroments expected in such a low symmetry molecule; the more symmetrical unfolded complex would be expected to show at most 8 peaks in its spectrum (see Figure 5.2). This isomer is thought to be a kinetic rather than thermodynamic product, with 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. UV/Vis spectroscopic and electrochemical studies suggest that the folded isomer isomerises slowly to one in which the secondary amines are essentially planar in neutral solution, and that eventual substitution of the unidentate ligand by the carboxylate occurs. This process is observable in the change in the cyclic voltammogram of the folded isomer with time. The initial voltammogram shows a single reversible wave at -0.46 V. After the solution is left standing for a number of days, a second reversible wave begins to form at a slightly less negative potential, corresponding to the wave observed for the hexadentate species (see Figure 5.3). In the visible spectrum, a similar effect can be seen with the absorbance at 524 nm diminishing with time concomitant with a shift in maxima for the other two peaks(477, 365 nm) to the positions found for the hexadentate species (481, 339). During any geometric isomerisation, inversion at some of the bound secondary amines must occur. In the isomer where the amine pendant and the unidentate donor occupy *trans* positions, the secondary amines would presumably adopt the more stable *RRSS* configuration, consistent with results found for the similar pendant arm hexadentate L1 bound as a quinquedentate.[22]

Figure 5.2 The ^{1}H and ^{1}H-decoupled ^{13}C NMR spectra of $[Co(L2)]^{2+}$.



The chloropentaamine complex $[Co(HL2)Cl](ClO_4)_2$ was defined by an X-ray crystal structure analysis. A view of the cation, together with numbering scheme, appears in Figure 5.4, and atomic coordinates in Table 5.1. The secondary amines N(2), N(3) and N(4) of the macrocycle lie in a common plane with the pendant amine N(5) and the metal ion, whereas one secondary amine, N(1), lies out of this plane and *trans* to the bound chloride ion. The donors 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[23] (dien = 3-azapentane-1,5-diamine)]. The Co-N distances (Table 5.2) 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).

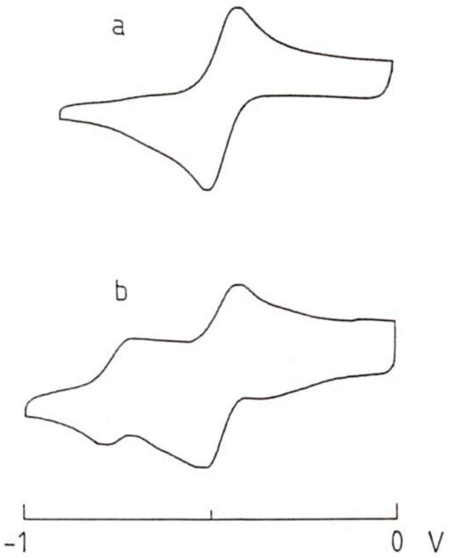


Figure 5.3 Cyclic voltammogram of a fresh solution of $[Co(L_2)H_2O]^{2+}$ (a) and the same solution after being left to stand for a day (b) to allow the formation of a second species.

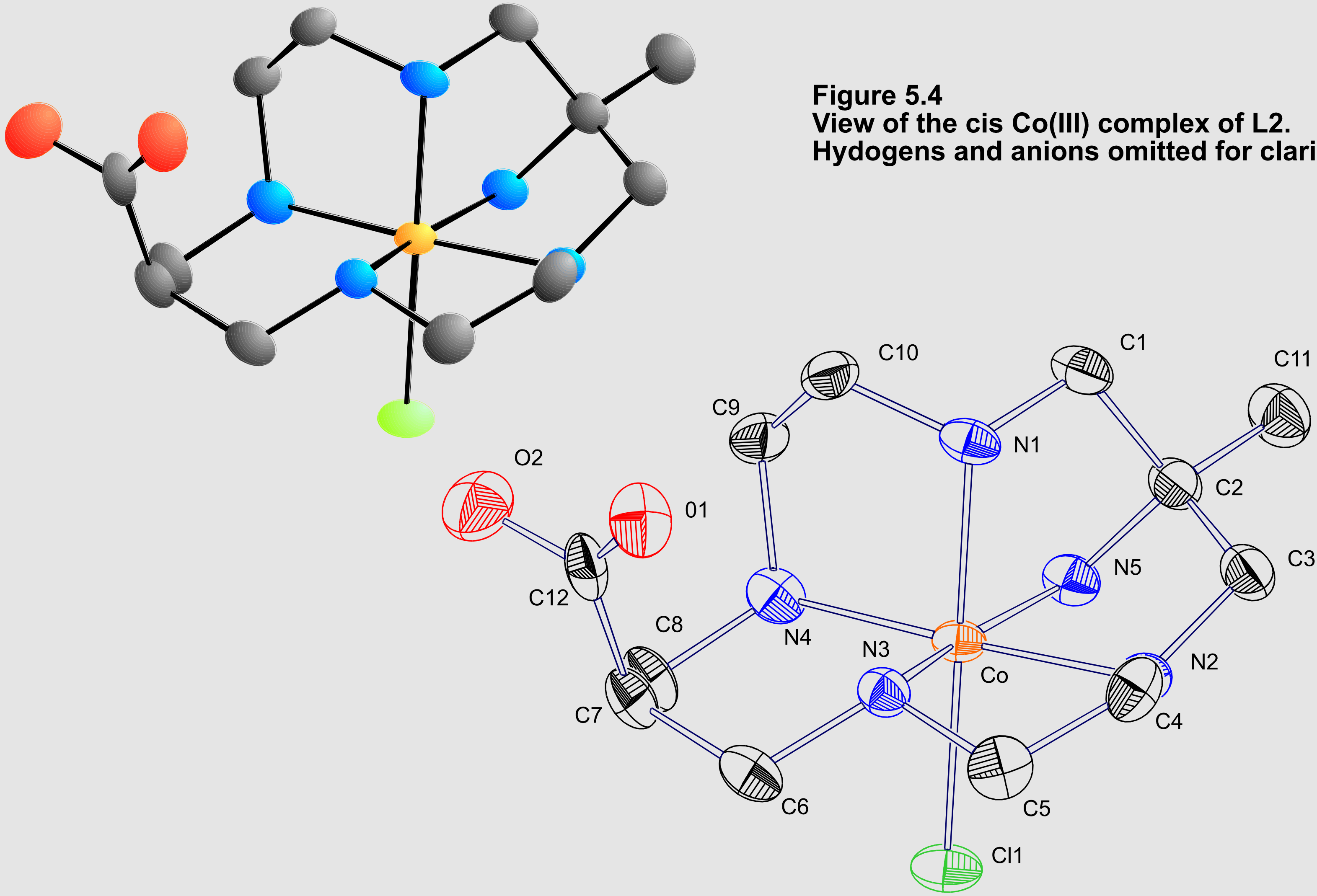


Figure 5.4
View of the cis Co(III) complex of L2.
Hydrogens and anions omitted for clarity.

Table 5.1 Positional parameters for $[Co(HL2)Cl](ClO_4)_2$.

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

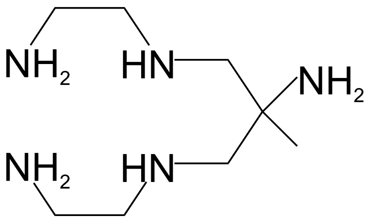
The Co-Cl distance of 2.266(2) Å is not significantly different from the distance of 2.261(1) Å reported in a structure of $[Co(L9)Cl]^{2+}$ (L9 = 5-methyl-3,7-diazanonane-1,5,9-triamine) where the primary central or 'cap' amine of the acyclic ligand was located *trans* rather than *cis* to the chloride ion,[24] but significantly longer than distances of 2.224(2) Å in *trans*-$[Co(L10)Cl]^{2+}$ and 2.236(2) Å in *cis*-$[Co(L10)Cl]^{2+}$ analogues (L10 = 6-methyl-1,4,8,11-tetra-

Table 5.2 Bond lengths (Å) for the cation of $[Co(L2)Cl](ClO_4)_2$.

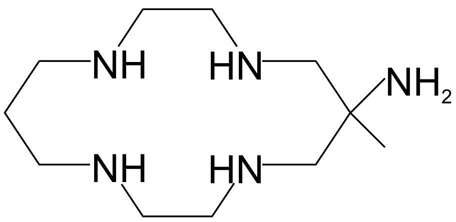
N(1)-Co(1)	1.960(5)	N(2)-Co(1)	1.940(6)
N(3)-Co(1)	1.975(5)	N(4)-Co(1)	1.975(5)
N(5)-Co(1)	1.968(5)	Cl(1)-Co(1)	2.266(2)
C(1)-N(1)	1.495(9)	C(10)-N(1)	1.481(8)
C(3)-N(2)	1.506(8)	C(4)-N(2)	1.480(8)
C(5)-N(3)	1.505(8)	C(6)-N(3)	1.486(8)
C(8)-N(4)	1.506(9)	C(9)-N(4)	1.488(8)
C(2)-N(5)	1.505(8)	C(71)-O(1)	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)		

azacyclotetradecane-6-amine) [25,26] which contain the identical macrocycle except for the absence of the uncoordinated pendant carboxylate. What is different in the latter *cis* complex is that the amine adopts the more favourable *RRSS* geometry compared with *RRRR* geometry in this case.

The octahedron is somewhat less distorted in the former (L10) case, but the average Co-N distance [1.95(4) Å] in the L10 complex is not significantly shorter than in the present example [1.96(3) Å]. Examination of Table 5.3 shows the distortion of the CoN_5Cl octahedron, with the N(5)-Co-N(3) axis being deformed towards a line joining the atoms N(1) and N(2); the angle of 167.3(2)° is essentially the same as that observed [167.4°] in the cobalt(III)



L9



L10

complex of the close analogue L10,[26] indicating a primary influence of the common coordinated pendant. Tied to this distortion is the observation that the N-Co-N angles in the five-membered rings formed on coordinating the pendant amine are small at 81.7(2) and 84.7(2)°. Coordination 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 coordinated 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 [109.0°] is normal (unlike the observation for the corresponding angle in the L10 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 expanded 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] near the pendant carboxylic acid group, whereas in the unsubstituted analogue L10 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

Table 5.3 Bond angles (°) for the cation of [Co(HL2)Cl](ClO_4)$_2$

N(2)-Co(1)-N(1)	91.1(2)	N(3)-Co(1)-N(1)	90.1(2)
N(3)-Co(1)-N(2)	86.9(2)	N(4)-Co(1)-N(1)	87.3(2)
N(4)-Co(1)-N(2)	176.9(2)	N(4)-Co(1)-N(3)	95.8(2)
N(5)-Co(1)-N(1)	84.7(2)	N(5)-Co(1)-N(2)	81.7(2)
N(5)-Co(1)-N(3)	167.3(2)	N(5)-Co(1)-N(4)	95.6(2)
Cl(1)-Co(1)-N(1)	176.7(2)	Cl(1)-Co(1)-N(2)	90.3(2)
Cl(1)-Co(1)-N(3)	93.0(2)	Cl(1)-Co(1)-N(4)	91.2(2)
Cl(1)-Co(1)-N(5)	92.5(2)	C(1)-N(1)-Co(1)	108.6(4)
C(10)-N(1)-Co(1)	109.0(4)	C(10)-N(1)-C(1)	114.1(5)
C(3)-N(2)-Co(1)	110.2(4)	C(4)-N(2)-Co(1)	109.7(4)
C(4)-N(2)-C(3)	116.3(5)	C(5)-N(3)-Co(1)	106.2(4)
C(6)-N(3)-Co(1)	118.7(4)	C(6)-N(3)-C(5)	111.4(5)
C(8)-N(4)-Co(1)	118.1(4)	C(9)-N(4)-Co(1)	108.3(4)
C(9)-N(4)-C(8)	115.7(6)	C(2)-N(5)-Co(1)	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)

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 L10 analogue, or whether there is some steric influence of the uncoordinated carboxylate group (which is absent in the analogous structure), is difficult to define, although both may contribute.

Coordination of the ligand L2 as a hexadentate necessarily involves binding of the pendant amine and carboxylate groups in *trans* dispositions, where the secondary amines must adopt *RRSS* stereochemistry as a consequence of the mode of binding of the pendants. This coordination mode has been achieved, and the geometry confirmed with an X-ray crystal structure of [Co(L2)]$(ClO_4)_2.H_2O$. A view of the molecular cation appears (with the numbering scheme) in Figure 5.5 and positional parameters in Table 5.4. Bond lengths and angles pertinent to the molecular cation appear in Tables 5.5 and 5.6 respectively.

The coordinated 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 significantly shorter than that in the quiquedentate [1.95(2) Å compared with 1.96(3) Å]; however, it is not obvious whether this is the result of the constraints of the additional coordination 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 coordination of the primary amine and the carboxylate. The equatorial five-membered chelate

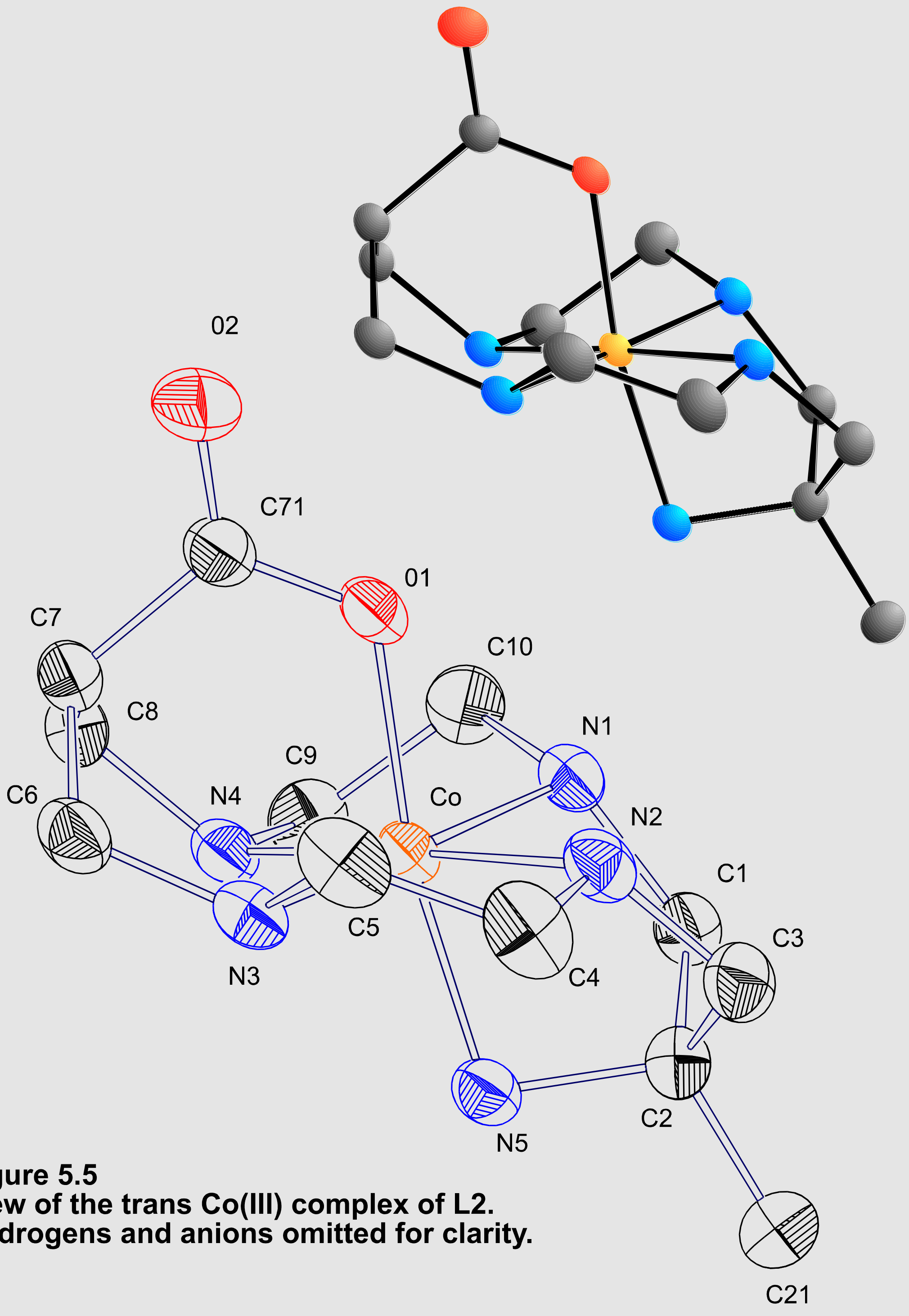


Figure 5.5
View of the trans Co(III) complex of L2.
Hydrogens and anions omitted for clarity.

rings are slightly flattened skew conformations, 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°, and in C(3)-N(2)-C(4) and C(1)-N(1)-C(10) [opened out to 113.3, 116.1° respectively] (see Table 5.6). The six-membered skew-boat rings formed by coordination of the carboxylate O(1) exhibit less strain, with angles around C(71) close to ideal [120°] 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 coordination 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 coordination 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 Å; 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.[27] In the latter case the short Co-N distances may reflect contraction of the octahedral face caused by the relatively short Co-O

Table 5.4 Positional parameters for $[Co(L2)](ClO_4)_2 \cdot H_2O$.

Atom	10^4x	10^4y	10^4z
Co(1)	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 5. 5 Bond lengths (Å) for the cation of [Co(L2)]$(ClO_4)_2 \cdot H_2O$.

N(2)-Co(1)	1.950(2)	O(1)-Co(1)	1.899(2)
N(3)-Co(1)	1.959(2)	N(5)-Co(1)	1.956(2)
N(4)-Co(1)	1.949(2)	N(1)-Co(1)	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)		

distances. Thus, overall, there is a modest 'compression' of the coordination sphere despite the evident angle strain introduced by hexadentate coordination. Both structures exhibit some significant non-bonded interactions involving hydrogen bonding between amine hydrogens and (where relevant) coordinated chloride, carboxylate, perchlorate and water oxygens. The NH...Y distances fall within the range 2.0 -2.7 Å, and may contribute to stabilisation 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 quiquedentate structure which may contribute to stabilisation of the uncommon *RRRR* geometry observed.

Table 5.6 Bond angles (°) for the cation of $[Co(L2)](ClO_4)_2 \cdot H_2O$.

O(1)-Co(1)-N(2)	90.6(1)	N(3)-Co(1)-N(2)	87.9(1)
N(3)-Co(1)-O(1)	88.8(1)	N(5)-Co(1)-N(2)	82.3(1)
N(5)-Co(1)-O(1)	170.5(1)	N(5)-Co(1)-N(3)	97.3(1)
N(4)-Co(1)-N(2)	176.3(1)	N(4)-Co(1)-O(1)	92.7(1)
N(4)-Co(1)-N(3)	93.7(1)	N(4)-Co(1)-N(5)	94.2(1)
N(1)-Co(1)-N(2)	90.0(1)	N(1)-Co(1)-O(1)	88.5(1)
N(1)-Co(1)-N(3)	176.5(1)	N(1)-Co(1)-N(5)	85.2(1)
N(1)-Co(1)-N(4)	88.5(1)	C(3)-N(2)-Co(1)	109.1(2)
C(4)-N(2)-Co(1)	108.1(2)	C(4)-N(2)-C(3)	113.3(2)
C(71)-O(1)-Co(1)	120.7(2)	C(5)-N(3)-Co(1)	105.3(2)
C(6)-N(3)-Co(1)	114.6(2)	C(6)-N(3)-C(5)	112.7(2)
C(2)-N(5)-Co(1)	100.8(2)	C(8)-N(4)-Co(1)	114.6(2)
C(9)-N(4)-Co(1)	107.9(2)	C(9)-N(4)-C(8)	113.6(2)
C(1)-N(1)-Co(1)	109.2(2)	C(10)-N(1)-Co(1)	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)		

No evidence for the *cis* isomer of acammac (L5) was found in the products of the complexation reaction. This is at first surprising, as the NMR studies of the crude acammac suggest that the proportion of L5 present in the original ligand synthesis may have been as high as 20%, as discussed in the previous chapter. NMR spectroscopy of all fractions from the complexation reaction show no evidence of a *cis* isomer, although the presences of a small percentage may go undetected. This outcome was a result of the synthetic method used to isolate this particular batch of the hydrochloride salt of the free ligand. In all early syntheses of the hydrochloride salt of acammac, the ligand was crystallised from very concentrated acidic solution. It was found for diammac that this procedure also resulted in the isolation of only the *trans* isomer (L1). Isolation of one isomer was not a concern, since at the time only one isomer was also known for diammac; indeed, stereospecificity in formation could be argued as more likely for acammac than diammac because of the potentially stronger axial interaction of the carboxylate group directing the final condensation. With the discovery of the highly soluble *cis* isomer of diammac, a search revealed the *cis* isomer of acammac as well. Later complexation reactions with other metal ions, if done without the ligand crystallisation step, resulted in the formation of complexes of the minor *cis* isomer. However, the dominant *trans* isomer (≥ 80%) remained the focus of most interest principally because of its accessibility and the more extensive parallel chemistry with *trans* diammac.

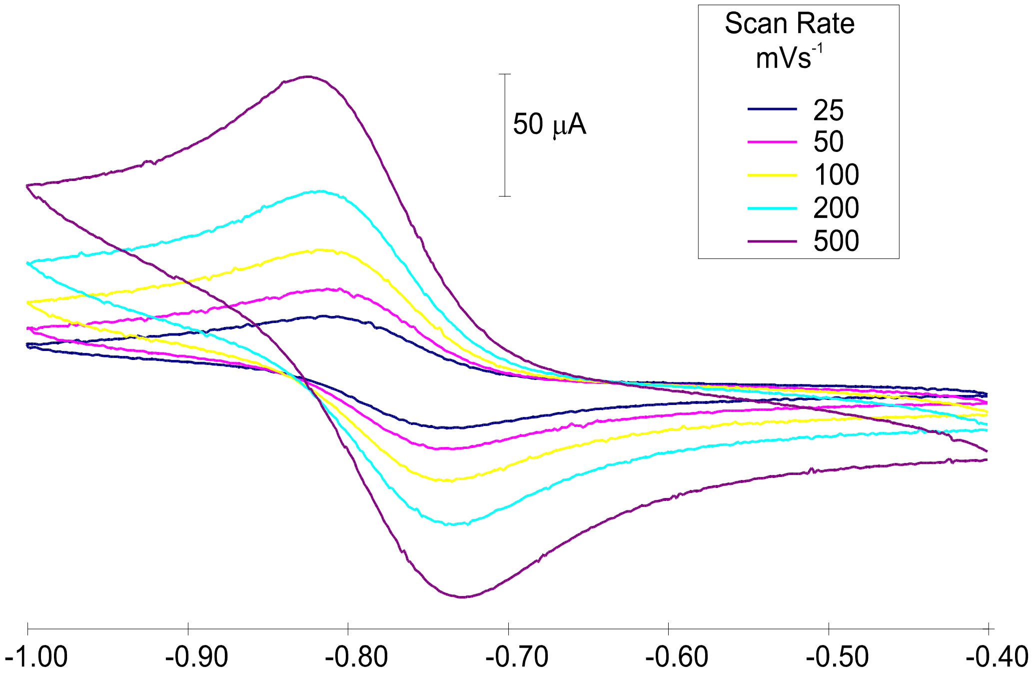


Figure 5.6 Cyclic voltammograms for the hexadentate Co(III) complex of L2 at different scan rates, demonstrating the diffusion controlled quasi-reversible behaviour of the $Co^{III/II}$ couple.

In the $[Co(L2)]^{3+}$ ion, physical properties do reflect the short Co-donor distances associated with an encapsulating macrocyclic ligand. The $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$ transitions are at slightly higher energy than for CoN_5O^{2+} chromophores generally [e.g. 481 nm and 339 nm versus 487 nm and 345 nm for $[Co(en)_2(gly)]^{2+}$][28] (gly = glycine). The cobalt(III)-cobalt(II) redox couple [$E_{1/2}$ -0.42 V vs Ag/AgCl] is quasi-reversible on the voltammetric timescale (see Figure 5.6), and more negative than for other acetatopentaamine ions [e.g. $E_{1/2}$ -0.32 V for acetatopentaamminecobalt(III)][29]. The difference in redox couples ($\Delta E_{1/2}$) for $[Co(L^n)^{m+}$ - $Co(NH_3)_5X^{m+}]$ varies from -0.10 V [L^n = L2, X = acetate] to -0.51 V [L^n = L1, X = ammonia]; likewise, shifts in the low-energy electronic transition maxima vary from 260 cm^{-1} for the acid to 1320 cm^{-1} for the amine. This is consistent with a less 'compressed' environment in L2 compared with L1. Although L2 is a sterically efficient ligand, it introduces less 'compression' than the hexaamine L1. Generality of this observation can be seen with a range of metal ions, and will be discussed later in the chapter.

Chromium(III)

Although both polyamine and polycarboxylate complexes of chromium(III) are quite common, coordination of macrocycles with carboxylate pendants involving all donors seems to be inherently more difficult than for macrocycles with amine pendants. Coordination of L1 to chromium with conventional synthetic methods was readily achieved,[4] whereas coordination of L2 with Cr(III) was not facile. Attempts to use the same procedure as employed with L1 for L2 results in very low yields of hexadentate complex as well as small amounts of tetradentate and quinquidentate forms, the major product being metal hydroxides. Variations to the method were not particularly helpful, but the target complex was obtained albeit in reduced yield.

The orange crystals produced from the synthesis were assigned as the hexadentate form of the complex. The infrared spectra of $[Cr(L2)]^{3+}$ confirms the presence of a coordinated $-COO^-$ group with an absorbance found at 1620 cm^{-1}. The expected primary amine stretch, observed at 1595 cm^{-1} in the case of the Cr(III) complex of L1, is masked for L2 by the large carboxylate peak. The infrared spectra was clearly analogous to that found for the hexadentate

Co(III) complex of L2, which has been structurally characterised by an X-ray crystal structure. Isomers other than the hexadentate species showed more complex spectra due to their lower symmetry.

The electronic spectrum of $[Cr(L2)]^+$ exhibited three transition from the $^4A_{2g}$ ground state in a manner consistent with that of an octahedraly coordinated but tetragonaly distorted d^3 ion. Strong quartet-quartet transitions to the $^4T_{1g}$ (365 nm) and $^4T_{2g}$ states (517 and 415 nm) were observed. Spin-forbidden transition to the $^2T_{1g}$ and ^2E_g states were not observed; however, these are usually very weak and may have been masked by the absorbance centred at 517 nm. The greater splitting of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition in the L2 complex (517 and 415 nm) compared with the L1 complex (a single absorbance at 427 nm) is related to the presence of the coordinated carboxylate oxygen lowering the symmetry. The higher molar absorptivities in the CrN_5O versus CrN_6 pendant arm macrocyclic complexes is also consistent with the lower symmetry in the former. The general trend of a lowering of the ligand field strength observed in the Co(III) complex of L2 compared with L1 is also apparent in the Cr(III) complex, especially in the transition to the $^4T_{1g}$ state which is moved from 332 nm in the complex of L1 to 365 for L2. The change in the position of the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition is more difficult to quantify due to the splitting, but a trend towards lower energy from L1 to L2 seems to apply. It may be assumed, by analogy to the Co(III) complex, that the lower field strength is in part the result of the reduction in steric strain by the introduction of the six membered chelate ring necessary to coordinate the deprotonated carboxylate together with the substitution of a different donor into the coordination sphere.

Iron(III)

Whereas a large number of polyimine complexes of Fe(III) have been reported, the few known hexaamine complexes of iron(III) tend to be relatively unstable in solution due to a tendancy to undergo oxidative dehydrogenation reactions. A notable exception to this trend is the Fe(III) complex of L1, which was found to be stable essentially indefinitely. The high stability of this complex has in part been related to the relatively rigid 'compressed' structure of the complex and a consequently much more negative redox couple than that found for other hexamines, thus making the reduction of Fe(III) to Fe(II) more difficult and consequently stopping any intermolecular oxidative dehydrogenation chemistry. The conversion of amines to imines through the reduction of iron(III) is thought to be the first step in the mechanism in which iron(III) hexamine complexes decompose. The mixed amine-carboxylate capped L2 complex is, like L1, stable for extensive periods. Replacing both pendant amines with carboxylate groups also allows the formation of a stable hexadentate complex, as is shown by the synthesis of the Fe(III) complex of L3 reported by Curtis and coworkers.[6]

The formulation of the complex isolated with L2 suggested by the microanalysis is consistent with that found for some other bound carboxylates in which the carboxylate oxygen not attached to the metal ion interacts with a proton, resulting in a third perchlorate being included in the molecule. For example, similar behaviour has been shown in a pendant carboxylate bound to a cobalt(III) ion and defined in that case by a crystal structure analysis.[20] The presence of the carboxylate absorbance at 1627 cm^{-1} in the infrared spectra rules out the possibility of a dangling protonated carboxylate and strongly suggests that the carboxylate is bound to the metal ion. The simplicity of the infrared spectra, as well as its close similarity to that of the structurally characterised cobalt(III) complex of the same ligand, also supports the premise that the ligand is in the arrangement in which both pendants are coordinated. The electronic spectra of the complex is consistent with the proposed structure, and is the quasi-reversible Fe$^{II/III}$ couple observed (see Figure 5.7), is indicative of the absence of oxidative dehydrogenation processes not expected to occur for the hexadentate complex.

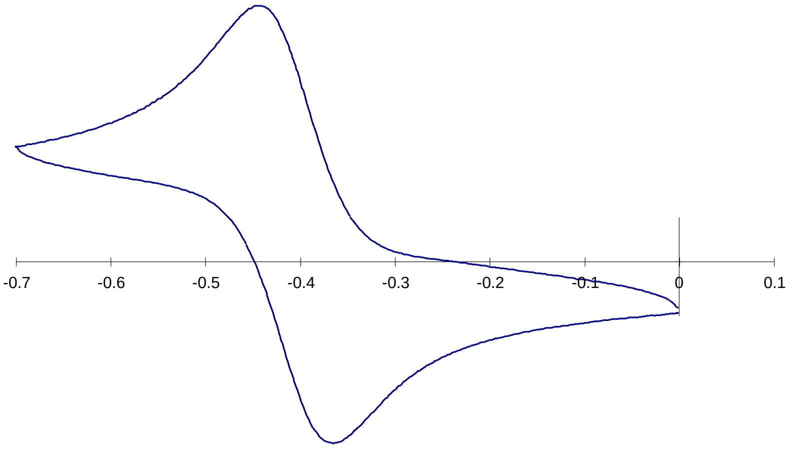


Figure 5.7 The cyclic voltammogram for the hexadentate Fe(III) complex of L2, demonstrating its quasireversible nature.

Rhodium(III)

While the hexadentate form of the complex of L1 forms, no evidence was found for the formation of the hexadentate form of L2 under similar reaction conditions. The complex isolated crystallised as the quiquedentate form $[Rh(HL2)Cl](ClO_4)_2$ with the carboxylate protonated and unbound, as is clearly shown by the infrared spectroscopy (-COOH stretch at 1720 cm^{-1}). Further, the electronic spectrum (λ_{max} 347, 278 and 230 nm) is consistent with a tetragonally distorted chromophore analogous to the spectrum of the known $[Rh(L1)Cl]^{2+}$ (λ_{max} 342, 294, 281 nm).[4] Attempts to force the carboxylate to coordinate by long periods of reflux (even months) in basic solution all failed. The apparent preference of rhodium for chloride donors may have some role to play. Previously, it has been observed that a branched acyclic pentaamine binds preferentially as a RhN_3Cl_3 complex, and only converts to the RhN_5Cl chromophore with extended reaction.[30] Apart from ligand preference, possible strain in the putative hexadentate complex of L2 with the larger rhodium(III) ion encapsulated may also act against its formation.

5.3.2 Metal Complexes of *trans*-Diacmac (L3)

The diacmac ligand is formed and recovered only in very low yield (<5%), and hence extensive examination of its chemistry is somewhat limited by ligand availability. Previously, Curtis and coworkers[5] have reported this ligand, isolated in equally low yield. The only complexes reported by that group were of the *trans* isomer (L3), which is the predominant geometric form and, like its analogues in the diammac and acammac systems, the least soluble as a hydrochloride salt. The only X-ray structural study of a hexadentate complex of diacmac extant before this work was of the Fe(III) complex of L3.[6] This showed clearly that the *trans* isomer of diacmac acts as an efficient pseudo encapsulating ligand, with both carboxylates bound in *trans* positions to the octahedral ion. The Fe-N bond lengths were substantially longer in this complex than those found in the analogous complex of L1 (1.996 Å for $Fe(L3)^+$ compared with 1.965 Å for $Fe(L1)^{3+}$), but still shorter than those observed for unsubstituted cyclam complexes of iron(III). The carboxylate pendants of L3 approach the metal ion much more closely (1.895 Å) than the primary amine pendants of L1 (1.982 Å), but this is to be expected considering the charged and sterically efficient nature of the carboxylate pendant. The present study has extended the coordination chemistry of diacmac by a brief examination of the Ni(II) chemistry, and, particularly, an investigation of the Co(III) chemistry where separation and finite identification of the *cis* and *trans* isomers has been achieved.

Nickel(II)

As with L2, it proved difficult to isolate the high spin Ni(II) complex of diacmac in which both pendants are coordinated. The yellow low spin square planar complex was readily isolated from solution, which is different from the high solubility exhibited by the majority of the square planar complexes of analogues. This yellow solid is most likely a mixture of both the *cis* and *trans* forms of the diacmac ligand, probably in proportions similar to that found for the original hydrochloride salt of the crude ligand employed in the synthesis.

This outcome is anticipated if one considers that in the square planar form the pendants are unable to contribute to the coordination sphere and hence the two geometric isomers are likely to have a modest effect on the solubility of their complexes.

The carboxylate groups in this complex show one absorbance at 1731 cm^{-1} in the infrared spectrum, suggesting both are unbound and protonated. Attempts to record NMR spectra of a solution of the yellow solid were unsuccessful since in both acid and basic pH conditions an equilibria with high spin products was apparently established, leading to paramagnetic broadening. The addition of base readily converted the solution to a pink colour which can be assumed to be a form where the pendants may be coordinated. However, on precipitation or slow crystallisation, only the yellow low-spin form was recovered. However, crystallisation from acidified D_2O yielded what appeared to be two high spin products. The first product that formed was a pink solid which shows evidence of two forms of carboxylate in the infrared spectrum, one unprotonated and hence probably coordinated (1605 cm^{-1}) and the other protonated and consequently uncoordinated (1728 cm^{-1}). It can be assumed in this species that only one of the carboxylates is coordinated, with the other site on the metal ion being occupied by solvent or another ion such as chloride. On further standing, violet crystals form. This species shows two carboxylate absorbances in the same region (1723 and 1702 cm^{-1}), consistant with carboxylate groups being protonated and hence not coordinated. Solubility differences between species in D_2O and H_2O presumably direct crystallisation of high-spin octahedral species in the former solvent system. Based purely on the amounts isolated, it could be proposed that the violet solid is the nickel complex of the *trans* isomer (L3) since at least four times as much of it forms as does the pink solid, which by analogy is possibly the complex of the *cis* isomer (L6). Although a simplistic proposal, the infrared spectra are sufficiently different overall to support separation of geometric isomers. Unfortunately, the small amounts of crystals isolated were not of a quality suitable for X-ray crystallography, which would appear the most effective way of confirming the proposals.

Cobalt(III)

The cobalt(III) complexes of L3 formed readily in a manner analogous to that found for L1. This was anticipated, since *bis* and *tris* amino acid complexes of cobalt(III) with up to three bound carboxylates are well know and form reasonably readily. In this case, the *cis* and *trans* isomers of the ligand were easily separated by cation exchange chromatography on Dowex 50Wx2 resin. The first 3 bands isolated from the column were all shown to be different complexes of the *trans* isomer L3 with the single complex of the *cis* isomer (L6) being isolated as a separate final band. NMR studies of complexes of L3 isolated as solids from the first three bands showed them to be isomerically pure, with no splitting or multiplicity of peaks suggestive of the presence of a complex of L6. The *cis* isomer isolated from the fourth band will be discussed later in the chapter. The inert complexes produced in this chemistry lend themselves to facile separation, with no rapid interconversions or equilibria to add to the complexity of the task. Although not pursued, the free ligands could be recovered from the cobalt complexes if required by zinc reduction and subsequent removal of the cobalt(II) ion with concentrated acid followed by chromatography, techniques employed for the ligand recovery from cobalt(III) macrocyclic cage complexes.[31]

The first band isolated produced an orange pink solid for which infrared spectroscopy showed an absorbance in the carboxylate region at 1613 cm^{-1} with a shoulder at approximately 1630 cm^{-1}. These absorbances are characteristic of coordinated deprotonated carboxylates. The ^{1}H NMR spectrum of the complex shows only a single poorly resolved peak at δ 6.9 in the amine region, suggesting that all the amine protons are in the same or a very similar environment and hence, as supported by the rest of the spectrum, that the molecule is highly symmetrical. The high symmetry of the complex is supported by the proton decoupled ^{13}C NMR spectrum, which has only 4 peaks (Figure 5.8). The ^{1}H-decoupled ^{13}C NMR shows a peak readily assignable to a carboxylate at 184.4 ppm. Three further signals at 50.0, 50.7 and 55.7 ppm arise from the two non-equivalent C-$\underline{C}$-N methylene groups (in the five- and six-membered chelate rings) and the -H$\underline{C}$(COO^{-})- group. The high symmetry of the molecule and the fact that both carboxylates are coordinated suggested that this is the octahedral complex of L3 with both pendant bound in a ‘vice-like’ configuration. This was later confirmed by an x-ray crystal structure of the complex. A view of the molecular cation appears in Figure 5.9, together with atom numbering, whereas atomic coordinates are given in Table 5.7. The

Figure 5.8 The ^{1}H and ^{1}H-decoupled ^{13}C NMR spectra of $[Co(L3)]^{1+}$.

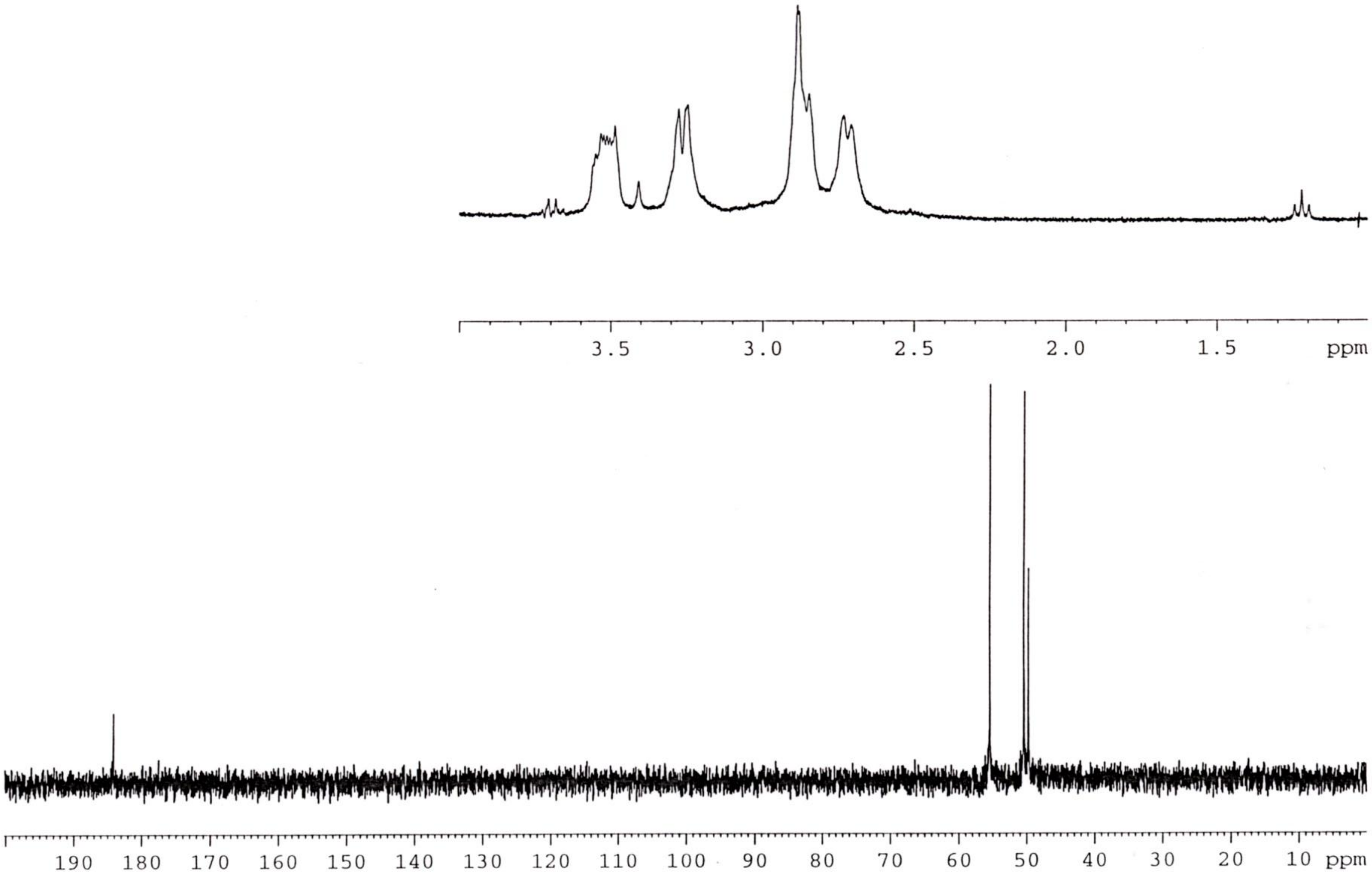
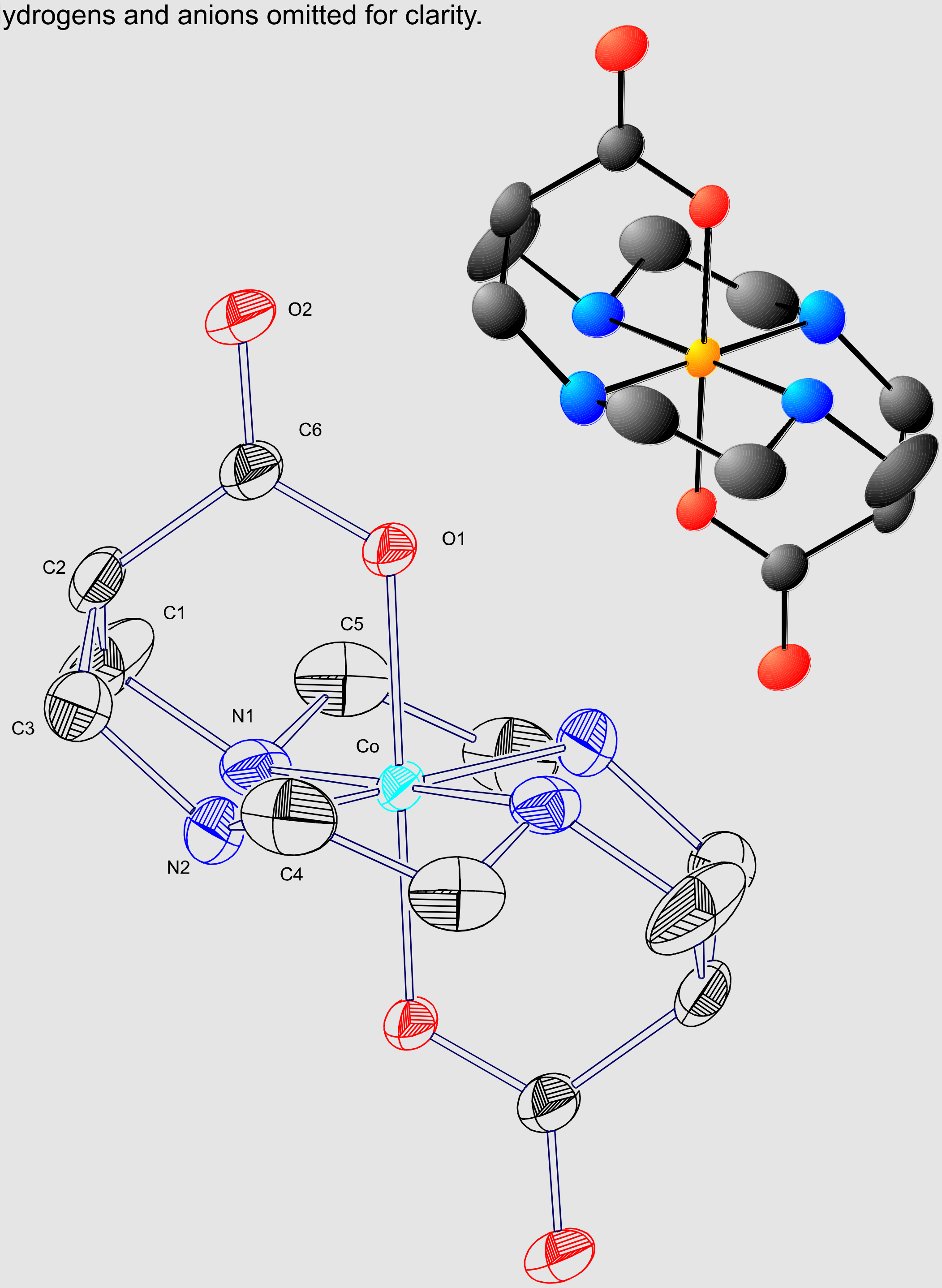


Figure 5.9
View of the trans Co(III) complex of L3.
Hydrogens and anions omitted for clarity.



bond distances and angles in the molecular cation appear in Table 5.8 and 5.9 respectively.

The two facially coordinated units in the structure involving two secondary amines and a pendant carboxylate group are symmetry-related and equivalent. The structure shows disorder within the uncoordinated perchlorate oxygens and, more importantly, disorder of the ethylene residues between the δ and λ configurations. The positions shown in Figure 5.9 for atom C(4) and C(5) are those assigned the highest occupancy (0.55). The Co necessarily lies within the plane defined by the nitrogen atoms. The N-Co-O bonds are all reasonably close to ideal (91.4(1), 88.6(1), 92.7(1) and 87.3(1)°), and the O(1)-Co bond is not bent back towards a line joining N(1) and N(2), as is the case in the strained diammac complex. The six membered chelate ring formed by the coordination of N(1) and N(2) to the Co is forced into a 'boat' conformation by the coordination of the pendant carboxylate oxygen. The bond angles in this ring (Co-N-C; 113.9(3), 116.3(3)° and N-C-C; 112.3(4), 114.7(4)°) are opened out slightly from the ideal 109.5° presumably to accommodate the preferred oxygen and nitrogen bond lengths. Coordination of O(1) creates two additional six-membered chelate rings, which display no significant strain. The O1-C6-C2 angle (121(4)°) is close to ideal, as are the C6-C2-C1 (110.0(5)°) and C6-C2-C3 (111.0(4) °) angles. Similar behaviour was observed for the carboxylate capped end of the *trans* acammac structure (Section 5.3.1). This contrasts with the significant strain in the amine capped component of

Table 5.7. Positional parameters for [Co(L3)]ClO_4

Atom	*x*	*y*	*z*
Co(1)	0.5000	0.0000	0.0000
Cl(1)	0.5000	0.5965(2)	0.2500
O(1)	0.6277(2)	-0.0055(3)	0.1674(2)
O(2)	0.7676(2)	0.1128(3)	0.3317(2)
O(3)	0.5862(3)	0.5150(5)	0.3487(4)
O(4)	0.5437(6)	0.7290(9)	0.2518(7)
O(4')	0.5557(6)	0.633(1)	0.2048(6)
N(1)	0.4525(3)	0.1898(4)	0.0131(3)
N(2)	0.5851(3)	0.0942(4)	-0.0310(3)
C(1)	0.5449(4)	0.3002(5)	0.0862(5)
C(2)	0.6601(4)	0.2425(5)	0.1462(4)
C(3)	0.6692(4)	0.2044(6)	0.0568(4)
C(4)	0.6536(9)	-0.033(2)	-0.021(1)
C(4')	0.608(1)	-0.013(2)	-0.087(1)
C(5')	0.359(1)	0.149(2)	0.016(1)
C(5)	0.4195(9)	0.166(1)	0.0758(10)
C(6)	0.6890(3)	0.1093(5)	0.2235(3)

acammac or the caps in diammac, and the presence of an addition atom in the coordinated pendant chelate rings in the carboxylate capped system is clearly important in relieving strain. The nitrogens in each six-membered chelate ring adopt a geometry with both associated hydrogens pointing to one side of the nitrogen plane in the view shown in Figure 5.9.

Table 5.8 Bond lengths (Å) for the cation of [Co(L3)]ClO_4.

Co(1) -O(1)	1.904(2)	Co(1) -N(1)	1.949(3)
Co(1) -N(2)	1.942(4)	O(1) -C(6)	1.280(4)
O(2) -C(6)	1.222(4)	N(1) -C(1)	1.485(6)
N(1) -C(5')	1.58(2)	N(1) -C(5)	1.41(1)
N(2) -C(3)	1.469(6)	N(2) -C(4)	1.53(2)
N(2) -C(4')	1.51(1)	C(1) -C(2)	1.504(7)
C(2) -C(3)	1.523(7)	C(2) -C(6)	1.525(6)
C(4) -C(5)	1.48(2)	C(4') -C(5')	1.49(3)

The Co-N bond lengths (1.942(4) and 1.949(3) Å) are somewhat shorter than found in non-macrocyclic species [as exemplified by Co-N 1.964(7) Å in $Co(en)_3^{3+}$ (en = ethane-1,2-diamine)], but similar to those found in other macrocyclic species, as will be discussed later in the chapter. The Co-O (1.904(2) Å) bond length is typical of that found for cobalt complexes of amino-acids [27] and for the other coordinated carboxylates discussed in this chapter. It is just slightly longer than that found for the complex of L2 (1.899(2)Å), the very slight 'compression' in the L2 complex possibly influenced by of a short Co-N bond in the *trans* position rather than, as in the present case, an equivalent Co-O bond in the *trans* position.

The electronic spectrum of the $[Co(L3)]^+$ complex is distinctively different to that found for L1 and L2 analogues, as is to be expected in the shift from N_6 to N_5O and to *trans*-N_4O_2 donor sets. The most obvious effect is the splitting of the

Table 5.9 Bond Angles (°) for the cation of [Co(L3)]ClO_4.

O(1) -Co(1) -O(1)i	180.00	O(1) -Co(1) -N(1)	91.4(1)
O(1) -Co(1) -N(1)i	88.6(1)	O(1) -Co(1) -N(2)	92.7(1)
O(1) -Co(1) -N(2)i	87.3(1)	N(1) -Co(1) -N(1)	180.00
N(1) -Co(1) -N(2)	92.2(2)	N(1) -Co(1) -N(2)i	87.8(2)
N(2) -Co(1) -N(2)	180.00	Co(1) -N(1) -C(1)	113.9(3)
Co(1) -N(1) -C(5')	104.6(6)	Co(1) -N(1) -C(5)	107.4(6)
C(1) -N(1) -C(5')	128.6(7)	C(1) -N(1) -C(5)	104.3(6)
Co(1) -N(2) -C(3)	116.3(3)	Co(1) -N(2) -C(4)	104.0(6)
Co(1) -N(2) -C(4')	110.7(7)	C(3) -N(2) -C(4)	105.3(6)
C(3) -N(2) -C(4')	121.9(8)	N(1) -C(1) -C(2)	114.7(4)
C(1) -C(2) -C(3)	112.0(4)	C(1) -C(2) -C(6)	110.0(5)
C(3) -C(2) -C(6)	111.0(4)	N(2) -C(3) -C(2)	112.3(4)
N(2) -C(4) -C(5)	107.7(8)	N(2) -C(4') -C(5')	102(1)
N(1) -C(5') -C(4')	110(1)	N(1) -C(5) -C(4)	105.9(9)
O(1) -C(6) -O(2)	123.0(4)	O(1) -C(6) -C(2)	115.7(3)
O(2) -C(6) -C(2)	121.3(4)		

symmetry generated i = 1-x, -y, -z

parent $^1T_{1g} \leftarrow {}^1A_{1g}$ transition into two ($^1E \leftarrow {}^1A_1$ and $^1A_2 \leftarrow {}^1A_1$) bands (421 and 511 nm). This is consistent with the introduction of two oxygen donors in the *trans* sites; splitting would be less for a *cis*-CoN_4O_2 chromophore.

The electrochemistry exhibits a quasi-reversible wave at -0.69 V which is consistent with observations for other macrocyclic complexes and can be assigned to a $Co^{III/II}$ couple. No other electroactive groups are present, consistent with the absence of other redox processes. The Co(II) reduction occurs only at very negative potentials (>-1.8 V).

The second band isolated from the reaction was a pink solution which changed to green on evaporation to dryness. Infrared and UV-visible spectroscopy showed it to be the same substance as isolated from the third band, and it has been identified as a *trans*-dichlorotetraaminocobalt(III) species. The green colour is characteristic of these compounds with the low-energy electronic maxima at 615 and 450 nm arising from splitting of the $^1T_{1g}\leftarrow{}^1A_{1g}$ parent transition. The ^1H-decoupled ^{13}C NMR spectrum, with only four signals at 45.7, 50.7, 53.7 and 175.5 ppm, is fully consistent with the *trans* geometry in the complex and also confirmed that this was an isomerically pure substance with no evidence of the other ligand isomer.

When the green solid was redissolved and the solution stirred at pH 10 overnight, an orange solution resulted, which had the same UV/Vis spectrum as band 1, further confirming the ligand species in this sample as the *trans* isomer (L3), and indicating that 'lid-on' reactions forming the hexadentate are reasonably facile. The original pink colour of the solution in band 2 was most probably that of an aqua complex which anated to produce the *trans*-dichlorocobalt(III) complex in the hydrochloric acid solution. The third band off the column also precipitated as a *trans*-dichlorocobalt(III) species. Once again, its purity was confirmed by NMR spectroscopy and the identity of the ligand as L3 was also confirmed by its conversion to the fully structurally characterised 'capped' version of the complex in basic solution.

5.3.3 Metal Complexes of the *cis*-Isomers of Diacmac and Acammac (L6 and L5)

The *trans* isomers of acammac and diacmac predominate, and the *cis* isomers are highly soluble as the hydrochloride salt. Complexes of the minor isomer can also differ substantially in solubility from those of the major isomer. However, with some metal ions, the solubility behaviour observed for the free ligand salts is reversed, and the minor isomer may be preferentially crystallised. Alternatively, complexation may permit effective chromatographic separation of the isomers.

During studies directed principally towards the octahedral complexes of the major isomers, L3 and L2, the Ni(II) complex of L5 and the Co(III) complex of L6 were isolated and structurally characterised. These form an interesting contrast to the octahedrally bound forms of L2 and L3 since the pendants, being on the same side of the macrocyclic ring, can force different coordination geometries. This has been clearly defined recently for diammac, where the *cis* isomer (L4), binds large metal ions in a 'nest like' geometry employing all donor groups, whereas the *trans* isomer (L1) cannot bind to the same metal ions as a hexadentate ligand.[19] In the case of the small cobalt(III) ion complex of L6, the result simply involves the metal being conventionally coordinated in the centre of the flat macrocyclic ring with one of the pendants occupying an axial position and the other remaining uncoordinated (see Figure 5.13). The sixth coordination site of the metal ion, inaccessible to the second pendant of the ligand in the geometry adopted, is occupied by a water molecule. However, in the case of the Ni complex of L5, a more novel outcome is favoured in which a dimer is formed with the two Ni centres linked by the two bridging carboxylate groups, leaving one of the ring nitrogens uncoordinated in each half of the dimer and each Ni with an N_4O_2 donor set (see Figure 5.10). In neither case is a 'nest-like' geometry such as achieved by *cis* diammac even with a relatively small chromium(III) ion[32] observed. However, this does not imply that such arrangements are forbidden, although such a shape would force the two charged carboxylate groups in diacmac close together, and thus may account for the alternate geometry encountered here. Further structural studies alone will allow detailed comment on this issue.

Ni(II) *cis*-acammac (L5)

The nickel complex of L5 crystallises preferentially from a solution containing both the *cis* and *trans* forms of the ligand as a dimer in which the carboxylate from each pendant bridges to the nickel centre of the other macrocycle, resulting in a dimer linked by two carboxylate bridges. A view of the molecular cation together with the atom numbering scheme is given in Figure 5.10. Positional parameters appear in Table 5.10 and bond lengths and bond angles for the cation in Tables 5.11 and 5.12 respectively.

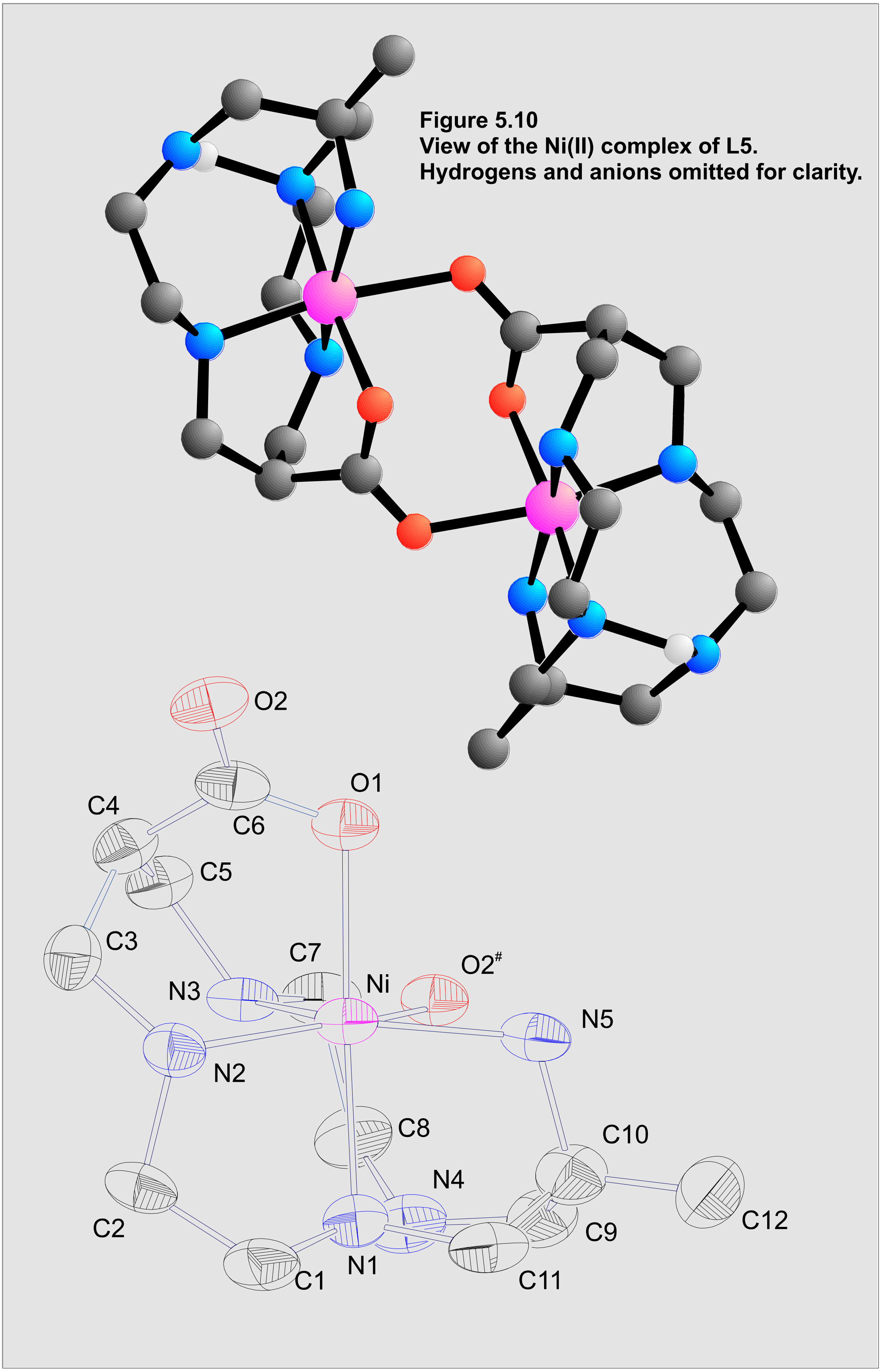


Figure 5.10
View of the Ni(II) complex of L5.
Hydrogens and anions omitted for clarity.

Table 5.10 Position parameters for [Ni(L5)]ClO_4.

Atom	10^4x	10^4y	10^4z
Ni	626(1)	1340(1)	834(1)
O(1)	-379(5)	1758(6)	62(2)
O(2)	457(6)	1044(6)	-713(2)
N(1)	1550(7)	718(8)	1611(2)
N(2)	2628(6)	351(7)	597(2)
N(3)	1708(7)	3571(7)	818(2)
N(4)	1076(8)	3365(8)	1969(2)
H	2164(9)	2110(9)	1964(3)
N(5)	-1353(7)	1711(8)	1220(2)
C(1)	2769(9)	-458(10)	1531(3)
C(2)	3703(8)	100(9)	1091(3)
C(3)	3285(9)	1272(11)	157(3)
C(4)	2158(9)	2531(9)	-97(3)
C(5)	2019(9)	4005(9)	254(3)
C(6)	648(9)	1725(8)	-272(3)
C(7)	876(10)	4903(10)	1069(3)
C(8)	1249(10)	4850(10)	1684(3)
C(9)	-451(9)	2853(11)	2096(3)
C(10)	-1040(9)	1329(10)	1803(3)
C(11)	214(9)	45(9)	1850(3)
C(12)	-2478(10)	735(13)	2021(4)
Cl(1)	5726(2)	5332(3)	1267(1)
O(11)	7139(11)	5892(16)	1424(5)
O(12)	4705(12)	6349(11)	1010(6)
O(13)	6003(19)	4184(16)	892(6)
O(14)	5229(12)	4335(18)	1659(6)

To accommodate the coordination of a second oxygen, the macrocycle adopts a folded *cis* configuration in which the pendant primary amine is bound, but one of the macrocyclic ring nitrogens is not bound to the metal ion. This arrangement appears to be stabilised by a hydrogen bonding as a superbase between one of the coordinated ring nitrogens and the uncoordinated nitrogen (Figure 5.10, white atoms), the hydrogen atom being located during the X-ray structure solution between the coordinated N(1) and free N(2). The bonds in this bridge are relatively short at 1.4872(6) (N(1)-H) and 1.4129(6) (N(4)-H), consistent with the structural role of the bridging hydrogen atom.

Table 5.11 Bond Lengths (Å) for the cation in [Ni(L5)]ClO_4.

Ni-O(1)	2.0650(4)	C(9)-C(10)	1.5248(7)
Ni-N(3)	2.0786(10)	C(10)-C(12)	1.5043(8)
Ni-N(2)	2.0796(11)	C(10)-C(11)	1.5257(7)
Ni-N(1)	2.0870(4)	N(3)-C(7)	1.4966(6)
Ni-N(5)	2.0990(11)	N(3)-C(5)	1.5116(2)
Ni-O(2)$^{\#a}$	2.1935(11)	N(4)-H	1.4129(6)
O(1)-C(6)	1.2912(5)	N(4)-C(8)	1.4374(6)
O(2)-C(6)	1.2387(2)	N(4)-C(9)	1.4730(9)
O(2)-Ni$^{\#a}$	2.1935(11)	N(5)-C(10)	1.4923(2)
N(1)-C(11)	1.4749(7)	C(1)-C(2)	1.5156(4)
N(1)-C(1)	1.4798(7)	C(3)-C(4)	1.5247(6)
N(1)-H	1.5163(6)	C(4)-C(6)	1.5091(8)
N(2)-C(2)	1.4872(5)	C(4)-C(5)	1.5151(6)
N(2)-C(3)	1.4999(3)	C(7)-C(8)	1.5362(2)

(a) symmetry generated atoms.

The Ni-O bond for the carboxylate oxygen attached to the parent macrocycle is 2.0650(4) while that from the adjacent macrocycle is 2.1935(11) Å. The 'internal' Ni-O bond is substantially shorter than that found for the internal bond of the similarly bridged Ni(II) complex of the 15-membered strapped ligand 1,5,9,13-tetraazabicyclo[1.1.2.2]heptadecane-7-carboxylate (2.104(3) Å),[33] whereas the external bond is longer than that in the strapped complex (2.168(3) Å). However, the same trend can be seen in comparative size, with the internal bond being smaller than the external one. In the more conventionally coordinated Ni(II) monomer complex of an analogue based on cyclohexane-1,2-diamine[20] (L8) in which the metal sits in the macrocyclic ring with both pendants coordinated in a *trans* manner, the Ni-O bond length (2.112(6) Å) falls between that found for the two Ni-O bonds in this molecule. The ring nitrogen-metal bond lengths are longer than those found for the analogous Ni complex of L8 (2.039(7), 2.073(7), 2.051(7) and 2.057(7) Å compared to 2.079(1), 2.080(1), 2.087(1)and 2.099(1) Å for L5), despite the greater steric bulk of L8. This is probably a consequence of location of the metal ion 'outside' of the macrocyclic ring which adopts a folded geometry in the present case. The Ni-N distances are also slightly longer than those found for $Ni(L1)^{2+}$ (2.075(3) and 2.069(3) Å).[34]

The pendant amine is located *trans* to one of the ring nitrogens (N(2)) and *cis* to the two coordinated oxygen atoms with a Ni-N bond length of 2.099(1) Å. This is once again a longer bond length than found with L8 (2.088(7) Å), but

Table 5.12 Bond Angles (°) for the cation in [Ni(L5)]ClO$_4$.

O(1)-Ni-N(3)	89.17(2)	C(7)-N(3)-Ni	113.88(4)
O(1)-Ni-N(2)	95.08(3)	C(5)-N(3)-Ni	110.873(11)
N(3)-Ni-N(2)	86.61(4)	H-N(4)-C(8)	121.19(3)
O(1)-Ni-N(1)	174.908(2)	H-N(4)-C(9)	114.90(4)
N(3)-Ni-N(1)	95.92(2)	C(8)-N(4)-C(9)	120.043(12)
N(2)-Ni-N(1)	85.10(3)	N(4)-H-N(1)	111.28(4)
O(1)-Ni-N(5)	96.47(3)	C(10)-N(5)-Ni	110.02(2)
N(3)-Ni-N(5)	106.27(3)	N(1)-C(1)-C(2)	110.66(3)
N(2)-Ni-N(5)	162.769(11)	N(2)-C(2)-C(1)	107.65(4)
N(1)-Ni-N(5)	82.28(3)	N(2)-C(3)-C(4)	111.70(4)
O(1)-Ni-O(2)$^{\#1}$	83.35(2)	C(6)-C(4)-C(5)	113.20(3)
N(3)-Ni-O(2)$^{\#1}$	170.706(5)	C(6)-C(4)-C(3)	109.12(4)
N(2)-Ni-O(2)$^{\#1}$	88.55(4)	C(5)-C(4)-C(3)	113.71(3)
N(1)-Ni-O(2)$^{\#1}$	91.57(2)	N(3)-C(5)-C(4)	112.51(3)
N(5)-Ni-O(2)$^{\#1}$	80.15(3)	O(2)-C(6)-O(1)	123.05(2)
C(6)-O(1)-Ni	109.87(3)	O(2)-C(6)-C(4)	119.42(2)
C(6)-O(2)-Ni$^{\#1}$	123.445(13)	O(1)-C(6)-C(4)	117.51(3)
C(11)-N(1)-C(1)	114.78(4)	N(3)-C(7)-C(8)	109.90(2)
C(11)-N(1)-H	107.34(2)	N(4)-C(8)-C(7)	120.081(14)
C(1)-N(1)-H	111.14(4)	N(4)-C(9)-C(10)	113.920(13)
C(11)-N(1)-Ni	103.23(3)	N(5)-C(10)-C(12)	110.41(3)
C(1)-N(1)-Ni	104.58(2)	N(5)-C(10)-C(9)	107.91(2)
H-N(1)-Ni	115.78(3)	C(12)-C(10)-C(9)	110.50(2)
C(2)-N(2)-C(3)	114.88(3)	N(5)-C(10)-C(11)	106.51(2)
C(2)-N(2)-Ni	107.45(3)	C(12)-C(10)-C(11)	112.06(4)
C(3)-N(2)-Ni	114.41(3)	C(9)-C(10)-C(11)	109.29(4)
C(7)-N(3)-C(5)	111.02(2)	N(1)-C(11)-C(10)	107.69(4)

$^{\#1}$ refers to symmetry generated atoms from adjacent molecule.

shorter than that found for the primary amine pendant in the hexadentate nickel complex of L1 (2.126(3) Å) . The nickel atom sits in a distorted octahedral environment with the metal ion pushed towards N(3) and away from O(2). The N(2)-Ni-N(5) angle (162.77 °) is substantially reduced from the ideal value, and particularly the N(5)-Ni-O(2)$^{\#}$ angle (80.15 °) is also far from ideal. The N(5)-Ni-N(3) angle (106.27 °) is opened considerably to compensate for the compressed N(5)-Ni-O(2)$^{\#}$ angle. All angles around the nickel reflect this distorted environment (Table 5.12). This distortion probably results from the strains associated with coordinating the macrocycle in a folded *cis* configuration, along with a need to accommodate the differences in oxygen bond lengths associated with the bridged carboxylate geometry, differences also seen in the much less strained nickel polymer discussed in Chapter 3.

The bridging nature of the carboxylate group is also reflected in the infrared spectrum with a value, typical of that observed for bridging carboxylates,[8] for the carboylate absorbance at 1602 cm^{-1}. This compares with absorbances near 1630 cm^{-1} in conventionally coordinated carboxylates, such as seen in the complex of L2 discussed earlier in the chapter. The UV/Vis spectrum of the complex, like most high spin Ni complexes is relatively complex. However, this situation is exacerbated by the fact that the dimer may not persist in aqueous solution, with several high-spin species possibly present in solution at any given time as well as the low-spin complex. Given the potential complexity, the solution chemistry was not pursued further.

During the precipitation of the dimer of L5, it was noted that the remaining solution turns to a yellow colour. It could be argued that this is the remaining *trans* isomer (L2),[20] forming as the thermodynamically stable low-spin species, which did not crystallise readily. It is interesting to note that the complexes of L8 tend to be of lower solubility in aqueous solution than those of L2. This decreased solubility, attributable to the presence of cyclohexane rings, probably contributed to L8 forming a readily isolable high-spin compound.

Co(III) *cis*-diacmac (L6)

The cobalt complex of L6 was synthesised by the complexation of a mixture of *cis* and *trans* diacmac to Co(II) followed by air oxidation of the metal centre. It was then separated from the various complexes of the *trans* isomer (L3) by cation exchange chromatography on strong-acid Dowex 50Wx2 resin. This was readily achieved, probably due to the different geometries achieved by L3 and L6 on coordination. In many ways, this is the preferable method for separating the two isomers, since the inert character of the Co(III) ion means that, once coordinated, it is difficult to remove donors, at least those which belong to a polydentate ligand. This means that the various complexes formed can be considered to be 'long-lived' and hence are suitable for chromatographic separation. It is interesting that only one L6 complex formed from the reaction as opposed to the three observed for L3, but this may simply reflect a particular thermodynamic stability under the experimental conditions employed for the isomer isolated in this case compared with other potential products. When taken to dryness, NMR spectroscopy of the red solid formed showed no evidence of the presence of other complexes (Figure 5.12), suggesting that all the available L6 ligand was converted to the one complexed geometrical isomer. Unless the complex adopts a 'nest' geometry (Figure 5.11), with the cobalt ion above the four nitrogen donors and the two carboxylates in *cis* coordination sites, the ligand cannot achieve hexadentate coordination. This particular geometry may be less preferred as a result of by the close approach of two charged carboxylates in adjacent sites. Any geometry where the cobalt ion lies in the plane of the four secondary nitrogens can achieve no greater than quinquedentate coordination, as observed in the complex isolated.

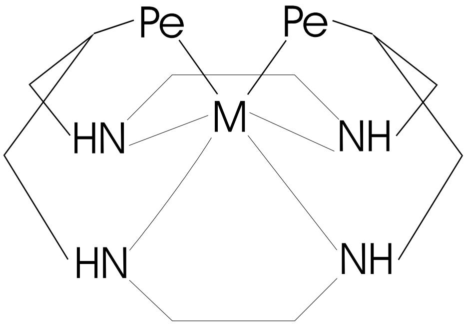
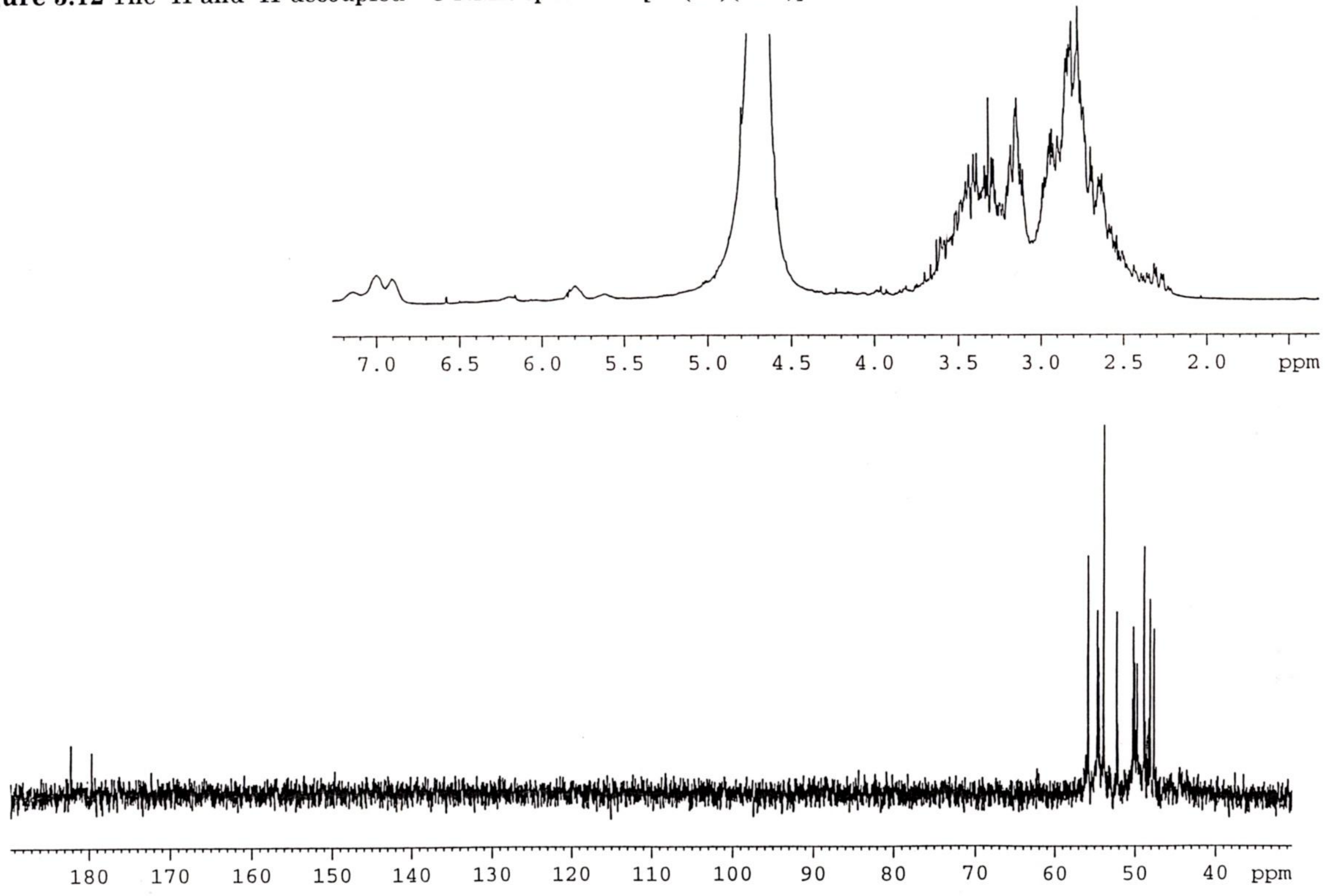


Figure 5.11 The 'nest' coordination geometry adopted by *cis* diammac (where Pe = NH_2) with some metal ions.

A view of the Co(III) complex of L6 crystalised and characterised by an X-ray crystal structure is shown in Figure 5.13, with atomic positional parameters given in Table 5.13. Bond lengths and bond angles for the cation appear in Tables 5.14 and 5.15 respectively. The cobalt atom sits in the macrocyclic plane defined by the four ring nitrogens. One of the axial sites is occupied by one carboxylate pendant. The other axial position is occupied by a water molecule,

Figure 5.12 The ^{1}H and ^{1}H-decoupled ^{13}C NMR spectra of $[Co(L6)(H_2O)]^{2+}$.



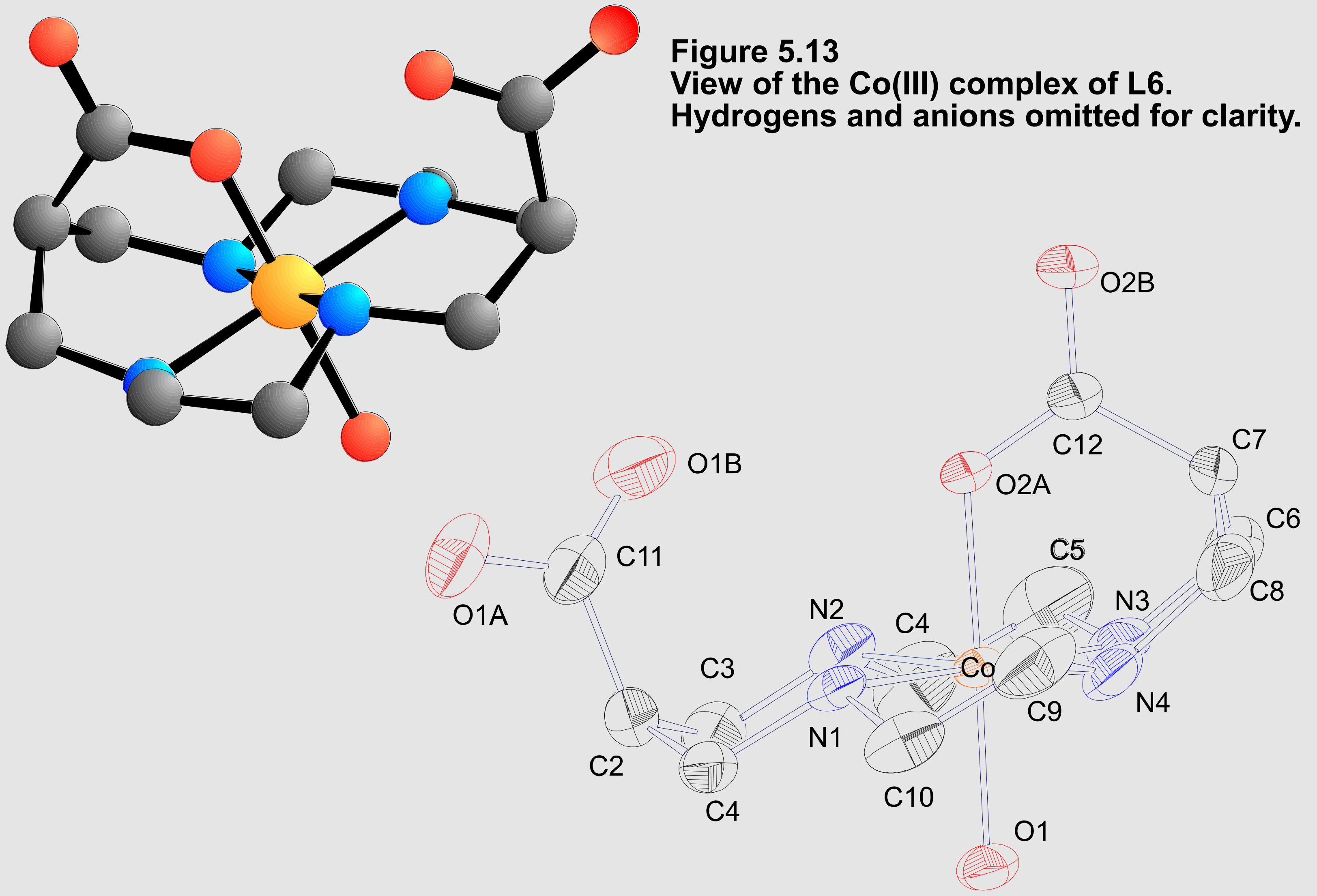


Figure 5.13
View of the Co(III) complex of L6.
Hydrogens and anions omitted for clarity.

with the second pendant unbound and unable to bind to its parent metal ion in this geometry. There is no evidence for interaction of the unbound carboxylate with any other metal centre. The free carboxylic acid group is attached to a six-membered chelate ring which adopts a preferred chair configuration, but the carboxylic acid group acts as an axial substituent. It is stabilised, to some extent, in this geometry by internal hydrogen bonding to the proton of N(2) which lies on the same side of the chelate ring as the carboxylate group (O(1B)-H(2) 2.28 Å (H(2) is the hydrogen on N(2))).

The only significant H-bonding contacts are, however, O(2)-H(1A1) (free water molecule and non-coordinated carboxylic acid H-atom), 1.78 Å, and O(2B)-H(11) (H-atom of aqua ligand), 1.70 Å. The coordinated carboxylate forces the six-membered chelate ring to which it is attached to adopt a boat conformation, with the hydrogen atoms attached to N(3) and N(4) both displaced to the opposite side of the CoN_4 plane to the bound carboxylate group. As can be inferred from the N(2)-Co-N(4) (177.04(10)°) and N(1)-Co-N(3) (179.20(10)°) bond angles, the cobalt lies almost exactly in the plane created by the four ring nitrogens. The cobalt is displaced slightly away from the nitrogens (N(3), N(4)) on the face of the octahedron involving the bound pendant, the Co-N average bond distance being slightly but significantly longer than those leading to the opposite face (average 1.971(3) compared to 1.964(3) Å). The coordinated carboxylate shows little strain, with the O(1)-Co-O(2A) angle (177.51(10)°) close to ideal, and internal angles in the chelate rings formed by its coordination (eg O(2B)-C(12)-C(7), 121.3(3)°) close to ideal.

Table 5.13 Position parameters for [Co(HL6)(OH_2)]ClO_4.Cl.H_2O.

Atom	10^4x	10^4y	10^4z	Atom	10^4x	10^4y	10^4z
Co(1)	1844(1)	2337(1)	3249(1)	O(1A)	3433(3)	4874(2)	5505(2)
N(1)	1159(2)	3434(1)	3635(2)	O(1B)	3676(3)	3525(2)	5512(2)
N(2)	3780(3)	2639(2)	3575(2)	C(12)	1245(5)	1289(2)	4854(2)
N(3)	2548(3)	1236(2)	2879(2)	O(2A)	1753(2)	1997(1)	4626(1)
N(4)	-113(3)	2033(2)	2999(2)	O(2B)	1204(4)	1055(2)	5762(2)
C(1)	1943(3)	4196(2)	3423(2)	O(1)	2024(2)	2683(1)	1840(1)
C(2)	3429(3)	4169(2)	3849(2)	O(2)	2976(3)	-1127(2)	-718(3)
C(3)	4260(3)	3489(2)	3368(3)	Cl(1)	6689(1)	1593(1)	5761(1)
C(4)	4642(4)	2030(3)	3041(3)	O(11)	6829(4)	972(2)	5025(3)
C(5)	4033(5)	1202(2)	3203(3)	O(12A)	5772(6)	2225(3)	5499(5)
C(6)	1774(5)	515(2)	3258(3)	O(13A)	6567(6)	1252(4)	6765(4)
C(7)	649(6)	762(2)	3964(2)	O(14A)	8135(5)	1977(4)	5878(4)
C(8)	-527(5)	1211(3)	3394(3)	O(12B)	6891(21)	1653(13)	6668(17)
C(9)	-967(3)	2715(3)	3404(3)	O(13B)	5014(18)	1420(11)	5735(13)
C(10)	-287(3)	3514(2)	3206(2)	O(14B)	6470(15)	2261(8)	5030(11)
C(11)	3529(3)	4160(2)	5025(2)	Cl(2)	218(1)	1135(1)	845(1)

The angles at the cobalt (O(2A)-Co-N(4) 89.48(10) and O(2A)-Co-N(3) 90.09(10)°) and the carbon angles within the ring (eg. N(4)-C(8)-C(7), 112.8(3)°) are also not unusual. This is in marked contrast to the strain imposed upon the formation of five-membered chelate rings by amine pendants such as found in L1 and L2. This parallels observations made in related structures reported earlier in the chapter.

Table 5.14 Bond lengths for the cation of [Co(HL6)(OH_2)]ClO_4.Cl.H_2O (Å).

Co(1)-O(2A)	1.876(2)	N(4)-C(9)	1.490(5)
Co(1)-O(1)	1.927(2)	C(1)-C(2)	1.517(5)
Co(1)-N(2)	1.964(3)	C(2)-C(3)	1.515(5)
Co(1)-N(1)	1.964(2)	C(2)-C(11)	1.524(4)
Co(1)-N(4)	1.970(3)	C(4)-C(5)	1.479(6)
Co(1)-N(3)	1.972(3)	C(6)-C(7)	1.514(7)
N(1)-C(1)	1.478(4)	C(7)-C(8)	1.510(7)
N(1)-C(10)	1.487(4)	C(7)-C(12)	1.524(4)
N(2)-C(3)	1.478(4)	C(9)-C(10)	1.477(5)
N(2)-C(4)	1.485(4)	C(11)-O(1B)	1.209(4)
N(3)-C(5)	1.479(5)	C(11)-O(1A)	1.316(4)
N(3)-C(6)	1.483(5)	C(12)-O(2B)	1.240(4)
N(4)-C(8)	1.485(5)	C(12)-O(2A)	1.283(4)

The metal-nitrogen bond lengths for the secondary nitrogens (1.964(3), 1.964(2), 1.970(3) and 1.972(3) Å) are all longer than those found for the cobalt complex of L2 (1.950(2), 1.959(2), 1.949(2) and 1.946(2) Å) and similar to the quinquedentate-bound L10 (1.954(5), 1.958(5), 1.964(5), 1.971(5) Å).[35] There is clearly a ‘shrinking’ of the ring of donors as at least one ‘tight’ amine cap is bound. However, the distances are close to those found for non-macrocyclic complexes such as Co(en)$_3^{3+}$ (Co-N 1.964(7) Å). This suggests there is little ‘compression’ of the coordination sphere associated with complexation of diacmac.

Table 5.15 Bond angles for the cation of $[Co(HL6)(OH_2)]ClO_4.Cl.H_2O$ (°).

O(2A)-Co(1)-O(1)	177.51(10)	C(6)-N(3)-Co(1)	116.0(3)
O(2A)-Co(1)-N(2)	87.67(10)	C(8)-N(4)-C(9)	111.9(3)
O(1)-Co(1)-N(2)	90.00(10)	C(8)-N(4)-Co(1)	116.2(3)
O(2A)-Co(1)-N(1)	89.31(9)	C(9)-N(4)-Co(1)	107.8(2)
O(1)-Co(1)-N(1)	91.71(9)	C(1)-C(2)-C(11)	112.0(3)
N(2)-Co(1)-N(1)	93.09(10)	N(2)-C(3)-C(2)	114.7(2)
O(2A)-Co(1)-N(4)	89.48(10)	C(5)-C(4)-N(2)	107.1(3)
O(1)-Co(1)-N(4)	92.86(10)	N(3)-C(5)-C(4)	108.4(3)
N(2)-Co(1)-N(4)	177.04(10)	N(3)-C(6)-C(7)	112.8(3)
N(1)-Co(1)-N(4)	86.05(11)	C(8)-C(7)-C(6)	112.3(3)
O(2A)-Co(1)-N(3)	90.09(10)	C(8)-C(7)-C(12)	110.5(4)
O(1)-Co(1)-N(3)	88.87(10)	C(6)-C(7)-C(12)	110.4(4)
N(2)-Co(1)-N(3)	86.35(12)	N(4)-C(8)-C(7)	112.8(3)
N(1)-Co(1)-N(3)	179.20(10)	C(10)-C(9)-N(4)	108.8(3)
N(4)-Co(1)-N(3)	94.47(13)	C(9)-C(10)-N(1)	106.2(3)
C(1)-N(1)-C(10)	110.0(2)	O(1B)-C(11)-O(1A)	120.3(3)
C(1)-N(1)-Co(1)	121.2(2)	O(1B)-C(11)-C(2)	122.1(3)
C(10)-N(1)-Co(1)	107.9(2)	O(1A)-C(11)-C(2)	117.6(3)
C(3)-N(2)-C(4)	109.9(3)	O(2B)-C(12)-O(2A)	121.5(3)
C(3)-N(2)-Co(1)	119.8(2)	O(2B)-C(12)-C(7)	121.3(3)
C(4)-N(2)-Co(1)	106.9(2)	O(2A)-C(12)-C(7)	117.2(3)
C(5)-N(3)-C(6)	112.2(3)	C(12)-O(2A)-Co(1)	121.2(2)
C(5)-N(3)-Co(1)	108.0(2)	N(1)-C(1)-C(2)	113.3(2)
C(3)-C(2)-C(11)	113.5(3)	C(3)-C(2)-C(1)	112.7(3)

The UV/Vis spectrum shows the classic splitting of the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ (O_h) parent transition into two bands, as is to be expected with the two axial sites of the coordination sphere occupied with a carboxylate and a water, forming a *trans*-CoN_4O_2 chromophore. However, all absorbances are at a lower energy than those found for the Co(III) complex of L3 (546, 448, and 357 nm for L6; 511, 421 and 343 nm for L3). This implies a lower ligand field strength in the present case compared to a ligand able to fully encapsulate the metal ion in a 'vice' configuration. However, direct comparison would only be possible for comparable hexadentate coordination of pairs of ligands.

The lower symmetry of the isolated complex is also shown in the NMR spectra by the presence of four peaks in the ^{1}H spectra (δ 6.9, 7.1, 7.2 and 7.4) associated with the amine and coordinated water protons (Figure 5.12). Although symmetry considerations suggest eight peaks would be the minimum number predicted, twelve peaks were found in the ^{1}H-decoupled ^{13}C spectra, suggesting that the free carboxylate may be interacting selectively with one amine site in solution, leading to inequivalence of the various carbon environments. This would also account for the multiplicity of the amine protons. A second peak also found in the carboxylate region of the of the ^{1}H decoupled ^{13}C spectrum (179 ppm), is probably associated with the unbound carboxylate. The presence of more than one peak in the υ_{asym} carboxylate region of the IR spectra is consistent with the two forms of carboxylate in the molecule.

5.3.4 Comparisons of the Hexadentate Metal Complexes of L1, L2 and L3

The *trans* isomers of all three ligands, diammac, acammac and diacmac (L1, L2 and L3) represent sterically efficient potentially hexadentate ligands where the pendant groups are attached at carbons of the macrocyclic ring rather than at the nitrogen heteroatoms. The capacity to totally encapsulate metal ions with a preference for octahedral coordination has been observed for all three ligands in the complexes of Co(III) and Fe(III). Presumably, the hexadentate Cr(III) complex of L3 is also accessible, as comparable complexes of L1 and L2 exist, but this chemistry is yet to be pursued. In general, for the hexadentate complexes, we see a gradual weakening of the ligand field as we move from the N_6 chromophore of L1 through the N_5O chromophore of L2 to the N_4O_2 case found in L3. This can be best seen in the spectroscopic data (Table 5.16) for Co(III), where a gradual shift to lower energy is seen for the absorbances as the number of oxygen donors is increased. As one progresses from hexadentate complexation of L1 to L2 to L3, apart from changes in donor, the strained five-membered rings introduced by coordination of the pendant primary amine are successively replaced by less strained six-membered rings formed by coordination of the pendant carboxylates. Since donors in the axial sites are changing, it is most reasonable to define the outcome of this change in the metal ion environment by examining the structures rather than comparing spectroscopic parameters. In the case of the Co(III) complexes of L1, L2 and L3 this is now possible.

The NMR spectra of the cobalt(III) complexes of L1, L2 and L3 are shown in Figures 5.14 (^1H spectra) and 5.15 (^1H-decoupled ^{13}C spectra). The latter reflect the high symmetry of the hexadentate diammac an diacmac complexes with only four peaks anticipated and observed. The intermediate acammac, of

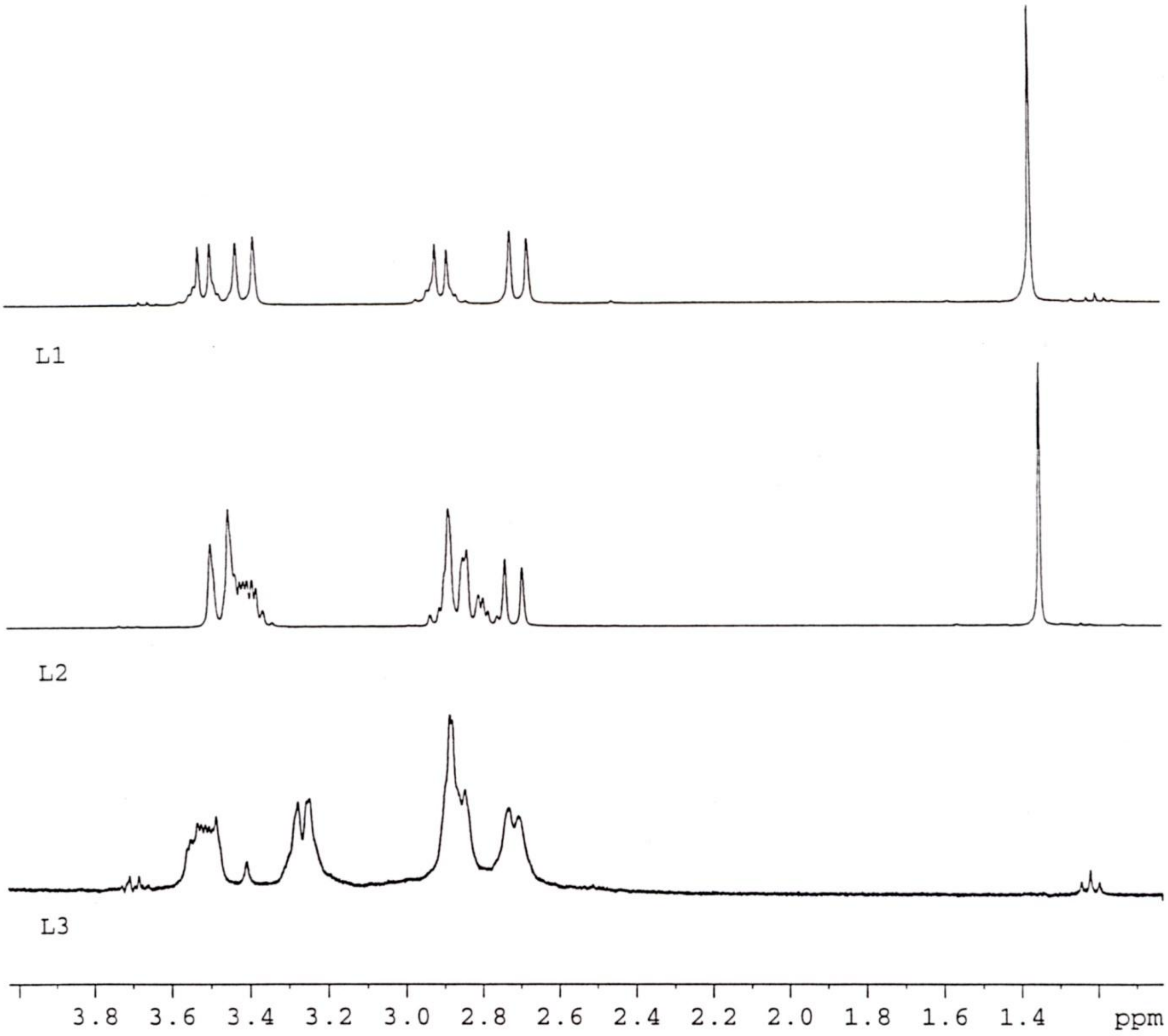


Figure 5.14 A comparison of the ^{1}H NMR spectra for the hexadentate Co(III) Complexes of L1, L2 and L3. (Traces of EtOH in some spectra.)

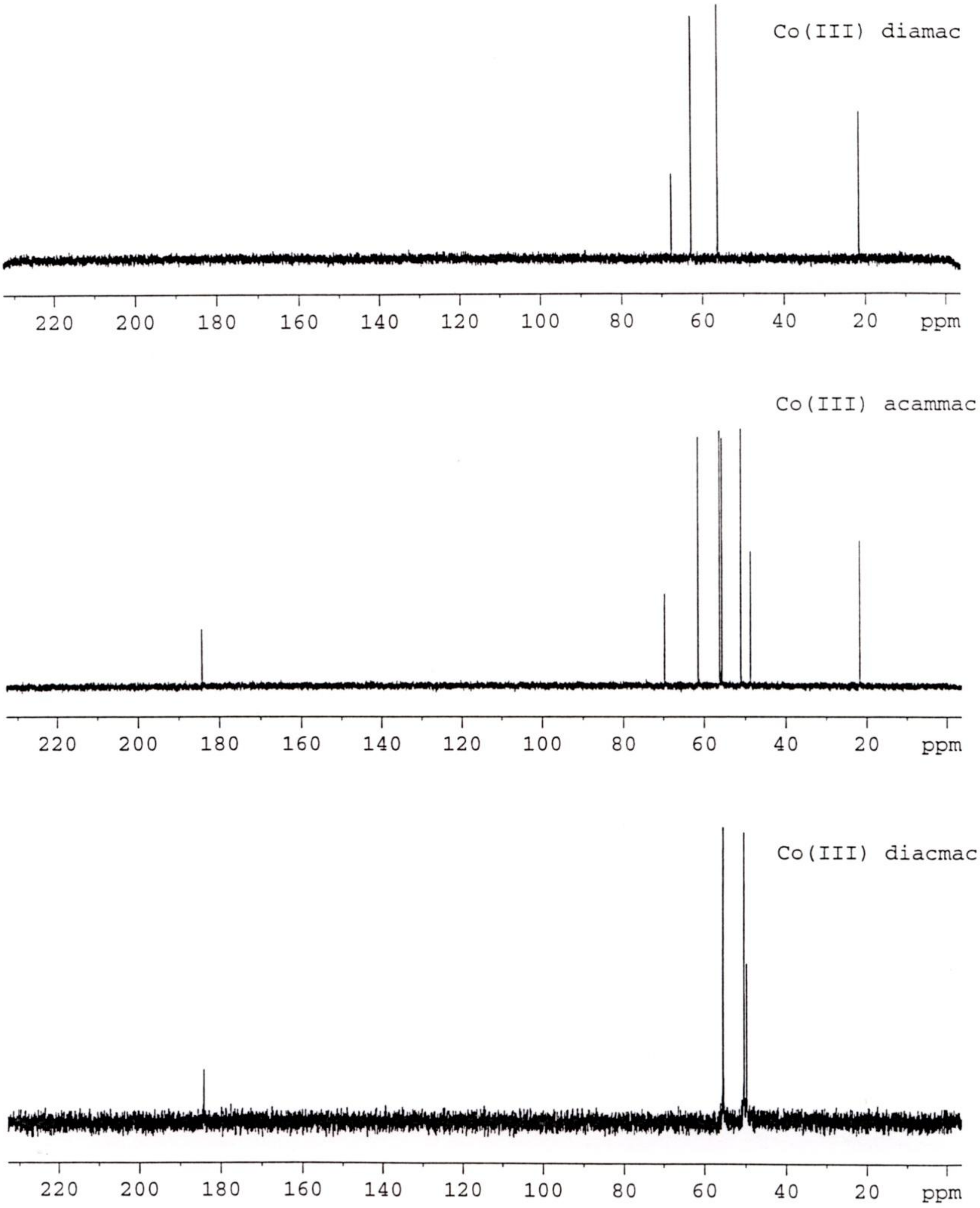


Figure 5.15 A comparison of the ^{1}H-decoupled ^{13}C NMR spectra for the hexadentate Co(III) Complexes of L1, L2 and L3.

inherently lower symmetry, yields eight peaks in the ^{13}C NMR, with the -CH_3 and -COO^- resonances comparable in position to those in the symmetric parents, and equivalent methylene resonances in each capping unit apparent. The ^{1}H NMR are less straight-forward, although the transition from effectively the two AB quartets in the L1 spectrum to a more complex pattern in L2 is clear and consistent with ^{13}C NMR behaviour. The ^{1}H NMR spectrum of L3 is more complex than that found for L1, because an additional hydrogen atom has been introduced on each carbon carrying a pendant.

Differences in the two 'caps' of the Co(III) complex of L2 have been discussed earlier, but it is notable that one apparent consequence of the introduction of the carboxylate group in L2 is a 'swelling' of the general coordination sphere relative to L1. The average distance for the secondary nitrogen donors in $Co(L2)^{2+}$ [1.951(2) Å] and $Co(L1)^{3+}$ [1.937(2) Å] are not equivalent, and even the primary amine cap exhibits a longer distance in the L2 complex [1.956(2) Å] compared with the L1 complex [1.946(2) Å]. [22] In $Co(L3)^+$, we see the average Co-N distance again shorten slightly to 1.946(3) Å, possibly influenced by the short Co-O distances. However, this is still longer than distances found in the L1 complex.

The slight shortening in the Co-N distances from $Co(L2)^{2+}$ to $Co(L3)^+$ may reflect the greater steric efficency of the carboxylate donors compared with the primary amine donors, permitting closer approach of the secondary amine donors to the metal ion along with the pendant donors. The effect differs from

Table 5.16 Comparison of selected physical properties for L1, L2 and L3 complexes.

cation		**λ_{max} (ε_{max}) [nm(dm^3 mol^{-1} cm^{-1})]**	**$E_{1/2}$ (V^a)**	**M-N$_{eq}$ (Å)**	**M-N$_{ax}$ (Å)**	**M-O (Å)**
Cr(III)	L1	427(55), 332(52)	-1.04	2.037	2.067	-
	L2	517(48), 415(32), 365(70)	-0.44			
	L3	n.r.	n.r.			
Fe(III)	L1	560(1), 480(30), 417(55), 332(140)	-0.35	1.965	1.982	-
	L2	681(16), 466(85), 402(124), 339(440)	-0.34			
	L3	498(35), 428(32), 332(~1000)	-0.18	1.996	-	1.895
Co(III)	L1	447(73), 328(76)	-0.79	1.937	1.946	-
	L2	481(87), 339(92)	-0.42	1.951	1.956	1.899
	L3	511(28), 421(35), 343 (90)	-0.69	1.946	-	1.904

[a] vs Ag/AgCl

the 'compression' introduced by the coordination of pendant -NH_2 as a result of the direct attachment of that donor to the macrocycle. A -CH_2-NH_2 pendant, forming six-membered chelate rings on coordination like the carboxylate pendant, may more properly comment on the comparative steric efficiency of the carboxylate and amine donors.

The ring nitrogen bond lengths in $Co(L2)^{2+}$ are much less symmetrical than found in the other two complexes, presumably related to the different natures of the two pendants. Two of the bonds fall within the range of the Co-N bond lengths of $Co(L3)^{+}$, suggesting that the limit for the 'swelling' of the coordination sphere is met at the introduction of one carboxylate. For both the L2 and L3 complexes the Co-O bond length are very similar (1.899(2) and 1.904(2) Å). As has been stated earlier, these are similar to (if slightly shorter than) those found for coordinated amino acids,[27] which supports the view that the six membered chelate rings produced in the coordination of the carboxylate pendants introduce very little strain into the molecule. 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'. Another structural feature demonstrating this reduction in strain is the change in the angle of the axial pendant bonds in relation to the nitrogen plane. In $Co(L1)^{3+}$ the axial bonds are bent towards the pendant to accommodate the greater strain associated with the five-membered chelate rings introduced, whereas in $Co(L3)^{+}$ they are almost perpendicular to the nitrogen plane (bent slightly away from the pendant by ~2.1°). Interestingly, even for the comparatively unstrained complex of L3, the bond lengths do not approach those found for the *cis* and *trans* isomers of unsubstituted cyclam bound to cobalt(III) [1.986(7) to 2.016(6) Å][36] (as clearly seen in Figure 5.16). This implies that, with the donors attached directly to the macrocyclic ring, their coordination involves a compensation by the ring donors towards a smaller coordination sphere to 'match' the short M-donor distances introduced by both a pendant amine and a pendant carboxylate, albeit arising from different sources. Consequently, L1, L2 and L3 can all be considered stronger field ligands than unsubstituted cyclam when the pendants are participating in binding. Only with metal ions such as copper(II), where useful axial interactions are limited by the Jahn-Teller elongation, does one possibly not see an effect. Similar features can be seen in the reported structures for the Fe(III) complexes of L1 and L3 to those discussed in the cobalt(III) set. While no structural data is available to quantify the differences between the Cr(III) complexes of the three ligands (to date only the structure for $Cr(L1)^{3+}$ has been reported[4]) the trend in λ_{max} is consistent with that found for the other two metals for L1 and L2, with a move towards lower energy with the increase in the number of oxygen donors. There seems little reason to assume that the trend would not extend to L3 for chromium(III), and to other metal ions.

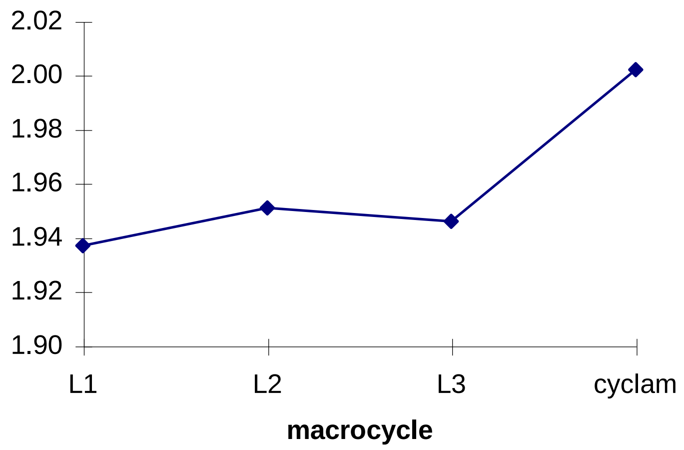


Figure 5.16 Variation in average Co-N (secondary) distances (Å) with ligand.

The chemistry of Ni(II) with the three ligands is complicated by the lability of the pendant donors and the apparent thermodynamic stability of the low spin complexes. Spectroscopic data for the high spin complexes is complicated by the mixed species existing in solution for L2 and L3. The hexadentate complex of L1 has been reported and characterised by an X-ray crystal structure.[37] Isolation of this species was probably aided by a lower solubility than that of the equivalent complexes of L3 and L2, with the charge on the hexadentate complex, dropping from 2+ in the case of L1 to zero in the case of L3, possibly having an influence.

There is some relationship between Co-N_{eq} distance and the $Co^{III/II}$ redox couple, with the least compressed (L2) displaying the most positive $E_{1/2}$ value (Table 5.16). As the ‘compression’ increases from L3 to L1, the $E_{1/2}$ becomes more negative. This may be associated with the larger cavity being able to accommodate the larger Co(III) ion more effectively. This relationship has been more extensively explored for a range of macrobicyclic hexamines,[38,39,40] and it is interesting to note that the correlation extends to the pseudo-encapsulating hexadentates discussed here. This relationship occurs despite the variation in donor groups, which must also make some contribution. With the Fe(III) complexes, there is, however, no clear trend. Apparent trends such as the one reported should be approached with caution.

The three *trans* isomers L1, L2 and L3 represent a close family of ligands whose coordination chemistry presents some interesting outcomes. The less abundant *cis* isomers L4, L5 and L6 have been studied only to a limited extent, and deserve attention in the future. The different encapsulation geometries demanded by the *trans* and *cis* isomers may lead to distinctive shape-directed chemistry for these ligands.

5.3.5 Comparative Formation Constants for Labile Metal Ions with Diammac, Acammac and Diacmac

The transition from two primary amine pendant donors to two carboxylate pendant donors via the species with one of each donor presents an opportunity to examine the influence of different pendants on the metal ion binding capabilities in a series where the pendants are attached directly to carbon atoms of the macrocycle ring. Selected inert metal complexes have been discussed earlier in the chapter; here, formation constants with labile d^{10} metal ions and the high spin d^5 metal ion Mn(II) are discussed.

Given the common framework linking L1 - L3 and cyclam (L7), it is not unreasonable to find that the protonation constants of all ligands are somewhat similar (Table 5.17).[41,42,43] The protonation behaviour of the ligands has already been discussed in Chapter 4. In the data presented in the table, L is the neutral hexamine (L1), or else the deprotonated amino acid (L2 and L3), and hence six protonation steps can be expected for each ligand. All titrations in the presence of metal ions have been modelled successfully essentially identically. Examples of the speciation diagrams for L2 and L3 are given with zinc(II) (Figure 5.17) and lead(II) (Figure 5.18). For most cases, ML is the dominant species present at neutral pH, as exemplified for zinc(II) in Figure

5.16. However, with large metal ions like lead(II) other species such as MLH_{-1} associated with a coordinated deprotenated water molecule as discussed later, are significant even at neutral pH (Figure 5.17).

Binding of the d^{10} metal ions show a significant difference in formation constants for L1 compared with L3, employing a common model for analysis of titration data, and imply that the pendant groups play a role in metal ion binding. Of the metal ions examined, only zinc(II) has been shown capable of (though not necessarily having a preference for) hexadentate coordination to L1,[2] and presumably this may be the case with L3 and L2 also. The significant difference for log K_{ML} with L3 and zinc ion compared to the other ligands probably reflects formation of a highly preferred neutral hexadentate complex with L3; L1 and L2 may not participate in hexadentate coordination at all under the conditions employed. The other metal ions are too large to be incorporated into the macrocycle ring, and thus differences between ligands are subsequently not generally so marked.

However, with L3, even where metal ions bind in a five-coordinate mode as a square-based pyramid, at least one of the carboxylate pendant groups must be coordinated, whereas L2 has a choice of amine or carboxylate axial donors and L1 only axial amine donors, accounting for differences between L1 and L3 with all metal ions and less substantial differences between L1 and L2. Both protonated species MLH and MLH_2 modelled exhibit significantly lower stabilities than ML species, consistent with proton incorporation into the

Table 5.17 The logarithms of the protonation and formation constants for L1, L2 and L3 with various metal ions; some comparative values for cyclam (L7) are included (charges are omitted for clarity)^a.

M	**Complex**	**L1**	**L2**	**L3**	**L7**
H^+	$H + L \Leftrightarrow HL$	11.0	10.5	10.6	11.6
	$HL + H \Leftrightarrow H_2L$	10.0	9.9	9.9	10.6
	$H_2L + H \Leftrightarrow H_3L$	6.2	6.4	4.0	-
	$H_3L + H \Leftrightarrow H_4L$	5.5	5.5	3.2	-
	$H_4L + H \Leftrightarrow H_5L$	1.5^b	3.2^c	3.1^c	1.6^d
Zn^{2+}	$M + L \Leftrightarrow ML$	14.9	14.7	26.3	15.5
	$ML + H \Leftrightarrow MLH$	6.8	6.6	5.4	
	$MLH + H \Leftrightarrow MLH_2$	6.0	5.0	4.8	
	$ML \Leftrightarrow MLH_{-1} + H$	10.5	10.8	10.5	
Cd^{2+}	$M + L \Leftrightarrow ML$	10.6	16.7	15.9	11.3
	$ML + H \Leftrightarrow MLH$	7.5	6.8	7.1	
	$MLH + H \Leftrightarrow MLH_2$	5.7	6.0	3.4	
	$ML \Leftrightarrow MLH_{-1} + H$	-	7.1	7.2	
Hg^{2+}	$M + L \Leftrightarrow ML$	10.5	17.3	21.8	23.0
	$ML + H \Leftrightarrow M$	7.5	6.8	8.2	
	$MLH + H \Leftrightarrow MLH_2$	5.7	6.0	5.9	
	$ML \Leftrightarrow MLH_{-1} + H$	-	7.8	13.4	
Pb^{2+}	$M + L \Leftrightarrow ML$	10.8	10.7	19.0	10.8
	$ML + H \Leftrightarrow MLH$	7.5	6.1	7.3	
	$MLH + H \Leftrightarrow MLH_2$	4.1	3.0	4.2	
	$ML \Leftrightarrow MLH_{-1} + H$	-	-	8.0	
Mn^{2+}	$M + L \Leftrightarrow ML$	6.2	12.0	18.3	-
	$ML + H \Leftrightarrow MLH$	8.2	8.6	8.9	
	$MLH + H \Leftrightarrow MLH_2$	-	5.9	3.7	
	$ML \Leftrightarrow MLH_{-1} + H$	4.6	8.7	9.3	

(a) 25 °C, I = 0.5 mol dm^{-3} KCl, standard errors are ±0.1 units.

(b) Approximate only; sixth protonation not determined (< 1.5).

(c) Sixth protonation not determined (< 2).

(d) Third protonation; fourth protonation not determined (< 1.5).

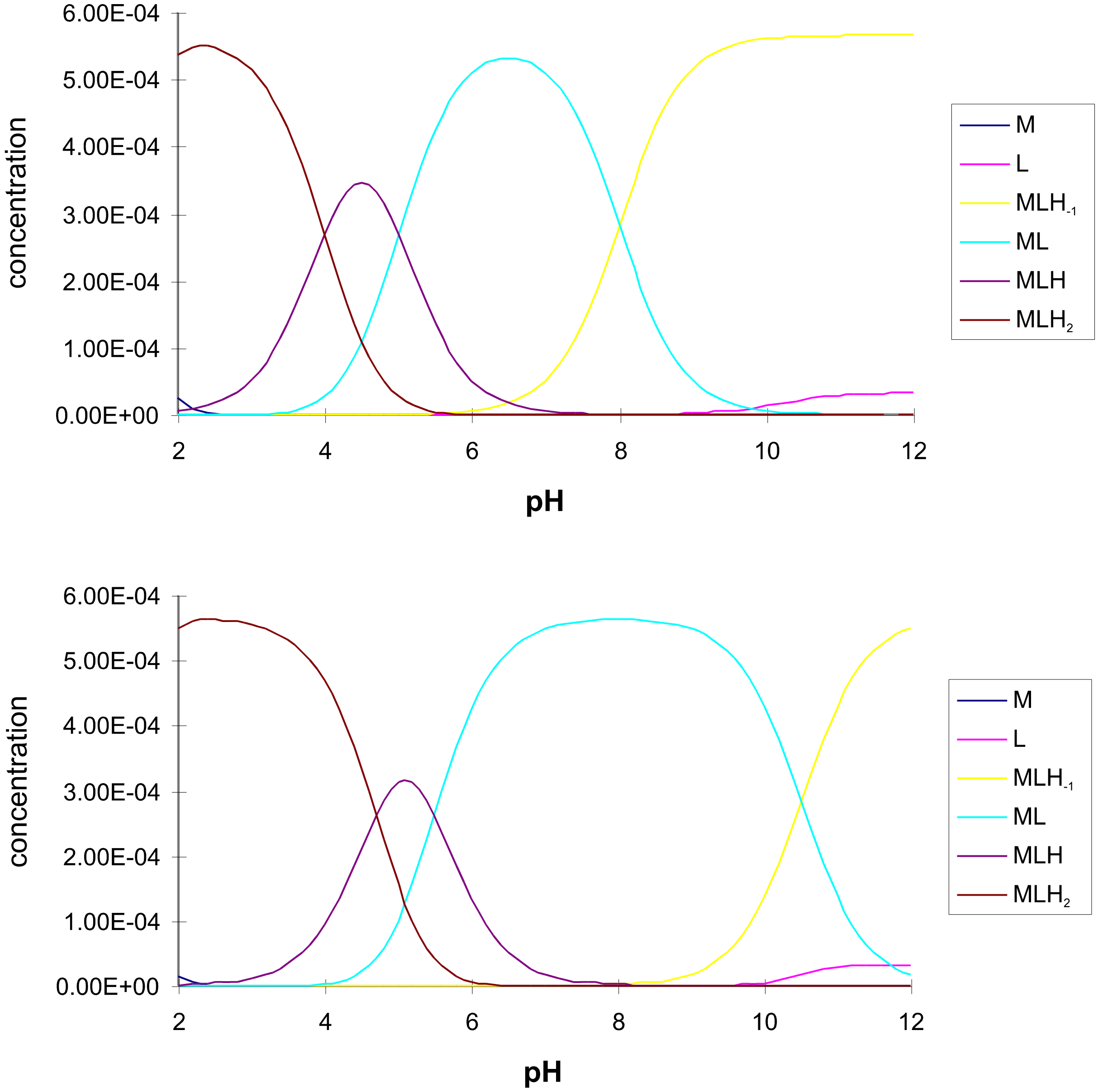
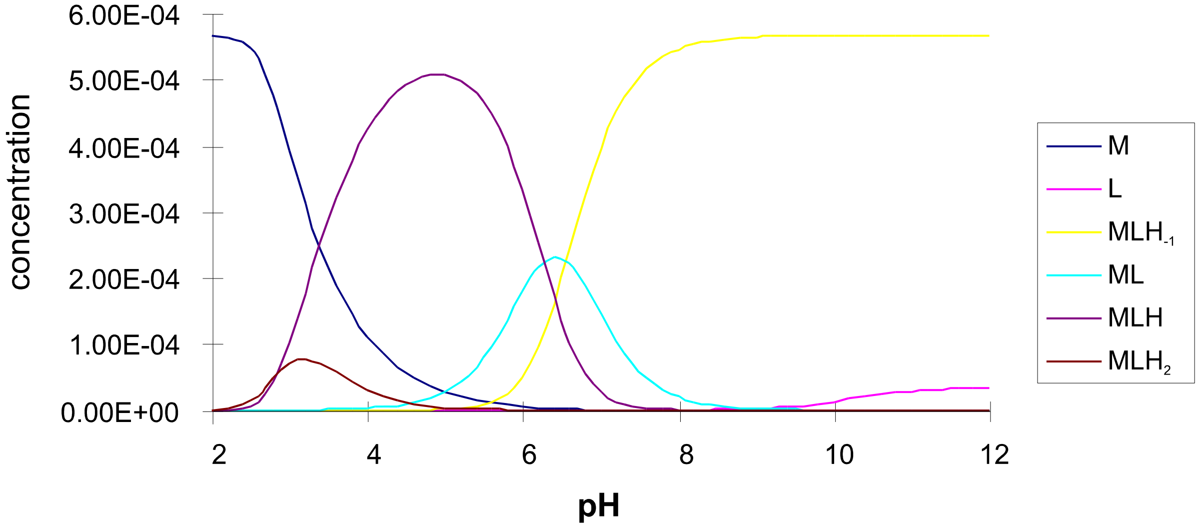


Figure 5.17 Speciation graphs for the complexation of zinc(II) with L2 (top) and L3 (bottom). Minor contributions from other protonated (but uncomplexed) forms of the ligand have been omitted for clarity.



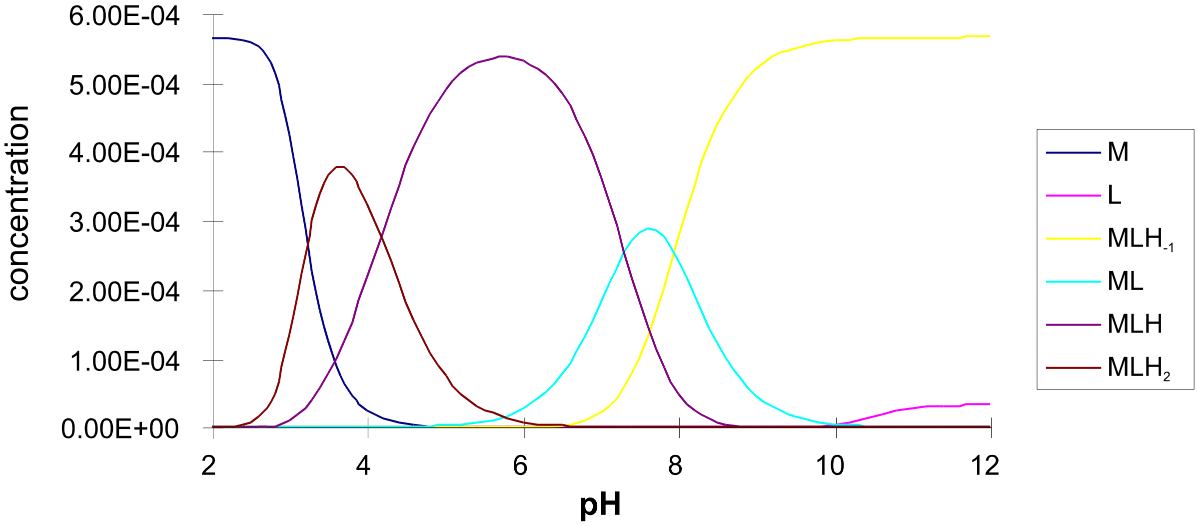


Figure 5.18 Speciation graphs for the complexation of lead(II) with L2 (top) and L3 (bottom). Minor contributions from other protonated (but uncomplexed) forms of the ligand have been omitted for clarity.

macrocycle which makes binding involving the ring unfavourable, without any obvious trends; these species may involve only simple chelation involving a pendant and one ring secondary amine exo to the ring. A MLH_{-1} species can be modelled reasonably consistently, presumably associated with a deprotonated coordinated water and either reduced coordination by the multidentate ligand or else 7-coordination. Formation constants for larger metal ions with both L3 and L2 are greater for these MLH_{-1} species than is the case with L1, presumably reflecting an enhanced stability of neutral or anionic complexes possible only with these ligands and not L1, which would still form a cationic complex.

Whereas zinc can be considered a special case because it alone can accommodate six-coordination, with all metal ions there will nevertheless be an interplay between O anion-donor versus N-donor preference in determining the size of the formation constant. With mercury(II), there is a trend of increasing formation constants for both ML and MLH_{-1} species with increasing number of available O-donors, in line with the expected behaviour for O anion-donor preference (Hg > Pb > Zn > Cd),[42,43] but opposed to the expected behaviour for N-donor preference (Hg > Cd > Zn > Pb).[42,43] Lead typically shows a relatively strong O versus N preference, consistent with the step in formation constant from L2 to L3, whereas by contrast Cd typically shows a relatively strong N versus O preference, again consistent with no major change from L2 to L3. The trend for L3, whereby $\log K_{ML}$ for Zn is significantly higher than that for Cd and Pb, inferring a strong selectivity towards zinc, is similar to that observed with the cyclic polyaminoacid 1,4,7-triazacyclononane-1,4,7-triacetate (log K_{ML} 26.6, Zn; 16.8, Cd; 16.6, Pb).[44] The trend with the d^5 manganese(II) ion is consistent with an expected preference for O anion donors. Overall, the polyaminoacid diacmac is both a stronger binder of the d^{10} and d^5 metal ions examined compared with diammac, but at the same time more selective, as a result of the mixed donor set offered, including the sterically more efficient carboxylate donors. A clear role for the pendant donors in the binding to labile metal ions is apparent, adding to the established evidence for coordination of the pendants found with inert metal ions. The pendant arm macrocycles discussed, with the pendant directly attached to ring carbon atoms, play an important role in the chemistry of their interaction with metal ions.

5.4 References

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