Synthesis and Crystallographic Characterisation of Pendant-arm Macrocyclic Complexes derived from 1,4,7-triazacyclononane: Mono- and Di-(3-aminopropyl)-1,4,7-triazacyclononane as Ligands†

Denis G. Fortier and Alexander McAuley *
Department of Chemistry, University of Victoria, Victoria, BC V8W 2Y2, Canada

Metal complexes based on pendant-arm ligands derived from triazacyclononane have been prepared and characterised. The ligands 1,4-di(3-aminopropyl)-1,4,7-triazacyclononane (daptacn) and 1-(3-aminopropyl)-1,4,7-triazacyclononane (maptacn) with two and one pendant arms have been complexed to cobalt(III), copper(II) and nickel(II) in the former system and with nickel(II) in the latter. X-Ray studies show the complex $[Co(daptacn)Cl][ClO_4]_2 \cdot H_2O$ to crystallise in the orthorhombic space group *Pbca* with $a = 19.538(4)$, $b = 16.813(4)$ and $c = 13.155(3)$ Å. Refinement converged at $R = 0.0855$ ($R' = 0.0724$) for 395 parameters using 1906 reflections with $I > \sigma(I)$. The complex ion is octahedral with the chloride *trans* to a tertiary nitrogen donor. The same structure is maintained in solution. Refinement of the complex $[Cu(daptacn)][ClO_4]_2$ (orthorhombic, space group *Pbca*), with $a = 17.358(4)$, $b = 14.262(3)$ and $c = 16.533(4)$ Å for 253 parameters using 1378 reflections with $I > 2\sigma(I)$ converged at $R = 0.0811$ ($R' = 0.0895$). The complex is square pyramidal with an axial Cu–N bond length of 2.251(12) Å. The tetradentate ligand maptacn forms a dinuclear complex $[Ni_2(maptacn)_2(\mu\text{-}Cl)_2][ClO]_2$ in which the remaining octahedral sites are filled by bridging chlorides. The perchlorate salt crystallised in the triclinic space group $P\bar{1}$ with $a = 10.235(2)$, $b = 11.373(3)$, $c = 7.150(2)$ Å, $\alpha = 81.84(2)$, $\beta = 99.36(2)$ and $\gamma = 109.96(2)°$. Refinement converged at $R = 0.0562$ ($R' = 0.0641$) for 269 parameters using all 2709 reflections collected. There is strong hydrogen bonding between the N(4) donors of the pendant arms and the counter perchlorate ions. The chloride ions may be replaced by a bridging oxalate group. For this complex, oxidation to nickel(III) takes place yielding an ESR spectrum containing evidence for the unpaired electron in a $d_{x^2-y^2}$ orbital ($g_{\parallel} = 2.184$, $g_{\perp} = 2.079$) but no hyperfine splitting.

A novel feature of recent co-ordination chemistry has been the appending of pendant arms to macrocyclic ring systems thereby increasing the number of co-ordination sites filled when metal complexes are formed. In many instances, functionalisation occurs at the nitrogen-donor sites and examples of derivatives of triazacyclononane ([9]aneN_3)[1–5] and tetraazamacrocycles are known.[6–10] In the case of the latter, although for many of the complexes based on cyclam (1,4,8,11-tetraazacyclotetradecane, [14]aneN_4) the metal ions are held within the macrocycle,[11] examples have been provided, *e.g.* *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane,[7,8] where exocyclic complexing to two metal centres is exhibited with no resulting incorporation into the cyclam ring. In several systems, extrapolations have involved extension of the arm from the carbon atom α to a secondary nitrogen. In this way, Kimura[11] has appended an imidazole group which can co-ordinate axially. (An extreme example of this extension is the joining of a second cyclam moiety to the first, leading to a different type of binuclear species. This has been achieved either on the carbon centres of the five-membered ring[12] or, *via* a C-spiro derivative,[13] at the central carbon of the six-membered ring of the macrocycle.)

In the case of the smallest macrocycle, 1,4,7-triazacyclononane ([9]aneN_3, tacn), three pendant arms originating from the nitrogen centres have led to six-co-ordinate complexes of Fe^{II}, Co^{III} and Ni^{II} with either N_6 or N_3O_3 donors.[3–5] In a previous study, the preparation of the ligand 1,4,7-tri(aminopropyl)-1,4,7-triazacyclononane (taptacn) was described,[3] together with the structures and reactivity of the nickel(II) and cobalt(III) complexes.

In the course of preparation of the above ligand, two other amines were formed, in which either two (daptacn) or one (maptacn) pendant arms are present. Complexes of these ligands are the subject of this paper. In the case of daptacn, not only are five- or six-co-ordinate species formed, but condensation of glyoxal with the $[Cu(daptacn)]^{2+}$ ion and subsequent reduction leads to the formation of a novel macrobicyclic ligand in which a triazacyclononane ring is 'fused' with a cyclam unit to produce six-co-ordinate complexes in which only one co-ordination site is available for substitution. A related set of complexes has been reported recently from this laboratory where the apical donor is a sulphur atom.[14] In the case of the maptacn ligand the possibility exists for tetrahedral co-ordination. However, in the complex formed with nickel(II) a dimeric structure has been identified.

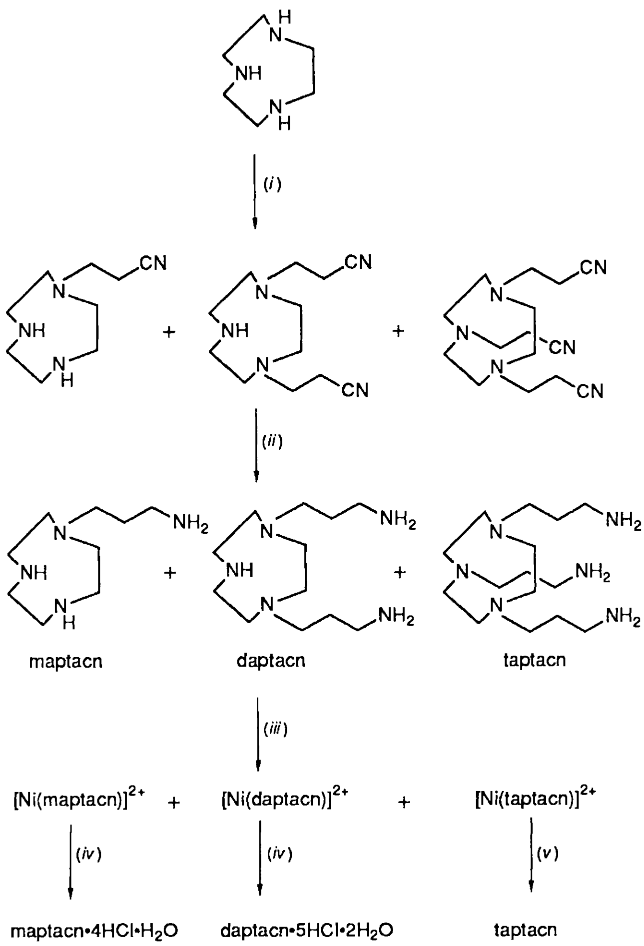
Experimental

All materials were of reagent grade, unless indicated otherwise. Electron spin resonance spectra were obtained using a Varian E6S spectrometer with diphenylpicrylhydrazyl (dpph, $g = 2.0037$) as a reference standard, IR spectra in KBr discs by using a Perkin-Elmer 283 grating spectrometer, and high-field ^{13}C and ^{1}H NMR spectra on a Bruker WM 250 instrument. All chemical shifts are reported relative to tetramethylsilane. Ultraviolet–visible spectra were run on either a Cary 17 or a Perkin-Elmer Lambda 4B dual-beam spectrometer. Elemental

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: G = 10^{-4} T.

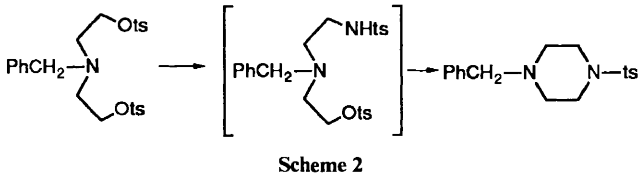


Scheme 1 (*i*) $CH_2{=}CHCN$; (*ii*) BH_3·thf; (*iii*) $[Ni(H_2O)_6]^{2+}$; (*iv*) (*a*) separation on Sephadex, (*b*) 6 mol dm ^{3} HCl, (*c*) elution on Dowex; (*v*) (*a*) separation on Sephadex, (*b*) NaCN, (*c*) extraction into CH_2Cl_2

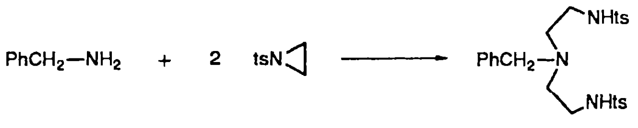
analyses were performed by Canadian Microanalytical Services, Vancouver, BC, Canada.

Syntheses.—The synthetic pathways are outlined in Scheme 1. Ligand [9]aneN_3 was prepared by a modification of the Richman–Atkins[15] synthesis and has been described previously.[16]

A simple route to daptacn hinges on functionalising [9]aneN_3 at only two of the three secondary amines. However, on reaction of [9]aneN_3 with acrylonitrile (2 mol) in a Michael addition, followed by reduction of the cyano groups to primary amines, a mixture of products (Scheme 1) was derived leading to a problem of separating the free ligands. Attempts were made using selective alkylation or benzylation. As an example, benzylation of diethanolamine followed by tosylation yielded the ditosylate, but, upon reaction with sodium toluene-*p*-sulphonamide, the product formed was the disubstituted piperazine owing to internal attack on the second Ots group (Scheme 2). Preparation of the desired diamine tosylate was achieved using tosylaziridine (Scheme 3) but, after cyclisation and detosylation, it was apparent that the benzyl group had also cleaved.



Scheme 2



Scheme 3

Since selective alkylation did not appear feasible, separation and isolation was achieved using column chromatography of the corresponding nickel(II) complexes.

Mono-, di- and tri-(2-*cyanoethyl*)-1,4,7-*triazacyclononane* (*mcetacn, dcetacn and tcetacn respectively*). To [9]aneN_3 (25.5 g, 0.20 mol) dissolved in refluxing benzene (500 cm^3) was added acrylonitrile (26 cm^3, 0.39 mol) and the solution was refluxed for 1 h. The solvent was removed under reduced pressure, yielding a pale yellow oil which was further dried under vacuum overnight. Yield: 48.5 g. NMR ($CDCl_3$): ^1H, δ 2.4 (t, CH_2CN), 2.85 (t, NCH_2CH_2CN) and 2.75 (s, NCH_2CH_2N); ^{13}C, consistent with a 1:5:13 ratio of the mono:di:tri adducts.

Mono-, di- and tri-(3-*aminopropyl*)-1,4,7-*triazacyclononane* (*maptacn, daptacn and taptacn respectively*). The crude oil from the reaction above was suspended in 1 mol dm^{-3} BH_3•thf in thf (550 cm^3) and refluxed overnight. Ethanol (200 cm^3) was then added cautiously to destroy any excess of BH_3. Subsequently, the solution was taken to dryness under reduced pressure, leaving a crusty residue which was in turn dissolved in a solution of HCl in methanol (4 mol dm^{-3} 600 cm^3) and refluxed for 1 h. The solution was again taken to dryness under reduced pressure. The products were not isolated at this stage, rather their nickel(II) complexes were synthesised and separated using an ion-exchange column.

The crude residue was dissolved in water (100 cm^3) and neutralised using NaOH (15 g) to pH *ca.* 11. This solution was diluted with 100% ethanol (1 l) then $Ni(CH_3CO_2)_2{\cdot}6H_2O$ (45 g, 0.18 mol) was added. The mixture was refluxed for 1 h after which the purple-blue solution was filtered to remove the precipitate of NaCl. The ethanol was then removed under reduced pressure, the residue dissolved in water (1 l), and NaOH added to pH 8. At this point the solution was divided into three fractions and charged on Sephadex-C50 columns (50 × 5 cm). Elution with increasing concentrations of sodium chloride solutions resulted in the isolation of seven distinct bands, the first two of which were $[Ni(tacn)_2]^{2+}$ and $[Ni(taptacn)]^{2+}$ respectively.

$[Ni(daptacn)(H_2O)][ClO_4]_2$. The third band from the column containing the reaction mixture was eluted using 0.25 mol dm^{-3} NaCl. After removing most of the NaCl by repeatedly taking the fractions to dryness under reduced pressure, redissolving the complex in 95% ethanol and filtering off the precipitate of NaCl, the complex was dissolved in a minimum amount of water (35 cm^3) and $NaClO_4$ (6.5 g) was added. A precipitate formed upon standing, which was filtered off, rinsed with cold water and air dried. Although more complex was present in solution, a second crop could not be obtained, so the complex was decomposed to isolate the ligand. Yield: 5.25 g (10.5 mmol, 5.8%) (Found: C, 27.90; H, 6.00; Cl, 13.35; N, 13.35. Calc. for $C_{12}H_{31}Cl_2N_5NiO_9$: C, 27.75; H, 6.00; Cl, 13.50; N, 13.50%).

Daptacn•5HCl•2H_2O. After reducing the volume of the supernatant from the $[Ni(daptacn)][ClO_4]_2$ preparation to 15 cm^3, an equal volume of concentrated HCl was added. The solution immediately discoloured from purple to pale blue, but heating at 60 °C for 3 h was required before the colour turned pale green, indicating complete decomplexation. The cooled solution was sorbed on an ion-exchange column (Dowex 50W-X8, 50–100 mesh, H^+ form, 4 × 10 cm). After removal of the $[Ni(H_2O)_6]^{2+}$ ions with 1.5 mol dm^{-3} HCl (500 cm^3), the column was eluted with 6 mol dm^{-3} HCl (1500 cm^3) to remove the hydrochloride salt of the ligand. The latter fraction was taken to dryness under reduced pressure, the residue was dissolved in a minimum amount of water (5 cm^3), then dimethylformamide (dmf) (50 cm^3) and concentrated HCl (1 cm^3) were added. The volume was reduced to 10 cm^3 under reduced pressure, whereupon the product precipitated as a white powder which was filtered off, rinsed with cold dmf, cold ethanol and air dried. Yield: 3.5 g (7.6 mmol, 4.2%) (Found: C, 30.80; H, 8.10; Cl, 38.35; N, 14.90. Calc. for $C_{12}H_{38}Cl_5N_5O_2$: C, 31.20; H, 8.30; Cl, 38.40; N, 15.15%). ^{13}C NMR (D_2O): δ 21.5 ($CH_2CH_2CH_2$) 36.7 ($CH_2CH_2CH_2NH_2$), 42.1, 48.3, 48.9 and 52.7 (CH_2N). The total yield of daptacn obtained was 18.1 mmol (10%).

$[Ni_2(maptacn)_2Cl_2][ClO_4]_2$. The fourth band from the column was eluted with 0.4 mol dm^{-3} NaCl. Most of the NaCl was removed upon repeatedly taking the solution to dryness, dissolving the complex in a minimum of 95% ethanol, and filtering off the precipitate of NaCl. The complex was then dissolved in water and $NaClO_4$ (8 g) added. Only a few crystals formed, which were intermixed with these of NaCl. The blue crystals were hand-picked, and judged suitable for X-ray crystal-structure analysis. The rest of the solution was treated with 6 mol dm^{-3} HCl in order to identify the ligand.

Maptacn·4HCl·H_2O. The solution containing $[Ni(maptacn)]^{2+}$ was taken to dryness, and the resulting solid was dissolved in 6 mol dm^{-3} HCl (60 cm^3). Upon heating at 60 °C for 1 h the solution changed from blue to pale green, indicating complete decomplexation. The cooled solution was sorbed on a cation-exchange column (Dowex 50W-X8, 50–100 mesh, H$^+$ form, 4 × 10 cm) and the $[Ni(H_2O)_6]^{2+}$ removed using 1 mol dm^{-3} HCl (1000 cm^3). Elution with 4 mol dm^{-3} HCl (1000 cm^3) released the ligand. After the 4 mol dm^{-3} HCl fraction was taken to dryness the residue was dissolved in a minimum amount of water (5–10 cm^3), then dmf (50 cm^3) and HCl (1 cm^3) were added. Upon removal of the solvent to 1/5th the original volume a white powder formed which was filtered off, rinsed with cold dmf, cold ethanol and air dried. Yield: 5.2 g (14.8 mmol, 8.3%) (Found: C, 31.30; H, 7.95; Cl, 39.85; N, 16.00. Calc. for $C_9H_{28}Cl_4N_4O$: C, 30.85; H, 8.05; Cl: 40.50; N, 16.00%). ^{13}C NMR (D_2O): δ 22.1 ($CH_2CH_2CH_2$), 37.2 ($CH_2CH_2CH_2NH_2$), 42.0, 47.3, 51.4 (ring CH_2N) and 52.8 ($NCH_2CH_2CH_2NH_2$) (intensity ratio 1:1:2:2:2:1).

$[Co(daptacn)Cl][ClO_4]_2·H_2O$. To a solution containing a mixture of maptacn, daptacn, and taptacn ligands (2 g) in water (90 cm^3) was added $CoCl_2·6H_2O$ (1.58 g, 6.6 mmol) and activated charcoal (0.6 g). Air was bubbled through this solution overnight, by which time the solution was reddish brown. After filtration to remove the charcoal, the solution was sorbed on an ion-exchange column (Dowex 50W-X8, 50–100 mesh, H$^+$ form, 25 × 3 cm). Elution with a mixture of 2 mol dm^{-3} HCl and 1 mol dm^{-3} NaCl (4 l) removed the desired complex. The fractions were taken repeatedly to dryness, dissolved in ethanol, and filtered to remove NaCl. After most of the NaCl had been removed the complex was dissolved in a minimum amount of water, $NaClO_4$ was added, and the solution was layered with Pr^{i}OH. Purple crystals were obtained, which were filtered off, rinsed with cold water, Pr^{i}OH and air dried. Yield: 70 mg (0.13 mmol, 2%) (Found: C, 26.10; H, 5.50, Cl, 19.55; N, 12.35. Calc. for $C_{12}H_{33}Cl_3CoN_5O_9$: C, 26.00; H, 5.65; Cl, 19.15; N, 12.60%). ^{13}C NMR (D_2O): δ 23.4, 24.7 ($CH_2CH_2CH_2$), 37.0, 38.4 (CH_2NH_2), 47.4, 55.1, 55.9, 58.6, 60.9, 62.8, 66.1 and 66.9 (CH_2N).

$[Cu(daptacn)][ClO_4]_2$. The ligand daptacn·5HCl·2H_2O (2.05 g, 4.44 mmol) was added to a solution of NaOH (1.03 g, 24.1 mmol) in water (20 cm^3). After dilution to 100 cm^3 with ethanol, the mixture was heated to 60 °C before a solution of $[Cu(H_2O)_6][ClO_4]_2$ (1.53 g, 4.81 mmol in 10 cm^3 50% ethanol) was added. The reaction mixture instantaneously turned dark blue, but stirring at 60 °C was continued for 20 min. The volume was reduced to 25 cm^3 under reduced pressure and the ensuing precipitate filtered off, rinsed with cold water, then ethanol and air dried. A second crop was obtained after reducing the volume further (to 5 cm^3) and allowing the solution to stand overnight. Total yield 1.79 g (3.53 mmol, 80%) (Found: C, 28.30; H, 5.75; Cl, 13.50; N, 13.60. Calc. for $C_{12}H_{29}Cl_2CuN_5O_8$: C, 28.50; H, 5.75; Cl, 14.00; N, 13.85%).

$[Ni_2(maptacn)_2(C_2O_4)][ClO_4]_2·H_2O$. To a solution of $[Ni(maptacn)]^{2+}$ (6.5 mmol) in water (100 cm^3) containing 0.01 mol dm^{-3} sodium tetraborate buffer (pH 9.18) was added sodium oxalate (460 mg, 3.3 mmol). The solution was refluxed for 1 h, after which the volume was reduced to 10 cm^3 and $NaClO_4$ (1 g) added. A pink precipitate formed immediately, which was filtered off, rinsed with cold water, and air dried. Yield: 2.09 g (2.63 mmol, 80%) (Found: C, 29.90; H, 5.65; Cl, 9.20; N, 13.90. Calc. for $C_{20}H_{46}Cl_2N_8NiO_{13}$: C, 30.20; H, 5.85; Cl, 8.90; N, 14.10%). IR: NH stretches, 3260, 3270, 3315 and 3340; CO stretch, 1635 cm^{-1}.

CAUTION: Transition-metal perchlorates are known to explode. These materials should be made only in small quantities and treated with extreme caution.

Crystallography.—Experimental parameters for the three complex ions studied are presented in Table 1. Crystals were mounted in glass Lindemann tubes and the unit cells and space groups determined by using Weissenberg and precession photography, after which the crystals were transferred to a Picker four-circle diffractometer automated with a PDP11/10 computer.

$[Co(daptacn)Cl][ClO_4]_2·H_2O$. Crystals were grown by slow evaporation of an aqueous solution containing the complex, $NaClO_4$ and traces of HCl.

The unit cell was refined by using 15 pairs of reflections in the range 2θ 14–39°. Intensity measurements were obtained by scanning in the θ–2θ mode using 120 steps of 0.01° in 2θ, counting for 0.5 s per step. Background counting was introduced for 30 s at the end of each scan. A set of three reflections preceded each batch of measurements with no noticeable change in intensity observed during the collection.

Solution of the phase problem was by direct methods using SHELX 76.[17] The atomic scattering factors used were those included in the SHELX 76 program together with the cobalt *f* curve.[18] The program used for absorption correction was a local modification of an existing procedure.[19] Completion and refinement of the structure were carried out by difference electron-density maps and least-squares techniques. All atoms were refined anisotropically except for the hydrogens which were observed and refined isotropically. The refinement converged with a maximum shift to estimated standard deviation (e.s.d.) of 0.340 (corresponding to the position of one of the hydrogen atoms) in the final cycle, and a maximum unassigned peak of 0.76 e Å^{-3} at an R value of 0.0855 (R' = 0.0724).

$[Cu(daptacn)][ClO_4]_2$. X-Ray quality crystals of $[Cu(daptacn)][ClO_4]_2$ were obtained from two different solvent systems, acetonitrile–diethyl ether and ethanol. Details of the former are described.

The unit cell was refined by using 15 pairs of reflections in 2θ from 16 to 36°. The intensity measurements were obtained by scanning in the θ–2θ mode using 200 steps of 0.01° in 2θ counting for 0.25 s per step. Background counting was introduced for 25 s at each end of the scan. A set of three standard reflections preceded each batch of 50 measurements, with no noticeable change in intensity during the collection. The structure was refined in a manner similar to that described above. All atoms were refined anisotropically except for the hydrogen atoms which were not included in the solution. The refinement converged with a maximum shift/e.s.d. of 0.114 in the final cycle, and a maximum unassigned peak of 0.62 e Å^{-3}, at an R 0.0811 (R' = 0.0895). The reason for the high R values is probably the extensive disorder in the perchlorate ions. No attempt was made to model this disorder.

$[Ni_2(maptacn)_2(\mu-Cl)_2][ClO_4]_2$. Crystals of $[Ni_2(maptacn)_2(\mu-Cl)_2][ClO_4]_2$ were obtained from an aqueous solution of the complex containing both sodium chloride and sodium perchlorate.

The unit cell was refined by using 25 pairs of reflections in 2θ in the range 15–48°. The intensity measurements were obtained by scanning in the θ–2θ mode using 176 steps of 0.01° in 2θ

Table 1 Experimental crystallographic data[a]

	$[Co(daptacn)Cl][ClO_4]_2{\cdot}H_2O$	$[Cu(daptacn)][ClO_4]_2$ (set a)	$[Ni_2(maptacn)_2(\mu\text{-}Cl)_2][ClO_4]_2$
Formula	$C_{12}H_{31}Cl_3CoN_5O_9$	$C_{12}H_{29}Cl_2CuN_5O_8$	$C_9H_{22}Cl_2N_4NiO_4$ ($\frac{1}{2}$ molecule)
M	554.70	505.8	379.9
Crystal colour	Magenta	Blue	Bluish purple
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pbca*	*Pbca*	$P\bar{1}$
Cell dimensions			
a/Å	19.538(4)	17.358(4)	10.235(2)
b/Å	16.813(4)	14.262(3)	11.373(3)
c/Å	13.155(3)	16.533(4)	7.150(2)
α/°			81.84(2)
β/°			99.36(2)
γ/°			109.96(2)
U/Å^3	4321.25	4093.2	768.55
Z	8	8	1
D_c/g cm^{-3}	1.705	1.647	1.641
D_m/g cm^{-3}	1.687	1.50	1.637
F(000)	2223.91	1159.94	395.98
Crystal dimensions/mm	0.38 × 0.11 × 0.21	0.87 × 0.15 × 0.11	0.30 × 0.28 × 0.23
Filter	Zirconium	Graphite	Zirconium
2θ range/°	2–45	2–45	2–50
Octants collected	*h,k,l*	*h,k,l*	±*h*,±*k*,*l*
Standard reflections	600, 602, 604	800, 060, 008	030, 004, 500
No. reflections collected	2825	2678	2709
No. observed [$I > n\sigma(I)$]	1906 (n = 1)	1378 (n = 2)	2709 (n = 0)
No. parameters	395	253	269
μ/cm^{-1}	12.78	12.98	16.18
Solution method	Direct	Direct	Patterson map
R^b	0.0855	0.0811	0.0562
R'^c	0.0724	0.0895	0.0641

[a] Details in common: Mo-Kα radiation (λ = 0.710 69 Å). [b] $\Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [c] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$ where $w = 1.41/(\sigma_F{}^2 + 0.001F^2)$ for Co, $2.30/(\sigma_F{}^2 + 0.001F^2)$ for Cu and $0.0289/(\sigma_F{}^2 + 0.001F^2)$ for Ni.

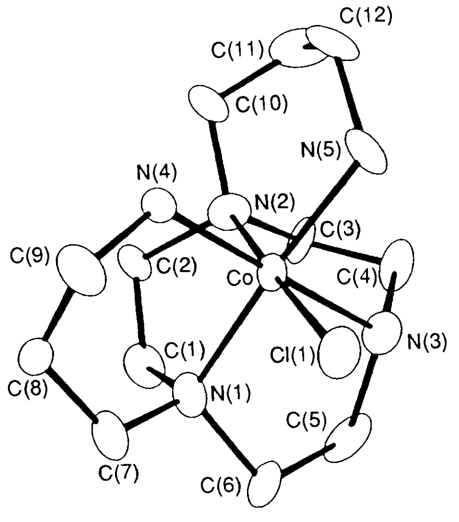


Fig. 1 ORTEP Diagram of $[Co(daptacn)Cl]^{2+}$ ion showing 25% thermal ellipsoids

counting for 0.25 s per step. Background counting was introduced for 22 s at the end of each scan. A set of three standard reflections preceded each batch of 50 measurements with no observable decay in intensity during the collection. Solution of the phase problem was achieved using the Patterson function. Completion and refinement of the structure was carried out by difference electron-density maps and by least squares. All atoms were refined anisotropically except for the hydrogen atoms which were observed and refined isotropically. The refinement converged with a maximum shift/e.s.d. of 0.05 in the final cycle, and a maximum unassigned peak of 0.90 e Å^{-3} at an R 0.056 (R' = 0.064).

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

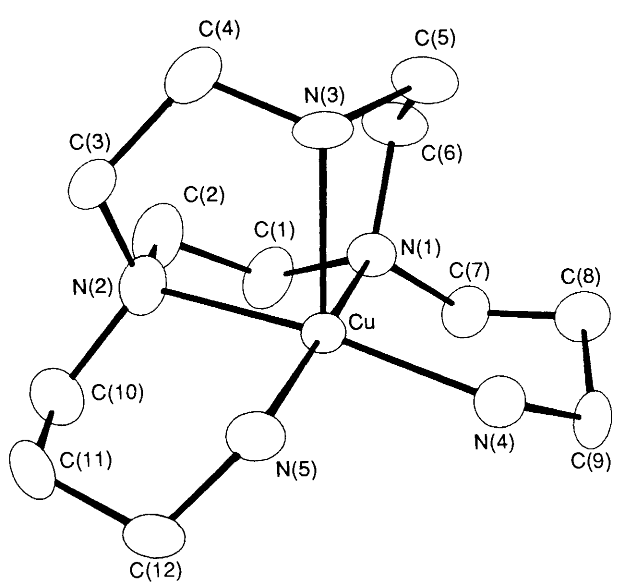


Fig. 2 ORTEP Diagram of the cation $[Cu(daptacn)]^{2+}$ showing 25% thermal ellipsoids

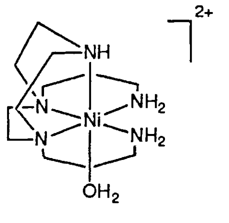
Results and Discussion

The method of preparation of the ligand hydrochlorides is shown in Scheme 1 and the metal complexes were synthesised as outlined. In the case of $[Cu(daptacn)]^{2+}$, reactions of the coordinated ligand have been carried out.[20] Reaction with glyoxal followed by reduction with tetrahydroborate provides the fully reduced macrocyclic cyclam ring. The reaction is of interest in

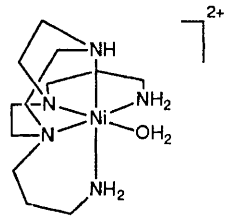
Table 2 Fractional atomic coordinates

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
(*a*) $[Co(daptacn)Cl][ClO_4]_2{\cdot}H_2O$							
Co	10 706(8)	11 115(8)	20 062(10)	N(3)	531(7)	2 020(7)	2 483(9)
Cl(1)	726(2)	1 358(2)	408(2)	N(4)	1 616(5)	193(6)	1 507(8)
Cl(2)	4 026(2)	1 966(2)	−505(3)	N(5)	1 871(7)	1 800(8)	1 698(11)
Cl(3)	1 732(2)	4 117(2)	1 927(3)	C(1)	296(11)	179(13)	3 414(12)
O(1)	3 973(7)	2 731(5)	−168(9)	C(2)	1 001(8)	195(8)	3 752(10)
O(2)	3 593(5)	1 822(6)	−1 346(7)	C(3)	1 051(11)	1 656(8)	4 093(11)
O(3)	4 718(5)	1 823(7)	−812(9)	C(4)	867(10)	2 348(9)	3 422(11)
O(4)	3 871(6)	1 405(7)	240(8)	C(5)	−208(10)	1 774(11)	2 694(12)
O(5)	1 167(6)	3 654(7)	1 733(9)	C(6)	−342(9)	1 013(11)	2 189(12)
O(6)	1 743(7)	4 777(6)	1 295(9)	C(7)	121(8)	−223(8)	1 601(13)
O(7)	1 683(9)	4 376(9)	2 883(9)	C(8)	694(8)	−800(9)	1 525(12)
O(8)	2 279(7)	3 688(9)	1 839(18)	C(9)	1 274(8)	−456(9)	926(12)
O(9)	2 631(9)	−1 025(11)	4 815(12)	C(10)	2 078(9)	913(9)	3 658(12)
N(1)	234(5)	459(6)	2 313(7)	C(11)	2 471(10)	1 634(11)	3 324(14)
N(2)	1 336(5)	978(6)	3 458(7)	C(12)	2 534(10)	1 695(11)	2 193(13)
(*b*) $[Cu(daptacn)][ClO_4]_2$							
Cu	42 525(10)	27 400(11)	11 084(10)	N(4)	5 370(7)	2 476(8)	839(9)
Cl(1)	448(3)	2 783(4)	1 507(3)	N(5)	4 484(7)	4 121(8)	949(9)
Cl(2)	1 665(3)	4 807(3)	4 074(3)	C(1)	3 458(11)	1 502(13)	2 123(12)
O(1)	635(9)	3 488(10)	978(10)	C(2)	2 832(11)	2 187(17)	1 871(14)
O(2)	−109(13)	2 978(14)	1 991(14)	C(3)	2 695(10)	3 379(14)	766(13)
O(3)	1 014(10)	2 455(21)	1 939(12)	C(4)	2 773(10)	2 642(15)	89(14)
O(4)	202(17)	2 087(12)	1 045(13)	C(5)	3 770(12)	1 347(12)	−91(11)
O(5)	1 144(10)	5 581(12)	4 084(9)	C(6)	3 616(11)	888(10)	709(12)
O(6)	1 626(12)	4 441(11)	4 833(10)	C(7)	4 640(12)	813(11)	1 764(12)
O(7)	1 500(12)	4 163(14)	3 524(12)	C(8)	5 316(12)	748(11)	1 173(12)
O(8)	2 369(9)	5 132(11)	3 893(9)	C(9)	5 824(10)	1 636(12)	1 150(11)
N(1)	3 997(8)	1 376(8)	1 419(8)	C(10)	3 162(11)	3 816(17)	2 177(12)
N(2)	3 152(8)	3 070(10)	1 517(11)	C(11)	3 508(15)	4 750(14)	1 894(12)
N(3)	3 593(8)	2 401(8)	−27(8)	C(12)	4 354(13)	4 717(12)	1 680(13)
(*c*) $[Ni_2(maptacn)_2(\mu\text{-}Cl)_2][ClO_4]_2$							
Ni(1)	12 539(4)	13 860(4)	11 602(6)	N(4)	2 616(4)	384(4)	2 242(7)
Cl(1)	760(1)	499(1)	−1 996(1)	C(1)	2 235(4)	3 695(3)	−1 106(5)
Cl(2)	−2 955(1)	3 025(1)	−3 804(2)	C(2)	912(4)	3 792(4)	−582(6)
O(1)	−2 607(5)	3 524(5)	−1 955(6)	C(3)	−595(4)	2 629(4)	1 907(6)
O(2)	−2 024(5)	2 373(4)	−3 828(8)	C(4)	537(4)	2 943(4)	3 596(6)
O(3)	−2 951(8)	3 938(5)	−5 214(8)	C(5)	3 001(4)	2 979(4)	3 983(5)
O(4)	−4 338(5)	2 099(5)	−3 830(8)	C(6)	3 462(4)	3 735(3)	2 141(5)
N(1)	2 917(3)	3 002(3)	441(4)	C(7)	4 068(4)	2 754(4)	−307(6)
N(2)	25(3)	2 551(3)	230(5)	C(8)	4 734(4)	1 894(4)	991(7)
N(3)	1 496(3)	2 202(3)	3 697(4)	C(9)	3 804(5)	540(4)	1 188(8)

Estimated standard deviations are given in parentheses. Coordinates × 10^n where $n = 5$ for M and 4 otherwise.



A



B

that it is one of the few examples of a successful glyoxal condensation promoted by copper(II). Barefield *et al.*[21] were unable to prepare the copper cyclam complex by glyoxal condensation because of precipitation of metallic copper in the BH_4^- reduction step. Subsequently our laboratory[14] using a copper(II) ion and Barefield and co-workers[22] [with the nickel(II) complex of 5-(3-aminopropyl)-8-methyl-1,5,8,12-tetraazadodecane] provided examples of functionalised tetraazadodecanes. What is noteworthy is that, in all three instances, five-co-ordinate metal centres are involved, leading to the possible increased stability of intermediates formed in the condensation process. There is a need for structural information on complexes of ligands of this type, since (see below) isomeric octahedral configurations are possible depending on whether the sixth substituent in the octahedral framework is *cis* or *trans* to the unsubstituted amine of the triazacyclononane.

Molecular Structures.—The structures of $[Co(daptacn)Cl]^{2+}$ and $[Cu(daptacn)]^{2+}$ are shown in Figs. 1 and 2. Significant differences are observed in that, as anticipated, the cobalt(III) complex is six-co-ordinate. However, the copper(II) ion shows pseudo-square-pyramidal five-co-ordinated geometry. Crystals of $[Ni(daptacn)(H_2O)][ClO_4]_2$ were obtained from an aqueous solution containing the complex and sodium perchlorate. The structure was solved only to an R value of 0.19, owing to the fact that the crystal contained two isomers, one in which the water molecule is *trans* to the unsubstituted amine on the ring (**A**), and one in which it is *cis* (**B**). The two structures were disordered and were not refined further.

$[Co(daptacn)Cl][ClO_4]_2{\cdot}H_2O$. The structure consists of the pseudo-octahedral ion $[Co(daptacn)Cl]^{2+}$, two perchlorate ions and a water molecule. Seven H atoms [H(1)–H(7)] are associated with N(3)[H(1)], N(4)[H(2),H(3)], N(5)[H(4),H(5)] and O[H(6),H(7)]. The water molecule is weakly hydrogen-

Table 3 Selected bond lengths (Å) and angles (°) for [Co(daptacn)Cl]-$[ClO_4]_2 \cdot H_2O$ with e.s.d.s. in parentheses

Cl(1)–Co	2.246(3)	N(3)–Co	1.960(12)
N(1)–Co	2.010(10)	N(4)–Co	1.988(10)
N(2)–Co	1.992(9)	N(5)–Co	1.987(13)
N(1)–Co–Cl(1)	92.6(3)	N(4)–Co–N(2)	95.1(4)
N(2)–Co–Cl(1)	175.2(3)	N(4)–Co–N(3)	179.4(5)
N(2)–Co–N(1)	87.6(4)	N(5)–Co–Cl(1)	86.4(4)
N(3)–Co–Cl(1)	89.7(4)	N(5)–Co–N(1)	177.4(5)
N(3)–Co–N(1)	85.6(5)	N(5)–Co–N(2)	93.2(5)
N(3)–Co–N(2)	85.5(5)	N(5)–Co–N(3)	92.0(6)
N(4)–Co–Cl(1)	89.7(3)	N(5)–Co–N(4)	87.9(5)
N(4)–Co–N(1)	94.5(4)		

Table 4 Selected interatomic distances (Å) and angles (°) for [Cu(daptacn)]$[ClO_4]_2$ with e.s.d.s in parentheses

N(1)–Cu	2.061(12)	N(4)–Cu	2.026(13)
N(2)–Cu	2.080(13)	N(5)–Cu	2.027(12)
N(3)–Cu	2.251(12)		
N(2)–Cu–N(1)	86.3(5)	N(4)–Cu–N(3)	105.3(6)
N(3)–Cu–N(1)	84.0(5)	N(5)–Cu–N(1)	172.9(6)
N(3)–Cu–N(2)	81.5(6)	N(5)–Cu–N(2)	90.2(6)
N(4)–Cu–N(1)	94.9(5)	N(5)–Cu–N(3)	101.6(5)
N(4)–Cu–N(2)	173.2(7)	N(5)–Cu–N(4)	87.8(5)

Table 5 Selected bond lengths (Å) and angles (°) for $[Ni_2(maptacn)_2(\mu\text{-}Cl)_2][ClO_4]_2$ with e.s.d.s in parentheses

Cl(1)–Ni(1)	2.507(1)	N(2)–Ni(1)	2.096(3)
Cl(1′)–Ni(1)	2.495(1)	N(3)–Ni(1)	2.093(3)
N(1)–Ni(1)	2.102(3)	N(4)–Ni(1)	2.080(3)
N(1)–Ni(1)–Cl(1)	96.4(1)	N(4)–Ni(1)–N(2)	174.0(2)
N(2)–Ni(1)–Cl(1)	92.7(1)	N(4)–Ni(1)–N(3)	93.8(2)
N(2)–Ni(1)–N(1)	83.9(1)	Cl(1′)–Ni(1)–C(1)	83.8(1)
N(3)–Ni(1)–Cl(1)	174.1(1)	Cl(1′)–Ni(1)–N(1)	178.5(1)
N(3)–Ni(1)–N(1)	84.4(1)	Cl(1′)–Ni(1)–N(2)	95.2(1)
N(3)–Ni(1)–N(2)	81.5(1)	Cl(1′)–Ni(1)–N(3)	95.2(1)
N(4)–Ni(1)–Cl(1)	92.1(1)	Cl(1′)–Ni(1)–N(4)	88.9(1)
N(4)–Ni(1)–N(1)	91.9(1)	Ni(1)–Cl(1)–Ni(1′)	96.2(1)

Primes denote atoms obtained through the symmetry element $-x$, $-y$, $-z$.

bonded to the primary amines on the pendant arms [O(9) ··· H(3) 2.24, O(9) ··· N(4) 3.012, H(3)–N(4) 0.86(9) Å, O(9)–H(3)–N(4) 149°; O(9) ··· H(4) 2.30, O(9) ··· N(5) 2.963, H(4)–N(5) 0.90(9) Å, O(9)–H(4)–N(5) 130°]. The atomic coordinates are listed in Table 2.

The co-ordination at the cobalt centre consists of the five nitrogens from daptacn and one chloride ion (Fig. 1). As was noted for the nickel complex, there are two possible isomers for octahedral complexes of daptacn. In this case, the only isomer observed is the one (**B**) with the chloride ion *cis* to the secondary amine. The bond lengths and angles are listed in Table 3. The Co–N bond lengths vary from 1.96 to 2.01 Å, which is slightly shorter than in the $[Co(taptacn)]^{3+}$ complex[3] [Co–Ni(primary) 1.99, Co–N(tertiary) 2.03 Å] indicating a relief from steric crowding upon replacement of a chelate ring with a chloride ion. In contrast to $[Co(taptacn)]^{3+}$, there is no clear distinction between the Co–N(ring) and the Co–N(pendant arm) distances. The bond angles at the cobalt centre average 86.2° for the chelate angles defined by nitrogens in the [9]aneN_3 ring, identical to that observed in $[Co(taptacn)]^{3+}$. The chelate angles of the six-membered ring average 83.9°, again similar to the value in $[Co(taptacn)]^{3+}$. The cobalt centre is only slightly distorted from an ideal octahedral co-ordination sphere as expected for a d^6 ion. The distortion is a result of the size of the [9]aneN_3 ring which is not quite large enough to occupy the three corners of the octahedron.

[Cu(daptacn)]$[ClO_4]_2$. X-Ray quality crystals of [Cu(daptacn)]$[ClO_4]_2$ were obtained in two different solvent systems. Photography was carried out on the two sets of crystals, and it was found that they belonged to the orthorhombic space group *Pbca* but with different unit-cell dimensions. Data were collected for both crystals, to investigate possible differences in the co-ordination geometry or in the co-ordination number. Both structures were solved and found not to have any major differences. The details of only one of the structures is discussed here, that for the crystal grown from acetonitrile–diethyl ether. The crystal data are provided in Table 1.

The atomic coordinates are listed in Table 2, and the bond lengths and angles in Table 4. The structure consists of a five-co-ordinate copper complex and two perchlorate ions. The molecular structure of the complex ion, shown in Fig. 2, is best described as a distorted square pyramid, with the copper atom above the plane described by the four basal nitrogen ligands, and the apical nitrogen tilted away from the position directly above the copper atom. The displacement of the copper atom out of the plane is 0.116 Å towards the apical position and the angle between the N(ap)–Cu vector and the normal to the N_4 plane is 14.5°. The latter deviation is a result of the inability of the ligand completely to reach over and occupy the apical position. As has been shown recently,[20] when the two pendant arms are linked to form a 14-membered macrocycle the copper atom is pushed further out of the N_4 plane and the degree of 'tugging' on the apical nitrogen increases.

The five-co-ordinate nature of the $[Cu(daptacn)]^{2+}$ ion is in contrast with the corresponding complexes of Ni^{II} and Co^{III} in which both metal centres are octahedral. The difference in co-ordination number is a result of the very small crystal-field stabilisation energy (c.f.s.e.) difference between octahedral and square-pyramidal complexes for d^9 ions, such that the c.f.s.e. would not compensate for the steric strain caused by the addition of a sixth ligand.

The Cu–N bond lengths fall in three categories, Cu–N(apical) being the longest at 2.251(12) Å. The basal nitrogens are differentiated among themselves; the bond lengths to the primary amines are significantly shorter [2.026(13) Å)] than those to the tertiary amines [2.07(1) Å], probably owing to increased steric crowding around the tertiary amines.

The bond lengths involving Cu and the [9]aneN_3 ring are consistent with values obtained for other five-co-ordinate copper complexes involving the [9]aneN_3 ring, such as $[Cu([9]aneN_3)(N_3)_2]$,[23] $[Cu([9]aneN_3)Br_2]$,[24] and $[Cu([9]aneN_3)Cl_2]$.[25] In these complexes the Cu–N(apical) distance ranges from 2.230 to 2.246 Å and Cu–N(basal) from 2.035 to 2.072 Å. The values of the N–Cu–N angles within the ring average 83.9°, slightly distended over those in the three complexes described above (average of nine angles: 82.8°). This distention is probably a result of a minor pull by the pendant arms. The chelate angles of the two pendant arms are different (90.2 and 94.9°). This asymmetry is a result of the non-planarity of the ethylenediamine chelate ring [N(1)–C(1)–C(2)–N(2)] which destroys the mirror-plane symmetry otherwise expected for this structure.

The bite distance between N(4) and N(5) is only 2.811 Å, comparable to that spanned between the nitrogens involved in five-membered chelate rings (average 2.85 Å) in this complex. Thus the $[Cu(daptacn)]^{2+}$ complex is predisposed towards ring closing to form another five-membered chelate ring. In contrast, the six-membered chelate bites average 2.96 Å.

$[Ni_2(maptacn)_2(\mu\text{-}Cl)_2][ClO_4]_2$. The atomic coordinates are listed in Table 2, and the bond lengths and angles in Table 5. The crystal structure consists of the $[Ni_2(maptacn)_2(\mu\text{-}Cl)_2]^{2+}$ dimeric cation packed with two perchlorate counter ions. The asymmetric unit consists of the dimer and one counter ion. The two halves of the dimer are related by a crystallographically

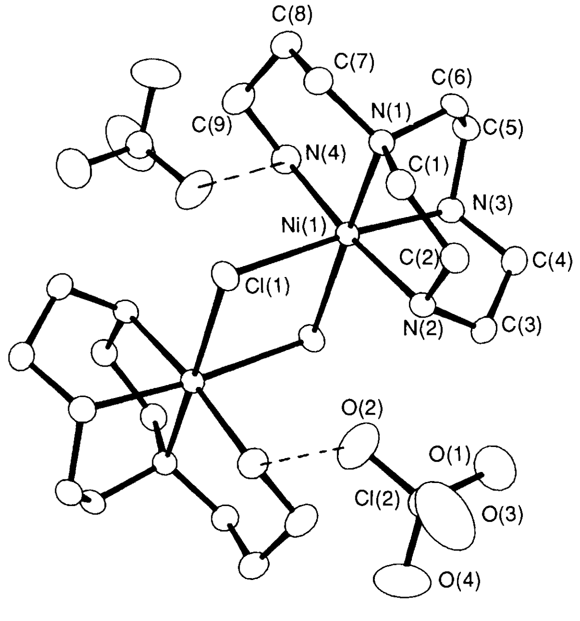


Fig. 3 ORTEP Diagram of the molecule $[Ni_2(maptacn)_2(\mu-Cl)_2][ClO_4]_2$ showing 25% thermal ellipsoids

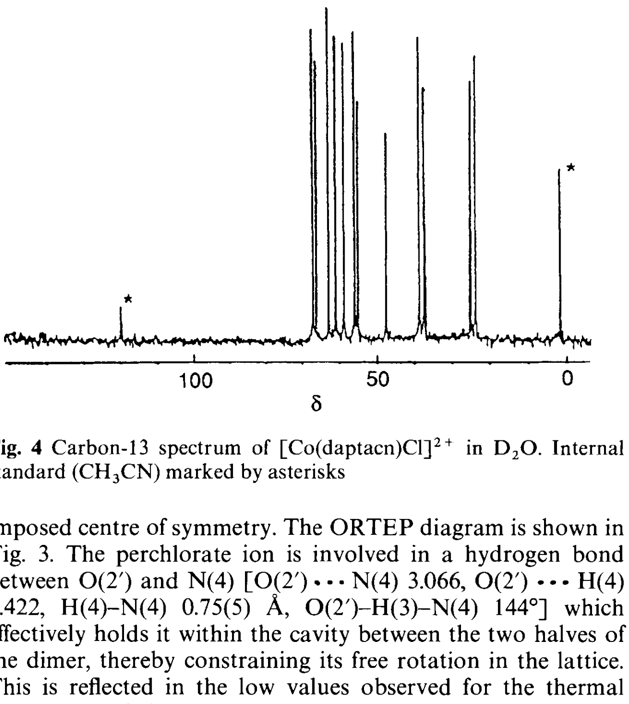


Fig. 4 Carbon-13 spectrum of $[Co(daptacn)Cl]^{2+}$ in D_2O. Internal standard (CH_3CN) marked by asterisks

imposed centre of symmetry. The ORTEP diagram is shown in Fig. 3. The perchlorate ion is involved in a hydrogen bond between O(2′) and N(4) [O(2′) ··· N(4) 3.066, O(2′) ··· H(4) 2.422, H(4)–N(4) 0.75(5) Å, O(2′)–H(3)–N(4) 144°] which effectively holds it within the cavity between the two halves of the dimer, thereby constraining its free rotation in the lattice. This is reflected in the low values observed for the thermal parameters of the oxygen atoms of the perchlorate ion. The hydrogen bond is indicated by a broken line in Fig. 3. The geometry around the nickel centre is distorted octahedral formed by co-ordination of the four nitrogens from maptacn and two bridging chloride ions in *cis* positions. The three Ni–N bond lengths to the nitrogens on the ring are the same within experimental error at 2.097(4) Å, whereas the bond to the primary amine of the pendant arm is shorter, 2.080(3) Å. These bond lengths are significantly shorter than the Ni–N bond lengths in $[Ni(taptacn)]^{2+}$.[3] However, it has previously been noted that there is a shortening of the Ni–N bond as nitrogens are replaced by oxygen centres, for example for the series $[Ni(en)(H_2O)_4]^{2+}$, $[Ni(en)_2(H_2O)_2]^{2+}$ and $[Ni(en)_3]^{2+}$ (en = ethylenediamine) the Ni–N bond lengths are 2.065,[26] 2.09[27] and 2.12 Å,[28] respectively. The principal cause of this shortening has been attributed to a decrease in steric strain[29] as the chelate ring is replaced by water molecules. The same effect can be expected when two of the nitrogen ligands are replaced by bridging *cis*-chloride ions as is the case in the present system. Since the Cl–Ni–Cl′ angle (83.8°) is quite small, the pair of chloride atoms occupy less of the co-ordination sphere than expected, allowing the N_4 ligand a closer approach.

The Ni–Cl bond lengths (2.495 and 2.507 Å) are comparable with those reported for similar nickel complexes containing *cis* bridging chlorides. For example, in $[Ni_2(en)_4(\mu-Cl)_2]X_2$[30] the Ni–Cl distances are 2.461 and 2.512 Å when X = ClO_4 and 2.461 and 2.551 Å when X = Cl. In the $[Ni_2(en)_4(\mu-Cl)_2]^{2+}$ system the bridge is quite asymmetric (the two Ni–Cl bonds differ by as much as 0.1 Å). This disparity between the Ni–Cl distances was attributed to hydrogen bonding.[30] In the present system the bridge is almost symmetric, probably owing to the absence of any hydrogen bonding. The shortest Cl ··· N contact is Cl(1′) ··· N(4) (3.234 Å), and is not through any of the hydrogens on the amine [Cl ··· H(3) 3.279 Å, Cl(1′) ··· H(3) ··· N(4) 80°; Cl(1′) ··· H(4) = 2.925 Å, Cl(1′)–H(4)–N(4) 107°]. (For a hydrogen bond the angle at the hydrogen should be close to 180°.)

The N–Ni–N angles where all the nitrogens are part of the $[9]aneN_3$ ring average 82.6°, typical of ethylenediamine chelate angles in high-spin nickel(II) complexes[26] and similar to the value obtained in $[Ni(taptacn)]^{2+}$ (83.3°). The N(1)–Ni–N(4) angle, representing the chelate angle for the six-membered ring, is 91.9°, again resembling the value obtained[3] in $[Ni(taptacn)]^{2+}$ (92.4°).

Solution Studies.—Details of the electronic spectra of the complexes are given in Table 6. The spectra of the $[Ni(daptacn)(H_2O)]^{2+}$ and $[Ni(maptacn)(H_2O)_2]^{2+}$ complexes in neutral aqueous media are typical of octahedral polyamine complexes of nickel(II).[31] However, addition of acid ($[H^+]$ *ca.* 0.1 mol dm^{-3}) causes rapid protonation of the labile primary amines. The resulting chromophore resembles very closely that of protonated nickel(II) taptacn,[3] $[Ni(H_3taptacn)(OH_2)_3]^{5+}$ suggesting that all three complexes must be closely similar upon protonation. The λ_{max} values obtained are reminiscent of those obtained by Melson and Wilkins[32] for facial triaminenickel(II) complexes. Thus, in the present systems, the pendant arms are all easily protonated, leaving an N_3O_3 chromophore at the nickel centre which is inert towards further protonation in 1 mol dm^{-3} $HClO_4$.

The electronic spectrum of $[Co(daptacn)Cl]^{2+}$ is also characteristic of octahedral Co^{III}, but with a noted decrease in the energy of the first d–d transition ($^1A_1 \longrightarrow {}^1T_1$) as a result of substituting a chloride ion for one of the amine nitrogens in the inner co-ordination sphere. Since it is diamagnetic, the complex was also characterised in solution by ^{13}C NMR spectroscopy. The complex shows 12 lines of equal intensity (Fig. 4), indicating that the ligand C_2 symmetry was lost upon co-ordination. This is a result of the chloride ion co-ordinating *cis* to the secondary amine from the $[9]aneN_3$ ring, rather than *trans*. Thus the complex retains the same structure in both solution and crystal environments.

The electronic spectra of $[Cu(daptacn)]^{2+}$ in aqueous sodium tetraborate buffer (pH 9.1) is characteristic of a square-pyramidal CuN_5 chromophore.[33] Upon addition of acid, decomposition is rapid initially to a species with λ_{max} 640 nm (ε *ca.* 40 dm^3 mol^{-1} cm^{-1}) corresponding to the diprotonated species $[Cu(H_2daptacn)(H_2O)_n]^{4+}$. Further protonation to $[Cu(H_2O)_6]^{2+}$ is somewhat slower, but complete decomposition is achieved in 0.10 mol dm^{-3} $HClO_4$. The lower acid stability of the $[Cu(H_2daptacn)(H_2O)_n]^{4+}$ species when compared to the nickel(II) analogue is in keeping with the lower formation constant for $[Cu([9]aneN_3)(H_2O)_n]^{2+}$ compared to $[Ni([9]aneN_3)(H_2O)_3]^{2+}$.[34]

Maintenance of the square-pyramidal structure at low temperatures has been confirmed by a solid solution (methanol–water, 2:1) ESR spectrum at 77 K where a normal copper(II) signal is derived $g_{\parallel} = 2.238$, $A_{\parallel} = 179(2)$ G, $g_{\perp} = 2.061$, with evidence for hyperfine splitting, $A_{\perp}$ *ca.* 38 G.

Owing to the instability of the nickel complex in acidic media

Table 6 Electronic spectroscopic data for pendant-arm complexes

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Ref.
$[Ni(daptacn)(H_2O)]^{2+}$ [a]	374 (11.2), 530 (7.6)	This work
$[Ni(taptacn)]^{3+}$	341 (8.9), 532 (7.2), 815 (sh) (14.5)	3
$[Ni(H_2daptacn)(H_2O)_3]^{4+}$ [b]	350 (7.6), 586 (4.7)	
$[Ni(H_3taptacn)(H_2O)_3]^{5+}$ [b]	363 (3.1), 598 (5.6), 785 (3.6)	3
$[Co(daptacn)Cl]^{2+}$	374 (77.3), 490 (sh), 548 (74.1)	This work
$[Co(taptacn)]^{3+}$	358 (92.5), 497 (77.4)	3
$[Cu(daptacn)]^{2+}$ [a]	578 (106), 865 (39)	This work
$[Cu(H_2daptacn)H_2O)_n]^{2+}$ [c]	640 (40)	

[a] In 0.01 mol dm^{-3} sodium tetraborate buffer, pH 9.1. [b] In 1.0 mol dm^{-3} $HClO_4$. [c] After 2 mol equivalents of acid were added.

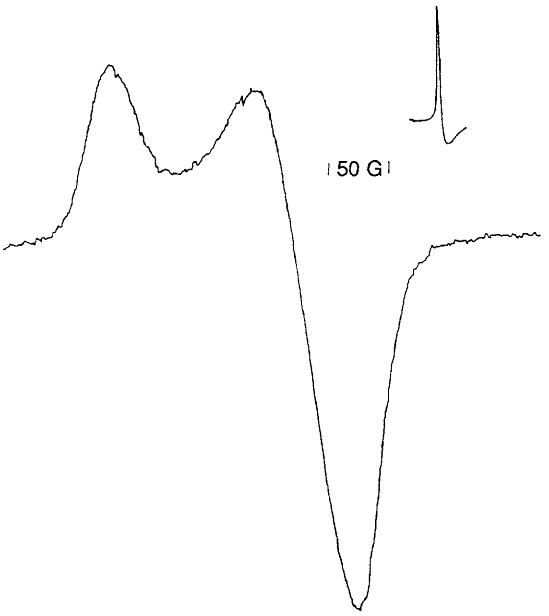
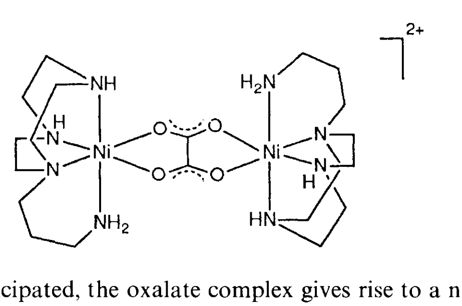


Fig. 5 ESR spectrum of $[Ni_2(maptacn)_2(\mu\text{-}C_2O_4)]^{4+}$ in frozen acetonitrile at 77 K

it was not possible to characterise the nickel(III) complexes of daptacn and maptacn. However, the nickel maptacn complex was treated with oxalate to chelate the two free co-ordination sites, thus forming a co-ordinatively saturated complex which permits formation of a more stable nickel(III) ion in aqueous media at neutral pH, as well as under non-aqueous conditions. The IR spectrum of the precipitate obtained from the reaction mixture contains only one C=O stretching vibration in the region 1600–1800 cm^{-1}, indicating that the oxalate is co-ordinated in a symmetric tetradentate fashion.[35] This species is closely similar to that reported recently involving *cis*-cyclam with an oxalate bridge.[36]



As anticipated, the oxalate complex gives rise to a nickel(III) complex when oxidised in aqueous media (neutral pH) with peroxodisulphate, or in acetonitrile with NO^+ as an oxidant. The resulting Ni^{III} is stable for only a few minutes, but upon freezing gives an ESR spectrum with $g_\perp = 2.079$ and $g_\parallel = 2.184$ (see Fig. 5). The ESR profile is the reverse of normal axial spectra obtained for Ni^{III}, *i.e.* $g_\parallel > g_\perp$. This is indicative[37] of a tetragonally compressed octahedral geometry, in which for a low-spin d^7 ion the unpaired electron is located primarily in the $d_{x^2-y^2}$ orbital. A number of nickel(III) complexes have been reported with this geometry,[38] most of which contain ligands which form *cis* complexes, such as $[Ni^{III}([12]aneN_4)(CH_3CN)_2]^{3+}$.[39] In our system the presence of the axially disposed unsubstituted secondary amine may prevent the bond rearrangement necessary for an axially symmetric ion. Although previous studies[36] have provided evidence for a transient mixed-valence (nickel(II,III) ion, this was not observed under our experimental conditions.

Acknowledgements

We thank Natural Sciences and Engineering Research Council (NSERC) (Canada) for financial support. D. G. F. acknowledges receipt of a Post-graduate NSERC Scholarship. The assistance of Mrs. K. Beveridge in the X-ray studies is gratefully acknowledged.

References

1 N. W. Alcock, R. G. Kingston, P. Moore and C. Pierpoint, *J. Chem. Soc., Dalton Trans.*, 1984, 1937.
2 T. A. Kaden, *Top. Curr. Chem.*, 1984, **121**, 157.
3 G. W. Bushnell, D. G. Fortier and A. McAuley, *Inorg. Chem.*, 1988, **27**, 2626.
4 K. Wieghardt, U. Bossek, P. Chandhuri, W. Herrmann, B. C. Menke and J. Weiss, *Inorg. Chem.*, 1982, **21**, 4308.
5 L. Christiansen, D. M. Hendrickson, H. Toftlund, S. R. Wilson and C. L. Xie, *Inorg. Chem.*, 1986, **25**, 2813.
6 L. Fabbrizzi, F. Forlini, A. Perotti and B. Seghi, *Inorg. Chem.*, 1984, **23**, 807.
7 J. Murase, M. Mikuriya, H. Sonoda and J. Kida, *J. Chem. Soc., Chem. Commun.*, 1984, 692.
8 A. Evers, R. D. Hancock and I. Murase, *Inorg. Chem.*, 1986, **25**, 2160.
9 L. Fabbrizzi, L. Montagna, A. Poggi, T. A. Kaden and L. C. Siegfried, *Inorg. Chem.*, 1986, **25**, 2672.
10 *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979.
11 E. Kimura, M. Shionoya, T. Mita and Y. Iitaka, *J. Chem. Soc., Chem. Commun.*, 1987, 1712.
12 E. K. Barefield, D. Chueng, D. G. Van Derveer and F. Wagner, *J. Chem. Soc., Chem. Commun.*, 1981, 302.
13 A. McAuley, S. Subramanian and T. W. Whitcombe, *J. Chem. Soc., Chem. Commun.*, 1987, 539.
14 D. G. Fortier and A. McAuley *Inorg. Chem.*, 1989, **28**, 655.
15 T. J. Atkins, J. E. Richman and W. F. Oettle, *Org. Synth.*, 1978, **58**, 86.
16 A. McAuley, P. R. Norman and O. Olubuyide, *Inorg. Chem.*, 1984, **23**, 1938.
17 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Refinement, University of Cambridge, 1976.
18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
19 P. Coppens, L. Lieserowitz and D. Rabinovitch; modified by G. W. Bushnell, University of Victoria, 1978.
20 D. G. Fortier and A. McAuley, *J. Am. Chem. Soc.*, 1990, **112**, 2640.
21 E. K. Barefield, F. Wagner and K. D. Hodges, *Inorg. Chem.*, 1976, **15**, 1370.
22 J. Franz, G. M. Freeman, E. K. Barefield, W. A. Volkent, G. J. Ehrhardt and R. A. Holmes, *Nucl. Med. Biol.*, 1987, **14**, 479.
23 P. Chandhuri, K. Oder, K. Wieghardt, B. Nuber and B. Weiss, *Inorg. Chem.*, 1986, **25**, 2818.
24 R. D. Bereman, M. R. Churchill, P. M. Schaber and M. E. Winkler, *Inorg. Chem.*, 1979, **18**, 3122.
25 W. J. Schwindinger, T. G. Fawcett, R. A. Lalancette, J. A. Patenza and H. J. Schugar, *Inorg. Chem.*, 1980, **19**, 1379.
26 G. J. McDougall and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1980, 654.
27 L. Kh. Minacheva, A. S. Antsyshkina and M. A. Porai-Koshits, *Struct. Chem.*, 1974, **15**, 408.
28 R. E. Cramer and J. T. Huneke, *Inorg. Chem.*, 1978, **17**, 365.
29 V. J. Thom, C. C. Fox, J. C. A. Boeyens and R. D. Hancock, *J. Am. Chem. Soc.*, 1984, **106**, 5947.

30 G. A. Bottomley, L. G. Glossop, C. L. Raston, A. H. White and A. C. Wills, *Aust. J. Chem.*, 1978, **31**, 285.
31 K. Wieghardt, W. Schmidt, W. Herrmann and H. J. Kuppers, *Inorg. Chem.*, 1983, **22**, 2953.
32 G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 1963, 2662.
33 B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, 1970, **5**, 1.
34 R. Yang and L. T. Zompa, *Inorg. Chem.*, 1976, **15**, 1499.
35 K. Nakamoto, *Infra-red and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley-Interscience, New York, 1978, p. 237.
36 L. P. Battaglia, A. Bianchi, A. B. Corradi, E. Garcia-Espana, M. Micheloni and M. Julve, *Inorg. Chem.*, 1988, **27**, 4174.
37 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.
38 S. A. Jacobs and D. W. Margerum, *Inorg. Chem.*, 1984, **23**, 1195 and refs. therein.
39 A. Bencini, L. Fabbrizzi and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.

Received 12*th June* 1990; *Paper* 0/02632H