Synthesis, Structure and Properties of Cobalt(III) Complexes of Pentadentate Ligands with Pyridyl Pendant Arms†

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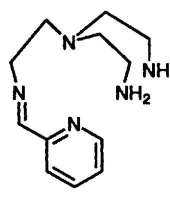
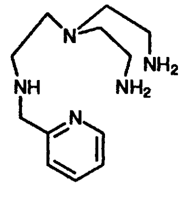
Cobalt(III) complexes of the pentadentate ligands 3-[4-(2-pyridyl)-3-azabut-3-enyl]-3-azapentane-1,5-diamine (L^1), 3-[4-(2-pyridyl)-3-azabutyl]-3-azapentane-1,5-diamine (L^2) and 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (L^4) have been synthesized. Various characterization studies have confirmed the formation of the complexes $[CoL^4(OH_2)]^{3+}$, $[Co(L^4)Cl]^{2+}$, $[Co(L^1)Cl]^{2+}$, $[Co(L^2)Cl]^{2+}$ and $[Co(HL^3)Cl]^{2+}$ (HL^3 = 3-{2-[hydroxy(2-pyridyl)methyleneamino]ethyl}-3-azapentane-1,5-diamine) the product of oxidation of $[Co(L^1)Cl]^{2+}$ in acidic solution. The structure of $[CoL^4(OH_2)][ClO_4]_3 \cdot H_2O$ has been determined by single crystal X-ray diffraction. The complex crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 15.090(3)$, $b = 16.659(4)$, $c = 10.192(4)$ Å and $Z = 4$. Refinement gave final R and R' values of 0.045 and 0.043, respectively, for 1708 observed reflections. The pyridyl pendant arms were found to introduce significant distortion from ideal octahedral geometry. The Co–N(tacn) distances are shorter than in related complexes of ligands derived from 1,4,7-triazacyclononane (tacn). The complex $[Co(HL^3)Cl][ClO_4]_2 \cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.496(5)$, $b = 10.253(3)$, $c = 15.371(6)$ Å, $\beta = 101.65(3)°$ and $Z = 4$. Refinement gave final R and R' values of 0.054 and 0.054, respectively, for 1686 observed reflections. The bond lengths within the amide portion of the pentadentate ligand are intermediate between keto and enol resonance forms. Protonation of the amide oxygen is implied by the number of counter ions present. No evidence of imine oxidation was observed in electrochemical studies. These studies indicated that some stabilization of the Co^{II} state relative to Co^{III} arises from the presence of pyridyl and imine π acceptors.

The co-ordination chemistry of a variety of long-chain and macrocyclic ligands with nitrogen donor atoms has been particularly well studied with considerable attention focussing on kinetically inert metal ions such as cobalt(III) and chromium(III).[1-6] We have been investigating the co-ordination chemistry of pentadentate ligands derived from the tripod ligand tris(2-aminoethyl)amine (tren) and 1,4,7-triazacyclononane (tacn) concentrating, in particular, on their application in the synthesis of singly bridged binuclear complexes.[7-10] These pentadentate ligands offer advantages over long-chain analogues in that co-ordination produces fewer geometric isomers and the products are usually more easily isolated.

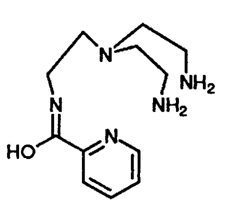
Conversion of tren into pentadentate ligands has not been extensively explored, apart from the attachment of various amine groups usually achieved by template reactions around cobalt(III). More recently, pyridyl arms have been attached to tren forming the pentadentate ligands 3-[4-(2-pyridyl)-3-azabut-3-enyl]-3-azapentane-1,5-diamine (L^1) and 3-[4-(2-pyridyl)-3-azabutyl]-3-azapentane-1,5-diamine (L^2), which have been applied in the synthesis of mononuclear and azido bridged binuclear nickel(II) complexes.[10] In this paper, we present the preparation and properties of cobalt(III) complexes of these ligands and an amide complex, $[Co(HL^3)Cl]^{2+}$ (HL^3 3-{2-[hydroxy(2-pyridyl)methyleneamino]ethyl}-3-azapentane-1,5-diamine), obtained through oxidation of $[Co(L^1)Cl]^{2+}$ solutions. Examples of the oxidation of imines to amides are quite rare. Two well known examples are the oxidation of $[Fe\{MeN{=}CHCH{=}NMe\}_3]^{2+}$ by cerium(IV), believed to proceed *via* an iron(III) intermediate,[11-13] and of *N*-aryl-(2-pyridylmethylene)amine chelated to rhenium(III) and ruthenium(II) to the *N*-aryl pyridine-2-carboxamide by reaction with H_2O_2.[14,15]



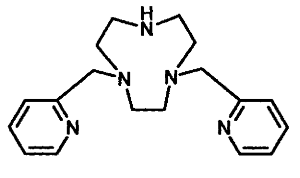
L^1



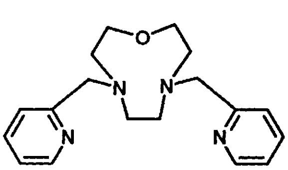
L^2



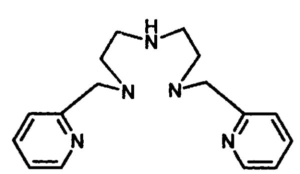
HL^3



L^4



L^5



L^6

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

N-Functionalization of tacn, 1-thia-4,7-diazacyclononane and 1-oxa-4,7-diazacyclononane has recently been recognized as an attractive method for generating pentadentate ligands with two pendant arms, such as, for example, L^4 and L^5. The range of pendant arms that have been attached include amines, carboxylates, pyridyls and phenols.[16–24] The macrocyclic backbones have been shown to bind strongly to one face of an octahedron giving rise to stable complexes with many metals and different oxidation states of the one metal. This is one attractive feature of these ligands and their pentadentate derivatives which has been exploited in the preparation of transition-metal complexes. Complexes of such ligands have been applied in the elucidation of biological reaction mechanisms. For example Busch and co-workers[21] have studied the reactivity of superoxide with $[Fe(L^5)]^{2+}$, where L^5 is 4,7-bis(2-pyridylmethyl)-1-oxa-4,7-diazacyclononane, and $[Fe(tmptacn)]^{2+}$, where tmptacn is 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane, in order to obtain information about the disproportionation of superoxide by superoxide dismutase. In both cases, direct attachment of superoxide to the Fe^{II} centre to form an Fe^{III}–peroxy adduct was proposed to be an important step in the overall process.

The synthesis of L^4 [1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane], the tacn analogue of L^5, has been achieved previously by treating 2-(chloromethyl)pyridine with tacn and the resulting ligand used to prepare Ni^{II} complexes. The preparation of $[Co(L^4)Cl]^{2+}$ and $[CoL^4(OH_2)]^{3+}$ has been undertaken in order to establish the co-ordination properties of the ligand through X-ray structural and NMR studies. The cyclic L^4 is a closed-chain analogue of 1,9-bis(2-pyridyl)-2,5,8-triazanonane (L^6) for which the structures of the aqua, chloro and nitrito Co^{III} complexes are known.[25,26]

Experimental

Reagents and Materials.—All materials were of reagent grade or better and were used without further purification. The compounds tacn·3HBr,[4,27] L^4, L^1 and L^2,[10] and $[Co(tren)Cl_2]Cl$[28] were all prepared by published methods. Salts of $[Co(trenenim)Cl]^{2+}$ [trenenim = 3-(5-amino-3-azapentyl)-3-azapentane-1,5-diamine] and $[Co(trenen)Cl]^{2+}$ [trenen = 3-(5-amino-3-azapent-3-enyl)-3-azapentane-1,5-diamine] were available from previous work.[7,8] The resin used for cation-exchange chromatography was Bio-Rad AG 50W-X2.

CAUTION: Although no problem was encountered in this work, transition-metal perchlorates are potentially explosive and should only be handled in small quantities.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Hitachi 150-20 or a Cary 3 spectrophotometer. The NMR spectra were recorded on a Bruker AC-200 spectrometer. Chemical shifts are reported relative to tetramethylsilane or sodium 3-trimethylsilylproprionate as internal references. Electron microprobe analyses were made with a JEOL JSM-1 scanning electron microscope through an NEC X-ray detector and pulse processing system connected to a Packard multichannel analyser. Solid samples were mounted on an aluminium planchette and covered with a very thin film of carbon by using a Balzer Union CED 010 carbon sputterer. Microanalyses were performed by Chemical and Micro-analytical Services (CMAS) Melbourne, Australia.

Syntheses.—$[Co(L^4)Cl][ClO_4]_2 \cdot H_2O$ *and* $[CoL^4(OH_2)][ClO_4]_3 \cdot H_2O$. The salt $CoCl_2 \cdot 6H_2O$ (1.19 g, 5 mmol) was added to an aqueous solution of L^4 (1.55 g, 5 mmol, 50 cm^3) under nitrogen. The solution was stirred for 15 min after which time it was diluted to 800 cm^3 and adsorbed onto a cation-exchange column. The column was washed thoroughly with water. Elution with 1.5 mol dm^{-3} HCl removed an orange band and further elution with 3 mol dm^{-3} HCl removed a red band. The solutions were concentrated on a Rotavac and $NaClO_4$ (2.3 g) was added to each. On standing, an orange compound precipitated from the first solution and a red compound from the second. They were collected separately and washed with ethanol and air dried. Yield red compound 1.68 g, 54%; orange compound 1.27 g, 37%. Relative amounts of the two products vary with each synthesis.

Red compound. {Found: C, 34.4; H, 4.4; N, 10.9. Calc. for $[Co(C_{18}H_{25}N_5)Cl][ClO_4]_2 \cdot H_2O$: C, 34.7; H, 3.7; N, 10.5%}. Electron microprobe: Co:Cl ratio 1:3. IR (KBr disc, cm^{-1}): 3230m (NH), 1612m, 1480m, 1465m (skeletal vibrations in pyridine ring), 1098vs, 627s, (ClO_4^-). UV/VIS (MeCN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 509 (171), 365 (252). ^{13}C NMR (D_2O): δ 165.7, 163.2, 154.3, 150.2 (C_{ortho} to N in pyridine ring), 142.1, 143.1 (C_{para} to N in pyridine ring), 127.8, 127.6, 126.1, 124.8 (C_{meta} to N in pyridine ring) 70.4, 68.5 ($CH_2NC_5H_4$), 64.9, 63.3, 62.6, 61.5, 54.9, 53.8 (C on tacn ring).

Orange compound. {Found: C, 30.8; H, 4.1; N, 10.0. Calc. for $[Co(C_{18}H_{25}N_5)(OH_2)][ClO_4]_3 \cdot H_2O$: C, 30.7; H, 4.0; N, 9.9%}. Electron microprobe: Co:Cl ratio 1:3. IR (KBr disc, cm^{-1}) 3422s (H_2O), 3219m (NH), 1607m, 1476m, 1447m (skeletal vibrations in pyridine ring), 1086vs, 622s (ClO_4^-). UV/VIS (MeCN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 476 (200). ^{13}C NMR $[(CD_3)_2SO]$: δ 165.0, 162.5, 151.4, 150.8 (C_{ortho} to N in pyridine ring), 141.9, 142.7 (C_{para} to N in pyridine ring), 127.2, 126.7, 125.9, 124.4 (C_{meta} to N in pyridine ring), 68.3, 67.6 ($CH_2NC_5H_4$), 63.1, 62.4, 61.5 (× 2), 53.9, 53.2 (C on tacn ring).

$[Co(L^1)Cl][ClO_4]_2$. *Method A.* To an aqueous solution of L^2 (3.16 mmol), prepared as described previously,[10] was added $CoCl_2 \cdot 6H_2O$ (0.75 g, 3.16 mmol). The solution was diluted to 750 cm^3, adsorbed onto a cation-exchange column and the column washed thoroughly with water. Elution with 2 mol dm^{-3} HCl removed a red fraction which was collected and concentrated to about half its volume. Sodium perchlorate (1.7 g) was added and the solution left to stand overnight. A red microcrystalline precipitate formed. It was collected by filtration and washed with ethanol. Yield 0.52 g, 31% {Found: C, 27.4; H, 4.0; N, 13.6. Calc. for $[Co(C_{12}H_{21}N_5)Cl][ClO_4]_2$: C, 27.3; H, 4.0; N, 13.3%}. Electron microprobe: Co:Cl ratio 1:3. IR (KBr disc, cm^{-1}): 3279m, 3237s, 3130s (NH), 1633s (C=N, imine) 1600s, 1475m, 1443s (skeletal vibrations in pyridine ring) 1085vs, 623s (ClO_4^-). UV/VIS (MeCN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 497 (169) 346(sh) (198). ^{13}C NMR (CD_3CN): δ 176.9 (C=N, imine), 159.8, 157.4 (C_{ortho} to N in pyridine ring), 143.7 (C_{para} to N in pyridine ring), 131.7, 131.5 (C_{meta} to N in pyridine ring), 65.5(× 2), 64.5 (C adjacent to tertiary N), 59.1 (C adjacent to imine N), 47.9 (× 2) (C adjacent to primary N).

Method B. To a refluxing solution of $[Co(tren)Cl_2]Cl$ (1.0 g, 3.17 mmol) in methanol (60 cm^3), was added pyridine-2-carboxaldehyde (0.340 g, 3.17 mmol). The solution was refluxed for 1 h and added to an aqueous solution of sodium perchlorate (2 g in 20 cm^3 of water). A red microcrystalline precipitate formed on cooling in an ice-bath. It was collected by filtration and washed with ethanol. Yield 1.44 g, 86%.

$[Co(HL^3)Cl][ClO_4]_2 \cdot H_2O$. A small number of dark red crystals suitable for single-crystal X-ray diffraction were collected after several weeks from the filtrate of $[Co(L^1)Cl][ClO_4]_2$ prepared by method A. IR (KBr disc, cm^{-1}): 3324m, 3265s, 3142s (NH), 2600–2400 (O ··· H–O H-bonding), 1652s (amide C–O), 1574s (amide C–N) 1607s, 1492s, 1457m (skeletal vibrations in pyridine ring), 1102vs, 626s (ClO_4^-).

$[Co(L^2)Cl][ClO_4]_2 \cdot 2H_2O$. *Method A.* To an aqueous solution of L^2 (3.16 mmol), prepared as described previously,[10] was added $CoCl_2 \cdot 6H_2O$ (0.75 g, 3.16 mmol) and the pH adjusted to 7 with dilute NaOH. Concentrated HCl (25 cm^3) was added and the brown solution was gently heated for 0.5 h. The solution was then diluted to 1 dm^3 and adsorbed onto a cation-exchange column which was washed thoroughly with water. Elution with 2 mol dm^{-3} HCl removed a red fraction

Table 1 Crystallographic data for $[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$ and $[Co(HL^3)Cl][ClO_4]_2{\cdot}H_2O$

	$[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$	$[Co(HL^3)Cl][ClO_4]_2{\cdot}H_2O$
Colour, habit	Orange, block	Red
Formula	$C_{18}H_{29}Cl_3CoN_5O_{14}$	$C_{12}H_{23}Cl_3CoN_5O_{10}$
M	704.7	562.6
a/Å	15.090(3)	13.496(5)
b/Å	16.659(4)	10.253(3)
c/Å	10.192(4)	15.371(6)
β/°		101.65(3)
U/Å^3	2562(1)	2083(1)
Z	4	4
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
λ(Mo-Kα)/Å	0.710 73	0.710 73
F(000)	1448	1152
D_c/g cm^{-3}	1.827	1.794
Crystal size/mm	0.10 × 0.20 × 0.20	0.26 × 0.12 × 0.08
μ/mm^{-1}	1.065	1.269
Max., min. transmission factors	1.095, 0.841	0.903, 0.828
Data collection instrument	Rigaku AFC6R	Nicolet R3m/V
Scan speed/° min^{-1}	32.0	3.97–19.53
Scan width/°	0.57	1.2
Scan method	ω–2θ	ω
Collection range/°	$2.0 \leqslant 2\theta \leqslant 50$	$3.5 < 2\theta < 50$
Data collected	$+h, +k, +l$	$\pm h, +k, +l$
No. unique data	2684	3686
No. observed data	1708	1686 $[F \geqslant 6.0\sigma(F)]$
R	0.045	0.054
R'	0.043	0.054
ρ/e Å^{-3}	0.42	0.63

which was collected and concentrated to about a third of the original volume. Sodium perchlorate (2.0 g) was added and the solution left to stand overnight. The red microcrystalline precipitate that formed was collected by filtration and washed with ethanol. Yield 0.83 g, 47%.

Method B. Excess of $NaBH_4$ (0.4 g) was added to a solution of $[Co(L^1)Cl][ClO_4]_2$ (1.0 g, 1.89 mmol) in water (50 cm^3). The mixture was stirred vigorously for 1 min, diluted to 1 dm^3 and adsorbed onto a cation-exchange column. The product was eluted and isolated as in method A. Yield 0.83 g, 83% {Found: C, 25.7; H, 5.0; N, 12.3. Calc. for $[Co(C_{12}H_{23}N_5)Cl][ClO_4]_2{\cdot}2H_2O$: C, 25.4; H, 4.8; N, 12.4%. Electron microprobe: Co:Cl ratio 1:3. IR (KBr disc, cm^{-1}): 3578m, 3414m (H_2O), 3294s, 3255s, 3213s, 3161m, 3114m (NH) 1593s, 1479m, 1457m (skeletal vibrations in pyridine ring), 1092vs, 625s (ClO_4^-). UV/VIS (MeCN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 512 (189), 365 (249). ^{13}C NMR (CD_3CN): δ 165.2, 154.1 (C_{ortho} to N in pyridine ring), 141.4 (C_{para} to N in pyridine ring), 126.0, 123.2 (C_{meta} to N in pyridine ring), 64.2, 63.2, 62.2 (C adjacent to tertiary N), 56.3, 53.1 (C adjacent to secondary N), 46.5, 45.9 (C adjacent to primary N).

Crystal Structure Determination.—Crystal data and refinement parameters for $[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$ and $[Co(HL^3)Cl][ClO_4]_2{\cdot}H_2O$ are given in Table 1.

Intensity data for $[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$ were measured at 290 K on a Rigaku AFC6R diffractometer using graphite-monochromated Mo-Kα radiation. A total of 2684 independent data (ω–2θ scan technique, 2θ_{max} 50.0°) were corrected for Lorentz and polarization effects[29] and for absorption employing an empirical method[30] (range of transmission coefficients 0.841–1.095). The structure was solved by direct methods[31] and refined by a full-matrix least-squares procedure based on F.[29] The non-H atoms were refined anisotropically and H atoms were included in the model at their calculated positions (C–H 0.97 Å). The refinement on 370 parameters converged with R 0.045 and R' 0.043 (sigma weights). Final atomic parameters, bond lengths and angles are given in Tables 2 and 3 and Fig. 1 (drawn with the ORTEP[32] program at 35% probability ellipsoids) shows the structure of the cation and atomic labelling scheme. Scattering factors for all atoms were as incorporated in the TEXSAN[29] package installed on an Iris Indigo workstation.

For $[Co(HL^3)Cl][ClO_4]_2{\cdot}H_2O$, intensity measurements were made on a Nicolet R3m/V diffractometer using graphite-monochromated Mo-Kα radiation with $3.5 < 2\theta < 50°$, operating in an ω scan mode with a scan range of 1.20°, at a scan rate between 3.97 and 19.53° min^{-1}. A total of 3686 unique data were collected, ($\pm h$, $+k$, $+l$), 1686 of which were considered to be observed $[F \geqslant 6\sigma(F)]$, and used in the final refinement. Three standard reflections monitored every 197 showed no significant variation in intensity over the data collection period. Intensity data were corrected for Lorentz and polarization effects. A face-indexed numerical absorption correction was applied[33] on six crystal faces, the maximum and minimum transmission factors being 0.903 and 0.828, respectively. The atomic scattering factors for neutral atoms were taken from ref. 34 and were corrected for anomalous dispersion by using values from ref. 34. The program used for least squares refinement was that due to Sheldrick.[34] The structure was solved by direct methods. Refinement was by full-matrix least squares employing anisotropic thermal parameters for Ni, Cl and O and isotropic thermal parameters for all other atoms (single isotropic thermal parameter for hydrogen in geometrically idealized positions fixed at 0.08 Å^2, C–H 0.96, N–H 0.90 Å). At convergence (190 variables, 1686 observed data) R was 0.054 and R' 0.054, where $R' = \Sigma(|F_o - F_c|)w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$ and $w = [\sigma^2(F_o) + 0.0006F^2]^{-1}$. The goodness of fit value $\{[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}\}$ was 1.33. Final atomic parameters, bond lengths and angles are given in Tables 4 and 5 and Fig. 2 shows the structure of the binuclear cations and atomic labelling scheme.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Complexes of L^4.—Cobalt(III) complexes were prepared by adding $CoCl_2{\cdot}6H_2O$ to an aqueous solution of L^4, such that the final Co–L^4 ratio was 1:1, followed by aerobic oxidation (Scheme 1). Cation-exchange chromatography separated a red

Table 2 Fractional atomic coordinates for $[CoL^4(OH_2)][ClO_4]_3\cdot H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	0.121 90(08)	−0.205 06(07)	0.208 19(12)	N(4)	0.078 3(05)	−0.135 4(05)	0.341 8(07)
Cl(1)	0.216 1(02)	0.118 92(17)	0.186 8(03)	N(5)	0.049 4(05)	−0.159 5(04)	0.070 4(07)
Cl(2)	0.244 0(02)	−0.554 08(16)	0.248 1(03)	C(1)	0.254 6(06)	−0.318 7(06)	0.252 5(11)
Cl(3)	0.566 25(17)	−0.650 16(16)	0.222 2(03)	C(2)	0.245 9(07)	−0.307 4(06)	0.108 8(11)
O(1)	0.213 2(04)	−0.131 4(04)	0.147 6(06)	C(3)	0.092 4(07)	−0.352 3(05)	0.089 6(09)
O(2)	0.316 1(05)	0.031 1(04)	0.466 8(07)	C(4)	0.007 8(06)	−0.328 5(05)	0.156 8(09)
O(11)	0.275 6(05)	0.054 5(05)	0.204 9(08)	C(5)	0.072 5(07)	−0.330 1(05)	0.375 4(09)
O(12)	0.196 1(05)	0.156 0(05)	0.308 6(09)	C(6)	0.151 3(07)	−0.290 5(06)	0.434 3(09)
O(13)	0.247 8(08)	0.170 0(06)	0.098 2(13)	C(7)	−0.040 0(06)	−0.229 2(06)	0.323 2(09)
O(14)	0.133 8(06)	0.087 5(05)	0.138 5(08)	C(8)	−0.003 2(07)	−0.156 0(06)	0.384 3(09)
O(21)	0.165 7(04)	−0.510 1(04)	0.270 2(09)	C(9)	−0.047 0(08)	−0.110 4(07)	0.475 7(10)
O(22)	0.272 7(08)	−0.539 4(09)	0.127 0(10)	C(10)	−0.006 3(09)	−0.041 7(06)	0.518 6(09)
O(23)	0.308 7(06)	−0.531 6(08)	0.332 2(12)	C(11)	0.075 6(09)	−0.021 7(06)	0.476 2(11)
O(24)	0.224 5(06)	−0.632 2(05)	0.267 6(15)	C(12)	0.115 6(07)	−0.068 7(06)	0.388 0(09)
O(31)	0.650 0(06)	−0.617 9(06)	0.191 3(10)	C(13)	0.145 2(06)	−0.243 3(06)	−0.051 1(09)
O(32)	0.571 0(07)	−0.670 5(05)	0.355 6(07)	C(14)	0.070 8(06)	−0.187 0(05)	−0.049 7(09)
O(33)	0.557 3(07)	−0.717 8(05)	0.148 7(08)	C(15)	0.031 5(08)	−0.154 8(07)	−0.159 5(09)
O(34)	0.504 6(08)	−0.597 9(08)	0.193 4(14)	C(16)	−0.030 9(08)	−0.096 8(07)	−0.146 8(11)
N(1)	0.203 6(05)	−0.257 7(04)	0.324 4(08)	C(17)	−0.054 0(07)	−0.069 3(06)	−0.022 9(11)
N(2)	0.153 4(05)	−0.285 2(05)	0.078 7(07)	C(18)	−0.012 7(06)	−0.102 2(06)	0.081 5(09)
N(3)	0.034 0(04)	−0.280 0(04)	0.272 0(07)				

Table 3 Bond distances (Å) and angles (°) for $[CoL^4(OH_2)][ClO_4]_3\cdot H_2O$

Co–O(1)	1.945(6)	N(5)–C(14)	1.35(1)	N(2)–C(2)	1.48(1)	C(10)–C(11)	1.35(2)
Co–N(1)	1.921(8)	N(5)–C(18)	1.34(1)	N(2)–C(3)	1.45(1)	C(11)–C(12)	1.34(1)
Co–N(2)	1.937(7)	C(1)–C(2)	1.48(1)	N(2)–C(13)	1.50(1)	C(13)–C(14)	1.46(1)
Co–N(3)	1.933(7)	C(3)–C(4)	1.50(1)	N(3)–C(4)	1.48(1)	C(14)–C(15)	1.37(1)
Co–N(4)	1.906(7)	C(5)–C(6)	1.49(1)	N(3)–C(5)	1.46(1)	C(15)–C(16)	1.36(1)
Co–N(5)	1.936(7)	C(7)–C(8)	1.48(1)	N(3)–C(7)	1.50(1)	C(16)–C(17)	1.39(1)
N(1)–C(1)	1.47(1)	C(8)–C(9)	1.37(1)	N(4)–C(8)	1.35(1)	C(17)–C(18)	1.35(1)
N(1)–C(6)	1.48(1)	C(9)–C(10)	1.37(1)	N(4)–C(12)	1.33(1)		
O(1)–Co–N(1)	91.7(3)	C(8)–N(4)–C(12)	119.0(8)	Co–N(1)–C(1)	110.1(6)	C(5)–N(3)–C(7)	111.5(7)
O(1)–Co–N(2)	92.6(3)	Co–N(5)–C(14)	113.0(6)	Co–N(1)–C(6)	107.1(6)	Co–N(4)–C(8)	112.9(6)
O(1)–Co–N(3)	178.1(3)	Co–N(5)–C(18)	127.8(6)	C(1)–N(1)–C(6)	113.7(7)	Co–N(2)–C(12)	127.9(7)
O(1)–Co–N(4)	95.0(3)	C(14)–N(5)–C(18)	119.0(8)	Co–N(2)–C(2)	105.3(6)	C(9)–C(10)–C(11)	121(1)
O(1)–Co–N(5)	85.6(3)	N(1)–C(1)–C(2)	111.0(8)	Co–N(2)–C(3)	108.8(5)	C(10)–C(11)–C(12)	119(1)
N(1)–Co–N(2)	87.0(3)	N(2)–C(2)–C(1)	108.8(9)	Co–N(2)–C(13)	105.1(6)	N(4)–C(12)–C(11)	122(1)
N(1)–Co–N(3)	86.4(3)	N(2)–C(3)–C(4)	111.8(7)	C(2)–N(2)–C(3)	113.0(8)	N(2)–C(13)–C(14)	110.7(7)
N(1)–Co–N(4)	93.4(3)	N(3)–C(4)–C(3)	106.2(7)	C(2)–N(2)–C(13)	112.3(7)	N(5)–C(14)–C(13)	114.2(8)
N(1)–Co–N(5)	171.6(3)	N(3)–C(5)–C(6)	110.8(7)	C(3)–N(2)–C(13)	111.9(7)	N(5)–C(14)–C(15)	120.3(9)
N(2)–Co–N(3)	87.3(3)	N(1)–C(6)–C(5)	106.6(8)	Co–N(3)–C(4)	105.6(5)	C(13)–C(14)–C(15)	124.9(9)
N(2)–Co–N(4)	172.4(3)	N(3)–C(7)–C(8)	109.5(7)	Co–N(3)–C(5)	109.8(5)	C(14)–C(15)–C(16)	120(1)
N(2)–Co–N(5)	85.1(3)	N(4)–C(8)–C(7)	114.7(8)	Co–N(3)–C(7)	105.3(5)	C(15)–C(16)–C(17)	119.9(9)
N(3)–Co–N(4)	85.2(3)	N(4)–C(8)–C(9)	121.1(9)	C(4)–N(3)–C(5)	111.4(7)	C(16)–C(17)–C(18)	118(1)
N(3)–Co–N(5)	96.3(3)	C(7)–C(8)–C(9)	124(1)	C(4)–N(3)–C(7)	112.7(7)	N(5)–C(18)–C(17)	123.1(9)
N(4)–Co–N(5)	94.8(3)	C(8)–C(9)–C(10)	118(1)				

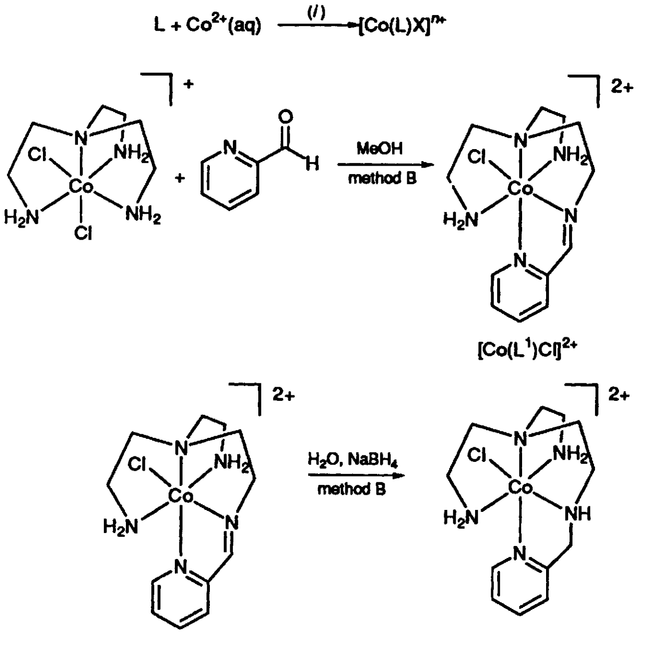
Table 4 Atomic coordinates (× 10^4) for $[Co(HL^3)Cl][ClO_4]_2\cdot H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	2021.5(8)	2005.7(12)	941.5(8)	C(9)	3500(8)	5249(10)	312(6)
Cl(1)	344(2)	1979(3)	455(2)	C(10)	2775(8)	6061(11)	−185(6)
N(1)	2131(5)	978(7)	−102(5)	C(11)	1799(8)	5663(10)	−370(6)
N(2)	2099(5)	375(7)	1590(4)	C(12)	1524(7)	4483(9)	−65(6)
N(3)	1800(5)	2802(7)	2029(4)	Cl(2)	4442(2)	3110(3)	3861(2)
N(4)	3427(5)	2081(7)	1285(4)	O(2)	4013(6)	1891(8)	3981(5)
N(5)	2217(5)	3689(7)	418(4)	O(3)	5421(7)	2982(9)	3827(10)
O(1)	4847(5)	3344(6)	1221(4)	O(4)	3942(8)	3670(9)	3062(6)
C(1)	2243(7)	−434(9)	139(6)	O(5)	4335(10)	3973(11)	4525(7)
C(2)	1763(7)	−661(9)	923(6)	Cl(3)	1284(2)	6091(3)	2344(2)
C(3)	1413(7)	491(9)	2232(6)	O(6)	546(6)	5551(10)	1658(5)
C(4)	1626(7)	1810(9)	2680(6)	O(7)	1383(7)	5240(8)	3062(5)
C(5)	3178(7)	143(9)	2086(6)	O(8)	1002(9)	7297(8)	2594(8)
C(6)	3929(6)	920(9)	1705(6)	O(9)	2208(6)	6120(10)	2037(6)
C(7)	3870(6)	3090(9)	1083(5)	O(10)	6202(5)	1613(7)	1494(6)
C(8)	3194(7)	4070(9)	593(6)				

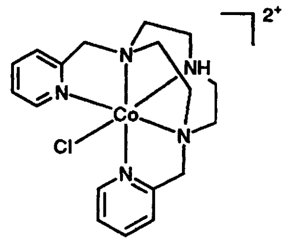
and an orange product which precipitated as the perchlorate salts following addition of $NaClO_4$. Elemental analyses indicated that the red and orange complexes were $[Co(L^4)Cl][ClO_4]_2\cdot H_2O$ and $[CoL^4(OH_2)][ClO_4]_3\cdot H_2O$, respectively.

Table 5 Bond distances (Å) and angles (°) for $[Co(HL^3)Cl][ClO_4]_2{\cdot}H_2O$

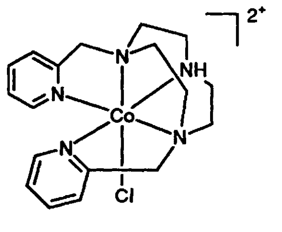
Co–Cl(1)	2.237(3)	N(4)–C(6)	1.455(11)	N(2)–C(2)	1.483(11)	C(5)–C(6)	1.497(13)
Co–N(1)	1.950(7)	N(4)–C(7)	1.265(12)	N(2)–C(3)	1.487(13)	C(7)–C(8)	1.460(12)
Co–N(2)	1.938(7)	N(5)–C(8)	1.349(11)	N(2)–C(5)	1.520(10)	C(8)–C(9)	1.375(14)
Co–N(3)	1.937(7)	N(5)–C(12)	1.345(11)	N(3)–C(4)	1.479(12)	C(9)–C(10)	1.391(14)
Co–N(4)	1.865(6)	O(1)–C(7)	1.319(10)	O(10)–O(1)	2.521(6)	C(10)–C(11)	1.353(14)
Co–N(5)	1.945(7)	C(1)–C(2)	1.497(14)			C(11)–C(12)	1.375(14)
N(1)–C(1)	1.494(12)	C(3)–C(4)	1.519(13)				
Cl(1)–Co–N(1)	87.6(2)	N(5)–C(8)–C(7)	112.8(8)	C(6)–N(4)–C(7)	125.3(7)	N(4)–Co–N(5)	82.3(3)
Cl(1)–Co–N(4)	176.5(2)	C(8)–C(9)–C(10)	118.4(9)	C(8)–N(5)–C(12)	118.5(8)	Co–N(2)–C(3)	107.3(5)
N(1)–Co–N(3)	171.3(3)	N(5)–C(11)–C(12)	121.0(8)	N(2)–C(3)–C(4)	106.6(8)	C(2)–N(2)–C(5)	111.2(6)
N(2)–Co–N(3)	85.5(3)	N(4)–C(7)–C(8)	114.4(7)	N(4)–C(6)–C(5)	108.5(7)	Co–N(4)–C(6)	116.6(5)
N(3)–Co–N(4)	93.7(3)	Cl(1)–Co–N(2)	96.2(2)	N(5)–C(8)–C(9)	122.4(8)	Co–N(5)–C(8)	112.5(5)
Co–N(1)–C(1)	109.9(5)	Cl(1)–Co–N(5)	94.9(2)	C(9)–C(10)–C(11)	118.8(10)	N(1)–C(1)–C(2)	108.2(8)
C(2)–N(2)–C(3)	111.8(7)	N(1)–Co–N(4)	90.8(3)	O(1)–C(7)–C(8)	116.6(8)	N(3)–C(4)–C(3)	110.3(8)
C(3)–N(2)–C(5)	110.0(6)	N(2)–Co–N(4)	86.8(3)	Cl(1)–Co–N(3)	88.4(2)	C(7)–C(8)–C(9)	124.8(8)
Co–N(4)–C(7)	117.9(6)	N(3)–Co–N(5)	92.3(3)	N(1)–Co–N(2)	87.3(3)	C(10)–C(11)–C(12)	120.8(9)
Co–N(5)–C(12)	128.9(6)	Co–N(2)–C(2)	106.5(5)	N(1)–Co–N(5)	95.8(3)	O(1)–C(7)–N(4)	129.0(8)
N(2)–C(2)–C(1)	108.9(7)	Co–N(2)–C(5)	109.9(5)	N(2)–Co–N(5)	168.7(3)		
N(2)–C(5)–C(6)	112.1(7)	Co–N(3)–C(4)	111.5(5)				



Scheme 1 Synthesis of the cobalt(III) complexes (L = L¹, L² or L⁴; X = Cl⁻ or H_2O): (*i*) O_2, HCl, ion-exchange chromatography



A



B

The infrared spectra of both complexes exhibit bands in the 1400–1600 cm^{-1} region (skeletal vibrations of the pyridyl ring), a stretching band at *ca.* 3230 cm^{-1} (NH) and bands at *ca.* 1100 and 625 cm^{-1} (ClO_4^-). For the chloro complex, a band at 3486 cm^{-1} indicated the presence of water of crystallization while for the aqua complex a band at 3422 cm^{-1} can be ascribed to co-ordinated water. The UV/VIS spectrum of $[Co(L^4)Cl][ClO_4]_2{\cdot}H_2O$ in water shows bands at 509 [$^1A_{1g} \longrightarrow {}^1T_{1g}(\nu_1)$] and 365 nm [$^1A_{1g} \longrightarrow {}^1T_{2g}(\nu_2)$] typical of Co^{III} complexes with a $Co^{III}N_5Cl$ chromophore (see Table 6). The first band in $[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$ is at higher energy (476 nm) because of the higher field strength of co-ordinated water compared with Cl^-. In this complex, the higher energy $^1A_{1g} \longrightarrow {}^1T_{2g}$ transition is masked by more intense transitions within the ligand.

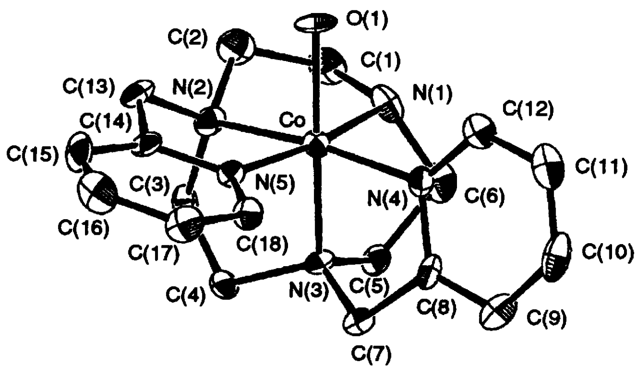


Fig. 1 Molecular structure and atomic numbering scheme for the cation in $[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$ (with 35% thermal ellipsoids)

An important feature of the ^{13}C NMR spectrum of $[Co(L^4)Cl][ClO_4]_2{\cdot}H_2O$ is that distinct signals are observed for each carbon on the ligand, *viz.* there are six resonances between δ 53.8 and 64.9 for the methylene carbons on the cyclononane backbone, two resonances at δ 68.5 and 70.4 for the methylene carbons on the pyridyl arms and ten resonances between δ 120 and 170 for pyridyl carbons. In contrast, the ^{13}C spectrum of unco-ordinated L⁴ shows only half the number of resonances which indicates that the ligand has C_2 symmetry. The fact that this symmetry is lost in the Co^{III} complex indicates that the chloride ion co-ordinates *cis* to the secondary amine on the tacn ring, as depicted in isomer **B**. This was confirmed for the corresponding aqua complex through a crystal-structure determination (see below). Isomer **A** is the only other possible isomer but this would result in retention of the ligand C_2 symmetry within the complex and the number of ^{13}C resonances would be the same as for the free ligand.

Molecular structure of $[CoL^4(OH_2)][ClO_4]_3{\cdot}H_2O$. The molecular structure of the $[CoL^4(OH_2)]^{3+}$ cation, Fig. 1, shows a slightly distorted-octahedral geometry about the Co^{III} centre. Five sites are occupied by the nitrogens of L⁴ with a water molecule completing the co-ordination sphere. The structure of the cation confirms that the aqua group is *cis* to the secondary amine as in isomer **B**. The structure is thus similar to that of *syn*-αβ-$[CoL^6(OH_2)][ClO_4]_2[NO_3]$.[25] The three

Table 6 Visible spectral data for Co^{III} complexes

Complex	λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1})	Ref.
$[Co(L^4)Cl]^{2+}$	509 (171), 365 (252)	This work
$[Co(daptacn)Cl]^{2+}$	548 (74.1), 374 (77.3)	35
$[Co(tmptacn)]^{3+}$	474 (296), 343 (284)	36
$[Co(tacn)_2]^{3+}$	458 (100), 333 (89)	37
$[Co(tacn)(L')Cl]^{2+}$ *	520 (87), 360 (85)	38
i-$[Co(L^1)Cl]^{2+}$	497 (169), 346sh (298)	This work
i-$[Co(trenenim)Cl]^{2+}$	494 (190), 356 (190)	7, 39, 40
$[Co(L^2)Cl]^{2+}$	512 (189), 365 (249)	This work
s-$[Co(trenen)Cl]^{2+}$	512 (151)	7, 39, 40
t-$[Co(mtrenen)Cl]^{2+}$	534 (512)	41
p-$[Co(tren)(NH_3)Cl]^{2+}$	512 (94)	42
t-$[Co(tren)(NH_3)Cl]^{2+}$	530 (136)	42

* L′ = 2,3-Diaminopropanol.

five-membered chelate rings of the 1,4,7-triazacyclononane backbone are not planar and they adopt the λλλ conformation. The two five-membered chelate rings formed by co-ordination of the pendant pyridyl arms to Co^{III} are also puckered and adopt the δδ configuration. Thus, resolution of the complex into one of the possible enantiomers has been achieved.

The Co–N(tacn), Co–N(C_5H_4N) and Co–OH_2 distances (Table 3) are similar to the corresponding distances in $[CoL^6(OH_2)]^{3+}$ [1.938(7), 1.954(7) and 1.951(6) Å, respectively].[25] However, the Co–N(tacn) bond lengths in $[CoL^4(OH_2)]^{3+}$ are significantly shorter than found in some other Co^{III} complexes of pendant-arm ligands derived from tacn, *viz.* $[Co(daptacn)Cl][ClO_4]_2$ [1.987(7) Å] and $[Co(taptacn)][ClO_4]_3$ [2.025(7) Å] [daptacn = 1,4-bis(3-aminopropyl)-1,4,7-triazacyclononane, taptacn = 1,4,7-tris(3-aminopropyl)-1,4,7-triazacyclononane].[35,43] The bite angles (Table 3) between the tacn nitrogens are less than 90° (average 86.9°) but they are equivalent to those found in the related complexes $[Co(daptacn)Cl]^{2+}$ and $[Co(taptacn)Cl]^{2+}$ (average 86.9°). The angles subtended by the five-membered chelate rings involving the pyridyl nitrogens are also less than 90°, averaging 85.2°. The trigonal twist angle (ϑ) is a measure of the rotation of the two N donors on the pyridyl arms and the aqua ligand relative to the tacn nitrogen donors. The angle ϑ is 52.7° for the pyridyl nitrogens indicating some distortion from ideal octahedral geometry ($\vartheta = 60°$). However, the water ligand is in a regular octahedral position, *viz.* $\vartheta \approx 60°$ with O(1)–Co–N(3) 178.1(3)°. The related complex $[Co(daptacn)Cl]^{2+}$ shows minimal distortion from regular octahedral geometry, with ϑ 59.6° due to the greater flexibility of the six-membered aminopropyl arms.

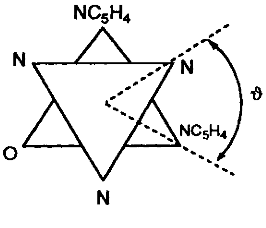
The crystal lattice of $[CoL^4(OH_2)][ClO_4]_3 \cdot H_2O$ features a number of close contacts between the component species. The H atoms of both the co-ordinated and free water molecules were not located in the X-ray study, however, the presence of H-bonding contacts between them is indicated by the O(1) ⋯ O(2^I) separation of 2.527(9) Å (symmetry operation: 0.5 − *x*, −*y*, −0.5 + *z*). Further contacts between O(1) and the perchlorate anions are noted, *i.e.* O(1) ⋯ O(31^{II}) 2.65(1) Å (symmetry operation: 1 − *x*, 0.5 + *y*, 0.5 − *z*) and, less significantly, O(1) ⋯ O(11) of 3.29(1) Å. The O(2) water molecule makes contacts with three perchlorate groups, O(2) ⋯ O(14^{III}) 2.75(1) Å (symmetry operation: 0.5 − *x*, −*y*, 0.5 + *z*), O(2) ⋯ O(11) 2.77(1) and O(2) ⋯ O(31^{II}) 3.00(1) Å. There are also H-bonding contacts involving the amine H atom and the perchlorate anions with N(1)H ⋯ O(13^{IV}) 2.36 [N(1) ⋯ O(13^{IV}) 3.21(1) Å, symmetry operation: 1 − *x*, −0.5 + *y*, 0.5 − *z*] and N(1)H ⋯ O(13^I) 2.57 Å [N(1) ⋯ O(13^I) 3.23(1) Å].

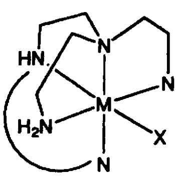
Complexes of L^1.—Two methods were used to prepare the cobalt(III) complexes of L^1. The most successful method involved a template reaction between $[Co(tren)Cl_2]Cl$ and pyridine-2-carboxaldehyde (Scheme 1) in refluxing methanol. The reaction was accompanied by a change in colour from blue to dark red and the product was isolated as the perchlorate salt, $[Co(L^1)Cl][ClO_4]_2$. A lower yield was obtained from reaction of a solution of tren and pyridine-2-carboxaldehyde (1 : 1 ratio) with equimolar quantities of Co^{II} salts (Scheme 1). This reaction gave several products separable by cation-exchange chromatography. Microanalyses of the main product obtained by each method were identical and supported the composition $[Co(L^1)Cl][ClO_4]_2$. The IR spectrum exhibited bands due to NH stretches at 3279, 3237 and 3130 cm^{-1}, a band at 1633 cm^{-1} due to the imine stretch and bands at 1600, 1475 and 1443 cm^{-1} due to the skeletal ring vibrations of the pyridyl groups. The UV/VIS spectrum (Table 6) shows bands at 497 and 346 nm in the typical region for $Co^{III}N_5Cl$ complexes, indicating that the complex incorporated a pentadentate ligand. In addition, the spectrum is very similar to that of $[Co(trenenim)Cl]^{2+}$ whose structure has been determined recently.[44]

In octahedral complexes of pentadentate ligands derived from tren, such as L^1, L^2, trenen and trenenim, three arrangements of the ligand around the metal are possible. In general, the preferred isomer is that with the sixth ligand *trans* to nitrogen supporting the pendant arm, as predicted from considerations of non-bonding interactions.[45] In the $[Co(L^1)Cl]^{2+}$ complex, this isomer (termed the i isomer to indicate the chloro group is *trans* to the imine) has C_2 symmetry while the p- and t-isomers, which have the chloro group *trans* to the primary or tertiary nitrogens, lack this symmetry.

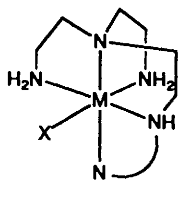
The ^{13}C NMR spectrum of $[Co(L^1)Cl][ClO_4]_2$, prepared by two methods, provides strong evidence for the formation of the i isomer. The spectrum shows an imine resonance at δ 176.9, five pyridyl resonances in the δ 130–60 region and only four resonances (δ 47.9, 59.1, 64.5, 65.5) due to the methylene carbons on the tren backbone. Three of these methylene resonances correspond closely to those observed in the ^{13}C spectrum of $[Co(tren)Cl_2]^+$ with the fourth appearing at lower field (δ 59.1 rather than 48) because it is adjacent to the imine moiety. The resonances in the tren backbone in $[Co(L^1)Cl]^{2+}$ also match those in i-$[Co(trenenim)Cl]^{2+}$ which occur at δ 48.1, 56.8, 61.7 and 62.5 as does the signal due to the imine carbon (δ 176.9 *vs.* 185). These considerations suggest that the mirror plane in the $[Co(tren)Cl_2]^+$ complex is preserved in $[Co(L^1)Cl]^{2+}$, as expected for the i isomer. If any of the p- and t-isomers had formed, the plane of symmetry would be removed rendering all the methylene carbons on the tren backbone inequivalent and eight resonances would be observed.

The reaction of $[Co(tren)Cl_2]^+$ and pyridine-2-carboxaldehyde generates the i isomer of $[Co(L^1)Cl]^{2+}$, the same isomer as is obtained from the reaction of $[Co(tren)Cl_2]^+$ with $H_2NCH_2CH(OEt)_2$. For both these reactions, Schiff-base condensation can, in principle, take place at the position *trans* to the primary amine regardless of whether condensation occurs before or after co-ordination of the pyridyl group. For the latter case, Sargeson and co-workers[39,46] have shown that substitution of a chloride ligand on $[Co(tren)Cl_2]^+$ occurs mainly at the position *trans* to the tertiary amine, due to the greater *trans* effect of the tertiary amine compared to the primary amines. With the pyridyl nitrogen co-ordinated *trans* to the tertiary amine the Schiff-base condensation could occur at any of the three primary amines. However, condensation at the

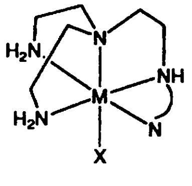




s isomer



p isomer



t isomer

NH_2 group *trans* to chloride is preferred because this group is either more acidic or it becomes a better nucleophile on deprotonation.

Complexes of L^2.—The cobalt(III) complex of L^2 was prepared either by reaction of a Co^{II} salt with L^2 (oxidation to Co^{III} occurred during the procedure) or by the reduction of the co-ordinated imine in $[Co(L^1)Cl]^{2+}$ with excess of tetrahydroborate (Scheme 1). In each case, the complex was purified by ion-exchange chromatography and ultimately precipitated as the perchlorate salt. Elemental analysis supported the empirical formula $[Co(L^2)Cl][ClO_4]_2 \cdot 2H_2O$. The IR spectrum is similar to that of the L^1 complex with the important exception that the C=N stretching band is absent indicating that reduction of the imine has occurred. Similarly, the imine carbon resonance is absent in the ^{13}C NMR spectrum of $[Co(L^2)Cl][ClO_4]_2 \cdot 2H_2O$. The spectrum shows five resonances due to the pyridyl carbons at δ 123.2, 126.0, 141.4, 154.1 and 165.2 and seven resonances in the methylene carbon region. One of these (δ 56.3) is attributed to the CH_2 adjacent to the pyridyl and the remaining six resonances to methylenes on the tren backbone. The presence of six such peaks, in contrast to i-$[Co(L^1)Cl]^{2+}$ which has only four, can be attributed to the generation of a chiral nitrogen centre which removes the plane of symmetry within the complex and renders each CH_2 inequivalent. It is also possible that the product formed is one of the p isomers (*syn* and *anti* configurations are possible) or the t isomer and not the expected s isomer. Two factors militate against this possibility (*i*) the reduction of the closely related complex, i-$[Co(trenenim)Cl]^{2+}$ occurs with a retention of stereochemistry,[8,39] and (*ii*) the visible spectrum (see below) indicates that the s isomer is formed.

The visible spectrum of the $[Co(L^2)Cl]^{2+}$ shows bands at 512 and 365 nm which correspond closely to those observed for the related s-$[Co(trenen)Cl]^{2+}$ [7,39] complex but are distinctly different to those observed for t-$[Co(mtrenen)Cl]^{2+}$ [mtrenen = 3-(5-amino-3-methyl-3-azapentyl)-3-azapentane-1,5-diamine] which has the chloro group *trans* to the tertiary nitrogen (see Table 6).[41] These data support the assignment of the $[Co(L^2)Cl]^{2+}$ complex as the s isomer. They also indicate that the ligand-field strengths of L^2 and trenen are comparable. Overall, L^1 has a similar field strength to trenenim and slightly stronger than L^4, L^2 and trenen.

Cobalt(III) *Complex of* L^3.—After several weeks, small amounts of red crystals deposited in the filtrate from the preparation of $[Co(L^1)Cl][ClO_4]_2$. These were initially believed to be the imine complex. However, the IR spectrum of these crystals was significantly different to that of $[Co(L^1)Cl][ClO_4]_2$. Bands at 1652 and 1574 cm^{-1} replaced the C=N stretching frequency at 1633 cm^{-1} present in the imine complex. Subsequent X-ray structural analysis (see below) revealed that the ligand L^1 had been oxidized to an amide. The two new bands in the IR spectrum are therefore due to the C–N and C–O bond stretches in the amido complex.

Molecular structure of a-$[Co(HL^3)Cl][ClO_4]_2 \cdot H_2O$. The molecular structure of the a-$[Co(HL^3)Cl]^{2+}$ cation is shown in Fig. 2 and a packing diagram of the unit cell is shown in Fig. 3. Each complex cation consists of a pentadentate amido ligand and chloride ligand co-ordinated to a Co^{III} centre in slightly distorted octahedral geometry. The arrangement of the ligand in the a-$[Co(HL^3)Cl]^{2+}$ cation is similar to that observed with other bifurcated tren-based ligands, {*e.g.* s-$[Co(trenen)Cl]^{2+}$ [8] and i-$[Co(trenenim)Cl]^{2+}$ [44]} in which the monodentate ligand is situated *trans* to the *N*-functionalized amine. In addition, the chloride ligand is *trans* to the amide nitrogen (a isomer) which supports the appended arm, as is the case for several Co^{III} complexes of tren-based pentadentate ligands (see earlier).

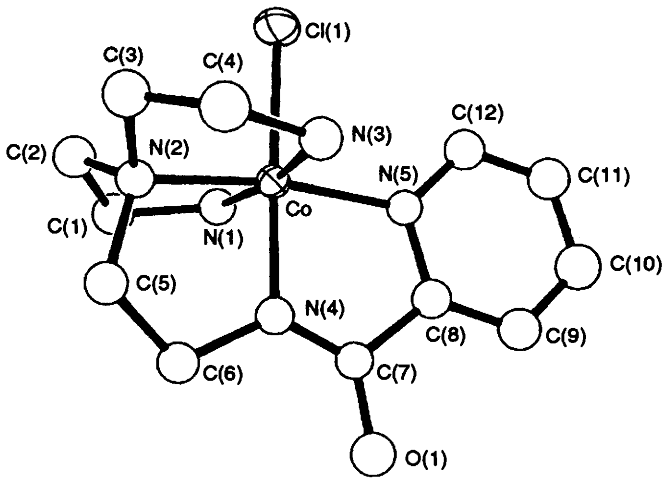


Fig. 2 Molecular structure and atomic numbering scheme for the cation in $[Co(HL^3)Cl][ClO_4]_2 \cdot H_2O$

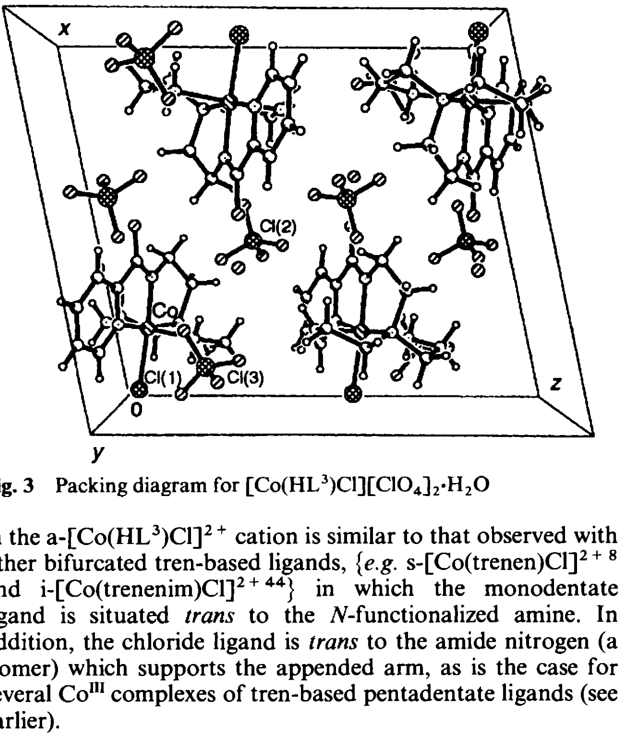
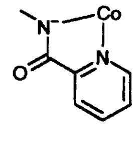


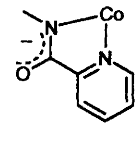
Fig. 3 Packing diagram for $[Co(HL^3)Cl][ClO_4]_2 \cdot H_2O$

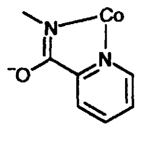
The Co–N(1), N(2) and N(3) bond lengths [average 1.942(3) Å] are comparable to those in related complexes, such as i-$[Co(trenenim)Cl]^{2+}$ [average 1.964(3) Å],[44] and s-$[Co(trenen)N_3]^{2+}$ [average 1.957(3) Å].[47] The Co–Cl(1) bond is also shorter at 2.237(3) Å than in i-$[Co(trenenim)Cl]^{2+}$ [2.273(1) Å] and $[Co(NH_3)_5Cl]^{2+}$ [48] [2.286(5) Å]. The three bond angles about the amide nitrogen, N(4), and the three about the amide carbon, C(7), are all close to 120°, and total 360°, confirming the planarity of the amide group. The bite angle of the five-membered chelate ring containing the amido group of 82.3(3)° is smaller than those for the other five-membered chelate rings [average 86.5(3)°], a reflection of the rigidity introduced by this group.[39,41,44–47]

The bond lengths within the amide portion of the ligand are unusual. For an N-co-ordinated, and therefore deprotonated, amide group it is expected that the negative charge would be delocalized along the amide C–N and C–O bonds, leading to two resonance forms[49] which have different C–N and C–O bond lengths. In resonance form **I**, C–N has single bond character, C–O double bond character and the Co–N(amide) bond is relatively short. Conversely, in resonance form **II**, C–N has



I





II

double bond character, C–O single bond character and the Co–N(amide) bond is longer. These bonds can also be intermediate between double and single bonds. In a-$[Co(HL^3)Cl]^{2+}$, the amide C–N and C–O bond lengths are not consistent with either of these resonance forms. The C(7)–N(4) bond length, 1.265(12) Å, is close to that expected for a C=N double bond,[44] indicating resonance form **II**. However, the amide C(7)–O(1) bond length, 1.32(1) Å, lies between the normal range of bond lengths for C=O (≈1.20 Å) and C–O (≈1.43 Å) and is suggestive of an intermediate resonance form. An extra positive charge is required to balance the charge in the complex. Since the complex was precipitated from concentrated HCl, the amide oxygen O(1) is likely to be protonated favouring resonance form **II**. Protonation of the amide oxygens in $[Co(Gly\text{-}Gly\text{-}O^-)_2]^-$ produces $[Co(HGly\text{-}Gly\text{-}O^-)_2]^+$ [where Gly-Gly-O^- represents $NH_2CH_2C(O)N^-CH_2CO_2^-$ and HGly-Gly-O^- represents $NH_2CH_2C(O)NHCH_2CO_2^-$],[50] which has different C–N, C–O and Co–N(amide) bond lengths.[51] The amide C–N bond in $[Co(HGly\text{-}Gly\text{-}O^-)_2]^+$, 1.250(15) Å, is shorter than that in $[Co(Gly\text{-}Gly\text{-}O^-)_2]^-$, 1.30(1) Å. Conversely, the amide C–O bond length in $[Co(HGly\text{-}Gly\text{-}O^-)_2]^+$, 1.360(15) Å, is much longer than that in $[Co(Gly\text{-}Gly\text{-}O^-)_2]^-$, 1.26(1) Å. In addition, the Co–N(amide) bond distances in $[Co(Gly\text{-}Gly\text{-}O^-)_2]^-$, 1.870(7) Å, are much shorter than in $[Co(HGly\text{-}Gly\text{-}O^-)_2]^+$, 1.940(7) Å. Thus, the short Co–N(4) distance in a-$[Co(HL^3)Cl]^{2+}$, 1.865(6) Å, indicates significant contribution from resonance form **I**.

Circumstantial evidence for protonation of the amide oxygen comes from the presence of oxygen O(10), presumably from a water molecule, in close proximity to O(1). The O(10) ··· O(1) distance of 2.521(6) Å is typical of systems with strong H-bonding, O–H ··· O.[52] The IR spectrum of a-$[Co(HL^3)Cl][ClO_4]_2$ exhibits strong sharp bands in the 2400–2600 cm^{-1} region which are absent in the Co^{III} complexes of related tren-based ligands and which, according to Nakamoto *et al.*,[52] can be attributed to strong H-bonding (O ··· O distance ≈2.6 Å). Thus, the proton could be stabilized by H-bonding to O(10) (from a H_2O molecule) located in the vicinity of O(1).

Table 7 Electrochemical data for cobalt complexes

Compound	E_c/V	E_a/V	$E_{\frac{1}{2}}$/V	ΔE/mV	i_{p_a}/i_{p_c}
$[Co(L^4)Cl]^{2+}$	−0.54	−0.43	−0.49	118	0.50
$[Co(L^1)Cl]^{2+}$	−0.67	−0.43	−0.55	240	0.82
$[Co(L^2)Cl]^{2+}$	−0.82	—	—	—	—
$[Co(tmptacn)]^{3+}$ [a]	—	—	−0.32	90	—
$[Co(tacn)_2]^{3+}$ [b]	—	—	−0.41 [c]	70	—

[a] Ref. 36. [b] Ref. 37. [c] *vs.* Normal hydrogen electrode.

Possible oxidation mechanisms. The oxidation of L^1 is a surprising result. Following precedents,[11–15] attempts were made to prepare deliberately the L^3 complex by reaction of solutions of either $[Co(L^1)Cl]^{2+}$ or $[CoL^1(OH_2)]^{2+}$ with strong oxidizing agents like hydrogen peroxide and cerium(IV). These have thus far proved unsuccessful. The oxidation of amine ligands to unsaturated ligands[53–55] is more common than oxidation of co-ordinated imines to amides, of which two examples are known. The oxidation of $[Fe(MeN{=}CHCH{=}NMe)_3]^{2+}$ by Ce^{IV} in strongly acidic solution results in some ligand oxidation yielding an amido ligand.[11–13] The reaction is complex but it was concluded that ligand oxidation did not proceed *via* direct attack on the imine by the Ce^{IV} rather it involves formation of an Fe^{III} complex, $[Fe(MeN{=}CH\text{-}CH{=}NMe)_3]^{3+}$, as an intermediate which undergoes intramolecular reduction to Fe^{II} with concomitant ligand oxidation. In the recently reported oxidation of imine groups co-ordinated to Re^{III} and Ru^{II} by hydrogen peroxide,[14,15] ligand oxidation was accompanied by a one-electron oxidation of the central metal to Re^{IV} and Ru^{III}, respectively. In both these amine oxidations, an intermediate with the metal in a higher oxidation state has been proposed. Electrochemical studies in the −2.0 to +1.7 V potential range (see below) showed no evidence for formation of Co^{IV}, which indicates that dioxygen is unlikely to oxidize Co^{III} to Co^{IV}, or the oxidation of the imine moiety. A more likely possibility is that the imine is partially hydrolysed in acidic solution forming an alcohol which is oxidized by dioxygen. Sargeson and co-workers[56] have shown that in acidic solutions $[Co(NH_3)_5\{NH_2CH_2CH(OH)Me\}]^{3+}$ can be oxidized to $[Co(NH_3)_5(NH_2CH_2COMe)]^{3+}$ by $Cr_2O_7^{2-}$. Our proposal for formation of $[Co(HL^3)Cl]^{2+}$ is reasonable since in acidic solution the oxidation potential for $Cr_2O_7^{2-}$ is very similar to that for dioxygen.

Electrochemistry of Cobalt(III) *Complexes*.—The redox behaviour of the Co^{III} L^4, L^1 and L^2 complexes has been studied by cyclic voltammetry in MeCN (potential range −2.0 to +1.7 V, scan rate 100 mV s^{-1}, 0.1 mol dm^{-3} NBu_4ClO_4 as supporting electrolyte). Only processes associated with the Co^{III}–Co^{II} redox couple were observed. Electrochemical data are summarized in Table 7 and are quoted with respect to the ferrocene–ferrocenium redox couple which was used as an internal standard.

The $[Co(L^4)Cl]^{2+}$ complex undergoes a quasi-reversible one-electron reduction at −0.49 V. The related complex, $[Co(tmptacn)]^{3+}$, where tmptacn is 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane, undergoes quasi-reversible reduction at −0.32 V.[56] Thus, replacement of one pyridyl pendant-arm, with π-acceptor properties, by a chloride ligand destabilizes the more electron rich Co^{II} state by ≈170 mV. The i-$[Co(L^1)Cl]^{2+}$ complex exhibits a quasi-reversible one-electron reduction at −0.55 V. No oxidation to Co^{IV} or redox processes attributable to oxidation or reduction of the imine group were observed. The complex $[Co(L^2)Cl]^{2+}$ exhibits an irreversible anodic wave at −0.82 V (cathodic E_c), due to the one-electron reduction of Co^{III} to Co^{II}. The corresponding reduction potential, E_c, for i-$[Co(L^1)Cl]^{2+}$ is −0.67 V. Thus, the imine moiety, which like pyridyl rings can act as a π-acceptor, stabilizes the Co^{II} state by 150 mV. The poor reversibility of redox processes involving i-$[Co(L^1)Cl]^{2+}$ and $[Co(L^2)Cl]^{2+}$ could be due to rapid ligand-exchange processes which accompany reduction to Co^{II}.

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