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Padlock macrocyclic complexes. The synthesis of a range of nickel(II) complexes of *N*-alkyl azacyclams and the crystal structure of (3-ethyl-1,3,5,8,12-penta-azacyclotetradecane) nickel(II) perchlorate

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Abstract—A range of (3-alkyl-1,3,5,8,12-penta-azacyclotetradecane)nickel(II) complexes [NiL] $(ClO_4)_2$ (R = Me, Et, *n*-Pr, *n*-Bu, *n*-octyl, *n*-tridecyl, *n*-octadecyl) has been prepared and characterised. The planar octahedral equilibrium in solution has been studied in detail for R = Et. For this equilibrium $\Delta H^0 = -19.2 \pm 0.5$ kJ mol^{-1} and $\Delta S^0 = -76.4 \pm 1.5$ JK^{-1} mol^{-1}, with $K = 0.24$ at 25°. The crystal structure of 3-ethyl-1,3,5,8,12-penta-azacyclotetradecane)nickel(II) perchlorate has been determined. The complex is square planar and the Ni—N bond lengths are 1.959(5) and 1.906(5) Å. Both six-membered chelate rings adopt a chair conformation and the five-membered rings are *gauche* with the *sec*-NH centres having the RSRS configuration. The N—Et group is axial. © 1997 Elsevier Science Ltd

Keywords: padlock macrocycle; *N*-alkyl-azacyclams; nickel(II) complex; crystal structure; planar-octahedral equilibria.

Suh and Kang [1] have developed a useful synthesis of two-dimensional macrocyclic complexes of the cyclam type by treating $[M(en)_2]^{2+}$ (M = Ni^{II} or Cu^{II}) with formaldehyde and a primary amine RNH_2 (R = CH_3 or C_2H_5). This condensation gave the 14-membered hexa-aza macrocycle (**1**) when methylamine was the primary amine employed. Similar reactions can be carried out with tetramine complexes $[Ni(2,3,2\text{-tet})]^{2+}$ (2,3,2-tet = 1,9-diamino-3,7-diazanonane) to give azacyclam derivatives such as (**2**) if $MeNH_2$ is used as the "padlocking" amine. In the present work we have extended this synthesis by the use of a series of primary amines RNH_2 with R = Me, Et, *n*-Pr, *n*-Bu, *n*-octyl, *n*-tridecyl and *n*-octadecyl. Such long-chain derivatives have the potential to form metallomicelles in aqueous solution which may display novel catalytic behaviour. In addition complexes of this type may also display interesting liquid crystal phenomena [3].

EXPERIMENTAL

Synthesis

(3-*Methyl*-1,3,5,8,12-*penta-azacyclotetradecane*) *nickel*(*II*) *perchlorate*. The synthetic procedure was essentially as described by Fabbrizzi *et al.* [2]. Nickel(II) chloride hexahydrate (6.0 g, 25.2 mmol) was dissolved in ethanol (150 cm^3) and 1,9-diamino-3,7-diaznonane (4.04 g, 25.2 mmol) added dropwise. Triethylamine (5.04 g, 50.4 mmol), aqueous methylamine (30%, 6 cm^3, 25.2 mmol) and aqueous formaldehyde solution (35%, 11.4 g, 140 mmol) were added to the violet solution which was then heated to reflux for 24 h. The resulting brown solution was cooled, filtered and reduced in volume by one third on a rotary evap-

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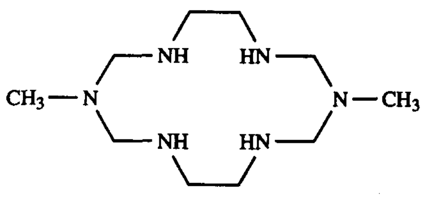
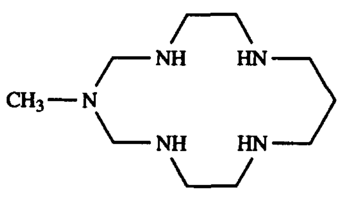


(1)



(2)

EXPERIMENTAL

Structure 1

orator. A saturated ethanolic solution (100 cm^3) of sodium perchlorate was added and the solution cooled in a refrigerator. The yellow crystalline product was filtered off, washed with diethyl ether and dried *in vacuo*. (Yield 5.7 g, 46%.) Found: C, 25.6; H, 5.5; N 15.0. Calc. for $C_{10}H_{25}N_5NiCl_2O_8$: C, 25.4; H, 5.3; N, 14.8%. The complex has λ_{max} 448 ($\varepsilon = 51$ dm^3 mol^{-1} cm^{-1}) in aqueous solution.

(3-*Ethyl*-1,3,5,8,12-*penta-azacyclotetradecane*) *nickel*(*II*) *perchlorate*. The preparation was essentially as described above substituting aqueous ethylamine (70%, 1.63 g, 25.2 mmol) for aqueous methylamine. (Yield 7.3 g, 60%.) Found: C, 27.3; H, 5.4; N, 14.2. Calc. for $C_{11}H_{27}N_5NiCl_2O_8$; C, 27.1; H, 5.6; N, 14.4%. The complex has λ_{max} 464 nm ($\varepsilon = 62.6$ dm^3 mol^{-1} cm^{-1}) in nitromethane.

The other complexes were prepared similarly using *n*-propylamine (1.49 g, 25.2 mmol), yield 7.7 g (61%); *n*-butylamine (1.85 g, 25.2 mmol), yield 8 g (62%); *n*-octylamine (3.26 g, 25.2 mmol), yield 6.1 g (42%); *n*-tridecylamine (5.03 g, 25.2 mmol), yield 7.6 g (47%) and *n*-octadecylamine (6.80 g, 25.2 mmol), yield 6.2 g (34%). Satisfactory analytical data was obtained for all of these complexes after recrystallisation. All of the complexes have λ_{max} near 460 nm in aqueous solution.

Crystal structure determination of (3-*ethyl*-1,3,5,8-12-*penta-azacyclo-tetradecane*)*nickel*(*II*) *perchlorate*

Crystal data. $C_{11}H_{27}N_5NiCl_2O_8$, M = 486.96, monoclinic, $a = 13.521(2)$, $b = 9.252(1)$, $c = 9.105(2)$ Å, $\beta = 117.226(8)°$, $V = 1012.8(2)$ Å^3 (by least squares refinement on diffractometer angles for 25 automatically centred reflections in the range $8.48 < 2\theta < 17.67°$, $\lambda = 0.71069$ Å, space group Cm (No. 8), $Z = 2$, $D_C = 1.60$ g cm^{-3}, $F(000) = 508.00$. Orange block. Crystal dimensions: $0.40 \times 0.25 \times 0.15$ mm, $\mu(\text{Mo-}K_\alpha) = 12.69$ cm^{-1}.

Data Collection and Processing. Rigaku AFC7S diffractometer, ω–2θ mode with ω scan width = $1.63 + 0.35 \tan\theta$, ω scan speed 16.0° min^{-1}, graphite monochromated Mo-K_α radiation; 1000 reflections measured (max. $2\theta = 50.0°$), 956 unique [merging $R = 0.012$ after absorption correction (max., min. transmission factors = 0.90, 1.00], giving 878 with $I > 3\sigma(I)$. Lorentz, polarisation and absorption corrections were made.

Structure analysis and refinement. Direct methods [4] followed by expansion using Fourier techniques [5]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Full-matrix least square refinement was based on 878 observed reflections and 158 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.031$ and $R_w = 0.027$. The standard deviation of unit weight was 2.87. The weighting scheme was based on counting statistics. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *vs* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.32 and -0.29 $e^-/\text{Å}^3$ respectively. The perchlorate anions were initially refined anisotropically, but after finding large anisotropic disorder about the O(3)—Cl(2) axis the model was replaced by one that allowed six positions about the axis of one perchlorate anion rather than three, and the model refined isotropically. In addition, the C(10) of the ethyl group refined very anisotropically, and was subsequently split into a disordered, half assigned site, off the mirror plane at $y = 1/2$. The R factor was lowered from 0.037 to 0.031. All calculations were performed using the teXsan [6] crystallographic software package of the Molecular Structure Corporation.

Physical measurements

UV-vis measurements were carried out using a Perkin Elmer Lambda 14P spectrophotometer equipped with a Peltier cell for variable temperature measurements.

RESULTS AND DISCUSSION

The reaction of the appropriate primary amine, RNH_2 with $[Ni(2,3,2\text{-tet})]^{2+}$ and formaldehyde gave reasonable yields of the azacyclam complexes. These complexes are yellow in colour, typical of low spin nickel(II) and have λ_{max} near 460 nm in aqueous solution. The intensity of the colour decreases as the alkyl chain length increases. This effect arises due to the lowered percentage of nickel(II) in the complex. The crystal structure of the N—Et derivative described below confirms the expected structure. The complex has the RSRS configuration of the chiral *sec*-NH centres with the N—Et group axial. The N—Et group is not involved in coordination to the metal. As previously noted by Fabbrizzi *et al.* [2] the tertiary amino group in complexes of this type is very weakly basic and does not bind protons at pH values as low as 2 so that $pK < 2$. This behaviour is unusual as tertiary amino functions are strongly basic in aqueous solution. Thus trimethylamine has a pK of 9.81 and triethylamine a pK of 11.01. The low basicity can be understood in terms of the difficulty in protonating a dication since the metal centre is only some 3.3 Å distant from the tertiary amino group and strong electrostatic repulsive effects will come into play as the proton approaches. In addition, the flattening of the N—Et group observed in the crystal structure indicates some sp^2 character in the nitrogen centre which should also substantially decrease its basicity.

Solution equilibria

The complex $[\mathrm{NiL_{Et}}]^{2+}$ displays a temperature-dependent visible spectrum which can be attributed to the existence of the planar octahedral equilibrium,

$$[\mathrm{NiL_{Et}}]^{2+} + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{NiL_{Et}(OH_2)_2}]^{2+}\ ;\quad K.$$

The concentration of the planar complex increases with increasing temperature (Fig. 1). The λ_{max} for the planar complex is 448 nm in the non-coordinating solvent nitromethane with an absorption coefficient of 62.6 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ which is assumed to be that of the pure planar species. The octahedral species has an absorption coefficient of *ca.* 6 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ at this wavelength [7]. The equilibrium constant K at each temperature can be calculated using the equation

$$K = (\varepsilon_{\mathrm{low\ spin}} - \varepsilon_{\mathrm{obs}})/(\varepsilon_{\mathrm{obs}} - \varepsilon_{\mathrm{high\ spin}}).$$

The values obtained are summarised in Table 1. A plot of $\ln K$ *vs* $1/T$ (Fig. 2), gives $\Delta H^0 = -19.2 \pm 0.5$ kJ $\mathrm{mol^{-1}}$ and $\Delta S^0 = -76.4 \pm 15$ $\mathrm{JK^{-1}\ mol^{-1}}$. The equilibrium constant $K = 0.24$ at 25°C. The ther-

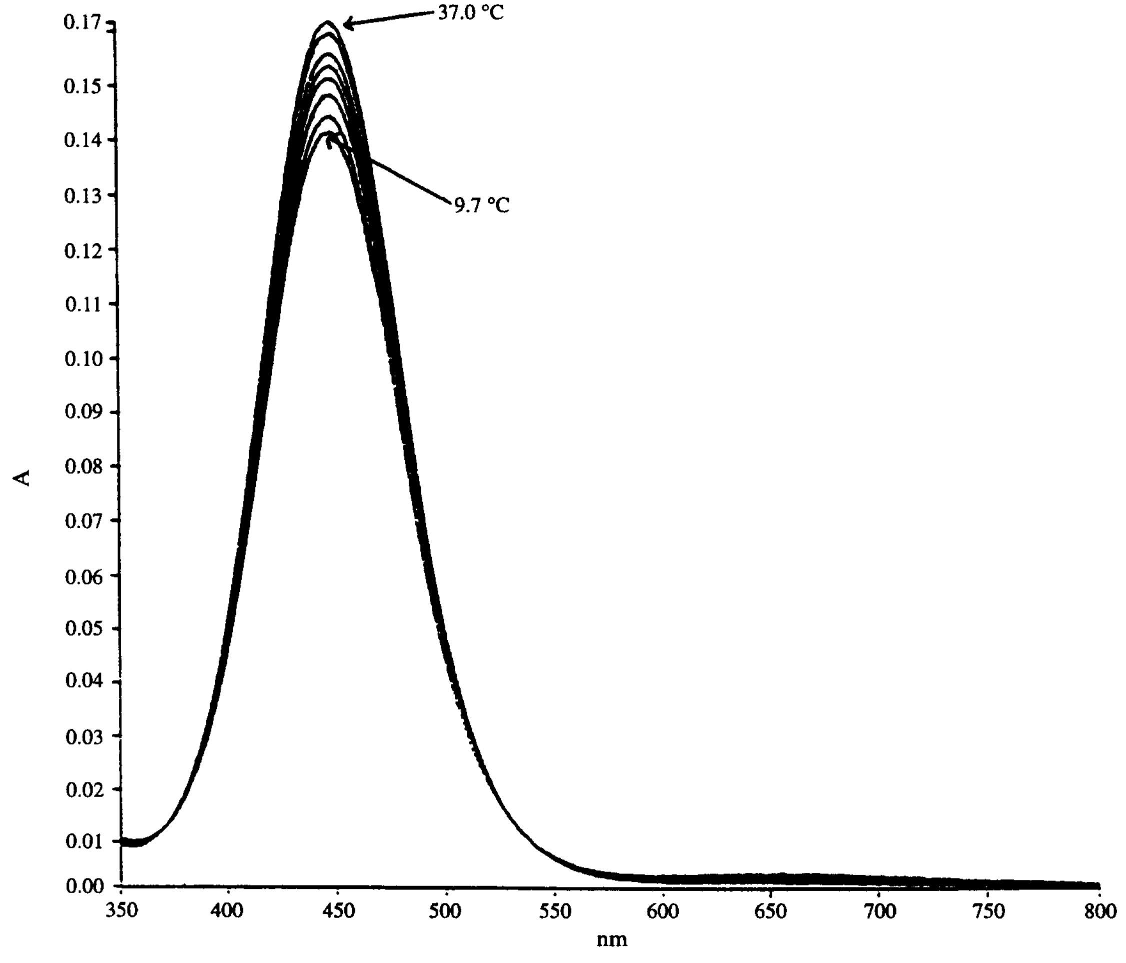


Fig. 1. Temperature dependence of the spectrum of $[\mathrm{NiL_{Et}}]^{2+}$ in aqueous solution. The temperatures employed were 9.7, 12.9, 16.9, 20.9, 23.7, 27.1, 33.2 and 37°C. The concentration of the complex employed was 3×10^{-3} mol $\mathrm{dm^{-3}}$.

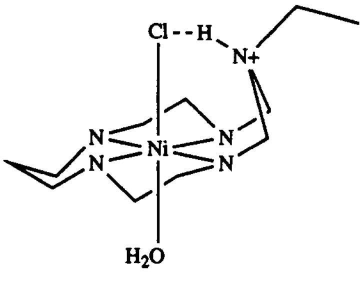
Table 1. The planar octahedral equilibrium in the complex [NiL$_{Et}$]

T (K)	10^3 $1/T$ (K^{-1})	Abs. at 448 nm	ε_{obs}	K
285.3	3.505	0.1446	48.2	0.34
287.6	3.477	0.1468	48.9	0.32
292.3	3.421	0.1509	50.3	0.28
298.0	3.356	0.1550	51.8	0.24
299.6	3.338	0.1566	52.2	0.23
301.7	3.315	0.1581	52.7	0.21
304.6	3.283	0.1597	53.2	0.20
307.1	3.256	0.1611	53.7	0.19
309.9	3.227	0.1626	54.2	0.17
313.2	3.193	0.1642	54.7	0.16
318.1	3.144	0.1662	55.4	0.15
324.1	3.085	0.1682	56.1	0.13

The concentration of the complex employed was 3×10^{-3} mol dm^{-3}.

modynamic parameters obtained are very similar to those previously determined for cyclam and other macrocyclic tetramine ligands, see Table 2. Thus for cyclam [8] $\Delta H^0 = -22.6$ kJ mol^{-1} and $\Delta S^0 = -83.7$ JK^{-1} mol^{-1}.

The square planar $\rightleftharpoons$ octahedral equilibrium in the presence of varying concentrations of HCl was also studied. As can be seen from the series of spectra in Fig. 3, the concentration of the planar species *decreases* as the concentration of HCl increases. High concentrations of HCl favour the formation of the octahedral complex [NiL$_{Et}$Cl$_2$]$^{2+}$. This behaviour contrasts with that observed with [Ni(cyclam)]$^{2+}$ where the addition of HCl increases the concentration of the planar species [8]. The behaviour observed with [NiL$_{Et}$]$^{2+}$ can be rationalised in terms of the formation of the protonated complex (3) in acidic solution. Intramolecular hydrogen bonding between the Et—NH$^+$ group and the axial chloride stabilises the octahedral complex.



(3)

Structure 2

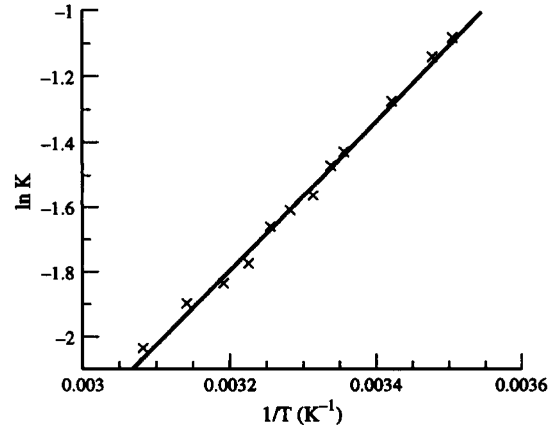


Fig. 2. Plot of ln K versus $1/T$ for the square planar octahedral equilibrium of [NiL$_{Et}$]$^{2+}$.

Crystal structure of (*3-ethyl*-1,3,5,8,12-*pentaazacyclotetradecane*) *nickel*(*II*)*perchlorate*

An ORTEP view of the complex with the atomic numbering scheme is shown in Fig. 4. Atoms O(1), O(2) and C(10) are shown as the non-disordered sites for clarity. Selected bond lengths and angles are listed in Table 3. The four secondary amine nitrogen atoms are bound to the nickel ion in an almost regular square planar geometry and adopt an RSRS configuration. The N—Ni—N bite angles deviate slightly from those expected for ideal square planar geometry; those in the six-membered chelate rings are expanded to 92.9(3)° with a bite distance of 2.84 Å and those in five-membered rings are contracted to 87.0(1)° with a bite distance of 2.66 Å. The Ni—N bond lengths are 1.959(5) Å and 1.906(5) Å and lie in the range expected for such low spin tetraamine complexes [9]. Both six-membered chelate rings adopt a chair conformation and the five membered rings are *gauche*. The ethyl group on the tertiary N(1) is axial. The tertiary amino group N(1) appears to exhibit some sp^2 character in that its geometry differs from that expected for an unstrained trialkylamino group. The

Table 2. Thermodynamic parameters for square planar $\rightleftharpoons$ octahedral equilibria in nickel(II) complexes of macrocyclic tetramine

Ligand	λ_{max} (nm)	ΔH^0 (kJ mol^{-1})	ΔS^0 (JK^{-1} mol^{-1})
Cyclam	444	−22.6	−83.7
Isocyclam	466	−22.6	−74
[12]aneN$_4$	430	−7.1	−23
[13]aneN$_4$	466	−31.4	−30
N—Et azacyclam	448	−19.2	−76.4

Data taken from Hay, R. W., Kinsman, B. and Smith, C. A., *Polyhedron*, 1995, **14**, 1245.

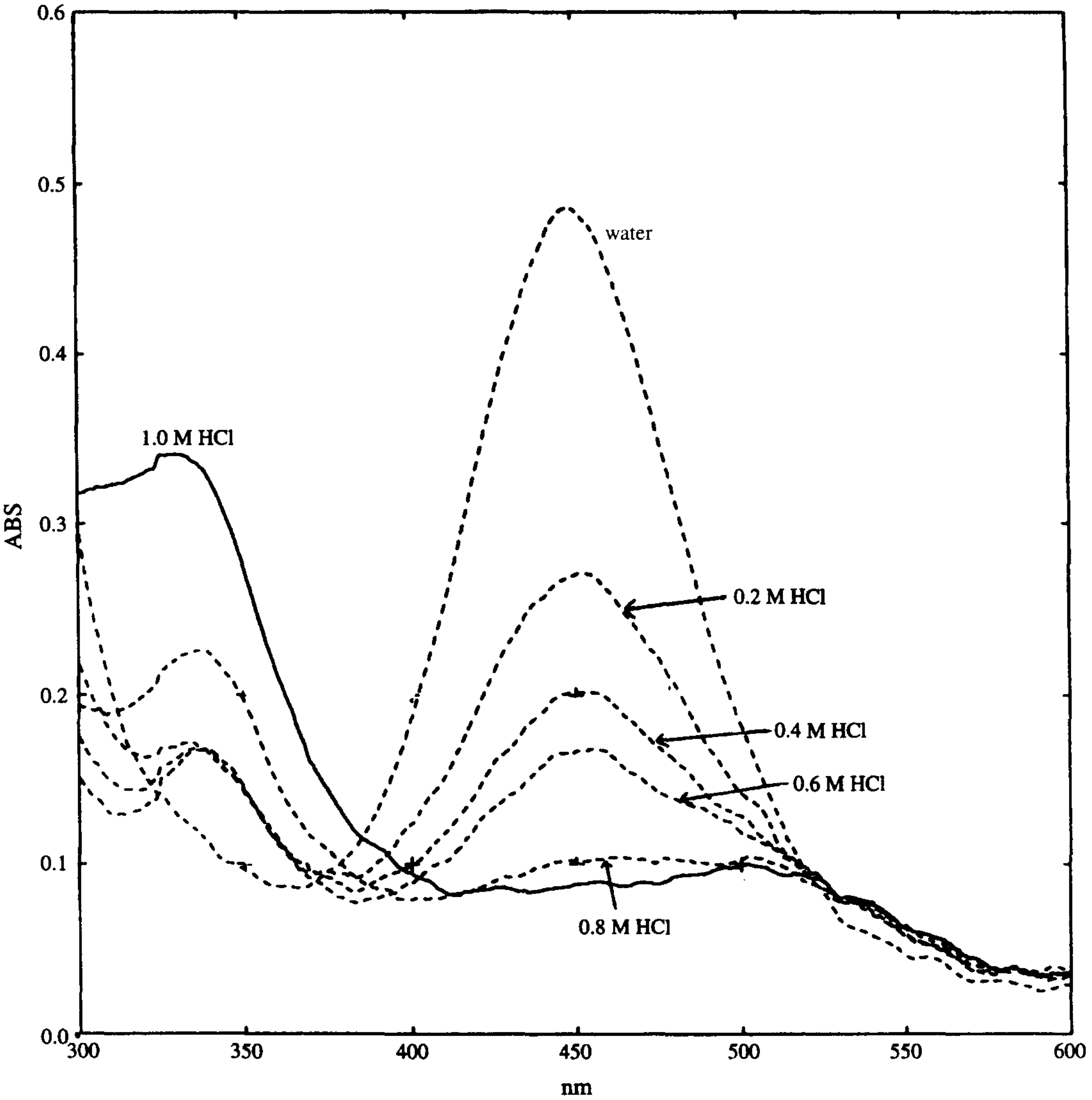


Fig. 3. Spectrum of $[NiL_{Et}]^{2+}$ at various HCl concentrations.

expected C—C bond angle for an sp^3 hybridised nitrogen atom is 109° which is observed in the crystal structure of the hexamethylenetriamine-thiourea adduct [10]. Significantly the C—N(1)—C angles found here have a mean value of 115.93°; two angles of 118.9(5)° and a third of 110.0(7)°. Such flattening of the NC_3 group has been observed previously in the analogous complex (3-methyl-1,3,5,8,12-pentaazacyclotetradecane)nickel(II) perchlorate [2] and in the sepulchrate complexes of nickel(II) [11], cobalt(II) [12] and cobalt(III) [13]. On the basis of molecular modelling calculations, Sargeson *et al.* [12] have attributed the flattening of the NC_3 groups in cobalt(II) sepulchrate to either steric constraints or to the electrostatic attraction between the metal centre and the tertiary nitrogen atom. Fabbrizzi *et al.* [2] have suggested that in the complex (3-methyl-1,3,5,8,12-pentaazacyclotetradecane)nickel(II) perchlorate the flattening of the tertiary N(1) nitrogen is due to long range M—N electrostatic interactions rather than steric effects as the $N(1)C_3$ group is incorporated into the macrocyclic ring by only two C—N bonds, the third being bound to a methyl group. The C—N—C bond angles and C—N bond lengths for several tertiary amine complexes which exhibit such flattening are given in Table 4.

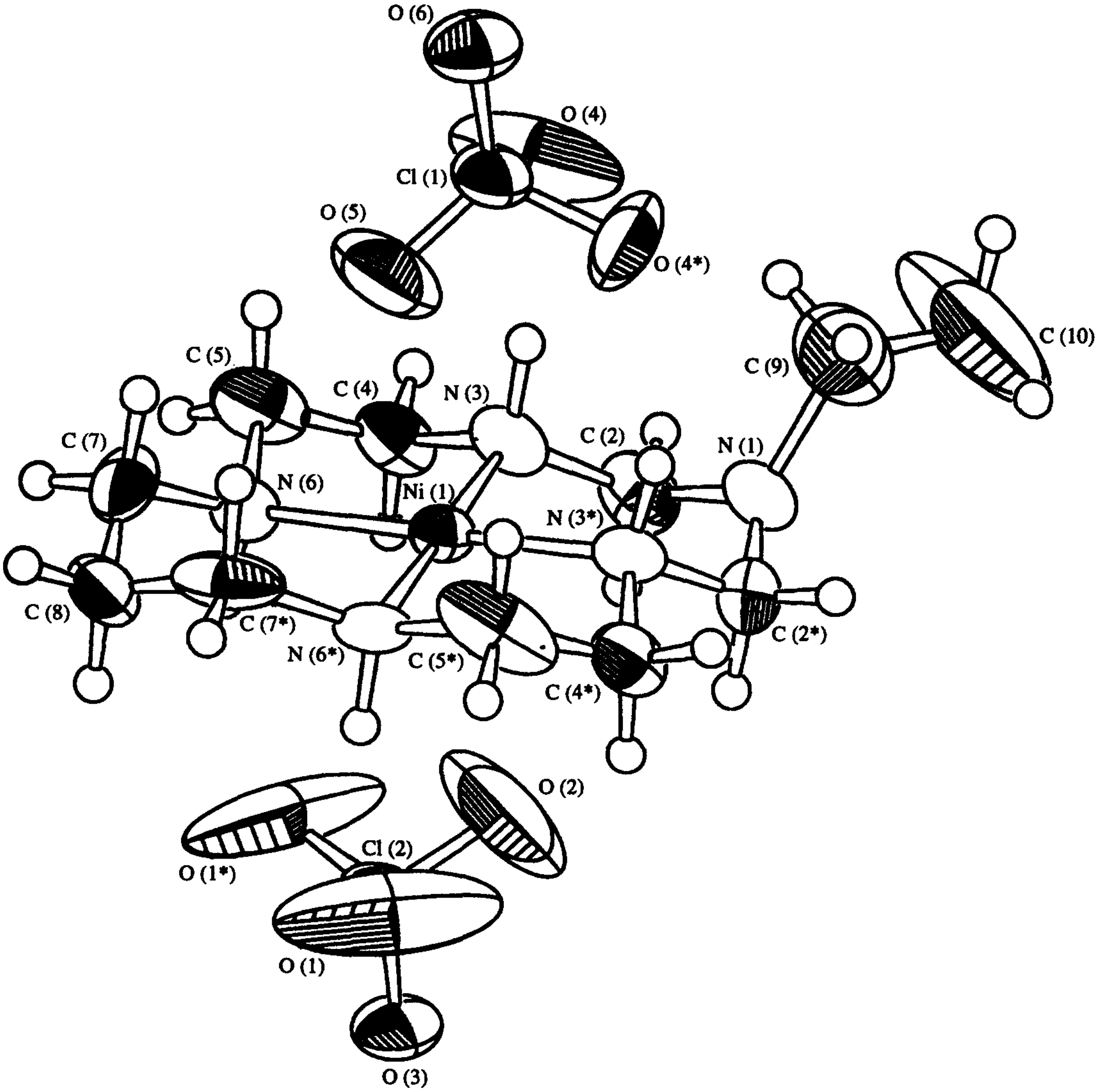
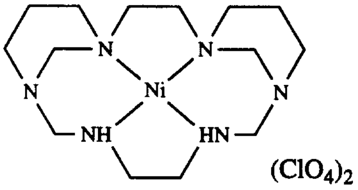
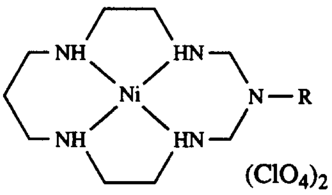


Fig. 4. ORTEP view of (3-ethyl-1,3,5,8,12-pentaazacyclotetradecane)nickel(II) perchlorate with the atomic numbering scheme. In the final model, atoms O(1), O(2) and C(10) are disordered, but the ordered structure is presented here for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for the cation

Ni(1)—N(3)	1.959(5)	N(6)—C(5)	1.522(9)
Ni(1)—N(6)	1.906(5)	N(6)—C(7)	1.561(7)
N(1)—C(2)	1.526(8)	C(4)—C(5)	1.495(6)
N(1)—C(9)	1.47(1)	C(7)—C(8)	1.41(1)
N(3)—C(2)	1.409(8)	C(9)—C(10)	1.51(2)
N(3)—C(4)	1.429(9)		
N(3)—Ni(1)—N(3)	92.9(3)	Ni(1)—N(6)—C(7)	120.2(5)
N(3)—Ni(1)—N(6)	87.0(1)	C(5)—N(6)—C(7)	111.9(6)
N(3)—Ni(1)—N(6)	179.4(3)	N(1)—C(2)—N(3)	113.0(6)
N(6)—Ni(1)—N(6)	93.0(3)	N(3)—C(4)—C(5)	110.8(7)
C(2)—N(1)—C(2)	110.0(7)	N(6)—C(5)—C(4)	102.8(6)
C(2)—N(1)—C(9)	118.9(5)	N(6)—C(7)—C(8)	114.0(6)
Ni(1)—N(3)—C(2)	117.7(5)	C(7)—C(8)—C(7)	114.3(9)
Ni(1)—N(3)—C(4)	106.0(4)	N(1)—C(9)—C(10)	112(1)
C(2)—N(3)—C(4)	109.8(6)		
Ni(1)—N(6)—C(5)	109.7(4)		

Table 4. Molecular geometry about the distal nitrogen atom of various penta- and hexa-aza macrocycles

Complex	C—N—C (°)	C—N (Å)	Reference
	113.67 ± 2.47	1.446 ± 0.022	14
			
R = —CH_3	114.97 ± 1.10	1.447 ± 0.014	2
R = —SO_2CH_3	118.93 ± 2.58	1.448	15
R = —SO_2—p—C_6H_4—Me	120.00 ± 3.51	1.443 ± 0.002	16
R = —CH_2CH_3	115.93 ± 5.13	1.507 ± 0.032	This work

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