Crystal and Molecular Structure and Solution Behaviour of Low-spin (3-Methyl-1,3,5,8,12-pentaazacyclotetradecane)-$\kappa^4N^1,N^5,N^8,N^{12}$)nickel(II) Diperchlorate†

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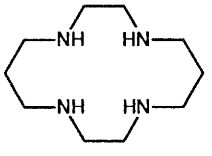
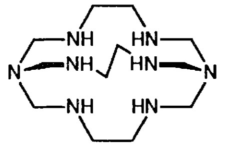
Template reaction of 3,7-diazanonane-1,9-diamine, formaldehyde and methylamine, in the presence of $Ni(ClO_4)_2$, gives the pentaazamacrocyclic low-spin complex $[Ni(azacyclam)][ClO_4]_2$ (azacyclam = 3-methyl-1,3,5,8,12-pentaazacyclotetradecane), whose crystal and molecular structure was determined from single-crystal X-ray diffraction data collected with the use of Cu-Kα radiation: space group $P2_12_12_1$ with a = 15.967(3), b = 13.497(3), c = 8.737(2) Å, $\alpha = \beta = \gamma = 90°$, Z = 4 (R = 0.0705). Only the four secondary amine nitrogen atoms of azacyclam are bound to the metal, according to a regular square-planar stereochemistry, the lone pair of the tertiary nitrogen atom, N(1), being exposed. In particular, the $N(1)C_3$ group is flattened, probably due to a long-range electrostatic interaction between N(1) and the metal. As a consequence, N(1) displays a very small affinity towards aqueous H^+ ($pK_a < 2$). The $[Ni(azacyclam)]^{2+}$ complex in aqueous solution displays the high spin–low spin (blue-to-yellow) interconversion, typical of complexes of cyclam. However, in contrast, addition of HCl favours formation of the high-spin form. This unusual behaviour is ascribed to protonation of the N(1) atom, at acid concentrations of 0.5–1.0 mol dm^{-3}, and to axial co-ordination of a hydrogen-bonded chloride ion. Addition of $HClO_4$ first favours formation of the high-spin species, then that of the low-spin complex: in this case, the hydrogen-bond-facilitated axial co-ordination of a water molecule is hypothesized.

Most convenient template routes to quadridentate amine macrocycles typically involve the Schiff-base condensation of the primary amine groups of a polyamine ligand, co-ordinated to Ni^{II}, with carbonyl derivatives. Hydrogenation of the resulting C=N double bonds gives the fully saturated macrocycle. The most famous and investigated system produced through this synthetic route is 1,4,8,11-tetraazacyclotetradecane (L^1, cyclam),[1] which is obtained in good yield from the nickel(II) template reaction between the open-chain tetramine 4,7-diazadecane-1,10-diamine and glyoxal.[2] It presents the most favourable structure arrangement for the co-ordination of divalent transition-metal ions: a tetraaza 14-membered cyclic framework, forming a 5,6,5,6 sequence of chelate rings.[3] The especially strong in-plane M^{II}–N interactions generate (*i*) the highest thermodynamic stability among metal complexes with macrocycles of varying ring size and denticity,[4] (*ii*) extreme inertness towards demetallation[5] and (*iii*) the easiest access to high, otherwise unstable, oxidation states of the encircled metal centre (*e.g.* Ni^{III} and Cu^{III}).[6] Features (*i*)–(*iii*) are commonly described as macrocyclic properties.[7]

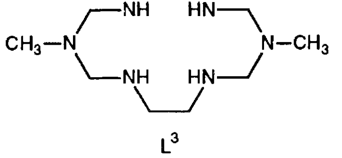
In 1977, Sargeson and co-workers[8] designed a new pathway to the metal template ring closure of polyamines: in particular, it was shown that condensation of the $[Co^{III}(en)_3]^{3+}$ complex (en = ethylenediamine) with ammonia and formaldehyde gives the octamine six-co-ordinating cage macrocycle L^2 (the so-called sepulchrand).[9] In the Sargeson reaction, NH_3 acts as a capping fragment and, being triprotic, causes a three-dimensional condensation to take place. More recently, Suh and Kang[10] successfully extended this type of reaction to the synthesis of two-dimensional systems, *i.e.* cyclam-like macrocycles, by treating $[M^{II}(en)_2]^{2+}$ (M = Ni or Cu) with formaldehyde and a primary amine RNH_2 (R = CH_3 or C_2H_5). This condensation produced the 14-membered hexaaza macrocycle L^3. Studies in solution showed that $[NiL^3]^{2+}$ exhibits properties very similar to $[Ni(cyclam)]^{2+}$, suggesting that L^3 behaves as a quadridentate ligand: the two tertiary amine nitrogen atoms seem to play only an architectural role and are not involved in the co-ordination.



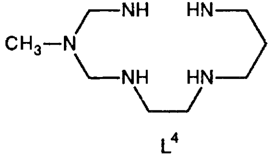
L^1



L^2



L^3



L^4

We were interested to clarify the nature and role of the bridging tertiary amine group in this type of macrocyclic complex. In this connection, we prepared, through the typical template procedure, the nickel(II) complex of the 14-membered pentaaza macrocycle L^4 (3-methyl-1,3,5,8,12-pentaazacyclotetradecane, azacyclam), which, in addition to the four secondary amine nitrogen atoms of cyclam, contains just one methylamino bridging group. We report here the crystal and

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

Table 1 Experimental data for the X-ray diffraction study

Formula	$C_{10}H_{25}Cl_2N_5NiO_8$
M	472.95
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	15.967(3)
b/Å	13.497(3)
c/Å	8.737(2)
$\alpha,\beta,\gamma/^\circ$	90
U/Å^3	1882.9(7)
Z	4
D_c/Mg m^{-3}	1.668
F(000)	984
μ/cm^{-1}	45.993
Diffractometer	Siemens AED
Scan type	θ–2θ
Scan speed/° min^{-1}	3–12
Scan width/°	$\theta - 0.65$ to $\theta + 0.65 + \Delta\lambda\cdot\lambda^{-1} \tan\theta]$
Radiation	Cu-Kα (λ 1.541 78 Å)
2θ Range/°	6–140
Reflections measured	$\pm h,k,l$
Total data measured	4016
Observed data [$I_{hkl} > 2\sigma(I)$]	3564
Unique observed data	3050
No. of variables	302
Final *R*	0.0705
Final *R'*	0.0705 (unit weights)

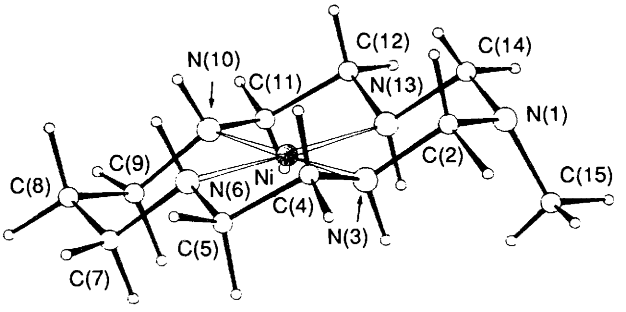

Fig. 1 Perspective view of the complex cation $[NiL^4]^{2+}$, with the atomic numbering scheme

Table 2 Fractional atomic coordinates (× 10^4) for the non-hydrogen atoms of $[NiL^4][ClO_4]_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ni	6 558(1)	2 637(1)	2 183(1)
Cl(1)	10 113(1)	2 254(2)	4 479(2)
Cl(2)	8 055(1)	2 269(2)	−1 038(2)
O(11)	9 456(4)	2 092(2)	3 435(8)
O(12)	10 879(5)	2 079(10)	3 753(11)
O(13)	10 044(9)	1 617(7)	5 748(11)
O(14)	10 067(7)	3 228(6)	5 003(14)
N(1)	7 779(4)	4 392(5)	3 631(8)
C(2)	7 768(6)	3 462(7)	4 459(11)
N(3)	7 550(4)	2 599(4)	3 458(6)
C(4)	7 510(7)	1 697(7)	4 469(11)
C(5)	7 195(7)	883(6)	3 417(13)
N(6)	6 426(4)	1 245(4)	2 671(8)
C(7)	6 179(7)	536(7)	1 370(14)
C(8)	5 369(7)	848(7)	656(13)
C(9)	5 430(6)	1 850(7)	−178(11)
N(10)	5 561(4)	2 662(5)	928(6)
C(11)	5 515(7)	3 641(7)	104(11)
C(12)	5 821(5)	4 391(6)	1 199(11)
N(13)	6 659(4)	4 027(4)	1 746(7)
C(14)	6 972(6)	4 717(6)	3 029(11)
C(15)	8 459(7)	4 520(8)	2 581(12)
O(21)	8 717(8)	2 688(10)	−1 972(14)
O(22)	7 475(8)	3 052(9)	−846(15)
O(23)	8 293(8)	1 812(9)	336(13)
O(24)	7 531(8)	1 552(9)	−1 836(16)
O(21b)	8 632(10)	2 049(13)	−2 104(16)
O(22b)	8 423(11)	2 372(14)	530(15)
O(23b)	7 450(10)	1 530(15)	−879(16)
O(24b)	7 664(13)	3 178(12)	−1 296(15)

molecular structure of the low-spin $[NiL^4][ClO_4]_2$ complex and an investigation on its solution behaviour. It will be shown that the tertiary amine nitrogen atom is not directly involved in co-ordination, but, as an ammonium group, has important and unexpected consequences on the electronic and stereochemical properties of the encircled metal centre, in solution.

Experimental

Synthesis of (3-*Methyl*-1,3,5,8,12-*pentaazacyclotetradecane*)-*nickel*(II) *Perchlorate*.—The synthesis is a slight modification of that already described by Suh and Kang[10] for 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane. The compound $NiCl_2\cdot 6H_2O$ (5.75 g, 24.15 mmol) was dissolved in ethanol (120 cm^3) and 3,7-diazanonane-1,9-diamine (3.87 g, 24.15 mmol) added in portions at room temperature. A violet solution formed, to which triethylamine (4.8 g, 48 mmol), 40% aqueous methylamine (4.3 cm^3, 24.15 mmol) and 40% aqueous formaldehyde (10 cm^3, 133 mmol) were slowly added. The solution was heated at reflux for 20 h: a brown mixture formed, which was cooled to room temperature and filtered. Ethanol (50 cm^3) was removed on a rotary evaporator and the resulting deep brown solution was treated with an equal volume of an ethanolic solution saturated in sodium perchlorate. The yellow-brown crystals which formed were filtered off, washed with diethyl ether and dried *in vacuo*, yielding 3.6 g (32%) of $[NiL^4][ClO_4]_2$ (Found: C, 25.6; H, 5.4; N, 14.6. Calc. for $C_{10}H_{25}Cl_2N_5NiO_8$: C, 25.4; H, 5.3; N, 14.8%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated water–ethanol (70:30) solution.

Crystal Structure of $[NiL^4][ClO_4]_2$.—The X-ray measurements were carried out at room temperature on a single crystal of about 0.5 × 0.3 × 0.2 mm. Crystal data and the most relevant parameters used in the data collection are summarized in Table 1.

The cell parameters were determined from 34 $I_{hkl}(\theta,\chi,\varphi)$ reflections in the range $34 < \theta < 45°$ found in a random search of the reciprocal lattice. In the systematic data collection the intensities I_{hkl} were determined by profile analysis with the method of Lehmann and Larsen.[11] The intensity of one standard reflection, checked every 100 measurements, showed no significant fluctuations. The 4016 collected reflections were corrected for Lorentz and polarization effects and 3569 with $I_{hkl} > 2\sigma(I_{hkl})$ were retained as observed and used in the structure refinement. Absorption effects were corrected using ABSORB[12] at the end of the isotropic refinement.

The structure was solved by Patterson and Fourier methods and refined using the SHELX[13] package of programs. The structure was refined by the blocked full-matrix least-squares method to a total of 302 parameters. Parameters refined were: the overall scale factor, positional parameters for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms with the exception of the oxygen atoms of one ClO_4^- anion, which was disordered between two different orientations and whose occupancy factors were also refined (0.766, 0.234 respectively). Seventeen hydrogens were found in the Fourier ΔF map and refined with isotropic thermal parameters. The others were taken in their calculated positions. The refinement converged at $R = 0.0705$. The highest peak in the final Fourier ΔF map was 0.34 e Å^{-3}.

An independent refinement with the $-x, -y, -z$ atomic coordinates was carried out to determine the absolute con-

Table 3 Molecular geometry dimensions (lengths in Å, angles in °)

Ni–N(3)	1.937(6)	Ni–N(10)	1.933(6)
Ni–N(6)	1.938(6)	Ni–N(13)	1.921(6)
N(1)–C(2)	1.449(12)	C(9)–N(10)	1.476(11)
C(2)–N(3)	1.498(11)	N(10)–C(11)	1.507(12)
N(3)–C(4)	1.506(11)	C(11)–C(12)	1.476(13)
C(4)–C(5)	1.518(14)	C(12)–N(13)	1.503(10)
C(5)–N(6)	1.474(13)	N(13)–C(14)	1.541(11)
N(6)–C(7)	1.537(13)	C(14)–N(1)	1.459(12)
C(7)–C(8)	1.496(16)	N(1)–C(15)	1.432(13)
C(8)–C(9)	1.539(14)		
N(3)–Ni–N(6)	86.4(3)	N(10)–Ni–N(13)	86.5(3)
N(6)–Ni–N(10)	93.0(3)	N(13)–Ni–N(3)	94.1(3)
N(6)–Ni–N(13)	178.1(3)	N(10)–Ni–N(3)	179.2(3)
C(2)–N(1)–C(14)	115.5(7)	C(8)–C(9)–N(10)	110.6(8)
N(1)–C(2)–N(3)	112.7(7)	C(9)–N(10)–C(11)	109.4(6)
C(2)–N(3)–C(4)	107.2(6)	C(9)–N(10)–Ni	118.4(6)
C(2)–N(3)–Ni	120.4(5)	C(11)–N(10)–Ni	109.1(5)
C(4)–N(3)–Ni	108.9(5)	N(10)–C(11)–C(12)	106.0(7)
N(3)–C(4)–C(5)	104.1(8)	C(11)–C(12)–N(13)	106.1(7)
C(4)–C(5)–N(6)	107.7(7)	C(12)–N(13)–C(14)	108.8(6)
C(5)–N(6)–C(7)	109.5(7)	C(12)–N(13)–Ni	107.9(5)
C(5)–N(6)–Ni	109.2(5)	C(14)–N(13)–Ni	118.2(5)
C(7)–N(6)–Ni	118.0(6)	N(13)–C(14)–N(1)	111.5(7)
N(6)–C(7)–C(8)	110.8(8)	C(14)–N(1)–C(15)	113.7(7)
C(7)–C(8)–C(9)	113.0(9)	C(15)–N(1)–C(2)	115.7(8)

Relevant intermolecular hydrogen bonds

N(3)···O(23)	3.16(1)	H(3)···O(23)	2.37(1)	N(3)–H(3)···O(23)	140.2(5)
N(6)···O(14′)	3.06(1)	H(6)···O(14′)	2.12(1)	N(6)–H(6)···O(14′)	153.4(4)
N(10)···O(21″)	3.12(1)	H(10)···O(21″)	2.36(1)	N(10)–H(10)···O(21″)	134.8(2)
N(13)···O(22)	2.93(1)	H(13)···O(22)	2.11(1)	N(13)–H(13)···O(22)	145.8(5)

Symmetry codes: ′ $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; ″ $-\frac{1}{2} + x, \frac{1}{2} - y, -z$.

figuration. In this case the refinement converged at $R = 0.0728$. On the basis of Hamilton's test,[14] in which the significance of the discrepancy between the R factors of the two absolute configurations is estimated, we may reject at the probability level of 0.005 the hypothesis that the absolute configuration is the second of the two tried. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

Geometrical calculations were performed using PARST.[15] The atomic scattering factors were taken from the literature.[16] All the calculations were performed on the GOULD 6040 POWERNODE of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

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

Studies in Solution.—Spectra of aqueous solutions were taken using a Cary 2300 spectrophotometer or an Hewlett-Packard 8452 diode array spectrophotometer. Thermostatted water was circulated through the jacketed cuvette holder. pH Measurements were performed with an Orion 720 potentiometer connected to a calibrated glass electrode (Orion 91-01) and to a calomel electrode.

Results and Discussion

Crystal Structure of $[NiL^4][ClO_4]_2$.—The X-ray investigation showed that in the $[NiL^4]^{2+}$ cation only the four secondary amine nitrogen atoms were co-ordinated, according to an almost regular square stereochemistry, as shown in Fig. 1. The four bound nitrogen atoms present an *RSRS* configuration. Relevant bond distances and angles are given in Table 3.

The metal atom is displaced by 0.018(1) Å out of the best plane of the four co-ordinated nitrogen atoms. The Ni^{II}–N distances range from 1.921(6) to 1.938(6) Å, as typically observed for low-spin tetramine complexes of Ni^{II}.[17] As observed in other cyclam-like systems,[18] the N–Ni^{II}–N angles are somewhat distorted from the ideal square-planar geometry: those in the five-membered rings are reduced to 86.4(3) and 86.5(3)°, whereas those involved in the six-membered rings are expanded to 93.0(3) and 94.1(3)°. The complex possesses a pseudo-symmetry plane which bisects the N(3)–Ni^{II}–N(13) and N(6)–Ni^{II}N(10) angles: the bis(ethylenediamine) complex originating from this bisection is in the λ–δ configuration.

Both six-membered chelate rings adopt a chair conformation and the methyl group on N(1) is axial. The five-membered rings adopt a *gauche* conformation. Similar conformations have been observed in the six- and five-membered rings in the *RRSS* configurational isomer, with two N–H bonds up and two down, in the high-spin $[Ni(cyclam)Cl_2]$ complex[19] and in the $[Ni(cyclam)]^{2+}$ moiety of a low-spin dinickel(II) bis(cyclam) complex.[20] Moreover, we wished to consider the effect of replacing the middle methylene group of one of the trimethylene chains of cyclam by a NCH_3 group. To do that we compared the structural features of $[NiL^4]^{2+}$ with those of the $[Ni(cyclam)]^{2+}$ subunit of the previously mentioned dimetallic bis(cyclam) complex.[20] The latter complex is well characterized from a structural point of view and is one of the few with the 14-membered unsubstituted ligand, among the numerous complexes with cyclam-like derivatives.

First, the average Ni^{II}–N bond length in the azacyclam complex [1.932(6) Å] is *ca.* 0.02 Å shorter than observed in the complex chosen as a reference [1.95(1) Å].[20] Moreover, the Ni^{II}···N(1) distance [3.319(7) Å] is shorter (by 0.03 Å) than the corresponding Ni^{II}···CH_2 distance observed in the reference system (3.35 Å).[20] The shortening of the Ni^{II}–N distances observed in the azacyclam complex as well as the slight deformation of the torsion angles of the chelate rings, compared to what is observed in the reference system,[20] seems to indicate that the unco-ordinated tertiary amine nitrogen

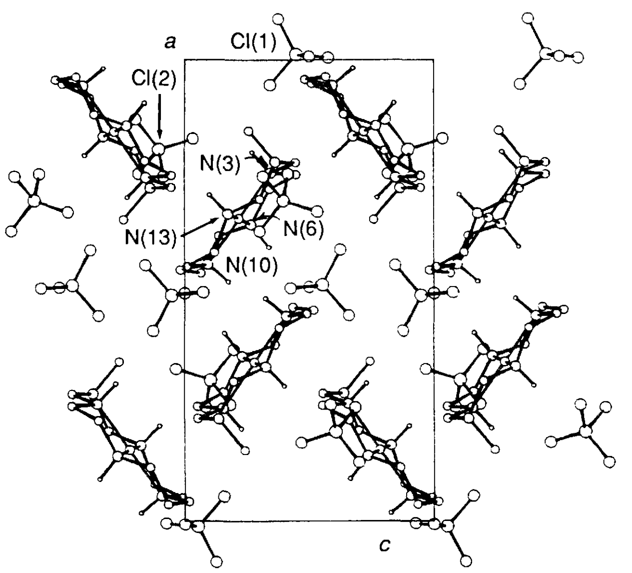

Fig. 2 Molecular packing along [010] showing only the hydrogen atoms [at N(3), N(6), N(10) and N(13)] involved in intermolecular hydrogen bonds

atom generates a significant strain in the azacyclam framework. In particular, the geometry of the NC_3 group [at the N(1) atom of the azacyclam system] substantially deviates from that of a normal 'unstrained' trialkylamino group. In this case, we chose as a reference system the NC_3 group of hexamethylenetetramine, in the X-ray investigated hexamethylenetetramine–thiourea adduct.[21] First, the mean value of the N(1)–C bond length in azacyclam [1.45(1) Å] is 0.02 Å shorter than the N–C distance observed in the reference system. Secondly, and more significantly, the C–N(1)–C angles in the azacyclam complex exhibit an average value [115.0(7)°] 7° larger than that observed for the C–N–C angles in the hexamethylenetetramine reference system (109°, *i.e.* the canonical value for an sp^3-hybridized nitrogen atom). These data would suggest that the N(1) nitrogen atom of the co-ordinated azacyclam system has partial sp^2 character, which can affect its properties and reactivity, in particular the affinity towards the aqueous H^+ ion (see below). It should be noted that an analogous distortion of the NC_3 group has been previously observed in the sepulchrand complexes of Co^{III},[8] Co^{II}[22] and Ni^{II}.[23] On the basis of molecular mechanics calculations, Sargeson and co-workers[22] pointed out that the flattening of the NC_3 group in sepulchrate complexes can be ascribed either to (*i*) steric constraints or (*ii*) the electrostatic attraction between the metal centre and the tertiary nitrogen atom. In the present system, in which the $N(1)C_3$ group is incorporated in the macrocyclic framework only through two N–C bonds, whereas the third N(1)–C bond is bound to a methyl group, steric constraints should be less effective than in the sepulchrate complexes. Thus, the fact that the NC_3 group is still substantially flattened stresses the role of the M–N(1) long-range electrostatic interaction, a rather new contribution to the bonding in metal amine complexes.

Finally, Fig. 2 shows the molecular packing of the $[NiL^4][ClO_4]_2$ complex. It emphasizes the existence of intermolecular hydrogen bonding between the $>$NH fragments of azacyclam and perchlorate ions.

The Solution Behaviour of $[NiL^4]^{2+}$.—X-Ray studies have shown that the tertiary amine group of the azacyclam ring is not involved in direct co-ordination to the metal centre, but its lone pair is exposed. Thus the tertiary nitrogen atom might behave as a rather strong base. To verify this we carried out a pH titration on a solution 10^{-2} mol dm^{-3} in $[NiL^4][ClO_4]_2$, 10^{-2} mol dm^{-3} in $HClO_4$ and adjusted to 0.1 mol dm^{-3} ionic strength with $NaClO_4$. Standard NaOH was added and the pH was measured by a calibrated glass electrode. In the investigated pH range no inflections were observed in the acidic part of the titration curve, which displayed a profile typical for the titration of a strong acid with a strong base. In particular, the curve superimposed well with that obtained, under the same conditions, using $[Ni(cyclam)][ClO_4]_2$. This indicates that the unco-ordinated tertiary amine group of the azacyclam complex does not bind protons down to pH 2, *i.e.* it has a $pK_a < 2$. This may be surprising, if one considers that tertiary amine groups are rather strongly basic in aqueous solution, displaying pK_a values of $\geqslant 10$, *e.g.* 9.81 for $N(CH_3)_3$ and 11.01 for $N(C_2H_5)_3$. However, two main effects may contrast and reduce the basicity of the unco-ordinated amine group of azacyclam: first, the dipositive metal centre, at a distance of 3.319(7) Å, should exert strong electrostatic repulsions towards positively charged species, making the approach of the hydrogen ion especially difficult. Moreover, the flattening of the $N(1)C_3$ group makes the tertiary amine nitrogen atom exhibit something intermediate between sp^3 and sp^2 hybridization. This should decrease its basicity substantially.

Further information about the basic nature of the N(1) atom of azacyclam can be obtained from an investigation of the spin interconversion equilibrium of the $[NiL^4]^{2+}$ complex. It is well known that the precursor complex $[Ni(cyclam)]^{2+}$ exists in aqueous solution as an equilibrium mixture of two main forms: a blue high-spin form and a yellow low-spin form.[24] The low-spin complex exhibits planar geometry, whereas in the high-spin complex two water molecules are thought to occupy the axial positions of an elongated octahedron. Thus, the high spin–low spin interconversion, as described by equation (1), involves the

$$[Ni^{II}L(H_2O)_2]^{2+} \rightleftharpoons [Ni^{II}L]^{2+} + 2H_2O \qquad (1)$$

release of two water molecules from the co-ordination sphere of the octahedral complex. The blue-to-yellow interconversion is endothermic and can be further displaced to the right by the bulk addition of an inert electrolyte (*e.g.* $NaClO_4$). This latter effect has been explained by admitting that the ions of the added salt compete for the water molecules bound to the high-spin complex, so favouring the formation of the planar species. Curiously, NaCl, which contains a co-ordinating anion, behaves as an inert electrolyte, and a bulk addition results in an increase in the concentration of the yellow form: this means that hydrogen-bond formation of Cl^- with water molecules (the 'dehydrating effect') predominates over the co-ordination tendency of Cl^- towards the metal centre. A similar effect is displayed by the acids $HClO_4$ and HCl.

We wished to verify whether such behaviour is displayed by the azacyclam complex. Thus its d–d spectra were recorded in aqueous solutions of varying concentration of HCl. For comparative purposes, the spectra of $[Ni(cyclam)]Cl_2$ were recorded under the same conditions. Fig. 3 reports the variation of the intensity of the absorption band at 450 nm with increasing concentration of HCl (from 10^{-3} to 6 mol dm^{-3}, logarithmic scale) for solutions 10^{-2} mol dm^{-3} in each complex.

The band at 450 nm corresponds to the low-spin square-planar $[Ni(macrocycle)]^{2+}$ complex and can be used to monitor its concentration. In the case of the cyclam complex the normal behaviour is observed: an increase in the HCl concentration results in a progressive increase in the concentration of the low-spin $[Ni(cyclam)]^{2+}$ species. Considering that the molar absorbance of this species is 64.5 dm^3 mol^{-1} cm^{-1}, the concentration of the yellow square-planar species changes from 78.4 (in 10^{-2} mol dm^{-3} HCl) to 93.4% (in 6 mol dm^{-3} HCl). Surprisingly, the $[NiL^4]^{2+}$ complex displays the opposite behaviour: on adding HCl the intensity of the band at 450 nm decreases, whereas bands at 342 and 516 nm gradually become stronger. The last two bands are pertinent to the high-spin octahedral complex. In particular, at $\geqslant 1$ mol dm^{-3} HCl the band of the yellow complex disappears and the bands of the blue

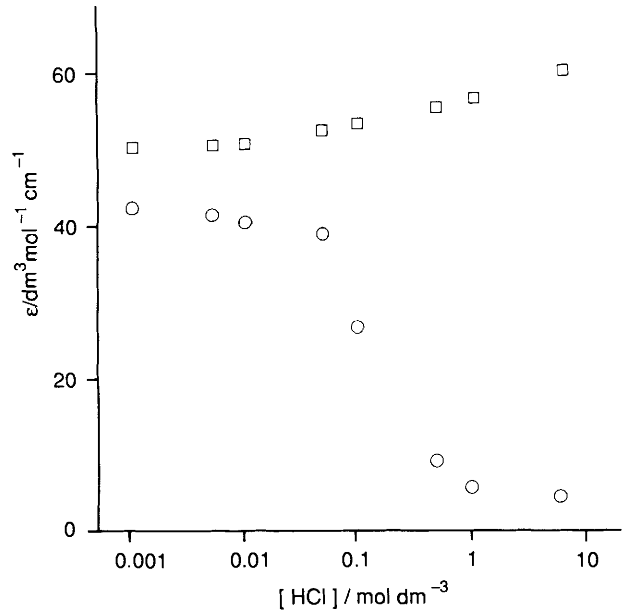

Fig. 3 Variation of the absorbance of the band at 450 nm, pertinent to the low-spin $[Ni(macrocycle)]^{2+}$ chromophore, with increasing concentration of HCl [macrocycle = cyclam (□); azacyclam (○)]

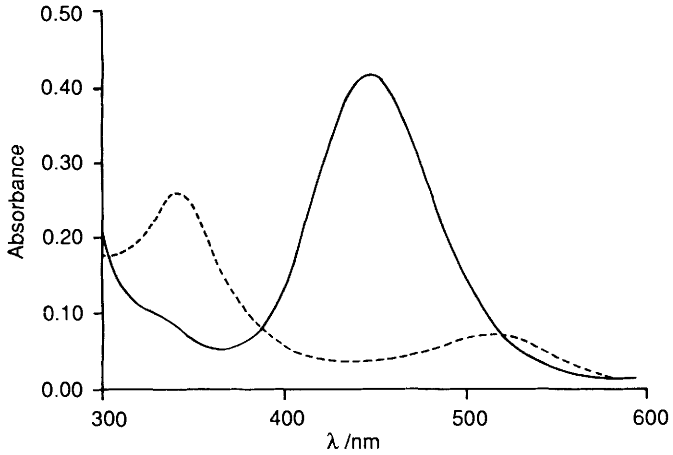

Fig. 4 Spectra of the $[NiL^4]Cl_2$ complex in aqueous solutions 0.01 (——) and 6 mol dm^{-3} in HCl (- - -)

species reach their limiting values. Fig. 4 reports the spectra of $[NiL^4]Cl_2$ solutions containing limiting concentrations of HCl: 0.01 and 6 mol dm^{-3}.

Thus, in the case of the azacyclam complex, in contrast to what observed for cyclam (and for the nickel(II) complexes with all the other tetraaza macrocycles investigated),[25] addition of the inert electrolyte (HCl) favours the formation of the blue complex. We believe that this anomalous behaviour is related to the protonation of the unco-ordinated tertiary amine nitrogen atom, which takes place under strongly acidic conditions, *i.e.* at HCl concentrations between 0.5 and 1.0 mol dm^{-3}. In these circumstances, the trialkylammonium group could interact through hydrogen bonding with a Cl^- ion, in such a way to force it to bind axially to the nickel(II) cation, so stabilizing the triplet state. To do this, the co-ordinated macrocycle, if existing in the conformation observed in the solid state, should rearrange in order so as to point the NH^+ bond (that is the lone pair in the unprotonated complex) in a direction more favourable for the formation of a bridge with the co-ordinated Cl^-. This could happen if the six-membered chelate ring containing the ammonium group, which in the solid state exists in a chair conformation, rearranges to a twist-boat conformation. Such a rearrangement, without any configurational change of the co-ordinated nitrogen atoms, should be quite easy, as the required energy is probably small. It is also possible that these two conformers exist in equilibrium in an aqueous solution of the unprotonated complex and just one is 'frozen' during the crystallization. After the protonation, the formation of the $N^+{-}H\cdots Cl{-}Ni^{II}$ system should stabilize the other conformer. A tentative sketch of the suggested stereochemical arrangement of the high-spin complex in strongly acidic solutions is shown in Fig. 6.

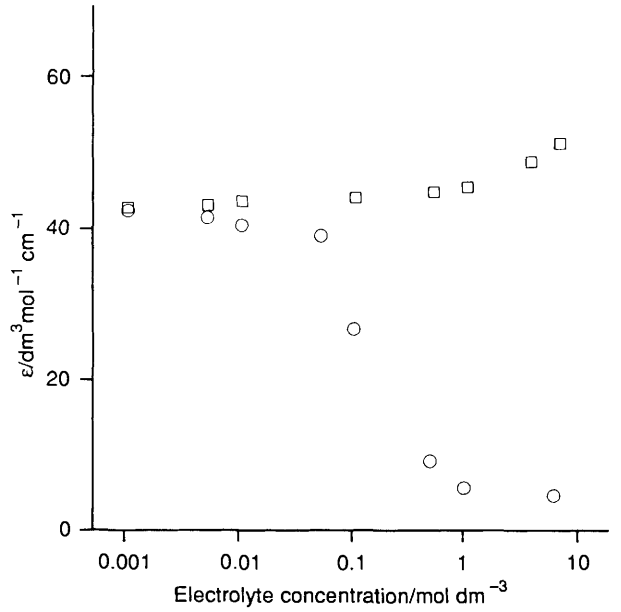

Fig. 5 Variation of the absorbance of the band at 450 nm of $[NiL^4]^{2+}$, pertinent to the low-spin chromophore, with increasing concentration of HCl (○) and NaCl (□)

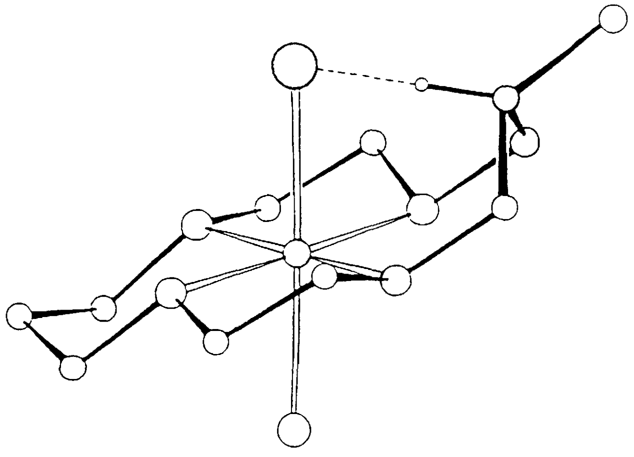

Fig. 6 Hypothesized stereochemical arrangement of the $[NiL^4]^{2+}$ complex in an aqueous solution of >1 mol dm^{-3} HCl. The unco-ordinated trialkylamino group is protonated and interacts through hydrogen bonding with a chloride ion, apically bound to the metal centre

It is worth noting that the curve reported in Fig. 3 can be considered as a titration profile. In this sense, the log c_{HCl} value at which the concentration of the yellow form has been reduced to 50% of its original value should correspond to a sort of apparent 'pK_a' value (*i.e.* 0.96 log units) corresponding to the acid–base equilibrium (L = azacyclam) (2). As indicated in the

$$\underset{\text{low spin}}{[Ni^{II}L]^{2+}} + H^+ + Cl^- + H_2O \rightleftharpoons \underset{\text{high spin}}{[Ni^{II}(HL)Cl(H_2O)_{ax}]^{2+}} \quad (2)$$

formula of the high-spin complex, it is assumed that a water molecule occupies the second axial position of the distorted octahedron.

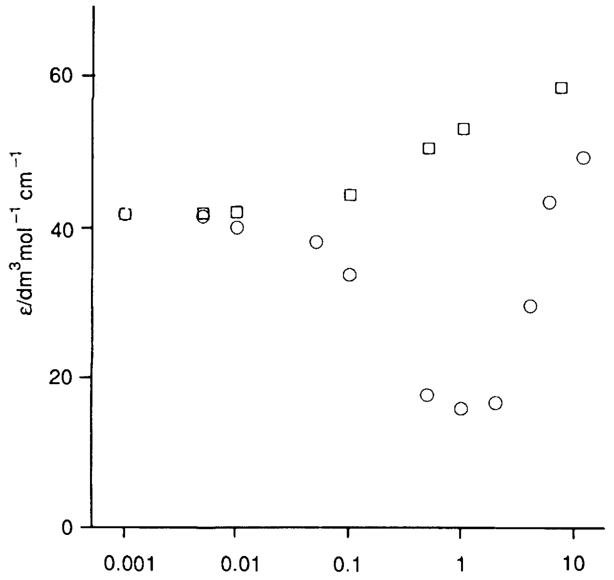

Fig. 7 Variation of the absorbance of the band at 450 nm of $[NiL^4]^{2+}$, pertinent to the low-spin chromophore, with increasing concentration of $HClO_4$ (○) and $NaClO_4$ (□)

It should be noted that the presence of a large excess of H^+ ions is essential for the formation of the high-spin azacyclam complex. Addition of NaCl to a neutral solution of $[NiL^4]Cl_2$ has the normal effect of increasing the intensity of the band of the yellow species (see Fig. 5). Moreover, the Ni^{II}–$Cl \cdots HN^+$ assembly seems a rather stable one. Increasing the temperature to 50 °C for a $[NiL^4]Cl_2$ solution containing $\geqslant 1$ mol dm^{-3} HCl does not induce any modification of the spectrum (pertinent to the 100% of the blue form) and, in particular, no band develops at 450 nm. On the contrary, heating a corresponding solution 0.1 mol dm^{-3} in HCl produces a detectable increase in the intensity of the band of the yellow chromophore, at 450 nm, as expected on the basis of the endothermic nature of equilibrium (1).[3]

To investigate the effect of the nature of the anion of the background electrolyte we carried out similar studies in solutions containing the much less strongly co-ordinating ClO_4^- ion. The effect of the variation of the $NaClO_4$ or $HClO_4$ concentration is illustrated in Fig. 7. Addition of bulk $NaClO_4$ salt has the normal 'dehydrating effect', resulting in a progressive increase in the intensity of the band at 450 nm (*i.e.* increasing the concentration of the low-spin complex). On the other hand, addition of $HClO_4$ induces a behaviour similar to that observed in the case of HCl solutions, at least at not too high values of the acid concentration. In particular, in the range $c_{HClO_4} = 0.1$–1 mol dm^{-3}, the low-spin species drastically decreases in concentration, almost disappearing, whereas the high-spin complex forms. Again, this behaviour has to be related to the protonation of the tertiary amine atom N(1), as is confirmed by the fact that, at lower acidity the curve of absorbance at 450 nm *vs.* log c_{HClO_4} superimposes upon that obtained in the case of HCl solutions. This leads to the same apparant pK_a value in both HCl and $HClO_4$ solutions. Thus, to account for the colour change and spin-state conversion, one should invoke, also in this case, a hydrogen-bonding controlled co-ordination of the anion. Such a situation is rather surprising, considering the very poor co-ordinating tendency of the perchlorate ion, especially in aqueous solution. However, analogy with the HCl solutions ends at an $HClO_4$ concentration of 1 mol dm^{-3}: here, the nearly 80% high-spin form is present; but further addition of acid results in formation of the yellow species and the intensity of its band increases steeply. At the highest c_{HClO_4} investigated (11.6 mol dm^{-3}), the concentration of the yellow square-planar species is higher than that observed in weakly acidic solution ($c_{HClO_4} = 10^{-3}$–10^{-2} mol dm^{-3}). This indicates that the axial ligand responsible for the stabilization of the high-spin form is released at $\geqslant 2$ mol dm^{-3} $HClO_4$. The above behaviour seems to exclude that this ligand is perchlorate. If perchlorate were bound, according to the hydrogen-bonding mechanism hypothesized for chloride, there is no reason why it should be displaced by further addition of perchlorate. We rather suggest that the ammonium group, which is completely formed at $c_{HClO_4} = 1$ mol dm^{-3}, is hydrogen bonded to a water molecule: this molecule is driven to occupy one of the axial positions, in a similar way as observed for Cl^- in hydrochloric acid solution. On further addition of acid, the strong 'dehydrating' ions H^+ and ClO_4^-, which are present in an overwhelming concentration compared to the ring-incorporated ammonium group, successfully compete for the apically bound water molecule, stabilizing again the low-spin form of the complex. In conclusion, the acidity-controlled low spin–high spin–low spin sequence can be described through the stepwise equilibra (3). The assembly $[Ni^{II}(HL) \cdots H_2O_{ax}]^{3+}$ seems less stable than the corresponding high-spin species formed in concentrated HCl solutions. It has been mentioned before that the assembly $[Ni^{II}(HL)Cl(H_2O)_{ax}]^{2+}$ does not decompose even on heating the solution to 50 °C. On the other hand, increasing the temperature of a solution of the nickel(II) azacyclam complex in 1 mol dm^{-3} $HClO_4$ (at which the highest concentration of the high-spin protonated complex is present) results in the appearance and subsequent increase in intensity of the band at 450 nm (pertinent to the low-spin complex). The process is fully reversible, as the original spectrum is restored on cooling.

$$\underset{\text{low spin}}{[\mathrm{Ni^{II}L}]^{2+}} + \mathrm{H^+} + 2\mathrm{H_2O} \rightleftharpoons \underset{\text{high spin}}{[\mathrm{Ni^{II}(HL)\cdots H_2O_{ax}(H_2O)_{ax}}]^{3+}} \rightleftharpoons \underset{\text{low spin}}{[\mathrm{Ni^{II}(HL)}]^{3+}} + 2\mathrm{H_2O} \quad (3)$$

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References

1 E. K. Barefield, *Inorg. Chem.*, 1972, **11**, 2273.
2 E. K. Barefield, E. Wagner, A. W. Herlinger and A. R. Dahl, *Inorg. Synth.*, 1976, **16**, 220.
3 L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, 1979, **18**, 438.
4 L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1980, **19**, 535.
5 D. H. Busch, *Acc. Chem. Res.*, 1978, **11**, 392.
6 L. Fabbrizzi, *Comments Inorg. Chem.*, 1985, **4**, 33.
7 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley Interscience, New York, 1988, p. 344.
8 I. I. Creaser, J. MacB. Harrowfield, A. J. Herlt, A. M. Sargeson, J. Springborg, R. J. Geue and M. R. Snow, *J. Am. Chem. Soc.*, 1977, **104**, 3181.
9 A. M. Sargeson, *Chem. Br.*, 1979, **15**, 23.
10 M. P. Suh and S.-G. Kang, *Inorg. Chem.*, 1988, **27**, 2544.
11 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
12 F. Ugozzoli, ABSORB, *Comput. Chem.*, 1987, **11**, 109.
13 G. M. Sheldrick, SHELX 76, Programs for Crystal Structure Determination, University of Cambridge, 1976; SHELX 86, Institut für Anorganische Chemie der Universität, Göttingen, 1986.
14 W. C. Hamilton, *Acta Crystallogr.*, 1965, **18**, 502.
15 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
16 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

17 N. F. Curtis, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979.

18 K. Henrik, P. A. Tasker and L. F. Lindoy, *Prog. Inorg. Chem.*, 1985, **33**, 1.

19 B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson and M. L. Tobe, *Chem. Commun.*, 1965, 97.

20 E. K. Barefield, D. Chüeng and D. G. Van der Veer, *J. Chem. Soc., Chem. Commun.*, 1981, 302.

21 T. C. W. Mak, O. W. Lau, M. F. C. Ladd and D. C. Povey, *Acta Crystallogr., Sect. B*, 1978, **34**, 1290.

22 I. I. Creaser, R. J. Geue, J. MacB. Harrowfield, A. J. Herlt, A. M. Sargeson, M. R. Snow and J. Springborg, *J. Am. Chem. Soc.*, 1982, **104**, 6016.

23 M. P. Suh, W. Shin, D. Kim and S. Kim, *Inorg. Chem.*, 1984, **23**, 618.

24 A. Anichini, L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chim. Acta*, 1977, **24**, L21.

25 L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1979, 1857.

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