Synthesis and Characterisation of 1,7-Dimethyl-1,4,7,10-tetra-azacyclododecane: Crystal Structure of the Nickel(II) Bromide Monohydrate Complex of this Macrocycle; Thermodynamic Studies of Protonation and Metal Complex Formation [†]

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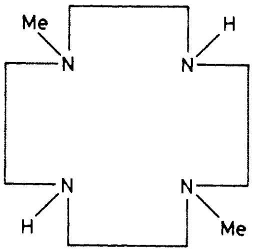
The synthesis and characterisation of the macrocycle 1,7-dimethyl-1,4,7,10-tetra-azacyclododecane (L^1) are reported. The basicity constants of L^1 and the stability constant of the complex $[CuL^1]^{2+}$ have been determined by potentiometry at 25 °C in 0.5 mol dm^{-3} KNO_3. The macrocycle L^1 behaves as a diprotic base in the pH range investigated; pD–^{13}C n.m.r. studies indicate that only the two secondary nitrogens are involved in the protonation process. Copper(II) and nickel(II) complexes with L^1 have been prepared and studied spectrophotometrically both in aqueous solution and in the solid state. The reflectance spectrum of dry yellow $NiL^1(ClO_4)_2$ shows that a square-planar geometry, with the nickel(II) in the low-spin state, is achievable also with this partially methylated twelve-macrocycle. The molecular structure of the complex $[NiBr(H_2O)L^1]Br$ has been determined by single-crystal *X*-ray analysis. The compound crystallises in an orthorhombic unit cell (space group $P2_12_12_1$) with lattice constants a = 13.478(5), b = 11.186(4), and c = 10.585(4) Å for Z = 4. Least-squares refinement converged at R = 0.046 for 910 observed reflections. The complex shows a *cis*-octahedral geometry, with the macrocycle co-ordinated in a folded configuration to four sites around the central nickel atom. The chirality of each nitrogen atom of the macrocycle is the same. The bromide ion and the oxygen atom of the water molecule are *cis* to each other. The chelate rings are all asymmetric.

Synthetic macrocyclic compounds and their metal complexes have been one of the most studied groups of compounds in recent years.[1-4] There are several reasons for this interest in macrocyclic complexes, *e.g.* the synthetic challenge, the exceptional kinetic and thermodynamic properties which enable practical applications of these compounds, and the possibility of using them as models for systems of biological interest.[1-4] Our own interest centres on the thermodynamics of complex formation with saturated macrocycles containing nitrogen-donor atoms.[5] Among the most important factors determining the thermodynamic behaviour of such metal–ligand systems are the relative dimensions of the metal ion and of the hole in the macrocyclic ligand,[6-8] the position of the donor atoms within the macrocyclic ring,[6-8] and the presence of substituent groups either on the donor atoms themselves or on the hydrocarbon bridges between them.[9] In the course of our studies we have synthesised the small, partially methylated macrocycle 1,7-dimethyl-1,4,7,10-tetra-azacyclododecane (L^1). Several authors have reported that neither the copper(II) nor nickel(II) can be accommodated within the cavity of a twelve-membered macrocycle,[10] but it has been found that 1,4,7,10-tetra-azacyclododecane can form a yellow complex with nickel(II) which is presumably square planar.[11] Moreover, an *X*-ray structure determination has definitely proved a slightly distorted square-planar co-ordination for the yellow nickel diperchlorate dihydrate complex of 1,4,7,10-tetramethyl-1,4,7,-10-tetra-azacyclododecane.[12] Actually, the nickel atom lies slightly out of the mean plane of the four nitrogen atoms.[12] The presence of the two methyl groups on the nitrogen atoms of this new ligand should stabilise the yellow, diamagnetic form and allow us to obtain information on the chirality of the nitrogen atoms.



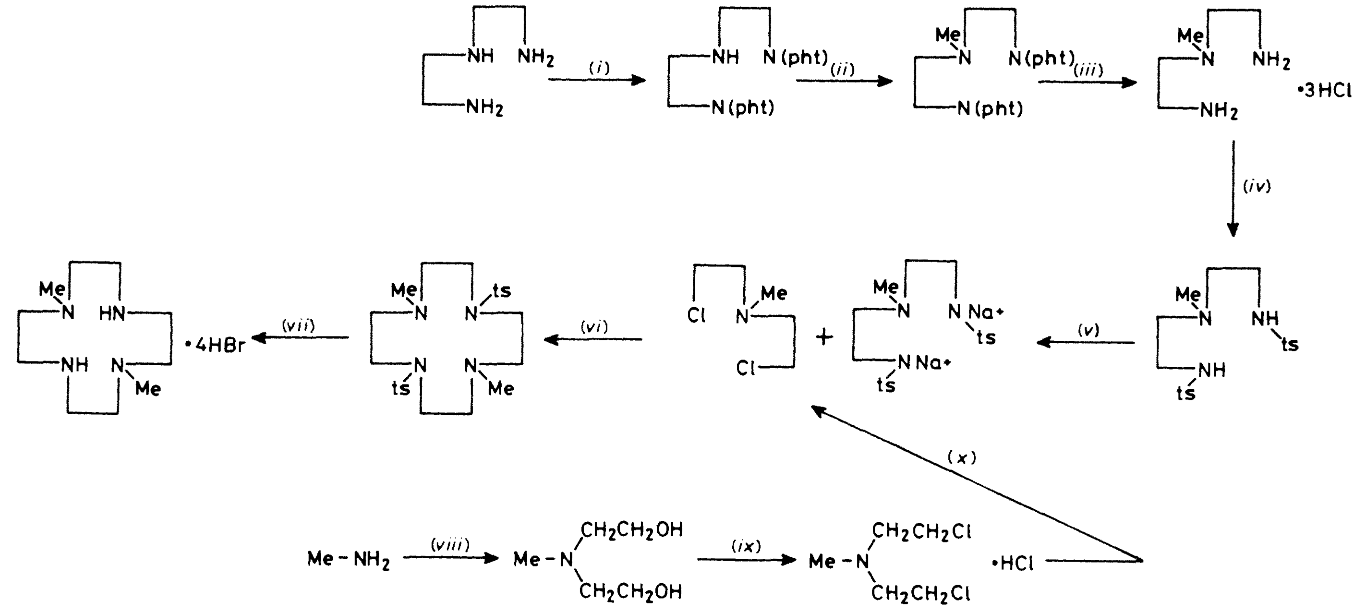
L^1

Experimental

Preparation of 1,7-*Dimethyl*-1,4,7,10-*tetra-azacyclododecane* (L^1) (*Scheme*).—The preparation of *N*,*N*′-iminodiethylenebisphthalimide, *N*,*N*′-methyliminodiethylenebisphthalimide, and 2,2′-methyliminodi(ethylamine) tris(hydrochloride) was performed as described previously.[13]

(*a*) N′-*Methyl*-N,N″-*bis*(*toluene*-p-*sulphonyl*)*diethylenetriamine*. A solution of sodium hydroxide (104 g, 2.6 mol) in water (250 cm^3) was added to a solution of 2,2′-methyliminodi(ethylamine) tris(hydrochloride) (117 g, 0.52 mol) in water (500 cm^3). Over a period of *ca.* 6 h a solution of toluene-*p*-sulphonyl chloride (198 g, 1.04 mol) in diethyl ether (1000 cm^3) was added. The reaction mixture was then stirred overnight. The crystalline product was filtered off, washed with water, recrystallised from ethanol, and dried to constant weight at 70 °C. Yield 180 g (82%), m.p. 113—114 °C (Found: C, 53.8; H, 6.3; N, 9.8. Calc. for $C_{19}H_{27}N_3O_4S_2$: C, 53.6; H, 6.40; N, 9.85%).

[†] *Supplementary data available* (No. SUP 23888, 11 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.



Scheme. Preparation of 1,7-dimethyl-1,4,7,10-tetra-azacyclododecane. pht = Phthaloyl [o-$C_6H_4(CO)_2$]; ts = tosyl (p-$MeC_6H_4SO_2$). (*i*) Heat, pht, $CHCl_3$; (*ii*) heat, HCO_2H-HCHO; (*iii*) HCl, reflux; (*iv*) p-$MeC_6H_4SO_2Cl$-NaOH; (*v*) NaOEt-EtOH; (*vi*) dmf, 110 °C; (*vii*) conc. H_2SO_4; (*viii*) $\overline{OCH_2CH_2}$, 0 °C; (*ix*) SO_2Cl_2, $CHCl_3$; (*x*) NaOH

(*b*) *Disodium salt of* N′-*methyl*-N,N″-*bis*(*toluene*-p-*sulphonyl*)*diethylenetriamine*. The reaction was carried out under nitrogen using deoxygenated solvents. The diethylenetriamine derivative (106.3 g, 0.25 mol) was suspended in ethanol (200 cm^3) and warmed. To this hot suspension was added a solution of sodium (11.5 g, 0.5 mol) in dry ethanol (300 cm^3). This was then refluxed for about 20 min and the solvent evaporated under reduced pressure.

(*c*) 1,7-*Dimethyl*-4,10-*bis*(*toluene*-p-*sulphonyl*)-1,4,7,10-*tetra-azacyclododecane*. The dry residue of the sodium salt prepared above was dissolved in dimethylformamide (dmf) (1 800 cm^3) (dried by distillation at reduced pressure over CaH_2) and the solution heated to 110 °C. A solution of bis(2-chloroethyl)-methylamine [14] (39 g, 0.25 mol) in dmf (500 cm^3) was added over a period of about 90 min, keeping the temperature at 110 °C. Following this addition the temperature was maintained at 110 °C for 45 min and then water (500 cm^3) was slowly added to the hot solution (70—80 °C). This was then stirred overnight giving a white solid which was filtered off, washed with dmf-water (3 : 1), ethanol, and finally ether. Yield 51 g (40%), m.p. 175—177 °C (Found: C, 56.5; H, 6.8; N, 11.0. Calc. for $C_{24}H_{36}N_4O_4S_2$: C, 56.65; H, 7.15; N, 11.0%). The i.r. spectrum showed that cyclisation had occurred, no bands in the N–H region (3 060—3 500 cm^{-1}) being observed.

(*d*) 1,7-*Dimethyl*-1,4,7,10-*tetra-azacyclododecane*. The above compound (30 g, 0.06 mol) was detosylated with sulphuric acid (60 cm^3) as described previously.[15] The resulting amine sulphate was dissolved in water, and made alkaline with sodium hydroxide solution. The amine was extracted with chloroform (5 × 40 cm^3), and the combined extracts were dried overnight over calcium sulphate. The chloroform was removed under reduced pressure, the oily residue dissolved in ethanol (40 cm^3) and cooled. 47% Hydrobromic acid (100 cm^3) was added carefully to the cold solution. This was now brought to its boiling point and left to cool overnight. The crystalline white precipitate which resulted was filtered off, washed with ethanol, and dried. Yield 27 g (90%), m.p. 268—270 °C. ^{13}C N.m.r.: δ 45.5 (CH_3), 45.0, 55.0 (CH_2N) (Found: C, 22.8; H, 5.6; Br, 60.4; N, 10.7. Calc. for $C_{10}H_{28}Br_4N_4$: C, 22.9; H, 5.40; Br, 61.0; N, 10.7%).

The free amine (L^1) was obtained by dissolving the tetrahydrobromide (10.5 g, 20 mmol) in water (30 cm^3) and adding 4 g of sodium hydroxide in water (10 cm^3). After extraction with chloroform (4 × 50 cm^3), drying over sodium sulphate, and solvent removal under reduced pressure, the residue was sublimed. White deliquescent crystals were obtained, m.p. 41—42 °C (Found: C, 60.1; H, 12.3; N, 28.0. Calc. for $C_{10}H_{24}N_4$: C, 59.95; H, 12.05; N, 27.95%).

Synthesis of Metal Complexes.—$Cu(L^1)(ClO_4)_2$. A solution of the ligand (1 mmol) in ethanol (10 cm^3) was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) in hot ethanol (10 cm^3). After cooling, the solid compound was filtered off, washed with ethanol and light petroleum, and dried at 45 °C under reduced pressure (Found: C, 25.6; H, 5.4; N, 11.7. Calc. for $C_{10}H_{24}Cl_2CuN_4O_8$: C, 25.95; H, 5.25; N, 12.1%).

$Ni(L^1)X_2\cdot nH_2O$ (X = Br *or* ClO_4). A solution of the ligand (1 mmol) in n-butanol (5 cm^3) was added to a solution of $NiX_2\cdot nH_2O$ (1 mmol) in hot n-butanol (25 cm^3). The mixture was then concentrated and the solid complex filtered off, washed with n-butanol and light petroleum, and dried overnight at 60 °C under reduced pressure. The bromide complex is very hygroscopic and crystallises with one water molecule (Found: C, 27.4; H, 5.9; N, 12.9. Calc. for $C_{10}H_{26}Br_2N_4NiO$: C, 27.5; H, 6.00; N, 12.8. Found: C, 26.0; H, 5.4; N, 12.3. Calc. for $C_{10}H_{24}Cl_2N_4NiO_8$: C, 26.25; H, 5.30; N, 12.25%).

^{13}C N.m.r. spectra were recorded at 25 °C in tubes (diameter 8 mm) on a Varian CFT 20 spectrometer operating at 20 MHz with proton-noise decoupling and a deuterium lock. The solvent was water with 15% (w/w) D_2O. The deuterium frequency of the solvent was used for internal heteronuclear stabilisation of the magnetic field. Shifts were referenced against external $SiMe_4$, upfield shifts being negative. A spectral width of 4 000 Hz covered by 8 192 data points was used.

The pH measurements were carried out with a Radiometer model PHM 84 potentiometer, equipped with a combined Radiometer model GK2401C electrode; the apparatus was

Table 1. Positional (× 10^4) parameters with estimated standard deviations in parentheses for $[NiBr(H_2O)L^1]Br$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ni	−231(2)	−176(2)	−917(2)	C(3)	−954(16)	−1 153(20)	1 458(19)
Br(1)	−1 068(2)	−1 807(2)	−2 322(2)	C(4)	−1 834(15)	−581(17)	869(19)
Br(2)	−5 351(2)	−387(2)	−616(2)	C(5)	−1 408(15)	1 597(18)	562(19)
O(1)	−328(9)	851(10)	−2 614(11)	C(6)	−327(15)	1 772(18)	934(18)
N(1)	1 318(10)	−634(14)	−1 043(15)	C(7)	1 380(15)	1 222(21)	219(19)
N(2)	−194(12)	−1 387(15)	537(14)	C(8)	1 832(17)	458(19)	−746(21)
N(3)	−1 591(11)	422(14)	−42(14)	C(9)	1 646(16)	−1 098(19)	−2 286(19)
N(4)	308(13)	1 364(14)	−74(15)	C(10)	−2 468(13)	560(16)	−841(17)
C(1)	1 512(15)	−1 629(19)	−139(18)	$H_w(1)$ *	−0.105	0.048	−0.277
C(2)	780(16)	−1 640(20)	915(20)	$H_w(2)$	−0.005	0.164	−0.282

* From ΔF Fourier synthesis.

Table 2. Basicity and stability constants at 25 °C in 0.5 mol dm^{-3} KNO_3 (standard state = 1 mol dm^{-3})

Reaction	Log K	
	$L = L^1$	$L = L^2$
$H^+ + L \rightleftharpoons HL^+$	10.76(1) [a,b]	10.97 [c]
$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$	9.41(1) [b]	9.87 [c]
$Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$	17.89(3) [b]	24.8 [d]
$Cu^{2+} + L + H^+ \rightleftharpoons [CuHL]^{3+}$	20.06(7) [b]	—

[a] Values in parentheses are standard deviations in the last significant figure. [b] This work. [c] Ref. 23. [d] M. Kodama and E. Kimura, *J. Chem. Soc., Chem. Commun.*, 1975, 326.

standardised by use of appropriate buffer solutions. No correction for pH/pD differences was made. The potentiometric titrations were carried out at 25 °C in 0.5 mol dm^{-3} KNO_3, using commercial KNO_3 (C. Erba, ACS grade). The fully automatic apparatus has already been described.[16] The computer program MINIQUAD [17] was used to process data and calculate both basicity and stability constants.

Electronic spectra were recorded on a Beckman DK2-A spectrophotometer in the solid state and on a Varian Cary model 17 spectrophotometer in solution.

Crystallography.—Crystal data. $C_{10}H_{26}Br_2N_4NiO$, M = 436.87, orthorhombic, space group $P2_12_12_1$, a = 13.478(5), b = 11.186(4), c = 10.585(4) Å, U = 1 595.85 $Å^3$, Z = 4, D_c = 1.818 g cm^{-3}, $F(000)$ = 880, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ = 61.76 cm^{-1}.

Data collection. A parallelepiped crystal of $[NiBr(H_2O)L^1]Br$ having dimensions 0.40 × 0.25 × 0.10 mm was chosen for data collection. Cell parameters were determined from the setting angles of 25 reflections, measured accurately on a Philips PW 1 100 automatic diffractometer, using Mo-K_α radiation. The intensities were collected, on the same diffractometer, in the range $6 \leqslant 2\theta \leqslant 50°$ by using graphite-monochromated Mo-K_α radiation and the ω–2θ scan technique. Variable scan widths of $(0.80 + 0.30 \tan \omega)°$ were used with a scan speed of 0.07 ° s^{-1}. The background counting time was a half the peak time for each side. Three standard reflections were measured every 100 min, but no systematic loss of intensity was noted during the data collection. Standard deviations of the intensities were calculated as described elsewhere,[18] using a value for the instability factor K of 0.03. The 910 independent reflections having $I \geqslant 3\sigma(I)$ (from a total of 1 537 reflections) were considered observed and used in the structure analysis. An absorption correction was applied using a numerical method [$\mu(\text{Mo-}K_\alpha)$ = 61.76 cm^{-1}].[19] The intensities were also corrected for Lorentz and polarisation effects. Atomic scattering factors were taken from ref. 20 for non-hydrogen atoms and from ref. 21 for hydrogen atoms. Corrections for anomalous dispersion effects were also applied; [22] the application of the $\Delta f''$ corrections allowed the determination of the absolute structure.

Structure determination and refinement. The structure was solved by the heavy-atom method which gave the positions of the bromine and nickel atoms. Successive F_o Fourier synthesis gave the positions of all non-hydrogen atoms. The structure was then refined by use of full-matrix least squares using the SHELX program.[19] The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where the weights w were assigned according to the expression $w = 1/\sigma^2(F_o)$. The hydrogen atoms of L^1 were introduced in calculated positions with an overall thermal parameter U of 0.05 $Å^2$, and were not refined. According to SHELX, the hydrogen atoms of the methyl group are fixed in staggered configuration. Their positions were varied in every cycle on the basis of the shift in the carbon atoms (C–H fixed at 1.08 Å). The positions of the hydrogen atoms of the water molecule were found from a ΔF Fourier synthesis calculated in the last stage of refinement. These positions, as well as the isotropic thermal parameter U 0.05 $Å^2$, were not refined. Isotropic thermal parameters were used for carbon atoms, whereas the other atoms were refined anisotropically. The absolute structure was determined by performing cycles on the two possible configurations. The configuration which gave the lower R and standard deviations was considered the correct one. The final conventional R was 0.046. For the other configuration the final R factor was 0.060; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ = 0.042. The final ΔF Fourier synthesis did not show any unusual features. The final values of the parameters are reported in Table 1.

Results and Discussion

Protonation.—All the small-to-medium sized tetra-aza macrocycles so far investigated exhibit high basicity in the first two steps of protonation and much lower basicity in the last two steps.[16,23,24] This behaviour has been rationalised in terms of electrostatic repulsion within highly protonated species such as H_3L^{3+} and H_4L^{4+}. With macrocycle L^1 such trend is exasperated by the presence of the small twelve-membered ring and two tertiary nitrogens which are less basic than the secondary nitrogens. As a result, L^1 behaves as a diprotic base in the pH range investigated in the potentiometric measurements. The protonation constants of L^1 are reported in Table 2. The value of the first protonation constant of L^1 (log K = 10.76) is similar to that of the related unmethylated macrocycle 1,4,7,10-tetra-azacyclododecane L^2 (log K = 10.97),[23] where all nitrogens are equivalent and secondary (see Table 2). Furthermore, it has been already shown that when the first protonation in a tetra-aza macrocycle involves a tertiary amino-group [24] the basicity constant is smaller than that found for both L^1 and L^2. These consider-

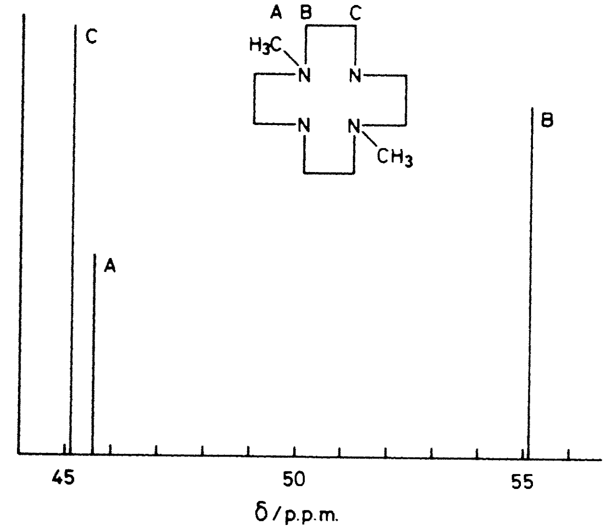


Figure 1. Proton-decoupled ^{13}C n.m.r. spectrum of $L^1 \cdot 4HBr$

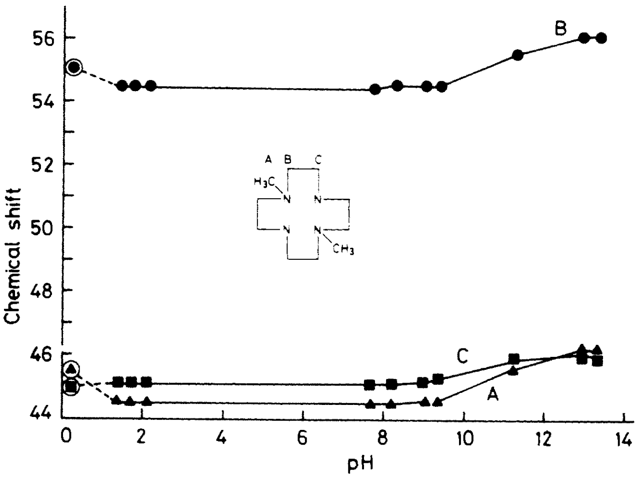


Figure 2. ^{13}C N.m.r. chemical-shift variation (p.p.m.) as a function of pH for L^1. Encircled points are the chemical shifts of $L^1 \cdot 4HBr$

ations suggest that the first nitrogen to be protonated in L^1 is one of the two secondary nitrogen atoms. The second step of protonation will automatically involve the other secondary amino-group which is farthest away (in *trans* position) from the one already protonated and positively charged.

In order to gain more insight into the protonation process we have carried out a ^{13}C n.m.r. pH study. The ^{13}C n.m.r. spectrum of $L^1 \cdot 4HBr$ shows three sharp peaks at 55.0, 45.5, and 45.0 p.p.m. (Figure 1), with relative intensities *ca.* 2 : 1 : 2. The assignment of these signals has been made on the basis of the relative intensities and by comparing them with the spectrum of the related macrocycle L^2. The chemical shifts (p.p.m.) of the carbon atoms of L^1 as function of pH are shown in Figure 2. At high pH (>12.5) the macrocycle can be considered unprotonated and the chemical shifts are that of the free amine. Invariably, all carbons show upfield protonation shifts,[25,26] 1.7 p.p.m. for methyl, 1.7 p.p.m. for carbon B and 1.1 p.p.m. for carbon C (Figure 1). In the range pH 10—12 the monoprotonated species HL^+ becomes important and the chemical shifts change rapidly. Below pH 10 the most important species are HL^+ and H_2L^{2+} with the latter becoming more important as the pH decreases. In the wide range pH 1.5—10 the chemical shifts are essentially unchanged. Considering the carbon atoms in the macrocyclic ring it can be seen that that most influenced by protonation is in the position B with respect to the protonation site. The ' B effect ' is also found in open-chain polyamines.[26,27]

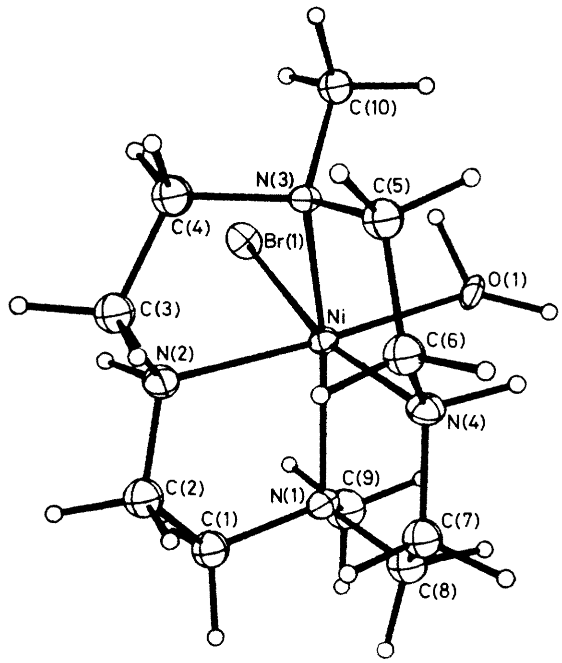


Figure 3. ORTEP drawing of the complex cation $[NiBr(H_2O)L^1]^+$ with the atom-labelling scheme

Metal Complexes.—The copper(II) complex $[CuL^1]^{2+}$ is less stable than $[CuL^2]^{2+}$ (see Table 2) as expected since two secondary amino-groups have been converted into more weakly co-ordinating tertiary amino-groups. The complex $Cu(L^1)(ClO_4)_2$ exhibits, in the solid state, a broad band with a peak at 17 400 cm^{-1}. In aqueous solution the complex shows a ligand-field absorption band at 16 700 cm^{-1} (ε 325 $dm^3 mol^{-1} cm^{-1}$) and a rather intense band at 35 200 cm^{-1} (ε 5 000 $dm^3 mol^{-1} cm^{-1}$) which can be confidently attributed to an electron-transfer transition $N \rightarrow Cu$.

The reflectance spectrum of $[NiBr(H_2O)L^1]Br$ is typical of an octahedral high-spin nickel(II) complex, exhibiting three band maxima at 10 400, 17 700, and 27 400 cm^{-1} (Δ_o = 1 040 cm^{-1}; nephelauxetic ratio, β = 0.87). In aqueous solution the complex behaves essentially as a 2 : 1 electrolyte, thus suggesting the occurrence of the $[Ni(H_2O)_2L^1]^{2+}$ cation. The absorption spectrum of this blue solution shows ligand-field bands at 10 500 (ε 31), 17 600 (ε 8), and 27 500 cm^{-1} (ε 15 $dm^3 mol^{-1} cm^{-1}$). It also exhibits a shoulder at 12 400 cm^{-1}, attributable to the spin forbidden $A_{2g} \rightarrow E_g$ transition in O_h symmetry. Of interest is the higher value of the molar absorbance for the first band with respect to those of the second and third bands. This feature must be considered diagnostic of *cis*-octahedral tetra-aminenickel(II) complexes.[28,29] The solid $NiL^1(ClO_4)_2 \cdot 2H_2O$ exhibits a reflectance spectrum almost identical to that of the dibromide complex. On heating, the complex turns yellow and diamagnetic and the reflectance spectrum exhibits only one ligand-field band at 22 500 cm^{-1}, typical of low-spin square-planar NiN_4 chromophores. When exposed to air it reverts to the blue octahedral complex. At room temperature, no evidence of the low-spin yellow form is apparent in aqueous solution. By contrast, the nickel(II) complex of 1,4,7,10-tetramethyl-1,4,7,10-tetra-azacyclodode-

Table 3. Selected bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses for [NiBr(H_2O)L^1]Br

Ni–Br(1)	2.610(2)	Ni–N(4)	2.072(12)	N(2)–C(3)	1.437(18)	N(4)–C(7)	1.487(19)
Ni–O(1)	2.136(9)	N(1)–C(1)	1.491(18)	N(3)–C(4)	1.515(18)	C(1)–C(2)	1.490(20)
Ni–N(1)	2.153(12)	N(1)–C(8)	1.440(19)	N(3)–C(5)	1.482(18)	C(3)–C(4)	1.485(21)
Ni–N(2)	2.051(12)	N(1)–C(9)	1.482(18)	N(3)–C(10)	1.462(16)	C(5)–C(6)	1.521(20)
Ni–N(3)	2.160(12)	N(2)–C(2)	1.401(19)	N(4)–C(6)	1.442(18)	C(7)–C(8)	1.465(22)

Br(1)–Ni–O(1)	82.5(3)	N(3)–Ni–N(4)	81.7(5)	Ni–N(2)–C(2)	111.7(10)	C(4)–N(3)–C(10)	105.8(11)
Br(1)–Ni–N(1)	102.6(4)	Ni–N(1)–C(1)	108.0(9)	Ni–N(2)–C(3)	111.8(10)	C(5)–N(3)–C(10)	106.9(11)
Br(1)–Ni–N(2)	88.7(4)	Ni–N(1)–C(8)	104.6(10)	C(2)–N(2)–C(3)	120.7(13)	Ni–N(4)–C(6)	111.9(10)
Br(1)–Ni–N(3)	95.4(3)	Ni–N(1)–C(9)	115.3(9)	Ni–N(3)–C(4)	103.1(8)	Ni–N(4)–C(7)	110.0(10)
Br(1)–Ni–N(4)	168.0(4)	C(1)–N(1)–C(8)	114.1(13)	Ni–N(3)–C(5)	108.6(9)	C(6)–N(4)–C(7)	117.2(12)
O(1)–Ni–N(1)	97.8(4)	C(4)–N(1)–C(9)	104.8(12)	Ni–N(3)–C(10)	118.1(9)	N(1)–C(1)–C(2)	111.7(13)
O(1)–Ni–N(2)	171.0(5)	C(8)–N(1)–C(9)	110.3(13)	C(4)–N(3)–C(5)	114.7(11)	N(2)–C(2)–C(1)	113.9(14)
O(1)–Ni–N(3)	98.2(4)					N(2)–C(3)–C(4)	111.3(13)
O(1)–Ni–N(4)	86.4(4)					N(3)–C(4)–C(3)	114.4(13)
N(1)–Ni–N(2)	82.3(5)					N(3)–C(5)–C(6)	112.6(13)
N(1)–Ni–N(3)	157.3(5)					N(4)–C(6)–C(5)	109.7(13)
N(1)–Ni–N(4)	83.4(5)					N(4)–C(7)–C(8)	108.7(14)
N(2)–Ni–N(3)	84.4(5)					N(1)–C(8)–C(7)	116.6(15)
N(2)–Ni–N(4)	102.6(5)						

cane is predominantly in the yellow square-planar form in aqueous solution [12] and the paramagnetic form, on the other hand, is reported to be five-co-ordinated.[12]

Crystal Structure.—The structure of [NiBr(H_2O)L^1]Br consists of [NiBr(H_2O)L^1]$^+$ cations and Br$^-$ anions. The complex shows a *cis*-octahedral geometry, with the macrocycle co-ordinated in a folded configuration to four sites around the central nickel atom, the other two sites being occupied by a bromine atom and the oxygen atom of a water molecule (Figure 3). The configuration of the four nitrogen atoms of the macrocycle is such that the four terminal groups of the nitrogen atoms, two hydrogens and two methyls, are on the same side with respect to the idealised macrocyclic plane. The chelate rings are all in the asymmetric configuration. Bond distances and angles are reported in Table 3. Of note is the significant difference between the Ni–N(secondary) and Ni–N(tertiary) distances [2.051(12) and 2.072(12) against 2.153(12) and 2.160(12) Å, respectively]. Some short intermolecular contacts between the two bromine atoms and hydrogen atoms have been found: Br(1)···H_w(2) 2.305, Br(1)···H[N(4)] 2.651, and Br(2)···H[N(2)] 2.647 Å. As far as the yellow low-spin species is concerned, no structural information was available until now. However, on the basis of molecular models and by analogy with the known structure of the tetramethyl analogue,[12] the less strained ligand (L^1) conformation for this kind of geometry seems to involve the macrocycle with all nitrogen atoms in the same configuration and with the chelate rings in asymmetric conformation.

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