

Tetraaza macrocycles containing pyridine and their copper(II) and nickel(II) complexes: X-ray, spectroscopic, molecular mechanics and molecular orbital studies †

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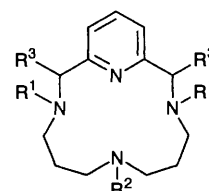
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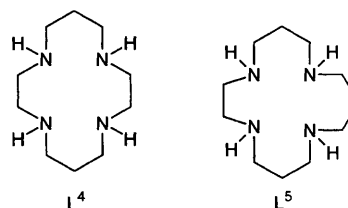
The behaviour in solution of nickel(II) complexes of the macrocycles L¹ {3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene} and L² {7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene} containing pyridine rings was investigated spectroscopically (UV/VIS/near IR and ¹H NMR) and several species were found. In order to understand these and previous experimental data concerning stability constants, some crystals were prepared. The crystal structures of L¹ and the complexes [CuL¹][PF₆]₂ **1** and [NiL²(ClO₄)] [ClO₄]₂ **2** were determined, the copper complex adopting a square-planar geometry and the nickel one a square-pyramidal geometry, where the four nitrogen atoms are planar and one perchlorate occupies the axial co-ordination position. Molecular mechanics calculations were performed in order to find the preferred conformations for square-planar and square-pyramidal complexes of both L¹ and L², and the related macrocycles which do not contain a pyridine ring. The electronic preferences were analysed with extended-Hückel calculations. The introduction of pyridine into macrocycle does not significantly affect its behaviour upon co-ordination in square-planar complexes. For square-pyramidal complexes, the structures where a fifth donor occupies the axial position are usually more stable, though the introduction of methyl groups as substituents on the nitrogen may favour the presence of this donor in an equatorial site and lead to folding of the macrocycle.

Macrocycles L¹ {3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene} and L² {7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene} and some of their metal complexes (Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺) have been studied in aqueous solution, by potentiometric techniques, and their stability constants determined.¹ When a pyridine nitrogen replaces one of the four nitrogen atoms of the tetraaza ring of the macrocycle the stability constants of the metal complexes formed decrease. In some cases the differences in stability between the two series are surprisingly large, as for instance for the complexes of Ni²⁺ and Cu²⁺ with L¹, when compared with those of cyclam (L⁴) or isocyclam (L⁵).¹

The lower overall basicity of the compounds containing pyridine (L¹ or L²) compared to that of the tetraaza series, L⁴ and L⁵, of about 1 log unit¹⁻³ only partially explains the large differences in stability constants found for complexes of Ni²⁺ (3.8–5.9 log units, depending on the authors¹⁻³) and Cu²⁺ (about 7 log units¹⁻³). The behaviour found for acyclic compounds is usually different. A comparison of two such compounds differing by the replacement of one or more of their secondary amines by the same number of pyridine nitrogens, *cf.* Table 1, shows a large difference on the overall basicity, but small ones in the stability constants of the complexes of Cu²⁺ or Ni²⁺. In some cases, *e.g.* the nickel(II) complexes listed in Table 1, the stability constant for the complex of the ligand containing



L¹ R¹ = R² = R³ = H
 L² R¹ = R³ = H, R² = Me
 L³ R¹ = R² = Me, R³ = H
 L⁶ R¹ = R² = H, R³ = Me
 L⁷ R¹ = H, R² = R³ = Me



the pyridine nitrogen is comparable or even higher than that of the corresponding complex of the polyamine. The enhanced stability of complexes of acyclic ligands containing pyridine donors was partially attributed to π -bonding interactions between the pyridine π or π^* orbitals and appropriate metal d

† Non-SI units employed: eV \approx 1.60 \times 10⁻¹⁹ J, cal = 4.184 J.

Table 1 Overall basicity ($\log \beta^H$) of some linear amines without or with pyridine nitrogen atoms and their stability constants with Cu^{2+} and Ni^{2+} ($\log K_{\text{ML}}$) taken from the literature⁴ (25 °C, $I = 0.1 \text{ mol dm}^{-3}$)

Ion	Equilibrium	A	B	$\Delta_1 = A - B$	C	$\Delta_2 = A - C$
		$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	$\text{NC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NH}_2$		$\text{NC}_5\text{H}_4\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4\text{N}$	
H^+	$[\text{H}_3\text{L}]/[\text{L}][\text{H}]^2$	16.97	13.45	3.52	9.79 ^a	7.18
Cu^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	10.50	7.5	3.0	3.41 ^a	7.09
Ni^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	7.31	5.2	2.11	1.4 ^a	5.91
		$[\text{ML}_2]/[\text{ML}][\text{L}]$	3.54 ^b	2.55		
		$[\text{ML}_3]/[\text{ML}_2][\text{L}]$	2.46 ^b	1.94		
		$\text{NH}[(\text{CH}_2)_2\text{NH}_2]_2$	$\text{NC}_5\text{H}_4(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$	Δ_1	$\text{NC}_5\text{H}_4\text{CH}_2\text{NHCH}_2\text{-C}_5\text{H}_4\text{N}$	Δ_2
H^+	$[\text{H}_3\text{L}]/[\text{L}][\text{H}]^3$	23.09	19.6	3.49	10.99	12.10
Cu^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	15.9	13.4	2.5	14.4	1.5
Ni^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	10.5	9.4	1.1	8.7	1.8
		$\text{H}_2\text{N}[(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2]$	$[\text{NC}_5\text{H}_4\text{CH}_2\text{NH}(\text{CH}_2)_2]$	Δ_1		
H^+	$[\text{H}_4\text{L}]/[\text{L}][\text{H}]^4$	28.67	17.02	11.65		
Cu^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	20.05	17.03	3.02		
Ni^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	13.8	14.48	-0.68		
		$\text{NH}[(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{-NH}_2]_2$	$\text{NH}[(\text{CH}_2)_2\text{NHCH}_2\text{-C}_5\text{H}_4\text{N}]_2$	Δ_1	$\text{NC}_5\text{H}_3(\text{CH}_2\text{NHCH}_2\text{-C}_5\text{H}_4\text{N})_2$	Δ_2
H^+	$[\text{H}_4\text{L}]/[\text{L}][\text{H}]^4$	31.59	21.14	10.45	14.41	4.43
Cu^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	22.8	20.9	1.9	18.4	4.4
Ni^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	17.4	19.2	-1.8		
		$\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$	$\text{N}(\text{CH}_2\text{C}_5\text{H}_4\text{N})_3$	Δ_1		
H^+	$[\text{H}_3\text{L}]/[\text{L}][\text{H}]^3$	27.98	13.07	14.91		
Cu^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	18.8	16.2	2.6		
Ni^{2+}	$[\text{ML}]/[\text{M}][\text{L}]$	14.6	14.5	0.1		

^a 20 °C, $I = 0.1 \text{ mol dm}^{-3}$. ^b 25 °C, $I = 0.5 \text{ mol dm}^{-3}$.

orbitals.⁵ The completely different situation found for the macrocyclic series (L^1 – L^5 inclusive) led us to search for an explanation based on electronic and/or structural features and to undertake studies in this direction.

Spectroscopic studies of the complexes of Co^{2+} , Ni^{2+} and Cu^{2+} in aqueous solution (UV/VIS/near IR, ^1H and ^{13}C NMR and EPR) had provided some structural information,¹ but some doubts persisted. In a further attempt to clarify the behaviour of the metal complexes of these macrocyclic ligands containing pyridine, an investigation of the structure of free L^1 , a L^1 –copper(II) complex, and a L^2 –nickel(II) complex, using single-crystal X-ray diffraction, was carried out. This study was complemented by molecular mechanics calculations,⁶ in order to investigate the reasons for the different conformations found in metal complexes of L^1 , compared to those of L^4 and L^5 . This difference is particularly striking for L^1 and L^5 , both of which have four donor nitrogen atoms bridged by two, two, three and three carbon atoms, respectively, thus forming 14-membered rings. While L^4 also provides a 14-membered ring and four donor nitrogen atoms, the bridge pattern is two, three, two, three. The effect of introducing substituents at N, such as methyl groups, was also analysed. The results were compared with the conformations experimentally observed, both in the complexes described in this work and those taken from the Cambridge Crystallographic Data Base.⁷ Molecular orbital calculations (extended-Hückel method)⁸ were used to investigate the influence of different types of donor atoms on the stability of the complexes.

Experimental

Reagents

The macrocycles L^1 and L^2 were synthesized and purified in our laboratory.¹ The other chemicals were of reagent grade and used without further purification. Organic solvents were purified by standard methods.⁹

Crystals of L^1 . The pure compound was dissolved in diethyl ether and the solution allowed to stand at 4 °C. White crystals were formed, m.p. 83–85 °C (Found: C, 66.5; H, 9.3; N, 23.6. $\text{C}_{13}\text{H}_{22}\text{N}_4$ requires C, 66.6; H, 9.5; N, 23.9%).

Synthesis of the copper complexes and preparation of crystals for X-ray analysis

$[\text{CuL}^1][\text{PF}_6]_2$ 1. A concentrated aqueous solution of CuCl_2 (0.1 mmol, 0.0136 g) was added to a stirred solution of L^1 (0.1 mmol, 0.024 g) dissolved in the minimum volume of water. An aqueous solution of TIPF_6 was then added (0.1 mmol, 0.3494 g) and the precipitate formed (TICl) filtered off. The solution was concentrated to dryness, the residue taken up in methanol and left to stand at room temperature. Violet crystals were formed after a few days of slow evaporation (Found: C, 26.3; H, 3.5; N, 9.3. $\text{C}_{13}\text{H}_{22}\text{CuF}_6\text{N}_4\text{P}$ requires C, 26.55; H, 3.75; N, 9.55%).

$[\text{NiL}^2][\text{ClO}_4]_2$ 2. The salt $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.492 mmol, 0.1802 g) was dissolved in the minimum volume of methanol and added to L^2 (0.492 mmol, 0.1222 g) dissolved in CHCl_3 (2 ml). The precipitate formed was filtered off, washed with a small amount of MeOH and dried under vacuum. A portion of this solid was dissolved in a mixture of methanol and light petroleum (b.p. 40–60 °C) and left to stand at room temperature. Red crystals were formed a few days later (Found: C, 33.0; H, 4.5; N, 10.9. $\text{C}_{14}\text{H}_{24}\text{Cl}_2\text{N}_4\text{NiO}_8$ requires C, 33.25; H, 4.8; N, 11.05%).

Spectroscopic studies

Proton and ^{13}C NMR spectra were recorded with a Bruker CXP-300 spectrometer, using solutions of the complexes prepared by the addition of the metal ion to the macrocycle at the appropriate pD value in D_2O (corresponding to the total formation of the metal complex). The concentration of the complexes was about 0.75–1.66 mmol dm^{-3} . Magnetic moments were determined in solution by the Evans method.¹⁰

Table 2 Room-temperature crystal data and details of refinement of compounds L¹, **1** and **2**

Compound	L ¹	1	2
Empirical formula	C ₁₃ H ₂₂ N ₄	C ₁₃ H ₂₂ CuF ₁₂ N ₄ P ₂	C ₁₄ H ₂₄ Cl ₂ N ₄ NiO ₈
<i>M</i>	234.95	587.83	505.98
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.669(2)	9.011(2)	10.539(2)
<i>b</i> /Å	8.885(2)	9.016(2)	14.964(1)
<i>c</i> /Å	10.382(3)	13.079(2)	13.172(2)
α /°	102.86(2)	81.06(2)	
β /°	99.23(2)	83.43(1)	98.307(7)
γ /°	117.86(1)	89.26(1)	
<i>U</i> /Å ³	656.0(3)	1042.7(4)	2055.5(4)
<i>Z</i>	2	2	4
<i>D_c</i> /g cm ⁻³	1.186	1.872	1.635
μ (Mo-K α)/mm ⁻¹	0.074	1.316	1.186
<i>F</i> (000)	256	590	1048
θ Range/°	2.1–33.9	1.6–26.0	2.1–29.9
Index ranges <i>hkl</i>	–13, –13, 0 to 13, 13, 16	–11, –10, 0 to 11, 11, 16	–14, 0, 0 to 14, 20, 18
Measured reflections	5564	4258	6175
Independent reflections (<i>R_{int}</i>)	5318 (0.0295)	4071 (0.0225)	5945 (0.0696)
Goodness of fit on <i>F</i> ²	1.288	1.035	1.094
<i>R</i> and <i>R'</i> [<i>I</i> > 2 σ (<i>I</i>) (all data)]	0.0792, 0.2304 0.1424, 0.3180	0.0965, 0.2606 0.1538, 0.3382	0.0700, 0.1624 0.1146, 0.2055
<i>a</i> and <i>b</i> in weighting scheme	0.1507, 0	0.1982, 6.94	0.0789, 4.18
Largest difference peaks and hole/e Å ⁻³	0.698, –0.428	1.302, –1.006	0.981, –0.577

Crystallography

The pertinent crystal data for compounds L¹, **1** and **2** are listed in Table 2. X-Ray data were collected with an Enraf-Nonius CAD-4 diffractometer equipped with a rotating molybdenum anode and a graphite monochromator. The unit-cell parameters and orientation matrix were calculated by least-squares refinement of 25 well centred reflections in the ranges 12 < θ < 18° for L¹ and **2** and 12 < θ < 17° for **1**. The intensity data were collected by ω -2 θ scan mode. Three strong reflections were measured after every 3600 s and their intensities did not show appreciable decay. The data were corrected for Lorentz-polarisation effects with CAD-4 software. Intensities of complexes **1** and **2** were corrected empirically for absorption effects, those of L¹ were not corrected for absorption effects.

Structure analysis and refinement. The crystal structure of the macrocycle L¹ was solved by direct methods, those of the metal complexes by using a combination of Patterson and Fourier methods. Two counter ions, namely the hexafluorophosphate of the copper complex and one perchlorate of the nickel complex, were disordered. These anions were introduced in refinement as disordered rigid bodies including two alternative positions for oxygen and fluorine atoms. To each position of the fluorine atoms was assigned an occupancy factor of 0.50. The oxygen atoms were refined with occupancy factors of 0.67 and 0.33 for major and minor components. The P–F and Cl–O distances were restrained to 1.56 and 1.45 Å, respectively. Anisotropic thermal parameters were used for all non-hydrogen atoms of all compounds, except for disordered oxygens and fluorines of complexes **1** and **2**. The hydrogens were introduced in the refinement in calculated positions, except for those bonded to nitrogen atoms which were found from Fourier-difference maps. The hydrogens bonded to nitrogen atoms were refined isotropically with a fixed isotropic thermal parameter of $U_{iso} = 0.05$ Å² for all compounds. The methylenic and aromatic hydrogens of the three compounds and the methyl hydrogens of complex **2** were refined with global isotropic thermal parameters. The structures were refined by least-squares methods to convergence. The final refinements were made on *F*² using a weighting scheme of the form $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (see Table 2). In the ΔF map calculated for compound **1** the

largest positive peak with an electronic density of 1.30 e Å⁻³ was close to one fluorine atom of a disordered hexafluorophosphate anion.

All calculations required to solve and refine the structures were carried out with SHELXS 86¹¹ and SHELXL 93.¹² The atomic scattering factors were taken from ref. 13. The molecular diagrams were drawn with ORTEP II.¹⁴ The geometric features of the intermolecular hydrogen-bonding networks were investigated by using the graphic program SCHAKAL 92¹⁵ and the suite of programs PLATON.¹⁶

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/240.

Molecular mechanics calculations

Molecular mechanics calculations were carried out using the universal force field within the CERIOUS 2 software.¹⁷ Default parameters were used apart from the terms involving the metal atom. In all cases the unstrained environment was considered to be an ideal geometry. The angle-bending terms at the metal centre were treated in the following manner. For planar macrocycle conformers with square-planar or square-pyramidal geometries the angles were restrained to 90 and 180° using a cosine periodic expansion term. This algorithm incorporates the possibility of more than one ideal angle, e.g. 90, 180 or 270° for a square-planar system. For a square-pyramidal geometry the angles were treated individually using a cosine Fourier-expansion term. For folded conformers with square-pyramidal geometries, angles L_{ax}–M–L_{eq}* were restrained to 100° and L_{eq}–M–L_{eq} to 90 and 160°. Torsion angles L–M–L–C were given zero force constant.

The starting coordinates for geometric isomers were obtained from X-ray determinations or alternatively by manipulation of the coordinates of complexes where macrocyclic ligands are coordinated in geometric environments similar to the present ones; so, all folded conformers for [ML¹Cl]²⁺ and

* L_{eq} and L_{ax} denote an axial and an equatorial ligand respectively.

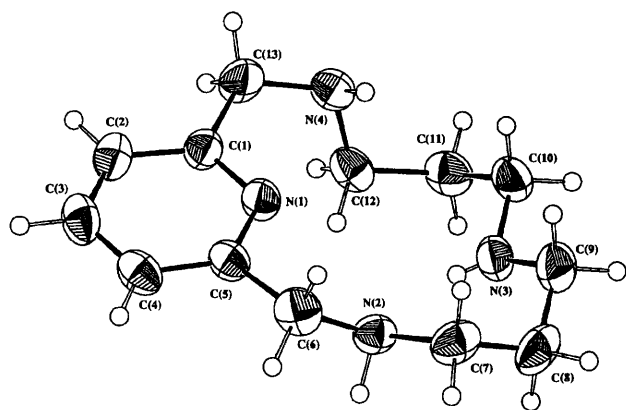


Fig. 1 Molecular structure of the free macrocycle L^1 with the labelling scheme adopted (50% ellipsoids)

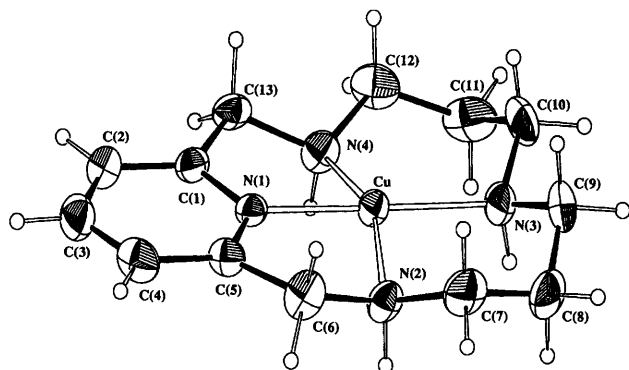


Fig. 2 Molecular structure of the $[CuL^1]^{2+}$ complex cation with the labelling scheme adopted (30% ellipsoids)

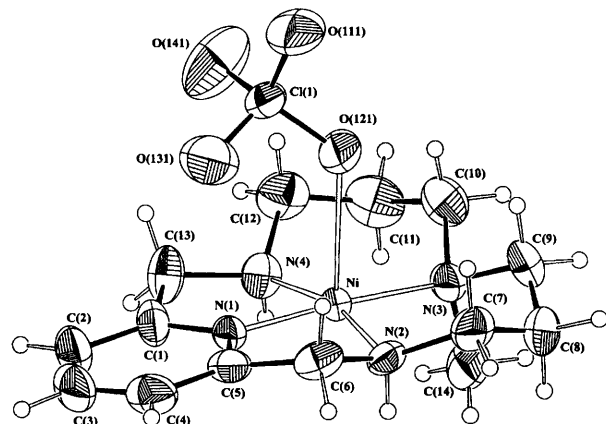


Fig. 3 Molecular structure of the $[NiL^2(ClO_4)]^+$ complex cation with the labelling scheme adopted (40% ellipsoids)

$[ML^3Cl]^{n+}$ derive from the square-pyramidal complex $[NiL^3Cl]^{n+}$ and planar conformers for $[ML^1Cl]^{n+}$ and $[ML^3Cl]^{n+}$ from the *trans*-octahedral complex $[IrL^3(Et)Cl]^{n+}$; conformers $----$ and $---+$ (see later for definition) for $[ML^1]^{n+}$ and $[ML^3]^{n+}$ from $[NiL^3]^{2+}$, $+-$ from $[NiL^3]^{2+}$; planar conformers $[ML^5Cl]^{n+}$ and $[ML^5]^{n+}$ from the square-pyramidal complex $[CuL^5(NCS)]^{n+}$; $+$ and $++$ from the square-pyramidal complex $[NiL^5(H_2O)]^{n+}$; $++$ conformers $[ML^5Cl]^{n+}$ from the *cis*-octahedral complex $[NiL^5(H_2O)]^{2+}$, $++$ conformations $++--$, $+++-$ and $+++$ for $[ML^4]^{n+}$ from $[NiL^8]^{2+}$ ($L^8 = 1,4,8,11$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane), $++++$ from $[NiL^8]^{2+}$, $++-$ from $[NiL^4]^{2+}$; planar conformers $[ML^4Cl]^{n+}$ from the *trans*-octahedral complex $[ZnL^4Cl_2]^{n+}$ and folded conformers from the *cis*-octahedral complex $[NiL^4(H_2O)_2]^{2+}$.

The strain energies of the different conformers were calculated as a function of the M–L bond length in the

following manner. The force constants for the M–L bond lengths were set at high values so that the bond lengths were fixed at the particular value. The structures were then minimised with these constraints. The ideal bond lengths were changed successively at 0.05 Å intervals over the range 1.5–2.5 Å so that an energy profile of the complex relative to distance was obtained.⁶ For conformers of L^1 and L^3 with square-planar geometry the force constants for the angles L–M–L were also set at high values, in order to restrict the geometry of the metal co-ordination sphere.

Molecular orbital calculations

All the molecular orbital calculations were done using the extended-Hückel method⁸ with modified H_{ij} values.¹⁸ The basis set for the metal atom consisted of ns , np and $(n-1)d$ orbitals. Only s and p orbitals were used for chlorine. The s and p orbitals were described by single Slater-type wavefunctions, and the d orbitals were taken as contracted linear combinations of two Slater-type wavefunctions. Standard parameters were used for H, C, O and Cl, while those for Ni were the following (H_{ii}/eV , ζ): 4s, -9.17 , 1.825; 4p, -5.15 , 1.125; 3d, -13.49 , 5.75, 2.000 (ζ_2), 0.5683 (C_1), 0.6292 (C_2).

Calculations were carried out using the experimental structure of $[NiL^2(ClO_4)]^+$, **2**, constructed models of $[Ni(NH_3)_4]^{2+}$ and $[Ni(NH_3)_3(py)]^{2+}$ ($py = \text{pyridine}$), for square-planar environments, and constructed models of $[Ni(NH_3)_4(H_2O)]^{2+}$, $[Ni(NH_3)_4(ClO_4)]^+$ and $[Ni(NH_3)_4Cl]^+$ for the square-pyramidal environments. The distances were taken from those observed in **2**.

Results and Discussion

Studies in solution

Spectroscopic studies of aqueous solutions of the nickel complexes of L^1 and L^2 , having nitrate as the counter ion, at room temperature (UV/VIS/near IR, and 1H NMR) have revealed the presence of a paramagnetic species, probably with the nickel ion in a square-pyramidal arrangement, although some other isomers in equilibrium with the main species were found but not identified.¹ On the other hand, it was known that the corresponding complex of the tetraaza macrocycle, L^4 , exists in solution as a mixture of a six-co-ordinated octahedral species and a four-co-ordinated square-planar diamagnetic species, the amount of the diamagnetic species increasing with increase in ionic strength or the temperature of the solution (as the addition of an electrolyte, *e.g.* $NaClO_4$, or increase in temperature slow the aquation process).¹⁹ In the solid state L^4 adopts a relatively strain-free $++--$ conformation (see later)²⁰ in the octahedral complex $[NiL^4Cl_2]^{2+}$.²¹ The conformational differences of the nickel complexes of each ligand were suggested to be the possible reason for the differences in stability constants,¹ as Ni^{II} is more stable when octahedral and a square-pyramidal arrangement around this metal ion is not favoured by crystal-field stabilisation energy.²² In the present work we pursued solution studies of the nickel(II) complex of L^1 , using perchlorate, the counter ion used to grow crystals, as the counter ion. Proton NMR studies in solution have shown the nickel(II) complex of L^1 to be involved in an equilibrium between a diamagnetic species, which should, in principle, have square-planar co-ordination, and a paramagnetic species. When the temperature or the ionic strength of the solution is increased another diamagnetic species appears with broad signals at δ 5.83, 5.10, 3.95, 3.66 and 2.86 ($I = 0.179 \text{ mol dm}^{-3}$), probably due to a five-co-ordinated species. Comparison of the spectra of the complex in the presence of nitrate¹ or perchlorate (this work) led to a better assignment of the spectrum of the nitrate containing solution and to the conclusion that broad signals of a diamagnetic species also appear with

Table 3 Selected bond lengths (Å) and angles (°) in the co-ordination sphere of complexes **1** and **2**

	1	2
	M = Cu ^{II}	M = Ni ^{II}
M–N(1)	1.904(8)	1.848(4)
M–N(2)	1.968(8)	1.936(4)
M–N(3)	2.041(9)	1.942(4)
M–N(4)	2.037(8)	1.955(4)
M–O(121)	—	2.590(4)
N(1)–M–N(3)	179.3(4)	175.9(2)
N(1)–M–N(4)	81.4(4)	84.0(2)
N(3)–M–N(4)	98.4(4)	95.4(2)
N(1)–M–N(2)	82.5(3)	83.3(2)
N(3)–M–N(2)	97.9(4)	96.6(2)
N(4)–M–N(2)	157.3(4)	164.5(2)
N(1)–M–O(121)	—	90.9(2)
N(2)–M–O(121)	—	88.0(2)
N(3)–M–O(121)	—	93.2(2)
N(4)–M–O(121)	—	101.2(2)

Table 4 Endocyclic torsion angles in compounds L¹, **1** and **2**

	L ¹	1	2
C(1)–N(1)–C(5)–C(6)	–177.1(2)	–174.8(9)	–172.4(5)
C(5)–N(1)–C(1)–C(13)	179.7(2)	176.5(8)	172.5(5)
C(12)–N(4)–C(13)–C(1)	67.6(3)	–163.4(9)	–152.1(6)
C(13)–N(4)–C(12)–C(11)	178.5(2)	171.1(12)	–172.8(6)
N(4)–C(12)–C(11)–C(10)	61.6(2)	–61.4(17)	–63.9(8)
N(3)–C(11)–C(10)–C(12)	58.6(3)	73.4(17)	68.3(9)
C(9)–N(3)–C(10)–C(11)	177.6(2)	172.8(12)	177.5(6)
C(10)–N(3)–C(9)–C(8)	–179.6(2)	–176.2(12)	175.1(6)
N(3)–C(9)–C(8)–C(7)	–72.4(3)	–68.6(17)	–69.6(8)
N(2)–C(7)–C(8)–C(9)	64.2(3)	65.8(16)	65.9(7)
C(6)–N(2)–C(7)–C(8)	–169.9(2)	–177.5(11)	176.8(5)
C(7)–N(2)–C(6)–C(5)	152.0(2)	153.9(10)	165.2(5)
N(1)–C(5)–C(6)–N(2)	–39.0(3)	–18.7(14)	–24.8(6)
N(1)–C(1)–C(13)–N(4)	14.9(3)	20.6(12)	17.6(8)

increasing temperature, as testified by the decrease in magnetic moment of the solution, in the more complex nitrate system.

For the nitrate copper complexes the spectroscopic studies in aqueous solution, electronic and EPR, did not reveal differences in the behaviour of the complexes of tetraaza polyamine macrocycles from those containing an amine replaced by one pyridine nitrogen atom.¹

Molecular and crystal structures

Molecular diagrams including the labelling scheme used are shown in Fig. 1 for the free macrocyclic L¹, and in Figs. 2 and 3 for the complex cations [CuL¹]²⁺ **1** and [NiL²(ClO₄)]⁺ **2**, respectively. Selected bond lengths and angles in the metal co-ordination spheres are listed in Table 3. The four nitrogen atoms of the macrocyclic ligands belong to the co-ordination plane of copper in square-planar **1** and the equatorial plane of nickel in square-pyramidal **2**.

The co-ordination of macrocycles L¹–L³ to a metal may lead to four different geometric isomers, depending on the positions of the NH hydrogen atoms or the *N*-methyl groups below (–) or above (+) the macrocycle. The metal often occupies a position slightly away from the plane of the donor atoms. One isomer is ---, the second – + –, and the two + --- arrangements lead to two enantiomers (see Fig. 5). In a square-pyramidal geometry the number of conformations is at least twice that of the square planar, depending on the orientation of the NH or NMe groups relative to the apical ligand, which may also occupy an equatorial or an axial position. Both L¹ and L² adopt a --- arrangement in the present complexes.

In complexes **1** and **2** the M–N distance to the pyridine nitrogen is shorter than that to the other nitrogen atoms. This bond-length pattern is typical of complexes with tetraazamacro-

cyclic ligands containing a pyridine moiety.²³ The best least-squares plane through the nitrogen atoms shows a small tetrahedral distortion of ±0.15 Å in the copper complex. In the nickel complex the nitrogen atoms are closer to planarity, the tetrahedral deviation from that plane being only of ±0.04 Å. The Cu and Ni atom lie out of the co-ordination N₄ plane by 0.133(5) and 0.114(2) Å, respectively, on the side opposite the hydrogen atoms or methyl groups.

The Ni–O distance of 2.590(4) Å in complex **2** is on the long side of the available distances, which range mainly between 1.95 and 2.15 Å, but for example in the complex [NiL⁶(ClO₄)]⁺ a very long Ni–O distance (2.77 Å) is reported.^{7,24}

Endocyclic torsion angles, listed in Table 4 for compound L¹, **1** and **2**, are close to the expected values of 60 or 180°, with the exception of N(1)–C(5)–C(6)–N(2) and N(1)–C(1)–C(13)–N(4). Though L² has a methyl group on the nitrogen atom in the *trans* position to the pyridine ring and L¹ has a hydrogen atom, the torsion angles observed for the nickel complex are comparable to those found for the copper complex and also for the free macrocycle L¹. In L¹ the torsion angle C(1)–C(13)–N(4)–C(12) is close to 60°, while co-ordination to the metal ions forces it to change to 163.4° in **1** and 152.1 in **2**.

In the free macrocycle L¹ the pyridine ring is tilted at an angle of 21.2(1)° relative to the N₄ plane. In the metal complexes the pyridine ring is required to be coplanar to the N₄ plane, so that the nitrogen lone pair is directed toward the metal and good overlap takes place. Indeed, this angle drops to only 1.4(6)° in the [CuL¹]²⁺ complex and 5.2° in the related *trans*-[CoL¹(Et)(H₂O)]²⁺.²⁵ A similar situation probably occurs for L², as this angle for the nickel complex is also small [6.8(2)°], but the absence of structural data for the free macrocycle precludes comparison.

A further study of the crystal structures was carried out. There is a short intramolecular distance in L¹ that might be considered to be a hydrogen bond, N(4)–H...N(1) [N(4)...N(1) 2.821(2), N(4)–H...N(1) 2.593(27) Å, 95.0(17)°]. Also observed are shorter contacts between C(12) and two of the nitrogen atoms that could also be considered as weak hydrogen bonds [C(12)...N(1) 3.168(3), C(12)–H...N(1) 2.599(3) Å, 117.7(1)°, C(12)...N(3) 2.996(3), C(12)–H...N(3) 2.682(3) Å, 99.3(1)°], which may help explain the particular conformation of the free macrocycle. Recall that C(12) has a very different position in the free macrocycle and in the complex. Some intermolecular hydrogen bonds are also observed, but no special stacking with the pyridine rings.

The complexes offer a more interesting pattern. Both form three-dimensional layered structures. In the copper complex layers of the cation alternate with layers of hexafluorophosphate anions, as shown in Fig. 4(a). Despite the disorder in this anion, full occupancy of one position by the fluorides is assumed). Short F...H contacts are present, but the disorder prevents a thorough analysis. A similar layered pattern is seen for the nickel derivative in Fig. 4(b). The disordered perchlorate anion is shown again with full occupancy of one set of tetrahedral positions. It is the other perchlorate, found in the same layer, which is of interest. One of the oxygen atoms forms a Ni–O covalent bond, relatively weak at 2.590(4) Å. Two of the other oxygen atoms are concomitantly involved in intermolecular O...H–N hydrogen bonds to the macrocycle [N(2)–H...O(111) (½ – x, ½ + y, ½ – z) 2.43(5) Å, 133(4)° and N(2)–H...O(141) (½ – x, ½ + y, ½ – z) 2.48(4) Å, 154(5)°]. The formation of the Ni–O bond is probably responsible for the ordering in this anion.

Molecular mechanics calculations

Hancock and co-workers²⁶ carried out molecular mechanics calculations on L⁴ square-planar complexes and have described the configurations of co-ordinated macrocycles in terms of the

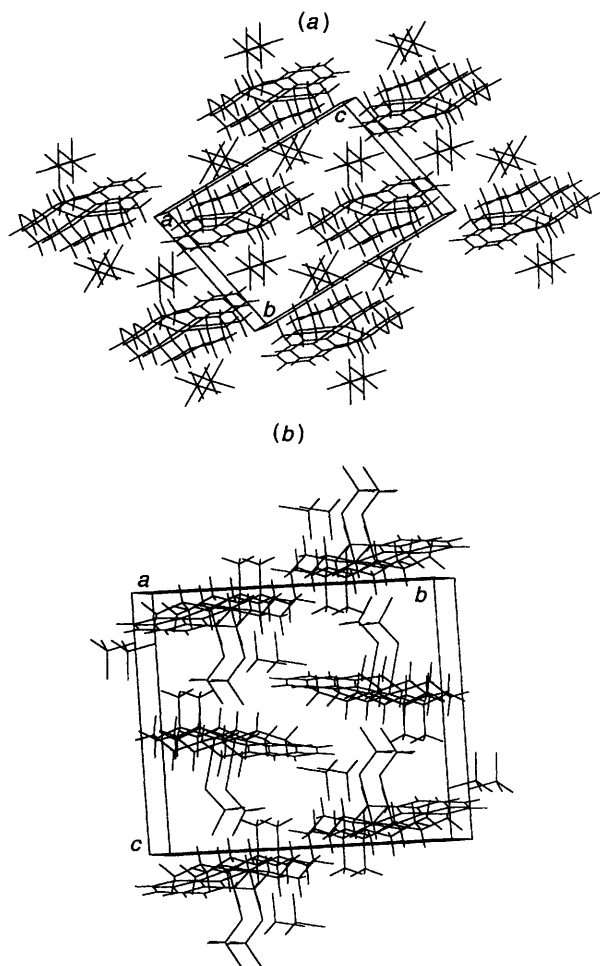


Fig. 4 Three-dimensional SCHAKAL plots depicting the layered structure and cation-anion interactions in $[\text{CuL}^1][\text{PF}_6]_2$ (a) and $[\text{NiL}^2(\text{ClO}_4)]\text{ClO}_4$ (b)

relative position of the hydrogen atoms bound to the nitrogen atoms. Thus, there are five possible structures: + + + + (*trans* I), + + + - (*trans* II), + - - + (*trans* III), + + - - (*trans* IV) and + - - - (the *cis* V form). Notice that + - - + and + + - - differ owing to the presence of two or three carbon bridges between nitrogen donor atoms.

We have carried out similar molecular mechanics calculations on L^4 complexes but with the universal force field,²⁷ so that the results can readily be compared with those on L^1 , L^2 and L^5 . It would not be possible to compare Hancock's results directly with ours on different macrocycles using a different force field.

Results for square-planar complexes $[\text{ML}^1]$ and $[\text{ML}^3]$ are shown in Fig. 5, and for $[\text{ML}^4]$ and $[\text{ML}^5]$ in Fig. 6. Changes of energy as a function of M-N distance are plotted in Fig. 5 (see Experimental section for further details), for the three conformations ---, -+- and +--, of L^1 and L^3 complexes. The --- and -+- forms are comparable, -+- being slightly more stable and presenting a minimum for a slightly shorter M-N distance. Introduction of methyl groups in the L^3 ligand gives rise to higher minimum energy with the three curves barely distinguishable, though the --- conformation has become a bit less stable than the other two forms.

Experimental data available⁷ include those for complexes of L^1 , L^3 , L^6 and L^7 , where L^6 and L^7 are the analogues of L^1 and L^3 with two extra methyl groups at the two ring carbon atoms adjacent to pyridine. Both the $[\text{CuL}^1]^+$ complex described above and $[\text{NiL}^6]^{2+}$ exhibit a --- conformation, while $[\text{NiL}^3]^{2+}$ appears in two different forms, --- and -+-; $[\text{NiL}^7]^{2+}$ also shows a -+- arrangement. There are a few octahedral complexes of these ligands, though only those which

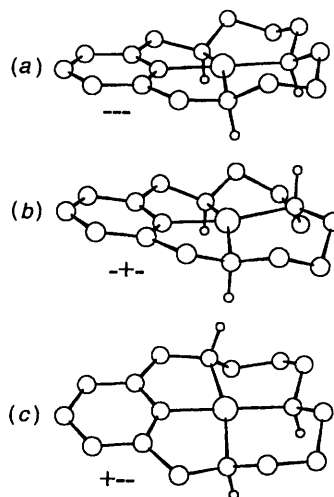
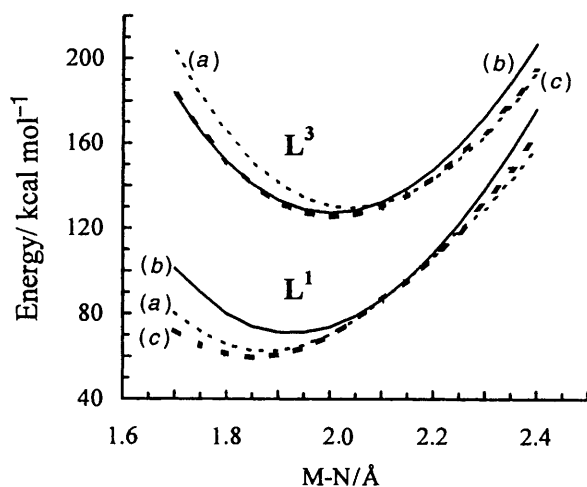


Fig. 5 Energy change as a function of the M-N distance, for square-planar complexes $[\text{ML}^1]$ and $[\text{ML}^3]$, with sketches of the relevant conformations

are *trans* and where the macrocycle occupies the equatorial plane interest us here. In $[\text{IrL}^3(\text{EtCl})]^+$, $[\text{CoL}^1(\text{Et})(\text{H}_2\text{O})]^{2+}$, and $[\text{NiL}^6(\text{ONO})(\text{NO}_2)]^{2+}$ the observed conformation is ---, while in $[\text{RuL}^7(\text{NCO})(\text{H}_2\text{O})]^+$ it is -+-.

The situation is more complicated for the complexes with 14-membered macrocyclic ligands without pyridine, L^4 and L^5 , especially the more asymmetric L^5 . Curves for their square-planar complexes are shown in Fig. 6, as well as the definitions of conformations. The curve for L^4 is qualitatively similar to that obtained by Hancock and co-workers,²⁶ considering that different force fields are being used. The most stable forms are + + + + and + + - -, the first for M-N distances shorter than ≈ 2.0 Å or longer than 2.35 Å, the second for the intermediate range. All the others have higher energies. Most structures have a + + - - arrangement,⁷ which is not surprising in view of the usual M-N distance being close to 2.0 Å. One striking exception is $[\text{NiL}^4][\text{ZnCl}_4]$. The macrocycle adopts a + - - - conformation, which was previously known only in the *cis* V conformation (with a folded macrocycle in octahedral environments). In this complex this conformation is observed for a planar macrocycle, in a square-planar complex with a Ni-N distance 1.92 Å, though it is 11 kcal mol⁻¹ less stable than + + + +, according to our calculations. The presence of N-H...Cl hydrogen bonds between the macrocycle and the anion may have contributed to this unusual behaviour. Octahedral complexes where the macrocycle occupies the equatorial plane also exhibit a + + - - conformation.⁷

For L^5 complexes there are three different conformers for + + + -, which are called + + - -a when the H below the N_4

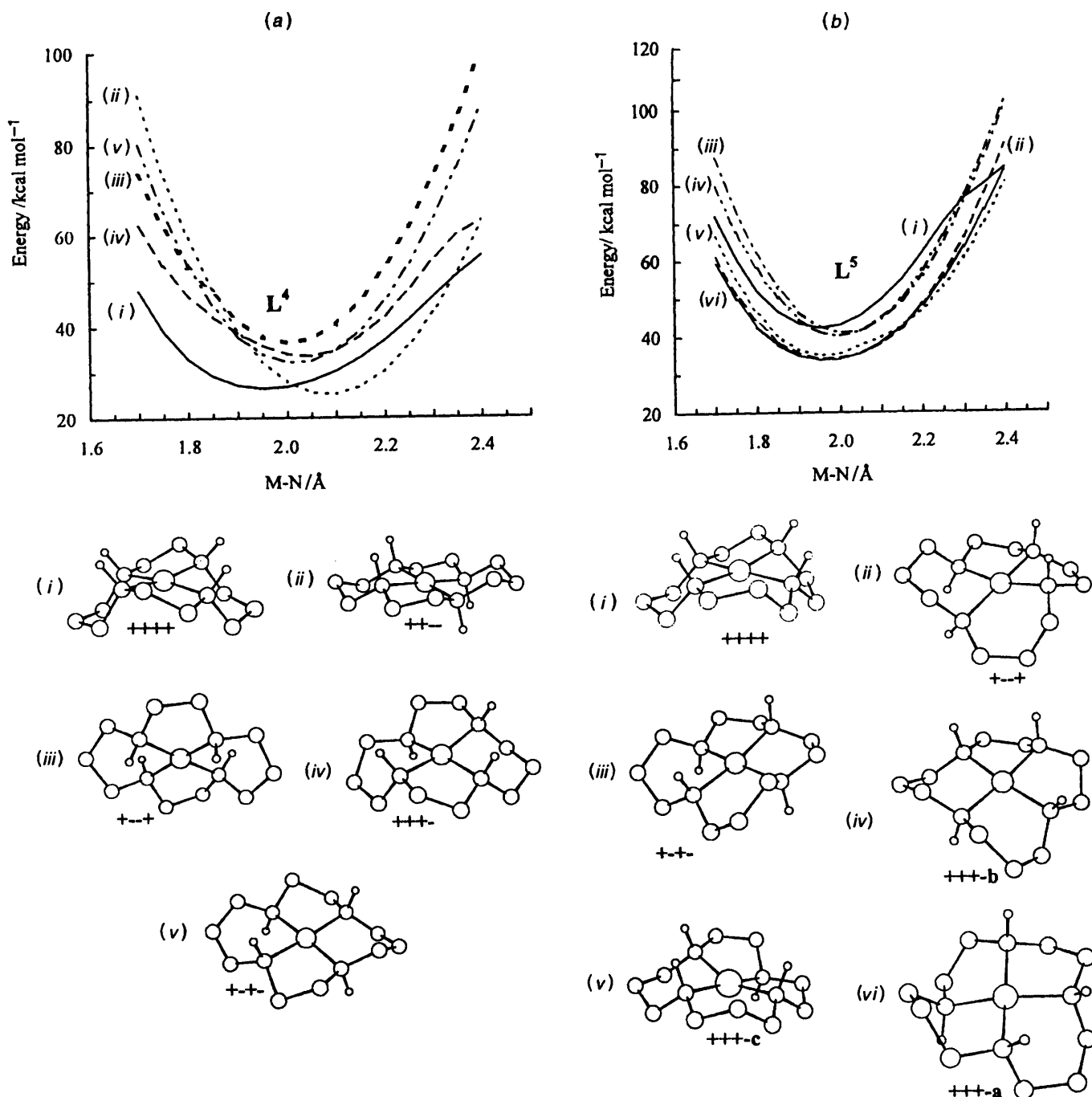


Fig. 6 Energy change as a function of the M-N distance, for square-planar complexes $[ML^4]$ (a) and $[ML^5]$ (b), with sketches the relevant conformations

plane is between one five-membered and one six-membered chelate ring, + + + - b when it is between two six-membered rings and + + + - c when it is between two five-membered rings, as drawn in Fig. 6. The curves are essentially the same for + + - -, + + + - a and + + + - c, which are significantly lower than the other three conformers, + - + -, + + + - b and + + + +. They are relatively shallow near the minimum and optimise for the same M-N distance. Although in the only compound known, $[NiL^5][ClO_4]_2$, the macrocycle is disordered,²⁸ it apparently has the + + + - c conformation, which is one of the low-energy set.

In the case of square-planar complexes the behaviour of the macrocycle is thus not significantly changed, according to these molecular mechanics calculations and also the experimental data, by the introduction of a pyridine in the ring.

Square-pyramidal geometries will now be analysed. The fifth

ligand, which was modelled by a chloride, can be axial (a conformations) or equatorial (e conformations); besides, each hydrogen atom or methyl group in the ring may be, for the same conformation, oriented toward (+) or away (-) from the fifth ligand. For instance, conformation + + + in L^1 square-planar complexes can lead to + + + a (axial ligand on the same side of the ring as H or Me) and - - - a (axial ligand on the opposite side). When the fifth ligand is equatorial, the macrocycle folds (Fig. 7). Some conformations are not specifically mentioned, because they are not stable to the geometry optimisation procedure.

Results for $[ML^1Cl]$ and $[ML^3Cl]$ are shown in Fig. 7. The preferred conformation is not very clear for $[ML^1(Cl)]$, where a few conformations, having in common the axial Cl ligand, share the lowest-energy range. The most stable conformation up to M-N distances of ≈ 1.9 Å is + + + a,

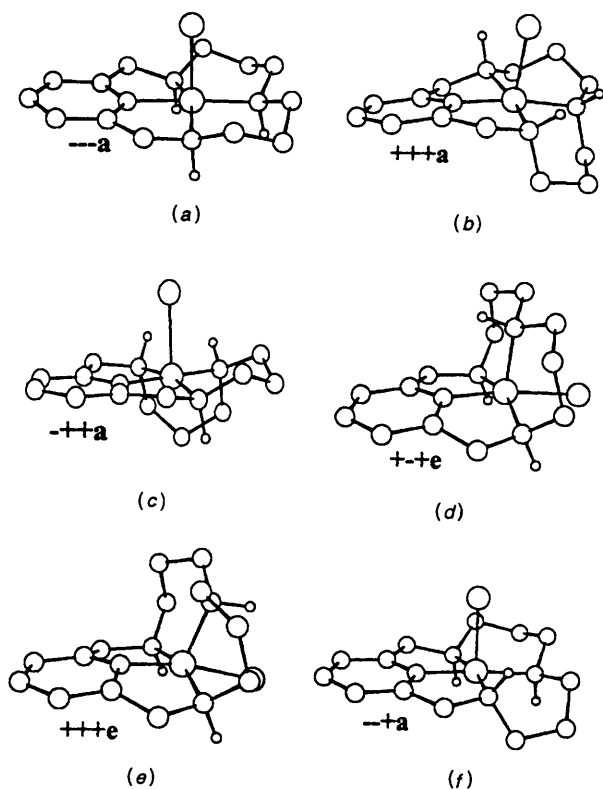
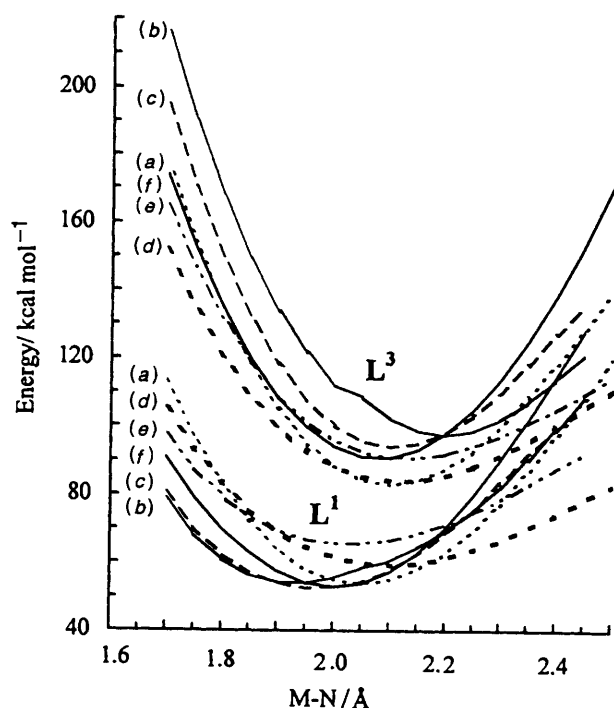


Fig. 7 Energy change as a function of the M-N distance, for square-pyramidal complexes $[ML^1Cl]$ and $[ML^3Cl]$, with sketches of the relevant conformations

followed by $---a$ between 1.9 and 2.05 Å, $---a$ between 2.05 and 2.15 Å, and finally $+++e$. The conformation observed in the nickel complex described in this work is $---a$ where all the hydrogen atoms point away from the axial oxygen ligand, even though the Ni-N distances range from 1.85 to 1.96 Å. Another related complex, $[NiL^6(ClO_4)]^+$, with an axial oxygen at 2.77 Å, exhibits the $-++a$ arrangement, most stable for M-N distances close to 1.85 Å.⁷ In conclusion, the conformations having an axial fifth ligand are more stable for complexes of L^1 having a M-N distance up to 2.15 Å. The equatorial $+++e$

conformation may be favoured at higher M-N distances, though neither $+++e$ or $+++e$ conformations are likely to occur at low M-N distances.

The effect of replacing the three hydrogens in L^1 by three methyl groups to give L^3 is given in the curves calculated for $[ML^3Cl]$ (Fig. 7). The most interesting result is the stabilisation of one of the $+++e$ equatorial forms in the complete range of distances studied, barely distinguishable from $---a$ near their minima, between 1.95 and 2.25 Å. Complexes $[NiL^3(dmsO)]^{2+}$ ($dmsO = Me_2SO$), $[NiL^3-(H_2O)]^{2+}$, $[NiL^3Cl]^+$, and $[NiL^7Cl]^+$ all exhibit the $+++e$ arrangement⁷ and confirm the validity of our calculations. The introduction of methyl groups has therefore an important effect in stabilising equatorial conformers.

Results for $[ML^4Cl]$ complexes are shown in Fig. 8 and for $[ML^5Cl]$ in Fig. 9, along with schemes of some of the possible conformers. In the case of the more symmetrical L^4 ligand derivatives, $++++a$ is the most stable form up to M-N distances of 2.1 Å, when $+++a$ becomes similar. Around 2.25 Å a very different conformation, $+-+e$, is preferred. The only known complex of this type is $[HgL^4Cl]^+$,⁷ with Hg-N distances of 2.38, 2.38, 2.28 and 2.42 Å and Hg-Cl of 2.46 Å. The positions of the carbon atom are disordered but a $++++a$ conformation is likely. Our calculations show that this is one of the three lowest-energy conformations within this range of M-N distances.

Only some of the results for square-pyramidal complexes $[ML^5Cl]$ are shown in Fig. 9, as the low symmetry required the calculation of a considerable number of independent conformations. When the fifth ligand occupies an equatorial position there are two types of *cis* arrangements for the macrocycle, depending on whether the five-membered (5) or the six-membered (6) chains are perpendicular to the M-Cl bond. The relevant conformations are drawn in Fig. 9(a) for conformers with axial Cl and in Fig. 9(b) for those with equatorial Cl.

The conformer $++++a$ is preferred for short M-N distances up to 2.0 Å, $+++a$ between 2.0 and 2.15 Å, $+++ac$ between 2.15 and 2.25 Å, and finally the equatorial $+-+e$ form has the lowest energy for long distances (> 2.25 Å). The only available structure is that of $[CuL^5(NCS)]NCS$ with an axial thiocyanate ($Cu-N_{ax}$ 2.292, $Cu-N_{eq}$ 2.022 Å) and exhibiting conformation $---+ac$. The corresponding curve has a minimum at M-N 2.15 Å where its energy approaches that of the most stable forms. Considering the difficulty of choosing the right M-N distance the result seems acceptable.

In conclusion, the conformers having the fifth ligand in an axial position are usually more stable for the square-pyramidal geometries. However, the introduction of methyl groups favours the macrocycle for the pyridine-containing ligands. On the other hand, for both L^4 and L^5 , the stabilisation of equatorial forms takes place for long M-N distances. Unfortunately, structural details of not many such complexes are known and this trend cannot yet be proven.

The molecular mechanics calculations are clearly consistent with all known experimental data and therefore it can be said with confidence that calculations carried out in systems not yet studied in detail are likely to be correct and indicate the type of conformer to be found.

The structures of all the complexes containing the L^1 macrocyclic ligand and its methylated derivatives mentioned in the previous discussion were optimised, in an attempt to check the reliability of the universal force field used. A list of the complexes, along with some experimental and calculated data, and the r.m.s. deviations (root-mean-square deviation for non-hydrogen atoms between the molecular mechanics structure and the X-ray experimental structure) for atomic coordinates are given in Table 5. The calculated M-N distances values appear under the 'Refined' heading as the first set of numbers, while those in italics refer to the X-ray determinations. Even for

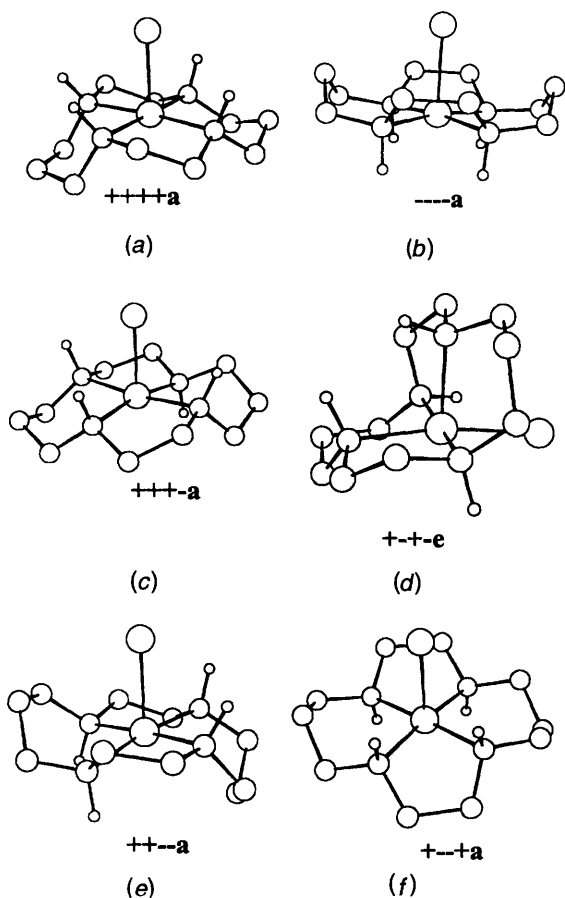
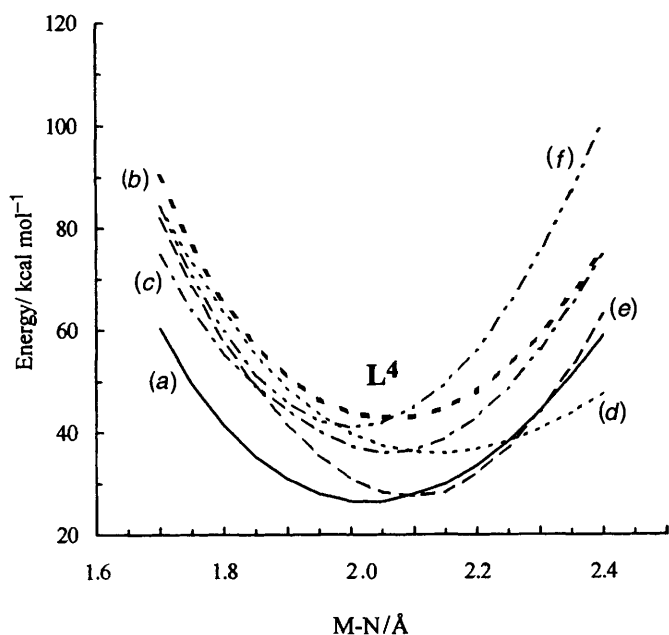


Fig. 8 Energy change as a function of the M-N distance, for square-pyramidal complexes $[ML_4(Cl)]$, with sketches of the relevant conformations

those structures with large r.m.s., the agreement between experimental and calculated M-N distances is rather good.

Molecular orbital calculations

Extended-Hückel molecular orbital calculations⁸ were performed on the $[NiL^2(ClO_4)]^+$ complex **2** and some models. It was stated in the introduction that the presence of pyridine rings does not lead to the same change in the stability constants

for cyclic and acyclic amines. The overlap population, an indicator of the strength of a bond, between Ni and a pyridine nitrogen is only slightly higher than that between Ni and an amine nitrogen. In a simple $[Ni(NH_3)_3(py)]^{2+}$ model and in the real complex **2** the calculated overlap populations are Ni-N (py) 0.328(model)/0.294(**2**), Ni-N (*trans*) 0.236/0.245, Ni-N (*cis*) 0.238/0.207, 0.257 (the two *cis* nitrogens are not equivalent in **2**), respectively. The trends are essentially the same and therefore the different behaviour of the stability constants should not arise from electronic factors, as they are not expected to change from cyclic to acyclic polyamines.

The calculations on the nickel complex were also aimed at probing the existence of a covalent bond between nickel and one of the perchlorate oxygen atoms. As pointed out earlier, though 2.590 Å is too long for a typical Ni-O bond, there is one example of a longer bond in a ClO_4^- group {2.77 Å in $[NiL^6(ClO_4)]^+$ } which was taken by the authors as belonging to the coordination sphere. Calculations on **2** using the experimentally determined coordinates led to a Ni-O overlap population of 0.076. In order to understand how strong such a bond is, two simple models, $[Ni(NH_3)_4(H_2O)]^{2+}$ and $[Ni(NH_3)_4(ClO_4)]^+$, were used. In these models either the water molecule or the perchlorate bind to nickel in an axial position. When the Ni-O distance was allowed to increase from 1.90 to 2.80 Å the Ni-O overlap population changed from 0.066/0.075 to 0.064/0.057, with a maximum of 0.088(2.25)/0.088(2.15 Å), respectively. At 2.60 Å, close to the experimental 2.590 Å, the overlap populations are respectively 0.077 and 0.071, in very good agreement with the value found for the real geometry. It appears that the axial Ni-O bond in this type of five co-ordinate complex is not very sensitive to the bond length.

Another interesting question to address is the relative stability of isomers containing the fifth ligand (modelled by a Cl^- ligand, to compare with the molecular mechanics results), equatorial or axial, from an electronic point of view. This problem has been addressed before and the trends obviously depend on the electronic configuration of the metal.²⁹ For d^8 metals in a square-pyramidal environment the stronger σ donors prefer the equatorial (or basal) position, which allows them to form stronger bonds (assuming the pyramidality is not too much, namely the $L_{eq}-M-L_{eq}$ angle does not exceed 165°). On the other hand, π effects are more difficult to rationalise, though for a nearly flat pyramid the π interaction is greatest in the basal position, changing as the pyramidality increases. Calculations for a simple model $[Ni(NH_3)_4Cl]^+$ showed the isomer having axial Cl to be the most stable (≈ 12 kcal mol⁻¹). Indeed, this arrangement leads to stronger Ni-N bonds, keeping a relatively strong Ni-Cl bond. When one N occupies the axial position the Ni-N bond becomes very weak and does not compensate for the increasing strength of the Ni-Cl bond. Therefore, the axial forms observed experimentally in most structures are preferred on both electronic and steric grounds. The availability of the equatorial isomer will increase as the pyramid becomes less flat.

Conclusion

The molecular mechanics calculations consistently describe the real geometries of the existing macrocycle complexes which have been examined. Of course these calculations are carried out on gas-phase structures and compared to structures in crystals, but packing effects should not be too important for bulky metal complexes and so good agreement is to be expected. For the square-planar isomers the presence of the pyridine in the macrocycle does significantly change the structural preferences. In the square-pyramidal geometries axial isomers are usually most stable on both electronic and steric grounds. The equatorial species become more stable, according to molecular mechanics calculations, in the case of pyridine-containing cycles, when methyl groups are introduced as

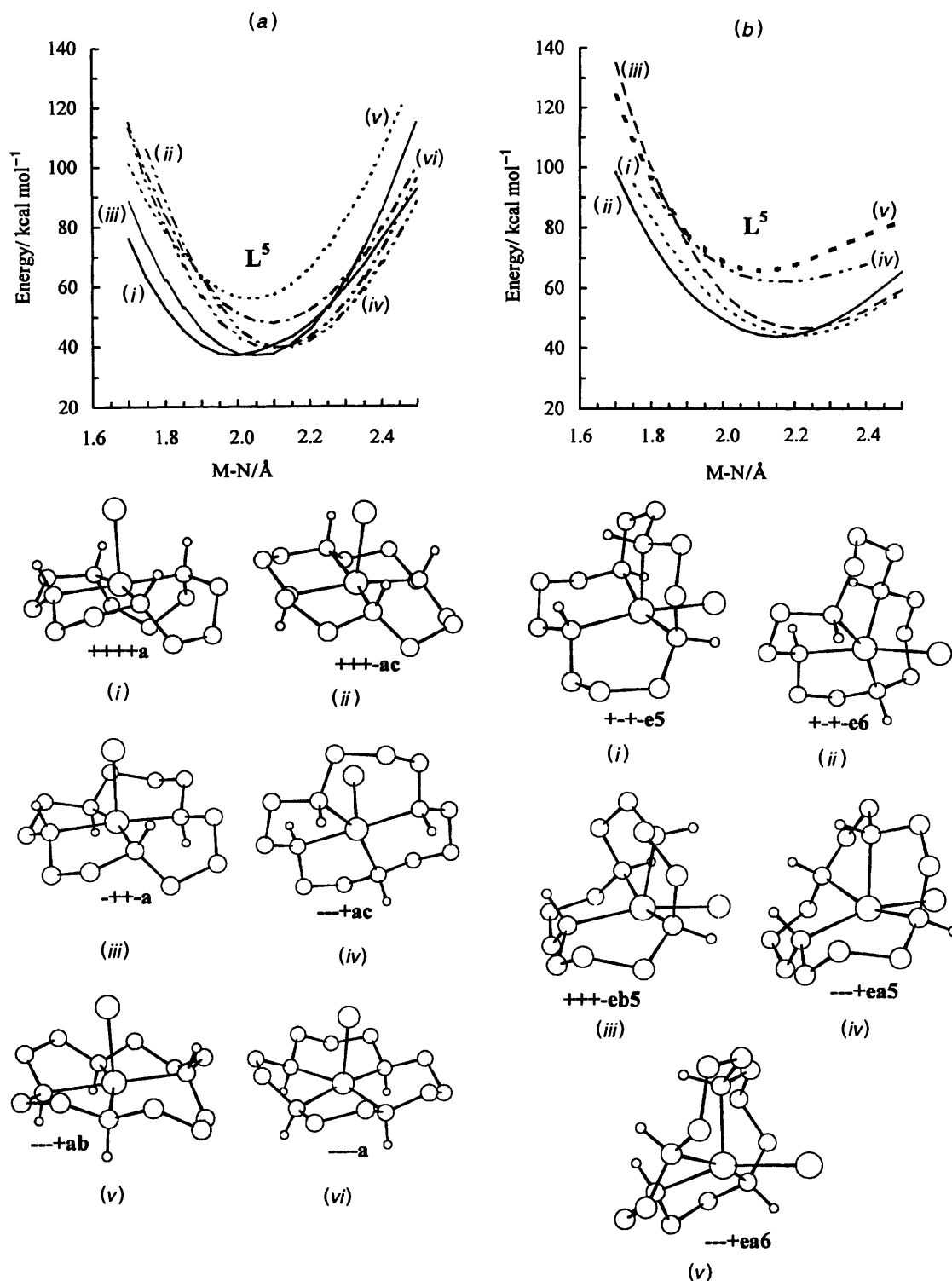


Fig. 9 Energy change as a function of the M-N distance, for square-pyramidal complexes $[ML^5(Cl)]$, with sketches of the relevant conformations: (a) fifth ligand axial; (b) fifth ligand equatorial

substituents (see L^1 vs. L^3 curves); and for L^4 and L^5 derivatives when the M-N distance is relatively long, in a range not available for most transition elements, certainly not first-row ones. In these type of geometries the macrocycle bends. This bending has also been observed in a few octahedral complexes of L^5 .

The question raised earlier about relative stabilities cannot therefore be answered in terms of different structural preferences due either to steric constraints, or to electronic preferences. The stability constants are related to Gibbs-free energy changes, while all our calculations take into account

only enthalpies. While a lot has been learnt about the group of complexes studied in this work, we feel that the difference in stability constants between cyclic and acyclic ligands must derive from other factors.

Acknowledgements

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Table 5 Comparison of molecular mechanics minimised structures and X-ray diffraction structures

Refcode	Compound	M–N(sp ³)/Å		M–N(sp ²)/Å		r.m.s./Å *
		Ideal	Refined	Ideal	Refined	
This work	L ¹					0.180
This work	[CuL ¹] ²⁺	2.00	2.024 2.015	1.94	1.911 1.904	0.115
This work	[NiL ³ (ClO ₄)] ²⁺	1.89	1.948 1.944	1.86	1.809 1.848	0.247
DOCVEW	[NiL ³] ²⁺	1.89	1.975 1.988	1.86	1.865 1.866	0.095
FEJMOW	[NiL ³] ²⁺	1.89	1.961 1.981	1.86	1.856 1.820	0.095
DOCVIA	[NiL ³ (H ₂ O)] ²⁺	1.89	1.952 2.084	1.86	1.859 1.974	0.185
FEJMUC	[NiL ³ (dmsO)] ²⁺	1.89	1.945 2.098	1.86	1.856 1.964	0.224
FEJNAJ	[NiL ³ Cl] ⁺	1.89	1.951 2.088	1.86	1.858 1.977	0.206
GEWPUT	[NiL ⁷] ²⁺	1.89	1.966 1.978	1.86	1.862 1.851	0.084
HALBOL	[CuL ⁵ (NCS)] ⁺	2.00	2.026 2.022			0.093
BUXSIW	[PdL ⁴] ²⁺	2.05	2.051 2.051			0.090
DUJSUW	[PdL ⁴] ²⁺	2.05	2.051 2.049			0.082
BUXSES	[PdL ⁴] ²⁺	2.05	2.051 2.055			0.151
COANEC	[CoL ⁴] ²⁺	1.95	1.981 1.978			0.066
HAFSUC	[CuL ⁴] ²⁺	2.00	2.015 2.020			0.061
FISKEX	[NiL ⁴] ²⁺	1.89	1.938 1.954			0.073
JIZTUH	[NiL ⁴] ²⁺	1.89	1.938 1.940			0.083
FAGWAL	[NiL ⁴] ²⁺	1.89	1.923 1.916			0.118

* Root-mean-square deviation between calculated and X-ray experimental structure (non-hydrogen atoms).

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