Ligand Design and Metal-ion Recognition. Comparison of the Interaction of Cobalt(II) and Nickel(II) with 16- to 19-Membered Mixed-donor Macrocycles†

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The interaction of cobalt(II) and nickel(II) with a range of 16- to 19-membered ring macrocycles incorporating nitrogen, oxygen and/or sulfur heteroatoms is reported. These ligands constitute an extensive array of related macrocyclic structures in which the positions of the donor atoms, their spacing, and the macrocyclic ring size all vary in a systematic manner. Emphasis has been given to the examination of structure–function relationships in the complexation behaviour. Physical measurements confirm the 1:1 metal to macrocyclic ligand stoichiometry of the respective complexes. Stability constants for the metal complexes have been determined potentiometrically in 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4). An X-ray crystallographic study of $[NiL^{18}(H_2O)][NO_3]_2$ (L^{18} = 5,6,7,8,10,11,12,13,19,20-decahydrodibenzo[*f*,*l*][1,8,11,4,15]oxadithiadiazacycloheptadecine) confirms that the nickel ion is six-co-ordinate with the complex cation exhibiting a distorted-octahedral geometry defined by all five donor atoms of the ON_2S_2 macrocycle and a water molecule; the macrocyclic backbone incorporating the N–O–N donor fragment is arranged meridionally. Molecular mechanics modelling of selected nickel(II) complexes has also been undertaken. As well as their considerable intrinsic interest, the results provide a potentially useful background upon which the design of new reagents for metal-ion discrimination may be based.

The design and synthesis of organic substrates that preferentially interact with particular metal ions is of fundamental importance to many areas of chemistry. Metal complex stability will be influenced by a range of factors, including (*i*) the number and nature of the donor atoms and their spatial arrangement, (*ii*) the backbone structure of the ligand and its ability to accommodate the preferred co-ordination geometries of the respective metal ions (including the degree of 'preorganisation' present in the system),[1] (*iii*) the number and size of the chelate rings formed on complexation, and (*iv*), for transition-metal ions, crystal-field effects of the type underlying the Irving–Williams stability order.[2]

Relative to their open-chain analogues, macrocyclic ligands have further stereochemical constraints associated with their cyclic nature which may influence their potental for metal-ion recognition.[3] For macrocycles incorporating rigid or semi-rigid cavities, recognition (and hence discrimination) may be associated with a close match or otherwise of the radius of the metal ion for the cavity. A further discrimination mechanism involves the use of a gradual change of properties (such as macrocycle hole size or degree of ligand substitution) along a ligand series to trigger a sudden change in the co-ordination geometry along the corresponding series of metal complexes. A process of this type may form the basis for discriminating between different metal ions and has been termed 'dislocation discrimination.[4] Several examples of structural dislocations have now been documented.[5–8]

In the present study a comparative investigation of the interaction of cobalt(II) and nickel(II) with the extensive array of 16- to 19-membered macrocycles, L^1–L^{20}, is reported. Incorporated in the comparison are data for the interaction of these metals with the O_2N_3-donor ligands L^4 and L^7–L^9; log K data for these systems have been reported previously (see below).[5] Taken together, all the above macrocycles form a matrix of structural types in which a systematic variation in donor-atom pattern and ring size occurs. One aim of the present study was to investigate structure–function relationships involving complex formation by this extensive ligand series. It has been our experience[4] that comparison of the co-ordination behaviour of a range of closely related ligand systems usually results in a more complete understanding of the often subtle factors underlying any observed discrimination. Such studies also provide a useful background upon which further ligand design may be based.

The earlier study of the stabilities of the nickel(II) complexes of 17-, 18- and 19-membered pentadentate macrocycles incorporating O_2N_3-donor sets (namely, L^4, L^7–L^9) strongly suggested that a structural dislocation occurs along the series on passing from the complex of the 18- to that of the 19-membered ring. Related dislocation behaviour may be induced by substituting the 'parent' 17-membered ring L^4 to yield its dimethylated derivative L^{21}; the stability constants (log K values) for the nickel(II) complexes of the last two ligands in 95% methanol are 10.0 and 6.9, respectively. In both the above examples the dislocations have been assigned to a change from facial to meridional co-ordination of the N_3-donor backbone in the respective octahedral co-ordination spheres.

Experimental

Physical Measurements.—Proton and ^{13}C NMR spectra

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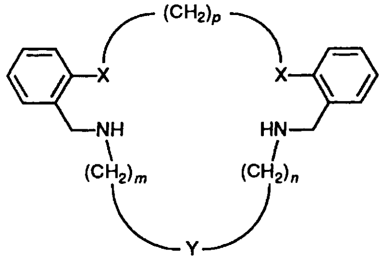
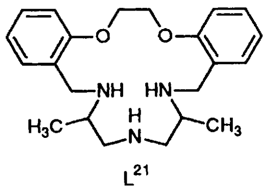
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI units employed: dyn = 10^{-5} N, D ≈ 3.33 × 10^{-30} C m.



	X	Y	m	n	p
L^1	O	NH	2	2	1
L^2	O	S	2	2	1
L^3	O	O	2	2	1
L^4	O	NH	2	2	2
L^5	O	S	2	2	2
L^6	O	O	2	2	2
L^7	O	NH	2	3	2
L^8	O	NH	3	3	2
L^9	O	NH	2	4	2
L^{10}	O	S	3	3	2
L^{11}	O	NH	2	2	4
L^{12}	O	S	2	2	4
L^{13}	O	O	2	2	4
L^{14}	S	NH	2	2	1
L^{15}	S	S	2	2	1
L^{16}	S	NH	2	2	2
L^{17}	S	S	2	2	2
L^{18}	S	O	2	2	2
L^{19}	S	NH	3	3	2
L^{20}	S	S	2	2	3



L^{21}

were obtained at 25 °C on a Bruker AM300 spectrometer at 300 and 75 MHz, respectively, infrared spectra as Nujol mulls on a Perkin-Elmer 197 spectrophotometer and positive-ion fast atom bombardment (FAB) mass spectra were determined by means of a JEOL-DX300 spectrometer (samples in 3-nitrobenzyl alcohol). Conductance measurements were obtained using a Philips conductivity bridge type PR 9501; all measurements were performed in methanol at *ca.* 10^{-3} mol dm^{-3} (and 23 °C). The UV/VIS spectra were obtained on a Beckman ACTA IV spectrophotometer; solid-state spectra were determined as Nujol mulls spread on filter-paper, solution spectra of the respective complexes at *ca.* 10^{-3} mol dm^{-3} in methanol. Magnetic moments were determined at 23 °C using a Faraday balance calibrated against Hg[Co(NCS)$_4$].

Macrocycle and Complex Synthesis.—The synthesis and characterisation of the macrocyclic ligands L^1–L^{20} have been described elsewhere.[5,9,10]

[Ni(NO$_3$)L^1]ClO$_4$·3H$_2$O. Nickel(II) nitrate hexahydrate (0.1 g) in boiling ethanol (10 cm^3) and solid lithium perchlorate (0.1 g) (**CAUTION**: perchlorates may be explosive) were added to a stirred boiling solution of L^1 (0.10 g) in ethanol (10 cm^3). The volume was reduced to 5 cm^3 and the solution was filtered and then cooled. On standing, blue crystals separated from the solution; yield 0.07 g (Found: C, 40.5; H, 4.9; N, 10.7. Calc. for $C_{19}H_{25}ClN_4NiO_9{\cdot}3H_2O$: C, 40.3; H, 4.8; N, 9.9%).

[Ni(NO$_3$)L^{11}]ClO$_4$·C$_2$H$_5$OH·H$_2$O. In a similar manner, Ni(NO$_3$)$_2$·6H$_2$O (0.08 g) and LiClO$_4$ (0.09 g) in ethanol (15 cm^3) were added to L^{11} (0.10 g in 10 cm^3 ethanol) to yield dark blue crystals; yield 0.05 g (Found: C, 44.0; H, 6.2; N, 8.5. Calc. for $C_{22}H_{31}ClN_4NiO_9{\cdot}C_2H_5OH{\cdot}H_2O$: C, 44.1; H, 6.0; N, 8.6%).

[Ni(NO$_3$)L^{14}]ClO$_4$·3H$_2$O. In a similar manner, Ni(NO$_3$)$_2$·6H$_2$O (0.09 g) and LiClO$_4$ (0.09 g) in butanol (10 cm^3) were added to L^{14} (0.10 g in 10 cm^3 butanol) to yield purple crystals; yield 0.03 g (Found: C, 35.6; H, 4.3; N, 8.4. Calc. for $C_{19}H_{25}ClN_4NiO_7S_2{\cdot}3H_2O$: C, 35.9; H, 4.9; N, 8.8%).

[Ni(NO$_3$)L^{16}]ClO$_4$·C$_2$H$_5$OH·0.5H$_2$O. In a similar manner, L^{16} (0.10 g) yielded dark blue crystals; yield 0.07 g (Found: C, 40.8; H, 5.0; N, 9.0. Calc. for $C_{20}H_{27}ClN_4NiO_7S_2{\cdot}C_2H_5OH{\cdot}0.5H_2O$: C, 40.8; H, 5.3; N, 8.6%).

[NiL^{18}(H$_2$O)][NO$_3$]$_2$. Nickel(II) nitrate hexahydrate (0.10 g) in boiling ethanol (15 cm^3) was slowly added to a stirred solution of L^{18} (0.10 g) in boiling ethanol (10 cm^3). The blue solution was filtered and butanol (10 cm^3) was added to the filtrate. The volume was reduced to 20 cm^3 and the solution was then filtered and cooled. On standing dark blue crystals formed; yield 0.05 g (Found: C, 41.6; H, 4.9; N, 9.7. Calc. for $C_{20}H_{28}N_4NiO_8S_2$: C, 41.8; H, 4.9; N, 9.7%).

Equilibrium Studies.—The reagents used for the equilibrium studies were all analytical grade or better. Analytical grade methanol was fractionated and distilled over magnesium before use. The potentiometric titration apparatus consisted of a water-jacketed titration vessel and a water-jacketed calomel reference electrode, connected by a salt bridge. A Philips glass electrode (GA-110) was used for all pH measurements. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the background electrolyte; the solvent was 95% methanol and the temperature was maintained at 25 ± 0.1 °C.

During the course of each measurement, methanol-saturated nitrogen was bubbled through the solution in the measuring cell. Tetraethylammonium hydroxide solution was introduced into the measuring cell using a Metrohm Dosimat 655 automatic titrator. A Corning model 130 Research pH meter was employed for the pH determinations. The microprocessor-controlled apparatus was calibrated daily by titration with a solution of standardised base. The data were processed using a local version of MINIQUAD[11] and selected data were also reprocessed using SUPERQUAD;[12] the two programs gave values showing no significant differences.

In a typical determination of protonation constants, ligand (1.3×10^{-3} mol dm^{-3}) in 25.00 cm^3 of perchloric acid solution (4.0×10^{-3} mol dm^{-3}, $I = 0.1$ mol dm^{-3}) was titrated with tetraethylammonium hydroxide solution (0.1 mol dm^{-3}). Each quoted value is the mean of values (weighted according to the corresponding 'R factors' as obtained from the respective MINIQUAD outputs) of at least three separate determinations (at different ligand concentrations). The stability constants for the metal complexes were obtained by a similar procedure except that each titration was performed in the presence of metal ion. Typically, for a given system, titrations were performed using at least two different metal to ligand ratios.

Crystallography for [NiL^{18}(H$_2$O)][NO$_3$]$_2$.—*Crystal data.* $C_{20}H_{28}N_4NiO_8S_2$, $M = 575.3$, crystallised from ethanol as purple crystals, crystal dimensions $0.21 \times 0.21 \times 0.17$ mm, monoclinic space group Cc ($C^4{}_s$, no. 9), $a = 11.073(2)$, $b = 14.588(3)$, $c = 15.561(3)$ Å, $\beta = 107.00(2)°$, $U = 2403.8(8)$ Å^3, $D_c = 1.59$ g cm^{-3}, $Z = 4$, graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.710\,69$), μ(Mo-Kα) = 9.66 cm^{-1}, $F(000) = 1200$.

Data were collected on a Philips PW1100 diffractometer in the range θ 3–25°, with a scan width of 0.80°, using the technique previously described.[13] No absorption corrections were applied. The metal atom was located from a Patterson synthesis.[14] The positions of the remaining non-hydrogen atoms and the N- and O-bonded H atoms were found from subsequent Fourier and Fourier difference syntheses. The

Table 1 Fractional atomic coordinates with estimated standard deviation in parentheses for $[NiL^{18}(H_2O)][NO_3]_2$

Atom	x	y	z
Ni	0.000 00	0.112 04(9)	0.000 00
S(1a)	0.198 7(3)	0.039 3(2)	0.057 9(2)
S(1b)	0.112 2(3)	0.244 3(2)	−0.029 9(2)
N(1a)	−0.009 5(8)	0.160 3(6)	0.123 5(6)
N(1b)	−0.049 2(8)	0.072 2(6)	−0.134 6(6)
O(1c)	−0.171 4(7)	0.178 7(5)	−0.044 5(5)
C(1a)	0.306 9(11)	0.113 3(8)	0.021 5(8)
C(2a)	0.250 5(10)	0.055 7(8)	0.178 0(7)
C(3a)	0.339 5(11)	−0.010 4(9)	0.223 2(9)
C(4a)	0.387 7(12)	−0.003 8(10)	0.316 0(9)
C(5a)	0.351 6(12)	0.061 7(9)	0.363 2(9)
C(6a)	0.257 8(11)	0.122 2(9)	0.318 2(8)
C(7a)	0.207 9(10)	0.123 3(8)	0.225 7(8)
C(8a)	0.109 0(10)	0.194 9(8)	0.185 2(8)
C(9a)	−0.108 9(10)	0.230 4(8)	0.105 1(8)
C(10a)	−0.220 7(11)	0.199 5(8)	0.030 4(8)
C(1b)	0.275 3(11)	0.215 2(8)	0.024 8(8)
C(2b)	0.104 5(10)	0.251 9(8)	−0.146 5(7)
C(3b)	0.129 3(12)	0.337 1(10)	−0.173 4(9)
C(4b)	0.120 1(12)	0.354 0(10)	−0.264 6(9)
C(5b)	0.089 7(12)	0.285 3(10)	−0.324 7(10)
C(6b)	0.065 5(11)	0.197 5(9)	−0.296 5(8)
C(7b)	0.071 3(11)	0.178 5(8)	−0.205 9(8)
C(8b)	0.042 0(12)	0.082 9(8)	−0.184 9(9)
C(9b)	−0.175 8(10)	0.114 5(8)	−0.181 3(8)
C(10b)	−0.251 9(10)	0.128 6(8)	−0.118 3(7)
H(N1a)	−0.035 70	0.103 30	0.147 30
N(N1b)	−0.057 30	0.017 20	−0.123 80
O(7)	−0.082 2(8)	−0.010 9(5)	0.028 0(6)
H(O71)	−0.162 80	−0.048 80	0.042 20
H(O72)	−0.072 30	−0.047 10	−0.012 90
N(1)	0.957 8(10)	0.818 1(8)	0.870 4(8)
O(1)	0.936 9(9)	0.879 9(6)	0.814 1(6)
O(2)	0.989 4(9)	0.838 0(7)	0.954 3(7)
O(3)	0.960 5(11)	0.737 9(6)	0.849 4(7)
N(2)	0.138 9(10)	0.459 1(8)	0.080 8(7)
O(4)	0.063 3(10)	0.427 6(7)	0.120 2(8)
O(5)	0.102 1(10)	0.507 6(8)	0.016 4(8)
O(6)	0.251 8(8)	0.439 6(9)	0.109 3(6)

aromatic and aliphatic C-bonded H atoms were placed in geometrically idealised positions (C–H 1.08 Å), and constrained to ride on the relevant C atom, with thermal parameters tied to single free variables which were refined [final values 0.047 (aliphatic) and 0.073 Å^2 (phenyl)]. The located N- and O-bonded H atoms were given fixed isotropic thermal parameters of 0.08 Å^2 and their positions not refined. In the final cycles of full-matrix refinement, using 1421 unique data with $I > 3\sigma(I)$, the nickel, water and nitrate oxygen atoms were assigned anisotropic thermal parameters and refinement converged at $R = 0.051$ and $R' = 0.049$ where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$ using a weighting scheme of $w = 1/[\sigma^2(F_o)]$. A final Fourier difference map showed no significant regions of electron density.

Atomic coordinates are given in Table 1 with bond distances and angles in Table 2.

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

Molecular Mechanics Calculations.—As well as the above structural data for the nickel(II) complex of the ON_2S_2-donor ligand L[18], X-ray data were also available for the corresponding complexes of the O_2N_3-donor[8] and N_3S_2-donor[15] macrocycles, L[4] and L[16]. Each of these systems has been the subject of molecular mechanics analysis in the present study. The provisional force-field parameter set for this series of complexes was largely based on the parameters derived previously for high-spin nickel(II) complexes of macrocyclic ligands incorporating N_4-, O_2N_2- and S_2N_2-donor systems.[16] The force-field parametrisation employed is listed in Table 3. The parametrisation for the nickel–nitrogen bonds was similar to that used previously for high-spin nickel(II) complexes of tetraazamacrocycles. The bending constants for angles about the oxygen and nitrogen donor atoms were also the same as those used for modelling the nickel(II) complexes of the (related) O_2N_2-donor structures. However, slight modification of other parameters associated with the metal ion from those used previously was found to improve the 'fit' of each of the present structures. No attempt was made to refine the nickel to water bond in each structure. Instead, the procedure employed was to fix the cartesian coordinates of the nickel and water molecule in space (based on the corresponding X-ray structure coordinates) while allowing the rest of the molecule to refine.

X-Ray data provided the basis for setting up the 'starting coordinates' for each of the three configurational isomers investigated while Drieding models were used to assist in the selection of likely conformations within individual structures. That is, for each isomer type different conformations of the co-ordinated ligand were investigated in an endeavour to ensure that the lowest-energy structure was identified in each case.

Results and Discussion

Isolation of Selected Metal Complexes.—Nickel(II) complexes of a selection of the present macrocycles have been isolated. In contrast, attempts to obtain cobalt(II) species using similar procedures were not successful. Complexes of the ligands L[1], L[11], L[14], L[16] and L[18] were prepared by the addition of a slight excess of nickel(II) nitrate in ethanol to a boiling solution of the appropriate macrocycle in ethanol. In four instances it proved necessary to add excess of lithium perchlorate to the reaction mixture to aid crystallisation of the products. Microanalytical data indicated that these latter complexes contained one nitrate ion per metal ion, with a perchlorate as the second anion.

It should be noted that the attempted syntheses of the nickel(II) complexes of many of the macrocyclic ligands containing other than an N_3-donor aliphatic fragment resulted in the isolation of colourless crystalline products which were soluble in water. These products gave sharply defined (that is, not contact shift broadened) ^1H NMR spectra in D_2O, their properties indicated that they are salts of the corresponding protonated ligands. The structure of one such product, the dihydronitrate salt of L[12], has recently been confirmed by X-ray analysis.[19] The isolation of these salts is very likely a result of the strongly basic nature of the respective ligands and the low solubilities of the salts in alcohol relative to the corresponding nickel complexes, coupled with the relatively moderate stabilities of the latter.

Physical data for six nickel complexes are included in Table 4. The magnetic moments of these species all fall in the normal range expected for complexes of high-spin nickel(II).

The infrared spectra of the complexes incorporating perchlorate anions give no clear indication of perchlorate co-ordination; that is, while the broad strong absorptions at *ca.* 1080 cm^{-1} are generally not symmetrical, no splitting of these bands was observed. The presence of peaks attributable to the ligand partially masked the nitrate absorptions in each case and no attempt was made to assign these resonances. All the spectra contained bands between 3200 and 3300 cm^{-1} arising from the presence of (co-ordinated) amine groups. In all cases where water and/or ethanol were suggested to be present (on the basis of their microanalytical data), the expected absorptions in the range 3400–3600 cm^{-1} were observed. In two complexes alcohol of crystallisation was postulated to be present. Similar association of solvent has been shown to occur in particular nickel complexes of other O_2N_3-macrocyclic ligands of the present type,[5] as well as in related N_2S_2-donor macrocyclic complexes reported previously.[20]

Table 2 Bond lengths (Å) and angles (°) for $[NiL^{18}(H_2O)][NO_3]_2$

Ni–O(7)	2.113(8)	Ni–S(1a)	2.370(3)	C(2a)–C(7a)	1.396(17)	C(3a)–C(4a)	1.388(18)
Ni–S(1b)	2.413(3)	Ni–N(1a)	2.078(9)	C(4a)–C(5a)	1.336(21)	C(5a)–C(6a)	1.385(17)
Ni–N(1b)	2.086(9)	Ni–O(1c)	2.063(7)	C(6a)–C(7a)	1.383(16)	C(7a)–C(8a)	1.512(15)
O(7)–H(O71)	1.126	O(7)–H(O72)	0.858	C(9a)–C(10a)	1.498(15)	C(2b)–C(3b)	1.364(19)
S(1a)–C(1a)	1.821(14)	S(1a)–C(2a)	1.804(11)	C(2b)–C(7b)	1.392(16)	C(3b)–C(4b)	1.414(20)
S(1b)–C(1b)	1.807(11)	S(1b)–C(2b)	1.795(12)	C(4b)–C(5b)	1.345(20)	C(5b)–C(6b)	1.404(20)
N(1a)–C(8a)	1.470(13)	N(1a)–C(9a)	1.467(14)	C(6b)–C(7b)	1.420(18)	C(7b)–C(8b)	1.489(17)
N(1a)–H(N1a)	0.988	N(1b)–C(8b)	1.457(18)	C(9b)–C(10b)	1.482(18)	N(1)–O(1)	1.231(15)
N(1b)–C(9b)	1.510(13)	N(1b)–H(N1b)	0.829	N(1)–O(2)	1.282(16)	N(1)–O(3)	1.218(15)
O(1c)–C(10a)	1.456(16)	O(1c)–C(10b)	1.431(12)	N(2)–O(4)	1.260(18)	N(2)–O(5)	1.197(16)
C(1a)–C(1b)	1.532(17)	C(2a)–C(3a)	1.411(16)	N(2)–O(6)	1.231(14)		
S(1a)–Ni–O(7)	87.1(2)	S(1b)–Ni–O(7)	174.5(2)	C(10b)–O(1c)–C(10a)	117.2(9)	C(1b)–C(1a)–S(1a)	113(1)
S(1b)–Ni–S(1a)	87.6(1)	N(1a)–Ni–O(7)	87.5(3)	C(3a)–C(2a)–S(1a)	113.0(9)	C(7a)–C(2a)–S(1a)	126.1(8)
N(1a)–Ni–S(1a)	95.3(2)	N(1a)–Ni–S(1b)	94.3(3)	C(7a)–C(2a)–C(3a)	121(1)	C(4a)–C(3a)–C(2a)	118(1)
N(1b)–Ni–O(7)	88.2(4)	N(1b)–Ni–S(1a)	101.4(3)	C(5a)–C(4a)–C(3a)	122(1)	C(6a)–C(5a)–C(4a)	119(1)
N(1b)–Ni–S(1b)	91.6(3)	N(1b)–Ni–N(1a)	162.5(3)	C(7a)–C(6a)–C(5a)	123(1)	C(6a)–C(7a)–C(2a)	117(1)
O(1c)–Ni–O(7)	93.4(3)	O(1c)–Ni–S(1a)	177.2(2)	C(8a)–C(7a)–C(2a)	126(1)	C(8a)–C(7a)–C(6a)	117(1)
O(1c)–Ni–S(1b)	91.9(2)	O(1c)–Ni–N(1a)	82.0(3)	C(7a)–C(8a)–N(1a)	115.7(9)	C(10a)–C(9a)–N(1a)	110.2(9)
O(1c)–Ni–N(1b)	81.4(3)	H(O71)–O(7)–Ni	150	C(9a)–C(10a)–O(1c)	105(1)	C(1a)–C(1b)–S(1b)	114.7(8)
H(O72)–O(7)–Ni	102	H(O72)–O(7)–H(O71)	97	C(3b)–C(2b)–S(1b)	114.4(9)	C(7b)–C(2b)–S(1b)	123.3(9)
C(1a)–S(1a)–Ni	103.8(4)	C(2a)–S(1a)–Ni	108.3(4)	C(7b)–C(2b)–C(3b)	122(1)	C(4b)–C(3b)–C(2b)	120(1)
C(2a)–S(1a)–C(1a)	101.9(5)	C(1b)–S(1b)–Ni	102.8(4)	C(5b)–C(4b)–C(3b)	120(1)	C(6b)–C(5b)–C(4b)	120(1)
C(2b)–S(1b)–Ni	111.7(4)	C(2b)–S(1b)–C(1b)	103.7(6)	C(7b)–C(6b)–C(5b)	122(1)	C(6b)–C(7b)–C(2b)	116(1)
C(8a)–N(1a)–Ni	116.4(8)	C(9a)–N(1a)–Ni	107.1(6)	C(8b)–C(7b)–C(2b)	127(1)	C(8b)–C(7b)–C(6b)	117(1)
C(9a)–N(1a)–C(8a)	111.3(8)	H(N1a)–N(1a)–Ni	99	C(7b)–C(8b)–N(1b)	117(1)	C(10b)–C(9b)–N(1b)	111.5(9)
H(N1a)–N(1a)–C(8a)	110	H(N1a)–N(1a)–C(9a)	111	C(9b)–C(10b)–O(1c)	105.1(9)	O(2)–N(1)–O(1)	120(1)
C(8b)–N(1b)–Ni	119.4(7)	C(9b)–N(1b)–Ni	107.6(7)	O(3)–N(1)–O(1)	122(1)	O(3)–N(1)–O(2)	118(1)
C(9b)–N(1b)–C(8b)	112.9(9)	H(N1b)–N(1b)–Ni	94	O(5)–N(2)–O(4)	121(1)	O(6)–N(2)–O(4)	119(1)
H(N1b)–N(1b)–C(8b)	110	H(N1b)–N(1b)–C(9b)	110	O(6)–N(2)–O(5)	120(1)		
C(10a)–O(1c)–Ni	110.6(6)	C(10b)–O(1c)–Ni	109.0(6)				

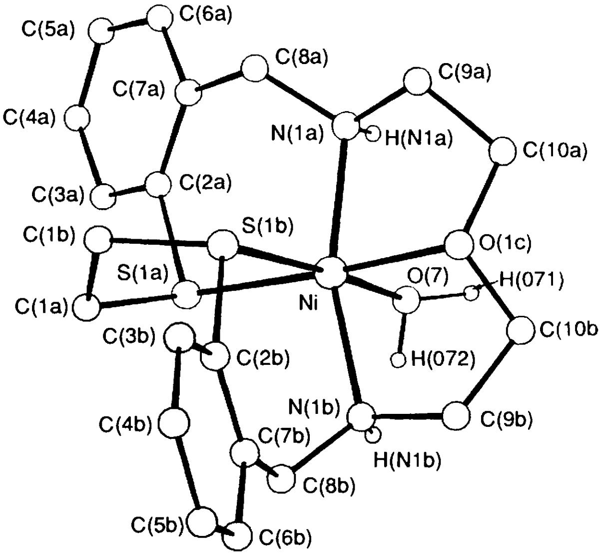


Fig. 1 The X-ray structure of the cation $[NiL^{18}(H_2O)]^{2+}$

Conductance values in methanol for the nickel(II) complexes {with the exception of $[NiL^{18}(H_2O)][NO_3]_2$} indicate or approximate to 1:1 electrolytes (80–115 S cm^2 mol^{-1}) in this solvent[21] (Table 4) and hence at least one anion is present in the co-ordination sphere. There is much evidence in the literature that nitrate co-ordination will be favoured over perchlorate co-ordination in such complexes. Consequently, a nitrate ion is postulated to occupy one co-ordination position in each complex in solution and it seems likely that such an arrangement persists in the solid state. The nickel complex of L^{18} is a 2:1 electrolyte in methanol, hence non-co-ordination of the anions occurs in solution (and also in the solid state as shown by the X-ray structure).

In accordance with the predicted structures, the positive-ion FAB source mass spectra of the mixed-anion complexes all show strong peaks corresponding to $[Ni(NO_3)L^n]^+$, although weaker peaks attributable to $[Ni(ClO_4)L^n]^+$ are also present for most complexes, presumably reflecting ion rearrangement in the vapour phase.

The solution and solid-state electronic spectra of the complexes are typical of octahedral or pseudo-octahedral nickel(II) species.[5] In the majority of cases the spectra contained three major bands which may be assigned to the following transitions in O_h symmetry: $^3A_{2g} \longrightarrow {}^3T_{1g}$ (P), $^3A_{2g} \longrightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \longrightarrow {}^3T_{2g}$. However, it is noted that in many cases the bands are somewhat broad and unsymmetrical, indicating that the real symmetry is, not unexpectedly, somewhat lower than octahedral. In particular, the solution spectra of $[Ni(NO_3)L^{16}]ClO_4{\cdot}C_2H_5OH{\cdot}0.5H_2O$, and $[NiL^{18}(H_2O)][NO_3]_2$ both show a clear splitting of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition, indicating that significant distortion from octahedral symmetry is present in these complexes. In the solution and solid-state spectra of the complex of the sulfur-containing ligand L^{16} the $^3A_{2g} \longrightarrow {}^3T_{1g}$ (P) transition is obscured by the edge of an intense charge-transfer band.

It is not possible to assign specific modes of macrocycle co-ordination in the respective complexes from the spectrophotometric data. However, with the possible exception of the complexes of L^1 and L^{18}, the strong similarities between the spectra of individual complexes in the solid and in solution suggest that similar geometries occur in both states.

X-Ray Crystal Structure.—The structure of $[NiL^{18}(H_2O)][NO_3]_2$ is shown in Fig. 1. The nickel atom is six-co-ordinate with the complex cation exhibiting a distorted-octahedral geometry comprising all five donor atoms of the ON_2S_2-donor macrocycle, and a water molecule *trans* to S(1b). The main distortions from regular octahedral geometry appear to result from the steric requirements of the macrocyclic ligand. The angles around the nickel in the five-membered chelate rings are, as usual, less than the ideal value of 90° [81.4(3), 82.0(3) and 87.6(1)°] whereas those in the six-membered rings are greater

Table 3 Force-field parameters for high-spin nickel(II) complexes of L^4, L^{16} and L^{18}

Non-bonded parameters[a]

Atom	r^*/Å	ε/kJ mol^{-1}
Ni	2.30	0.711

Bond stretching parameters and bond moments

Bond type	r_0/Å	k_r/mdyn Å^{-1} molecule^{-1}	μ/D
Ni–N	2.05	1.80	0.014
Ni–O(aromatic ether)	2.14	0.60	0.000
Ni–O(aliphatic ether)[b]	2.11	0.80	0.290
Ni–S	2.49	0.65	0.800
O(aromatic ether)–Lp[c]	0.60	6.10	0.600
O(aliphatic ether)–Lp[b]	0.60	4.60	0.600
S–Lp	0.60	5.30	0.800
C(sp^3)–N(sp^3)	1.46	4.00	0.027

Bond bending parameters

Bond angle	θ_0/°	k_θ/mdyn Å rad^{-2} molecule^{-1}
Ni–N–C	109.5	0.50
Ni–N–H	109.5	0.50
Ni–O–C	109.5	0.35
Ni–O–Lp	109.5	0.10
Ni–O(aliphatic ether)–C	109.5	0.40
Ni–O(aliphatic ether)–Lp	105.16	0.35
Ni–S–C	100.0	0.50
Ni–S–Lp	115.0	0.50
N–Ni–N	90.0	0.25
N–Ni–O	90.0	0.50
N–Ni–S	90.0	0.50
O–Ni–O	90.0	0.50
O–Ni–S	90.0	0.50
S–Ni–S	90.0	0.50
C–S–C	100.0	0.50
C–S–Lp	115.0	0.50

Stretch-bond constants

Bond angle	k_{sb}/mdyn rad^{-1} molecule^{-1}
C–N–Ni	0.12
H–N–Ni	0.09
C–O–Ni	0.12
C–S–Ni	0.25

Torsional constants

Torsion	V_1/kJ mol^{-1}	V_2/kJ mol^{-1}	V_3/kJ mol^{-1}
C–C–N–Ni	−0.84	3.05	3.35
H–C–N–Ni	0.00	0.00	2.18
C–C–O–Ni	1.67	2.18	1.95
H–C–O–Ni	0.00	0.00	2.22
C–C–S–Ni	−2.59	1.26	1.05
H–C–S–Ni	0.00	0.00	2.26

[a] The same values were used by Drew *et al.*[17] [b] Based on Allinger's values.[18] [c] Lp = Lone pair.

[91.6(3) and 95.3(2)°]. The two longest bonds to the metal atom are from the sulfur donors with Ni–S(1b) at 2.413(3) being significantly longer than Ni–S(1a) at 2.370(3) Å. The ether oxygen O(1c) lies closer to the nickel ion than the oxygen of the water molecule [Ni–O(1c) 2.063(7) *versus* Ni–O(7) 2.113(8) Å], which is in accordance with the operation of a chelate effect involving the co-ordinated $N(CH_2)_2O(CH_2)_2N$ fragment of the molecule. The nitrogen and sulfur donor groups are effectively chiral in the crystal with prochiral *RSSS* (or *SRRR*) configurations for N(1a), S(1a), S(1b) and N(1b), respectively. The nitrate anions are strongly hydrogen-bonded to the complex with H(N1b) $\cdots$ O(1) 2.22, H(O72) $\cdots$ O(2) 1.93 and H(O71) $\cdots$ O(6) 1.61 Å.

Stability Constants.—The protonation constants for L^1–L^3, L^5, L^6 and L^{10}–L^{20} were obtained by potentiometric titration in 95% methanol, containing 2 or 3 equivalents of perchloric acid (I = 0.1 mol dm^{-3}, NEt_4ClO_4), with tetraethylammonium hydroxide at 25 °C. The corresponding constants for the macrocycles L^4 and L^7–L^9, have been determined previously and are also listed in Table 5 for comparison.[6]

Stability constants for the 1 : 1 (L : M) complexes of cobalt(II) and nickel(II) of the macrocyclic ligands were also determined potentiometrically in 95% methanol. A summary of the respective values is given in Table 5. From the data listed it is apparent that the systematic changes in the macrocyclic ligand structures (variation of the donor-atom set, the macrocyclic ring size and/or the chelate ring sizes) are clearly reflected in the stabilities of the resultant metal complexes and the following general observations may be made.

First, in accordance with the Irving–Williams order[2] (and related earlier studies),[5,22] the nickel(II) complex in each case is more stable than the corresponding cobalt(II) complex. Secondly, the observed log K values for the complexes of L^1–L^{21} show the expected dependence on the nature of the donor atom Y. Thus, when Y = NH, the stabilities of the corresponding complexes are invariably higher than for complexes involving ligands where Y is a thioether sulfur or an ether oxygen. This is clearly seen on comparing the stabilities of the nickel(II) complexes of the 17-membered rings L^4–L^6 (YN_2O_2-donor set) or L^{16}–L^{18} (YN_2S_2-donor set): each series spans a stability range of 10^6–10^7 as Y varies from NH, through S, to O. In this context it is noted that thermodynamic studies on nickel complexes of linear polyamines of the type $H_2NCH_2CH_2ZCH_2CH_2NH_2$ (for which Z = NH, O or S) indicate that the enhanced stability of the triamine complex derives primarily from an enhanced enthalpic contribution to binding by the NH group, relative to the complexes in which S or O donors are present.[23–25] Thus, co-ordination of the ether oxygen or thioether donors, with the concomitant displacement of water ligand(s), appears to be an endothermic process in the formation of these complexes.[25]

Thirdly, the stabilities of the respective metal complexes tend not to depend greatly on whether X = O or S. This is in accordance with the well documented weak donor capacity of ether and thioether groups towards most divalent, first-row transition-metal ions.[26,27] Affinities are expected to be even less in the present systems which contain aryl moieties adjacent to the X donor groups. However, it is noted that these donors are still sufficiently different to influence the configuration adopted by the macrocycle on co-ordination around five positions of octahedral nickel(II) (see later).

Fourthly, the dependence of metal complex stability on the size of the chelate rings formed by individual macrocyclic ligands is also apparent. As expected (if it is assumed that all donors co-ordinate), the complexes of L^1–L^3, L^{14} and L^{15} incorporating four-membered chelate rings tend to be less stable than the complexes of ligands (incorporating the same donor set) in which the corresponding chelate rings are five-membered (L^4–L^6, L^{16}, L^{17}). In turn, complexes of the latter ligands tend to be more stable than complexes of ligands in which the corresponding chelate rings are six- or seven-membered (L^{11}–L^{13}, L^{20}). It needs to be kept in mind that the overall macrocyclic ring size will also usually vary concomitantly with chelate ring size; this may in turn influence complex stability by restricting the number of possible conformations and/or configurations of the ligand about the central metal. The dislocation behaviour as reported previously for the nickel(II) complexes [and, to a less obvious degree, the cobalt(II) complexes] of the O_2N_3-donor ligand series (L^4, L^7 and L^8) appears to be associated with the 'sudden' release of ligand strain along the series of complexes.[5] While this might be

Table 4 Physical data for the nickel(II) complexes of selected macrocyclic ligands

			IR (cm^{-1})^c			Electronic spectra, λ/nm		
Complex	Λ^a/s cm^2 mol^{-1}	μ^b	ν(OH)	ν(NH)	Anion	Solid	Solution^d	m/z^e
$[Ni(NO_3)L^1]ClO_4 \cdot 3H_2O$	95	3.05	3460	3250, 3220	1030	360 (sh) 555 895	365 (25) 600 (13) 965 (10)	447
$[Ni(NO_3)L^{11}]ClO_4 \cdot C_2H_5OH \cdot H_2O$	117	3.16	3450	3270, 3260	1065	360 (sh) 550 985	365 (27) 585 (15) 965 (12)	489
$[Ni(NO_3)L^{14}]ClO_4 \cdot 3H_2O$	117	3.07	3600, 3520	3340, 3290	1090	345 (sh) 530 860	350 (22) 540 (6) 870 (6)	479
$[Ni(NO_3)L^{16}]ClO_4 \cdot C_2H_5OH \cdot 0.5H_2O^f$	134	3.13	3545	3380, 3245	1070	555 805 900	535 (8) 860 (5) 1015 (5)	493
$[NiL^{18}(H_2O)][NO_3]_2$	205	3.10	3360	3260		355 (sh) 590 1070	340 (sh) 615 (29) 870 (29) 1055 (10)	494

^{a} In methanol (23 °C). ^{b} At 23 °C. ^{c} Nujol mull. ^{d} In methanol; ε/dm^3 mol^{-1} cm^{-1} given in parentheses. ^{e} Positive-ion FAB mass spectral peak for $[ML(NO_3)]^+$. ^{f} The related species $[NiL^{16}(H_2O)][ClO_4]_2$ has recently been investigated by X-ray diffraction (ref. 15).

Table 5 Ligand protonation constants and stability constants for the complexes of cobalt(II) and nickel(II) with L^1–L^{20} [95% MeOH, I = 0.1 mol dm^{-3} (NEt_4ClO_4) at 25 °C]

	Free ligand			log $K_{ML}{}^a$ ($M^{2+} + L \rightleftharpoons ML^{2+}$)	
Ligand	log $K_1{}^H$	log $K_2{}^H$	log $K_3{}^H$	M = Co^{II}	Ni^{II}
L^1	9.38	8.27	2.3	6.1	8.3
L^2	8.31	7.12		b	≈3.0
L^3	8.95	7.91		<3.5	<3.5
L^4	9.69^c	8.45^c	2.0^c	7.7	10.0
L^5	8.64	7.39		≈3.3	5.5
L^6	8.67	7.68		<3.5	<3.5
L^7	10.05^c	8.22^c	3.73^c	7.3^d	9.8^d
L^8	10.33^c	8.36^c	5.59^c	5.1^d	≈6.2
L^9	10.24^c	7.84^c	4.42^c	>5.0^d	5.1^d
L^{10}	9.38	8.36		≈3.4	<3.5
L^{11}	9.56	8.32	2.4	7.3	9.7
L^{12}	8.91	7.68		≈3.4	b
L^{13}	9.13	8.01		≈3.5	3.5
L^{14}	8.96	6.86	1.9	5.5	8.4
L^{15}	7.82	6.52		<3.5	b
L^{16}	9.13	7.05	2.1	b	9.5
L^{17}	7.79	6.46		<3.5	<3.5
L^{18}	8.13	6.87		<3.5	≈3.4
L^{19}	10.28	7.37	5.31	≈3.4	5.7
L^{20}	7.91	6.70		<3.5	

^{a} Unless otherwise indicated, the error is estimated to be ±0.1 for each log K value. ^{b} Precipitation prevented usable data being obtained. ^{c} Value fron ref. 6. ^{d} Value from ref. 5 (95% MeOH, I = 0.1 mol dm^{-3}, NMe_4Cl).

considered to be primarily a function of macrocyclic ring size, the situation is unlikely to be quite this simple and contributions from a number of sources are also undoubtedly important.

Fifthly, the 'dislocation' study just mentioned gave log K values for the nickel(II) complexes of L^4 and L^8 in 95% methanol (with I = 0.1 mol dm^{-3} and NEt_4Cl as background electrolyte) which indicated that the complex of L^4 was a factor of about 10^4 more stable than the corresponding complex of L^8.[5] As expected, the values obtained in the present study (for which I = 0.1 mol dm^{-3} NEt_4ClO_4) (Table 5) confirm that this effect is essentially independent of the background electrolyte.

Sixthly, a related pattern to that just described is present when the ether oxygen donors of L^4 and L^8 are replaced by thioether donors to yield L^{16} and L^{19}; the nickel(II) complex of L^{16} is again a factor of about 10^4 more stable than the complex of L^{19}.

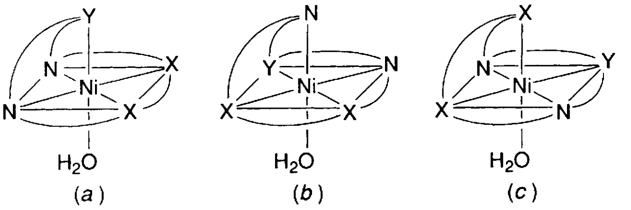
Finally, in the present study, a dislocation was not observed between the complexes of the 17- and 19-membered ring structures L^4 and L^{11} (in contrast with that which occurs between the complexes of L^4 and L^5). In this case, however, the 19-membered ring of L^{11} is achieved by increasing the number of methylene carbons between the oxygen donors rather than between the amine donors as in the case of L^8; the log K difference between the nickel complexes of L^4 and L^{11} is only about 0.3. This result supports the previous postulate[9] that the co-ordination geometries adopted by the O_2N_3-donor ligand series are largely associated with steric factors involving the chelate rings formed by the respective N_3 backbones.

Molecular Mechanics Study.—The force-field parameters for a wide range of low- and high-spin nickel(II) complexes of tetraaza macrocycles together with parameters for high-spin complexes of O_2N_2- and S_2N_2-donor macrocycles, based on a somewhat restricted number of X-ray structures, have been derived recently.[16,28,29] These prior results have now been used

Table 6 Bond distances (Å) and angles (°) involving nickel(II) in the X-ray structures and the structures calculated using molecular mechanics[a]

Distance	X-Ray	Calculated	Angle	X-Ray	Calculated
$[NiL^4(H_2O)][ClO_4]_2$[b]					
Ni–O(1a)	2.23	2.20	O(1a)–Ni–O(1b)	78	81
Ni–O(1b)	2.13	2.15	O(1a)–Ni–N(1a)	89	92
Ni–N(1a)	2.05	2.07	O(1b)–Ni–N(1b)	89	90
Ni–N(1b)	2.06	2.08	N(1a)–Ni–N(1b)	105	97
Ni–N(1c)	2.07	2.08	N(1a)–Ni–N(1c)	85	86
			N(1b)–Ni–N(1c)	85	86
			N(1c)–Ni–O(1a)	93	94
			N(1c)–Ni–O(1b)	101	98
$[NiL^{16}(H_2O)][ClO_4]_2$[c]					
Ni–N(1)	2.07	2.06	N(1)–Ni–N(2)	84	86
Ni–N(2)	2.08	2.07	N(1)–Ni–N(3)	100	100
Ni–N(3)	2.09	2.09	N(1)–Ni–S(1)	91	93
Ni–S(1)	2.40	2.42	N(2)–Ni–N(3)	82	85
Ni–S(2)	2.43	2.41	N(2)–Ni–S(2)	102	97
			N(3)–Ni–S(1)	93	93
			N(3)–Ni–S(2)	93	95
			S(1)–Ni–S(2)	84	85
$[NiL^{18}(H_2O)][NO_3]_2$[d]					
Ni–O(1c)	2.06	2.06	O(1c)–Ni–N(1a)	82	83
Ni–N(1a)	2.08	2.07	O(1c)–Ni–N(1b)	81	82
Ni–N(1b)	2.09	2.06	O(1c)–Ni–S(1b)	92	92
Ni–S(1a)	2.37	2.39	N(1a)–Ni–S(1a)	95	95
Ni–S(1b)	2.41	2.40	N(1a)–Ni–S(1b)	94	97
			N(1b)–Ni–S(1a)	101	100
			N(1b)–Ni–S(1b)	92	92
			S(1a)–Ni–S(1b)	88	85

[a] Atom labels correspond to those used originally for the X-ray structure determination. [b] Crystallographic *R* factor = 0.073 (ref. 8). [c] Crystallographic *R* factor = 0.085 (ref. 15). [d] Crystallographic *R* factor = 0.051 (this work).



(*a*) (*b*) (*c*)

Fig. 2 The three configurational isomers investigated by molecular mechanics: (*a*) facial **I**, (*b*) facial **II** and (*c*) meridonal

as a basis for the development of a provisional force-field parametrisation for use in calculations involving nickel(II) complexes of the present macrocycles. Further refinement of the force field for these pentadentate systems was limited by the availability of only three X-ray structures. As well as the structural data for the nickel(II) complex of the ON_2S_2-donor ligand L^{18} discussed above, previously determined data for the corresponding complexes of the O_2N_3- and S_2N_3-donor ligands, L^4 and L^{16},[8,15] were also available. It is noted that particular parameters from those developed previously proved satisfactory for use in modelling the present species without modification.

Inspection of molecular models (Drieding) indicated that three major isomers appeared likely for the 17-membered ring complexes of L^4, L^{16} and L^{18}. These are illustrated in Fig. 2 and, interestingly, each arrangement corresponds to that in one of the X-ray structures mentioned above. The starting co-ordinates for the respective molecular mechanics calculations were either the X-ray coordinates themselves or were generated by modification of the appropriate set of X-ray coordinates.

The nickel to donor atom bond distances as well as the angles about nickel for the calculated structures and the corresponding X-ray structures are presented in Table 6. The co-ordination sphere is modelled reasonably well in each complex.

The total strain energies for the three geometric isomers of each of the three complexes are listed in Table 7 and overall data describing the respective 'fits' of individual isomers to the X-ray structures are given as footnotes to this table (torsional angles involving bond angles above 170° were not included in the analysis since they are usually associated with an unrealistically high error).[28]

As already discussed, in our previous study it was proposed that the difference in the stability of the nickel(II) complexes of the 17-membered macrocyclic ligand L^4 and its 19-membered analogue L^8 arises from a 'structural dislocation'.[9] For the complex of L^4 the X-ray study shows that the three amine donors are arranged facially (and this arrangement was postulated to be maintained in solution) while it was proposed that, for the complex of L^8, the amine donors are arranged meridionally. The present molecular mechanics study of the 17-membered ring complex (of L^4) indicates that the facial isomer observed in the X-ray investigation appears indeed to be preferred over the second facial or the meridional isomer (Table 7) even though the calculated energy difference between the two facial forms is small. Similarly, the calculations predict that the corresponding complex of L^{18} will have its meridional isomer as the lowest-energy form and this isomer is also the one found to occur in the solid state. For the complex of L^{16} the calculations predict that the lowest-energy isomer will also be the meridional form. However, the X-ray structure shows that the complex is in fact facial **II** in the solid state. Nevertheless, the apparent strain-energy difference between the meridional and facial **II** forms is not great (at approximately 6.5 kJ mol^{-1}) and this difference may not be significant given the approximate nature of the present calculations.

Previously we have demonstrated that energy differences between isomeric metal complexes can be quite dependent on relatively minor changes in the force field employed.[16,28] Further, with respect to the above result, it is important to keep

Table 7 Relative strain energies of facial and meridional isomers of the nickel(II) complexes of L^4, L^{16} and L^{18}

Structure	Geometric isomer	Relative[a] strain energy (kJ mol^{-1})
$[NiL^4(H_2O)]^{2+}$	Facial **I**	0.0[b,c]
	Facial **II**	3.6
	Meridional	12.8
$[NiL^{16}(H_2O)]^{2+}$	Facial **I**	17.5
	Facial **II**	6.5[b,d]
	Meridional	0.0
$[NiL^{18}(H_2O)]^{2+}$	Facial **I**	18.3
	Facial **II**	11.2
	Meridional	0.0[b,e]

[a] Relative to the lowest-energy isomer. [b] Geometry observed in X-ray structure. [c] An earlier study (ref. 8) based on the modified MM1 force field also gave the same relative order for the facial **I** and meridional isomers while this order was reversed for the corresponding isomers incorporating the dimethylated derivative, L^{21}, a result which was confirmed on use of the present (updated) force field. Total bond distance root mean square (r.m.s.) differences = 0.019 Å, total bond angle r.m.s. differences = 2.7°, total torsional angle r.m.s. differences = 4.7°. [d] Total bond distance r.m.s. differences = 0.033 Å, total bond angle r.m.s. differences = 2.4°, total torsional angle r.m.s. differences = 5.5°. [e] Total bond distance r.m.s. differences = 0.025 Å, total bond angle r.m.s. differences = 1.7°, total torsional angle r.m.s. differences = 5.9°.

in mind two general limitations of the molecular mechanics method for determining the strain energies of metal complexes of the present type. First, there is an absence of proper thermodynamic calibration for those parts of the structures associated with the metal ion and the calculated energy differences between corresponding isomers will be, at best, only semiquantitative. Secondly, the calculated steric energies refer to gas-phase structures and intermolecular interactions, such as those arising from crystal packing, are not taken into account.

In summary, it is clear that molecular mechanics calculations on metal-containing systems of the present type are useful for predicting likely complex structures (and hence for ligand design) provided appropriate caution is exercised when interpreting small differences in the calculated strain energies between particular isomers.

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