Intramolecular Hydrogen-bond Formation in Nickel(II) Complexes with Macrocyclic Ligands containing Non-co-ordinating Nitrogen Atom(s): New Ditopic Receptors differentiating Hydrogensulfate and Hydrogenphosphates†

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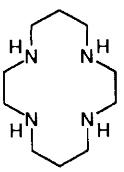
A comparative study of a series of nickel(II) complexes with structurally related tetradentate 14-membered tetra-, penta- and hexa-aza macrocycles has shown that the non-co-ordinating (remote) nitrogen atoms in the ligand backbones drastically influence the solution equilibria between the four- and six-co-ordinated forms of the complexes. This phenomenon is interpreted in terms of the formation of intramolecular, along with co-ordinative, hydrogen bonds between the axial ligand and remote nitrogen. Such specific two-centred interactions result in relatively high formation constants of mono(hydrogensulfate) complexes $[NiL(HSO_4)(H_2O)]^+$. For the tricyclic complex, with L = 1,3,6,9,11,14-hexaazatricyclo$[12.2.1.1^{6,9}]$octadecane, the formation of both mono- and bis-(hydrogensulfate) adducts has been detected with $K_1 = 7 \pm 1$ and $K_2 = 36 \pm 5$ dm^3 mol^{-1}, thus indicating the allosteric effect in this system. The high differentiating effect for hydrogensulfate *versus* hydrogenphosphates, which is especially evident for the tricyclic complex, has been established.

Polytopic molecules (receptors) which are able to participate in multipoint (in the simplest case, two-point) binding of additional species (substrates) in supramolecular complexes are very suitable objects for study of the selectivity of intermolecular interactions. A rich variety of such ditopic receptors has been synthesized to date (see, for example, refs. 1 and 2), among which macrocyclic compounds play an important role.[1,3–8]

As a rule, two types of relatively strong non-covalent interactions, co-ordinative[3,4] or hydrogen[5] bonds, are exploited in these systems as the driving forces causing the formation of receptor–substrate complexes. Macrocyclic receptors interacting with substrates *via* both these types of bonding *simultaneously* are rather limited in number.[6–8] As the substrates for such receptors, the amino acids and their derivatives,[6b,c] ammonium and hydrazonium salts,[6c,7a] nucleobases,[7b] urea[8] or chloride[7c] have been investigated.

Complexes of 14-membered penta- and hexa-aza macrocycles possessing non-co-ordinated sp^3-hybridized nitrogen atom(s) [so-called remote or distal nitrogen(s)[9]] may also be considered as potentially ditopic receptor systems. It is reasonable to expect that such distal atoms could form hydrogen bonds with additional molecules (*i.e.* substrates) occupying axial positions in the co-ordination sphere of the metal, thus realizing a two-point attachment of the substrate. To elucidate this possibility, a comparative study of axial ligation of the series of tetragonal nickel(II) complexes with structurally related macrocycles L^1–L^6‡ differing in the number and in the chemical nature of the distal nitrogen atoms, as well as in the ligand conformations in the complexes, was undertaken. Our preliminary results on the behaviour of $[NiL]^{2+}$ ($L = L^1$–L^4) in perchlorate- and sulfate-containing acidic solutions[10] as well as the data of other authors concerning $[NiL^1]^{2+}$ and $[NiL^3]^{2+}$ in perchloric and hydrochloric acids[11] have been communicated previously.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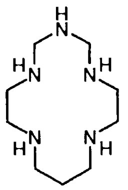
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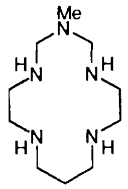
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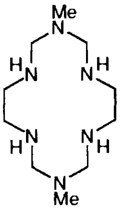
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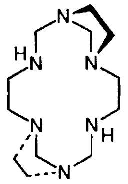
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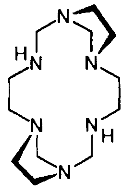
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Results and Discussion

Absorption Spectra and Spin Equilibria in Organic Solvents and Neutral Aqueous Solutions.—The absorption spectra of the complexes both in neutral aqueous solutions and in organic solvents are very similar (Table 1) and typical of square-planar low-spin nickel(II) species with equatorially co-ordinated tetradentate macrocycles.[12] Two main conclusions can be

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† *Supplementary data available:* (No. SUP 57094, 5 pp.): pH dependence of molar absorption coefficients of the complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

‡ Abbreviations used: L^1 = 1,4,8,11-tetraazacyclotetradecane (cyclam); L^2 = 1,3,5,8,12-pentaazacyclotetradecane; L^3 = 3-methyl-1,3,5,8,12-pentaazacyclotetradecane; L^4 = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane; L^5 and L^6 = 1,3,6,9,11,14-hexaazatricyclo$[12.2.1.1^{6,9}]$octadecane.

Table 1 d–d Absorption bands (10^{-3} $\tilde{\nu}/cm^{-1}$, $\varepsilon_{eff}/dm^3\ mol^{-1}\ cm^{-1}$) for the nickel(II) complexes

	Solvent		
Complex	$MeNO_2$	Water*	MeCN
$[NiL^1]^{2+}$	22.0 (62)	22.2 (48)	21.8 (18)
$[NiL^2]^{2+}$	22.1 (65)	22.2 (57)	21.8 (20)
$[NiL^3]^{2+}$	22.1 (60)	22.3 (50)	21.7 (21)
$[NiL^4]^{2+}$	22.3 (59)	22.2 (41)	22.0 (26)
$[NiL^5]^{2+}$	22.4 (80)	22.6 (73)	22.3 (75)
$[NiL^6]^{2+}$	22.4 (120)	22.0 (115)	21.8 (110)

* $I = 0.1$ mol dm^{-3} $NaClO_4$, pH $\approx$ 5.

drawn from these data. (*i*) The similarity of the spectrochemical characteristics, at least for the four monocyclic complexes $[NiL]^{2+}$ ($L = L^1$–L^4), indicates similar conformations for the co-ordinated macrocycles. Most likely, it is the most thermodynamically stable one with the *R,R,S,S* (*trans*-III) configuration of the co-ordinated nitrogen atoms.[13] This suggestion is in accordance with the molecular structure of $[NiL^3][ClO_4]_2$[11] and several derivatives of $[NiL^4][ClO_4]_2$.[14] The higher values of the molar absorption coefficient ε for the tricyclic complexes $[NiL^5]^{2+}$ and $[NiL^6]^{2+}$ seem to be caused by the lower symmetry of the chromophores arising from the rigidity of the ligand.[15,16]

(*ii*) The nature of the solvent strongly influences the value of ε for the d–d band at *ca.* 22 000 cm^{-1}, attributable to the low-spin nickel(II) species. It is well documented[12a,17] that this effect is caused by the formation of paramagnetic six-co-ordinated nickel(II) [equation (1)] since the absorbance of high-spin forms

$$\underset{\text{low-spin}}{\underset{\text{four-co-ordinated}}{[NiL]^{2+}}} + 2\,\text{solv} \xrightleftharpoons{K^{(\text{solv})}} \underset{\text{high-spin}}{\underset{\text{six-co-ordinated}}{[NiL(\text{solv})_2]^{2+}}} \quad (1)$$

at this wavenumber is an order of magnitude lower. Assuming that the value of ε_{eff} in nitromethane corresponds to the pure low-spin form,[14b,15a] the equilibrium constants in acetonitrile can be estimated from $K^{MeCN} = (\varepsilon^{MeNO_2} - \varepsilon^{MeCN})/\varepsilon^{MeCN}$. The following sequence reflecting the increasing affinity of the complexes towards acetonitrile as axial ligand can be obtained: $[NiL^6]^{2+} \approx [NiL^5]^{2+} \ll [NiL^4]^{2+} < [NiL^3]^{2+} < [NiL^2]^{2+} < [NiL^1]^{2+}$. Based on a more rigorous treatment of spectral data, quite analogous series may be constructed for neutral aqueous solutions, though the equilibrium constants in this medium are essentially lower [$K^{(H_2O)} < 0.5$].[18] It is well established[12] that the conversion of the nickel ion from its low- to high-spin form is accompanied by considerable (up to 0.2 Å) lengthening of the Ni–N distances. Thus, the lower tendency of $[NiL^5]^{2+}$ and $[NiL^6]^{2+}$ to axial ligation may be the consequence of the greater energy consumption needed for the rearrangement of the rigid tricyclic ligand as compared with flexible monocyclic ones.

Spin Equilibria in Acidic Aqueous Solutions.—As already noted, the complexes under study are predominantly four-co-ordinated in neutral aqueous solutions. From our, as well as from the literature,[11] data it follows that $[NiL^1]^{2+}$ displays such behaviour also in strongly acidic solutions. However, for the complexes with distal nitrogen atom(s), increasing the acidity of the solutions results in a decrease in ε_{eff} of the band at 22 000 cm^{-1} and the appearance of new bands typical of six-co-ordinated nickel(II) complexes (Fig. 1). These spectral changes are fully reversible upon readjustment of pH, with two isosbestic points in the visible region. Thus, we can conclude that the formation of the high-spin form of nickel(II) is connected with acid–base equilibria. The only group able to participate in such equilibria is the distal amine and its unusually low pK_a value (*ca.* 1, see Fig. 2) can be explained by electrostatic effects (see also ref. 11).

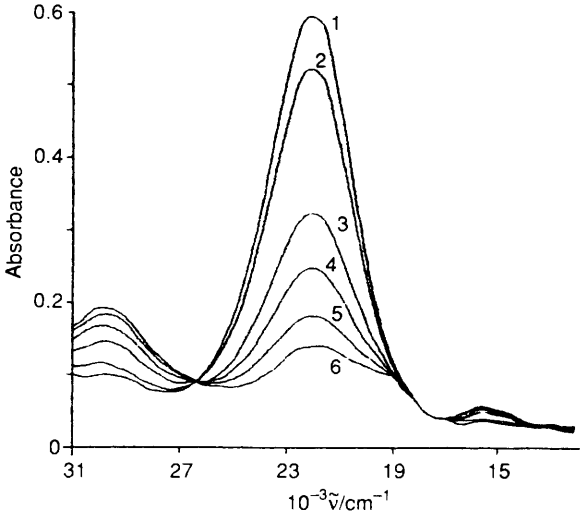

Fig. 1 Spectra of $[NiL^3][ClO_4]_2$ in aqueous solution at different pH values; 2.7 × 10^{-3} mol dm^{-3} complex, 0.2 mol dm^{-3} Na_2SO_4, l = 5 cm. pH 5.0 (1), 3.3 (2), 2.5 (3), 2.2 (4), 1.9 (5) and 0.7 (6)

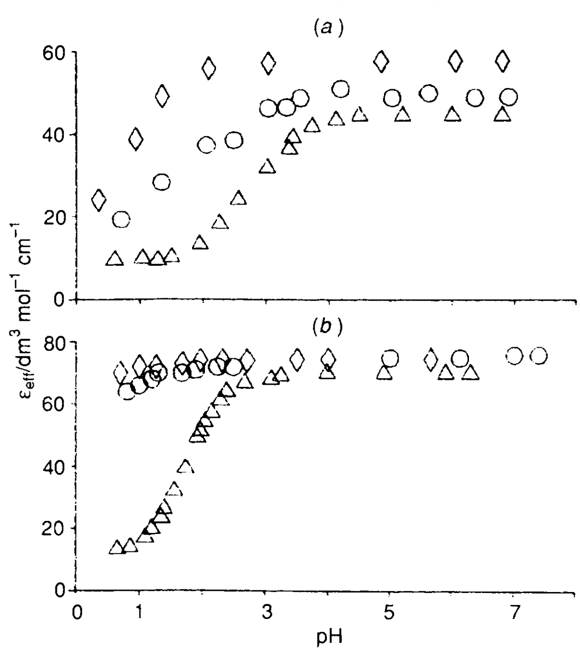

Fig. 2 Variation of the effective molar absorption coefficient ε_{eff} with pH at 22 °C for $[NiL^3]^{2+}$ (*a*) and $[NiL^5]^{2+}$ (*b*) in 0.5 mol dm^{-3} perchlorate (◇); 0.2 mol dm^{-3} sulfate (△) and 0.15 mol dm^{-3} phosphate media (○)

On the other hand, the data obtained show that the positions of the inflection points in the plots of ε_{eff} *vs.* pH do not depend on the electrolyte used (perchlorate, chloride, bromide, nitrate) except with sulfate and phosphate (see below). This behaviour clearly indicates the non-participation of anions in the formation of high-spin species so that only water molecules must be regarded as potential ligands. In our opinion, the structure schematically depicted in Fig. 3(*a*) may be assigned to the high-spin complexes and the equilibria occurring must be written as in equation (2).

$$[NiL]^{2+} + 3H_2O + H^+ \rightleftharpoons [Ni(HL)(H_2O)_2{\cdot}H_2O]^{3+} \quad (2)$$

The data obtained show that the nickel complexes with the

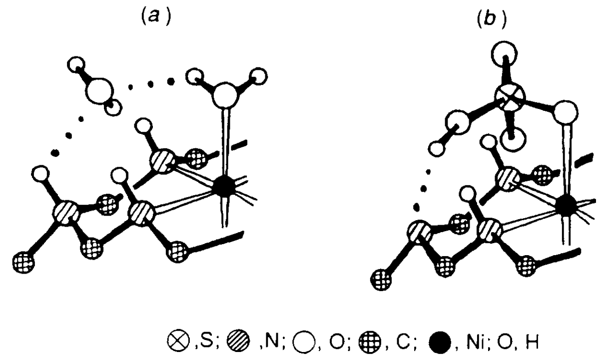

Fig. 3 Schematic representation of the co-ordination and hydrogen-bond geometry proposed for the six-co-ordinated nickel(II) complexes (only one distal nitrogen atom is shown; the second axial position in the co-ordination sphere of the metal ion is occupied by a water molecule; CH hydrogens are omitted for clarity)

tricyclic ligands, $[\mathrm{NiL^5}]^{2+}$ and $[\mathrm{NiL^6}]^{2+}$, are little prone to formation of high-spin species even in strongly acidic solutions. Most likely, protonation of the distal nitrogen takes place in these systems too, but is not accompanied by formation of high-spin forms since either the spatial directions of the nitrogen lone pairs are unfavourable for the formation of the network of intramolecular hydrogen bonds or the enthalpy gain owing to formation of the network does not compensate for the loss in ligand reorganization energy.

Significant displacement of the $\varepsilon_{\mathrm{eff}}$ *vs.* pH curves in sulfate-containing solutions as compared with those containing other anions unambiguously indicates the participation of sulfate in the formation of high-spin species. Taking into account its second protonation constant (1.30 at ionic strength $I = 0.6$ mol dm^{-3})[19] and the fact that the content of the six-co-ordinated species increases with increasing sulfate concentration at constant pH and I,[10] it must be assumed that the interconversion of nickel(II) from the low- into the high-spin form is connected with the co-ordination of hydrogensulfate* [equations (3a) and (3b)]. The lack of such an interaction for

$$[\mathrm{NiL}]^{2+} + \mathrm{HSO_4}^- + \mathrm{H_2O} \overset{K_1^{(\mathrm{HSO_4})}}{\rightleftharpoons} [\mathrm{NiL(HSO_4)(H_2O)}]^+ \quad (3a)$$

$$[\mathrm{NiL(HSO_4)(H_2O)}]^+ + \mathrm{HSO_4}^- \overset{K_2^{(\mathrm{HSO_4})}}{\rightleftharpoons} [\mathrm{NiL(HSO_4)_2}] + \mathrm{H_2O} \quad (3b)$$

$[\mathrm{NiL^1}]^{2+}$ suggests a crucial role of the distal nitrogen in such equilibria, and the specific mechanism of hydrogensulfate binding may involve a two-centre interaction, *i.e.* with metal ion and remote nitrogen [Fig. 3(*b*)].

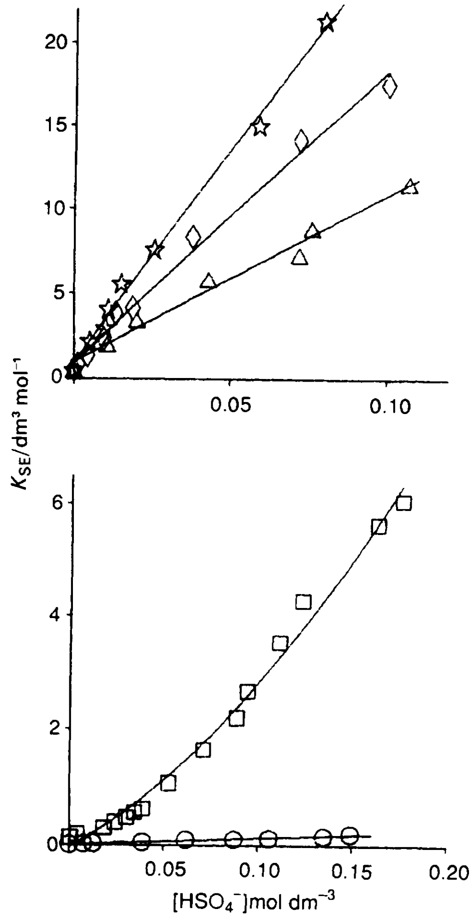

Fig. 4 Plot of K_{SE} *vs.* hydrogensulfate concentration for $[\mathrm{NiL^2}]^{2+}$ (☆), $[\mathrm{NiL^3}]^{2+}$ (△), $[\mathrm{NiL^4}]^{2+}$ (◇), $[\mathrm{NiL^5}]^{2+}$ (□) and $[\mathrm{NiL^6}]^{2+}$ (○) at 22 °C in 0.2 mol dm^{-3} sulfate-containing solution

It is obvious that the strongest hydrogen bond between a distal nitrogen and an axial ligand will be formed when the fragment O–H ⋯ :N (or O: ⋯ H–N) is approximately linear, *i.e.* with an axially orientated lone pair in a six-membered chelate ring. Despite the fact that the limited X-ray data for nickel complexes of this type indicate equatorial directivity of the lone pairs,[11,14,20] this does not present an impenetrable barrier to the formation of, though weaker, hydrogen bonds with distal nitrogen, and our data concerning the behaviour of $[\mathrm{NiL^5}]^{2+}$, in which the lone pairs are strictly equatorial,[15,16] confirm such a suggestion.

Evidence in support of the existence of the structure depicted in Fig. 3(*b*), at least for monocyclic complexes, is provided by the values of $K_1^{(\mathrm{HSO_4})}$. Assuming that the values of $\varepsilon^{\mathrm{hs}}$ are very similar for all kinds of high-spin species present simultaneously in solution (this seems quite reasonable in the light of their analogous *trans*-$\mathrm{NiN_4O_2}$ chromophores), it is easily shown that the value of $\varepsilon_{\mathrm{eff}}$, and thereby K_{SE} [where K_{SE} is a cumulative parameter reflecting the equilibria (1) and (3), see Experimental section], is determined by three terms [equation (4)]. Linear

$$K_{\mathrm{SE}} = K^{(\mathrm{H_2O})} + K_1^{(\mathrm{HSO_4})}[\mathrm{HSO_4}^-] + K_1^{(\mathrm{HSO_4})}K_2^{(\mathrm{HSO_4})}[\mathrm{HSO_4}^-]^2 \quad (4)$$

plots of the K_{SE} *vs.* hydrogensulfate concentration were constructed based on the dependences of $\varepsilon_{\mathrm{eff}}$ on pH (Fig. 4). They gave the values $K_1^{(\mathrm{HSO_4})} = 249 \pm 5$, 95 ± 4, 165 ± 6 and *ca.* 1 dm^3 mol^{-1} for $[\mathrm{NiL^2}]^{2+}$, $[\mathrm{NiL^3}]^{2+}$, $[\mathrm{NiL^4}]^{2+}$ and $[\mathrm{NiL^6}]^{2+}$, respectively. The only system displaying non-linearity of the K_{SE} *vs.* $[\mathrm{HSO_4}^-]$ plot, thus indicating a

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* As was mentioned by a referee, the effect observed may be treated as being induced by interaction of $[\mathrm{Ni(HL)}]^{3+}$ with $\mathrm{SO_4}^{2-}$ giving $[\mathrm{Ni(HL)(SO_4)(H_2O)}]^+$. However, from a thermodynamic point of view it is not relevant which mechanism results in the formation of high-spin species, either co-ordination of the hydrogensulfate to the dicationic four-co-ordinated complex or 'compulsory' protonation of distal nitrogen in the six-co-ordinated sulfate complex. If the species $[\mathrm{Ni(HL)(SO_4)(H_2O)}]^+$ $[K_1^{(\mathrm{SO_4})}]$ and $[\mathrm{NiL(HSO_4)(H_2O)}]^+$ $[K_1^{(\mathrm{HSO_4})}]$ are treated as one, it is easy to show that a simple relationship holds, $K_1^{(\mathrm{SO_4})} = K_1^{(\mathrm{HSO_4})}(K_{\mathrm{p}}^{\mathrm{SO_4}}/K_{\mathrm{p}}^{\mathrm{complex}})$, where $K_{\mathrm{p}}^{\mathrm{SO_4}}$ and $K_{\mathrm{p}}^{\mathrm{complex}}$ are the corresponding protonation constants. However, we believe that the lack of co-ordination of any form of phosphate, especially in neutral solutions where the electrostatic interaction $[\mathrm{NiL}]^{2+} \cdots \mathrm{PO_4}^{3-}$ must be the same as $[\mathrm{Ni(HL)}]^{3+} \cdots \mathrm{SO_4}^{2-}$, clearly indicates that the formation of an intramolecular hydrogen bond is the driving force for anion co-ordination.

measurable contribution from equilibrium (3b), is $[NiL^5]^{2+}$. Regression analysis for this complex gave the values $K_1^{(HSO_4)} = 7 \pm 1$ dm^3 mol^{-1} and $K_1^{(HSO_4)}K_2^{(HSO_4)} = 244 \pm 5$ dm^6 mol^{-2}. Though these constants in themselves are not very large, they seem rather high in the light of the very reduced tendency of a square-planar nickel(II) ion in a 14-membered tetraaza macrocyclic environment to bind axially oxo anions in aqueous solutions.[12a,17] To our knowledge, such constants have not been reported.

Most likely, the differences in equilibrium constants depending on the number (*cf.* $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$) and the nature (*cf.* $[NiL^2]^{2+}$ and $[NiL^3]^{2+}$) of the distal nitrogen atoms can be explained on a statistical basis. The probability of forming the structure in Fig. 3(*b*) for $[NiL^4]^{2+}$ must be twice that for $[NiL^3]^{2+}$ and this corresponds well with the 50% lower value of $K_1^{(HSO_4)}$ in the latter case. On the other hand, the orientation of the lone pair in $[NiL^2]^{2+}$ has little effect because the exchange of protons at the secondary nitrogen atom is very fast and both limiting conformers can readily form the hydrogen-bond structures. Assuming all other factors to be the same, one would expect similar values of $K_1^{(HSO_4)}$ for $[NiL^2]^{2+}$ and $[NiL^4]^{2+}$. However, the *ca.* 1.5 times larger value in the former case may reflect the different energetics of hydrogen bonding with participation of either secondary *vs.* tertiary nitrogen groups or axial *vs.* equatorial lone pairs on distal nitrogen, or both.

Comparison of the data for the two closely related systems, $[NiL^4]^{2+}$ and $[NiL^5]^{2+}$, reveals two essential differences between them. The first is a much weaker interaction with HSO_4^- of the tricyclic complex as compared with the monocyclic analogue. Presumably, the loss in free energy upon axial ligation (*cf.* $\Delta G^\circ = -12.5$ and -4.5 kJ mol^{-1} for $[NiL^4]^{2+}$ and $[NiL^5]^{2+}$, respectively) is connected with the enthalpic term, although it is difficult to decide what factor, either a weaker hydrogen bond when the lone pair is strictly equatorial or greater energy consumption needed for rearrangement of a more rigid macrocycle, is responsible for this free-energy difference.

The second difference is the lack of formation of bis(hydrogensulfate) complexes for $[NiL^4]^{2+}$ in contrast to $[NiL^5]^{2+}$, at least in the concentration ranges studied.* Moreover, some sort of allostery is observed for $[NiL^5]^{2+}$ [$K_2^{(HSO_4)} = 36$ dm^3 mol^{-1} is greater than $K_1^{(HSO_4)} = 7$ dm^3 mol^{-1}]. This may be connected with the rigidity of the tricyclic compound L^5. The energy which is needed for the rearrangement of *both* six-membered chelate rings in L^5 is consumed during the addition of the first axial ligand, so that the second hydrogensulfate co-ordinates to an already reorganized complex molecule. This effect would be the smaller the more flexible is the ligand molecule.

Additional comments are merited on the behaviour of the complexes in solutions containing phosphate ions. Considering the very similar structural parameters of sulfate and phosphate[21] and identical charges of HSO_4^- and $H_2PO_4^-$, the formation of high-spin species in phosphate media should be observed at higher, closer to neutral, pH values because the maximum content of $H_2PO_4^-$ ions in solution is reached at pH *ca.* 7.[22] However, this is not the case and the behaviour of the monocyclic complexes in phosphate-containing media is intermediate between those in perchlorate- and sulfate-containing ones (Fig. 2).

Furthermore, this difference is very pronounced for tricyclic $[NiL^5]^{2+}$ which exhibits negligible interaction with any forms of phosphate. We believe that this effect is related to the different stereochemical characteristics of the anions under consideration. From *ab initio* calculations,[23] the dihedral angle in O–P–O–H and O–S–O–H fragments differs by 46° and this can prevent simultaneous formation of co-ordination and hydrogen bonds between nickel complexes and $H_2PO_4^-$, especially in rigid systems with equatorial lone pairs. To our knowledge, $[NiL^5]^{2+}$ represents the first example of a low-molecular-weight metallocomplex system exhibiting efficient differentiation between sulfate and phosphate.

Thus, the results obtained show that the non-co-ordinating nitrogen atoms in the backbones of the macrocycles play not only an architectural role but also influence the axial interaction of the metal ion with additional ligands due to the formation of intramolecular hydrogen bonds. Macrocyclic complexes of a given type may be regarded as new ditopic receptors capable of differentiating between anions having very similar spatial characteristics. In addition, recent results have demonstrated the essential influence of such ligand structural features on the oxidation of nickel(II) complexes,[24,25] their catalytic properties in the electroreduction of carbon dioxide[9b] and the stabilization of tervalent nickel in aqueous solutions.[26] In all the above-mentioned cases the binding and positioning of the reagents near the metal centre as a result of hydrogen-bond formation with the non-co-ordinated amino group can be suggested.

Experimental

Reagents.—All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The solvents for spectroscopic measurements were purified according to literature methods.[27] The complexes $[NiL^1][ClO_4]_2$,[28] $[NiL^2][ClO_4]_2\cdot0.5EtOH$,[29] $[NiL^3][ClO_4]_2$,[30,31] $[NiL^4][ClO_4]_2$,[31] $[NiL^5][ClO_4]_2$[15] and $[NiL^6][ClO_4]_2$[16] were prepared as described. **CAUTION**: Some of the compounds containing perchlorate anions are potentially explosive and should be handled with care.

Instrumentation.—Electronic absorption spectra were recorded on a Specord M-40 (Carl Zeiss, Jena) spectrophotometer. An OP-213 pH-meter (Radelkis, Budapest) was used for pH measurements. The pH of the solutions was adjusted with $HClO_4$, HNO_3, H_2SO_4 or NaOH. Ionic strength was maintained by $NaClO_4$ or Na_2SO_4.

Thermodynamic Measurements.—All thermodynamic measurements were carried out spectrophotometrically in a thermostatted (22.0 ± 0.1 °C) quartz cell. Only freshly prepared solutions of complexes were used. The equilibrium constants for the four-co-ordinate–six-co-ordinate interconversion of the nickel complexes in acidic sulfate solutions were determined using the values of the effective molar absorption coefficients ε_{eff} of the band near 22 000 cm^{-1}, according to equation (5) where ε^{ls} and ε^{hs} are the molar absorption

$$K_{SE} = (\varepsilon^{ls} - \varepsilon_{eff})/(\varepsilon_{eff} - \varepsilon^{hs}) \qquad (5)$$

coefficients at this wavenumber of the four- (low-spin) and six- (high-spin) co-ordinated forms, respectively. Nickel(II) complexes in nitromethane are completely in the square-planar form[14b,31] and the value of ε^{ls} is weakly dependent on the nature of the solvent.[12] Since 100% content of high-spin forms in solution was not reached, the values of ε^{hs} were calculated through iterative resolution of the experimental spectra. In all cases values equal to 6.0 dm^3 mol^{-1} cm^{-1} were obtained. In general, spectral changes caused by variations of the pH of aqueous solutions are very similar for all the penta- and hexaaza macrocyclic complexes and a typical example is shown in Fig. 1. Analogously, only selected plots of ε_{eff} *vs.* pH are presented in Fig. 2. The complete set of these data is available as SUP 57094.

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* Unfortunately, we were unable to exceed *ca.* 0.1 mol dm^{-3} HSO_4^- in solutions of $[NiL^4]^{2+}$ because of the formation of precipitates, irrespective of what acid ($HClO_4$, HNO_3 or H_2SO_4) was used to adjust the pH. This can indicate the formation of sparingly soluble neutral $[NiL^4(HSO_4)_2]$, and is currently being examined in our laboratory.

Acknowledgements

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