Selectivity of Tetra-aza Macrocycles towards Metal Spin States. The High-spin–Low-spin Equilibrium for Nickel(II) Complexes with 13- and 14-Membered Ligands

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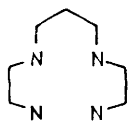
Nickel(II) complexes with 13- and 14-membered tetra-aza macrocycles exist in aqueous solution as an equilibrium mixture of a blue high-spin and a yellow low-spin species: the blue-to-yellow conversion is endothermic and predominance of the yellow form stems from a large positive entropy term, due to the release of two or more water molecules. The energy of the in-plane Ni–N interactions for low-spin complexes with 12- to 15-membered macrocycles is related to the size of the aperture in the cyclic ligand.

TETRAGONAL nickel(II) complexes with multidentate amine ligands can be either paramagnetic or diamagnetic according to their stereochemical features.[1] The high-spin form, normally *blue*, has distorted octahedral geometry, four co-ordination sites being occupied by amine nitrogen atoms, preferably coplanar, and the remaining two by appropriate counter ions (in the solid state) or solvent molecules (in solution). In the *yellow* low-spin form the nitrogen atoms are coplanar giving a square stereochemistry. Spin pairing also involves a reduction in the Ni–N bond distance (Ni–N for high spin, 2.10; low spin, 1.90 Å). For a given complex, the octahedral and the square-planar forms are in equilibrium [Scheme 1, where L represents a quadridentate amine].

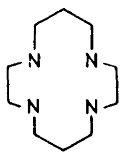
$$\underset{\text{blue, high spin}}{[\mathrm{NiL(OH_2)_2}]^{2+}} \rightleftharpoons \underset{\text{yellow, low spin}}{[\mathrm{NiL}]^{2+} + 2\mathrm{H_2O}}$$

SCHEME 1

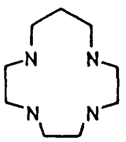
For instance, when L is the linear tetramine L^1, 77% of the blue high-spin and 23% of the yellow low-spin species are present at equilibrium, at 25 °C and in 0.1 mol dm^{-3} Na[ClO$_4$].[2] The reaction in Scheme 1 is *endothermic* and displaced to the right by either an increase in temperature or by an increase of the concentration of inert salt.[3] The thermodynamic parameters associated with Scheme 1 have been determined for a series of linear tetramines of various lengths [2,4] and have been interpreted in terms of several contributions: the change of metal–nitrogen bond enthalpy, the breaking of Ni–OH$_2$ bonds, and the variations in the number of particles.



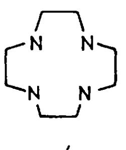
L^1



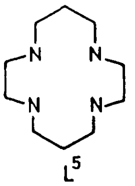
L^2



L^3



L^4



L^5

It has recently been shown that complexes with cyclic tetramines also give rise to equilibrium mixtures of blue and yellow species in aqueous solution.[4,5] For these complexes the cyclic nature of the ligand introduces another factor which can affect the position of equilibrium in Scheme 1, namely the nature of the match between the size of the encircled nickel(II) ion (high or low spin) and the hole in the macrocyclic ligand. In fact, among the tetra-aza macrocycles, the 14-membered ligand L^2 should have the most appropriately sized aperture for a high-spin nickel(II) ion: the ideal M–N distance corresponding to a complex in which the macrocyclic ligand is in its minimum energy configuration with all four nitrogen atoms coplanar (2.07 Å) [6] is identical with the Ni–N distance found in the structure of [Ni(L^2)Cl$_2$] in its blue high-spin form.[7] On the other hand, for low-spin complexes, in which the average Ni–N distance is 1.89 ± 0.03 Å (evaluated from a series of square-planar tetramine complexes [8–10]) the most appropriate ligand would be the 13-membered L^3, for which the ideal M–N distance is 1.92 Å.[6]

Therefore, a comparison of the solution spin equilibria for nickel(II) complexes with L^2 and L^3 will permit the evaluation from a thermodynamic standpoint of the effect of the size of the macrocyclic hole on the ligand preference for the larger (high-spin) or smaller (low-spin) nickel(II) ions. The thermodynamic parameters for the [Ni(L^2)]$^{2+}$ blue-to-yellow interconversion have been previously reported.[4,5] I have now synthesized the [Ni(L^3)]$^{2+}$ complex and report here a thermodynamic study of its solution behaviour. The relationship between the energy of the Ni–N in-plane interactions (spectroscopically evaluated) for low-spin complexes of 12- to 15-membered macrocycles is presented and discussed.

It should be remembered that several naturally occurring ring systems contain metal ions as macrocyclic complexes (*e.g.* in porphyrins and corrins) and that a given spin state is often essential for their functional behaviour.

EXPERIMENTAL

Synthesis of 1,4,7,10-*Tetra-azacyclotridecane* (L^3).—The preparation is based on the condensation of the appropriate tosylated segments according to a general method previously outlined.[11] Synthesis of (a) and (b), as well as detosylation of (c), was carried out as follows.

NN′N″-*Tris(toluene-p-sulphonyl)-3-azahexane-*1,6-*diamine*. An ether solution of toluene-*p*-sulphonyl chloride (tosyl chloride) (Erba RPE, Milan) [100 g, 0.52 mol; in diethyl ether (525 cm^3)] was added dropwise to a cold vigorously stirred solution of 3-azahexane-1,6-diamine (EGA Chemie) (21.3 g, 0.17 mol) and sodium hydroxide (21.0 g, 0.52 mol) in water (170 cm^3). The addition was completed in 6 h and followed by stirring for 1 h. The white precipitate was recrystallized from a large volume of ethanol, yield 82% (Found: C, 53.5; H, 5.85; N, 7.05. Calc. for $C_{26}H_{33}N_3O_6S$: C, 53.85; H, 5.75; N, 7.25%).

The disodium salt of NN′N″-*tris(toluene-*p*-sulphonyl)-*3-*azahexane-*1,6-*diamine* (a). The tritosylated triamine (57 g, 0.1 mol) was added in small portions (*ca*. 0.5 g) to a stirred solution, under nitrogen, of sodium (5 g) in absolute ethanol (500 cm^3). The white pasty precipitate was sucked onto a funnel under nitrogen, then washed with large portions of anhydrous diethyl ether, yield 80% (Found: C, 51.5; H, 5.00; N, 6.35. Calc. for $C_{26}H_{31}N_3Na_2O_6S_3$: C: 51.9; H, 5.20; N, 7.00%).

NOO′-*Tris(toluene-*p*-sulphonyl)bis(2-hydroxyethyl)amine* (b). An ether solution of tosyl chloride (11.4 4 g, 0.6 mol; in 600 cm^3) was added slowly to a stirred solution of bis(2-hydroxyethyl)amine (diethanolamine; Erba RPE) (20.4 g, 0.2 mol) in triethylamine (200 cm^3) (Erba RPE). The reaction was carried out in an open beaker; after stirring for 1 h, water was added to dissolve unchanged materials. The white precipitate was recrystallized from the minimum amount of ethanol, yield 60% (Found: C, 52.2; H, 5.40; N, 2.60. Calc. for $C_{25}H_{29}NO_8S_3$: C, 52.9; H, 5.15; N, 2.45%).

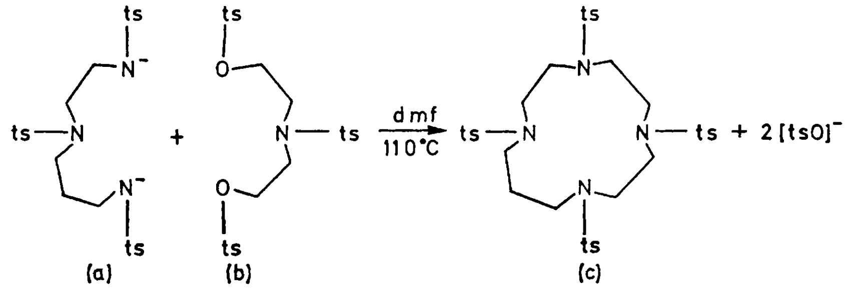
1,4,7,10-*Tetrakis(toluene-*p*-sulphonyl)*-1,4,7,10-*tetra-aza-cyclotridecane* (c). A solution of (b) (68 g, 0.12 mol) in dimethylformamide (dmf) (450 cm^3) was added dropwise to a stirred solution of (a) (69 g, 0.12 mol) in dmf (900 cm^3), kept at 110 °C. When addition was complete (2 h) stirring was continued for 1 h. The volume of the clear yellow solution was reduced on a rotary evaporator to 100 cm^3 and 1 dm^3 of water was added. The yellowish gummy precipitate was dissolved in hot benzene (800 cm^3). The solution was kept for 1 d over anhydrous sodium sulphate (20 g), then evaporated to 120 cm^3. The viscous solution which was obtained was then dissolved in hot absolute ethanol (400 cm^3). A crystalline product precipitated on cooling, yield 32% (Found: C, 54.9; H, 5.65; N, 7.20. Calc. for $C_{37}H_{46}N_4O_8S_4$: C, 55.35; H, 5.75; N, 7.00%), m.p. 194—197 °C.

Hydrolysis of (c), *free-ligand extraction, and complex formation*. A solution of (c) (1.3 × 10^{-2} mol dm^{-3}) in acetic acid–hydrobromic acid (1 100—1 900 cm^3) was heated under reflux for 3 d with stirring. The red solution was then evaporated to 300 cm^3. The addition of diethyl ether–ethanol (600—1 800 cm^3) caused the precipitation of a white powder of $L^3 \cdot 4HBr$. This compound was converted into the corresponding tetrahydrochloride by repeated crystallization from 37% hydrochloric acid (Found: C, 32.05; H, 7.60; N, 16.6. Calc. for $C_9H_{26}Cl_4N_4$: C, 32.55; H, 7.90; N, 16.85%).

The compound $L^3 \cdot 4HCl$ was dissolved in 6 mol dm^{-3} Na[OH] (100 cm^3) and 15—20 extractions in chloroform (100 cm^3 portions) were carried out; the $CHCl_3$ was removed on a rotary evaporator. Following this, diethyl ether (100 cm^3) was added and the solution was filtered. The filtrate was flash distilled to leave an oil, which solidified when refrigerated (Found: C, 60.1; H, 12.6; N, 32.85. Calc. for $C_9H_{22}N_4$: C, 59.95; H, 12.3; N, 31.05%).

When hot ethanolic solutions of L^3 (0.3 g) and $Ni[ClO_4]_2 \cdot 6H_2O$ were mixed a bright yellow precipitate formed. Recrystallization from methanol produced bright yellow needles (Found: C, 24.3; H, 4.85; N, 12.75. Calc. for $C_9H_{22}Cl_2N_4NiO_8$: C, 24.7; H, 5.05; N, 12.8%).

Spectrophotometric Measurements.—Measurements were made with a Beckman DK-2A apparatus, using 1-cm silica cells. During measurements, the cells containing solutions to be investigated were maintained in a temperature-controlled air-bath. The temperature of the solution was determined by the resistance of a calibrated thermistor.



SCHEME 2 ts = Toluene-*p*-sulphonyl

RESULTS

An aqueous solution of $[Ni(L^3)][ClO_4]_2$ is pale yellow. The visible spectrum shows an intense band (ε = 93 dm^3 mol^{-1} cm^{-1}) at 23 530 cm^{-1} attributable to the square-planar chromophore. The presence of a very weak band at *ca*. 18 200 cm^{-1} (ν_2) indicates the coexistence of a small amount of the ' octahedral ' high-spin species (ν_1, which is expected between 28 000 and 29 000 cm^{-1}, is obscured by the intense low-spin complex band). Increase of either the temperature and/or the ionic strength is expected to favour the formation of the yellow species: in fact, both increasing the temperature and adding Na[ClO$_4$] strengthened the band at 23 530 cm^{-1}, whereas the intensity of the band at *ca*. 18 200 cm^{-1} progressively decreased, producing an isosbestic point. On addition of more Na[ClO$_4$] the absorption coefficient of the band at 23 530 cm^{-1} eventually reaches a limiting value (ε = 107.2 dm^3 mol^{-1} cm^{-1}), which is taken as the molar absorption coefficient of the square-planar chromophore. Moreover, heating this solution does not increase the absorbance any further, thus indicating that the ε value is not temperature dependent.

A temperature-dependent study has been carried out for solutions of $[Ni(L^3)][ClO_4]_2$ (*ca*. 2 × 10^{-2} mol dm^{-3}) in 0.1 mol dm^{-3} Na[ClO$_4$]. At 25 °C, 87% of the yellow square-

TABLE 1

Thermodynamic parameters for the blue-to-yellow interconversion of [Ni(macrocycle)]$^{2+}$ complexes (Scheme 1), in aqueous 0.1 mol dm^{-3} Na[ClO$_4$] at 25 °C [a]

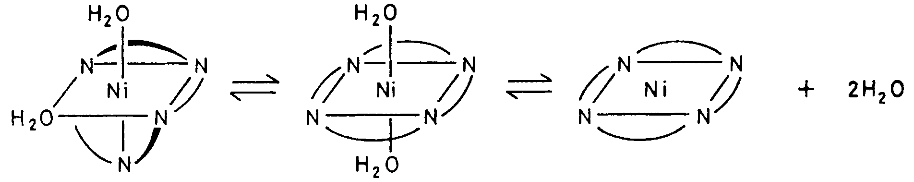
Macrocyclic ligand	$\Delta G^{\ominus}$ / kcal mol^{-1}	$\Delta H^{\ominus}$ / kcal mol^{-1}	$\Delta S^{\ominus}$ / cal K^{-1} mol^{-1}
L^3	-1.14 ± 0.02	7.5 ± 0.1 [b]	30.0 ± 0.5
L^2 [c]	-0.5	5.4	20

[a] For *ca.* 2×10^{-2} mol dm^{-3} solution of complex perchlorate salt. [b] Calculated from a plot of ln K against $1/T$: 21.0 °C, ln $K = 1.75$; 25.2 °C, 1.93; 32.1 °C, 2.23; 38.0 °C, 2.43; 43.2 °C, 2.64; 48.5 °C, 2.86. [c] Ref. 4.

planar complex is present. The equilibrium constant [$K = \varepsilon/(\varepsilon_{\text{lim}} - \varepsilon)$] was determined at different temperatures in the range 21—49 °C (see footnote *b* of Table 1). $\Delta H^{\ominus}$ was calculated from a plot of ln K against $1/T$ (correlation coefficient = 0.9995). The thermodynamic parameters for the high-spin–low-spin interconversion (Scheme 1) are given in Table 1.

DISCUSSION

(a) 13- *and* 14-*Membered Macrocycles*.—Formation of the yellow form is favoured with L^3 (87%, at 25 °C) compared to L^2 (71%). This is not the result of a relatively favourable enthalpy change (Table 1), as one might expect from a consideration of bond energies and of the matching of the metal ion and the macrocycle dimensions, but on a relatively much larger (*ca.* 50%) entropy contribution.



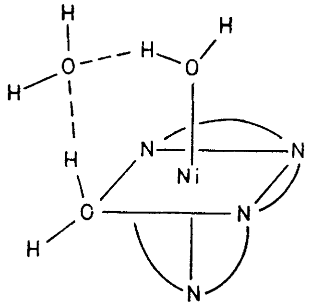
(I) high spin (II) high spin (III) low spin

SCHEME 3

Compound L^2 has the appropriate size to accommodate the high-spin nickel(II) ion and a coplanar arrangement of the four nitrogen atoms occurs in the blue high-spin solid [Ni(L^2)Cl$_2$], as shown by *X*-ray analysis.[7] Therefore, the blue-to-yellow equilibrium for the 14-membered system can be presumed to occur between forms (II) and (III) of Scheme 3.

The endothermicity of the reaction (Table 1) shows that the favourable enthalpy contribution due to the strengthening of the Ni–N in-plane bonds, going from the blue to the yellow form, must be more than compensated by the endothermic breaking of the two Ni–OH$_2$ axial bonds. A further endothermic enthalpy contribution will arise from the unfavourable configurational change experienced by the co-ordinated 14-membered ligand during the spin conversion: L^2 is forced to leave its preferred minimum-strain configuration (Ni–N 2.07 Å) and contract its macrocyclic hole to the Ni–N distance required by low-spin Ni$^{\text{II}}$ (*ca.* 1.90 Å).[8-10] This increase in internal energy, of steric origin, is not, however, experienced by the more flexible and unconstrained open-chain tetramine L^1, for which the blue-to-yellow conversion is much less endothermic ($\Delta H^{\ominus} = 3.5$ kcal mol^{-1}).[2,4,*] Conversely, the unfavourable entropy contribution due to the reduction of the spin multiplicity ($R \ln 1 - R \ln 3 = -2.18$ cal K^{-1} mol^{-1}) is cancelled out by the favourable increase in translational entropy, associated with the increase in the number of particles. The positive entropy change associated with the liberation of a water molecule from a solute in aqueous solution has been evaluated by several workers to be between 8 and 10 cal K^{-1} mol^{-1}.[2,12,13] The value found for L^2 (20 cal K^{-1} mol^{-1}) agrees with the stoicheiometry of (II) $\longrightarrow$ (III).

In view of its small aperture, L^3 is not able to accommodate high-spin nickel(II) ion in a coplanar fashion and evidence for a *cis*-octahedral ligand arrangement has been reported.[14] Thus, the blue-to-yellow conversion for this aqueous complex must occur between forms (I) and (III). The *trans*-octahedral form (II) ought to be absent from the equilibrium mixture and the existence of a sharp isosbestic point in the spectra in the visible region recorded at different temperatures precludes the existence of a third species. The entropy change (30 kcal mol^{-1}) for this *cis*-octahedral-to-square conversion would suggest the release of three water molecules and one might assume that the third water molecule could be hydrogen bonded by the two *cis*-co-ordinated water molecules, as shown below. Alternatively, one might argue that, since the *cis*-diaqua-complex ion will have a larger dipole moment than its *trans*-diaqua-isomer, it will be able to influence a larger number of second-sphere



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[*] Throughout this paper: 1 cal = 4.184 J.

water molecules. Therefore we can reasonably expect a more effective mobilization of solvent molecules when L^3 rearranges to give coplanar co-ordination to low-spin Ni^{II} and a correspondingly greater entropy change.

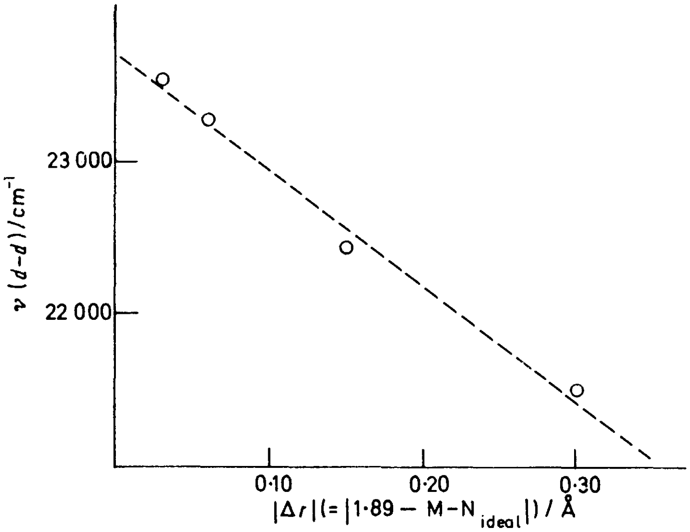
It can be inferred from spectroscopic data (see below) that L^3 establishes stronger in-plane interactions to Ni^{II} than its larger homologue L^2. In spite of this, the conversion into the low-spin complex is much more endothermic for the 13-membered ligand (see Table 1). This seems to be ascribed to: (*i*) the increase in strain energy experienced by L^3 during its *cis–trans* rearrangement; (*ii*) the more conspicuous dehydration (endothermic breaking of second-sphere hydrogen bonds).

In conclusion, the low-spin form predominates with most ideally sized 13-membered macrocycles (87% against 71% for the 14-membered system). However, this appears not to arise as much from the formation of stronger Ni–N bonds than from the large entropy change associated with the release of a larger number of water molecules into the solvent.

(b) *Other Macrocycles.*—The smallest macrocycle L^4 has an ideal M–N distance [6] of 1.83 Å and this prevents coplanar chelation of high-spin Ni^{II}, and for both solid and solvated $[Ni(L^4)]^{2+}$ complexes a *cis*-octahedral geometry has been inferred on the basis of spectroscopic data.[15] An aqueous solution (0.1 mol dm^{-3} $Na[ClO_4]$) of $[Ni(L^4)(ClO_4)_2]$ contains almost 99% of the blue form, but the concentration of the yellow species can be increased to detectable limits by increasing both the temperature and the ionic strength.[16] The low concentration of the low-spin form, as well as the impossibility of reaching the limiting ε value, did not allow the determination of the thermodynamic parameters for this blue-to-yellow equilibrium. We can infer that it should be of the (I) $\longrightarrow$ (III) type: in this case, the particularly favourable entropy change should be annulled by, among other contributions, the rearrangement of L^4 to give four coplanar nitrogen atoms, a process which has been predicted to be strongly endothermic.[6,16]

The low-spin species in the aqueous $[Ni(L^5)]^{2+}$ system with the larger 15-membered macrocycle is also present in very small amounts (1% at room temperature and low ionic strength). In this case, the blue complex has *trans*-octahedral stereochemistry [14] and a (II) $\longrightarrow$ (III) conversion will occur. The very low value of *K* must arise from the large configurational energy which must be expended by the ligand (ideal M–N distance, 2.22 Å) [6] in rearranging itself to the real Ni–N bond distance in the low-spin complex.

(c) *In-plane* Ni–N *Interactions and the Size of the Ligand Aperture.*—It has been reported previously [14] that the energy of the Ni–N plane interactions for macrocyclic *high-spin* nickel(II) complexes, measured by the Dq^{xy} value, decreases as the size of aperture increases in a series of complexes with ligands of 14—16-membered macrocycles. This study could not be extended to 12- and 13-membered ligands, since they co-ordinate high-spin Ni^{II} in a *cis*-octahedral geometry. The above Dq^{xy} sequence can be rationalized in terms of the relative sizes of the metal ion and the macrocyclic holes: enlargment of the ideally sized 14-membered aperture involves a weakening of the Ni–N in-plane interactions. The present study allows us to evaluate how the size of the macrocyclic aperture affects the energy of the metal–ligand interactions for low-spin nickel(II) complexes. The visible spectra of yellow nickel(II) tetramine complexes show a single absorption band, which envelops three *d–d* transitions. The energy of all these transitions is dependent on the value of the in-plane *Dq*. Therefore, the energy of the visible band, ν(*d–d*), should reflect the Dq^{xy} value, and has been used as an empirical parameter to express the intensity of Ni–N in-plane interactions.[16] In the case of yellow nickel(II) complexes with tetrapeptides, it has been shown through circular dichroism studies that ν(*d–d*) is equal to 1.1 10*Dq*.[17,18]



Plot of ν(*d–d*), the energy of the visible band of low-spin [Ni(macrocycle)]$^{2+}$ complexes, against Δ*r*, the difference between the ideal M–N distance [6] and the mean experimentally determined Ni–N distance (1.89 ± 0.03 Å) [8–10] in square low-spin nickel(II) tetramine complexes

The ν(*d–d*) values (see Table 2) decrease in the following order: $L^3 > L^4 > L^2 > L^5$. This sequence reflects the fact that L^3 has the most appropriate cavity size (ideal M–N distance: 1.92 Å) [6] to encircle low-spin Ni^{II} and thus to establish the strongest interactions. Any variation in macrocyclic hole size, whether an increase (L^2, L^5) or a decrease (L^4), will lead to a weakening of the Ni–N interaction and the extent of this decrease should be related to the magnitude of the deviation from the

TABLE 2

Energy of the *d–d* absorption band for low-spin complexes with 12- to 15-membered tetra-aza macrocycles

Ligand (ring members)	ν(*d–d*) [a]/cm^{-1}	Ideal M–N distance [b]/Å
L^4 (12)	23 260	1.83
L^3 (13)	23 530	1.92
L^2 (14)	22 470	2.07
L^5 (15)	21 510	2.22

[a] Measured in aqueous solution. [b] Ref. 6.

ideal macrocyclic size. When ν(*d–d*) values (Figure) are plotted against the difference between the ideal M–N distance and the ' experimental ' Ni–N distance (assumed to be the mean value of the Ni–N bond distance for yellow tetramine complexes, whose structures are known from *X*-ray analysis,[8-10] namely 1.89 ± 0.03 Å) a reasonable linear relationship is obtained (correlation coefficient for the least-squares straight line: 0.994). The intercept (23 690 cm^{-1}) gives the ν(*d–d*) value for the complex of the tailor-made macrocycle, which should have a size quite similar to L^3.

The above empirical correlation does not necessarily mean that the Ni–N interaction energy decreases progressively as the nitrogen atoms get either further away from or closer to the metal ion. In fact, in real complexes, the Ni–N bond distance remains close to the mean ' experimental value ' of 1.9 Å and the macrocycle, in rearranging itself to place the four donor atoms in the required positions, will experience serious distortions. These can take the form of an unfavourable conformation of chelate rings, a deviation from the ideal square-planar arrangement of the nitrogen atoms, or of a poor orientation of donor-atom lone pairs. The extent of the distortions will depend on how far the macrocyclic ligand departs from the ideal size.

In this connection, L^5 (ideal size: 2.22 Å),[6] when complexed to copper(II) has a much shorter M–N bond distance (mean value: 2.03 Å) [in the range expected for copper(II) polyamine complexes], but the ligand configuration seriously deviates from its minimum-energy arrangement.[19] For low-spin nickel(II) complexes, some interdependence is reasonably expected between the Ni–N interaction and the deviation from the ideal macrocyclic arrangement: it is curious that it manifests itself as a straight-line correlation.

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