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Determination of the Equilibrium Constant for Binding Hydroxide to Tetraazamacrocyclic–Nickel(II) Complexes

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Abstract

The pK_b for the equilibria $NiL(OH)^+ \rightleftarrows NiL^{2+} + OH^-$ for L ≡ 1,4,7,10-tetraazacyclotridecane, 1,4,8,12-tetraazacyclopentadecane, C-β-racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and C-β-racemic-1,4,5,7,7,8,11,12,14,14,-decamethyl-1,4,8,11-tetraazacyclotetradecane are 0.95, 1.9, 0.2 and 0.65 respectively. The results are compared with data for analogous complexes reported earlier. The results indicate that the main factors affecting these equilibrium constants are the in plane ligand field strengths of the square planar complexes and steric factors.

Introduction

Complexes of divalent nickel with tetraazamacrocyclic ligands exist in aqueous solutions in an equilibrium mixture between a low-spin, yellow form and a high-spin, blue form [1–9].

$$NiL^{2+} + 2H_2O \rightleftarrows NiL(H_2O)_2^{2+} \qquad (1)$$

yellow blue

The equilibrium constant for reaction (1) decreases with the increase of the in plane ligand field of the macrocycle [7] and with the increase in the steric repulsions between the alkyl portions of the ligand and the axially bound water [7]. In alkaline solutions a further equilibrium between two high spin forms of the complexes was observed [7].

$$NiL(H_2O)_2^{2+} + OH^- \rightleftarrows NiLOH^+ + 2H_2O \qquad (2)$$

blue green

It was proposed that in the alkaline form the nickel is pentacoordinated and probably somewhat displaced from the plane defined by the four amine donor ligands [7]. The equilibrium constants for reaction (2) were suggested to decrease with the increase in the in plane ligand field strength of the macrocyclic ligand [7]. Recent results [10] seemed to suggest that this equilibrium reaction is also affected by steric repulsions by the alkyl part of the ligand.

It seemed of interest to extend the study of the equilibrium reaction of nickel complexes with analogous ligands to those reported thus far. We report here the equilibria for four such complexes and compare the results with those reported earlier. It should be noted that there is no evidence that the pentacoordinated complexes, $NiL(OH)^+$, are formed from the aquo complexes, which are hexacoordinated for most complexes studied. Alternatively the pentacoordinated complexes might be formed via

$$NiL^{2+} + OH^- \rightleftarrows NiL(OH)^+ \qquad (3)$$

and this might be the only route for complexes with large steric repulsions by the alkyl portion of the ligand, e.g. for L = *trans*(III)-C-*meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane. We shall therefore report our results as the pK_b for the dissociation of $NiL(OH)^+$ *i.e.* for the reverse reaction (3).

$$K_b = \frac{([NiL]_T - [NiL(OH)^+])[OH^-]}{[NiL(OH)^+]}$$

where $[NiL]_T$ equals the total complex concentration.

Experimental

Materials

The synthesis of the complexes used in this study has been described in previous reports [11, 12]. All other materials used were of A.R. grade and were used without further treatment. Solutions were prepared with heat distilled water which was passed through a Milli-Q Millipore water purification system.

Spectra were measured using a spectronic 2000 Bausch and Lomb Spectrophotometer. pH values were determined using a Metrohm pH meter equipped

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with a stable alkaline glass electrode. For solutions at pH ⩾ 13.0 the pH was calculated from the amount of KOH added. In the pH range 12–13 the electrode was calibrated by conventional techniques. All spectrophotometric titrations were carried out in 1.0 M KNO_3 solutions.

Results and Discussion

Typical results of the spectrophotometric titrations are shown in Figs. 1 and 2. The clear isosbestic points obtained indicate that only one equilibrium process is observed. If a second equilibrium occurs it involves no further observable change in the spectrum of the complexes in the region studied and this is highly unlikely. In the case of 1,4,7,10-tetraazacyclotridecane a slight deviation from the isosbestic point was observed in solutions with $[OH^-] > 1.0$ M. These results are in accord with the suggestion that the hydroxo complexes of tetraazamacrocyclic nickel(II) are pentacoordinated [7].

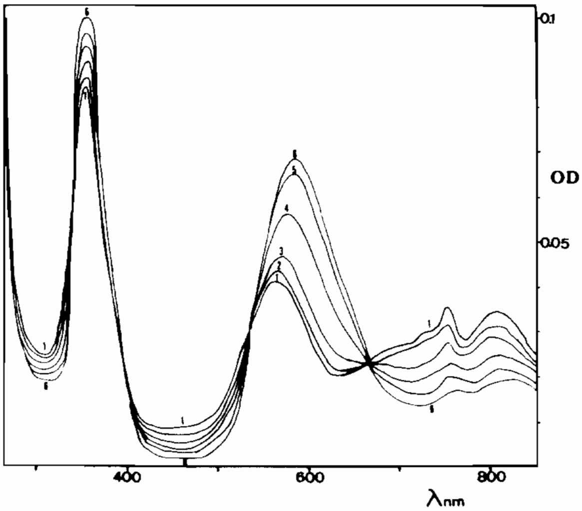

Fig. 1. Spectrophotometric titration of NiL_3^{2+}. 2.6 × 10^{-3} M $NiL_3(ClO_4)_2$; 1.0 M KNO_3. 1, pH 8.6; 2, pH 10.9; 3, pH 11.6; 4, pH 12.1; 5, pH 12.6; 6, pH 13.0.

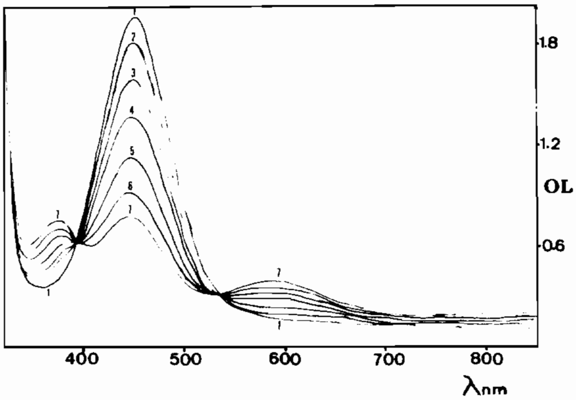

Fig. 2. Spectrophotometric titration of NiL_7^{2+}. 2.0 × 10^{-2} M $NiL_7(ClO_4)_2$; 1.0 M KNO_3. 1, pH 9.1; 2, pH 12.4; 3, pH 13.1; 4, pH 13.4; 5, pH 13.6; 6, pH 13.8; 7, pH 14.0.

The results are summarized in Table I. The Table also contains the λ_{max} of the absorption band in the visible of the low-spin isomers of the NiL^{2+} complexes in nitromethane as a measure of the in plane ligand field strength [13]. It should be pointed out that in all the NiL^{2+} complexes included in the Table the nickel is in the plane of the four nitrogens of the ligand, NiL_5^{2+} and NiL_{10}^{2+} excluded.

The results point out that the pK_b values are affected not only by the change in the in plane ligand field as measured by the absorption spectra of the NiL^{2+} complexes. Several effects are observed.

TABLE I. pK_b for the Dissociation of $NiL(OH)^+$

Ligand	pK_b	λ_{max} in CH_3NO_2 (nm)
1,4,7,10-tetraazacyclotridecane (L_1)	0.95[b]	426[b]
1,4,8,11-tetraazacyclotetradecane (L_2)	0.33[d]	455[c]
1,4,8,12-tetraazacyclopentadecane (L_3)	1.90[b]	460[b]
trans-III (*R*,*S*,*S*,*R*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L_4)	2.06[d]	492[c]
trans-I (*R*,*S*,*R*,*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L_5)	3.18[d]	–
trans-III c-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L_6)	<–0.5[c]	468[c]
trans-I c-*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L_7)	0.2[b]	461[e]
trans-III (*R*,*S*,*S*,*R*)-c-*meso*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane (L_8)	0.4[c]	516[e]
trans-I (*R*,*S*,*R*,*S*)-c-*rac*-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane (L_9)	0.65[b]	546[e]
1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane (L_{10})	3.8[f]	

[a] Accuracy of pK_b ± 0.15, λ_{max} of the low spin isomer of NiL^{2+}. [b] This work. [c] Ref. 10. [d] Ref. 7. [e] Ref. 12. [f] Refs. 15 and 16.

(a) When the size of the macrocyclic ligand is increased along the series L_{10}, L_1, L_2 and L_3 the change in the pK_b is not monotonous. The value of pK_b decreases from NiL_3^{2+} to NiL_2^{2+} as expected but then increases again, though the ligand field splitting in NiL_1^{2+} is larger than that of NiL_2^{2+}. This deviation from expectation stems most probably from the fact that the cavity of L_1 is too small to keep a high-spin divalent nickel cation in the plane of the nitrogens. Indeed all known high-spin complexes of NiL_1X_2 have the *cis* configuration [14]. Most probably also the hydroxo complex formed in alkaline solution is *cis*-$NiL_1(H_2O)(OH)^+$. The slight deviation from the isosbestic points at $[OH^-] \geqslant 1.0$ M suggests that *cis*-$NiL_1(OH)_2$ is formed in strong alkaline solutions. The smaller cavity of L_{10} enhances these effects and so the complex is present also in neutral solutions as the *cis* isomer of $NiL_{10}(H_2O)_2^{2+}$ and pK_b increases accordingly [15].

(b) Methyl substituents on the carbon atoms of the macrocyclic ligands decrease the value of pK_b though they decrease also the ligand field splitting induced by the ligand, compare NiL_2^{2+} with NiL_6^{2+} and NiL_7^{2+}. This effect is attributed to the hydrophobic nature of the methyl substituent, which due to steric factors decreases the tendency of the hydroxide to bind to the central nickel cation. As expected the effect is smaller for the *trans*-I isomer than that observed for the *trans*-III isomer as in the former a larger cavity is available for the hydroxide.

(c) Methyl substituents on the nitrogens of the macrocyclic ligand increase the value of pK_b in accord with the decrease in the ligand field splitting caused by the *N*-methylated ligands, compare NiL_5^{2+} and NiL_4^{2+} with NiL_2^{2+}; NiL_8^{2+} with NiL_6^{2+} and NiL_9^{2+} with NiL_7^{2+}. The effect is larger for NiL_5^{2+} than for the isomeric NiL_4^{2+}, as the former is already pentacoordinated. The result for NiL_8^{2+} is quite surprising as a model of this complex suggests that there is no space available for axial binding to the nickel. The small ligand field splitting caused by this ligand seems to supply enough driving force to allow axial binding of a hydroxide to enforce a distortion of the ligand coordination sphere which opens enough space for the approaching hydroxide. NiL_9^{2+} has a less crowded coordination sphere than its NiL_8^{2+} isomer and accordingly the pK_b of the former is somewhat higher.

The results thus point out that steric repulsions between methyl substituents on the ligand and the axial bound hydroxide affect the value of pK_b in analogy to their effect on ΔH_1^0 and ΔS_1^0 [7].

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References

1 E. K. Barefield, D. H. Busch and S. M. Nelson, *J. Chem. Soc., Quart. Rev.*, 457 (1968).

2 A. Anichini, L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chim. Acta, 24,* L21 (1977).

3 L. Fabbrizzi, P. Paoletti and R. M. Clay, *Inorg. Chem., 17,* 1042 (1978).

4 L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem., 19,* 535 (1980).

5 L. Fabbrizzi, M. Micheloni and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 134 (1980).

6 M. Micheloni, P. Paoletti, A. Poggi and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 61 (1982).

7 N. Herron and P. Moore, *Inorg. Chim. Acta, 36,* 89 (1979).

8 K. E. Newman, *Inorg. Chim. Acta, 89,* L3 (1984).

9 J. K. Beattie, M. T. Kelso, W. E. Moody and P. A. Tregolan, *Inorg. Chem., 24,* 415 (1985).

10 N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh and D. Meyerstein, *Inorg. Chem., 24,* 251 (1985).

11 N. Jubran, H. Cohen and D. Meyerstein, *Isr. J. Chem., 25,* 118 (1985).

12 N. Jubran, H. Cohen and D. Meyerstein, *Inorg. Chim. Acta,* in press.

13 F. Wagner and E. K. Barefield, *Inorg. Chem., 15,* 408 (1978).

14 L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1857 (1979).

15 J. H. Coates, D. A. Hadi and S. F. Lincoln, *Aust. J. Chem., 35,* 903 (1982).

16 M. Micheloni, P. Paoletti, S. Burki and T. A. Kaden, *Helv. Chim. Acta, 65,* 587 (1982).