Formation of Five-coordinate Ni(II) Complexes with 2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene Analogs and Halide Ions in Nitromethane

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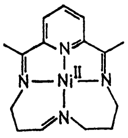
(Received May 11, 1979)

Synopsis. Formation of 5-coordinate Ni(II) complexes of the title quadridentate ligands and halide ions (Cl^-, Br^-, and I^-) in nitromethane was investigated. Some of the formation constants were estimated by means of curve-fitting method.

Nickel(II) complexes of the title ligand, L, and its analogs, $[Ni(L+nH)](ClO_4)_2$ ($n=-2$ (**1**), 0 (**2**), 2 (**3**), and 4 (**4**)) form 5- and 6-coordinate complexes with halide ions in nitromethane solutions. In the absence of halide ions, these complexes exist as 4-coordinate, diamagnetic species in nitromethane, which were confirmed by means of the ^1H NMR and electronic spectra. The present note discusses the solution equilibria between the complexes **1**—**4** and halide ions (Cl^-, Br^-, and I^-) in nitromethane.



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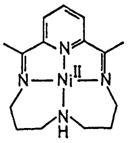

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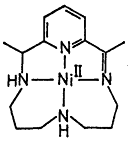

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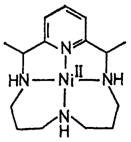

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The electronic spectra of the complexes **1**—**4** in nitromethane solutions were measured in the presence of various amounts of tetraethylammonium halides. The equilibria attained rapidly under the experimental conditions.[1]

Figure 1 shows the typical spectra of $[Ni(L+2H)](ClO_4)_2$ in the absence and the presence of halide ions. The results of the molar-ratio methods are shown in Fig. 2(a). In the chloride system, a 6-coordinate 1 : 2 complex forms predominantly, a small amount of a 1 : 1 complex being also formed. The decrease in the spectral intensity of the chloride system as compared with that of the 4-coordinate species also supports the above result.[7] In the iodide system, the spectrum is quite different from both that of a 4-coordinate and of a 6-coordinate complex, *viz.*, a single broad absorption with much larger extinction coefficient is observed around 520 nm. This feature suggests the formation of a 5-coordinate complex with a square-pyramidal structure.[2] The formation of a 5-coordinate 1 : 1 iodo complex was confirmed by the molar-ratio method (Fig. 2(a)). The behavior of the bromide system was intermediate between those of the chloride and the iodide systems. The spectrum changed markedly, depending on the amount of the added Et_4NBr. As is clear from Fig. 2(a), the 5-coordinate complex and then the 6-coordinate complex form with an increase in the concentration of the added Et_4NBr.

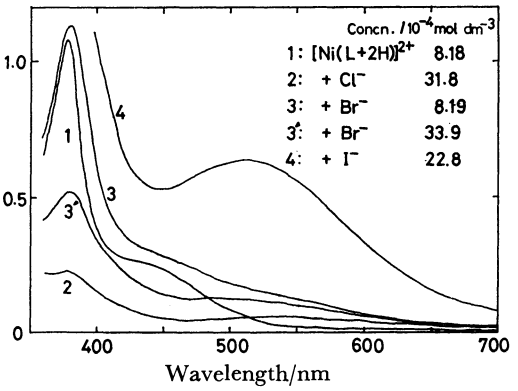

Fig. 1. Absorption spectra of the nitromethane solutions of $[Ni(L+2H)](ClO_4)_2$ (1) and in the presence of Et_4NX (2, 3, 3′, and 4) at 25±0.2 °C.

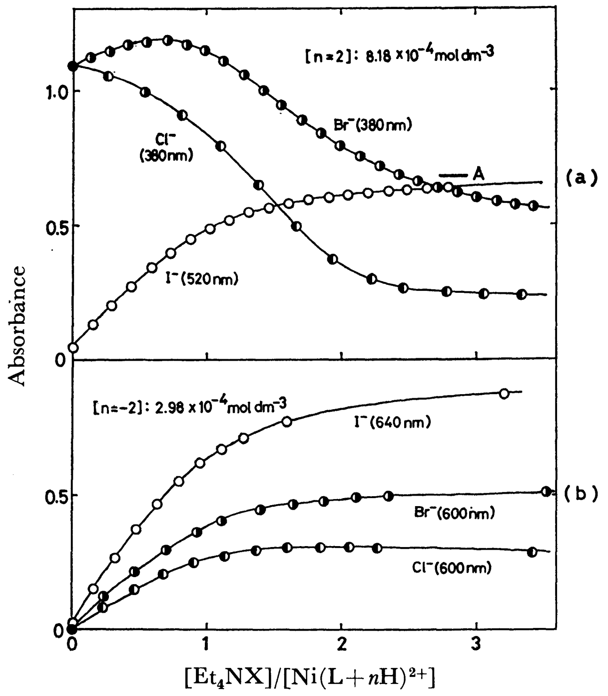

Fig. 2. The molar-ratio method applied to the systems, $[Ni(L+nH)](ClO_4)_2$ and Cl^-(◐), Br^-(◑), and I^-(○) for $n=2$ (a) and -2 (b). The horizontal line **A** indicates the calculated limiting value (see the text).

In contrast to the $[Ni(L+2H)](ClO_4)_2$ system, the complexes in $[Ni(L-2H)](ClO_4)_2$–halide system exist predominantly as 5-coordinate species, regardless of the kind of halide ions (Fig. 2(b)). Incorporation of the double bonds in the macrocyclic skeleton causes an increase in the in-plane ligand field strength.[3] The tendency to form the 6-coordinate complex would be thereby decreased in the $[Ni(L-2H)]^{2+}$ system.

TABLE 1. EQUILIBRIUM CONSTANTS AT 25±0.2 °C FOR THE REACTIONS, $[\mathrm{Ni(L}+n\mathrm{H)}]^{2+}+\mathrm{X}^- \rightleftharpoons [\mathrm{Ni(L}+n\mathrm{H)X}]^+$ ($\mathrm{X}=\mathrm{Cl}^-$, Br^-, AND I^-), AND THE MOLAR EXTINCTION COEFFICIENTS OF $[\mathrm{Ni(L}+n\mathrm{H)I}]^+$

	$\frac{K_1(\mathrm{Cl}^-)}{10^4\ \mathrm{mol}^{-1}\ \mathrm{dm}^3}$	$\frac{K_1(\mathrm{Br}^-)}{10^4\ \mathrm{mol}^{-1}\ \mathrm{dm}^3}$	$\frac{K_1(\mathrm{I}^-)}{10^3\ \mathrm{mol}^{-1}\ \mathrm{dm}^3}$	$\frac{\varepsilon_\mathrm{p}}{\mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{cm}^{-1}}\left(\frac{\lambda}{\mathrm{nm}}\right)$
Ni(L+4H)[a]	—	—	1—2	108—123 (550)
Ni(L+2H)	—	—	8.5	831 (520)[b]
Ni(L)	—	3.2	140	2500 (600)
Ni(L−2H)	3—4	2.6	19	3138 (640)

a) *α-C-meso* isomer (see Ref. 7). b) See the text and Fig. 2(a).

As a result of similar experiments for other systems, it was found that a relatively large amount of 5-coordinate complex forms in the systems, $[\mathrm{Ni(L}-2\mathrm{H)}]^{2+}$–$\mathrm{I}^-$, –$\mathrm{Br}^-$, –$\mathrm{Cl}^-$; $[\mathrm{Ni(L)}]^{2+}$–I^-, –Br^-; and $[\mathrm{Ni(L}+2\mathrm{H)}]^{2+}$–$\mathrm{I}^-$.

For the equilibria of $[\mathrm{Ni(L}+n\mathrm{H)}]^{2+}$,

$$[\mathrm{Ni(L}+n\mathrm{H)}]^{2+} + \mathrm{X}^- \overset{K_1}{\rightleftharpoons} [\mathrm{Ni(L}+n\mathrm{H)X}]^+, \qquad (1)$$

the formation constant of the 5-coordinate complex, K_1, and the observed absorbance of the solution, A, are expressed as follows.[4]

$$K_1[\mathrm{X}^-] = \frac{A-\varepsilon_\mathrm{s}[\mathrm{Ni(L}+n\mathrm{H)}^{2+}]_\mathrm{t}}{\varepsilon_\mathrm{p}[\mathrm{Ni(L}+n\mathrm{H)}^{2+}]_\mathrm{t}-A} = Y, \qquad (2)$$

where [ ] and $[\ ]_\mathrm{t}$ denote the equilibrium and the total concentration, respectively, and ε_s and ε_p the molar extinction coefficient for the 4- and 5-coordinate species, respectively. The values of $[\mathrm{X}^-]$ and Y can be calculated on the basis of the assumed ε_p. The values of K_1 and ε_p were determined by varying values of ε_p until a straight line was obtained for the plot of Y against $[\mathrm{X}^-]$. The values of K_1 and ε_p thus obtained are listed in Table 1. For some of the systems, the linear plots were not obtained due to the predominant formation of the more stable 6-coordinate 1:2 complex.

For the $[\mathrm{Ni(L}+2\mathrm{H)}]^{2+}$–$\mathrm{I}^-$ system, the value of ε_p seemed to be reasonable judging from the position of the horizontal line **A** in Fig. 2(a), which indicates the limiting value of the absorbance for the 5-coordinate iodo complex as calculated from the evaluated ε_p. The values of $K_1(\mathrm{I}^-)$ and $K_1(\mathrm{Br}^-)$ lie in the range 10^3—10^5 $\mathrm{mol}^{-1}\ \mathrm{dm}^3$. These values are in the same order of magnitude as corresponding values of $K_1^{-1}=2.5\times10^{-4}$ $\mathrm{mol\ dm}^{-3}$ for the analogous reaction of 1,4,8,11-tetrathiacyclotetradecane, ttp, $[\mathrm{Ni(ttp)I}]^+ \rightleftharpoons [\mathrm{Ni(ttp)}]^{2+} + \mathrm{I}^-$.[5] The values of the equilibrium constants in Table 1 indicate that the 5-coordinate complexes $[\mathrm{Ni(L)X}]^+$ and $[\mathrm{Ni(L}-2\mathrm{H)X}]^+$ are more stable than $[\mathrm{Ni(L}+4\mathrm{H)X}]^+$ and $[\mathrm{Ni(L}+2\mathrm{H)X}]^+$. In fact, the isolation of crystalline $[\mathrm{Ni(L)Br}]\mathrm{Br}\cdot\mathrm{H_2O}$ was reported.[6] The relative stabilities of the 5-coordinate complexes should be related also to the values of the equilibrium constants, $K_2(\mathrm{X}^-)$, for the step $[\mathrm{Ni(L}+n\mathrm{H)X}]^+ + \mathrm{X}^- \rightleftharpoons [\mathrm{Ni(L}+n\mathrm{H)X_2}]$. The value of $K_2(\mathrm{Br}^-)$ for the formation of $[\mathrm{Ni(L)Br_2}]$ was evaluated by an analogous method to be *ca.* $3\times10^3\ \mathrm{mol}^{-1}\ \mathrm{dm}^3$. This value is nearly 1/10 of $K_1(\mathrm{Br}^-)$, suggesting that the increased relative stability of 5-coordinate species compared with the 6-coordinate species in the solution containing comparable concentrations of $[\mathrm{Ni(L)}]^{2+}$ and Br^-.

The tendency to form the 5-coordinate complexes depends on the nature of the axial as well as the in-plane ligands, and also on the easiness with which the 6-coordinate species form. For the present systems in the nitromethane solutions, 5-coordinate complexes form predominantly when the in-plane ligand field is strong and the axial ligand field is weak.

Experimental

Reagent grade nitromethane (Wako) was dried with calcium chloride and distilled. Reagent grade tetraethylammonium halides were dried over phosphorus pentaoxide and kept in the dark. The complexes **1**—**4** were prepared according to the literature.[7] The purity was confirmed by elemental analysis. The absorption spectra were measured at 25±0.2 °C with a Hitachi recording spectrophotometer model EPS-3T.

References

1) The stopped-flow measurements revealed that the formation of the 5-coordinate complexes proceeds too fast to be observed.

2) E. B. Fleischer and S. W. Hawkinson, *Inorg. Chem.*, **7**, 2312 (1968); E. K. Barefield and D. H. Busch, *ibid.*, **10**, 1216 (1971).

3) For the detailed discussion, see L. Y. Martin, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 2968 (1977).

4) The contribution of the ion-pairs and/or the undissociated species could be regarded as negligible based on the linear relationship (Eq. 2).

5) W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694 (1969).

6) J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966). The 5-coordinate iodide species, $[\mathrm{Ni(L}+n\mathrm{H)I}]\mathrm{I}$, $n=-2$ and 0, was also isolated in our laboratory. The details will be reporated elsewhere.

7) J. L. Karn, Ph.D. Dissertation, The Ohio State University, 1966; J. L. Karn and D. H. Busch, *Inorg. Chem.*, **8**, 1149 (1969); E. Ochiai and D. H. Busch, *ibid.*, **8**, 1798 (1969); E. K. Barefield, F. V. Lovecchio, N. E. Tokel, E. Ochiai, and D. H. Busch, *ibid.*, **11**, 283 (1972).