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Effect of Trace Water in Chloroform on Coordination Mode of the Tetraazamacrocyclic Complex Comprised of Nickel(II) Bromide and 7*R*(*S*),14*S*(*R*)-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane

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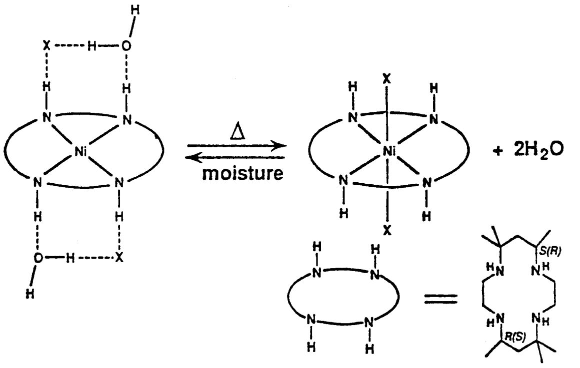
Synopsis. *Trans*-[$NiBr_2L$](L= the titled macrocyclic ligand) dissolves in freshly purified chloroform containing a very small amount of water to give an equilibrium mixture between the low-spin four coordinate and the high-spin six coordinate complexes. High temperature favors the high-spin form. This is opposite to the well-known behavior of equilibria in H_2O between low-spin four coordinate and high-spin six coordinate nickel(II) complexes with similar tetraaza macrocyclic ligands. Trace water in chloroform facilitates the formation of the low-spin species.

It has been reported that the titled tetraaza macrocyclic ligand (hereafter abbreviated as L) forms two types of complexes with NiX_2 ($X=Cl^-$ and Br^-), orange dihydrate ([NiL]$X_2 \cdot 2H_2O$) and violet anhydride *trans*-[NiX_2L].[1,2] The former is a square planar four coordinate complex having a singlet ground state (low-spin form), whereas the latter is a pseudo-octahedral complex having a triplet ground state (high-spin form). The two complexes, [NiL]$X_2 \cdot 2H_2O$ and [NiX_2L], are interconvertible in the solid state as in Eq. 1.



(1)

In Eq. 1, are shown schematic X-ray structures of the orange dihydrate, [NiL]$X_2 \cdot 2H_2O$,[3] and the violet anhydride, *trans*-[NiX_2L].[4] The solid orange dihydrate is converted upon heating to the violet anhydride through losing water of crystallization. Conversely, the solid violet anhydride reverts to the orange dihydrate unless the anhydride is carefully protected from moisture. The ΔH values for the dehydration reactions have been reported to be ca. 100 kJ mol^{-1}, which is as large as that for the solid-vapor equilibrium in water where strong hydrogen-bonds operate in the ice state.[2] In the dihydrate, neither halide ion nor water coordinates to the Ni(II) ion. Instead, "hydrogen-bonded chelate rings,"[3] comprized of the secondary amine groups, water molecules, and halide ions, have been formed. The hydrogen bonds are strong enough to prevent the coordination of water and halide ion.

All the above results indicate that water molecules in the vicinity of the central Ni(II) ion play an important role on the coordination mode, viz. on the molecular and electronic structure of the complex. The presence of water causes a decrease in the coordination number, shortening of the Ni–N distance, and the singlet ground state. In this note, we report a similar phenomenon observed in the solution state.

Results and Discussion

Figure 1 shows temperature dependent electronic spectra of *trans*-[$NiBr_2L$] in freshly purified chloroform which contains 4.7 mM H_2O added on purpose (M=mol dm^{-3}). The spectral change is reversible and has isosbestic points at 408 and 564 nm, showing that two species coexist in equilibrium in the solution. Judging from the spectral patterns of these types of complexes, which have been studied in detail,[5] the bands around 361, 534, and 670 nm are due to the six-coordinate high-spin form (*trans*-[$NiBr_2L$]), whereas the band around 500—520 nm is due to the four-coordinate low-spin form ([NiL]$^{2+}$) and is largely

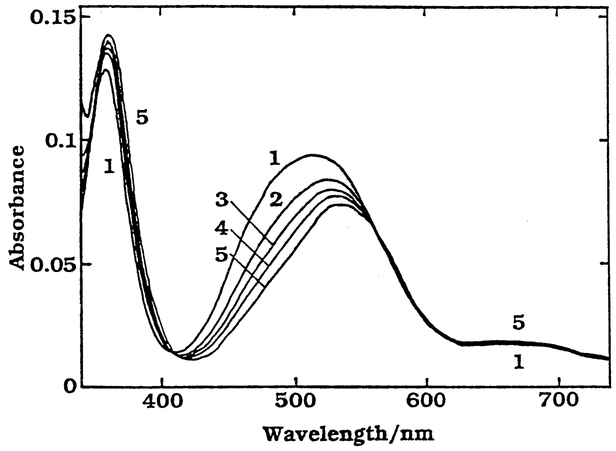


Fig. 1. Electronic absorption spectra of *trans*-[$NiBr_2L$] in a chloroform solution containing 4.7 mM H_2O at various temperatures (K): (1) 284.5, (2) 294.9, (3) 301.1, (4) 308.2, and (5) 323.1. The concentration of the complex is 10.0 mM.

overlapped with a component of the high-spin species.[6] In fact, a diffuse reflectance spectrum of solid *trans*-[$NiBr_2L$] shows bands at 365 (shoulder), 545, and 675 nm. On the other hand, the solid violet *trans*-[$NiBr_2L$] dissolves in water to give a yellow solution, which shows a single electronic absorption band at 461 nm in the visible region. This band has been known to be due to the four-coordinate low-spin species, $[NiL]^{2+}$, which is formed through the complete dissociation of the Br^- ligands from *trans*-[$NiBr_2L$] in H_2O.[7]

Of particular interest in Fig. 1 is the fact that the high-spin form (*trans*-[$NiBr_2L$]) increases with an increase in temperature. It is well known that nickel(II) complexes with tetraaza macrocyclic ligands such as cyclam (L′) dissolves in H_2O to give an equilibrium mixture between high-spin ($[NiL'(H_2O)_2]^{2+}$) and low-spin ($[NiL']^{2+}$) forms. In all the instances reported for such equilibria of macrocyclic nickel(II) complexes in H_2O, high temperature favors the low-spin four coordinate form.[8-16] This temperature dependency in H_2O is opposite to that found for the chloroform solution of *trans*-[$NiBr_2L$] in the present study.

We carried out experiments to obtain spectra of *trans*-[$NiBr_2L$] in chloroform containing a small amount of water as a function of the water concentration at a constant temperature. Change in the water content was accomplished by mixing water-saturated chloroform ([H_2O]=ca. 42 mM) and dried chloroform ([H_2O]=1.7 mM) in an appropriate ratio. Because of the very low solubility of *trans*-[$NiBr_2L$] in chloroform with the relatively high water content and the very low molar extinction coefficient of the compound, it was difficult to carry out the experiments quantitatively. However, we observed a clear trend that an incerase in the water content brings about the increase in the low-spin four coordinate species (Fig. 2). Namely, the dissociation of the bromo ligands from *trans*-[$NiBr_2L$] is facilitated as the water content in the chloroform solution increases.

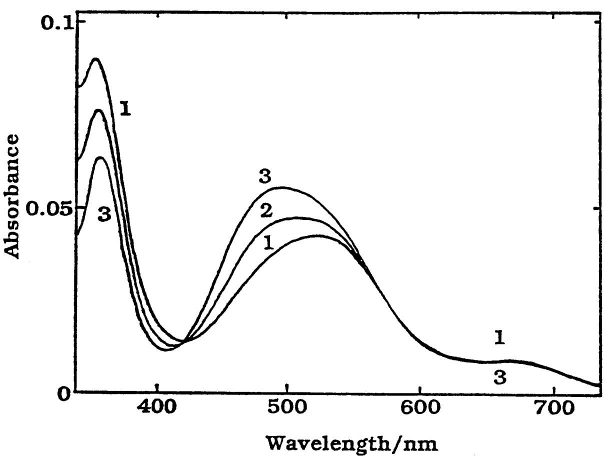


Fig. 2. Electronic absorption spectra of *trans*-[$NiBr_2L$] in a chloroform solution with various water contents: [H_2O]=9.3 (1), 25.6 (2), and 41.9 (3) mM. The concentration of the complex is 3.34 mM.

The present experimental results indicate clearly that the presence of trace water in chloroform affects the coordination number around the Ni(II) ion and thereby its spin state. The water content in the chloroform solution is comparable to the concentration of the nickel(II) complex under the experimental conditions. The molar ratio between water and the complex is nearly 1:2 under the conditions of Fig. 1. Under such circumstances, water molecules in chloroform solvate preferentially the solute complex, and the complex *trans*-[$NiBr_2L$] exists along with the small number of water molecules within the chloroform solvent cage. The solvated water causes the dissociation of the Br^- ligands from *trans*-[$NiBr_2L$]. However, the amount of available water in the cage is so little that the dissociation occurs partly, giving a mixture of the low- and high-spin complexes. Such situations within the cage should resemble at least partly those in the solid dihydrate state, [NiL]-$Br_2 \cdot 2H_2O$, where strong "hydrogen-bonded chelate rings" prevent both Br^- and water from coordination. Exact structure of the low-spin four coordinate species in the cage is uncertain. But it is highly possible that similar hydrogen-bonds operate in the cage among the secondary amine groups, the dissociated Br^- ions, and water molecules. At a given temperature, such hydrogen-bonds are expected to be stronger than the Ni-Br bond even in a solution state as has been proved in the solid dihydrate. At an elevated temperature, some water molecules in the cage go into the bulk solution, facilitating the formation of the six-coordinate species in the cage. Such a model is consistent with the observed facts that the high temperature favors the high-spin form and a solution with high water content favors the low-spin form.

Approximate thermodynamic parameters[17] for the equilibrium in the chloroform solution were estimated from the temperature dependent electronic spectra in the same way as reported previously.[14] Under the conditions of Fig. 1, the equilibrium constant (K=[high-spin]/[low-spin]) was found to be 16 at 25 °C (94% high-spin species and 6% low-spin species), and ΔH=16 kJ mol^{-1} and ΔS=77 JK^{-1} mol^{-1}. It should be emphasized the signs of both ΔH and ΔS are opposite to those of corresponding values for the well-known high- and low-spin equilibria of similar tetraaza macrocyclic nickel(II) complexes in H_2O.[8-16]

The chloro derivative, *trans*-[$NiCl_2L$], dissolves in chloroform very easily to give a violet solution irrespective of the water content. Its electronic spectrum consists almost exclusively of the components of the high-spin six-coordinate species (λ_{max}/nm(ε_{max}/M^{-1} cm^{-1})=353(14), 538(8), 689(5)). Furthermore, the spectrum is essentially temperature independent. The reason why the dichloro complex does not show a similar equilibrium is that the Ni-Cl bond is much stronger than the Ni-Br bond in [NiX_2L].

Experimental

Materials. *Trans*-[$NiBr_2L$] was prepared[2] by heating the dihydrate, [NiL]$Br_2 \cdot 2H_2O$,[3] in an oven at 90 °C for 10h, and was again dried before use. Reagent grade chloroform was purified before use in a reported manner[18] and finally distilled over CaH_2.

Measurements. Electronic absorption spectra were recorded on a Hitachi 340 spectrophotometer. The temperature of a sample solution was thermostated within ±0.1 °C.

The water content in a chloroform solution was determined immediately after spectral measurement by use of Trace Water Analyzer (Mitubishi Chemical Industry Model CA-02).

References

1) D. H. Busch, *Adv. Chem. Ser.*, **62**, 616 (1967).

2) T. Ito, Y. Tsutsumi, Y. Hiratsuka, K. Mochizuki, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **54**, 931 (1981).

3) T. Ito, K. Toriumi, and H. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 1096 (1981).

4) T. Ito and K. Toriumi, *Acta Crystallogr., Sect. B*, **37**, 88 (1981).

5) a) L. Y. Martin, C. R. Sperati, and D. H. Busch, *J. Am. Chem.Soc.*, **99**, 2968 (1977), and references cited therein; b) C. R. Sperati, Ph. D. Thesis, The Ohio State University, Columbus, Ohio, USA, 1971.

6) The band around 500—520 nm arises from overlapping the band at 461 nm due to a small amount (6% at 25 °C) of the low spin species with large ε and the band at 545 nm due to a large amount (94% at 25 °C) of the high spin species with small ε (less than 10 $M^{-1} cm^{-1}$). See the text and Ref. 7.

7) Four coordinate low-spin complexes, $[NiL]X_2 \cdot 2H_2O$ and $[NiL](ClO_4)_2$, with and without, respectively, the hydrogen-bonded chelate ring, have similar broad electronic spectra in H_2O (λ_{max}=461 nm, ε=56 $M^{-1} cm^{-1}$) and in the solid state (λ_{max}=466—468 nm).

8) L. Fabbrizzi, *Inorg. Chem.*, **16**, 2667 (1977).

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

10) L. Sabatini and L. Fabbrizzi, *Inorg. Chem.*, **18**, 438 (1979).

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

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

13) R. G. Swisher, J. P. Dayhulf, D. J. Stuehr, and E. L. Blinn, *Inorg. Chem.*, **19**, 1336 (1980).

14) K. Mochizuki, M. Fujimoto, H. Ito, and T. Ito, *Bull. Chem. Soc. Jpn.*, **53**, 2535 (1980).

15) J. H. Coates, D. A. Hadi, S. F. Lincoln, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **20**, 707 (1981).

16) M. Sugimoto, M. Nonoyama, T. Ito, and J. Fujita, *Inorg. Chem.*, **22**, 950 (1983).

17) Because of the experimental difficulties (the low solubility and the low molar extinction coefficient), errors for estimated values are of the order of 20%.

18) M. Pestmer, *Angew. Chem.*, **63**, 118 (1951).