Cis–Trans Isomerism among the Octahedral Anionobis(*C*-substituted ethylenediamine)nickel(II) Complexes Obtained by Thermal Reactions

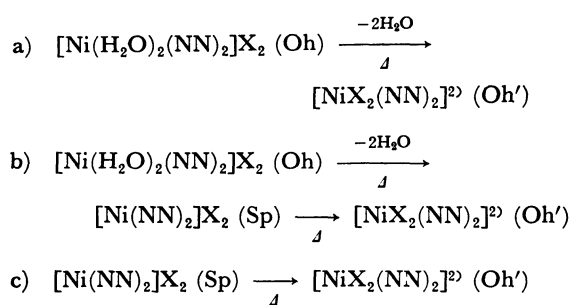Yoshinori Ihara,* Yutaka Fukuda,† and Kozo Sone†

Laboratory of Chemistry, Faculty of Education, Kanazawa University, Marunouchi, Kanazawa 920

†Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112

(Received December 24, 1985)

Ten octahedral anionobis(*C*-substituted ethylenediamine)nickel(II) complexes were obtained by thermal reactions of corresponding diaqua salts, and their electronic and IR spectra were examined to see whether they are cis or trans. Most of them were found to be trans, but [Ni(NO₃)(*m*-bn)₂](NO₃) and [NiCl₂(*i*-bn)₂] were cis.

We have previously reported on the thermal reactions of the nickel(II) complexes with *C*-substituted ethylenediamines in solid phase.[1] It was found that octahedral anionobis(diamine) complexes, [NiX₂(NN)₂],[2] are obtained as the final products of the following thermal reactions:

a) $[\text{Ni(H}_2\text{O})_2(\text{NN})_2]\text{X}_2$ (Oh) $\xrightarrow[\varDelta]{-2\text{H}_2\text{O}}$

$[\text{NiX}_2(\text{NN})_2]^{2)}$ (Oh′)

b) $[\text{Ni(H}_2\text{O})_2(\text{NN})_2]\text{X}_2$ (Oh) $\xrightarrow[\varDelta]{-2\text{H}_2\text{O}}$

$[\text{Ni(NN)}_2]\text{X}_2$ (Sp) $\xrightarrow{\varDelta}$ $[\text{NiX}_2(\text{NN})_2]^{2)}$ (Oh′)

c) $[\text{Ni(NN)}_2]\text{X}_2$ (Sp) $\xrightarrow{\varDelta}$ $[\text{NiX}_2(\text{NN})_2]^{2)}$ (Oh′)

Here Oh (or Oh′) and Sp represent an octahedral species and square planar one, respectively.

Whether these aniono complexes are cis or trans is an interesting problem, which is also fundamental for understanding the nature of their formation reactions. Unfortunately, the literature on such geometrical isomers of octahedral Ni(II)–bis(diamine) complexes is scanty; the number of known examples of such isomers is not so many, and the methods of their identification by means of the visible and IR spectra are not so well-established as in the case of the Co(III) and Cr(III) complexes.

Recently, however, there appeared several experimental and theoretical works on the electronic spectra of tetragonal Ni(II) complexes.[3-7] In particular, Lever et al. studied the electronic states of the bis(*N*-substituted ethylenediamine)nickel(II) complexes by the normalized spherical harmonic Hamiltonian (NSH) method in detail,[8-13] showing that the feature of the electronic spectrum in near IR region is especially useful for the identification of a cis or a trans isomer of such a complex. In this study, we tried to apply their results to our nickel(II) complexes with *C*-substituted ethylenediamines to see whether each of them is cis or trans.

Experimental

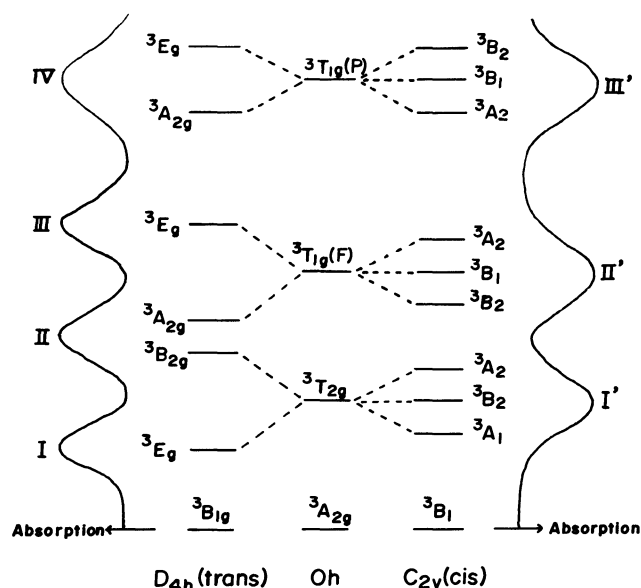Preparation of the ligands(1-phenyl-1,2-ethanediamine

Fig. 1. Energy level diagrams of a d⁸ system in ligand fields of different symmetries.[16] Sketches of the absorption spectra of the cis and trans isomers of NiX₂(diamine)₂ are also given. (After Lever[13]).

(phenen), 2-methyl-1,2-propanediamine(*i*-bn), *meso*- or *dl*-butanediamine(*m*-bn or *dl*-bn), and *dl*-1,2-diphenyl-1,2-ethanediamine(*dl*-stien)), and that of the anionobis(diamine)-nickel(II) complexes with them were described in the literature.[1,14,15] The electronic spectra in solid phase were measured by the diffuse reflectance method with a Hitachi 340 spectrophotometer equipped with reflection attachments for the visible (800—300 nm) and near IR (1400—800 nm) parts of the spectrum. The latter region was measured with special care for the discussion of the complex geometry. Common IR spectra were recorded with a JASCO IR-A3 spectrophotometer in Nujol mulls.

Results and Discussion

The energy levels derived from F and P terms of a d⁸ system (Ni²⁺) in ligand fields of different symmetries (Oh, D₄ₕ(trans), and C₂ᵥ(cis)) are shown in Fig. 1. In a tetragonal system(D₄ₕ), six spin-allowed transitions are anticipated, among which four or sometimes five bands are observed in practice.[7,8,13] The band due to the ³B₁g→³A₂g (from ³T₁g(P)) transition is scarcely observable as a discrete band, but may appear as a

shoulder of the band of $^3B_{1g}\rightarrow ^3E_g$ (from $^3T_{1g}$(P)) transition (Band IV shown in Fig. 1, which is sometimes obscured under the strong CT or ligand band in near UV region). The band due to $^3B_{1g}\rightarrow ^3E_g$ (from $^3T_{1g}$(F)) transition, Band III, is normally observed at ca. 17—18×10³cm⁻¹. The band of $^3B_{1g}\rightarrow ^3A_{2g}$ (from $^3T_{1g}$(F)) transition seems to lie very close to that of $^3B_{1g}\rightarrow ^3B_{2g}$ transition, giving only one peak, also around this region (Band II). The band at the lowest energy, Band I, is assigned to the $^3B_{1g}\rightarrow ^3E_g$ transition.

On the other hand, in a C_{2v} system, the splittings of the respective terms are small; so, when the complex is cis, three rather broad bands (bands I′, II′, and III′ shown in Fig. 1) are observed as in the case of the regular Oh system.[7,12,13,18]

The electronic spectra of the three aniono complexes are now shown in Fig. 2, where the Roman numerals on the curves are the band assignments shown in Fig. 1. The spectra of [NiBr₂(dl-stien)₂] and [Ni(NO₃)₂(phenen)₂] have the same feature, differing from that of Ni(NO₃)₂(m-bn)₂ in the near IR
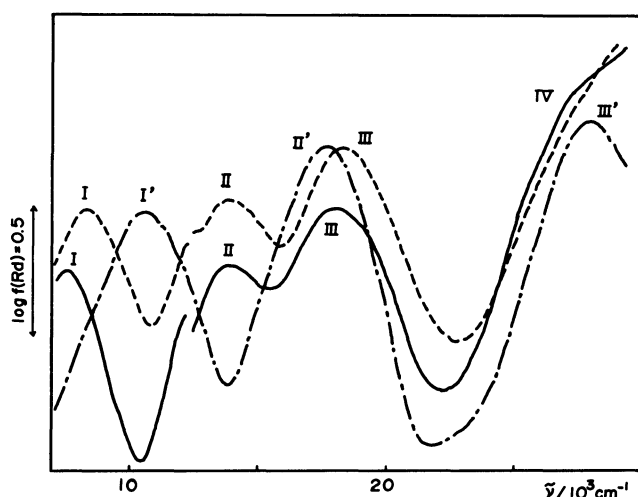
Fig. 2. Reflectance spectra of [NiBr₂(dl-stien)₂] (——), [Ni(NO₃)₂(phenen)₂] (----), and [Ni(NO₃)(m-bn)₂]-(NO₃) (———).

region. The additional band observed at ca. 13×10³ cm⁻¹ in the dl-stien and phenen complexes can be attributed to Band II, i. e., the overlapping of the transition to $^3A_{2g}$ from $^3T_{1g}$(F)) and $^3B_{2g}$ (from $^3T_{2g}$) levels. The four bands observed are thus assigned to the transitions from $^3B_{1g}$ to the lowest ^3E_g (band I), $^3B_{2g}$ and $^3A_{2g}$ (band II), ^3E_g (band III), and $^3A_{2g}$ (from $^3T_{1g}$(P)) and ^3E_g (from $^3T_{1g}$(P)) (band IV), respectively, in the order of increasing energy. The shoulder at 12.5×10³ cm⁻¹ of the phenen complex is probably the transition to $^3B_{2g}$ state. Consequently, both of these complexes are clearly trans. On the other hand, the m-bn complex, whose spectrum scarcely show any splitting, is clearly cis.

Table 1 summarizes the coordination structures of ten complexes deduced in the same way, their electronic spectral data and the thermochemical reactions used to prepare them. Most of these complexes are trans, and only two, i.e., Ni(NO₃)₂(m-bn)₂ and NiCl₂(i-bn),[19,20] are cis.

The mode of coordination in the three nitrato complexes in Table 1 was also studied by means of their IR spectra. In general, an NO₃⁻ ion in a metallic complex gives rise to a weak combination band in the range of 1700—1800 cm⁻¹. When it exists as an uncoordinated ion, this band is not split, but when it is coordinated as a monodentate ion, a small splitting into two components (less than 25 cm⁻¹) takes place. When it acts as a bidentate ligand, the splitting becomes much larger (20—50 cm⁻¹).[21,22]

Figure 3 indicates the IR spectra of the nitrate complexes of dl-stien and m-bn, together with those of their mother complexes having the free nitrate ions, [Ni(H₂O)₂(diamine)₂](NO₃)₂. A peak at 1746 cm⁻¹ assignable to the free NO₃⁻ ions in the spectrum of the mother complex with dl-stien is split into two peaks at 1749 and 1767 cm⁻¹ with a separation of 18 cm⁻¹ in that of the nitrato complex. This indicates that, in the latter, the two NO₃⁻ ions are coordinated at the axial positions as a unidentate ligands to form the trans-octahedral complex.[23] On the other hand, the nitrato

Table 1. Electronic Spectral Data of the Complexes

Complex	Absorption Bands $\bar{\nu}/10^3$ cm⁻¹				Preparation Method[a]
	I	II	III	IV	
trans-[NiCl₂(phenen)₂]	7.9	13.5	17.6	27.8 sh	(a)
trans-[NiBr₂(phenen)₂]	7.6	13.5	17.4	27.2	(a)
trans-[Ni(NO₃)₂(phenen)₂]	8.3	13.7	18.3	27.0<	(b)
trans-[NiCl₂(dl-bn)₂]	8.2	14.3	18.2	28.1	(b)
trans-[NiBr₂(dl-bn)₂]	7.6	14.3	17.9	29.4 sh	(b)
trans-[NiCl₂(dl-stien)₂]	8.1	14.3	17.9	26.5 sh	(b)
trans-[NiBr₂(dl-stien)₂]	7.6	13.9	18.1	26.1 sh	(b)
trans-[Ni(NO₃)₂(dl-stien)₂]	8.6	14.3	18.4	26.6 sh	(b)
	I′	II′	III′		
cis-[NiCl₂(i-bn)₂]	10.5	17.7	28.0		(c)
cis-[Ni(NO₃)(m-bn)₂](NO₃)	10.2	17.2	27.2		(c)

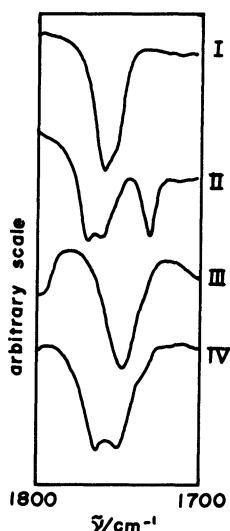a) The symbols a, b, or c correspond to the thermal reactions used to obtain the complexes (see text).

Fig. 3. IR spectra of [Ni(m-bn)₂](NO₃)₂(I), [Ni-(NO₃)(m-bn)₂](NO₃)(II), [Ni(H₂O)₂(dl-stien)₂]-(NO₃)₂(III), and [Ni(NO₃)₂(dl-stien)₂](IV).

complex with m-bn has the three peaks at 1732, 1758, and 1768 cm⁻¹. The peak at 1758 cm⁻¹ appears at nearly the same position as that of the mother complex, showing that a part of the NO₃⁻ ions remains uncoordinated. The large separation (36 cm⁻¹) between the other two peaks indicates that the coordinated NO₃⁻ ions are acting as bidentate ligand. Therefore, the nitrato m-bn complex can be formulated as cis-[Ni-(NO₃)(m-bn)₂](NO₃), having both free and bidentate nitrate ions.

The problem why only the nitrato complex of bis(m-bn) and the chloride complex of bis(i-bn) form the cis-octahedral structure is of interest. It is well known that the bis-type Ni(II) complexes with m-bn or i-bn strongly prefer a diamagnetic square planar structure,[1,24,25] so the generation of octahedral species with these diamines is quite unusual. In particular, the nitrato complex is the first example of an octahedral bis(m-bn) complex. Both of these novel complexes of cis-octahedral structure can be obtained only by the same type of thermal reaction (c), and they are converted into the original square planar complexes on cooling for some days, showing the reversibility of the structural changes.[26]

The work was partially supported by a Grant-in-Aid for Scientific Research No. 60303009 from the Ministry of Education, Science, and Culture.

References

1) Y. Ihara, T. Kamishima, and R. Tsuchiya, Thermochim. Acta, 67, 28 (1983).

2) If X⁻ ion (e.g. NO₃⁻) acts as a bidentate ligand, the formula is reperesented by [NiX(NN)₂]X (see text).

3) I. Bertini, D. Gatleschi, and A. Scozzafava, Inorg. Chem., 15, 203 (1976).

4) D. A. Cruse and M. Gerboch, J. Chem. Soc., Dalton Trans., 1977, 152.

5) L. Y. Martin, C. R. Sperati, and D. H. Busch, J. Am. Chem. Soc., 99. 2968 (1977).

6) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, Spectrosc. Lett., 12, 739 (1979).

7) A. B. P. Lever, Coord. Chem. Rev., 43, 63 (1982).

8) A. B. P. Lever, G. London, and P. J. McCarthy, Can. J. Chem., 55, 3172 (1977).

9) J. C. Donini, B. R. Hollebone, and A. B. P. Lever, Prog. Inorg. Chem., 22, 225 (1977).

10) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, Inorg. Chim. Acta, 44, L143 (1980).

11) I. M. Walker, A. B. P. Lever, and P. J. McCarthy, Can. J. Chem., 58, 823 (1980).

12) A. B. P. Lever, I. M. Walker, and P. J. McCarthy, Can. J. Chem., 60, 495 (1982).

13) A. B. P. Lever, "Inorganic Electronic Spectroscopy," 2nd ed., Elsevier, Amsterdam, 1985.

14) Y. Ihara and R. Tsuchiya, Bull. Chem. Soc. Jpn., 57, 2829 (1984).

15) Y. Ihara, Bull. Chem. Soc. Jpn., 58, 3248 (1985).

16) It is important to recognize that, depending upon the specific operators which survive from the cubic parent, there are three distinguishable C₂ᵥ systems, C₂ᵥ(I), C₂ᵥ(II), and C₂ᵥ(III), where the Roman numerals designate the surviving operators.[17] For example, trans(X,Y)-MX₂Y₂ZZ' is a C₂ᵥ(I) system, while trans-M(X-X)₂ZZ' is a C₂ᵥ(II) one. The geometry of the cis complexes described in this study(cis-M(X-X)₂Z₂) just belongs to C₂ᵥ(III), and here the ground state(^{3}A₂g) and ^{3}T₂g state of Oh system are transformed into ^{3}B₁ and ^{3}A₁+^{3}A₂+^{3}B₂, respectively,[9] as shown in Fig. 1.

17) J. C. Hempel, J. C. Donini, B. R. Hollebone, and A. B. P. Lever, J. Am. Chem. Soc., 96, 1693 (1974).

18) M. E. Farago, J. M. James, and V. C. G. Trew, J. Chem. Soc., (A), 1967, 820.

19) M. E. Farago, J. M. James, and V. C. G. Trew, J. Chem. Soc., (A), 1968, 48.

20) A. S. Antsyshkina and M. A. Porai-Koshits, Dokl. Akad. Nauk. SSSR, 143, 105 (1962).

21) A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, Can. J. Chem. 49, 1957 (1971).

22) Y. Fukuda, R. Morishita, and K. Sone, Bull. Chem. Soc. Jpn., 49, 1017 (1976).

23) The situation is quite similar in the case of trans-[Ni(NO₃)₂(phenen)₂], the data of which are not shown in Fig. 3.

24) H. Nishimoto, T. Yoshikuni, A. Uehara, E. Kyuno, and R. Tsuchiya, Bull. Chem. Soc. Jpn., 51, 1068 (1978).

25) L. D. Pettit and J. L. M. Swash, J. Chem. Soc., Dalton Trans., 1977, 697.

26) The cis-trans isomerism among the diaqua complexes, which are the starting complexes of the thermal reactions, is also an interesting problem. Here, however, the situation is more complicated than in this study, and, in certain cases, mixtures of cis-trans isomers are obtained according to the preparative methods. Details on this topic will be reported elsewhere.