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Studies of the Metal Complexes of Cyclohexane Derivatives. IV.[1] Copper(II) and Nickel(II) Complexes of 1,2-Cyclohexanediamine Isomers

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Two types of copper(II) complexes, Cu(*c*-chxn)$_2$X$_2$·*n*H$_2$O and Cu(*t*-chxn)$_2$X$_2$·*n*H$_2$O (X=Cl^-, Br^-, NO_3^-, and ClO_4^-, *n*=0—2), and three types of nickel(II) complexes, [Ni(*c*-chxn)$_2$]X$_2$, [Ni(*c*-chxn)$_3$]X$_2$·*n*H$_2$O (X=Cl^-, Br^-, NO_3^-, and ClO_4^-, *n*=0.5—1.5) and [Ni(*t*-chxn)$_2$(H$_2$O)$_2$]X$_2$ (X=Br^- and ClO_4^-), were synthesized. Here, *c*-chxn and *t*-chxn stand for *cis*- and *trans*-1,2-cyclohexanediamine respectively. Based upon the analyses of the electronic spectra and magnetic moments, the structures of the copper(II) complexes synthesized were found to be distorted octahedrons. The influence of the steric configurations of the diamine isomers on the structures of the copper(II) complexes is small. The three types of nickel(II) complexes were found to have square planar, octahedral, and distorted octahedral structures respectively. The steric influence of the ligands on the properties of the nickel(II) complexes was also considered.

Although the properties of various metal complexes of *trans*-1,2-cyclohexanediamine (abbreviated as *t*-chxn), but not the 1 : 2 complexes of copper(II) and nickel(II), have been studied so far,[2] no investigation of the metal complexes of *cis*-1,2-cyclohexanediamine (*c*-chxn) has been reported. These ligands may be regarded as C,C′-disubstituted ethylenediamine derivatives, but their steric properties due to the cyclohexane ring are quite different from one another. In the *c*-chxn complexes, the two amino groups are bound to the cyclohexane ring with axial and equatorial orientations simultaneously, so that the cyclohexane ring exists much closer to the chelate ring than in the *t*-chxn complexes. The present authors have prepared copper(II) and nickel(II) complexes of *c*-chxn and *t*-chxn and studied their properties by means of the electronic and infrared spectra, as well as the magnetic moments.

Experimental

Materials. From the Tokyo Kasei Co., Ltd., we purchased 1,2-cyclohexanediamine, which was then separated into *cis*- and *trans*-isomers according to the procedure described in previous paper.[3] The copper(II) and nickel(II) perchlorates were prepared from the corresponding metal basic carbonates and perchloric acid. The other metal salts used were of the highest grade available.

Preparation of Complexes. *Cu(*c*-chxn)$_2$X$_2$·nH$_2$O and Cu(*t*-chxn)$_2$X$_2$·nH$_2$O (X=Cl^-, Br^-, NO_3^-, and ClO_4^-, n=0—2)*: These complexes were synthesized by the reaction of 2 mmol of copper(II) salt and 4 mmol of *c*- or *t*-chxn in methanol. The violet product obtained was recrystallized from methanol-water.

[Ni(c-chxn)$_2$]X$_2$ (X=Cl^-, Br^-, NO_3^-, and ClO_4^-): The syntheses of these complexes were carried out much like those employed for the copper(II) complexes. The yellow crystals obtained were recrystallized from water. In the process of the recrystallization of [Ni(*c*-chxn)$_2$](NO$_3$)$_2$ and [Ni(*c*-chxn)$_2$](ClO$_4$)$_2$, a small amount of the yellow crystals occasionally turned violet. The violet complexes were completely transformed back to the yellow crystals, though, when they were kept in desiccated atmosphere.

[Ni(t-chxn)$_2$(H$_2$O)$_2$]X$_2$ (X=Br^- and ClO_4^-): The bromide complex was obtained by adding 15 ml of a 0.75 M ligand solution in methanol to 15 ml of a 0.5 M aqueous nickel(II) bromide solution. A blue violet precipitate was recrystallized from methanol–water. The perchlorate complex was prepared according to the following procedure. Six mmol of *t*-chxn in 6 ml of methanol were added to a solution of 4 mmol nickel(II) perchlorate in 8 ml of methanol. After removing a small amount of the tris-complex, the solution was heated on a water bath and concentrated until a small amount of product was deposited. The mixture was then allowed to stand at room temperature to give blue violet complex.

[Ni(c-chxn)$_3$]X$_2$·nH$_2$O (X=Cl^-, Br^-, NO_3^-, and ClO^-_4, n=0.5—1.5): To 3 mmol of *c*-chxn in 2 ml of ethanol we added 1 mmol of nickel(II) halide in 1 ml of water. The violet crystals thus obtained were recrystallized from ethanol–water to give [Ni(*c*-chxn)$_3$]Cl$_2$·1.5H$_2$O·0.5C$_2$H$_5$OH and [Ni(*c*-chxn)$_3$]Br$_2$·H$_2$O·0.5C$_2$H$_5$OH. The ethanol was removed by heating at 100 °C in the air for a few hours. [Ni(*c*-chxn)$_3$](NO$_3$)$_2$·0.5H$_2$O and [Ni(*c*-chxn)$_3$](ClO$_4$)$_2$·H$_2$O were readily obtained by mixing 3 mmol of the ligand in methanol with 1 mmol of nickel(II) salt in water.

[Ni(t-chxn)$_2$(H$_2$O)$_2$]X$_2$ (X=Cl^- and NO_3^-): These complexes were synthesized according to the methods described in the literature.[4]

Measurements. The magnetic moments were measured with a Shimadzu MB-2 magnetic balance at room temperature. Measurements of the electronic spectra of the copper(II) complexes in solution and the temperature dependence on the ε of the diamagnetic nickel(II) complexes were carried out using a Hitachi 124 spectrophotometer. The absorption and reflectance spectra of the nickel(II) complexes were measured with a Hitachi EPS-3T spectrophotometer. The infrared spectra in the range of 600—4000 cm^{-1} were recorded with a JASCO IRA-2 spectrophotometer by means of the KBr disc method. The far-infrared spectra in the range of 200—600 cm^{-1} were recorded on a JASCO DS-710G spectrophotometer in Nujol mulls.

Results and Discussion

Properties of the Complexes. The results of the elemental analyses, the magnetic moments, and the colors of the complexes newly synthesized in the present study are listed in Table 1. The copper(II) complexes with Cl^- and Br^- have 1—2 moles of water, while those with NO_3^- and ClO_4^- are anhydrous. From the values of the magnetic moments, the copper(II) complexes may be considered to be mononuclear.

The facility of the nickel(II) complex formation depends on the geometrical structure of the ligand, as well

Table 1. Colors, elemental analyses, and magnetic moments of the complexes

Complex	Color[a)]	Elemental analyses[b)] C%	H%	N%	μ (B.M.)
$Cu(c\text{-chxn})_2Cl_2 \cdot H_2O$	V	37.98(37.81)	8.08(7.94)	14.94(14.71)	1.86
$Cu(c\text{-chxn})_2Br_2 \cdot H_2O$	V	30.98(30.68)	6.57(6.44)	12.00(11.93)	1.87
$Cu(c\text{-chxn})_2(NO_3)_2$	V	34.75(34.65)	7.11(6.79)	20.55(20.20)	1.84
$Cu(c\text{-chxn})_2(ClO_4)_2$	V	29.11(29.37)	5.57(5.75)	11.26(11.41)	1.88
$Cu(t\text{-chxn})_2Cl_2 \cdot 2H_2O$	V	35.93(36.13)	7.75(8.08)	14.35(14.04)	1.88
$Cu(t\text{-chxn})_2Br_2 \cdot 2H_2O$	V	30.04(29.54)	6.87(6.61)	11.33(11.49)	1.84
$Cu(t\text{-chxn})_2(NO_3)_2$	V	34.70(34.65)	6.54(6.79)	20.53(20.20)	1.84
$Cu(t\text{-chxn})_2(ClO_4)_2$	V	29.69(29.37)	6.02(5.75)	11.27(11.41)	1.85
$[Ni(c\text{-chxn})_2]Cl_2$	Y	40.06(40.26)	7.93(7.88)	15.73(15.65)	dia
$[Ni(c\text{-chxn})_2]Br_2$	Y	31.83(32.25)	6.08(6.32)	12.53(12.54)	dia
$[Ni(c\text{-chxn})_2](NO_3)_2$	Y	34.87(35.06)	6.77(6.87)	20.59(20.44)	dia
$[Ni(c\text{-chxn})_2](ClO_4)_2$	OY	29.59(29.66)	5.97(5.81)	11.79(11.53)	dia
$[Ni(t\text{-chxn})_2(H_2O)_2]Br_2$	BV	30.15(29.85)	6.92(6.68)	11.40(11.60)	3.23
$[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$	BV	27.59(27.61)	6.11(6.18)	10.77(10.73)	3.20
$[Ni(c\text{-chxn})_3]Cl_2 \cdot 1.5H_2O$	V	43.15(43.30)	8.68(9.09)	16.45(16.83)	3.12
$[Ni(c\text{-chxn})_3]Br_2 \cdot H_2O$	V	37.71(37.33)	7.78(7.66)	14.16(14.51)	3.03
$[Ni(c\text{-chxn})_3](NO_3)_2 \cdot 0.5H_2O$	V	40.34(40.46)	8.25(8.11)	21.27(20.97)	3.15
$[Ni(c\text{-chxn})_3](ClO_4)_2 \cdot H_2O$	V	35.02(34.97)	7.18(7.17)	13.88(13.59)	3.16

a) V=violet, BV=blue violet, Y=yellow, OY=orange yellow. b) Calculated values in parentheses.

as on the counter anion concerned. The diamagnetic nickel(II) complexes of *c*-chxn were preferentially synthesized by the reaction of a 1:2 molar ratio of nickel(II) salt and ligand in a methanol solution. Tsuchida[4)] reported the preparation of two types of bis complexes, $[Nichxn_2]X_2$ ($X=Cl^-$, Br^-, and ClO_4^-) and $[Nichxn_2(H_2O)_2]X_2$ ($X=Cl^-$ and NO_3^-), and described the chxn as *t*-chxn. The synthetic method and the electronic and magnetic properties of $[Ni(c\text{-chxn})_2]X_2$ obtained here are almost the same as those of Tsuchida' s$[Nichxn_2]X_2$. Therefore, the $[Nichxn_2]X_2$ obtained by Tsuchida seems to consist of the *c*-chxn complexes formed with a small amount of the *cis* isomer contained in chxn.[3)] On the other hand, the *t*-chxn ligand afforded paramagnetic dihydrated bis-complexes. The isolation of $[Ni(t\text{-chxn})_2(H_2O)_2]X_2$ ($X=Br^-$ and ClO_4^-) was a little more difficult than that of the same type of the complexes with Cl^- and NO_3^-, because less soluble $[Ni(t\text{-chxn})_3]X_2 \cdot nH_2O$ substances were precipitated during the syntheses of the bis-complexes. The $[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$ shows a tendency to change to the orange yellow form in the dried atmosphere, losing almost 2 mol of coordinated water, which were, on the contrary, taken up by the complex when it was kept in the air. The $[Ni(c\text{-chxn})_3]Cl_2 \cdot 1.5H_2O$ and $[Ni(c\text{-chxn})_3]Br_2 \cdot H_2O$ are a little less stable than the corresponding tris-complexes of *t*-chxn and tend to change to yellow complexes when refluxed in methanol. The magnetic moments of all the nickel(II) complexes except for the yellow complexes of the *c*-chxn are around 3.1 B. M., and they indicate octahedral structures.

Electronic Spectra. The electronic spectra of the complexes were studied either in solution or in the solid state. Some typical spectra are shown in Figs.1—2, and the numerical results, in Tables 2—3. The absorption spectra of the *c*-chxn and *t*-chxn complexes with copper(II) halides show a d-d transition band at around 17700 cm^{-1}. The corresponding bands of the nitrate and perchlorate complexes appear in a somewhat shorter-wavelength region than those of the halide complexes. The reflectance spectra of the copper(II) complexes show a band in the region of 17900—19400 cm^{-1}. It is generally recognized that the electronic spectra of the copper(II) complexes of ethylenediamine derivatives exhibit a broad d-d band in the region of 14000—22000 cm^{-1}.[5)] The structures of the copper(II) complexes obtained are considered to be tetragonally distorted octahedrons, with diamine ligands to form a square planar structure. The degrees of the tetragonal distortion in the structures of the complexes with NO_3^- and ClO_4^- seem to be larger than those of Cl^-

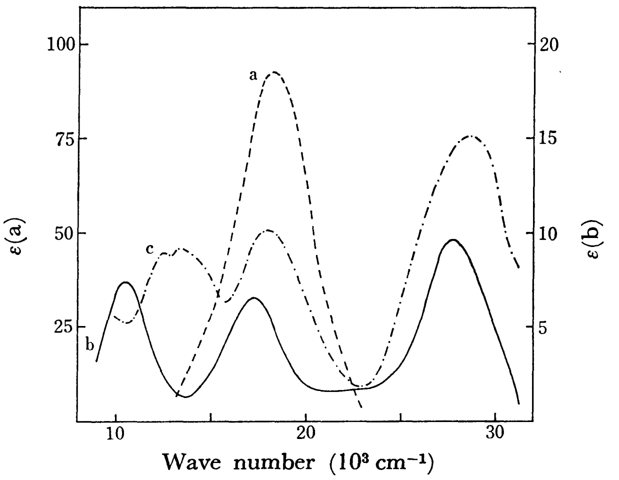

Fig. 1. Electronic spectra of (a) $Cu(t\text{-chxn})_2(ClO_4)_2$ (MeOH soln), (b) $[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$ (MeOH soln), and (c) $[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$ (Solid).

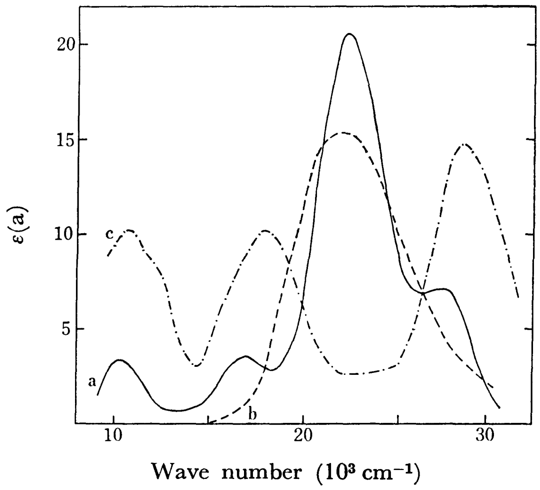

Fig. 2. Electronic spectra of (a) [Ni(*c*-chxn)$_2$](ClO$_4$)$_2$ (H$_2$O soln), (b) [Ni(*c*-chxn)$_2$](ClO$_4$)$_2$ (Solid), and (c) [Ni(*c*-chxn)$_3$](ClO$_4$)$_2$·H$_2$O (Solid).

and Br$^-$. The former two polyatomic anions were assumed to coordinate very weakly toward the copper(II) ion, because no appreciable distortion of the free ion was found in their infrared spectra. For the structures of the copper(II) complexes containing both X$^-$ and H$_2$O, it was difficult to know which ligand, X$^-$ or H$_2$O, coordinates in the tetragonal positions. The spectral properties suggest, however, that the steric configurations of the ligands have little effect on the coordination tendencies toward copper(II) ions. These results agree with the stability constants of the copper(II) complexes of the chxn isomers, whose values are nearly equal to each other.[6]

The electronic spectra of [Ni(*c*-chxn)$_2$]X$_2$ (X=Cl$^-$, Br$^-$, NO$_3^-$, and ClO$_4^-$) in the solid state show a relatively strong band at around 22000 cm^{-1} which is characteristic of a square planar structure. In aqueous solutions of these complexes, three additional bands (Bands I, III, and IV) corresponding to the octahedral structure are observed. These results indicate that [Ni(*c*-chxn)$_2$]$^{2+}$ and [Ni(*c*-chxn)$_2$(H$_2$O)$_2$]$^{2+}$ coexist in water. The [Ni(*c*-chxn)$_2$(H$_2$O)$_2$]$^{2+}$ cation can be assigned to the *cis* configuration because its spectral features are very similar to those of the [Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$ cation which exists as the *cis* form in solution.[7] Thermochromism is found in aqueous solutions of four [Ni(*c*-chxn)$_2$]X$_2$ complexes. As is shown in Fig.3, the intensity of Band V increases with an increase in the temperature. This reveals that the equilibrium between square planar and octahedral structures proceeds toward a dehydration reaction with a rise in the temperature. Similar behavior has been reported for ethylenediamine–nickel(II) complexes.[8]

The structures of the [Ni(*t*-chxn)$_2$(H$_2$O)$_2$]X$_2$ (X=Br$^-$ and ClO$_4^-$) complexes in the solid state are regarded as tetragonally distorted octahedrons, with water molecules coordinating in the axial positions, since these spectra show a splitting of Band I, although the peak at the lower wave number has not been measured in the present study, and since the spectra resemble those of [Ni(en)$_2$(H$_2$O)$_2$]X$_2$ (X=NO$_3^-$ and ClO$_4^-$) and of *t*-chxn complexes of the same type previously

Table 2. Electronic spectra of the copper(II) complexes

Complex	ν 10^3 cm^{-1} (ε)	
	Solid	in Methanol
Cu(*c*-chxn)$_2$Cl$_2$·H$_2$O	18.7	17.7 (119)
Cu(*c*-chxn)$_2$Br$_2$·H$_2$O	17.9	17.8 (122)
Cu(*c*-chxn)$_2$(NO$_3$)$_2$	19.0	18.3 (110)
Cu(*c*-chxn)$_2$(ClO$_4$)$_2$	19.4	18.3 (107)
Cu(*t*-chxn)$_2$Cl$_2$·2H$_2$O	18.4	17.7 (108)
Cu(*t*-chxn)$_2$Br$_2$·2H$_2$O	17.9	17.8 (105)
Cu(*t*-chxn)$_2$(NO$_3$)$_2$	19.2	18.3 (91)
Cu(*t*-chxn)$_2$(ClO$_4$)$_2$	18.7	18.3 (93)

Table 3. Electronic spectra of the nickel(II) complexes

Complex	State	ν 10^3 cm^{-1} (ε)				
		I	II	III	IV	V
[Ni(*c*-chxn)$_2$]Cl$_2$	Solid	—	—	—	—	22.6
	H$_2$O[a)]	10.3 (4.9)	—	17.1 (4.2)	27.4 (7.8)	22.4 (21.1)
[Ni(*c*-chxn)$_2$]Br$_2$	Solid	—	—	—	—	22.3
	H$_2$O[a)]	10.4 (3.3)	—	17.1 (3.5)	27.0 (7.7)	22.2 (21.9)
[Ni(*c*-chxn)$_2$](NO$_3$)$_2$	Solid	—	—	—	—	22.8
	H$_2$O[a)]	10.3 (4.6)	—	17.1 (4.7)	27.0 (9.2)	22.2 (22.5)
[Ni(*c*-chxn)$_2$](ClO$_4$)$_2$	Solid	—	—	—	—	21.8
	H$_2$O[a)]	10.4 (3.3)	—	16.9 (3.6)	27.4 (7.1)	22.2 (20.7)
[Ni(*t*-chxn)$_2$(H$_2$O)$_2$]Br$_2$	Solid	13.0	12.2	17.4	28.1	—
[Ni(*t*-chxn)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	Solid	13.3	12.5	18.0	28.6	—
	MeOH	10.5 (7.4)	—	17.1 (6.6)	27.8 (9.7)	—
[Ni(*c*-chxn)$_3$]Cl$_2$·1.5H$_2$O	Solid	10.6	12.2[b)]	17.7	28.1	—
	MeOH	10.6 (7.5)	12.3[b)]	17.5 (7.9)	28.1 (12.1)	—
[Ni(*c*-chxn)$_3$]Br$_2$·H$_2$O	Solid	10.6	12.2[b)]	17.6	28.2	—
[Ni(*c*-chxn)$_3$](NO$_3$)$_2$·0.5H$_2$O	Solid	10.6	12.3[b)]	17.8	28.4	—
[Ni(*c*-chxn)$_3$](ClO$_4$)$_2$·H$_2$O	Solid	10.9	12.3[b)]	17.8	28.4	—

a) The values of ε vary with the temperature. b) Shoulder.

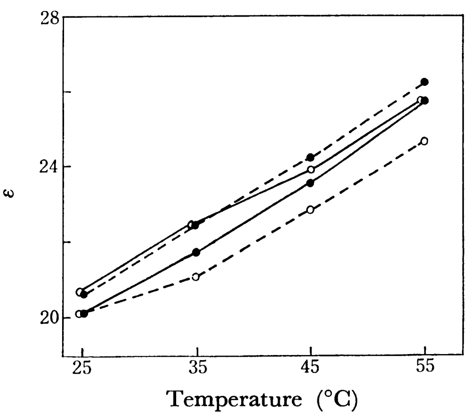

Fig. 3. Temperature dependence of the ε of Band V in the electronic spectra of the nickel(II) complexes (H_2O soln).
●(——): $[Ni(c\text{-chxn})_2]Cl_2$, ●(- - -): $[Ni(c\text{-chxn})_2]Br_2$, ○(——): $[Ni(c\text{-chxn})_2](ClO_4)_2$, ○(- - -): $[Ni(c\text{-chxn})_2](NO_3)_2$.

reported.[4,7] In a methanol solution, they are transformed to the *cis* form as well as $[Ni(c\text{-chxn})_2(H_2O)_2]^{2+}$.

The spectra of a series of tris-complexes of *c*-chxn have three main peaks typical of octahedrally coordinated nickel(II). Although these structures are analogous to those of the *t*-chxn and ethylenediamine complexes, the tris-complexes of *c*-chxn are thermodynamically less stable and the successive stability constant, k_3, has not been measured.[6] The instability of the tris-complexes of the *c*-chxn may be ascribable to the configuration of the ligand. The structures of the tris-complexes of *c*-chxn are more puckered due to the axial amino groups than those of the *t*-chxn. Similarly, the fact that hardly no paramagnetic bis-complexes of the *c*-chxn were obtained may also be explained by their unfavorable *cis* form in solution.

Infrared Spectra. All the nickel(II) complexes with the NO_3^- group show a broad strong absorption near 1350 cm^{-1} in their infrared spectra and seem to contain free nitrate ions.[9] Similarly, the $[Ni(c\text{-chxn})_2](ClO_4)_2$, $[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$, and $[Ni(c\text{-chxn})_3](ClO_4)_2 \cdot H_2O$ complexes were assumed to have ionic perchlorate ions on the basis of the ν_{Cl-O} band at around 1080 cm^{-1}.[10] Therefore, in octahedral $[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$, water molecules were regarded as coordinating to the nickel(II) ion. The ν_{O-H} bands, overlapping the two ν_{N-H} bands, were observed in a lower frequency region than that of water of crystallization. In the spectra of the copper(II) complexes containing NO_3^- and ClO_4^-, hardly any splitting of ν_{N-O} and ν_{Cl-O} was observed.

Table 4 summarizes the infrared frequencies of these complexes. The ν_{N-H} frequencies are found to shift toward higher frequencies in the order of $Cl^- \leqq Br^- < NO_3^- < ClO_4^-$. This shift is considered to arise mainly from the hydrogen bond between the amino group and the anion. The δ_{NH_2} of the bromide complexes shifted to frequencies lower by 2—11 cm^{-1} than those of the corresponding chloride complexes. The deformation frequency may be affected by the strength of the M–N bond and the structural difference of the complexes, in addition to the extent of the hydrogen bond; hence, a systematic trend of band shifts has not been deduced for all the complexes prepared. The rocking modes of the NH_2 groups, which were assigned by means of the deuteration of the representative complexes, are distinctly metal-sensitive as has been described in the literature.[10] Figure 4 illustrates some typical far-infrared spectra of the 1:2 copper(II) and nickel(II) complexes. The assignment of the metal nitrogen stretching bands has been subject to great confusion; however, two bands located at 370—420 and 240—280 cm^{-1} have been found to be fairly metal-sensitive. These bands are illustrated as (A) and (B) in Fig. 4 and are summarized in the last two columns in Table 4. Lever and Mantovani[11] studied the far-infrared spectra of metal complexes of ethylenediamine

TABLE 4. THE MAIN INFRARED BANDS OF THE BIS-COMPLEXES (cm^{-1})

Complex	ν_{N-H}	δ_{NH_2}	ρ_{rNH_2}	Unassigned	
$Cu(c\text{-chxn})_2Cl_2 \cdot H_2O$	3210, 3120[a]	1593	—[b]	417	282
$Cu(c\text{-chxn})_2Br_2 \cdot H_2O$	3220, 3130[a]	1582	—[b]	417	288
$Cu(c\text{-chxn})_2(NO_3)_2$	3310, 3260, 3170	1602, 1590 sh	730	420	288
$Cu(c\text{-chxn})_2(ClO_4)_2$	3340, 3300	1603, 1592	734	418	285
$Cu(t\text{-chxn})_2Cl_2 \cdot 2H_2O$	3270, 3230, 3150[a]	1592	—[b]	418	283
$Cu(t\text{-chxn})_2Br_2 \cdot 2H_2O$	3280, 3230, 3150[a]	1592, 1580	—[b]	418	300
$Cu(t\text{-chxn})_2(NO_3)_2$	3340, 3290, 3170	1603	733	420	293
$Cu(t\text{-chxn})_2(ClO_4)_2$	3340, 3290, 3170 sh	1592	711	420	289
$[Ni(c\text{-chxn})_2]Cl_2$	3190, 3090	1605, 1595	665	382	259
$[Ni(c\text{-chxn})_2]Br_2$	3200, 3100	1598, 1588	662	379	251
$[Ni(c\text{-chxn})_2](NO_3)_2$	3260, 3170	1602	660	378	245
$[Ni(c\text{-chxn})_2](ClO_4)_2$	3330, 3180	1600	664	371	240
$[Ni(t\text{-chxn})_2(H_2O)_2]Cl_2$	3340, 3260, 3180[a]	1605	669 sh, 661	408	278
$[Ni(t\text{-chxn})_2(H_2O)_2]Br_2$	3330, 3270, 3170[a]	1603	668 sh, 661	409	276
$[Ni(t\text{-chxn})_2(H_2O)_2](NO_3)_2$	3350, 3290, 3200 sh[a]	1598	692, 670 sh	412	280
$[Ni(t\text{-chxn})_2(H_2O)_2](ClO_4)_2$	3360, 3300, 3180 sh[a]	1596	660	412	276

sh = shoulder. a) These bands seem to be overlapped with the neighboring ν_{O-H} bands. b) 1—2 bands were observed assignable to ρ_{rNH_2} or ρ_{rH_2O} in the 650—750 cm^{-1} region.

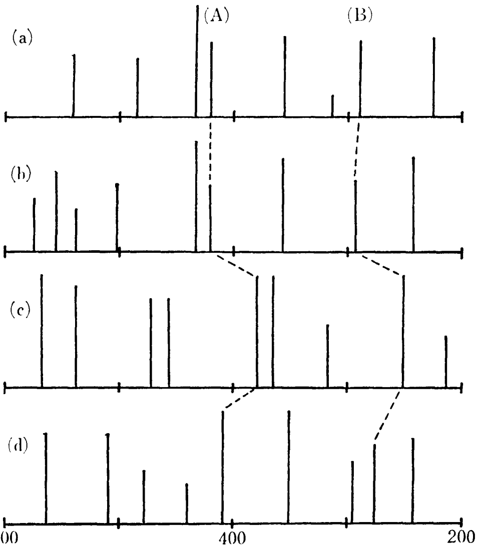

Fig. 4. Observed bands in the infrared spectra in the region between 200 and 600 cm^{-1}. (a): Cu(c-chxn)$_2$-(NO$_3$)$_2$, (b): Cu(t-chxn)$_2$(NO$_3$)$_2$, (c): [Ni(c-chxn)$_2$]-Br$_2$, (d): [Ni(t-chxn)$_2$(H$_2$O)$_2$]Br$_2$.

and its derivatives extensively and assigned the peaks in the regions of 403—421 and 309—331 cm^{-1} to $\nu_{\mathrm{Cu-N}}$, while the peaks in the region of 275—395 cm^{-1} were assigned to $\nu_{\mathrm{Ni-N}}$. Omura *et al.*[12] assigned the two bands at 412 and 472 cm^{-1} to the $\nu_{\mathrm{Cu-N}}$ of [Cu(en)$_2$]$^{2+}$. Therefore, the bands observed around 370—420 cm^{-1} may be regarded one consisting dominantly of the $\nu_{\mathrm{M-N}}$ band. The other lower metal-sensitive bands are supposed to be characteristic of the δ_{NMN} vibration, considering the values of the same type of complex. It is of interest that the frequency order of the metal-sensitive bands is Cu(t-chxn)$_2$X$_2$>Cu(c-chxn)$_2$X$_2$>[Ni(t-chxn)$_2$(H$_2$O)$_2$]X$_2$>[Ni(c-chxn)$_2$]X$_2$, which is consistent with the order of the stability constants.

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References

1) Part III of this series: R. Saito and Y. Kidani, *Nippon Kagaku Kaishi*, **1975**, 1734.

2) For example (a) F. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966); (b) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 2584 (1967); (c) E. Pedersen, *Acta Chem. Scand.*, **24**, 3362 (1970); (c) M. J. Harding, S. F. Mason, and B. J. Peart, *J. Chem. Soc., Dalton Trans.*, **1973**, 955.

3) R. Saito and Y. Kidani, *Chem. Lett.*, **1976**, 123.

4) M. Tsuchida, *Natural Science Report Ochanomizu Univ.*, **24**, 13 (1972).

5) I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc., A*, **1968**, 1678.

6) C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phy. Chem.*, **62**, 445 (1958).

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

8) K. Sone and M. Kato, *Z. Anorg. Allg. Chem.*, **301**, 277 (1959).

9) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

10) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York (1970).

11) B. P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 817 (1971).

12) Y. Omura, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, **27**, 2227 (1970).