Chelate Complexes of Nickel (II) and Copper (II) with trans-1, 2-Diaminocyclohexane

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Several nickel chelates with trans-1, 2-diaminocyclohexane (=cyclo-hexanediamine ; abbreviated as chxn), Ni $chxn_2X_2 \cdot nH_2O$ (X=Cl, Br, NO_3 or ClO_4 ; n=0 or 2) and Ni $chxn_3X_2 \cdot nH_2O$ (X=Cl, Br or NO_3 ; n=1 or 2.5) were prepared, together with some copper (II) chelates with the same ligand, Cu $chxn_2(NO_3)_2$ and Cu chxn L $(NO_3)_2 \cdot nH_2O$ (L=2, 2'-bipyridine : bip or 1, 10-phenanthroline : phen ; n=0 or 1). Two types of the bis-chxn nickel complexes are obtained, one is yellow diamagnetic and square planar [Ni $chxn_2$]X_2 and the other, purple, paramagnetic and octahedral [Ni $chxn_2(H_2O)_2$]X_2. These two chelates are in equilibrium in the aqueous solution.

Ni (II) forms many kinds of 4-, 5- or 6-coordinated complexes, showing nearly every kind of stereochemistries for these coordination numbers. Examples of tetrahedral, square planar, trigonal bipyramidal, square pyramidal, octahedral and tetragonal complexes are all known, among which the square planar (D_{4h}) diamagnetic complexes and the octahedral (O_h) paramagnetic ones are most common and have been most extensively investigated. Generally speaking, the former complexes are yellow, orange or red, while the latter ones are purple, blue or green, although exceptions to this rule sometimes occur. Whether the reaction of a nickel salt with a particular ligand leads to the formation of a diamagnetic complex or to a paramagnetic one depends primarily on the coordination ability (ligand field strength, ability of π-bond formation etc.) of the ligand, although the effects of the anion in the original nickel salt and of the steric properties of the ligand cannot be neglected in many cases.

Ethylenediamine (en) and its derivatives are known to yield both of these types of complexes, depending on the nature of the substituents in the ligands and that of the anions. Studies have been made

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on the complexes with propylenediamine (pn)[1], 2-methylpropylene-diamine (2-mepn)[2] and other C-substituted ethylenediamines[3], and also with N, N-dimethylethylenediamine (a-dimen)[4] and N, N-diethylethyl-enediamine (a-dien)[5].

Trans-1, 2-diaminocyclohexane (chxn) is a C-substituted ethylene-diamine which has special steric properties owing to its cyclohexane ring. Recently a number of Au (III), Pd (II), Pt (II) and Co (III) chelates of this ligand have been prepared and their properties have been reported by H. Ito et al.[6], and R. G. Asperger and C. F. Liu[7], but studies on its nickel chelates seem to be few[8].

In this paper, the results of a preparative study of the nickel-chxn complexes will be reported, and their spectral and magnetic properties will be discussed in comparison with other nickel-diamine complexes.

Experimental

Two samples of cyclohexanediamine were used in this work. One is trans-1, 2-cyclohexanediamine sulfate (c. p. grade) of Tokyo Kasei Co., and the other is 1, 2-cyclohexanediamine of Aldrich Chemical Co. which seems to be very predominantly trans.* To prepare complexes from the diamine sulfate, it was first dissolved in boiling water with the calculated amount of $Ba(OH)_2 \cdot 8H_2O$. After cooling, the thick $BaSO_4$ precipitate was removed by centrifugation and the resulting aqueous solution of the free diamine was used for complex formation.

All the other compounds used were reagent grade chemicals, except for $Ni(ClO_4)_2 \cdot 6H_2O$ which was prepared from $Ni(NO_3)_2 \cdot 6H_2O$ by precipitating $NiCO_3$, dissolving with $HClO_4$ and concentrating with a rotary evaporator.[10]

Preparation of the Nickel Complexes

(a) Ni $chxn_2Cl_2$

20 mmol of the diamine and 10 mmol of $NiCl_2 \cdot 6H_2O$ were mixed with stirring in methanol. A greenish blue solution was obtained, which became deep blue after two hours. A yellow precipitate separated out during this change, which was filtered and washed with methanol and recrystallized from hot water. (Found: C, 40.22; N, 15.76; H, 7.37%; Calcd: C, 40.26; N, 15.65; H, 7.88%)

(b) Ni $chxn_2Cl_2 \cdot 2H_2O$

This purple complex was obtained by concentrating the deep blue filtrate obtained in the preparation of (a), and recrystallized from methanol. (Found: C, 36.40; N, 14.22; H, 7.66%; Calcd: C, 36.58; N,

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* J. Fujita, private communication.

14.22 ; H, 8.18%)

If the reaction mixture in the preparation of (a) was set aside for one day or more, the complexes (a) and (b) precipitated together, but they could be separated by fractional dissolution with methanol.

(c)   Ni chxn$_2$Br$_2$

This yellow complex was prepared and recrystallized in the same manner as in the preparation of (a), using anhydrous NiBr$_2$ instead of NiCl$_2$·6H$_2$O. In this case no purple form complex corresponding to (b) could be obtained. (Found : C, 32.56 ; N, 12.59 ; H, 6.42% ; Calcd : C, 32.25 ; N, 12.54 ; H, 6.32%)

(d)   Ni chxn$_3$(ClO$_4$)$_2$

This yellow complex was also prepared and recrystallized in the same manner as in the preparation of (a), using Ni(ClO$_4$)$_2$·6H$_2$O instead of NiCl$_2$·6H$_2$O. In this case, the purple Ni chxn$_3$(ClO$_4$)$_2$ which was soluble in methanol but insoluble in water, was formed so easily that repeated washing was needed for purification. (Found : C, 29.54 ; N, 12.00 ; H, 5.28% ; Calcd : C, 29.66 ; N, 11.53 ; H, 5.81%)

(e)   Ni chxn$_2$(NO$_3$)$_2$·2H$_2$O

This purple complex was prepared as in the preparation of (a), using Ni(NO$_3$)$_2$·6H$_2$O instead of NiCl$_2$·6H$_2$O. The product was recrystallized from hot water or ethanol. The yellow form complex corresponding to (a), (c) or (d) was not obtained in this case. (Found : C, 32.48 ; N, 18.64 ; H, 7.45% ; Calcd : C, 32.24 ; N, 18.79 ; H, 7.21%)

(f)   Ni chxn$_3$Cl$_2$·2.5H$_2$O

The ligand and metal chloride were mixed in 3 : 1 molar ratio in methanol solution. The resulting purple precipitate was filtered, washed with methanol and dried in vacuo. (Found : C, 41.76 ; N, 16.11 ; H, 8.82% ; Calcd : C, 41.80 ; N, 16.25 ; H, 9.16%)

(g)   Ni chxn$_3$Br$_2$·2.5H$_2$O

This was prepared in the same manner as in the preparation of (f), using anhydrous nickel bromide instead of the chloride. (Found : C, 34.94 ; N, 13.85 ; H, 7.38% ; Calcd : C, 35.66 ; N, 13.87 ; H, 7.82%)

(h)   Ni chxn$_3$(ClO$_4$)$_2$·H$_2$O

Attempts to prepare the complex (d) in aqueous solution, using the ligand solution obtained from its sulfate, resulted in the precipitation of this tris-complex because of its insolubility in water. The purple precipitate was washed with water and dried in vacuo. (Found : C, 34.67 ; N, 13.86 ; H, 6.71% ; Calcd : C, 34.97 ; N, 13.59 ; H, 7.17%)

Preparation of the Copper Complexes

(i)   Cu chxn$_2$(NO$_3$)$_2$

20 mmol of the diamine in an aqueous solution obtained from its sulfate and 10 mmol of Cu(NO$_3$)$_2$·3H$_2$O in another aqueous solution were

mixed with stirring. A deep blue solution obtained was concentrated with a rotary evaporator to precipitate the chelate, which was then filtered, washed with water and recrystallized from hot water. (Found : C, 34.70 ; N, 20.02 ; H, 6.56% ; Calcd : C, 34.66 ; N, 20.21 ; H, 6.78%)

(j) Cu chxn bip(NO_3)$_2$·H_2O

Aqueous solutions of $Cu(NO_3)_2$·$3H_2O$, chxn obtained from its sulfate and bip were mixed in 1 : 1 : 1 molar ratio. The deep blue reaction mixture was concentrated and the resulting crystals were filtered, washed with water and recrystallized from hot water. (Found : C, 40.36 ; N, 17.34 ; H, 4.97% ; Calcd : C, 40.38 ; N, 17.66 ; H, 5.08%)

(k) Cu chxn phen(NO_3)$_2$

This was prepared in the same manner as in the preparation of (j), using phen instead of bip. (Found : C, 44.64 ; N, 17.29 ; H, 4.97% ; Calcd : C, 44.86 ; N, 17.44 ; H, 4.60%)

Physical Measurements

The electronic absorption spectra of the solutions were recorded with a Shimadzu Multiconvertible spectrophotometer DOUBLE-40 and a Shimadzu MPS-50 recording spectrophotometer, using 1 cm and 5 cm cells.

The diffuse reflectance spectra of finely ground solid samples were obtained with a Shimadzu MPS-50L recording spectrophotometer, using $KClO_4$ as the reference.

The infrared spectra were recorded with a JASCO-Infrared-G spectrophotometer with Nujol or hexachlorobutadiene mulls, using a polystyrene film for calibration.

Magnetic susceptibilities were measured by the Gouy method at room temperature using water as the standard, and calibrating with $HgCo(NCS)_4$. The molar susceptibility in each case was corrected for the diamagnetism of the ligand, water and anions.

Results and Discussion

Formulation of the Obtained Chelates

From the compositions of the obtained nickel chelates and their colors, magnetic moments, electronic spectra listed in Table 1, IR spectra and from the well-known fact that the coordination abilities of the ligands in these chelates decrease in the order diamine→H_2O →anions, the formulas in the first column of Table 1 can be readily derived.

The correlation between the coordination number (4 or 6) and magnetic moment or color was already mentioned in the Introduc-

Table 1. Formulas, colors, magnetic moments and electronic absorption spectra of the obtained complexes at room temperature.

Formula (Color)	μ(B.M.)	State*	Absorption Max. (10^3 cm^{-1}, ϵ in parenthesis)			
			ν_1	ν_2	ν_{dia}	ν_3
(a) [Ni chxn$_2$]Cl$_2$ (yellow)	dia	solid			23.1	
		H$_2$O	10.8 (4.6)	17.2 (4.1)	22.6(18.0)	27.7 (7.3)
(b) [Ni chxn$_2$(H$_2$O)$_2$]Cl$_2$ (purple)	3.10	solid	9.2 12.9	17.5		28.2
		H$_2$O	10.9 (6.5)	17.7 (5.6)		28.2 (8.3)
		MeOH	10.6 (7.1)	17.4 (6.0)		27.9 (8.7)
(c) [Ni chxn$_2$]Br$_2$ (yellow)	dia	solid			23.0	
		H$_2$O	10.7 (5.2)	17.5 (5.0)	22.5(21.3)	27.5(19.0)
(d) [Ni chxn$_2$](ClO$_4$)$_2$ (yellow)	dia	solid	11.0		22.1	
		H$_2$O	10.8 (4.4)	17.3 (3.9)	22.5(15.8)	27.5 (6.9)
		MeNO$_2$			22.3(48.0)	
		DMF	10.8(13.3)	17.4 (9.0)	23.0 (3.7)	28.2(15.8)
(e) [Ni chxn$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (purple)	3.28	solid	8.5 13.3	18.0		28.4
		H$_2$O	10.8 (7.0)	17.6 (5.8)	22.5 (4.9)	28.1(11.2)
		MeOH	10.4 (6.1)	17.3 (5.7)	22.4 (3.7)	27.9 (9.5)
		DMF	10.8(11.4)	17.7 (9.2)		28.3(16.9)
(f) [Ni chxn$_3$]Cl$_2$·2.5H$_2$O (reddish purple)	3.04	solid	8.3sh 11.4	18.0		28.4
		MeOH	11.4 (7.3)	18.1 (7.0)		28.7 (9.8)
(g) [Ni chxn$_3$]Br$_2$·2.5H$_2$O (reddish purple)	3.04	solid	8.3sh 11.6	18.4		29.4
		MeOH	11.7	18.3		29.0
(h) [Ni chxn$_3$](ClO$_4$)$_2$·H$_2$O	3.21	solid	8.3sh 11.4	18.3		29.2
(i) [Cu chxn$_2$](NO$_3$)$_2$ (violet)	1.90	solid	19.1			
		H$_2$O	18.4(83.2)			
		MeOH	18.5(61.5)			
(j) [Cu bip chxn](NO$_3$)$_2$·H$_2$O (grayish blue)	1.82	solid	17.2			
		H$_2$O	17.3(67.4)			
		MeOH	17.3(75.1)			
(k) [Cu chxn phen](NO$_3$)$_2$ (deep blue)	1.87	solid	17.4			
		H$_2$O	17.2(63.6)			
		MeOH	17.2(67.8)			

* H$_2$O, MeOH, MeNO$_2$ and DMF mean, respectively, aqueous, methanolic, nitromethane and dimethylformamide solutions.

tion; as to the spectra, it is known that a square planar complex shows usually a band of relatively high intensity ($\varepsilon \sim 50$) in the visible, while an octahedral one shows usually three weak bands (and sometimes four owing to the splitting of the first band, i. e., the band with the lowest energy). It can be seen that, in the solid state, all the yellow diamagnetic complexes in Table 1 show only one band (ν_{dia}), while all the purple paramagnetic ones show three to four ($\nu_1-\nu_3$), in conformity with expectation.

As to the copper chelates the formulation is quite simple since their colors and electronic absorption spectra are very similar to those of the common tetrammines of copper (see later). The formulas [Cu chxn$_2$](NO$_3$)$_2$, [Cu chxn bip](NO$_3$)$_2 \cdot$H$_2$O and [Cu chxn phen](NO$_3$)$_2$ are thus most probable.

Correlation between Spectra and Structures of the Nickel Chelates in Various States

From the foregoing discussion, it seems evident that, among the nickel complexes, (a), (c) and (d) are all square planar, while all others are octahedral in structure. Among the latter, the complexes (f), (g) and (h) are expected to have approximately O$_h$ symmetry, but (b) and (e) may have eitner cis- or trans-configuration (C$_{2v}$ and D$_{4h}$, respectively). The structures of all the bis-chelates, moreover, seem to change in various ways when they are dissolved in different solvents.

(1) Square Planar Complexes

[Ni chxn$_2$]Cl$_2$ (Fig. 1) and [Ni chxn$_2$]Br$_2$ show very similar spectra. In solid state they show only one band at 433–434 nm (23.0–23.1 kK),

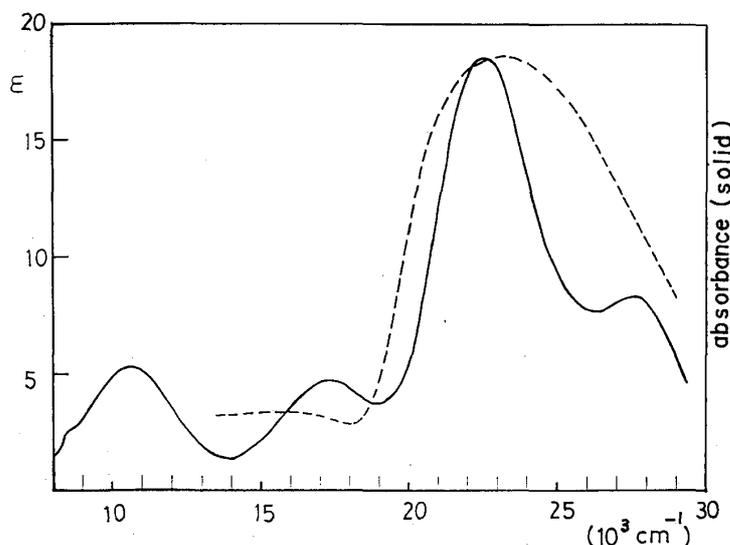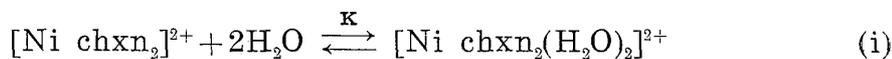Fig. 1. Spectra of [Ni chxn$_2$]Cl$_2$.

———— H$_2$O soln., − − − − − − solid.

while in aqueous solutions both of them show four. The one at 445-448 nm seems to correspond to that of the solid state, and the other three are found in the neighborhood of the bands observed in the aqueous solution of $[Ni\ en_2(H_2O)_2]^{2+}$, so that an equilibrium

$$[Ni\ chxn_2]^{2+} + 2H_2O \underset{\longleftarrow}{\overset{K}{\longrightarrow}} [Ni\ chxn_2(H_2O)_2]^{2+} \tag{i}$$

seems to be established in aqueous solution. An essentially similar situation is observed with $[Ni\ chxn_2](ClO_4)_2$ (Fig. 2); since this chelate is soluble in some organic solvents, the spectra in nitromethane and
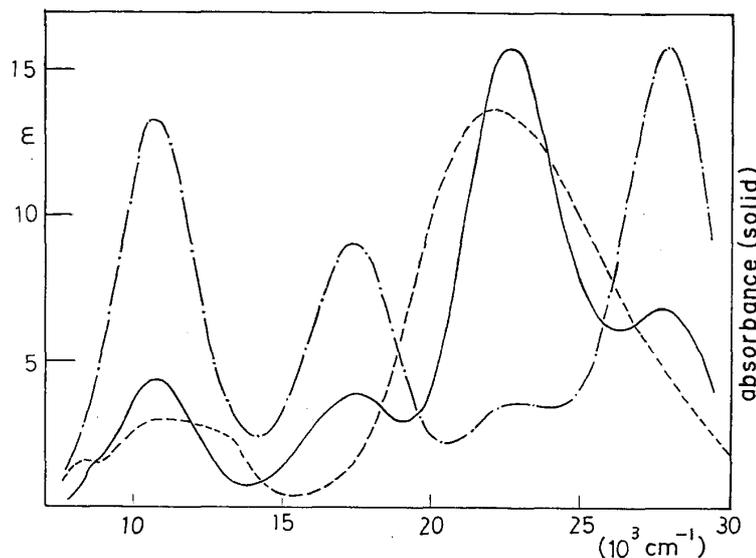
Fig. 2.   Spectra of $[Ni\ chxn_2](ClO_4)_2$.

———— H_2O soln.,   —————— solid,   ——·—— - DMF soln.

N, N-dimethylformamide were also measured. Interestingly, it was found that the $MeNO_2$ solution shows only the band ν_{dia} strongly, indicating that, in this solvent of poor coordination ability, nearly 100% of the dissolved chelate exist in the form of $[Ni\ chxn_2]^{2+}$, while in DMF which has a higher coordination ability than water, ν_{dia} appears only very weakly, and most part of the dissolved chelates exists as $[Ni\ chxn_2(DMF)_2]^{2+}$. If we assume that the ε value of ν_{dia} band of $[Ni\ chxn_2]^{2+}$ observed in $MeNO_2$ solution does not change appreciably in other solvents, the apparent intensities of the same band in H_2O and DMF indicates that approximately 33% of the dissolved chelate exist unsolvated in water, while the corresponding value in DMF is only 8% (cf. Fig. 3). From the effect of elevated temperature on the spectra listed in Table 2, it can be seen, in aqueous solutions, that the intensity of ν_{dia} increases remarkably with temperature, while that of ν_2 slightly decreases (the apparent increase of ν_3 in Table 2 is certainly due to the proximity of ν_3 and ν_{dia} and
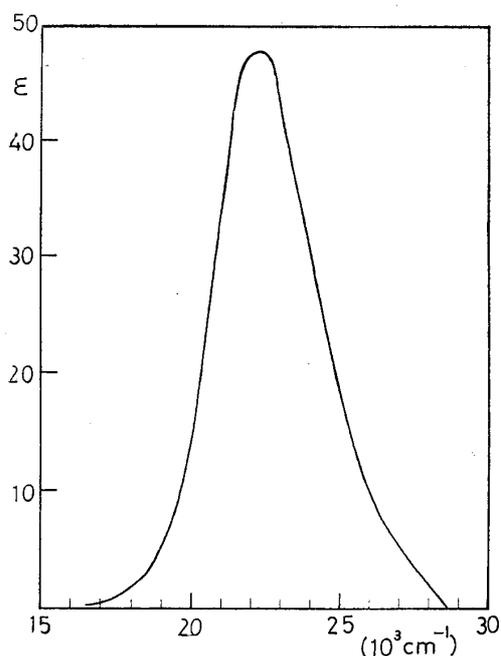
Fig. 3.   Spectrum of [Ni chxn$_2$](ClO$_4$)$_2$.
MeNO$_2$ soln.

their mutual overlapping). Thus the equilibrium (i) is displaced to the left-hand side with the rise of temperature. This reversible spectral change with temperature (thermochromism) is very similar to that observed in [Ni en$_2$(H$_2$O)$_2$]$^{2+}$ or [Ni pn$_2$(H$_2$O)$_2$]$^{2+}$ [1] ; in these latter cases, however, the change is observed only at a relatively high temperature (e.g. 80°C) in some special media (concentrated Na ClO$_4$ solution or ethanol), indicating that water molecules in them are bound more tightly than in [Ni chxn$_2$(H$_2$O)$_2$]$^{2+}$. This difference can be attributed to the effect of cyclohexane ring which makes the NH$_2$ groups more negative, increasing the ligand field strength and stabilizing the unsolvated form ; in fact, it is known that the ligand "TetraMeen" (C, C'-tetramethyl-ethylenediamine), which is expected to show the same effect more

Table 2.   Variation of the ε_{max} values of [Ni chxn$_2$]Cl$_2$
in aqueous solution with temperature.

Temp.	$\varepsilon(\nu_3)$	$\varepsilon(\nu_{dia})$	$\varepsilon(\nu_2)$
25°C	7.3	18.0	4.1
35	7.3	20.1	3.8
45	7.3	21.9	3.8
55	7.5	23.5	3.7

Note : Similar spectral changes were also observed in solutions of [Ni chxn$_2$]Br$_2$, [Ni chxn$_2$](ClO$_4$)$_2$ and [Ni chxn$_2$(H$_2$O)$_2$](NO$_3$)$_2$.
The spectra of [Ni chxn$_2$(H$_2$O)$_2$]Cl$_2$ (MeOH and H$_2$O solutions) and those of tris complexes were nearly independent of temperature.

strongly, forms only yellow [Ni TetraMeen$_2$]$^{2+}$ complex in aqueous solution.[3]   Therefore, we can arrange these and related ligands in the following series of increasing stability of the yellow form [Ni diamine$_2$]$^{2+}$ with respect to its purple hydrated form [Ni diamine$_2$(H$_2$O)$_2$]$^{2+}$:

en < pn[1] < chxn ~ 2-mepn[2] < TetraMeen.
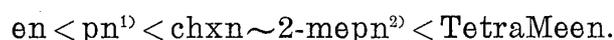
(2)   Octahedral Complexes

Among these chelates, the octahedral structure of the tris chelates is evident and seems to remain the same both in solid state and in

methanolic solution (Fig. 4), but the two diaquo-chelates [Ni chxn₂ (H₂O)₂]Cl₂ and [Ni chxn₂(H₂O)₂](NO₃)₂ present some problems (Figs. 5 and 6). The first band ν_1 in the solid spectra of these chelates splits into two components, which indicates that the two H₂O molecules in these chelates occupy trans positions.[9]

On the other hand the octahedral species produced in their solutions (and also those in the solutions of the square planar chelates described above) show no such splitting of the first band, so all these species seem to have the cis structure. If this type of reasoning is
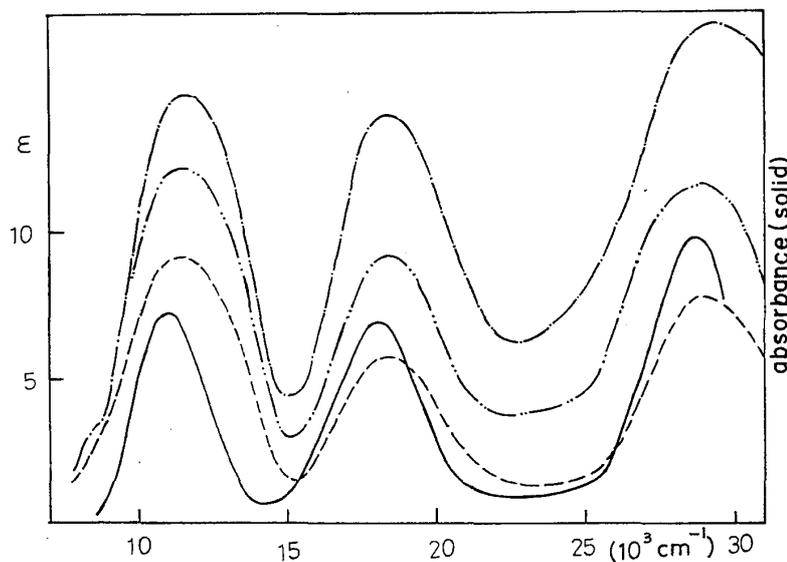
Fig. 4.   Spectra of [Ni chxn₃]X₂.

——————— X=Cl, MeOH soln.,   ——— ·· ——— X=Cl, solid,
— — — — — X=ClO₄, solid,   ——— · ——— · X=Br, solid.
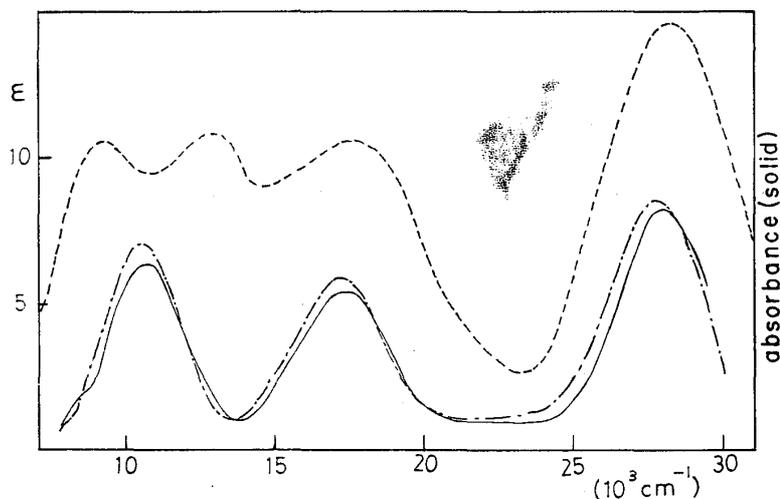
Fig. 5.   Spectra of [Ni chxn₂(H₂O)₂]Cl₂.

——————— H₂O soln.,   ——— · ——— · MeOH soln.,   — — — — — solid.
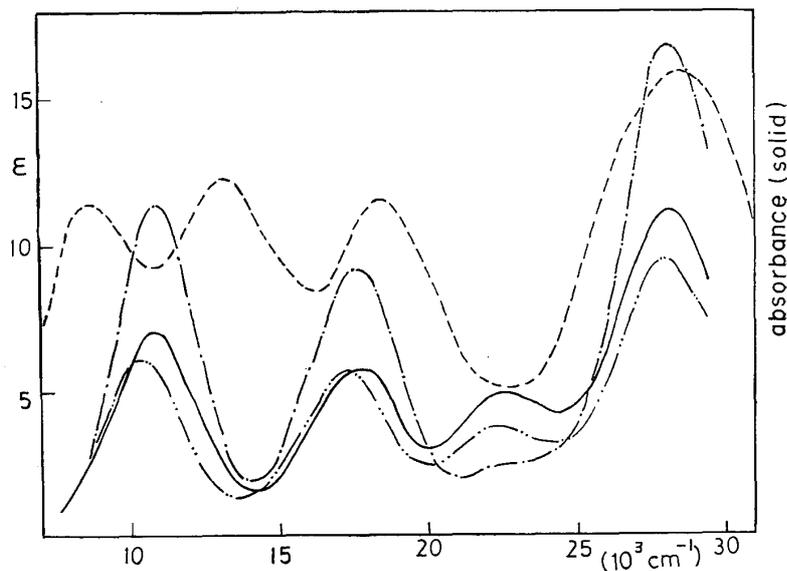
Fig. 6.   Spectra of [Ni chxn₂(H₂O)₂](NO₃)₂.

———— H₂O soln.,   —— · —— · DMF soln.,   —— · · —— MeOH soln.,

— — — — solid.

justificable, the structures of the bis-chelates in the last section can be shown as follows.

Complex	Solid	Aq. Solution
[Ni chxn₂]Cl₂		planar [Ni chxn₂]²⁺ (Y₁)
[Ni chxn₂]Br₂	planar	
[Ni chxn₂](ClO₄)₂		cis-oct. [Ni chxn₂(H₂O)₂]²⁺ (P₁)
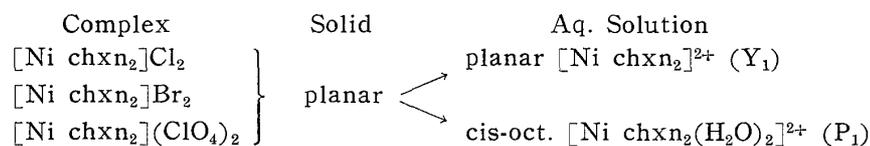
Now both of the chelates [Ni chxn₂(H₂O)₂]Cl₂ and [Ni chxn₂(H₂O)₂] (NO₃)₂ show the three bands ν_1, ν_2 and ν_3 in aqueous solutions; in the spectrum of the nitrate, the band ν_{dia} also appears, but its intensity is very much weaker than in the solutions of the complexes (a), (c) and (d) and is dependent on temperature, indicating that the equilibrium (i) also exists in the solution of the nitrate but the apparent value of K is larger than in the case of the complexes (a), (c) and (d). In contrast to this, in the spectrum of [Ni chxn₂(H₂O)₂]Cl₂, ν_{dia} does not appear at 25–45°C and no visible color change is observed even when the solution is heated to 90°C. Thus it seems probable that there are at least two kinds of purple cis-octahedral chelate species. One is the species P_1 which is formed by the dissolution of yellow square planar complexes and reversibly changes into the square planar species Y_1 in aqueous solution, and the other is the species P_2 which is formed by the dissolution of [Ni chxn₂(H₂O)₂]Cl₂ and does not easily change into the square planar form in solution. The octahedral species produced in the solution of the nitrate may be a mixture of P_1 and P_2, the former being in equilibrium with the square planar form.

Complex   Solid   Aq. Solution

[Ni chxn$_2$(H$_2$O)$_2$]Cl$_2$ trans-octahedral ⟶ cis-oct. [Ni chxn$_2$(H$_2$O)$_2$]$^{2+}$ (P$_2$)

                                                    ↗ planar (Y$_1$)

[Ni chxn$_2$(H$_2$O)$_2$](NO$_3$)$_2$ trans-oct.   ⟶ cis-oct. (P$_1$) ⎫
                                                    ↘ cis-oct. (P$_2$) ⎭ ?

The reason why such two kinds of diaquo-bis-chelates exist is, however, by no means clear at present.

(3) Dehydration of the Diaquo-bis-Chelates

In addition to the existence of two kinds of purple cis diaquo-bis-chelates described above, it seems that two kinds of yellow planar bis-chelates also exist, at least in the case of chloride. When the purple diaquo chelates, [Ni chxn$_2$(H$_2$O)$_2$]Cl$_2$ and [Ni chxn$_2$(H$_2$O)$_2$](NO$_3$)$_2$, are dehydrated at 80°C for 24 hours in vacuo, all the water molecules are lost from both of them; during this process a remarkable color change from purple to yellow is observed in the case of the chloride, but there is no visible change in the case of the nitrate. The appearance of the yellow material obtained from the chloride is very similar to that of the complex (a), but when this material is dissolved in H$_2$O, a purple solution is obtained and the spectra is practically the same as that of the original complex (b), [Ni chxn$_2$(H$_2$O)$_2$]Cl$_2$. This material, moreover, reverts gradually to the purple diaqno chelate on exposure to the atmosphere, while the complex (a) does not. These results show that there are distinct differences between this material and the complex (a).

As to the nitrate, an additional heating at 100°C for 24 hours were carried out, but no further change was observed. The original dihydrate and obtained anhydride have the same color and solution spectrum. Infrared spectrum of the anhydride shows no bands of water, but no reliable proof could be obtained on the coordination of NO$_3^-$ ion in it.[11] Thus the coordination structure of the anhydride is still not clear.

Visible Spectra of the Copper Chelates

The copper chelates of chxn were studied in connection with the problems of mixed chelates. Recently Sone and collaborators[12] have found that, while bulky diamines like bip or phen form in general only relatively unstable bis-chelate of copper (II), they form stable mixed chelates with non-bulky ligands like en, gly, ox and aca, and in many such cases, the rule of Kida[13] does not hold, i. e., the ν_{max} value of the visible absorption band of [CuAB]$^{m+}$ is remarkably larger than the mean of the ν_{max} values of the parent chelates [CuA$_2$]$^{p+}$ and [CuB$_2$]$^{q+}$. Although chxn is a bulky molecule itself, it has no bulky
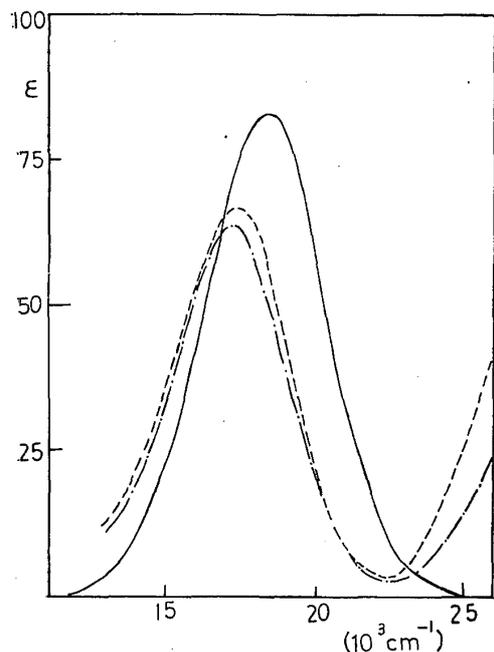
Fig. 7.   Spectra of [Cu chxn L](NO$_3$)$_2$
in H$_2$O solns.

L : ———— chxn, —————— bip,
—— · —— · phen.

groups around the coordinating atoms, so we can expect that the steric repulsion between it and the partner diamine in the mixed chelates will be quite small. In agreement with this expectation, it was found that the mixed chelates containing chxn and bip or phen can be readily obtained, and that their spectra do not obey the rule of Kida.

From the data shown in Table 1 and Fig. 7, it can be seen that the three obtained chelates show essentially similar spectra in the solid state, in MeOH and in aqueous solutions, and comparing them with the spectra of [Cu bip$_2$]$^{2+}$ and [Cu phen$_2$]$^{2+}$ (ν_{max} =13.5 and 13.9 kK, respectively), it becomes clear that the ν_{max} values of the mixed chelates lie in the neighborhood of that of [Cu chxn$_2$]$^{2+}$ and far from those of [Cu bip$_2$]$^{2+}$ or [Cu phen$_2$]$^{2+}$. This fact gives an additional support to the rule of Sone et al.. The magnetic moments of these chelates were found to be quite normal (1.8–1.9 B. M.).

Acknowledgements

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(Appendix)

Structural Parameters of the Nickel Chelates from the Spectral Data

The band ν_{dia} of a square planar complex is usually assigned to the transition: $^1A_{2g}(G) \leftarrow {}^1A_{1g}(D)$. If we assume trans structure (D_{4h}) for $[Ni\ chxn_2(H_2O)_2]Cl_2$ and $[Ni\ chxn_2(H_2O)_2](NO_3)_2$, the three bands are assigned to the following transitions.

$$\nu_1:\ ^3B_{2g} \leftarrow {}^3B_{1g}\ (\nu_1'),\quad {}^3E_g \leftarrow {}^3B_{1g}\ (\nu_1'')$$
$$\nu_2:\ ^3A_{2g} \leftarrow {}^3B_{1g},\quad \nu_3:\ {}^3A_{2g}(P) \leftarrow {}^3B_{1g}$$

According to Lever[14], it follows that

$$\nu_1' = 10Dq^E,\quad \nu_1'' = 10Dq^E - 35/4 \cdot Dt,\quad Dt(D_{4h}) = 4/7 \cdot Dq^E - Dq^A$$

where Dq^E, Dq^A and Dt denote, respectively, in-plane (equatorial) and out-of-plane (axial) field strengths and the tetragonal radial parameters. Thus we can get the following values of Dq^E, Dt and Dq^A.

	$Dq^E(cm^{-1})$	Dt	$Dq^A(cm^{-1})(H_2O)$
$[Ni\ chxn_2(H_2O)_2]Cl_2$	1290	+423	314
$[Ni\ chxn_2(H_2O)_2](NO_3)_2$	1330	+549	211

In the case of the octahedral complexes, the assignment is

$$\nu_1:\ ^3T_{2g} \leftarrow {}^3A_{2g},\quad \nu_2:\ {}^3T_{1g} \leftarrow {}^3A_{2g},\quad \nu_3:\ {}^3T_{1g}(P) \leftarrow {}^3A_{2g}$$

so that the values of Dq, $B = (\nu_2 + \nu_3 - 3\nu_1)/15$ and nephelauxetic parameters β_{35} are as follows.

	$Dq(cm^{-1})$	$B(cm^{-1})$	β_{35}
$[Ni\ chxn_3]Cl_2 \cdot 2.5H_2O$	1140	873	0.84
$[Ni\ chxn_3]Br_2 \cdot 2.5H_2O$	1160	867	0.83
$[Ni\ chxn_3](ClO_4)_2 \cdot H_2O$	1140	887	0.85