Studies of the Metal Complexes of Cyclohexane Derivatives. V.[1)] Copper(II) and Nickel(II) Complexes of *cis*-1,3-Cyclohexanediamine

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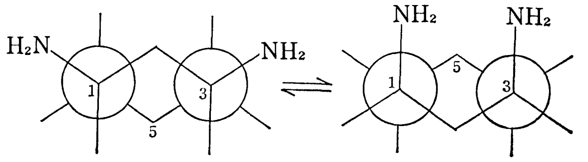
A series of 1,3-chxn(*cis*-1,3-cyclohexanediamine) copper(II) and nickel(II) complexes have been prepared and studied using spectroscopic and magnetic techniques. The violet and red copper(II) complexes of 1,3-chxn were found to consist of monomeric distorted octahedra and slightly distorted square planers, respectively. The nickel(II) complexes have a square planar structure. The conformational change of the ligand from diequatorial to diaxial on coordination has been confirmed by infrared analysis.

cis-1,3-Cyclohexanediamine(abbreviated as 1,3-chxn[2)]) is



(a) diequatorial conformation (b) diaxial conformation

known to take exclusively the diequatorial conformation(a). Assuming that the transformation to the less stable diaxial form(b) occurs, this diamine is able to form metal complexes containing six membered rings as bidentate ligands. The Pd(II) and Pt(II) complexes of 1,3-chxn have been prepared and there is some evidence for the square planar structure in which the ligand exists as the diaxial conformer(b).[3)] Kamisawa *et al.*[4)] recently determined the molecular structure of $[Pd(1,3\text{-chxn})_2]Cl_2$ by X-ray diffraction. A similar structure for the mixed Pt(II) complex with 1,3-chxn and 2,2′-bipyridyl has been reported by Sarneski *et al.*[5)]

The copper(II) and nickel(II) complexes with *cis*- and *trans*-1,2-cyclohexanediamine(abbreviated to *c*- and *t*-chxn) have been studied and it has been found that the structures of the bis complexes of nickel(II) were greatly affected by the steric configuration of these ligands.[1)] In a series of studies examing the influence of the stereochemistry of the cyclohexane derivatives upon complex formation, the copper(II) and nickel(II) complexes of 1,3-chxn were prepared and studied.

Experimental

Materials. 1,3-chxn was prepared from *cis*-1,3-cyclohexanedicarboxylic acid according to the procedure in the literature.[6)] *cis*-1,3-Cyclohexanedicarboxylic acid used was isolated by the method of Skita[7)] from the mixed *cis*- and *trans*-diacid resulting from hydrogeneration of isophthalic acid.

Measurements. The magnetic moments were measured with a Shimadzu MB-2 magnetic balance at room temperature. Measurements of the absorption spectra were carried out using a Hitachi 124-spectrophotometer. The reflectance spectra were measured with a Shimadzu MPS-5000 spectrophotometer. The infrared spectra were recorded with a JASCO IR-2A spectrophotometer using a KBr disc.

Preparation of the Complexes. $Cu(1,3\text{-chxn})_2Cl_2$: Copper(II) chloride dihydrate (2 mmol in 2 ml of MeOH) and 1,3-chxn (4 mmol in 2 ml of MeOH) were mixed together. The resulting violet product was recrystallized from methanol–ethanol.

$Cu(1,3\text{-chxn})_2ClClO_4$: Dihydrochloride of 1,3-chxn (6 mmol) and $CuCl_2\cdot 2H_2O$ (1.2 mmol) were dissolved in H_2O (7.5 ml) and the pH was adjusted to approximately 10 by 1 mol l^{-1} NaOH solution. To this solution $NaClO_4$ (6 mmol) was added. On warming the solution, a blue violet complex began to precipitate, and this was recrystallized from methanol.

$Cu(1,3\text{-chxn})_2Br_2$ *(A) and* $Cu(1,3\text{-chxn})_2Br_2$ *(B)*: Copper(II) bromide (2 mmol in 15 ml of EtOH) and 1,3-chxn (4 mmol in 2 ml of EtOH) were mixed together. This method predominantly produced the violet complex, Recrystallization from ethanol gave violet crystalline powder of (A), while, recrystallization from methanol afforded the wine red needles of (B).

$Cu(1,3\text{-chxn})_2(NO_3)_2$: Copper(II) nitrate trihydrate (1 mmol in 5 ml of H_2O) and 1,3-chxn (2 mmol in 10 ml of MeOH) were mixed and the resulting violet solution was warmed. The wine red crystals were recrystallized from methanol.

$[Ni(1,3\text{-chxn})_2]X_2$ $(X=Cl^-, Br^-, NO_3^-, \text{and } ClO_4^-)$: All the nickel(II) complexes were prepared in a similar manner as described here. To an ethanoic solution of the ligand (4—5 mmol), an ethanoic solution of the Ni(II) salt (2 mmol) was added. The yellow crystals obtained were recrystallized from methanol.

Results and Discussion

Properties of the Complexes. The results of the elemental analyses, the magnetic moments, and the colors of the complexes prepared are listed in Table 1. The copper(II) complexes are magnetically normal and are assumed to consist of monomeric species. The 1,3-chxn ligand was found to produce two forms of copper(II) complexes, a violet and a red, depending on the anion. The copper(II) complexes coordinating Br^- exist in two forms, however, the violet complex was recrystallized with some difficulty. On the other hand, this ligand afforded only diamagnetic nickel(II) complexes. The tris and bis nickel(II) complexes having octahedral or tetragonally distorted octahedral structures were not obtained.

Electronic Spectra. Some typical electronic spectra of the complexes obtained are shown in Fig. 1 and the numerical data, in Table 2. The band maxima of the red copper(II) complexes in the solid state were observed at 20400—20600 cm^{-1}, higher in energy than

TABLE 1. ELEMENTAL ANALYSES, MAGNETIC MOMENTS, AND COLORS OF THE COMPLEXES

Complex	Color[a)]	Found (Calcd) %			μ (B.M.)
		C	H	N	
$Cu(1,3\text{-chxn})_2Cl_2$	V	39.61 (39.72)	7.54 (7.78)	15.53 (15.44)	1.84
$Cu(1,3\text{-chxn})_2ClClO_4$	BV	33.66 (33.77)	6.71 (6.61)	13.35 (13.13)	1.86
$Cu(1,3\text{-chxn})_2Br_2$ (A)	V	32.06 (31.91)	6.22 (6.25)	12.31 (12.40)	1.84
$Cu(1,3\text{-chxn})_2Br_2$ (B)	WR	31.63 (31.91)	5.98 (6.25)	12.21 (12.40)	1.85
$Cu(1,3\text{-chxn})_2(NO_3)_2$	WR	34.73 (34.65)	7.06 (6.79)	20.52 (20.20)	1.83
$[Ni(1,3\text{-chxn})_2]Cl_2$	Y	39.96 (40.26)	8.15 (7.88)	15.51 (15.65)	dia
$[Ni(1,3\text{-chxn})_2]Br_2$	Y	32.10 (32.35)	6.07 (6.32)	12.72 (12.54)	dia
$[Ni(1,3\text{-chxn})_2](NO_3)_2$	Y	35.08 (35.06)	7.03 (6.87)	20.64 (20.44)	dia
$[Ni(1,3\text{-chxn})_2](ClO_4)_2$	OY	29.55 (29.66)	5.77 (5.81)	11.55 (11.53)	dia

a) V=violet, BV=blue violet, WR=wine red, Y=yellow, OY=orange yellow.

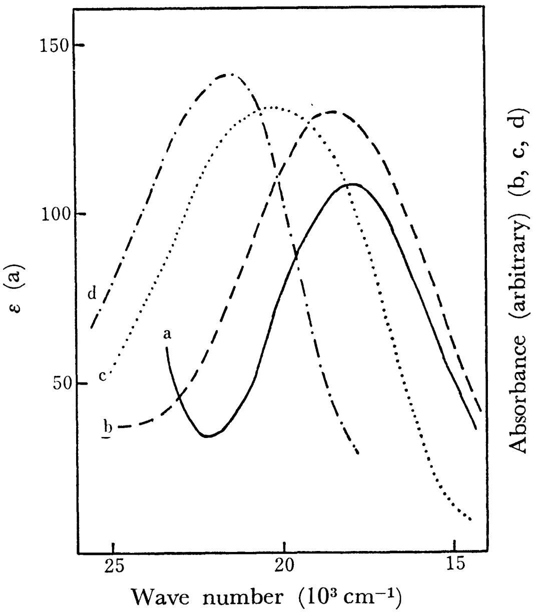


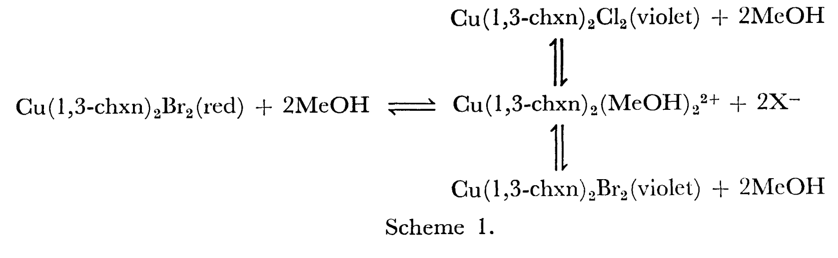
Fig. 1. Electronic spectra of (a) $Cu(1,3\text{-chxn})_2Br_2$(B) (MeOH soln.), (b) $Cu(1,3\text{-chxn})_2ClClO_4$ (Solid), (c) $Cu(1,3\text{-chxn})_2(NO_3)_2$ (Solid), and (d) $[Ni(1,3\text{-chxn})]_2$ (Solid).

TABLE 2. ELECTRONIC SPECTRA OF THE COMPLEXES

Complex	ν 10^3 cm^{-1} (ε)	
	Solid	Solution
$Cu(1,3\text{-chxn})_2Cl_2$	19.0	18.0 (106)[a)]
$Cu(1,3\text{-chxn})_2ClClO_4$	18.4	18.0 (107)[a)]
$Cu(1,3\text{-chxn})_2Br_2$ (A)	18.9	18.0 (107)[a)]
$Cu(1,3\text{-chx})_2Br_2$ (B)	20.6	18.0 (108)[a)]
$Cu(1,3\text{-chxn})_2(NO_3)_2$	20.4	18.5 (133)[b)]
$[Ni(1,3\text{-chxn})_2]Cl_2$	21.5	21.5 (46.2)[a)]
$[Ni(1,3\text{-chxn})_2]Br_2$	21.5	—[c)]
$[Ni(1,3\text{-chxn})_2](NO_3)_2$	21.6	—[c)]
$[Ni(1,3\text{-chxn})_2](ClO_4)_2$	21.4	—[c)]

c) In MeOH solution. b) In DMF solution. c) The absorption spectrum could not be measured because of the low solubility of the complex.

those of the violet complexes which were considered to have tetragonally distorted octahedral structures. The d-d bands of the former were sufficiently high compared to the copper(II) complexes of other diamines, *e.g.*, *c*-chxn,[1)] *t*-chxn,[1)] and 1,3-propanediamine[8)] thought to have a similar structure to 1,3-chxn. Asuming that 1,3-chxn coordinates to the copper(II) ion as a result of interconversion to the diaxial conformation(b) and that the chelate ring takes a chair conformation in the same way as $[Pd(1,3\text{-chxn})_2]Cl_2$,[4)] then the considerable large steric hindrance by a H_{5a} proton occurs in the z-axis. Consequently, only the anionic X group which has strong bond strength would be expected to occupy tetragonal positions. As the axial field strength weakens, the in-plane field strength increases. That the structure of the red form complexes is very close to being square planar is supported and this is unusual for $Cu(diamine)_2X_2$.[9,10)] In methanol solution, the copper(II) complexes of both forms, except the nitrate, have essentially the same ν_{max} and ε_{max}. It can be said that the equilibrium in the methanol solution shifts greatly towards the formation of $Cu(1,3\text{-chxn})_2(MeOH)_2^{2+}$ (Scheme 1). With the violet complexes having a distorted octahedral structure ligand-substitution reactions between the coordinated anions and solvent molecules appears to hold, while, in the case of the red complexes, the square planar structure appears to transform to the distorted octahedral structure by bonding solvent molecules.



Scheme 1.

As Table 2 shows, the visible spectrum of [Ni(1,3-chxn)$_2$]Cl$_2$ in methanol is similar to the reflectance spectra of all the nickel(II) complexes prepared. The spectral properties of the nickel(II) complexes with 1,3-chxn suggested that only reasonable structure for these complexes is square planar. This trend has been known for the nickel(II) complexes of the bulky diamine involved.[11]

Infrared Spectra. The representative infrared spectra of the complexes in the δ_{NH_2}, ρ_{rCH_2}, ρ_{rNH_2} region are shown in Fig. 2, and the main bands are listed in Table 3. The three copper(II) complexes of the violet form exhibit a very similar infrared spectra. The characteristic bands assignable to the rocking vibration of NH$_2$ are observed at 600—750 cm^{-1}. For the analogue of the violet complexes, the ρ_{rNH_2} values appear due to the anionic groups bonded in the tetragonal positions. Therefore, more than four peaks corresponding to ρ_{rNH_2} appear in the spectra of Cu(1,3-chxn)$_2$ClClO$_4$. No relationship between the frequencies of ρ_{rNH_2} and structures of the red copper(II) and nickel(II) complexes have been found.

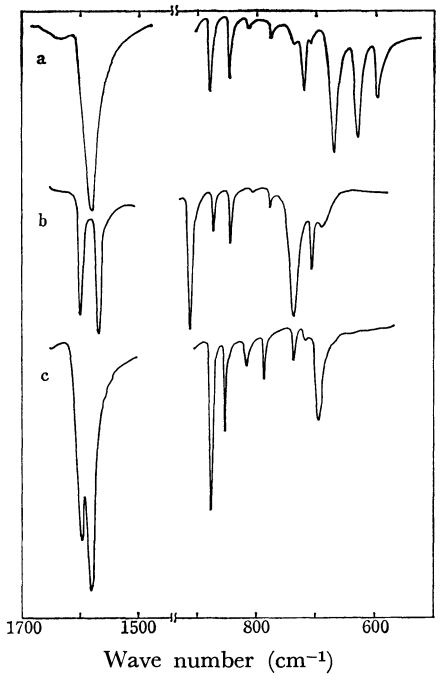


Fig. 2. Infrared spectra of (a) Cl(1,3-chxn)$_2$Br$_2$ (A), (b) Cu(1,3-chxn)$_2$Br$_2$ (B), and (c) [Ni(1,3-chxn)$_2$]Br$_2$ in the δ_{NH_2}, ρ_{rCH_2}, and ρ_{rNH_2} region.

The δ_{NH_2} of the nickel(II) complexes described here show two peaks. The similar frequency separation for the red copper(II) complexes is significantly larger than that for the violet copper(II) complexes. The splitting of this band may be due to the distortion of the chelate ring or the degree of hydrogen bonding between the NH$_2$ groups and the anion. In the spectra of a similar type of complexes having stronger metal–N bonds, such as [Pt(1,3-chxn)$_2$]Cl$_2$ and [Pd(1,3-chxn)$_2$]-Cl$_2$, the corresponding band shows no splitting.[3] From the δ_{NH_2} data, the structure of the red copper(II) complexes is thought very similar to the square planar complexes of nickel(II).

It is generally recognized that the degenerated stretching mode of the perchlorate ion splits into two bands on coordination.[12] As shown in Fig. 3, the infrared spectrum of Cu(1,3-chxn)$_2$ClClO$_4$ gives evidence of the covalently bonded perchlorate group. The same band of [Ni(1,3-chxn)$_2$](ClO$_4$)$_2$ appears to be single and broad, reflecting the existence of free ions. The infrared spectra of Cu(1,3-chxn)$_2$(NO$_3$)$_2$ shows a broad profile of ν_{N-O} ascribable to the free ion[13] at 1300—1400 cm^{-1}, which is very similar to that of [Ni(1,3-chxn)$_2$](NO$_3$)$_2$. This suggests that in the former complex the copper(II) ion is present in a planar rather than a distorted octahedral configuration.

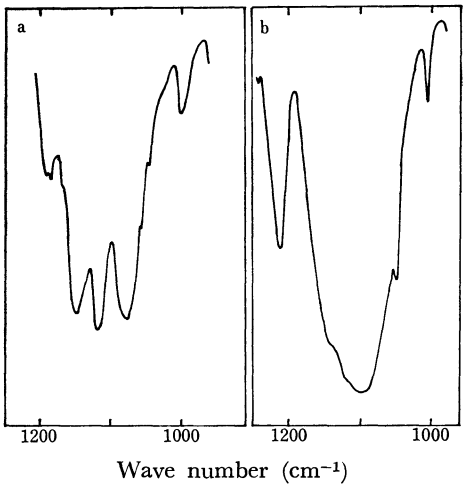


Fig. 3. Infrared spectra of (a) Cu(1,3-chxn)$_2$ClClO$_4$ and (b) [Ni(1,3-chxn)$_2$](ClO$_4$)$_2$ in the ν_{Cl-O} region.

TABLE 3. THE MAIN INFRARED BANDS OF THE COMPLEXES (cm^{-1})

Complex	ν_{NH}	δ_{NH_2}	ρ_{rCH_2}	ρ_{rNH_2}
Cu(1,3-chxn)$_2$Cl$_2$	3230, 3110[a]	1590, 1583	817, 777	727, 678, 637, 601
Cu(1,3-chxn)$_2$ClClO$_4$	3230, 3110[a]	1583, 1577[a]	812, 773	737, 719, 670, 632, 595[a]
Cu(1,3-chxn)$_2$Br$_2$ (A)	3230, 3120[a]	1580	812, 775	719, 670, 630, 596[a]
Cu(1,3-chxn)$_2$Br$_2$ (B)	3230, 3130[a]	1596, 1567	810, 777	738, 709, 690
Cu(1,3-chxn)$_2$(NO$_3$)$_2$	3260, 3150[a]	1619, 1602, 1585	777	740^{sh}, 692, 648, 608
[Ni(1,3-chxn)$_2$]Cl$_2$	3180, 3100	1607, 1584	810^{sh}, 795	715, 640
[Ni(1,3-chxn)$_2$]Br$_2$	3170, 3100	1594, 1580	817, 787	738, 720, 695
[Ni(1,3-chxn)$_2$](NO$_3$)$_2$	3280, 3140[a]	1620, 1583	810	746, 719, 645[a]
[Ni(1,3-chxn)$_2$](ClO$_4$)$_2$	3300, 3260, 3200[a]	1601, 1580	778	742, 710

a) A shoulder was observed besides these bands. sh = shoulder.

As previously discussed, for coordination of the 1,3-chxn ligand to the metal ion the interconversion from the diequatorial(a) to the diaxial(b) conformer is necessary. In the infrared spectra of the cyclohexane derivatives involving axially bonded substituents, the weak rocking vibration of CH_2 appears around 800 cm^{-1}.[14)] It has been found that the *c*-chxn complexes show these characteristic bands which are absent in the *t*-chxn complexes.[15)] Dihydrochloride of 1,3-chxn have no bands in the region of 560—840 cm^{-1}. However, in the spectra of the complexes one or two bands were observed around 770—810 cm^{-1} as shown in Table 3 and Fig. 2. These results support the complexes involve ligands with diaxial conformation(b). Similar complex formation of 1,3,5-triaminocyclohexane taking conformational inversion have been revealed in several investigations.[16—18)]

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