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167. Kozo Nagano, Hisashi Kinoshita, and Akiko Hirakawa :

Metal Complexes of Isonicotinoylhydrazine and Related Compounds. IV.*[1] Composition Formulae and Infrared Absorption Spectra of Metal Complex Crystals of Isonicotinoylhydrazine and Related Compounds.

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In the previous paper,*[1] the authors have reported two relations between the equilibrium constants of metal complexes and acid dissociation constants of the corresponding ligands for isonicotinoylhydrazine (INH) and related compounds. The first relation between log K_{M1} and pKa (H) or between log K_{M1} and pKa (P) indicates that INH, nicotinoylhydrazine (NH), 1-isonicotinoyl-1-methylhydrazine (N-Me-INH) and 1-isonicotinoyl-2-methylhydrazine (N′-Me-INH) more probably form addition complexes to hydrazide nitrogens similar to benzoylhydrazine (BH) and *p*-nitrobenzoylhydrazine (PNBH), and that isonicotinamide (INA) forms an addition complex to pyridine nitrogen. The second relation between pk_1 and pKa (A_2) indicates that an addition complex to hydrazide dissociates a proton from amide nitrogen in proportion to pKa (A_2) of the corresponding ligand except picolinoylhydrazine (PH). In other words, INH-Cu(II) addition complex changes into a chelate with dissociation of a proton but BH-Cu(II) complx does not change so easily, while PH-Cu(II) complex dissociates a proton very easily and changes into a chelate along another unknown reaction route. The chelate ring of INH-Cu(II) will be composed of the C-O bond, C=N bond, tetrahedral NH_2 group and Cu(II) as suggested by Cymerman-Craig, *et al.*[1)] and Albert.[2)] These are, however, only proposals without proofs of structural chemistry. The authors intend, therefore, to ensure the view from infrared spectral data of those complex crystals and to deduce the structure of PH-Cu(II) chelate. It must be noticed that the structure in crystalline state does not coincide necessarily with that in aqueous solution. The authors, however, consider that the view is supported if it is consistent with the spectral data of metal complex crystals.

At first, the complexes were isolated, and their composition formulas were investigated by elemental analyses. Isolation methods and composition formulas of INH-metal complexes have been reported by Foye, *et al.*[3)] and Taguchi,[4)] whose procedure was adopted here. As the spectra of those complexes are very complicated, complete analyses are impossible. It was therefore examined in detail by comparing the spectra of metal complex crystals with those of N-deuterated derivatives and those of ligands themselves. The latter will be described in Part V,[5)] showing how the main bands (*e.g.*, of the CO stretching, amide II and III, $-NH_2$ deformation and pyridine ring vibrations) differ from one another.

Experimental

Materials——Commercially available pyridine was distilled. (Py). b.p. 115°. INH, NH, PH, BH, PNBH,

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*[1] A part of this work was presented at the 13th Symposium on Co-ordination Chemistry, Nagoya, 1963. Part III: This Bulletin, **11**, 999 (1963).

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1) J. Cymerman-Craig, S.D. Rubbo, D. Willis, J. Edgar : Nature, **176**, 34 (1955).

2) A. Albert : *Ibid.*, **177**, 525 (1956).

3) W.O. Foye, R.N. Duvall : J. Am. Pharm. Assoc., Sci. Ed., **47**, 285 (1958).

4) K. Taguchi : This Bulletin, 8, 212 (1960).

5) Part V : *Ibid.*, **12**, 1207 (1964).

INA and N-Me-INH were the same as those used in Part II,[6] but N′-Me-INH was omitted owing to its instability. Nicotinamide (NA), m.p. 127.5°,[7] and picolinamide (PA), m.p. 103.5°,[7] were purchased from Shoko Chemical Co. and Tokyo Kasei Co., respectively, and used without further purification. $CuCl_2 \cdot 2H_2O$ and $CdCl_2 \cdot 2\frac{1}{2}H_2O$ were analytical grade and used without further purification.

Preparation of Metal Complex Crystals——i) Py-Cu (II). This substance was prepared by Lang's method.[8,9] The composition formula: $(C_5H_5N)_2CuCl_2$. The structure of this crystal has been reported.[10,11]

ii) Py-Cd (II). This substance was also prepared by Lang's method.[8] The composition formula: $(C_5H_5N)_2CdCl_2$.

iii) INH-Cu (II). A solution of 275 mg. (2 mmoles) of INH in 10 ml. of H_2O was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 10 ml. of H_2O, and shaked vigorously. A blue precipitate occurred instantly. This was collected on a glassfilter, washed with H_2O, EtOH and Et_2O successively, and dried over P_2O_5 *in vacuo*. The color turned green slowly. m.p. 260~262° (decomp.). *Anal.* Calcd. for $C_6H_6ON_3CuCl \cdot H_2O$: C, 28.47; H, 3.19; N, 16.60; Cl, 14.01; Cu, 25.10. Found: C, 28.89; H, 2.96; N, 15.65; Cl, 14.1; Cu, 25.4.

iv) INH-Cd (II). A solution of 275 mg. (2 mmoles) of INH in 10 ml. of H_2O was added to that of 457 mg. (2 mmoles) of $CdCl_2 \cdot 2\frac{1}{2}H_2O$ in 10 ml. of H_2O. A white precipitate was collected, washed with H_2O, EtOH and Et_2O, and dried. m.p. >280° (decomp.). *Anal.* Calcd. for $(C_6H_7ON_3)_2CdCl_2$: C, 31.49; H, 3.08; N, 18.37; Cl, 15.50; Cd, 24.56. Found: C, 31.13; H, 3.03; N, 18.18; Cl, 15.0; Cd, 24.2.

v) NH-Cu (II). A solution of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 10 ml. of H_2O and 5 ml. of EtOH were added to that of 275 mg. (2 mmoles) of NH in 10 ml. of H_2O. A bluish green precipitate was collected, washed with EtOH and Et_2O, and dried. The color turned green slowly. m.p. 265~266° (decomp.). *Anal.* Calcd. for $C_6H_6ON_3CuCl$: C, 30.65; H, 2.57; N, 17.87; Cl, 15.08; Cu, 27.02. Found: C, 30.76; H, 2.25; N, 17.25; Cl, 15.2; Cu, 26.1.

vi) PH-Cu (II)-1. A solution of 275 mg. (2 mmoles) of PH in 10 ml. of EtOH was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH. A blue precipitate occurred instantly, and turned light green through agitation. This was collected, washed with EtOH and dried. m.p. 211~212° (decomp.). *Anal.* Calcd. for $C_6H_7ON_3CuCl_2$: C, 26.53; H, 2.60; N, 15.47; Cl, 26.11; Cu, 23.39. Found: C, 27.49; H, 3.01; N, 15.25; Cl, 25.2; Cu, 23.0.

vii) PH-Cu (II)-2. A solution of 550 mg. (4 mmoles) of PH in 3 ml. of H_2O was added to that of 682 mg. (4 mmoles) of $CuCl_2 \cdot 2H_2O$ in 2 ml. of H_2O. A dark blue precipitate was collected, washed with H_2O and dried. m.p. 193~195° (decomp.). *Anal.* Calcd. for $C_6H_6ON_3CuCl \cdot H_2O$: C, 28.47; H, 3.19; N, 16.60; Cl, 14.01; Cu, 25.10. Found: C, 28.13; H, 3.37; N, 16.31; Cl, 14.4; Cu, 25.5.

viii) BH-Cu (II). A solution of 273 mg. (2 mmoles) of BH in 5 ml. of EtOH was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH. A blue precipitate occurred in a few minutes. This was collected, washed with EtOH and Et_2O, and dried. m.p. 179~180° (decomp.). *Anal.* Calcd. for $C_7H_8ON_2CuCl_2$: C, 31.07; H, 2.98; N, 10.35; Cl, 26.25; Cu, 23.48. Found: C, 31.08; H, 3.25; N, 9.88; Cl, 26.0; Cu, 23.4.

ix) BH-Cd (II). A solution of 273 mg. (2 mmoles) of BH in 5 ml. of H_2O was added to that of 457 mg. (2 mmoles) of $CdCl_2 \cdot 2\frac{1}{2}H_2O$ in 5 ml. of H_2O. A white precipitate was collected, washed with H_2O, EtOH and Et_2O, and dried. m.p. >280° (decomp.). *Anal.* Calcd. for $C_7H_8ON_2CdCl_2$: C, 25.06; H, 2.40; N, 8.35; Cl, 21.14; Cd, 33.51. Found: C, 25.90; H, 2.53; N, 8.54; Cl, 21.6; Cd, 35.3.

x) PNBH-Cu (II). A solution of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH was added to that of 363 mg. (2 mmoles) of PNBH dissolved in 20 ml. of warm EtOH. A green precipitate was quickly collected, washed with EtOH and Et_2O, and dried. m.p. >280° (decomp.). *Anal.* Calcd. for $C_7H_6O_3N_3CuCl \cdot H_2O$: C, 28.29; H, 2.71; N, 14.14; Cl, 11.93; Cu, 21.38. Found: C, 28.33; H, 2.58; N, 13.98; Cl, 12.0; Cu, 21.3.

xi) INA-Cu (II). A solution of 244 mg. (2 mmoles) of INA in 5 ml. of EtOH was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH. A light blue precipitate was collected, washed with EtOH and Et_2O, and dried. m.p. 275~276° (decomp.). *Anal.* Calcd. for $(C_6H_6ON_2)_2CuCl_2$: C, 38.06; H, 3.19; N, 18.37; Cl, 18.73; Cu, 16.78. Found: C, 37.83; H, 3.11; N, 18.18; Cl, 18.9; Cu, 16.5.

xii) N-Me-INH-Cu (II). A solution of 303 mg. (2 mmoles) of N-Me-INH in 5 ml. of EtOH was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH. A blue precipitate was collected, washed with EtOH and Et_2O, and dried. m.p. 170~172° (decomp.). *Anal.* Calcd. for $C_7H_9ON_3CuCl_2 \cdot H_2O$: C, 27.69; H, 3.65; N, 13.84; Cl, 23.35; Cu, 20.93. Found: C, 27.70; H, 4.28; N, 13.09; Cl, 22.5; Cu, 20.8.

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[6] Part II: This Bulletin, **11**, 797 (1963).

[7] C. Engler: Ber., **27**, 1786 1787, (1894).

[8] W. Lang: *Ibid.*, **21**, 1578 (1888).

[9] E. G. Cox, E. Sharratt, W. Wardlaw, K. C. Webster: J. Chem. Soc., **1936**, 129.

[10] S. S. Kabalkina: Doklady Acad. Nauk. U. S. S. R., **110**, 1013 (1956).

[11] J. D. Dunitz: Acta Cryst., **10**, 307 (1957).

xiii) NA-Cu (II). A solution of 488 mg. (4 mmoles) of NA in 10 ml. of EtOH was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH. A pale blue precipitate was collected, washed with EtOH and Et_2O, and dried. m.p. 285~288°(decomp.). *Anal.* Calcd. for $(C_6H_6ON_2)_2CuCl_2 \cdot H_2O$: C, 36.33 H, 3.56; N, 14.12; Cl, 17.87; Cu, 16.02. Found : C, 37.60; H, 3.98; N, 13.79; Cl, 17.9; Cu, 15.9.

xiv) PA-Cu (II). A solution of 244 mg. (2 mmoles) of PA in 5 ml. of EtOH was added to that of 341 mg. (2 mmoles) of $CuCl_2 \cdot 2H_2O$ in 5 ml. of EtOH. A light green precipitate was collected, washed with EtOH and Et_2O, and dried. m.p. >290°(decomp.). *Anal.* Calcd. for $C_6H_6ON_2CuCl_2$: C, 28.09; H, 2.36; N, 10.92; Cl, 27.64; Cu, 24.76. Found : C, 28.37; H, 2.47; N, 10.74; Cl, 26.6; Cu, 24.5.

xv) INH-Na. This substance was prepared by drying an equimolar solution of INH and NaOH in H_2O from the frozen state. The IR spectra of this yellow powder was measured in the Nujol mull as soon as it was prepared. Though its purity was not checked by elemental analyses owing to its instability, the spectra was considerably sharp.

Preparation of N-Deuterated Metal Complex Crystals——N-Deuterated metal complex crystals were prepared on a scale of one fifth to the method of the corresponding metal complex crystals by the use of D_2O or EtOD in stead of H_2O or EtOH without attentive washing with Et_2O. EtOD was prepared from EtONa and D_2O.

Elemental Analyses——Analyses of C, H and N were carried out at the Elemental Analysis Center of this faculty. Cl was determined by Volhard method. EDTA titration was used for determination of Cu (II) with murexide and of Cd (II) with eriochrome black T.[12]

Infrared Absorption Spectra——The IR absorption spectra were obtained using a Koken Model DS-301 spectrophotometer with a NaCl prism in the Nujol mulls, hexachlorobutadiene (HCB) mulls, mainly for N-deuterated metal complexes, and KBr disks, mainly for undeuterated ones.

Results and Discussion

The complexes were precipitated more easily as chlorides than as nitrates, and the elemental composition of the chlorides also agreed more closely to the calculated values than those of the nitrates. Metal complexes obtained are tabulated in Table I, where the results of INH-Cd (II) complex obtained in Part I[13] are also tabulated.

TABLE I. Composition Formulae and Other Characteristics of Isolated Metal Complex Crystals of INH and Related Compounds

Complex	Composition formula	Color	m.p. (°C)[a] (decomp.)	Type
Py-Cu (II)	$(C_5H_5N)_2CuCl_2$	greenish blue	>290	M(HZ)$_2$
Py-Cd (II)	$(C_5H_5N)_2CdCl_2$	colorless	>290	〃
INH-Cu (II)	$C_6H_6N_3OCuCl \cdot H_2O$	green	260~262	MZ
INH-Cd (II)	$(C_6H_7N_3O)_2CdCl_2$	colorless	>280	M(HZ)$_2$
	$(C_6H_7N_3O)_2Cd(NO_3)_2 \cdot 2H_2O$	pale yellow		〃
NH-Cu (II)	$C_6H_6N_3OCuCl$	green	265~266	MZ
PH-Cu (II)-1	$C_6H_7N_3OCuCl_2$	light green	211~212	MHZ
PH-Cu (II)-2	$C_6H_6N_3OCuCl \cdot H_2O$	dark blue	193~195	MZ
BH-Cu (II)	$C_7H_8N_2OCuCl_2$	blue	179~180	MHZ
BH-Cd (II)	$C_7H_8N_2OCdCl_2$	colorless	>280	〃
PNBH-Cu (II)	$C_7H_6N_3O_3CuCl \cdot H_2O$	green	>280	MZ
INA-Cu (II)	$(C_6H_6N_2O)_2CuCl_2$	light blue	275~276	M(HZ)$_2$
N-Me-INH-Cu (II)	$C_7H_9N_3OCuCl_2 \cdot H_2O$	bluish green	170~172	MHZ
NA-Cu (II)	$(C_6H_6N_2O)_2CuCl_2 \cdot H_2O$	pale blue	285~288	M(HZ)$_2$
PA-Cu (II)	$C_6H_6N_2OCuCl_2$	light green	>290	MHZ

a) All melting points are uncorreted.

Assignments of vibrational spectra of metal complex crystals of INH and related compounds were made from a comparison of the spectra of the complexes with those of N-deuterated derivatives and with those of the corresponding ligands, assignments of

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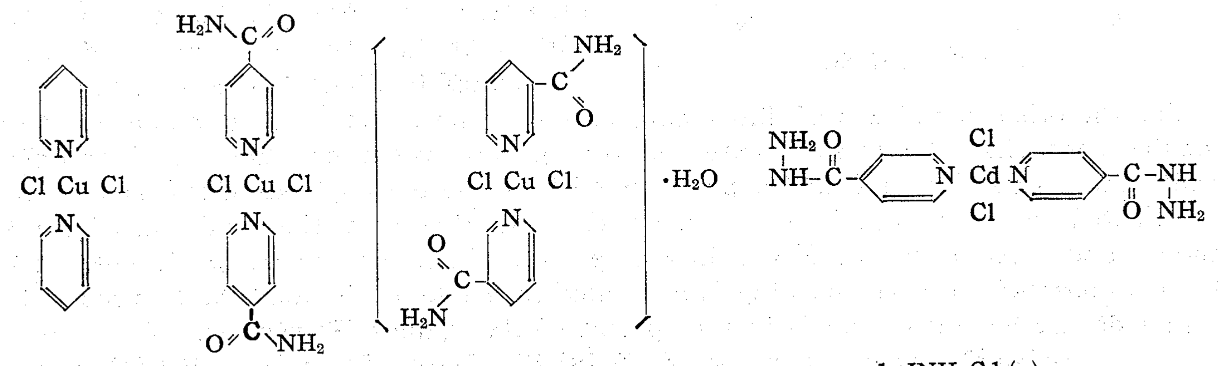
12) K. Ueno : "Kileto Tekitei Ho," p. 250, 233 (1962), Nankodo Co., Tokyo.

13) Part I : This Bulletin, **11**, 793 (1963).

which shall be described in Part V.[5] As the result of such investigations, it was clarified that the complexes can be roughly divided into two groups according to the direction of frequency shift of the strong CO stretching band; *i.e.*, (i) complexes in which the CO stretching frequency is higher or (ii) lower than that of the ligand.

INA-Cu(II) and NA-Cu(II) belong to the former group (i), and the bands of the $-NH_2$ deformation vibrations appear in the same regions as those of INA and NA respectively. A further detailed investigation of the bands in the region of $1350\sim650\,cm^{-1}$ reveals a noteworthy fact that the bands of the pyridine ring vibrations near $1000\,cm^{-1}$ shifts towards higher frequency by about $30\,cm^{-1}$ than those of INA and NA respectively, and that the same tendency is confirmed in the case of Py-Cu(II) and Py-Cd(II). The shifts of the CO stretching and the ring vibrations for metal complex crystals of INH and related compounds are listed in Tables II and III respectively. The shift of the C=O double-bond stretching vibration towards higher frequency will be explained as the result of electron attraction to the pyridine ring owing to co-ordination of Cu(II) to pyridine nitrogen, and will be understood similarly to the cases of INA·HCl, NA·HCl, and PA·HCl.[5] These findings are consistent with the view of the structure of INA-Cu(II) in aqueous solution. INH-Cd(II) also belongs to this group and may have the co-ordination at pyridine nitrogen. The structures of INA-Cu(II), NA-Cu(II), and INH-Cd(II) in crystalline state are inferred as illustrated in Chart 1, with that of Py-Cu(II), which has been determined by the X-ray analysis.[10,11] The elemental compositions of all the complexes of group (i) are a type of $M(HZ)_2$ as shown in Table II. In Fig. 1 are shown the infrared absorption spectra of INA-Cu(II) and INA-d_2-Cu(II) as a representative of this group.



a. Py-Cu(II) b. INA-Cu(II) c. NA-Cu(II) d. INH-Cd(II)

Chart 1.

The complexes which belong to the latter group (ii) are listed in Table II in sequence of the shift of the CO stretching frequency. The elemental analyses divides them again into two groups; *i.e.*, (iia) a MZ type (a deprotonated 1:1 complex) and (iib) a MHZ type (a 1:1 addition complex). It is interesting to note that the complexes of (iia) group show the larger frequency shift than those of (iib) group, and that the sequence agrees well with that of pk_1 of the addition complexes.

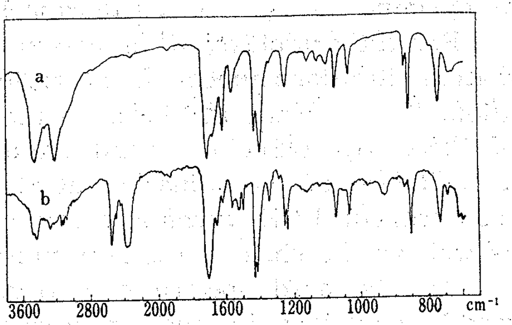


Fig. 1.

a. Isonicotinamide(INA)-Cu(II) (KBr disk)
b. INA-d_2-Cu(II) (Nujol mull, HCB mull)

The band at $1096\,cm^{-1}$ in the spectra of INH-Na may be assigned to the CO stretching frequency, which is as low as that of methanol

Table Ⅱ. Band of the CO Stretching Vibration, Shift of the Frequency, Complex Type, pk_1 Value and Classification of Metal Complexes of INH and Related Compounds

Complex	CO str. (cm^{-1})	$\Delta\nu$ (CO str.) (cm^{-1})	Type	pk_1	Class
INH-Na	1096	572	MZ		iia
PH-Cu (II)-2	1152	523	〃	1.34	
INH-Cu (II)	1210	455	〃	4.16	
PNBH-Cu (II)	1228	407	〃	4.72	
NH-Cu (II)	1380	280	〃	5.06	
BH-Cu (II)	1555	105	MHZ	5.49	iib
PH-Cu (II)-1	1630	45	〃		
BH-Cd (II)	1625	35	〃		
PA-Cu (II)	1643	25	〃		
N-Me-INH-Cu (II)	1628	− 3	〃	—	
INH-Cd (II)	1693	− 25	$M(HZ)_2$	8.69	i
INA-Cu (II)	1710	− 34	〃		
NA-Cu (II)	1720	− 35	〃		

at 1033 cm^{-1},[14] and can be considered to be almost single-bonded. In addition to this fact, the $-NH_2$ rocking frequency shifts towards higher frequency by 15 cm^{-1} and the ring vibration frequency towards higher frequency by 12 cm^{-1} than that of INH. These suggest the structure of INH-Na as illustrated in Chart 2, being consistent with that in alkaline aqueous solution (illustrated in Chart 1 of Part Ⅱ[6]).

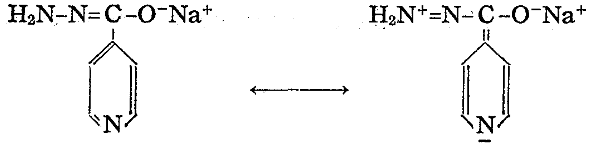


Chart 2. INH-Na

For the other complexes of (iia) group, however, the CO stretching frequency bears a double-bond character to some extent according to the resonance state, which probably decides the corresponding value of pk_1. In each of these complexes Cu(II) is strongly co-ordinated to the carbonyl oxygen, a proton dissociates from the amide nitrogen and amide Ⅱ and Ⅲ bands do not appear in the spectra, while, for (iib) group, BH-Cu(II) and BH-Cd(II) possess the corresponding bands listed in Table Ⅲ and the others except PH-Cu(II)-1 do not have such bands in the spectra of the ligands themselves. The co-ordinations at carbonyl oxygens may be weak for BH-Cu(II), PH-Cu(II)-1, BH-Cd(II), and PA-Cu(II), as the shifts of the CO stretching frequency are small. Although small shift is recognized for the frequency of N-Me-INH-Cu(II), its elemental composition agrees with the complex type of (iib) group. For this complex, the shift owing to co-oridination at pyridine nitrogen seems to cancel the effect of weak co-ordination at carbonyl oxygen.

For the complexes of (ii) except INH-Na and PA-Cu(II), the bands of the NH_2 deformation vibrations appear in the region of 1380~1160 cm^{-1}, which disappear on N-deuteration. These bands fall between the frequency of the tetrahedral NH_2 wagging vibration of $(CH_3)_2NH_2I$, 1421 cm^{-1},[15] and that of $HgNH_2Br$, 1022 cm^{-1},[16] These facts can be regarded as evidence of co-ordination at the terminal hydrazide nitrogen. The frequencies of the tetrahedral NH_2 wagging vibration, the amide Ⅱ and Ⅲ bands and the ring vibrations as well as the shift of the ring vibrations are listed in Table Ⅲ.

The infrared spectra of (iia) group, INH-Cu(II), PNBH-Cu(II), and NH-Cu(II), are readily explained by the structures illustrated in Chart 3, which are consistent with

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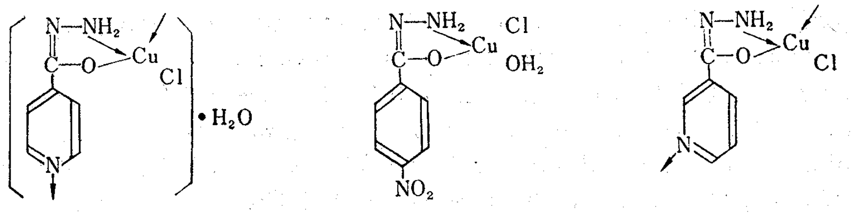
[14] C. Tanaka, K. Kuratani, S. Mizushima: Spectrochim. Acta, **9**, 265 (1957).
[15] E. A. V. Ebsworth, N. Sheppard: *Ibid.*, **13**, 261 (1959).
[16] I. Nakagawa, R. B. Penland, S. Mizushima, T. J. Lane, J. V. Quagliano: *Ibid.*, **9**, 199 (1957).

Table III. Amide II and III Bands, Band of the Tetrahedral NH_2 Wagging Vibration, Bands of the Ring Vibration and Shift of the Ring Vibration of Metal Complexes of INH and Related Compounds

Complex	Amide II (cm^{-1})	Amide III (cm^{-1})	NH_2 wag., tetr. (cm^{-1})	Ring vib. (cm^{-1})	$\Delta\nu$ (ring vib.) (cm^{-1})
INH-Na			(1156)[b]	1008	12
PH-Cu (II)-2			1226	1050	0
				1026	23
INH-Cu (II)			1376	1037	41
PNBH-Cu (II)			1198	1037 (w)[c]	
				1010 (m)	− 6
NH-Cu (II)			1192	1058	16
				1036 (vw)	3
BH-Cu (II)	1489	1323	1194, 1181	1025 (m)	− 2
				1004 (w)	− 2
PH-Cu (II)-1			1232	1052	2
				1032	29
BH-Cd (II)	1540	1344	1182	1023	− 4
				1003 (vw)	− 3
PA-Cu (II)		(1438)[a]	(1123)	1057	11
				1029	30
N-Me-INH-Cu (II)		(1267)	1165	1031	34
INH-Cd (II)	1513	1321	(1108, 1093)	1032 (w)	29
				1019 (s)	23
INA-Cu (II)		(1390)	(1121, 1096)	1030	25 or 34
NA-Cu (II)		(1385)	(1158, 1148)	1064	24
				1038	6
Py-Cu (II)				1046 (s)	12
				1020 (m)	26
Py-Cd (II)				1039 (s)	5
				1012 (vs)	18

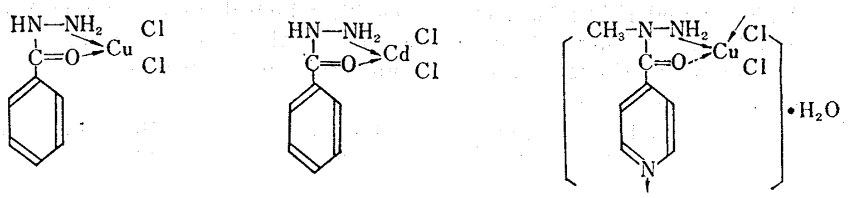
a) The frequency of the CN stretching vibration of Cu (II) complexes of INA, NA, PA, and N-Me-INH are listed in parentheses.
b) The frequency of the planar NH_2 rocking vibration of INH-Na and Cu (II) complexes of INA, NA, and PA are listed in parentheses.
c) w: weak; m: medium; vw: very weak; s: strong; vs: very strong.

those suggested by Cymerman-Craig, *et al.*[1] and Albert.[2] On the other hand, the spectra of (iib) group suggest either a chelate or a chain form. However, considering the process of proton dissociation from a (iib) type complex to a (iia) type in aqueous solution with increasing pH, it seems reasonable that each complex of the (iib) group has a chelate ring, which explains well the considerable stability of an addition complex to hydrazide. Thus, the structures of BH-Cu (II), BH-Cd (II), and N-Me-INH-Cu (II) in crystalline state are inferred as illustrated in Chart 4. The process proposed in Part III,



a. INH-Cu (II) b. PNBH-Cu (II) c. NH-Cu (II)

Chart 3.



a. BH-Cu (II) b. BH-Cd (II) c. N-Me-INH-Cu (II)

Chart 4.

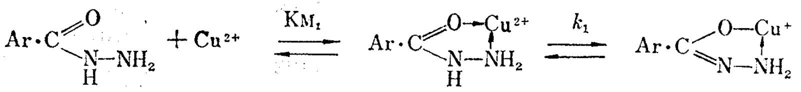


Chart 5.

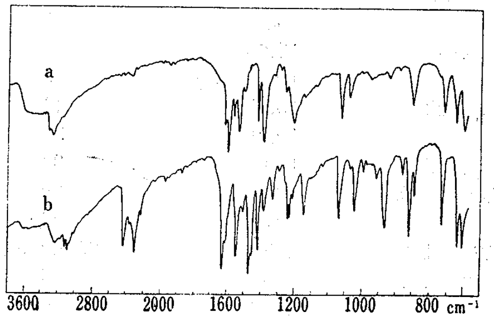


Fig. 2a. Isonicotinoylhydrazine(INH)-Cu (II) (Nujol mull, HCB mull)
b. INH-d_2-Cu (II) (Nujol mull, HCB mull)

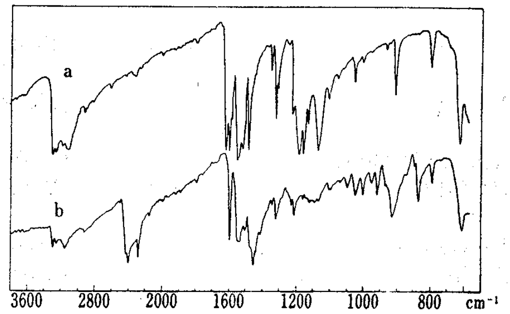


Fig. 3a. Benzoylhydrazine(BH)-Cu (II) (Nujol mull, HCB mull)
b. BH-d_3-Cu (II) (Nujol mull, HCB mull)

p. 1011,*[1] should be rewritten as shown in Chart 5. The infrared absorption spectra of INH-Cu (II) and INH-d_2-Cu (II) are shown in Fig. 2, and those of BH-Cu (II) and BH-d_3-Cu (II) are in Fig. 3.

The structue of PA-Cu (II) seems quite different from those of INA-Cu (II) and NA-Cu (II). This complex is a MHZ type. The band of the C=O stretching vibration is found to shift slightly towards a lower frequency, and that of the C-N stretching vibration towards a higher frequency than that of PA. The shift of the ring vibrations is also recognized for this complex. These facts suggest the structure of this complex as illustrated in Chart 6a.

PH-Cu (II)-2 can be obtained from aqueous solution, pH of the filtrate falls to 0.85, and the elemental composition of the complex agrees with a MZ type chelate. The very low frequency of the CO stretching vibration, the shift of the ring vibrations and the bands of the tetrahedral NH_2 deformation vibrations support strongly the structure of the complex in crystalline state as illustrated in Chart 6c.

On the other hand, PH-Cu (II)-1 can be obtained from ethanolic solution. Though this complex is a MHZ type, it does not possess the amide II and III bands. The bands of the C-H in-plane and out-of-plane bending and ring vibrations bear a resemblance to those of PA-Cu (II) and considerably to those of PH-Cu (II)-2. Nevertheless, the bands of PH-Cu (II)-1, 1630, 1475, (1394, 1384), 1011, and 917 cm^{-1}, and of PH-d_3-Cu (II)-1, 1628, (1395, 1383), 1120, 960, and 916 cm^{-1}, agree well with the bands of *cis*-planar N-substituted amides which were predicted by a normal vibration calculation of *cis* N-methylacetamide and observed for diketopiperazine by Miyazawa, *et al.*[17] (Table IV). Testing the product

TABLE IV. Calculated Frequencies of the *cis* N-Methylacetamide (*c*N-Me-AA) and Observed Frequencies of PH-Cu (II)-1 and Diketopiperazine (DKP)

Assignment	Undeuterated species (cm^{-1})			N-Deuterated species (cm^{-1})		
	*c*N-Me-AA	PH-Cu-1	DKP	*c*N-Me-AA	PH-Cu-1	DKP
C=O str.	1650	1630	1690	1632	1628	1675
NH bend., in-.	1445	1475	1443			
C-N str.	1386	1394, 1384	1340	1386	1395, 1383	1349
C-C str.	1066		1075	1203		1232
		1011			1120	
ND bend., in-.				944	960	970
		917			916	
N-CH_3 str. or N-CH_2- str.	827		910	810		887

rule with 5 bands in Table IV, the ratio 1.390 calculated for PH-Cu (II)-1 agrees well with 1.400 for *cis* N-methylacetamide. In addition, the bands of the tetrahedral NH_2 deformation vibrations and the shift of the ring vibrations suggest the structure of PH-Cu (II)-1 in crystalline state illustrated in Chart 6b.

The mechanism of complex fomation of PH-Cu (II)-1 and PH-Cu (II)-2 is inferred as illustrated in Chart 7. The structure of PH-Cu (II)-B corresponds to that of PA-Cu (II) and probably exists in small amounts in aqueous solution but can be very easily deprotonated to become PH-Cu (II)-2. It is natural to consider that an addition complex to hydrazide, PH-Cu (II)-A, might be formed to some extent considering that the first relation illustrated in Fig. 10 of Part III*[1] holds, but that it might change into a more stable chelate form illustrated in Chart 6b and deposit in ethanolic solution. The infrared absorption spectra of PH-Cu (II)-1, PH-d_3-Cu (II)-1, PH-Cu (II)-2 and PH-d_2-Cu (II)-2 are shown in Fig. 4.

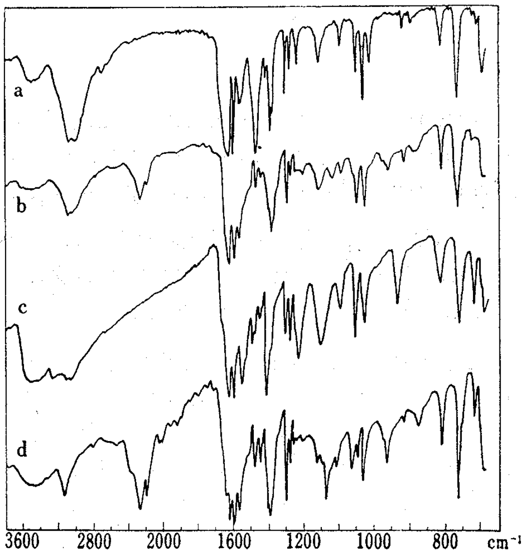
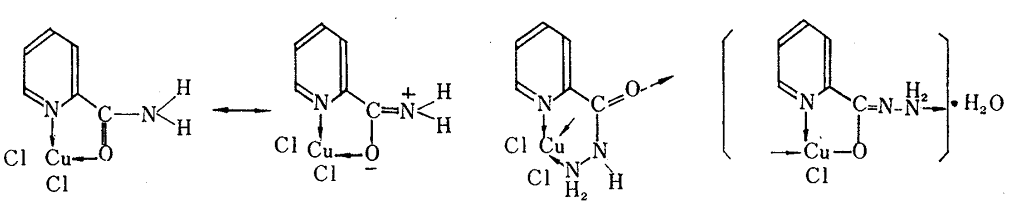


Fig. 4a. Picolinoylhydrazine(PH)-Cu (II)-1 (KBr disk)
b. PH-d_3-Cu (II)-1 (Nujol mull, HCB mull)
c. PH-Cu (II)-2 (KBr disk)
d. PH-d_2-Cu (II)-2 (Nujol mull, HCB mull, KBr disk)



a. PA-Cu (II)   b. PH-Cu (II)-1   c. PH-Cu (II)-2

Chart 6.

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17) T. Miyazawa, T. Shimanouchi, S. Mizushima: J. Chem. Phys., **29**, 611 (1958).

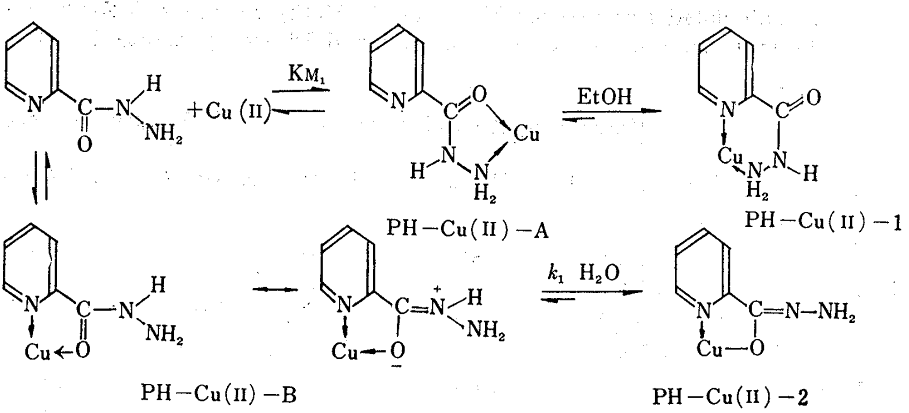

Chart 7.

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Summary

The following complexes were isolated by mixing metal chloride and ligand in water or ethanol. Their composition formulae were determined from the data of elemental analyses and their complex types are shown in parentheses.

INH-Cu (MZ); INH-Cd ($M(HZ)_2$); NH-Cu (MZ); PH-Cu (MHZ and MZ); BH-Cu (MHZ); BH-Cd (MHZ); PNBH-Cu (MZ); INA-Cu ($M(HZ)_2$); N-Me-INH-Cu (MHZ); NA-Cu ($M(HZ)_2$); PA-Cu (MHZ).

The infrared spectra of these complexes were investigated by comparing with those of ligands themselves and those of N-deuterated metal complexes. The behavior of the main bands (the bands of amide I, II, and III, $-NH_2$ deformation and pyridine ring vibrations) were discussed in relation to the structure of the complexes and their constitutional formulae were postulated.

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