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The 1:1 Complexes of Pyridine-2-carboxamide with Bivalent Metals

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The 1 : 1 complexes of pyridine-2-carboxamide (piaH) with the bivalent metals, nickel, copper, cobalt, zinc and cadmium, were prepared and their structures determined through measurements of diffuse reflectance spectra, magnetic moments and infrared spectra. In these complexes, MX_2-(piaH) (X=halogen), pyridine-2-carboxamide is likely to be coordinated to the metal through N(pyridine) and O(amide) atoms with two halogen atoms in the cis-position.

In preceding reports,[1-5] the 1 : 2 complexes of pyridine-2-carboxamide (picolinic acid amide, piaH) with nickel, copper, cobalt, iron and palladium having the general formulae, $[M(pia)_2]$ and $[M(H_2O)_2(piaH)_2]Cl_2$ were studied by various methods. The former complex had N(pyridine) and N(amide) coordination, while the latter N(pyridine) and O(amide) coordination. The 1 : 1 complexes, however, have scarcely been studied except for a copper complex.[6] In the present paper, the syntheses, properties and structures of the 1 : 1 complexes of nickel, copper, cobalt, cadmium and zinc with pyridine-2-carboxamide will be reported.

Experimental

Materials. Pyridine-2-carboxamide is the product of Tokyo Kasei Co. and was used without further purification.

Preparation of Complexes. 1) $CuCl_2(piaH)$*1: This complex was prepared by mixing together an ethanolic solution of 2.4 g (0.02 M) of the ligand and that of 3.4 g (0.02 M) of copper(II) chloride dihydrate.[6] A blue-green powder precipitated. Yield 4 g.

Found: Cu, 24.87; N, 11.35%. Calcd for $C_6H_6N_2OCuCl_2$: Cu, 24.76; N, 10.92%.

2) $CuBr_2(piaH)$: To an ethanolic solution of 2.2 g (0.01 M) of copper(II) bromide, 1.2 g (0.01 M) of the ligand dissolved in ethanol was added. The reddish-brown powder which precipitated was washed with ethanol. Yield 3 g.

Found: Cu, 18.45; N, 8.04%. Calcd for $C_6H_6N_2OCuBr_2$: Cu, 18.39; N, 8.11%.

3) $NiCl_2(piaH)\cdot 2.5H_2O$: Four grams (0.017 M) of nickel chloride hexahydrate, which had been partially dehydrated at 40°C for an hour, was dissolved in ethanol and an ethanolic solution of the ligand (1.2 g, 0.01 M) was added. The mixed solution was concentrated on a water bath until yellowish-green crystals precipitated. Yield 1.4 g.

Found: Ni, 19.88; N, 9.38; Weight loss *in vacuo* at 150°C: 15.33%. Calcd for $C_6H_6N_2ONiCl_2 2.5H_2O$: Ni, 19.78; N, 9.43; H_2O, 15.18%.

4) $CoCl_2(piaH)\cdot 2H_2O$: To an ethanolic solution of 10 g (0.04 M) of cobalt chloride hexahydrate, 1.2 g (0.01 M) of the ligand dissolved in ethanol was added. The purple powder which precipitated on concentrating the solution on a water bath was washed with ethanol. Yield 2 g.

Found: Co, 20.40; N, 9.44; Weight loss *in vacuo* at 150°C: 12.94%. Calcd for $C_6H_6N_2OCoCl_2 2H_2O$: Co,

1) K. Yamasaki and M. Sekizaki, This Bulletin, **38**, 2206 (1965).

2) M. Sekizaki and K. Yamasaki, *Nippon Kagaku Zasshi* (*J .Chem. Soc. Japan, Pure Chem. Sect.*), **87**, 1053 (1966).

3) M. Sekizaki and K. Yamasaki, *Spectrochim. Acta*, in press.

4) A. Masuko, T. Nomura and Y. Saito, This Bulletin, **40**, 511 (1967).

5) Y. Nawata, H. Iwasaki and Y. Saito, *ibid* **40**, 515 (1967).

6) K. Nagano, H. Kinoshita and A. Hirakawa, *Chem. Pharm. Bull.*, **12**, 1198 (1964).

*1 Dichloro(pyridine-2-carboxamide) copper(II). Other complexes are named in a similar way.

20.46; N, 9.73; H_2O, 12.51%.

5) $ZnCl_2$(piaH): Ethanolic solutions of 3 g (0.02 M) of zinc chloride and of 1.2 g (0.01 M) of the ligand were mixed together. The white powder which precipitated after one day was washed with ethanol. Yield 0.9 g.

Found: Zn, 25.03; N, 10.57%. Calcd for $C_6H_6N_2OZnCl_2$: Zn, 25.30; N, 10.84%.

6) $CdCl_2$(piaH): To an aqueous solution of 1.2 g (0.01 M) of the ligand, an aqueous solution of 2.5 g (0.01 M) of cadmium chloride was added. White crystals which precipitated were recrystallized from water. Yield 2.3 g.

Found: Cd, 36.58; N, 9.11%. Calcd for $C_6H_6N_2OCdCl_2$: Cd, 36.80; N, 8.77%.

The deuterated complex, $CdCl_2$(piaD) was prepared by recrystallizing $CdCl_2$(piaH) from 99.75% D_2O.

7) $CdBr_2$(piaH): This complex was prepared in a similar way to the corresponding chloro complex.

Found: Cd, 28.48; N, 7.16%. Calcd for $C_6H_6N_2OCdBr_2$: Cd, 28.50; N, 7.10%.

8) CdI_2(piaH): This complex was prepared in a similar way to the corresponding chloro complex.

Found: Cd, 22.85; N, 5.87%. Calcd for $C_6H_6N_2OCdI_2$: Cd, 23.02; N, 5.74%.

9) $Cd(NCS)_2$(piaH): To a mixture of 2.6 g (0.01 M) of cadmium sulfate 8/3 hydrate and 1.2 g (0.01 M) of the ligand dissolved in warm water, a warm aqueous solution of 2 g (0.02 M) of potassium thiocyanate was added. White crystals which precipitated were recrystallized from water. Yield 1.9 g.

Found: Cd, 32.26; N, 15.90%. Calcd for $C_6H_6N_2OCd(NCS)_2$: Cd, 32.05; N, 15.98%.

Magnetic and Spectroscopic Measurements. Magnetic moments were determined by the Gouy method at room temperature (17.5—20°C). Diffuse reflectance spectra were obtained using a Hitachi EPU-2A spectrophotometer equipped with attachments. Infrared spectra were measured with a JASCO DS-402G spectrophotometer (4000—700 cm^{-1}) and a Hitachi EPI-L spectrophotometer (700—200 cm^{-1}) using Nujol or hexachlorobutadiene mulls.

Results and Discussions

1. General Properties of the Complexes. Among the 1 : 1 complexes studied, only the cadmium complexes (Nos. 6—9) are soluble in water, while the others (Nos. 1—5) are all insoluble and readily decompose in water. All complexes are difficult to dissolve in ethanol and stable in air up to 150°C.

2. Magnetic Moments. The magnetic moments measured are listed in Table 1. The values for nickel and cobalt complexes correspond to two and three unpaired electrons, respectively, and suggest octahedral structures.[7] The values for the copper complexes are normal, indicating square planar or distorted octahedral structures without interaction between copper atoms. Zinc and cadmium complexes are all diamagnetic.

Table 1. Magnetic moments of the 1 : 1 complexes (17.5—20°C)

	Complex	Moment observed	Moment calcd. by the spin-only formula
1	$CuCl_2$(piaH)	1.88 B.M.	1.73 B.M.
2	$CuBr_2$(piaH)	1.82	1.73
3	$NiCl_2$(piaH)·2.5H_2O	3.21	2.82
4	$CoCl_2$(piaH)·2H_2O	4.97	3.88
5	$ZnCl_2$(piaH)	diamagnetic	
6	$CdCl_2$(piaH)	diamagnetic	
7	$CdBr_2$(piaH)	diamagnetic	
8	CdI_2(piaH)	diamagnetic	
9	$Cd(NCS)_2$(piaH)	diamagnetic	

3. Diffuse Reflectance Spectra. The diffuse reflectance spectra of the nickel complexes are shown in Fig. 1. The bands at 1300, 700 and 415 mμ for the 1 : 1 complex are assigned to the transitions $^3A_{2g}\rightarrow{}^3T_{2g}$ $^3A_{2g}\rightarrow{}^3T_{1g}$(F) and $^3A_{2g}\rightarrow{}^3T_{1g}$(P), respectively.[8] The corresponding bands for the 1 : 2 complex, $[Ni(H_2O)_2(piaH)_2]Cl_2$ appear at 875, 625 and 350 mμ.

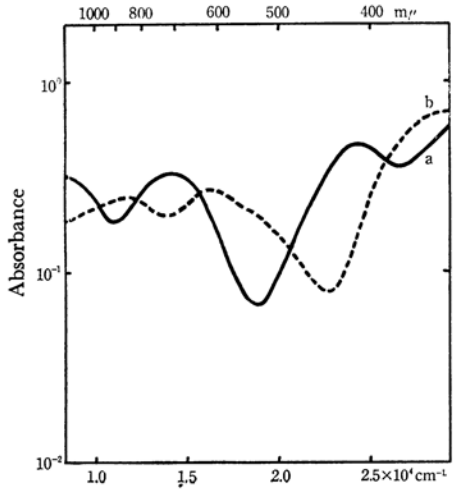

Fig. 1. Diffuse reflectance spectra of the nickel complexes.
a: $NiCl_2$(piaH)·2.5H_2O
b: $[Ni(H_2O)_2(piaH)_2]Cl_2$

The diffuse reflectance spectra of the cobalt complexes are shown in Fig. 2. Spectroscopic and magnetic data for the 1 : 1 complexes strongly suggest the octahedral coordination of cobalt compared with the 1 : 2 complex, $[Co(H_2O)_2(piaH)_2]Cl_2$. Absorption bands beyond 1100 mμ and at 550 mμ are assigned to the transitions

7) N. S. Gill and R. S. Nyholm, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

8) J. R. Miller, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 4, ed. by Emeleus and Sharpe, 133 (1962).

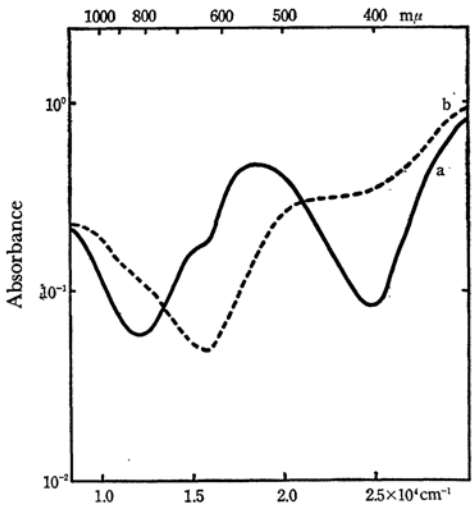

Fig. 2. Diffuse reflectance spectra of the cobalt complexes.
a: $CoCl_2(piaH)\cdot 2H_2O$
b: $[Co(H_2O)_2(piaH)_2]Cl_2$

$^4T_{1g}\rightarrow{}^4T_{2g}$ and $^4T_{1g}\rightarrow{}^4T_{1g}(P)$, respectively, and the shoulder at 650 mμ to the transition $^4T_{1g}\rightarrow{}^4A_{2g}$, which is weak because of the two-electron jump.[9]

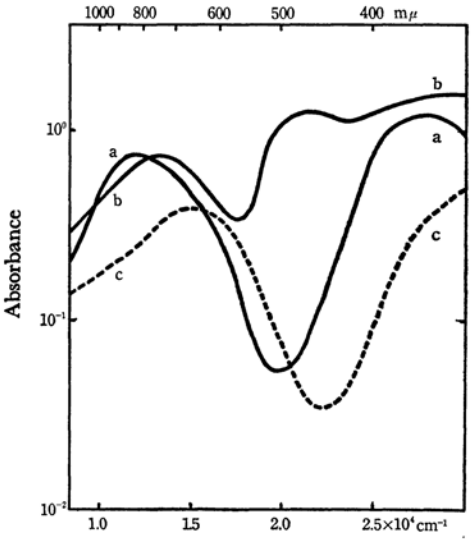

Fig. 3. Diffuse reflectance spectra of the copper complexes.
a: $CuCl_2(piaH)$, b: $CuBr_2(piaH)$,
c: $[Cu(H_2O)_2(piaH)_2]Cl_2$

All the 1 : 1 complexes of nickel and copper show d–d transition bands at longer wavelengths than the corresponding 1 : 2 complexes. This may be due to the coordination of two halogen atoms in the 1 : 1 complexes instead of a pyridine-2-carboxamide molecule.

As shown in Fig. 3, the 1 : 1 complexes of copper, $CuX_2(piaH)$, give two bands in the visible region. The band at 370 mμ for the chloro complex shifts to 470 mμ for the bromo complex and this band is not found for the 1 : 2 complex, $[Cu(H_2O)_2(piaH)_2]Cl_2$. Therefore this band may be assigned to a charge transfer band related to the coordination of halogen atoms. The band due to the d–d transition is observed at 830 mμ for the chloro complex, at 750 mμ for the bromo complex and at 660 mμ for the 1 : 2 complex. These 1 : 1 copper complexes are all thought to be of distorted octahedral or square planar structures, but it is difficult to decide from spectroscopic and magnetic data alone.

Zinc and cadmium complexes show no absorption bands in the visible region.

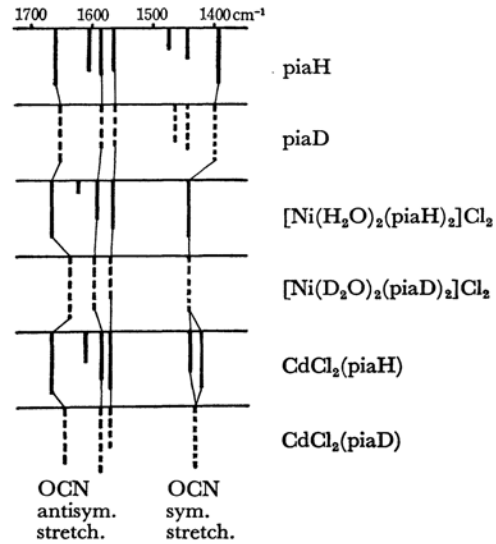

Fig. 4. Infrared spectra of ligands, nickel (1 : 2) and cadmium (1 : 1) complexes.

4. Infrared Spectra. Infrared spectra of the 1 : 1 complexes shown in Figs. 4, 5 and 6 are similar to each other, indicating similar structures; namely octahedral structures for nickel, cobalt, zinc and cadmium complexes, and probably for copper complexes as well.

In the region 4000—700 cm^{-1} some characteristic bands due to the amide group of the ligand are observed. The spectra of the free ligand, the 1 : 1 complexes $MX_2(piaH)$ and 1 : 2 complexes $[M(H_2O)_2(piaH)_2]X_2$,[3] and their deuterated compounds are shown in Fig. 4 and Table 2. In comparing the amide bands of the 1 : 1 complexes with those of the 1 : 2 complexes which had been found to be N and O coordination, a close similarity is observed in the following points: (1) Upon

9) S. Koide, *Phil. Mag.*, [8], **4**, 243 (1959).

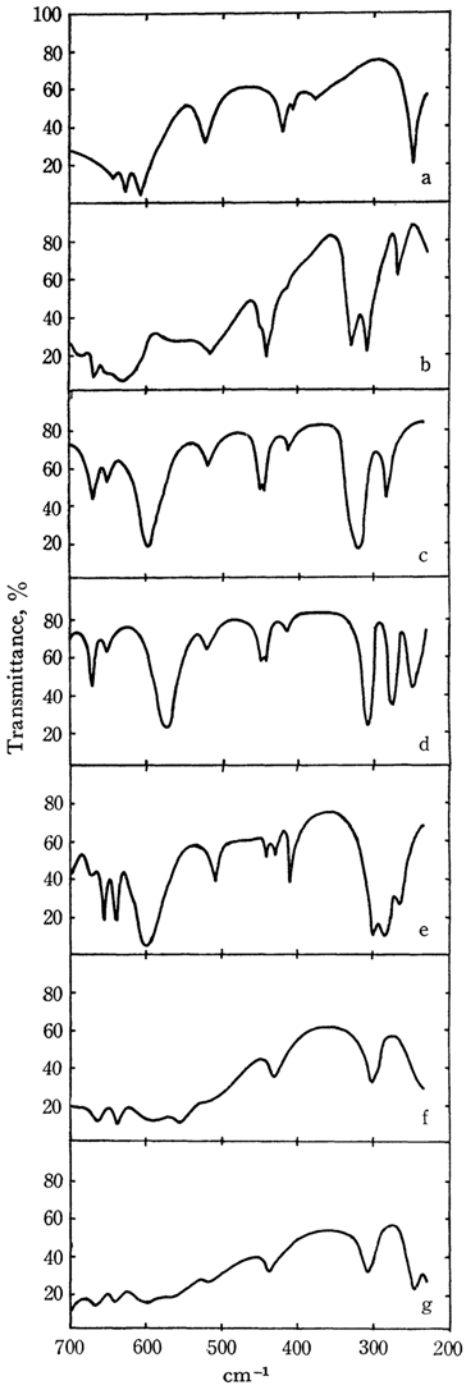

Fig. 5. Far infrared spectra.
a: piaH, b: $[Ni(H_2O)_2(piaH)_2]Cl_2$, c: $CuCl_2$-(piaH), d: $CuBr_2(piaH)$, e: $ZnCl_2(piaH)$, f: $CoCl_2(piaH)\cdot 2H_2O$, g: $NiCl_2(piaH)\cdot 2.5H_2O$

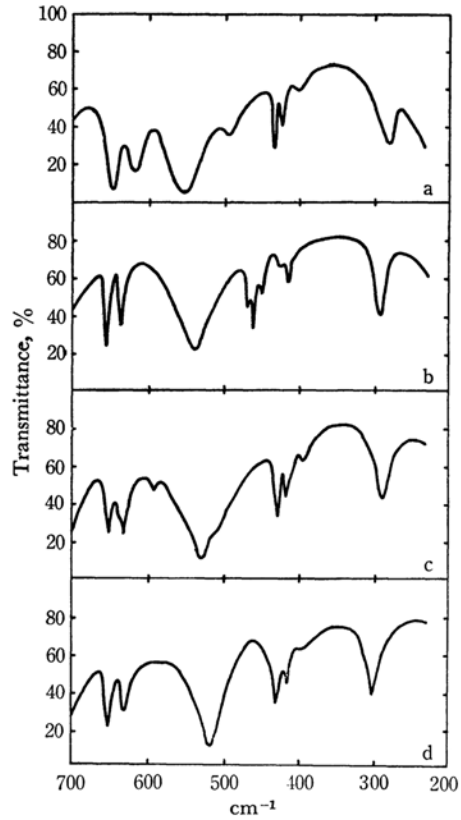

Fig. 6. Far infrared spectra.
a: $CdCl_2(piaH)$, b: $Cd(NCS)_2(piaH)$, c: $CdBr_2(piaH)$, d: $CdI_2(piaH)$

deuteration, the band of OCN antisymmetric stretching vibration mode of both the 1 : 1 and 1 : 2 complexes at 1670—1640 cm^{-1} shifts to lower frequency by 20—30 cm^{-1}, while the shift for the free ligand is small; (2) The band of OCN symmetric stretching vibration mode at 1440-1410 cm^{-1} is observed in a region higher than that of the free ligand by about 40 cm^{-1}, and the shift upon deuteration is small; (3) The band at about 1600 cm^{-1}, which is due to NH_2 scissoring is observed almost at the same position for various complexes. The close similarity of spectra between the 1 : 1 and 1 : 2 complexes suggests similar structures, *i. e.* N(pyridine) and O(amide) coordination for the 1 : 1 complexes, $MX_2(piaH)$, as well as for the 1 : 2 cationic complexes, $[M(H_2O)_2$-$(piaH)_2]X_2$. Entirely different spectra for the 1 : 2 non-ionic complexes, $M(pia)_2$, reported earlier,[3] rule out the possibility of N(pyridine) and N(amide) coordination for the 1 : 1 complexes.

Far infrared spectra (700—200 cm^{-1}) are shown in Figs. 5 and 6 and Table 3, with tentative assignments. The spectra of the 1 : 2 complexes of nickel and the free ligand[3] are also shown for comparison. In this region two characteristic bands due to the amide group are found at about 600 and 500 cm^{-1}. The former band is assigned to the CO in-plane bending mode and the latter to the CO out-of-plane bending mode. The frequency of

TABLE 2. INFRARED SPECTRA OF AMIDE GROUPS IN THE REGION 4000—700 cm^{-1}

1	piaH	3420 s	3155 s	1659 s	1602 m	1391 s	1164 w	1097 s
2	piaD	2550 s	2360 s	1650 s	1204 m	1400 s	920 s	
3	$[Ni(H_2O)_2(piaH)_2]Cl_2$	3300 s	3120 s	1664 s	1616 w	1434 s	1132 w	1109 w
4	$[Ni(D_2O)_2(piaD)_2]Cl_2$	2490 s	2300 s	1636 s	1221 m	1438 s	935 s	
5	$NiCl_2(piaH)\cdot 2.5H_2O$	3320 br	3200 br	1670 s	1610 w	1431 s	1183 w	1110 m
6	$CuCl_2(piaH)$	3395 s	3275 s	1643 s	1608 m	1432 s	1182 w	1123 m
7	$CoCl_2(piaH)\cdot 2H_2O$	3325 br	3195 br	1666 s	1625 m	1430 s	1181 w	1112 m
8	$ZnCl_2(piaH)$	3390 s	3290 s	1660 s	1612 m	1427 s	1177 w	1113 m
9	$CdCl_2(piaH)$	3460 s	3370 s	1666 s	1612 m	1438 m 1414 s	1176 w	1116 w
10	$CdCl_2(piaD)$	2580 s	2430 s	1644 s	1219 w	1427 s	926 w	914 w
	Assignment	NH_2 anti sym. stretch.	NH_2 sym. str.	OCN anti sym. str.	NH_2 sciss.	OCN sym. str.	NH_2 in-plane bend.	

Data for 1—4 were taken from Ref. 3.

TABLE 3. FAR INFRARED SPECTRA OF THE COMPLEXES IN THE REGION 700—200 cm^{-1}

1	piaH	627 s	645 m	607 s	520 m		420 m	411 w		252 s	
2	$[Ni(H_2O)_2](piaH)_2]Cl_2$	667 s	652 sh	632 s	515 m	440 s			328 s 311 s	269 m	230 s
3	$NiCl_2(piaH)\cdot 2.5H_2O$	664 br	641 br	600 br	560 br	436 m			307 m	245 s	
4	$CuCl_2(piaH)$	667 m	650 w	597 s	517 w	445 m 448 m		411 w	321 s	282 m	
5	$CuBr_2(piaH)$	670 m	650 w	576 s	518 w	443 m 447 m		410 w	307 s	275 s	251 m
6	$CoCl_2(piaH)\cdot 2H_2O$	662 br	637 br	595 br	555 br	431 m			302 m	235 s	
7	$ZnCl_2(piaH)$	653 m	639 m	600 s	509 m	439 w	428 w	410 m	300 s	286 s	270 m
8	$CdCl_2(piaH)$	646 s	617 m	552 s	495 w	434 m	422 w	400 w		282 m	
9	$CdBr_2(piaH)$	653 s	634 s	527 s	510 sh	430 s	418 m	396 w		290 m	
10	$CdI_2(piaH)$	655 s	633 m	519 s		430 m	417 w	397 sh		303 m	
11	$Cd(NCS)_2(piaH)$*4	656 s	635 m	538 s	467 w	452 w	415 w			294 m	
	Assignment	NH_2 twist.		CO in-plane bend.	CO out- of-plane bend.	py. ring out- of-plane bend.			*1	*2	*3

*1 chelate ring vibration.
*2 pyridine-amide torsion
*3 chelate ring vibration + M–X stretching (X = halogen)
*4 $Cd(NCS)_2(piaH)$ shows a band at 461 cm^{-1} due to the NCS bending

the CO in-plane bending mode for the 1 : 1 chloro complexes decreases in the following order: Ni~Zn>Co≥Cu>Cd. If the corresponding band is compared for different halogen-substituted complexes of the same metal, the frequency decreases in the following order for copper and cadmium: Cl>NCS>Br>I. On the other hand, frequencies of the CO out-of-plane bending mode show only small differences from each other, and there is no regularity in the shift. Therefore, some correlation between the coordination of halogen atoms and the CO in-plane bending mode seems to exist. Based on the above results, the structure shown in Fig. 7 is proposed for the 1 : 1 complexes, in which the metal, halogen atoms and the am ide group of the ligand are all situated in the same plane.

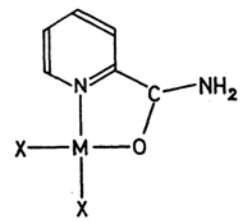

Fig. 7. The proposed structure for the 1 : 1 complex.

Several strong bands observed in the region 320—200 cm^{-1} are assigned to the skeletal vibration correlated with the chelate ring vibration. Of these bands, the one observed for the free ligand at 252 cm^{-1} and the band observed for 1 : 1 complexes at 235—303 cm^{-1} are assigned to the pyridine-amide torsional mode. Several bands are observed at 300 and 250—200 cm^{-1} for the 1 : 1 complexes, but not for the free ligand. These bands are mainly due to the metal - N (pyridine) or metal - O(amide) stretching vibration modes coupled with metal - halogen stretching. For the nickel and cobalt complexes, strong and broad absorptions due to the libration of lattice waters are present in the region 800—200 cm^{-1}.

Far infrared spectra were measured in the laboratory of Professor Shimanouchi, the University of Tokyo, and in the Naka Works, the Hitachi Ltd. The present authors wish to thank for their kindness shown during the measurements, and the Ministry of Education for a research grant.