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Cobalt(II) and Copper(II) Complexes of Several Potentially Terdentate N-Substituted Picolinamides

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Cobalt(II) and copper(II) complexes with several potentially terdentate N-substituted picolinamides: R–(CH$_2$)$_n$–NHCOC$_5$H$_4$N (R = coordinating group) have been studied. Coordination of the amide nitrogen with deprotonation can occur when the coordinating power of the R group to a metal ion is sufficiently strong. The coordinating mode of the amide group is affected not only by R and the central metal, but also by the preparative conditions.

Introduction

In the previous papers[1,2] we have reported the preparation of palladium(II) and nickel(II) complexes of potentially terdentate N-substituted picolinamides, R–(CH$_2$)$_n$–NHCOC$_5$H$_4$N (abbreviated generally as LH), where R is NH$_2$, NHCH$_3$, N(CH$_3$)$_2$, SC$_2$H$_5$, or OCH$_3$, and have studied mainly the effect of substituents of the amide nitrogen on the coordinating mode of amide groups. Palladium(II) formed only one type of complex, PdXL mH$_2$O, whereas nickel(II) formed two types, NiXL · mH$_2$O and NiX$_2$(LH)$_2$ · mH$_2$O, depending upon R and n. In the present work, copper(II) and cobalt(II) complexes with the above ligands were prepared, and the coordinating mode of amide groups was investigated in connection with the substituents, central metals, and preparative conditions.

Experimental Section

1. *Preparation of ligands.* The preparative methods of all the ligands were reported in the previous papers[1,2].

2. *Syntheses of the complexes.* (a) CuXL · mH$_2$O. To an aqueous solution (15 ml) of the respective ligand (5 mmol) was added an aqueous solution (15 ml) of a copper salt (5 mmol), and then an equivalent amount of sodium hydroxide (5 mmol) dissolved in a small amount of water. From the filtered solution fine crystals were obtained at room temperature after a few days. The product was recrystallized from water and dried in air(yield 30-60 %). The ligands forming the complexes of this type are those with R=NH$_2$, N(CH$_3$)$_2$, and SC$_2$H$_5$ for n=2, and those with R=NH$_2$ and N(CH$_3$)$_2$ for n=3. For the ligand moepH(R=OCH$_3$, n=2) no complex of this type was obtained.

Table I. Abbreviation of ligands: R-(CH$_2$)$_n$-NHCOC$_5$H$_4$N.

	R	n	Abbreviation
1	NH$_2$	2	enpH
2	NH$_2$	3	tnpH
3	N(CH$_3$)$_2$	2	dmepH
4	N(CH$_3$)$_2$	3	dmppH
5	SC$_2$H$_5$	2	etepH
6	OCH$_3$	2	moepH

(b) CuX$_2$(LH). To a warm ethanolic solution (20 ml) of a copper salt (10 mmol) was added an ethanolic solution (15ml) of the ligand (5 mmol). The precipitate formed was filtered off after cooling the solution to room temperature, washed with ethanol, and then dried in air(yield 80%). Only etepH and moepH formed complexes of this type.

(c) CuX$_2$(LH)$_2$. The complex CuCl$_2$(etepH)$_2$ was obtained by mixing 3 mmol of copper chloride and the ligand (5 mmol) in water. When a few drops of concentrated perchloric acid were added to a mixture of an aqueous solution of copper perchlorate (3 mmol) and of the ligand (5 mmol), the species Cu(ClO$_4$)$_2$(LH)$_2$ · 2HClO$_4$ were obtained, LH being dmepH and dmppH. The yield was ca. 55%.

(d) CoX$_2$(L)$_2$ · mH$_2$O. Only etepH and moepH formed this type of complex. The complexes were prepared by mixing an ethanolic solution of a cobalt salt (3 mmol) with the ligand (5 mmol). The yield was about 80%.

3. *Measurements.* Instruments used were the same as reported in the previous paper[3].

Results and Discussion

1. *General consideration.* The ligands and the complexes prepared are given in Tables I and II

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Table II. Prepared complexes and their analytical results.

	Complex	Colour	M %(Calcd.)	Analysis N %(Calcd.)	H_2O %(Calcd.)
1	$CuCl(enp)\cdot 2H_2O$	Blue	21.24(21.24)	14.00(14.04)	12.05(12.04)
2	$CuBr(enp)$	Dark blue	20.83(20.66)	13.68(13.66)	
3	$CuCl(tnp)$	Violet	22.84(22.92)	15.27(15.16)	
4	$CuBr(tnp)$	Violet	19.69(19.76)	13.05(13.06)	
5	$CuCl(dmep)\cdot 2H_2O$	Blue	19.43(19.42)	12.99(12.84)	11.14(11.01)
6	$CuBr(dmep)\cdot 2H_2O$	Blue	17.06(17.09)	11.37(11.30)	9.88(9.69)
7	$CuClO_4(dmep)$	Blue-violet	17.90(17.89)	11.60(11.83)	
8	$CuClO_4(dmpp)$	Blue-violet	17.32(17.21)	11.17(11.38)	
9	$CuCl(etep)\cdot H_2O$	Blue	19.66(19.47)	8.73(8.59)	5.63(5.52)
10	$CuCl_2(etepH)$	Green	18.27(18.43)	8.07(8.12)	
11	$CuBr_2(etepH)$	Brown	14.41(14.65)	6.56(6.46)	
12	$CuCl_2(moepH)$	Green	20.18(20.20)	8.77(8.90)	
13	$Cu(ClO_4)_2(dmepH)_2\cdot 2HClO_4$	Blue	7.43(7.48)	10.49(9.89)[a]	
14	$Cu(ClO_4)_2(dmppH)_2\cdot 2HClO_4$	Blue	7.28(7.24)	10.07(9.57)[b]	
15	$CuCl_2(etepH)_2$	Blue	11.58(11.45)	10.08(10.09)	
16	$Co(NCS)_2(etepH)_2$	Purple	9.75(9.89)	13.92(14.11)	
17	$Co(NCS)_2(moepH)_2$	Orange	10.88(11.00)	15.16(15.69)	
18	$CoBr_2(moepH)_2\cdot 4H_2O$	Orange	8.82(9.05)	8.60(8.60)	11.55(11.07)

[a] C, 28.31(28.27); H, 3.91(3.56%). [b] C,30.29(30.10); H, 4.31(4.13%).

Table III. Magnetic moments and diffuse reflectance spectra.

	Complex	μ_{eff} B.M.	Absorption maximum ($\times 10^3$ cm^{-1})
1	$CuCl(enp)\cdot 2H_2O$	1.83	15.3
1'	Anhydride of 1	1.83	16.8 21.0sh*
2	$CuBr(enp)$	1.90	16.1 18.5sh
3	$CuCl(tnp)$	1.83	16.5sh 18.7 25.5sh
4	$CuBr(tnp)$	1.82	17.7 19.5sh 24.5sh
5	$CuCl(dmep)\cdot 2H_2O$	1.85	14.8
6	$CuBr(dmep)\cdot 2H_2O$	1.84	14.7
7	$CuClO_4(dmep)$	1.86	16.8
8	$CuClO_4(dmpp)$	1.84	16.4 19.5sh 25.8sh
9	$CuCl(etep)\cdot H_2O$	1.83	15.2
10	$CuCl_2(etepH)$	1.88	13.1 25.0sh
11	$CuBr_2(etepH)$	1.73	9.6 12.8sh 21.0sh
12	$CuCl_2(moepH)$	1.86	13.4 24.7sh
13	$Cu(ClO_4)_2(dmepH)_2\cdot 2HClO_4$	1.93	15.7
14	$Cu(ClO_4)_2(dmppH)_2\cdot 2HClO_4$	1.87	15.9
15	$CuCl_2(etepH)_2$	1.87	14.1
16	$Co(NCS)_2(etepH)_2$	4.85	8.9 16.7sh 19.5 20.5sh
17	$Co(NCS)_2(moepH)_2$	4.77	9.6 17.0sh 19.3sh 20.8
18	$CoBr_2(moepH)_2\cdot 4H_2O$	4.60	9.5 21.9

* sh = shoulder.

together with the results of elemental analyses. Magnetic moments and diffuse reflectance spectral data are given in Table III. The three cobalt(II) complexes, $CoBr_2(moepH)_2\cdot 4H_2O$, $Co(NCS)_2(moepH)_2$, and $Co(NCS)_2(etepH)_2$, are of the high-spin type, and all the copper(II) complexes have normal magnetic moments. The orange colour of $CoBr_2(moepH)_2\cdot 4H_2O$ turned to red on dehydration, indicating coordination of water molecules.

2. *Infrared spectra.* The infrared spectral data of some of the complexes are shown in Table IV. The complexes studied are divided into two types by the pattern of the amide bands[4]. In the type A the amide group is coordinated via its oxigen atom (Fig. 1A), while in the type B coordination occurs via the deprotonated amide nitrogen atom (Fig. 1B).

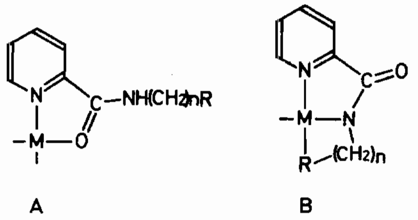

Figure 1. Two coordinating modes of an amide group.

The presence of a coordinated NH_2 group in CuCl(enp) is indicated by the bands ν(N-H) at 3147, 3250, and 1617 cm^{-1}, which shift on deuteration to 2319, 2440, and 1198 cm^{-1} respectively[5]. Similar bands are also observed for other enpH and tnpH complexes to show the presence of the NH_2 group.

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Table IV. Infrared spectra of the complexes (in cm^{-1}).

	Complex	νN-H	Amide bands I	II	III	Other bands (assignment)	
	Type A						
10	$CuCl_2(etepH)$	3285	1632	1550	1332	304(νCu-Cl)	
12	$CuCl_2(moepH)$	3280	1627	1550	1324	$\left\{\begin{matrix}1105\\1110\end{matrix}\right.$(νC-O)	313(νCu-Cl)
13	$Cu(ClO_4)_2(dmepH)_2 . 2HClO_4$	3310	1635	1556	1357	3116(νN-H)	1100(νClO$_4$)
16	$Co(NCS)_2(etepH)_2$	3220	1630	1548	1326	2087(νC≡N) 474(δNCS)	798(νC-S) 275(νCo-NCS)
17	$Co(NCS)_2(moepH)_2$	3255	1630	1540	1330	2075(νC≡N) 1099(νC-O)	472(δNCS) 246(νCo-NCS)
18	$CoBr_2(moepH)_2 . 4H_2O$	*	1633	1557	1327	$\left\{\begin{matrix}1102\\1113\end{matrix}\right.$(νC-O)	
	Type B						
1	CuCl(enp)		1631	1413		$\left\{\begin{matrix}3147\\3250\end{matrix}\right.$(νN-H)	1617(δNH$_2$)
3	CuCl(tnp)		1586	1393 1384		$\left\{\begin{matrix}3127\\3250\end{matrix}\right.$(νN-H)	1620(δNH$_2$)
5	$CuCl(dmep) . 2H_2O$		1618	1408			
7	$CuClO_4(dmep)$		1596	1410		$\left\{\begin{matrix}1113\\1102(\nu ClO_4)\\1053\end{matrix}\right.$	484(δClO$_4$)
8	$CuCl_4(dmpp)$		1586	1412		1092(νClO$_4$)	

* Obscured by the bands of H_2O.

The two $HClO_4$ adducts, $Cu(ClO_4)_2(LH)_2 \cdot 2HClO_4$ (LH = dmepH and dmppH), show two ν(N-H), one of which is due to the amide group, and the other to the terminal $NH(CH_3)^{2+}$ group. Thus it is shown that the terminal dimethylamino group is not coordinated.

Infrared spectra of the perchlorate complexes (Table II, Nos. 7, 8, 13, and 14) show bands at ca. 1100, ca. 930, and at ca. 620 cm^{-1}, which are similar to those of the free perchlorate ion and indicate non-coordination of the ClO_4 group. The complex, $CuClO_4(dmep)$, is exceptional in that the band at 1100 cm^{-1} splits into three components indicating the probable coordination of the ClO_4 group (Table IV)[6]. The coordination of the ClO_4 group is also supported by the appearance of a band at 484 cm^{-1} which is infrared-inactive when ClO_4 is free, but becomes active when the symmetry of ClO_4 is reduced by coordination[6]. The infrared spectra of the thiocyanato complexes show coordination of the NCS group through the N atom (Table IV)[7]. If the ether-O atom of moepH were coordinated, the ν(C-O) at 1095 cm^{-1} of free moepH[8] should shift to lower frequencies by ca. 50 cm^{-1}, but for $Co(NCS)_2(moepH)_2$ the band hardly shifts thus showing non-coordination of the ether-O atom (Table IV)[9]. The slight difference in frequency of ν(C-O) between this complex and other complexes such as $CuCl_2(moepH)$ and $CoBr_2(moepH)_2 \cdot 4H_2O$ may be due to hydrogen bonding between the ether-O and the amide-H atoms.

3. *Far infrared spectra.* The coordination of the pyridine ring is indicated by the shift of the deformation vibration a cat 620 cm^{-1} to higher frequencies by 25-35 cm^{-1}, as was reported for the complexes of pyridine derivatives[10].

In the complexes of type A the out-of-plane deformation vibration of the amide-carbonyl group of the free ligands at ca. 510 cm^{-1} shifts to higher frequencies by 15-30 cm^{-1}. This supports the amide-O coordination[3] which is consistent with the result obtained from the analysis of the amide I, II, and III bands, while in the type B complexes the whole spectra change so markedly on coordination that the assignment of the deformation band is difficult. Similary the assignment of of ν(Cu-X) of the type B complexes is difficult bacause several bands move to lower frequencies when a chloro ligand is replaced by a bromo ligand This is probably due to the coupling of ν(Cu-X) with other vibrations (Fig. 2). A remarkable spectral

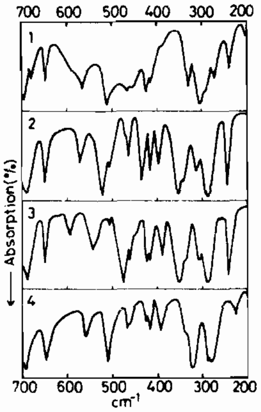

Figure 2. Far infrared spectra of (1) $CuCl(enp) . 2H_2O$, (2) CuCl(enp), (3) deuterated CuCl(enp) and (4) BuBr(enp).

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(6) K. Nakamoto, «Infrared Spectra of Inorganic and Coordination Compounds», 2nd ed., Wiley, New York (1970), p. 175.

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(10) R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, *4*, 350 (1965).

change is observed in the region 400-200 cm^{-1} when the hydrated type B complexes (Table II, Nos. 1, 5, 6, and 9) are dehydrated indicating marked structural change.

The bands ν(M-X) for the type A complexes are shown in Table IV. These ν(M-X) bands are similar in position to those of the corresponding complexes of other picolinamide derivatives[3] and this indicates a structural similarity, except for the complex $Co(NCS)_2(moepH)_2$ in which this band appears at slightly lower frequencies. Thus for $Co(NCS)_2(LH)_2$ and CuX(LH) may be assigned the structures shown in Figs. 3A and 3B respectively[3]. The ν(Cu-Cl) of $CuCl_2(etepH)_2$ is not observed down to 200 cm^{-1} probably due to the weak Cu-Cl bond in the tetragonally distorted copper complex[11].

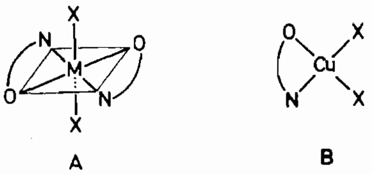

Figure 3. The structures proposed for $[MX_2(LH)_2]^{p+}$(A) and $[CuX_2(LH)]$(B), where $\overset{\frown}{N\ O}$ corresponds to the partial structure shown in Fig. 1A.

For CuCl(enp) the isotopic shifts due to the substitution of NH_2 with ND_2 are as shown in Fig. 2. The band at 523 cm^{-1} which shifts to 475 cm^{-1} upon deuteration is assigned to the rocking mode of the NH_2 group which is observed at 509 cm^{-1} for CuBr(enp). Three bands at 433, 397, and 314 cm^{-1} of CuCl(enp) show the shifts due to the D and Br substitution, too. The presence of such a coupling makes the assignment of ν(Cu-N) and ν(Cu-X) quite difficult.

4. Electronic spectra. (*a*) *Copper complexe.* The diffuse reflectance spectra of the type B complexes (Fig. 1B, the fourth site = X) have a broad absorption, the position of which depends upon the ligand L, anion X and the degree of hydration (Table III). The absorption maximum of the hydrate complexes (Table III, Nos. 1, 5, 6, and 9) occurs at lower frequencies than that of the corresponding anhydrous compounds. When the water molecules are coordinated (cf. 3) the ligand field around the copper ion may be closer to that characteristic of octahedral complexes. On the contrary, in the anhydrous complexes the ligand field may be similar to that of square-planar complexes[12,13].

On the basis of the infrared spectral data it was found that the acid amide ligands in the two complexes, $CuClO_4$(dmep) and $CuClO_4$(dmpp), are coordinated as sown in Fig. 1B, and that the ClO_4 ion of the former is coordinated at the fourth site, while that of the latter is not coordinated. The diffuse reflectance spectrum of the later complex has shoulders at 19.5 and 25.8 × 10^3 cm^{-1}, which indicate a different structure. Generally the copper complex with a subnormal magnetic moment shows a band in the near ultraviolet region[14,15] which may be correlated with a copper-copper interaction. The shoulder at 25.8 × 10^3 cm^{-1} of $CuClO_4$(dmpp), however, seems to have a different origin, since the magnetic moment of the complex is normal. Thus for $CuClO_4$(dmpp) a dimeric structure[16] with uncoordinated ClO_4 groups may be excluded. The question of what group occupies the fourth coordinating site in $CuClO_4$(dmpp) is difficult to solve by spectral studies alone.[17]

The absorption maxima in both diffuse reflectance and absorption spectra appear at higher frequencies for CuX(tnp) than for CuX(enp) (Tables III and V), whereas Ni(NCS)(tnp) . 1/4H_2O has the maximum at lower frequencies than Ni(NCS)(enp). This means that tnp is a stronger ligand than enp for copper(II), while for nickel(II) the order is reversed. The higher molar extinction coefficient of the copper complexes with a fused 5-5 membered chelate ring compared to that of the complexes with a fused 5-6 membered chelate ring has been interpreted to arise from the strain of the chelate rings.[18] A similar interpretation seems to be applicable for the complexes of acid amide (Table V).

Table V. Electronic spectra of the complexes.

	Complex	Solvent	Absorption maximum in ×10^3 cm^{-1}(log ε^a)	
1	CuCl(enp) . 2H_2O	$CHCl_3$	16.7(2.11)	
3	CuCl(tnp)	$CHCl_3$	17.6(1.87)	18.7sh ^{b}
5	CuCl(dmep) . 2H_2O	$CHCl_3$	16.4(2.21)	
6	CuBr(dmep) . 2H_2O	$CHCl_3$	16.2(2.21)	
9	CuCl(etep) . H_2O	$CHCl_3$	16.3(2.47)	19.5sh
10	$CuCl_2$(etepH)	H_2O	16.0(1.87)	
		c	16.3(2.18)	
12	$CuCl_2$(moepH)	H_2O	13.5(1.31)	
		c	16.8(1.72)	
16	$Co(NCS)_2(etepH)_2$	CH_3OH	8.9 (0.81)	16.0sh
			19.3(1.59)	21.0sh
17	$Co(NCS)_2(moepH)_2$	CH_3OH	8.9(0.81)	16.0sh
			19.3(1.59)	21.0sh

^{a}ε = molar extinction coefficient. ^{b}sh = shoulder. ^{c}0.1 N sodium hydroxide solution.

The diffuse reflectance spectra of CuX_2(LH) are very similar to those of CuX_2(mepiaH)*, suggesting non-coordination of the N-substituent on the acid amide in the solid state. Thus these complexes may have a structure involving the bidentate ligand LH, with the third and fourth sites occupied by halide ions (Figures 1A and 3B).[3] In aqueous solutions however, the absorption spectrum of $CuCl_2$(moepH) is almost identical to that of $CuCl_2$(mepiaH), while that of $CuCl_2$(etepH) is different. Even in 0.1 N sodium hydroxide solution the situation is the same (Table V). These results indicate that the sulfur atom of etepH has an

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(14) M. Kato, H.B. Jonassen, and J.C. Fanning, *Chem. Rev.*, *64*, 99 (1964).
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* mepiaH = N-methylpicolinamide.

appreciably high coordinating tendency, while the oxygen atom of moepH has only a low tendency to coordinate. Thus etepH acts as the terdentate ligand and forms a fused chelate ring with deprotonation of the amide group (Figure 1B), while moepH does not form such a chelate ring and coordinates only with the ring-N and amide-O atoms. This view is supported by the fact that the pH of the 0.005 M aqueous solution of $CuCl_2(etepH)$ is 2.9 due to the hydrogen ion released by deprotonation of the amide group, while that of $CuCl_2(moepH)$ is 4.0. The difference is also reflected by the isolation of the solid $CuCl(etep) . H_2O$ and the failure to isolate solid CuCl(moep).

In the complexes $Cu(ClO_4)_2(LH)_2 . 2HClO_4$ (LH = dmepH and dmppH) the ClO_4 groups are not coordinated, and the terminal dimethylamino groups are protonated and so are no longer potential ligands (cf. 2). The similarity of the diffuse reflectance spectrum (Table III) of $Cu(ClO_4)_2(LH)_2 . 2HClO_4$ to that of $[Cu(mepiaH)_2]^{2+}$ shows that both have an almost square-planar structure (Figure 3A, X = vacant).[3] The tetragonal distortion of $CuCl_2(etepH)_2$ may be smaller than that of $Cu(ClO_4)_2(LH)_2 . 2HClO_4$, since the absorption maximum of the former is at lower frequencies than that of the latter.[12,19] This is probably due to weak coordination of the chloride ions at the axial positions (Figure 3A, X = Cl).

(b) *Cobalt(II) complexes.* The diffuse reflectance spectra of the cobalt(II) complexes indicate an octahedral structure (Table III), and the spectra of $CoBr_2(moepH)_2 . 4H_2O$ and $Co(NCS)_2(etepH)_2$ are very similar to those of $[Co(mepiaH)_2(H_2O)_2]^{2+}$ and $[Co(NCS)_2(mepiaH)_2]$, respectively.[3] This indicates a structural similarity for each pair, namely, the N-substituent of the amide group of moepH and etepH is free from coordination similar to the methyl group of mepiaH (Figure 1A). The structure of $[Co(mepiaH)_2(H_2O)_2]^{2+}$ and $[Co(NCS)_2(mepiaH)_2]$ are shown in Figure 3A (X = H_2O or NCS).[3]

The spectrum of the orange complex $Co(NCS)_2(moepH)_2$ is similar to that of the orange complex $[Co(mepiaH)_2(H_2O)_2]^{2+}$ (trans 2N4O type), and different from that of the purple complex $[Co(NCS)_2(mepiaH)_2]$ (trans 4N2O type) (Figure 3A, X = H_2O and NCS respectively). This implies coordination of the ether-O atom of moepH. As has been discussed in section 2, infrared spectral data have disproved the coordination of the ether-O atom of moepH and that of the NCS group through S atom. A probable structure of the cobalt complex is the *cis*-coordination of two NCS groups and/or that of two moepH groups, but this is not confirmed by the electronic spectrum. If the two complexes, $Co(NCS)_2(etepH)_2$ and $Co(NCS)_2(moepH)_2$, are dissolved in methanol, the absorption spectra resemble that of $[Co(NCS)_2(mepiaH)_2]$. In solution, therefore, the ether-O atom of moepH has no specific influence on the structure.

Conclusions

In the study on the complexes of potentially terdentate picolinamides, $R\text{-}(CH_2)_n\text{-}NHCOC_5H_4N$, palladium(II), nickel(II), copper(II), and cobalt(II) complexes have been prepared and characterized. The coordinative behaviour of the representative ligands is summarized in Table VI.

Table VI. The coordinating mode of the amide group.

		Bivalent metal ion		
Ligand	Pd	Cu	Ni	Co
piaH[a]	N	N,O	N,O	O
mepiaH[b]	N	N,O	O	O
dmepH	N	N,O[c]	N	*
dmppH	N	N,O[c]	*	*
etepH	N	N,O	O	O
moepH	*	O	O	O

The amide-O and the amide-N coordination are indicated by O and N respectively. When the both coordinating modes are possible, the symbol N,O is used.
[a] Picolinamide. [b] N-Methylpicolinamide. [c] The amide-O coordinating mode can occur only when the terminal dimethylamino group is protected from coordination. * No isolation of a solid complex is possible.

For this series of picolinamides, the trend to form a complex coordinated with the amide-N atom increases in the order: $Co^{III*} > Co^{II} < Ni^{II} < Cu^{II} < Pd^{II}$. The same trend is also noticed for the coordinating group on the substituent, R = $NH_2 > NHCH_3 > N(CH_3)_2 > SC_2H_5 > OCH_3$. When the amide-N coordination occurs, the ligand is generally terdentate and anionic (Figure 1B), and a large tendency is found to provide easily a square-planar complex. On the other hand, when the amide-O coordination occurs, the substituent R is completely free from coordination and the ligand is bidentate and neutral (Figure 1A). These two categories are distinguished by infrared spectra of the amide groups as well as by the chemical composition of the complex formed.

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

* A dark red crystalline cobalt(III) complex, $CoClO_4(dmep)_2 . HClO_4 . 3/2H_2O$ was obtained by standing an aqueous solution of a mixture of cobalt perchlorate and the ligand in the 1:2 ratio. In this cobalt(III) complex, the ligand is coordinated through the deprotonated amide-N atom (cf. Figure 1B), whereas cobalt(II) does not form a complex with this ligand, dmepH. This fact indicates that cobalt(III) is more effective in enhancing deprotonation of an acid amide group than cobalt(II).