Contribution from the Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Nagoya, 464 Japan

Syntesis of Several N-Substituted Picolinamides and Their Nickel(II) Complexes

M. Nonoyama and K. Yamasaki

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Ten potentially terdentate N-substituted picolinamides, $R-(CH_2)_n-NHCOC_5H_4N$ where R is NH_2, $NHCH_3$, $N(CH_3)_2$, $N(C_2H_5)_2$, NHC_6H_5, OCH_3, or SC_2H_5 for n=2, and R is NH_2, $NHCH_3$, or $N(CH_3)_2$ for n=3 were prepared and their nickel(II) complexes were studied for the magnetic susceptibilities, infrared and electronic spectra. In the 1 : 2 complexes of the type $NiX_2(LH)_2 . mH_2O$ which are paramagneytic and octahedral, the bidentate ligand coordinates through its amide-O and ring-N atoms. In the diamagnetic square-planar 1 : 1 complexes, $[Ni(NCS)L] . xH_2O$, the ligand acts as a terdentate one with N,N,N-coordination except mppH($R=NHCH_3$, n=3). The exceptional mppH forms a paramagnetic and tetragonally distorted octahedral complex which becomes diamagnetic upon dehydration. The transition between square-planar and octahedral complexes seems to occur at the point where R is NH_2 or $NHCH_3$ and n is 3 depending on the ligand field strength.

Introduction

Picolinamide (Figure 1, n=0 and R=H) forms a stable five-membered chelate with metal ions, coordinating through the amide-O or amide-N atoms.[1] In order to study the coordinating ability of N-substituted picolinamides, ten potentially terdentate ligands with the general formula $R-(CH_2)_n-NHCOC_5H_4N$ (where R is a coordinating group: NH_2, $NHCH_3$, $N(CH_3)_2$, $N(C_2H_5)_2$, NHC_6H_5, OCH_3, or SC_2H_5 for n=2; and NH_2, $HNCH_3$, or $N(CH_3)_2$ for n=3) were synthesized. The palladium(II) complexes of these ligands, except those with $R=NH_2$ and OCH_3, were prepared and their electronic, infrared, and p.m.r. spectral properties studied. For palladium(II) only square-planar complexes of the type $[PdXL] . mH_2O$ (X = Cl, Br, and L = deprotonated ligand) were obtained.[2] Nickel(II), on the other hand, formed with these ten ligands octahedral and tetragonally distorted octahedral complexes in addition to square-planar complexes depending chiefly on the strength of the in-plane ligand field. These results will be compared with the previous report[3] and reported here.

The Schiff bases which have the similar skeletal structure as the ligands studied here were also compared in their coordinating properties.

Experimental Section

1. *Syntheses of the ligands.* The ligands with R = $NHCH_3$, $N(CH_3)_2$, $N(C_2H_5)_2$, NHC_6H_5, OCH_3, and SC_2H_5 for n=2, and R = $NHCH_3$ and $N(CH_3)_2$ for n=3 were prepared by refluxing for 6 hours a mixture of methyl picolinate (0.1 mole) and the respective amine (0.1 mole) ($R-(CH_2)_n-NH_2$), followed by vacuum distillation or recrystallization from ethanol.[2] The abbreviated names and b.p. or m.p. of the prepared ligands are given in Table I.

Table I. Chemical formulae of N-substituted picolinamides, $R-(CH_2)_n-NHCOC_5H_4N$, and their b.p. or m.p.

R	n	Abbreviation	b.p. (°C/mmHg)
NH_2	2	enpH	—
$NHCH_3$	2	mepH	184/20
$N(CH_3)_2$	2	dmepH	174/16.5
$N(C_2H_5)_2$	2	deepH	164/6
NHC_6H_5	2	aepH	92.0(m.p.)
NH_2	3	tnpH	—
$NHCH_3$	3	mppH	197/22
$N(CH_3)_2$	3	dmppH	179/13
OCH_3	2	moepH	183/22
SC_2H_5	2	etepH	178/6

The two ligands enpH($R=NH_2$, n=2) and tnpH-($=NH_2$, n=3), which have a terminal NH_2 group, were prepared by protecting one of the amino groups of reacting ethylenediamine or trimethylenediamine with hydrochloric acid. The products of the reaction with methyl picolinate were used for the preparation of the nickel complex without isolation of the pure ligands.*

2. *Preparation of the nickel(II) complexes.* (a) The 1:1 complexes with the general formula, Ni(NCS)L .

(1) M. Sekizaki and K. Yamasaki, *Nippon Kagaku Zasshi, 87,* 1053 (1966).
(2) M. Nonoyama and K. Yamasaki, *Nippon Kagaku Zasshi, 91,* 1085 (1970).
(3) M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta, 5,* 124 (1971).

(*) If unprotected, reaction of ethylenediamine and methyl picolinate gave 2-pyridylimidazoline[4] of N,N'-dipicolinoylethylemediamine,[5] not the desired enpH.
(4) J.L. Walter and H. Freiser, *Anal. Chem., 26,* 217 (1954).
(5) H. Ojima, *Nippon Kagaku Zasshi, 88,* 333 (1967).

Table II. Prepared complexes and their analytical results.

No.	Complex	Colour	Analysis* Ni %	C %	H %	N	H_2O %	Others %
1	$[Ni(NCS)(enp)]$	Yellow-brown	20.98	38.53	3.63	20.31		
			(20.89)	(38.47)	(3.59)	(19.94)		
2	$[Ni(NCS)(mep)] \cdot 5/4H_2O$	Orange	18.22	37.50	4.72	17.10	7.07	
			(18.49)	(37.83)	(4.60)	(17.64)	(7.09)	
3	$[Ni(NCS)(dmep)]$	Red	19.02	43.16	4.76	18.07		
			(19.00)	(42.75)	(4.57)	(18.13)		
4	$[Ni(NCO)dmep)] \cdot 3H_2O$	Reddish orange	16.96	38.89	5.89	15.94	15.40	
			(16.92)	(38.07)	(5.81)	(16.25)	(15.57)	
5	$[Ni(NCS)(deep)] \cdot 3/4H_2O$	Reddish orange	16.65	44.63	5.64	15.55	4.14	
			(16.75)	(44.54)	(5.61)	(15.98)	(3.85)	
6	$[Ni(NCS)(tnp)] \cdot 1/4H_2O$	Red	19.58	39.96	4.41	18.85	1.55	
			(19.60)	(40.10)	(4.21)	(18.71)	(1.50)	
7	$[Ni(NCS)(mpp)(H_2O)_2]$	Blue-violet	16.75	38.33	5.36	16.50	10.43	
			(17.01)	(38.29)	(5.26)	(16.24)	(10.43)	
8	$[NiBr_2(mepH_. HBr)_2]$	Green	8.07	29.24	3.88	11.25		Br: 42.63
			(7.95)	(29.26)	(3.82)	(11.83)		(43.26)
9	$[Ni(mppH \cdot HCl)_2(H_2O)_2]Cl_2 \cdot 2H_2O$	Blue-violet	8.83	36.30	6.31	12.16	11.02	Cl: 21.19
			(8.87)	(36.29)	(6.09)	(12.70)	(10.89)	(21.42)
10	$[Ni(NCS)_2(aepH_2]$	Blue	8.88	54.28	4.77	16.28		
			(8.93)	(54.81)	(4.60)	(17.04)		
11	$[Ni(NCS)_2(etepH)_2]$	Blue	9.74	44.09	4.76	13.57		
			(9.86)	(44.38)	(4.74)	14.11)		
12	$[NiCl_2(etepH)_2]$	Blue	10.61	43.65	5.16	10.22		
			(10.67)	(43.66)	(5.13)	(10.18)		
13	$[Ni(NCS)_2(moepH)_2]$	Blue-violet	10.97	44.75	4.67	15.29		
			(10.97)	(44.88)	(4.52)	(15.70)		
14	$[Ni(NCS)_2(moepH)_2] \cdot 6/5H_2O$	Blue	10.64	42.95	4.79	14.83	3.86	
			(10.61)	(43.14)	(4.78)	(15.09)	(3.88)	

* Calculated values are in parentheses.

Table III. Infrared spectra of the amide groups in the free ligand and the complexes (in cm^{-1}).

Compound	νN-H	Amide I	Amide II	Amide III
Free ligand(LH)	3350	1660	1520	1245
$Ni(LH)_2X_2 \cdot mH_2O$	3200	1630	1550	1340
$NiXL \cdot mH_2O$	—*	1635	1400	—*

* Not observed.

mH_2O (L = deprotonated ligand).

These complexes except those of enp and tnp were prepared by mixing a warm ethanol solution of the ligand and a warm aqueous solution of nickel thiocyanate in a 1:1 mole ratio and then adding an equivalent amount of potassium hydroxide to the ligand used. The solution was filtered and fine crystals formed upon standing for one day. If necessary, the filtered solution was concentrated. Complexes with other anions were obtained by using as the starting material other nickel salts, for instance nickel chloride, bromide, or cyanate.

(b) $[Ni(NCS)(enp)]$ and $[Ni(NCS)(tnp)] \cdot 1/4H_2O$. To a mixture of 1.2 g of ethylenediamine and 2.7 g of its dihydrochloride in 20 ml ethanol a minimum amount of water was added to dissolve the latter. Methyl picolinate (4.1 g) was added and the solution was refluxed for 2 hours. To the light yellow solution obtained were added 8.9 g of nickel nitrate dissolved in 40 ml of ethanol, 3.2 g of solid potassium thiocyanate and then 4.0 g of potassium hydroxide dissolved in 20 ml of water under vigorous stirring at room temperature. The turbid solution formed was extracted with 120 ml of chloroform, and the complex $[Ni(NCS)(enp)]$ (2.4 g) was obtained as yellow-brown crystals by evaporating the chloroform layer.

The ligand tnpH was prepared in the same way as enpH, and to thus prepared tnpH solution nickel nitrate and potassium hydroxide were added. Then potassium thiocyanate was added to the solution heated at 60°C to precipitate the red crystals of $[Ni(NCS)(tnp)] \cdot 1/4H_2O$.

(c) The 1:2 complexes, $[Ni(NCS)_2(LH)_2] \cdot mH_2O$ (LH = protonated ligand).

These complexes were prepared in the same way as 2(a) without the addition of potassium hydroxide. For the preparation of $[Ni(NCS)_2(moepH)_2] \cdot 6/5H_2O$ an excess amount of potassium thiocyanate was required.

3. *Analytical results.* The chemical compositions of all the complexes obtained are listed in Table II together with their colours.

4. *Measurements.* Instruments used for the measurement of infrared and electronic spectra, and magnetic susceptibilities were the same as reported in the previous paper.[3]

Results and Discussion

1. *Infrared spectra.* All the ligands show similar infrared spectra due to amide groups (Table III), and from the comparison of these spectra with those of the complexes $NiX_2(LH)_2 . mH_2O$ and $NiXL . xH_2O$, the acid amide group in the former complexes seems to be coordinated through O atoms, while in the latter through N atoms (Figures 1A and 1B).[3]

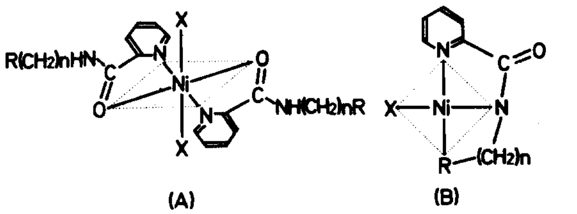

Figure 1. Proposed structures for (A) $[NiX_2(LH)_2]^{p+}$ and (B) $[NiXL] . mH_2O$.

The complexes No. 8 and No. 9 in Table II which contain HBr and HCl groups respectively show several bands at 2400~2800 cm^{-1} due to the terminal amino groups, $NHCH_3 . HX$.[6]

The band at ca. 620 cm^{-1} of all the ligands which is due to the deformation of a pyridine ring shifts on coordination to the higher frequency by ca. 35 cm^{-1} (Figures 1A and 1B).[7]

The two complexes [Ni(NCS)(enp)] and [Ni(NCS)-(tnp)] . $1/4H_2O$, both ligands of which have a terminal NH_2 group, show bands of medium intensity at 3120 and 3261 cm^{-1} (the former), and 3040 and 3160 cm^{-1} (the latter). These bands are assigned to the symmetric and asymmetric vibrations of NH_2, respectively (Figure 1B, $R=NH_2$).[8]

All the complexes containing NCS groups show bands νC≡N at ca. 2100, νC–S at ca. 790 cm^{-1} which is often obscured by the bands of the ligands, and δNCS at ca. 475 cm^{-1} which often splits into two. These bands indicate the coordination of thiocyanate ion through the N atom.[9] The complex No. 4 (Table II) with a NCO group shows νC≡N at 2255^{-1} and δNCO at 593 cm^{-1}, indicating coordination through the N atom.[9]

In the far infrared region the coordination of NCS groups[10] is further proved by the presence of νNi–NCS at 285 cm^{-1} for $[Ni(NCS)_2(aepH)_2]$, 255 cm^{-1} for $[Ni(NCS)_2(moepH)_2]$, 267 cm^{-1} for $[Ni(NCS)_2(moepH)_2] . 6/5H_2O$ and 278 cm^{-1} for $[Ni(NCS)_2(etepH)_2]$. Since the metal-ligand bond is generally stronger for the square-planar complexes than for the octahedral complexes,[11] the νNi–NCS is expected to be in the higher frequency for diamagnetic square-planar $[Ni(NCS)L] . mH_2O$ than for octahedral $[Ni(NCS)_2(LH)_2] . mH_2O$. The assignment of the νNi–NCS, however, is difficult due to its coupling with other vibrations. For $[NiCl_2(etepH)_2]$ the νNi–Cl is found at 220 cm^{-1}, indicating the coordination of Cl ions (Figure 1A, X=Cl).[12]

2. *Electronic spectra.* (1) The diamagnetic 1:1 complexes, $[NiXL] . mH_2O$. The diffuse reflectance spectra and the absorption spectra in chloroform of all the complexes of this type show features of a diamagnetic square-planar nickel(II) complex (Table IV).[11] The absorption spectra of both [Ni(NCS)-(enp)] and [Ni(NCS)(tnp)] . $1/4H_2O$ were measured in dimethylformamide because of their very low solubilities in chloroform (Figure 2). Based on the band intensity and frequency the weak band at 13.6~15.1 $\times 10^3$ cm^{-1} is tentatively assigned to a spin-forbidden transition and the more intense bands at 17~22$\times 10^3$ cm^{-1} to spin-allowed transitions. These bands shift to the lower frequencies in the order of R: $NH_2 > NHCH_3 > N(CH_3)_2 > N(C_2H_5)_2$ when the size of the chelate ring is the same. The order is identical to that of the increasing steric hindrance of R.[13] The bands also shift to the lower frequencies on replacing the coordinated NCS with NCO, and with the change of the chelate ring size from five to six. These trends are consistent with the usual spectrochemical series and chelate effect.

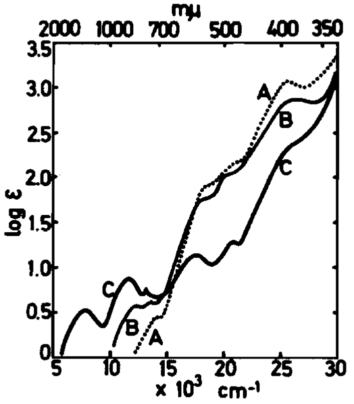

Figure 2. Absorption spectra of (A) [Ni(NCS)(tnp)] . $1/4H_2O$ in dimethylformamide, (B) $[Ni(NCS)(mpp)(H_2O)_2]$ in dimethylformamide, and (C) $[Ni(NCS)(mpp)(H_2O)_2]$ in dimethylsulfoxide.

There is no possibility for dimethylformamide coordinating to [Ni(NCS)(enp)] and [Ni(NCS)(tnp)] . $1/4H_2O$ in solution, since the weak absorption at 14~15$\times 10^3$ cm^{-1} of these two complexes does not appreciably shift from that in the solid state, and the whole absorption spectra are similar to those of the other complexes of the same type in chloroform. The fact that the absorption spectrum of [Ni(NCS)-(dmep)] in dimethylformamide is almost identical to that in chloroform also provides another evidence of non-coordination of dimethylformamide.

(2) The paramagnetic 1:1 complex, $[Ni(NCS)(mpp)(H_2O)_2]$. Among the 1:1 complexes of the composition $NiXL . mH_2O$, $[Ni(NCS)(mpp)(H_2O)_2]$

(6) L.J. Bellamy, « The Infrared Spectra of Complex Molecules », Methuen, London (1966), p. 248.
(7) R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, *4*, 350 (1965).
(8) T.G. Appleton and J.R. Hall, *Inorg. Chem.*, *9*, 1800 (1970).
(9) J.L. Burmeister, *Coordin. Chem. Rev.*, *3*, 225 (1968).
(10) D. Forster and D.M.L. Goodgame, *Inorg. Chem.*, *4*, 715 (1965).
(11) L. Sacconi, « Transition Metal Chemistry », *4*, ed. by R.L. Carlin, Marcel Dekker, New York (1968), p. 199.
(12) C.W. Schläpfer, Y. Saito, and K. Nakamoto, *Inorg. Chim. Acta*, *6*, 284 (1972).
(13) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, *6*, 262 (1967) and references therein.

Table IV. Magnetic moments and electronic spectra.

No.	Complex	μ_{eff} (B.M.)	Solvent[a]	Absorption maximum in $\times 10^3$ cm^{-1}(log ε^b)
1	[Ni(NCS)(enp)]	Dia.	Refl.	15.1
			DMF	15.2(0.56) 19.4sh[c] 21.6sh 25.7(3.21)
2	[Ni(NCS)(mep)] . 5/4H_2O	Dia.	Refl.	14.8
			$CHCl_3$	14.7(0.57) 18.7sh 21.7sh 25.8(3.24)
3	[Ni(NCS)(dmep)]	Dia.	Refl.	14.6
			$CHCl_3$	14.5(0.60) 18.5sh 21.5(2.49) 25.6(3.22)
			DMF	14.4(0.58) 18.6sh 21.5(2.49) 25.5(3.15)
4	[Ni(NCO)(dmep)] . 3H_2O	Dia.	Refl.	13.6
			$CHCl_3$	13.6(0.33) 17.8sh 21.0(2.44) 25.2(3.16)
5	[Ni(NCS)(deep)] . 3/4H_2O	Dia.	Refl.	13.9
			$CHCl_3$	14.4(0.57) 18.3sh 21.3(2.49) 25.5(3.23)
6	[Ni(NCS)(tnp)] . 1/4H_2O	Dia.	Refl.	14.3sh
			DMF	14.1(0.42) 18.5sh 21.2sh 25.6(3.08)
7	[Ni(NCS)(mpp)(H_2O)$_2$]	3.17	Refl.	9.0 12.4 13.4w 17.5 20.2sh
			DMF	12.4(0.65) 13.6(0.67) 18.1sh 21.3sh 25.9(2.88)
			DMSO	7.95(0.49) 11.6(0.88) 13.1(0.85) 17.5(1.12) 20.9srh 25.8sh(2.36)
	Anhydride (red)	Dia.	Refl.	14.0
8	[$NiBr_2$(mepH . HBr)$_2$]	3.24	Refl.	8.5 11.0 14.9 16.7sh
9	[Ni(mppH . HCl)$_2$(H_2O)$_2$]Cl_2 . 2H_2O	3.17	Refl.	11.1 13.5sh,w 16.7br
10	[Ni(NCS)$_2$(aepH)$_2$]	3.15	Refl.	10.5 13.3w 16.8
11	[Ni(NCS)$_2$(etepH)$_2$]	3.18	Refl.	10.5 13.2w 16.5
12	[$NiCl_2$(etepH)$_2$]	3.22	Refl.	9.2 14.9 17.0sh
13	[Ni(NCS)$_2$(moepH)$_2$]	3.18	Refl.	10.5 13.5w 15.7~17.7br 19.2sh
14	[Ni(NCS)$_2$(moepH)$_2$] . 6/5H_2O	3.23	Refl.	10.3 13.3w 16.7

[a] Refl. = diffuse reflectance spectra, DMF = dimethylformamide, and DMSO = dimethylsulfoxide. [b] ε = molar extinction coefficient. [c] sh = shoulder, w = weak, and br = broad.

alone is paramagnetic and shows a colour and diffuse reflectance spectrum different from other complexes (Tables II and IV). The spectrum of this complex indicates the octahedral structure with the approximate D_{4h} symmetry[14] with two coordinated water molecules (Figure 1B) which gave following ligand field parameters: Dq_{xy} = 1240, Dq_z = 661, and Dt = 331 cm^{-1}. These values seem to be reasonable compared with the known values.[14] When heated to 100 °C this complex is converted into the diamagnetic [Ni(NCS)(mpp)] by losing the coordinated water, and at the same time the diffuse reflectance spectrum changes into the one similar to that of [Ni(NCS)(tnp)].

The colour of this complex is red in dimethylformamide and yellowish green in dimethylsulfoxide. The absorption spectrum of the former solution (Figure 2) indicates the presence of a square-planar complex. The lower frequency of the spin-forbidden band at ca. 13×10^3 cm^{-1} compared with that of other diamagnetic square-planar nickel complexes (Table IV) reveals that this ligand mppH has the weakest ligand field. On the other hand, the absorption spectrum in dimethylsulfoxide is characteristic of a tetragonally distorted complex, and it is shifted to the lower frequencies compared with the diffuse reflectance spectrum. This fact may be due to the coordination of dimethylsulfoxide instead of water. The coordinating ability of dimethylformamide is only slightly weaker than that of dimethylsulfoxide as was reported,[15] but even this slight difference is distinguishable for this mpp complex.

All the complexes of the composition NiXL . mH_2O are diamagnetic when n of the ligand R–$(CH_2)_n$–$NHCOC_5H_4N$ is 2, but they are paramagnetic when n is 3 and R is $NHCH_3$ (L = mpp) and diamagnetic when n is 3 and R is NH_2 (L = tnp). Therefore the borderline between a diamagnetic square-planar complex and a paramagnetic distorted octahedral complex lies between the ligand mppH and tnpH for X = NCS.

(3) The paramagnetic 1:2 complexes, $NiX_2(LH)_2$. mH_2O. The diffuse reflectance spectra of the paramagnetic 1:2 complexes are characteristic of the hexacoordinated nickel(II) complexes.[11] The thiocyanato complexes except [Ni(NCS)$_2$(moepH)$_2$] show nearly the same spectrum as the blue [Ni(NCS)$_2$(picolinamide)$_2$], in which two NCS groups are coordinated in the trans-position and the amide is coordinated through the ring-N and amide-O atoms (Figure 1A, X = NCS).[16,17] Consequently the same structure is assigned to these 1:2 complexes, and the infrared spectral studies also support this structure. The structure of the exceptional [Ni(NCS)$_2$(moepH)$_2$] is difficult to be determined since its diffuse reflectance spectrum shows an unusually broad band at 16.5×10^3 cm^{-1} and is different from others.

The complex [$NiCl_2$(etepH)$_2$] has the bands at the lower frequencies than those of the thiocyanato complexes, and this may be due to the replacement of NCS with Cl which is the lower member of the spectrochemical series. This conclusion is borne out by the appearance of νNi–Cl in the region of hexa-coordinated nickel(II) complexes (Figure 1A, X=Cl).[12]

The diffuse reflectance spectrum of [$NiBr_2$(mepH . HBr)$_2$] is appreciably different from that of [Ni-

(14) A.B.P. Lever, *Coordin. Chem. Rev.*, 3, 119 (1968).
(15) V. Gutmann, *Angew. Chem..*, 82, 858 (1970).
(16) M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta*, 3, 585 (1969).
(17) A. Masuko, T. Nomura, and Y. Saito, *Bull. Chem. Soc. Japan*, 40, 511 (1967).

mppH . HCl)$_2$(H$_2$O)$_2$]Cl$_2$. 2H$_2$O (Table IV). In the former complex the first band ($^3A_{2g} \rightarrow ^3T_{2g}$ in O_h symmetry) splits into two (8.5 and 11.0×10^3 cm^{-1}), while it does not in the latter. This splittings suggests that effective symmetry around the nickel atom may be approximately D_{4h} due to the coordination of two bromide ions (Figure 1A, X=Br).[14]

The unsplit first band of [Ni(mppH . HCl)$_2$(H$_2$O)$_2$]-Cl$_2$. 2H$_2$O lies close to that of [Ni(mepiaH)$_2$(H$_2$O)$_2$]$^{2+}$ (11.0×10^3 cm^{-1}),[16] mepiaH being N-methylpicolinamide. Furthermore no νNi–Cl was found in the infrared spectrum. These facts supports the above formula and the structure as shown in Figure 1A (X = H$_2$O).

The ligand with n=2 and R=OCH$_3$, SC$_2$H$_5$, or NHC$_6$H$_5$ does not form the complex Ni(NCS)L . mH$_2$O even in an alkaline solution, whereas tnpH (n=3, R=NH$_2$) and mppH (n=3, R=NHCH$_3$) form the complex of this type, indicating the influence of R on the coordinating ability of the acid amide group.

3. *Comparison with the Schiff bases.* Terdentate Schiff bases of pyridine-2-aldehyde R–(CH$_2$)$_2$–N=CH–C$_5$H$_4$N, where R is N(CH$_3$)$_2$ or N(C$_2$H$_5$)$_2$, have a similar skeletal structure with the derivatives of picolinamide R–(CH$_2$)$_2$–NHCOC$_5$H$_4$N studied here, but the Schiff bases coordinate always through R, azomethine-N and ring-N atoms to nickel(II) forming paramagnetic penta- and hexa-coordinated complexes,[18] whereas the acid amides form diamagnetic square-planar complexes when they coordinate through R, amide-N, and ring-N atoms. Both the Schiff bases and acid amides act similarly as the N,N,N-terdentate ligand, but these two groups of ligands form the complexes with different structures. The factors governing the structures of the complexes may be a larger basicity of the deprotonated amide-N atom[19] compared with that of the azomethine-N atom,[20] and also a different formal charge on the donor nitrogen atom, namely, a negatively charged deprotonated amide-N atom and uncharged azomethine-N atom.

(18) G. Zakrzewski and L. Sacconi, *Inorg. Chem.*, 7, 1034)1968).
(19) R.B. Homer and C.D. Johnson, « The Chemistry of Amides », ed. by J. Zabickey, Interscience, London (1970), p. 187.
((20) J.W. Smith, « The Chemistry of the Carbon-Nitrogen Double Bond », ed. by S. Patai, Interscience, London (1970), p. 235.