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The Bivalent Nickel, Cobalt, Copper and Palladium Complexes of N-Methyl Derivatives of Pyridine-2-carboxamide

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Nickel(II), cobalt(II), copper(II) and palladium(II) complexes with pyridine-2-(N-methylcarboxamide)(abbreviated as mepiaH) and pyridine-2-(N,N-dimethylcarboxamide)(abbreviated as dimepia) as ligands were prepared and their properties and structures studied by spectroscopic and magnetic methods. With the former ligand, mepiaH, the 1:1(Cu), 1:2(Cu, Ni, Co), and 1:3(Ni, Co) complexes, and with the latter ligand, dimepia, 1:1(Cu), and 1:2(Cu, Ni, Co) complexes were obtained. Only with palladium a complex with the deprotonated ligand, Pd(mepia)$_2$2H$_2$O was obtained. The structures of the 1:1 complexes are presumed to be square planar, and those of the 1:2 and 1:3 complexes to be distorted octahedral respectively.

Introduction

The bivalent metal complexes of pyridine-2-carboxamide (picolinic acid amide, piaH) have been extensively studied[1-4] and their structures determined.[5] In the present paper nickel(II), cobalt(II) and copper(II) complexes of pyridine-2-(N-methylcarboxamide)(N-methylpicolinic acid amide, mepiaH), and pyridine-2-(N,N-dimethylcarboxamide)(N,N-dimethylpicolinic acid amide, dimepia) were prepared and their properties studied to find the effects of methyl group substitution on the amide nitrogen. The abbreviations, piaH, mepiaH and dimepia are used throughout the present paper.

Experimental Section

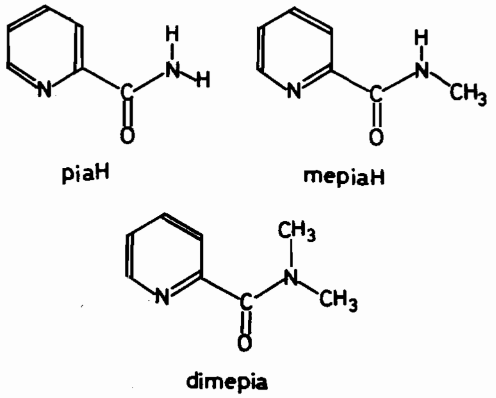
Ligands. MepiaH and dimepia were prepared by the reaction of pyridine-2-carboxylic acid methyl ester with anhydrous monomethylamine and dimethylamine respectively.[6] The reaction time and temperature were 5 hours at 100°C for the former, and 6 hours at 150°C for the latter. Thus prepared mepiaH and dimepia showed the b.p. 143°/20 mm Hg and 154°/21 mm Hg respectively.

Complexes. A solution of the respective metal halide or perchlorate was mixed with a solution of the ligand in the stoicheiometric ratio. On concentrating the mixture on a water bath the product was obtained. According to the solvent used the preparation methods are divided into A, B and C. In the method A water was used, while in the methods B and C 99.5% and 50% ethanol were used respectively (Table I).

Measurements. The absorption spectra of solutions and diffuse reflectance spectra of solids were obtained using a Hitachi EPU-2A spectrophotometer and the attachment. Magnesium oxide was used as the reference standard of the latter spectrum. The infrared spectrum was obtained by a Jasco-DS402G infrared spectrophotometer using Nujol and hexachlorobutadiene mulls. The magnetic susceptibility was measured by the Gouy method at room temperature.

Results and Discussion

Prepared complexes. The complexes prepared are listed in Table I and the structure of the ligands, piaH, mepiaH and dimepia are shown in Figure 1. The former two ligands have hydrogen atoms on the amide nitrogen which are exchanged in heavy water with deuterium, and dissociate in alkaline me-


piaH

mepiaH

dimepia

Figure 1. Structures of the ligands.

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(1) K. Nagano, H. Kinoshita and H. Hirokawa, *Chem. Pharm. Bull.*, *12*, 1198 (1964).
(2) K. Yamasaki and M. Sekizaki, *Bull. Chem. Soc. Japan*, *38*, 2206 (1965); M. Sekizaki and K. Yamasaki, *Nippon Kagaku Zasshi*, *87*, 1053 (1966); idem., *Spectrochim. Acta*, *25A*, 475 (1969).
(3) H. L. Conley, Jr. and R. B. Martin, *J. Phys. Chem.*, *69*, 2914 (1965).
(4) E. Uhlig and V. Neugebauer, *Z. anorg. Chem.*, *351*, 286 (1967).
(5) A. Masuko, T. Nomura and Y. Saito, *Bull. Chem. Soc. Japan*, *40*, 511 (1967); Y. Nawata, H. Iwasaki and Y. Saito, *ibid.*, *40*, 515 (1967).
(6) B. Prijs, R. Gall, R. Hinderling and H. Erlenmeyer, *Helv. Chim. Acta*, *37*, 90 (1954).

Table I. Prepared complexes. Compositions, Colors and Magnetic Moments

Complex	Method	Color	Analysis (%)[a]			Magnetic moment
			metal	N	H_2O	
$Ni(piaH)_2(NCS)_2$	C	blue	13.95 (14.01)	20.01 (20.05)		3.18 B.M.
$Co(piaH)_2(NCS)_2$	B	red. violet	14.00 (14.05)	20.24 (20.04)		4.89
$Cu(mepiaH)Cl_2$	B	green	23.48 (23.48)	10.13 (10.35)		1.90
$Cu(mepiaH)Br_2$	B	brown	17.63 (17.67)	8.09 (7.79)		1.88
$Cu(OH)(mepia)2H_2O$	—	violet	24.98 (25.24)	11.26 (11.23)	14.13 (14.31)	1.65
$Cu(mepiaH_2Cl_2 4H_2O$	A	blue	13.14 (13.27)	11.48 (11.70)	15.14 (15.05)	1.92
$Cu(mepiaH)_2(ClO_4)_2$	A	blue	11.75 (11.88)	10.18 (10.30)		1.91
$Ni(mepiaH_2Cl_2 4H_2O$	A	blue	12.33 (12.39)	11.54 (11.82)	15.04 (15.20)	3.26
$Ni(mepiaH)_2(ClO_4)_2 2H_2O$	A	blue	10.44 (10.37)	9.99 (9.94)	6.38 (6.37)	3.17
$Ni(mepiaH)_2(NCS)_2$	C	blue	13.00 (13.13)	18.77 (18.79)		3.16
$Co(mepiaH)_2Cl_2 4H_2O$	A	orange	12.39 (12.43)	11.79 (11.81)	15.55 (15.20)	4.65
$Co(mepiaH)_2(NCS)_2$	B	red. violet	12.92 (13.17)	18.58 (18.78)		4.81
$Co(mepiaH)_2(NCO)_2$	C	red. violet	14.17 (14.19)	19.93 (20.24)		4.76
$Pd(mepia)_2 2H_2O$	A	yellow	25.98 (25.78)	13.63 (13.58)	9.11 (8.72)	diamag.
$Ni(mepiaH)_3(ClO_4)_2 \frac{1}{2} H_2O$	A	blue	8.80 (8.70)	12.36 (12.45)	1.27 (1.33)	3.14
$Co(mepiaH)_3(ClO_4)_2 \frac{1}{2} H_2O$	A	pink	8.73 (8.73)	12.63 (12.44)	1.30 (1.33)	4.88
$Cu(dimepia)Cl_2$	B	green	22.31 (22.32)	9.61 (9.84)		1.92
$Cu(dimepia)Br_2$	B	black	17.06 (17.01)	7.27 (7.50)		1.92
$Cu(dimepia)_2(ClO_4)_2$	B	blue	11.00 (11.29)	9.55 (9.96)		1.92
$Ni(dimepia)_2(ClO_4)_2 2H_2O$	A	blue	9.92 (9.88)	9.35 (9.43)	6.05 (6.06)	3.22
$Ni(dimepia)_2(NCS)_2$	C	purple	12.21 (12.35)	17.77 (17.68)		3.16
$Co(dimepia)_2(ClO_4)_2 2H_2O$	A	orange	9.98 (9.91)	9.48 (9.43)	6.31 (6.06)	4.73
$Co_2(dimepia)_3(NCS)_4$	B	blue	14.56 (14.72)	17.32 (17.49)		4.61

[a] Analytical data in ( ) indicate the calculated values.

dia to combine with metals, while dimepia has no such a hydrogen atom. Since the ligand, piaH was found to form a complex $M(pia)_2$ in alkaline solution with Pd, Ni and Cu, isolation of the same type of complex $M(mepia)_2$ was attempted, but only the palladium complex, $Pd(mepia)_2 2H_2O$ was obtained. Formation of this palladium complex has added another example to the well known fact that palladium forms more stable complexes than nickel. In the case of copper a violet complex, $Cu(OH)(mepia)2H_2O$ was precipitated as small crystals by the addition of sodium hydroxide to the warm solution of $Cu(mepiaH)_2Cl_2 4H_2O$. By the same treatment of $Ni(mepiaH)_2Cl_2 4H_2O$ only a hydroxide-like substance was precipitated.

Electronic spectra. The diffuse reflectance spectra of the 1:1 copper complexes show two peaks at *ca.* 13×10^3 and 26×10^3 cm^{-1} for the chloride, and 13×10^3 and 20×10^3 cm^{-1} for the bromide complexes respectively (Table II). The former peak at 13×10^3 cm^{-1} is assigned to the d-d transition and the latter peak which shifts with the change of halogen atoms seems to be the charge transfer band. In ethanolic solutions the absorption bands are found at 12.5×10^3 cm^{-1} which are almost at the same positions as the bands of diffuse reflectance spectra, and the band of the bromide complex is more intense than that of the chloride complex (Table II).

The d-d transition bands of the 1:2 complexes, $Cu(mepiaH)_2Cl_2 4H_2O$ and $Cu(mepiaH)_2(ClO_4)_2$ are in the higher wave number region than those of the 1:1 complexes. This may be due to the difference of coordinated ligands between these 1:1 and 1:2 complexes. In the 1:2 chloride complex, $Cu(mepiaH)_2Cl_2 4H_2O$ two water molecules are supposed to coordinate to the square planar $Cu(mepiaH)_2$ from top and bottom making an approximate octahedral O_h symmetry.

In the 1:2 perchlorate complex the structure is supposed to be square planar without coordination of perchlorate ions. This structure is also supported

Table II. Electronic Spectra.

Complex	Absorption Spectra (in 10^3 cm^{-1})		Solvent	Diffuse Reffectance Spectra (in 10^3 cm^{-1})		
$Ni(piaH)_2(NCS)_2$				16.8	10.5	
$Co(piaH)_2(NCS)_2$	19.3(1.63)	8.9(0.84)	MeOH	19.6	9.1	
$Cu(mepiaH)Cl_2$	12.5(1.84)		EtOH	12.4	*ca.* 26	
$Cu(mepiaH)Br_2$	12.3(2.05)		EtOH	12.9	*ca.* 20	
$Cu(OH)(mepia)2H_2O$	*			17.5		
$Cu(mepiaH)_2Cl_24H_2O$	14.2(1.42)		Water	14.8		
$Cu(mepiaH)_2(ClO_4)_2$	14.4(1.42)		Water	16.3		
$Ni(mepiaH)_2Cl_24H_2O$	16.0(0.75)	9.8(0.75)	Water	15.9	11.1	
$Ni(mepiaH)_2(ClO_4)_22H_2O$	16.0(0.75)	9.7(0.75)	Water	15.8	11.0	
$Ni(mepiaH)_2(NCS)_2$	*			16.4	10.2	
$Co(mepiaH)_2Cl_24H_2O$	20.0(1.05)	8.8(0.53)	Water	22.7	9.2	
$Co(mepiaH)_2(NCS)_2$	19.2(1.59)	8.9(0.81)	MeOH	19.4	8.6	
$Co(mepiaH)_2(NCO)_2$	*			19.2	8.5	
$Pd(mepia)_22H_2O$	23.5(3.58)		$CHCl_3$	n.d.		
$Ni(mepiaH)_3(ClO_4)_2½H_2O$	16.3(0.89)	9.9(0.84)	Water	16.7	10.1	
$Co(mepiaH)_3(ClO_4)_2½H_2O$	20.0(1.08)	8.9(0.56)	Water	20.5	9.3	
$Cu(dimepia)Cl_2$	12.3(1.95)		EtOH	12.8	*ca.* 26	
$Cu(dimepia)Br_2$	**					
$Cu(dimepia)_2(ClO_4)_2$	13.0(1.24)		Water	16.0		
$Ni(dimepia)_2(ClO_4)_22H_2O$	15.3(0.49)	8.9(0.47)	Water	15.8	11.2	
$Ni(dimepia)_2(NCS)_2$	*			18.0	16.3	11.1
$Co(dimepia)_2(ClO_4)_22H_2O$	19.7(0.72)	8.7(0.15)	Water	22 sh	9.1	
$Co_2(dimepia)_3(NCS)_4$	20 sh	17.7 sh	MeCN	20 sh	16.1	8.2
	16.2(2.75)	8.8(1.90)				
		8.3(1.91)				

* No appropriate solvent was found. ** No satisfactory spectrum was obtained due to the black color. Molar extinction coefficient, log ε is given in ( ). sh means a shoulder.

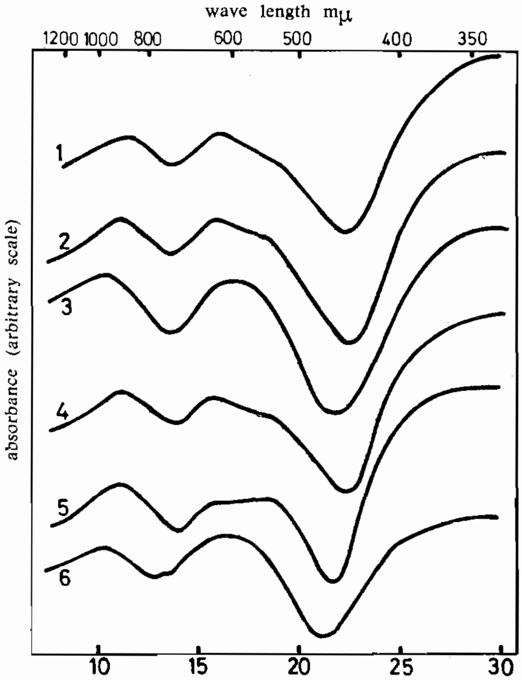

Figure 2. Diffuse reflectance spectra of 1: $Ni(piaH)_2Cl_22H_2O$; 2: $Ni(mepiaH)_2Cl_24H_2O$; 3: $Ni(mepiaH)_3(ClO_4)_2½H_2O$; 4: $Ni(dimepia)_2(ClO_4)_22H_2O$; 5: $Ni(dimepia)_2(NCS)_2$; 6: $Ni(mepiaH_2)(NCS)_2$; *cf.* Table II.

by infrared spectral evidences. To account for the difference of the d-d transition bands between $Cu(mepiaH)_2Cl_24H_2O$ and $Cu(mepiaH)_2(ClO_4)_2$ the energy level diagrams of the d^9 metal ion, Cu^{II}, are considered. The separations of the energy levels between the ground state $^2B_{1g}$ and the excited states (^2E_g, $^2B_{2g}$ and $^2A_{1g}$) are larger in the square planar field than in the tetragonally distorted octahedral field. This will explain the presence of bands of square planar $Cu(mepiaH)_2(ClO_4)_2$ in the higher wave number region that that of octahedral $Cu(mepiaH)_2Cl_24H_2O$.

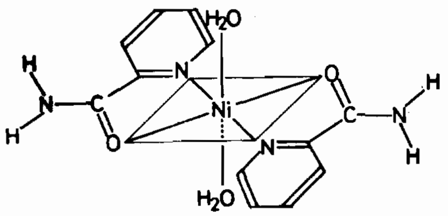

Figure 3. The structure of $[Ni(H_2O)_2(piaH)_2]Cl_2$ determined by X-rays.

Since the diffuse reflectance spectra of the 1:2 chloride and perchlorate complexes of nickel with piaH, mepiaH and dimepia are similar as shown in Table II and Figure 2, the structures of complexes of the latter two ligands in the solid state seem to be similar to that of the piaH complex, $[Ni(H_2O)_2(piaH)_2]Cl_2$ whose structure had been determined by X-rays[5] (Figure 3). In solution, however, the absorption spectrum of $Ni(dimepia)_2(ClO_4)_22H_2O$ is different from those of the piaH and mepiaH complexes of the same metal probably because of the dissociation of the dimepia complex in water, which is less stable due to the steric hindrance of methyl groups. The similar results are found for the dimepia complexes of copper and cobalt as well (Table II). The diffuse reflectance spectra of the 1:2 complexes of cobalt(II) with these three ligands are also similar to each other indicating the analogous structures (Figure 4).

The diffuse reflectance spectra of the thiocyanate complexes of nickel and cobalt are shown in Figures 2 and 4. The cobalt dimepia complex has an unusual composition $Co_2(dimepia)_3(NCS)_4$ with an intense blue color and it suggests the presence of a tetrahedral ionic species,[7] $[Co(NCS)_4]^{2-}$, while the spectra of other cobalt complexes show the characteristic octahedral features. The similarity of reflectance spectrum of the cobalt thiocyanate complex, $Co(mepiaH)_2(NCS)_2$ with that of $Co(mepiaH)_2(NCO)_2$ indicates the similar coordination around the cobalt atom, that is, nitrogen coordination of both cyanate and thiocyanate groups.

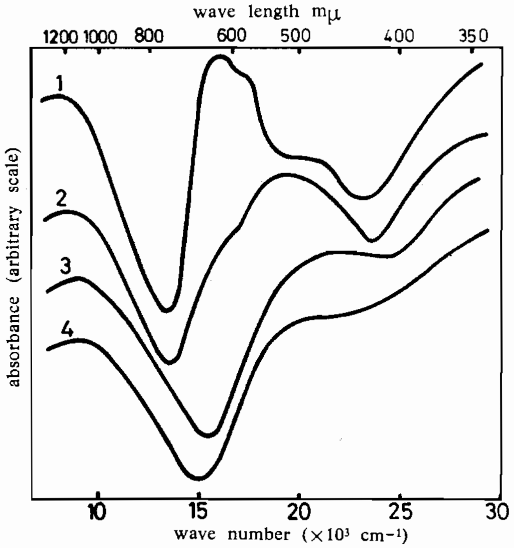

Figure 4. Diffuse reflectance spectra of 1: $Co_2(dimepia)_3(NCS)_4$; 2: $Co(mepiaH)_2(NCS)_2$; 3: $Co(mepiaH)_2Cl_24H_2O$; 4: $Co(dimepia))_2(ClO_4)_22H_2O$; *cf.* Table II.

The spectra of the 1:3 mepiaH complexes of nickel and cobalt are similar to those of the corresponding 1:3 piaH complexes[4] (Table II).

Infrared spectra. The characteristic bands of free ligands and some complexes in the region 4000-650 cm^{-1} are given in Table III. The free mepiaH has characteristic bands at 1672, 1532 and 1244 cm^{-1} which shifted on deuteration to 1659, 1486 and 934 cm^{-1}. They are assigned to the amide I (mainly $\nu_{C=O}$), amide II (mainly ν_{C-N}) and amide III (mainly δ_{N-H}) bands respectively.[8] By coordination to metals the amide I band of mepiaH shifted to lower frequencies by about 30 cm^{-1}, and the amide II band to higher frequencies by about 20 cm^{-1} and the amide III band split into two bands at 1335 and 1180 cm^{-1}. These facts may be explained by the decrease of the double bond character of C=O and the subsequent increase of the C–N double bond character[9] (Figure 5). The infrared spectrum of $Pd(mepia)_22H_2O$ in which the deprotonated ligand, mepia, coordinates is quite different from those of other mepiaH complexes: the N–H stretching vibration at *ca.* 3200 cm^{-1} disappeared and the characteristic amide bands changed their positions.

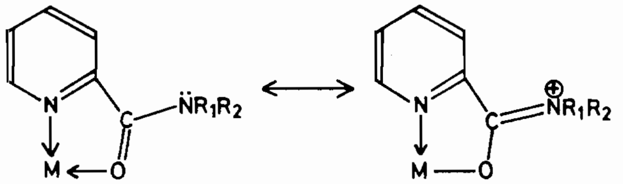

Figure 5. The resonance structures proposed for the complexes: $R_1=R_2=H$ for piaH. $R_1=H$, $R_2=CH_3$ for mepiaH, $R_1=R_2=CH_3$ for dimepia.

All the thiocyanato complexes have bands at *ca.* 2100 and 800 cm^{-1} except for $Co_2(dimepia)_3(NCS)_4$ which showed a somewhat higher C–S stretching frequency, 833 cm^{-1}, than others, suggesting its different structure, that is, the presence of $[Co(NCS)_4]^{2-}$ ion.[10] This conclusion is borne out by the electronic spectra as well. All the complexes containing perchlorate ion have a strong band at *ca.* 1100 cm^{-1}, a weak band at 930 cm^{-1} and a medium band at *ca.* 620 cm^{-1}. These characteristic bands of the free perchlorate ion indicate its non-coordination in these complexes.

Far-infrared spectra. Some of the far-infrared spectral data are listed in Table IV. For the hydrated complexes like $Cu(mepiaH)_2Cl_24H_2O$ the spectra are complicated due to the water of crystallization and are not discussed here. The in-plane and out-of-plane deformation frequencies of pyridine ring are at 620 and 439 cm^{-1} for free mepiaH, and 618 and 436 cm^{-1} for free dimepia respectively, and they shifted to higher frequencies by coordination to metals. The shift of the band at 620 cm^{-1} of mepiaH is relatively small for the complexes like $Cu(mepiaH)_2Cl_2$ and $Cu(mepiaH)_2(NCO)_2$, while it is large for the complexes such as $Cu(mepiaH)_2(ClO_4)_2$ and $Pd(mepia)_22H_2O$. The larger shifts for the latter complexes may indicate larger interaction between metals and the pyridine ring of the ligand.

The shoulder at 610 cm^{-1} of mepiaH which shifted to 485 cm^{-1} on deuteration is considered to be the N–H out-of-plane deformation and the bands at 486 and 695 cm^{-1} to the C=O out-of-plane and C=O in-plane deformations respectively. By coordination the former band shifted to higher frequencies, while the latter remained almost at the same positions. The bands at 363 and 307 cm^{-1} of mepiaH which were not found for piaH[2] and scarcely shifted on deuteration are considered to be the N–CH_3 in-plane and out-of-plane deformation vibrations respectively.

For the 1:1 copper halide complexes and nickel and cobalt thiocyanate complexes with these three

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(7) F. A. Cotton, D. M. L. Goodgame, M. Goodgame and A. Sacco, *J. Am. Chem. Soc.*, *83*, 4157 (1961).

(8) T. Miyazawa, *Nippon Kagaku Zasshi*, *77*, 171, 526, 619 (1956); L. J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London (1958).

(9) R. S. Drago, Physical Methods in Inorganic Chemistry, Reinhold Publ. Corp. New York. 1965. p. 230.

(10) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, *4*, 823 (1965).

Table III. Infrared spectra of mepiaH, mepiaD and their complexes in 4000-650 cm^{-1}

Complex	Amide I	Amide II	Amide III		Other bands		
MepiaH	1672	1532	1244		3380	3340 [a]	
MepiaD	1659	1486	934		2590	2513	2490 [b]
$Cu(mepiaH)Cl_2$	1635	1549	1337	1181			
$Cu(mepiaH)Br_2$	1632	1545	1334	1178			
$Cu(OH)(mepia)2H_2O$	1611 [c]						
$Ni(mepiaH)_2Cl_24H_2O$	1644	1554	1339	1184			
$Ni(mepiaD)_2Cl_24D_2O$	1639	1502	1118	950			
$Co(mepiaH)_2(NCS)_2$	1641 sh 1632	1549	1331	1181	2085 [d]	790 [e]	785 [e]
$Co(mepiaD)_2(NCS)_2$	1648 sh 1633	1495	1113	948	2085 [d]	791 [e]	785 [e]
$Co(mepiaH)_2(NCO)_2$	1640	1568	1339	1187	2208 [d]	907 [f]	
$Co(mepiaD)_2(NCO)_2$	1639	1497	1121	961	2205 [d]	906 [f]	
$Pd(mepia)_22H_2O$	1625 [c]						
$Ni(mepiaH)_2(ClO_4)_2½H_2O$	1639	1558	1338	1184	1107	930 [g]	
$Ni(mepiaD)_2(ClO_4)_2½D_2O$	1639	1501	[h]	953	1106	930 [g]	

[a] N—H stretching frequency; [b] N—D stretching frequengcy; [c] C=O stretching frequency; [d] C≡N stretching frequency; [e] C—O stretching frequency; [g] ClO_4 ion bands; [h] Covered with ClO_4 ion absorption.

Table IV. Far infrared spectra (in cm^{-1})

Compound	$\delta_{C=O}$	π_{N-H}	Py. ring [a]	$\pi_{C=O}$	NCS [b] NCO	Py. ring [c]	δ_{N-CH_3}	π_{N-CH_3}	ν_{M-X} [d]	
mepiaH	695 s	610 sh	620 s	486 m		439 m	363 w	307 m		402 m
mepiaD	699 s	485 m	621 s	460 w		440 w	365 w	304 m		403 m
$Cu(mepiaH)Cl_2$	691 s	620 sh 595 s	647 s	516 s		453 m	413 m	363 m	310 s 275 s	423 m, 251 w, 239 w, 208 w
$Cu(mepiaH)Br_2$	690 s	617 m 582 s	646 m	515 s		452 m	413 m	361 m	276 s 250 m	421 m, 227 w, 209 w
$Cu(mepiaH)_2(ClO_4)_2$	709 m	676 s	664 m	532 m		461 m 447 s	381 w	339 m		622 s [e], 417 w, 211 w
$Cu(mepiaD)_2(ClO_4)_2$	690 s	511 m	664 m	531 m		459 m 446 s	379 w	340 m		623 s [e], 417 w, 245 w
$Ni(mepiaH)_2(NCS)_2$	699 m	667 s	646 m	509 m	481 s 473 m 469 m	447 s	396 m	353m	285 s 276 s	412 sh, 218 w, 262 m
$Co(mepiaH)_2(NCS)_2$	698 s	663 s	642 m	504 m	480 s 472 m	446 s	392 m	349 m	270 s 263 s	410 sh, 400 sh, 250 w, 235 m, 220 sh
$Co(mepiaD)_2(NCS)_2$	693 s	513 s	642 m	500 m	476 m	445 s	390 w	346 m	270 s 263 s	410 sh, 251 w. 235 m, 220 sh
$Co(mepiaH)_2(NCO)_2$	700 m	697 s	641 m	506 m	613 s 596 w	446 m	395 w	346 m	291 s 284 s	410 w, 251 w, 227 sh, 219 w
$Co(mepiaD)_2(NCO)_2$	695 s	524 s	641 m	501 s	613 s 596 w	445 m	395 w	346 m	291 s 284 s	410 w. 250 w, 226 sh, 219 w
$Pd(mepia)_22H_2O$	683 s		661 m	529 s		447 m	378 w	331 m		643 w, 478 w, 421 m, 299 m

[a] Pyridine ring in-plane deformation; [b] NCS and NCO bending; [c] Pyridine ring out-of-plane deformation; [d] M=Cu, Co and X=Cl, Br, NCS, NCO; [e] ClO_4 band; s: strong; m: medium; sh: shoulder; δ: in-plane deformation; π: out-of-plane deformation; ν: stretching.

ligands strong bands are found between 320 and 200 cm^{-1}. These bands are assigned to the metal-anion vibrations coupled with other vibration modes. Appearance of two ν_{M-X} bands for some complexes such as thiocyanate and cyanate complexes are supposed to be due to, (1) depression of the symmetry around the metal, (2) crystal lattice effects, (3) coupling with other vibration modes, and/or (4) hydrogen bonding.

Effects of methyl substitution. Nickel and cobalt perchlorates formed the 1:2 and 1:3[4] complexes with piaH and mepiaH, while with dimepia only the 1:2 complexes. In the solid state their diffuse reflectance spectra are similar, but in solution the absorption bands of dimepia are in the lower wave number region with lower intensity. In alkaline media piaH formed complexes of the type, $M(pia)_2$ with palladium, nickel and copper, while mepiaH formed only one complex, $Pd(mepia)_22H_2O$. These effects of methyl groups on the amide nitrogen may be explained in the following way: an amide group shows the resonance between following structures:

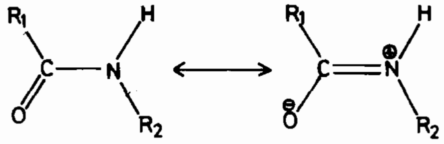

Figure 6. The resonance structures of an amide.

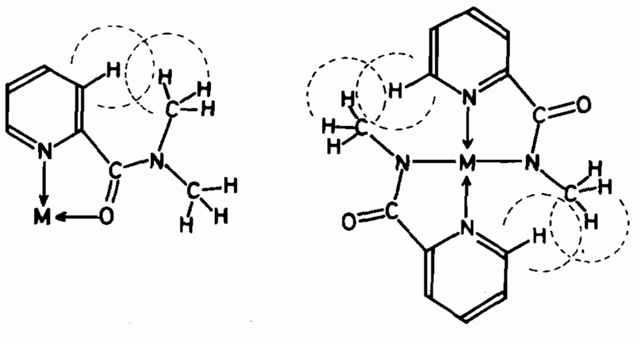

Figure 7. Van der Waal's interaction between the methyl groups and the hydrogen atoms of pyridine rings.

where C=O group interacts with the lone pair electron of the nitrogen atom.[9] The requirement for the resonance is that the amide nitrogen must have electronic configuration of sp^2 hybridization, that is, an amide group should be in the same plane with H, R_1 and R_2 (Figure 6). Three ligands, piaH, mepiaH and dimepia must have the same resonance structures with respect to the amide group. If the models are set up by taking these facts into account, the methyl groups of the coordinated dimepia molecule have interactions with the 3-H of the pyridine ring (Figure 7). In the complex, $M(mepia)_2$ a methyl group of the ligand interacts with the 6-H of the pyridine ring of the other ligand. These interactions may make the complexes less stable in solution, and the formation of the 1:3 complexes more difficult, and thus may give explanation to the experimental facts observed above.

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