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A Study of 2-Cyanopyridine Addition Products in the Coordination Sphere of Ni(II)

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Abstract

The coordination of 2-cyanopyridine molecule to Ni(II) atom promotes a nucleophilic addition of solvent molecules (water, methanol, ethanol) to the nitrile group. The addition of water leads to the formation of solid complexes containing pyridine-2-carboxamide as a chelate ligand. An analogous reaction of 2-cyanopyridine with NiX_2 (X = Cl, Br, I, NCS) in methanolic solutions gives, however, complexes containing two or three molecules of *O*-methylpyridine-2-carboximidate. No nucleophilic addition of solvent occurred with 3- and 4-cyanopyridine under the same reaction conditions.

The complexes under study exhibit an octahedral geometry. The structure and the mode of the ligand coordination have been determined by IR spectra.

Introduction

Increased reactivity of coordinated nitriles has been observed in a number of instances [1–4]. The complex formation ability of 2-cyanopyridine with Ni(II), Co(II), Zn(II), Cd(II), Hg(II), Pd(II), and Pt(II) both halides and thiocyanates [5–7] as well as with perchlorates of Cu(I), Ag(I) and Au(I) [8] has been examined but no evidence for any metal promoted reactions was found. On the other hand it was observed that the reactions of 2-cyanopyridine with some Ni(II), Cu(II) and Cr(III) chlorides in aqueous or alcoholic solutions yielded solid complexes containing different addition products of 2-cyanopyridine [9–11]. Furthermore, pyridine-2-carboxamide (piaH) was isolated from the aqueous solutions, having been formed by addition of water molecules to the initial 2-cyanopyridine. The compositions of the solid complexes obtained from alcoholic solutions as well as the structures of the coordinated addition products of 2-cyanopyridine have been investigated only partially till now. The observed nucleophilic addition of solvent molecules to 2-cyanopyridine in the coordination sphere of transition metals gives possibilities of preparing some types of organic compounds using new methods.

Experimental

Starting Chemicals

The solid 2-cyanopyridine (2-CNpy) was purified by distillation under reduced pressure. *O*-Methylpyridine-2-carboximidate (*O*-CH_3pii) and *N*-methylpyridine-2-carboxamide (*N*-CH_3pia) were prepared according to the methods given in the literature [12, 13]. The purity of the samples was checked by infrared spectra.

Analysis and Measurements

Nickel was determined by EDTA titration; carbon, hydrogen, and nitrogen by microanalytical methods (Carlo Erba Model 11-02).

Measurements of magnetic moments, electronic and infrared spectra are described elsewhere [14]. Colours, analytical data, magnetic moments (at 293 K) and the electronic spectral data of the solid complexes are given in Tables I and II.

Preparation of the Complexes

By the reaction of 2-CNpy with NiX_2 (X = Cl, Br, I, NCS) several new coordination compounds were prepared depending on the solvent used, on the nickel to organic ligand molar ratio (usually 1:2 or 1:4), as well as on temperature and reaction time. The reaction of 2-CNpy with NiX_2 in aqueous solutions leads to the isolation of complexes **I**, **II**, **V**, and **VI**, which contain pyridine-2-carboxamide. Yellow complexes **III** and **IV** were prepared by heating complexes with composition $[Ni(H_2O)_2(piaH)_2]X_2$ (X = Cl and Br) in an oven at 440 K. The complexes **VII**–**X** were prepared directly from *N*-CH_3pia in methanolic solutions. Analogous reactions of *O*-CH_3pii with NiX_2 gives complexes **XIV**, **XV**, **XX**, and **XXI**. The other complexes (**XI**–**XIII** and **XVI**–**XIX**) were prepared by the reactions of anhydrous Ni(II) salts with 2-CNpy in methanolic solutions. In preparing some tris-complexes it was necessary to add acetone to the final reaction solution.

We failed in our attempts to prepare from aqueous or methanolic solutions complexes containing 2-CNpy.

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TABLE I. Colours and Analytical Data for Complexes

No.	Complex	Colour	Calculated (%) Found (%)			
			Ni	C	H	N
I	$[\mathrm{Ni(H_2O)_2(piaH)_2]Cl_2}$	blue	14.33	35.17	3.94	13.67
			14.10	34.97	3.90	13.66
II	$[\mathrm{Ni(H_2O)_2(piaH)_2]Br_2}$	blue	11.77	28.90	3.23	11.24
			11.70	28.52	3.15	11.16
III	$[\mathrm{NiCl_2(piaH)_2}]$	yellow	15.70	38.55	3.24	14.99
			15.85	38.79	3.32	14.94
IV	$[\mathrm{NiBr_2(piaH)_2}]$	yellow	12.69	31.15	2.61	12.11
			12.45	31.32	2.84	12.32
V	$[\mathrm{NiI_2(piaH)_2}]$	green-blue	10.43	25.60	2.15	9.95
			10.29	26.15	2.47	9.75
VI	$[\mathrm{Ni(NCS)_2(piaH)_2}]$	blue	13.98	40.04	2.88	20.01
			13.92	39.87	2.78	19.89
VII	$[\mathrm{NiCl_2}(N\text{-}\mathrm{CH_3pia})_2]$	green	14.61	41.86	4.01	13.95
			14.35	41.47	4.39	13.70
VIII	$[\mathrm{Ni}(N\text{-}\mathrm{CH_3pia})_3]\mathrm{Br_2 \cdot 2H_2O}$	blue	8.86	38.04	4.26	12.68
			8.77	37.65	4.10	12.52
IX	$[\mathrm{Ni}(N\text{-}\mathrm{CH_3pia})_3]\mathrm{I_2}$	blue	8.14	34.98	3.36	11.66
			8.20	34.60	3.40	11.48
X	$[\mathrm{Ni(NCS)_2}(N\text{-}\mathrm{CH_3pia})_2]\cdot N\text{-}\mathrm{CH_3pia}$	blue	10.06	47.36	4.15	19.21
			10.20	46.95	3.90	18.95
XI	$[\mathrm{NiCl_2}(O\text{-}\mathrm{CH_3pii})_2]$	green	14.61	41.86	4.01	13.95
			14.48	41.40	4.09	13.70
XII	$[\mathrm{NiBr_2}(O\text{-}\mathrm{CH_3pii})_2]$	green	11.97	34.27	3.29	11.42
			11.70	33.95	3.49	11.49
XIII	$[\mathrm{Ni(NCS)_2}(O\text{-}\mathrm{CH_3pii})_2]$	blue–violet	13.13	42.95	3.61	18.80
			13.22	42.35	3.59	18.63
XIV	$[\mathrm{NiI_2}(O\text{-}\mathrm{CH_3pii})_2]$[a]	yellow–green	10.04	28.75	2.76	9.59
			10.20	28.45	2.86	9.32
XV	$[\mathrm{Ni(NCS)_2}(O\text{-}\mathrm{CH_3pii})_2]$[a]	blue–violet	13.13	42.95	3.61	18.80
			12.85	43.59	3.99	19.11
XVI	$[\mathrm{Ni}(O\text{-}\mathrm{CH_3pii})_3]\mathrm{Cl_2 \cdot 2H_2O}$	pink	10.23	43.95	4.92	14.64
			10.30	43.87	4.99	14.35
XVII	$[\mathrm{Ni}(O\text{-}\mathrm{CH_3pii})_3]\mathrm{Br_2 \cdot 2H_2O}$	pink	8.86	38.04	4.26	12.68
			8.81	38.60	4.36	12.74
XVIII	$[\mathrm{Ni}(O\text{-}\mathrm{CH_3pii})_3]\mathrm{I_2}$	pink	8.14	34.98	3.36	11.66
			7.91	35.06	3.65	11.36
XIX	$[\mathrm{Ni}(O\text{-}\mathrm{CH_3pii})_3]\mathrm{(NCS)_2}$	pink	10.09	47.46	4.16	19.25
			10.16	47.56	4.05	19.43
XX	$[\mathrm{Ni}(O\text{-}\mathrm{CH_3pii})_3]\mathrm{Cl_2 \cdot 2H_2O}$[a]	pink	10.23	43.95	4.92	14.64
			10.16	43.50	4.77	14.46
XXI	$[\mathrm{Ni}(O\text{-}\mathrm{CH_3pii})_3]\mathrm{Br_2 \cdot 2H_2O}$[a]	pink	8.86	38.04	4.26	12.68
			9.19	37.91	3.97	12.85

[a] Complex was prepared directly from *O*-methylpyridine-2-carboximidate.

Although it is not mentioned in this paper in more detail, the same method, when used in ethanolic solutions, gives *O*-ethylpyridine-2-carboximidate as the addition product.

In agreement with previous papers [7, 14], the complexes containing 3-CNpy or 4-CNpy molecules

TABLE II. Magnetic Moments and Electronic Spectral Data of Complexes

No.	Complex	μ_{eff} (BM)	Maxima of absorption bands[a] (cm^{-1})		
I	$[Ni(H_2O)_2(piaH)_2]Cl_2$	3.25	11500 9600sh	15950 18600sh	
II	$[Ni(H_2O)_2(piaH)_2]Br_2$	3.21	11300	15850 18500sh	
III	$[NiCl_2(piaH)_2]$	3.20	9200 8200sh	15200	
IV	$[NiBr_2(piaH)_2]$	3.19	8500 6800sh	15200 17000sh	
V	$[NiI_2(piaH)_2]$	3.20	8000 6800sh	15400	
VI	$[Ni(NCS)_2(piaH)_2]$	3.20	10500	16750	25500–27000
VII	$[NiCl_2(N\text{-}CH_3pia)_2]$	3.25	8200	15000 17200sh	
VIII	$[Ni(N\text{-}CH_3pia)_3]Br_2 \cdot 2H_2O$	3.24	10600	16500	
IX	$[Ni(N\text{-}CH_3pia)_3]I_2$	3.22	10300	16400	
X	$[Ni(NCS)_2(N\text{-}CH_3pia)_2] \cdot N\text{-}CH_3pia$	3.24	10500	16300	
XI	$[NiCl_2(O\text{-}CH_3pii)_2]$	3.07	8400	16100	
XII	$[NiBr_2(O\text{-}CH_3pii)_2]$	3.13	8200	16400	25000–27000
XIII	$[Ni(NCS)_2(O\text{-}CH_3pii)_2]$	3.18	10800	18000 16400sh	
XIV	$[NiI_2(O\text{-}CH_3pii)_2]$[b]	3.13	7700	13300	
XV	$[Ni(NCS)_2(O\text{-}CH_3pii)_2]$[b]	3.13	10900	18000 16400sh	
XVI	$[Ni(O\text{-}CH_3pii)_3]Cl_2 \cdot 2H_2O$	3.03	11700	18500	
XVII	$[Ni(O\text{-}CH_3pii)_3]Br_2 \cdot 2H_2O$	2.99	11600	18400	
XVIII	$[Ni(O\text{-}CH_3pii)_3]I_2$	3.00	11600	18400	
XIX	$[Ni(O\text{-}CH_3pii)_3](NCS)_2$	3.15	11700	18400	
XX	$[Ni(O\text{-}CH_3pii)_3]Cl_2 \cdot 2H_2O$[b]	3.12	11700	18500	
XXI	$[Ni(O\text{-}CH_3pii)_3]Br_2 \cdot 2H_2O$[b]	3.14	11600	18400	

[a] sh = shoulder. [b] Complex was prepared directly from $O\text{-}CH_3pii$.

as organic ligands can only be obtained by the reactions of aqueous or alcoholic solutions of NiX_2 with 3-CNpy or 4-CNpy.

Results and Discussion

Based on electronic spectra and magnetic moments values, an octahedral configuration of Ni(II) was assigned to all complexes under investigation. A greater deviation from this symmetry was only observed for complexes with piaH and $N\text{-}CH_3pia$.

Compositions and structures of the investigated complexes, as well as the coordination modes of ligands were determined on the basis of IR spectra. The spectra of the complexes no longer exhibit the most characteristic band assigned to valence vibration $\nu(C{\equiv}N)$ of the nitrile group of 2-CNpy (at 2235 cm^{-1}). At the same time, however, there appear several new, often very intense, characteristic bands.

The Complexes with piaH

A comparison of the IR spectra of the complexes prepared in aqueous solutions of 2-CNpy with that of piaH itself (Table III) shows that the complexes contain coordinated piaH molecules as organic ligands only. Their coordination through the nitrogen atom of the pyridine ring as well as via the oxygen atom of the amide group is indicated by a shift of $\nu_s(OCN)$ and $\tau(NH_2)$ vibrations to higher values by 32–44 and 36–45 cm^{-1}, respectively. Moreover,

TABLE III. IR Spectra of Amido Group (in cm^{-1}) for Complexes with Pyridine-2-carboxamide[a]

No.	Compound	ν(NH)	ν_a(OCN)	$\delta(NH_2)$	ν_s(OCN)	$\tau(NH_2)$	δ(CO)	π(CO)
	piaH	3420s 3155s	1659s	1602m	1391s	627s	607s	520m
I	$[Ni(H_2O)_2(piaH)_2]Cl_2$	3270s 3125s, br	1660s	1610w	1435s	672m	636s	515w
II	$[Ni(H_2O)_2(piaH)_2]Br_2$	3310s 3140s	1658s	1610w	1435s	668m	608s	503w
III	$[NiCl_2(piaH)_2]$	3290s 3130s	1660s	1615w	1440s	665m	642m	513w
IV	$[NiBr_2(piaH)_2]$	3300s 3135s	1657s	1615w	1425m	662m	618s	511w
V	$[NiI_2(piaH)_2]$	3305s 3130s, br	1655s	1608w	1423m	663m	581m	510w
VI	$[Ni(NCS)_2(piaH)_2]$	3380s 3290s 3200s	1661s	1612m	1431s	667m	563m	500w

[a] s, strong; m, medium; w, weak; br, broad; ν, stretching; δ, in-plane deformation; π, out-of-plane deformation; τ, twisting.

N,O-coordination has also been proved by X-ray structure analysis [15] for complex **I** prepared directly with piaH.

The Complexes with N-CH_3pia

Table IV presents the most important bands of the amide group in *N*-CH_3pia as well as in complexes prepared directly with this ligand. The IR spectra of complexes **VII–IX** allow us to assume that all organic molecules are coordinated to the central atoms of Ni(II) as chelates through the nitrogen and oxygen atoms. This has been proved by the characteristic shift of the amide I band to lower wavenumbers but those of amide II and amide III bands to higher wavenumbers [16,17].

The Complexes with O-CH_3pii

IR spectra observed for complexes prepared in methanolic solutions of 2-CNpy (Table V) when compared with those of complexes prepared directly with *O*-CH_3pii, give evidence that the addition of methanol leads to the formation of *O*-CH_3pii but not to the isomeric compound *N*-CH_3pia. This finding was also proved by the reaction of $NiCl_2$ in methanolic solution with a considerable excess of 2-CNpy, when pure *O*-CH_3pii was separated. The most significant spectra changes after coordination of *O*-CH_3pii molecules were observed as shifts of the bands ν_a(COC) and δ(NH) to higher values. The present knowledge of IR spectra do not allow us to determine unambiguously the coordination mode of the imine etheric group. Nevertheless the significant shift of the ν_a(COC) vibration to higher values could be considered as a consequence of the coordination of the imine etheric group through the nitrogen atom. The suggested N,N-coordination of *O*-CH_3pii is also in agreement with the opinion

TABLE IV. IR spectra of Amido Group (in cm^{-1}) for Complexes with *N*-Methylpyridine-2-carboxamide[a]

No.	Compound	ν(NH)	Amide I	Amide II	Amide III	δ(CO)	π(NH)	π(CO)
	N-CH_3pia	3340s	1672s	1532s	1244s	695s	610w	486m
VII	$[NiCl_2(N\text{-}CH_3pia)_2]$	3168s, br	1640s	1548m, br	1337m	701w	673m	510w
VIII	$[Ni(N\text{-}CH_3pia)_3]Br_2 \cdot 2H_2O$	3233s, br	1635s	1552m	1340m	703w 688w	677w	512w
IX	$[Ni(N\text{-}CH_3pia)_3]I_2$	3180s, br	1634s	1545m	1337m	702w	665w	505w
X	$[Ni(NCS)_2(N\text{-}CH_3pia)_2] \cdot N\text{-}CH_3pia$	3215s, br	1680s 1642s, br	1551m, br	1335m	695w	668m	510w

[a] s, strong; m, medium; w, weak; br, broad; ν, stretching; δ, in-plane deformation; π, out-of-plane deformation.

TABLE V. IR Spectra of Iminoetheric Group (in cm^{-1}) for Complexes with *O*-Methylpyridine-2-carboximidate[a]

No.	Compound	ν(NH)	ν(C=N)	δ(NH)	ν_a(COC)	ν_s(COC)	π(NH)
	O-CH$_3$pii	3280s	1650s	1368s	1085s	961s	878s
XI	[NiCl$_2$(*O*-CH$_3$pii)$_2$]	3208s	1652s	1385s	1146m 1141s	970m	849s
XII	[NiBr$_2$(*O*-CH$_3$pii)$_2$]	3233s	1647s	1388s	1147m 1141s	958m	836s
XIII	[Ni(NCS)$_2$(*O*-CH$_3$pii)$_2$]	3268s	1650s	1380s	1134s	958m	811s
XIV	[NiI$_2$(*O*-CH$_3$pii)$_2$][b]	3278s 3250s	1650s	1375s	1151s 1142m	968m	823m
XV	[Ni(NCS)$_2$(*O*-CH$_3$pii)$_2$][b]	3270s	1656s	1382s	1133s	963m	820m
XVI	[Ni(*O*-CH$_3$pii)$_3$]Cl$_2$·2H$_2$O	3128s, br	1647s	1385s	1142m	960m	885m, br
XVII	[Ni(*O*-CH$_3$pii)$_3$]Br$_2$·2H$_2$O	3140s, br	1648s	1381s	1140m	960m	867w, br
XVIII	[Ni(*O*-CH$_3$pii)$_3$]I$_2$	3175s, br	1642s	1378s	1137m	957m	836m, br
XIX	[Ni(*O*-CH$_3$pii)$_3$](NCS)$_2$	3150s, br	1645s	1376s	1133m	962m	850m 885sh
XX	[Ni(*O*-CH$_3$pii)$_3$]Cl$_2$·2H$_2$O[b]	3150m, br	1650s 1660sh	1380s	1142s	963m	890m, br
XXI	[Ni(*O*-CH$_3$pii)$_3$]Cl$_2$·2H$_2$O[b]	3140m, br	1642s	1378s	1135m	955m	860m, br

[a] s, strong; m, medium; sh, shoulder; br, broad; ν, stretching; δ, in-plane deformation; π, out-of-plane deformation. [b] Complex was prepared directly from *O*-CH$_3$pii.

of other authors studying analogous complexes [10].

Conclusions

In studying the products isolated after the reaction of 2-cyanopyridine with Ni(II) compounds in aqueous or methanolic solutions was finished, we have elucidated the composition of these addition products of 2-cyanopyridine as pyridine-2-carboxamide and *O*-methylpyridine-2-carboximide, respectively. Moreover, we have succeeded in obtaining high yields of the latter addition products (80% and 90%, respectively) from reaction mixtures containing a considerable excess of the starting 2-cyanopyridine.

The results of a kinetic study of the above reactions (partially presented already [18]) pointed also to a high catalytic activity of the Ni(II) compounds used. This depends to a great extent on the anionic ligand and the type of nucleophilic reagent (water, methanol, and ethanol). The other factors which affect the rates of the reactions, were investigated at constant values of ionic strength and pH of the solutions. A supposed mechanism of the reactions was also suggested. The results of the kinetic study will be presented in more detail in another paper.

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