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PYRIDINE TYPE COMPLEXES OF TRANSITION-METAL-HALIDES II.

Preparation, characterisation and thermal analysis studies of cobalt(II)-bromides and iodides with 2-,3-,4-methylpyridines

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Abstract

In the preparation of cobalt(II)-picoline-bromide and iodide three different solvents were tested. Some new ternary mixed complexes were prepared containing different picolines using solid-gas phase preparation method. Themal and spectroscopic properties of the tittle compounds were investigated.

1. INTRODUCTION

This work is a continuation of previously reported study [1] on the coordination compounds formed between the cobalt(II)-chlorides and 2-,3-,4-methylpyridines (picolines).

While the chemistry and the thermal properties of these complexes are well documented [2-7] it was possible to prepare some new complexes either by the freezing-out technique reported earlier or by the solid-gas phase chemisorbtion. In the classical preparative work three different solvents were tested to measure the effect of the reaction media on the complex formation. Thermal and spectral properties of the complexes were investigated by means of simultaneous TG-DTG-DTA and far infrared spectroscopy.

2. EXPERIMENTAL

In the preparation of cobalt(II)-picoline-bromides and iodides an excess of picoline (A) , ethanol (B) and acethonitrile (C) were used as solvents. The Co:picoline molar

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ratio was, in each case,1:4. The cobalt(II)-halides were used as anhydrate, but in the case of ethanolic solutions the hexahydrates were also applied (B^*).

The thermal intermediates were prepared at 100 °C from the tetrakis-complexes.

The mixed complexes were prepared from these intermediates by leaving them in a vacuum desiccator under the vapour of different picolines for several days.

The cobalt content of the compounds were determined by means of complexometric titration.

Thermal properties were measured by MOM OD-2 Derivatograph with the heating rate of β=5°C/min, and a sample weight of 100 mg in a platinum crucible and nitrogen atmosphere was applied.

The melting point of the complexes was determined by a Micro-Heiztisch-Boetius type thermomicroscope (β=4°C/min).

Far infrared spectra was obtained on a Digilab FTS spectrophotometer equipped by TGS detector and 6 μm hylar beam splitter. For sample preparation nujol mulls and polyethylene matrix have been used.

3. RESULTS AND DISCUSSION

The complexes formed in solutions are collected in Table 1.

The solvent has no effect on the complexation of the cobalt-halides except in the case of β-picoline complexes, because of the charge distribution and charge densities of the pyridine ring. Pyridine type complexes can stabilize by back donation (Co $d\pi$-$p\pi$ N) which localize mainly on 2, 4 and 6-positions. In the case of β-picoline the electron-repelling effect of the methyl substituent already increases the charge density of these positions, while the back coordination is inhibited. In the case of γ-picoline complexes the 2, 4 and 6-positions have the less electron density, thus, the back coordination can stabilize the complexes [8].

With this possible explanation we were able to understand the fact that cobalt(II)-bromide and iodide as well as chloride [1] form only bis-complexes with β-picoline in ethanolic solutions, while γ-picoline complexes four ligands are bonded in all solvents.

The substituent position can also influence the composition of the compounds. Because of the steric hindrance the the methyl-group of α-picoline prevents the formation of the tetrakis derivates analogously to the bis-complexes [7].

In the case of preparation method B^*, where the Co-halides were used as hexahydrates, the water was accommodated only in one case, when the complex has a probable stochimetry of $[Co(\beta\text{-pic})_4(H_2O)_2]I_2$ according to the thermal and spectroscopic results. According to our knowledge this complex obtained first time.

Pyridine type complexes of transition-metal-halides have the following decomposition scheme [5]:

$$ML_4X_{2(s)} \longrightarrow ML_2X_{2(s)} + 2L_{(g)} \quad (1)$$

$$ML_2X_{2(s)} \longrightarrow ML_2X_{2(l)} \quad (2)$$

$$ML_2X_{2(l)} \longrightarrow ML_1X_{2(l)} + L_{(g)} \quad (3)$$

$$ML_1X_{2(l)} \longrightarrow ML_{2/3}X_{2(l)} + 1/3\ L_{(g)} \quad (4)$$

$$ML_{2/3}X_{2(l)} \longrightarrow MX_{2(s)} + 2/3\ L_{(g)} \quad (5)$$

$$ML_2X_{2(l)} \longrightarrow MX_{2(s)} + 2L_{(g)} \quad (6)$$

Table 1.

Compound	Method	Yield	Colour	Co-cont.	n
	[-]	[%]	[-]	[mg/g]	[-]
[Co(α-pic)$_n$Br$_2$]	A	68.1	blue	157.2	2
	B	89.8	blue	148.6	2
	B*	78.7	blue	152.9	2
	C	81.2	blue	145.3	2
[Co(β-pic)$_n$Br$_2$]	A	91.3	pink	100.3	4
	B	84.6	blue	149.1	2
	B*	81.4	pink	99.9	4
	C	92.1	pink	100.5	4
[Co(γ-pic)$_n$Br$_2$]	A	91.6	pink	98.9	4
	B	94.0	pink	97.7	4
	B*	94.0	pink	100.1	4
	C	94.8	pink	99.2	4
[Co(α-pic)$_n$I$_2$]	A	34.5	green	117.3	2
	B	75.5	green	119.5	2
	B*	70.5	green	115.9	2
	C	78.8	green	118.2	2
[Co(β-pic)$_n$I$_2$]	A	75.5	brown	85.3	4
	B	85.6	brown	119.1	2
	B*	55.7	orange-brown	80.1$^+$	4
	C	92.0	brown	86.2	4
[Co(γ-pic)$_n$I$_2$]	A	71.0	brown	85.3	4
	B	80.0	brown	88.2	4
	B*	91.0	brown	87.4	4
	C	93.0	brown	86.1	4

$^+$A probable stochiometry is [Co(β-pic)$_4$(H$_2$O)$_2$]I$_2$.

The results of the thermal studies are shown in Table 2.

The α-picoline complexes of the CoBr$_2$ and CoI$_2$ are melted at about the same temperature range. The releasing of the last two-third moles of α-picoline (Eq. (5)) immediately follows the first two overlapped decomposition steps (Eq. (3)+(4)).

The tetrakis-complexes of cobalt(II)-bromides and iodides decompose in three steps. The first endothermic peak, representing the releasing of the first two ligands (Eq. (1)), is overlapped by the melting of the complex (Eq. (2)) on the DTA-curve in the case of γ-picoline derivates , while on the

Table 2.

Compound	Eq. No.	DTG-peak temperature	Resulting compound	Melting point
	[-]	[C°]	[-]	[C°]
$[Co(\alpha\text{-pic})_2Br_2]$	(2)	-	$[Co(\alpha\text{-pic})_2Br_2]$	168
	(3)+(4)	250	$[Co(\alpha\text{-pic})_{2/3}Br_2]$	-
	(5)	300	$CoBr_2$	-
$[Co(\beta\text{-pic})_4Br_2]$	(1)	105	$[Co(\beta\text{-pic})_2Br_2]$	-
	(2)	-	$[Co(\beta\text{-pic})_2Br_2]$	153
	(6)	300	$CoBr_2$	-
$[Co(\gamma\text{-pic})_4Br_2]$	(1)	127,143	$[Co(\gamma\text{-pic})_2Br_2]$	-
	(2)	-	$[Co(\gamma\text{-pic})_2Br_2]$	115
	(6)	325	$CoBr_2$	-
$[Co(\alpha\text{-pic})_2I_2]$	(2)	-	$[Co(\alpha\text{-pic})_2I_2]$	168
	(3)+(4)	240	$[Co(\alpha\text{-pic})_{2/3}I_2]$	-
	(5)	320	$CoBr_2$	-
$[Co(\beta\text{-pic})_4I_2]$	(1)	105	$[Co(\beta\text{-pic})_2I_2]$	-
	(2)	-	$[Co(\beta\text{-pic})_2I_2]$	165
	(6)	>300	CoI_2	-
$[Co(\gamma\text{-pic})_4I_2]$	(1)	128,152	$[Co(\gamma\text{-pic})_2I_2]$	-
	(2)	-	$[Co(\gamma\text{-pic})_2I_2]$	110
	(6)	310	CoI_2	-

derivatograms of the β-picoline complexes the peaks are separated. The next two moles of ligand decompose in one step (Eq. (6)).

The decomposition of $[Co(\beta\text{-pic})_4(H_2O)_2]I_2$ starts with the releasing of the water (Eq. (7) See Fig.1.):

$$[Co(\beta\text{-pic})_4(H_2O)_2]I_{2(s)} \longrightarrow [Co(\beta\text{-pic})_4I_2]_{(s)} + 2H_2O_{(g)} \qquad (7)$$

The observed melting points (See Table 2.) are different from the earlier reported data [2] in some cases.

The thermal stability of the cobalt(II)-bromide complexes are similar to those of the appropriate chloride derivates; however, a slow decreasing can be observed in the thermal stability from the chlorides to iodides. This is probably due to the polarizability of the anions, which increase in the same order. The high charge aquired by the cobalt-ion, caused by the increasing charge transfer from Cl to I, further reduces the affinity for pyridine.

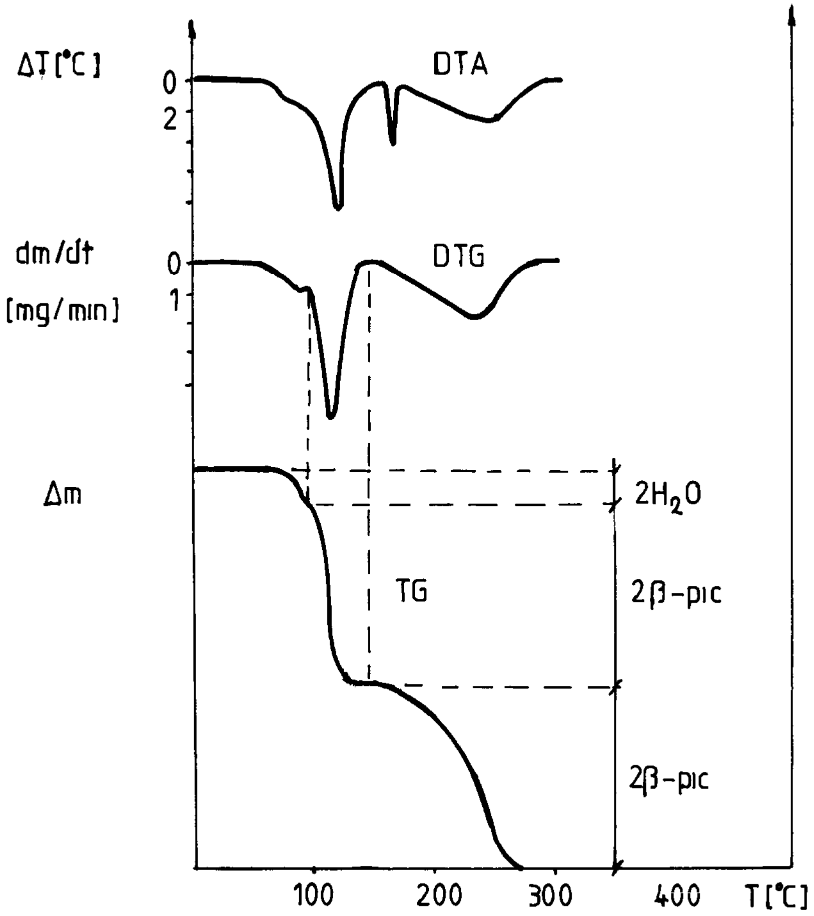

Fig.1. Thermal decomposition of $[Co(\beta\text{-pic})_4(H_2O)_2]I_2$

At 100°C we were able to prepare the thermal intermediates (See Table 3.), which contain two moles of picoline except for the iodide γ-picoline complex where the tris-compound was obtained. The decomposition of the tetrakis-complexes to bis-compounds (octahedral-tetrahedral transition) can be easily followed by the change in colour from pink to deep blue for the bromides, and from brown to green for the iodides. The bis-complexes of α-picoline suffered no change at this temperature.

The chemisorbtion from the vapour phase and the formation of the ternary mixed complexes or the total ligand exchange (See Table 3.) can be explained by the charge densities and steric hindrance described earlier i.e. the stability of the complexes.

Table 3.

Heating at 100°C	Vapour
$[Co(\beta\text{-pic})_4Br_2] \longrightarrow [Co(\beta\text{-pic})_2Br_2]$	$\xrightarrow{\alpha\text{-pic}} [Co(\beta\text{-pic})_2(\alpha\text{-pic})_2Br_2]$
	$\xrightarrow{\beta\text{-pic}} [Co(\beta\text{-pic})_4Br_2]$
	$\xrightarrow{\gamma\text{-pic}} [Co(\gamma\text{-pic})_4Br_2]$
$[Co(\gamma\text{-pic})_4Br_2] \longrightarrow [Co(\gamma\text{-pic})_2Br_2]$	$\xrightarrow{\alpha\text{-pic}} [Co(\gamma\text{-pic})_2(\alpha\text{-pic})_2Br_2]$
	$\xrightarrow{\beta\text{-pic}} [Co(\gamma\text{-pic})_2(\beta\text{-pic})_2Br_2]$
	$\xrightarrow{\gamma\text{-pic}} [Co(\gamma\text{-pic})_2Br_2]$
$[Co(\beta\text{-pic})_4I_2] \longrightarrow [Co(\beta\text{-pic})_2I_2]$	$\xrightarrow{\alpha\text{-pic}} [Co(\beta\text{-pic})_2I_2]$
	$\xrightarrow{\beta\text{-pic}} [Co(\beta\text{-pic})_4I_2]$
	$\xrightarrow{\gamma\text{-pic}} [Co(\gamma\text{-pic})_4I_2]$
$[Co(\gamma\text{-pic})_4I_2] \longrightarrow [Co(\gamma\text{-pic})_3I_2]$	$\xrightarrow{\alpha\text{-pic}} [Co(\gamma\text{-pic})_3I_2]$
	$\xrightarrow{\beta\text{-pic}} [Co(\gamma\text{-pic})_3(\beta\text{-pic})_1I_2]$
	$\xrightarrow{\gamma\text{-pic}} [Co(\gamma\text{-pic})_4I_2]$

α-picoline complexes can not adopt more α-picoline from the vapour phase, because of the steric hindrance of the tetrakis-complex formation, but undergo a total ligand exchange in β- and γ-picoline vapour, forming the appropriate tetrakis-complex of the ligand from the gas-phase.

β-picoline bis-complex of cobalt(II)-bromide forms ternary mixed complex with α-picoline, while the β-picoline complex of iodide suffers no change in α-picoline vapour, because of the larger radius of the anion. Due to the highest stability of the cobalt(II)-halide γ-picoline complexes, the β-picoline complexes suffered total ligand exchange in γ-picoline vapour, forming $[Co(\gamma\text{-pic})_4X_2]$ (where X=Cl [1],Br or I).

γ-picoline bis-complex of cobalt(II)-bromide forms ternary mixed complexes with α- and β-picoline and neither the α-, nor the β-picoline can not exchange the γ-substituated picoline, because of the highest stability of these compound. In the case of $[Co(\gamma\text{-pic})_3I_2]$ the formation of the miscellaneous complex with α-picoline is inhibited by the steric hindrance and the large ionic radius of the anion.

The thermal decomposition of the ternary mixed complexes are collected in Table 4.

Table 4.

Compound	Eq. No.	DTG-peak temperature	Resulting compound	Melting point
	[-]	[C°]	[-]	[C°]
$[\mathrm{Co}\substack{(\beta\text{-pic})_2\\(\alpha\text{-pic})_2}\mathrm{Br}_2]$	(2)	-	$[\mathrm{Co}\substack{(\beta\text{-pic})_2\\(\alpha\text{-pic})_2}\mathrm{Br}_2]$	140
	(8)	250	CoBr_2	-
$[\mathrm{Co}\substack{(\gamma\text{-pic})_2\\(\alpha\text{-pic})_2}\mathrm{Br}_2]$	(1)	100	$[\mathrm{Co}(\gamma\text{-pic})_2\mathrm{Br}_2]$	-
	(2)	-	$[\mathrm{Co}(\gamma\text{-pic})_2\mathrm{Br}_2]$	150
	(6)	330	CoBr_2	-
$[\mathrm{Co}\substack{(\gamma\text{-pic})_2\\(\beta\text{-pic})_2}\mathrm{Br}_2]$	(1)	115	$[\mathrm{Co}(\gamma\text{-pic})_2\mathrm{Br}_2]$	-
	(2)	-	$[\mathrm{Co}(\gamma\text{-pic})_2\mathrm{Br}_2]$	150
	(6)	325	CoBr_2	-
$[\mathrm{Co}\substack{(\gamma\text{-pic})_3\\(\beta\text{-pic})_1}\mathrm{I}_2]$	(9)	95	$[\mathrm{Co}(\gamma\text{-pic})_3\mathrm{I}_2]$	-
	(10)	135	$[\mathrm{Co}(\gamma\text{-pic})_2\mathrm{I}_2]$	-
	(6)	310	CoI_2	-

In the case of $[\mathrm{Co}(\beta\text{-pic})_2(\alpha\text{-pic})_2\mathrm{Br}_2]$ the decomposition is a one step process:

$$[\mathrm{Co}(\beta\text{-pic})_2(\alpha\text{-pik})_2\mathrm{Br}_2] \xrightarrow{\qquad\qquad} \mathrm{CoBr}_2 \qquad (8)$$

The decomposition of the other bromide ternary mixed complexes start with the releasing of the sorbated ligand (See Fig. 2.):

$$[\mathrm{Co}(\gamma\text{-pic})_2(\beta\text{-pic})_2\mathrm{Cl}_2] \xrightarrow{\qquad\qquad} [\mathrm{Co}(\gamma\text{-pic})_2\mathrm{Cl}_2] \qquad (1)$$

The endothermic peak of the first decomposition is overlapped with the effect of melting.

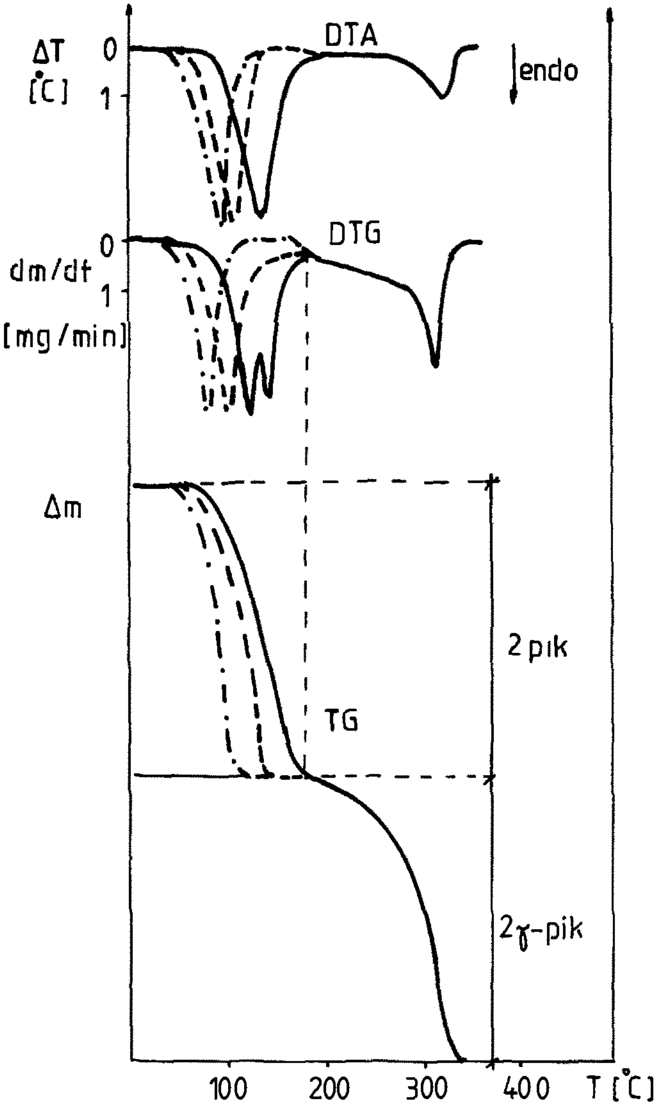

Figure 2. Thermal decomposition of quaternary mixed complexes

—— [Co(γ-pic)$_4$Br$_2$] – – [Co(γ-pic)$_2$(β-pic)$_2$Br$_2$]

—·— [Co(γ-pic)$_2$(α-pic)$_2$Br$_2$]

The decomposition of the iodide ternary mixed complex is somewhat different:

$$[Co(\gamma\text{-pic})_3(\beta\text{-pic})_1I_2] \longrightarrow [Co(\gamma\text{-pic})_3I_2] \qquad (9)$$

$$[Co(\gamma\text{-pic})_3I_2] \longrightarrow [Co(\gamma\text{-pic})_2I_2] \qquad (10)$$

After the releasing of the sorbated ligand the thermal decomposition is identical with the appropriate thermal intermediate.

In the region of 4000-400 cm^{-1} a small changes in ligand bans can be observed, but in the case of $[Co(\beta\text{-pic})_4(H_2O)_2]I_2$ the rocking vibration of coordinated water (545 cm^{-1}) appears in the infrared spectrum. In addition to the rocking band the OH stretching (3300,3220 cm^{-1}) and the HOH bending vibrations (with low intensity at approximately 1650 cm^{-1}) can be assigned as well. Due to the thermal and spectroscopic properties we may explain, that the iodides are in the outer coordination sphere.

The ring vibration of pyridine [9] and picolines [10] has been extensively studied, the two lowest ring vibrations are the ring in-plane (δ) and the out-of-plane (γ) deformation modes (See Table 5.). As a consequence of the complexation these bands are shifted to higher frequencies [11]. The in-plane deformation is more sensitive to the changes of symmetry [12] than the other, but the bonding of halogen atom showed no significant changes in this region. The in-plane ring deformation band appears as a doublet in tetrahedral (C_{2v}) γ-picoline complexes, while octahedral compounds showed only one deformation band.

In addition to the bands described earlier other characteristic frequencies can be seen in the spectra of the compounds. Due to the coordination of the picolines to the cobalt some new vibrations become IR active. These bands can be observed low intensity ones in the 650-300 cm^{-1} region (See Table 5.). By the careful study of pyridine ring vibrations we are able to demonstrate the existence of the ternary mixed complex, both ligand bands were observed in these cases (See Fig. 3.). When total ligand exchange was suggested from the thermal investigation, we found only the vibration of the ligand, which was absorbed from the vapour phase, and it was identical with the spectra of the compound with appropriate stochiometry.

The data of the Co-halogen, Co-ligand and ligand-Co-ligand vibration are collected in Table 6. The assignment was based on papers reported earlier [12-16] especially on isotopic labelling studies [17-20].

The Co-ligand stretching vibrations occur at approximately the same frequencies in the chloro [1], bromo and iodo analogs of cobalt. In the spectra of trans-octahedral complexes only one Co-nitrogen stretching band (207-210 cm^{-1}) was observed, while two vibrations (243-203 cm^{-1})can be detected for tetrahedral compounds.

The Co-halogen stretching vibrations showed strong halogen dependence. The ratios of $\nu(Co\text{-}Br)/\nu(Co\text{-}Cl)\approx0.78$ and $\nu(Co\text{-}I)/\nu(Co\text{-}Cl)\approx0.62$ are in good agreement with the data reported earlier [12].

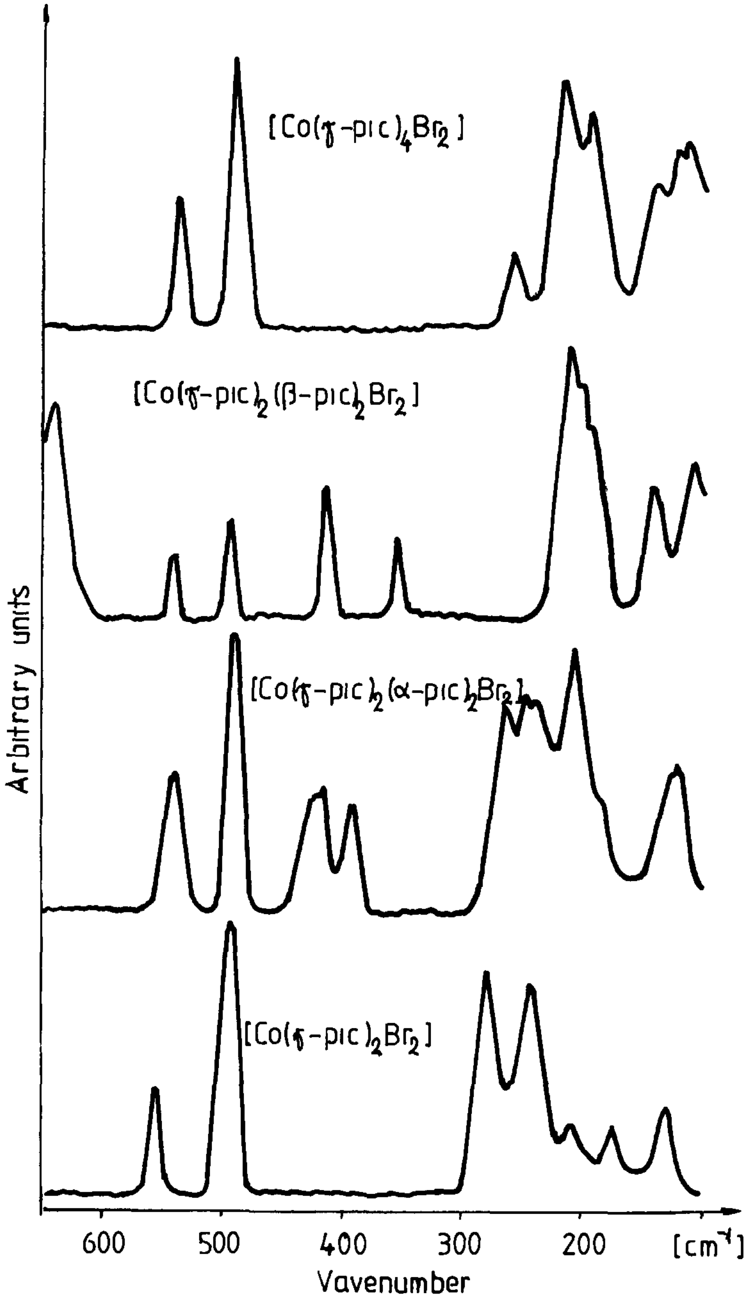

Figure 3. Low frquency vibration of ternary mixed complexes

Table 5.

Compund	In plane def.(δ) [cm^{-1}]	Out of plane def.(γ) [cm^{-1}]	Other ring vibrations [cm^{-1}]
α-picoline	628	403	-
β-picoline	629	402	-
γ-picoline	515	485	-
$[Co(\alpha\text{-pic})_2Br_2]$	>650	420	554,471,390
$[Co(\beta\text{-pic})_4Br_2]$	>650	448	537,475,412,355
$[Co(\beta\text{-pic})_2Br_2]$	>650	448	538,476,411,356
$[Co(\beta\text{-pic})_2(\alpha\text{-pic})_2Br_2]$	>650	424	555,473,393
$[Co(\gamma\text{-pic})_4Br_2]$	538	493	-
$[Co(\gamma\text{-pic})_2Br_2]$	539	495	555
$[Co(\gamma\text{-pic})_2(\alpha\text{-pic})_2Br_2]$	540	495,422	472,417,392
$[Co(\gamma\text{-pic})_2(\beta\text{-pic})_2Br_2]$	647,539	493,454	476,415,357
$[Co(\alpha\text{-pic})_2I_2]$	>650	420	554,472,392
$[Co(\beta\text{-pic})_4I_2]$	>650	448	538,474,411,354
$[Co(\beta\text{-pic})_2I_2]$	>650	448	538,473,410,353
$[Co(\gamma\text{-pic})_4I_2]$	539	496	-
$[Co(\gamma\text{-pic})_3I_2]$	539	495	554
$[Co(\beta\text{-pic})_1(\gamma\text{-pic})_3I_2]$	648,536	497,455	467,414,355

The study of the ternary mixed complexes are of interest. When α-picoline was bounded from the vapour phase, the original tetrahedral symmetry of the bis-intermediate has not been changed. In the case of β- and γ-picoline containing miscellaneous complexes, trans-octahedral symmetry was found according to the Co-N and Co-X stretching vibrations.

The ligand-Co-ligand deformation modes are expected around 180cm^{-1}, the other two sets of bands tentatively can be assigned to X-Co-N and X-Co-X bending modes as it was shown in the previous studies of Zn [21-22] and Ni [23-24] complexes.

4. SUMMARY

Cobalt(II)-picoline-halides were prepared from different reaction media using different conditions. The solvent has no effect on the complexation, however the charge distribution of the pyridine ring and the steric hindrance sometimes supported the formation of the tetrakis complexes.

Table 6.

Compound	ν(Co-X)	ν(Co-N)	δ(N-Co-N)	Unassigned bands [cm^{-1}]
$[Co(\alpha\text{-pic})_2Br_2]$	264,240	240,203	175	130
$[Co(\beta\text{-pic})_4Br_2]$	198	208	-	123
$[Co(\beta\text{-pic})_2Br_2]$	273,242	242,208	180	143,120
$[Co(\beta\text{-pic})_2(\alpha\text{-pic})_2Br_2]$	271,240	243,227	180	140,120
$[Co(\gamma\text{-pic})_4Br_2]$	195	207	158	147,125
$[Co(\gamma\text{-pic})_2Br_2]$	279,244	210,244	175	140,128
$[Co(\gamma\text{-pic})_2(\alpha\text{-pic})_2Br_2]$	265,245	239,207	-	128
$[Co(\gamma\text{-pic})_2(\beta\text{-pic})_2Br_2]$	198	213,207	182	143,104
$[Co(\alpha\text{-pic})_2I_2]$	210,180	240,236	180	145,88
$[Co(\beta\text{-pic})_4I_2]$	180	211	177	130,98
$[Co(\beta\text{-pic})_2I_2]$	-	248,236	178	147,90
$[Co(\gamma\text{-pic})_4I_2]$	180	210	-	133,102
$[Co(\gamma\text{-pic})_3I_2]$	212,179	245,239	-	145,97
$[Co(\gamma\text{-pic})_3(\beta\text{-pic})_1I_2]$	195	235	-	135,84

Either by the earlier reported freezing-out technique or by the new solid-gas phase preparation method, we prepared five new cobalt(II)-picoline-halide complexes.

The thermal and spectral properties showed that γ-picoline vapour exchanged β- and α-picoline ligands from their complexes, or formed tetrakis complex with the γ-picoline intermediates, while β-picoline vapour formed mixed complexes with γ-picoline intermediates and exchanged α-picoline derivates to $[Co(\beta\text{-pic})_4X_2]$. The formation of the ternary mixed complexes in α-picoline vapour depend on the anion. While for chloride [1] and bromide intermediates of β- and γ-picolines chemisorbtion of the ligand from the vapuor phasehas been observed, in the case of the iodide analogous formation of mixed complexes have not been detected as a possible consequence of larger ionic radius of the iodide.

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