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PYRIDIN TYPE COMPLEXES OF TRANSITION -METAL-HALIDES

I. Preparation, characterization and thermal analysis studies of cobalt(II)-chlorides with 2,3,4-methylpyridines

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A large number of Co-picoline-chlorides were prepared from different reaction media by changing the Co: picoline molar ratio.

A new solid-gas phase method is described to prepare ternary mixed Co-picoline complexes containing different picolines.

According to the thermal and spectral investigations the ligand chemisorption from the vapour phase depends on the stability of the solid complex and the complex formation ability of the ligand in the gas phase.

Keywords: complexes of transition-metal-halides, TA studies, far-IR

Introduction

The complexes between cobalt(II)-chlorides and α-, β- and γ-picolines have been prepared [1] and their thermal [1–6], spectral [1, 2,7–15] and magnetic [7, 16] properties were studied earlier.

Previously reported papers agree on the fact, that only the bis- and tetrakis-complexes can be obtained from solutions [1, 3].

This work deal with the picoline complexes of $CoCl_2$, systematic preparative work was carried out, and a new producing method was described to obtain ternary mixed complexes, containing different picolines.

The thermal and structural properties of the title compounds were measured by means of simultaneous TG-DTG-DTA and far infrared spectroscopy.

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Table 1 Preparation of Co-picoline-chloride complexes from solution

Compound	Method [–]	Yield [–]	Colour [–]	Co-cont. [mg/g]	n [–]
$\mathrm{Co}(\alpha-\mathrm{pic})_n\mathrm{Cl}_2$	A	51.5	blue	189	2.0
	B	71.0	blue	191	2.0
	B*	76.0	blue	185	2.0
	C	70.8	blue	186	2.0
$\mathrm{Co}(\beta-\mathrm{pic})_n\mathrm{Cl}_2$	A	73.8	pink	114	4.0
	B	96.0	blue	182	2.0
	B*	77.5	pink	116	4.0
	C	88.0	pink	120	4.0
$\mathrm{Co}(\gamma-\mathrm{pic})_n\mathrm{Cl}_2$	A	80.0	pink	119	4.0
	B	91.0	pink	116	4.0
	B*	87.8	pink	115	4.0
	C	86.0	pink	119	4.0

New compounds	Method	Co:pic	Colour	n
$\mathrm{Co}(\beta-\mathrm{pic})_n\mathrm{Cl}_2$	D	1:1	blue	1.33
	D	2:1	lilac	1.0
	D	4:1	lilac	0.67
$\mathrm{Co}(\gamma-\mathrm{pic})_n\mathrm{Cl}_2$	D	1:3	blue	3.0
	D	1:2	blue	2.33
	D	1:1.5	blue	1.67
	D	1:1	lilac	1.0
	D	3:1	lilac	0.67

Method	Co:pic	$\mathrm{CoCl_2}$	Solvent
A	1:4	unhydrate	excess of picoline
B	1:4	unhydrate	ethanol
B*	1:4	$6\mathrm{H_2O}$	ethanol
C	1:4	unhydrate	$\mathrm{CH_3CN}$
D	4:1–1:20	unhydrate	$\mathrm{CH_3CN}$

Experimental

In the preparation of Co-picoline-halides three different solvents were tested, using five different methods (Table 1). The thermal intermediates were prepared from tetrakis complexes, at the temperature obtained from thermal studies (see below). The mixed complexes were prepared from these intermediates leaving them in a vacuum dessicator in a vapour of different picolines for a few days (Table 2).

Table 2 Preparation of Co(II)-picoline-chloride mixed complexes

Heating			Vapour	
		$Co(\alpha-pic)_2Cl_2$	α	$Co(\alpha-pic)_2Cl_2$
			β	$Co(\beta-pic)_2Cl_2$
			γ	$Co(\gamma-pic)_2Cl_2$
$Co(\beta-pic)_4Cl_2$	$\xrightarrow{100^\circ C}$	$Co(\beta-pic)_2Cl_2$	α	$Co(\beta-pic)_2(\alpha-pic)_2Cl_2$
			β	$Co(\beta-pic)_4Cl_2$
			γ	$Co(\gamma-pic)_4Cl_2$
$Co(\beta-pic)_4Cl_2$	$\xrightarrow{100^\circ C}$	$Co(\gamma-pic)_2Cl_2$	α	$Co(\gamma-pic)_2(\alpha-pic)_1Cl_2$
			β	$Co(\gamma-pic)_2(\beta-pic)_2Cl_2$
			γ	$Co(\gamma-pic)_4Cl_2$

The Co contents were determined by means of complexometric titration.

The thermal properties were measured by MOM-OD2 Derivatograph (sample weight: 100 mg, β=5 deg/min, in platinum crucible, under N_2 atmosphere).

The melting points of the complexes were determined by Micro-Heiztisch-Boetius type thermomicroscope (β= 4 deg/min).

Far infrared spectra were obtained on Digilab FTS spectrophotometer using polyethylene matrix.

Results

In addition to the well-known bis and tetrakis complexes some new compounds were prepared (Table 1). The X-ray powder diffraction data show them to be crystalline and unique.

The thermoanalytical curves of $Co(\gamma\text{-pic})_xCl_2$ complexes, prepared by method D, are presented in Fig. 1.

The decomposition of $Co(\gamma\text{-pic})_4Cl_2$ is a five step process:

$$Co\ (L_4)\ Cl_{2(s)} \rightarrow Co\ (L_2)\ Cl_{2(s)} + 2L_{\ (g)} \tag{1}$$

$$Co\ (L_2)\ Cl_{2(s)} \rightarrow Co\ (L_2)\ Cl_{2(l)} \tag{2}$$

$$Co\ (L_2)\ Cl_{2(l)} \rightarrow Co\ (L_1)\ Cl_{2(l)} + 1L_{\ (g)} \tag{3}$$

$$\mathrm{Co\ (L_1)\ Cl_{2(l)} \rightarrow Co\ (L_{2/3})\ Cl_{2(l)} + 1/3L_{(g)}} \quad (4)$$

$$\mathrm{Co\ (L_{2/3})\ Cl_{2(l)} \rightarrow CoCl_{2(l)} + 2/3L_{(g)}} \quad (5)$$

The endothermic peak representing the releasing of the first two ligands (1) is overlapped by the melting of the complex (2) on the DTA curve. The next one (3) and the one-third (4) mole of ligands decompose afterwards. The last two-third (5) picoline released above 300°C. The TG curves of the new complexes containing between four and two, or less than two ligands are connected to the curve of the corresponding tetrakis-γ-picoline-complexes with respect to the temperature range which is appropriate with their stoichiometries.

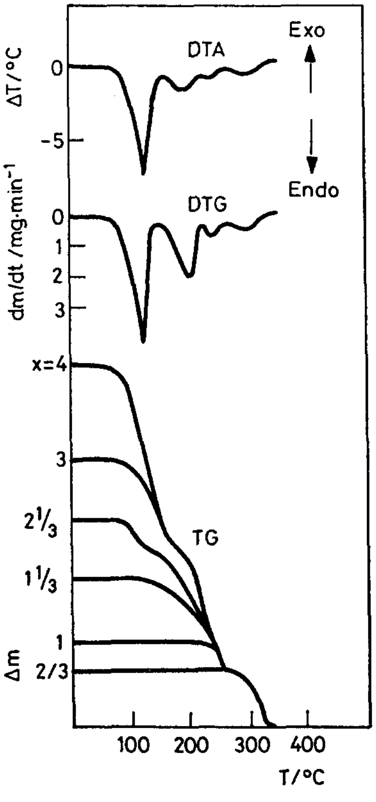

Fig. 1 Thermal decomposition of $\mathrm{Co(\gamma\text{-}pic)_xCl_2}$ prepared by method D

Co-chloride mixed complexes containing different picolines are listed in Table 1.

The thermoanalytical curves of the thermal intermediate $\mathrm{Co(\gamma\text{-}pic)_2Cl_2}$ and its mixed complexes are shown in Fig. 2.

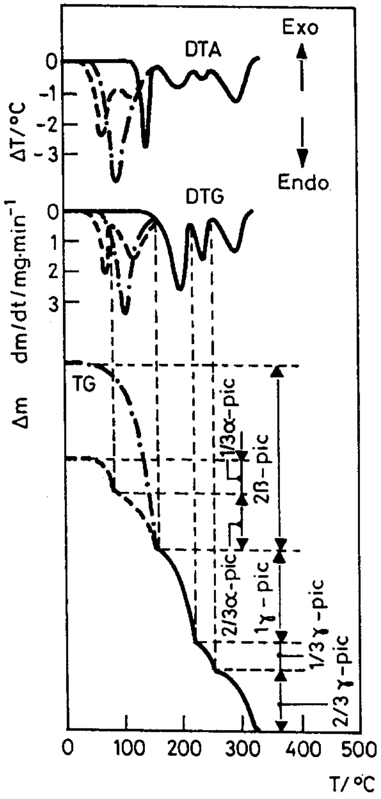

Fig. 2 Thermal decomposition of Co(γ-pic)$_2$Cl$_2$ and its ternary mixed complexes

Co(γ-pic)$_2$Cl$_2$ ————

Co(γ-pic)$_2$(α-pic)$_1$Cl$_2$ ··············

Co(γ-pic)$_2$(β-pic)$_2$Cl$_2$ – – – – –

The thermal decomposition of Co(γ-pic)$_2$Cl$_2$ – prepared by heating at 100°C – is analogue with the last two steps described above.

The decomposition of mixed complexes start with the releasing of the ligand absorbed from the vapour phase. The Co(γ-pic)$_2$ (α-pic)$_2$Cl$_2$ liberates at first the α-picoline in two steps and Co(γ-pic)$_2$ (β-pic)$_2$Cl$_2$ starts by releasing two β-picoline. The melting and degradation enthalpy effects are very close to each other according to the DTA character.

The first step of the thermal decomposition of Co(γ-pic)$_2$(γ-pic)$_2$Cl$_2$ is identical with Co(γ-pic)$_4$Cl$_2$. The last two moles of γ-picoline leave in the same temperature range and mechanism is similar to previously observed case of Co(γ-pic)$_2$Cl$_2$.

The far infrared spectra of the complexes are listed in Table 3. The spectra of Co(γ-pic)$_2$Cl$_2$ and its mixed complexes are shown in Fig. 3.

Table 3

Compounds	Ring vibrations	Co–N	Co–Cl
	[cm^{-1}]	[cm^{-1}]	[cm^{-1}]
Co(α–pic)$_2$Cl$_2$	392, 421	240	308, 333
Co(β–pic)$_4$Cl$_2$	354, 417, 646	208	125
Co(γ–pic)$_4$Cl$_2$	479, 536	215	136
Co(β–pic)$_2$Cl$_2$	344, 417, 650	208	304, 343
Co(β–pic)$_2$	421, 650		
(α–pic)$_2$Cl$_2$	392, 421	209, 240	307, 336
Co(γ–pic)$_2$Cl$_2$	491, 554	215	312, 343
Co(γ–pic)$_2$	491, 554		
(α–pic)$_1$Cl$_2$	392, 421	210, 239	308, 332
Co(γ–pic)$_2$	494, 537		
(β–pic)$_2$Cl$_2$	354, 416, 645	209, 214	133

In the case of Co(γ-pic)$_2$Cl$_2$ the Co–Cl bands showed C_{2v}, symmetry and tetrahedral environment around the Co-ion. The γ-picoline bands can be observed as well as Co–N band.

In the case of Co(γ-pic)$_2$(α-pic)$_1$Cl$_2$ which also exhibits the tetrahedral coordination, but the wavenumbers of Co–Cl are identical with Co(α-pic)$_2$Cl$_2$. By the side of γ-picoline bands the α-picoline vibrations can be seen in the spectra.

The spectra of Co(γ-pic)$_2$(β-pic)$_2$Cl$_2$ is showing octahedral environment around the Co-ion. The β-picoline bands can be observed as well as that of γ-picoline.

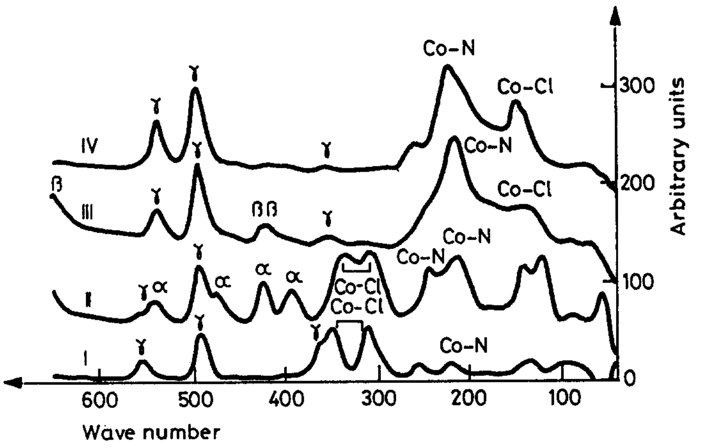

Fig. 3 Far infrared spectra of Co(γ-pic)$_2$Cl$_2$ and its mixed complexes I. Co(γ-pic)$_2$Cl$_2$, II. Co(γ-pic)$_2$(α-pic)$_1$Cl$_2$, III. Co(γ-pic)$_2$(β-pic)$_2$Cl$_2$, IV. Co(γ-pic)$_2$(γ-pic)$_2$Cl$_2$

The Co–Cl bands also show octahedral symmetry in the case of Co(γ-pic)$_2$(γ-pic)$_2$Cl$_2$.

The transition between octahedral and tetrahedral symmetry can be easily followed by the change in colour from pink to deep blue.

When Co(α-pic)$_2$-chloride and Co(β-pic)$_2$-chloride were placed in a γ-picoline vapour or Co(α-pic)$_2$-chloride in a β-picoline vapour, pink complexes were obtained, but the thermal and FIR properties showed total ligand exchange, Co(γ-pic)$_4$-chloride or Co(β-pic)$_4$-chloride were identified. However Co(γ-pic)$_2$-chloride and Co(β-pic)$_2$-chloride in α-picoline vapour or Co(γ-pic)$_2$-chloride in β-picoline vapour form mixed complexes i.e. different picolines (Table 2).

These facts are in a good agreement with the stability of the complexes formed with the ligands in the following order: α-<β-<γ-picolines.

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Zusammenfassung In verschiedenen Reaktionsmedien wurden unter Änderung des Co : Pikolin Verhältnisses eine große Anzahl verschiedener C-Pikolinchloride hergestellt.
Es wird eine neue Fest-Gas-Phasenmethode zur Herstellung ternärer Co-Pikolinmischkomplexe mit verschiedenen Pikolinen beschrieben.
Entsprechend den thermischen und spektralen Untersuchungen hängt die Chemisorption der Liganden aus der Dampfphase von der Stabilität des festen Komplexes und vom Komplexbildungsvermögen des Liganden in der Gasphase ab.