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THE PREPARATION, CHARACTERIZATION AND THERMAL ANALYSIS STUDIES ON COMPLEXES OF COBALT(II) WITH 2-, 3-, 4-CYANOPYRIDINES

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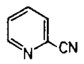
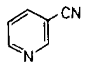
Some complexes of the thiocyanates, chlorides, bromides, iodides, nitrates and sulphates of cobalt(II) with 2-, 3-, 4-cyanopyridines have been prepared. The stereochemical configurations of the complexes were deduced using spectral and magnetic properties. The decomposition of the complexes was studied by thermogravimetry and differential thermal analysis.

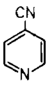
While the coordination chemistry of the cyanopyridines with some transition elements is well documented [1–3] relatively few complexes of cobalt have been studied [4]. This paper describes an investigation into the preparation, thermal analysis, spectroscopic and magnetic properties of the chloride, bromide, iodide, sulphate, nitrate and thiocyanate of cobalt(II) with the 2-, 3- and 4-cyanopyridines.



2-cyanopyridine



3-cyanopyridine



4-cyanopyridine

The cyanopyridines possess two potential donor sites: the pyridine ring nitrogen and the nitrile group, and could thus act as unidentate or bidentate ligands.

Experimental

Four methods of preparation were used to prepare the complexes:

(A) 8 g (33.6 mmol) of the cobalt salt was dissolved in 40 cm^3 ethanol. 5 g (48.0 mmol) of cyanopyridine was dissolved in 40 cm^3 ethanol. The two solutions were then mixed together and heated on a steam bath for 20 minutes. The resulting precipitate was filtered, washed with 20 cm^3 ethanol, 10 cm^3 diethyl ether and dried over calcium chloride.

(B) 7 g (25.0 mmol) of cobalt sulphate was initially dissolved in the minimum amount of water then warmed in 30 cm^3 ethanol. 5 g (48.0 mmol) of cyanopyridine was dissolved in 40 cm^3 ethanol. The two solutions were mixed together and heated on a steam bath for 20 minutes. The resulting precipitate was filtered, washed with ethanol, then diethyl ether and dried over calcium chloride.

(C) 8 g (33.6 mmol) of cobalt salt (Table 1) was dissolved in 30 cm^3 water. 5 g (48.0 mmol) of cyanopyridine was dissolved in 30 cm^3 water. The two solutions were mixed and heated on a steam bath for 30 minutes. The resulting precipitates were filtered, washed with ethanol then diethyl ether and dried over calcium chloride.

(D) The complexes prepared by methods (A)–(C) were heated on a thermobalance at a fixed temperature until a constant weight was obtained.

The complexes prepared by these methods are listed in Table 1. Thermal decomposition studies (Table 2, Figs 1–9) were carried out in static air at a heating rate of

Table 1 Analyses

Complex	Colour	% Cobalt expt	% Cobalt theory	% Anion expt	% Anion theory	Method of preparation
$Co(2\text{-}cypy)_2(NCS)_2$	blue	15.38	15.40	30.28	30.30	A
$Co(3\text{-}cypy)_2(NCS)_2H_2O$	red	14.66	14.70	28.86	28.90	C
$Co(3\text{-}cypy)_2(NCS)_2$	red	15.34	15.40	30.24	30.30	D
$Co(4\text{-}cypy)_2(NCS)_22H_2O$	pink	14.08	14.10	27.68	27.70	C
$Co(4\text{-}cypy)_2(NCS)_2$	pink	15.34	15.40	30.24	30.30	D
$Co(2\text{-}cypy)_4Cl_2H_2O$	yellow	10.42	10.44	12.52	12.56	A
$Co(2\text{-}cypy)_4Cl_2$	yellow	10.76	10.79	12.96	12.97	D
$Co(3\text{-}cypy)_2Cl_2$	violet	17.36	17.43	20.92	20.97	A
$Co(3\text{-}cypy)Cl_2$	lilac	25.60	25.62	30.81	30.83	D
$Co(4\text{-}cypy)_2Cl_2$	violet	17.40	17.43	20.94	20.97	A
$Co(4\text{-}cypy)Cl_2$	lilac	25.60	25.62	30.81	30.83	D
$Co(2\text{-}cypy)_4Br_2$	yellow	9.24	9.27	25.12	25.16	A
$Co(3\text{-}cypy)_4Br_2$	violet	9.25	9.27	25.10	25.16	A
$Co(3\text{-}cypy)_2Br_2$	lilac	13.84	13.90	37.20	37.25	D
$Co(4\text{-}cypy)_2Br_2$	violet	13.86	13.90	37.21	37.25	A
$Co(4\text{-}cypy)Br_2$	yellow	18.20	18.24	49.40	49.49	D
$Co(2\text{-}cypy)_3I_2$	yellow	9.40	9.43	40.56	40.60	A
$Co(3\text{-}cypy)_4I_2$	brown	8.02	8.08	34.72	34.77	A
$Co(4\text{-}cypy)I_24H_2O$	green	12.04	12.06	51.90	51.92	A
$Co(4\text{-}cypy)I_2$	green	14.10	14.13	60.86	60.88	D
$Co(2\text{-}cypy)_2(NO_3)_2$	orange	15.04	15.06	31.66	31.70	A
$Co(3\text{-}cypy)_4(NO_3)_2$	pink	9.76	9.80	20.66	20.70	A
$Co(4\text{-}cypy)_2(NO_3)_2$	pink	15.01	15.06	31.62	31.70	A
$Co(3\text{-}cypy)_2SO_4$	pink	16.18	16.23	25.40	26.43	B
$Co(4\text{-}cypy)_2SO_4$	orange	16.20	16.23	26.41	26.43	A

(cypy = cyanopyridine)

Table 2 TG data

Complex	Expected loss	Calculated	Actual %
Co(2-cypy)$_2$(NCS)$_2$	1 x cypy	27.1	25.3
	1 x cypy + 2 x NCS	62.9	67.4
Co(3-cypy)$_2$(NCS)$_2$H$_2$O	1 x H$_2$O	4.5	4.1
	2 x cypy + 2 x NCS	79.8	78.0
Co(4-cypy)$_2$(NCS)$_2$2H$_2$O	2 x H$_2$O	8.6	8.4
	2 x cypy + 2 x NCS	77.3	76.0
Co(2-cypy)$_4$Cl$_2$H$_2$O	1 x H$_2$O	3.2	5.5
	4 x cypy + Cl$_2$	95.9	93.2
Co(3-cypy)$_2$Cl$_2$	1 x cypy	30.8	31.0
	1 x cypy	30.8	30.4
	Cl$_2$	20.9	15.2
Co(4-cypy)$_2$Cl$_2$	1 x cypy	30.8	29.4
	1 x cypy	30.8	31.4
	Cl$_2$	21.0	15.4
Co(3-cypy)$_4$Br$_2$	2 x cypy	32.8	32.2
	2 x cypy	32.8	33.5
	Br$_2$	25.1	22.2
Co(4-cypy)I$_2$4H$_2$O	4 x H$_2$O	14.7	10.3
	1 x cypy + I$_2$	73.2	72.4
Co(4-cypy)$_2$Br$_2$	1 x (4-cypy)	24.4	24.1
	1 x (4-cypy)	24.4	23.8
	Br$_2$	37.5	34.1

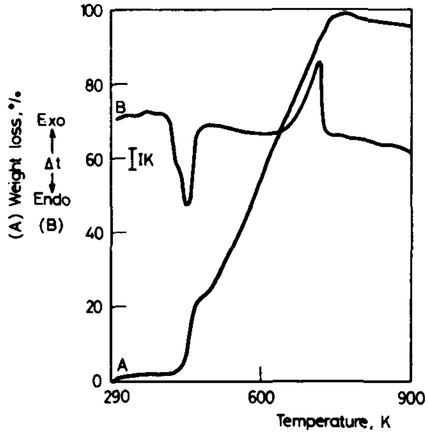


Fig. 1 TG and DTA curves of Co-2-cyanopyridine thiocyanate; sample weight: 54.2 mg

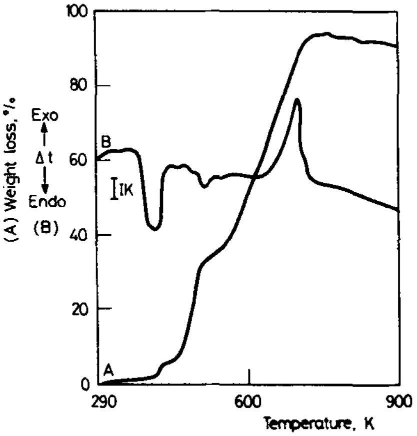


Fig. 2 TG and DTA curves of Co-3-cyanopyridine thiocyanate monohydrate; sample weight: 32.9 mg

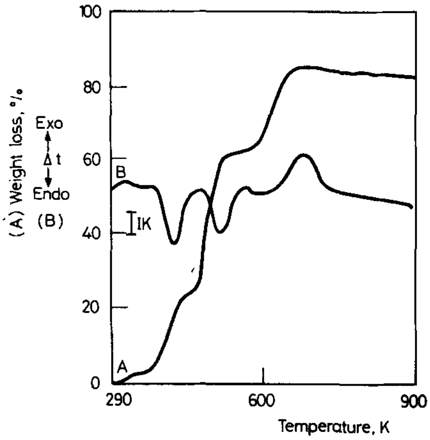


Fig. 3 TG and DTA curves of Co-4-cyanopyridine thiocyanate dihydrate; sample weight: 67.5 mg

6°C/min on a Stanton Redcroft Model TR-01 Thermobalance working at a chart speed of 6 in/hr with DTA attachment. The theoretical weight loss of a ligand was obtained by taking the molecular weight of the ligand being lost over the molecular weight of complex times the actual weight of the complex. This value was then compared to weight loss of ligand from the TG curve. Solid state diffuse electronic spectra (Table 4) were obtained on a Beckmann ACTA M-IV spectrophotometer. Infrared absorption

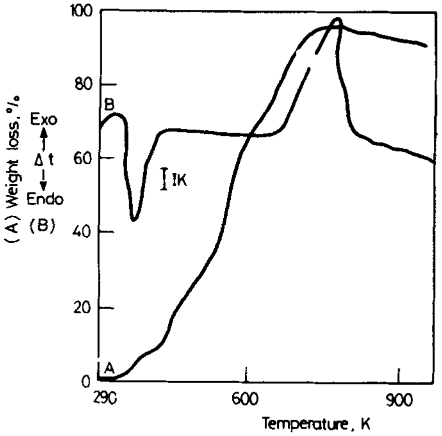


Fig. 4 TG and DTA curves of Co-2-cyanopyridine chloride monohydrate; sample weight: 43.0 mg

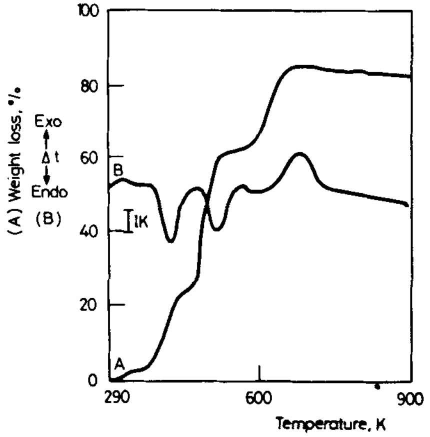


Fig. 5 TG and DTA curves of Co-3-cyanopyridine chloride; sample weight: 32.9 mg

spectra, (Table 5) using KBr discs, 2000–600 cm^{-1} and polyethylene matrix 600–200 cm^{-1} were obtained with a Perkin–Elmer Infrared Spectrophotometer Model 598. Magnetic susceptibility measurements (Table 3) were made by the Gouy Method using a Newport Variable Temperature Balance over the range 300–100 K, and the calibrant $Hg[Co(SCN)_4]$. Diamagnetic corrections were applied using the atomic diamagnetic susceptibilities tabulated by Figgis and Lewis [5]. Corrections

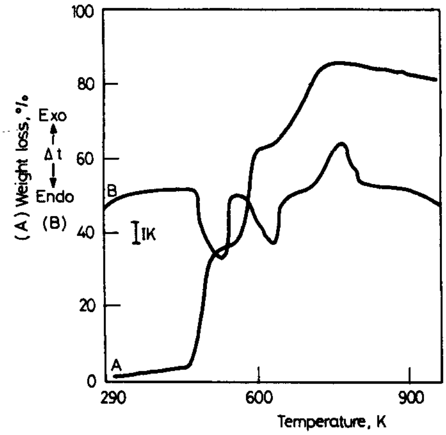


Fig. 6 TG and DTA curves of Co-4-cyanopyridine chloride; sample weight: 56.2 mg

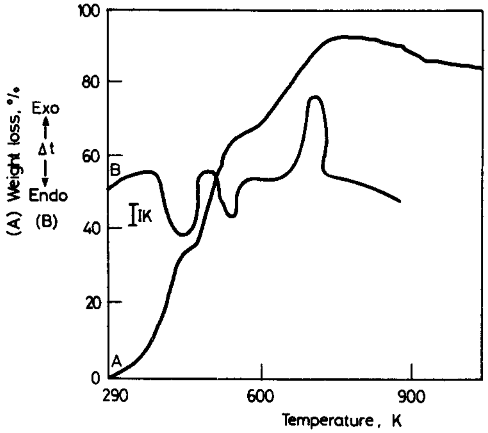


Fig. 7 TG and DTA curves of Co-3-cyanopyridine bromide; sample weight: 74.5 mg

were made for Temperature Independent Paramagnetism in the tetrahedral complexes [6]. The analyses of the cobalt ion was determined by a Perkin–Elmer 373 atomic absorption spectrophotometer using a wavelength of 240.7 nm, the thiocyanate ion using mercuric nitrate [7a], the sulphate ion using barium chloride [7b], the nitrate ion using nitron [7c], the chloride, bromide and iodide ions using Volhards method [7d].

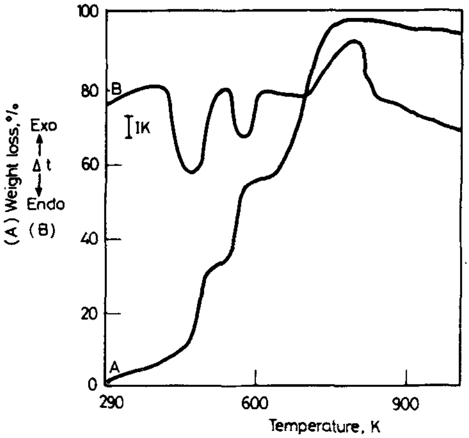


Fig. 8 TG and DTA curves of Co-4-cyanopyridine iodide tetrahydrate; sample weight: 94.0 mg

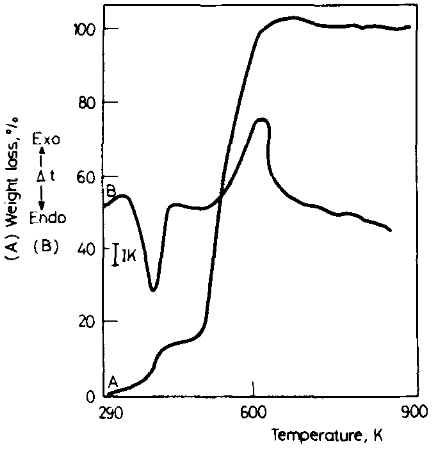


Fig. 9 TG and DTA curves of Co-4-cyanopyridine bromide; sample weight: 112.7 mg

Table 3 Magnetic data

Compound	Temp., K	Diamagnetic correction/10^{-6}	χ_M^{corr} 10^{-6}	μ, Am^2	θ
Co(2-cypy)$_2$(NCS)$_2$	303	130.06	9359	4.36×10^{-23}	6.93
Co(3-cypy)$_2$(NCS)$_2$H$_2$O	296	144.06	9662	4.44×10^{-23}	37.5
Co(4-cypy)$_2$(NCS)$_2$2H$_2$O	293	157.06	11920	4.88×10^{-23}	20.6
Co(2-cypy)$_4$Cl$_2$H$_2$O	298	185.12	12249	4.92×10^{-23}	1.3
Co(3-cypy)$_2$Cl$_2$	296	115.86	12097	4.85×10^{-23}	3.92
Co(4-cypy)$_2$Cl$_2$	293	115.86	12521	4.98×10^{-23}	9.72
Co(2-cypy)$_4$Br$_2$	298	194.52	10782	4.61×10^{-23}	−6.99
Co(3-cypy)$_4$Br$_2$	296	194.52	11652	4.87×10^{-23}	16.2
Co(4-cypy)$_2$Br$_2$	293	138.26	12755	5.07×10^{-23}	20.2
Co(2-cypy)$_3$I$_2$	298	108.39	9809	4.45×10^{-23}	10.4
Co(3-cypy)$_4$I$_2$	300	226.52	12566	5.18×10^{-23}	46.1
Co(4-cypy)$_4$I$_2$4H$_2$O	293	194.13	11553	4.85×10^{-23}	10.9
Co(2-cypy)$_2$(NO$_3$)$_2$	296	106.86	7379	4.23×10^{-23}	−7.38
Co(3-cypy)$_4$(NO$_3$)$_2$	295	163.12	13139	5.17×10^{-23}	16.2
Co(4-cypy)$_2$(NO$_3$)$_2$	297	106.86	10040	4.44×10^{-23}	23.8
Co(3-cypy)$_2$SO$_4$	293	109.16	11573	4.84×10^{-23}	13.0
Co(4-cypy)$_2$SO$_4$	293	109.16	12346	4.70×10^{-23}	6.43

Results and discussion

The complexes prepared, their analyses and methods of preparation are listed in Table 1.

The stoichiometry of the complexes shows that the maximum number of organic ligands present in any one complex is four. All of the complexes are anhydrous with the exception of bis(3-cyanopyridine)cobalt(II)thiocyanate, bis(4-cyanopyridine)cobalt(II)chloride and tris(4-cyanopyridine)cobalt(II)iodide which have respectively one, two and four molecules of water of crystallization attached. The infrared spectrum of the hydrated complexes have a broad band from 3380–3200 cm^{-1} and this is considered to be due to a O—H stretching vibration of the water molecule. Evidence for the water being purely lattice water is given by the absence of a band at 315 cm^{-1} [8]. Furthermore the water is lost below 373 K while coordinated water is lost at a higher temperature [9].

The results of the thermogravimetric studies are given in Figs 1–9 and Table 2. Bis(2-cyanopyridine)cobalt(II)thiocyanate undergoes an endothermic reaction at 443 K with loss of one molecule of 2-cyanopyridine followed by an exothermic reaction at 702 K with the loss of the remaining 2-cyanopyridine, thiocyanate and the formation of Co_3O_4. Bis(3-cyanopyridine)cobalt(II)thiocyanate monohydrate undergoes an endothermic reaction at 373 K with loss of one molecule of water followed by endothermic and exothermic reactions at 431 K and 702 K re-

Table 4 Electronic spectra (cm^{-1})
(a) Octahedral complexes

Complex	$^4T_{1g}(F) \rightarrow$ $^4T_{2g}(F)$	$^4T_{1g}(F) \rightarrow$ $^4A_{2g}(F)$	$^4T_{1g}(F) \rightarrow$ $^4T_{1g}(P)$	Dq	B	β
$Co(4\text{-}cypy)_2(NCS)_2$	7460	16000	20000	857	909	0.83
$Co(2\text{-}cypy)_4Cl_2$	9090	17390	19420	1023	765	0.70
$Co(3\text{-}cypy)_2Cl_2$	8333	16810	23500	1037	958	0.94
$Co(3\text{-}cypy)Cl_2$	6666	15038	17241	763	769	0.70
$Co(4\text{-}cypy)_2Cl_2$	8330	16583	18903	943	778	0.71
$Co(4\text{-}cypy)Cl_2$	8930	17390	19420	1006	775	0.71
$Co(2\text{-}cypy)_4Br_2$	8804		22220	1006	978	0.89
$Co(3\text{-}cypy)_2Br_2$	8330	15160	18900	943	778	0.71
$Co(3\text{-}cypy)_2Br_2$	8333	15504	19417	945	813	0.74
$Co(4\text{-}cypy)_2Br_2$	8333	15698	18382	940	741	0.68
$Co(4\text{-}cypy)Br_2$	8620	16260	18350	970	720	0.68
$Co(3\text{-}cypy)_4I_2$	9090	14390	18350	1017	689	0.63
$Co(4\text{-}cypy)I_2$	6849	14306	24271	784	1005	0.91
$Co(3\text{-}cypy)_2(NO_3)_2$	8930		19610	1007	788	0.72
$Co(3\text{-}cypy)_2SO_4$	8772		20000	993	826	0.75
$Co(4\text{-}cypy)_2SO_4$	8583		20284	975	858	0.78

(b) Tetrahedral complexes

Complex	$^4A_2(F) \rightarrow {}^4T_1(F)$	$^4A_2(F) \rightarrow {}^4T_1(P)$	Dq	B	β
$Co(2\text{-}cypy)_2(NCS)_2$	7463	16000	404	756	0.37
$Co(3\text{-}cypy)_2(NCS)_2$	6060	17300 sh	330	896	0.30
$Co(2\text{-}cypy)_2(NO_3)_2$	6494	19650	354	1033	0.32

spectively with loss of the 3-cyanopyridines, thiocyanate and the formation of Co_3O_4. Bis(4-cyanopyridine)cobalt(II)thiocyanate dihydrate undergoes an endothermic reaction at 339 K with loss of two molecules of water followed by endothermic and exothermic reactions at 443 K and 702 K respectively with loss of the 4-cyanopyridines, thiocyanate and the formation of Co_3O_4.

Tetrakis(2-cyanopyridine)cobalt(II)chloride monohydrate undergoes an endothermic reaction at 360 K with the loss of one molecule of water followed by endothermic and exothermic reactions at 454 K and 773 K respectively with loss of the 2-cyanopyridines, chlorine and the formation of Co_3O_4. Bis(3-cyanopyridine)cobalt(II)chloride undergoes endothermic reactions at 454 K and 510 K with loss of one molecule of 3-cyanopyridine followed by the loss of the other molecule of 3-cyanopyridine to give cobalt(II)chloride. An exothermic reaction takes place at 813 K with loss of chlorine and the formation of Co_3O_4. Bis(4-cyanopyridine)cobalt(II)chloride undergoes two endothermic reactions at 454 K and 527 K with loss of one molecule of 4-cyanopyridine followed by the loss of the other molecule of 4-cyanopyridine and the formation of cobalt(II)chloride. An exothermic

Table 5 Infrared spectra

	$\nu(C\equiv N)$	$\nu(C-C)$ and $\nu(C-N)$			Ring vibrations		$\nu(O-H)$
2-cypy	2242	1585		1436	1048	996	
$\mathrm{Co(2\text{-}cypy)_2(NCS)_2}$	2080	1596		1422	1060	1018	
$\mathrm{Co(2\text{-}cypy)(NCS)_2}$	2100	1602		1412	1066	1012	
$\mathrm{Co(2\text{-}cypy)_4Cl_2H_2O}$	2026	1600		1422	1060	1022	3600–2800
$\mathrm{Co(2\text{-}cypy)_4Cl_2}$	2050	1602		1423	1060	1022	
$\mathrm{Co(2\text{-}cypy)_2Cl_2}$	2005	1604		1422	1050		
$\mathrm{Co(2\text{-}cypy)_4Br_2}$	2020	1600		1422	1060	1022	
$\mathrm{Co(2\text{-}cypy)_3I_2}$	2040	1600		1424	1060	1018	
$\mathrm{Co(2\text{-}cypy)_2(NO_3)_2}$	2060	1600		1422	1060	1027	
3-cypy	2236	1592	1472	1423	1024	974	
$\mathrm{Co(3\text{-}cypy)_2(NCS)_2H_2O}$	2238	1595	1470	1415	1032	970	3400–3260
$\mathrm{Co(3\text{-}cypy)_2(NCS)_2}$	2240	1598	1476	1419	1037	972	
$\mathrm{Co(3\text{-}cypy)_2Cl_2}$	2262	1596	1472	1420	1034	970	
$\mathrm{Co(3\text{-}cypy)Cl_2}$	2264	1600		1420 sh	1040	990	
$\mathrm{Co(3\text{-}cypy)_4Br_2}$	2242	1596	1472	1420	1036	972	
$\mathrm{Co(3\text{-}cypy)_2Br_2}$	2242	1600	1474	1422	1037	988	
$\mathrm{Co(3\text{-}cypy)_4I_2}$	2241	1598	1472	1420	1038	973	
$\mathrm{Co(3\text{-}cypy)_4(NO_3)_2}$	2243	1596	1472	1420	1036	972	
$\mathrm{Co(3\text{-}cypy)_2SO_4}$	2242	1596	1472	1420	1037	975	
4-cypy	2240	1540	1494	1413	1079	988	
$\mathrm{Co(4\text{-}cypy)_2(NCS)_22H_2O}$	2100	1541		1413	1062	1010	3380–3200
$\mathrm{Co(4\text{-}cypy)(NCS)_2}$	2232	1546	1494	1413	1073	1012	
$\mathrm{Co(4\text{-}cypy)_2Cl_2}$	2200	1548	1494	1413	1056	1017	
$\mathrm{Co(4\text{-}cypy)Cl_2}$	2289	1555	1494	1418	1070	1018	
$\mathrm{Co(4\text{-}cypy)_2Br_2}$	2236	1548	1490	1414	1058	1014	
$\mathrm{Co(4\text{-}cypy)Br_2}$	2294	1550	1494	1418	1068	1018	
$\mathrm{Co(4\text{-}cypy)I_24H_2O}$	2262	1548	1492	1412	1058	1018	3300–3350
$\mathrm{Co(4\text{-}cypy)I_2}$	2268	1548	1492	1414	1060	1012	
$\mathrm{Co(4\text{-}cypy)_2(NO_3)_2}$	2282	1548	1490	1413	1061	1012	
$\mathrm{Co(4\text{-}cypy)_2SO_4}$	2236	1542	1496	1412		1012	

reaction takes place at 646 K with loss of chlorine and the formation of Co_3O_4. Tetrakis(3-cyanopyridine)cobalt(II)bromide undergoes an endothermic reaction at 421 K with loss of two molecules of 3-cyanopyridine followed by an endothermic reaction at 477 K with loss of the remaining two molecules of 3-cyanopyridine. An exothermic reaction at 664 K corresponds to the loss of the bromine and the formation of Co_3O_4. Bis(4-cyanopyridine)cobalt(II)bromide undergoes an endothermic reaction at 454 K with loss of one molecule of 4-cyanopyridine followed by another endothermic reaction at 564 K with loss of the remaining molecule of 4-cyanopyridine. A further exothermic reaction at 702 K corresponds to the loss of the bromine and the formation of Co_3O_4. 4-cyanopyridine cobalt(II)iodide tetrahydrate undergoes an endothermic reaction at 395 K with loss of four water molecules and a further exothermic reaction at 780 K with loss of the molecule of 4-cyanopyridine and the iodine.

The complexes would appear to fall into three groups: the hydrated complexes which first dehydrate below 373 K and then decompose at temperatures between 702 K and 773 K directly to Co_3O_4; the anhydrous complexes which similarly decompose between 340 K and 670 K to Co_3O_4 and the anhydrous complexes which give intermediate decomposition products between 420 K and 530 K and eventually decompose to give cobalt(II)chloride and cobalt(II)bromide. Comparison of these complexes to those reported previously for pyridine methylpyridines, ethylpyridines and cobalt(II) [10, 11] show that the trend in decomposition is similar.

The visible spectra of the complexes in Table 4(a) are characteristic of the cobalt(II) ion in an octahedral environment [12]. The observed transitions are ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The absorption bands due to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ were observed for all the complexes and using the values for these bands 10 Dq, β, B were calculated [19]. The absorption band due to the transitions ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ was generally not observed. The complexes have values of 10 Dq > 4400 cm^{-1} [13]. The presence of the ${}^4T_{1g}(F)$ ground state term for these complexes is shown by the variation of the magnetic moment with temperature over the temperature range 300–100 K for the complexes. The complexes have magnetic moments which agree with an octahedral environment for the cobalt ion [5]. The exception is bis(4-cyanopyridine)cobalt(II)nitrate which has a magnetic moment of 444×10^{-23} Am^2. The variation of the magnetic moment for this complex over the temperature range 300–100 K agrees with a T ground state term. The complexes obey the Curie–Weiss law with positive values for θ. The exception is tetrakis(2-cyanopyridine)cobalt(II)bromide which has a negative value for θ. The visible spectra of the complexes in Table 4(b) are characteristic of the cobalt(II) ion in a tetrahedral environment [12]. The observed transitions are ${}^4A_2(F) \rightarrow {}^4T_1(F)$ and ${}^4A_2(F) \rightarrow {}^4T_1(P)$. The values for the absorption bands due to these transitions was used to calculate 10 Dq, β and B [19]. The complexes have values of 10 Dq < 4400 cm^{-1} [13]. The presence of the ${}^4A_2(F)$ ground state term is shown by the fact that the magnetic moments for the complexes do not vary over the temperature range 300–100 K. The compounds have magnetic moments between $4.23–4.45 \times 10^{-23}$ Am^2 which agree with a tetrahedral environment for the cobalt(II) ion [10] and obey the Curie–Weiss law with positive values of θ. The visible spectrum of tris(2-cyanopyridine)cobalt(II)iodide would suggest a trigonal bipyramidal structure [14]. The observed transitions are ${}^4A_2(F) \rightarrow {}^4E(F)$; ${}^4A_2(F) \rightarrow {}^4A_2(P)$. The complex has a magnetic moment which agrees with this structure [14] and obeys the Curie–Weiss law with a positive value of θ. The infrared spectra of the complexes are listed in Table 5. A comparison of the bands in the infrared spectra of the complexes to those of the organic ligand shows that the spectra are similar. The C≡N stretching frequency decreases in the 2-, 4-cyanopyridine complexes while in the 3-cyanopyridine complexes a slight increase is observed for the C≡N stretching vibrations. This is assumed to be due to a resonance effect [2]. This suggests that the organic ligand is not nitrile bonded to the cobalt atom. A conclusion which is further supported by the fact that the vibrations associated with the C—C and C—N bonds do not undergo any appreciable change in wavenumber. This would suggest that the bonding has taken place through the pyridine nitrogen and not through the nitrile nitrogen [1]. This view is further supported by the fact that the infrared spectra shows a change to higher frequency of the bands due to the ring vibrations of the pyridine ring.

Without X-ray analysis no definite structures can be described for the complexes. However chemical analyses as well as spectroscopic and magnetic data enable us to propose structures. The complexes CoL_4X_2 and CoL_2X_2 have octahedral structures. The exceptions are bis(2-cyanopyridine)cobalt(II)thiocyanate, bis(3-cyanopyridine)cobalt(II)thiocyanate and bis(2-cyanopyridine)cobalt(II)nitrate which have tetrahedral structures. The infrared spectrum of bis(2-cyanopyridine) cobalt(II)nitrate has bands at 1390, 830, 1050, 712 cm^{-1} suggesting that the nitrate group is covalently bonded through one oxygen atom [15]. The complex bis(4-cyanopyridine)cobalt(II)nitrate has an octahedral structure. The infrared spectrum of this complex has bands at 782, 1031, 1290 (sh) and 1499 cm^{-1} indicating a bidentate nitrate group [3]. Thus the complex attains six coordinations by chelating with the nitrate groups. The low value for the magnetic moment may be due to packing effect in the crystal [16]. The poor solubility of the other octahedral complexes of stoichiometry CoL_2X_2 would suggest that they have polymer structures [17]. This is further supported by a band at 2142 cm^{-1} in the infrared spectrum of bis(4-cyanopyridine)cobalt(II)thiocyanate which agrees with the presence of bridging thiocyanate groups in the complex [18]. It is suggested that the polymer chain consists of Co—X atoms with the organic ligands bonded above and below the plane of the chain to each cobalt atom through a lone pair of electrons on the ring nitrogen.

The complexes $CoLX_2$ have a double layer chain structure in which each X atom is acting as a bridge between three cobalt atoms with the organic ligands in trans positions [11]. Tris(2-cyanopyridine)cobalt(II)iodide has a trigonal bipyramidal structure.

References

1 R. A. Walton, J. Inorg. Nucl. Chem., 20 (1966) 2229.

2 R. Farha and R. T. Iwamoto, Inorg. Chem., 4 (1965) 844.

3 B. K. Mohapatra and D. V. Ramana Rao, Indian J. Chem., 9 (1971) 715.

4 (a) P. P. Singh and S. A. Khan, Indian J. Chem., 14A (1976) 176.
(b) J. Burgess, Spectrochim. Acta, 24A (1968) 1645.

5 B. N. Figgis and J. Lewis, Modern Coordination Chemistry, ed. J. Lewis & R. G. Wilkins, Interscience, New York, p. 403, 1960.

6 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Co., London, p. 326, 1968.

7 A. I. Vogel, Quantitative Inorganic Analysis, (a) p. 266, (b) p. 402, (c) p. 505, (d) p. 258.

8 M. Goodgame and P. J. Hayward, J. Chem. Soc., (A) (1966) 859.

9 J. R. Allan, G. M. Baillie, N. S. Middlemist and M. J. Pendlowski, J. Thermal Anal., 22 (1981) 3.

10 J. R. Allan and G. M. Baillie, J. Thermal Anal., 14 (1978) 291.

11 J. R. Allan, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, J. Inorg. Nucl. Chem., 26 (1964) 1895.

12 J. R. Allan, D. H. Brown and M. Lappin, J. Inorg. Nucl. Chem., 32 (1970) 2287.

13 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Co., London, p. 324, 1968.

14 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier Publishing Co., London, p. 330, 1968.

15 B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, J. Chem. Soc., (1957) 4222.

16 F. A. Cotton and R. H. Soderberg, J. Am. Chem. Soc., 85 (1963) 2402.

17 J. R. Allan, N. D. Baird and A. L. Kassyk, J. Thermal Anal., 16 (1979) 79.

18 H. N. Ramaswamy and H. B. Jonassen, Inorg. Chem., 11 (1965) 1595.

19 A. B. P. Lever, J. Chem. Educ., 45 (1968) 711.

Zusammenfassung — Komplexe mit 2-, 3-, 4-Zyanopyridinen mit den Chloriden, Bromiden, Jodiden, Nitraten und Sulphaten von Kobalt(II) wurden hergestellt. Die stereochemische Konfigurationen der Komplexe wurden aus spektralen und magnetischen Eigenschaften abgeleitet. Die Zersetzung der Komplexe wurde durch Thermogravometrie und Differentialthermoanalyse untersucht.

Резюме — Получены некоторые комплексы тиоцианатов, хлоридов, бромидов, иодидов, нитратов и сулфатов двухвалентного кобальта с 2-, 3- и 4-цианпиридинами. На основе спектральных и магнитных свойств комплексов, выведены их стереохимические конфигурации. Термическое разложение комплексов было изучено методом термогравиметрии и дифференциального термического анализа.