

Pyridine-Type Complexes of Transition-Metal Halides VII.† Thermal and Structural Properties of Cobalt(II) Halide Complexes Formed with 2-Halogenopyridines

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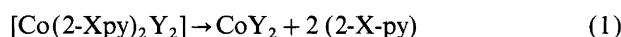
The [Co(2-Xpy)₂Y₂]-type solid, tetrahedral complexes where X = Cl, Br and Y = Cl, Br, I have been prepared from solution, and their thermal properties have been described using the simultaneous TG–DTG–DTA and DSC technique. Vibrations in the mid- and far-infrared spectra have been assigned, and an extra A₂ deformation band was found, reflecting a possible distortion from the C_{2v} symmetry. From the indexed X-ray powder diffractograms of the title compounds the unit cell parameters were calculated. The electronic properties and steric factors which effect the stability of the complexes are described in detail.

Recently there has been much interest in the factors which effect the properties of solid octahedral and tetrahedral complexes of cobalt(II) halides. In some earlier published papers we studied steric effects,¹ ligand polarizability² and the existence of back donation³ in transition-metal(II) halide complexes formed with substituted pyridines.

On the basis of the electronic spectra McWhinnie⁴ suggested tetrahedral coordination for dihalogenobis(2-halogenopyridine)cobalt(II) complexes. The results of Billing and Underhill⁵ and those of Gill and Kingdon⁶ also support the expected symmetry around the central cobalt(II) ion, found to be C_{2v} or lower.

In the far-infrared spectra of these complexes only the metal–ligand and metal–halide stretching vibrations have so far been described,^{7,8} however, eight infrared-active modes would be expected on the basis of C_{2v} symmetry for [M(L)₂X₂]-type complexes.

Mortimer and McNaughton reported the single-step thermal decomposition pathway [eqn. (1)] for the title compounds.⁹



where X = Cl, Br and Y = Cl, Br.

From the results of calorimetric measurements, the mean dissociation energies of the Co–N bonds were calculated⁹ for the cobalt(II) chloride and bromide complexes of 2-chloro- and 2-bromopyridine. Substitution in the second position was found to weaken the Co–N dative bond, although this effect was not marked for the cobalt(II) bromide derivatives.⁹

Recently, we reported on the single-crystal structure of dibromobis(2-bromopyridine)cobalt(II).¹⁰ The present work also deals with the thermal and spectroscopic properties and X-ray powder diffraction characteristics for the title compounds, from which the cobalt(II) iodide derivatives are described for the first time.

Experimental

Preparation of the complexes. The pink hexahydrates of cobalt(II) chloride and bromide and the green cobalt(II) iodide were dehydrated at 300 °C and the anhydrous cobalt(II) halides (0.05 mol) were dissolved in acetonitrile (20 cm³, freshly purified by distillation from P₂O₅). The 2-halogenopyridines, dried over KOH, were blended with 20 cm³ of acetonitrile and added to the reaction mixture from a dropping funnel under stirring.

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Part V. L. Hiltunen, L. Niinistö, G. Kenessey, G. M. Keserü, G. Liptay, *Acta Chem. Scand.* 48 (1994) 456.

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The solutions thus formed were heated and kept at their boiling point for 1 h. During slow cooling crystals were formed and then collected on a glass filter, washed with a small amount of a cool solvent and dried in a desiccator over CaCl_2 . $[\text{Co}(\text{2-Clpy})_2\text{Cl}_2]$, Found: Co 16.3, C 33.7, H 2.3, N 7.9; Calc.: Co 16.51, C 33.65, H 2.26, N 7.85; $[\text{Co}(\text{2-Clpy})_2\text{Br}_2]$, Found: Co 13.4, C 26.8, H 1.7, N 6.3; Calc.: Co 13.22, C 26.94, H 1.81, N 6.28; $[\text{Co}(\text{2-Clpy})_2\text{I}_2]$, Found: Co 10.7, C 22.3, H 1.5, N 5.2; Calc.: Co 10.92, C 22.25, H 1.49, N 5.19; $[\text{Co}(\text{2-Brpy})_2\text{Cl}_2]$, Found: Co 13.1, C 26.7, H 1.9, N 6.3; Calc.: Co 13.22, C 26.94, H 1.81, N 6.28; $[\text{Co}(\text{2-Brpy})_2\text{Br}_2]$, Found: Co 11.1, C 22.9, H 1.4, N 5.2; Calc.: Co 11.02, C 22.96, H 1.51, N 5.24; $[\text{Co}(\text{2-Brpy})_2\text{I}_2]$, Found: Co 9.2, C 19.2, H 1.3, N 4.5; Calc.: Co 9.37, C 19.10, H 1.28, N 4.46.

Thermal analysis. Simultaneous TG–DTG–DTA measurements were made in an argon atmosphere on Seiko TG/TDA 320 equipment of the SSC 5200 series using a sample weight of 5 mg and a heating rate of 5 K min^{-1} . Standard opened-cup aluminium crucibles were used, and $\alpha\text{-Al}_2\text{O}_3$ was chosen as DTA reference.

The quantitative determination of the enthalpy changes were performed using a Perkin–Elmer DSC-7 instrument with a sample weight of 5 mg and a heating rate of 5 K min^{-1} in closed-cup aluminium crucibles. Small holes were made on the lid of the crucible in order to avoid elevated pressure and to let the gaseous products emanate.

Infrared spectra. The far-infrared spectra ($650\text{--}40 \text{ cm}^{-1}$) were obtained on a Digilab FTS spectrophotometer equipped with TGS detector and $6\text{-}\mu\text{m}$ Hylar beam splitter. For sample preparation a Nujol mull and polyethylene matrix were used. Mid-infrared spectra ($4000\text{--}400 \text{ cm}^{-1}$) were measured using KBr pellets.

X-Ray powder diffraction. Solid complexes were analysed in a Guinier–Hägg focusing camera with a diameter of 50 mm, quartz monochromator and $\text{Cu K}\alpha_1$ radiation. Silicon ($a = 5.430880 \text{ \AA}$) was always added as internal standard and used for the correction of the 2θ scale. Film strips were measured with an automatic optical reader¹¹ yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR90, a trial-and-error indexing program.¹² The relatively low de Wolff figures of merit¹³ are more related to the large differences in scattering power of the atoms within these compounds than to inaccuracies in diffraction angles. These refined and indexed monophase X-ray patterns can be obtained upon request from one of the authors (G.K.), or found in the near future in the JCPDS database.

Results

Thermal properties. In Table I we summarize the results of the thermal investigations. T_{max} is the temperature

corresponding to the peak temperature of the DTA and DSC curves. Because of the different experimental conditions (See above) the T_{max} value of the DSC curve is at a higher temperature (maximum 10%) compared to the T_{max} value of the DTA curve for the same compound. This is mainly because of the increased ligand pressure in the DSC closed-cup crucible compared to the opened-cup crucible in the case of the TG–DTG–DTA simultaneous investigation. For the 2-halogenopyridine complexes formed with cobalt(II) halides we observed a single-step decomposition scheme, in agreement with the earlier work of Mortimer and McNaughton.⁹ The pathway was also characteristic for the analogous iodides, which are described for the first time. The differences between our findings and those of Mortimer and McNaughton⁹ were within 5°C for the DSC peak temperature (Table I). However, significant differences are apparent for the enthalpies of the decompositions. These values decrease from the chloride to the iodide derivatives, with the exception of dibromobis(2-chloropyridine)cobalt(II), which has a slightly higher ΔH value than the chloride analogue. The enthalpy values were found to be lower for the 2-bromopyridine complexes than in the case of the 2-chloropyridine analogues, except for the iodide derivatives, where diiodobis(2-bromopyridine)cobalt(II) has a higher enthalpy of decomposition compared to the 2-chloropyridine analogue.

Infrared spectra. The mid- and far-infrared spectra of the compounds are described and assigned for the first time; however, the metal–ligand and metal–halide stretching vibrations have been described earlier,^{7,8} except for the 2-chloro- and 2-bromopyridine complexes of the cobalt(II) iodide.

In the mid-infrared spectra the ligand vibrations were shifted to higher wavenumbers due to coordination (Tables 2 and 3). The only exceptions were the ligand deformation vibrations, which occur at 450, 428 and 444, 415 cm^{-1} in the spectra of the free 2-chloro- and 2-bromopyridine, respectively, and were shifted to lower wavenumbers. In addition to these bands, some new ligand vibrations with low intensities occur in the spectra of the complexes. On the basis of the C_{2v} point group eight infrared-active metal–ligand vibrations are expected. The two $\nu(\text{Co–N})$ stretching vibrations are approximately the same wavenumbers for those complexes having the same 2-halogenopyridine as a ligand, but different halides, although the observed wavenumbers were higher for the 2-chloropyridine derivatives compared to the 2-bromopyridine analogs, representing a stronger coordinative bond. The two $\nu(\text{Co–X})$ (where $X = \text{Cl, Br, I}$) stretching modes were shifted to lower wavenumbers from the chloride to the analogous iodide, as expected. In addition to these four stretching modes four deformation vibrations were assigned, in agreement with the C_{2v} symmetry. These are the $\delta(\text{N–Co–N}) A_1$, $\delta(\text{N–Co–Br}) B_1$ and B_2 and $\delta(\text{Br–Co–Br}) A_1$ bands at relatively low wavenumbers. In each spectrum an extra

Table 1. Summary of the thermoanalytical investigations.

Compounds	TG			DTG	DTA	$\Delta H/\text{mVs mol}^{-1}$	DSC	
	Δm , calc. (%)	Δm , found (%)	$\Delta(\Delta m)$	$T_{\text{max}}/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$		$T_{\text{max}}/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
[Co(2-Clpy) ₂ Cl ₂]	63.6	63.2	-0.4	194	195	146.3	202(207)*	104.8(115.2)*
[Co(2-Clpy) ₂ Br ₂]	50.7	50.9	+0.2	200	203	149.8	222(227)*	109.1(124.8)*
[Co(2-Clpy) ₂ I ₂]	42.1	41.1	-1.0	172	177	143.6	195	45.3
[Co(2-Brpy) ₂ Cl ₂]	70.9	69.9	-1.0	197	201	134.6	225(222)*	105.6(126.5)*
[Co(2-Brpy) ₂ Br ₂]	59.1	58.9	-0.2	201	203	10.9	242(237)*	100.6(129.5)*
[Co(2-Brpy) ₂ I ₂]	50.3	49.6	-0.7	203	204	174.8	234	58.9

* Values in parentheses are from Ref. 9.

Table 2. The infrared spectra of the 2-chloropyridine complexes.

2-Clpy ^a	[Co(2-Clpy) ₂ Cl ₂]	[Co(2-Clpy) ₂ Br ₂]	[Co(2-Clpy) ₂ I ₂]	Assignment
3080	3094	3091	3084	$\nu(\text{CH})$, ν_{20b}
3057	3073	—	3064	$\nu(\text{CH})$, ν_{20a}
1577	1595	1595	1593	$\nu(\text{CC})$, ν_{8a}
1568	1558	1558	1555	$\nu(\text{CC})$, ν_{8b}
1452	1459	1458	1457	$\nu(\text{CC})$, ν_{19a}
1420	1422	1422	1421	$\nu(\text{CC})$, ν_{19a}
1363	1367	1369	1371	$\nu(\text{CC})$, ν_{14}
1288	1293	1291	1289	$\beta(\text{CH})$, ν_3
1150	1175	1174	1174	$\beta(\text{CH})$, ν_{9a}
—	1153	1153	1153	$\beta(\text{CH})$, ν_{9b}
1120	1130	1130	1130	Cl-sens.
—	1110	1110	1110	Cl-sens.
1083	1087	1086	1086	$\beta(\text{CH})$, ν_{18b}
1048	1055	1057	1055	$\beta(\text{CH})$, ν_{18a}
994	1022	1021	1020	Ring
881	888	886	883	$\gamma(\text{CH})$, ν_{10a}
763	763	765	766	$\gamma(\text{CH})$, ν_{10b}
724	729	728	728	$\phi(\text{CC})$, ν_4
620	643	643	642	$\alpha(\text{CCC})$, ν_{6b}
480	480	480	480	$\phi(\text{CC})$, ν_{11}
450	447	445	445	Ring
428	421	420	420	Cl-sens.
313	347	348	347	Cl-sens.
—	333, 312 (334, 313) ^b	259, 244 (259, 254) ^b	239, 203	$\nu(\text{Co-X})$
—	228, 212 (222) ^b	228, 209 (222) ^b	225, 209	$\nu(\text{Co-N})$
—	187	169	150	$\delta(\text{N-Co-X})$ ^c
—	133, 117	126, 95	122, 88	$\delta(\text{N-Co-X})$
—	109	91	84	$\delta(\text{N-Co-X})$
—	140	137	137	$\delta(\text{N-Co-N})$

^aGreen, J. H. S. and Barnard, P. W. B. *J. Chem. Soc.* (1963) 640. ^bValues in parentheses are from Ref. 4. ^cRaman-active only in the C_{2v} point group.

band occurs with increased intensity and lowered wavenumber on going from the chloride to the analogous iodide, indicating a possible anion effect. These bands have higher wavenumbers for the analogous 2-chloropyridine than for the 2-bromopyridine compounds, showing nitrogen participation. We assigned these bands as $\delta(\text{N-Co-X})$ A_2 modes, which are Raman-active only in the C_{2v} point group. The appearance of these bands shows a possible distortion from ideal C_{2v} symmetry.

X-Ray powder diffraction. In Table 4 we summarize the results of the structural investigations. All complexes have triclinic symmetry and are closely related to each other, especially the cobalt(II) chloride and bromide

derivatives of 2-bromopyridine. The volume of the unit cell increases on going from the chloride to the analogous iodide, as does the molecular weight, resulting in increasing densities.

Discussion

The stabilities of the substituted pyridine complexes are mainly interpreted in terms of the basicity of the ligand, the effect of the substituents and the choice of anion.

Because of the negative inductive effect of the halogeno substituent the basicity of halogenopyridines are small compared to pyridine or other substituted pyridines having substituents with a positive inductive effect.

Table 3. The infrared spectra of the 2-bromopyridine complexes.

2-Brpy ^a	[Co(2-Brpy) ₂ Cl ₂]	[Co(2-Brpy) ₂ Br ₂]	[Co(2-Brpy) ₂ I ₂]	Assignment
3069	3090	3088	3081	v(CH), v _{20a}
1573	1588	1587	1586	v(CH), v _{8a}
1565	1553	1552	1551	v(CC), v _{8b}
1452	1457	1456	1454	v(CC), v _{19a}
1417	1417	1416	1415	v(CC), v _{19b}
1282	1289	1289	1287	β(CH), v ₃
1146	1152	1153	1153	β(CH), v _{9a}
1104	1117	1114	1115	Br-sens.
1079	1080	1080	1079	β(CH), v _{18b}
1041	1056	1055	1054	β(CH), v _{18a}
991	1020	1019	1018	Ring
882	887	885	—	γ(CH), v _{10a}
761	759	760	763	γ(CH), v _{10b}
722	724	723	—	φ(CC), v ₄
701	703	703	703	Br-sens.
615	642	642	642	α(CCC), v _{6b}
457	467	469	466	φ(CC), v _{16b}
444	441	440	440	Ring
415	414	416	416	Ring
404	407	406	406	φ(CC), v _{16a}
315	339	339	339	Br-sens.
—	330, 319 (327, 319) ^b	252, 237 (246, 234) ^b	228, 194	v(Co-X)
265	278	278	280	Br-sens.
—	219, 206 (222) ^b	216, 202 (222) ^b	218, 203	v(Co-N)
—	178	162	147	δ(N-Co-X) ^c
—	125, 119	122, 97	122, 91	δ(N-Co-X)
—	91	77	67	δ(X-Co-X)
—	134	134	128	δ(N-Co-N)

^aGreen, J. H. S., Kynastom, W. and Bailey, H. M. *Spectrochim. Acta* (1963) 549. ^bValues in parentheses are from Ref. 4. ^cRaman-active only in the C_{2v} point group.

Table 4. Summary of the structural studies.

Compound	[Co(2-Clpy) ₂ X ₂]			[Co(2-Brpy) ₂ X ₂]		
	Cl	Br	I	Cl	Br	I
X ₂	Cl	Br	I	Cl	Br	I
Symmetry	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	7.54(1)	8.62(1)	8.83(3)	7.992(6)	8.019(7)	7.521(9)
b/Å	7.889(9)	9.61(1)	8.09(2)	8.574(5)	8.694(3)	7.8705
c/Å	10.70(2)	10.57(1)	13.90(8)	11.134(7)	11.352(7)	7.294(9)
α/°	91.5(2)	93.1(1)	94.0(4)	84.7(1)	84.71(6)	102.4(1)
β/°	111.7(2)	71.8(1)	124.6(3)	78.26(9)	78.43(5)	106.57(8)
γ/°	67.2(2)	128.59(7)	69.7(2)	69.16(4)	69.80(5)	97.14(8)
V/Å ³	547.0	638.2	756.3	697.9	727.5	396.2
M	356.9	445.8	539.8	445.8	534.7	628.7
Z	2	2	2	2	2	1
D ₀ /g cm ⁻³	2.17	2.32	2.37	2.12	2.44	2.63
x (no. of lines)	20	20	20	20	20	14
M(x) ^a	9	9	10	16	12	16
F(x) ^b	19	19	19	29	21	12

^aSee Ref. (13). ^b*J. Appl. Crystallogr.* 12 (1979) 60.

Therefore the σ-bonding properties of the halogenopyridines are weaker and the enthalpy of the decomposition thus smaller than for the analogous pyridine.¹⁴

For pyridine-type complexes there is a possibility of stabilization via back donation of electrons from the central metal ion to the non-bonding π-orbitals of the nitrogen. These back-donated electrons enter into the delocalized π-system of the pyridine ring and stabilize mainly in the 2-, 4- and 6-positions. Electron-with-

drawing substituents, such as halogeno groups, in the second position increase the electron density in the 2-, 4- and 6-positions, back donation is hindered. This also weakens the metal-nitrogen bond.

These effects are more marked for the more polarizable bromide, as is apparent from the smaller enthalpy of decomposition and the lower v(Co-N) wavenumbers for the 2-bromopyridine complexes compared to the 2-chloropyridine derivatives.

On the other hand, there is no anion effect according to the $\nu(\text{Co-N})$ stretching frequencies, although the temperature and the enthalpy of the decomposition are strongly dependent on the anion. These observations can be interpreted taking into account steric interactions, which are marked for those pyridine complexes having a substituent in the second position. The steric hindrance increases with the increasing ionic radii of the halides, i.e. from the chloride to the iodide, and are larger for the 2-bromopyridine than for the 2-chloropyridine. The steric interaction causes a deviation from the C_{2v} symmetry, which was proved by the assignment of the $\delta(\text{N-Co-X}) A_2$ band and the observed increase in its intensity from the chloride to the iodide derivatives. This distortion was also found in the structure of dibromobis(2-bromopyridine)cobalt(II).¹⁰ The greater space requirement of the larger halides can also be easily seen from the larger cell volumes. However, it is noteworthy that these effects mainly reflect the properties of the iodide complexes and are much less marked for the analogous chloride and bromide.

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