Thermochimica Acta, 113 (1987) 161–169
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOGRAVIMETRIC ANALYSIS OF COBALT(II) HALIDE COMPLEXES WITH A SERIES OF SUBSTITUTED PYRIDINE LIGANDS

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(Received 4 August 1986)

ABSTRACT

In this study we compare the thermal decompositions and the presence of stable intermediates for $Co(R{-}py)_2X_2$ complexes where R-py are variously substituted pyridines and X is Cl or Br.

INTRODUCTION

The CoL_2X_2 complexes exist either as tetrahedral monomers or as octahedral polymers containing bridging halide groups. The factors which determine the occurrence of one stereochemistry over another have been discussed by various authors [1–3]. The observed coordination number of the cobalt ion depends upon: (1) the nature and position of the substituents in the pyridine ring; (2) the halides of the cobalt salt; and (3) in some cases, the controlled heating of the reaction mixture [4]. Some thermochemical work on a limited series of $Co(R{-}py)_2X_2$ complexes have been reported by various investigators [5–7]. An idealised scheme of decomposition was proposed as:

$$CoL_2X_2(tet) \rightarrow CoL_2X_2(oct) \rightarrow CoL_{2/3}X_2(oct) \rightarrow CoX_2(oct)$$

Bearing in mind the difficulties associated with the reproducibility and the accuracy obtainable in quantitative thermogravimetric studies of previous reports and because no thermochemical analysis of an extensive series of cobalt pyridine complexes had ever been reported, we have carried out this study.

0040-6031/87/$03.50

EXPERIMENTAL

The $Co(R{-}py)_2X_2$ complexes were prepared by direct reaction in ethanol of the cobalt halide with the substituted pyridine ligand in a 1 : 2 ratio, as described in the literature [8,9]. Precipitation of the crystalline product occurred either immediately or after cooling the solution. Where possible, the compounds were recrystallised from ethanol, washed with dry ether and allowed to dry overnight over silica gel under reduced pressure. The thermal measurements were recorded on a DuPont R90 thermal analyzer equipped with a 951 TGA balance in a N_2 gas flow (20 ml min^{-1}) at ambient pressure. A heating rate of 10°C min^{-1} was chosen. In cases where the TG curve indicated the possibility of stable intermediates, a heating rate of 5°C min^{-1} or 1°C min^{-1} was applied, because at this rate it may be determined whether or not successive reactions can be separated [10].

RESULTS

Thermogravimetric data of 39 cobalt–pyridine complexes are reported in Tables 1–4. The majority of the coordination compounds decompose to their appropriate cobalt halides directly, or by way of intermediates which were characterised by the stoichiometric compounds assigned to the inflections in the thermal decomposition curves. In some cases, a distinct plateau was observed, which indicates some thermal stability of the intermediate products over a defined temperature region. The decomposition of the complexes occurs according to the following reactions:

$$ML_2X_2(s) \rightarrow MLX_2(s) \quad + L(g) \qquad (1)$$

$$ML_2X_2(s) \rightarrow ML_{5/3}X_2(s) \quad + 1/3L(g) \qquad (1a)$$

$$ML_{5/3}X_2(s) \rightarrow MLX_2(s) \quad + 2/3L(g) \qquad (1bc)$$

$$MLX_2(s) \rightarrow MX_2(s) \quad + L(g) \qquad (2)$$

$$MLX_2(s) \rightarrow ML_{2/3}X_2(s) \quad + 1/3L(g) \qquad (2a)$$

$$ML_{2/3}X_2(s) \rightarrow ML_{1/3}X_2(s) \quad + 1/3L(g) \qquad (2b)$$

$$ML_{1/3}X_2(s) \rightarrow MX_2(s) \quad + 1/3L(g) \qquad (2c)$$

$$ML_2X_2(s) \rightarrow MX_2(s) \quad + 2L(g) \qquad (3)$$

where, by definition, the numbers 1 and 2 refer to the loss of the first and second pyridine ligands, respectively, and a, b and c define the partial decomposition of the ligand. Reaction (3) refers to the simultaneous separation of the two pyridine ligands without the formation of a stable intermediate, as no stoichiometric compound can be assigned to the curve inflections. In Table 3, reaction (4) stands for the decomposition of the

TABLE 1

Decomposition according to the general scheme

Complex	Reaction	Stable product	Temperature-range (°C)			Weight loss (%)	
			T_i	T_m	T_f	Obs.	Calc.
$Co(3\text{-}Clpy)_2Cl_2$	(1)	yes	149	169	174	32.0	31.8
	(2)	yes	221	243	249	32.0	31.8
$Co(3\text{-}Clpy)_2Br_2$	(1)	yes	156	176	183	26.0	25.5
	(2)	yes	208	235	240	26.0	25.5
$Co(3\text{-}Brpy)_2Cl_2$	(1)	yes	164	185	192	35.5	35.4
	(2)	yes	225	247	257	34.5	35.4
$Co(3\text{-}Brpy)_2Br_2$	(1)	yes	163	183	190	29.5	29.5
	(2)	yes	218	241	250	29.5	29.5
$Co(4\text{-}NCpy)_2Cl_2$	(1)	yes	171	188	195	30.0	30.8
	(2ab)	yes	247	265	272	22.5	20.5
	(2c)	yes	314	331	340	9.5	10.3
$Co(4\text{-}NCpy)_2Br_2$	(1)	yes	156	181	186	22.3	24.4
	(2ab)	no	238	262	269	17.6	16.3
	(2c)	yes	295	310	321	7.0	8.1
$Co(py)_2Cl_2$	(1a)	no	109	124	–[c]	27.5	27.5
	(1bc)	yes	–	143	148		
	(2a)	yes	191	205	210	9.0	9.2
	(2bc)	yes	243	263	270	17.0	18.3
$Co(py)_2Br_2$	(1a)	no	170	196	–[c]	21.0	21.0
	(1bc)	no	–	201	202		
	(2a)	no	204	218	221	6.8	7.0
	(2bc)	yes	230	249	254	13.5	14.0
$Co(3\text{-}CH_3py)_2Cl_2$	(1)	no	140	166	171	29.0	29.5
	(2a)	yes	174	184	187	10.0	9.8
	$(\text{-}CH_3)$[a]	no	217	228	237	≈ 5	4.7
	(2bc)	yes	236	262	269	20.0	19.6
$Co(4\text{-}CH_3py)_2Cl_2$	(1)	yes	139	162	166	29.3	29.5
	(2a)	yes	197	213	218	9.5	9.8
	(2b)	no	247	265	–[c]	19.8	19.6
	(2c)	yes	–	277	281		
$Co(3\text{-}HOOCpy)_2Cl_2$[e]	(1) + (2a)	yes	229	241	245	42.8	43.6
	(2bc)	no[b]	365	375	379	24.4	21.8
$Co(3\text{-}HOOCpy)_2Br_2$	(1) + (2a)	no	243	275	291	36.0	35.3
	(2bc)	no[b]	373	403	413	22.0	17.7
$Co(3,4\text{-}di\text{-}CH_3py)_2Cl_2$	(1) + (2a)	yes	200	232	239	42.0	41.5
	(2bc)	yes	289	301	305	20.3	20.8
$Co(4\text{-}C_2H_5py)_2Cl_2$	(1) + (2ab)	no	225	263	–	50.0	51.9
	(2c)	yes	–	283	289	10.5	10.4
$Co(4\text{-}C_6H_5COpy)_2Cl_2$	(1) + (2a)	no	234	258	–	49.0	49.2
	(2bc)	yes	–	310	314	23.8	24.6
$Co(4\text{-}C_6H_5py)_2Cl_2$	(1) + (2a)	no	241	269	276	≈ 47	47.0
	(2b)	no	298	310	–[c]	≈ 23	23.5
	(2c)	yes	–	346	353		

TABLE 1 (continued)

Complex	Reaction	Stable product	Temperature-range (°C)			Weight loss (%)	
			T_i	T_m	T_f	Obs.	Calc.
Co(3-CH_3COpy)$_2$$Cl_2$	(1)+(2a)	no	199	225	233	41.0	43.4
	(2b)	no	264	289	–[c]	21.5	21.7
	(2c)	yes	–	331	338		
Co(4-CH_3COpy)$_2$$Cl_2$	(1)	no	219	245	249	32.0	32.6
	(2a)	no	276	340	346	10.0	10.9
	(2bc)+(4)	no	438	516	–		
Co(3-CH_3OCOpy)$_2$$Cl_2$	(1)	yes	162	182	187	33.5	33.9
	(2ab)	yes	248	265	270	24.0	22.6
Co(3-CH_3OCOpy)$_2$$Br_2$	(1)	no	161	181	188	27.3	27.8
	(2a)	yes	219	230	233	11.6	9.2
Co(4-CH_3OCOpy)$_2$$Cl_2$	(1)+(2a)	no	174	195	200	45.3	45.2
	(-Ac)	yes	235	248	256	≈16	14.6
Co(4-CH_3OCOpy)$_2$$Br_2$	(1a)	no	172	185	–[c]	25.5	27.8
	(1bc)	yes	–	194	206		
Co(3-H_2NCOpy)$_2$$Cl_2$	(1)+(2a)	no	267	291	296	43.5	43.5
	(2bc)	no	320	346	–[d]		
Co(3-H_2NCOpy)$_2$$Br_2$	(1)+(2ab)	no	257	278	303		44.0
Co(4-H_2NCOpy)$_2$$Cl_2$	(1)	no	278	304	–[c]	54.0	54.0
	(2ab)	no	–	326	336		
Co(4-H_2NCOpy)$_2$$Br_2$	(1)	no	266	281	–[c]	42.0	44.0
	(2a)	no	–	290	–[c]		
	(2b)	no	–	310	318		

[a] An intermediate step is observed corresponding to a weight loss of the methyl group.
[b] The cobalt halides start to decompose above 380°C.
[c] Impossible to determine because of absence of plateau.
[d] Beyond the range studied.
[e] Recorded at a heating rate of 1°C min^{-1}.

TABLE 2

Decomposition with no characterisable intermediates and formation of stable cobalt halides

Complex	Reaction	Temperature-range (°C)			Weight loss (%)	
		T	T_m	T_f	Obs.	Calc.
Co(4-C_6H_5COpy)$_2$$Br_2$	(3)	233	269 295 [a]	301	63.5	62.6
Co(3-C_6H_5COpy)$_2$$Cl_2$	(3)	182	228 [a] 272	277	75.0	73.8
Co(3-C_6H_5COpy)$_2$$Br_2$	(3)	231	291 [a] 320	322	61.5	62.6
Co(3-CH_3py)$_2$$Br_2$	(3)	217	289	293	45.0	46.0
Co(4-CH_3py)$_2$$Br_2$	(3)	218	293	296	46.0	46.0
Co(3,4-di-CH_3py)$_2$$Br_2$	(3)	230	304	313	49.0	49.5
Co(4-C_2H_5py)$_2$$Br_2$	(3)	215	290	295	49.5	49.5
Co(4-C_6H_5py)$_2$$Br_2$	(3)	246	311	336	56.5	58.7

[a] A second maximum on the DTG curve is observed.

TABLE 3

Decomposition with no characterisable intermediates and decomposition of the cobalt halides ($T > 300°C$)

Complex	Reaction	Temperature-range (°C)			
		T	T_i	T_m	T_f
$Co(4\text{-}HOpy)_2Cl_2$	(3)	265	280	363 [a]	488
	(4)	–	–	473	–
$Co(4\text{-}H_2Npy)_2Cl_2$	(3)	253	279	334	413
	(4)	–	–	385	–
$Co(4\text{-}(CH_3)_2Npy)_2Cl_2$	(3)	253	267	286	420
	(4)	–	–	403	–
$Co(4\text{-}(CH_3)_2Npy)_2Br_2$	(3)	268	277	293	420
	(4)	–	–	398	–

[a] A second maximum on the DTG curve is observed.

TABLE 4

Irregular thermal behaviour and decomposition

Complex	Stable product	Temperature-range (°C)			Weight loss (%)	
		T_i	T_m	T_f	Obs.	Calc.
$Co(4\text{-}(CH_3)_3Cpy)_2Cl_2$	no	229	273	278	52.5	52.5
	no	302	319	325	13.0	15.0
$Co(3\text{-}CH_3COpy)_2Br_2$	see text					
$Co(4\text{-}CH_3COpy)_2Br_2$	see text					

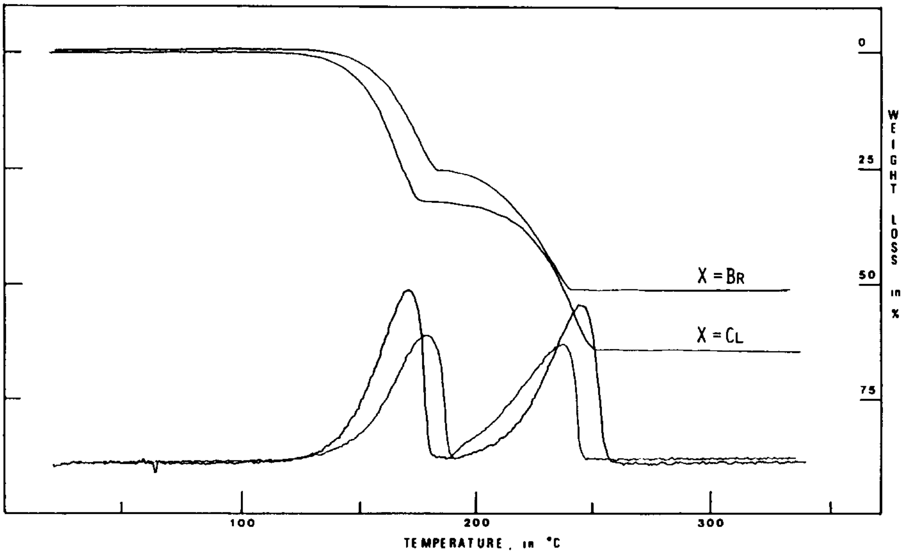

Fig. 1. TG and DTG of $Co(3\text{-}Clpy)_2X_2$.

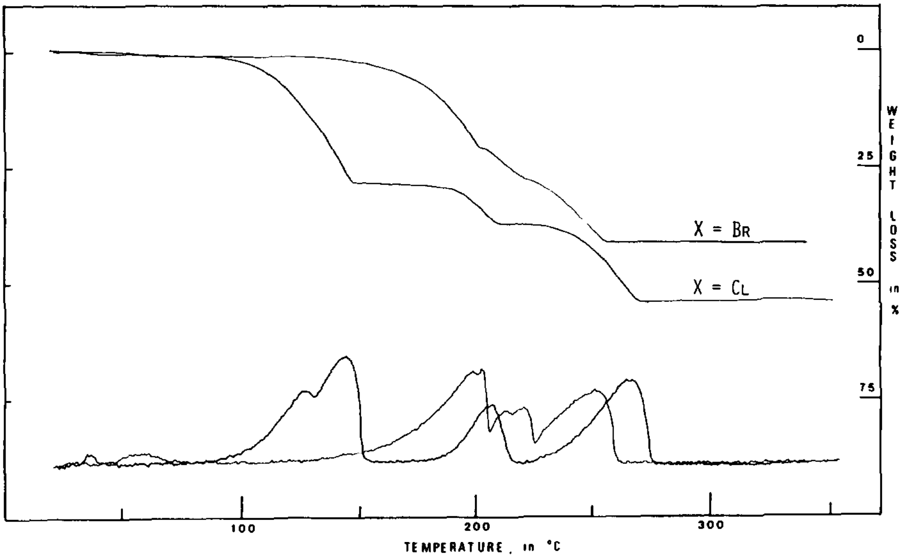

Fig. 2. TG and DTG of Co(py)$_2$X$_2$.

cobalt halides. No thermal measurements could be obtained for Co(3-CH$_3$COpy)$_2$Br$_2$ and Co(4-CH$_3$COpy)$_2$Br$_2$, even by the lowest heating rate available (1°C min^{-1}), because of their spattering behaviour. Some exam-

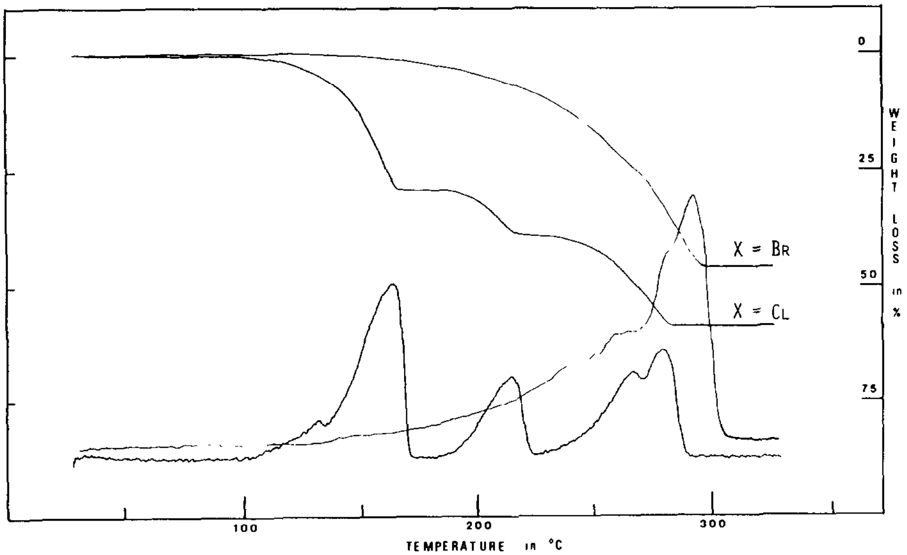

Fig. 3. TG and DTG of Co(4-CH$_3$py)$_2$X$_2$.

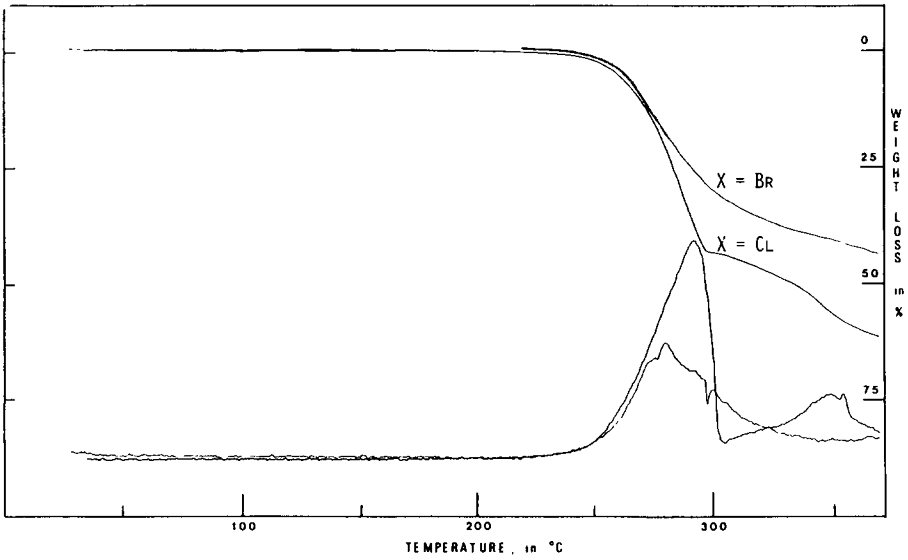

Fig. 4. TG and DTG of $Co(3\text{-}H_2NCOpy)_2X_2$.

ples of the thermograms are shown in Figs. 1–4, together with the curve derivative (DTG).

DISCUSSION

Stable intermediates of the thermal decomposition of $Co(R\text{–}py)_2X_2$ complexes are expected, as the intermediates of type $Co(R\text{–}py)_1X_2$ and $Co(R\text{–}py)_{2/3}X_2$ can form double and triple chain structures, respectively, in which each halogen is acting as a bridge between three cobalt ions [11]. The double chain structure of $Co(R\text{–}py)_1X_2$ with R–py = L is shown in Fig. 5. The fact that for the $Co(py)_2X_2$ complexes the first weight loss corresponds to the partial decomposition reactions (1a) and (1bc), rather than to the separation of a whole ligand unit which is observed for most substituted pyridine complexes, may imply the strong bonding between Co and N in the $Co(py)_2X_2$ complexes.

This is supported by: (1) Gill's statement [12] that pyridine can behave as π-acceptor; and (2) the proposition of King et al. [8] that the extent of M–L π-bonding was dependent on the π-acceptor capacity of the ligand, which in the case of substituted pyridines is controlled by the effect of its substituents. It is apparent from the data in the tables that most chloro-complexes start to decompose at a lower initial temperature and also extend over a longer temperature range than the corresponding bromo analogues. A possible explanation for the greater thermal stability of the CoL_2Br_2 com-

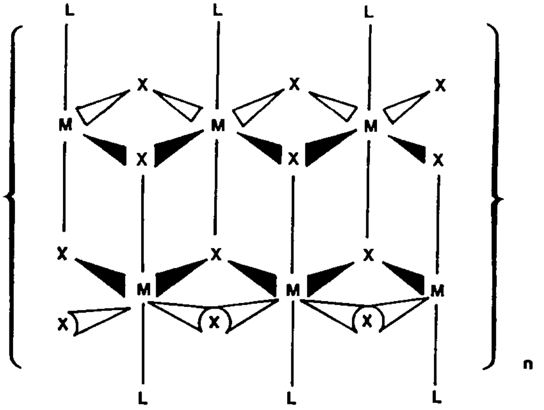

Fig. 5. Diagrammatic view of the structure of $CoLX_2$ polymers.

plexes lies in the more readily polarizable bromine atom which allows total Co–N bond strengthening by encouraging any back-bonding from the cobalt to the nitrogen in pyridine. The analysis of the force constants of $[Zn(py)_2Cl_2]$ and $[Zn(py)_2Br_2]$ performed by Wong [13], showed indeed that the Zn–N bond in the bromo complex is stronger than in the chloro complex. The cyanopyridine complexes decompose via the $CoLX_2$ and $CoL_{1/3}X_2$ intermediates to their cobalt halides. However, the decomposition of such intermediates occurs at relatively high temperatures when compared to other complexes of the same group. We must consider the possibility that cyanopyridines may coordinate through the nitrile or the ring nitrogen atoms and both may be involved in coordination to produce thermally stable polymers. Polymerization of cobalt complexes by coordination of the nitrile groups have been reported by Farha and Iwamoto [14].

Of special interest is the fact that decomposition temperatures are influenced by the stereochemistry, they are reportedly higher for smaller coordination number (CN). Examples are found in Table 5, together with some relevant spectroscopic data.

TABLE 5

Decomposition temperature, coordination number and some spectroscopic data of some cobalt(II) halide pyridine complexes

Compound	T (°C)	νCo–N (cm^{-1})	*CN*	λ_{max} (nm)
$Co(py)_2Cl_2$	104	233	6	525
$Co(py)_2Br_2$	166	253	4	620
$Co(4\text{-}C_6H_5py)_2Cl_2$	223	210	6	
$Co(4\text{-}C_6H_5py)_2Br_2$	248	235	4	

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