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THE THERMAL DECOMPOSITION OF TRANSITION-METAL COMPLEXES CONTAINING HETEROCYCLIC LIGANDS

3. SUBSTITUTED PYRIDINE COMPLEXES OF COBALT

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ABSTRACT

Enthalpies of the overall decomposition reactions

$$CoX_2L_2(c) \rightarrow CoX_2(c)+2L(g)$$

and of the intermediate stepwise loss of ligand, L, where X is Cl or Br, and L is 3-chloropyridine, 3-bromopyridine, 2-chloropyridine, 2-bromopyridine, or 2-methoxypyridine have been measured by use of a differential scanning calorimeter. Enthalpies of sublimation of $CoCl_2$(3-chloropyridine)$_2$, $CoBr_2$(3-chloropyridine)$_2$, $CoCl_2$(3-bromopyridine)$_2$, $CoCl_2$(2-chloropyridine)$_2$, $CoCl_2$(2-bromopyridine)$_2$, $CoBr_2$(2-bromopyridine)$_2$, $CoCl_2$(2-methylpyridine)$_2$ and $CoBr_2$(2-methylpyridine)$_2$ have been determined. Values of the cobalt–nitrogen bond dissociation energies have been calculated. Specific heats of a number of the complexes are reported.

INTRODUCTION

In the first[1] and second[2] papers of this series we reported enthalpies of thermal decomposition of complexes CoX_2L_2, where X is Cl or Br, and L is benzothiazole or benzoxazole. From these data and enthalpies of sublimation, values of the cobalt–nitrogen and cobalt–oxygen bond dissociation energies in the complexes were calculated. We now present corresponding data for complexes in which the ligand L is 3-chloropyridine (3Clpy), 3-bromopyridine (3Brpy), 2-chloropyridine (2Clpy), 2-bromopyridine (2Brpy), 2-methoxypyridine (2MeOpy), and 2-methylpyridine (2Mepy).

The overall decomposition reaction (1) was divided into two stages, reactions (2) and (3). For the complex $CoBr_2(2MeOpy)_2$, decomposition resulted in the loss of one ligand to yield a liquid product, reaction (4).

$$CoX_2L_2(c) \rightarrow CoX_2(c) + 2L(g) \qquad (1)$$

$$CoX_2L_2(c) \rightarrow CoX_2L(c) + L(g) \qquad (2)$$

$$\mathrm{CoX_2L(c)} \rightarrow \mathrm{CoX_2(c)} + \mathrm{L(g)} \qquad (3)$$

$$\mathrm{CoBr_2(2MeOpy)_2(c)} \rightarrow \mathrm{CoBr_2(2MeOpy)(liq)} + \mathrm{2MeOpy(g)} \qquad (4)$$

EXPERIMENTAL

The complexes were prepared by the addition of alcoholic solutions of ligands and metal halide, and purity was established by microanalysis for C, H and N. The Perkin-Elmer differential scanning calorimeter (DSC-1) was used to measure the enthalpies of thermal decompositions in a nitrogen atmosphere, by a procedure referred to previously[3]. The scan rate was 16 K min^{-1} in all experiments and the sensitivity was 2, 4, or 8 mcal(full scale deflection)$^{-1}$ sec^{-1}. The instrument was calibrated by use of the enthalpy of fusion of indium (0.78 kcal mol^{-1}) and checked as before[1]. Specific heat data were obtained by use of the differential scanning calorimeter according to the method described by O'Neill[4]. Enthalpies of sublimation were obtained by use of a Dupont thermal analyser according to Ashcroft's method[5].

RESULTS

Enthalpies of the stepwise and overall decomposition reactions are shown in Table 1. The symbols T_i, T_p, and T_f refer to the initial, peak (where the rate of ΔH change was greatest), and final temperatures of the dissociation reaction, respectively,

TABLE 1

ENTHALPIES OF STEPWISE AND OVERALL DECOMPOSITION OF $\mathrm{CoX_2L_2}$

Complex	*Reaction*	*ΔH (kcal mol^{-1})*	*T_i (K)*	*T_p (K)*	*T_f (K)*	*Weight loss (%)*	
						obs.	*calc.*
$\mathrm{CoCl_2(3Clpy)_2}$	(2)	14.6±0.3	425	490	500	32.8±0.1	31.81
	(3)	17.6±0.3	520	585	595		
	(1)	32.2±0.6	(T_m = 540 K)			65.0±0.6	63.63
$\mathrm{CoBr_2(3Clpy)_2}$	(2)	17.0±0.2	430	505	515	26.8±0.1	25.46
	(3)	17.1±0.4	515	580	590		
	(1)	34.1±0.6	(T_m = 545 K)			51.4±0.3	50.92
$\mathrm{CoCl_2(3Brpy)_2}$	(2)	14.3±0.2	470	520	530	40.1±0.4	35.44
	(3)	17.8±0.1	540	600	610		
	(1)	32.1±0.3	(T_m = 560 K)			71.5±0.2	70.88
$\mathrm{CoBr_2(3Brpy)_2}$	(2)	15.7±0.2	460	520	530	33.1±0.1	29.54
	(3)	18.4±0.2	530	590	595		
	(1)	34.1±0.4	(T_m = 555 K)			59.1±0.9	59.09
$\mathrm{CoCl_2(2Clpy)_2}$	(1)	27.5±0.2	420	480	490	63.2±0.5	63.63
$\mathrm{CoBr_2(2Clpy)_2}$	(1)	29.8±0.3	430	500	520	51.1±0.3	50.92
$\mathrm{CoCl_2(2Brpy)_2}$	(1)	30.2±0.3	430	495	510	69.0±0.2	70.88
$\mathrm{CoBr_2(2Brpy)_2}$	(1)	30.9±0.4	440	510	520	57.6±0.2	59.09
$\mathrm{CoCl_2(2MeOpy)_2}$	(2)	13.2±0.4	390	430	440	28.7±2.2	31.35
$\mathrm{CoBr_2(2MeOpy)_2}$	(4)	12.7±0.3	405	440	480	27.0±1.1	24.97

and T_m is the mean of the T_p values of the two successive reactions. In all cases the ΔH values, which refer to the temperatures T_p or T_m, are the mean of at least five experiments and the associated uncertainties are standard deviations of the mean values.

It is noted from Table 1 that, for the overall decomposition reaction (1), the values of T_m or T_p lie in the range 480–555 K (with the exception of the 2-methoxypyridine complexes for which the values are a little lower). We might expect that the Kirchoff corrections to refer the ΔH values to 298 K would be similar and that differences between these corrections would be small, compared with the quoted uncertainties. Unfortunately, it has not been possible to make these corrections because of the absence of specific heat data for the gaseous ligands. Nevertheless, we have obtained such data for a selection of the complexes, so that the Kirchoff corrections could be made when specific heats of the ligands are known. The values obtained are as follows, where the temperature ranges to which they refer are shown in parenthesis. $CoBr_2(3Clpy)_2$ $C_p = 18.3 + 0.149T$ (320–400 K), $CoCl_2(3Brpy)_2$ $C_p = 28.8 + 0.134T$ (320–410 K), $CoBr_2(2Clpy)_2$ $C_p = 28.9 + 0.138T$ (320–400 K), $CoCl_2(2Brpy)_2$ $C_p = 15.2 + 0.177T$ (330–390 K), $CoBr_2(2Brpy)_2$ $C_p = 26.7 + 0.134T$ cal·deg^{-1} mol^{-1} (330–410 K).

Determination of enthalpies of sublimation of the complexes is difficult because of their low vapour pressure at room temperature and decomposition at higher temperatures. However, enthalpies of sublimation of six of the complexes, together with those of $CoCl_2(2Mepy)_2$ and $CoBr_2(2Mepy)_2$ have been determined over the temperature ranges indicated, as follows:

$CoCl_2(3Clpy)_2$ 22.9±0.8 (363–381 K), $CoBr_2(3Clpy)_2$ 11.7±1.5 (345–371 K),

$CoCl_2(3Brpy)_2$ 18.4±1.0 (344–383 K), $CoCl_2(2Clpy)_2$ 24.2±1.6 (337–368 K),

$CoCl_2(2Brpy)_2$ 28.8±1.1 (351–376 K), $CoBr_2(2Brpy)_2$ 24.1±0.5 (348–382 K),

$CoCl_2(2Mepy)_2$ 20.7±0.9 (335–358 K), $CoBr_2(2Mepy)_2$ 16.6±0.7 kcal mol^{-1} (353–374 K)

Very slight decomposition of the complexes $CoCl_2(3Clpy)_2$, $CoCl_2(2Clpy)_2$, $CoCl_2(2Mepy)_2$ and $CoBr_2(2Mepy)_2$ was observed, so that enthalpies of sublimation of these compounds are likely to be maximum values. Assuming that these enthalpies are close to those at 298 K and that they refer to monomeric species in the gas phase, and taking the enthalpy of sublimation[6], $CoCl_2$ 56.0±0.4 kcal mol^{-1} and that[7] of $CoBr_2$ 53±1 kcal mol^{-1}, we obtain the mean bond dissociation energies, $\bar{D}$(Co–N), shown in Table 2. This table also lists the bonds dissociation energies of other cobalt complexes, which have been reported previously[1,2].

From these results it is seen that the strength of the cobalt–nitrogen bond in the pyridine complexes is reduced by substitution in the 2-position of the pyridine ring. This is presumably due to steric interaction between the substituent (Cl, Br, or CH_3) and the halogen (Cl or Br) bonded directly to the cobalt. The effect is less marked for the $CoBr_2$ than for the $CoCl_2$ complexes. Substitution in the 3-position of the pyridine

TABLE 2

MEAN BOND DISSOCIATION ENERGIES OF Co–N AND Co–O BONDS

Complex	*$\bar{D}$(Co–N)* *(kcal mol^{-1})*	*Complex*	*$\bar{D}$(Co–N)* *(kcal mol^{-1})*
$CoCl_2(py)_2$	34.3 ± 1.0[a]	$CoBr_2(BT)_2$[e]	30.8 ± 1.2
$CoBr_2(py)_2$	29.8 ± 1.2[b]	$CoCl_2(2MeBT)_2$[f]	33.5 ± 1.0
$CoCl_2(2Mepy)_2$	30.8 ± 0.8[c]	$CoBr_2(2MeBT)_2$	32.0 ± 1.2
$CoBr_2(2Mepy)_2$	28.8 ± 1.0[d]		
$CoCl_2(2Clpy)_2$	29.7 ± 1.0		$\bar{D}$(Co–O)
$CoCl_2(2Brpy)_2$	28.7 ± 0.8	$CoCl_2(2MeBO)_2$[g]	34.5 ± 0.7
$CoBr_2(2Brpy)_2$	29.9 ± 0.7	$CoBr_2(2MeBO)_2$	32.4 ± 1.4
$CoCl_2(3Clpy)_2$	32.7 ± 0.8	$CoC_2(25DiMeBO)_2$[h]	35.3 ± 1.0
$CoBr_2(3Clpy)_2$	37.7 ± 1.3	$CoBr_2(25DiMeBO)_2$	30.6 ± 1.5
$CoCl_2(3Brpy)_2$	34.9 ± 0.8		

[a] Uncertainties are the standard deviations of mean values. [b] Based on the value[3] $\Delta H(1) = 27.3 \pm 0.9$ kcal mol^{-1}, and an estimated enthalpy of sublimation of 20.8 ± 1.0 kcal mol^{-1}. [c] Based on the value[3] $\Delta H(1) = 26.2 \pm 0.5$ kcal mol^{-1}. [d] Based on the value[3] $\Delta H(1) = 21.2 \pm 0.9$ kcal mol^{-1}. [e] BT = benzothiazole. [f] 2MeBT = 2-methylbenzothiazole. [g] 2MeBO = 2-methylbenzoxazole. [h] 25DiMeBO = 2,5-dimethylbenzoxazole.

ring has little effect in the case of $CoCl_2(3Clpy)_2$, $\bar{D}$(Co–N) = 32.7 ± 0.8 kcal mol^{-1}, and $CoCl_2(3Brpy)_2$, $\bar{D}$(Co–N) = 34.9 ± 0.8 kcal mol^{-1}, as compared with the value $\bar{D}$(Co–N) = 34.3 ± 1.0 kcal mol^{-1} in $CoCl_2(py)_2$. The bond dissociation energy in $CoBr_2(3Clpy)_2$, $\bar{D}$(Co–N) = 37.7 ± 1.3 kcal mol^{-1} is especially high. Presumably, Co–N π-bonding is encouraged by the polarisable bromine and the electron-withdrawing chlorine substituent, so strengthening the bond. It is also noted that the strength of the Co–N bond in the benzothiazole complex, $CoBr_2(BT)_2$, 30.8 ± 1.2 kcal mol^{-1}, is similar to that in the pyridine complex, $CoBr_2(py)_2$, 29.8 ± 1.2 kcal mol^{-1}, but that methyl substitution in the 2-position of benzothiazole tends to increase rather than decrease the bond strength[1]. A further point, already made[2], is that the Co–O bond strength in the benzoxazole complexes is similar to the Co–N bond strength in the pyridine and benzothiazole complexes.

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