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THE THERMAL DECOMPOSITION OF TRANSITION-METAL COMPLEXES CONTAINING HETEROCYCLIC LIGANDS

2. BENZOXAZOLE COMPLEXES

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ABSTRACT

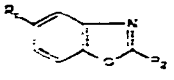
Enthalpies of the overall decomposition reactions

$$MX_2L_2(c) \rightarrow MX_2(c)+2L(g),$$

and of the intermediate reactions involving stepwise loss of ligand, L, where M is Mn, Co, Ni, Cu, or Cd, X is Cl or Br, and L is benzoxazole, 2-methylbenzoxazole, or 2,5-dimethylbenzoxazole have been measured by use of a differential scanning calorimeter. Specific heats of $CoCl_2$(2-methylbenzoxazole)$_2$ and $CoBr_2$(2-methylbenzoxazole)$_2$ are reported together with enthalpies of sublimation of $CoCl_2$(2-methylbenzoxazole)$_2$, $CoBr_2$(2-methyl-benzoxazole)$_2$, $CoCl_2$(2,5-dimethylbenzoxazole)$_2$ and $CoBr_2$(2,5-dimethylbenzoxazole)$_2$. Enthalpies of decomposition of benzoxazole complexes are found to be greater than those of the corresponding pyridine complexes, but less than those of the analogous benzothiazole complexes. However, the mean bond dissociation energies of the cobalt–nitrogen and cobalt–oxygen bonds in these complexes are all in the region 33 ± 2 kcal mol^{-1}.

INTRODUCTION

In this paper we report results of our continued study[1] of complexes of first-series transition metals with ligands containing a nitrogen atom bonded within a five-membered ring fused to a benzene ring. Thermochemical data are given for complexes, MX_2L_2, where L is one of the following benzoxazoles, and X is either chlorine or bromine.



$R_1 = R_2 = H$	benzoxazole (BO)
$R_1 = Me, R_2 = H$	2-methylbenzoxazole (2MeBO)
$R_1 = R_2 = Me$	2,5-dimethylbenzoxazole (25DiMeBO)

The overall thermal decomposition reaction (1) occurs in two stages, reactions (2) and (3), except for the complex $CdCl_2(BO)_2$, where decomposition follows the reactions (4) and (5). The complex $CuCl_2$(25DiMeBO) decomposes according to reaction (3).

$$MX_2L_2(c) \rightarrow MX_2(c)+2L(g) \tag{1}$$

$$MX_2L_2(c) \rightarrow MX_2L(c)+L(g) \tag{2}$$

$$MX_2L(c) \rightarrow MX_2(c)+L(g) \tag{3}$$

$$CdCl_2(BO)_2(c) \rightarrow CdCl_2(BO)_{\frac{1}{2}}(c)+1\tfrac{1}{2}(BO)(g) \tag{4}$$

$$CdCl_2(BO)\tfrac{1}{2}(c) \rightarrow CdCl_2(c)+\tfrac{1}{2}(BO)(g) \tag{5}$$

In an attempt to obtain data for selenium analogues, we have prepared the complexes of some transition metal halides with 2-methyl-5-methoxybenzoselenazole. These complexes appear not to have been reported previously. Unfortunately, their thermal decomposition reactions were not amenable to study by differential scanning calorimetry.

EXPERIMENTAL

The complexes were prepared by the method described previously[2,3] and purity was established by microanalysis for C, H, and N. The complexes $MnX_2(BO)_2$ and $NiX_2(BO)_2$ gave poor analyses, whilst $CuCl_2(BO)_2$ (blue) and $CuBr_2(BO)_2$ (green) changed colour on standing in air. Although $ZnCl_2(BO)_2$ could be prepared pure and was stable, its thermal decomposition was not reproducible. None of these compounds was investigated further.

TABLE 1

ANALYTICAL DATA FOR 2-METHYL-5-METHOXYBENZOSELENAZOLE AND 2,5-DIMETHYLBENZOXAZOLE COMPLEXES

Complex	*Analyses* (%)					
	C		*H*		*N*	
	calc.	*found*	*calc.*	*found*	*calc.*	*found*
L = 2-methyl-5-methoxybenzoselenazole						
$CoCl_2L_2$ (blue)	37.14	38.3	3.12	3.52	4.81	4.9
$CoBr_2L_2$ (jade/blue)	32.22	31.9	2.70	3.05	4.18	4.1
$CuCl_2L_2$ (green/brown)	36.85	36.9	3.09	3.80	4.77	4.8
$CuBr_2L_2$ (red/brown)	32.00	32.9	2.69	3.08	4.15	4.2
L = 2,5-dimethylbenzoxazole						
$CoCl_2L_2$ (blue)	50.97	51.2	4.28	4.49	6.61	6.7
$CoBr_2L_2$ (blue)	42.14	42.4	3.54	3.92	5.46	5.4
$NiCl_2L_2$ (v. pale yellow)	50.99	53.1	4.28	4.50	6.61	6.8
$CuCl_2L$ (orange/brown)	38.39	39.2	3.22	3.45	4.98	4.9

Analytical data for complexes involving 2,5-dimethylbenzoxazole and 2-methyl-5-methoxybenzoselenazole ligands, L, not previously reported in the literature, are shown in Table 1.

The Perkin-Elmer differential scanning calorimeter (DSC-1) was used to measure the enthalpies of thermal decompositions in a nitrogen atmosphere. The scan rate was 16 K min^{-1} 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 and checked by measuring the enthalpies of (i) dehydration of $CuSO_4 \cdot 5H_2O$, (ii) fusion of Pb foil, and (iii) decomposition of $CoCl_2$(pyridine)$_2$ (tetrahedral form) as described previously[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 successive stages of the decomposition reactions are shown in Table 2, where 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. Enthalpies of the overall decomposition reactions (1) are shown in Table 3, where the temperature T_m is an approximate mean of the values of T_p for successive reactions. In all cases the ΔH values, which refer to the temperature T_p or T_m, are the mean of at least five experiments, and the associated uncertainties are standard deviations of mean values.

It is noted from Table 3 that for all the complexes the values of T_m lie in the narrow temperature range 475–540 K. We might expect that the Kirchoff corrections to refer the ΔH values to a common temperature within this range would be similar and small, compared with the quoted uncertainties. In the absence of specific heat data for the benzoxazoles it has not been possible to make these corrections, even though specific heat values for the complexes can be obtained by use of the scanning calorimeter.

We have obtained such data for two complexes as follows. $CoCl_2(2MeBO)_2$ $C_p = 30.2 + 0.19T$, $C_{p,298} = 86.8$ cal deg^{-1} mol^{-1}, $CoBr_2(2MeBO)_2$ $C_p = 24.3 + 0.23T$, $C_{p,298} = 92.8$ cal deg^{-1} mol^{-1}. These values (at 298 K) are close to those obtained previously[1] for the corresponding 2-methyl-benzothiazole complexes, $CoCl_2$ $(2MeBT)_2$ $C_{p,298} = 92.9$, $CoBr_2(2MeBT)_2$ $C_{p,298}$ 91.6 cal deg^{-1} mol^{-1}.

When using the enthalpies of reaction as a measure of bond strength, it is preferable that the data refer to the gas phase. Enthalpies of sublimation of four complexes have been measured, over the temperature ranges indicated, as follows. $CoCl_2(2MeBO)_2$ 22.1±0.6 kcal mol^{-1} (327–348 K), $CoBr_2(2MeBO)_2$ 26.6±1.0 kcal mol^{-1} (344–368 K), $CoCl_2(25DiMeBO)_2$ 22.8±1.1 kcal mol^{-1} (326–349 K), and $CoBr_2(25DiMeBO)_2$ 25.0±1.2 kcal mol^{-1} (345–364 K). Assuming that these enthalpies are close to those at the decomposition temperatures, and taking the enthalpy of sublimation[6] of $CoCl_2$ 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 $\bar{D}$(Cl_2Co–2MeBO) = 34.5±0.7, $\bar{D}$(Br_2Co–2MeBO) = 32.4±1.4, $\bar{D}$(Cl_2Co–25DiMeBO) = 35.3±1.0, and $\bar{D}$(Br_2Co–25DiMeBO) = 30.6±1.5 kcal mol^{-1}. There is evidence[3] that in these complexes the ligand is bonded to the metal through the oxygen atom, so that these dissociations energies refer to cobalt–oxygen bonds. Nevertheless, the values are close to those found[1] for the strength of the cobalt–nitrogen bond in the benzothiazole complex, $\bar{D}$(Br_2Co–BT) = 30.8±1.2, the 2-methylbenzothiazole complexes, $\bar{D}$(Cl_2Co–2MeBT) = 33.5±0.7 and $\bar{D}$(Br_2Co–2MeBT) = 32.0±1.2 kcal mol^{-1}, and in the

TABLE 2

ENTHALPIES OF STEPWISE DECOMPOSITION OF BENZOXAZOLE 2-METHYLBENZOXAZOLE AND 2,5-DIMETHYLBENZOXAZOLE COMPLEXES

Complex	*Reaction*	*ΔH (kcal mol^{-1})*	*T_i (K)*	*T_p (K)*	*T_f (K)*	*Weight loss (%)*	
						obs.	*calc.*
Benzoxazole complexes							
$CoCl_2(BO)_2$	2	16.0 ±0.3	400	460	470	32.5 ±0.2	32.4
	3	18.1 ±0.3	470	530, 580	590		
$CoBr_2(BO)_2$	2	16.4 ±0.1	420	490	500	27.6 ±1.7	26.1
	3	17.9 ±0.1	500	555	565		
$CdCl_2(BO)_2$	4	24.7 ±0.5	370	440, 455	490	42.7 ±0.2	42.4
	5	9.9 ±0.3	500	540	560		
2-Methylbenzoxazole complexes							
$MnCl_2(2MeBO)_2$	2	18.2 ±0.3	365	395, 440	480	33.9 ±0.9	34.0
	3	16.2 ±0.2	485	540, 565	575		
$CoCl_2(2MeBO)_2$	2	15.0 ±0.1	405	450	460	33.5 ±0.1	33.6
	3	20.1 ±0.2	495	565	575		
$CoBr_2(2MeBO)_2$	2	18.8 ±0.4	450	505	515	27.2 ±0.2	27.5
	3	19.5 ±0.4	515	570	580		
$ZnCl_2(2MeBO)_2$	2	~16	420	470	480	32.3 ±0.3	33.1
$CdCl_2(2MeBO)_2$	2	11.4 ±0.4	380	420	430	28.7 ±1.0	29.6
	3	20.0 ±0.3	460	525	545		
2,5-Dimethylbenzoxazole complexes							
$CoCl_2(25DiMeBO)_2$	2	17.0 ±0.3	395	445	465	35.8 ±0.2	34.7
	3	20.4 ±0.2	510	585	595		
$CoBr_2(25DiMeBO)_2$	2	15.4 ±0.3	440	480	510	29.4 ±0.2	28.7
	3	17.8 ±0.4	530	585	590		
$NiCl_2(25DiMeBO)_2$[a]	2	17 ±2[a]	380	465	490	43.1 ±0.4	34.7
	3	17.0 ±0.2	515	565	590		
$CuCl_2(25DiMeBO)$	3	25.2 ±0.6	440	475	515	50.1 ±0.9	52.3

[a] A long and straggly thermogram made it difficult to determine the conclusion of reaction (2) and the start of reaction (3), which lead to inaccuracy in the ΔH value and analytical data.

TABLE 3

ENTHALPIES OF THE OVERALL DECOMPOSITION REACTION (I)

Complex	ΔH (I) (*kcal mol*$^{-1}$)	T_m (*K*)	*Weight loss* (%)	
			obs.	*calc.*
L = benzoxazole				
$CoCl_2L_2$	34.1 ±0.6	505	63.5 ±0.2	64.8
$CoBr_2L_2$	34.3 ±0.2	520	51.9 ±0.4	52.1
$CdCl_2L_2$	34.6 ±0.8	495	57.8 ±0.5	56.5
L = 2-methylbenzoxazole				
$MnCl_2L_2$	34.4 ±0.5	500	65.9 ±1.4	67.9
$CoCl_2L_2$	35.1 ±0.3	520	67.1 ±0.1	67.2
$CoBr_2L_2$	38.3 ±0.8	540	54.8 ±0.1	54.9
$CdCl_2L_2$	31.4 ±0.7	475	57.7 ±0.2	59.2
L = 2,5-dimethylbenzoxazole				
$CoCl_2L_2$	37.4 ±0.5	515	69.7 ±0.2	69.4
$CoBr_2L_2$	33.2 ±0.7	530	57.2 ±0.1	57.4
$NiCl_2L_2$	34 ±2.2	515	73.4 ±0.4	69.4

tetrahedral form of the pyridine complex, $CoCl_2(py)_2$, for which we calculate $\bar{D}(Cl_2Co{-}py) = 34.3 \pm 1.0$ kcal mol^{-1}. This value is derived from the enthalpy of decomposition[8], $\Delta H(1) = 28.6 \pm 0.5$ kcal mol^{-1}, and an enthalpy of sublimation, $\Delta H = 16 \pm 1$ kcal mol^{-1}, which is estimated from an extrapolation of the plot of enthalpies of sublimation of cobalt complexes, given above and previously[1], against molecular weight.

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