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THERMAL ANALYSIS OF HETEROCYCLIC THIONE DONOR COMPLEXES. PART III. COBALT(II) COMPLEXES OF IMIDAZOLIDINE-2-THIONE

BARBARA M. JORDAN, ERIC S. RAPER and JAMES R. CREIGHTON

School of Chemical and Life Sciences, Newcastle-upon-Tyne Polytechnic, Newcastle-upon-Tyne NE1 8ST (Gt. Britain)

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ABSTRACT

The thermal decomposition of the cobalt(II) complexes of imidazolidine-2-thione (Imdt), $Co(Imdt)_2X_2$ (X = Cl, Br, and I) have been studied in air and argon by means of TG and DTG as well as in nitrogen by DTA. Decomposition schemes have been proposed for the complexes in both air and inert atmospheres. Reaction enthalpies have been derived from the melting and decomposition endotherms by means of quantitative DTA. A mean coordinate bond dissociation energy, $\bar{D}$, has been estimated for the Co–Imdt bond in the chloro complex. Reaction products in air have been identified by X-ray powder diffraction.

INTRODUCTION

The S-donating character of the imidazolidine-2-thione (Imdt) molecule (Fig. 1) towards transition and other metals has been established by spectroscopic and single-crystal X-ray methods [1,3–7]. With cobalt(II) halides Imdt forms pseudo-tetrahedral complexes of general formula, $Co(Imdt)_2X_2$ (X = Cl, Br, and I).

Previous reports in this series have dealt with the thermal analysis of unsaturated imidazole-thione complexes of cobalt and nickel [8–10]. This report deals with the thermochemistry of the cobalt(II) complexes of the saturated imidazole (imidazolidine)-2-thione molecule (Fig. 1) and compares the results with others in this series [8,9].

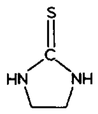

Fig. 1. Imidazolidine-2-thione.

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EXPERIMENTAL

Preparation and characterisation of the complexes

The complexes were prepared according to literature methods and characterised by chemical (C, H and N) analyses and IR spectra. This established the stoichiometries of the complexes, $Co(Imdt)_2X_2$, to be as reported in the literature [1]. Low-frequency IR spectra (1000–200 cm^{-1}) confirmed the S-donating character of the ligands [2,9,10].

TG and DTG

A Stanton-Redcroft TG 750 thermobalance and DTG unit were used together with open Pt crucibles (6 mm diameter). The atmosphere was column dried (molecular sieve, 13X) flowing air or argon (15–20 cm^3 min^{-1}). Sample masses were in the range 2–6 mg; the heating rate was 10°C min^{-1} and the recorder speed was 2 mm min^{-1}.

DTA

A Stanton-Redcroft 673/4 instrument was used together with quartz crucibles [3 cm (length) × 0.3 cm (internal diameter)]. The atmosphere was flowing nitrogen (200 cm^3 min^{-1}) and the heating rate was 20°C min^{-1}. Sample masses were in the range 4–6 mg and the reference material was Al_2O_3 (5 mg in a quartz crucible). Amplifier sensitivity was 50 μV (0.5°C) f.s.d., and the recorder speed was 5 mm min^{-1}.

Reaction enthalpies were obtained from the melting and decomposition endotherms by means of the relationship

$$\Delta H_R = AM/Kw \times 10^3$$

where A is the peak area (mm^2) of the appropriate endotherm; M is the molar mass of the complex; K is an experimental constant (mm^2 mJ^{-1}) for a specific reaction temperature [8]; and w is the sample mass (mg).

Variations in the derived (ΔH_R) values are in the range ±3–10% and are based on three runs per complex. The melting endotherms have regular shapes with variations in the lower end of the range (±3–5%) whereas the irregularly shaped decomposition endotherms generate variations in the higher end of the range (±5–10%). Calibration data and enthalpy values for relevant reactions have been reported previously [8].

X-Ray powder diffraction

A Philips XDC-700 Guinier–Hägg parafocussing camera, monochromatised CuK_α, (λ = 154.05 pm) radiation and Kodirex single-coated X-ray

TABLE 1

Thermogravimetric analysis in air

Compound	M/g mole^{-1}	Overall mass losses				Stepped mass losses	
		Temp. range (T/°C)	End-product	Theory (%)	Expt. (%)	Temp. range (T/°C)	Mass loss (%)
Co(Imdt)$_2$Cl$_2$	333.8	170–600	Co_3O_4	77.5	76.5	170–420	51.0
						420–600	25.5
Co(Imdt)$_2$Br$_2$	422.7	250–650	Co_3O_4	82.3	83.5	250–500	45.0
						500–650	38.5
Co(Imdt)$_2$I$_2$	516.7	225–800	CoO	84.5	85.5	250–425	45.0
						425–550	38.0
						550–800	2.5

film were employed in identifying the end-products in air which were either Co_3O_4 (JCPDS reference 9-0418) or CoO (JCPDS reference 9-402).

RESULTS AND DISCUSSION

Data from the TG and DTG curves in air and argon are summarised in Tables 1 and 2; DTA data in nitrogen are summarised in Table 3. Specimen curves are shown in Figs. 2 and 3.

TABLE 2

Thermogravimetric analysis in argon

Compound	Overall mass losses		Stepped mass losses	
	Temp. range (T/°C)	Mass loss (%)	Temp. range (T/°C)	Mass loss (%)
$Co(Imdt)_2Cl_2$	0–1000	63	300–400	30
			400–650	22
			650–1000	11
$Co(Imdt)_2Br_2$	0–1000	68	300–400	20
			400–600	33
			600–1000	15
$Co(Imdt)_2I_2$	0–1000	74	350–680	59
			680–1000	15

TABLE 3

Differential thermal analysis in nitrogen

Compound	Peak temp. (°C)			Peak character [b]	Reaction enthalpy, ΔH_R (kJ mole^{-1})
	T_i	$T_p(T_m$ [a]$)$	T_f		
$Co(Imdt)_2Cl_2$	180	204	230	M	38
	300	400	500	D	121
$Co(Imdt)_2Br_2$	170	190	220	M	47
	300	340	380	D	39
	380	430	480	D	75
$Co(Imdt)_2I_2$	160	181	190	M	36
	300	370	440	D	194
Imdt	180	192	200	M	15
	260	330	400	D	60

[a] $T_m = 1/2[T_i + T_f]$ for decomposition endotherms, T_p is peak maximum temperature.
[b] M = Melting endotherm, D = decomposition endotherm.

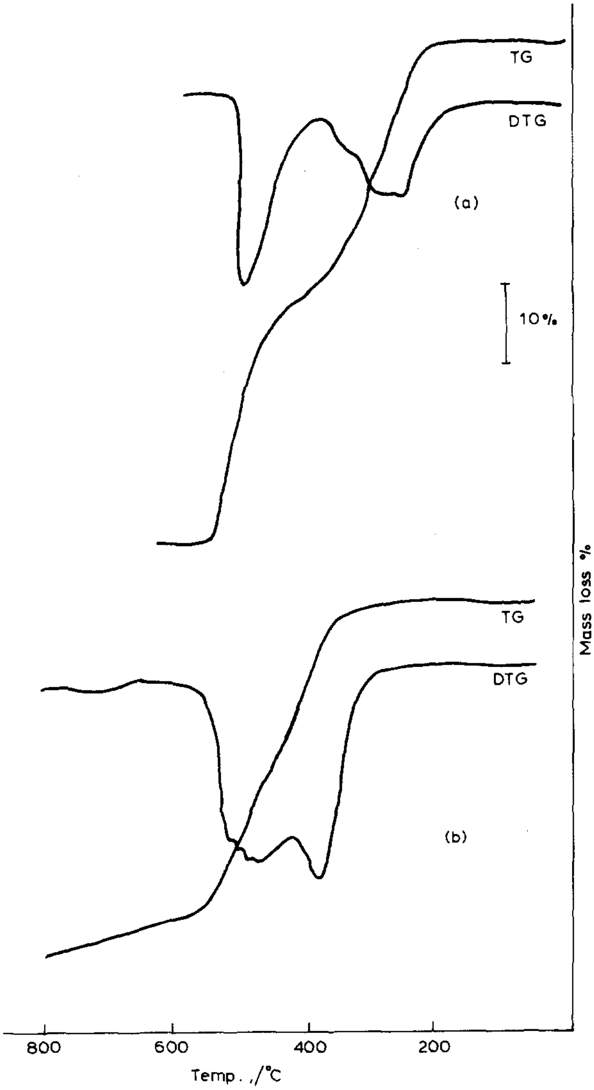

Fig. 2. TG and DTG curves for Co(Imdt)$_2$Br$_2$ in air (a) and argon (b).

Analysis of the end-products by XRPD has shown that the complexes degrade to Co_3O_4 in air over the temperature range 170–800°C. Agreement between observed and calculated mass losses for the process

$$3\ Co(Imdt)_2X_2(s) + 2\ O_2(g) \rightarrow Co_3O_4(s) + 6\ Imdt(g) + 3\ X_2(g)$$

is within experimental error (±2%) for all of the complexes. The TG and DTG curves suggest that the decomposition in air is essentially a two-stage process. Slight splitting of the first DTG curve occurs for the bromo and iodo complexes. The iodo complex exhibits an additional mass loss (2.5%) in

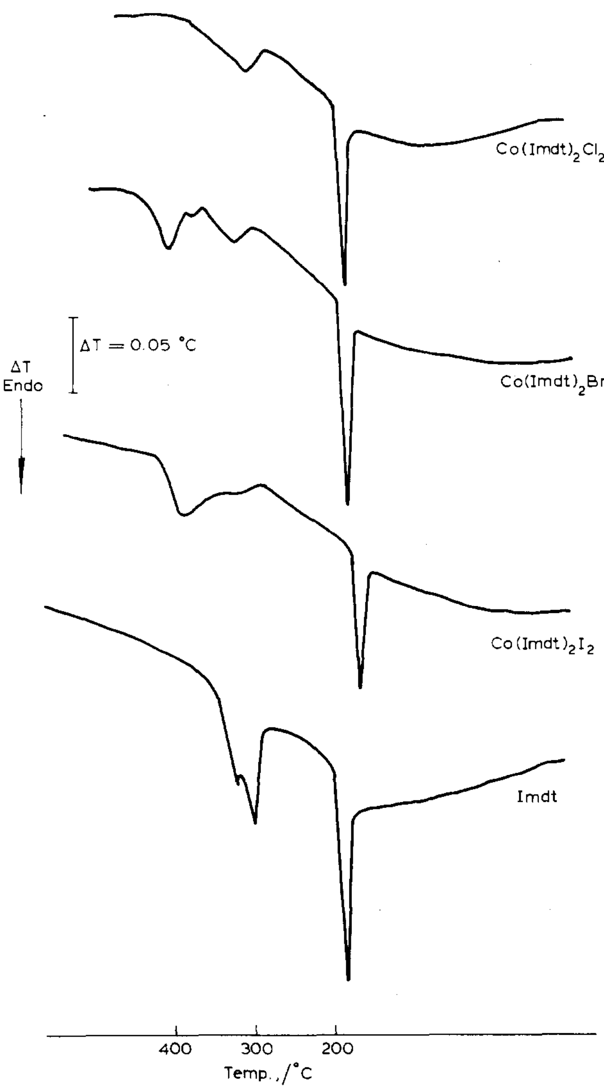

Fig. 3. Selected DTA curves in nitrogen.

the temperature range 500–800°C which is consistent with further degradation of Co_3O_4 to CoO.

Analysis of the stepped mass losses from the DTG and TG curves suggests that the two stages involved are broadly consistent with initial loss of the heterocyclic molecules

$$Co(Imdt)_2X_2(s) \rightarrow CoX_2(s) + 2\ Imdt(g)$$

in the temperature range 170–500°C, followed by conversion of the halide to the oxide. Overlap of the two processes, however, is clearly indicated from the stepped mass losses and by the absence of a well-defined intermediate plateau between the two components of the TG curves (Fig. 2).

In none of these complexes, however, do the stepped mass losses suggest the fractional decomposition of the heterocyclic molecules previously observed for the cobalt(II) complexes of 1-methylimidazoline-2-thione [8].

In argon the temperature range at which decomposition occurs is higher than in air, also, no clearly defined end-plateau is observed for any of the complexes. The end-products, on cooling, become amorphous vitreous solids. Overall mass losses are variable and increase with increasing molar mass of the complexes (Table 2). The major mass loss, for all the complexes (52–59%), occurs in the temperature range 300–680°C and is essentially consistent with Imdt evolution. However the mass loss at this stage for $Co(Imdt)_2I_2$ suggests that some metal iodide decomposition accompanies loss of Imdt for this complex. The major DTG peak is split in all cases, clear resolution into two components occurs only for the bromo complex where the peak heights are in the ratio of 1 : 1. This suggests sequential, rather than simultaneous loss of the heterocyclic molecules.

The DTA data (Table 3) show that all of the complexes exhibit a melting endotherm with T_p values in the range 181–204°C, in addition to a decomposition endotherm with T_m values in the range 340–420°C. The decomposition endotherm for $Co(Imdt)_2Br_2$ is clearly resolved into two components.

The temperature range of the decomposition endotherm in nitrogen broadly parallels that at which Imdt evolution occurs in argon. The reaction enthalpies of the complexes ($159–230 \pm 15$ kJ mole^{-1}) are similar to those reported ($150–240 \pm 15$ kJ mole^{-1}) for related complexes [ML_2X_2; ($M = Co$ and Ni; $L =$ MImt and DmImt; $X = Cl$, Br and I)] in this series [8,9]. The large value observed for $Co(Imdt)_2I_2$ is also common for this series and supports the contention that decomposition of the metal iodide accompanies Imdt loss for this complex.

In the absence of the sublimation energies of the complexes the bond strength of the Co–Imdt bond in the chloro complex may be estimated by using an averaged value (110 ± 15 kJ mole^{-1}) from the literature [8] together with the literature value for the sublimation energy of $CoCl_2$ (226 ± 4 kJ mole^{-1}) [11]. This produces a gas phase reaction enthalpy for the reaction

$$Co(Imdt)_2Cl_2(g) \rightarrow CoCl_2(g) + 2\ Imdt(g)$$

of 275 ± 15 kJ mole^{-1} and a mean coordinate bond dissociation energy, $\overline{D}$, of 138 ± 15 kJ mole^{-1} for the Co–Imdt bond in $Co(Imdt)_2Cl_2$, assuming the complex to be monomeric and no further stereochemical changes occur. This value is comparable to that obtained for the Co–MImt bond in $Co(MImt)_2Cl_2$ (134 ± 15 kJ mole^{-1}) [8] and slightly, but not necessarily significantly less than the value obtained for the Co–DmImt bond in $Co(DmImt)_2Cl_2$, (153 ± 15 kJ mole^{-1}) [9].

In view of the assumptions and experimental errors inherent in the derivation of the above values, the range obtained ($134–153 \pm 15$ kJ mole^{-1}) suggests a fairly uniform thermal bond strength for these complexes which is broadly in agreement with the range of Co–S bond lengths 232 ± 2 pm obtained for both saturated (Imdt) [5] and unsaturated (MImt and DmImt) [12,13] imidazole-thione molecules.

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