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THERMAL ANALYSIS OF HETEROCYCLIC THIONE DONOR COMPLEXES. PART V. NICKEL(II) COMPLEXES OF IMIDAZOLIDINE-2-THIONE

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ABSTRACT

The thermal decomposition of the nickel(II) complexes of imidazolidine-2-thione (Imdt), $Ni(Imdt)_4X_2$ (X = Cl and Br), have been studied in air and in argon by means of TG and DTG, as well as in nitrogen by DTA. Decomposition schemes have been proposed for the complexes in air and inert atmospheres. End-products have been identified for the reactions in air by means of X-ray powder diffraction. Quantitative DTA has been used to derive reaction enthalpies (ΔH_R) from the melting and decomposition endotherms of Imdt and the complexes in nitrogen. The factors which govern the reaction enthalpies of these complexes have been discussed.

INTRODUCTION

The monodentate S-donating character of the imidazolidine-2-thione (Imdt) (Fig. 1) molecule towards transition and other metals has been established by spectroscopic and single-crystal X-ray methods [1–4]. With Ni(II), Imdt forms complexes of general formula, $Ni(Imdt)_4X_2$ (X = halide, nitrate, perchlorate or tetrafluoroborate) [5]. These complexes may be either tetragonal paramagnetic or square diamagnetic in the solid. This report deals with the thermochemistry of the yellow *trans*-$Ni(Imdt)_4X_2$ (X = Cl or Br) complexes.

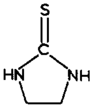

Fig. 1. Imidazolidine-2-thione.

EXPERIMENTAL

Preparation and analysis of the complexes

The complexes were prepared according to literature methods and characterised by chemical (C, H and N) analyses and IR spectra. Chemical analysis established the stoichiometries to be as stated in the literature [6] and the low-frequency (1000–200 cm^{-1}) IR spectra confirmed the S-donating characters of the ligands.

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 (15–25 cm^3 min^{-1}). Sample weights were in the range 2–6 mg; the furnace 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) and 0.3 cm (internal diameter)]. The latter were chosen in preference to Pt crucibles because of sample swelling and creep as well as the frequent production of tenacious deposits. The furnace atmosphere was flowing nitrogen (200 cm^3 min^{-1}) and the heating rate was 20°C min^{-1}. Sample weights 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}.

The relationship

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

where A is the peak area of a reaction endotherm (mm^2); M is the molar mass of the compound; K is a calibration constant (mm^2 mJ^{-1}) for a given reaction temperature [6]; and w is the sample weight (mg) used for the determination of reaction enthalpies (kJ mole^{-1}) from the appropriate endotherms. Variations in ΔH_R are in the range ±5–9% and are based on three runs per complex.

X-Ray powder diffraction

A Philips XDC-700 Guinier-Hägg parafocussing camera, monochromatised CuK_α, ($\lambda = 1.5405$ Å) radiation and Kodirex single-coated X-ray film were employed in identifying the end-products in air which were invariably NiO (JCPDS reference 4-0835).

RESULTS AND DISCUSSION

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

End-product identification by XRPD shows that the complexes degrade to NiO in air over the temperature range 180–820°C.

$$Ni(Imdt)_4X_2(s) + 1/2O_2(g) \rightarrow NiO(s) + 4\ Imdt(g) + X_2(g) \qquad (1)$$

Agreement between observed and theoretical overall mass losses for the above reaction is within experimental error (±2%) for both complexes. In addition to the loss of three Imdt molecules at 400°C, the chloro complex shows an intermediate mass loss at 82.0% (580°C) which is consistent with NiS formation (theoretical mass loss 83.1%); subsequent heating produced NiO at 820°C. The bromo complex also loses its organic molecules in two stages but without NiS formation.

The major mass losses in argon occur in the temperature range 280–650°C

TABLE 1

Thermogravimetric analysis

(a) In air

Compound	Overall mass losses			Stepped mass losses	
	Temp. range (T/°C)	Theory (%)	Exptl. (%)	Temp. range (T/°C)	Mass loss (%)
$Ni(Imdt)_4Cl_2$	200–820	86.1	86.0	200–400	54.0
				400–580	28.0
				580–820	4.0
$Ni(Imdt)_4Br_2$	180–550	88.1	86.5	180–280	22.0
				280–400	27.0
				400–550	37.5

(b) In argon

Compound	Overall mass losses		Stepped mass losses	
	Temp. range (T/°C)	Mass loss (%)	Temp. range (T/°C)	Mass loss (%)
$Ni(Imdt)_4Cl_2$	0–1000	83	300–400	40
			400–650	27
			650–1000	16
$Ni(Imdt)_4Br_2$	0–1000	76	280–380	30
			380–550	36
			650–1000	10

TABLE 2

Differential thermal analysis data in nitrogen and reaction enthalpies

Compound	Peak temp. (T/°C)			Peak character[b]	Reaction enthalpy ΔH_R (kJ mole^{-1})[c]	Reaction enthalpies (ΔH_L)(kJ mole^{-1})[d] for the process $ML_nX_2(s) \rightarrow MX_2(s) + nL(g)$ (with ΔH_B in parentheses)
	T_i	T_p(T_m[a])	T_f			
$Ni(Imdt)_4Cl_2$	180	192	220	M	108	97(22)
	260	345	430	D	280	
$Ni(Imdt)_4Br_2$	150	170	190	M	74	97(22)
	300	375	450	D	312	
Imdt(L)	180	192	200	M	15	
	260	330	400	D	60	

[a] $T_m = 1/2[T_i + T_f]$ for decomposition endotherms. T_p = peak maximum temperature for melting endotherms.

[b] M = Melting endotherm, D = decomposition endotherm.

[c] Variations are in the range ±5–9% and are based on three runs per complex.

[d] $\Delta H_L = \Delta H_R / n$; $\Delta H_B = \Delta H_L - \Delta H_S$.

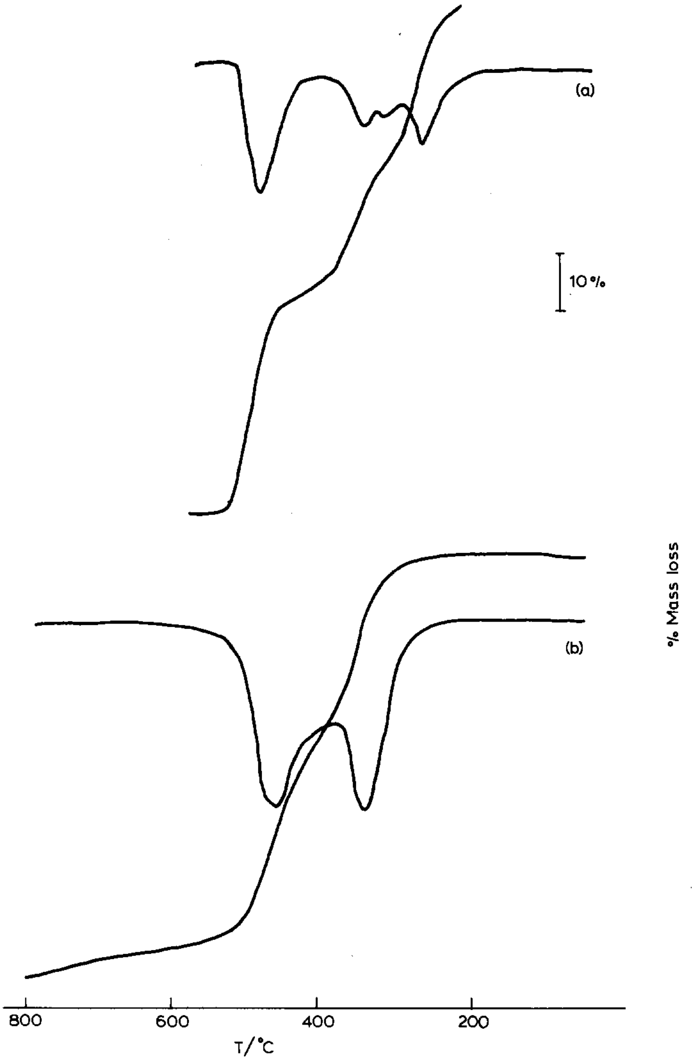

Fig. 2. TG and DTG curves of $Ni(Imdt)_4Br_2$ in air (a) and argon (b).

and correspond to the loss of the Imdt molecules. The presence of two essentially equal DTG components for $Ni(Imdt)_4Br_2$ (Fig. 2) suggests that the Imdt molecules are evolved sequentially, and in pairs.

The DTA curves of the complexes consist of a melting endotherm followed by a broad decomposition endotherm (Fig. 3). The heterocyclic molecule also exhibits a combination of melting (ΔH_M) and decomposition endotherms (ΔH_D), the sum of these enthalpies correspond to the sublimation enthalpy (ΔH_S) for the molecule (Table 2). Similarly, the sum of the melting and decomposition enthalpies for the complexes represents the total

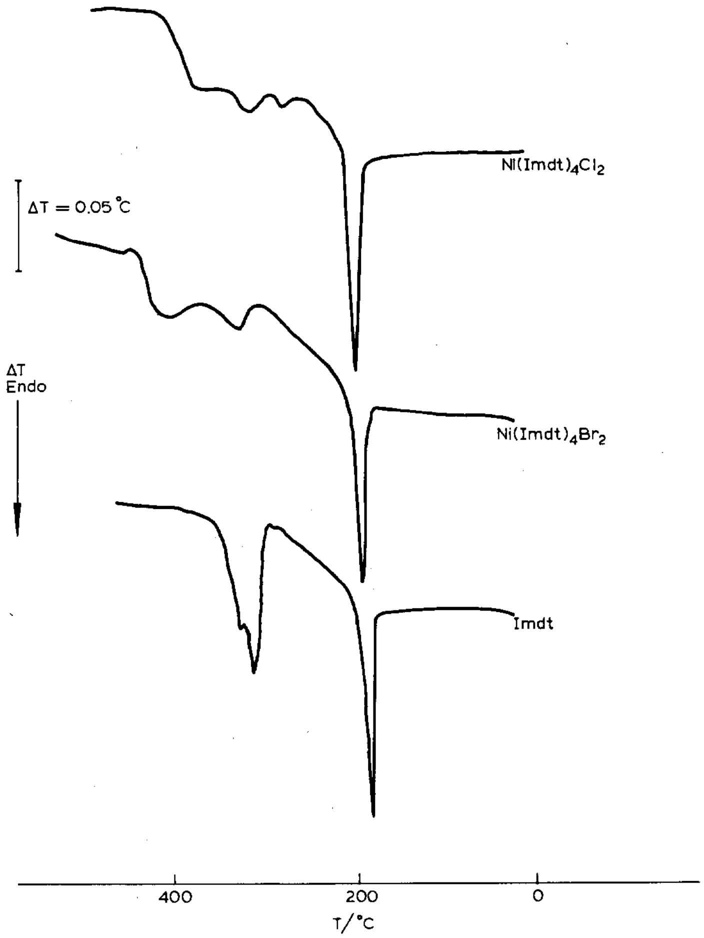

Fig. 3. DTA curves in nitrogen.

reaction enthalpy (ΔH_R) for the reaction

$$\text{Ni(Imdt)}_4\text{X}_2\text{(s)} \rightarrow \text{NiX}_2\text{(s)} + 4\ \text{Imdt(g)} \tag{2}$$

The values of ΔH_R for the two complexes are within experimental error ($\pm$5–9%), although the component, and anion dependent, ΔH_M and ΔH_D values do show significant differences. In addition, the ΔH_R values represent the resultant of several reaction enthalpies which are summarised in Fig. 4 and below:

ΔH_1, the Ni–Imdt bonding enthalpy;
ΔH_2, the Ni $\cdots$ X′ bonding enthalpy;
ΔH_3, the H-bonding (NH $\cdots$ X′) enthalpy; and
ΔH_4, the Ni–X bond formation enthalpy.

The resultant of these four values, (per mole Imdt; ΔH_L), is obtained from ΔH_R and the number of Imdt molecules evolved [eqn. (2) and Table 2]. A

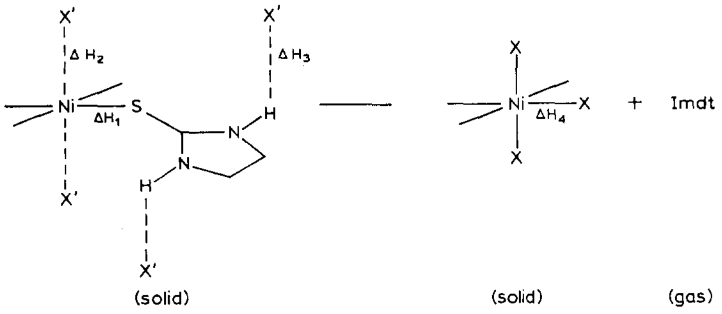

Fig. 4. Enthalpy terms contributing to the decomposition scheme.

measure of the Ni–Imdt bond strength (ΔH_B) may then be estimated by allowing for the sublimation enthalpy of the heterocyclic molecule ($\Delta H_B = \Delta H_L - \Delta H_S$).

The resultant values of ΔH_L and ΔH_B (97 and 22 kJ mole^{-1}) are the same and suggest similar bond strengths for the Ni–Imdt bonds in both complexes. The values are comparable with other tetragonal, paramagnetic NiL_4X_2 complexes where L is a heterocyclic molecule [7,8].

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