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THERMAL ANALYSIS OF HETEROCYCLIC THIONE DONOR COMPLEXES. II. COBALT(II) AND NICKEL(II) COMPLEXES OF 1,3-DIMETHYL (*N*,*N*′)-IMIDAZOLINE-2-THIONE

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ABSTRACT

The thermal decompositions of the cobalt and nickel complexes of 1,3-dimethyl (*N*,*N*′)-imidazoline-2-thione, $M(DmImt)_2X_2$ [M=Co(II) and Ni(II); 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. Reaction enthalpies (ΔH_R) have been determined from the melting and decomposition endotherms in nitrogen by means of quantitative DTA. Decomposition schemes have been proposed for the complexes in air as well as for inert atmospheres. Mean coordinate bond dissociation energies, $\bar{D}$, have been estimated for the Co–DmImt and the Ni–DmImt bonds in the chloro complexes. Reaction products in air have been identified by X-ray powder diffraction.

INTRODUCTION

Dimethyl (*N*,*N*′)-imidazoline-2-thione (DmImt) is one of a series of thione substituted imidazole derivatives whose coordination chemistry has been investigated recently [1–9]. The DmImt molecule is an exclusive thione S-donor [1,6]. In this respect it is similar to the fully saturated imidazolidine-2-thione molecule, Imdt [8,9], but differs from the unsaturated parent molecule of this series, imidazoline-2-thione, Imt [3,5], and its 1-methyl derivative, MImt [2,4], both of which may be either S-donating or S,N-chelating in character.

Reacting DmImt with Co(II) and Ni(II) halides produces complexes of general stoichiometry, $M(DmImt)_2X_2$ (M = Co and Ni; X = Cl, Br and I) [1]. The pseudo-tetrahedral structures of these complexes and the S-donating character of the ligand have been established by a combination of spectrochemical and X-ray methods [1]. This report is concerned with the thermochemistry of these complexes.

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EXPERIMENTAL

Preparation and analysis of the complexes

The complexes were prepared according to literature methods [1] and characterized by chemical (C, H and N) analyses, IR spectroscopy, electronic spectroscopy and magnetic measurements [10,11]. These procedures verified that the stoichiometries and structures of the complexes corresponded to those already described in the literature [1].

TG and DTG

A Stanton-Redcroft TG 750 thermobalance and DTG unit were used together with open Pt crucibles (6 mm diameter). The furnace atmosphere was column-dried flowing air or argon (15 cm^3 min^{-1}); sample masses varied from 2 mg to 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 latter were chosen in preference to Pt crucibles because of sample swelling and creep as well as the production of tenacious deposits. The furnace atmosphere was column-dried flowing nitrogen (200 cm^3 min^{-1}); the heating rate was 20°C min^{-1}; sample masses were 5–6 mg; the recorder speed was 5 mm min^{-1}; sample reference was Al_2O_3 (5 mg also in a quartz crucible); and the amplifier sensitivity was 50 μV f.s.d.

Reaction enthalphies (ΔH_R, kJ $mole^{-1}$) for the complexes have been derived from the peak areas of the melting and decomposition endotherms by means of the expression

$$\Delta H_R = A\,M/K\,m\;10^3$$

where, A is the peak area (mm^2); M is the molar mass of the complex; K is a calibration constant (mm^2 mJ^{-1}) for a given reaction temperature (T/°C) [12]; and m is the sample mass (mg). Variations in ΔH_R are in the range 3–8%.

The melting endotherms were invariably in the lower end of this range (3–5%; 2–3 kJ $mole^{-1}$) whereas the decomposition endotherms were in the upper end of the range (5–8%; 10–15 kJ $mole^{-1}$). This variation is primarily a consequence of peak shape, with melting endotherms being invariably sharp and regular and the decomposition endotherms being broad and irregular.

X-Ray powder diffraction

A Guinier–Hägg parafocussing camera, monochromatized Cu*Kα* ($\lambda = 1.5405$ Å) radiation, and Kodirex single-coated X-ray film were employed in identifying the end-products: Co_3O_4 (JCPDS reference 9-0418) and NiO (JCPDS reference 4-0835).

RESULTS AND DISCUSSION

Data from the TG and DTG curves in air and argon are summarized in Tables 1 and 2; DTA data in nitrogen are summarized in Table 3. Specimen curves are shown in Figs. 1–4.

Both sets of complexes degrade to the respective oxides (Co_3O_4 or NiO) in air over the temperature range 155–800°C. Agreement between observed and theoretical overall mass losses for these processes is within experimental

TABLE 1

Thermogravimetric analysis in air

Compound	Temp. Range T(°C)	Overall mass loss (%)		Stepped mass losses	
		Theoret.	Exptl.	Temp. range (°C)	Mass loss (%)
$Co(DmImt)_2Cl_2$	200–525	80.6	82.0	200–400	65.0
				400–525	17.0
$Co(DmImt)_2Br_2$	270–670	84.2	86.0	270–520	51.0
				520–670	35.0
$Co(DmImt)_2I_2$	180–800	86.8	87.0	180–425	61.0
				425–600	21.5
				600–800	4.5
$Ni(DmImt)_2Cl_2$	155–625	80.6	80.0	155–220	9.0
				220–270	8.0
				270–350	11.0
				350–520	34.0
				520–625	18.0
$Ni(DmImt)_2Br_2$	350–725	84.3	85.0	320–500	53.0
				500–755	32.0
$Ni(DmImt)_2I_2$	160–585	86.9	85.0	160–250	15.0
				300–350	47.0
				350–585	23.0

TABLE 2

Thermogravimetric analysis in argon

Compound	Temp. Range T(°C)	Overall mass loss (%)	Stepped mass losses	
			Temp. range (°C)	Mass loss (%)
Co(DmImt)$_2$Cl$_2$	0–1000	79.0	250– 500	63.0
			500–1000	16.0
Co(DmImt)$_2$Br$_2$	0–1000	80.0	230– 420	51.0
			420– 480	14.0
			480–1000	15.0
Co(DmImt)$_2$I$_2$	0–1000	82.0	250– 450	50.0
			430– 550	18.0
			550–1000	14.0
Ni(DmImt)$_2$Cl$_2$	0–1000	80.0	0– 50	2.0
			50– 210	12.0
			210– 290	18.0
			290– 430	35.0
			430–1000	14.0
Ni(DmImt)$_2$Br$_2$	0–1000	77.0	120– 140	1.0
			200– 450	60.0
			450–1000	16.0
Ni(DmImt)$_2$I$_2$	0–1000	84.0	200– 450	63.0
			450–1000	21.0

TABLE 3

Differential thermal analysis in nitrogen

Compound	DTA peaks,[a] T_m(°C)	Reaction enthalpy, ΔH_R (kJ mole^{-1})	
		Solid	Gas
Co(DmImt)$_2$Cl$_2$	204 M	47	306
	410 D	143	
Co(DmImt)$_2$Br$_2$	205 M	43	
	450 D	127	
Co(DmImt)$_2$I$_2$	192 M	23	
	450 D	170	
Ni(DmImt)$_2$Cl$_2$	192 M	32	307
	350 D	140	
Ni(DmImt)$_2$Br$_2$	204 M	36	
	360 D	180	
Ni(DmImt)$_2$I$_2$	235 M	47	
	340 D	190	

[a] M=melting endotherm; D=decomposition endotherm.

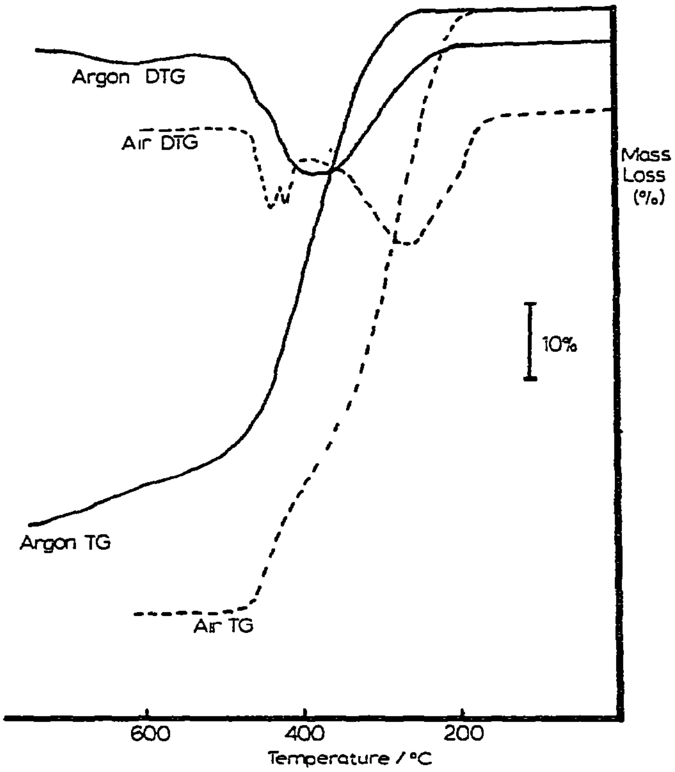

Fig. 1. TG and DTG curves of $Co(DmImt)_2Cl_2$ in air and argon

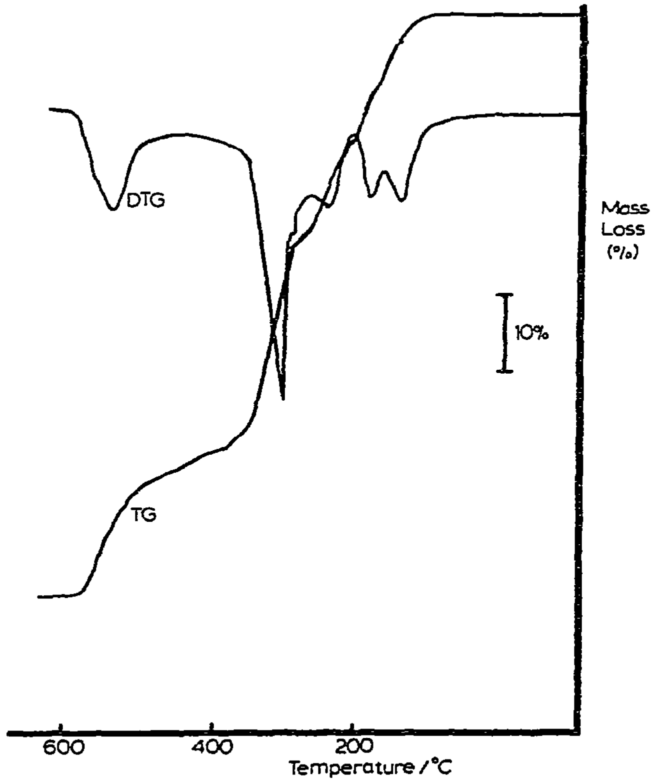

Fig. 2. TG and DTG curves of $Ni(DmImt)_2Cl_2$ in air.

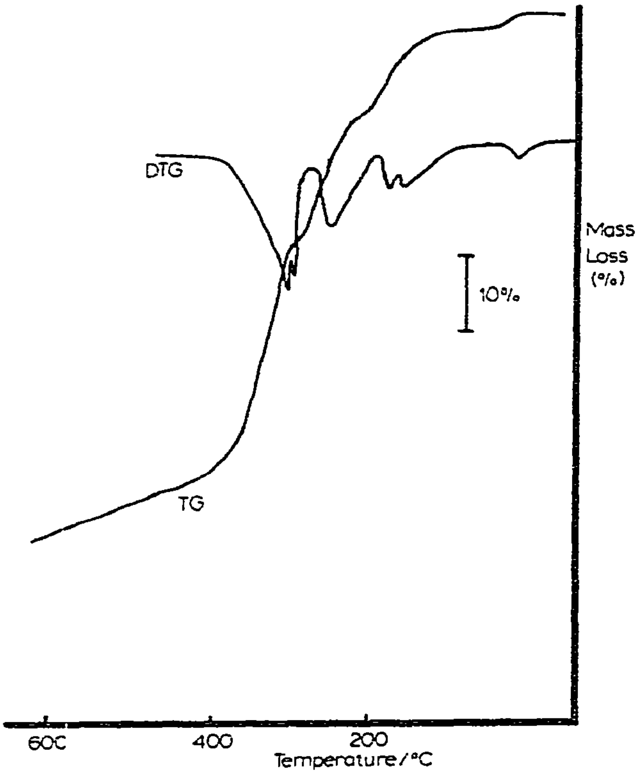

Fig. 3. TG and DTG curves of Ni(DmImt)$_2$Cl$_2$ in argon.

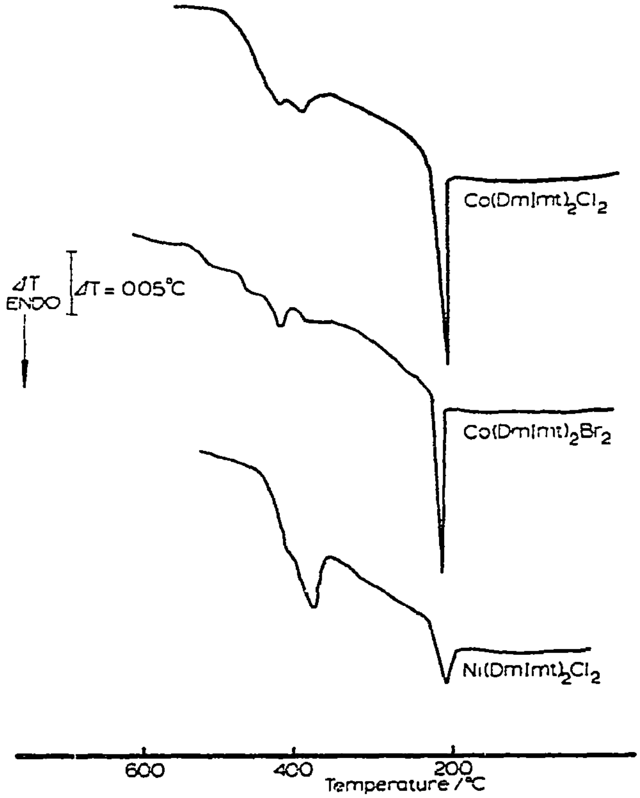

Fig. 4. Selected DTA curves in nitrogen.

error (± 1–2%) in all cases. The final stage (4.5%) observed for $Co(DmImt)_2I_2$ is consistent with further degradation of Co_3O_4 to CoO.

Stepped mass losses obtained from the DTG curves suggest that the first of the two stages is consistent with ligand loss

$$M(DmImt)_2X_2(s) \rightarrow MX_2(s) + 2\ DmImt(g)$$

However, exceptions to this behaviour occur for $Ni(DmImt)_2Cl_2$ and $Ni(DmImt)_2I_2$. The chloro complex exhibits a four-stage decomposition over the temperature range 155–520°C. The first three stages are effectively equivalent and account for one ligand molecule, while the fourth (34.0%) stage accounts for the second ligand.

The first decomposition stage of the iodo complex corresponds to the loss of two-thirds of a ligand molecule

$$Ni(DmImt)_2I_2(s) \rightarrow Ni(DmImt)_{4/3}I_2(s) + 2/3\ DmImt(g)$$

The second stage, however, accounts for the remaining ligand fractions together with some degradation of the residual metal iodide. Overlap of ligand removal and metal salt degradation also occurs for $Co(DmImt)_2I_2$ where the first decomposition stage (61.0%) exceeds the ligand composition in the complex (45.0%).

In argon the total mass losses are in the range 77.0–84.0%. The final downward drift and the absence of clearly defined end-plateaux both signify gradual reduction of the residual metal halide to the metal. The major mass loss for all the complexes occurs in the range 200–500°C and is largely consistent with the removal of both ligand molecules.

The DTG curves show some slight splitting for $Co(DmImt)_2I_2$; major discontinuities occur for $Ni(DmImt)_2Cl_2$. In the latter case four clearly defined stages are indicated; the first (2%) is attributed to absorbed moisture, the remaining three relate to the decomposition of the complex and suggest that the two ligands are evolved in three unequal stages, with the final (35%) stage equivalent to one ligand molecule (33.2%). The first two stages account for the other ligand molecule. Thus the degradation of this complex in argon is similar but not identical to that which occurs in air. It is likely that both decomposition processes involve complicated auto-catalytic degradations, with the oxidizing atmosphere (air) accounting for the slight differences between them.

The DTA curves consist of a melting endotherm with T_p values in the range 192–235°C and a broad decomposition endotherm whose T_m values range from 340 to 450°C. Thus for all of these complexes melting and decomposition are effectively separate processes; in addition, the intermediate molten phase is highly viscous.

Melting point enthalpies range from 23 to $47 \pm 2–3$ kJ $mole^{-1}$ and the decomposition endotherms range from 127 to $190 \pm 10–15$ kJ $mole^{-1}$; total decomposition enthalpies ($170–240 \pm 15$kJ $mole^{-1}$) are similar to those which have been obtained for other pseudo-tetrahedral cobalt(II) complexes (150–240 ± 15kJ mole^{-1}) in this series [12,13].

Gas phase decomposition enthalpies for the process

$$ML_2Cl_2(g) \rightarrow MCl_2(g) + 2\,L(g)$$

where L is a monodentate heterocyclic molecule, may be estimated by assuming the sublimation enthalpy for both the chloro complexes to be the same and in the range (110 ± 15 kJ mole^{-1}) previously obtained for similar cobalt (II) complexes containing heterocyclic molecules [12], sublimation enthalpies of the relevant metal halides ($CoCl_2$, 226 ± 4 kJ mole^{-1}; $NiCl_2$ 245 ± 4 kJ mole^{-1}) are taken from the literature [14].

The values so obtained (Table 3) yield mean gas phase coordinate bond dissociation energies, $\bar{D}$, of 153 ± 15 kJ mole^{-1} for the Co–DmImt bond and 154 ± 15 kJ mole^{-1} for the Ni–DmImt bond. These two values are within experimental error and provide further evidence of the structural similarity between the complexes. The corresponding $\bar{D}$ value for the Co–MImt bond is 134 ± 15 kJ mole^{-1}, which suggests that the additional steric hindrance expected of the DmImt molecule does not result in any significant weakening of the resultant Co–S bond. This conclusion is also supported by X-ray data which have revealed a Co–S distance of 2.320 ± 0.009 Å for the Co–DmImt bond [1] and a mean value of 2.32 ± 0.02 Å for the Co–MImt bond in its complexes [15,16].

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