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THERMAL ANALYSIS OF COBALT, NICKEL AND COPPER COMPLEXES OF 2-AMINOTHIAZOLE

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ABSTRACT

The thermal decomposition of 2-aminothiazole (2-amt) complexes of general formula $M(2\text{-amt})_2X_2$ [M = Co(II) and Cu(II)] and $Ni(2\text{-amt})_4X_2$ [X = Cl and Br] have been studied in air and argon by TG and DTG as well as by DTA in nitrogen; end products from the decompositions in air have been characterised by X-ray powder diffraction. Decomposition stoichiometries have been proposed and factors governing the thermal decomposition have been discussed.

INTRODUCTION

Thiazole and its derivatives have an extensively studied coordination chemistry which has been stimulated primarily as a consequence of the biochemical importance of the compounds [1]. In particular, 2-aminothiazole (2-amt) has considerable coordination potential with heterocyclic N, amino N and heterocyclic S as possible donor sites. With transition and other metals, 2-amt has N-donating monodentate character [2–7]. The nature of the donating N atom is controversial. Hetero N has been suggested for Co(II) and Cu(II) complexes [2,3] and has been demonstrated to be so by X-ray studies for $Co(2\text{-amt})_2Cl_2$ [8] and $Co(2\text{-amt})_4(NCS)_2$ [9]. Both hetero N [2,3] and amino N [7] have been suggested as donor sites for the Ni(II) complexes.

A thermal analysis study has previously been made of some complexes of benzothiazole (bzt) [10], but we believe this to be the first thermal analysis report for complexes of 2-amt. We are interested in the factors which govern the formation, structures and thermal behaviour of metal complexes with S,N-containing heterocyclic molecules.

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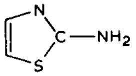

2—Aminothiazole

EXPERIMENTAL

The complexes were prepared as described previously [2,3] and were characterised by chemical analysis (Table 1).

TG and DTG

A Stanton Redcroft TG 750 thermobalance and DTG unit were used together with open Pt crucibles (diam. 6 mm). The atmosphere was column-dried (molecular sieve, 13X) flowing air or argon (15 cm^3 min^{-1}). Sample masses varied from 2 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 (length 2 cm, internal diam. 0.3 cm). The latter were chosen in preference to Pt crucibles because of swelling of the sample, sample creep during the molten phase and also the frequent production of tenacious deposits. The atmosphere was flowing nitrogen (200 cm^3 min^{-1}) with a heating rate of 20°C min^{-1}. Sample masses were 5 mg, the reference material was Al_2O_3, amplifier sensitivity was 50 μV (0.5°C) f.s.d. and the recorder speed was 5 mm min^{-1}. The relationship

$$\Delta H = A/K \cdot w$$

and

$$\Delta H_R = A \cdot M/K \cdot w \cdot 10^3$$

where A = peak area (mm^2), K = calibration constant (mm^2 mJ^{-1}), w = sample weight and M = molecular mass, were used for instrumental calibration [11] and the determination of reaction enthalpies ΔH_R (kJ $mole^{-1}$), respectively; reaction enthalpies were determined from peak areas. Variations in the enthalpies are of the order ±3–5% (melting) and ±5–9% (decomposition).

X-Ray powder diffraction

A Guinier Hagg parafocussing camera, monochromatised CuK_α (λ =

TABLE 1

Analytical data

Compound	Colour	M	C (%)		H (%)		N (%)	
			Found	Calcd.	Found	Calcd.	Found	Calcd.
Co(2-amt)$_2$Cl$_2$	Blue	330.1	22.0	21.8	2.29	2.37	16.9	17.0
Co(2-amt)$_2$Br$_2$	Blue	419.0	17.3	17.2	3.00	2.90	13.3	13.4
Ni(2-amt)$_4$Cl$_2$	Beige	530.2	27.2	27.2	3.11	3.0	21.2	21.1
Ni(2-amt)$_4$Br$_2$	Beige	619.1	23.1	23.3	2.73	2.5	18.0	18.1
Cu(2-amt)$_2$Cl$_2$	Brown	334.7	21.4	21.5	2.4	2.4	16.8	16.7
Cu(2-amt)$_2$Br$_2$	Brown	423.6	17.0	17.0	1.9	1.9	13.1	13.2

1.5405 Å) radiation and Kodirex single-coated X-ray film were employed in identifying the end products, Co_3O_4, NiO and CuO.

RESULTS

Decompositions in air

Data from the TG and DTG curves are summarised in Table 2. Specimen curves are shown in Figs. 1–3.

The complexes degrade to their respective oxides in air over the temperature range 80–805°C. Agreement between observed and theoretical mass losses for the various processes is within experimental error ($\pm 2.0\%$) in all cases.

The TG curves show essentially two-stage processes for the cobalt complexes. It is also clear from the shape of the curves linking the major mass losses that the two processes overlap. In addition, the fine detail from the

TABLE 2

Thermogravimetric analysis data in air

Compound	Overall mass losses			Stepped mass losses	
	Temp. range (T/°C)	Theory (%)	Expt. (%	Temp. range (T/°C)	Mass loss (%)
Co(2-amt)$_2$Cl$_2$	130–585	75.7	75.2	130–300	32.8
				300–585	42.4
Co(2-amt)$_2$Br$_2$	170–620	80.9	82.0	170–350	29.5
				350–620	52.5
Ni(2-amt)$_4$Cl$_2$	155–660	86.0	84.0	155–280	54.0
				280–430	10.8
				430–660	19.2
Ni(2-amt)$_4$Br$_2$	80–660	87.9	87.0	80–200	32.0
				200–280	8.6
				280–350	8.1
				350–660	38.3
Cu(2-amt)$_2$Cl$_2$	50–805	76.2	75.5	50–120	3.5
				120–350	27.0
				350–600	40.0
				600–805	5.0
Cu(2-amt)$_2$Br$_2$	105–755	81.2	83.5	105–220	12.0
				220–480	51.7
				520–580	17.5
				580–755	2.3

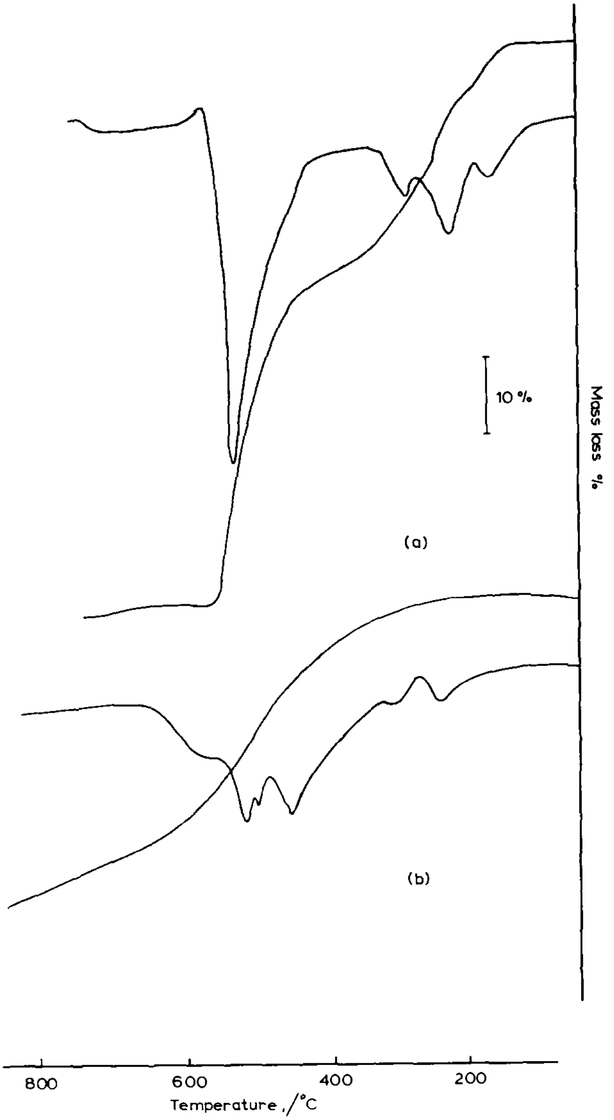

Fig. 1. TG and DTG curves for Co(2-amt)$_2$Cl$_2$ (a) in air and (b) in argon.

DTG curves show that the major processes are occasionallt split into two or more components. Stepped mass losses for Co(2-amt)$_2$Cl$_2$ suggest that one heterocyclic ligand is lost initially (130–300°C) and that the final stage involves further loss of 2-amt, together with production of the oxide (Co_3O_4). The DTG profile for this complex (Fig. 1) also suggests that the first 2-amt ligand is lost in three stages. Fractional heterocyclic ligand loss, ($1\frac{1}{3}$ molecules), and splitting of the first stage have also been observed for the bromo complex.

Consideration of the mass losses leads to the following proposed stoichio-

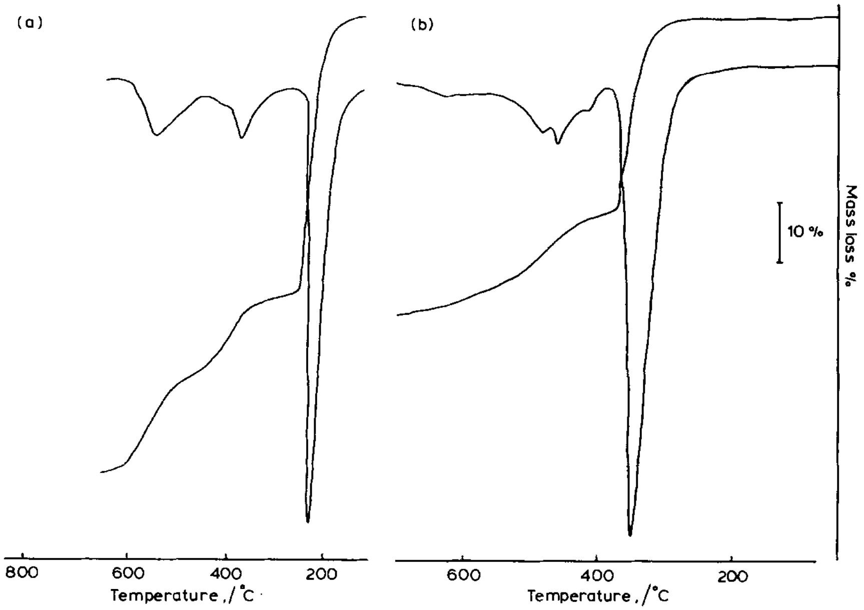

Fig. 2. TG and DTG curves for Ni(2-amt)$_4$Cl$_2$ (a) in air and (b) in argon.

TABLE 3

Thermogravimetric analysis data in argon

Compound	Temp. range (T/°C)	Overall mass loss (%)	Stepped mass losses	
			Temp. range (T/°C)	Mass loss (%)
Co(2-amt)$_2$Cl$_2$	0–1000	65.0	200– 450	32.0
			450–1000	33.0
Co(2-amt)$_2$Br$_2$	0–1000	58.0	220– 650	34.4
			550–1000	23.6
Ni(2-amt)$_4$Cl$_2$	0–1000	60.0	230– 470	36.0
			470– 590	16.0
			590–1000	8.0
Ni(2-amt)$_4$Br$_2$	0–1000	64.0	360– 420	20.3
			420– 520	8.0
			520– 680	17.7
			680–1000	18.0
Cu(2-amt)$_2$Cl$_2$	0–1000	63.0	180– 300	8.0
			300– 500	32.0
			500–1000	23.0
Cu(2-amt)$_2$Br$_2$	0–1000	60.0	50– 250	10.0
			250– 410	20.2
			410–1000	30.0

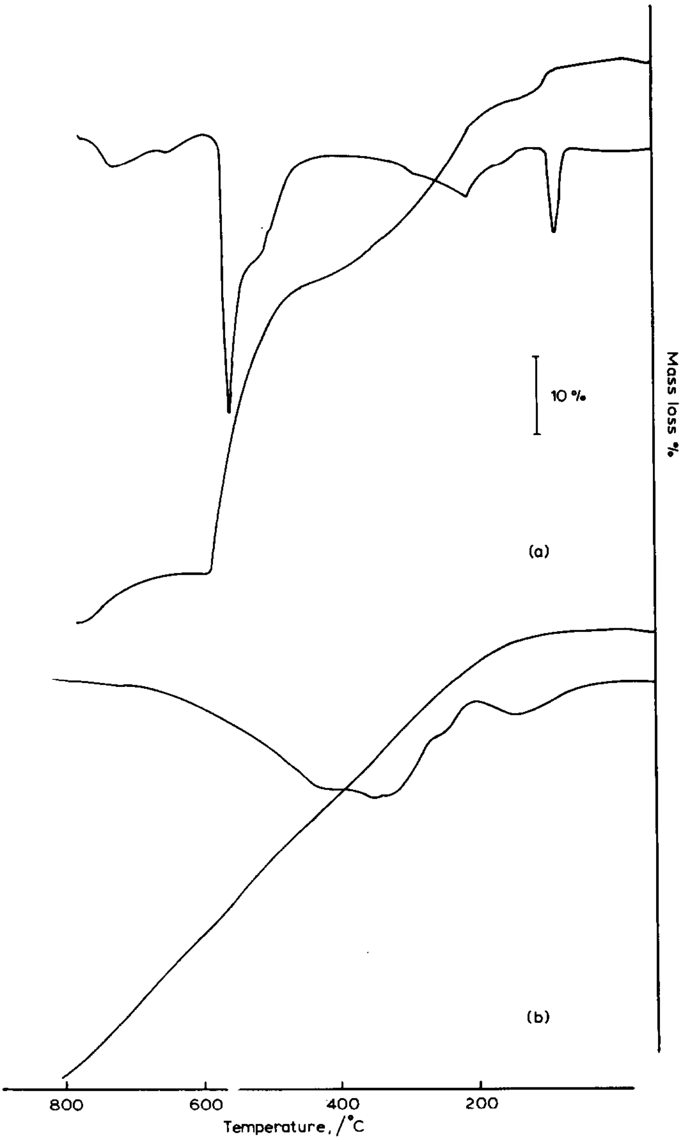

Fig. 3. TG and DTG curves for $Cu(2\text{-amt})_2Cl_2$ (a) in air and (b) in argon.

metric decomposition for $Ni(2\text{-amt})_4Cl_2$.

$NiL_4Cl_2(s) \rightarrow NiL_{4/3}Cl_2(s) + 2\frac{2}{3}\ L(g)$ (155–280°C)

$NiL_{4/3}Cl_2(s) \rightarrow NiL_{2/3}Cl_2(s) + \frac{2}{3}\ L(g)$ (280–430°C)

$NiL_{2/3}Cl(s) \rightarrow NiO(s) + Cl_2(g) + \frac{2}{3}\ L(g)$ (430–660°C)

In contrast to this behaviour, $Ni(2\text{-amt})_4Br_2$ initially (80–200°C) loses

TABLE 4

Differential thermal analysis data in nitrogen and argon

Compound	Nitrogen		Argon	
	DTA peaks (T_m/°C)	Character, ΔH_R/kJ mole^{-1}	DTA peaks (T_m/°C)	Character, ΔH_R/kJ mole^{-1}
Co(2-amt)$_2$Cl$_2$	170	endo, 24.4(±2.0)	170	endo, 26.3(±2.0)
	258	exo	258	exo
			310	exo
Co(2-amt)$_2$Br$_2$	185	endo, 27.4(±2.0)	185	endo, 27.8(±2.0)
	263	exo	263	exo
	428	exo	310	exo
			406	exo
			480	exo
Ni(2-amt)$_4$Cl$_2$	230	endo, 36.5(±3.0)	215	endo, 33.0(±3.0)
	247	exo	226	exo
	300	exo	269	exo
	325	endo, 106(±8.0)	310	endo, 102(±8.0)
Ni(2-amt)$_4$Br$_2$	204	endo, 35.7(±3.0)	204	endo, 36.5(±2.0)
	215	exo	226	exo
	320	exo	310	exo
	360	endo, 109(±8.0)	350	endo, 100(±8.0)
Cu(2-amt)$_2$Cl$_2$	120	endo		
	130	exo		
	250	exo		
Cu(2-amt)$_2$Cl$_2$	100	endo		
	200	exo		
2-amt	93	endo, 13.0(±1.0)		
	237	endo, 31.0(±2.0)		

two ligands; the next ligand is evolved in two effectively equal parts (200–350°C) and the final stage (350–660°C) accounts for the remaining heterocyclic ligand in addition to oxide production.

Cu(2-amt)$_2$Cl$_2$ shows some evidence of solvent retention (50–120°C). The ensuing losses account for one 2-amt ligand (120–350°C) followed by further degradation to the sulphide (CuS, 350–600°C) then to the oxide (CuO, 600–805°C). Cu(2-amt)$_2$Br$_2$ decomposes to the oxide (CuO, 150–580°C) with no clearly defined discontinuities on the TG curve. The DTG curves do suggest the presence of three components, but the associated mass losses produce unsatisfactory intermediate decomposition stoichiometries.

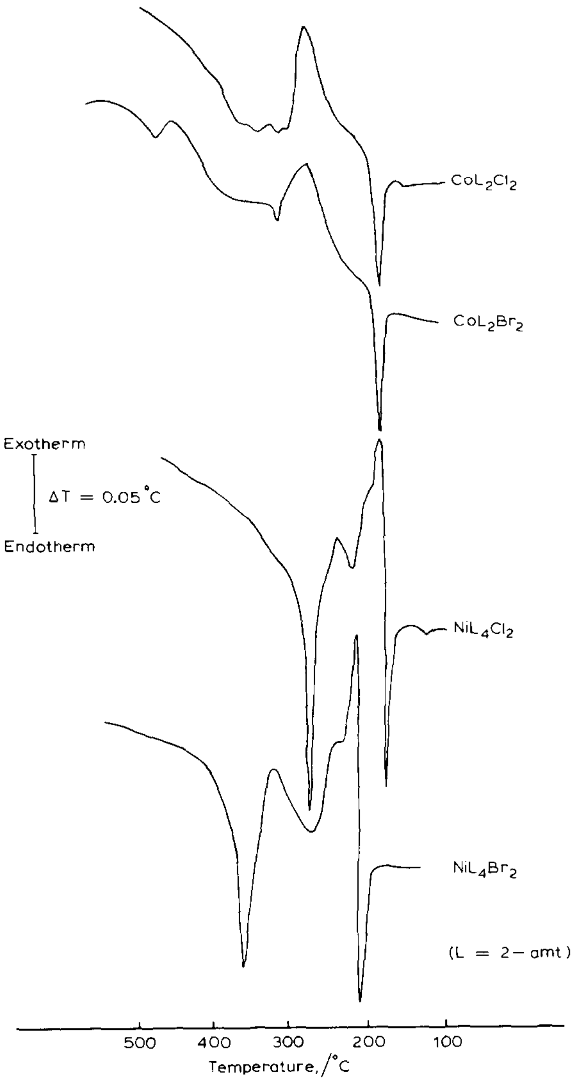

Fig. 4. DTA curves in nitrogen.

Decompositions in argon

Data from the TG and DTG curves in argon are summarised in Table 3. Specimen curves are shown in Figs. 1–3.

Overall mass losses in argon vary between 58.0 and 65.0% over the temperature range 200–1000°C and correspond to the removal of the bulk of the ligands for most of the complexes. The absence of clearly defined end plateaux is typical of all the complexes. The bulk of the mass losses in most cases occur in the temperature range 200–700°C. For the chlorides, this corresponds to approximately half of the heterocyclic molecules, but for the

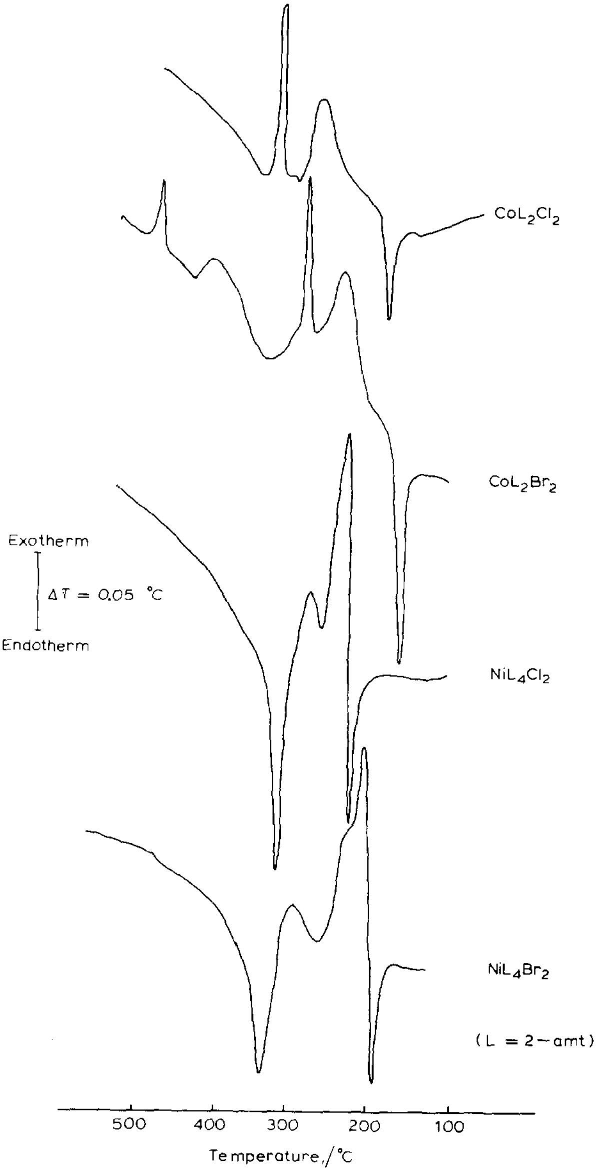

Fig. 5. DTA curves in argon.

bromides, rather more than half of the 2-amt ligands are lost in the same temperature range. The TG curves of the cobalt and copper complexes are essentially featureless, while their DTG curves contain occasional peaks superimposed upon a broad background (Figs. 1 and 3). For the nickel complexes, however, discrete mass losses are indicated on the TG curves, which are matched by relatively sharp DTG peaks (Fig. 2).

DTA curves in nitrogen and argon

Data from the DTA curves in nitrogen and argon are summarised in Table 4. Specimen curves are shown in Figs. 4 and 5.

The essential features of these curves consist of a melting endotherm with T_m values ranging from 170°C [Co(2-amt)$_2$Cl$_2$] to 215°C [Ni(2-amt)$_4$Cl$_2$] followed by a sequence of exotherms; the nickel complexes also exhibit endotherms in their final stages of decomposition. In the case of the cobalt complexes, there is a temperature interval of about 100°C between melting and exothermic degradation, but for the nickel complexes exothermic degradation immediately follows the melting process. Quantitative DTA has been used to determine the melting enthalpies in both nitrogen and argon (Table 4). The resultant values are in agreement, within experimental error ($\pm 5\%$), and are typical of transition metal complexes with heterocyclic ligands [11,12].

No quantitative measurements were attempted on the curves from the copper complexes since they were rather poorly defined. Consequently, only the data in nitrogen are reported (Table 4).

Due to the rather unexpected nature of the DTA curves in nitrogen, the work was repeated in argon in order to obtain a genuinely inert atmosphere. However, the results obtained were very similar. Only in the case of Co(2-amt)$_2$Cl$_2$ were any significant differences observed and they consisted of rather more well-defined exotherms in argon in the temperature range 310–480°C.

DISCUSSION

The major difference between the thermal decomposition of the complexes in air and inert atmospheres appears to be that they are readily converted to the appropriate oxide (Co_3O_4, NiO or CuO) in air but decompose less readily in the absence of oxygen. Co(2-amt)$_2$Cl$_2$, for example, is converted to Co_3O_4 in air between 130 and 585°C, whereas only one heterocyclic molecule (32.0% mass loss) is lost between 200 and 450°C in argon, and at 1000°C the mass loss (65.0%) corresponds to the loss of both heterocyclic molecules. In addition, Ni(2-amt)$_4$Cl$_2$ is converted to NiO in air between 155 and 660°C, whereas at 590°C in argon, the mass loss (52.6%) corresponds to slightly less than three heterocyclic molecules. Similar differences are observed for the copper complexes, although a significant intermediate in the decomposition of Cu(2-amt)$_2$Cl$_2$ in air is CuS, which suggests that ligand decomposition occurs, at least in this instance.

The DTA curves show that, in both nitrogen and argon, thermal decomposition is characterised by endothermic melting followed by exothermic decomposition. In addition, the nickel complexes show an endotherm in their final decomposition stage. These general features contrast markedly with the free ligand, 2-amt, and the corresponding benzothiazole complexes [10], both of which show endothermic melting and decomposition.

The presence of decomposition exotherms for the Co(2-amt)$_2$X$_2$ complexes suggests that the endothermic requirements of ligand removal are exceeded by exothermic reactions, which may possibly arise from reaction between the decomposition products of the heterocyclic molecules. In the initial stages, the DTA curves of the nickel complexes parallel those of the cobalt complexes, the major difference being the presence of an endotherm for the nickel complexes in both nitrogen and argon in the region 350–360°C. The fact that these endotherms all have similar enthalpies suggests a common decomposition process, probably resulting from a common stoichiometric–structural relationship. The mass loss studies in argon suggest that the likely cause of this relationship is the production of polymeric Ni(2-amt)X$_2$ upon the loss of three 2-amt molecules from the original complexes. The endothermic requirements for removal of the heterocyclic ligand then exceed those for the conventionally bonded molecules in the monomeric, tetragonal Ni(2-amt)$_4$X$_2$ complexes [13].

The ill-defined DTA curves for the Cu(2-amt)$_2$X$_2$ complexes probably result from redox reactions and appropriate structural changes in the solid, which render such systems difficult to study [13].

The major features of this study, namely decomposition exotherms, fractional ligand decomposition stoichiometry and the production of a sulphide intermediate all point towards decomposition of the 2-amt molecules during thermal decomposition of the complexes. Consequently, the dominant factor governing the thermal decomposition of the complexes in this study is the thermal stability of the 2-amt molecule [14]. In view of the endothermic decomposition of the free molecule, it is probable that the M(II) ions catalyse the exothermic degradation of the coordinated 2-amt molecules.

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