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THERMAL ANALYSIS OF SOME METHYLHYDRAZINE AND METHYLHYDRAZINIUM COMPLEXES OF COPPER(II), COPPER(I) AND MIXED VALENCE SPECIES

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ABSTRACT

Novel methylhydrazine and methylhydrazinium chloride complexes of copper in various oxidation states (1, 4/3, 2) have been prepared and characterised by elemental analyses and magnetic data. The thermal decomposition of these complexes was studied by simultaneous DTA, TG and DTG. The complex $Cu(II)Cl_2(NH_2NH_2CH_3Cl)$ decomposes on heating with reduction to Cu(I)Cl. Significantly the complex $Cu_3(2I, II)Cl_6(NH_2NH_2CH_3)_2$ on heating disproportionates as follows $3Cu(4/3) \rightarrow 2\ Cu(I) + Cu(II)$.

INTRODUCTION

A number of thermal analysis studies of hydrazine and hydrazinium complexes of transition metal halides have been reported [1–7]. This paper outlines the preparation and study of some methylhydrazine NH_2NHCH_3 and methylhydrazinium chloride $NH_2NH_2CH_3Cl$ complexes of copper. Like hydrazine, methylhydrazine can potentially act as a unidentate or bridging ligand. It forms polymeric complexes which are insoluble in solvents except those causing decomposition. To date, thermal decomposition studies of methylhydrazine complexes have been confined to those of the $MCl_2(NH_2NHCH_3)_6$ complexes (M = Co, Ni), which decompose to the corresponding bis complexes when heated in vacuo [8,9]. Protonation of NH_2NHCH_3 to form the methylhydrazinium cation can take place either at the amino or imino nitrogen; the most likely site is at the imino nitrogen because the adjacent methyl group can help to delocalise the positive charge. The $NH_2\overset{+}{N}H_2CH_3$ cation can still coordinate through the amino nitrogen.

No methylhydrazinium complex of transition metal halides has been reported previously, although analogous hydrazinium complexes with copper have been prepared by Brown et al. [10]. These hydrazinium complexes were

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found to have polymeric structures, copper atoms being linked by halide bridges.

EXPERIMENTAL

$NH_2NH_2CH_3Cl$ preparation. To 15 cm^3 of concentrated HCl in 200 cm^3 of absolute ethanol, 3 cm^3 0.08 M methylhydrazine (MMH) was added dropwise. After stirring for ca. 1 h, the clear solution was placed in a refridgerator, where white needlelike crystals of the salt formed.

Complex preparation

$Cu_3(2I, II)Cl_6(NH_2NH_2CH_3)_2$ and $(Cu(I)Cl)_2(NH_2NH_2CH_3Cl)$. To a mixture of $CuCl_2 \cdot 2H_2O$ (0.02 M) and $NH_2NH_2CH_3Cl$ (0.02 M) was added 30 cm^3 of 3 M HCl. The black solution was heated to 75 °C for five min before refrigeration; white crystals of $(CuCl)_2(NH_2NH_2CH_3Cl)$ formed (Table 1, Analysis a). These were filtered and the filtrate concentrated to ca. 20 cm^3 on a hot water bath under suction from a water pump; upon refrigeration black crystals of $Cu_3Cl_6(NH_2NH_2CH_3)_2$ formed. Note: 1.5 g of the

TABLE 1

Analysis of complexes

Compound	Colour		Analytical data found (theoretical)				
			C (%)	H (%)	N (%)	X (%)	Cu (%)
$NH_2NH_2CH_3Cl$	White		14.23	8.76	33.47	43.12	–
			(14.56)	(8.55)	(33.95)	(42.94)	–
$CuCl(NH_2NH_2CH_3Cl)$	White		7.04	3.83	15.75	39.06	35.21
			(6.62)	(3.88)	(15.43)	(39.04)	(35.01)
$(CuCl)_2(NH_2NH_2CH_3Cl)$	White	(a)	4.55	2.45	9.79	38.40	45.13
	White	(b)	4.13	2.44	10.02	37.69	44.85
	Dark grey	(c)	4.55	2.59	10.57	37.25	45.37
			(4.28)	(2.52)	(9.99)	(37.90)	(45.31)
$Cu_3Cl_6(NH_2NH_2CH_3)_2$	Black	(a)	4.68	2.77	11.28	42.39	38.48
	Black	(b)	4.74	2.83	11.53	42.24	38.45
			(4.83)	(2.84)	(11.26)	(42.74)	(38.33)
$CuCl_2(NH_2NH_2CH_3Cl)$	Green	(a)	5.90	3.24	12.88	48.66	29.69
		(b)	5.60	3.08	13.16	48.91	29.78
			(5.54)	(3.25)	(12.91)	(49.00)	(29.29)
$CuCl_2(NH_2NH_2CH_3Cl)_2$	Brown		7.60	4.53	18.38	47.08	22.75
			(8.02)	(4.71)	(18.71)	(47.33)	(21.22)
$(CuBr)_2(NH_2NHCH_3)$	Pale brown		3.66	1.81	8.67	47.66	38.12
			(3.61)	(1.82)	(8.41)	(48.00)	(38.17)
$(CuCl)_2(NH_2NHCH_3)$	White		4.84	2.40	11.47	28.85	52.31
			(4.92)	(2.48)	(11.48)	(29.04)	(52.08)

$CuCl_2(NH_2NH_2CH_3Cl)$ complex dissolved in 6 cm^3 of 3 M HCl to give a black solution; on refrigeration black crystals of $Cu_3Cl_6(NH_2NH_2CH_3)_2$ and white crystals of $(CuCl)_2(NH_2NH_2CH_3Cl)$ formed (Analysis b).

Cu(II)Cl₂(NH₂NH₂CH₃Cl). This complex was prepared from both CuCl (a) and $CuCl_2 \cdot 2H_2O$ (b). To a solution of 0.0059 moles of metal salt in 30 cm^3 of concentrated HCl, was added dropwise a solution of 0.0059 moles of MMH in 30 cm^3 of absolute ethanol. Green crystals of the complex formed after stirring for a few minutes. In concentrated HCl, both Cu(I)Cl and $Cu(II)Cl_2$ form $CuCl_4^{2-}$ which is a plausible explanation for the same product being obtained from both salts. The UV spectra of both Cu(I)Cl and $Cu(II)Cl_2$ in concentrated HCl are identical.

Cu(II)Cl₂(NH₂NH₂CH₃Cl)₂. The procedure for the preparation of $CuCl_2(NH_2NH_2CH_3Cl)$ was repeated except that only 10 cm^3 of concentrated HCl was used. A green precipitate of the mono product formed initially, however this changed to the brown of the bis product after stirring for 30 min. It was not possible to prepare this complex in an analytically pure form.

Cu(I)Cl(NH₂NH₂CH₃Cl). Refluxing 0.01 moles of $CuCl_2 \cdot 2H_2O$ with 0.02 moles of MMH in 40 cm^3 of absolute ethanol at ca. 82 °C gave a white solid and a clear solution. Analysis of the white solid showed it to be impure $(CuCl)_2(NH_2NHCH_3)$. The hot mixture was filtered and, on cooling, a white precipitate of $CuCl(NH_2NH_2CH_3Cl)$ formed in the filtrate. It is interesting that the chloride for this hydrochloride formation arose due to the reduction of $Cu(II)Cl_2$ to Cu(I)Cl.

(Cu(I)X)₂(NH₂NHCH₃) (X = Cl, Br). The preparation of $(CuCl)_2(NH_2NHCH_3)$ from ethanolic solution has been previously reported [11]. We prepared this complex successfully by reacting 0.006 moles of $CuCl_2 \cdot 2H_2O$ in 20 cm^3 of 0.88 M NH_3 with 0.012 moles of MMH. After stirring for 30 min, the resulting blue solution was evaporated to dryness on a water bath under suction from a water pump, leaving a residue of the required product. The ability of methylhydrazine to act as a reducing agent was further demonstrated by the fact that stirring the above blue ammonical solution under nitrogen for a few days resulted in the gradual formation of Cu metal. The reaction when repeated with Cu(I)Cl did not yield pure $(CuCl)_2(NH_2NHCH_3)$ complex due to the presence of excess Cu metal produced by reduction of Cu(I)Cl after a few minutes of stirring.

DISCUSSION

Methylhydrazinium chloride $NH_2NH_2CH_3Cl$ dissolves in water and warm ethanol without decomposition. It is deliquescent and when exposed to the air absorbs enough water vapour in a few hours to form a solution. Both the methylhydrazine and methylhydrazinium complexes were found to be

TABLE 2

Thermal analysis data

Compound	Thermogravimetry temp. range (°C)	Weight loss (calc.) (%)	DTA peak temp. (°C)	Inference
$NH_2NH_2CH_3Cl$		–	76 (endo)	Melting
	165–410	100	207 (exo)	$NH_2NH_2CH_3Cl \rightarrow NH_2CH_3Cl$
			263 (endo)	$NH_3CH_3Cl \rightarrow$ vaporized
$CuCl(NH_2NH_2CH_3Cl)$		–	72 (endo)	Melting
	154–419	45.5	218 (exo)	$CuCl(NH_2NH_2CH_3Cl) \rightarrow CuCl(NH_3CH_3Cl)$
			257 (endo)	$CuCl(NH_3CH_3Cl) \rightarrow CuCl$
			407 (endo)	CuCl phase change
			418 (endo)	CuCl melting
$(CuCl)_2(NH_2NH_2CH_3Cl)$	165–419	–	75 (endo)	Melting
			216 (exo)	$(CuCl)_2(NH_2NH_2CH_3Cl) \rightarrow (CuCl)_2(NH_3CH_3Cl)$
			270 (endo)	$(CuCl)_2(NH_3CH_3Cl) \rightarrow 2CuCl$
			407 (endo)	CuCl phase change
			418 (endo)	CuCl melting
$Cu_3Cl_6(NH_2NH_2CH_3)_2$	100–127	12.6 (15.4)	111 (endo)	$Cu_3Cl_6(NH_2NH_2CH_3)_2 \rightarrow (CuCl)_2(NH_2NH_2CH_3Cl)$
			114 (endo)	
	165–456	27.7 (24.9)	218 (exo)	$(CuCl)_2(NH_2NH_2CH_3Cl) \rightarrow (CuCl)_2(NH_3CH_3Cl)$
			274 (endo)	$(CuCl)_2(NH_3CH_3Cl) \rightarrow 2CuCl$
			407 (endo)	CuCl phase change
			418 (endo)	CuCl melting
			223 (endo)	$CuCl(NH_3CH_3Cl) \rightarrow CuCl$
			266 (endo)	
			407 (endo)	CuCl phase change
			418 (endo)	CuCl melting

$CuCl_2(NH_2NH_2CH_3Cl)$		–	72 (endo)	Melting
	96–136	25.1 (23.3)	111 (endo)	$CuCl_2(NH_2NH_2CH_3Cl) \rightarrow CuCl(NH_3CH_3Cl)$
	184–420	29.3 (31.1)	114 (endo)	
	Continuous gradual wt. loss to melting of CuCl			
$(CuCl)_2(NH_2NHCH_3)$	124–418	27.0	152 (endo)	
			166 (exo)	$(CuCl)_2(NH_2NHCH_3) \rightarrow CuCl$ (18.9%)
			225 (exo)	Also loss of some chloride
			263 (endo)	
			349 (endo)	
			407 (endo)	$\beta \rightarrow \gamma$ phase change
			418 (endo)	Cu(I)Cl melting
$(CuBr)_2(NH_2NHCH_3)$	Continuous graduate wt. to melting of CuBr		145 (endo)	
	118–484	27.7	181 (exo)	$(CuBr)_2(NH_2NHCH_3) \rightarrow CuBr$ (13.8%)
			218 (exo)	Also loss of some bromide
			266 (endo)	
			322 (endo)	
			385 (endo)	$\gamma \rightarrow \beta$ phase change
			468 (endo)	$\beta \rightarrow \alpha$ phase change
			484 (endo)	Cu(I)Br melting

insoluble in organic solvents, as expected for polymeric structures. In water the $(CuCl)_2(NH_2NH_2CH_3Cl)$, $Cu_3Cl_6(NH_2NH_2CH_3)_2$ and $CuCl(NH_2NH_2CH_3Cl)$ complexes decompose giving a white precipitate which was found from analysis to be largely Cu(I)Cl and some Cu metal. The other complexes dissolved in water decomposing to give clear solutions. With the exception of the $Cu_3Cl_6(NH_2NH_2CH_3)_2$ and $CuCl_2(NH_2NH_2CH_3Cl)$ complexes, all the complexes prepared were found to decompose on exposure to air. The $CuCl(NH_2NH_2CH_3Cl)$ complex is particularly unstable.

The mixed valence complex $Cu_3Cl_6(NH_2NH_2CH_3)_2$ is analogous to the hydrazinium complex $Cu_3Cl_6(N_5H_5)_2$ prepared by Brown et al. [10], containing one Cu(II) and two Cu(I) ions. The magnetic moment of $Cu_3Cl_6(NH_2NH_2CH_3)_2$ at 20 °C was found to be 2.15 BM per formula unit; that for the $CuCl_2(NH_2NH_2CH_3Cl)$ complex was 1.99 BM. Both these values are in the 1.75–2.20 BM range generally found for Cu(II) complexes, regardless of stereochemistry.

Thermal analysis

The DTA, TG and DTG experiments were carried out on a Stanton Redcroft simultaneous thermal analyzer. The 10–20 mg samples were heated in platinum crucibles at 5 °C min^{-1} in a nitrogen atmosphere, with a flow rate of 50 cm^3 min^{-1}. The inert reference sample used was α-alumina. Thermal analysis was carried out on $NH_2NH_2CH_3Cl$ and the copper complexes with the exception of $CuCl_2(NH_2NH_2CH_3Cl)_2$; the results are given in Table 2.

$NH_2NH_2CH_3Cl$. The DTA endotherm at 76 °C has no associated weight loss and occurs as an exotherm on cooling; it is therefore due to melting. Although this melting endotherm for several runs consistently occurred at the same temperature the associated exotherm, a very sharp peak much sharper than the melting peak, on subsequent freezing at 5 °C min^{-1} varied from 57 °C to ca. 20 °C; this effect is due to supercooling. Total weight loss occurs in a single step between 165 and 410 °C; however 96% of this loss is observed up to 300 °C. The associated DTG peak appears as a doublet and the exo and endo DTA peaks indicate that the decomposition takes place in two steps. Thermal analysis of the hydrazinium halides N_2H_5X (X = Cl, Br) exothermally yields ammonium halides as decomposition intermediates [2]. Similarly methylhydrazinium nitrate forms methyl ammonium nitrate as a decomposition product [12]. Therefore a likely intermediate in the decomposition of $NH_2NH_2CH_3Cl$ is NH_3CH_3Cl; this would account for a weight loss of 18% occurring at 222 °C, approximately midway between the DTA exo and endo peaks.

$CuCl(NH_2NH_2CH_3Cl)$ and $(CuCl)_2(NH_2NH_2CH_3Cl)$. The thermograms for these complexes are very similar and, like the thermogram for

$NH_2NH_2CH_3Cl$, have DTA peaks associated with melting, and exo and endo peaks associated with the ligands decomposition. The final loss of ligand coincides with the melting and initial vaporization of Cu(I)Cl; therefore the TG curves show a continual gradual weight loss. This effect was observed for all the methylhydrazium complexes studied. Table 3 gives the melting and subsequent freezing temperatures of these methylhydrazinium complexes and for the Cu(II) complex on heating and cooling at 5 °C min^{-1}.

The freezing point consistently occurs at the same temperature, and its depression is probably due to the presence of a mixture of two components in the melt, i.e. melted ligand and Cu(I)Cl. The DTA endotherm at 407 °C is attributed to the phase transition from the gamma cubic zincblende structure of Cu(I)Cl to the hexagonal wurtzite structure. The endotherm at 418 °C is due to melting of Cu(I)Cl; both these endotherms are reversible. They appear as exotherms on cooling at the same temperature. There is inconsistency in the literature as to the exact temperature of the phase change and melting of Cu(I)Cl [13–15]. Values of 403 and 407 °C have been reported for the phase change, and 415 and 430 °C for melting. The values of 403 and 415 °C determined using DTA [15] are the closest to the results found for these complexes.

$Cu_3Cl_6(NH_2NH_2CH_3)_2$. Unlike the other methylhydrazinium complexes, this complex has no endotherm due to melting at ca. 72 °C. As shown in Fig 2 a stable intermediate exists between 127 and 175 °C. Formation of this intermediate takes place in two steps as suggested by the doublet DTA and DTG peaks. A possible intermediate is $(CuCl)_2(NH_2NH_2CH_3Cl)$, as both complexes were prepared from the same reaction. Although the observed weight loss of 12.61% is lower than the theoretical value of 15.4% for this conversion, evidence for the intermediate comes from comparison of the DTA, DTG and TG curves above 127 °C with those for the $(CuCl)_2(NH_2NH_2CH_3Cl)$ complex (Fig. 1). Heating $Cu_3Cl_6(NH_2NH_2CH_3)_2$ in air was found to give the same thermogram as that obtained by heating under nitrogen to 275 °C. Subsequently, the sample heated in air exhibited a large DTA exotherm at 290 °C associated with the oxidation of the ligand. Analysis of the dark grey compound obtained on heating in air to 127 °C showed it to be pure $(CuCl)_2(NH_2NH_2CH_3Cl)$ (Table 1, Analysis c).

TABLE 3

Melting and subsequent freezing temperatures of complexes

Complex	Melting temp. (° C)	Freezing temp (° C)
$CuCl(NH_2NH_2CH_3Cl)$	72	50
$(CuCl)_2(NH_2NH_2CH_3Cl)$	75	52
$CuCl_2(NH_2NH_2CH_3Cl)$	72	50

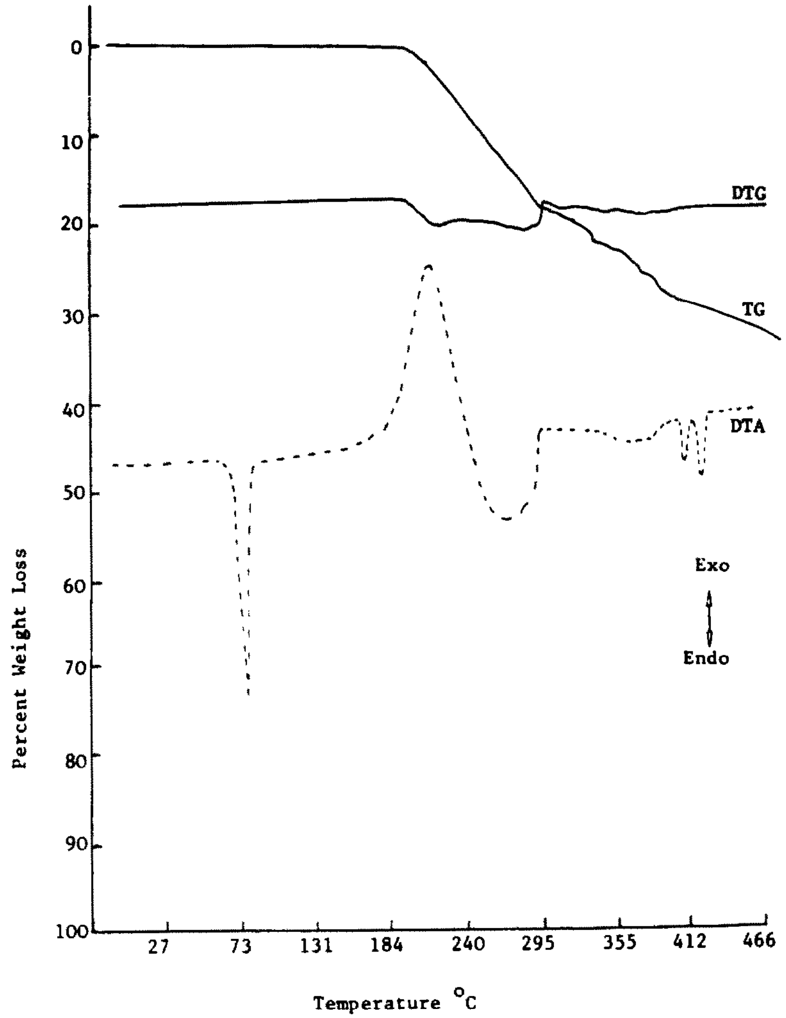

Fig. 1. Simultaneous TG-DTG-DTA of $(CuCl)_2(NH_2NH_2CH_3Cl)$.

$CuCl_2(NH_2NH_2CH_3Cl)$ [1]. The endotherm (Fig. 3) at 72°C is due to melting. The initial weight loss of 22.1% has associated doublet DTA and DTG peaks indicating that the decomposition takes place in two steps. Possible intermediates are $Cu(II)Cl_2(NH_2CH_3)$ (wt. loss = 23.7%) or $Cu(I)Cl(NH_2CH_3 \cdot HCl)$ (wt. loss = 23.3%). The latter compound's formation is more likely as the doublet DTA endotherms at 407 and 418°C are characteristic of a Cu(I) complex. The exotherm and endotherm at 223 and 266°C are similar to those found for the other methylhydrazinium complexes, again suggesting a compound of the type $CuCl(NH_2CH_3 \cdot HCl)$. Therefore decomposition takes place with reduction of Cu(II) to Cu(I).

$(CuX)_2(NH_2NHCH_3)(X = Cl, Br)$. These methylhydrazine complexes have no DTA endotherm associated with melting. The first endotherm for the

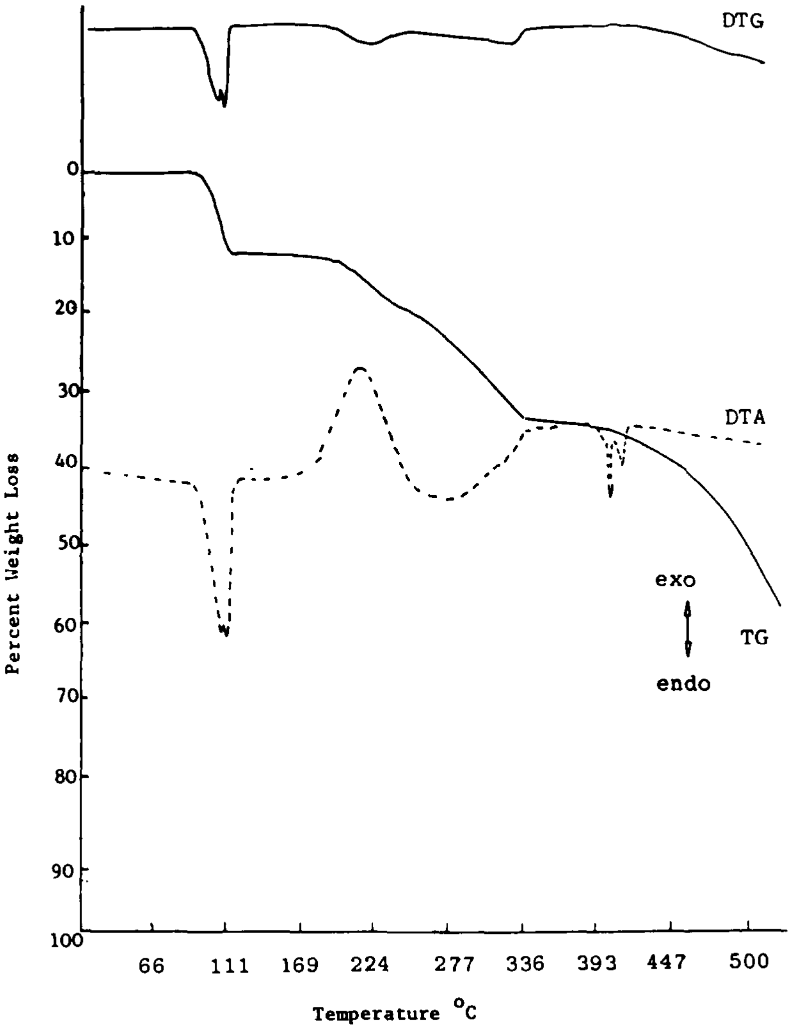

Fig. 2. Simultaneous TG–DTG–DTA of $Cu_3Cl_6(NH_2NH_2CH_3)_2$.

bromide complex occurs at 145 ° C whereas that for the chloride is at 152 ° C, showing that the latter complex is the more stable. From the start of the weight loss on decomposition, the TG curve has a continuous gradual slope up to the melting of the metal salt, even after all the ligand is lost. This indicates that some halogen from CuBr and CuCl is also evolved. The DTA curves for both complexes exhibit sharp endotherms immediately followed by a broad doublet exotherm and a broad doublet endotherm. The chloride complex has DTA endotherms associated with the gamma to beta phase transition, and melting of CuCl as observed for the other complexes. The bromide complex has three endotherms, at 385 ° C due to the conversion of CuBr from the gamma cubic zincblende structure to the beta hexagonal

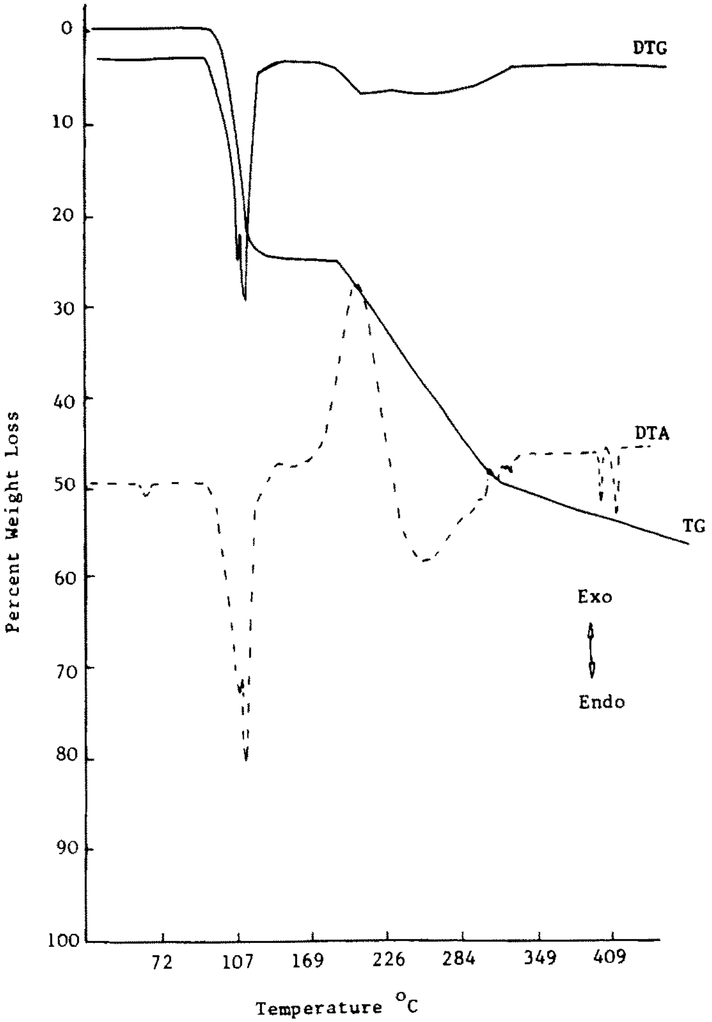

Fig. 3. Simultaneous TG–DTG–DTA of $CuCl_2(NH_2NH_2CH_3Cl)$.

wurtzite structure, followed at 468°C by conversion of the alpha cubic structure; the final endotherm at 484°C is due to the melting of CuBr [14]. These three endotherms appear as exotherms at the same temperature on cooling at 5°C min^{-1}.

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