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STUDY OF THE THERMAL DECOMPOSITIONS ON N,N-DIALKYL-N'-BENZOYLTHIOUREA COMPLEXES OF Cu(II), Ni(II), Pd(II), Pt(II), Cd(II), Ru(III) AND Fe(III)

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Abstract

The thermal decompositions of the complexes of N,N-dialkyl-N'-benzoylthioureas with Cu(II), Ni(II), Pd(II), Pt(II), Cd(II), Ru(III) and Fe(III) were studied by TG and DTA techniques. These metal complexes decompose in two stages: elimination of dialkylbenzamide, and total decomposition to metal sulphides or metals. The influence of the alkyl substituents in these benzoylthiourea chelates on the thermal behaviour of the metal complexes was investigated.

Keywords: metal complexes, N,N-dialkyl-N'-benzoylthiourea, thermal decomposition

Introduction

In earlier work, the complexes of N,N-dialkyl-N'-benzoylthiourea (DEBT) with metals (*M*=Cu, Ni, Pt, Pd and Ru) were characterized [1] and their thermal behaviour was studied [2]. The anhydrous products decomposed in a well-defined step in the range 195–280°C, with a narrow endothermic peak, corresponding to the loss of diethylbenzamide.

The present work is concerned with the influence of the alkyl substituents propyl and hexyl in the benzoylthiourea chelates on the thermal behaviour of their metal complexes, where *M*=Cu, Ni, Pt, Pd, Cd, Fe and Ru.

Experimental

The syntheses of N,N-dialkyl-N'-benzoylthiourea (where alkyl=propyl (DPBT) and hexyl (DHBT)) and the preparative methods for the studied complexes $M(DPBT)_2$ and $M(DHBT)_2$ (where *M*=Cu, Ni, Pt, Pd, Cd, Fe and Ru) were the same

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as described previously [2]. All the chemicals were commercial analytical grade reagents and were used without further purification.

TG and DTA studies were carried out under a nitrogen stream at a flow rate of 100 mL min^{-1} on a Shimadzu DT-40 thermal analyzer, with a simultaneous DTA-TG module, at a heating rate of 10°C min^{-1}. The temperature range employed was 25–1000°C. The mass of samples employed in this study was 5–10 mg. α-Al_2O_3 was used as a reference material.

GC-MS analyses were performed with a Hewlett-Packard 5890 HP gas chromatograph and a 5971 HP mass spectrometer, using an HP-1 capillary column, at a heating rate of 15°C min^{-1} in the temperature range 50–250°C.

X-ray powder diffraction patterns were obtained with a Siemens F diffractometer with a Philips PW1010 generator, using CuK_α radiation.

Results and duscussion

Thermogravimetric analysis is a very useful method with which to study the thermal decompositions of solid substances, including simple metal salts and complex compounds [3]. The curves obtained depict the decrease in sample mass with linear increase in treatment temperature.

In the present investigation, the heating rate was fixed at 10°C min^{-1}. Depending on the total mass loss at around 550°C, the sample mass was monitored in the range 5–10 mg during the experimental runs.

TG and DTA curves for DPBT and DHBT are given in Fig. 1. DPBT decomposed with a mass loss of 99.6% in the range 145–380°C, exhibiting similar thermal decomposition behaviour to that of DEBT [2]. The DTA curve of DPBT has only one endothermic peak, which corresponds to the elimination of dipropylbenzamide.

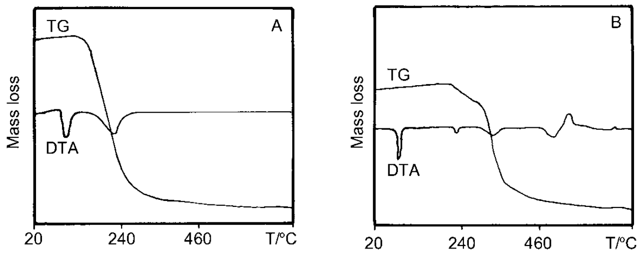

Fig. 1 TG and DTA curves of A – DPBT; B – DHBT

The TG curve for DHBT indicates that decomposition takes place in two steps. In the range 140–195°C, DHBT decomposed to yield dihexylbenzamide and thiocyanic acid, release of which resulted in a mass loss of 17.15%. The calculated mass loss for this is 16.95%. In the second stage, dihexylbenzamide, which is liquid at the final temperature of the first stage, disappears completely in the range 195–414°C with an observed mass loss of 82.46%. Overall, this corresponds to the theoretically expected total mass loss of 100%.

The DTA curve for DHBT exhibits three endothermic effects, centred at 60, 150 and 280°C, and one exothermic peak at around 460°C. The first endothermic peak corresponds to the fusion process and the other two to the decompositions of thiocyanic acid and dihexylbenzamide, respectively. The final peak may indicate a possible dimerization of dihexylbenzamide.

The values obtained as melting points from the DTA curves for DPBT and DHBT are 71 and 60°C, respectively, which are in good agreement with the literature data (DPBT: 71°C, DHBT: 60°C) [4]. The melting point of DEBT is 98°C [2]. The melting points of the N,N-dialkyl-N'-benzoylthiourea ligands decrease as the alkyl group becomes longer. This can be explained by the decreasing intramolecular attractive forces with increase in free volume for a longer alkyl group.

For all the isolated complexes of DPBT and DHBT, the TG and DTA curves (Figs 2 and 3) are similar, with two types of thermal behaviour; thus, these anhydrous complexes display only two effects: elimination of dialkylbenzamide and total decomposition to metal sulphide or metal. The first endothermic peaks in the DTA curves of the metal complexes relate to their melting points. The melting points of

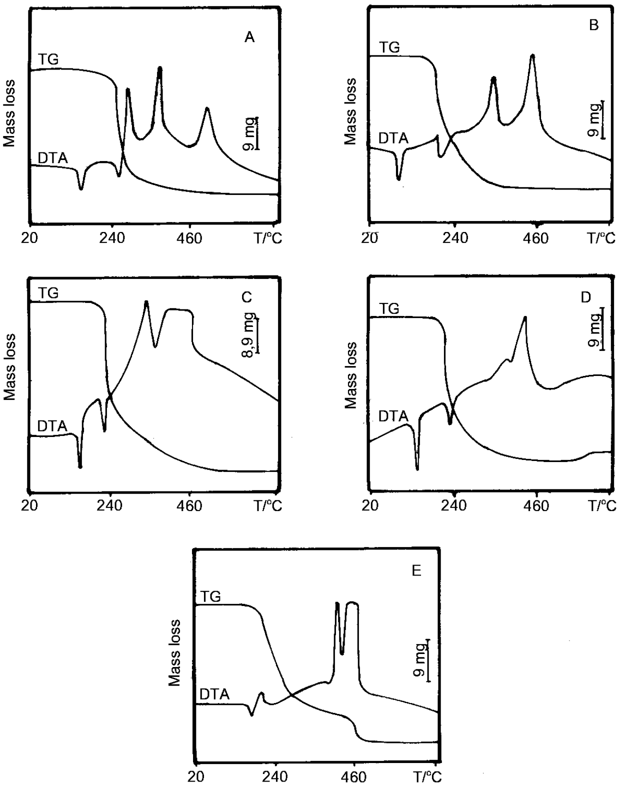

Fig. 2 TG and DTA curves of A – Ni(DPBT)$_2$; B – Cu(DPBT)$_2$; C – Pd(DPBT)$_2$; D – Cd(DPBT)$_2$; E – Pt(DPBT)$_2$

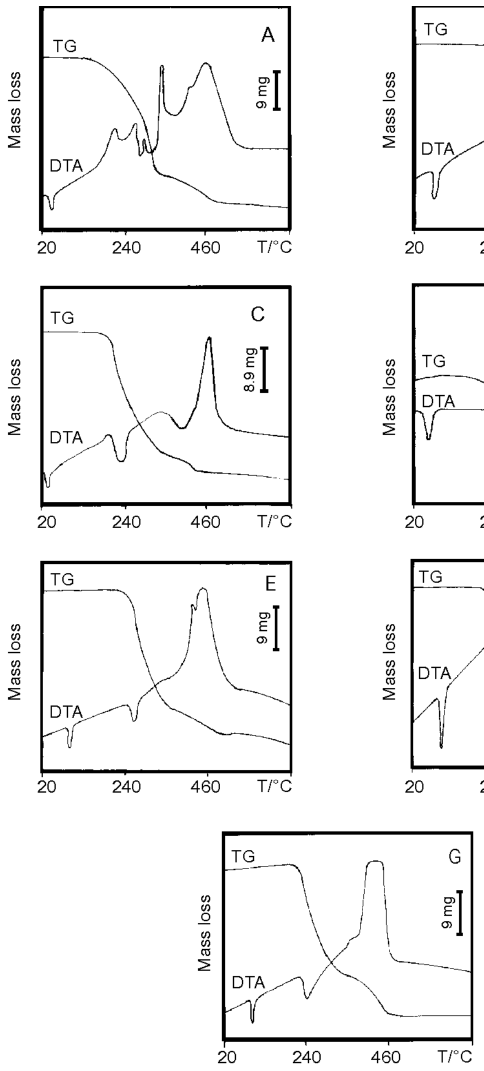

Fig. 3 TG and DTA curves of A – Fe(DHBT)$_3$; B – Ni(DHBT)$_2$; C – Cu(DHBT)$_2$; D– Ru(DHBT)$_3$; E – Pd(DHBT)$_2$; F – Cd(DHBT)$_2$; G– Pt(DHBT)$_2$

the metal-DHBT complexes are lower than those of the metal-DPBT complexes. The Ru and Fe(III)-DPBT complexes were not crystallized. As observed for the free ligands, increase in length of the alkyl group causes a decrease in the melting point of the metal complex.

The thermal decomposition products, the temperature range concerned and the estimated and the calculated mass losses are listed in Tables 1 and 2 for DPBT and DHBT, respectively. The estimated mass losses were based on TG analysis.

Table 1 Mass losses of DPBT complexes in different temperature ranges

Metal complex	Temp. range/ °C	Decomposition product lost	Mass loss/%	
			found	calcd
$Cu(DPBT)_2$	163–330	2 DPB*	69.67	69.54
	330–525	SCN+CN	14.31	14.25
$Cd(DPBT)_2$	181–348	2 DPB	65.14	64.22
	348–491	2 CN	6.8	8.15
$Pd(DPBT)_2$	205–293	2 DPB	63.4	64.83
	293–521	SCN+CN	15.17	13.23
$Pt(DPBT)_2$	191–394	2 DPB	56.66	56.85
	394–494	2 SCN	17.22	16.10
$Ni(DPBT)_2$	181–299	2 DPB	70.82	70.12
	299–557	SCN+CN	13.49	14.47

*DPB: dipropylbenzamide

Table 2 Mass losses of DHBT complexes in different temperature ranges

Metal complex	Temp. range/ °C	Decomposition product lost	Mass loss/%	
			found	calcd
$Cu(DHBT)_2$	150–378	2 DPH*	76.21	76.3
	378–530	SCN+CN	11.75	11.09
$Cd(DHBT)_2$	163–340	2 DHB	70.00	71.68
	340–475	2 CN	10.56	10.42
$Pd(DHBT)_2$	190–376	2 DHB	72	72.22
	376–488	SCN+CN	11.2	10.50
$Pt(DHBT)_2$	202–408	2 DHB	66.2	65
	408–476(488)	2 SCN	12.15	13.05
$Ni(DHBT)_2$	213–315	2 DHB	76.9	76.80
	315–553	SCN+CN	11.27	11.16
$Ru(DHBT)_3$	140–494(340)	3 DHB	72.27	75.91
	340–800	3 SCN	12.2	15.23
$Fe(DHBT)_3$	150–351	3 DHB	75.6	79.04
	351–450	3CN	7.50	7.11
	450–540	3S	10.62	8.75

*DHB: dihexylbenzamide

The first decomposition stage, involving the loss of dialkylbenzamide, appeared as an endothermic effect in the corresponding DTA curves of the Cu, Cd, Pd and Ru complexes. However, this decomposition was seen as an exothermic effect for the Pt and Fe complexes. Only for the Ni complexes did this stage involve two peaks, the first endothermic and the second exothermic. This decomposition stage was also identified by GC-MS, with which the ligands and metal complexes were analyzed between 50 and 250°C. In the GC chromatograms, two peaks were obtained, at 5.71 and 6.75 min for DPBT, and at 6.85 and 10.96 min for DHBT. Two peaks were similarly observed for the metal complexes of these ligands, e.g. at 7.65 and 8.38 min for Cu-DPBT, and at 8.66 and 11.25 min for Fe-DHBT. These peaks were determined by MS to be due to benzoylthiocyanate and N,N-dialkylbenzamide. The percentage quantities of these products varied with the nature of the metal. Mostly the latter product was formed, depending on the stabilities of the metal thiocyanate complexes of DPBT and DHBT. Great similarity was observed in this decomposition stage between the metal complexes of both these ligands and those of DEBT [2]. The estimated and calculated mass losses were in reasonable agreement, varying between 56 and 78% in this stage.

In the range 300–800°C (second decomposition stage), a mass loss of about 10–15% occurs. This reflects qualitatively the loss of SCN and CN radicals, indicated by two exothermic effects for all the metal complexes. These findings are also in good agreement with the behaviour observed for the DEBT complexes of Ni, Cu, Pd, Pt and Ru, as reported previously [2]. As a result, it can be concluded that all N,N-dialkylbenzoylthioureas decompose in two stages in a similar way. There is

Table 3 Residues from the pyrolysis

Complexes	Residue	$T_{\text{final TG}}$/°C	Residue/% found	Residue/% calcd.
DPBT				
Cu	CuS	525	16.02	16.21
Cd	CdS	491		
Ni	NiS	557	15.79	15.51
Pd	PdS	521	21.43	21.88
Pt	Pt	494	26.12	27.05
DHBT				
Cu	CuS	530	12.04	12.61
Cd	CdS	475	19.44	17.91
Ni	NiS	553	11.83	12.05
Pd	PdS	488	16.8	17.29
Pt	Pt	476	21.65	21.94
Fe	Fe	540	6.28	5.1
Ru	Ru	800	15.59	8.85

only a slight shift to higher temperature in the first decomposition step with decrease in length of the alkyl group.

The final residues of pyrolysis were the corresponding metallic sulphides for the Cu, Ni, Cd and Pd complexes; and the metal for the Pt and Ru complexes (also containing certain amounts of metal oxides, as indicated by the X-ray diffraction patterns). The results are listed in Table 3.

The X-ray diffraction pattern data indicated that the residues from the Cu and Pd complexes of both ligands contain some Cu_2S and Pd_2S. The residue from $Fe(DHBT)_3$, was converted to metallic iron above 540°C because Fe_2S_3 decomposes above this temperature. The identity of the final products of the complexes was confirmed by comparing the X-ray diffraction data with those given in the literature [5]. They were all in good agreement.

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