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# THERMAL BEHAVIOUR OF SOME METAL COMPLEXES OF N,N-DIETHYL-N'-BENZOYL THIOUREA

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## Abstract

The thermal behaviour of the complexes of N,N-diethyl-N'-benzoylthiourea (DEBT) with Ni(II), Cu(II), Pt(II), Pd(II) and Ru(III) was studied using differential thermal analysis (DTA) and thermogravimetry (TG). These complexes undergo only a pyrolytic decomposition process. A gas chromatography-mass spectrometry combined system was used for the verification of the first decomposition product and X-ray diffraction method for the characterization of the final products of pyrolysis.

**Keywords**: complexes, N,N-diethyl-N'-benzoylthiourea, thermal behaviour

## Introduction

The applications of thermal analysis have contributed to advances made in the fields of explosives, polymers, soil studies, space research, agrochemicals, organometallics, etc. [1]. N,N-dialkyl-N'-benzoylthioureas are selective analytical reagents especially for the determination of platinum group metals in complex interfering matrices [2, 3]. The complexation capacity of N,N-diethyl-N'-benzoylthiourea (DEBT) has also been reported in several papers [4, 5]. However, there is no information in the literature about their thermal behaviour.

For this reason, the thermal behaviour of Ni(II), Cu(II), Pt(II), Pd(II) and Ru(III)-DEBT complexes has been studied and will be described in this paper.

## Experimental

DEBT was synthesized and isolated complexes M-$(DEBT)_2$ (where $M$=Cu(II), Ni(II), Pt(II), Pd(II)) and $Ru(DEBT)_3$ were prepared using a previously described method [4]. All chemicals used were of analytical reagent grade or chemically pure.

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The thermal studies were carried out on a Shimadzu DT-40 Thermal Analyzer with simultaneous DTA-TG module.

Thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded in a nitrogen atmosphere at a heating rate of 10°C $min^{-1}$ in the temperature range 25–1000°C, with samples varying in mass from 5 to 10 mg. $\alpha$-$Al_2O_3$ was used as reference.

X-ray powder diffraction patterns were obtained by means of a Siemens F Model diffractometer with Philips PW1010 Model generator using $CuK_\alpha$ radiation.

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

## Results and discussion

The thermal analysis curves for DEBT are shown in Fig. 1. Decomposition starts at 143 and ends at 374°C, when all the sample disappears from the reaction crucible. On the other hand, the DTA curve of DEBT exhibits two endothermic effects centred at 101 and 208°C, which correspond to the fusion and decomposition process, respectively. The value found for the melting point (99°C) is in good agreement with literature data (98°C) [4]. Once DEBT has melted, it undergoes a rapid decomposition process responsible for the single endothermic effect in the DTA curve described above.

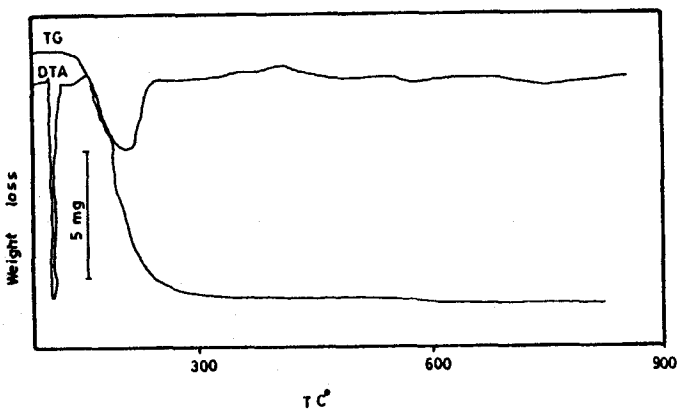


**Fig. 1** DTA and TG curves of DEBT

The TG and DTA curves for Ni(II), Cu(II), Pt(II), Pd(II) and Ru(III)-DEBT complexes are given in Fig. 2.

The thermal decomposition of all the complexes occurs in 2 steps above 170°C: (i) elimination of molecules of diethylbenzamide in the temperature range 195–280°C; (ii) decomposition of metal thiocyanate or cyanide and metal sulphide, metal oxide or metal formation.

The first endothermic peak in the DTA curve of all the complexes corresponds to fusion. The melting points of the complexes are in good agreement with those

given in the literature except for Ru(III) (Table 1) [6]. In the DTA curve of $Ru(DEBT)_3$, the temperature observed as melting point on an Electrothermal 9200 Model digital melting point apparatus which agreed with literature was seen as a decomposition peak. Since the data of DTA analysis are more reliable, it can be stated that $Ru(DEBT)_3$ decomposes at about 170°C, not showing a definite melting point.

**Table 1** Melting points of metal-DEBT chelates

| Metal chelates | $mp_{obs}$/°C | $mp_{ref}$/°C |
|---|---|---|
| $Ni(DEBT)_2$ | 139 | 138 |
| $Cu(DEBT)_2$ | 118 | 117–118 |
| $Pt(DEBT)_2$ | 168 | 164–165 |
| $Pd(DEBT)_2$ | 157 | 156 |
| $Ru(DEBT)_3$ | – | 194–196 |

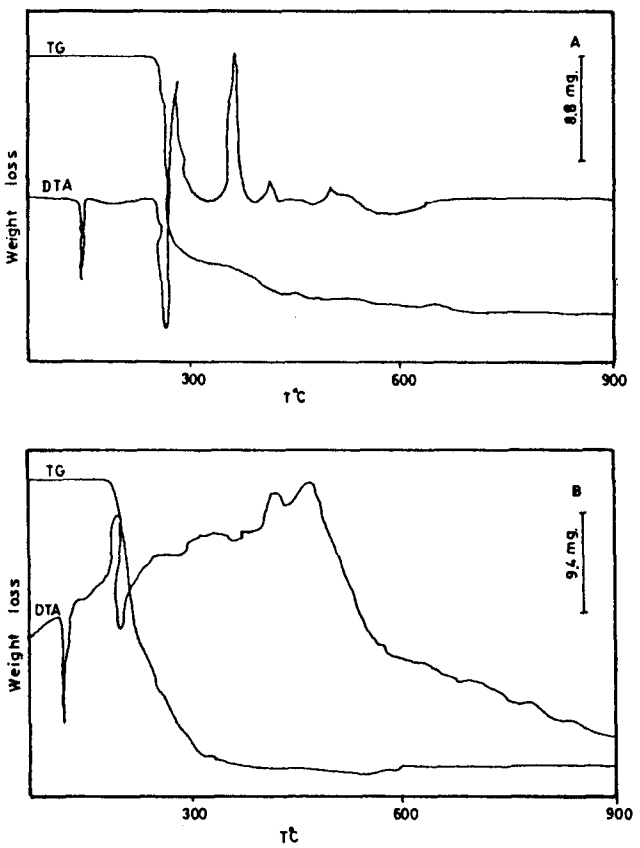


**Fig. 2** DTA and TG curves of A) $Ni(DEBT)_2$; B) $Cu(DEBT)_2$

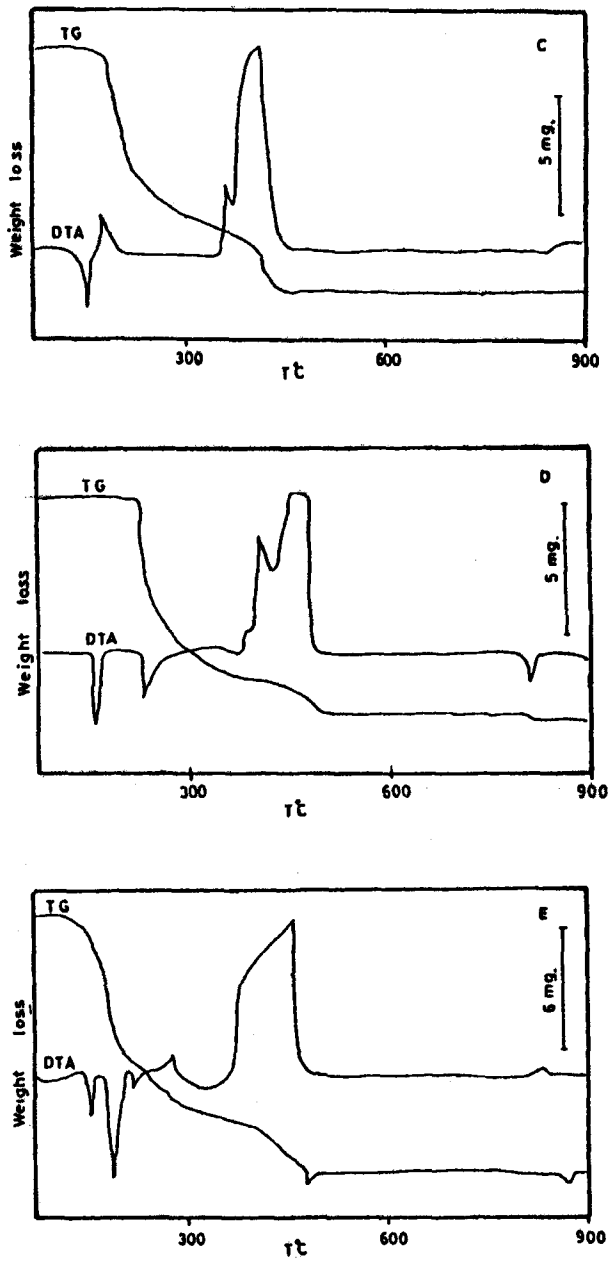


**Fig. 2** DTA and TG curves of C) $Pt(DEBT)_2$; D) $Pd(DEBT)_2$; E) $Ru(DEBT)_3$

All the isolated complexes decompose in the 170–900°C temperature range. In the first decomposition step connected with elimination of benzamide from the ligand, the DTA curve of Ni(II) exhibits one endothermic and one exothermic peak

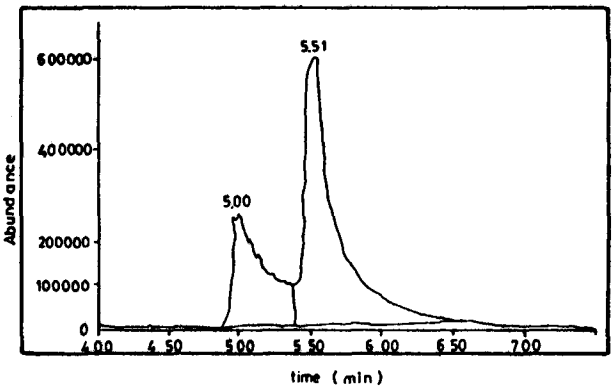


Fig. 3 GC-MS chromatogram of $Ru(DEBT)_3$

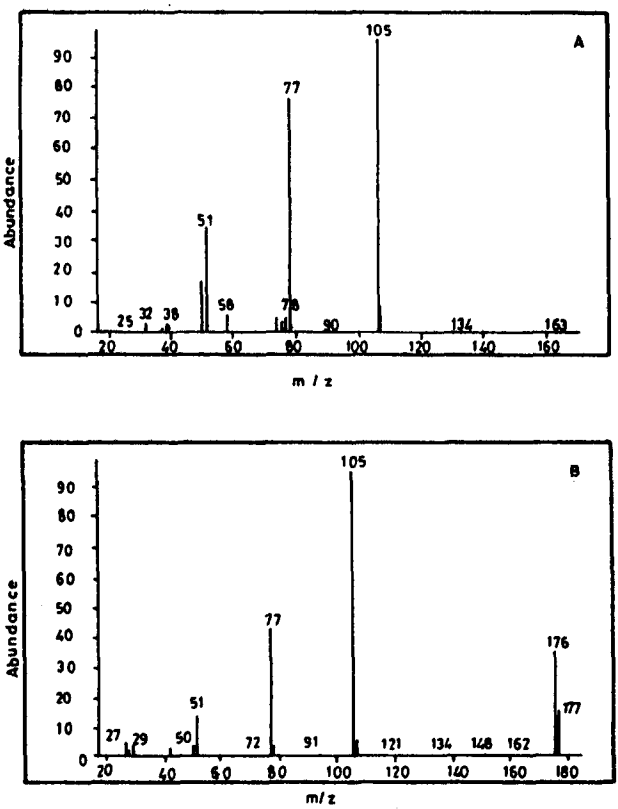


Fig. 4 Mass spectrum of $Ru(DEBT)_3$; A) the peak at $t_R=5$; B) the peak at $t_R=5.51$

at 262 and 278°C. The DTA profile of the Cu(II) chelate shows one exothermic and one endothermic effect at 197 and 202°C. In the DTA curve of the Pt(II) and Pd(II)-DEBT chelates, one exothermic peak was exhibited at 204°C and an endothermic peak at 232°C. The Ru(III)-DEBT chelate showed two endothermic peaks at 160 and 199°C and one exothermic peak at 223°C in the DTA curve.

The decomposition products were identified by GC-MS. The complexes were analyzed between 50 and 250°C but only the GC-MS chromatogram and the mass spectra of $Ru(DEBT)_3$ at different retention times are given in Fig. 3 and Fig. 4, respectively, because of the similarity of the decomposition processes of all the metal complexes studied. Two kinds of decomposition products, benzoylisocyanate and diethylbenzamide, were formed in different ratios, depending on the metal ion. The reason is that during the formation of the latter products, the residual part of the metal complex could be metal thiocyanate. The percentage of the latter decomposition product depends on the stability of the metal thiocyanate compounds because the higher the degree of formation of metal thiocyanate the higher the formation percentage of diethylbenzamide.

The next decomposition process, in which the CN and SCN radicals are lost and metal sulphides or metals are obtained residue between 295° and 600°C, occurs in exothermic effects centered at 367, 413 and 497°C for Ni(II), one or two steps causing exothermic effects centered at 434 and 491°C for Cu(II) and three exothermic effects centered at 382, 407 and 480°C for Pd(II), exothermic effects centered at 384 and 432°C for Pt(II), an exothermic effect centered at 437°C for Ru(III)-DEBT complexes.

Calculated and observed mass losses and the corresponding temperature ranges for the pyrolitic decomposition are given in Table 2.

**Table 2** Thermogravimetric data for pyrolytic processes

| Process | $T_{range}$/°C | Mass loss/% | |
|---|---|---|---|
| | | calcd. | found |
| $Ni(DEBT)_2 \rightarrow 2DEB^*$ | 200–295 | 66.87 | 67.61 |
| $\rightarrow SCN$ | 295–430 | 10.96 | 10.23 |
| $\rightarrow CN$ | 430–562 | 4.91 | 4.54 |
| $Cu(DEBT)_2 \rightarrow 2DEB+SCN$ | 172–380 | 77.12 | 78.14 |
| $\rightarrow CN$ | 380–547 | 4.87 | 4.79 |
| $Pt(DEBT)_2 \rightarrow 2DEB$ | 197–365 | 53.23 | 52.71 |
| $\rightarrow 2SCN$ | 365–480 | 17.44 | 18.86 |
| $Pd(DEBT)_2 \rightarrow 2DEB$ | 223–365 | 61.42 | 59.79 |
| $\rightarrow 2SCN+CN$ | 365–517 | 14.57 | 15.03 |
| $Ru(DEBT)_3 \rightarrow 3DEB$ | 175–308 | 65.87 | 65.62 |
| $\rightarrow 3SCN$ | 311–900 | 21.59 | 22.26 |

*diethylbenzamide

The TG curves of Ni(II), Cu(II), Pt(II), Pd(II) and Ru(III) complexes show 67.61, 78.14, 52.71, 59.79 and 65.62% mass loss which correspond to the theoretical value required for the elimination of two or three moles of diethylbenzamide per mole of compound except for the Cu-DEBT complex (theoretical values, 66.87, 79.00, 53.23, 61.42 and 65.87%). The mass loss of the Cu(II) complex also includes SCN radical in addition to the elimination of benzamide groups.

In the second step of pyrolytic decomposition, the elimination of SCN and CN radicals from Ni(II), Cu(II), Pt(II), Pd(II) and Ru(III) complexes gives 10.23, 4.79, 18.86, 15.06 and 22.26% mass loss. As can be observed, the experimental values of the percentage mass loss in all steps of TG are in good agreement with those calculated for the decomposition process of the complexes above.

**Table 3** Residual mass percentages after the decomposition process

| Complex | Residual compound | $T_{final\ TG}$/ °C | Residual mass/% | |
|---|---|---|---|---|
| | | | calcd. | found |
| $Ni(DEBT)_2$ | NiS | 562 | 17.26 | 17.62 |
| $Cu(DEBT)_2$ | CuS | 547 | 18.01 | 18.13 |
| $Pt(DEBT)_2$ | Pt | 480 | 29.33 | 28.43 |
| $Pd(DEBT)_2$ | PdS | 517 | 24.01 | 25.15 |
| $Ru(DEBT)_3$ | Ru | 900 | 12.54 | 12.12 |

The TG studies reveal that the Ni(II), Cu(II), Pt(II), Pd(II) and Ru(III) complexes yield the respective metal sulphides or metals, NiS, CuS, Pt, PdS and Ru at the end of two decomposition steps. These final residues were identified by comparing their X-ray diffraction data with those given in literature [7]. The residue of the Ru-DEBT complex was identified as a mixture of $Ru+RuO_2$ from its X-ray diffraction powder pattern. The differences between the experimental and the theoretical values (Table 3) for the pyrolitic residues of metal comlexes can be ascribed to partial reduction of the corresponding metallic sulphide to metal.

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## References

1 W. W. Wendlandt, 'Thermal Methods of Analysis', 2nd Ed., John Wiley, New York 1974.
2 M. Schuster, Fresenius J. Anal. Chem., 342 (1992) 791.
3 M. Merdivan, Ph. D. Thesis, Middle East Technical University, Turkey, 1994.
4 M. Schuster, B. Kugler and K. H. König, Fresenius J. Anal. Chem., 338 (1990) 717.
5 K. H. König, M. Schuster, G. Schneeweis and B. Steinbrech, Z. Anal. Chem., 319 (1984) 66.
6 M. Schuster, Ph. D. Thesis, Goethe University, Germany, 1986.
7 ASTM (1981), Index (Inorganic) to the Powder Diffraction File, 81 (Ed.) The Joint Committee on Powder diffraction Standard.