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THERMAL ANALYSIS OF HETEROCYCLIC THIONE DONOR COMPLEXES. PART VII *. PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF THIAZOLE-THIOLATES

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ABSTRACT

The thermal decomposition of benzothiazoline-2-thiolate, thiazolidine-2-thiolate and thiazoline-2-thiolate complexes of general formula M_2L_4, where M = Pd and Pt, were studied in air by means of TG and DTG, and by means of DTA in dinitrogen; end-products from the decompositions in air were characterised by X-ray powder diffraction. A combined TG/mass spectroscopy study was carried out for the platinum benzothiazoline-2-thiolate complex. Decomposition enthalpies were determined by quantitative DTA. Decomposition processes were proposed for the complexes and factors governing the thermal decomposition were discussed.

INTRODUCTION

Previous reports in this series have dealt with the thermal analysis of complexes resulting from the interaction of metal halides with neutral S-donating heterocyclic thiones. Compound stoichiometries reported so far are either ML_2Cl_2 (M = Co(II), Ni(II), Cu(I); L = imidazole-thione [2–5]) or ML_4X_2 (M = Ni(II); L = imidazole-thione [6] and M = Pd(II), Pt(II); L = thiazole-thione [1]). The metals concerned adopt either a tetrahedral [2–5], square [1] or tetragonal stereochemistry [1,6]. The copper (I) complexes are binuclear and the remainder are mononuclear.

Deprotonation of the heterocyclic thiones, by the removal of the thioamido proton, generates the corresponding thiolato anion. These anions having both *exo*-S and *hetero*-N available for coordination, have a richer coordination chemistry than the corresponding neutral thione [7].

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* For Part VI see ref. 1.

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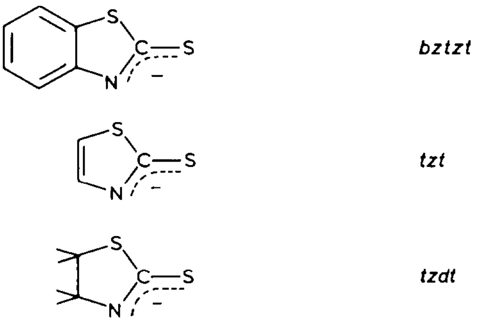

Fig. 1. Molecular formulae and abbreviations of the ligands.

We now report the thermal analysis of the Pd(II) and Pt(II) complexes of thiazoline-2-thiolate (tzt), benzothiazoline-2-thiolate (bztzt) and thiazolidine-2-thiolate (tzdt). The structural formulae of the ligands are shown in Fig. 1.

EXPERIMENTAL

Materials

All of the ligands were obtained commercially: bztztH as 2-mercaptobenzothiazole and tzdtH as 2-mercaptothiazoline from Ralph N. Emanuel Ltd.; tztH as 2-mercaptothiazole from Lancaster Synthesis. The metal salts, potassium tetrachloroplatinate(II) (K_2PtCl_4) and potassium tetrachloropalladate(II) (K_2PdCl_4), were obtained from the Aldrich Chemical Company Ltd. All reagents were used without further purification.

Preparation and analysis of the complexes

All of the complexes were prepared according to the following general scheme: 1 mmol K_2MCl_4 (M = Pd or Pt) was dissolved in 10 ml of distilled water. The ligand, 2 mmol, was dissolved in aqueous ethanol. The metal salt solution was then added to the ligand solution dropwise, which resulted in immediate precipitation of the relevant complex. The product was filtered, washed with ethanol, dried at 70 °C, and stored over $CaCl_2$.

The complexes were characterised by chemical (C, H and N) analyses (Table 1) and IR spectroscopy (4000–200 cm^{-1}, recorded as CsI discs using a Perkin–Elmer 684 IR grating spectrophotometer).

TG and DTG

A Stanton–Redcroft TG 750 thermobalance and DTG unit were used together with open Pt crucibles (6 mm diameter). The atmosphere was

TABLE 1

Analytical data

Complex	No.	Colour	R.M.M.	Carbon (%)		Hydrogen (%)		Nitrogen (%)		Metal (%) [a]	
				Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$[Pt(bztzt)_2]_2$	**(1)**	Yellow	1054	32.82	32.88	2.15	2.05	6.29	6.18	36.2	34.8
$[Pd(bztzt)_2]_2$	**(2)**	Orange	876	38.10	38.36	1.65	1.82	6.20	6.39	24.3	24.2
$[Pt(tzdt)_2]_2$	**(3)**	Mustard	862	16.30	16.70	1.75	1.90	6.05	6.50	44.0	45.2
$[Pd(tzdt)_2]_2$	**(4)**	Orange	684	20.70	21.10	2.25	2.30	7.90	8.20	32.0	31.0
$[Pt(tzt)_2]_2$	**(5)**	Beige	854	16.41	16.86	1.02	0.94	6.19	6.56	54.5	54.3
$[Pd(tzt)_2]_2$	**(6)**	Dark red	676	20.84	21.30	1.22	1.18	8.02	8.28	30.8	31.4

[a] Percentage metal calculated from TG.

column dried (molecular sieve, 13 ×) in flowing air (20 cm^3 min^{-1}). Sample masses were in the range 2–6 mg, the furnace heating rate was 20 °C min^{-1} and the recorder speed was 5 mm min^{-1}.

DTA

A Stanton–Redcroft 673/4 instrument was used together with quartz crucibles (3 cm length and 0.3 cm internal diameter). The latter were chosen in preference to Pt crucibles because of sample swelling and creep, as well as the frequent production of tenacious deposits. The furnace atmosphere was flowing dinitrogen (100 cm^3 min^{-1}) and the heating rate was 20 °C min^{-1}. Sample masses were approximately 10 mg and the reference material was Al_2O_3 (5 mg in a quartz crucible). Amplifier sensitivity was 50 μV (0.5 °C) f.s.d. and the recorder speed was 5 mm min^{-1}.

Details of the quantitative DTA method are found in ref. 2.

TG / mass spectroscopy

A Stanton–Redcroft STA 1500 instrument involving combined TG/DTA/MS techniques was used in an argon atmosphere (50 ml min^{-1}), the heating rate was 10 °C min^{-1} and chart speed was 5 mm min^{-1}. The results quoted in this report were provided by Dr. S. Waddington of the Stanton–Redcroft Consultancy Service, Copper Mill Lane, London SW17 OBN, Gt. Britain.

RESULTS AND DISCUSSION

The complexes, together with their stoichiometries, colours and microanalytical data are summarised in Table 1. Data from the TG/DTG curves are summarised in Table 2 and illustrated in Fig. 2. DTA data, in N_2, for complexes **1** and **2** only are summarised in Table 3 and illustrated in Fig. 3. Results of the combined TG/MS study of $[Pt(bztzt)_2]_2$ (**1**) are illustrated in Fig. 4.

Ligands and complexes

The free ligands adopt the thione tautomeric form in the solids as shown by their IR spectra [7] and X-ray studies on bztztH [8] and tzdtH [9]. With pK_a values in the region of 7 [10] the free ligands are readily deprotonated. The resultant thiolate anions (Fig. 1) have both *exo*-S and *hetero*-N available for coordination to the metal, many complexes have been reported for both bztztH and tzdtH [7]. With Pd(II) and Pt(II) bztzt has been reported to form complexes of empirical formulation $M(bztzt)_2$ with S,N-chelating ligands

TABLE 2

Thermogravimetric analysis in air

Complex	No.	Overall mass losses			Stepped mass losses	
		Temp. range (°C)	Theo. (%)	Expt. (%)	Temp. range (°C)	Mass loss (%)
$[Pt(bztzt)_2]_2$	**(1)**	169–512	63.0	64.0	169–360	13
					360–512	51
$[Pd(bztzt)_2]_2$	**(2)**	33–526	72.2	72.0	33–380	36
					380–526	36
$[Pt(tzdt)_2]_2$	**(3)**	35–475	54.6	56.0	35–284	16
					284–414	23
					414–475	17
$[Pd(tzdt)_2]_2$	**(4)**	35–566	69.0	68.0	35–360	37
					360–548	31
$[Pt(tzt)_2]_2$	**(5)**	80–512	54.3	54.5	80–360	12
					360–447	21
					447–557	21.5
$[Pd(tzt)_2]_2$	**(6)**	120–456	63.9	64.5	120–331	25
					331–456	39.5

TABLE 3

DTA in dinitrogen

Complex	No.	DTA peak (°C)	Peak Range (°C)	Enthalpy (kJ mol^{-1})
$[Pt(bztzt)_2]_2$	**(1)**	204	163–226	85.4 (±0.2)
		466	390–484	191.6 (±3.4)
$[Pd(bztzt)_2]_2$	**(2)**	360	331–380	212.5 (±8.5)

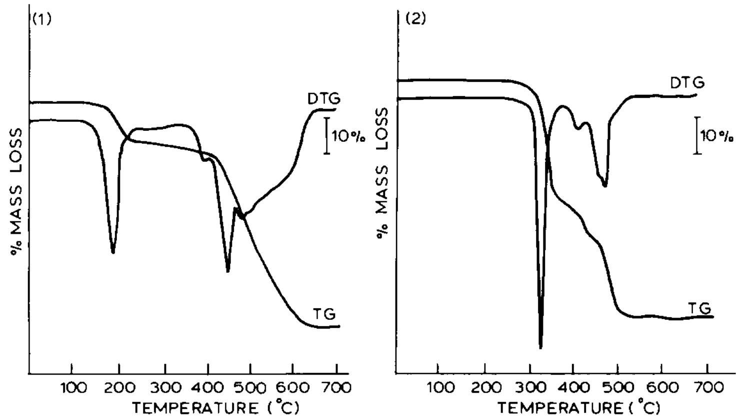

Fig. 2. TG and DTG curves in flowing air at a heating rate of 20 °C min^{-1}: (1), $[Pt(bztzt)_2]_2$; (2), $[Pd(bztzt)_2]_2$.

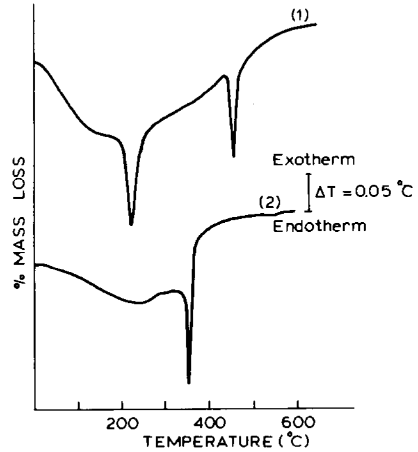

Fig. 3. DTA curves in flowing dinitrogen at a heating rate of 20 ° C min^{-1}: (1), $[Pt(bztzt)_2]_2$; (2), $[Pd(bztzt)_2]_2$.

and square-planar environments about the metal [11]. However, structural studies have shown the complexes to be dinuclear with planar *cis*-S_2N_2 environments about the metal and S,N-bridging ligands [12,13]. Similar structures are proposed for the corresponding tzt and tzdt complexes in this study since all of the complexes have similar IR spectra with $\nu(M-S)$ and $\nu(M-N)$ in the ranges 300–370 cm^{-1} and 245–280 cm^{-1} respectively.

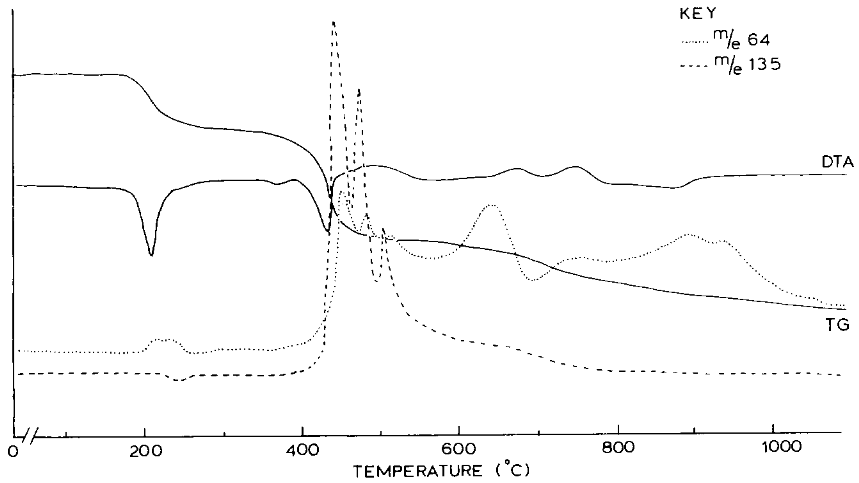

Fig. 4. Combined TG/DTA/MS study of $[Pt(bztzt)_2]_2$ with molecular fragments *m/e* 64 and 135.

Thermogravimetric curves (TG and DTG) in air

*$[PtL_2]_2$ series (**1**, **3** and **5**)*

These complexes thermally degrade to the metal in air. The agreement between experimental and theoretical mass losses (Table 2) are within experimental error (±2.0%).

The complexes decompose over the temperature range 35–557 °C. Complex **1** shows a two-stage decomposition over the temperature range 169–512°C. A 13% mass loss occurs between 169 and 360 °C, with the remaining 51% mass loss occurring between 360 and 512°C. The DTG curve shows that the second major mass loss consists of three distinct components.

Similar decomposition pathways are observed for complexes **3** and **5**. The DTG curves show that both complexes decompose in three distinct stages. An initial mass loss (12–16%) is observed between 35 and 360 °C, followed by a slightly greater loss (21–23%) over the temperature range 248–447 °C and a final mass loss (17–21.5%) between 414 and 557 °C (Table 2).

*$[PdL_2]_2$ series (**2**, **4** and **6**)*

In air the complexes thermally degrade to the metal oxide, PdO. Experimental and theoretical mass losses are in good agreement and within experimental error (±2.0%).

The complexes degrade over the temperature range 33–566 °C. The TG profile for all of the palladium complexes shows a two-stage thermal decomposition, with an initial 25–37% mass loss (33–380 °C) followed by 31–39.5% mass loss (331–548 °C). Complexes **2** and **6** exhibit similar DTG curves, also involving a two-stage decomposition with the second stage consisting of two distinct components. Complex **4** also shows two stages with the first appearing to consist of several components (Table 2).

DTA curves in N_2

Thermal data for the neutral ligands have been previously reported [1]. DTA data are reported here for complexes **1** and **2** only, because the remaining four complexes gave broad and essentially non-reproducible DTA curves.

*$[Pt(bztzt)_2]_2$ (**1**)*

The complex decomposes in the temperature range 163–484 °C and exhibits two distinct endotherms with an overall enthalpy of 277.0 kJ mol^{-1}. The endotherms are sharp in character; however, hot-stage microscopy indicates that melting does not occur. The total reaction enthalpy is less than that expected for ligand sublimation (386 kJ mol^{-1}) [1]. Consequently, the thermal degradation probably involves a more complicated pathway consist-

Fig. 5. Benzothiazole (C_7H_5NS).

ing of a combination of ligand loss (endothermic process) and metal sulphide (PtS) formation (exothermic process).

[Pd(bztzt)$_2$]$_2$ (2)

The complex degrades over the temperature range 331–380 °C exhibiting only one sharp endotherm, with an enthalpy of 212.5 kJ mol^{-1}. Hot-stage microscopy again revealed that the complex decomposed without melting.

TG/DTA/MS study

A combined TG/DTA/MS study of **1** was undertaken to provide detailed information of the breakdown products and to provide an understanding of the processes which determine the thermal decomposition of these complexes. An initial TG/MS study at four different temperatures (204, 438, 495 and 566 °C) indicated the presence of many fragments which appeared at increasing concentration with increasing temperature. Some of the fragments, identified on the basis of their *m/e* values, are CS (44), H_2S (34), HCN (27), CN (26), S_2 (64), H_4S_2 (68), C_6H_5–CN (103) and C_7H_5NS (135). The production of the dominant fragments *m/e* 64 (S_2) and *m/e* 135 (C_7H_5NS) was then monitored with a simultaneous TG/DTA study (Fig. 4). The initial mass loss (13% at 205 °C) is accompanied by modest concentrations of S_2 and C_7H_5NS, the second major mass loss (50% at 449 °C) is accompanied by substantial concentrations of S_2 and C_7H_5NS. This second emission coincides with the second endotherm of the DTA curve. At higher temperatures (ca. 670 °C) further increases in the concentrations of the evolved species occur. The presence of these monitored species, as well as those indicated in the preliminary study, are indicative of the thermal degradation of the ligands. The evolution of elemental sulphur and benzothiazole (Fig. 5) and the production on PtS in the residues suggest that ligand desulphurisation is a major feature of the thermal degradation. At higher temperatures, PtS is converted to the metal and more S_2 is evolved.

FINAL COMMENTS

The decomposition processes proposed for the thiazole-thiolate complexes of palladium and platinum are similar to those previously suggested for the thiazole-thione complexes of the metals [1]. This study has, however, unequivocally demonstrated that the ligands decompose during thermal degradation of the metal complexes. Production of the metal sulphides in the residues is a major factor in the decomposition, although the metal centres are initially coordinated by both the heterocyclic nitrogen and the thione sulphur of the thiolate ligands.

Differences between the TG/DTG and DTA curves of the complexes are attributed to the differing catalytic behaviour of palladium and platinum. The detection of benzothiazole and elemental sulphur (S_2) during the combined TG/DTA/MS study of $[Pt(bztzt)_2]_2$, has confirmed that desulphurisation of the ligand is a primary feature of its decomposition.

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