THERMAL AND STRUCTURAL PROPERTIES OF COORDINATION COMPOUNDS OF 2-MERCAPTO-1-METHYLIMIDAZOLE WITH PALLADIUM(II) AND PLATINUM(II)

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(Received November 25, 1993; in revised form October 21, 1994)

Abstract

Complexes of 2-mercapto-1-methylimidazole (TMZ) with Pd^{II} and Pt^{II} of the general formula $M(TMZ)_nX_2$ (where M=Pd, Pt and X=Cl, Br, I or SO_4 and n=2 or 4) were obtained. The thermal stabilities of the compounds were estimated by derivatographic measurements and lattice constants were estimated from their X-ray powder diffraction patterns.

Keywords: 2-mercapto-1-methylimidazole, Pd(II), Pt(II)

Introduction

Some platinum-group metal complexes obtained as solids, in particular Pt^{II} and Pt^{IV} compounds, have been known as potent anticancer drugs, highly effective against transplanted neoplasms induced either by carcinogens or by viruses. The *cis*-$[Pt(NH_3)_2Cl_2]$ compound, known as *cis*-platin, has been capable of causing complete remission of carcinogenesis [1]. The anticancer effectiveness of these compounds rests on the inhibition of DNA synthesis in cancer cells. The structure of the complex formed resembles interchain cross linking [2]. In this situation it seemed worthwhile to study the bromide, iodide and sulphate Pd^{II} and Pt^{II} complexes of 2-mercapto-1-methylimidazole (thiamazole, TMZ) a compound used for the treatment of thyroid disorders. Previously, chloride complexes of this ligand with Pd^{II}, Pt^{II}, Ru^{III} and Rh^{III} were obtained [3].

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0368–4466/95/ $ 4.00

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Experimental

Materials

2-Mercapto-1-methylimidazole (Aldrich-Europe, Belgium) was recrystallized from redistilled H_2O. The m.p. of the purified compound was 387 K. The complexes were prepared from $PdCl_2$ (AR grade, POCH, Gliwice, Poland) and K_2PtCl_4 obtained by the method of Livingstone [4].

Samples

Redistilled water was used throughout.

$Pd(TMZ)_4Cl_2$

The synthesis of the complex was described in paper [3].

$Pd(TMZ)_4Br_2$ and $Pd(TMZ)_4I_2$

One mmol of $PdBr_2$ (PdI_2) was dissolved in 5 cm^3 of DMF on a water bath. The solution was then diluted to 50 cm^3 with Me_2CO and 4 mmoles of TMZ were added. The solution was then concentrated and left for 12 h. Then, the precipitated red complex was filtered off, washed with Me_2CO and Et_2O and dried in vacuo at 323 K. The yields were 70% and 80%, respectively.

$Pd(TMZ)_4SO_4$

One mmol of K_2PdCl_4 and 4 mmoles of TMZ were dissolved separately in 1*M* H_2SO_4. The solutions were then mixed together and left for crystallization in a refrigerator. The dark-red complex was filtered off, washed successively with dilute H_2SO_4, EtOH and Et_2O and dried in vacuo at 323 K. The yield was 75%.

cis-$Pt(TMZ)_2Cl_2$

The preparation of the complex was described previously [3].

cis-$Pt(TMZ)_2Br_2$ and *cis*-$Pt(TMZ)_2I_2$

One mmol of K_2PtCl_4 was dissolved in 20 cm^3 H_2O, 3 g of KBr (4 g KI) were added and the solution was thoroughly mixed. Separately, 2 mmol of TMZ were dissolved in 20 cm^3 of water. Both solutions were mixed together. A yellow bromide complex fell out within one minute, whereas the yellow-orange iodide complex appeared immediately. After 2 h the precipitates were filtered, washed successively with H_2O, Me_2CO and Et_2O. The bromide complex was dried in vacuo at 323 K and the iodide complex in a desiccator over conc. H_2SO_4. The yields were 62 and 53%, respectively.

Method

TG, DTA and DTG curves were recorded simultaneously with dynamic heating using a derivatograph MOM Budapest. The sample weight was 100–200 mg, the heating rate was 5 deg·min^{-1}, from 20 to 1000°C, the sensitivity was 100 or 200 mg in TG, 1/5 in DTA and DTG. Calcined Al_2O_3 was used as reference material.

X-ray powder diffraction patterns were taken on a DRON-2 (USSR) diffractometer equipped with a scintillation counter, connected with an IBM computer, step by step method, over the 2θ angle range of 4–80°. Powdered Al (AnalaR grade, POCh, Gliwice, a = 4.049(3) Å) was added as an inert reference.

The composition of coordination compounds was determined on a Model 240 CHN Perkin Elmer analyzer.

The melting points of the compounds were measured on a Boetius apparatus.

Results and discussion

To establish the composition of the co-ordination compounds, the contents of carbon, hydrogen, nitrogen, chloride, bromide, iodide and metal were determined. The results are listed in Table 1.

The $Pd(TMZ)_4Cl_2$ complex is stable up to about 373 K. The endothermic effects at 533, 553 and 593 K, as well as the strong exothermic effect at ca. 791 K depends on redox-processes with final metallic Pd, due to combustion of the ligands (Fig. 1a), are accompanied by an 80% loss in weight.

The $Pd(TMZ)_4Br_2$ complex is thermally stable up to 526 K. At this temperature it melts with decomposition. The loss in weight taken from the TG trace is 30.47%, this corresponding to two TMZ molecules (31.59%). An endothermic peak at 598 K accompanied by an 8.62% loss in weight can be due to liberation of one bromine atom (11.05%). The very strong exothermic peak over the range 773–993 K which depends on redox-processes with final metallic Pd, (Fig. 1b) is due to combustion of the organic ligand and is accompanied by a 45.84% loss in weight.

The $Pd(TMZ)_4I_2$ complex is thermally stable up to 473 K where it melts. This process is accompanied by an endothermic peak with no loss in weight. At 543K an endothermic peak appears which is accompanied by a 32.19% loss in weight suggesting liberation of two iodine atoms (31.07%). Over the 793–993 K range, a strong exothermic effect which depends on redox-processes with

Table 1 Analytical and physical data for the complex

Complex	Colour	*m.p.*/K	Found (Calculated) %					Ref.
			C	H	N	X^a	M^b	
$Pd(TMZ)_4Cl_2$	brick-red	> 523 dec.	30.2	3.8	17.5	11.3	17.0	[3]
			(30.3)	(3.8)	(17.7)	(11.2)	(16.8)	
$Pd(TMZ)_4Br_2$	red	526	26.7	3.6	15.6	22.7	15.4	this paper
			(26.6)	(3.3)	(15.5)	(22.1)	(14.7)	
$Pd(TMZ)_4I_2$	red	473	23.6	3.2	13.2	31.4	14.0	this paper
			(23.5)	(3.0)	(13.7)	(31.1)	(13.0)	
$Pd(TMZ)_2SO_4$	dark-red	468	28.0	3.7	16.7	–	16.7	this paper
			(29.1)	(3.9)	(16.9)		(16.1)	
$Pt(TMZ)_2Cl_2$	yellow	> 448 dec.	21.0	2.5	11.2	14.1	39.6	[3]
			(20.7)	(2.4)	(11.3)	(14.3)	(39.5)	
$Pt(TMZ)_2Br_2$	yellow	> 423 dec.	16.7	2.3	9.7	30.6	34.0	this paper
			(16.5)	(2.1)	(9.6)	(27.4)	(33.5)	
$Pt(TMZ)_2I_2$	yellow-	> 493 dec.	14.4	1.9	8.3	36.1	30.1	this paper
	orange		(14.2)	(1.8)	(8.3)	(37.5)	(28.8)	

[a] X = Cl, Br or I
[b] M = Pd or Pt

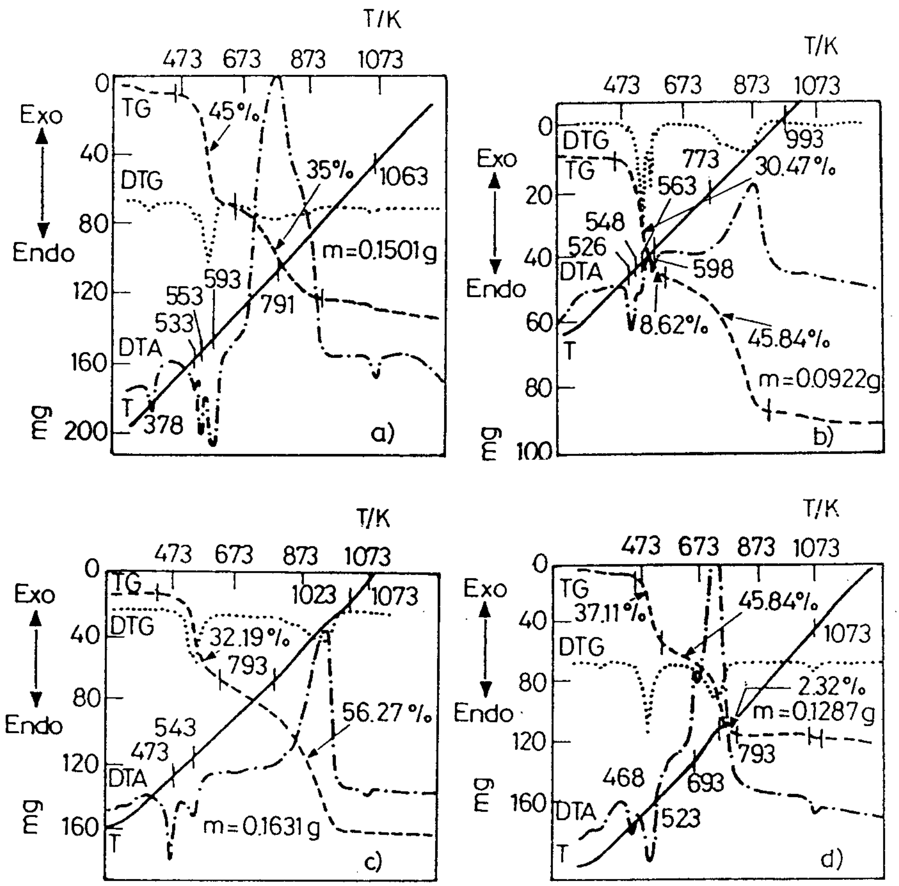

Fig. 1 T, DTA, TG and DTG curves of the complexes: a) $Pd(TMZ)_4Cl_2$; b) $Pd(TMZ)_4Br_2$; c) $Pd(TMZ)_4I_2$; d) $Pd(TMZ)_4SO_4$

final metallic Pd, takes place due to combustion of the organic ligand (Fig. 1c). The over-all loss in weight is 88.46% (86.98%).

The $Pd(TMZ)_4SO_4$ complex melts at 468 K. At 523 K two TMZ molecules are lost, whereas the remaining two leave over the range 693–793 K with accompanying combustion of the organic ligand (Fig. 1d). The respective losses in weight are 37.11 (34.64%) and 45.84% (49.21%).

As has been demonstrated by XRD analysis, the ultimate product of the thermal degradation of all these complexes is palladium metal [5].

The results of thermal analysis for all of the palladium complexes studied together with the mechanism of their thermal degradation are presented in Table 2.

The $Pt(TMZ)_2Cl_2$ complex is thermally stable up to ca. 423K. The endothermic effects at ca. 453 and 588 K and the exothermic one at ca. 773K are accompanied by a 57% loss in weight (TG curve) corresponding to abstraction of both chloride ions and both ligands. The exothermic effect (DTA trace) due to combustion of the ligands is very broad and intense (Fig. 2a).

Table 2 TG data for the Pd(II) and complexes with 2-mercapto-1-methylimidazole

Stable phase or thermal reaction*	Temperature range / K	Effect	Total % of mass loss	
			Found	Theoretical
$Pd(TMZ)_4Cl_2$	293–373	–	–	–
$Pd(TMZ)_4Cl_2 \rightarrow Pd(TMZ)_2$	533–593	endo	45.00	47.20
$Pd(TMZ)_2 \rightarrow Pd$	663–813	exo	35.00	36.01
			80.00	83.21
$Pd(TMZ)_4Br_2$	293–520	–	–	–
$Pd(TMZ)_4Br_2(c) \rightarrow Pd(TMZ)_4Br_2$ (l)	526	endo	–	–
$Pd(TMZ)_4Br_2 \rightarrow Pd(TMZ)_2Br$	548–568	endo	30.47	31.59
$Pd(TMZ)_2Br_2 \rightarrow Pd(TMZ)_2Br$	598	endo	8.63	11.05
$Pd(TMZ)_2Br_2 \rightarrow Pd$	773–993	exo	45.85	42.64
			84.94	85.28
$Pd(TMZ)_4I_2$	293–473	–	–	–
$Pd(TMZ)_4I_2(c) \rightarrow Pd(TMZ)_4I_2(l)$	473	endo	–	–
$Pd(TMZ)_4I_2 \rightarrow Pd(TMZ)_4$	543	endo	32.19	31.07
$Pd(TMZ)_4 \rightarrow Pd$	793–993	exo	56.27	55.91
			88.46	86.98
$Pd(TMZ)_4SO_4$	293–433	–	–	–
$Pd(TMZ)_4SO_4(c) \rightarrow Pd(TMZ)_4SO_4(l)$	468	endo	–	–
$Pd(TMZ)_4SO_4 \rightarrow Pd(TMZ)_2SO_4$	523	endo	37.11	34.64
$Pd(TMZ)_2SO_4 \rightarrow Pd$	693–793	exo	45.84	–
	1073	endo	2.32	49.21
			85.27	83.85

*Symbols used: c – crystal, l – liquid

The $Pt(TMZ)_2Br_2$ complex is stable up to 423 K. Over the range 773–873 K it undergoes complete degradation and the overall loss in weight is 62.68(66.55%) (Fig. 2b).

The $Pt(TMZ)_2I_2$ complex loses most probably one iodine atom at ca. 573 K. The observed loss in weight (18.32%) agrees well with the theoretical one (18.74%). Further degradation of the complex occurs at ca. 883 K where another iodine atom is liberated and organic ligands are combusted to produce a strong exothermic DTA peak.

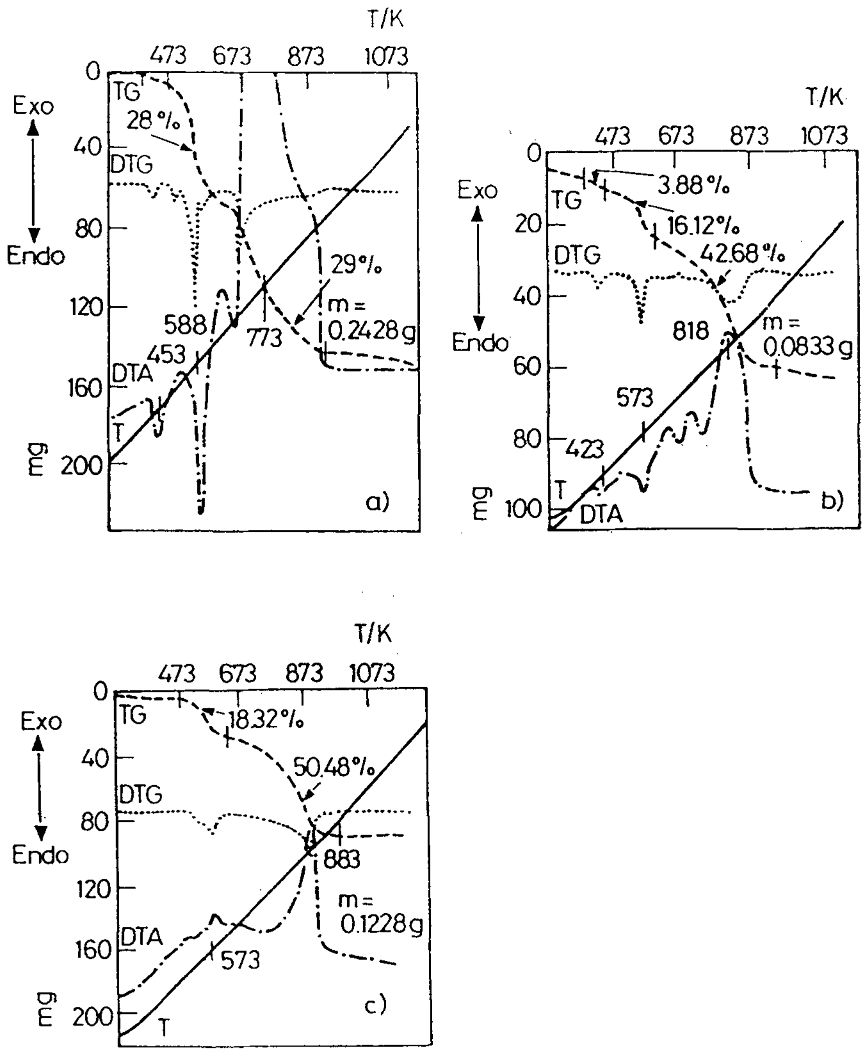

Fig. 2 T, DTA, TG and DTG curves of the complexes: a) $Pt(TMZ)_2Cl_2$; b) $Pt(TMZ)_2Br_2$; c) $Pt(TMZ)_2I_2$

All these complexes are reduced to platinum metal [6] shown by the exothermic effects in the range of 693–900 K.

The results of thermal analysis for all of the platinum complexes studied together with the mechanism of their thermal degradation are presented in Table 3.

The X-ray diffraction data showed that the investigated Pd^{II} and Pt^{II} complexes crystallize in a different system. In Table 4 the unit cell dimensions are

Table 3 TG data for the Pt(II) and complexes with 2-mercapto-1-methylimidazole

Stable phase or thermal reaction	Temperature range / K	Effect	Total % of mass loss	
			Found	Theoretical
$Pt(TMZ)_2Cl_2$	293–423	–	–	–
$Pt(TMZ)_2Cl_2 \rightarrow Pt(TMZ)Cl$	453	endo	28.00	30.27
	588	endo		
$Pt(TMZ)Cl \rightarrow Pt$	670–923	exo	29.00	30.27
			57.00	60.54
$Pt(TMZ)_2Br_2$	293–423	–	–	–
$Pt(TMZ)_2Br_2 \rightarrow Pt$	423–588	endo	62.68	66.55
	588–873	exo		
$Pt(TMZ)_2I_2$	293–493	–	–	–
$Pt(TMZ)_2I_2 \rightarrow Pt(TMZ)_2I$	573	exo	18.32	18.74
$Pt(TMZ)_2I \rightarrow Pt$	883	exo	50.48	52.45
			68.80	71.19

Table 4 Lattice parameters of the palladium and platinum complexes with TMZ

Compounds	Parameters			Ref.
	a /Å α /°	b /Å β /°	c /Å γ /°	
$Pd(TMZ)_4Cl_2$	16.91(6)	17.24(8)	15.74(3)	[3]
	107.05(1)	111.05(9)	95.33(6)	
	17.62(9)	17.68(8)	13.17(4)	this p.
	95.87(8)	98.42(3)	117.00(4)	
$Pd(TMZ)_4Br_2$	13.69(4)	19.52(0)	9.80(1)	
	–	–	–	this p.
$Pd(TMZ)_4I_2$	14.58(0)	26.93(1)	13.78(7)	
	–	–	–	this p.
$Pd(TMZ)_4SO_4$	22.60(3)	39.37(1)	12.93(6)	
	–	101.82(7)	–	this p.
$Pt(TMZ)_2Cl_2$	16.55(4)	16.11(7)	15.79(4)	[3]
	97.39(6)	98.28(8)	88.93(7)	
	15.74(8)	5.77(7)	8.33(0)	
	–	98.49(5)	–	this p.
$Pt(TMZ)_2Br_2$	11.50(1)	13.72(8)	9.40(1)	
	–	–	–	this p.

listed, with the exception of $Pt(TMZ)_2I_2$ which gave poorly legible powder pattern. Both the indexation and calculation of the unit cell dimensions were performed by the ITO–12 method using a Visser program [7].

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Zusammenfassung — Komplexe von 2-Merkapto-1-methylimidazol (TMZ) mit Pd^{II} und Pt^{II} der allgemeinen Formel $M(TMZ)_nX_2$ (mit M=Pd, Pt und X= Cl, Br, I oder SO_4 und n= 2 oder 4) wurden hergestellt. Mittels derivatografischen Messungen wurde die thermische Stabilität der Verbindungen geschätzt und anhand von Debye-Scherrer-Aufnahmen Gitterkonstanten geschätzt.