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Crystal Structures and Thermal Decomposition of *trans*-$Pd(Creat)_2Cl_2 \cdot 2H_2O$ and *cis*-$Pt(Creat)_2I_2 \cdot 3H_2O$

Paul T. Beurkens[a], **Aurea Perales**[b], **Francisco J. Martín-Gil**[c], and **J. Martín-Gil**[c,*]

[a] Crystallography Laboratory Toernooiveld, Nijmegen, Holland
[b] Crystallography Department, Instituto "Rocasolano", Madrid, Spain
[c] Department of Inorganic Chemistry, ETSII, University of Valladolid, E-47011 Valladolid, Spain

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New complexes of the formulae *trans*-$Pd(Creat)_2Cl_2 \cdot 2H_2O$ (**I**) and *cis*-$Pt(Creat)_2I_2 \cdot 3H_2O$ (**II**) have been prepared and their structures and stabilities studied by X-ray diffraction and thermal analysis. Both compounds have a square-planar geometry, the two Cl atoms and N1 creatinine atoms are coordinated to Pd in *trans* configuration, while in compound **II** the I atoms and N1 atoms are coordinated in *cis* configuration. In spite of the earlier differences, the TG and DTA curves of the complexes show that their stability is very similar. Since an extended hydrogen bond system is present in the crystals, especially in **II**, the possible consequences in biological media are discussed briefly.

(Keywords: Creatinine; Palladium(II) complexes; Platinum(II) complexes; Crystal structures; Thermal analysis)

Kristallstrukturen und thermische Zersetzung von trans-$Pd(Creat)_2Cl_2 \cdot 2H_2O$ *und cis-*$Pt(Creat)_2I_2 \cdot 3H_2O$

Es wurden neue Komplexe der Formeln *trans*-$Pd(Creat)_2Cl_2 \cdot 2H_2O$ (**I**) und *cis*-$Pt(Creat)_2I_2 \cdot 3H_2O$ (**II**) hergestellt und ihre Strukturen und Stabilitäten mittels Röntgenstrukturanalyse bzw. thermischer Analyse untersucht. Beide Komplexe haben quadratisch-planare Struktur, die zwei Cl-Atome und die N1-Creatinin-Atome sind an Pd in *trans*-Konfiguration koordiniert, währenddessen in Verbindung **II** die I-Atome und die N1-Atome in *cis*-Konfiguration zueinander stehen. Trotz früherer Differenzen zeigen die TG- und DTA-Kurven der Komplexe, daß ihre Stabilitäten sehr ähnlich sind. Da besonders in **II** ein ausgedehntes Wasserstoffbindungssystem vorhanden ist, werden auch mögliche Konsequenzen bezüglich biologischer Wirksamkeit kurz diskutiert.

Introduction

Palladium and platinum compounds have attracted attention as a consequence of their application in homogeneous and heterogeneous

catalysis. The structure, stereochemistry and bonding in these compounds cover an area of considerable research since the discovery of antitumor properties in certain *cis* Pd/Pt complexes. The structure determination of a series of palladium and platinum complexes with substituted anilines and amino-acids ligands using X-ray diffraction and spectroscopic techniques has been taken up in order to study the substituent effects on coordination and the interaction of these ions with biologically significant ligands. On the other hand, creatinine: $H_3C—N—C(NH)—NH—CO—CH_2$, plays and important role in protein metabolism and is as such of considerable biological interest. It has more than one bonding site towards metal ions and is capable of forming cationic, neutral and anionic metal complexes similar to adenine [1]. In this paper we firstly report the synthesis and the crystal structure of palladium and platinum creatinine complexes. Next, a thermoanalytical study of the complexes is also included in order to define their stability in solid state and to complete this pharmacological requisite in view of the possible utility of such products as antineoplasic drugs.

Experimental

Preparation of the Complexes

trans-$Pd(Creat)_2Cl_2 \cdot 2H_2O$ (**I**): the complex was obtained by mixing in aqueous medium free creatinine with $PdCl_2 \cdot 2H_2O$ in the respective stoichiometry 2/1.

cis-$Pt(Creat)_2I_2 \cdot 3H_2O$ (**II**): the preparation was carried out in dim light, which seemed to minimize formation of dark iodoplatinum precipitates. A total of 415 mg (1 mmol) of K_2PtCl_4 was dissolved in 20 ml of water, and 4 g (about 24 mmol) of KI was added to yield a solution of 0.05 *M* PtI_4^{2-} and 1 *M* I^-. To this solution 226 mg (2 mmol) of creatinine was added. The *cis* compound precipitated inmediately and was filtered, washed with ethanol and dry diethyl ether, and dried in vacuum at room temperature.

Both complexes gave satisfactory elemental analysis.

Crystal Structures

Reflections were measured employing a Philips PW 1100 diffractometer. Calculations were carried out with the computer programs and the X-ray system [2–6] on the Univac 1108 computer of the MEC (Madrid).

Calorimetry

Measurements were carried out with a Perkin-Elmer 3600. Instrument calibration was by a standard indium sample of known temperature (156 °C) and enthalpy (+ 6.79 kcal g^{-1}) of melting.

Results and Discussion

Structures

The crystal analysis parameters are listed in Table 1, while the system of numbering of the atoms in both molecules is shown in Fig. 1. The final

Table 1. *Crystal analysis parameters for compounds* **I** *and* **II**

Crystal data	Compound **I**	Compound **II**
Formula	$C_8H_{12}N_6O_2Cl_2Pd \cdot 2\,H_2O$	$C_8H_{12}N_6O_2I_2Pt \cdot 3\,H_2O$
Crystal habit	transparent yellow needles	transparent red prismatic
Crystal size	$0.15 \times 0.18 \times 0.07$ mm	$0.14 \times 0.18 \times 0.06$ mm
Symmetry	triclinic $P\bar{1}$	monoclinic $P2_1/a$
Unit cell dimensions	$a = 7.272(3)$ Å	$a = 13.807(4)$ Å
	$b = 9.110(4)$	$b = 9.097(1)$
	$c = 7.023(1)$	$c = 16.250(4)$
	$\alpha = 107.93(5)°$	
	$\beta = 118.25(7)$	$\beta = 114.082(5)°$
	$\gamma = 74.23(5)$	
Dc. ($g\,cm^{-3}$), M, $F(000)$	1.885, 437.56, 218	2.592, 727.16, 1 328
Z, μ (cm^{-1})	2, 15.596	4, 109.144
Experimental data		
technique	Four-circle diffrac. CAD-4. Monochromated MoKα, up θ max. 35	Four-circle diffrac. CAD-4. Monochromated MoKα, up θ max. 35
Number of reflexions		
Independent	3 383	6 406
Observed	3 206 [2σ (I) criterion]	4 232 [2σ (I) criterion]
Solution and refinement	*Patterson* L.S. on F obs. with 1 block	*Patterson* L.S. on F obs. with 1 block
Absorption correction	Empirical absorption correction [1]	Empirical absorption correction [1]
Parameters		
Number of variables	91	181
Degrees of freedom	3 115	4 051
Ratio of freedom	35	23
H atoms	difference synth.	calculated positions
Final shift error	0.19	0.02
w-scheme	empirical as to give no trends in $\langle w\Delta^2F\rangle$ vs. $\langle F$ obs.$\rangle$ and $\langle \sin\theta/\lambda\rangle$	empirical as to give no trends in $\langle w\Delta^2F\rangle$ vs. $\langle F$ obs.$\rangle$ and $\langle \sin\theta/\lambda\rangle$
Max. ther. values	U11 (C4) 0.066(2) $Å^2$	U11 (OW3) 0.20 (1.8) $Å^2$
Final R and Rw values	3.1, 3.5	4.2, 4.7
Computer and programs	VAX 11/750, X-Ray 76 [3] Mithril, Dirdiff.	VAX 11/750, X-Ray 76 Mithril, Dirdiff.
Scattering factors	International Tables X-Ray Crystallography [6]	International Tables X-Ray Crystallography

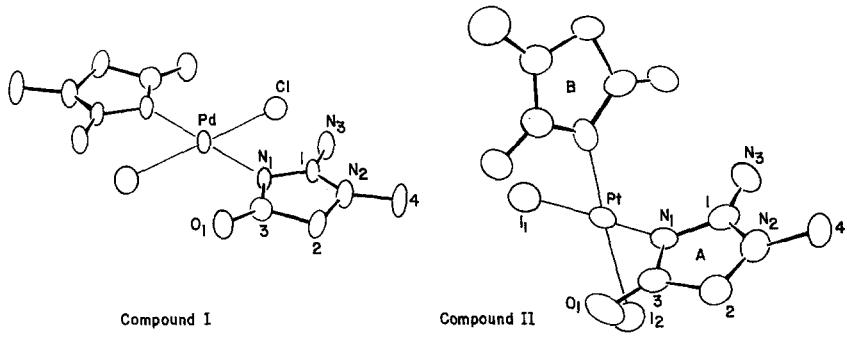

Fig. 1. View of the molecules for compound **I** and compound **II**

structural parameters with their e.s.d's of non-H atoms are reported in Table 2. Bond distances and angles are listed in Table 3.

In both compounds the central Pd and Pt atoms are four coordinated. Both compounds have a square-planar geometry, the two Cl atoms and N1 creatinine atoms are coordinated to Pd in *trans* configuration, while in compound **II** the I atoms and N1 atoms are coordinated in *cis* configuration. The Pd—Cl and Pd—N distances [2.30(1) Å] and [2.03(1) Å] agree well with the values found in similar *trans* PdN_2Cl_2 configurations [7]. Pt—I bond lengths [2.568(9) Å] and Pt—N bond length [2.069(4) Å] lie within the range that has been observed previously [8]. The bond distances and angles within the creatinine molecule are comparable to those obtained for biscreatinine-silver(I) perchlorate dihidrate [9] and creatininium cation [10]. The results suggest an extensive electron delocalitation in the creatinine molecule with the exception of N2—C2, N2—C4 and C2—C3, thus the molecule is quite planar, the maximum deviations from the plane of N1, C1, N2, C2, C3, N3, C4 and O1 are 0.08 Å for N2 and 0.09 Å for C4 for **I** and **II** respectively. In **II** the creatinine moities are not coplanar, the interplanar angle between them is 98.7(2)°. An extended hydrogen bond system is present in the crystals especially in compound **II**. The scheme of hydrogen bonds in the unit cells is shown in Figs. 2 and 3.

H atoms for compound **I** were located on difference *Fourier* maps, but in **II** the H atoms positions were included at calculated sites (C—H = 1.00 Å). Although the H positions could not be determined directly, H-bridges are evident from the interatomic distances. Table 4, gives the geometry for the H-bonds*.

* Lists of structure factors, anisotropic temperature factors, H-atom parameters and additional details of molecular geometry may be obtained from the authors.

Table 2. *Fractional atomic coordinates (Å) ($\cdot 10^4$) with e.s.d's in parenthesis*

Compound **I**			
Atom	*X*	*Y*	*Z*
Pd	5000 (0)	5000 (0)	5000 (0)
C11	2556 (12)	3537 (9)	4349 (11)
O1	780 (38)	7785 (30)	4153 (35)
O3	1332 (38)	6489 (31)	382 (38)
N1	3812 (33)	6776 (25)	6877 (32)
N2	3743 (41)	8594 (27)	9861 (37)
N3	6467 (41)	6455 (32)	10417 (37)
C1	4750 (41)	7249 (29)	9137 (38)
C2	1788 (51)	9012 (34)	8031 (49)
C3	2016 (45)	7804 (32)	6095 (43)
C4	4169 (62)	9303 (39)	12163 (50)

Compound **II**			
Atom	*X*	*Y*	*Z*
Pt	−1024 (2)	1257 (0)	2404 (2)
I1	−1911 (6)	−1176 (8)	1653 (5)
I2	−2428 (5)	1703 (8)	3053 (5)
O1A	−945 (0)	4673 (0)	1695 (0)
O1W	2019 (86)	2562 (126)	6260 (60)
N1A	−300 (0)	3271 (0)	2955 (0)
N2A	661 (69)	4827 (93)	3987 (58)
N3A	666 (78)	2369 (105)	4430 (59)
C1A	341 (76)	3428 (98)	3819 (65)
C2A	195 (86)	5657 (114)	3153 (71)
C3A	−435 (0)	4439 (0)	2516 (0)
C4A	1413 (123)	5435 (159)	4837 (85)
O1B	1109 (60)	−836 (86)	3075 (53)
O2W	257 (77)	6331 (118)	912 (69)
O3W	298 (159)	−764 (215)	4371 (125)
N1B	147 (54)	837 (76)	1981 (46)
N2B	1047 (62)	747 (97)	1104 (54)
N3B	−379 (70)	2396 (97)	714 (56)
C1B	255 (64)	1388 (95)	1232 (58)
C2B	1588 (80)	−272 (111)	1818 (75)
C3B	937 (70)	−144 (96)	2371 (62)
C4B	1451 (84)	1211 (143)	442 (65)

Table 3. *Bond distances (Å) and bond angles (°) with e.s.d's in parenthesis*

Compound **I**		Compound **II**	
Pd—C11	2.299 (1)	Pt—I1	2.582 (8)
Pd—N1	2.026 (2)	Pt—I2	2.589 (11)
N1—C1	1.372 (3)	Pt—N1A	2.104 (3)
N1—C3	1.363 (3)	Pt—N1B	2.035 (9)
O1—C3	1.226 (3)	O1B—C3A	1.247 (0)
N2—C1	1.333 (3)	N1A—C1A	1.327 (9)
N2—C2	1.448 (3)	N1A—C3A	1.251 (0)
N2—C4	1.455 (4)	N2A—C1A	1.338 (12)
N3—C1	1.318 (3)	N2A—C2A	1.452 (13)
C2—C3	1.509 (4)	N2A—C4A	1.458 (14)
		N3A—C1A	1.323 (13)
		C2A—C3A	1.523 (10)
		O1B—C3B	1.241 (13)
		N1B—C1B	1.379 (13)
		N1B—C3B	1.351 (11)
		N2B—C1B	1.328 (14)
		N2B—C2B	1.434 (13)
		N2B—C4B	1.462 (16)
		N3B—C1B	1.310 (11)
		C2B—C3B	1.513 (18)
N1—Pd—N1′	179.9 (1)	N1A—PT—N1B	90.2 (2)
C1—Pd—C1′	180.0 (1)	I2—Pt—N1B	175.8 (2)
C1′—Pd—N1′	90.0 (1)	I2—Pt—N1A	89.7 (1)
C1′—Pd—N1	90.0 (1)	I1—Pt—N1B	88.2 (2)
C1—Pd—N1′	90.0 (1)	I1—Pt—N1A	177.2 (1)
C1—Pd—N1	90.0 (1)	I1—Pt—I2	92.2 (1)
Pd—N1—C3	125.6 (2)	Pt—N1A—C3A	124.2 (2)
Pd—N1—C1	126.5 (2)	Pt—N1A—C1A	122.7 (4)
C1—N1—C3	107.6 (2)	C1A—N1A—C3A	113.1 (4)
C2—N2—C4	123.0 (3)	C2A—N2A—C4A	124.1 (9)
C1—N2—C4	125.8 (3)	C1A—N2A—C4A	127.0 (9)
C1—N2—C2	109.0 (2)	C1A—N2A—C2A	108.7 (8)
N2—C1—N3	124.7 (3)	N2A—C1A—N3A	123.9 (9)
N1—C1—N3	123.0 (3)	N1A—C1A—N3A	126.2 (8)
N1—C1—N2	112.3 (2)	N1A—C1A—N2A	109.8 (8)
N2—C2—C3	101.7 (3)	N2A—C2A—C3A	99.7 (7)
O1—C3—C2	124.6 (3)	N1A—C3A—C2A	108.6 (4)
N1—C3—C2	108.7 (3)	O1A—C3A—C2A	121.3 (4)
N1—C3—O1	126.7 (3)	O1A—C3A—N1A	130.0 (4)
		Pt—N1B—C3B	124.5 (6)
		Pt—N1B—C1B	128.0 (6)
		C1B—N1B—C3B	107.3 (8)
		C2B—N2B—C4B	123.6 (9)
		C1B—N2B—C4B	125.0 (9)
		C1B—N2B—C2B	110.4 (8)
		N2B—C1B—N2B	125.7 (9)
		N1B—C1B—N3B	122.5 (9)
		N1B—C1B—N2B	111.7 (8)
		N2B—C2B—C3B	101.0 (8)
		N1B—C3B—C2B	109.5 (8)
		O1B—C3B—C2B	124.9 (9)
		O1B—C3B—N1B	125.6 (9)

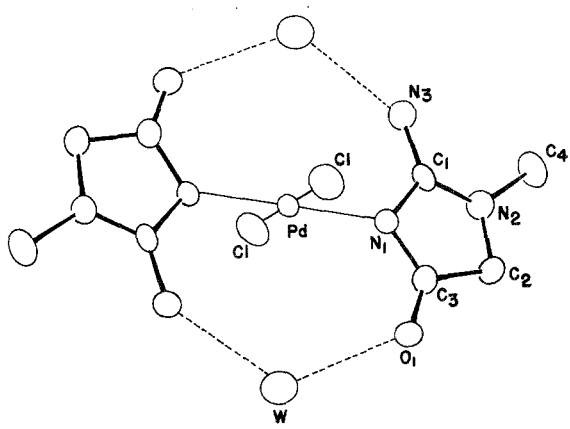

Fig. 2. Perspective view showing the packing of molecules for compound I

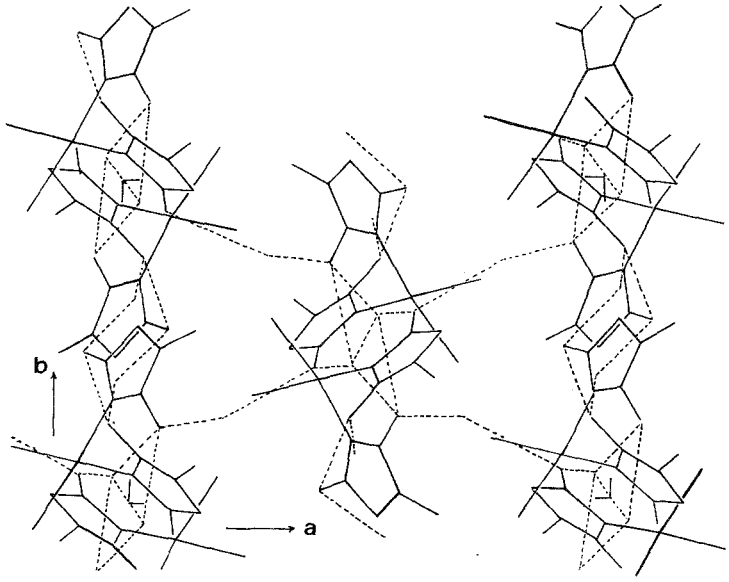

Fig. 3. Perspective view showing the packing of molecules for compound II

Table 4. *Hydrogen-bonding schemes in* **I** *and* **II**; *e.s.d's in parenthesis*

Compound **I**		Compound **II**	
OW .....O1 (i)	= 2.728 (3) Å	OW1.....N3A (i)	= 2.80 (6) Å
OW .....N3 (ii)	= 2.765 (3)	OW1.....O1B (iv)	= 2.77 (1)
OW .....CL (iii)	= 3.183 (3)	OW2.....N3B (ii)	= 2.95 (2)
		OW2.....O1A (i)	= 2.89 (3)
		OW3.....N3A (i)	= 2.89 (2)
		OW3.....O1B (i)	= 2.76 (4)
		OW3.....N3A (iii)	= 3.13 (4)
		OW3.....OW3 (iii)	= 2.86 (4)
		N3B .....O1 (i)	= 2.91 (2)

* Symmetry code:
(i) x, y, z
(ii) $1-x, 1-y, 1-z$
(iii) $-x, 1-y, -z$

* Symmetry code:
(i) x, y, z
(ii) $-x, 1-y, -z$
(iii) $1/2-x, 1/2+y, 1/2-z$
(iv) $1/2-x, -1/2+y, 1-z$

Thermal Study

The TG and DTG curves of *trans*-$Pd(Creat)_2Cl_2 \cdot 2\,H_2O$ (**I**) in static air and N_2 (Fig. 4) show that after dehydratation the complex is stable between 75 °C and 250 °C, above which temperature a decomposition in two consecutive stages (250–390 and 390–550 °C) occurs.

In static air, and as the DTA curve shows, the decomposition of **I** is exothermic whereas in N_2 it is endothermic. To understand this feature it is necessary to remember that an endothermic effect results from dissociation and consequent sublimation of the dissociation products while an exothermic effect results from the decomposition and/or the reaction of the dissociation products. In N_2 the exothermic effect is more than compensated by the endothermic process because the reaction products can diffuse away from the hot reaction zone, while in air the time of residence of the oxidizing and oxidizable species in the reaction zone is longer.

The thermal characteristics (TG and DTA) of *cis*-$Pt(Creat)_2I_2 \cdot 3\,H_2O$ (**II**) in static air and N_2 (Fig. 5) are more or less the same as reported for **I**: the complex loses water up to 110 °C above which temperature it shows constant weight up to 235 °C. The weight losses in the dehydratation stage (maxima at 51 °C in static air and at 60 °C in N_2) take place in two separate steps, in good accordance with the theoretical values of $-1\,H_2O$ and $-3\,H_2O$. Between 235 °C and 380 °C a net weight loss of 31% is observed. Such loss is sensitized in DTA by two small opposite and consecutive effects at 246 and 272 °C corresponding to the crystallization and melting.

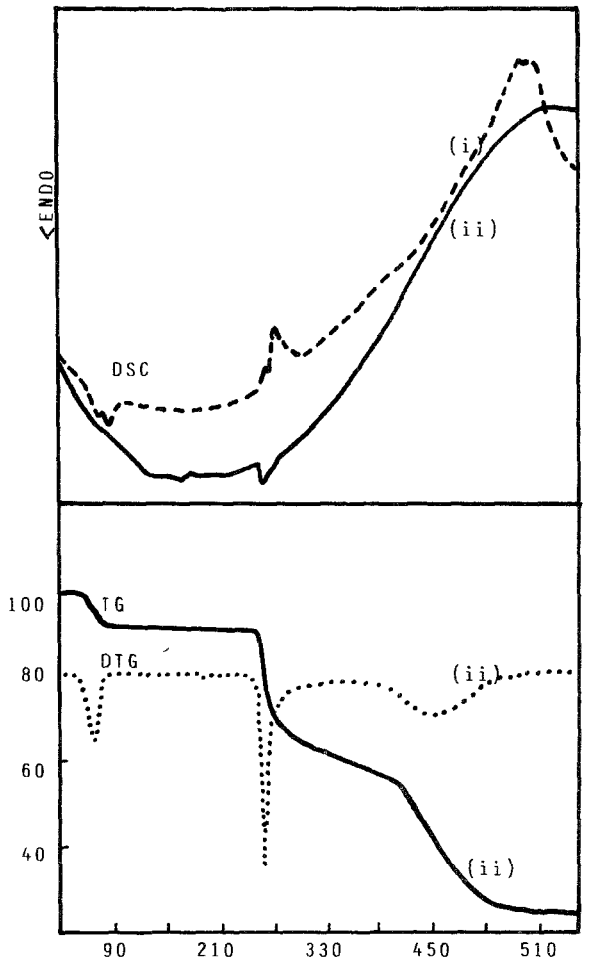

Fig. 4. TG, DTG and DTA curves for compound **I** from 30 °C to 600 °C in static air (*i*) and N_2 (*ii*); heating rate 5 °C min^{-1}

The subsequent weight loss that occurs above 380 and up to 520 °C is attributed to the thermolysis of PtI_2 (the release of I_2 has been evidenced at 350 °C in N_2). The decomposition maxima for the latter process are at 480 °C in static air and at 700 °C in N_2. The final product was platinum metal.

Table 5 gives the thermodynamic data of the two complexes.

The results of the present study form a reference system for other complexes, e.g. the hydrolysis products of blue solutions of *cis*-dichlorobiscreatinineplatinum(II). Such compounds present difficulties in

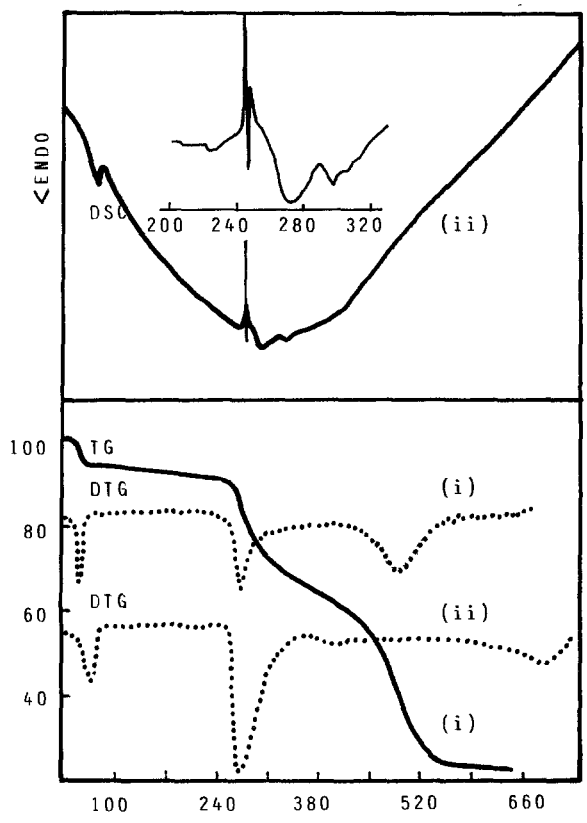

Fig. 5. TG, DTG and DTA curves for compound **II** from 30 to 730 °C in static air (*i*) and N_2 (*ii*); heating rate 2 °C min^{-1}

Table 5. *Thermodynamic data of compounds* **I** *and* **II**

	T_f (°C)	ΔH_f (cal mol^{-1})
trans-$Pd(Creat)_2Cl_2 \cdot 2H_2O$ (**I**)	256	167
cis-$Pt(Creat)_2I_2 \cdot 3H_2O$ (**II**)	266	48

the structural characterisation, but they are thermally more stable than **I** and **II** (m.p. 280 °C versus 256 and 266 °C, respectively). All these complexes are in accordance with those considered by *Lippert* [11] and *Rosenberg* [12] as "model metal complexes" to test cytostatic activities.

Acknowledgement

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