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THERMAL STUDIES ON METAL COMPLEXES OF 5-NITROSOPYRIMIDINE DERIVATIVES

V. Thermal behaviour of Zn(II), Cd(II), Hg(II) and Hg(I) complexes of 4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidine

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New 4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidine (TANH) complexes of Zn(II), Cd(II), Hg(II) and Hg(I) were prepared and their thermal behaviour was studied by TG and DSC techniques.

The dehydration and deamination enthalpies of the corresponding complexes were calculated.

Studies on the interaction of antitumour-active metal complexes with DNA and its constituents are now a very interesting subject in relation to an understanding of the mechanism by which metal ions are involved in the function of nucleic acids [1–8].

Several studies on anticarcinostatic metal complexes of thiopyrimidines and thiopurines have recently been reported [9–12]. These compounds have been exhaustively studied by spectroscopic and X-ray diffraction techniques, which have shown preferential coordination through one of the nitrogen atoms, the exocyclic sulphur atom or both [13–22]. However, investigations on the thermal behaviour of these complexes are scanty. For this reason and following the thermal studies on compounds containing metal ions and 5-nitrosopyrimidine derivatives [23–25], in this paper we probe into the thermal behaviour of Zn(II), Cd(II), Hg(II) and Hg(I) complexes with 4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidine TANH.

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Experimental

The pyrimidine derivative (TANH) was prepared by methods reported previously [26]. All the chemicals used in this work were of analytical reagent grade.

Preparation of the complexes

The syntheses of the zinc(II), cadmium(II) and mercury(II) complexes were carried out by mixing 10 ml (2 mmol) of aqueous solutions of zinc acetate, $CdCl_2 \cdot 2.5H_2O$ or $HgCl_2$ with an aqueous solution (100 ml) (2 mmol) of the ammonium salt of TANH ($TANNH_4$). In all three cases, the final metal/ligand ratio was 1/1. The resulting solutions were heated at 60° with continuous stirring. After a few minutes, powdery precipitates appeared, which were filtered off, washed consecutively with water, ethanol and ether, and air-dried.

In aqueous ammonia (7.5 *N*) and using the above preparative methods, a new Cd(II) complex was obtained. The purple complex was filtered off, washed with dilute ammonia and air-dried.

The mercury(I) complex was obtained in nitric acid (2.5 *N*) by mixing 10 ml (4 mmol) of $Hg_2(NO_3)_2$ with 100 ml (2 mmol) of TANH. The brown powdery precipitate was immediately isolated. The chemical analyses of these complexes are detailed in Table 1.

Table 1 Chemical analysis of the complexes

Compound	Colour	C, %		H, %		N, %		M, %	
		calcd.	found	calcd.	found	calcd.	found	calcd.	found
$Zn(TAN)_2 \cdot 2H_2O$	orange	21.65	21.48	2.25	2.28	25.26	25.22	14.73	15.18
$Cd(TAN)_2$	red	21.13	21.17	1.32	1.31	24.65	24.68	24.74	24.77
$Cd_2(TAN)_2 \cdot 4NH_3$	purple	15.17	15.20	2.52	2.61	26.55	27.13	35.52	35.36
$Hg(TAN)_2$	red	17.69	17.64	1.11	1.08	20.64	19.54	36.97	—
$Hg_2(TANH)_2(NO_3)_2$	brown	11.04	11.84	0.82	0.79	16.11	15.92	46.21	—

Apparatus

Chemical analysis of C, H and N was performed in a Carlo Erba 1106 microanalyzer.

Thermogravimetric analyses were made in a dynamic atmosphere of pure air or nitrogen with a Mettler TG–50 thermobalance at a heating rate of 10 deg min^{-1}.

The DSC curves were recorded in air on a Mettler DSC–20 differential scanning calorimeter at a heating rate of 5 or 10 deg $\min^{-1}$, in the temperature range 35–550°. Thermolytic reactions were obtained with samples varying in weight from 3.40 to 18.60 mg.

Results and discussion

IR studies carried out in this laboratory [27] have shown that TANH is coordinated to Cd(II) and Hg(II) ions in bidentate form, while with Zn(II) and Hg(I) it is monodentate.

In $Hg_2(TANH)_2(NO_3)_2$, the pyrimidine derivative acts as a monodentate molecular ligand through the sulphur atom substituent in position 2, as proved by IR [27]. In the remaining complexes, the pyrimidine ligand is always coordinated to the metal ions through the sulphur atom, except in the Zn(II) complex, where the coordination occurs through the oxygen atom of the substituent in position 6 of the pyrimidine ring.

Thermogravimetric analysis and DSC curves for the isolated Zn(II) and Cd(II) complexes are given in Fig. 1, and for the Hg(II) and Hg(I) complexes in Fig. 2.

In Fig. 1A it can be observed that the dehydration process for $Zn(TAN)_2 \cdot 2H_2O$ takes place in only one step, at 181°, which suggests that the water molecules are equivalent. The dehydration enthalpy was calculated from the area of the corresponding endothermic peak in the DSC curve (Table 2).

The dehydrated compound decomposes in the temperature range 250–775°. At this last temperature the residual weight corresponds to 18.9% of the initial weight of the sample (Table 3). Assuming that the pyrolytic residue of this compound is zinc oxide, as indicated by the IR spectra, the theoretical value (18.35%) is in good agreement with the experimental one. When the TG curve of $Zn(TAN)_2 \cdot 2H_2O$ was recorded in a nitrogen atmosphere, a residue of ZnO was again obtained.

The thermogravimetric curves of the cadmium complexes (Fig. 1B and 1C) are very different. The TG curve of $Cd(TAN)_2$ displays a very strong weight loss effect, followed by other, slow ones. The pyrolysis occurs in two steps: a fast decomposition between 250 and 350°, followed by another at around 500°. The residue obtained at the end of the pyrolysis (775°) was 28.3% of the original weight and corresponds to CdO (theoretical value 28.26%).

On the other hand, the TG of $Cd_2(TAN)_2 \cdot 4NH_3$ (Fig. 1C) shows a progressive and slow weight loss from 175° to 750°. The first step corresponds to a deamination process. The observed weight loss from 175° to 350°, was 10.2% of the original weight, which was assigned to the elimination of 4 NH_3 molecules (theoretical value 10.74%). The expected endothermic behaviour for the deami-

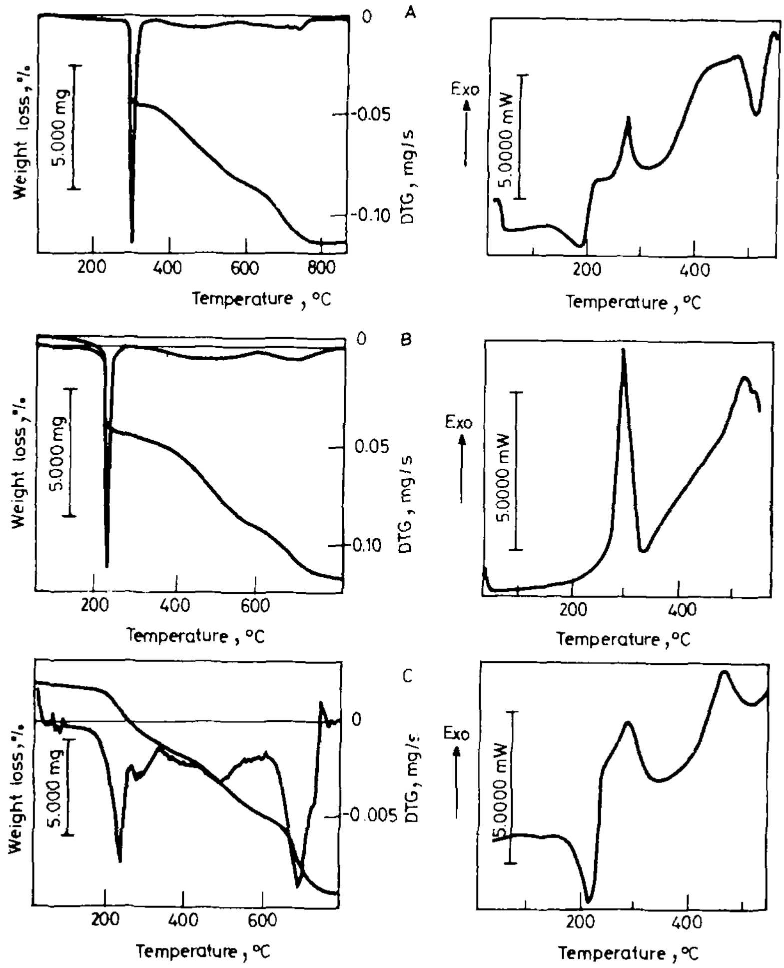

Fig. 1 TG and DSC curves of Zn(II) and Cd(II) complexes. A: $Zn(TAN)_2 \cdot 2H_2O$; B: $Cd(TAN)_2$; C: $CD_2(TAN)_2 \cdot 4NH_3$

Table 2 Thermoanalytical data for dehydration and deamination processes

Process	Weight loss, %		Peak temperature DSC, °C	Dehydration or deamination enthalpy (kJ·mol^{-1})
	calcd.	found		
$Zn(TAN)_2 \cdot 2H_2O \rightarrow Zn(TAN)_2 + 2H_2O$	8.12	8.20	181	38.5
$Cd_2(TAN)_2 \cdot 4NH_3 \rightarrow Cd_2(TAN)_2 + 4NH_3$	10.74	10.02	223	43.1

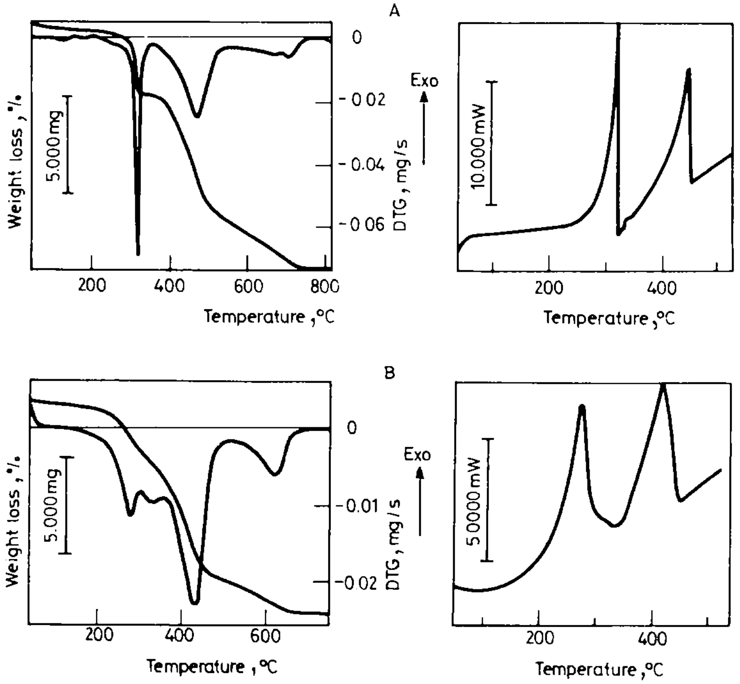

Fig. 2 TG and DSC curves of Hg(II) and Hg(I) complexes. A: $Hg(TAN)_2$; B: $Hg_2(TANH)_2(NO_3)_2$

Table 3 Thermogravimetric and DSC data for the pyrolytic processes (pure air)

Complex	Oxide residue, %		Final temperature TG, °C	DSC peak temperature, °C Exo		
	found	calcd.				
$Zn(TAN)_2 \cdot 2H_2O$	18.9	18.35	775	275	460	>545
$Cd(TAN)_2$	28.3	28.26	775	300	>550	
$Cd_2(TAN)_2 \cdot 4NH_3$	40.4	40.60	750	290	470	
$Hg(TAN)_2$		—	750	318	442	
$Hg_2(TANH)_2(NO_3)_2$		—	700	272	417	

nation process associated with this compound is supported by the DSC curve, which shows an endothermic effect centred at 223°. The corresponding enthalpy value, calculated from the area of this endothermic effect, was 43.1 kJ(Mol NH_3)$^{-1}$.

The deaminated compound decomposes in the temperature range 260–750°, with two exothermic effects in the corresponding DSC curve, at 290° and 470°. These effects must be attributed to the combustion of the organic matter. At 750° the experimental percentage of residue was 40.4%, which was assigned to CdO, as was proved by IR spectroscopy, and corresponds closely to the theoretical value required for CdO (40.60%) (Table 3).

The TG curves of both cadmium complexes in a dynamic N_2 atmosphere are similar to those recorded in pure air, but two observations can be made: i) in N_2 atmosphere the pyrolytic processes finished at higher temperatures than in air, and ii) the pyrolytic residue was CdS, as revealed by IR. At 850° the experimental residue was lower than expected, due to the partial volatilization of CdS in nitrogen atmosphere [28].

Finally, the TG and DSC curves of $Hg(TAN)_2$ and $Hg_2(TANH)_2 \cdot (NO_3)_2$ are recorded in Fig. 2A and 2B.

The TG of $Hg(TAN)_2$ shows that the pyrolytic decomposition takes place in two steps. The complex is stable up to 225°. At this temperature the first process begins; this consists of an intense effect with weight loss, which finishes at 375°. The second process corresponds to a slow weight loss from 375° to 500°, and the end of the pyrolysis occurs at 750°. At this point a residue was not obtained. In the DSC curve these processes appear as exotherms at 318° and 442° (Table 3) and can be assigned to the pyrolytic decomposition of the pyrimidine ring.

The decomposition of $Hg_2(TANH)_2(NO_3)_2$ see TG and DSC curves, Fig. 2B occurs in some steps with overlapping. At 700° no residue was obtained. The DSC curve shows two exothermic effects. The first process appears at 272° (Table 3), probably due to the pyrolysis of the nitrate ion (the enthalpy calculated was 290.3 kJ mol^{-1}). The second exothermic effect is centered at 417°, which suggests the pyrolytic decomposition of the resulting compound. The enthalpy calculated was similar to the above one (298.3 kJ mol^{-1}).

The TG curves recorded in N_2 atmosphere had similar features, but the pyrolytic process ended at a higher temperature than in air.

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Zusammenfassung — Neue 4-Amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidin-Komplexe (TANH) von Zn(II), Cd(II), Hg(II) und Hg(I) wurden dargestellt und ihr thermisches Verhalten mittels TG und DSC untersucht. Die Dehydratisierungs- und Deamminierungsenthalpien der Komplexe wurden berechnet.

Резюме — С помощью методов ТГ и ДСК изучено термическое поведение новых комплексов 4-амино-5-нитрозо-6-оксо-1,2,3,6-тетрагидро-2-тиопиримидина с цинком, кадмием, одновалентной и двухвалентной ртутью. Вычислены энтальпии реакций дегидратации и деамминирования.