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THERMAL STUDIES ON METAL COMPLEXES OF 5-NITROSOPYRIMIDINE DERIVATIVES

VI. Thermal behaviour of Zn(II), Cd(II), Hg(II) and Hg(I) complexes of 4-amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxopyrimidine

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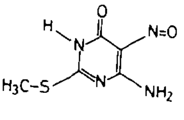
The following Zn(II), Cd(II), Hg(II) and Hg(I) complexes of 4-amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxopyrimidine (MTH) have been prepared and their thermal behaviour studied by TG and DSC techniques: $Zn(MT)_2 \cdot 3H_2O$, $Cd(MT) \cdot H_2O$, $Cd(MTH)Cl_2$, $Hg(MTH)Cl_2$ and $Hg_2(MT)(NO_3)$. The dehydration and dehalogenation enthalpy values were calculated.

In connection with previous studies on the metal complexes of pyrimidines [1–12], we have investigated the Zn(II), Cd(II), Hg(II) and Hg(I) complexes of 4-amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxopyrimidine (MTH), a pyrimidine derivative of potential biological interest. Our study has been centred on the thermal behaviour of these complexes because many papers have appeared on the interactions of ions with pyrimidine bases in recent years [1, 2, 13–16], whereas no investigation of the thermal behaviour has been reported. For this reason and following the thermal studies on compounds containing metal ions and 5-nitrosopyrimidine derivatives [17–19], we present a thermal study of five new complexes of MTH.



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Experimental

Materials

The pyrimidine derivative (MTH) was prepared by methods previously reported [21]. All the inorganic materials used were of analytical reagent grade.

The infrared spectra of the compounds studied were recorded in KBr medium in the region 4000–200 cm^{-1} using a Beckman 4250 spectrophotometer.

The TG studies were carried out in dynamic atmospheres of pure air and nitrogen on a Mettler TG–50 thermobalance, using samples varying in weight from 5.585 to 18.700 mg and heating rates of 10 deg min^{-1} and 20 deg min^{-1}. The DSC curves were recorded on a Mettler differential scanning calorimeter (model DSC 20) at a heating rate of 5 deg min^{-1}.

Microanalyses of C, H and N were performed in a Carlo Erba model 1106 microanalyzer.

Preparation of the complexes

Zn(II), Cd(II) and Hg(II) complexes of MTH were obtained by mixing 100 ml (2 mmole) of MTH and a solution containing 20 ml (2 mmole) of the corresponding metal ion ($ZnAc_2$, $CdCl_2 \cdot 2.5/2H_2O$ and $HgCl_2$, respectively). The resulting solutions were heated at 60° for one hour with stirring. On cooling to room temperature, powder precipitates were deposited; an exception was the cadmium complex, which precipitated when the solution volume was reduced to 1/5 of the initial volume.

Another cadmium complex was isolated by working in ammonia medium and using the same amounts of MTH and Cd(II), as indicated above.

To obtain the Hg(I) complex of MTH, 100 ml (2 mmole) of MTH was added to 20 ml (4 mmole) of $Hg_2(NO_3)_2$ solution in 2.5 mM NHO_3 medium. A light-brown powder precipitate was obtained immediately. All precipitates isolated were washed with water and ethanol and dried with ether.

Results and discussion

Recent studies by spectral methods (IR and ^1H–NMR) [20] have shown that the coordination of this pyrimidine derivative to Zn(II), Cd(II), Hg(II) and Hg(I) ions takes place an anionic and bidentate form, except for $Hg(MTH)Cl_2$, where it occurs in molecular form.

Table 1 Chemical analyses of the complexes

Compound	Colour	C %		H %		N %		M %	
		calcd.	found	calcd.	found	calcd.	found	calcd.	found
$Zn(MT)_2 \cdot 3H_2O$	orange	24.52	25.56	3.27	3.20	22.89	23.27	13.56	13.29
$Cd(MT^-) \cdot H_2O$	brown	19.02	19,08	1.91	2.06	17.81	18.00	35.64	35.19
$Cd(MTH)Cl_2$	red	16.24	16.46	1.62	1.52	15.16	15.51	30.51	24.60
$Hg(MTH)Cl_2$	yellow	13.11	12.94	1.31	1.23	12.24	12.02	43.84	--
$Hg_2(MT)(NO_3)$	brown	9.26	9.15	0.77	0.87	8.64	9.12	30.95	—

From the IR and ^{1}H-NMR spectra of the Zn(II) and Cd(II) complexes, we have concluded that the sulphur atom always participates in the binding.

The principal bands of the infrared spectra were assigned by comparison with the spectrum of the free pyrimidine, and the ^{1}H-NMR spectra of the Zn(II) and Cd(II) complexes in DMSO-d_6 were also compared with the ^{1}H-NMR spectrum of the free pyrimidine [20–21].

On the other hand, the IR and ^{1}H-NMR data on the mercury complexes suggest that the binding occurs through the nitrogen and oxygen atoms of the 5-nitroso and 6-oxo groups.

Thermogravimetric curves of all the isolated complexes were recorded in air and nitrogen atmospheres to observe the behaviour of these complexes in the different media. From these curves, two observations can be made: (i) the residue was metal oxide in the oxidant atmosphere, and metal sulphide under the inert atmosphere; (ii) under a N_2 flow, the pyrolytic process finished at temperatures higher than in pure air.

The TG curve of $Zn(MT)_2 \cdot 3H_2O$ (Fig. 1A) shows that the three water molecules are equivalent. The observed weight loss was 11.0% (theoretical weight loss for elimination of the three water molecules: 11.03%). After the dehydration process, the pyrolytic decomposition begins; this is completed at 800°, a residue of zinc oxide (16.5%) being obtained. This experimental percentage is in good agreement with the theoretical one (16.42%). The nature of the residue was proved by recording its IR spectrum.

In the DSC curve of this complex, the expected endothermic behaviour of the dehydration process was observed as a unique endothermic effect at 160°. The dehydration enthalpy calculated was 45.0 $kJ/mol \cdot H_2O^{-1}$ (see Table 2). The decomposition of the anhydrous complex, occurs in three steps (exothermics at 250°, 430° and 540°) and finishes at $>550°$.

The cadmium complexes show a different thermal behaviour (Figs 1B and 1C). Thus, the complex prepared in ammonia medium contains one water molecule, loss of which can be seen in the TG and DSC curves, while the complex prepared in

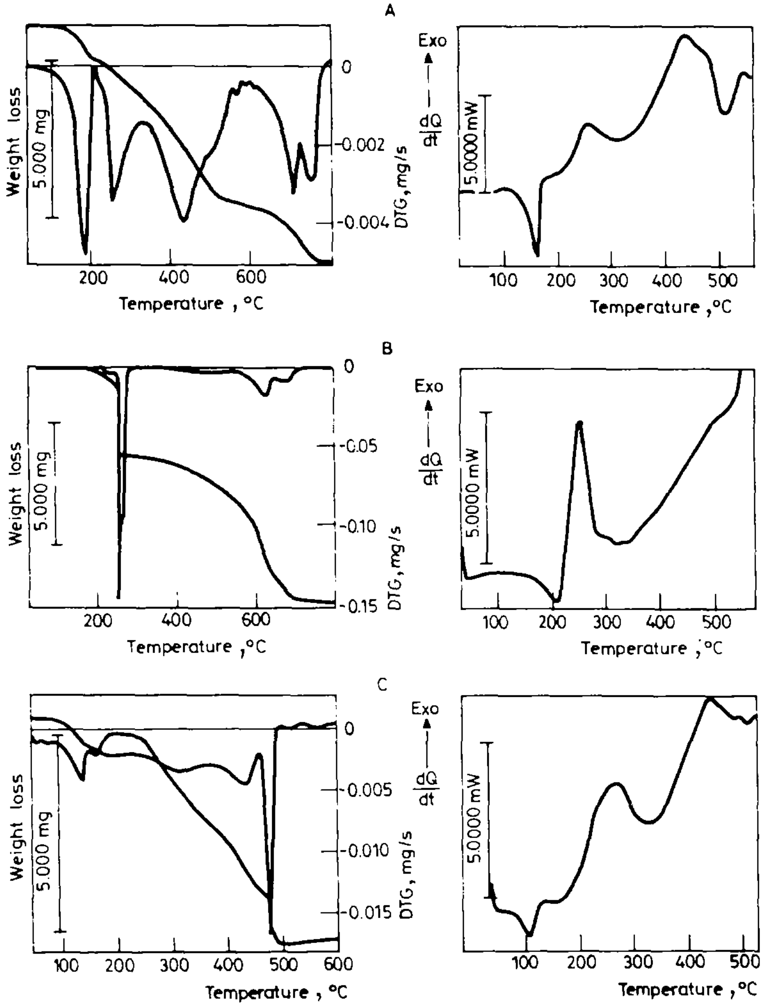

Fig. 1 TG and DSC curves of Zn(II) and Cd(II) complexes. A: $Zn(MT)_2 \cdot 3H_2O$; B: $Cd(MTH)Cl_2$; C: $Cd(MT)H_2O$

neutral medium is anhydrous and contains two chlorine atoms, loss of which can not be observed in the TG curve because the dehalogenation process occurs in a temperature range which overlaps with the beginning of pyrolytic decomposition of the pyrimidine ring.

The complex $Cd(MT) \cdot H_2O$ is completely dehydrated in the temperature range 60–150° (peak centred at 109°). The dehydration enthalpy was calculated from the area of the endothermic effect in the DSC diagram, being 22.7 $kJ \cdot mol \cdot H_2O^{-1}$.

Table 2 Thermoanalytic data for dehydration and dehalogenation processes of isolated compounds

Compound	Weight loss, %		DSC peak temperature, °C	Dehydration or dehalogenation enthalpy, kJ·mol^{-1}
	calcd.	found		
$Zn(MT)_2 \cdot 3H_2O$	11.03	11.0	160	45.0
$Cd(MT^-) \cdot H_2O$	5.71	5.11	109	22.7
$Cd(MTH)Cl_2$	19.22	a	210	55.3
$Hg(MTH)Cl_2$	15.52	a	189	b

a: overlapped with decomposition process
b: not possible to calculate

For this process the calculated weight loss from the TG curve was 5.1%, which is in good agreement with the theoretical one (5.71%). The dehydrated compound decomposes to the accompaniment of exothermic effects in the DSC curve, which must be attributed to combustion of the organic matter. The final residue was CdO in air CdS in nitrogen, as corroborated by IR spectroscopy. The thermogravimetric and DSC data on the pyrolytic process are given in Table 3.

The TG curve of the complex $Cd(MTH)Cl_2$ shows a first weight loss at 250°, where the dehalogenation and the beginning of pyrolytic processes overlap. However, in the DSC curve obtained at 5 deg min^{-1} we can observe an endothermic effect corresponding to the dehalogenation process, and an exothermic effect immediately appears. The last effect is due to a decomposition process which finishes at > 550°. From the area of the endothermic effect, we have calculated the dehalogenation enthalpy (55.3 kJ/g Cl). At 700°, a residue of CdO was obtained (Table 3). The experimental value is not in accordance with the calculated one, due to the partial volatilization of cadmium chloride, as we have

Table 3 Thermogravimetric and DSC data for the pyrolytic processes

Reaction	Residue %		Final temperature from TG, °C	DSC peak temperature, °C exo
	calcd.	obsd.		
$Zn(MT)_2 \rightarrow ZnO$	16.62	15.6	800	250 430 540
$Zn(MT)_2 \rightarrow ZnS$	19.90	19.4	850	
$Cd(MT^-) \rightarrow CdO$	40.84	40.2	675	270 450
$Cd(MT^-) \rightarrow CdS$	45.92	26.6	800	
$Cd(MTH) \rightarrow CdO$	34.76	28.2	700	250 500
$Cd(MTH) \rightarrow CdS$	45.94	26.4	850	

observed in a previous paper [22]. Under a nitrogen atmosphere, the pyrolytic decomposition followed the same course, but two weight loss effects can be seen in the TG curve from 150 to 300°: (i) dehalogenation, and (ii) the beginning of pyrolytic decomposition. The two processes overlap when the TG curve is recorded in a pure air atmosphere, due to the experimental conditions. At temperatures higher than 300°, the TG curve in a nitrogen atmosphere shows the same behaviour as that obtained in pure air, finishing at above 800°. At this temperature the residue was CdS. For both Cd(MT) · H_2O and Cd(MTH)Cl_2, the percentage of the residue was less than the calculated one, due to the partial sublimation of CdS.

The TG curve of Hg(MTH)Cl_2 (Fig. 2A) shows that this compound is stable up to 175°, after which an intense weight loss effect starts, followed by three slower weight losses, at 300°, 420° and 560°, which are due to pyrolytic decomposition. The dehalogenation process should be included in the first step. At the end of the pyrolysis (600°), no residue was obtained.

The DSC curve of Hg(MTH)Cl_2 shows the processes corresponding to the pyrolysis as exothermic effects (189° and 440°).

Under a nitrogen atmosphere we obtained the same results, but the end of the pyrolysis occurs above 600°.

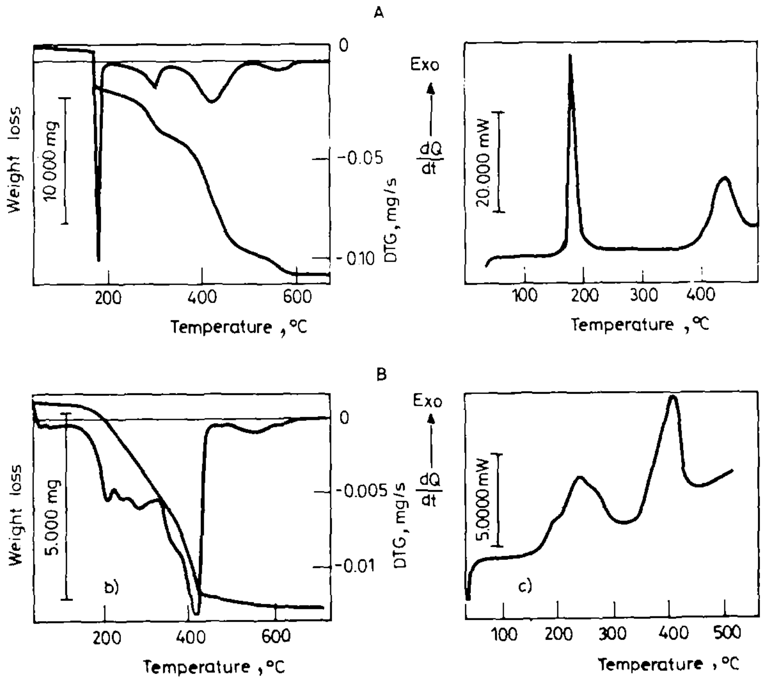

Fig. 2 TG and DSC curves of Hg(II) and Hg(I) complexes. A: Hg(MTH)Cl_2; B: Hg_2(MT)(NO_3)

Finally, the TG and DSC curves for the Hg(I) compound isolated are presented in Fig. 2B.

The decomposition of the Hg(I) compound takes place in overlapping steps. This process exhibits intense weight loss effects, which occur in the temperature range 175° to 600°. At this latter temperature, a residue was not obtained.

In the DSC curve, these processes appear as two exotherms, at 242° and 413°. The first process (242°) is probably due to the pyrolysis of the nitrate ion.

From a comparison of the thermoanalytical data obtained under pure air and nitrogen atmospheres, a tentative coordination mode for the pyrimidine ligand has been proposed, which is in agreement with that established from spectroscopic data.

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Zusammenfassung — Die folgenden Komplexe von Zn(II), Cd(II), Hg(II) und Hg(I) mit 4-Amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxopyrimidin (MTH) wurden dargestellt und hinsichtlich ihres thermischen Verhaltens durch TG und DSC untersucht: $Zn(MT)_2 \cdot 3H_2O$, $Cd(MT) \cdot H_2O$, $Cd(MTH)Cl_2$, $Hg(MTH)Cl_2$ und $Hg_2(MTH)(NO_3)$. Die Werte der Enthalpie der Dehydratisierung und Dehalogenisierung wurden berechnet.

Резюме — Получены комплексы состава $Zn(MT)_2 \cdot 3H_2O$, $Cd(MT)_2 \cdot H_2O$, $Cd(MTH)Cl_2$, $Hg(MTH)Cl_2$ и $Hg_2(MT)NO_3$, где MTH — 4-амино-1,6-дигидро-2-метилтио-5-нитрозо-6-оксопиримидин. Термическое поведение комплексов изучено методами ТГ и ДСК. Вычислены энтальпии реакций дегидратации и дегалогенирования.