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THERMAL STUDIES ON PURINE COMPLEXES.
XI. THERMAL BEHAVIOUR OF 2-THIOXANTHINE, ITS CHLOROHYDRATE AND SOME THIOXANTHINE COMPLEXES OF Ag(I), Cd(II), Hg(II) AND Hg(I)

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ABSTRACT

The chlorohydrate of 2-thioxanthine has been prepared in an acid medium, as well as some Ag(I), Cd(II), Hg(II) and Hg(I) 2-thioxanthine complexes. These compounds have been characterized by spectroscopic techniques and thermal analysis.

The thermal behaviour of 2-thioxanthine (TXH), its chlorohydrate (TXH_2Cl) and the above complexes has been studied by TG, DTG and DSC techniques. Dehalogenation enthalpies have been calculated.

INTRODUCTION

6-Thiopurine is currently used as an effective chemotherapeutic agent against human leukemias [1,2]. In some cases metal complexes of various sulphur-containing purines have been seen to be more active than the free ligand [3–9]. For this reason the interaction of metal ions with sulphur purine derivatives has been the subject of several investigations in order to understand the structural nature of those interactions [9–16], and also to check their carcinostatic properties; whereas no investigations of the thermal behaviour of these compounds have been reported.

In this work, and following the thermal studies on compounds containing metal ions and purine derivatives [17–24] we report the synthesis, characterization and thermal behaviour of 2-thioxanthine (TXH), its chlorohydrate and the six complexes isolated in the reactions between 2-thioxanthine and Ag(I), Cd(II), Hg(I) and Hg(II) ions.

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EXPERIMENTAL

Materials

2-Thioxanthine (6-oxo-2-thiopurine) was purchased from Sigma. All the inorganic products used in this work were analytical reagent grade.

Preparation of the compounds

2-Thioxanthine chlorohydrate (TXH_2Cl) was obtained by treating TXH with concentrated HCl. After ten days, colourless crystalline needles appeared, which were filtered, washed consecutively with water and ethanol and dried with ether.

Silver complexes of TXH were prepared in basic and acidic media. The preparative methods were as follows.

Basic medium. 3 mmol of TXH were dissolved in 100 ml of 7.5 N ammonium hydroxide. To this solution was added another containing 3 mmol of $AgNO_3$ dissolved in the minimum amount of 7.5 N NH_4OH. Both solutions were mixed, heated at 60°C and stirred for 20 min. After stirring a light brown solid was collected by filtration, washed with water and ethanol, and dried with diethyl ether.

Acid medium. To a solution of 2-thioxanthine (2 mmol) in 100 ml of 5 N HNO_3 was added a solution of silver nitrate (4 mmol) in 5 ml of 5 N HNO_3. The mixture was heated at 60°C, with stirring, and in a few minutes a yellow precipitate was obtained, which was collected by filtration, washed with water and ethanol and dried with diethyl ether.

A mercury(II) complex of 2-thioxanthine was obtained by mixing 3 mmol of TXH and 6 mmol of $HgCl_2$ in 250 ml of water. The mixture was stirred and heated at 60°C for 30 min. A yellow precipitate was formed immediately.

Solutions of Cd(II) and Hg(II) complexes in acidic media (4.8 N HCl) were also prepared in the same way. The precipitation occurred after 24 h. Light brown needles of the Cd(II) complex and colourless crystalline needles of the Hg(II) complex were obtained.

The mercury(I) complex was obtained in an aqueous medium by mixing 3 mmol TXH and 6 mmol $Hg_2(NO_3)_2 \cdot 2H_2O$ in 200 ml of water. In all cases the precipitates were filtered successively, washed with water and ethanol and dried with ether.

Analytical data for the 2-thioxanthine, its chlorohydrate and its silver(I), cadmium(II), mercury(II) and mercury(I) complexes, are shown in Table 1.

Apparatus

A chemical analysis of C, H and N was done in a Carlo Erba model 1106 microanalyzer. Infrared spectra of these compounds were recorded in a KBr

TABLE 1

Analytical data for 2-thioxanthine, its chlorohydrate and the TXH complexes of Ag(I), Cd(II), Hg(II) and Hg(I)

Compound	C%		H%		N%		M%		Colour
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
TXH	35.67	35.22	2.38	2.39	33.29	33.02	–	–	Light pink
TXH_2Cl	25.39	25.46	3.70	3.60	36.03	36.77	–	–	Colourless
Ag_3TX^{-})(TX)	18.27	18.24	0.76	0.80	17.05	16.08	50.11	49.59	Light brown
$Ag_3(TX)(NO_3)_2(TXH)$	15.33	16.60	0.89	0.96	17.89	18.27	41.40	42.00	Yellow
$Cd(TXH)_2Cl_2$	23.10	24.54	1.54	1.32	21.56	21.45	22.45	21.64	Light brown
$Hg(TXH)Cl_2$	13.64	14.07	0.91	0.84	12.73	13.07	45.95	–	Yellow
$Hg(TXH)_2Cl_2$	19.72	19.90	1.64	1.64	18.40	17.94	32.96	–	Colourless
$Hg_2(TX)(NO_3)$	9.52	10.06	0.48	0.58	11.12	11.27	63.66	–	Yellow

medium in the region 4000–200 cm^{-1} and in a polyethylene medium in the region 600–200 cm^{-1} using a Perkin-Elmer 4250 spectrophotometer. ^{1}H-NMR spectra were recorded on a Hitachi-Perkin-Elmer model R-600 FT-NMR spectrometer, using DMSO-d_6 as the solvent and TMS as the internal standard.

Thermogravimetric (TG) studies were made with a Mettler TG-50 thermobalance in pure air and dynamic nitrogen atmospheres (100 ml min^{-1}) using samples varying in weight from 3.999 to 19.195 mg and a heating rate of 10°C min^{-1}.

DSC curves were recorded in a Mettler DSC differential scanning calorimeter model DSC-20, in static air atmosphere and at a heating rate of 10°C min^{-1} in the 35–550°C temperature range. These samples varied in weight from 2.412 to 7.078 mg.

RESULTS AND DISCUSSION

In aqueous solutions, TXH shows a weakly acidic character; pK values for its dissociation process were calculated by the application of the methods of Bjerrum and Robinson to potentiometric data (pK_1 = 6.02, pK_2 = 9.64 at 25°C) and published in a previous work [25].

The ^{1}H-NMR spectrum of TXH shows a signal at 12.40 ppm, probably corresponding to the protons bonding to N(1) and N(3) and a new signal over 8.10 ppm corresponding to the proton bonding to C(8). Both of them shifted downfield with respect to the spectrum of xanthine [26] due to the lower screening effect of C=S compared with C=O.

In the ^{1}H-NMR spectrum of TXH_2Cl we observed signals at 10.40 ppm and 9.00 ppm, corresponding to the protons bonding to N atoms and C(8), respectively. These results are in agreement with those expected for the protonation on a nitrogen atom of the imidazolic ring N(9).

The most significant IR absorption bands for 2-thioxanthine and its chlorohydrate, as well as the principal absorption bands of the isolated complexes, are given in Table 2.

The IR spectrum of the $Ag_3(TX)(TX^-)$ complex did not show two of the bands corresponding to ν(N–H) present in the infrared spectrum of free TXH. This observation suggests that coordination of TXH to metal ions takes place in an anionic form.

Likewise, the IR of $Ag_3(TX)(TXH)(NO_3)_2$ shows (as the most significant) a new strong band at 1380 cm^{-1} corresponding to a stretching vibration, ν(N–O), of the nitrate ion.

Both of the two isolated silver complexes show new bands in the 225–235 cm^{-1} range which were assigned to ν(Ag–N).

Infrared data (Table 2) suggest that the coordination of TXH to Ag(I) takes place in an anionic (or molecular) form through the pyrimidine and

TABLE 2

Infrared data of the isolated compounds (cm^{-1})

Compound	ν(N–H) + ν(C–H)	ν(C=O)	ν(C=C)	ν(C=N)	$\nu(NO_3^-)$	ν(N–CS–N) + ν(HN–CS) + ν(C=S)	ν(M–X)
TXH	3090					1120	
	3000	1680	a	1575	–	1160	–
	2940					1210	
	2840						
TXH_2Cl	3065					1120	
	2970	1685	1635	1595	–	1160	–
	2830					1205	
$Ag_3(TX)(TX^-)$	3100–2870	1660	a	a	–	1120	225–235
						1180	
						1210	
$Ag_3(TX)(TXH)(NO_3)_2$	3100–2840	1680	a	1570	1380	1195	225–235
$Cd(TXH)_2Cl_2$	3040–2840	1690	a	1575	–	1120	245–255
						1165	
						1210	
$Hg(TXH)Cl_2$	3200–2700	1700	a	1575	–	1110	230,360,380
						1160	
						1190	
$Hg(TXH)_2Cl_2$	3200–2800	1710	1640	1580	–	1110	235–290
						1160	
						1200	
$Hg_2(TX)(NO_3)$	3200–2800	1725	–	a	1380	1210	–
						1170	

[a] Overlap with the ν(C=O) band.

TABLE 3

Thermogravimetric data of the compounds [a]

Compound	Decomposition temperature range (°C)	Other effects (°C)	DSC peak temperature (°C)	
			Endo	Exo
TXH	325–725	420,480,640	401.6	500
	(325–850)			
TXH_2Cl	175–725	237,420,480,640	237,401.6	500
$Ag_3(TX^-)(TX)$	370–675	450,580	–	500
	(370–800)	(460,610,700)		
$Ag_3(TX)(NO_3)_2(TXH)$	200–600	320,560	–	333
	(200–800)	(320,460,700)		530
$Cd(TXH)_2Cl_2$	225–675	275,375,440,490,660	275	520
	(225–800)	(275,325,390,450)		
$Hg(TXH)Cl_2$	300–625	375,400,550	–	460
	(300–800)	(380,410,600)		
$Hg(TXH)_2Cl_2$	175–575	258,465,550	258,401.6	480
	(175–750)	(240,450)		500
$Hg_2(TX)(NO_3)$	150–675	250,335,400,650		270
				312
	(150–800)	(275,350,400,700)		420

[a] Thermogravimetric data in a nitrogen atmosphere are given in parentheses.

imidazole ring nitrogens but it is not possible to propose any definitive structure for these compounds. Probably the complexes result from a strong polymerization step due to the numerous coordination positions that TX^-, TX and TXH ligands present.

The IR spectrum of $Cd(TXH)_2Cl_2$ shows a great similarity with the IR of the free ligand which indicates that coordination of TXH to Cd(II) takes place in molecular form. On the other hand, the donor capacity of basic atoms of the purine ring [27] suggests that sulphur and imidazole ring nitrogens are the most favoured positions to link TXH to Cd(II).

The IR spectrum of $Cd(TXH)_2Cl_2$ in the region of 600–200 cm^{-1} shows absorption bands at 245 cm^{-1} and 255 cm^{-1} assigned to stretching vibrations ν(Cd–Cl). The position of these bands is in accord with the literature data for a tetrahedral structure [28].

In the ^1H-NMR spectrum of the $Cd(TXH)_2Cl_2$ complex there is no shift of the C8–H signal which appears at 8.10 ppm; the signals of the N–H hydrogens are, practically, in the same position compared with the free ligand. This indicates that, according to the literature [29,30], the coordination of TXH is neither through N7 nor N9 atoms.

The above data, together with the thermal studies (Tables 3–6), suggests a tetrahedral structure for this compound in which the TXH is coordinated to Cd(II) through the sulphur atom.

The IR spectra of Hg(II) compounds suggest that coordination of the

TABLE 4

Thermogravimetric and DSC data for the pyrolytic processes of TXH and its chlorohydrate (TXH_2Cl)

Compound	T (°C) range for the decomposition	T (°C)	Dehalogenation weight loss(%)		ΔH (kJ mol^{-1})	MP (°C)	ΔH (kJ mol^{-1})	DSC peak temperature (°C) Exo
			Found	Calcd.				
TXH	300–725	–	–	–	–	401.6	58 [a]	490
TXH_2Cl	175–725	237	17.8	17.83	54.9	401.6		490

[a] See text.

TABLE 5

Thermogravimetric and DSC data for the pyrolytic processes of Ag(I) and Cd(II) complexes

Complex	Residue expected (%)						DSC peak temperature (°C) Exo
	Air			Nitrogen			
	Found	Calcd.	Natur.	Found	Calcd.	Natur.	
$Ag_3(TX)(TX)$	49.5	50.80	Ag	50.2	50.80	Ag	500
$Ag_3(TX)(NO_3)_2(TXH)$	41.0	41.36	Ag	41.5	41.36	Ag	333,530
$Cd(TXH)_2Cl_2$	11.4 [a]	24.72	CdO	10.2 [a]	27.80	CdS	520

[a] See text.

2-thioxanthine base to ion takes place in molecular form, due to the similarity of IR spectra of these compounds with the IR spectrum of free TXH. For Hg(II) complexes IR spectra show the same bands corresponding to stretching vibrations ν(N–H) compared with the position of these bands in the free 2-thioxanthine. Both of these two complexes are also present in the band in the region over 1700 cm^{-1} which was assigned to ν(C=O). Likewise, they show the same bands from 1000 to 1210 cm^{-1}, assigned to stretching vibrations of –N–CS–N, –NH–CS and C=S groups, but displaced to a lower wave-number with respect to the position of the bands in the free ligand. This fact suggests that the 2-thioxanthine would be coordinated through the sulphur atom, which is in accord with the literature data for analogous compounds [13,16,31]. Besides, this position is also in accord with the characteristics of soft acid and soft base that Hg and S atoms respectively present.

The IR spectrum of $Hg_2(TX)(NO_3)$ does not show the same number of bands corresponding to ν(N–H) that the IR spectrum of free TXH shows, which suggests that the coordination of TXH to Hg(I) takes place in the anionic form through one of the imidazole ring nitrogens. On the basis of X-ray studies carried out on complexes analogous to other thiopurine-derivatives, where this base acts in anionic form [27], we believe that the N(7) atom is the most likely binding site to the Hg(I) ion, but on the other hand the coordination will also be possible through N(3) due to the greater acidity

TABLE 6

Thermogravimetric and DSC data for the dehalogenation processes

Complex	Weight loss (%)			DSC peak temperature (°C)	ΔH dehalog. (kJ mol^{-1})
	Found	Calcd.	Natur.		
$Cd(TXH)_2Cl_2$	13.3	13.59	2Cl	275	60.2
$Hg(TXH)Cl_2$	–	61.78	$HgCl_2$	–	–
$Hg(TXH)_2Cl_2$	44.6	44.63	$HgCl_2$	258	192.5

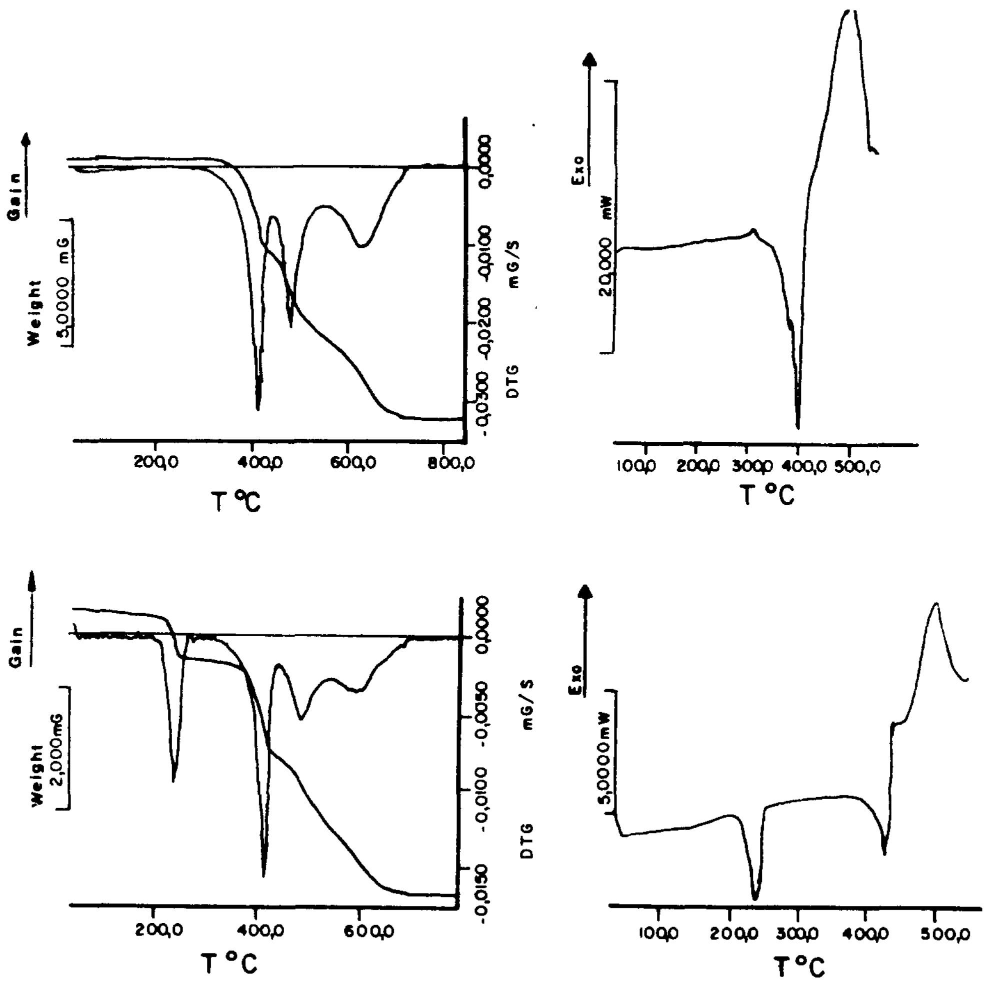

Fig. 1. TG and DSC curves for (top) TXH; (bottom) TXH_2Cl.

of the hydrogen atom joined to N(3) [32]. Finally, the IR spectrum of this complex shows a new band at 1380 cm^{-1} due to the presence of nitrate ions.

Thermogravimetric analysis and differential scanning calorimeter curves for TXH and its chlorohydrate are presented in Fig. 1; TG and DSC curves for Ag(I) and Cd(II) complexes are recorded in Fig. 2 and, for Hg(II) and Hg(I) compounds, in Fig. 3.

The TG curve of TXH (obtained in air), shows that the thermal decomposition of this purine derivative takes place with three weight loss effects (Table 3) at 420, 480 and 640°C, and at 725°C the complete elimination of the sample occurs. In a nitrogen atmosphere, the end of the decomposition process takes place at a higher temperature ($>$ 850°C).

The DSC curve of 2-thioxanthine shows one endothermic effect centred at 401.6°C corresponding to the fusion of the sample. Overlapped with this

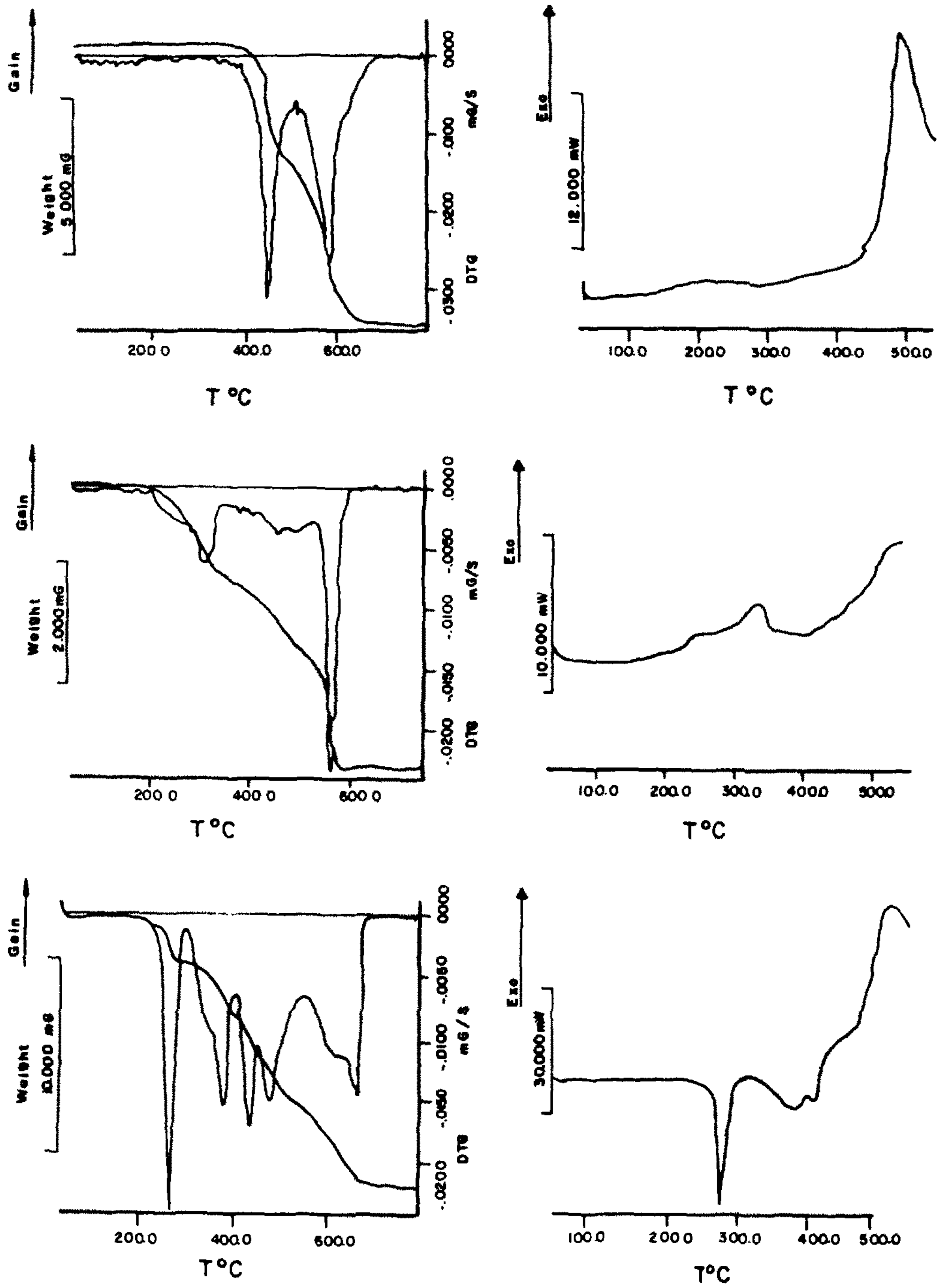

Fig. 2. TG and DSC curves for (top) $Ag_3(TX)(TX^-)$; (centre) $Ag_3(TX)(TXH)(NO_3)_2$; (bottom) $Cd(TXH)_2Cl_2$.

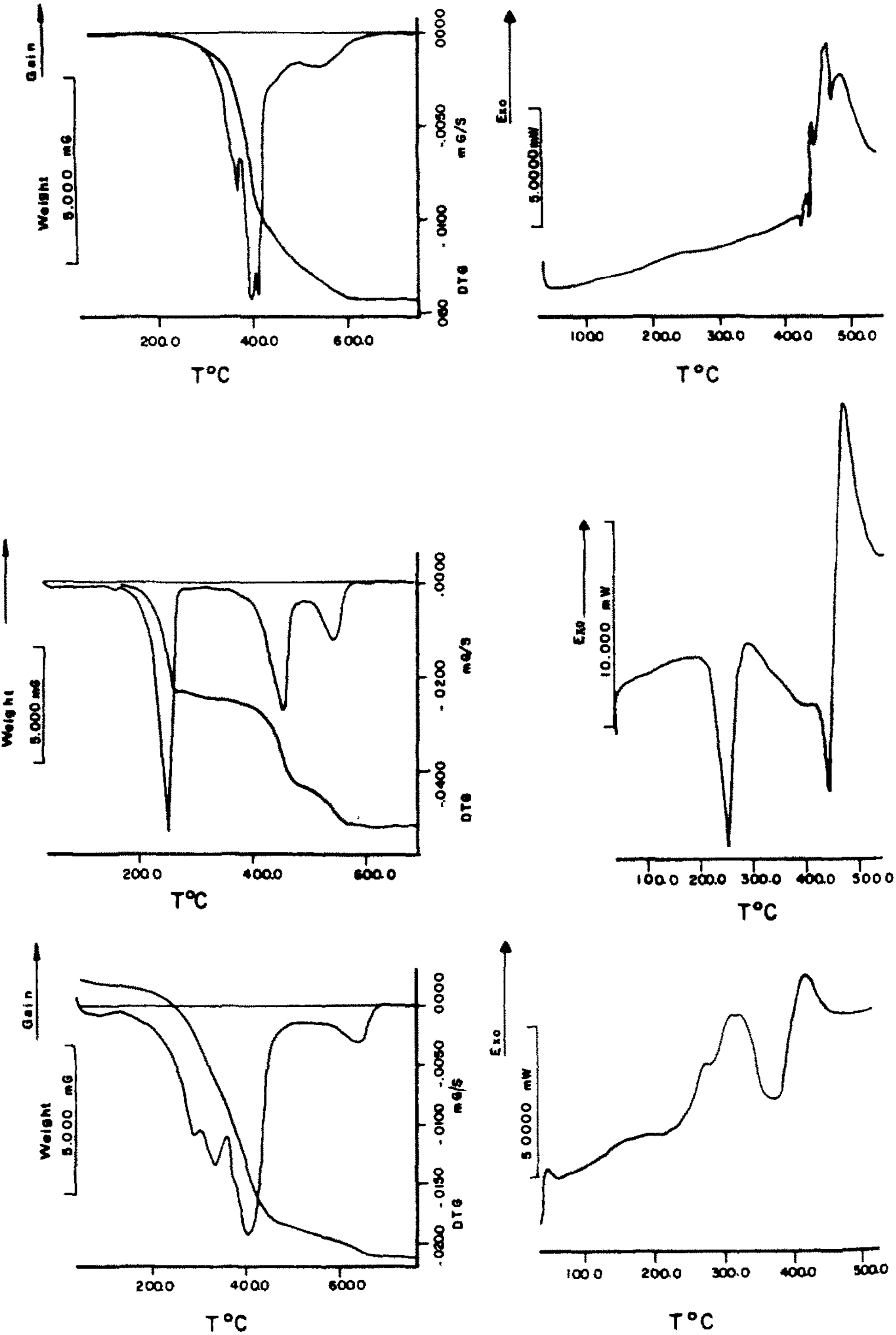

Fig. 3. TG and DSC curves for (top) $Hg(TXH)Cl_2$; (centre) $Hg(TXH)_2Cl_2$; (bottom) $Hg_2(TX)(NO_3)$.

effect appears an intense exothermic effect, due to the initiation of the pyrolytic decomposition of TXH. This fact interferes with the endothermic effect integration, and this must be taken into account when considering the calculated fusion enthalpy (58 kJ mol^{-1}).

The TG of TXH_2Cl (Fig. 1B) shows a first weight loss effect which starts at 175°C and finishes at 250°C. The observed weight loss (see Table 4) was 17.8% (theoretical weight loss for elimination of the chlorine atom, 17.83%). The expected endothermic behaviour for this dehalogenation process can be observed from the DSC curve (endothermic effect centred at 237°C); the dehalogenation enthalpy value was 54.9 kJ mol^{-1}. After this effect, the TG curve of TXH_2Cl follows the same pattern as that corresponding to 2-thioxanthine.

The TG and DSC curves (recorded in air) for silver and cadmium compounds of 2-thioxanthine are shown in Fig. 2.

The TG curves of both Ag(I) compounds (Fig. 2A and 2B) clearly show two weight loss effects (Table 3). At the end of the second effect, the residual weight corresponds to 49.5% (silver compound made in basic medium) and 41.0% (silver compound made in acidic medium) of the initial weight of the samples. The pyrolytic residue of these compounds is metallic silver, and was corroborated by IR spectra. The experimental values are in good agreement with the theoretical ones: 50.80% and 41.36%, respectively (Table 5). Besides, in the TG curve of the silver compound obtained in basic medium we can see that the pyrolytic decomposition begins at 370°C, showing the great stability of this compound. The DSC curve of this compound displays an exothermic effect centred at 480°C, but it is not completed due to the technical characteristics of the apparatus employed.

On the other hand, the first weight loss effect (15.4%), in the TG curve of the silver compound in acidic medium (Fig. 2B) has been assigned to the elimination of nitrate (theoretical weight loss 15.33%). The DSC curve shows the pyrolysis of nitrate anions as an exothermic effect centred at 333°C. After this elimination, the compound decomposes (530°C), finishing the pyrolytic process at 600°C in air and > 800°C in a nitrogen atmosphere. In both cases, at the end of the TG curve, metallic silver was obtained.

The TG and DSC curves for the cadmium complex are given in Fig. 2C. In this cadmium complex, two processes can occur: dehalogenation and pyrolytic decomposition.

Dehalogenation process

The dehalogenation process occurs in one step in the temperature range 240–320°C. The observed weight loss in this temperature range is shown in Table 6. The expected endothermic behaviour for the dehalogenation process associated with this compound can be observed from the DSC curve. Under the experimental conditions used in the present work, the two chlorine atoms are eliminated in one step as Cl_2. The calculated value of the dehalogenation enthalpy for $Cd(TXH)_2Cl_2$ was 602 kJ mol^{-1} which is in accord with that found for analogous compounds.

Pyrolytic process

Thermogravimetric and DSC data for the pyrolytic process are given in Tables 3 and 5. The dehalogenation complex decomposes in the temperature range 320–700°C, showing exothermic effects in the DSC curve. This must be attributed to the combustion of the organic matter. The final residue was cadmium sulphide, as revealed by IR spectroscopy, and the accumulated weight loss was higher than expected due to the partial sublimation of cadmium sulphide in the experimental conditions (nitrogen atmosphere).

The TG and DSC curves (recorded in air) for mercury compounds of 2-thioxanthine are shown in Fig. 3.

From these curves we extracted the data given in Tables 3 and 6.

The TG curve (Fig. 3) of $Hg(TXH)Cl_2$ shows that this compound is stable up to 250°C. At this temperature its thermal decomposition starts, which takes place in three steps which overlap. These processes correspond to the pyrolysis of the compound which was observed in the DSC curve. At the end of the pyrolysis (550°C) no residue was obtained.

The TG curve of the $Hg(TXH)_2Cl_2$ complex (Fig. 3B) clearly shows three weight loss effects. The complex is stable up to 175°C, after which an intense weight loss effect starts, followed by two slower weight losses over 450°C and 550°C, respectively, finishing at 575°C with no residue.

The first process has been assigned to the sublimation of $HgCl_2$. The weight loss value (Table 5) observed was 44.6% which is in good agreement with the calculated weight loss for sublimation of Hg as $HgCl_2$ (44.63%). The second and third processes correspond to the pyrolysis of 2-thioxanthine.

The DSC curve (Fig. 3B) shows at 258°C the endothermic effect corresponding to the first process. The sublimation enthalpy of $HgCl_2$ calculated from the area was 192.5 kJ mol^{-1}. Likewise, another endothermic effect appears at 401.6°C, corresponding to the fusion of the sample remains and, finally, an exothermic effect at 490°C assigned to pyrolysis of the sample in which the sample is completely eliminated.

The TG and DSC curves for the Hg(I) isolated compound are presented in Fig. 3C.

The TG curve shows that the decomposition of the Hg(I) compound takes place in four steps which overlap. The three first processes consist of a progressive and intense effect of weight loss which occurs in the temperature range 150–450°C. The fourth step corresponds to a slow weight loss over 650°C. The end of pyrolysis occurs at 675°C and no residue was obtained.

In the corresponding DSC curve, above 270°C, an exothermic effect appears. This effect is due to pyrolysis of the nitrate ion. The other exothermic effects above 312°C and 420°C, have been assigned to the combustion of the purine derivative.

REFERENCES

1 P. Calabresi and R.E. Parks, Jr. in L.S. Goodman and A. Gilman (Eds.), The Pharmacological Basis of Therapeutics, Macmillan, New York, 1975, Ch. 62.
2 G.B. Elion, E. Burgi and G.H. Hitchings, J. Am. Chem. Soc., 74 (1952) 411.
3 S. Kischner, Y. Wei, D. Francis and J.G. Bergman, J. Med. Chem., 9 (1966) 369.
4 E. Sletten, J. Sletten and L.H. Jensen, Acta Crystallogr. B, 25 (1969) 1330.
5 G.M. Brown, Acta Crystallogr. B, 25 (1969) 1338.
6 M. Das and S.E. Livingstone, Br. J. Cancer, 38 (1978) 325.
7 M. Maeda, N. Abiko and T. Sasaki, J. Pharm. Dyn., 5 (1982) 81.
8 S.M. Skinner, J.M. Swatzell and R.W. Lewis, Res. Commun. Chem., Pathol. Pharmacol., 19(1) (1978) 165.
9 R. Barbieri, E. Rivarola and F. Di Biana, Inorg. Chim. Acta, 57 (1982) 37.
10 H.I. Heitner and S.J. Lippard, Inorg. Chem., 13(4) (1974) 815.
11 M.R. Caira and L.R. Nassimbeni, J. Chem. Soc. Dalton Trans., 4 (1974).
12 P. Singh and D.J. Hodgson, Acta Crystallogr. B, 32 (1976) 979.
13 P. Lavertue, J. Hubert and A.L. Beauchamp, Inorg. Chem., 15(2) (1976) 322.
14 N. Kottmair and W. Beck, Inorg. Chim. Acta, 34 (1979) 137.
15 E.A.H. Griffith and E.L. Amma, J. Chem. Soc. Chem. Commun., 1013 (1979).
16 N.B. Behrens and D.M.L. Goodgame, Inorg. Chim. Acta, 46 (1980) 45.
17 J.M. Salas-Peregrin, E. Colacio-Rodríguez, J.D. López-González and C. Valenzuela Calahorro, Thermochim. Acta, 63 (1983) 145.
18 E. Colacio-Rodríguez, J.M. Salas-Peregrín, M.P. Sânchez-Sânchez and A. Mata-Arjona, Thermochim. Acta, 66 (1983) 245.
19 J.M. Salas-Peregrín, E. Colacio-Rodríguez, M.A. Romero-Molina and M.P. Sânchez-Sânchez, Thermochim. Acta, 69 (1983) 313.
20 E. Colacio Rodríguez, J.M. Salas-Peregrín, R. López-Garzón and J.D. López-González, Thermochim. Acta, 71 (1983) 139.
21 E. Colacio-Rodríguez and J.M. Salas-Peregrín, Thermochim. Acta, 74 (1984) 45.
22 E. Colacio-Rodríguez, J.M. Salas-Peregrín, M.A. Romero-Molina and R. López-Garzón, Thermochim. Acta, 76 (1984) 373.
23 J.M. Salas-Peregrín, E. Colacio-Rodríguez, F. Girela-Vilchez and M. Roldán Medina, Thermochim. Acta, 80 (1984) 323.
24 E. Colacio-Rodríguez, J.D. López-González and J.M. Salas-Peregrín, J. Therm. Anal., 28 (1983) 3.
25 M.P. Sânchez-Sânchez, J.M. Salas-Peregrín, M.A. Romero-Molina and A. Mata-Arjona, Thermochim. Acta, 88 (1985) 355.
26 E. Colacio-Rodríguez, J.M. Salas-Peregrín and J.D. López-González, Can. J. Chem., 65(1) (1983) 2506.
27 D.J. Hodgson, Progr. Inorg. Chem., 23 (1977) 211.
28 J.R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York, 1971.
29 W.M. Beck, J.C. Calabrese and N. Kottmair, Inorg. Chem., 18 (1979) 176.
30 E.H. Griffith and E.L. Amma, J. Chem. Soc. Chem. Commun., (1979) 324.
31 N.B. Behrens, D.M.L. Goodgame and Z. Warnke, Inorg. Chim. Acta, 31 (1978) 257.
32 R.B. Martin and Y.H. Mariam, in Metal Ions in Biological Systems, Vol. 8, M. Dekker, New York, 1977, p. 57.