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THERMAL STUDIES ON PURINE COMPLEXES. II. THERMAL BEHAVIOUR OF SOME METAL COMPLEXES OF THEOPHYLLINE

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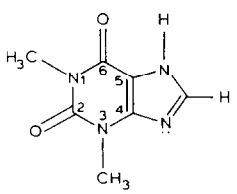
ABSTRACT

The thermal behaviour of the complexes of theophylline with Co(II), Cu(II), Ag(I), Zn(II) and Cd(II) was studied by thermogravimetry (TG), differential scanning calorimetry (DSC) and IR spectroscopy.

The complexes decompose in three steps, dehydration, deammination and decomposition of the anhydrous complexes to metal or metal oxide.

INTRODUCTION

According to data in the literature [1], the molecular structure of theophylline (TH) can be represented as



Studies on theophylline complexes indicate that bonding of the purine base to the metal ions takes place, in most cases, through the N_7 atom [2–5]. Although the interactions of metal ions with purine bases have been studied extensively by spectroscopic and X-ray diffraction techniques, their thermal behaviour has not been described in the literature. For this reason and as part of our work on the coordination of purine derivatives to metal ions, we recently reported the thermal behaviour of some Co(II), Cu(II) and Cd(II) complexes of xanthine [6]. In the present paper, a description is given of the preparation of some Co(II), Cu(II), Ag(I), Zn(II) and Cd(II) theophyllinato

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complexes, which have been obtained in order to study their thermal behaviour by TG and DSC techniques.

EXPERIMENTAL

Materials

Theophylline(1,3-dimethyl-2,6-dioxo purine), was purchased from Carlo Erba. All the chemicals used in this work were analytical reagent grade.

Preparation of the complexes

Theophyllinato complexes of Cu(II), Ag(I) and Cd(II) were obtained by mixing solutions of 7 M ammonia containing 5×10^{-3} mole of theophylline and 7 M ammonia containing 3×10^{-3} mole of metal nitrate. In all cases, precipitation was immediate. The isolated complexes were washed with water and ethanol and dried with ether. Their chemical analysis and colour were: $(C_7H_7N_4O_2)_2(NH_3)_2Cu \cdot H_2O$ (blue), calcd., C = 35.47%; H = 4.64%; N = 29.56%; Cu = 13,42%: found, C = 34.99%; H = 4.76%; N = 30.00%; Cu = 13.70%. $(C_7H_7N_4O_2)Ag \cdot H_2O$ (white), calcd., C = 27.56%; H = 2.95%; N = 18.37%; Ag = 35.37%: found, C = 28.10%; H = 2.72%; N = 18.74%; Ag = 35.12%. $(C_7H_7N_4O_2)_2(NH_3)(H_2O)_3Cd$ (white), calcd., C = 31.03%; H = 4.25%; N = 23.37; Cd = 20.76%. found, C = 32.17%; H = 4.26%; N = 22.98%; Cd = 19.70%.

Theophyllinato complexes of Co(II) and Zn(II) were synthesized as described. 5×10^{-3} mole of theophylline was dissolved in 50 ml of 0.25 M NH_4OH. This solution was added to a solution containing 3×10^{-3} mole of $M(NO_3)_2$ (M = Co and Zn) in 100 ml of 0.1 M NH_4Cl. In both cases the complexes precipitated immediately. The solid complexes were filtered with suction, washed several times with water and ethanol and dried with ether. The chemical analysis data for these complexes are: $(C_7H_7N_4O_2)_2(H_2O)_3$ Co(pink), calcd., C = 35.68%; H = 4.25%; N = 23.78%; Co = 12.51%: found, C = 35.28%; H = 4.24%; N = 23.56%; Co = 12.85%. $(C_7H_7N_4O_2)_2(NH_3)_2Zn$ (white), calcd., C = 36.73% H = 4.37%; N = 30.61%; Zn = 14.29%: found, C = 37.08%; H = 4.17%; N = 31.09%; Zn = 14.59%.

Apparatus

Chemical analysis of C, H and N was realized in a Carlo Erba model 1106 microanalyzer. The determination of metal ions was carried out in a Perkin Elmer model 290 absorption spectrometer.

Infrared spectra were recorded with a Beckman 4250 IR spectrophotome-

ter in the 4000–200 cm^{-1} range, using the KBr pellet technique.

TG studies were made in a static atmosphere of air, in a Mettler TG-50 thermobalance, using samples varying in weight from 4.44 to 12.56 mg and a heating rate of 10°C min^{-1}.

The DSC curves were recorded in a Mettler differential scanning calorimeter model DSC-20 at a heating rate of 5°C min^{-1}, in the 35–550°C temperature range.

RESULTS AND DISCUSSION

In recent research carried out in this laboratory [7] the authors have isolated some theophyllinato complexes of Co(II), Cu(II) Ag(I), Zn(II) and Cd(II). In these complexes theophylline bonding to the metal ion occurs through N_7. The most significant absorption bands for free theophylline and the isolated complexes are given in Table 1.

Thermogravimetric analysis curves for theophylline and some of their metal complexes are given in Fig. 1 and differential scanning calorimeter curves are given in Fig. 2.

The TG curve of anhydrous theophylline shows a single weight loss effect which starts at 275°C and finishes at 380°C. At 380°C no theophylline remains in the reaction crucible. On the other hand, the DSC curve of anhydrous theophylline exhibits two endothermic effects centred at 270 and 334°C. The first corresponds to fusion of the sample. The value found for the melting point (270.7°C) is in good agreement with the literature data [8]. The fusion enthalpy calculated from the area of the corresponding endothermic effect is 28.2 kJ $mole^{-1}$. The absence of exothermic effects in the DSC curve of theophylline indicates that in this purine base experiment a single vaporization process occurs after fusion, this vaporization being responsible for the endothermic effects at 334°C.

In the isolated theophyllinato complexes, three processes can occur: dehydration, deammination and pyrolytic decomposition.

Dehydration processes

At the first step of the thermal decomposition of hydrated complexes, water is eliminated. The data for calculated and observed weight losses and the corresponding temperature ranges for dehydration processes are given in Table 2.

The expected endothermic behaviour for the dehydration processes associated with these complexes has been observed from DSC curves in the same temperature range (Fig. 2). The corresponding dehydration enthalpies and temperature peaks are also given in Table 2. The high dehydration enthalpy and temperature peak values for the cobalt(II) theophylline complex suggests

TABLE 1

Infrared data for the theophyllinato complexes

All values are in cm^{-1}.

Substance	$\nu_{(O-H)}$	$\nu_{(NH)}$	$\nu_{(CH_3)}$	$\nu_{(C=O)}$	$\nu_{(C=C)}$	$\nu_{(C=N)}$	$\delta_{s(NH_3)}$	$\rho_{(NH_3)}$	ν_{M-OH_2}
Theophylline		3120 [c]	2960 2820	1715 1665	1605	1560			
$CoT_2 \cdot 3\ H_2O$	3440 3370 3240		2935	1650 1600	1560	1520			320
$CuT_2(NH_3)_2 \cdot H_2O$	3440	3340 3260 3180	2960	1690 1640	1580	1530	1220	680	[a]
$AgT \cdot H_2O$	3560 3520		[a]	1685 1635	1580	1530			[a]
$ZnT_2(NH_3)_2$		3355 3315 3210 3170	2950	1690 1625	1575	1520	1100 1050	645	
$CdT_2(NH_3) \cdot 3\ H_2O$	3460	3380 3260	2960	1665	1575	1535	1100	685	[a]

[a] Not observed.

[b] Not observed due to the overlapping with the $\delta_{as(NH)}$ and $\delta_{as(OH)}$ bands.

[c] Corresponds to (N_7-H).

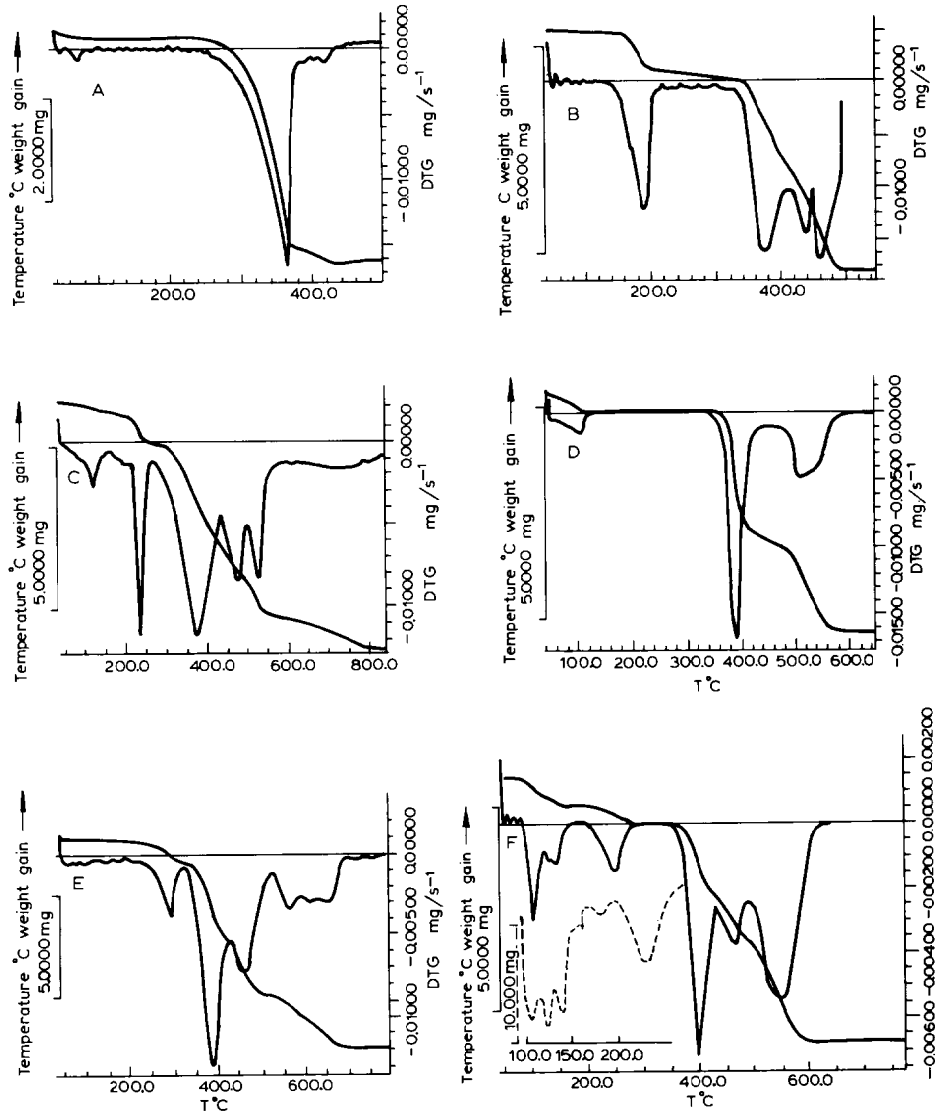

Fig. 1. TG and DTG curves of: A, theophylline; B, $CoT_2 \cdot 3\ H_2O$; C, $CuT_2(NH_3)_2 \cdot H_2O$; D, $AgT \cdot H_2O$; E, $ZnT_2(NH_3)_2$; F, $CdT_2(NH_3) \cdot 3\ H_2O$.

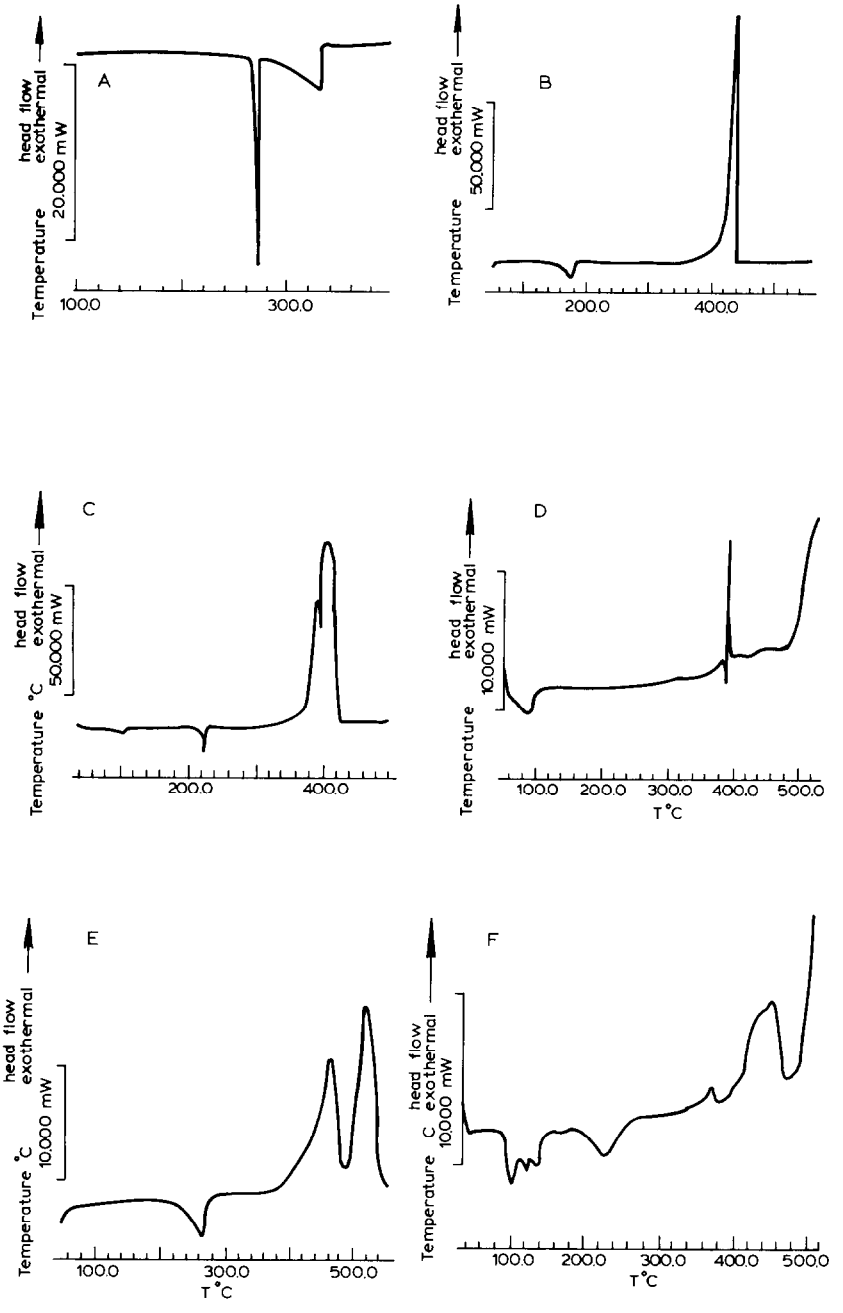

Fig. 2. DSC curves of: A, theophylline; B, $CoT_2 \cdot 3\ H_2O$; C, $CuT_2(NH_3)_2 \cdot H_2O$; D, $AgT \cdot H_2O$; E, $ZnT_2(NH_3)_2$; F, $CdT_2(NH_3) \cdot 3\ H_2O$.

TABLE 2

Thermoanalytic data for dehydration processes of isolated complexes

Process [a]	Weight loss (%)		Temperature range (°C)	Peak temperature, DSC (°C)	Dehydration enthalpy (kJ mole^{-1})
	Calcd.	Obs.			
$CoT_2 \cdot 3\ H_2O \rightarrow CoT_2 + 3\ H_2O$	11.5	12.6	135–220	172	73.4
$CuT_2(NH_3)_2 \cdot H_2O \rightarrow CuT_2(NH_3)_2 + H_2O$	3.8	3.7	70–160	105	32.3
$AgT \cdot H_2O \rightarrow AgT + H_2O$	5.9	4.8	50–120	86	23.8
$CdT_2(NH_3) \cdot 3\ H_2O \rightarrow CdT_2(NH_3) \cdot 2\ H_2O + H_2O$				99	
$CdT_2(NH_3) \cdot 2\ H_2O \rightarrow CdT_2(NH_3) \cdot H_2O + H_2O$	9.9	9.7	70–160	120	45.6
$CdT_2(NH_3) \cdot H_2O \rightarrow CdT_2(NH_3) + H_2O$				136	

[a] T = Theophyllinato anion $(C_7H_7N_4O_2)^-$.

that the three water molecules are directly coordinated to Co(II). The lower values of the dehydration enthalpies of the copper and silver theophyllinato complexes indicate water of crystallization. Finally, the cadmium complex becomes completely dehydrated in three consecutive steps which are clearly shown in the DTG and DSC curves. The average enthalpy for the elimination of these three water molecules is given in Table 2.

Deammination processes

The second step of the decomposition of theophyllinato complexes of Cu(II), Zn(II) and Cd(II) is a deammination process.

Copper, zinc and cadmium theophyllinato complexes become deamminated in the temperature ranges 200–270°C, 240–325°C and 195–275°C, respectively. The observed weight losses in these temperature ranges are shown in Table 3. The expected endothermic behaviour for the deammination process associated with these compounds is supported by DSC curves in almost the same temperature ranges. Temperature peaks and enthalpies of deammination are also given in Table 3.

Pyrolytic processes

All the isolated complexes, the dehydrated and deamminated intermediates, decompose in the temperature range 370–850°C, showing one, two or three exothermic effects in DSC curves (with the exception of the silver complex, which presents an endothermic effect centered at 388°C). This must be attributed to the combustion of the organic matter. The final residues were oxides (except for the copper and silver complexes, which gave residues of Cu^0 and Ag^0), as revealed by IR spectroscopy. The thermogravimetric and DSC data for these pyrolytic processes are given in Table 4.

The endothermic effect of the silver complex, can be attributed to fusion

TABLE 3

Thermogravimetric and DSC data for the prepared complexes in the deammination processes

Process	Weight loss (%)		Temperature range TG (°C)	Temperature peak DSC (°C)	ΔH (kJ (mole^{-1})
	Calcd.	Obs.			
$CuT_2(NH_3)_2 \rightarrow CuT_2 + 2\ NH_3$	7.2	7.4	200–270	223	38
$ZnT_2(NH_3)_2 \rightarrow ZnT_2 + 2\ NH_3$	7.4	6.8	240–325	261	59
$CdT_2(NH_3) \rightarrow CdT_2 + NH_3$	3.1	3.6	195–275	227	82

TABLE 4

Thermogravimetric and DSC data for the pyrolytic processes

Reaction	Oxide or metal residue expected (%)		DSC peak temperature (°C)	
	Calcd.	Obs.	Endo	Exo
$CoT_2 \rightarrow Co_3O_4$	17.0	17.6		443
$CuT_2 \rightarrow Cu$	13.4	13.0		406
$AgT \rightarrow Ag$	35.4	35.1	388	390 > 500
$ZnT_2 \rightarrow ZnO$	17.8	17.2		458 > 517
$CdT_2 \rightarrow CdO$	23.7	22.9		370 445 > 500

of the dehydrated compound. The melting point is 388°C and the fusion enthalpy calculated from the area of the endothermic effect is 24.7 kJ $mole^{-1}$.

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