THERMAL STUDIES ON PURINE COMPLEXES. I. THERMAL BEHAVIOUR OF SOME XANTHINE COMPLEXES OF COBALT(II), COPPER(II) AND CADMIUM(II)

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ABSTRACT

Cobalt, copper and cadmium xanthinate tetrahydrates have been prepared in aqueous medium, and characterized on the basis of elemental analysis, IR and ^{1}HNMR studies. The thermal behaviour of these compounds has been studied using TG, DTG and DSC techniques. Heats of dehydration have been calculated from DSC curves.

INTRODUCTION

The interaction of metal ions with purines has been the subject of several investigations. Most of this work has been carried out on the complexes in solution by spectroscopic and potentiometric titration methods [1–4]. More recently a few X-ray crystallographic structure determinations of metal complexes of purines have appeared in the literature [5–8]. In the present work some metal complexes of xanthine have been prepared in order to elucidate their binding sites to the metal and to study their thermal behaviour by TG and DSC techniques.

EXPERIMENTAL

Materials

Xanthine (2,6-dioxo-purine) was purchased from E. Merck. All the inorganic products used were of analytical reagent grade.

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Methods

Infrared spectra of the studied compounds were recorded in KBr medium, in the region 4000–200 cm^{-1}, using a Beckman 4250 spectrophotometer. The TG studies were carried out in air on a Mettler TG-50 thermobalance, using samples varying in weight from 6 to 13 mg and at 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 temperature range 40–560°C. The ^{1}HNMR spectra were recorded on a Hitachi-Perkin-Elmer Model R-600 FT-NMR spectrometer.

Preparation of the compounds

Xanthinates of the type $MX_2 \cdot 4\ H_2O$ [where X = xanthinate ion, M = Co(II), Cu(II) and Cd(II)], were obtained by mixing an aqueous solution of xanthine with an aqueous solution of the respective metal nitrate. The cloudy mixture was heated at 70°C with continuous stirring until all the xanthine was dissolved. The resulting clear solution was allowed to cool slowly to room temperature. After a few hours precipitates appeared which were filtered, washed consecutively with water, ethanol and ether, and dried in air. The xanthinates prepared, along with their elemental analysis, are presented in Table 1.

RESULTS AND DISCUSSION

The IR data of the studied compounds are tabulated in Table 2, together with those corresponding to free xanthine. The principal IR bands have been assigned by comparison with the IR spectrum of free xanthine [9,10]. The shifts of the bands ν(C=O) at 1630 cm^{-1} and 1580–1595 cm^{-1} can be attributed to the formation of hydrogen bonds between the carbonyl groups of the pyrimidine ring and the water molecules linked to the metal.

The ^{1}HNMR spectra of $CdX_2 \cdot 4\ H_2O$ in DMSO-d_6 was compared with the ^{1}HNMR spectra of free xanthine [11]. The chemical shift of the proton H(8) in this compound is the same as that in free xanthine, which is compatible with the coordination of the xanthinate ion through N(1) or N(3), although coordination by N(3) will be favoured according to bibliographic data [12].

Figures 1 and 2 show TG and DSC plots of xanthine and some metal xanthinates. The thermal behaviour of these compounds consists of two major processes: (i) dehydration of the hydrated compounds, and (ii) decomposition of the anhydrous complexes to the respective metal oxide.

Under the experimental conditions used in the present work, the dehydration process occurs in one step for $CoX_2 \cdot 4\ H_2O$ and $CdX_2 \cdot 4\ H_2O$, whereas

TABLE 1

Analytical data for some xanthinate complexes

Compound	Colour	Analysis (%)							
		Found				Calcd.			
		C	H	N	M	C	H	N	M
Xanthine	White	39.75	2.72	36.63		39.44	2.63	36.81	
$CoX_2 \cdot 4 H_2O$	Pink	27.86	3.25	26.00	13.10	27.71	3.23	25.85	13.60
$CuX_2 \cdot 4 H_2O$	Green	27.55	3.21	25.71	14.18	27.41	3.20	25.58	14.51
$CdX_2 \cdot 4 H_2O$	White	24.77	2.89	23.12	23.25	24.66	2.88	23.02	23.10

TABLE 2

Infrared data of some xanthinate complexes

Compound	$\nu(OH)$	$\nu(N-H)$ [a]	$\nu(=C-H)$	$\nu(C=O)$	$\nu(C=C)$	$\nu(C=N)$	$\nu(M-OH_2)$	$\nu(M-N)$
Xanthine		3200–2700(s)	3000(s)	1700 and 1650(vs)	1615m	1570m		
$CoX_2 \cdot 4 H_2O$	3210(s)	3200–2700(s)	3000(s)	1635 and 1580(vs)	b	b	380(w)	285(w)
$CuX_2 \cdot 4 H_2O$	3310(s)	3200–2700(s)	3010(s)	1630 and 1595(vs)	b	b	390(w)	305(w)
$CdX_2 \cdot 4 H_2O$	3210(s)	3200–2700(s)	3000(s)	1630 and 1585(vs)	b	b	370(vw)	c

[a] Few bands.
b Not observed due to the overlapping with the carbonyl bands.
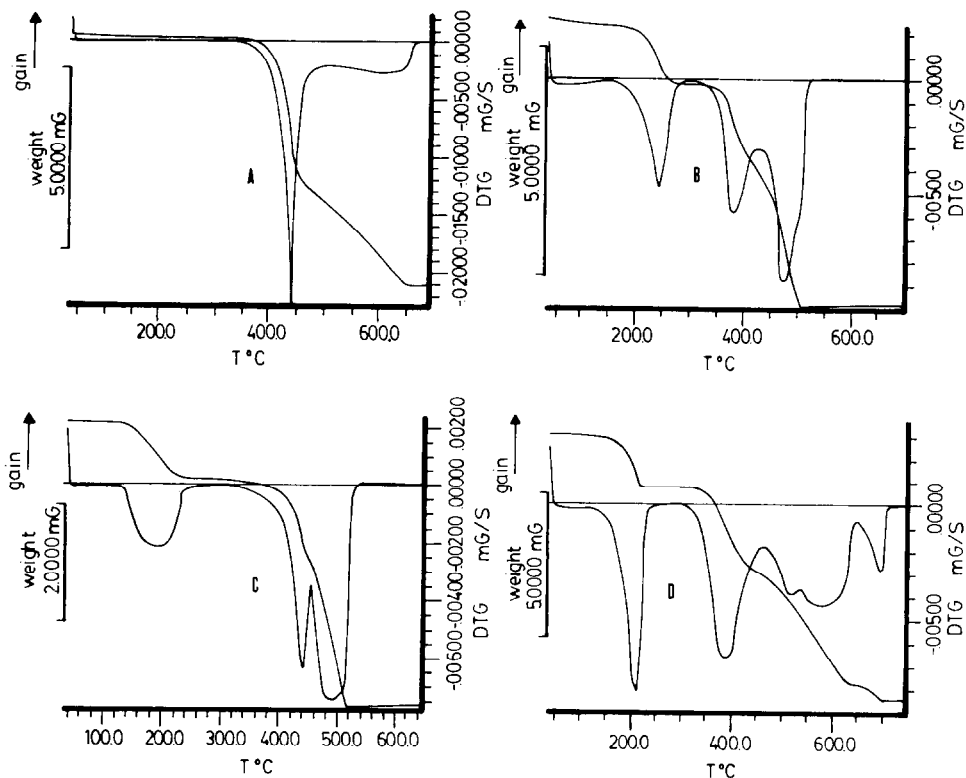c Not observed.

Fig. 1. TG and DTG plots of xanthine (A); $CoX_2 \cdot 4 H_2O$ (B); $CuX_2 \cdot 4 H_2O$ (C); and $CdX_2 \cdot 4 H_2O$ (D).

for $CuX_2 \cdot 4 H_2O$ this dehydration apparently occurs in two steps, as observed from its DSC curve.

The dehydration of $CoX_2 \cdot 4 H_2O$, $CuX_2 \cdot 4 H_2O$ and $CdX_2 \cdot 4 H_2O$ occurs in the temperature ranges 175–280°C, 130–230°C and 145–240°C, respectively. The observed weight losses in these temperature ranges show the tetrahydrate nature of the three compounds. The expected endothermic behaviour for the dehydration process associated with these compounds has been observed from DSC curves in almost the same temperature ranges. The dehydration temperatures, observed weight losses, calculated weight losses and dehydration enthalpies calculated from the DSC curves of Fig. 2 are indicated in Table 3.

The coordination around the metal centre for the Cd and Co compounds is possibly octahedral, with the four water molecules in the equatorial plane and the xanthinate ions in axial positions (Fig. 3). In the copper complex, dehydration occurs in two steps, which suggests for this complex a distorted octahedral symmetry due to a Jahn–Teller effect.

The TG curve of xanthine (Fig. 1) shows that this compound is anhydrous and stable in the 50–375°C temperature range. The pyrolytic destruction of the purine ring occurs in two steps: a fast decomposition between 375 and
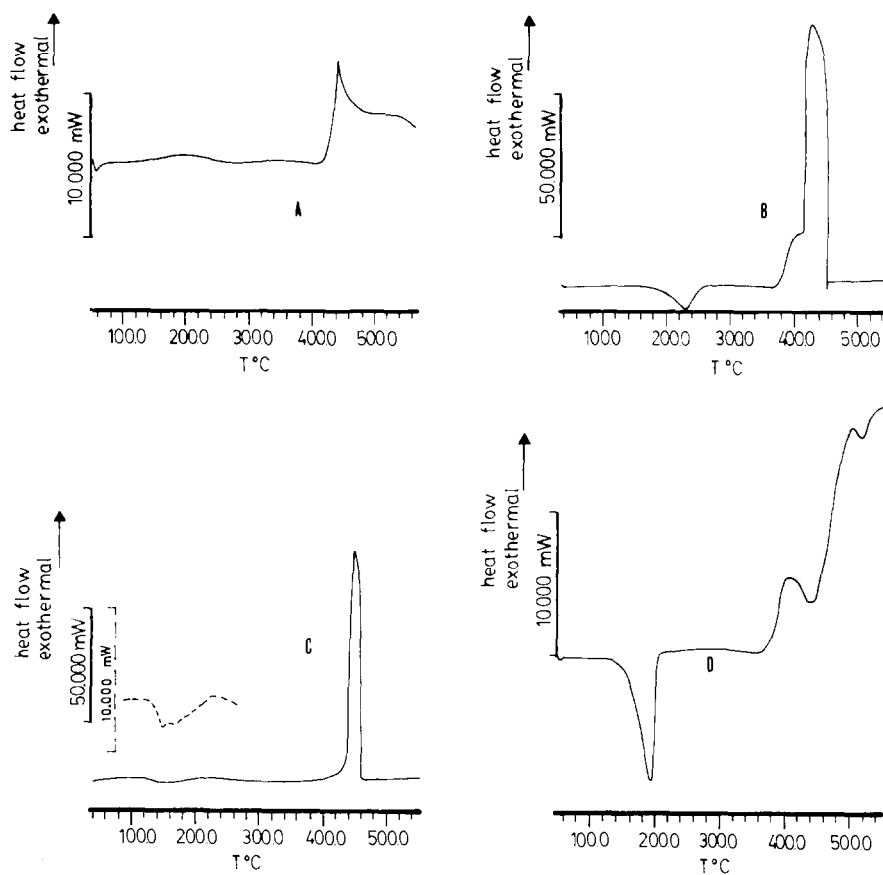
Fig. 2. DSC curve of xanthine (A); $CoX_2 \cdot 4\ H_2O$ (B); $CuX_2 \cdot 4\ H_2O$ (C); $CdX_2 \cdot 4\ H_2O$ (D).

480°C, followed by a slow decomposition from 480°C to the end of the pyrolysis around 600°C.

The anhydrous cobalt xanthinate is stable from 280°C to 315°C. The TG curve shows a fast decomposition in two steps in the temperature range

TABLE 3

TG and DSC data for the dehydration of some xanthinate complexes

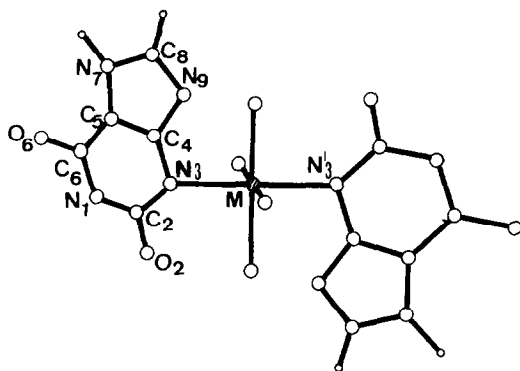| Complex	Dehydration temp. (°C)	wt. loss (%)		$\Delta H_{\text{dehydr.}}$ (kJ mole^{-1} H$_2$O)
		Found	Calcd.	
$CoX_2 \cdot 4\ H_2O$	228.0	16.39	16.63	64.33
$CuX_2 \cdot 4\ H_2O$	147.0	16.45	16.41	47.85
$CdX_2 \cdot 4\ H_2O$	191.8	13.80	13.22	57.75

Fig. 3. Possible structure of $MX_2 \cdot 4 H_2O$. Hydrogen atoms on the coordinated water molecules are omitted for clarity.

315–520°C. At this point the residual weight is 17.8% of the original weight, which corresponds narrowly with the theoretical value required for Co_3O_4 (18.5%).

The anhydrous copper xanthinate is stable up to 360°C; from this temperature to the end of the run a very rapid weight loss occurs in two steps. The percentage weight of the residue at 530°C (19.03%) corresponds to CuO.

The anhydrous cadmium xanthinate is stable from 240°C to 320°C. A fast decomposition occurs between 320 and 450°C, followed by a slower decomposition from 450°C to the end of the run at 715°C. The residue obtained at the end of the pyrolysis (28.9% of the original weight) corresponds to CdO.

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