

THERMAL BEHAVIOUR OF METAL-XANTHOSINE COMPLEXES

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ABSTRACT

Several complexes of xanthosine, 9- β -D-ribofuranosylxanthine (Xao) with 3d metal ions have been prepared. The new complexes appear to be generally monomeric, involving terminal N3-bonded Xao ligands. The thermal behaviour of these complexes has been studied by TG, DTG and DSC techniques.

INTRODUCTION

Xanthosine (9- β -D-ribofuranosylxanthine) is a stronger acid ($pK=5.6$) than other similar purine nucleosides. This can be due to the formation of a strong hydrogen bond $N3-H \rightarrow O5'$, that facilitates the loosing of this proton (1,2).

Because of its acidity, xanthosine easily undergo substitution of this proton by metal ions giving different metal complexes. We have recently reported the results of our research on the thermal behaviour of some metal-purine derivatives complexes (3-5). Now we have extended our work to study the thermal behaviour of several metal-nucleoside complexes. The result of our spectroscopic and thermal studies on six new metal-xanthosinato complexes are presented here.

EXPERIMENTAL

Xanthosine was purchased from Aldrich-Chemie. Cobalt, nickel, copper and zinc xanthosinato complexes were obtained by treating a slight excess of the adequate metal carbonate with a hot aqueous solution of xanthosine during thirty minutes. Unreacted carbonate is then filtered off and the clear solution is left to evaporate at room temperature. After 24 h. the solids were filtered, washed with cold water and dried at room temperature. The nickel complex, because of its poor solubility, is better obtained by mixing stoichiometric amounts of xanthosine and nickel nitrate in 1 M ammonia. Cadmium and mercury complexes were obtained dissolving xanthosine by the dropwise addition of 0.05 M sodium hydroxide and subsequent addition of cadmium or mercury chloride until to reach a 2:1 molar ratio.

The chemical analysis of C, H and N were carried out by microanalytical methods at the Technical Services of the University of Granada. Analytical and colour data of the complexes are given in table 1.

^1H -NMR and ^{13}C -NMR spectra of Zn(II) and Cd(II) complexes were recorded on a Bruker AM300 spectrometer using DMSO-d_6 as solvent and TMS as internal standard. IR spectra were recorded using KBr pellets (4000-250 cm^{-1} range) and polyethylene pellets (650-180 cm^{-1} range) on a Perkin-Elmer 983G spectrophotometer.

Thermogravimetric studies were carried out in a dynamic air atmosphere (100 ml.min^{-1}) on a Mettler TG-50 thermobalance at a heating rate of 10 deg.min^{-1} , while the DSC runs were obtained using a Mettler DSC-20 differential scanning calorimeter in the 35-450°C temperature range at the same heating rate. The weight of the samples used varied between 4 and 20 mg.

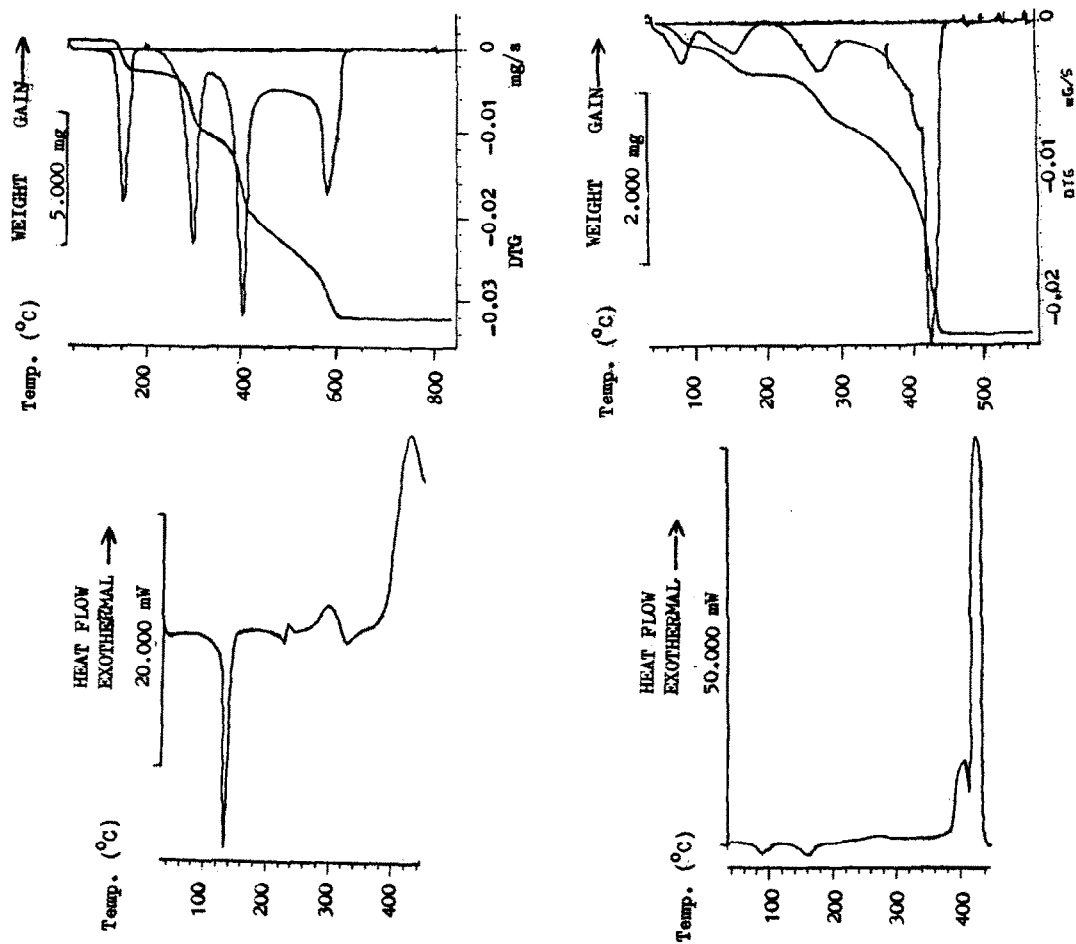


Figure 1: TG and DSC curves for xanthosine (left) and its cobalt complex (A) (right).

RESULTS AND DISCUSSION

IR spectra of the isolated complexes show two significant features: First, the splitting of the signal due to $\nu(\text{C}=\text{O})$ which appears in the IR spectrum of free xanthosine as a single band at 1682 cm^{-1} . This fact can be explained by the deprotonation of the ligand at N3 and the interaction of water molecules with $\text{C2}=\text{O}$ group. Second, the appearance of a new band in the $300\text{--}250\text{ cm}^{-1}$ range, assigned to $\nu(\text{M-N})$.

On the other hand, $^1\text{H-NMR}$ spectra of Zn(II) and Cd(II) complexes are very similar, being quite different of the one of free xanthosine (6). The more important differences are the loss of the signal due to N3 proton and the very big downfield shift of C4 resonance (20 ppm.). These facts strongly suggest monodentate coordination through N3.

Thermal decomposition of these metal-xanthosinato complexes has been studied from their TG, DTG and DSC curves. As a title, in fig. 1 thermogravimetric and DSC curves for xanthosine and $[\text{Co}(\text{Xao})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ have been collected. The thermal decomposition of the $[\text{M}(\text{Xao})_2(\text{H}_2\text{O})_4] \cdot n\text{H}_2\text{O}$ complexes begins with a dehydration process in two steps which gives an important information about the structure of the complexes.

The first of these steps consists in the elimination of hydration water; it takes place in the $55\text{--}90^\circ\text{C}$ temperature range. Together with this process, cobalt, copper and zinc complexes loose their crystalline look, although their colour only changes slightly. The second dehydration step takes place in the $105\text{--}170^\circ\text{C}$ temperature range, in which coordinated water is eliminated. At the end of this process, the cobalt complex changes its colour from pale rose to deep purple, nickel one changes from blue to yellow

TABLE 1: Colour and analytical data for isolated complexes.

Compound	Colour	C%	H%	N%
$[\text{Co}(\text{Xao})_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ (A)	pale rose	31.85 (31.94)	5.04 (4.79)	16.14 (14.91)
$[\text{Ni}(\text{Xao})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}$ (B)	pale blue	29.85 (29.81)	4.87 (5.22)	13.82 (13.91)
$[\text{Cu}(\text{Xao})_2(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (C)	green	30.64 (31.01)	4.18 (4.91)	13.72 (13.83)
$[\text{Zn}(\text{Xao})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (D)	white	32.18 (32.44)	4.66 (4.59)	15.42 (15.14)
$[\text{Cd}(\text{Xao})_2(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$ (E)	white	29.21 (29.82)	4.43 (4.47)	13.53 (13.92)
$[\text{Hg}(\text{Xao})\text{Cl}] \cdot 2\text{H}_2\text{O}$ (F)	white	23.70 (23.11)	2.47 (2.89)	11.29 (10.78)

Calculated values in parentheses.

TABLE 2: Thermoanalytical data.*

Compound	First dehydration				Second dehydration			
	Weight loose		Peak	ΔH	Weight loose		Peak	ΔH
	Exp.	Theor.	temp.		Exp.	Theor.	temp.	
(A)	7.1	7.2	89.0	51	15.3	16.8	162.5	66
(B)	14.1	13.4	63.7	21	23.0	22.3	165.7	24
(C)	9.5	9.3	63.3	27	18.2	18.6	132.2	51
(D)	4.7	4.9	109.0	40	13.1	14.6	145.5	**
(E)	6.6	6.2	81.8	26	14.7	15.6	109.2	29
(F)	7.3	6.9	57.4	17	--	--	--	--

(*) Temperatures in deg. and enthalpies in kJ mol^{-1} .

(**) Overlapping with the exothermic effects of ribose pyrolysis.

and copper one changes from green to brown. The observed and calculated weight losses, dehydration temperatures as well as dehydration enthalpies calculated from DSC plots, for both steps have been tabulated in table 2. The analysis of these data let us to propose an octahedral configuration around the central metal ion for these complexes.

The pyrolytic decomposition of dehydrated compounds shows a similar pattern for all these complexes, taking place in two main steps. The first step begins at 250°C and it is associated to small exothermal effects, that can be assigned to the incomplete burning of the ribose moiety because, in the infrared spectra of the intermediate compound, the corresponding bands due to $\nu(\text{C-O})$ and $\nu(\text{O-H})$ of the sugar are lost. In the case of free xanthosine, the IR spectrum of a sample heated at 320°C is analogous to the one of xanthine. Associated weight losses are smaller than expected probably due to the presence of unburned carbon. Finally, all TG curves show one or two more steps due to the pyrolytic decomposition of purine ring, leaving the corresponding metal oxide as residue, except mercury complex that leaves no residue.

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