

THERMAL BEHAVIOUR OF XANTHINIUM SALTS OF Zn(II), Cd(II) AND Hg(II)

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Salts $[\text{XanH}^+]_2[\text{MCl}_4]^{2-}$ (where XanH^+ = protonated form of xanthine and $M = \text{Zn(II)}$, Cd(II) and Hg(II)) have been synthesized and studied by IR, $^1\text{H-NMR}$, TG and DSC. The metal is not coordinated to the ligand and forms a salt-like structure. The cationic proton is on N(7). Thermal decomposition of these salts occurs in two steps: (i) dehalogenation and (ii) decomposition. Dehalogenation enthalpies have been calculated from DSC curves.

The biological importance of purine bases (constituents of the nucleic acids) is well known. The interaction of metal ions with nucleic acids, nucleosides and nucleotides has been an active research area in inorganic and structural chemistry during the last few years, and a number of recent reviews exist on the subject [1, 2].

This research increased in importance with the discovery that some platinum compounds exhibit carcinostatic properties [3]. Although the interactions of metal ions with purine bases have been studied extensively by spectroscopy and X-ray diffraction techniques, however, no investigation of the thermal behaviour has been reported. For this reason as part of our work on the interaction of xanthine derivatives with metal ions, we recently reported the thermal behaviour of some Co(II), Cu(II) and Cd(II) compounds of xanthine [4]. We now describe the preparation of some Zn(II), Cd(II) and Hg(II) salts of xanthine (Fig. 1), which have been studied by TG and DSC techniques, in order to propose a thermal decomposition mechanism. These salts of xanthine are similar to those obtained in the reactions between hypoxanthine and $[\text{AuCl}_4^-]$ [5], and theophylline or 9-ethylguanine and $[\text{PtCl}_4]^{2-}$ [6, 7].

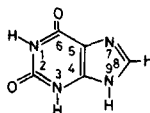


Fig. 1 Structure of xanthine (2,6-dioxopurine)

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Experimental

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

Infrared spectra were recorded in the range 4000–200 cm^{-1} using a Beckman-4250 spectrophotometer, in KBr pellets. The 600–200 cm^{-1} range was also recorded in polyethylene pellets.

The TG studies were made in a static atmosphere of air (in the case of the mercury compound a pure air flow of 100 ml/min was used) and under an inert atmosphere of N_2 on a Mettler TG-50 thermobalance, using samples of 3–14 mg and a heating rate of 10 deg/min. The DSC curves were recorded in air on a Mettler DSC-20 differential scanning calorimeter at a heating rate of 5 deg/min in the temperature range 40–560°, of 1.7–5 mg. The $^1\text{H-NMR}$ spectra were recorded on a Hitachi–Perkin–Elmer R-600 FT-NMR spectrometer, using DMSO-d_6 as solvent and TMS as internal standard.

The microanalyses of C, H and N were performed with a Carlo Erba model 1106 microanalyzer. Metal ions were determined with a Perkin–Elmer 290 absorption spectrometer.

Preparation of salts

A solution of 3 mmol MCl_2 ($\text{M} = \text{Zn, Cd or Hg}$) in 10 ml water was added to 6 mmol xanthine in 50 ml water containing 15 ml concentrated HCl. The cloudy mixture was heated at 70° until all xanthine had dissolved. The resulting clear solution was allowed to cool slowly to room temperature. After a few hours, colorless needles appeared in each of the three cases. These were filtered off, washed consecutively with water, ethanol and ether, and dried in air. The crystal needles are very soluble in water. None of the isolated compounds presents a definite melting point.

Analysis. Calcd. for $[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}]$: C = 23.46; H = 1.95; N = 21.88; Zn = 12.73; Cl = 27.64. Found: C = 23.82; H = 1.86; N = 21.76; Zn = 13.29; Cl = 28.17%.

Analysis. Calcd. for $[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$: C = 21.40; H = 1.78; N = 19.97; Cd = 20.05; Cl = 25.33. Found: C = 21.85; H = 1.73; N = 19.91; Cd = 18.96; Cl = 25.70%.

Analysis. Calcd. for $[\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$: C = 18.5; H = 1.54; N = 17.26. Found: C = 19.26; H = 1.51; N = 17.35%.

$^1\text{H-NMR}$ data for $\text{C}_8\text{-H}$ in $[\text{XanH}^+]_2[\text{MCl}_4^{2-}]$: $\delta(\text{ppm})$: 8.23 (1H).

Results and discussion

Under the experimental conditions employed in this work (very low pH) the new xanthine compounds contain exclusively monoprotonated xanthine. All the compounds show practically the same infrared spectra. The principal bands were assigned by comparison with the spectrum of free xanthine [8, 9]. The absorption in the 3260–2600 cm^{-1} range (few bands of combination) is assigned to $\text{N}^+\text{—H}$ stretching. The xanthine bands at 1620 and 1565 cm^{-1} , involving contributions of the stretching modes of the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ groups, respectively, are slightly shifted, to 1650 and 1590 cm^{-1} , in the xanthinium compounds. These shifts are attributed to the protonation at N(7), since an increase in the electron density at the carbon atoms adjacent to the protonated nitrogen has been calculated theoretically for some nitrogen heterocyclic molecules [10].

In the 600–200 cm^{-1} region the infrared spectra show absorption bands at 250 cm^{-1} ($[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}]$), 235 cm^{-1} ($[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$) and 205 cm^{-1} ($[\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$), assigned to metal-halogen tension vibration. The positions of these bands accord to the literature data [11]. The ratio $\nu_3(\text{Cd—Cl})/\nu_3(\text{Zn—Cl})$ is 0.94 and $\nu_3(\text{Hg—Cl})/\nu_3(\text{Zn—Cl})$ is 0.82. These values are equal to those obtained for tetraethylammonium compounds of type $[\text{Et}_4\text{N}^+]_2[\text{MCl}_4^{2-}]$ (where $\text{M} = \text{Zn(II)}$, Cd(II) and Hg(II) , and MCl_4^{2-} is a tetrahedral anion) [12], and suggest that these compounds have similar structures that of to the $[\text{XanH}^+]_2[\text{MCl}_4^{2-}]$ isolated.

The $^1\text{H-NMR}$ spectra of $[\text{XanH}^+]_2[\text{MCl}_4^{2-}]$ in DMSO-d_6 were compared to the $^1\text{H-NMR}$ spectra of free xanthine [13, 14]. The downfield shift of H(8) (0.3 ppm) in the three isolated salts is compatible with the positive character of the imidazole ring, due to protonation at N(7). A downfield shift has also been observed in the $^1\text{H-NMR}$ spectrum of the salt $(9\text{EG})_2[\text{PtCl}_4] \cdot 2\text{H}_2\text{O}$ (where 9EG = 9-ethyl-guaninium) [6].

Likewise, all the compounds present a new signal above 10 ppm corresponding to two protons, probably protons of the imidazole ring (N(7)—H and N(9)—H). These protons are equivalent due to (A) and its resonance-equivalent form (B), which places the positive charge on N(9) (Fig. 2).

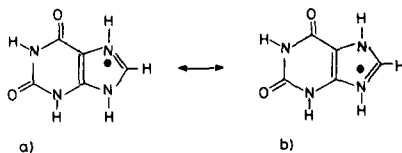


Fig. 2 Resonance forms for the protonation of xanthine in the imidazole ring

The TG curves of $[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}]$ in pure air and N_2 (Fig. 3a) are very similar, showing that this compound is completely dehalogenated in the temperature range 315–390°. This dehalogenation occurs in two steps which overlap. The dehalogenated

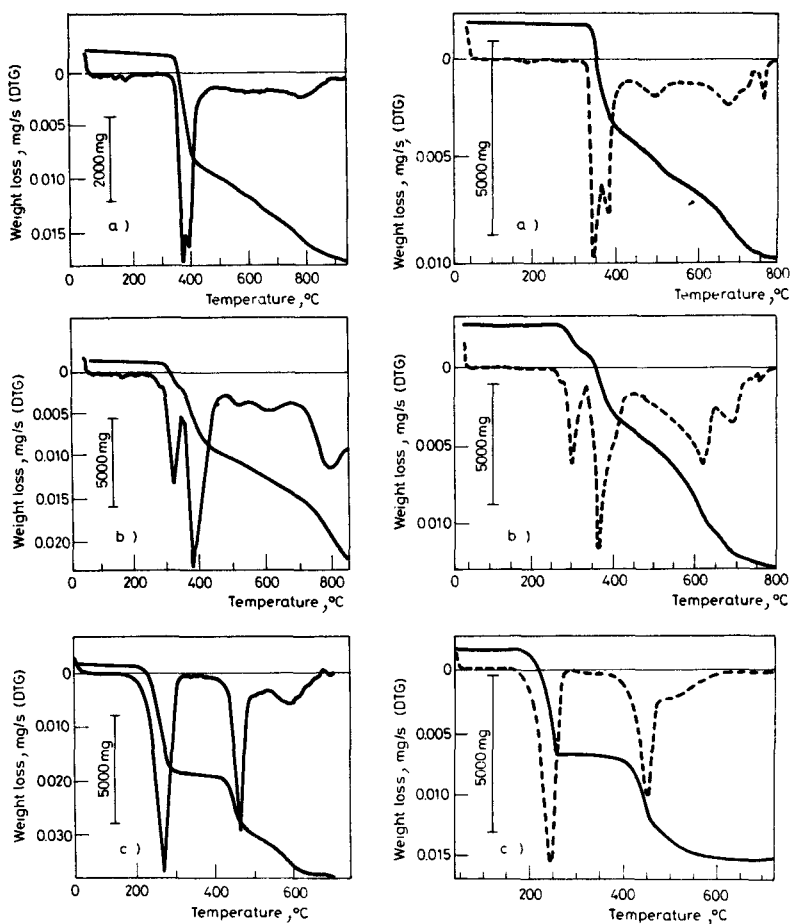


Fig. 3 TG curves for a = $[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}]$; b = $[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$; c = $[\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$, in air (left hand side) and nitrogen (right hand side)

compound is very unstable and immediately starts to decompose. The residue obtained at the end of the pyrolysis (total weight loss 83.5%) has been proved by IR examination to be ZnO (theoretical weight loss 84.15%).

The DSC curve of $[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}]$ (Fig. 4a) shows two endothermic effects, indicating that the four chlorine atoms are not equivalent (endothermic effects at 338° and 375°). The dehalogenation enthalpies for the two effects were 131.9 and $150.5 \text{ kJ} \cdot \text{mol}^{-1}$, respectively.

The TG curves of $[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$ in pure air and N_2 (Fig. 3b) are analogous. These curves show that $[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$ starts to lose weight around 280° . The observed weight loss in the temperature range $290\text{--}350^\circ$ (12.9%) can be assigned to the elimination of two chlorine atoms as HCl (theoretical weight loss 13.02). At 360°

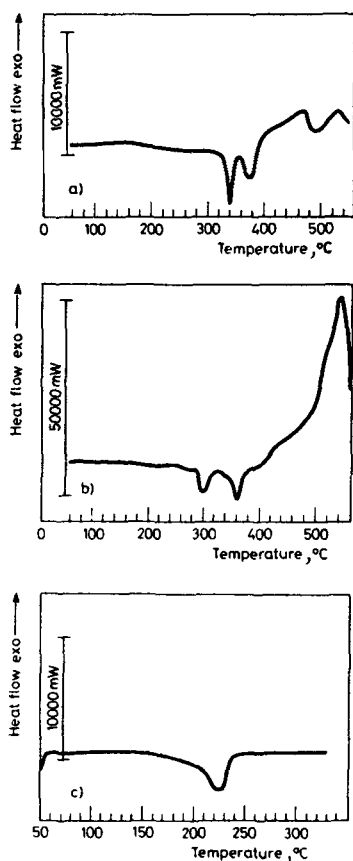


Fig. 4 DSC curves for a = $[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}]$; b = $[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$; c = $[\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$

the compound is very unstable and rapidly undergoes total dehalogenation and pyrolysis of the organic moiety to give CdO (17.6%) at the end of the pyrolysis; part of the CdCl₂ sublimes during the dehalogenation process.

In the DSC curve of $[\text{XanH}^+]_2[\text{CdCl}_4^{2-}]$ (Fig. 4b) the dehalogenation occurs in two steps (endothermic effects at 295° and 358°, respectively). The enthalpies associated with these endothermic effects were 54.0 and 87.2 kJ · mol⁻¹, respectively.

Finally, the TG curves of $[\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$ in pure air and N₂ (Fig. 3c) are also very similar, showing two processes: the process in the temperature range 200–300° (experimental weight loss 51.2%) has been assigned to elimination of two chlorine atoms as HCl and simultaneously sublimation of HgCl₂ (theoretical weight loss 52.82%). The temperature range of the sublimation of HgCl₂ (Fig. 5a) is 180–290°, which is in good agreement with the temperature range observed for the sublimation of HgCl₂ from $[\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$.

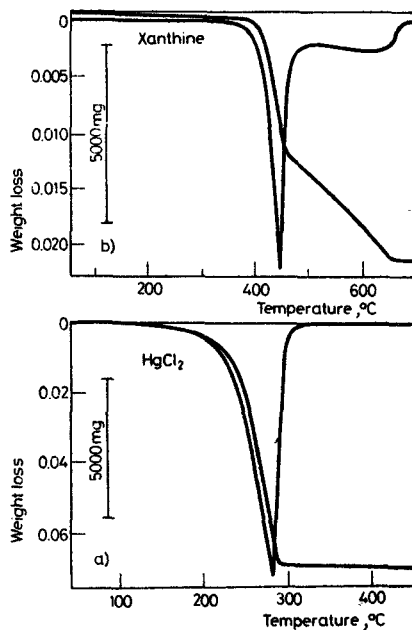
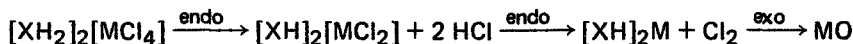


Fig. 5 Thermogravimetric curves of HgCl₂ (a) and xanthine (b)

The second process occurs in the temperature range 400–650° (48.8% weight loss), which corresponds to the pyrolysis of xanthine (theoretical weight loss 47.18%). The temperature range for the pyrolysis of xanthine (Fig. 5b) is in good agreement with the temperature range obtained for the pyrolysis of xanthine in [XanH⁺]₂[HgCl₄²⁻]. At 700°, the residue was practically equal to that obtained from pure xanthine. The expected endothermic behaviour for dehalogenation and HgCl₂ sublimation from [XanH⁺]₂[HgCl₄²⁻] was observed in almost the same temperature range on DSC (endothermic effect at 225°). The enthalpy associated with this endothermic effect was 202.8 kJ · mol⁻¹.

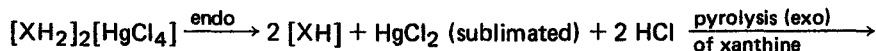
From the TG and DSC data we suggest the following thermal decomposition mechanisms for these compounds:

(i) Zn and Cd compounds:



where M = Zn or Cd.

(ii) Hg compound:



where [XanH⁺] = [XH₂].

The non-equivalence of the four chlorine atoms would suggest [15, 16] a light distortion in the tetrahedral structure of [MCl₄²⁻], due to hydrogen-bonding inter-

actions with the xanthinium cation. On the basis of the decomposition temperatures, the thermal stability sequence is given as $[\text{XanH}^+]_2[\text{ZnCl}_4^{2-}] > [\text{XanH}^+]_2[\text{CdCl}_4^{2-}] > [\text{XanH}^+]_2[\text{HgCl}_4^{2-}]$. This sequence is analogous to that obtained from the ionic radii, since, for equivalent environments, as the ionic radii increase, the strength of the bond decreases. In this case the sequence of the ionic radii is $\text{Zn(II)} < \text{Cd(II)} < \text{Hg(II)}$, and therefore the order of stability will be the contrary.

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Zusammenfassung – $(\text{XanH}^+)_2(\text{MCl}_4^{2-})$ -Salze (worin XanH^+ die protonisierte Form von Xanthin bedeutet und $\text{M} = \text{Zn(II)}$, Cd(II) oder Hg(II) ist) wurden synthetisiert und mit IR, $^1\text{H-NMR}$, TG und DSC untersucht. In diesem Fall liegt keine Koordination des Metalls mit dem Liganden vor, und es bildet sich eine salzartige Struktur aus. Das kationische Proton ist an N(7) lokalisiert. Die thermische Zersetzung dieser Salze erfolgt in zwei Schritten: (i) Dehalogenisierung und (ii) Zersetzung. Dehalogenierungsenthalpien wurden aus DSC-Kurven berechnet.

Резюме – Синтезированы и изучены с помощью ИК- и ПМР-спектроскопии, а также методами ТГ и ДСК соли $[\text{XanH}^+]_2[\text{MCl}_4^{2-}]$, где XanH^+ – протонированная форма ксантина, а M – двухвалентные цинк, кадмий и ртуть. В этих солях металл не образует координационной связи с лигандом, а образует солеобразную структуру. Протонирование ксантина происходит по азоту в седьмом положении. Термическое разложение солей происходит в две стадии: дегалогенирование и разложение. Из ДСК-кривых были вычислены энтальпии реакции дегалогенирования.