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THERMAL STUDIES ON PURINE COMPLEXES. VI. THERMAL BEHAVIOUR OF SOME Ag(I) AND Hg(I) COMPLEXES OF XANTHINE DERIVATIVES

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ABSTRACT

The complexes AgL (L = theobromine, 1,3,8-trimethylxanthine and 3,8-dimethylxanthine), $Hg_2L \cdot NO_3$ (L = 3,8-dimethylxanthine and 1,3,8-trimethylxanthine) and $Hg_2C_2(NO_3)_2$ (C = caffeine), were prepared in aqueous and HNO_3 medium. These complexes were characterized by IR, ^{1}H-NMR, TG, DTG and DSC techniques.

INTRODUCTION

Several studies on the metal complexes of xanthine, minor constituents of RNA, have appeared in recent years [1–3]. Several authors have shown great interest in the metal complexes of *n*-methylxanthines, such as theophylline, theobromine, caffeine [1–14], and 8-alkyl-*N*-methylxanthines [15,16]. These xanthine derivatives are not nucleic acid constituents but can be employed as models of biologically important analogs, such as guanine [1]. For this reason, and following the thermal studies of metal complexes of xanthine derivatives [2,15,17,18], this communication reports the synthesis, study and thermal behaviour of three new complexes of Ag(I) with 1,3,8-trimethylxanthine (TMH), 3,8-dimethylxanthine (DMH) and theobromine (TBH), and three new complexes of Hg(I) with TMH, DMH and caffeine (C).

EXPERIMENTAL

Materials

Theobromine (TBH) and caffeine (C), were purchased from Carlo Erba. 3,8-Dimethylxanthine (DMH) and 1,3,8-trimethylxanthine (TMH) were synthesized according to previously described methods [15]. All inorganic products used were of analytical reagent grade.

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Methods

Chemical analysis of C, H and N was performed on a Carlo Erba microanalyzer (model 1106). The determination of Ag(I), was carried out using the Volhard method [19].

The IR spectra of the compounds studied were recorded in KBr medium in the region 4000–200 cm^{-1} using a Beckman 4250 spectrophotometer. ^1H-NMR spectra were recorded on a Hitachi–Perkin-Elmer spectrometer (model R-600 FT-NMR), using dimethyl sulfoxide-d_6 as solvent and TMS as internal standard.

The TG studies were carried out on a Mettler TG-50 thermobalance, using samples varying in weight from 5.09 to 11.98 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}. The TG and DSC studies were carried out in a dynamic atmosphere of pure air (100 ml min^{-1})

Preparation of the compounds

Mercurous compounds

The Hg(I) compounds were obtained by mixing solutions of 2.5 M HNO_3, containing 5 mmol of xanthine derivative, and 2.5 M HNO_3, containing 3.1 mmol of mercury(I) nitrate. In all cases, the precipitation was immediate. The compounds were filtered, washed consecutively with water and ethanol, and dried with ether. Their chemical analyses were:

Hg_2DMNO_3 (white). Anal. Calc. (%): C, 13.08; H, 1.09; N, 10.90. Anal. Found (%): C, 13.16; H, 1.09; N, 9.98.

$Hg_2C_2(NO_3)_2$ (colorless needles). Anal. Calc. (%): C, 21.02; H, 2.19; N, 15.32. Anal. Found (%): C, 21.63; H, 2.06; N, 15.14.

$Hg_2(TM)(NO_3)$ (white). Anal. Calc. (%): C, 14.63; H, 1.37; N, 10.67. Anal. Found (%): C, 15.78; H, 1.38; N, 10.49.

Silver compounds

Silver(I) theobromine compound was obtained by mixing solutions of 0.25 M NH_4OH, containing 3 mmol of theobromine, and 0.25 M NH_4OH, containing 3 mmol of $AgNO_3$. The precipitation was immediate. The compound was filtered, washed consecutively with water and ethanol, and dried with diethylether. The chemical analysis was:

$Ag(TB) \cdot 2\,H_2O$ (white). Anal. Calc. (%): C, 26.02; H, 3.40; N, 17.35; Ag, 33.39. Anal. Found (%): C, 25.83; H, 2.92; N, 17.42; Ag, 33.70.

The silver(I) compounds of DMH and TMH, were obtained by mixing aqueous solutions containing 1.3 mmol of xanthine derivative and 4 mmol of $AgNO_3$. In both cases, white precipitates were obtained immediately, which were filtered, washed consecutively with water and ethanol and dried with diethylether. Their chemical analyses were:

AgDM. Anal. Calc. (%): C, 29.28; H, 2.44; N, 19.52; Ag, 37.58. Anal. Found (%): C, 29.08; H, 2.45; N, 20.00; Ag, 37.21.

AgTM. Anal. Calc. (%): C, 31.91; H, 2.99; N, 18.61; Ag, 35.83. Anal. Found (%): C, 32.10; H, 2.98; N, 18.58; Ag, 35.12.

RESULTS AND DISCUSSION

Hg(I) compounds

The IR data of the isolated compounds are tabulated in Table 1, together with those corresponding to the respective xanthinic bases.

The IR spectrum of $Hg_2(TM)(NO_3)$ does not show the band corresponding to ν(N–H), which, in the IR spectrum of TMH, appears at 3180 cm^{-1}. This observation suggests that the coordination of TMH to Hg(I) takes place in the anionic form through one of the imidazole ring nitrogens. In view of the numerous crystal structure determinations reported for the complexes with theophylline (analogous to TMH) where this base acts in anionic form [1] it is reasonable to conclude that the coordination of TMH to the Hg(I) ion occurs through the N_7 atom.

TABLE 1

Infrared data for the isolated compounds (all values are in cm^{-1})

Substance	ν(O–H)	ν(N–H)	ν(C=O)	ν(C=C)	ν(C=N)	$\nu(NO_3^-)$
Theobromine (TBH)	–	3120	1710 1675	1600	1550	–
AgTB·2 H_2O	3340	–	1630 [a]	1580	1535	–
3,8-Dimethyl-xanthine (DMH)	3470	3150 3100 3040	1705 1660	1600	1565	–
AgDM	–	3160 3040	1680 [a]	1585	1530	
$Hg_2(DM)(NO_3)$	–	[b]	1630 [a]	1575	1505	1380
1,3,8-Trimethyl-xanthine (TMH)	–	3180	1700 1630	1590	1550	–
AgTM	–	–	1695 1640	[c]	1535	–
$Hg_2(TM)(NO_3)$		–	1690 1645	[c]	1525	1380 835
Caffeine (C)	–	–	1700 1650	1595	1540	–
$Hg_2C_2(NO_3)_2$	–	–	1705 1660	1595	1540	1380 810

[a] Broad band.

[b] Not observed.

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

The IR spectrum of $Hg_2(DM)(NO_3)$, also presents no bands corresponding to ν(N–H). In this case N_1, N_7 and N_9 would be equally likely to act as the binding site, but the imidazole nitrogens (N_7 and N_9) are stronger ligating atoms than the pyrimidine nitrogen [1]. From this fact, we believe that one of the imidazole ring nitrogens is the binding site. On basis of X-ray studies on complexes of analogous xanthine derivatives, we think that the N_7 atom is the most likely binding site to the Hg(I) ion. However, this is only a tentative assignation, since crystal structure determinations proved that binding site assignments made on the basis of spectral evidence for metal purine complexes were incorrect [20,21].

Likewise, in the spectra of $Hg_2(TM)(NO_3)$ and $Hg_2(DM)(NO_3)$ compounds, the bands corresponding to ν(C=C) and ν(C=N) are displaced to a lower wavenumber with respect to the position of the bands in the free ligands. This fact suggests that the ligands coordinate through one of the imidazole ring nitrogens [22,23].

Another marked difference in the IR spectra of these compounds, is the presence of new bands due to uncoordinated nitrate ion. Therefore, the most likely structure for these compounds consists of NO_3^- anions and $[HgDM]^+$ and $[HgTM]^+$ cations, respectively. This structure is analogous to that presented for the complex of the ligand *o*-phenanthroline (Phen), $Hg_2(Phen)(NO_3)_2$, for which an X-ray study has shown that the solid adduct consists of NO_3^- anions and $[Hg_2(Phen)]^{2+}$ cations. The ligand is chelated to just one mercury atom [24].

The ^{1}H-NMR spectra of these compounds have not been obtained due to their insolubility in the solvents used: Cl_3CD, D_2O and DMSO-d_6.

In caffeine (1,3,7-trimethylxanthine), only the N_9 atom is available as a binding site. The bands of caffeine remain intact in the IR spectrum of the $Hg_2C_2(NO_3)_2$ complex, as was expected for adducts of the neutral xanthine derivative ligands [14,16]. Likewise, the IR spectrum also presents the new bands due to uncoordinated nitrate ion.

In the ^{1}H-NMR spectrum of $Hg_2C_2(NO_3)_2$, there are no shifts of the C_8–H signal, which could probably be explained by assuming the break of metal–N_9 bonding under the experimental conditions (strong heating due to low solubility of the complex in the solvents used).

This compound is analogous to $Hg_2(Phen)_2(NO_3)_2$, obtained in 0.1 M HNO_3 by reaction between $Hg_2(NO_3)_2$ and *o*-phenanthroline [24].

The TG and DSC curves for Hg(I) isolated compounds are presented in Fig. 1.

The TG curves show that the decomposition of Hg(I) compounds takes place, in all cases, in two steps which overlap. The first process consists of an intense effect of weight loss, which occurs in the temperature ranges 210–355, 205–270 and 225–305°C for DMH, C and TMH compounds, respectively. The second process corresponds to a slow weight-loss from 355, 270 and 305°C to the end of the pyrolisis at 620, 550 and 700°C, respectively. At this

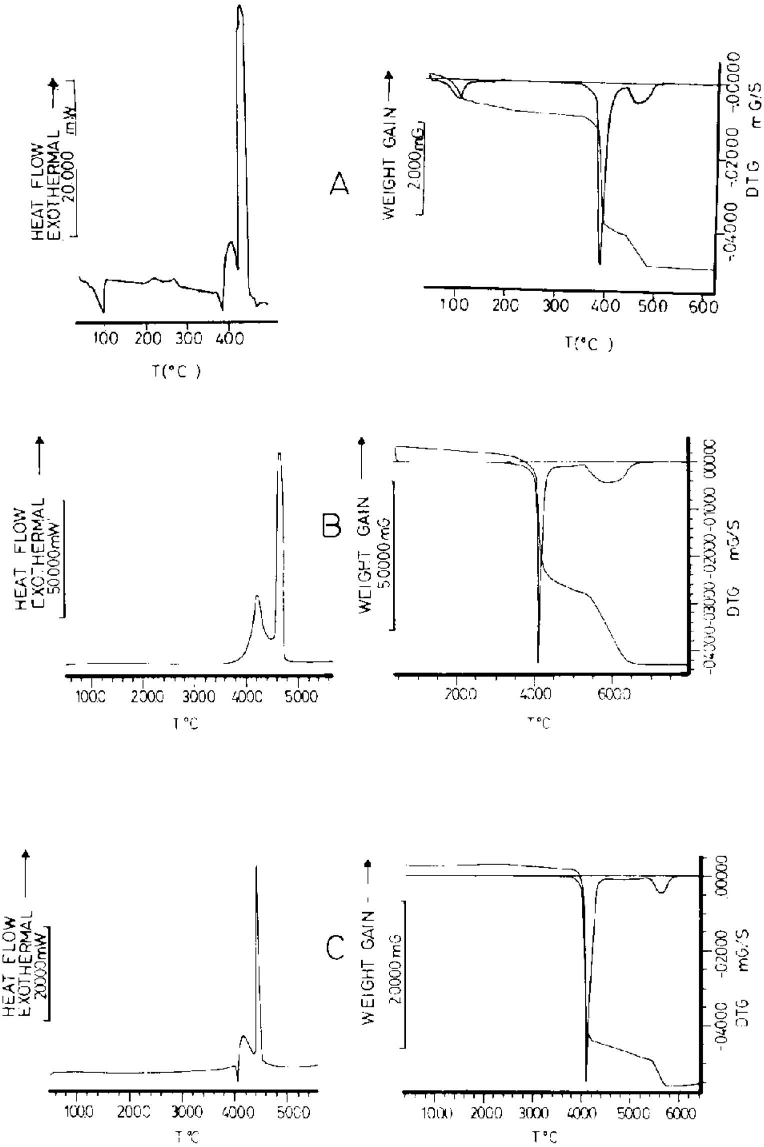

Fig. 1. TG and DSC curves for (A) AgTB·2 H_2O; (B) AgDM; and (C) AgTM.

point, in all cases, a residue was not obtained. In the DSC curves, these processes appear as exotherms at 273 and 282°C (TMH compound) and 305 and 400°C (DMH compound), which indicates that these processes correspond to the pyrolitic decomposition of the compounds.

In the DSC curve of $Hg_2C_2(NO_3)_2$, the first process appears as an endotherm at 234°C, probably due to the sublimation of the caffeine present in the compound. Above 250°C, an exotherm appears due to pyrolisis of the nitrate ion.

Ag(I) compounds

The most significant absorption bands for these compounds are also given in Table 1. These bands were assigned by comparison with the spectra of the respective free bases.

The IR spectrum of AgTB · 2 H_2O did not present the band corresponding to $\nu(N_1-H)$, which suggests that the coordination of TBH to Ag(I) takes place in the anionic form through the N_1 atom, since only this nitrogen is protonated in the free base.

The IR spectrum of DMH presents three bands assignable to $\nu(N-H)$ at 3150, 3100 and 3040 cm^{-1}, whereas the corresponding spectrum of AgDM only shows two bands at 3160 and 3040 cm^{-1}. This fact also indicates an anionic coordination of DMH to the Ag(I) ion, probably through the N_7 atom [in view of that indicated for $Hg_2(DM)(NO_3)$].

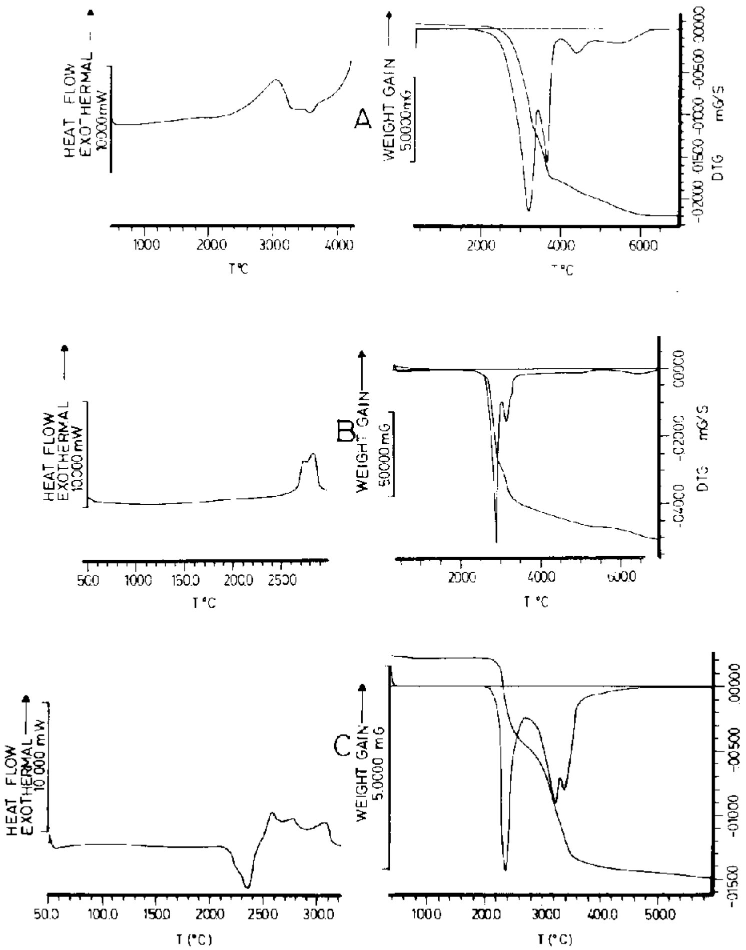

Fig. 2. TG and DSC curves for (A) $Hg(DM)(NO_3)$; (B) $Ag(TM)(NO_3)$; and (C) $Hg_2(C)_2(NO_3)_2$.

TABLE 2

Thermogravimetric and DSC data for the pyrolitic processes

Substance	Metal residue (%)		DSC peak temperature (°C) for the combustion of the compounds	
	Found	Calcd.		
AgTB·2 H_2O	32.7	33.39	411	430
AgDM	38.6	37.58	422	473
AgTM	34.5	35.83	420	450

Finally, the IR spectrum of AgTM did not show the band corresponding to $\nu(N_7–H)$ [23] which indicates an anionic coordination of this base to the Ag(I) ion through the N_7 atom as in the complex Hg(TM)(NO_3).

TG and DSC curves of the Ag(I) compounds are given in Fig. 2. The TG curve of AgTB · 2 H_2O shows that this compound becomes completely dehydrated in the temperature range 60–120°C. The calculated weight-loss for the dehydration process (11.15%) is in good agreement with the observed value (10.3%). The DSC curve shows the endotherm corresponding to this process at 96.6°C. The dehydration enthalpy was 39.9 kJ mol^{-1} H_2O.

The TG curves of AgTB, AgDM and AgTM are very similar, showing that the decomposition of these compounds takes place in two steps: (1) partial elimination of the ligand (very fast effect of weight loss); and (2) elimination of the remaining ligand and reduction of Ag_2O to Ag, due to the reaction between the carbon resulting from the oxidation of the organic matter and the Ag_2O.

The DSC curves of these compounds show two exothermic effects, which correspond to the combustion of the ligands. In all cases, the final residue was metallic silver, as revealed by X-ray patterns. The TG and DSC data for these processes are given in Table 2.

The DSC curves of AgTB · 2 H_2O and AgTM also present an endothermic effect centred at 387 and 405°C, respectively, which can be attributed to the fusion of the compounds. The fusion of AgTM calculated from the area of the endothermic effect was 32 kJ mol^{-1}.

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