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THERMAL AND SPECTRAL STUDIES ON HEXACHLOROPLATINATES(IV) OF SOME ALKYL-XANTHINES

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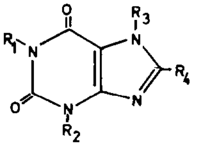
ABSTRACT

Hexachloroplatinates of xanthine (XH), theobromine (TBH), theophylline (TFH), 1,3,8-trimethyl-xanthine (TMH), caffeine (CF) and 8-ethyl-theophylline (ETH) have been synthesized and studied by IR, H-NMR, TG and DSC techniques. In all cases, the purine derivatives acts in monoprotonated for and is not bound to metal ion, forming a salt-like structure.

INTRODUCTION

Recently, the study of interactions of hexachloroplatinate (IV) anion with some important biologically molecules has aroused a great interest due to antitumor properties that some of these compounds have shown (1,2). Thus, the 8-dialkylamino-alkoxy-caffeine hexachloroplatinates (IV) have significant antitumor activity against various tumor systems in animals, and minimal toxicity (3,4). By these reasons, we have synthesized and studied some alkyl-xanthine hexachloroplatinates (IV) (Scheme I).



$R_1=R_2=R_3=R_4=H$ (XH) $R_3=H$; $R_1=R_2=R_4=CH_3$ (TMH)

$R_1=R_4=H$, $R_2=R_3=CH_3$ (TBH) $R_4=H$; $R_1=R_2=R_3=CH_3$ (CF)

$R_3=R_4=H$; $R_1=R_2=CH_3$ (TFH) $R_3=H$; $R_1=R_2=CH_3$; $R_4=CH_2-CH_3$ (ETH)

EXPERIMENTAL

Preparation of the compounds Hexachloroplatinates (IV) were

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obtained by mixing solutions of 0.5M HCl containing alkylxanthine derivative and H_2PtCl_6 in molar ratio ½. After a few days, crystals appeared which were filtered off, washed consecutively with ethanol and diethylether and dried in air. Their chemical analyses were in according with the following formulas: $PtCl_6(XH_2)_2.2Cl(XH_2).8H_2O$, $PtCl_6(TBH_2)_2.2H_2O$, $PtCl_6(TFH_2)_2.2H_2O$, $PtCl_6(TMH_2)_2.2H_2O$, $PtCl_6(CFH)_2$ and $PtCl_6(ETH_2)_2.2H_2O$.

The new compounds contain exclusively monoprotonated xanthine derivatives, since their IR spectra show few bands in the 3200-2700 cm^{-1} range due to $\nu(N^+-H)$ stretching vibration. Likewise, the $\nu(C=C)$ and $\nu(C=N)$ bands are shifted to lower frequencies with respect to the position of these bands in IR spectra of the free ligands, which may be due to the increase of the electronic density on the imidazole ring as consequence of the protonation in a nitrogen atom of this ring, probably N-9. This fact is also corroborated by H-NMR data, since in the isolated salts, the ^{1}H-NMR spectra show a downfield shift of the signals corresponding to the protons of the sustituents bonding to C-8, which is compatible with the positive character of the imidazole ring. The protonation of xanthine derivatives is consistent with the experimental conditions of the synthesis of these compounds (very low pH).

In the 600-200 cm^{-1} region, the isolated hexachloroplatinates (IV) present, in their IR spectra, a new band in 310-315 cm^{-1} range, which can be assigned to $\nu(Pt-Cl)$ stretching vibration in the octahedral $PtCl_6^{2-}$ anion (5). The presence of two bands for this vibrational mode suggests that chlorine atoms are not equivalent probably due to their interaction by hydrogen bonds with the hydrogen atoms of xanthine derivatives and water molecules.

TG and DSC curves have been carried out using a Mettler TG-50 thermobalance and a Mettler DSC-20 differential scanning calorimeter, respectively. The thermal behaviour of these compounds consists of three major processes: dehydration, dehalogenation and pyrolitic decomposition.

The observed and calculated weight losses, as well as, DSC peak temperatures and enthalpy values for these

TABLE 1.- TG and DSC data for the isolated compounds

Compound	Dehydration				Dehalogenation					Pyrolisis		
	Wt. loss(%)		DSC	ΔH	Wt. loss(%)		Process	DSC	ΔH	Effects	% Residue	
	found	calcd	T(ºC)	$(Kj.mol^{-1}.H_2O)$	found	calcd		T(ºC)	$(Kj.mol^{-1})$	T(ºC)	found	calcd
$PtCl_6(XH_2)_2.2Cl(XH_2).8H_2O$	10.6	11.66	182	45.6	6.7	5.91	-2HCl	261	66.2	410exo	14.9	15.80 Ptº
					19.4	17.24	-6Cl	351	528.0	500exo		
$PtCl_6(TBH_2)_2.2H_2O$	4.8	4.47	121	43.6	26.0	25.67	-2HCl + -4Cl	342	243.0	450exo 500exo	23.2	24.20 Ptº
$PtCl_6(TFH_2)_2.2H_2O$	4.1	4.47	201	62.2	9.2	9.06	-2HCl	287	45.3	440exo	23.6	24.20 Ptº
					16.4	17.62	-4Cl	334	114.5	500exo		
$PtCl_6(TMH_2)_2.2H_2O$	4.3	4.32	122	25.5[a]	17.3	17.26	-2HCl	252	145.3	420exo	22.4	23.39 Ptº
			164		7.7	8.51	-2Cl -2Cl	300	b			
$PtCl_6(CFH\ )_2$					27.0	26.93	-2HCl + -4Cl	293	305.6	430exo 500exo	23.4	24.44 Ptº
$PtCl_6(ETH_2)_2.2H_2O$	4.2	4.18	158	56.2	25.2	24.93	-2HCl + -4Cl	283	249.5	425exo	22.2	22.63 Ptº

(a) Average value; (b) No calculated due to overlapping with the exothermic effects.

processes are given in table 1.

Dehalogenation processes have been confirmed by recording of IR spectra of heated samples above just to the temperatures corresponding to the end of weight loss effects assigned to this process. In all cases, these IR spectra show the dissappearance of the bands corresponding to $\nu(N^+-H)$ and $\nu(Pt-Cl)$, which indicates that dehalogenation processes take place with the loss of Cl_2 and HCl. Likewise, the bands corresponding to $\nu(C=C)$ and $\nu(C=N)$ stretching vibration are shifted to higher frequencies with respect to their position in the IR of the initial products, as consequence of deprotonation on the imidazolic ring.

On the other hand, the endothermic effects corresponding to dehalogenation of TBH, CF and ETH compounds are asymetric which confirms, according with the IR data, that the chlorine atoms are not exactly equivalent, although in the corresponding TG plots, the loss of these atoms takes place in one step.

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