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THERMAL, SPECTRAL AND BIOLOGICAL STUDIES ON METAL COMPLEXES OF ISOOROTIC AND 2-THIOISOOROTIC ACIDS

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ABSTRACT

From reaction, in aqueous medium, of isoorotic (H_2CU) and 2-thioisoorotic (H_2CTU) acids with several first row transition metal ions, complexes of general formula $M(HL)_2.2H_2O$ have been obtained. These were studied by thermal (TG, DTG and DSC) and spectral methods (IR). Likewise, the antibacterial activity of these compounds is reported.

INTRODUCTION

The orotic acid has been largely used as analytical reagent for the determination of several ions [1-4]. The complexation capacity of orotic and 2-thioorotic acids has also been reported in several papers [5-7], which include the determination, by X-ray diffraction methods, of the molecular structure of some of these complexes [8-11]. However, there are no reports about their thermal behaviour.

Because of this reason, and as an extension of our previous studies on the thermal behaviour of pyrimidine complexes containing uracil derivatives as ligands [12-13], we report in this paper the results obtained from the structural study of some metal complexes of isoorotic (5-carboxy-uracil, H_2CU) and 2-thioisoorotic (5-carboxy-2-thio-uracil, H_2CTU) acids with Co(II), Ni(II), Cu(II) and Zn(II) ions.

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EXPERIMENTAL

Isoorotic and 2-thioisoorotic acids were purchased from Sigma and used without further purification. In all cases, metallic salts were analytical reagent grade.

Synthesis of the complexes

The preparative method was as follows: An aqueous solution (10 ml) of metal chloride (1 mmol) was added, slowly with stirring to a hot aqueous solution (100 ml) of the corresponding ligand (1 mmol). When the resulting solutions are cooled to room temperature, products precipitate. These were filtered off, washed with water and ethanol and dried with diethylether. The analytical results are in good concordance with the general formula $M(HL)_2.2H_2O$ (L=CU M=Co,Cu,Zn; L=CTU M=Co,Ni,Zn).

Apparatus

Microanalyses were performed in the Instituto de Química Bioorgánica (C.S.I.C., Barcelona) and the Servicios Técnicos de la Universidad de Granada. Infrared spectra were recorded in a Perkin Elmer 983-G spectrophotometer, using KBr pellets (4000-600 cm^{-1}) and polyethylene pellets (600-180 cm^{-1}). TG and DSC plots were obtained in a Mettler TA-3000 system with a TG-50 thermobalance and a DSC-20 differential scanning calorimeter, using a heating rate of 10 $deg.min^{-1}$. The weight of samples was comprised between 2 mg and 17 mg and the investigated temperature ranges were 30-850 (TG) and 30-450 deg (DSC).

Biological studies

Biological studies carried out on isolated compounds have been forwarded to the assesment of their antibacterial activity. The determination of CMIs was performed according to the method prescribed by the National Comittee for Clinical Laboratory Standards (1985).

RESULTS AND DISCUSSION

IR spectra of isolated complexes are very similar, which is indicative that all of them present the same structure. The most important IR bands (stretching, cm^{-1}) are: ≈3500 sharp (O-H,H_2O), 3300-2400 few bands (N-H,C-H), ≈1700 broad (C=O), ≈1600 (C=C+C-O asym. carboxylate) and ≈1380 (C-O sym.,carboxylate). Likewise, the H_2CTU complexes show a band in the 1161-1171 cm^{-1} wavenumber range, which would be assigned to the stretching vibration of C=S bond. These data are in accordance with the coordination of ligands through one carboxylate oxygen. This also suggests that formation of a chelate six-membered ring with O4 atom occurs, in spite of the possible shift to lower wavenumber of the band corresponding to stretching vibration of C4=O cannot be observed, due to this vibration mode appears overlapping with those corresponding to other two carbonyl groups that are present in the free ligand. This coordination behaviour also takes place in complexes with the same formula, in which ligands are 5-formyl-uracil derivatives [12].

Thermal studies on isolated complexes have been carried out from their TG, DTG and DSC plots. As an example, those corresponding to free ligands and their cobalt complexes are given in Figure 1. The most interesting thermoanalytical data are collected in Table 1.

From obtained data, it can be seen that,on heating these complexes, two major processes occur : dehydration and pyrolytic decomposition.

Dehydration of H_2CU complexes is complete at about 250 deg, whereas this process, for H_2CTU complexes, cannot be discerned since it is overlapping with the pyrolytic process. These facts suggest that the water molecules are strongly linked to the metal ion. Thus, the structure of the complexes seems be a distorted octahedron with the equatorial positions occupied by two

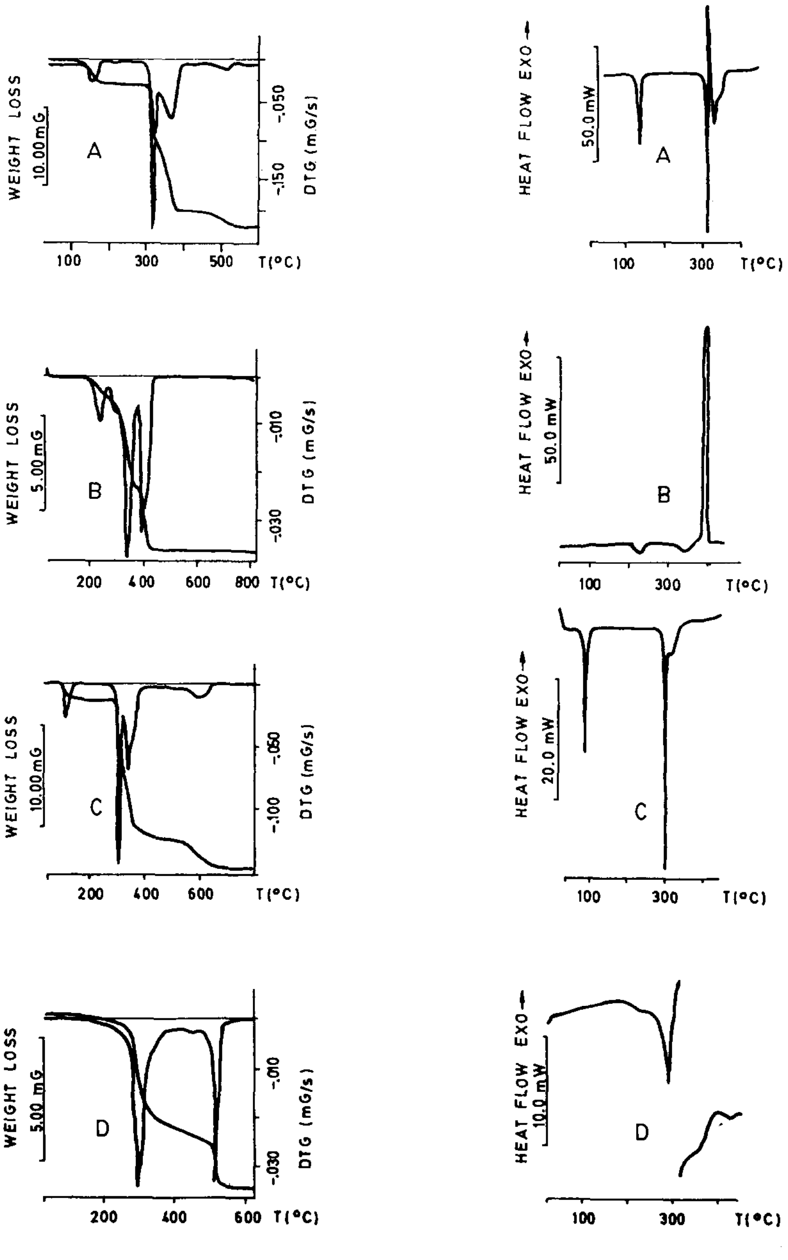

Figure 1: TG and DSC plots for (a) $H_2CU.H_2O$, (b) $Co(HCU)_2.2H_2O$, (c) $H_2CTU.H_2O$ and (d) $Co(HCTU)_2.2H_2O$.

Table 1: Thermoanalytical data*

Compound	Dehydration				Pyrolysis			
	% H_2O	T(TG)	T([illegible])	ΔH	T_f	%wl	Residue	T(DSC)
$H_2CU.H_2O$	9.9 (10.3)	125-210	28	43	550	100	--	304end 310exo 327end
$Co(HCU)_2.2H_2O$	9.5 (8.9)	175-265	228	84	425	79.9 (80.2)	Co_3O_4	337end 400exo
$Cu(HCU)_2.2H_2O$	9.3 (8.8)	100-200	156	76	375	81.0 (80.6)	CuO	365exo
$Zn(HCU)_2.2H_2O$	9.8 (8.8)	130-240	230	66	600	80.3 (80.2)	ZnO	300end
$H_2CTU.H_2O$	8.9 (9.5)	70-160	86	51	650	100	--	297end
$Co(HCTU)_2.2H_2O$	a	a	a	a	530	79.7 (81.6)	Co_3O_4	287end 390exo
$Ni(HCTU)_2.2H_2O$	a	a	a	a	510	81.4 (82.9)	NiO	276end 440exo
$Zn(HCTU)_2.2H_2O$	a	a	a	a	800	82.0 (81.7)	ZnO	257end 295end 315end

(*) Temperatures in deg and enthalpies in $kJ.mol^{-1}$.
(*) In parentheses, calculated values.
(a) Overlapping with other effects.

O4,O5-bidentate ligands. The octahedron is completed by two water molecules which occupy apical positions. The enthalpies corresponding to the loss of these water molecules, in the cases in which they can be calculated, are listed in Table 1.

After dehydration, anhydrous species undergo decomposition. These processes appear in DSC curves as several effects. The first of these, with the exception of $Cu(HCU)_2.2H_2O$, is an endothermic effect, which could be assigned to a decarboxylation process, since the IR spectrum of heated compounds at the temperature in which the weight loss associated is finished, shows no C=O stretching vibrations bands. However, other processes may be included in this first endothermic effect, since the weight loss is, in all cases, greater than that calculated for only CO_2 loss.

The thermal decomposition of these complexes is completed in the 425-800 deg temperature range. In all cases, the final residue of pyrolysis was the corresponding metallic oxide, which has been verified by IR spectroscopy.

Finally, the results of antibacterial activity of these compounds reveal that $Cu(HCU)_2.2H_2O$ and $Ni(HCTU)_2.2H_2O$ share some activity. The first compound has activity on the Gram positive bacteria, specially on the genus **Micrococcus**, whereas the second shows antibacterial activity on the Gram negative bacteria and in the genus **Candida** (yeast).

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