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THERMAL STUDIES ON METAL COMPLEXES OF 2-THIOPYRIMIDINES

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ABSTRACT

Some metal complexes of 4-amino-1,6-dihydro-2-methylthio -5-nitroso-6-oxo-pyrimidine (MTH_2) and 4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidine ($TANH_2$) have been prepared in neutral and basic media. The structures of these complexes have been established from IR, ^{1}H-NMR, TG and DSC data.In the cases of Cd(II) complexes the comparation between TG diagrams realized in dynamic atmosphere of air and nitrogen alloved to know the pyrimidine binding site.

INTRODUCTION

Experimental work of the past thirty years has led to the awareness that metal ions are essential to a large variety of biological processes in general and in the biochemistry of nucleic acids, specifically (1). Metal ions have been found to play crucial role at some stages of gene expression and in the production of metalloenzimes or other metal-proteine complexes.

By theses reasons, binding studies of metal ions interactions with components of nucleic acids (bases, nucleosides and nucleotides) are currenty of great interest (1-5), specially in view of the antitumoral actions that some platinum (II) complexes have show (6-7).

As a contribution to the study of the interactions between metal ions and pyrimidine derivatives, we report in this communication the some spectral properties and thermal behaviour of complexes formed by 4-amino-1,6-dihydro 2-methylthio-5-nitroso-6-oxo-pyrimidine (MTH_2) and 4-amino-5-nitroso-6-oxo-1,2,3,6-tetrahydro-2-thiopyrimidine ($TANH_2$)

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with Zn(II), Cd(II) and Hg(II) ions.

MEASURING METHODS

Microanalyses of C, H and N were carried out in a Carlo Erba microanalyser model 1106; metal ions were determined gravimetrically. The IR spectra of solid were obtained on a Beckman 4250 spectrophotometer using KBr and polyethylene as dispersant agents. ^{1}H-NMR spectra were taken with a Hitachi Perkin-Elmer model R-600-FT-NMR spectrometer. TG studies were made using pure air and nitrogen (flow rate of 100 $ml.min^{-1}$) on a Mettler thermobalance model TG-50 at a heating rate of $10ºC.min^{-1}$ in the temperature range 35-750ºC. DSC curves were obtained on a DSC-20 scanning calorimeter at a heating rate of $5ºC.min^{-1}$ in the temperature range 35-550ºC.

RESULTS AND DISCUSSION

Complexes of simplified formulas. $Zn(MTH)_2.3H_2O$, $Cd(MTH_2)Cl_2$; $*Cd(MT).H_2O$, $Hg(MTH_2)Cl_2$, $Zn(TANH)_2.2H_2O$; $Cd(TANH)_2$; $*Cd_2(TAN)_2(NH_3)_4$ and $Hg(TANH)_2$ are obtained from the reactions between MTH_2 and $TANH_2$ with Zn(II), Cd(II) and Hg(II) ions in aqueous medium (complexes noted by * were obtained in basic medium).

From TG and DSC diagrams of the isolated complexes data of table 1 have been obtained. According these data the following facts can be established:

a) For Zn(II) complexes, the thermal decomposition starts with a dehydration process, which occurs in the 100-200ºC temperature range. Anhydrous compounds decompose between 200 and 750ºC. At this temperature, the residual products is ZnO in air atmosphere, likewise ZnS is obtained when pyrolitic process take place in nitrogen atmosphere.

b) Complexes $Cd(MTH_2)Cl_2$, $Cd(MT).H_2O$ and $Cd_2(TAN)_2(NH_3)_4$ show, previous to their pyrolitic decomposition, a dehalogenation, dehydration or deammination process respectivelly. In the four Cd(II) complexes the final products obtained at 750ºC is CdO (in air) and CdS (in nitrogen).

TABLE 1.- Thermoanalytical data for the isolated metal complexes

Process	T(ºC)	$\Delta H(Kj.mol^{-1})$	% acumulate loss weigth exp.	teor.
$Zn(MTH)_2.3H_2O \longrightarrow Zn(MTH)_2$	170(endo)	45.0	11.0	11.03
$Zn(MTH)_2 \xrightarrow{air} ZnO$	250,430,540(exo)		83.5	83.38
$Zn(MTH)_2 \xrightarrow{N_2} ZnS$			80.6	80.10
$Cd(MTH_2)Cl_2 \longrightarrow Cd(MTH_2)$	170(endo)			
$Cd(MTH_2) \xrightarrow{air} CdO$	260, 500(exo)		71.8	65.15
$Cd(MTH_2) \xrightarrow{N_2} CdS$			75.8	60.80
$Cd(MT).H_2O \longrightarrow Cd(MT)$	109(endo)	22.7	5.1	5.71
$Cd(MT) \xrightarrow{air} CdO$	270,450(exo)		59.8	59.30
$Cd(MT) \xrightarrow{N_2} CdS$			73.4	54.34
$Zn(TANH)_2.(H_2O)_2 \longrightarrow Zn(TANH)_2$	181(endo)	38.5	8.2	8.12
$Zn(TANH)_2 \xrightarrow{air} ZnO$	275,460,545(exo)		81.1	81.65
$Zn(TANH)_2 \xrightarrow{N_2} ZnO$			81.3	81.65
$Cd(TANH)_2 \xrightarrow{air} CdO$	297,520(exo)		72.4	71.87
$Cd(TANH)_2 \xrightarrow{N_2} CdS$			77.9	68.36
$Cd_2(TAN)_2(NH_3)_4 \longrightarrow Cd_2(TAN)_2$	223(endo)	43.1	10.2	10.74
$Cd_2(TAN)_2 \xrightarrow{air} CdO$	290,470(exo)		59.6	59.40
$Cd_2(TAN)_2 \xrightarrow{N_2} CdS$			70.2	54.36

Differences between exp. and teor. values of the residues are due to a partial sublimation of CdS

c) $Hg(MTH_2)Cl_2$ and $Hg(TANH)_2$ complexes are stables up to 160 and 225ºC, respectivelly. At these temperatures the pyrolitic decomposition starts. According to the DSC curves, the decomposition of the complexes originates two exothermic effects centered at 190, 450ºC and 310 and 440ºC, respectivelly. In both cases, for temperatures above 700ºC none residue is obtained.

From above considerations, can be established that in the $Zn(MTH)_2.3H_2O$, $Cd(MTH_2)Cl_2$, $Cd(MT).H_2O$, $Cd(TANH)_2$ and $Cd_2(TAN)_2(NH_3)_4$ complexes, coordination of the pyrimidine base to metal ions ake place through the sulphur atom substituent in 2 position. This affirmation is in agreement with the ^{1}H-NMR and IR spectral data. For $Zn(TANH)_2.2H_2O$ TG and DSC data suggest that coordination of pyrimidine to metal ion occurs through a oxygen atom.

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