

PREPARATION AND THERMAL DECOMPOSITION OF COPPER(II), ZINC(II) AND CADMIUM(II) CHELATES WITH 8-HYDROXYQUINOLINE

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Through TG-DTA, DSC, elemental analysis, IR spectroscopy and X-ray, was verified that copper(II), zinc(II) and cadmium(II) 8-hydroxyquinolate chelates prepared in acid medium present uncoordinated ligand into the crystal lattice. When the compounds are heated in an inert atmosphere it can be verified the consecutive partial sublimation, fusion, partial volatilization and partial thermal decomposition of the anhydrous complexes. When in an oxidating atmosphere the above process is only verified to Cu(II) chelates. Anhydrous copper(II) complexes present a monoclinic structure in the β form and the volatilized compound in a α form. Zinc(II) and cadmium(II) hydrated complexes are isomorphous and they present different cell dimensions from those reported previously.

Keywords: 8-hydroxyquinolines; TG; DTA.

INTRODUCTION

Borrel and Paris¹ have studied the synthesis and stoichiometry of some metal oxinate complexes and their associated thermal stability by using thermogravimetric analysis. The effect of alpha methyl substitution on the oxine ligand in Cu(II) and Zn(II) complexes² over the solubility products of Cu(II) and Zn(II) oxinates and methylloxinates has been investigated by potentiometric neutralization of acid solutions containing oxine or methylloxine and metallic cations³. The thermal stability and volatilization on vacuum of metallic chelates which derived from 8-hydroxyquinoline were investigated by Charles and Langer⁴. The total volatilization of complexes such as copper (200-260°C), zinc (250-320°C) and cadmium (350-450°C) by using vacuum Thermobalance showed products with color and composition similar to the anhydrous complexes. It was observed that the temperature range of volatilization depends on the metallic ion electronegativity for the divalent metal 8-hydroxyquinolates. The thermal stability of these complexes was also studied by Wendlandt and Horton⁵ using differential thermal analysis (DTA). It was verified the presence of endothermic and exothermic peaks corresponding to fusion and thermal decomposition, respectively. These 8-hydroxyquinolates hydrates were also studied by Gore and Wendlandt⁶ by using thermogravimetry, differential scanning calorimetry and reflectance spectra. The thermogravimetric data applied on different types of solid state kinetics equation and calorimetric data showed that water is bonded in different ways in these complexes.

Studies of the crystalline structures in this kind of complexes⁷⁻⁹ described monoclinic in the a and b forms for the copper(II) complexes regardless of the hydration degree. Zinc(II) and cadmium(II) complexes^{10,11} were found to be monoclinic structures, but it was verified that these structures depend on the hydration. The Zn(II) and Cd(II) anhydrous complexes could show the same b form found for the copper(II) complexes. Several papers have indicated characteristic IR bands for these compounds¹²⁻¹⁸.

Studies about copper(II), zinc(II) and cadmium(II) complexes with 8-hydroxyquinoline give little information about

the several possible mechanisms of thermal decomposition when they are heated in an inert or oxidating atmosphere or when they were obtained by different synthesis methods. This work presents the study of solid complexes of Cu(II), Zn(II) and Cd(II) with 8-hydroxyquinoline obtained by precipitation at pH values 5 and 9. It is studied the stoichiometry, thermal dehydration, thermal stability and thermal decomposition in a synthetic air and nitrogen atmosphere by using TG-DTG, DTA and DSC. X-ray diffraction patterns and Infrared spectroscopy were used for the characterization of the complexes and residues of the thermal decomposition.

EXPERIMENTAL

The complexes were prepared by reaction of the aqueous solution of the metallic ion with an excess of an acetic solution of 8-hydroxyquinoline. It was obtained a solid when the pH was increased to values of 5 and 9, by using a diluted ammonia aqueous solution. The solids were filtered, washed with water (pH 5) and ammonia aqueous solution (pH 9) to remove both the excess of ligand and of the anion chloride (copper and cadmium) or sulphate (zinc), dried at 60°C and stored in a desiccator over CaCl₂.

The compounds were decomposed by wet digestion at 340°C with sulphuric acid and hydrogen peroxide. The metallic ion contents in this solution were determined by complexometric titration with standard 0,01 mol L⁻¹ EDTA solution using xilenol orange as an indicator¹⁹. The metal contents as well as the hydration water were also obtained from the TG curves. The 8-hydroxyquinoline content was obtained by determining the contents of C, H, N by microanalytical procedures.

TG-DTA curves were obtained by using a TA Instruments SDT 2960 Thermoanalyser with both synthetic air and N₂ flux of 100 mL min⁻¹, heating rate at 10°C min⁻¹, sample mass \approx 7 mg and alumina pan.

DSC curves were obtained by using TA Instruments DSC 2910 on the same conditions set before but using open aluminum pan. Standard reference material (Indium metal) has been used to calibrate the temperature and energy scale of the instrument.

The X-ray powder diffraction patterns were performed on a HGZ 4/B horizontal diffractometer in a Bragg-Bretano arrangement and Co K α radiation ($\lambda = 1.7889$ Å), with proportional counter and pulse-height discriminator.

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Infrared absorption spectra were obtained in the region 4000 - 400 cm^{-1} by using a Nicolet Infrared Spectrophotometer, model 400 with 4 cm^{-1} of resolution. The solid complexes were run as pressed disks using KBr as the diluent.

RESULTS AND DISCUSSION

Table 1 presents both analytical and thermoanalytical data for the synthesized complexes and Table 2 shows the onset and peak temperatures of fusion for the compounds and the respective enthalpies of fusion in a N_2 atmosphere. The corresponding TG - DTA and DSC curves are shown in Figures 1-3 and Figures 4-5, respectively. IR spectra and X-ray powder diffraction patterns are shown in Figures 6 and 7-8, respectively.

1. TG-DTA AND DSC CURVES

1.1. Copper(II) complexes

TG curves of $\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{1.2} \cdot \text{H}_2\text{O}$ in a N_2 atmosphere, Figure 1b, show mass losses in two steps. The first step occurs up to 188°C and it is attributed to dehydration process followed by elimination of the uncoordinated ligand, and it is observed through two endothermic peaks, 128.8 and 172.4°C, in DTA curves. The second step, between 276 and 483°C, is initially attributed to the loss of the complex by partial volatilization followed by partial decomposition of the anhydrous complex which was not completed even up to 900°C. In this step it is observed two endothermic peaks in DTA curve, the first at 329°C indicates the fusion and the second at 361°C, the partial volatilization of the complex.

DSC curve, Figure 4a, shows two endothermic peaks due to the dehydration and to the elimination of the uncoordinated ligand, 131.8 and 146.7°C, respectively. A peak at 334.6°C due to fusion of the anhydrous complex, preceded by a peak at 324°C due to partial sublimation of the compound are also observed. Several peaks at 348.8, 352 and 402°C are due to volatilization of the complex and finally one endothermic peak

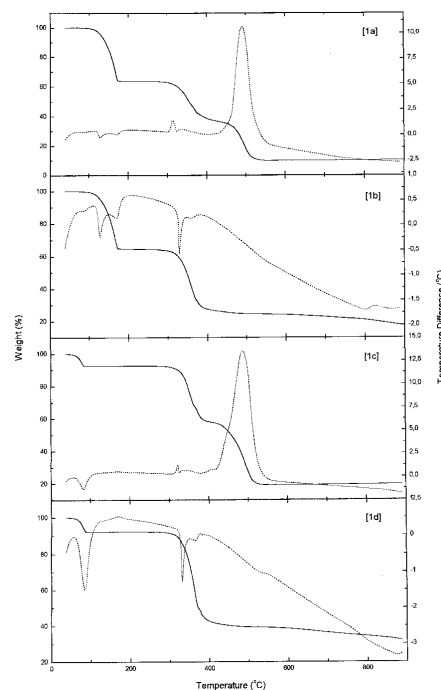


Figure 1.

up to 516°C is due to the thermal decomposition of the remaining compound.

Sublimation and volatilization of the complex can be observed by little mass losses in the TG curve just before and after the fusion peak in the DTA curve.

The TG Curve of $\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{1.2} \cdot \text{H}_2\text{O}$, Figure 1a, in a synthetic air atmosphere shows three mass-loss steps. The first step occurs up to 188°C and corresponds to dehydration

Table 1. Analytical and thermoanalytical (TG) results.

Compounds	Metal %		C %		N %		H %		H ₂ O		
	theor.	exper. ¹	exper. ²	theor.	exper. ³	theor.	exper. ³	theor.	exper. ³	theor.	exper. ⁴
$\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{1.2} \cdot \text{H}_2\text{O}$ pH 5, FW=541.74	11.72	11.55	9.40	63.79	63.60	8.27	10.17	4.18	3.80	3.31	3.27
$\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 1.5\text{H}_2\text{O}$ pH 9, FW=378.69	16.78	16.67	14.84	57.04	54.47	7.39	9.44	4.00	3.98	7.14	7.17
$\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{0.6} \cdot 2.5\text{H}_2\text{O}$ pH 5, FW=483.56	13.52	12.69	13.63	55.84	54.29	7.24	8.72	4.28	4.03	9.32	9.53
$\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ pH 9, FW=389.53	16.78	16.33	17.44	55.45	54.29	7.19	7.11	4.15	4.00	9.25	8.97
$\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{0.7} \cdot 1.5\text{H}_2\text{O}$ pH 5, FW=529.10	21.24	20.67	22.00	55.11	53.40	7.14	7.80	3.80	3.90	5.11	5.22
$\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2.25\text{H}_2\text{O}$ pH 9, FW=441.07	25.48	25.76	26.97	48.97	49.15	6.35	6.38	3.78	3.65	9.19	9.11

¹Complexometric Titration Analysis; ²From oxide residue in TG curves; ³From elemental analysis; ⁴From TG curves

Table 2. Melting temperature and melting enthalpy (ΔH_m) in a N_2 atmosphere.

Compounds	Melting Temperature		ΔH_m (Kcal mol ⁻¹)
	Tonset (°C)	Tpeak (°C)	
$\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{1.2} \cdot \text{H}_2\text{O}$	333.5	334.6	7.17
$\text{Cu}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 1.5\text{H}_2\text{O}$	335.0	336.2	8.84
$\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{0.6} \cdot 2.5\text{H}_2\text{O}$	372.7	375.3	5.54
$\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$	367.0	370.1	6.77
$\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2 \cdot (\text{C}_9\text{H}_7\text{ON})_{0.7} \cdot 1.5\text{H}_2\text{O}$	453.1	467.9	—
$\text{Cd}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2.25\text{H}_2\text{O}$	457.4	472.4	—

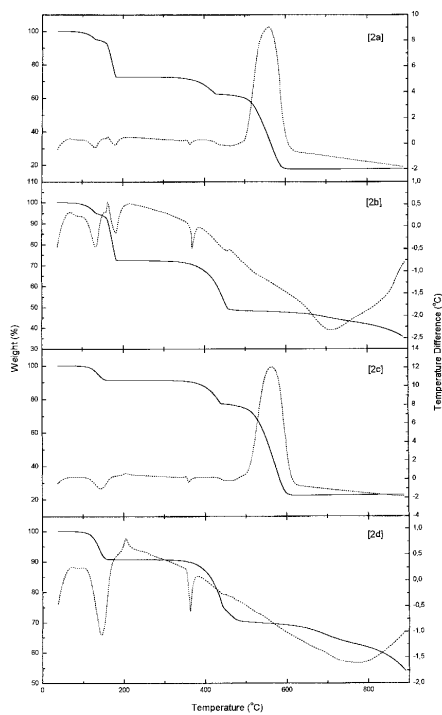


Figure 2.

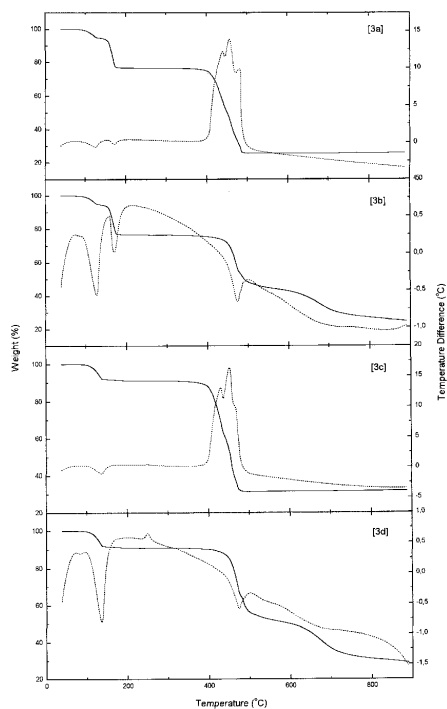


Figure 3.

and volatilization of the uncoordinated ligand. The respective DTA curve shows two endothermic peaks at 128.8 and 172.4°C, consistent with the TG data. The second step in the TG curve, between 276-375°C, was attributed to the partial volatilization (22.4%) of the anhydrous complex, followed by the thermal decomposition of the remaining compound. It was verified the presence of CuO and also of the anhydrous complex which was not decomposed at 375°C. The decomposition is complete at 584°C. This is due to the presence of a protecting layer of CuO around the remaining complex that prevents the ligand oxidation.

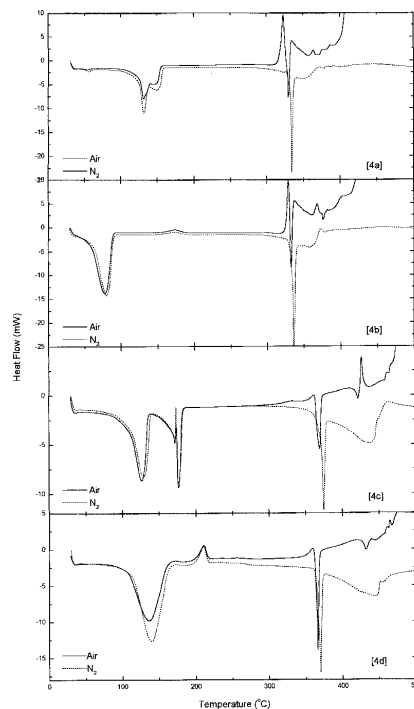


Figure 4.

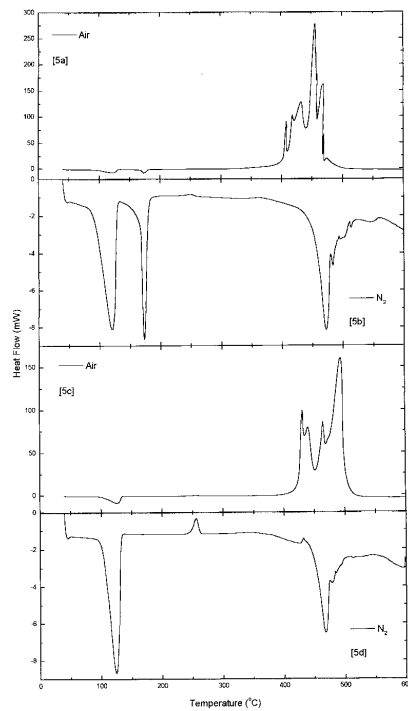


Figure 5.

DTA curve confirms this step through one exothermic peak at 314°C, indicating a small oxidation of the complex before its fusion at 324°C, followed by partial volatilization of the complex at 491.4°C. The use of an air atmosphere leads to a fusion temperature that is 10°C lower than the one observed in a nitrogen atmosphere. The DSC curve, Figure 4a, shows a more defined peak due to the initial oxidation. This leads to the displacement of the fusion peak toward a lower temperature.

The presence of the complex in the first intermediate product at 370°C and in the volatilized product was verified by infrared

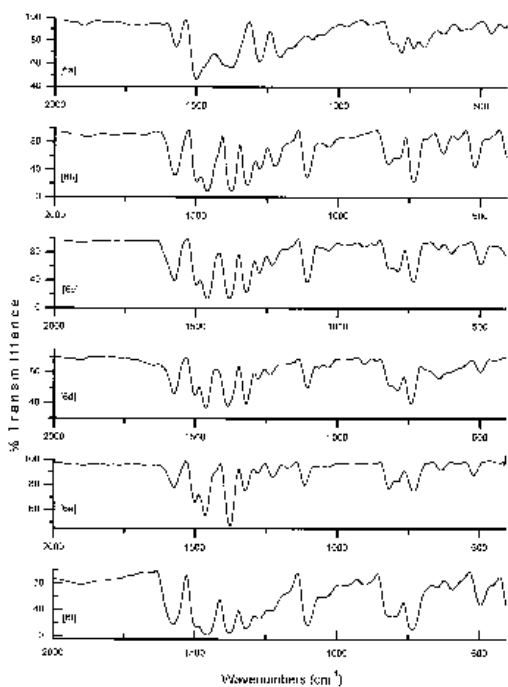


Figure 6.

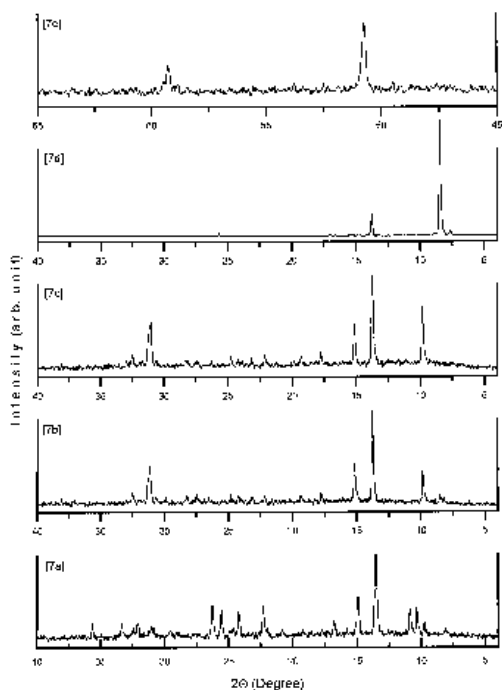


Figure 7.

spectroscopy. The Figure 6b shows the infrared spectra of the anhydrous complex that shows similar bands to the bands observed for the infrared spectra of the volatilized product, Figure 6e. The kind of structure founded on basis of X-ray diffraction patterns by the volatilized product was the monoclinic in a form. The hydrated and anhydrous complexes were characterized as monoclinic structure in b form. The residue at 370°C was found to have no crystalline form.

The difference between the values of the metal content obtained by conventional methods and those obtained by TG

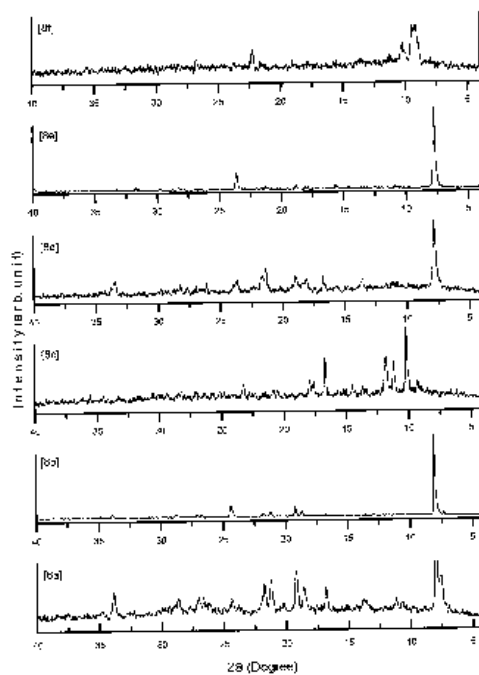


Figure 8.

analysis, Table 1, also confirms the partial loss of the complex by volatilization.

The TG and DTA curves obtained in a N_2 atmosphere, Figure 1d, show a similar thermal behavior such as the dehydration process, volatilization and thermal decomposition of the anhydrous complex. However, it was verified a little displacement of temperature peaks or temperature values in both of these processes. The sublimation step is not well defined as it is for the Cu(II) compound obtained in acid pH. At 171°C, it can be observed an exothermic peak which was attributed on the basis of X-ray diffraction of the product as being due to crystallization. The DSC curve, Figure 4a, shows an exothermic peak at 173.5°C assigned to the crystallization and another endothermic peak at 336.2°C due to fusion of the anhydrous complex.

In synthetic air, the crystallization peak at 171°C can also be observed in DTA curves, Figure 1c. The other mass-loss steps in the TG curve, and exothermic and endothermic peaks in the DTA curve were similar to the Cu(II) compound obtained in the acid pH. However, the amount of volatilized compound was smaller (10.7%) than that obtained for the $Cu(C_9H_6ON)_2 \cdot (C_9H_7ON)_{1.2} \cdot H_2O$.

1.2. Zinc complexes

The TG curves of $Zn(C_9H_6ON)_2 \cdot (C_9H_7ON)_{0.6} \cdot 2.5H_2O$ in a N_2 atmosphere, Figure 2b, show a two step mass loss. The first step occurs up to 141.6°C and it is ascribed to the loss of H_2O ; the second, up to 192°C, to the loss of 1.5 H_2O followed by the elimination of the uncoordinated ligand, respectively. It can be observed through three endothermic peaks at 92, 132 and 181°C, in DTA curve. The last mass-loss step, between 320°C and 512°C, is due to the partial volatilization followed by partial thermal decomposition of the anhydrous complex which could not be completed even at 900°C. In this step, two endothermic peaks in DTA curve in a N_2 atmosphere can be verified. The first intense peak at 370°C, is attributed to the fusion and the second broad peak at 455°C, to partial volatilization of the anhydrous compound.

The DSC curves in a N_2 atmosphere, Figure 4c, show five

endothermic peaks. The first two at 129.5 and 172.3°C are ascribed to dehydration process and another at 177.2°C, to the elimination of the uncoordinated ligand. The fourth peak at 375.3°C is ascribed to the fusion of the anhydrous complex and the last well defined one at 439°C, to partial volatilization.

The TG curve in a synthetic air atmosphere, Figure 2a, shows four mass-loss steps. The first two steps show similar behavior of the compound in a N₂ atmosphere. The third mass-loss step, between 320 and 462°C, is ascribed to the partial thermal decomposition of the anhydrous compound with formation of ZnO. The remaining compound, characterized on the basis of infrared spectra, figure 6f, presents still IR bands of the anhydrous complex, which is decomposed, between 462 to 620°C, with formation of the ZnO.

In DTA curve, Figure 2a, it can be verified peaks corresponding to the mass-loss in the TG curve. In that DTA curve it can also be verified a dislocation of the fusion peak of the anhydrous complex toward a lower temperature due to the presence of a little amount of the oxidizer compound.

The DSC curve in a synthetic air, Figure 4c, shows the dislocation of the fusion peak to a lower temperature (370°C), as well as the small exothermic peak before the fusion peak which could not be easily seen under other conditions. After the peak of fusion, it can be verified a small endothermic peak at 423°C followed by another exothermic peak at 427.5°C, and these two peaks can be verified in the same interval as the DSC curve in N₂ atmosphere and which had been attributed to the volatilization process.

The TG and DTA curves to the compound Zn(C₉H₆ON)₂.2H₂O in a synthetic air and N₂ atmospheres, Figures 2c and 2d, show a similar thermal behavior when it is compared to anhydrous compound obtained in acid pH. The dehydration process occurs in only one mass-loss step up to 170°C with correspondent endothermic peak at 146°C in the DTA curves. At 207°C one exothermic peak appears which was attributed on the basis of X-ray diffraction patterns of this product as been due to crystallization.

The DSC curves, Figure 4d, shows the first two peaks, one endothermic at 140°C and one exothermic at 211°C, ascribed to dehydration and crystallization processes, respectively. In a N₂ atmosphere, it is observed the fusion peak at 370°C, followed by a broad endothermic peak at 441°C attributed to volatilization process. In a synthetic air atmosphere, the fusion peak is dislocated to 366°C due probably to a reaction of oxidation that occurs before the fusion process. At 432.8°C it can be observed an endothermic peak followed by another at 454°C, ascribed to a possible volatilization that could be confirmed when the compound was heated in a muffle furnace using a larger crucible. The last intense exothermic peak at 540°C is attributed to the thermal decomposition of the remaining compound with the formation of the ZnO.

1.3. Cadmium complexes

The TG curve of Cd(C₉H₆ON)₂.(C₉H₇ON)_{0.7}.1.5H₂O, Figure 3b, in a N₂ atmosphere shows four mass-loss steps. The first two steps occur up to 133°C and 188°C, and they are ascribed to a loss of 1.5 water molecules and to the elimination of the uncoordinated ligand. The respective DTA curve shows two endothermic peaks at 125 and 172°C consistent with the TG data. The two other steps, from 408 to 570°C and from 570 to 900°C, are ascribed to partial volatilization of the anhydrous complex followed by its partial thermal decomposition, respectively. Two endothermic peaks, an intense one at 479°C and another broad one at 570-770°C, are in correspondence to those mass losses.

In the DSC curve, Figure 5b, in a N₂ atmosphere, the peak at 467.9°C is in correspondence with the first thermal decomposition step in the TG curve, may be due to simultaneous fusion and volatilization processes.

The TG curve, Figure 3a, in a synthetic air atmosphere shows the same initial behavior verified when in a N₂ atmosphere, such as dehydration and elimination of the uncoordinated ligand. The next consecutive mass-loss steps which occur from 358 to 500°C are ascribed to the thermal decomposition of the anhydrous compound with formation of CdO.

The DTA curve shows the same two endothermic peaks concerning to dehydration and elimination of the uncoordinated ligand. The three consecutive exothermic peaks from 385°C to 540°C are in correspondence to the thermal decomposition steps in TG curve. The DSC curve, Figure 5a, shows five exothermic peaks from 385 to 530°C, regarding the thermal decomposition step of the anhydrous complex.

The TG curve of Cd(C₉H₆ON)₂.2.25H₂O, Figure 3d, in a N₂ atmosphere shows three mass-loss steps. The first, up to 203°C, is ascribed to dehydration process. The two others, from 400 to 570°C and from 570 to 900°C are ascribed to consecutive mass losses by sublimation, volatilization and thermodecomposition processes, respectively.

The DTA curve, Figure 3d, shows an endothermic peak at 136°C, according to the first mass-loss in the TG curve. At 255°C one exothermic peak appears which was attributed on the basis of X-ray diffraction patterns of this product as been due to crystallization. The endothermic peaks at 474°C and other broad ones from 497 to 780°C are ascribed to consecutive sublimation, fusion, volatilization of the anhydrous compound and to the partial thermal decomposition of the remaining compound, respectively. The DSC curve, Figure 5d, shows a broad endothermic peak at 424.9°C ascribed to sublimation which could not be observed in DTA curve.

The TG curve in a synthetic air shows the same behavior as the thermal decomposition step of the anhydrous complex obtained in acid pH. Intense exothermic peaks can be verified from 380°C to 540°C in DTA curve consistent with the mass-losses in TG curve. The DSC curve, Figure 5c, shows several consecutive exothermic peaks from 395 to 530°C regarding to the thermodecomposition steps in the TG curves.

2. INFRARED ABSORPTION SPECTRA

These kinds of metallic complexes exhibit a very strong main IR band in the 1100 cm⁻¹ region^{12,13} which has been attributed to the electronic distribution change around C-O group due to Me-O-C bond. This IR band varied from 1100 to 1107 cm⁻¹ depending either on the metallic ion or on the conditions under which the complexes were obtained and besides, whether they were anhydrous or hydrated, Figures 6a-f. At 1093 cm⁻¹ there is a weak IR band referring to C-O vibration mode of the uncoordinated ligand. To the volatilized copper complex, Figure 6e, the Me-O-C bond occurs at 1114 cm⁻¹. At 1030 cm⁻¹ there is a medium IR band, which has been attributed to C-N stretch in the metallic complexes and not present in the IR spectra of the uncoordinated 8-hydroxyquinoline, Figure 6a. To the zinc complex, heated up to 450°C, Figure 6f, it can be observed a IR band at 1050 cm⁻¹ ascribed to uncoordinated ligand, probably due to partial thermal decomposition of the complex and to the presence of ZnO. At 1320 cm⁻¹ occurs an intense IR band attributed to axial deformation of C-N from the ring, which is not observed to uncoordinated ligand. At 1460 cm⁻¹, intense band to the complexes can be found but not to uncoordinated ligand which has been assigned to C-N deformation in the ring and to C-C stretching. IR band resulting from Me-O-Me bond between 700-800 cm⁻¹, could not be observed because of the presence of 8-hydroxyquinoline band in the same region^{12,15}. At 800 cm⁻¹, a strong IR band can be observed, possibly a Me-O stretching frequency due to a diatomic vibration^{13,15}. Between 450-525 cm⁻¹ these complexes have shown two intense bands due to Me-N and Me-O vibration modes¹⁴. In the case of the copper(II) complex, Figures 6b and

6e, they have been verified by an intense IR band at 520 cm^{-1} and another moderate IR band around 470 cm^{-1} , whereas to the cadmium(II) and zinc(II) complexes these IR bands appear at 500 cm^{-1} and 450 cm^{-1} , Figures 6d and 6c respectively. The other IR bands observed to these metallic complexes present similar aspects to the 8-hydroxyquinoline.

3. X-RAY POWDER DIFFRACTION

The β -form^{7,9,10} to copper(II) complex had been defined as the one which the copper atom forms four normal bonds to the anion and a fifth longer bond to an oxygen of another molecule related to the first by a center of symmetry resulting a dimer type unit. The unusual α -form⁸ presents a six coordinate copper atom which lies on a symmetry center. It is bonded to the two 8-hydroxyquinolinolate anion through the nitrogen atoms and hydroxyl oxygen atoms in trans-planar configuration and to the oxygen atoms from adjacent molecules. It has been verified on the basis of X-ray patterns, Figure 7a-c, that the hydrated and anhydrous copper(II) complexes, present a monoclinic structure in the β -form, spatial group $P2_1/c$ with $a_0=10.644$, $\beta_0=8.593$, $c_0=15.239$ and $\beta=102.18^\circ$ ⁷. The copper(II) complex obtained by volatilization of the anhydrous compounds at 370°C , Figure 7d, has also presented monoclinic structure but in the α -form, spatial group $P2_1/c$ with $a_0=7.40$, $\beta_0=3.84$, $c_0=24.37$ and $\beta=98^\circ 6'$ ⁸. In these two forms it has not been verified the influence of the hydration degree.

Zinc(II) complexes were described by Merritt et al^{10, 11} as a monoclinic unit cell with $a_0=11.28$, $\beta_0=5.42$, $c_0=13.16$ and $\beta=106^\circ 18'$. To hydrated complex there would be a sort of distorted octahedral arrangement of bonds around the central zinc ion while the anhydrous compound would be essentially planar.

Although the compound prepared hasn't shown the same cell dimensions, it can't be attributed to hydration degree. Zinc(II) and cadmium(II) complexes, Figures 8a-b and 8d-e respectively, prepared in either acid or basic pH were found to be isomorphous. The anhydrous compounds, Figures 8c and 8f respectively, have shown different interplanar distances from initial compounds and different from one another. Anhydrous zinc(II) compound has been found to be more crystalline than the anhydrous cadmium(II) complex .

4. CONCLUSION

All the complexes achieved in acid pH present uncoordinated ligand into crystal lattice.

The colors of the metallic complexes in the acid pH are lighter than the compounds obtained in the basic pH.

All the compounds present the sublimation, fusion and volatilization processes when in a nitrogen atmosphere. When

in an oxidating atmosphere these processes are only observed in the case of the copper(II) complexes.

To the cadmium(II) complex, it has been verified that the thermal decomposition of the anhydrous complex is very different whether in inert or oxidating atmospheres. It denotes a distinct mechanism of the thermal decomposition which depends on the atmosphere and different from that behavior observed to copper(II) and zinc(II) complexes.

The enthalpy of fusion calculated to copper(II) and zinc(II) complexes in a N_2 atmosphere indicates higher values to compounds obtained in acid pH, and lower values from copper(II) to zinc(II) compounds. It was not been possible to obtain the enthalpy values to the cadmium compounds because several reactions occurred together with the fusion process.

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