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SYNTHESIS AND THERMAL STUDY OF THE BARIUM COMPLEXES WITH 8-HYDROXYQUINOLINATE DERIVATIVES

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Abstract

In this present work, barium ion was reacted with different ligands which are 5,7-dibromo, 5,7-dichloro, 7-iodo and 5-chloro-7-iodo-8-hydroxyquinoline, in acetone/ammonium hydroxide medium under constant stirring and the obtained compounds were as follows: (I) $Ba[(C_9H_4ONBr_2)_2]\cdot 1.5H_2O$; (II) $Ba[(C_9H_4ONCl_2)(OH)]\cdot 1H_2O$; (III) $Ba[(C_9H_5ONI)_2]\cdot 1H_2O$ and (IV) $Ba[(C_9H_4ONICl)_2]\cdot 5H_2O$, respectively. The compounds were characterized by elemental analysis, infrared absorption spectrum (IR), inductively coupled plasma spectrometry (ICP), simultaneous thermogravimetry–differential thermal analysis (TG-DTA) and differential scanning calorimeter (DSC).

The final residue of the thermal decomposition was characterized as orthorhombic $BaBr_2$ from (I); the intermediate residue, as a mixture of orthorhombic $BaCO_3$ and $BaCl_2$ and cubic BaO and the final residue, as a mixture of cubic and tetragonal BaO and orthorhombic $BaCl_2$ (II); the intermediate residue, as orthorhombic $BaCO_3$ and as a final residue, a mixture of cubic and tetragonal BaO from (III); and the intermediate residue, as a mixture of orthorhombic $BaCO_3$ and $BaCl_2$ and as a final residue, a mixture of cubic and tetragonal BaO and orthorhombic $BaCl_2$ from (IV).

Keywords: barium, DTA, TG, thermal decomposition

Introduction

8-Hydroxyquinoline and its halogen derivatives present a particular behavior to obtain stable complexes with many metallic cations [1, 2]. This behavior resulted in several applications of these ligands as analytical reactants whose studies have been published by Hahn [3] and Berg [4].

The thermal stability of the earth alkaline chelates with 8-hydroxyquinoline was studied by Charles in 1961 [6]. The anhydrous chelates were heated in air absence and the thermal decomposition occurred around 500°C with H_2 evolution. Charles also established a decrease in the thermal stability order and concluded that all of them were thermally more stable than the 8-hydroxyquinoline. Charles and Langer in 1959 [5] studied the pyrolysis of earth alkalines of the chelates with 8-hydroxyquinoline. MgO was presented as a result from the pyrolysis of the magnesium oxinate.

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In 1999, Guerreiro, Ribeiro, Crespi and Torres [7] synthesized and studied the compounds $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$ (I), $Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$ (II), $Sr[(C_9H_5ONI)_2]\cdot 5H_2O$ (III) and $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$ (IV), through termogravimetry (TG), differential thermal analysis (DTA) and others. It was proposed $SrBr_2$ from (I); mixture of $SrCl_2$, $SrCO_3$ and SrO from (II); $SrCO_3$ from (III) and SrO from (IV) as intermediate and final residues from the thermal decomposition.

In this work, the synthesis of the compounds of barium with 5,7-dibromo, 5,7-dichloro, 7-iodo and 5-chloro-7-iodo-8-hydroxyquinoline are presented. The influences of halogen in the formation of the complexes and in the process of thermal decomposition are investigated.

Experimental

The reaction of 8-hydroxyquinoline with the respective halogen in medium of acetic acid/water resulted in the ligands 5,7-dibromo, 5,7-dichloro and 7-iodo-8-hydroxyquinoline [8]; the reaction of 7-iodo-8-hydroxyquinoline with chlorine in aqueous medium resulted in 5-chloro-7-iodo-8-hydroxyquinoline. The melting point of the compounds through DSC curves was determined by using the mass of the samples between 1.5 and 2.0 mg, aluminum crucible, empty crucible as reference, nitrogen atmosphere (90 ml min^{-1}) and heating rate of 5°C min^{-1}. $C_9H_4ONBr_2$ (mp=199°C, N=4.56%; C=36.25%, H=1.41%); $C_9H_4ONCl_2$ (mp=182°C, N=6.51%; C=50.6%; H=2.37%); C_9H_5ONI (mp=136°C, N=5.49%; C=33.3%; H=1.56%) and C_9H_4ONICl (N=4.80%; C=34.5%; H=1.47%).

The solid state compounds of barium with 8-hydroxyquinolinate derivatives were prepared by mixing, under constant stirring, the aqueous solution of the dehydrated barium nitrate with the acetone solution of the derivatives of 8-hydroxyquinoline. The pH was adjusted to 9, with concentrated aqueous ammonia solution under constant stirring and heating for one h. After keeping the solution standby at room temperature until its complete sedimentation, it was filtered and the precipitates were washed with diluted aqueous ammonia solution several times in order to eliminate the excess of the ligands. They were dried at 60°C and stored in a desiccator containing anhydrous $CaCl_2$.

The water molecule number was obtained from TG curves; 8-hydroxyquinoline derivative contents from both the TG curves and elemental analysis; and barium from TG curves and ICP.

TG and DTA curves were obtained through simultaneous module of thermal analysis, SDT 2960 from TA Instruments, able to operate from room temperature to 1500°C. The thermocouples to sample and to reference are of Pt–Pt/Rh 13%, with 0.1 μg of sensibility of the balance, around 1% of precision, 200 mg of the mass capacity (350 mg including the crucibles), 0.001°C of sensibility ΔT(DTA). The system was calibrated with relation to mass, base line DTA and temperature (by using In of high purity). Curves were obtained with 7 mg mass sample, alumina crucible of 40 μL, α-Al_2O_3, as reference material, synthetic air and nitrogen atmospheres, heating rate of 5, 10 and 20°C min^{-1}. TG and DTA curves were obtained through TA Instruments, SDT 2960, on synthetic air atmosphere, with flux of 100 mL min^{-1}, heating rate of 20°C min^{-1}, samples mass around 8 mg and alumina crucible.

The barium content present in the complexes was determined by using an inductively coupled plasma spectrometry (ICP), Thermojarrel Ash, model CID – DUO, line 189.989{136}.

Infrared absorption spectra (IR) were obtained in the region 4000–400 cm^{-1} by using a Nicolet Infrared Spectrophotometer model 400 with 4 cm^{-1} of resolution, having the solid complexes been run as pressed pellets using KBr as diluent.

Elemental analysis data were obtained from CHNS-O, model Ea 1110 of the CE Instruments.

X-ray diffractograms were obtained by using the Horizontal Diffractometer HGZ 4/B with proportional counter and discrimination of height of pulses in Bragg-Bretano, with cobalt tube (λ=1.7889 nm), submitted to 36 kV and 20 mA. Samples were put in a proper support of the equipment and exposed to radiation up to 60°C (2θ).

Results and discussion

TG-DTA curves

Figure 1 presents TG-DTA curves obtained to the compounds of barium with 5,7-dibromo, 5,7-dichloro, 7-iodo and 5-chloro-7-iodo-8-hidroxyquinolina, in dynamic synthetic air atmosphere.

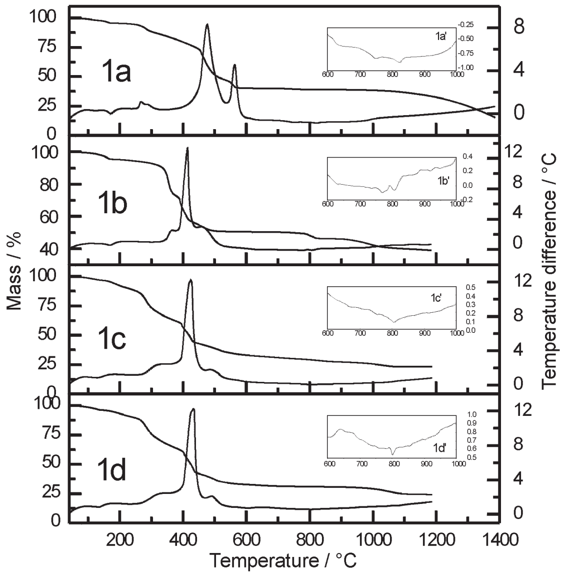

Fig. 1 TG-DTA curves of the compounds, 20°C min^{-1}, synthetic air atmosphere: a – $Ba[(C_9H_4ONBr_2)_2]\cdot 1.5H_2O$; b – $Ba[(C_9H_4ONCl_2)(OH)]\cdot 1H_2O$; c – $Ba[(C_9H_5ONI)_2]\cdot 1H_2O$ and d – $Ba[(C_9H_4ONICl)_2]\cdot 5H_2O$

To $Ba[(C_9H_4ONBr_2)_2]\cdot1.5H_2O$, Fig. 1a, it is verified that the dehydration occurs in the first step up to nearly 200°C, with an endothermic peak corresponding to 170°C in DTA curve, Table 1. Next three exothermic peaks are observed at 266, 477 and 562°C related to the thermal decomposition of the anhydrous compound and formation, above 600°C, of exclusively $BaBr_2$ as residue. Diffraction scan of this residue obtained above 600°C shows the presence of orthorhombic $BaBr_2$, Fig. 2a, which is also verified to qualitative test of brometo ion [9]. At 747 and 820°C it is observed two small endothermic peaks without any mass loss in the TG curve ascribed to possible phase transitions including fusion [10] of $BaBr_2$. Immediately after the fusion, at 834°C, slow volatilization of $BaBr_2$ is verified, which is incomplete up to 1400°C.

Table 1 Metal, ligand and water contents from analytical and thermogravimetric (TG) data

Compound	Barium/%			Water/%		Ligand/%	
	Theor.	TG	ICP	Theor.	TG	Theor.	TG
$Ba[(C_9H_4ONBr_2)_2]\cdot1.5H_2O$	17.5	17.8	17.5	5.73	5.24	55.6	56.1
$Ba[(C_9H_4ONCl_2)(OH)]\cdot1H_2O$	35.6	35.2	35.2	4.68	4.53	48.4	49.2
$Ba[(C_9H_5ONI)_2]\cdot1H_2O$	19.7	20.7	19.9	2.59	2.31	75.4	74.9
$Ba[(C_9H_4ONICl)_2]\cdot5H_2O$	16.4	16.1	16.2	10.8	10.5	65.3	64.3

Table 2 Results from elemental analysis

Compound	C/%		H/%		N/%	
	Theor.	Exper.	Theor.	Exper.	Theor.	Exper.
$Ba[(C_9H_4ONBr_2)_2]\cdot1.5H_2O$	22.4	22.1	1.46	1.49	2.90	2.78
$Ba[(C_9H_4ONCl_2)(OH)]\cdot1H_2O$	29.4	28.5	1.92	2.27	3.81	3.73
$Ba[(C_9H_5ONI)_2]\cdot1H_2O$	31.1	31.1	1.74	1.56	4.03	3.93
$Ba[(C_9H_4ONICl)_2]\cdot5H_2O$	25.9	24.5	2.17	2.26	3.35	2.74

In the TG-DTA curve of $Ba[(C_9H_4ONCl_2)(OH)]\cdot1H_2O$, six mass loss steps can be observed, Fig. 1b. The first step is attributed to the dehydration of the initial compound up to 200°C, with a corresponding endothermic peak in DTA curve. The three steps following the exothermic peaks at 357, 411 and 462°C, Table 1, with corresponding mass loss in TG curves, are related to the thermal decomposition of the anhydrous compound with the formation of a mixture of $BaCl_2$, $BaCO_3$ and BaO at 600°C as verified through the diffraction scan. Above 800°C a mass loss, which corresponds to the partial decomposition of $BaCO_3$, can be seen caused by the presence of $BaCl_2$ in the mixture. This behavior was confirmed through TG-DTA curve of the physical mixture of $BaCl_2/BaCO_3$, Fig. 3c, which is not observed in the individual curves of $BaCl_2$ and $BaCO_3$, Figs 3a and 3b, respectively. Above 950°C, there is a continuous mass loss which does not reach its total decomposition up to 1200°C. This reaction corresponds to the partial volatilization of $BaCl_2$. Residues obtained at 850 and 1150°C were identified through diffraction scan as a mixture of cubic BaO,

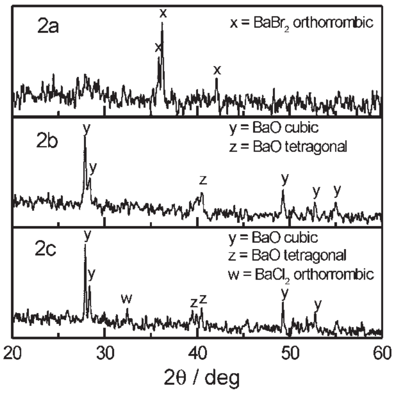

Fig. 2 X-Ray diffractometry of residues from thermal decomposition obtained through TG: a – Ba[$(C_9H_4ONBr_2)_2$]·1.5H_2O at 900°C; b – Ba[$(C_9H_5ONI)_2$]·1H_2O at 1100°C and c – Ba[$(C_9H_4ONICl)_2$]·5H_2O at 1150°C

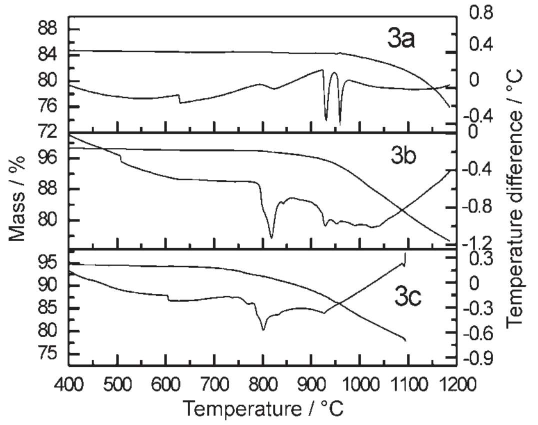

Fig. 3 TG-DTA curves of the compounds, 20°C min^{-1}, synthetic air atmosphere: a – $BaCl_2$; b – $BaCO_3$ and c – physical mixture of $BaCl_2$ and $BaCO_3$

orthorhombic $BaCO_3$, Fig. 4b, and as a mixture of cubic and tetragonal BaO and orthorhombic $BaCl_2$, Fig. 4c, respectively.

The thermal behavior of Ba[$(C_9H_5ONI)_2$]·1H_2O can be verified through TG-DTA curve, Fig. 1c. The dehydration of the compound occurs in the first step of the mass loss, with an endothermic peak at 133°C, observed in DTA curve. The following four steps were attributed to the thermal decomposition of the anhydrous compound in the TG curve and it corresponds to a wide endothermic peak around 260°C followed by three exothermic peaks at 329, 432 and 490°C, Table 1, with the only formation of $BaCO_3$ at 700°C. In the last step occurs the thermal decomposition from $BaCO_3$ to BaO up to 1100°C, which can be seen through the endothermic peak at 802°C, in DTA curve. No presence of iodine was found in the residue at 700°C [9].

Diffraction scan of the residue at 1100°C, Fig. 2b, shows the presence of cubic and tetragonal BaO.

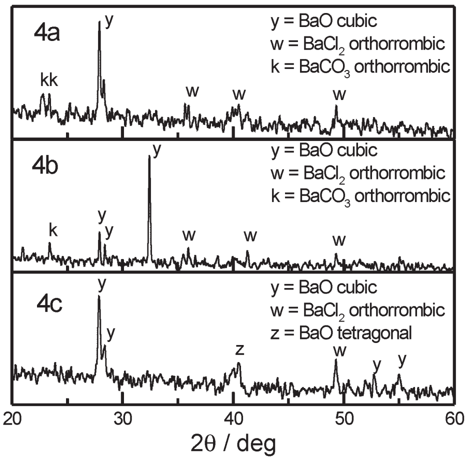

Fig. 4 X-Ray diffractometry of residues from thermal decomposition obtained through TG to Ba[($C_9H_4ONCl_2$)(OH)]·1H_2O at: a – 600°C; b – 850°C and c – 1150°C

In TG-DTA curves of Ba[(C_9H_4ONICl)$_2$]·5H_2O, Fig. 1d, six mass loss steps can be verified, being the first related to the dehydration of the compound up to 160°C. Following, four steps of mass loss with a corresponding wide endothermic peak around 260°C are observed and three exothermic peaks at 326, 437 and 490°C, Table 1, with the formation of a mixture of $BaCO_3$ and $BaCl_2$ up to 750°C. This mixture decomposes above 900°C with the formation of BaO and still the presence of $BaCl_2$. Residue obtained at 1150°C shows the presence of cubic and tetragonal BaO and orthorhombic $BaCl_2$, confirmed through diffraction scan, Fig. 2c. The small endothermic peak in the DTA curve, Fig. 1d, at 810°C, is attributed to the transition from γ to β $BaCO_3$ [11].

Infrared absorption spectrum

IR have shown characteristic bands [12] to each obtained complex (Figs 5a–d). The compound Ba[($C_9H_4ONBr_2$)$_2$]·1.5H_2O presented bands of medium intensity in 720 and in 654 cm^{-1} which have been clearly related to the equatorial and axial C–Br stretching vibration, respectively. To the compound which contains chloride-ion, the absorption band in the region of 800 cm^{-1} was ascribed to the stretching of C–Cl axial and to the compound which contains iodine-ion; the absorption bands in 730 and in 600 cm^{-1} are due to the stretching of C–I bond. When iodine-ion and chloride-ion are present in the same compound, Ba[(C_9H_4ONICl)$_2$]·5H_2O, weak bands were verified in the region 669–500 cm^{-1}, which could be attributed to the vibration of the stretching of the C–Cl axial as to the vibration of the C–I stretching of the C–I equatorial;

however, only stretching of C–Cl equatorial can be ascribed to 820 cm^{-1} and stretching of C–I to C–I to 569 cm^{-1}.

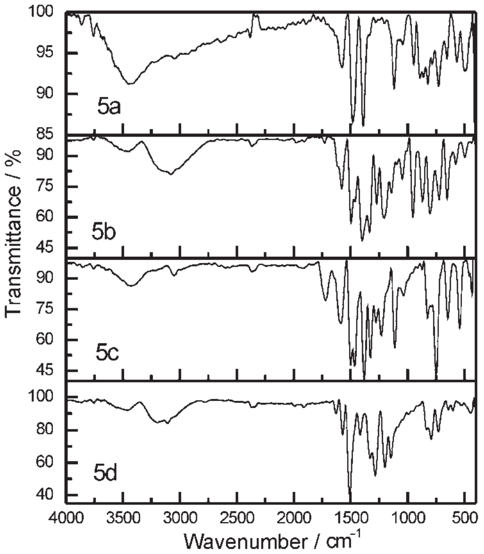

Fig. 5 Infrared absorption spectra of the original compounds:
a – Ba[($C_9H_4ONBr_2$)$_2$]·1.5H_2O; b – Ba[($C_9H_4ONCl_2$)(OH)]·1H_2O;
c – Ba[(C_9H_5ONI)$_2$]·1H_2O and d – Ba[(C_9H_4ONICl)$_2$]·5H_2O

Absorption bands around 1600–1300 cm^{-1}, to all the compounds, are related to the stretching of the C–O bonds as well as with the C–N bond, both of which allow to confirm the barium coordination of these atoms in each ligand used.

Conclusions

The presence of halogen in the 8-hydroxyquinoline ring caused not only changes in the thermal decomposition of the complexes, but also diversity in the formation of the intermediate and final residues.

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