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SYNTHESIS AND THERMAL STUDY OF MAGNESIUM COMPLEXES WITH 8-HYDROXYQUINOLINATE DERIVATIVES

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Abstract

Magnesium ion was reacted with 5,7-dibromo-, 5,7-dichloro-, 7-iodo- and 5-chloro-7-iodo-8-hydroxyquinoline, in acetone/ammonium hydroxide medium under constant stirring to obtain (I) $Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$; (II) $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$; (III) $Mg[(C_9H_5ONI)_2]\cdot 2H_2O$ and (IV) $Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$ complexes. The compounds were characterized by elemental analysis, IR spectra, ICP, TG-DTA and DSC.

Through thermal decomposition residues were obtained and characterized, by X-ray diffractometry, as a mixture of hexagonal $MgBr_2$ and cubic MgO to the (I) compound at 850°C; cubic MgO to the (II), (III) and (IV) compounds at 750, 800 and 700°C, respectively.

Keywords: 8-hydroxyquinolinate derivatives, magnesium, thermal decomposition

Introduction

The thermal stability of earth alkaline chelates with 8-hydroxyquinoline was studied by Charles in 1961 [1]. 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 8-hydroxyquinoline. The same author *et al*. [2] studied the pyrolysis of earth alkaline of chelates with 8-hydroxiquinoline. MgO was presented as a result from the pyrolysis of the magnesium oxinate.

In 1998, Guerreiro *et al.* [3] studied the metallic complexes of strontium with 5,7-dibromo-, 5,7-dichloro-, 7-iodo- and 5-chloro-7-iodo-8-hydroxyquinoline through thermogravimetry (TG), differential thermal analysis (DTA) and others. It was proposed $SrBr_2$; a mixture of $SrCl_2$, $SrCO_3$ and SrO; $SrCO_3$ and SrO as intermediates and residues from thermal decomposition of the compounds $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$, $Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$, $Sr[(C_9H_5ONI)_2]\cdot 5H_2O$ and $Sr[(C_9H_4ONICl)(OH)]\cdot 25H_2O$, respectively.

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In this work, the synthesis of the compounds of magnesium with 5,7-dibromo-, 5,7-dichloro-, 7-iodo- and 5-chloro-7-iodo-8-hydroxyquinoline are presented and the influence of halogen in the formation of the complexes and in the process of thermal decomposition were 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 [4]; the reaction of 7-iodo-8-hydroxyquinoline with chlorine in aqueous medium resulted in 5-chloro-7-iodo-8-hydroxyquinoline. $C_9H_4ONBr_2$ (*m.p.*=199.1°C, N=4.56%; C=36.25%; H=1.41%); $C_9H_4ONCl_2$ (*m.p.*=182.1°C, N=6.51%; C=50.6%; H=2.37%); C_9H_5ONI (*m.p.*=136.5°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 magnesium with 8-hydroxyquinolinate derivatives were prepared by mixing, under constant stirring, the aqueous solution of $MgCl{\cdot}6H_2O$ with acetone solution of the derivatives of 8-hydroxyquinoline. pH was adjusted to 9 with concentrated aqueous ammonia solution under constant stirring and heating for one hour. After the solution was kept at room temperature until its complete sedimentation, it was filtered and the precipitates washed with diluted aqueous ammonia solution several times in order to eliminate the excess of the ligands. They were dried at 60°C and kept 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 magnesium from TG curves and ICP, Table 1.

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

Compound	Magnesium/%			Water/%		Ligand/%	
	Theor.	TG	ICP	Theor.	TG	Theor.	TG
$Mg[(C_9H_4ONBr_2)_2]{\cdot}2H_2O$	3.66	3.81	3.73	5.43	5.24	80.9	80.7
$Mg[(C_9H_4ONCl_2)_2]{\cdot}3H_2O$	8.64	8.28	8.28	9.60	9.75	75.5	76.0
$Mg[(C_9H_5ONI)_2]{\cdot}2H_2O$	4.05	4.02	3.71	6.00	6.35	87.3	86.9
$Mg[(C_9H_4ONICl)_2]{\cdot}2.5H_2O$	3.58	3.41	3.32	6.64	6.86	87.4	87.5

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 magnesium 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 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 run as pressed pellets using KBr as diluent.

Table 2 Results from elemental analysis

Compound	C/%		H/%		N/%	
	Theor.	Exper.	Theor.	Exper.	Theor.	Exper.
$Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$	32.6	33.4	1.21	1.49	4.22	4.24
$Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$	40.9	39.5	3.05	2.89	5.30	5.31
$Mg[(C_9H_5ONI)_2]\cdot 2H_2O$	36.0	34.6	2.35	2.49	4.66	4.29
$Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$	31.9	31.2	1.93	2.16	4.13	4.40

Elemental analysis data were obtained from CHNS-O, model Ea 1110 of the CE Instruments, Table 2.

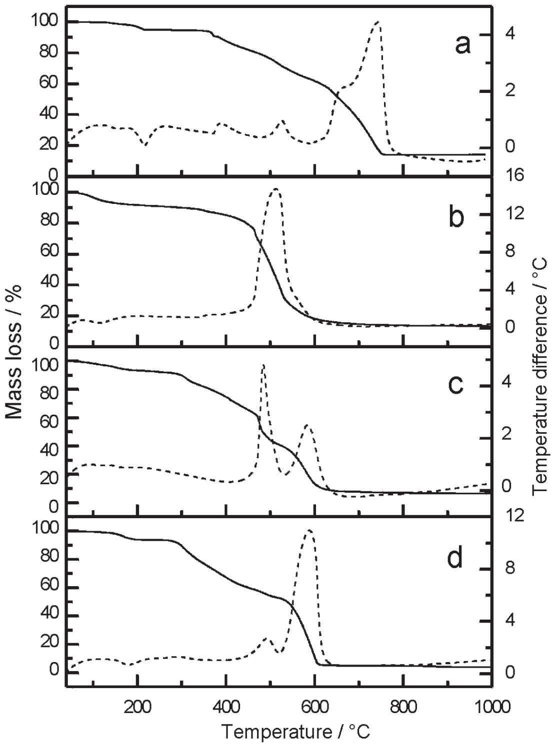

Fig. 1 TG-DTA curves of the compounds, 20°C min^{-1}, synthetic air atmosphere; a – $Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$; b – $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$; c – $Mg[(C_9H_5ONI)_2]\cdot 2H_2O$ and d – $Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$

Results and discussion

TG-DTA curves

TG-DTA curves of 5,7-dibromo-, 5,7-dichloro-, 7-iodo- and 5-chloro-7-iodo-8-hydroxyquinolinates of magnesium, in synthetic air atmosphere, are presented in Fig. 1.

$Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$ presents five mass loss steps in TG curve, Fig. 1a. The two first steps up to 240°C, can be attributed to the dehydration of the compound, corresponding to the endothermic peaks in DTA curve (150 and 212°C), when there is the beginning of the thermal decomposition of the anhydrous compound in three mass loss steps, with formation of 35% of $MgBr_2$ and 65% of MgO at 850°C. This residue was analyzed through X-ray diffractometry, Fig. 2a, where peaks related both to the cubic MgO and to the tetragonal $MgBr_2$ can be observed. The presence of bromide ion was also tested at 850°C and confirmed in the obtained residue through a qualitative test [5].

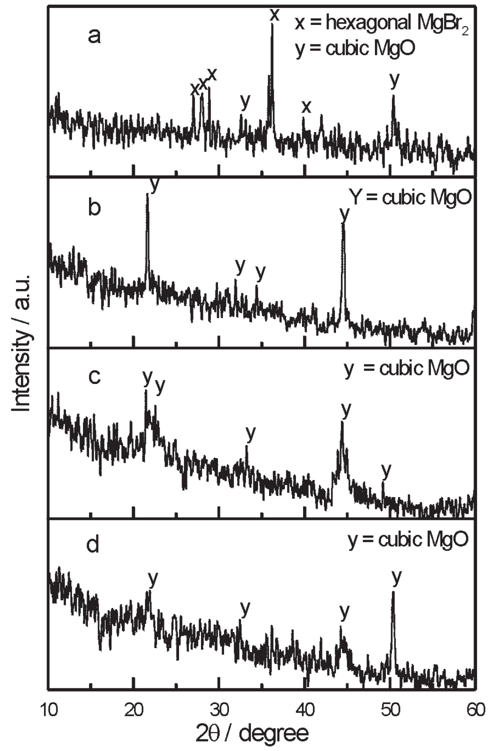

Fig. 2 X-ray diffractometry of residues from thermal decomposition obtained through TG curves; a – $Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$ at 850°C; b – $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$ at 750°C; c – $Mg[(C_9H_5ONI)_2]\cdot 2H_2O$ at 800°C and d – $Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$ at 700°C

To $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$, the endothermic peak observed at 115°C in DTA curve, Fig. 1b, can be ascribed to the dehydration of the compound, according to the first step of mass loss, observed in TG curve. The thermal decomposition of the anhydrous compound occurs in two consecutive steps up to approximately 750°C, with exothermic peaks at 360 and 512°C, related to the formation nearly total of cubic MgO, Fig. 2b. After 750°C mass loss is observed due to the presence of a small percent of $MgCl_2$ contained in the residue, which sublimes slowly and continuously. The presence of chloride ion in the final residue was confirmed through a qualitative test [5].

In Fig. 1c, TG-DTA curve of $Mg[(C_9H_5ONI)_2]\cdot 2H_2O$ is presented, through which it can be verified that the dehydration of the compound occurs in only one mass loss step as verified through an endothermic peak around 170°C. At 250°C, the thermal decomposition of the anhydrous compound takes place in two steps up to nearly 800°C, corresponding to exothermic peaks at 483 and 584°C in DTA curve. The obtained residue was identified as cubic MgO, Fig. 2c.

The thermal behavior of $Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$ can be analyzed through TG-DTA curve, Fig. 1d. The dehydration of the compound occurs in the first step up to 260°C, with an endothermic peak at 180°C in DTA curve. After that, two consecu-

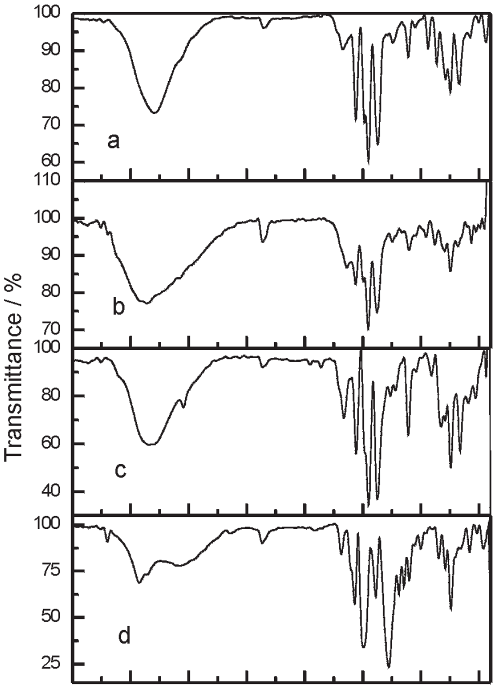

Fig. 3 Infrared spectra of the original compounds; a – $Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$; b – $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$; c – $Mg[(C_9H_5ONI)_2]\cdot 2H_2O$ and d – $Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$

tive steps of the thermal decomposition occur, with formation of cubic MgO at 700°C, Fig. 2d, with corresponding exothermic peaks at 491 and 587°C.

IR spectra

The magnesium complexes with halogen derivatives of 8-hydroxyquinoline present characteristic bands in their spectra, Figs 3a–3d. For $Mg[(C_9H_4ONBr_2)_2]\cdot 2H_2O$, it is verified medium intensity bands in 740 cm^{-1} region, Fig. 3a, which corresponds to the stretching mode of equatorial C–Br bond [6]. The compound containing the chloride ion, $Mg[(C_9H_4ONCl_2)_2]\cdot 3H_2O$, presents medium absorption band in 800 cm^{-1}, related to the stretching mode of axial C–Cl bond, Fig. 3b, that can also be observed in spectrum of $Mg[(C_9H_4ONICl)_2]\cdot 2.5H_2O$ in 820 cm^{-1}, Fig. 3c. In the spectrum of 7-iodo-8-hydroxyquinolinate of magnesium, the bands in 730–600 cm^{-1} region, medium intensity can be attributed to the stretching mode of C–I bond, Fig. 3d.

The strong intensity bands in 1700–1300 cm^{-1} region appear in the spectrum of all these compounds, and can be related to the stretching of C–O and C–N bonds indicating that the magnesium is coordinated through the oxygen and nitrogen atoms of each ligand.

Conclusions

The presence of halogen in 8-hydroxyquinoline ring caused not only changes in the thermal decomposition of the complexes, with the formation of MgO with exception of the bromo derivative which led to a mixture of oxide residue and magnesium bromide. This behavior is different from that observed for the strontium complexes with 8-hydroxyquinolinate derivatives, where the formation of bromide, chloride, along with metallic oxides and carbonates was verified [3].

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