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SYNTHESIS AND THERMAL STUDY OF 8-HYDROXY-QUINOLINE DERIVATIVES OF THE ALKALINE EARTH METALS

I. Strontium complexes

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Abstract

Strontium complexes of 5,7-dibromo-, 5,7-dichloro-, 7-iodo- and 5-chloro-7-iodo-8-hydroxyquinoline were precipitated from an aqueous ammonia and acetone medium. The complexes obtained were $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$; $Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$; $Sr[(C_9H_5ONI)_2]\cdot 5H_2O$ and $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$. The residues of their thermal decomposition were $SrBr_2$; a mixture of $SrCl_2$, $SrCO_3$ and SrO; $SrCO_3$ and $SrCO_3$, respectively. All were characterized by means of thermogravimetry, differential thermal analysis, complexometry with EDTA, atomic absorption spectroscopy, IR spectroscopy and X-ray diffraction.

Keywords: DTA, 8-hydroxyquinoline and its halogenated derivatives, strontium, TG, thermal behaviour

Introduction

8-Hydroxyquinoline forms complexes with more than forty metal ions in different oxidation states. For each metal ion, there is a pH interval in which complete precipitation occurs; the use of different conditions can lead to complexes with different degrees of hydration and different crystal structures [1–5].

Halogenated derivatives of 8-hydroxyquinoline have been investigated as analytical reagents for the determination of metals under different conditions, such as precipitation agents in absorptiometry and extraction from solvents [6].

Wendlandt and Horton studied the thermal behaviour of 8-hydroxyquinoline, 5,7-dichloro-, 2-methyl-, 5-iodo-, 5,7-dibromo- and 5,7-diiodo-8-hydroxyquinoline and 8-hydroxyquinoline complexes of Cu, Zn and Cd and also the 8-hydroxyquinoline derivative complexes of Th, Al and Cu. The peaks observed in the DTA curves were attributed to dehydration, fusion and/or thermal decomposition of the chelate agents and to thermal decomposition of the metal complexes [7].

The present work reports the synthesis of strontium complexes with some 8-hydroxyquinoline derivatives.

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The influence of the halogen in the formation of the complexes and in the thermal decomposition processes was investigated.

Experimental

The reactions of 8-hydroxyquinoline with the respective halogen in a 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 furnished 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%) and C_9H_5ONI (*m.p.*=136.5°C, N=5.49%, C=33.3%, H=1.56%).

The solid-state compounds of strontium with these 8-hydroxyquinoline derivatives were prepared by mixing, under constant stirring, an aqueous solution of strontium nitrate and an acetone solution of the relevant 8-hydroxyquinoline derivative. The pH was adjusted to 9 with concentrated aqueous ammonia solution under constant stirring and the mixture was heated for 1 h and then allowed to stand at room temperature until complete sedimentation had occurred. It was next filtered and the precipitate was washed several times with dilute aqueous ammonia solution in order to eliminate the excess of the ligand. The precipitate was dried at 60°C and stored in a desiccator containing anhydrous $CaCl_2$.

The number of water molecules was established from the TG curves; the 8-hydroxyquinoline derivative contents were found from the TG curves and from elemental analysis; and the strontium contents were determined from the TG curves and atomic absorption spectrophotometry.

TG and DTA curves were obtained with an SDT 2960 apparatus (TA Instruments) in a synthetic air atmosphere, with a flux of 150 ml min^{-1}, at a heating rate of 20°C min^{-1}, with a sample mass of around 8 mg, in an alumina crucible.

The strontium contents in the complexes were determined by using inductively coupled plasma spectrometry (ICP) (Thermojarrel Ash, model CID-DUO, line 189.989 {136}).

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

Elemental analysis data were obtained with a CHNS-O, model Ea 1110 instrument (CE Instruments).

Results and discussion

TG-DTA curves

$Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$ (Fig. 1a) displayed one step of mass loss in the TG curve up to 220°C, reflecting the dehydration of the compound, with a corresponding endothermic peak at 139°C in the DTA curve. The thermal decomposition of the anhydrous complex occurred in three consecutive steps of mass loss up to 675°C, with the formation of $SrBr_2$ (37.9%) plus a carbonized residue. In this temperature

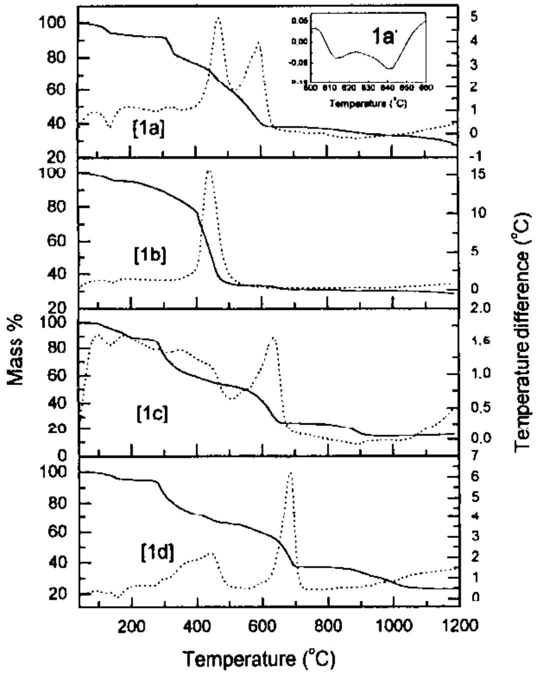

Fig. 1 TG and DTA curves of the complexes: a – $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$; b – $Sr[(C_9H_4ONCl_2)_2]\cdot 1.5H_2O$; c – $Sr[(C_9H_5ONI_2)]\cdot 5H_2O$ and d – $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$

interval, the DTA curve contained an endothermic peak at 274°C, followed by two intense exothermic peaks, at 468 and 594°C. The presence of $SrBr_2$ as the residue of the thermal decomposition was verified through the fusion peak at 641°C in a cooling/heating DTA curve (Fig. 1a') and through qualitative tests for bromide ion [9]. Mass losses above 700°C were attributed to $SrBr_2$ volatilization, which was not completed up to 1200°C.

$Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$ (Fig. 1b) gave an endothermic peak at 145°C in response to the dehydration of the complex. Following this process, consecutive mass losses were verified, with a corresponding intense exothermic peak at 442°C, which reflects the thermal decomposition of the complex up to 545°C, with the formation of a residue containing $SrCO_3$, SrO and a small amount of $SrCl_2$. Between 545 and 900°C, $SrCO_3$ underwent thermal decomposition to SrO. The mass losses observed above 900°C were due to the volatilization of $SrCl_2$ present in the residue. The presence of $SrCl_2$ was verified through qualitative tests for chloride ion [9]; $SrCO_3$ and SrO were identified by X-ray diffractometry (Fig. 2a).

The TG-DTA curves of $Sr[(C_9H_5ONI)_2]\cdot 5H_2O$ (Fig. 1c) indicated two consecutive mass losses up to 240°C, with only one endothermic peak, at 138°C, which characterizes the dehydration of the complex. Between 240 and 740°C, there were two mass loss steps, with corresponding exothermic peaks at 222–523°C and 634°C, accompanying the formation of $SrCO_3$, which decomposes between 750 and 990°C, as seen in the TG curve, and an endothermic peak at 888°C in the DTA curve, associated with the formation of SrO. The presence of SrO in the final residue was verified by X-ray diffractometry (Fig. 2b).

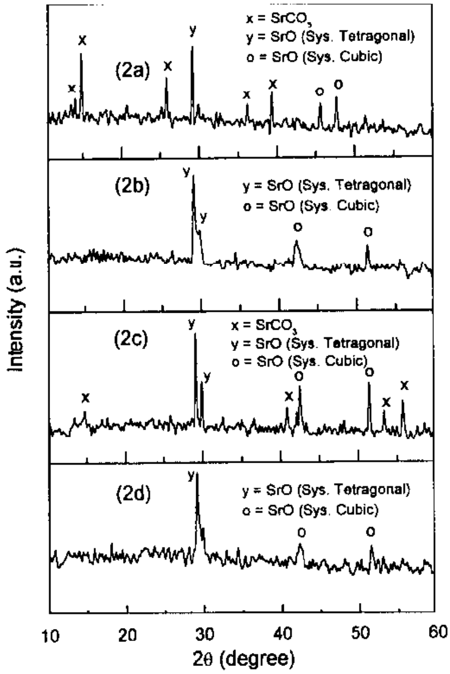

Fig. 2 XRD patterns of the complexes residue: a – $Sr[(C_9H_4ONCl_2)_2]\cdot 1.5H_2O$ at 800°C; b – $Sr[(C_9H_5ONI_2)]\cdot 5H_2O$ at 750°C; c – $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$ at 800°C and d – $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$ at 1200°C

The TG-DTA curves of $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$ (Fig. 1d) contained two consecutive mass losses up to 220°C, with corresponding endothermic peaks at 115 and 156°C, relating to the dehydration of the compound. At around 300°C, the beginning of thermal decomposition of the anhydrous complex in two main steps was observed, with exothermic peaks at 274–519°C and 686°C, corresponding to the formation of $SrCO_3$, and also that of $SrCl_2$ at 725°C. The $SrCO_3$ formed decomposed and the $SrCl_2$ volatilized above 800°C in two mass loss steps up to 1100°C, where the presence of SrO could be observed, as revealed by X-ray diffractometry (Figs 2c, d). Corresponding endothermic peaks occurred at 850–950°C and at 950–1060°C, respectively. The presence of $SrCl_2$ in the final residue at 725°C was verified through qualitative tests for chloride ion [9].

IR spectra

The IR spectra exhibited characteristic bands [10] for each of the complexes (Figs 3a–d). $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$ gave bands of medium intensity at 731 and 675 cm^{-1}, clearly related to the equatorial and the axial C–Br stretching vibration, respectively. The absorption bands at 928 and 858 cm^{-1} can be attributed to the deformation vibrations of the C–C bond corresponding to the carbon–bromo bond. For the compound containing two chlorine atoms, the absorption bands in the region of 789 and 742 cm^{-1} were ascribed to the stretching of C–Cl axial, while for the compound containing iodine, the absorption bands at 723 and 653 cm^{-1} are due to the stretching of the C–I bond. For $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$, weak bands were verified at 653 and 548 cm^{-1}, and were attributed to the stretching vibration of the C–Cl axial and of the C–I equatorial; however, only stretching of the C–Cl equatorial can be ascribed to 820 cm^{-1} and stretching of the C–I to 569 cm^{-1}.

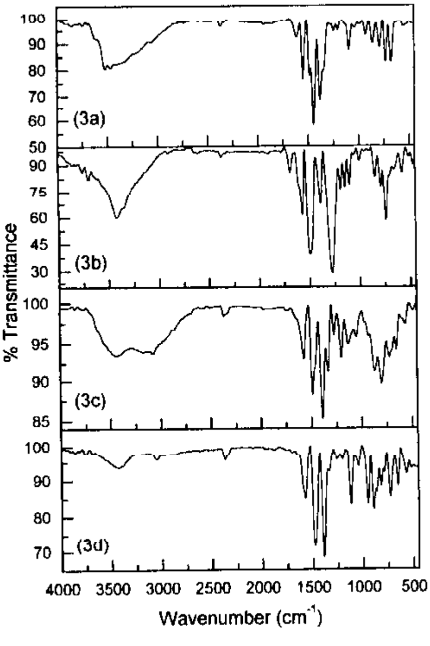

Fig. 3 IR Spectra of the complexes: a – $Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$; b – $Sr[(C_9H_4ONCl_2)_2]\cdot 1.5H_2O$; c – $Sr[(C_9H_5ONI_2)]\cdot 5H_2O$ and d – $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$

$Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$ and $Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$ should present bands due to symmetric and asymmetric H–OH stretching vibrations, but they could not be identified: all of the spectra contain bands in the region 3500 to 300 cm^{-1} that relate to the moisture content of the KBr used to prepare the pressed disks of the chelates.

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

Compound	Strontium %			Water %		Ligand %	
	Theor.	TG	AAS	Theor.	TG	Theor.	TG
$Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$	11.90	12.80	12.43	6.11	6.50	81.99	80.70
$Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$	25.42	25.15	25.33	7.84	7.21	66.74	67.64
$Sr[(C_9H_5ONI)_2]\cdot 5H_2O$	12.21	12.26	12.20	12.55	12.00	75.24	75.74
$Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$	20.30	19.65	19.83	5.22	5.01	74.48	75.34

Table 2 Results from elemental analysis

Compound	C %		H %		N %	
	Theor.	Exper.	Theor.	Exper.	Theor.	Exper.
$Sr[(C_9H_4ONBr_2)_2]\cdot 2.5H_2O$	29.35	31.91	1.79	1.83	3.80	3.93
$Sr[(C_9H_4ONCl_2)(OH)]\cdot 1.5H_2O$	31.36	33.73	2.34	2.08	4.06	4.27
$Sr[(C_9H_5ONI)_2]\cdot 5H_2O$	30.12	29.61	3.10	2.67	3.90	4.10
$Sr[(C_9H_4ONICl)(OH)]\cdot 1.25H_2O$	25.04	27.37	1.75	1.29	3.24	2.60

Conclusions

The presence of halogen on the 8-hydroxyquinoline ring resulted in changes in the thermal decompositions of the complexes, and also in diversity in the residues formed.

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References

1 J. F. Flagg, Organic Reagents used in Gravimetric and Volumetric Analysis, Interscience, New York, 1948.
2 J. I. Hoffman, Chemist. Analyst, 49 (1960) 126.
3 T. Moeller, Industrial and Engineering Chemistry, Analytical Edition, 15 (1943) 253.
4 K. Motojima and H. Has Hitan, Analytical Chemistry, 33 (1961) 48.
5 V. Alexeév, Análise Quantiativa, Livraria Lopes da Silva, 3ª Edição, Porto, 1983.
6 H. Irving and A. R. Pinnington, Journal of the Chemical Society, (1975) 285.
7 W. W. Wendlandt and G. R. Horton, Anal. Chem., 34 (1962) 1098.
8 C. T. Ramelo, R. Faez, C. A. Ribeiro and M. Spirandeli Crespi, Eclética Química, 20 (1995) 49.
9 A. I. Vogel, Textbook of Macro and Semimicro Qualitative Inorganic Analysis, 5th Ed. Longman London, 1979.
10 A. D. Cross and R. A. Jones, An Introduction to Practical Infra-Red Spectroscopy, 3rd Ed. Butterworths London, 1969.