



Spectroscopic characteristics and thermal properties of the complexes of 2-hydroxyphenylhydrazoacetanilide (2-HPHAAA) with Uranyl(II), and Thorium (IV)

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ABSTRACT

The spectroscopic characteristics (IR) and the thermal properties (TGA, DTG and DTA) of the solid complexes obtained by the reaction of 2-hydroxyphenylhydrazoacetanilide (2-HPHAAA) with Uranyl(II), and Thorium (IV) are reported and discussed.

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Keywords

Uranyl,
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Thermal analysis.

Introduction

The complexation reactions of lanthanides and actinides have been actively studied during last two to three decades. Increased interest in the separation of nuclear fission products in the fuel reprocessing and in the safe burial of reprocessing and in the safe burial or radioactive waste materials has created the need for understanding the behavior of these metal ions in aqueous solution [1,2].

The behavior of the lanthanides and actinides is mainly electrostatic in character and largely dependent upon the changes in metal ion hydration during the complex formation process.

Although the chemical properties of the lanthanides and actinides are quite similar but significant differences exist because the 5f-orbitals are less shielded than 4f-orbitals.

However in the solid state, the coordination number of the f-element cations can differ significantly from that in solution. Factors such as charge, size, and number of the ligands play an important role both in solid and solution systems. For example, in solid, the lack of shielding by the bulk solvent from the effect of other cations and ligands can result in different electrostatic balance within a crystal compared to solution systems.

Organic ligands form stronger complexes with the lanthanides and actinides than do inorganic ligands [3,4].

Experimental

Materials

Most of the chemicals used were of Analar grade, materials which are not generally provided into Analar grade were of the highest available purity.

Preparation of 2-HPHAAA

The ligand under investigation was prepared by coupling the diazonium salt of 2-aminophenol with acetoacetanilide in sodium acetate medium to give 2-hydroxyphenylhydrazoacetanilide (2-HPHAAA). The

crude product was recrystallized several times from dioxane. Brilliant brown crystals have been collected filtered and dried the melting point was 162°C. The results of elemental analysis were as follows: %cal./(found), %C 64.6/(64.89), %H 5.05/(5.21), and %N14.14/(14.46).

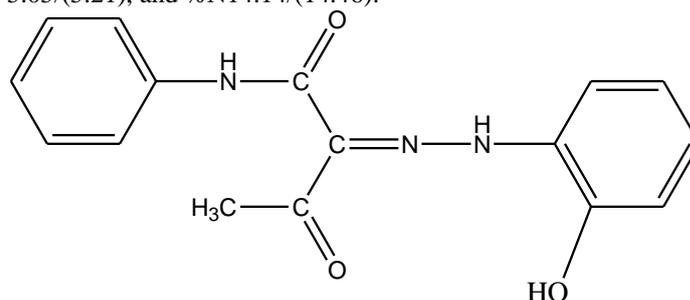


Fig.(1): Structure of 2-hydroxyphenylhydrazoacetanilide (2-HPHAAA)
Preparation of solid complexes

The solid complexes were prepared by mixing 40 ml of 0.2M solution of the ligand with 20 ml of 0.2M of metal ion solution as nitrate, at pH 5.00. The metal – ligand mixture was refluxed for about half an hour and then kept overnight to separate the metal complexes.

The collected complexes were washed several times with water and suitable solvent (ethanol or dioxane) to get rid of the excess ligand. Then the products were dried in air and stored in vacuum desiccator for several days. The measured melting points were found to be over 250°C.

Quantitative analysis of carbon, hydrogen, nitrogen, and metal were carried out at microanalysis center, Cairo University, Egypt. Table (1) gives the elemental analysis of the complexes.

The IR spectra were recorded as KBr discs on a Perkin – Elmer spectrometer 1430 radio recording at the central laboratory of faculty of girls, Ain shams university.

Table (1): Elemental analysis of the complexes.

Compound	%C	%H	%N	%M
[UO ₂ (C ₃₂ N ₆ O ₆ H ₂₆).2H ₂ O]	42.76 (42.90)	3.56 (3.69)	9.35 (9.48)	26.50 (26.15)
[Th(C ₃₂ N ₆ O ₆ H ₂₆).2H ₂ O]	44.76 (44.47)	3.03 (3.29)	9.79 (9.91)	27.04 (27.33)

The thermal stability of the solid complexes has been studied using TG, DTG, and DTA techniques. The measurements were made with Shimadzu TGA- 50 with sensitivity TG=10mg and both DTG, and DTA 1/5. The samples were heated in platinum crucibles, in nitrogen atmosphere at a heating rate of 20 deg. min⁻¹ up to 800°C using Al₂O₃ as a reference compound.

Results and Discussion

IR study:

When Hydrazo-β-diketone ligand is coordinated to a metal ion at least one additional atom is introduced to the ligand and vibrating system. It thus expected that the bond lengths, angles and interacting forces within the ligand would be altered at least slightly. This means that the infrared of the coordinated 2-HPHAAA ligand within UO₂²⁺ and Th⁴⁺ ions will differ from the free one. In this way the spectrum of the 2-HPHAAA will differ from that of the complexes compounds, due to its bonding to the central metal ion.

The comparison of the infrared of the organic ligand and its uranyl and thorium complexes will be helpful in identifying the structure of the solid complexes. In this investigation the meaningful characteristic region of the IR spectra will be discussed.

2-HPHAAA has various coordination sites as -OH, -NH-N=C-, and >C=O groups. The infrared of 2-HPHAAA shows a medium band around 3300cm⁻¹ due to the phenolic -OH and intramolecular hydrogen bonded stretch, is completely disappeared in the spectrum of uranyl and thorium complexes showing the coordination of hydroxyl group. In addition, the infrared spectra of these two solid complexes are characterized by the presence of strong band between 3600-2900 cm⁻¹ attributed to the presence of coordinated water molecules. The coordinated water bond band is overlapped with both stretching frequencies of -NH and -CH bands. The appearance of new medium band at 847cm⁻¹ in both complexes spectra, is attributed rocking modes of coordinated water [5-9].

The other coordination site which can take part in complexation is the hydrazone group (-NH-N=). The strong evidence of sharing of this group can be seen from the band at 1598 cm⁻¹ in the spectrum of ligand which may be due to (ν_{>C=N}) azomethine 1593cm⁻¹, shifts to lower frequencies at 1590 cm⁻¹ and 1591 cm⁻¹ for uranyl and thorium respectively. This confirms the conclusion that coordination occurs through nitrogen atom of hydrazone group.

Also, the appearance of a new band for both complexes at lower frequencies between 500- 600 cm⁻¹ may be taken as an evidence for the presence of M-N band.

The (ν_{>C=O}) observed at 1642 cm⁻¹ in the spectrum of the free ligand is shifted to lower frequencies at 1634 cm⁻¹ and 1637 cm⁻¹ for both uranyl and thorium chelates respectively, denoting the rule of this group in coordination processes. Other evidence confirming this argument, is the appearance of metal-oxygen vibration at 440 cm⁻¹ and 439 cm⁻¹ for uranyl and thorium complexes respectively as those given by Nokamoto [5,10].

The weak band of hydrazone structure at 300-3400 cm⁻¹ may be overlapped with the broad ν_{OH} band. Also, the band

position of conjugated >C=N [3,11] was variable in the region 1500-1600 cm⁻¹ for the investigated ligand [12].

A new band appears between 500-600 cm⁻¹ which may be due to the presence of metal-nitrogen bond [13]. The IR spectra of the solid complexes indicate the presence of coordinated water molecules, since there is a strong broad band in the frequency range 3300-3600 cm⁻¹.

The strongest evidence for the complexation of uranyl ion with 2-HPHAAA is the appearance of characteristic stretching frequency of dioxouranium ion in the IR spectra of the formed complex. The strong frequency (ν_{O=U=O}) at 875 cm⁻¹ appeared in the spectra of the uranyl complex can be assigned to the asymmetric stretching frequency of UO₂²⁺ [8,10,14-16].

Table(2): Infrared absorption spectra of organic ligand and its Uranyl(II) and Thorium(IV) complexes.

Compound	ν _{OH}	π _{H₂O}	>C=N	>C=O	M-N	M-O
Ligand 2HPHAAA	3350 w.b	--	1598 m.b	1642 s.b	--	--
UO ₂ ²⁺ -Complex	3340 b.b	847 m.b	1590 s.b	1634 s.b	518 w.b	440 w.b
Th ⁴⁺ -Complex	3345 b.b	847 s.b	1592 s.b	1637 s.b	525 w.b	439 w.b

TGA and DTA study of the complexes:

The pyrolysis curve of the solid complex is characterized as follows: At the temperature range 105-135°C, the corresponding weight loss equals to 3.90% which is attributed to the loss of two moles of coordinated water (exothermic process). At the temperature range between 280-420°C, the weight loss which equals to 35.40%, results from melting, decomposition of four phenyl rings from ligand molecules (exothermic process). The final stage at the temperature range between 420-550°C with the percentage weight loss equaling 28.20% is due to the decomposition of the complex with the formation of UO₃ as final pyrolysis product (exothermic process).

In case of thorium ion complex, the observed weight loss (4.00%) within the temperature range 105 -140°C may correspond to loss of two coordinated water molecules (exothermic process). After that, in the range 230 - 325°C, the observed weight loss (36.00%) is due to loss of four phenyl groups (exothermic process). In the range 370 - 490°C the observed weight loss (25.40%) includes the decomposition of the complex along the chelate bond with the consequent loss of the formation of ThOCO₃ as a final product (exothermic process) [14, 17].

Conclusion

The IR spectra for 2-HPHAAA and its complex with UO₂²⁺ and Th⁴⁺ have been recorded. It gives good evidence about the coordination of the components. Thermal analysis was carried out for the complexes of UO₂²⁺ and Th⁴⁺ with 2-HPHAAA to show the chemical changes and physical processes in order to have a complete information about the structure of the prepared complexes.

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