

## Synthesis and Characterization of Dioxouranium (VI) complexes with Salicylyl hydrazine based Mixed Ligands

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**Abstract:** Mixed ligand complexes of Dioxo Uranium [UO<sub>2</sub>(VI)] with Salicylyl hydrazine (SH) and its derivatives as primary ligands and two different anions viz., nitrate and thiocyanate as secondary ligands were synthesized. These complexes were characterized by elemental analysis, molar conductance, IR spectra TG and DTG data. In these complexes the primary ligands salicylyl hydrazine (SH), acetyl salicylyl hydrazine (ASH) and benzoyl salicylyl hydrazine (BSH) act as neutral bidentate ligand and the secondary ligands, viz., the monovalent ions NO<sub>3</sub><sup>-</sup> and NCS<sup>-</sup> act as unidentate ligands.

**Keywords:** BSH, DTG, Molar conductance, SH, TG

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### I. INTRODUCTION

The ligands salicylyl hydrazine(SH), acetyl salicylyl hydrazine(ASH) and benzoyl salicylyl hydrazine(BSH) can act either as monovalent bidentate ligands or neutral bidentate ligands towards the lanthanide(III) ions under different experimental conditions <sup>[1,2]</sup>. A search through the literature has revealed that no actinide complexes with these ligands have been prepared so far. Therefore, synthesis of some complexes of actinide ion UO<sub>2</sub>(VI) is worthwhile.

The carbonyl oxygen atom in the ligands SH, ASH and BSH is H-bonded to the phenolic -OH group as evident from IR spectral studies. Hence of special interest in these ligands. Also, four potential donor atoms, viz., carbonyl oxygen, phenolic oxygen, imino nitrogen and amino nitrogen present in ligand SH as shown in Fig.1. The H-bonded structure of BSH (Fig.2) and keto-enol tautomerism exhibited by ASH (Fig.3) are shown below. The ligands ASH and BSH are structurally similar to the ligand SH and thus the study of these ligands towards Dioxo uranium metal ion in presence of two coordinating ions needs attention.

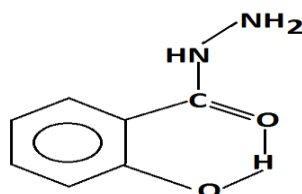


Fig.1 Structure of ligand SH

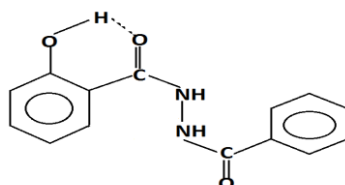


Fig.2 Structure of BSH

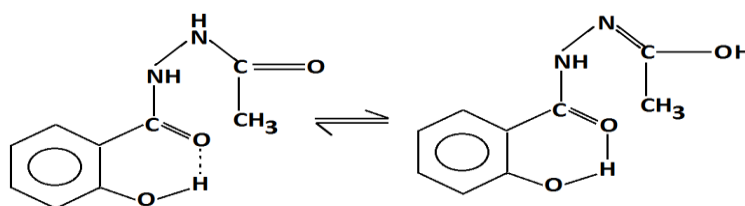


Fig.3 Keto- Enol tautomerization in ASH

## II. MATERIALS AND METHODS

### 2.1 Chemicals and Methods

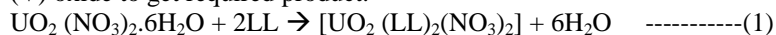
All the chemicals used were of GR/AR grade quality obtained from Merck chemicals. All the solvent used were purified by standard methods<sup>[3]</sup>. The metal content of the complexes was estimated by oxalate- oxide method<sup>[4]</sup>. The nitrate content of the complexes was determined gravimetrically by using nitron reagent<sup>[5]</sup>. The thiocyanate content was determined gravimetrically as AgSCN<sup>[4]</sup>. TG- DTG techniques have been used for the comparison of the thermal behaviour of complexes viz., [UO<sub>2</sub> (ASH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] and [UO<sub>2</sub> (BSH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]. IR spectra of the ligand and complexes were recorded in KBr on a Perkin- Elmer 882 IR spectrometer in the range 4000-400 cm<sup>-1</sup>. In order to determine the molar mass of complexes Rast method was employed, where camphor is used as the solvent

### 2.2 Synthesis of Ligand

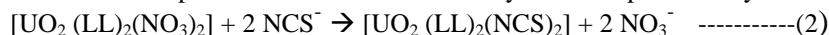
The ligands SH, ASH and BSH were prepared by standard methods<sup>[2]</sup>.

### 2.3 Synthesis of Metal complexes

The complexes were prepared by refluxing methanolic solution of the nitrates of UO<sub>2</sub> (VI) with primary ligands in the mole ratio 1:2 according to the equation (1). The complexes have to be dried in vacuo over phosphorus (V) oxide to get required product.



The nitrate complexes are converted into thiocyanate complexes<sup>[6]</sup> by substitution reaction based on eqn. (2)



Where LL = SH, ASH, BSH

## III. RESULTS AND DISCUSSION

### 3.1 Elemental analysis

All the complexes are non- hygroscopic solids, with varying colours. The complexes are moderately soluble in acetonitrile, ethanol, methanol and nitrobenzene. Also, these are insoluble in benzene and petroleum ether. The analytical data are given in Table.1

Table.1 Analytical data of UO<sub>2</sub> (VI) Complexes

Complex	Colour	Mol. Wt. Found (Calcd.)	Percentage Analysis Found (Calcd.)		
			Metal	Nitrate	Thio cyanate
[UO <sub>2</sub> (SH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Yellow	680 (698)	33.9 (34.0)	17.3 (17.6)	-
[UO <sub>2</sub> (SH) <sub>2</sub> (NCS) <sub>2</sub> ]	Pale Brown	679 (690)	34.1 (34.4)	-	16.1 (16.7)
[UO <sub>2</sub> (ASH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Yellow	778 (782)	29.1 (29.6)	14.9 (15.7)	-
[UO <sub>2</sub> (ASH) <sub>2</sub> (NCS) <sub>2</sub> ]	Brown	768 (774)	29.1 (29.9)	-	14.1 (14.8)
[UO <sub>2</sub> (BSH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Pale Brown	891 (906)	25.7 (26.2)	13.2 (13.7)	-
[UO <sub>2</sub> (BSH) <sub>2</sub> (NCS) <sub>2</sub> ]	Pale Yellow	880 (897)	25.9 (26.5)	-	12.6 (12.9)

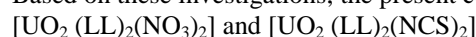
### 3.2 Molar Conductivity

Molar conductance values of Dioxo uranium complexes in acetonitrile, methanol and nitrobenzene are in a range (Table.2). which corresponds to those of non- electrolyte in these solvents<sup>[7]</sup>. The conductance values suggest that both the anions act as additional ligands in these complexes and therefore all the complexes are neutral.

**Table 2.** Molar Conductance data of the complexes

Complex	Molar conductance ( $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )		
	$\text{CH}_3\text{CN}$	$\text{CH}_3\text{OH}$	$\text{PhNO}_2$
$[\text{UO}_2(\text{SH})_2(\text{NO}_3)_2]$	64	100	6.5
$[\text{UO}_2(\text{SH})_2(\text{NCS})_2]$	60	103	7.2
$[\text{UO}_2(\text{ASH})_2(\text{NO}_3)_2]$	61	108	12
$[\text{UO}_2(\text{ASH})_2(\text{NCS})_2]$	55	110	16
$[\text{UO}_2(\text{BSH})_2(\text{NO}_3)_2]$	41	99	7
$[\text{UO}_2(\text{BSH})_2(\text{NCS})_2]$	46	98	12

Based on these investigations, the present complexes can be formulated as follows.



Where LL= SH, ASH, BSH

### 3.3 IR Spectra

IR Spectrum provides valuable information regarding the nature of functional groups coordinated to the metal atom. The selected IR spectral data of the ligand and complexes given in the Table 3.

**Table.3** IR spectral data of SH, ASH, BSH and their  $\text{UO}_2(\text{VI})$  Complexes

Ligand SH	SH Complexes		Ligand ASH	ASH Complex		Ligand BSH	BSH Complex		Tentative Assignments
	$\text{UO}_2(\text{NO}_3)_2$	$\text{UO}_2(\text{NCS})_2$		$\text{UO}_2(\text{NO}_3)_2$	$\text{UO}_2(\text{NCS})_2$		$\text{UO}_2(\text{NO}_3)_2$	$\text{UO}_2(\text{NCS})_2$	
3440 br	3410 br	3410 br	-	-	-	-	-	-	$\nu_{(\text{NH})}$ amine
3370 w	3360 w	3360 w	-	-	-	-	-	-	
-	-	-	3330 br	-	-	-	-	-	$\nu_{(\text{OH})}$ enolic
3300 w	3300 w	3300 w	3427 s	3427 s	3427 s	3300 vs	3325 vs	3328 vs	$\nu_{(\text{NH})}$ imine
3275 br	3275 br	3275 br	3200 br	3198 br	3198 br	3230 br	3230 br	3230 br	$\nu_{(\text{OH})}$ phenolic
-	-	2050 vs	-	-	2050 vs	-	-	2050 vs	$\nu_{(\text{CN})}$ of NCS
-	-	-	1684 s	1670 s	1671 s	-	-	-	$\nu_{(\text{C}-\text{O})}$ acetyl
-	-	-	-	-	-	1682 vs	1666 s	1668 s	$\nu_{(\text{C}-\text{O})}$ benzoyl
1668 s	1641 s	1640 s	1648 s	1633 s	1635 s	1648 s	1633 s	1633 s	$\nu_{(\text{C}-\text{O})}$ salicylyl
-	-	-	1575 s	-	-	-	-	-	$\nu_{(\text{C}-\text{N})}$
1540 s	1538 s	1540 s	1535 s	1535 s	1535 s	1520 s	1518 s	1520 s	$\nu$ phenyl
1490 m	1490 m	1490 m	1495 s	1495 s	1495 s	1492 s	1492 s	1492 s	
-	1450 s	-	-	1455 m	-	-	1452 m	-	$\nu_4(\text{NO}_3)$
1370 vs	1384 vs	1384 vs	1370 vs	1385 vs	1385 vs	1384 vs	1387 vs	1387 vs	$\nu_{(\text{C}-\text{N})}$
-	1320 m	-	-	1310 m	-	-	1320 m	-	$\nu_1(\text{NO}_3)$
1185 s	1188 s	1188 s	1168 m	1168 m	1168 m	1168 w	1168 w	1168 w	$\nu_{(\text{N}-\text{N})}$
-	935 vs	930 vs	-	935 vs	930 vs	-	935 vs	932 vs	$\nu_3(\text{O}=\text{U}=\text{O})$
-	1050 w	-	-	1030 s	-	-	1030 s	-	$\nu_2(\text{NO}_3)$
-	-	790 m	-	-	800 m	-	-	850 m	$\nu_{(\text{CS})}$ of NCS
-	-	450 w	-	-	450 w	-	-	450 w	$\nu_{(\text{NCS})}$

br – broad; m – medium; s -strong; vs -very strong; w – weak

IR spectra of ligand (SH) exhibits two strong bands at  $3440 \text{ cm}^{-1}$  and  $3370 \text{ cm}^{-1}$  which corresponds to  $\nu_{(\text{NH})}$  mode of amino and imino group respectively. In the spectra of complexes  $\nu_{(\text{NH})}$  mode of amino group has lower values, on the other hand  $\nu_{(\text{NH})}$  mode of imine is retained. It suggests the coordination of nitrogen atom of primary amino group of the ligand to the metal ion. A broad band at  $3275 \text{ cm}^{-1}$  of the ligand SH is attributed to stretching vibration of phenolic OH. Broad nature of the band indicates that H-bonding is present between the phenolic OH and carbonyl oxygen. This band is retained in the complexes and indicates the non- involvement of phenolic oxygen in bonding.

A strong band at  $1668 \text{ cm}^{-1}$  in the spectrum of ligand is assigned to stretching vibration of the carbonyl group. In the complexes, the carbonyl stretching frequency is present at a lower region ( $1650\text{-}1630 \text{ cm}^{-1}$ ) indicating the metal- ligand coordination through carbonyl oxygen atoms.

The IR spectra of ASH and its complexes exhibit a strong intense peak at  $3427\text{ cm}^{-1}$ . This band is assigned to NH mode of vibration of imino groups. The sharp band at  $3330\text{ cm}^{-1}$  in the ligand is assigned to the stretching vibration of O- H group present in the enol form of the ligand. This has no parallel band in the complexes suggesting the existence of ligand as keto form only. Therefore, it is suggestive that although ASH can exist in the Keto- enol form (Fig.2) when it is free, it can only exist in the keto form when it is complexed with the metal ions. This is further supported by the appearance of a band at  $1575\text{ cm}^{-1}$  in the spectrum of the ligand characterizing the  $\nu_{(C-N)}$  mode of vibration which has no parallel band in the spectra of the complexes. The broad band at  $3200\text{ cm}^{-1}$ , both in the ligand and in the complexes, is assigned to the stretching vibration of phenolic O- H which is hydrogen bonded to the carbonyl oxygen as shown in Fig.2

The strong band at  $1684\text{ cm}^{-1}$  in the spectrum of the ligand is attributed to the acetyl- carbonyl stretching frequency in the keto form of the ligand. This band is shifted to a lower region in the complexes ( $1670\text{ cm}^{-1}$ ) indicating that ASH is coordinated to the metal ion through acetyl- carbonyl oxygen atom. The strong band at  $1648\text{ cm}^{-1}$  in the spectrum is assigned to the stretching frequency of salicylyl carbonyl group. This band appears in the lower region than the expected region due to strong intra molecular hydrogen bonding with the phenolic -OH group. In the spectra of the complexes, this band is slightly shifted to lower region at  $1635\text{ cm}^{-1}$  which indicates that the salicylyl carbonyl group is coordinated to the metal ions. Another strong band at  $1370\text{ cm}^{-1}$  in the spectrum of the ligand is assigned to  $\nu_{(C-N)}$  which has a higher value in the complexes due to slight increase in its bond order because of the coordination of carbonyl oxygen. Thus, ASH acts as the bidentate neutral ligand coordinating through the carbonyl oxygen atoms of both the acetyl and salicylyl groups.

IR spectra of BSH and its complexes exhibit a strong intense band at  $3330\text{ cm}^{-1}$  corresponds to the  $\nu_{(NH)}$  bond. The broad band at  $3230\text{ cm}^{-1}$  of the ligand and the complexes corresponds to the stretching vibration of phenolic - OH. The broad nature of this band indicates that hydrogen bonding is present between the phenolic OH and carbonyl oxygen like the other two ligands. The structure of this ligand is given in the Fig.3

The strong band at  $1682\text{ cm}^{-1}$  in the ligand BSH is assigned to the stretching vibration of the benzoyl carbonyl group. This carbonyl stretching vibration is present at a lower region in the complexes ( $1666\text{ cm}^{-1}$ ) indicating that the ligand is coordinated to the metal ion through this carbonyl oxygen. The strong band at  $1648\text{ cm}^{-1}$  is assigned to the  $\nu_{(C-O)}$  mode of the salicylyl carbonyl. This band appears in the lower region than the expected region due to strong intra molecular hydrogen bonding with the phenolic - OH group. This band is also slightly shifted to the lower region ( $1633\text{ cm}^{-1}$ ) in the complexes which shows the coordination of the salicylyl carbonyl group of BSH with the metal ion. These data prove the neutral bidentate nature of BSH coordinating through the carbonyl oxygen atoms of benzoyl and salicylyl groups.

In addition to the bands assigned above, the nitrate complexes of these ligands with  $UO_2(VI)$  show three additional bands at  $1450, 1320$  and  $1030\text{ cm}^{-1}$  which are absent in the spectra of the ligand and in the thiocyanate complexes. These three bands are  $\nu_4, \nu_1$  and  $\nu_2$  modes of the coordinated nitrate ion. A difference of  $130\text{ cm}^{-1}$  between  $\nu_4$  and  $\nu_1$  mode of vibration shows the coordination of nitrate ion in a unidentate fashion<sup>[8]</sup>.

The IR spectra of all the three thiocyanate complexes of these ligands with  $UO_2(VI)$  exhibit three additional bands at  $2050, 850$  and  $450\text{ cm}^{-1}$  which are assigned to  $\nu_{(CN)}, \nu_{(CS)}$  and  $\nu_{(NCS)}$  modes respectively of the coordinated thiocyanate ions. It has been established that  $\nu_{(CN)}$  acquires around  $2050\text{ cm}^{-1}$  in N- bonded complexes. Whereas the S- bonded complexes appear around  $2100\text{ cm}^{-1}$ . Moreover,  $\nu_{(CS)}$  mode appears in the range  $860-750\text{ cm}^{-1}$  for N- bonded complexes while it appears in the range  $720-680\text{ cm}^{-1}$  for S- bonded complexes. N- bonded complexes also exhibit a single sharp band corresponding to  $\nu_{(NCS)}$  mode at  $450\text{ cm}^{-1}$  whereas S- bonded complexes show several bands around  $460\text{ cm}^{-1}$ . In these evidences, thiocyanate ions of the present complexes are coordinated unidentately through N- atom and not through S- atom<sup>[9,10]</sup>. The IR spectra of Dioxo uranium (VI) complexes have an additional strong band around  $935-930\text{ cm}^{-1}$  which have no parallel band in the spectra of the ligand. The band is assigned to the asymmetric stretching vibration of  $UO_2(VI)$  ions. Absence of  $\nu_3(O=U=O)$  shows that oxygen atoms of  $UO_2(VI)$  moiety are in trans position in the present complexes.

### 3.4 Thermal Study

The Thermal behaviour of the complexes has been investigated using thermogravimetric techniques in the temperature range from ambient to  $700^\circ\text{C}$ . Thermal decomposition data of complexes is given in Table.4

**Table.4** Thermal Decomposition Data of the Complexes

Complex	Plateau in TG (0C)	Peaks in DTG (0C)	Peak width in DTG (0C)	Final Residue	Final Loss (%)		
					TG	Independent pyrolysis	Theoretical
[UO <sub>2</sub> (ASH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Up to 180	190	170- 210	U <sub>3</sub> O <sub>8</sub>	67	66.3	65.5
	Above 540	530	470- 550				
[UO <sub>2</sub> (BSH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ]	Up to 220	270	210- 300	U <sub>3</sub> O <sub>8</sub>	70	70.8	69.0
	Above 490	480	470- 500				

UO<sub>2</sub> (VI) complexes undergoes two stage decomposition. The complexes are stable up to 220<sup>0</sup>C with a slightly lower stability for [UO<sub>2</sub>(ASH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]. The decomposition is over by 540<sup>0</sup>C for [UO<sub>2</sub>(ASH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] and 490<sup>0</sup>C for [UO<sub>2</sub>(BSH)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]. The final residues obtained for uranyl complexes are found to be U<sub>3</sub>O<sub>8</sub>. The TG-DTG data supports the 1:2 ratios between the metal and ligand in the complex and has displayed the composition of the thorium complex.

#### IV. CONCLUSION

Mixed ligand complexes of UO<sub>2</sub> (VI) with Salicylyl hydrazine (SH) and its derivatives as primary ligands and two different anions viz., nitrate and thiocyanate as secondary ligands were synthesized. These complexes were characterized with analytical data and spectral studies. Conductivity measurements showed that all thorium complexes are non-electrolytes. IR spectral studies revealed the unique character of ligands- SH, ASH, BSH towards Th(IV) metal ion. They act as neutral bidentate ligands towards UO<sub>2</sub>(VI) in presence of anionic ligands viz., nitrate and thiocyanate. In all these complexes nitrate and thiocyanate ions act as monovalent unidentate ligands. Thus, a coordination number of 8 has been assigned to the metal ion in these complexes.

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