Synthesis and Characterization of Some Mixed Ligand Complexes of Thorium(IV) and Dioxouranium(VI) with Salicylylhydrazine and its Dervatives

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A series of 12 mixed ligand complexes of Th(IV) and UO_2(VI) with salicylylhydrazine (SH) and its derivatives as primary ligands and two different anions, *viz.*, nitrate and thiocyanate as secondary ligands have been synthesised and characterised on the basis of elemental analysis, molecular weight, molar conductance, IR spectral, TG and DTG data. These complexes have the general formulae $[Th(LL)_2(NO_3)_4]$, $[Th(LL)_2(NCS)_4]$, $[UO_2(LL)_2(NO_3)_2]$ and $[UO_2(LL)_2(NCS)_2]$ where LL = SH, ASH, BSH. In these complexes the primary ligands salicylylhydrazine (SH), acetyl salicylylhydrazine (ASH) and benzoyl salicylylhydrazine (BSH) act as neutral bidentate ligand and the secondary ligands, *viz.*, the monovalent anions NO_3^- and NCS^- act as unidentate ligands.

INTRODUCTION

It has been reported that the ligands salicylylhydrazine (SH), acetyl salicylylhydrazine (ASH) and benzoyl salicylylhydrazine (BSH) can act either as monovalent bidentate ligands or neutral bidentate ligands towards the lanthanide(III) ions under different experimental conditions.[1, 2] A search through the literature has revealed that no actinide complexes with these ligands have been prepared so far. Therefore, as part of our programme of the synthesis and characterization of Th(IV) and UO_2(VI) complexes, we thought it would be fruitful to synthesize some complexes of two actinide ions, Th(IV) and UO_2(VI) using salicylylhydrazine and its acetyl as well as benzoyl derivative such as ASH and BSH as the primary ligands and two different coordinating anions, *viz.*, nitrate and thiocyanate as the secondary ligands.

The ligands SH, ASH and BSH are of special interest in that the carbonyl-oxygen atom is H-bonded to the phenolic-OH group as evident from the IR spectral studies. Moreover the ligand SH has four potential donor atoms, viz., carbonyl-

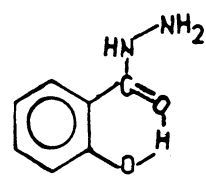


Fig. 1

oxygen, phenolic-oxygen, imino-nitrogen and amino-nitrogen as shown in Fig. 1. The ligands ASH and BSH are structurally similar to SH except that one of the H atoms of imino group in SH is replacted by an acetyl or benzoyl group. Therefore ASH and BSH have five donor atoms each *viz.*, two carbonyl oxygen atoms, phenolic oxygen and two imino nitrogen atoms. ASH undergo keto-enol

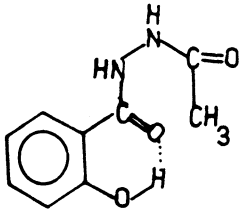
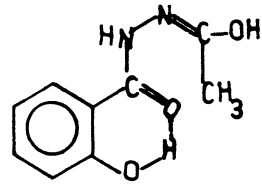


Fig. 2



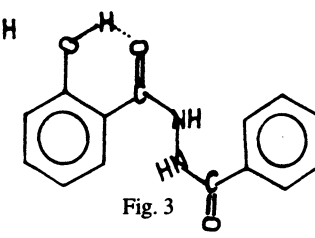


Fig. 3

tautomerism as shown in Fig. 2. The H-bonded structure of BSH can be represented as shown in Fig. 3.

Therefore it is interesting to investigate the coordination behaviour of these three closely related primary ligands towards two different metal ions, Th(IV) and UO_2(VI) in presence of two coordinating anions, nitrate and thiocyanate.

EXPERIMENTAL

The ligands SH, ASH and BSH are prepared by literature method.[2] On treatment of the nitrates of Th(IV) and UO_2(VI) with the primary ligands in the mole ratio 1:2 in methanol, the corresponding nitrato complexes are formed as per equations (1) and (2).

$$Th(NO_3)_4 \cdot 4H_2O + 2LL \rightarrow [Th(LL)_2(NO_3)_4] + 4H_2O \quad (1)$$

$$UO_2(NO_3)_2 \cdot 6H_2O + 2LL \rightarrow [UO_2(LL_2)(NO_3)_2] + 6H_2O \quad (2)$$

The complexes have to be dried *in vacuo* over phosphorus(V) oxide to get required products.

The nitrate complexes are converted to thiocyanate[6] complexes by substitution reaction (3) and (4).

$$[Th(LL)_2(NO_3)_4] + 4NCS^- \rightarrow [Th(LL)_2(NCS)_4] + 4NO_3^- \quad (3)$$

$$[UO_2(LL)_2(NO_3)_2] + 2NCS^- \rightarrow [UO_2(LL)_2(NCS)_2] + 2NO_3^- \quad (4)$$

where LL may be SH, ASH or BSH.

Analytical, molecular weight and molar conductance data of the complexes are presented in Table-1, while IR spectral details are given in Table-2 and TG-DTG data in Table-3. A total of 12 complexes have been isolated, all of which are non-hygroscopic solids, with varying colours (Table-1). The complexes are moderately soluble in acetonitrile, ethanol, methanol and nitrobenzene and insoluble in benzene, carbon tetrachloride and petroleum ether.

In the present investigation, the TG-DTG techniques have been used for the comparison of the thermal behaviour of some representative complexes of Th(IV) and UO_2(VI), *viz.*, $[Th(SH)_2(NO_3)_4]$, $[UO_2(ASH)_2(NO_3)_2]$ and $[UO_2(BSH)_2(NO_3)_2]$. The TG and DTG curves of these complexes were recorded simultaneously on a thermal analyser from ambient to 700°C. The weight % *vs.* temperature curves obtained were redrawn in approprite scales. Independent pyrolysis experiment in air was also carried out for each of the complexes studied. For this a known weight of the complex (0.2 g) was heated in a silica crucible up to 700°C for 2 h. From the weight of the residue the percentage loss of weight was calculated in each case, which was compared with the percentage loss of weight obtained from the respective TG experiment.

TABLE-1
ANALYTICLA DATA OF COMPLEXES

Complex (Colour)	Mol. wt. Found (Calcd.)	% Analysis, Found (Calcd.)			Melting point (°C)	Molar conductance in ohm^{-1} cm^2 $mole^{-1}$		
		Metal	Nitrate	Thio-cyanate		CH_3CN	CH_3OH	$PhNO_2$
$[Th(SH)_2(NO_3)_4]$ (white)	742 (784)	29.1 (29.5)	31.2 (31.6)	—	205	67	108	7.5
$[Th(SH)_2(NCS)_4]$ (pale pink)	782 (768)	29.8 (30.2)	—	29.8 (30.2)	225	57	106	8.5
$[Th(ASH)_2(NO_3)_4]$ (dark pink)	850 (868)	26.3 (26.7)	27.8 (28.5)	—	180	48	112	6.5
$[Th(ASH)_2(NCS)_4]$ (cream)	840 (852)	26.9 (27.2)	—	26.8 (27.2)	169	52	115	14
$[Th(BSH)_2(NO_3)_4]$ (pale pink)	975 (992)	22.8 (23.3)	24.8 (25.0)	—	272	40	102	10
$[Th(BSH)_2(NCS)_4]$ (cream)	865 (876)	23.1 (23.7)	—	23.1 (23.7)	280	38	98	8
$[UO_2(SH)_2(NO_3)_2]$ (yellow)	680 (698)	33.9 (34.0)	17.3 (17.7)	—	240	64	100	6.5
$[UO_2(SH)_2(NCS)_2]$ (pale brown)	679 (690)	34.1 (34.4)	—	16.1 (16.8)	229	60	103	7.2
$[UO_2(ASH)_2(NO_3)_2]$ (yellow)	778 (782)	29.1 (29.6)	14.9 (15.8)	— —	195	61	108	12
$[UO_2(ASH)_2(NCS)_2]$ (brown)	768 (774)	29.1 (29.9)	—	14.1 (14.9)	175	55	110	16
$[UO_2(BSH)_2(NO_3)_2]$ (pale brown)	891 (906)	25.7 (26.2)	13.2 (13.6)	—	265	41	99	7
$[UO_2(BSH)_2(NCS)_2]$ (pale yellow)	880 (898)	25.9 (26.5)	—	12.6 (12.9)	275	46	98	12

Thorium and uranium contents of the complexes were determined by oxalate-oxide method.[7] Nitrate was determined as nitron-nitrate using nitron reagent.[8]

Thiocyanate was determined as silver thiocyanate from alkali thiocyanate solution using $AgNO_3$ in presence of HNO_3. Molar conductances of the complexes in acetonitrile, methanol and nitrobenzene (10^{-3} M solutions) were measured at room temperature (28 ± 2°C). The IR spectra of the ligand and the complexes were recorded in KBr on a Perkin-Elmer 882 IR spectrometer in the range 4000–400 cm^{-1}. Molecular weights of the complexes were determined by Rast method using camphor as the solvent.[8] The TG and DTG curves of the complexes were recorded on a thermal analyser from ambient to 700°C.

RESULTS AND DISCUSSION

Molar conductance values of the complexes in acetonitrile, methanol and nitrobenzene are in the ranges corresponding to those of non-electrolytes in these solvents.[3] The conductance values suggent that both the anions act as additional ligands in these complexes and therefore all the complexes are neutral. From the analytical, molecular weight and conductance data (Table-1), the complexes have one of the following general formulae:

$[Th(LL)_2(NO_3)_4]$, $(Th(LL)_2(NCS)_4]$, $[UO_2(LL)_2(NO_3)_2]$ and $[UO_2(LL)_2(NCS)_2]$

where LL= bidentate neutral ligands, viz., SH, ASH and BSH.

Important IR spectral bands of the ligands and the complexes are presented in Table-2. The spectrum of the ligand salicylylhydrazine (Table-2) exhibits two strong bands at 3440 cm^{-1} and 3370 cm^{-1} which correspond to the ν(NH) mode of the amino and the imino group respectively. In the spectra of the complexes ν(NH) mode of amino group has lower values (3410 cm^{-1} and 3360 cm^{-1}) and ν(NH) mode of imine is retained, suggesting that the nitrogen atom of primary amino group of the ligand is coordinated to the metal ion. The broad band at 3275 cm^{-1} of the ligand SH is attributed to the stretching vibration of phenolic OH. The broad nature of this band indicates that H-bonding is present between the phenolic —OH and carbonyl oxygen. This band is retained in the complexes. Hence the phenolic oxygen is not involved in bonding.

The strong band at 1668 cm^{-1} observed in the spectrum of the ligand is assigned to the stretching vibration of the carbonyl group. In the complexes, the carbonyl stretching frequency is present at a lower region (1650–1640 cm^{-1}) indicating that the ligand is coordinated to the metal ion through the carbonyl oxygen. Hence SH acts as a bidentate neutral ligand coordinating through the amino-nitrogen and the carbonyl-oxygen atoms.

The IR spectra of acetyl salicylylhydrazine (ASH) and its complexes (Table-2) exhibit a strong intense peak at 3472 cm^{-1}. This band is assigned to the NH mode of vibration of imino groups. The sharp band at 3330 cm^{-1} in the ligand is assigned to the stretching vibration of the O—H group present in the enol form of the ligand. This has no parallel band in the complexes suggesting that the ligand exists only in the keto form in complexes. Therefore, it is suggestive that although ASH can exist in the keto-enol form (Fig. 2) when it is free, it can exist only in the keto form when it is complexed with the metal ions. This is further supported by the appearance of a band at 1575 cm^{-1} in the spectrum of the ligand characterizing

TABLE-2
IR SPECTRAL BANDS (cm^{-1}) OF SH, ASH, BSH AND THEIR Th^{4+} and UO_2^{2+} COMPLEXES

Ligand SH	SH complexes				Ligand ASH	ASH complexes				Ligand BSH	BSH complexes				Tentative assignments
	$Th(NO_3)_4$	$Th(NCS)_4$	$UO_2(NO_3)_2$	$UO_2(NCS)_2$		$Th(NO_3)_4$	$Th(NCS)_4$	$UO_2(NO_3)_2$	$UO_2(NCS)_2$		$Th(NO_3)_4$	$Th(NCS)_4$	$UO_2(NO_3)_2$	$UO_2(NCS)_2$	
3440 br 3370 w	3410br 3360 w	3410 br 3360 w	3410 br 3360 w	3410 br 3360 w	—	—	—	—	—	—	—	—	—	—	ν(NH) (amine)
—	—	—	—	—	3330 br	—	—	—	—	—	—	—	—	—	ν(OH) (enolic)
3300 w	3300 w	3300 w	3300 w	3300 w	3427 s	3427 s	3425 s	3427 s	3427 s	3330 vs	3320 vs	3325 vs	3325 vs	3328 vs	ν(NH) (imine)
3275 br	3275 br	3275 br	3275 br	3275 br	3200 br	3198 br	3198 br	3198 br	3198 br	3230 br	3230 br	3230 br	3230 br	3230 br	ν(OH) (phenolic)
—	—	2050 vs	—	2050 vs	—	—	2050 vs	—	2050 vs	—	—	2050 vs	—	2050 vs	ν(CN) (of NCS)
—	—	—	—	—	1684 s	1670 s	1672 s	1670 s	1671 s	—	—	—	—	—	ν(C–O) (acetyl)
—	—	—	—	—	—	—	—	—	—	1682 vs	1666 s	1668 s	1666 s	1668 s	ν(C–O) (benzoyl)
1668 s	1640 s	1650 s	1641 s	1640 s	1648 s	1635 s	1635 s	1633 s	1635 s	1648 s	1635 s	1633 s	1633 s	1633 s	ν(C–O) (salicylyl)

Ligand SH	SH complexes				Ligand ASH	ASH complexes				Ligand BSH	BSH complexes				Tentative assignments
	$Th(NO_3)_4$	$Th(NCS)_4$	$UO_2(NO_3)_2$	$UO_2(NCS)_2$		$Th(NO_3)_4$	$Th(NCS)_4$	$UO_2(NO_3)_2$	$UO_2(NCS)_2$		$Th(NO_3)_4$	$Th(NCS)_4$	$UO_2(NO_3)_2$	$UO_2(NCS)_2$	
—	—	—	—	—	1575 s	—	—	—	—	—	—	—	—	—	ν(C–N)
1540 s 1490 m	1540 s 1490 m	1540 s 1490 m	1538 s 1490 m	1540 s 1490 m	1535 s 1495 s	1535 s 1495 s	1535 s 1495 s	1535 s 1495 s	1535 s 1495 s	1520 s 1492 s	1510 s 1492 s	1520 s 1492 s	1518 s 1492 s	1520 s 1492 s	ν(phenyl)
—	1451 s	—	1450 s	—	—	1450 m	—	1455 m	—	—	1450 m	—	1452 m	—	$\nu_4(NO_3)$
1370 vs	1385 vs	1384 vs	1384 vs	1384 vs	1370 vs	1385 vs	1385 vs	1385 vs	1385 vs	1384 vs	1387 vs	1388 s	1387 s	1387 s	ν(C–N)
—	1320 m	—	1320 m	—	—	1320 m	—	1310 m	—	—	1320 m	—	1320 m	—	$\nu_1(NO_3)$
1185 s	1188 s	1188 s	1188 s	1188 s	1168 m	1168 m	1168 m	1168 m	1168 m	1168 w	1168 w	1168 w	1168 w	1168 w	ν(N–N)
—	1050 w	—	1050 w	—	—	1030 s	—	1030 s	—	—	1030 s	—	1030 s	—	$\nu_2(NO_3)$
—	—	—	935 vs	930 vs	—	—	—	935 vs	930 vs	—	—	—	935 vs	932 vs	$\nu_3(O{=}U{=}O)$
—	—	790 m	—	790 m	—	—	800 m	—	800 m	—	—	850 m	—	850 m	ν_{CS} (of NCS)
—	—	450 w	—	450 w	—	—	450 m	—	450 w	—	—	450 w	—	450 w	δ(NCS)

br—broad; m—medium; s—strong; vs—very strong; w—weak

the ν(C=N) mode of vibration which has no parallel band in the spectra of the complexes. The broad band at 3200 cm^{-1}, both in the ligand and in the complexes is assigned to the stretching vibration of phenolic O—H which is H-bonded to the carbonyl oxygen as shown in Fig. 2.

The strong band at 1684 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 cm^{-1}) indicating that ASH is coordinated to the metal ion through the acetyl-carbonyl oxygen.

The strong band at 1648 cm^{-1} in the spectrum of the ligand is assigned to the stretching frequency of the salicylyl carbonyl group. This band appears in the lower region than the expected region due to strong intramolecular hydrogen bonding with the phenolic —OH group. In the spectra of the complexes, this band is slightly shifted to lower region at 1635 cm^{-1} which indicates that the salicylyl carbonyl group is coordinated to the metal ions. Another strong band at 1370 cm^{-1} in the spectrum of the ligand is assigned to the ν(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 a bidentate neutral ligand coordinating through the carbonyl oxygen atoms of both the acetyl and salicylyl groups.

The IR spectral data of the benzoyl salicylyl hydrazine (BSH) and its complexes are presented in Table-2. The strong intense band at 3330 cm^{-1} in the spectra of the ligand and complexes corresponds to the ν(NH) mode. The broad band at 3230 $cm^{-1}$of the ligand and 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 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 cm^{-1}) indicating that the ligand is coordinated to the metal ion through this carbonyl oxygen. The strong band at 1648 cm^{-1} is assigned to the ν(C=O)) mode of the salicylyl carbonyl. This band appears in the lower region than in the expected region due to strong intramolecular hydrogen bonding with the phenolic —OH group. This band is also slightly shifted to the lower region (1633 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 nitrato complexes of these ligands with Th(IV) and UO_2 (VI) show three additional bands at *ca.* 1450 cm^{-1}, *ca.* 1320 cm^{-1} and *ca.* 1030 cm^{-1} which are absent in the spectra of the ligand and in the thiocyanate complexes. These three bands are ν_4, ν_1 and ν_2 modes of the coordinated nitrate ion. A difference of 130 cm^{-1} between ν_4 and ν_1 mode of vibration shows the coordination of nitrate ion in a unidentate fashion.[4]

The IR spectra of all the three thiocyanate complexes of these ligands with Th(IV) and UO_2(VI) exhibit three additional bands at 2050 cm^{-1}, 850 cm^{-1} and 450 cm^{-1} which are assigned to ν(CN), ν(CS) and δ(NCS) modes respectively of

the coordinated thiocyanate ions. It has been established that ν(CN) occurs around 2050 cm^{-1} in N-bonded complexes. Whereas the S-bonded complexes appear around 2100 cm^{-1}. Moreover, ν(CS) mode appears in the range 860–750 cm^{-1} for N-bonded complexes while it appears in the range 720–680 cm^{-1} for S-bonded complexes. N-bonded complexes also exhibit a single sharp band corresponding to δ(NCS) mode at 450 cm^{-1} whereas S-bonded complexes show several bands around 460 cm^{-1}. In these evidences, thiocyanate ions of the present complexes are coordinated unidentately through N-atom and not through S-atom.[5] Coordination of these anions, nitrate and thiocyanate is further supported by the non-electrolytic behaviour of these complexes.

The IR spectra of dioxouranium(VI) complexes have an additional strong band around 935–930 cm^{-1} which have no parallel band in the spectra of the ligand as well as in the spectra of thorium(VI) complexes. This band is assigned to the asymmetric stretching vibration of UO_2(VI) ions. Absence of ν_3(O=U=O) shows that oxygen atoms of UO_2(VI) moiety are in *trans* position in the present complexes.

On the basis of the above observations and discussion it can be concluded that all three ligands SH, ASH and BSH have unique character towards both the metal ions, Th(IV) and UO_2(VI) in presence of two coordinating anions, *viz.*, nitrate and thiocyanate. They act as neutral bidentate ligands towards both Th(IV) and UO_2(VI) in presence of these anionic ligands. In all the complexes, nitrate and thiocyanate ions act as monovalent unidentate ligands. Thus a coordination number of 8 has been assigned to both the metal ions in these complexes.

TABLE-3
THERMAL DECOMPOSITION DATA OF THE COMPLEXES

Complex	Plateau in TG (°C)	Peaks in DTG (°C)	Peak width in DTG (°C)	Final residue	Final loss (%)		
					TG	Independent pyrolysis	Theoretical
$[Th(SH)_2(NO_3)_4]$	Upto 230	240	220-260	ThO_2	68	67.5	66.3
		290	260-330				
	Above 450	440	400-470				
$[UO_2(ASH)_2(NO_3)_2]$	Upto 180	190	170-210	U_3O_8	67	66.3	65.5
	Above 540	530	470-550				
$[UO_2(BSH)_2(NO_3)_2]$	Upto 220	270	210-300	U_3O_8	70	70.8	69.0
	Above 490	480	470-500				

Thermal decomposition data of the complexes including the plateau in TG, peak temperatures and peak width in DTG are given in Table-3. Thorium(IV) complex undergoes three-stage decomposition and the uranyl(VI) complexes undergo two-stage decomposition. The complexes are stable up to *ca.* 220°C with a slightly lower stability for $[UO_2(ASH)_2(NO_3)_2]$ (*ca.* 180°C). The decomposition is over by 450°C for $[Th(SH)_2(NO_3)_4]$, 540°C for $[UO_2(ASH)_2(NO_3)_2]$ and 490°C for $[UO_2(BSH)_2(NO_3)_2]$. The final residues obtained for thorium and uranyl complexes are found to be ThO_2 and U_3O_8 respectively.

From the thermal decomposition studies of these representative complexes it can be concluded that all the complexes prepared in the present investigation are stable up to *ca.* 180°C and hence they can be conveniently dried at *ca.* 150°C without any change in their composition. The TG-DTG data also supports the 1:2 ratio between the metal and the ligand in these complexes and has displayed the composition of the complexes.

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