

Synthesis and Characterization of Some Mixed Ligand Complexes of Th(IV) with Salicylyl hydrazine and its Derivatives

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ABSTRACT

Some mixed ligand complexes of Th (IV) with Salicylyl hydrazine (SH) and its derivatives as primary ligands and two different anions viz., nitrate and thiocyanate as secondary ligands have been synthesized and characterized on the basis of elemental analysis, molecular weight, 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 NO³⁻ and NCS act as unidentate ligands.

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

I. INTRODUCTION

It has been reported that the ligands salicylyl hydrazine(SH), acetyl salicylyl hydrazine(ASH), benzoyl salicylyl hydrazine(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 prepares so far. Therefore, it would be fruitful to synthesize some complexes of actinide ion, Th(IV).

The ligands SH, ASH, BSH are of special interest in that the carbonyl oxygen atom is H- bonded to the phenolic -OH group as evident from IR spectral studies. Moreover, the ligand SH has four potential donor atoms ^[3], viz., carbonyl oxygen, phenolic oxygen, imino nitrogen and amino nitrogen as shown in Fig.1. The structural similarity of ligands ASH and BSH with SH makes the study of coordination behaviour of these complexes more relevant.

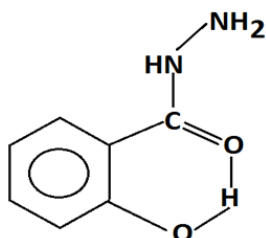


Figure 1. Structure of ligand SH

II. METHODS AND MATERIAL

2.1 Chemicals and Methods

All chemical used were of Analar grade. The metal content of the complexes was estimated by oxalate-oxide method ^[4]. The nitrate content of the complexes was determined gravimetrically by using nitron reagent ^[5]. The thiocyanate content was determined gravimetrically as AgSCN ^[4]. TG- DTG techniques have been used for the comparison of the thermal behaviour of complexes viz., [Th(SH)₂(NO₃)₄] and [Th(ASH)₂(NO₃)₄]. IR spectra of the ligand and complexes were recorded in KBr on a Perkin- Elmer 882 IR spectrometer in the range 4000-400 cm⁻¹. Inorder to determine the molar mass of complexes Rast method was employed, where camphor is used as the solvent

2.2 Synthesis of Ligand

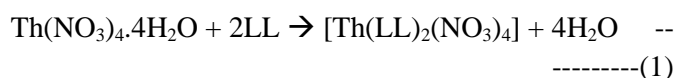
The ligands SH, ASH and BSH were prepared by standard methods ^[2].

2.3 Synthesis of Metal complexes

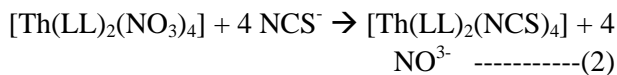
The complexes were prepared by refluxing methanolic solution of the nitrates of Th(IV) with primary ligands in the mole ratio 1:2 according to the equation (1). The

complexes have to be dried in vacuo over phosphorous (V) oxide to get required product.

III. RESULTS AND DISCUSSION



The nitrate complexes are converted into thiocyanate complexes^[6,7] by substitution reaction based on eqn. (2)



Where LL = SH, ASH, BSH

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 Th (IV) Complexes

Complex	Colour	Mol. Wt. Found (Calcd)	Percentage Analysis Found (Calcd)		
			Metal	Nitrate	Thio cyanate
[Th(SH) ₂ (NO ₃) ₄]	White	742 (784)	29.1 (29.5)	31.2 (31.6)	-
[Th(SH) ₂ (NCS) ₄]	Pale Pink	782 (768)	29.8 (30.2)	-	29.8 (30.2)
[Th(ASH) ₂ (NO ₃) ₄]	Dark Pink	850 (868)	26.3 (26.7)	27.8 (28.5)	-
[Th(ASH) ₂ (NCS) ₄]	Cream	840 (852)	26.9 (27.2)	-	26.8 (27.2)
[Th(BSH) ₂ (NO ₃) ₄]	Pale Pink	975 (992)	22.8 (23.3)	24.8 (25.0)	-
[Th(BSH) ₂ (NCS) ₄]	Cream	865 (876)	23.1 (23.7)	-	23.1 (23.7)

3.2 Molar Conductivity

Molar conductance values of the complexes in acetonitrile, methanol and nitrobenzene are in a range

(Table.2). which corresponds to those of non- electrolyte in these solvents^[8]. 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 (Ohm ⁻¹ cm ² mol ⁻¹)		
	CH ₃ CN	CH ₃ OH	PhNO ₂

[Th(SH) ₂ (NO ₃) ₄]	67	108	7.5
[Th(SH) ₂ (NCS) ₄]	57	106	8.5
[Th(ASH) ₂ (NO ₃) ₄]	48	112	6.5
[Th(ASH) ₂ (NCS) ₄]	52	115	14
[Th(BSH) ₂ (NO ₃) ₄]	40	102	10
[Th(BSH) ₂ (NCS) ₄]	38	98	8

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



Where LL= SH, ASH, BSH

3.3 IR Spectra

The IR Spectrum provides the 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 Th(IV) Complexes

Ligand SH	SH Complexes		Ligand ASH	ASH Complex		Ligand BSH	BSH Complex		Tentative Assignments
	Th(NO ₃) ₄	Th(NCS) ₄		Th(NO ₃) ₄	Th(NCS) ₄		Th(NO ₃) ₄	Th(NCS) ₄	
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	3425 s	3300 vs	3320 vs	3325 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	1672 s	-	-	-	$\nu_{(\text{C}-\text{O})}$ acetyl
-	-	-	-	-	-	1682 vs	1666 s	1668 s	$\nu_{(\text{C}-\text{O})}$ benzoyl
1668 s	1640 s	1650 s	1648 s	1635 s	1635 s	1648 s	1635 s	1633 s	$\nu_{(\text{C}-\text{O})}$ salicylyl
-	-	-	1575 s	-	-	-	-	-	$\nu_{(\text{C}-\text{N})}$
1540 s	1540 s	1540 s	1535 s	1535 s	1535 s	1520 s	1510 s	1520 s	ν phenyl
1490 m	1490 m	1490 m	1495 s	1495 s	1495 s	1492 s	1492 s	1492 s	
-	1451 s	-	-	1450 m	-	-	1450 m	-	$\nu_4(\text{NO}_3)$
1370 vs	1385 vs	1384 vs	1370 vs	1385 vs	1385 vs	1384 vs	1387 vs	1388 vs	$\nu_{(\text{C}-\text{N})}$
-	1320 m	-	-	1320 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	$\nu_{(\text{N}-\text{N})}$
-	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 cm⁻¹ and 3370 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 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 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 cm^{-1} . This band is assigned to NH mode of vibration of imino groups. The sharp band at 3330 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 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 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 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 acetyl- carbonyl oxygen atom. The strong band at 1648 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 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 $\nu_{(C=N)}$ 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 cm^{-1} corresponds to the $\nu_{(NH)}$ bond. The broad band at 3230 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 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 $\nu_{(C-O)}$ 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 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 Th(IV) show three additional bands at $1450, 1320$ and 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^[9].

The IR spectra of all the three thiocyanate complexes of these ligands with Th (IV) exhibit three additional bands at $2050, 850$ and 450 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 cm^{-1} in N- bonded complexes. Whereas the S- bonded complexes appear around 2100 cm^{-1} . Moreover, $\nu_{(CS)}$ 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 $\nu_{(\text{NCS})}$ 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^[10,11].

3.4 Thermal Study

The Thermal behaviour of the complexes has been investigated using thermogravimetric techniques in the temperature range from ambient to 700°C. Thermal decomposition data of complexes is given in Table.4

Table 4. 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]	Up to 230 Above 450	240 290 440	220 - 260 260 - 330 400 - 470	ThO ₂	68	67.5	66.3

Th (IV) complexes undergoes three stage decomposition. The decomposition is over by 450°C for [Th(SH)₂(NO₃)₄]. The final residues obtained for thorium is found to be ThO₂. 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 Th (IV) 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 Th (IV) 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.

V. REFERENCES

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