

Synthesis and Characterization of Thorium(IV) Complexes with Salicylaldehyde N(4)-Phenylthiosemicarbazone

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Some thorium(IV) complexes with salicylaldehyde N (4)-phenylthiosemicarbazone (SPT) were synthesized and characterized. The compositions of the complexes were ascertained from elemental analysis, molar conductivity measurements and spectral investigations to be $[\text{ThL}_2\text{X}_n]$ ($\text{X} = \text{NO}_3^-, \text{NCS}^-, \text{ClO}_4^-, \text{CH}_3\text{COO}^-$ or $\text{CH}_3\text{CHOHCOO}^-$, $n = 2$ and $\text{X} = \text{SO}_4^{2-}, \text{C}_2\text{O}_4^{2-}$, $n = 1$ and $\text{L} =$ salicylaldehyde N (4)-phenylthiosemicarbazone). Thermal studies were conducted on two representative complexes. The ligands along with a few complexes were screened for their antifungal activity against *Fusarium oxysporum* which causes wilt in tomato.

Key Words: Thorium(IV) complexes, Antifungal activity, Salicylaldehyde N (4)-phenylthiosemicarbazone.

INTRODUCTION

Thiosemicarbazones and their complexes exhibit a great variety of biological activity¹. The biological activity of thiosemicarbazones is due to their ability to form chelates with trace metals². Owing to the wide range of medicinal properties of thiosemicarbazones and their ability to form chelates with metal ions, it was considered worth while to synthesize some new thorium(IV) complexes of this class of ligands.

EXPERIMENTAL

The reagents and solvents used were of analytical grade and used without further purification.

Preparation of salicylaldehyde N(4)-phenylthiosemicarbazone (SPT): The compound 4-phenyl thiosemicarbazide was prepared from N-phenylthiourea and hydrazine hydrate using standard method³.

Salicylaldehyde N (4)-phenyl thiosemicarbazone was prepared by refluxing equimolar (0.01 mol) mixture of N-phenyl thiosemicarbazide and salicylaldehyde in methanol for 3 h. The light yellow solid separated was filtered, washed and dried. It was recrystallized from methanol (yield ca. 75%; m.p. 178°C).

Preparation of complexes: The nitrate and perchlorate complexes were prepared by refluxing a methanolic solution of ligand (SPT) with the metal salt in 2 : 1 stoichiometric ratio for 4 h. The solid complex separated on concentration

was filtered and washed with methanol and dried over P_4O_{10} *in vacuo*. The other anionic complexes were prepared from the nitrate complex by substitution methods^{4,5}, by refluxing stoichiometric amounts of nitrate complex with respective anionic salts for 3 h.

The thorium, nitrate and perchlorate contents of the complexes were determined gravimetrically by oxalate-oxide⁶, nitron⁷ and Kurz's⁸ methods, respectively. The sulphate and thiocyanate contents were determined as $BaSO_4$ and $AgNCS$ ⁷, respectively. Carbon, hydrogen, nitrogen and sulphur contents of the complexes were determined by microanalytical methods using Elementar-Vario EL III Carlo-Erba 1108 Analyzer at SAIF, CDRI, Lucknow, India.

RESULTS AND DISCUSSION

Thiosemicarbazone and its thorium(IV) complexes were characterized by elemental analysis, conductivity measurements, infrared and 1H NMR spectra and thermal studies. The analytical data of complexes are given in Table-1. The electrical conductivity measurements in nitrobenzene, methanol and acetonitrile indicate that the complexes are essentially non-electrolytes.

TABLE-1
ANALYTICAL DATA OF Th(IV) COMPLEXES OF THIOSEMICARBAZONE

Complex	Analysis %, Found (Calcd.)					
	Th	C	H	N	S	Anion
$[Th(SPT)_2(NO_3)_2]$	25.49 (25.83)	19.21 (18.70)	1.89 (1.45)	8.11 (7.79)	3.93 (3.56)	14.18 (13.80)
$[Th(SPT)_2(SO_4)]$	26.79 (26.60)	20.90 (19.31)	1.72 (1.49)	4.03 (4.83)	8.01 (7.37)	10.89 (11.01)
$[Th(SPT)_2(NCS)_2]$	26.49 (26.06)	22.93 (21.57)	1.92 (1.46)	7.90 (7.87)	11.10 (10.78)	12.97 (13.00)
$[Th(SPT)_2(C_2O_4)]$	26.84 (26.91)	41.42 (41.66)	3.69 (3.24)	9.91 (9.72)	3.01 (3.71)	—
$[Th(SPT)_2(OAc)_2]$	25.99 (26.01)	37.70 (40.00)	4.20 (3.80)	10.13 (9.39)	2.90 (3.60)	—
$[Th(SPT)_2(C_3H_5O_3)_2]$	23.91 (24.37)	44.48 (42.76)	4.36 (3.98)	10.03 (8.80)	3.25 (3.36)	—
$[Th(SPT)_2(ClO_4)_2]$	24.01 (23.84)	18.03 (17.27)	1.52 (1.37)	5.01 (4.32)	3.90 (3.29)	19.97 (20.45)

IR spectrum of the ligand shows a medium intensity band at 2988 cm^{-1} due to intramolecular hydrogen bonded $\nu(OH)$ group⁹. This band is absent in the spectra of complexes indicating dissociation of phenolic proton and coordination through deprotonated phenolic oxygen⁹. Another band observed at 1201 cm^{-1} in the ligand spectrum, assigned to $\nu(C-O)$ stretching¹⁰ (phenolic) has been shifted to higher frequency by $20-30\text{ cm}^{-1}$ in the spectra of complexes. This shift supports

the formation of (Th—O) bond^{9, 10}. The IR spectrum of the free ligand does not display the $\nu(\text{S—H})$ mode at about 2600 cm^{-1} indicating that in the solid state the ligand remains in thioketo form¹¹ or —SH is not present in the ligand and the two bands observed at 1285 and 781 cm^{-1} are assigned to $\nu(\text{C—S})$ vibrations¹². The shift of these bands to lower frequencies in the spectra of complexes indicates the coordination of the ligand through thioketo sulphur. The $\nu(\text{C=N})$ observed at 1627 cm^{-1} in the spectrum of ligand shows a downward shift by $15\text{--}20\text{ cm}^{-1}$ in complexes, suggesting the participation of this group in coordination¹³. The mode of coordination through deprotonated phenolic oxygen, azomethine nitrogen and thioketo sulphur is further manifested by the appearance of new bands in the region $480\text{--}525$, $405\text{--}420$ and $320\text{--}360\text{ cm}^{-1}$, due to $\nu(\text{Th—O})$, $\nu(\text{Th—N})$ and $\nu(\text{Th—S})$ vibrations, respectively. Thus the ligand SPT behaves as a monobasic tridentate chelating agent in these complexes. The nitrate complex exhibited three new bands at 1465 , 1365 and 1024 cm^{-1} which are absent in the spectra of SPT and other complexes. These three bands are attributed to ν_4 , ν_1 and ν_2 modes of the coordinated nitrate ions. The magnitude of separation between the split bands ν_4 and ν_1 is of the order of 100 cm^{-1} indicating that the nitrate ions are coordinated unidentately¹⁴ to the metal ions. In the sulphato complex three bands are observed around 1200 , 1188 and 1078 cm^{-1} which are assigned to stretching frequencies of bidentate sulphate ions. The IR spectra of acetato and lactato complexes show ν_{asym} stretching vibrations at 1614 and 1615 cm^{-1} and ν_{sym} stretching vibrations at 1389 and 1384 cm^{-1} , respectively. Since the difference between ν_{asym} and ν_{sym} is far greater than that for ionic complexes, these ions are coordinated to the metal ion in a monodentate fashion. The oxalato complex exhibited additional bands at 1651 and 1404 cm^{-1} which are assigned to $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ modes of the bidentately coordinated dicarboxylate ion. In the present complex oxalate anion is coordinated bidentately to the metal ion with a chelate structure. The 'N' coordinated nature of thiocyanate is indicated by $\nu(\text{C—N})$ at 2065 cm^{-1} , $\nu(\text{C—S})$ at 829 cm^{-1} and $\delta(\text{NCS})$ at 476 cm^{-1} , respectively. Spectrum of perchlorato complex shows three additional bands at 1112 , 1083 and 624 cm^{-1} assigned to ν_4 , ν_1 and ν_3 modes of unidentately coordinated perchlorate ion. The nature of bonding of the various anions is further supported by the nonelectrolytic nature of all the complexes.

The ¹H NMR spectra of the ligand (SPT) and its complex have been recorded in DMSO-d₆. The OH proton signal at δ 11.50 present in the ligand is absent in the spectrum of the complex indicating that SPT behaves as a monobasic ligand coordinating through deprotonated phenolic oxygen. A strong signal at δ 8.50 due to CH=N of ligand undergoes a downfield shift on complexation indicating the participation of azomethine nitrogen in bonding. Aromatic protons occur as multiplet in the ligand, showing characteristic shift on complexation. SPT does not show any peak attributable to (S—H) proton indicating that it exists in the thioketo form.

Thermal studies were conducted on the complexes $[\text{Th}(\text{SPT})_2(\text{NO}_3)_2]$ and $[\text{Th}(\text{SPT})_2(\text{C}_2\text{O}_4)]$. Thermogravimetric curves were recorded in the temperature range from room temperature to 1000°C . For the complex $[\text{Th}(\text{SPT})_2(\text{NO}_3)_2]$ the TG plateau up to 210°C shows its stability. There are two stages of decomposition as shown by DTG peaks at 229 and 580°C . The decomposition at 229°C is due to the dissociation of the organic moiety making a mass loss of 60%. The decomposition continues with a gradual decrease in weight and the metal nitrate is converted into oxide (ThO_2) at 580°C and a constant weight is obtained at about 600°C . The residual mass is about 28% which indicates that the decomposition product is ThO_2 . Independent pyrolysis also confirms that the final product is ThO_2 .

For the complex $[\text{Th}(\text{SPT})_2(\text{C}_2\text{O}_4)]$ the plateau is up to 200°C indicating that the complex is stable up to 200°C . The DTG curve has three peaks at 224 , 401 and 573°C showing that the complex undergoes decomposition in three stages. The decompositions at 224 and 401°C are due to the dissociation of the ligand molecules. The decomposition continues with a decrease in weight and a constant weight due to the formation of ThO_2 is obtained at about 580°C . The residual mass is 30% which shows that the final product is ThO_2 , which is in agreement with the independent pyrolysis experiment.

All these studies confirm the composition of the complexes as $[\text{Th}(\text{SPT})_2\text{X}_2]$ with $\text{X} = \text{NO}_3^-$, NCS^- , CH_3COO^- , $\text{CH}_3\text{CHOHCOO}^-$ and ClO_4^- and $[\text{Th}(\text{SPT})_2\text{X}]$ with $\text{X} = \text{SO}_4^{2-}$ and $\text{C}_2\text{O}_4^{2-}$, respectively. Thus a coordination number of 8 is assigned to thorium in these complexes.

Antifungal activity

The ligand (SPT) and the complexes $[\text{Th}(\text{SPT})_2(\text{NO}_3)_2]$ and $[\text{Th}(\text{SPT})_2(\text{C}_2\text{O}_4)]$ were screened for their antifungal activity using poisoned food technique¹⁵. The ligand and the complexes were found to be active against *Fusarium oxysporum* which is a common plant pathogen.

Test solutions have been prepared by dissolving appropriate amounts of complexes in ethanol. The test solution in the desired concentration was taken and appropriate volume mixed with molten potato agar medium to have a resultant concentration of 100 ppm. This chemical amended medium was poured into 9 cm petri plates. Mycelial discs of actively growing fusarium culture were cut with cork borer and placed at the centre of petri plates. In control sets appropriate quantities of ethanol were incorporated in place of test solution. Three plates were kept for each sample. The fungal growth was measured at every 24 h, at two points along the diameter of the colony. The growth of the colony in control sets was compared with that of the various treatments and percentage inhibition was calculated. Results show that the complexes exhibited significant antifungal profile and more activity than the ligand (Table-2).

TABLE-2
EFFECT OF SPT AND ITS THORIUM(IV) COMPLEXES ON MYCELIAL GROWTH OF
FUSARIUM OXYSPORUM

Samples taken	Mycelial growth (cm)	Inhibition (%)
Control	9.2	—
SPT	5.0	45.00
[Th(SPT) ₂ (NO ₃) ₂]	1.7	81.52
[Th(SPT) ₂ (C ₂ O ₄)]	2.1	77.17

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AJC-4784

As per the current regulatory requirement, resolution between two components should be more than 3.0, tailing factor should be less than 2.0 and theoretical plate should be more than 2000. It is evident from Table-4 that the proposed method for two drugs in combination is satisfying the regulatory requirement.

TABLE-4
OPTIMIZED CHROMATOGRAPHIC CONDITION

S.No.	Parameters	Ranitidine hydrochloride	Ondansetron hydrochloride
1.	Capacity factor (K')	0.35	2.05
2.	Resolution (Rs)	1.72	5.90
3.	Tailing factor (T)	1.10	0.97
4.	Theoretical plate (N)	2931	2247
5.	Calibration range ($\mu\text{g/mL}$)	35.0–195.0	1.0–5.0
6.	Limit of detection ($\mu\text{g/mL}$)	1.25	0.517
7.	Limit of quantitation ($\mu\text{g/mL}$)	3.75	1.515

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