

## NOTE

## Studies of Thorium(IV) Complexes of Schiff Base Derived from Fluoroaniline and *p*-(N,N'-Dicyanoethyl) Amino Benzaldehyde

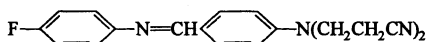
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A series of new thorium(IV) complexes with a Schiff base derived from fluoroaniline and *p*-(N,N'-dicyanoethyl) amino benzaldehyde have been synthesized. Analytical, conductance, molecular weight and spectral data reveal that the complexes have the general composition  $(\text{ThX}_4 \cdot n\text{L})$  ( $\text{X} = \text{NO}_3^-$ ,  $\text{NCS}^-$ ,  $n = 2$ ;  $\text{X} = \Gamma^-$ ,  $n = 4$ ;  $\text{X} = \text{ClO}_4^-$ ,  $n = 6$ ). Thorium atom is 6 or 10 coordinated depending upon the anions present in these complexes.

Recently the studies on Th(IV) metal salts with various Schiff bases have been reported<sup>1-5</sup>. In the present work we wish to report the studies on coordination compounds of a Schiff's base (L) derived from fluoroaniline and *p*-(N,N'-dicyanoethyl) amino benzaldehyde with Th(IV) metal salts. The ligand (L) is expected to function as a monodentate ligand.



The metal salt  $\text{Th}(\text{NO}_3)_4$  used was of BDH, AR grade and all other metal salts were prepared by respective reported methods<sup>6-9</sup>.

The ligand was prepared by condensing the corresponding amine and aldehyde in equimolar ratio and refluxing the reaction mixture for 3-4 h.

The metal complexes were prepared by the following general method: An ethanolic solution of the corresponding metal salt (0.01 mol in 10 mL) was refluxed with a solution of the ligand (0.022 mol) dissolved in the same solvent (20 mL) on a steam bath for about 1 h. From the refluxate the complexes were separated gradually either on standing or by concentrating and cooling at room

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temperature. The products were collected, washed with cold ethanol and finally with ether and dried in *vacuo* over  $\text{CaCl}_2$ .

The analytical and conductivity data (Table-1) indicate that the perchlorate and iodo complexes are ionic in nature while all others are nonionic in nature indicating that iodo and perchlorate complexes are conducting in nature. The complexes are fairly stable at room temperature except the iodo complex which converts into sticky mass after some time.

The complexes are characterized on the basis of their IR spectra. It is clear from spectral data that on complexation there is considerable shift in  $\nu(\text{C}=\text{N}-)$  which shows that the bonding site is the azomethine nitrogen through which the ligand binds to the metal ion<sup>10, 11</sup>. The  $\nu(\text{C}=\text{N})$  shifts towards lower frequency, which is due to involvement of unshared pair of electrons of N-atom in coordination to metal atom. The important IR spectral bands are given in Table-1.

TABLE-1  
ANALYTICAL AND INFRARED SPECTRAL DATA ( $\text{cm}^{-1}$ ) FOR THE Th(IV) COMPLEXES OF SCHIFF'S BASE DERIVED FROM FLOUROANILINE AND *p*-(N,N'-DICYANOETHYL) AMINO BENZALDEHYDE

Complex	m.p. (°C)	m.w. found (calcd.)	Analysis, found (calcd) %			$\Lambda$ ( $\text{ohm}^{-1} \text{cm}^2$ ) mole <sup>-1</sup>	$\nu(\text{C}=\text{N})/\nu(\text{C}-\text{N})/\nu(\text{M}-\text{N})$
			M	N	Anion		
Ligand (L)	210	-	-	-	-	-	1662 s, 1170 m, -
Th(NO <sub>3</sub> ) <sub>4</sub> ·2L	240	1089 (1100)	20.05 (21.09)	13.72 (15.27)	-	3.9	1640 s, 1175 m, 550 m
ThI <sub>4</sub> ·4L	215	650 (1980)	10.80 (11.71)	10.13 (11.31)	24.50 (25.66)	50.9	1649 m, 1180 m, 478 m
Th(NCS) <sub>2</sub> ·2L	190	1080 (1084)	20.02 (21.40)	14.40 (15.49)	20.04 (21.40)	4.3	1639 s, 1160 w, 518 m
Th(ClO <sub>4</sub> ) <sub>4</sub> ·6L	220	552 (2490)	8.12 (9.31)	11.50 (13.49)	14.20 (15.98)	93.4	1640 s, 1170 m, 550 m

The preferred coordination number of thorium(IV) metal atom is 6 or 10 but higher coordination numbers have also been observed<sup>12</sup>. In thiocyanato complex coordination number of thorium(IV) is found to be six which is suggested by conductance and molecular weight value. In the iodo complex 1 : 2 electrolyte nature suggests that two iodine atoms are present outside the coordination sphere and hence the coordination number of Th(IV) is six. It has been observed from a single crystal X-ray structure determination of  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  that the nitrate groups are linked to thorium through two oxygen atoms, each nitrate group

functioning as a bidentate ligand<sup>13, 14</sup>. In the nitrate complex of this ligand the thorium metal is ten-coordinated as it is surrounded by eight-coordinated oxygen atoms (from four nitrate ions) and two azomethine nitrogen atoms. In perchlorato complex, conductance, molecular weight and infrared studies reveal that all the four perchlorato groups are present outside the coordination sphere and hence suggest the presence of six-coordinated thorium in this complex.

### ACKNOWLEDGEMENT

One of the authors (RCG) sincerely acknowledges the financial support from UGC, Central Regional Office, Bhopal, India.

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(Received: 7 February 2000; Accepted: 29 April 2000)

AJC-2030