

## Synthesis and Characterization of Thorium(IV) and Dioxouranium(VI) Complexes of a Schiff Base: Part 1

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A new series of Th(IV) and UO<sub>2</sub>(VI) with a Schiff base derived from condensation of *m*-methyl aniline and *p*-(*N,N'*-dicyanoethyl)amino benzaldehyde having general composition ThX<sub>4</sub>nL (X = NO<sub>3</sub><sup>-</sup>, n = 2; X = NCS<sup>-</sup>, n = 2; X = Γ<sup>-</sup>, n = 4; X = ClO<sub>4</sub><sup>-</sup>, n = 6); and UO<sub>2</sub>X<sub>2</sub>·2L (X = NO<sub>3</sub><sup>-</sup>, Γ<sup>-</sup>, NCS<sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup>) and UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·4L where L is the Schiff base. The complexes were characterized on the basis of analytical conductance molecular weight and spectral studies. The Schiff base behaves as a neutral monodentate ligand which coordinates to the central metal atom through azomethine nitrogen.

**Key Words:** Thorium(IV), Dioxouranium(VI), Schiff base, *m*-methylaniline, *p*-(*N,N'*-dicyanoethyl)amino benzaldehyde, Complexes.

### INTRODUCTION

A number of complexes with linear dioxouranium(VI) ion in 6- or 8-coordination number and with thorium(IV) in 6-, 8-, or 10-coordination number are known<sup>1-6</sup>. In the present paper, the synthesis and characterization of a series of complexes of these metals with a Schiff base ligand (L) which is derived from the condensation of *m*-methyl aniline and *p*-(*N,N'*-dicyanoethyl)amino benzaldehyde is reported (Fig. 1).

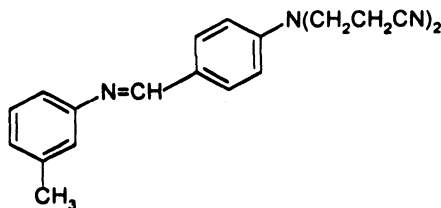


Fig. 1. Schiff base ligand (L)

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## EXPERIMENTAL

Uranyl nitrate, uranyl acetate and thorium nitrate were obtained from BDH and all other salts were prepared by the respective methods<sup>7-11</sup>. The ligand was prepared by condensing the corresponding amine and aldehyde in equi-molar ratio and refluxing the reaction mixture for 3-4 h.

The metal complexes were prepared by the following general method:

The respective metal salt solutions were treated with ligand solution in the required molar concentrations (*i.e.*, 1 : 2, 1 : 4 or 1 : 6). The complexes were isolated immediately in cold while in some cases in hot solutions. In some cases refluxing for 2-3 h at *ca.* 65-75°C is required. The solvents used were ethanol, isopropanol or acetone. The complexes were collected, washed with the solvent and finally with ether and dried *in vacuo* over CaCl<sub>2</sub>.

All other physico-chemical studies were performed by the usual methods<sup>12</sup>.

## RESULTS AND DISCUSSION

The analytical and conductance data (Table-1) indicate that the perchlorato and iodo complexes are ionic in nature while all other complexes are nonionic in nature. The complexes are fairly stable at room temperature except the iodo complexes which convert into sticky mass after some time. .

TABLE-1  
ANALYTICAL, CONDUCTANCE AND MOLECULAR WEIGHT DATA  
FOR Th<sup>4+</sup> AND UO<sub>2</sub><sup>2+</sup> COMPLEXES OF THE SCHIFF BASE

Compound (colour)	m.p. (°C)	m.w. found (calcd.)	Analysis %			Λ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			found	(calcd.)		
			C	H	N	
L	97	—	—	—	—	—
(Yellow)						
Th(NO <sub>3</sub> ) <sub>4</sub> ·2L	140	1078	40.83	4.17	14.38	3.2
(Orange yellow)		(1112)	(44.11)	(3.67)	(15.44)	
Th(NCS) <sub>4</sub> ·2L	115	1087	47.12	4.14	15.06	2.7
(Dark yellow)		(1096)	(49.17)	(3.64)	(15.32)	
Th <sub>4</sub> ·L	146-147	989	45.09	4.32	11.07	51.8
(Dark yellow)		(2004)	(47.90)	(3.99)	(11.17)	
Th(ClO <sub>4</sub> ) <sub>4</sub> ·6L	155	708	52.69	4.54	13.89	98.4
(Orange yellow)		(2528)	(56.96)	(4.74)	(13.29)	
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2L	150	996	45.23	4.01	13.08	3.5
(Yellow)		(1026)	(47.33)	(3.94)	(13.18)	
UO <sub>2</sub> I <sub>2</sub> ·2L	127-128	1142	49.72	4.15	10.57	2.1
(Orange yellow)		(1156)	(41.52)	(3.46)	(9.68)	
UO <sub>2</sub> (NCS) <sub>2</sub> ·2L	176-177	1012	45.62	4.13	12.42	3.2
(Light yellow)		(1018)	(49.50)	(3.92)	(13.75)	
UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ·2L	191	1012	49.68	4.16	10.12	3.4
(Yellow)		(1020)	(51.76)	(4.50)	(10.98)	
UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·4L	142-143	683	50.34	4.06	10.19	52.1
(Yellow)		(1734)	(55.36)	(4.61)	(12.91)	

The complexes are characterized on the basis of their IR spectra. It is clear from the spectral data that on complex formation there is a considerable shift in the azomethine  $\nu(\text{—C=N—})$  shows that the bonding site is the azomethine nitrogen through which the ligand binds to the metal ion<sup>13,14</sup>. The  $\nu(\text{—C=N—})$  shifts towards the 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-2.

TABLE-2  
PARTIAL IR DATA FOR THORIUM(IV) AND DIOXOURANIUM(VI) COMPLEXES OF THE SCHIFF BASE LIGAND

Compound	$\nu(\text{C=N})$	$\nu(\text{C—N})$	$\nu(\text{M—N})$
L	1597 s	1195 s	—
Th(NO <sub>3</sub> ) <sub>4</sub> ·2L	1528 m	1192 s	511 w
Th(NCS) <sub>4</sub> ·2L	1527 m	1188 m	513 w
ThI <sub>4</sub> ·4L	1528 m	1192 s	517 m
Th(ClO <sub>4</sub> ) <sub>4</sub> ·6L	1531 w	1193 s	522 w
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2L	1532 m	1193 s	523 w
UO <sub>2</sub> I <sub>2</sub> ·2L	1527 m	1194 sh	516 w
UO <sub>2</sub> (NCS) <sub>2</sub> ·2L	1525 m	1186 s	501 w
UO <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub> ·2L	1525 s	1192 w	521 m
UO <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> ·4L	1532 m	1192 s	520 w

The preferred coordination number of thorium(IV) metal atom is 6 or 10 but higher coordination numbers have also been observed<sup>15</sup>. In thiocyanato complex coordination number of thorium(IV) is found to be six which is suggested by the conductance and molecular weight value. In the iodo complex 1 : 2 electrolytic 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 Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O that the nitrate groups are linked to the thorium through two oxygen atoms, each nitrate group functioning as a bidentate ligand<sup>16,17</sup>. In the nitrate complex of this ligand the thorium metal is then coordinated as it is surrounded by eight coordinated oxygen atoms (from four nitrate ions) and two azomethine nitrogen atoms. In perchlorato complex of thorium(IV) conductance, molecular weight and infrared data reveal that all the perchlorato ions are present outside the coordination sphere and hence suggest the presence of six-coordinated thorium in this complex.

In case of dioxouranium(IV) halo and isothiocyanato complexes both the anions are covalently bonded to the central atom thereby generating six coordinated uranium atoms in these cases. In case of dioxouranium(VI) nitrate complex IR data reveal that both the anions are bidentately covalently bonded to the metal atom thereby suggesting coordination number eight of the uranium atom. In case of perchlorato complex the conductance data show that both the perchlorato groups are present outside the coordination sphere. Thus, the coordination number of uranium in this case is found to be six<sup>18</sup>.

## REFERENCES

1. W.H. Zachariasen, *Acta Cryst.*, **1**, 795 (1954).
2. K. Arora, *Asian J. Chem.*, **7**, 424 (1995).
3. R.K. Agrawal, K. Arora, H. Agarwal and R.K. Sarin, *Synth. React. Inorg. Met. Org.-Chem.*, **25**, 899 (1995).
4. R.K. Agarwal, K. Arora and P. Dutt, *Proc. Nat. Acad. Sci. (India)*, **67A**, II, (1997).
5. R.K. Agarwal and K. Arora, *Pol. J. Chem.*, **67**, 25 (1993).
6. ———, *Pol. J. Chem.*, **67**, 219 (1993).
7. S.S. Sandhu and S.S. Sandhu (Jr.), *Indian J. Chem.*, **11A**, 369 (1973).
8. N.V. Sidgewick, *The Chemical Elements and their Compounds*, Oxford University Press (1952).
9. V.V. Savant and C.C. Patel, *J. Inorg. Nucl. Chem.*, **34**, 1462 (1972).
10. P. Ramamurthy and C.C. Patel, *Can. J. Chem.*, **42**, 856 (1964).
11. ———, *J. Inorg. Nucl. Chem.*, **25**, 310 (1963).
12. R.K. Agarwal, K. Arora and P. Dutt, *Polyhedron*, **13**, 957 (1994).
13. R.C. Goyal, K. Arora, D.D. Agarwal and K.P. Sharma, *Asian J. Chem.*, **12**, 919 (2000).
14. K. Arora, D.D. Agarwal and R.C. Goyal, *Asian J. Chem.*, **12**, 893 (2000).
15. B.C. Smith and M.A. Wassef, *J. Chem. Soc. (A)*, 1817 (1968).
16. J.R. Ferraro and A. Walker, *J. Chem. Soc.*, **45**, 550 (1960).
17. T. Ueki, A. Zalkin and Templeton, *Acta Cryst.*, **20**, 836 (1966).
18. K. Arora and K.P. Sharma, *Synth. React. Inorg. Met-Org. Chem.*, **32**, 913 (2002).

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