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Studies of Thorium(IV) and Dioxouranium(VI) Complexes of a Schiff Base: Part 2

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A new series of Th(IV) and UO_2(VI) with a Schiff base derived from condensation of *p*-amino ethylbenzoate and *p*-(N,N′-dicyanoethyl)amino benzaldehyde having general composition $ThX_4 \cdot nL$ ($X = NO_3^-$, n = 2; $X = NCS^-$, n = 2; $X = I^-$, n = 4; $X = ClO_4^-$, n = 6) and $UO_2X_2 \cdot 2L$ ($X = NO_3^-$, I^-, NCS^- or CH_3COO^-) and $UO_2(ClO_4)_2 \cdot 4L$ 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 coordinate to the central metal atom through azomethine nitrogen.

Key Words: Thorium(IV), Dioxouranium(VI), Schiff base, *p*-Aminoethylbenzoate, *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-, 10-coordination number are known[1–5]. In the present paper we wish to report 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 *p*-amino ethylbenzoate and *p*-(N,N′-dicyanoethyl)amino benzaldehyde (Fig. 1).

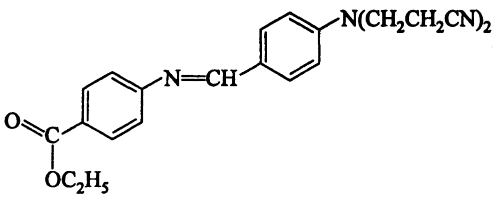

Fig. 1. Schiff base ligand (L)

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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[6–10]. 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:

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 heating is required. In some cases the resulting solutions were refluxed for 2–3 h at *ca.* 65–75°C for isolating the complexes. 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 $CaCl_2$.

All other physico-chemical studies were performed by the usual methods[11].

RESULTS AND DISCUSSION

The analytical data (Table-1) indicate that the perchlorato and iodo complexes are ionic in nature while all other complexes are nonionic in nature indicating that the perchlorato and iodo complexes are conducting 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 THORIUM(IV) AND DIOXOURANIUM(VI) COMPLEXES
OF THE SCHIFF BASE LIGAND

Compound (colour)	Yield (%)	m.p. (°C)	m.w. found (calcd.)	Analysis % found (calcd.) C	H	N	Λ $(ohm^{-1}\ cm^2\ mol^{-1})$
L	90	108–	—	—	—	—	—
(Yellow)		109					
$Th(NO_3)_4\cdot 2L$	90	164–	1210	40.66	4.25	13.05	3.4
(Brown)		165	(1228)	(43.85)	(3.65)	(13.95)	
$Th(NCS)_4\cdot 2L$	76	166	1217	43.12	4.24	13.06	2.3
(Orange yellow)			(1212)	(47.52)	(3.63)	(13.86)	
$ThI_4\cdot 4L$	84	168	1123	42.19	4.22	11.01	51.9
(Brown)			(2236)	(47.22)	(3.93)	(10.01)	
$Th(ClO_4)_4\cdot 6L$	97	204–	854	51.07	4.12	11.89	99.4
(Orange yellow)		205	(2876)	(55.06)	(4.58)	(11.69)	
$UO_2(NO_3)_2\cdot 2L$	77	169	1121	45.23	4.23	12.19	2.5
(Yellowish green)			(1142)	(46.73)	(3.89)	(12.38)	
$UO_2I_2\cdot 2L$	93	139	1227	39.99	4.17	9.57	3.1
(Orangish brown)			(1272)	(41.50)	(3.46)	(8.80)	
$UO_2(NCS)_2\cdot 2L$	80	111–	1124	43.62	4.23	12.42	3.3
(Orangish brown)		112	(1134)	(48.67)	(3.88)	(12.34)	
$UO_2(CH_3COO)_2\cdot 2L$	97	182–	1124	44.68	5.16	10.80	3.1
(Yellow)		183	(1136)	(50.70)	(4.40)	(9.85)	
$UO_2(ClO_4)_2\cdot 4L$	97	206–	698	48.19	4.19	10.84	55.1
(Orange)		207	(1966)	(53.71)	(4.47)	(11.39)	

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 ν(—C═N—) which shows that the bonding site is the azomethine nitrogen through which the ligand binds to the metal ion [12, 13]. The ν(—C═N—) shifts towards the lower frequency, which is due to involvement of unshared pair of electrons of N-atom in the coordination to metal atom. The important IR spectral bands are given in Table-2.

TABLE-2

PARTIAL IR BANDS (cm^{-1}) FOR Th^{4+} AND UO_2^{2+} COMPLEXES OF SCHIFF BASE

Compound	ν(C═N)	ν(C—N)	ν(M—N)
L	1588 s	1168 s	—
$Th(NO_3)_4 \cdot 2L$	1527 m	1181 s	526 w
$Th(NCS)_4 \cdot 2L$	1528 m	1179 m	527 w
$ThI_4 \cdot 4L$	1528 m	1176 s	525 m
$Th(ClO_4)_4 \cdot 6L$	1531 w	1184 m	528 w
$UO_2(NO_3)_2 \cdot 2L$	1525 s	1179 s	508 w
$UO_2I_2 \cdot 2L$	1526 m	1176 s	534 w
$UO_2(NCS)_2 \cdot 2L$	1524 s	1179 s	536 w
$UO_2(CH_3COO)_2 \cdot 2L$	1524 s	1171 s	539 m
$UO_2(ClO_4)_2 \cdot 4L$	1529 s	1183 s	530 w

The preferred coordination number of thorium(IV) metal atom is 6 or 10 but higher coordination numbers have also been observed[14]. 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 $Th(NO_3)_4 \cdot 5H_2O$ that the nitrato groups are linked to the thorium through two oxygen atoms, each nitrato group functioning as a bidentate ligand[15–16]. In the nitrato 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 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 atom in these cases.

In case of dioxouranium(VI) nitrato and complexes IR data reveal that both the anions are bidentately covalently bonded to the metal atom thereby generating coordination number eight on the central 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 six[17].

REFERENCES

1. W.H. Zachariasan, *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. K. Arora, R.C. Goyal, D.D. Agarwal and M.C. Pathak, *J. Indian. Chem*. Soc., **69**, 686 (2002).
6. S.S. Sandhu and S.S. Sandhu (Jr.), *Indian J. Chem.*, **11A**, 369 (1973).
7. N.V. Sidgewick, The Chemical Elements and their Compounds, Oxford University Press (1952).
8. V.V. Savant and C.C. Patel, *J. Inorg. Nucl. Chem.*, **34**, 1462 (1972).
9. P. Ramamurthy and C.C. Patel, *Can. J. Chem.*, **42**, 856 (1964).
10. ———, *J. Inorg. Nucl. Chem.*, **25**, 310 (1963).
11. R.K. Agarwal, K. Arora and P. Dutt, *Polyhedron*, **13**, 957 (1994).
12. R.C. Goyal, K. Arora, D.D. Agarwal and K.P. Sharma, *Asian J. Chem.*, **12**, 919 (2000).
13. K. Arora, D.D. Agarwal and R.C. Goyal, *Asian J. Chem.*, **12**, 893 (2000).
14. B.C. Smith and M.A. Wassef, *J. Chem. Soc. (A)*, 1817 (1968).
15. J.R. Ferraro and A. Walker, *J. Chem., Soc.*, **45**, 550 (1960).
16. T. Ueki, A. Zalkin and Templeton, *Acta Cryst.*, **20**, 836 (1966).
17. K. Arora and K.P. Sharma, *Synth. React. Inorg. Met-Org. Chem.*, **32**, 913 (2002).

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