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Synthesis and Spectral Studies of Thorium(IV) and Dioxouranium(VI) Complexes of Schiff Base Derived from Benzocain and *p*-Dimethyl Amino Benzaldehyde

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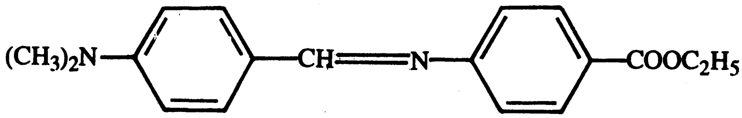
A new series of complexes of Th(IV) and UO_2(VI) with a Schiff base derived from condensation of benzocain and *p*-dimethylamino benzaldehyde having general composition $ThX_4 \cdot nL$ ($X = Cl^-$, Br^-, NCS^- or I^-, $n = 4$; $X = ClO_4^-$, $n = 6$; $X = NO_3^-$, $n = 2$) and $UO_2X_2 \cdot 2L$ ($X = NO_3^-$, Br^-, I^-, NCS^- and CH_3COO^-) or $UO_2X_2 \cdot 4L$ ($X = ClO_4^-$), where L is Schiff base. The complexes were characterised on the basis of elemental analysis, molecular weight determination, magnetic moment, infrared and electronic spectral studies and conductivity measurement. In all the complexes, ligand behaves as monodentate neutral ligand which coordinate to metal by azomethine nitrogen.

INTRODUCTION

A number of complexes with linear dioxouranium ion in 6-, 7- or 8-coordination number and with thorium(IV) in 6-, 8- or 10-coordination number are known[1–4]. In the present work we wish to report the synthesis and characterization of a series of complexes of these metals with a Schiff base ligand (I) which is derived from benzocain and *p*-dimethyl amino benzaldehyde on condensation.



(I)

EXPERIMENTAL

Uranyl nitrate, uranyl acetate and thorium nitrate were obtained from B.D.H. and other salts were prepared by respective reported methods[5–9]. Benzocain and *p*-dimethyl amino benzaldehyde were also obtained commercially.

Preparation of ligand

The Schiff base was prepared by refluxing benzocain and *p*-dimethyl amino benzaldehyde in equimolar ratio (1 : 1) in ethanolic medium for 3 h. The reaction mixture was then cooled in ice bath and on prolonged cooling the product was obtained.

M.p. –228°C, yield 80%, colour—brown; Found: C, 72.1; H, 6.2; N, 9.1; Calcd. for C, 72.9; H, 6.7; N, 9.4%.

Preparation of complexes

$Th(NO_3)_4 \cdot 2L$: The complex was prepared by mixing $Th(NO_3)_4$ (1 mmol) and ligand (2 mmol) in (20 mL) in butanol and refluxing the reaction mixture at *ca.* 75°C for 1 h. On cooling the reaction mixture, desired product was collected which was than washed with ether and finally dried *in vacuo* over P_4O_{10}.

$ThX_4 \cdot 4L$ ($X = Cl^-, Br^-$) and $UO_2X_2 \cdot 2L$ ($X = NO_3^-, CH_3COO^-$ and Br^-): These complexes were prepared by mixing corresponding uranyl salt with ligand in 1:2 molar ratio and thorium salt with ligand in 1:4 molar ratio in isopropanol (20 mL) and refluxing the reaction mixture at *ca.* 75°C for 1 h and treated as above.

$ThX_4 \cdot nL$ ($n = 4, X = I^-$ or NCS^-) and $UO_2X_2 \cdot 2L$ ($X = I^-$ or NCS^-): These complexes were prepared by mixing ThX_4 with ligand in 1:4 molar ratio and UO_2X_2 and ligand in 1:2 molar ratio in methanol (20 mL) and refluxing the reaction mixture at *ca.* 70°C for 1 h. On cooling the reaction mixture, desired product was collected which was then washed with the solvent and finally with ether and dried *in vacuo* over P_4O_{10}.

$Th(ClO_4)_4 \cdot 6L$ and $UO_2(ClO_4)_2 \cdot 4L$: The complexes were prepared by refluxing $UO_2(ClO_4)_2$ (1 mmol) with ligand (4 mmol) and $Th(ClO_4)_4$ (1 mmol) with ligand (6 mmol), respectively in methanolic medium and concentrating the solvent to a certain extent. The complexes were collected and washed with ethanol and ether and finally dried *in vacuo* over P_4O_{10}.

All physico-chemical studies were performed by usual methods[10] and uranium and thorium were estimated as U_3O_8 and ThO_2.

RESULTS AND DISCUSSION

The interaction of Schiff base with the respective metal salts results in the formation of adducts $ThX_4 \cdot nL$ ($X = Cl^-$, Br^-, NCS^-, n = 4; $X = I^-$ or ClO_4^-, n = 6; $X = NO_3^-$, n = 2) and $UO_2X_2 \cdot 2L$ ($X = NO_3^-$, Br^-, I^-, NCS^- or CH_3COO^-) and $UO_2(ClO_4)_2 \cdot 4L$.

The analytical data of these complexes are presented in Table-1. The complexes are quite stable and can be stored for a long period at room temperature (*ca.* 30°C) except the iodide complexes which decompose to a sticky mass after a few weeks. The complexes are sufficiently soluble in common organic solvents.

In order to understand the nature of complexes in solution their electrical conductivities were determined in $PhNO_2$ medium. All the complexes are essentially non-electrolytes except $ThI_4 \cdot 4L$, $Th(ClO_4)_4 \cdot 6L$ and $UO_2(ClO_4)_2 \cdot 4L$. The conductivity values for all other complexes are too low to account for any dissociation but these complexes behave like 1:2 electrolytes while $Th(ClO_4)_4 \cdot 6L$ behaves as 1:4 electrolyte. This suggests that the perchlorato and iodo groups in these three complexes are ionic in ntaure. The molecular weight data of these complexes in nitrobenzene are also contained in Table-1 along with their values calculated on the basis of established formula for the complexes.

These complexes are found to be diamagnetic in nature[11, 12]. Their magnetic susceptibilities are independent of field strength and temperature[13]. The ground state of dioxouranium and thorium complexes contained no unpaired electrons. The compounds are therefore expected to be weakly diamagnetic as observed[12, 14, 15].

TABLE-1
ANALYTICAL CONDUCTIVITY AND MOLECULAR WEIGHT DATA FOR COMPLEXES OF SCHIFF'S BASE (L)

Compound/colour	m.p. (°C)	Analysis: Found (calcd.) %			Ω_M M ohm^{-1} cm^2 mole^{-1}	Mol. wt. found (calcd.)
		Metal	N	Anion		
$Th(NO_3)_4 \cdot 2L$	213	20.50	10.24	—	2.7	1065
(yellow)		(21.60)	(10.44)			(1072)
$ThCl_4 \cdot 4L$	215	14.20	7.50	9.13	3.4	1548
(yellowish brown)		(14.80)	(7.18)	(9.11)		(1558)
$ThBr_4 \cdot 4L$	224	12.90	6.30	18.67	4.1	1727
(yellow)		(13.30)	(6.45)	(18.43)		(1736)
$ThI_4 \cdot 4L$	203	11.90	5.10	25.20	50.8	640
(orange)		(12.05)	(5.85)	(26.40)		(1924)
$Th(ClO_4)_4 \cdot 6L$	207	9.80	6.80	16.30	91.2	408
(yellow)		(9.60)	(6.98)	(16.50)		(2406)
$Th(NCS)_4 \cdot 4L$	232	14.80	10.90	14.80	3.8	1632
(orange)		(14.07)	(10.19)	(14.07)		(1648)
$UO_2(NO_3)_2 \cdot 2L$	202	23.60	8.10	—	4.2	980
(orange)		(24.13)	(8.51)			(986)
$UO_2(OAc)_2 \cdot 2L$	199	24.80	5.10	12.60	4.5	974
(brown)		(24.20)	(5.71)	(12.40)		(980)
$UO_2Br_2 \cdot 2L$	195	23.90	4.90	15.10	3.3	1011
(blood red)		(23.20)	(5.47)	(15.65)		(1022)
$UO_2I_2 \cdot 2L$	230	20.90	4.80	21.90	3.8	1110
(reddish yellow)		(21.30)	(5.01)	(22.70)		(1116)
$UO_2(NCS)_2 \cdot 2L$	224	24.10	7.90	11.10	2.9	972
(brick red)		(24.30)	(8.58)	(11.80)		(978)
$UO_2(ClO_4)_2 \cdot 4L$	220	14.50	6.20	11.60	50.2	548
(yellow)		(14.20)	(6.77)	(12.00)		(1653)

Electronic spectral studies: A comparison of spectral of the free Schiff base with some of the uranyl complexes in methanol solution shows that there is a change in the position of the bands. The Schiff base show the absorption near 244, 290 and 498 nm and the corresponding bands in the complexes appear at

261, 294 and 388 nm. The first two transitions 244 and 290 nm are due to $\phi \rightarrow \phi^*$ and $\pi \rightarrow \pi^*$ benzenoid[16–18] and $\pi \rightarrow \pi^*$ (axomethine)[17, 18] respectively. The third band observed at 388 nm in complexes and correspondingly at 398 nm in Schiff base. The shift of this band towards lower wavelength may be due to coordination of azomethine nitrogen to metal atom[16].

Infrared spectral studies: The partial IR data for these complexes is given in Table-2. As it is clear from the data that there is no considerable shift in ν(C═O) str., so, it may be concluded that C═O of the ester group is not involved in the bonding with metal. The second possibility of tertiary amine nitrogen for coordination can also be ruled out on the same reason. But there is a change in ν(C═N) which shows that the bonding site may be the azomethine nitrogen through which this ligand binds to the metal ion[19, 20]

TABLE-2
PARTIAL IR DATA (cm^{-1}) FOR Th(IV) AND UO$_2^{2+}$(VI) COMPLEXES OF SCHIFF BASE

Complex	ν(C═O)	ν(C═N)	ν(C—N)	ν(M—N)
Ligand (L)	1690 s	1625 s	1170 m	—
$Th(NO_3)_4 \cdot 2L$	1685 s	1640 s	1170 m	580 m
$ThCl_4 \cdot 4L$	1684 s	1642 s	1175 sh	585 m
$ThBr_4 \cdot 4L$	1687 s	1636 s	1172 m	585 m
$ThI_4 \cdot 4L$	1688 s	1635 s	1173 sh	580 m
$Th(NCS)_4 \cdot 4L$	1689 s	1640 s	1174 m	580 m
$Th(ClO_4)_4 \cdot 6L$	1690 s	1645 s	1175 m	589 m
$UO_2(NO_3)_2 \cdot 2L$	1684 s	1640 s	1170 m	550 m
$UO_2Br_2 \cdot 2L$	1688 s	1645 s	1178 m	560 m
$UO_2I_2 \cdot 2L$	1680 s	1642 s	1175 m	570 m
$UO_2(NCS)_2 \cdot 2L$	1689 s	1648 s	1177 sh	565 sh
$UO_2(OAc)_2 \cdot 2L$	1684 s	1644 m	1172 m	568 sh
$UO_2(ClO_4)_4 \cdot 4L$	1684 s	1640 s	1176 m	570 m

s = strong, m = medium, sh = shoulder.

The shift to higher wave number is due to unshaired pair of electrons of N-atom being attached to the metal atom, breaking the N, π conjugation with aniline ring and developing a partial positive charge on the nitrogen atom. The aniline ring becomes coplaner in the molecule, but the positive charge on the N atom hinders the usual $\pi \rightarrow \pi^*$ conjugation of the azomethine group with aniline nucleus. The removal of the azomethine group from conjugation with its electronic structure analogous to $\text{—CH=}\overset{+}{\text{N}}\text{H—}$ increases the frequency of its absorption in IR spectra[21, 22].

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