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Dioxouranium(VI) and Thorium(IV) Complexes with Potential Tetradentate Schiff Base Ligand

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A series of dioxouranium(VI) and thorium(IV) complexes were synthesised with the tetradentate Schiff base ligand (N_2O_2 donor set) obtained by the condensation of *o*-phenylenediamine with salicylaldehyde (H_2-Salophen). The complexes formed are of the type $[UO_2(H_2L)_2]X_2$, where $X = Cl^-, I^-$, $[UO_2H_2L(NO_3)_2]\cdot H_2O\cdot C_2H_5OH$, $[UO_2(HL)_2]\cdot 2CH_3CO,CH_3$, $[UO_2(HL)CH_3COO\cdot H_2O]$, $[UO_2(H_2L)SO_4]$, $UO_2H_2L(SCN)_2$, $[Th(H_2L)_2(NO_3)_2](NO_3)_2$ and $Th(H_2L)_2(SCN)_4$. The complexes contain 6-coordinated UO_2^{2+} group with anions inside the coordination sphere and 12-coordinated thorium. Analytical, UV-visible, IR, molar conductance, molecular weight determination and TGA data are presented in support of the strucures of the complexes.

INTRODUCTION

Much work has been reported on the transition metal complexes of tetradentate Schiff bases derived from substituted aromatic carbonyl compounds and a number of diammines, such as ethylene diamine and propylenediamine [1–6], but those for uranium and other actinides are not so frequent. The coordination chemistry of dioxouranium(VI) and thorium(IV) ion has been less extensively investigated[7, 8] even though they present an excellent area of research because of the possibility of forming coordination number greater than 6 and hence attracted wide attention in recent years[9, 10]. The UO_2^{2+} group coordinates 2 to 8 other atoms, ions or molecules in the equatorial plane with a strong tendency to make these ligating atoms coplanar[11]. The large thorium(IV) ion with ionic radii of 0.99 Å and high charge form complexes of higher coordination number[12]. With this fact we are engaged in synthesising Th(IV) and UO_2(VI) complexes with Schiff base ligands. Some recent publications show that UO_2(VI) and Th(IV) form Schiff base complexes of the type $[UO_2LX_2]$[13, 14] and $[ThL_2X_4]$[15], where L = bis(salicylidene) ethylenediamine, bis(acetylacetone) ethylenediamine, bis(benzoylacetone) ethylenediamine and $X = Cl^-, I^-, NO_3^-, NCS^-, 0.5SO_4^{2-}$, $[UO_2(H_2L)X_2]$[16], $[Th(H_2L)X_4]$[16] where H_2L = bis(salicylidene)ehylene diamine and $X = Cl^-, I^-, NO_3^-, NCS^-$ and $0.5SO_4^{2-}$.

This paper reports the results of investigation of series of thorium(IV) and uranyl(VI) complexes with bis(salicylidene) *ortho*-phenylene diamine-(H_2 salophen)

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EXPERIMENTAL

Details of materials and physico-chemical techniques are similar to reported method.[17]

Preparation of complexes

$[UO_2(H_2L)NO_3)_2]\cdot H_2O, C_2H_5OH$: Uranyl nitrate hexahydrate (0.5 g, 1 mmol) solution in absolute ethanol (5 mL) was added to a solution containing the ligand (0.62 g, 2 mmol) in absolute ethanol (50 mL) in boiling condition with constant stirring. It was then refluxed for 1 h. On cooling, the resulting orange coloured solid obtained was washed with ethanol and ether and dried under reduced pressure.

$[UO_2(H_2L)SO_4]$: Hydrated uranyl sulphate (0.43 g, 1 mmol) solution in absolute ethanol (10 mL) was added to a solution containing the ligand (0.62 g, 2 mmol) in absolute ethanol (50 mL) in boiling condition with constant stirring. It was then refluxed for $\frac{1}{2}$ h. On cooling, the orange coloured solid obtained was washed with ethanol and ether and dried in vacuum.

$[UO_2(H_2L)_2]Cl_2$: Ethanolic solution of uranyl chloride (0.37 g, 1 mmol) was added dropwise with constant stirring to ethanolic ligand (0.62 g, 2 mmol) solution. It was then refluxed for $\frac{1}{2}$ h. On cooling, the resulting orange coloured solid obtained was suction filtered washed in ethanol and ether and dried under reduced pressure.

$[UO_2(H_2L)_2]I_2$: Ethanolic solution of UO_2I_2 was obtained by mixing uranyl nitrate hexahydrate (0.5 g, 1 mmol) with ethanolic KI (0.34 g, 2 mmol) soln. in ethanol (5 mL). The potassium nitrate precipitate was filtered off and the filtrate was concentrated by slow evaporation. This solution was added dropwise to the ligand (0.62 g, 2 mmol) in ethanol (50 mL). The colour of the solution was changed to deep red. On stirring the solution for $\frac{1}{2}$ h, the deep orange solid appeared was suction filtered, washed in ethanol and ether and dried under reduced pressure.

$[UO_2H_2L(SCN)_2]$: Ethanolic solution of $UO_2(SCN)_2$ was obtained by mixing uranyl nitrate hexahydrate (0.5 g, 1 mmol) in absolute ethanol (3 mL) with KSCN (0.19 g, 2 mmol) in absolute ethanol (5 mL) and filtering off the insoluble white precipitate of potassium nitrate. This solution was added dropwise to the ligand (0.62 g, 2 mmol) in ethanol (50 mL) in hot condition. On refluxing the resulting solution for $\frac{1}{2}$ h the orange coloured solid obtained was suction filtered, washed in ethanol and ether and dried under reduced pressure.

$[UO_2(HL)(CH_3COO)H_2O]$: Uranyl acetate (0.32 g, 1 mmol) in ethanol-methanol mixture (10 mL) was added dropwise to the ligand (0.62 g, 2 mmol) in ethanol-methanol (50 mL) with constant stirring. The orange precipitate obtained was filtered, washed in ethanol and ether and dried under reduced pressure (0.45 g).

$[UO_2(HL)_2]2CH_3COCH_3$: Sodium acetate (2 g) was added to acetone-ethanol mixture (50 mL) ligand (0.62 g, 2 mmol) solution and warmed for 5 min. To that uranyl acetate (0.32 g, 1 mmol) in acetone-ethanol (10 mL) mixture solvent was added slowly. It was then refluxed for 2 h, cooled overnight at about 0°C in the fridge. The deep red amorphous compound obtained was suction filtered, washed in acetone and ether and dried under reduced pressure.

TABLE-1

ANALYTICAL, CONDUCTANCE MEASUREMENT AND ANALYTICAL DATA OF Th^{4+} AND UO_2^{2+} COMPLEXES

Compound	Empirical formula/Colour	mol. wt.	m.p. (°C)	% Analysis, found (calcd.)					in mho (10 M^{-3})	
				M	C	H	N	% of H_2O loss	MeOH	$PhNO_2$
Ligand (H_2L)	$C_{20}H_{16}N_2O_2$ (yellow)	325 (316)	162	—	76.37 (75.94)	5.40 (5.06)	8.89 (8.86)	—	—	—
$[UO_2(H_2L)(NO_3)_2]H_2O\cdot C_2H_5OH$	$UC_{22}H_{24}N_4O_{12}$ (orange crystalline)	760 (774)	>250	30.30 (30.74)	34.50 (34.10)	3.50 (3.10)	7.10 (7.23)	8.50 (8.26)	30	14
$[UO_2(H_2L)SO_4]$	$UC_{20}H_{16}N_2O_8S$ (orange crystalline)	699 (682)	>250	35.10 (34.98)	34.80 (35.19)	2.60 (2.34)	4.50 (4.10)	—	16	Insol.
$[UO_2(H_2L)_2]Cl_2$	$UC_{40}H_{32}N_4O_6Cl_2$ (orange crystalline)	958 (973)	>250	24.75 (24.46)	49.80 (49.33)	3.63 (3.28)	5.34 (5.75)	—	235	105
$[UO_2(H_2L)_2]I_2$	$UC_{40}H_{32}N_4O_6I_2$ (deep orange crystalline)	1174 (1156)	>250	20.12 (20.58)	40.60 (41.52)	2.75 (2.76)	4.53 (4.84)	—	260	106
$[UO_2(HL)CH_3COO\cdot H_2O]$	$UC_{22}H_{20}N_2O_7$ (orange crystalline)	648 (662)	>250	35.53 (35.95)	40.20 (39.87)	2.65 (3.02)	4.60 (4.22)	3.10 (2.71)	40	15
$[UO_2(H_2L)(SCN)_2]$	$UC_{22}H_{16}N_4O_4S_2$ (orange crystalline)	723 (702)	>250	33.45 (33.90)	38.21 (37.60)	2.42 (2.27)	7.30 (7.97)	—	23	10
$[UO_2(HL)_2(CH_3COCH_3)_2$	$UC_{46}H_{42}N_4O_8$ (red amorphous)	998 (1016)	150	23.10 (23.42)	53.71 (54.33)	4.40 (4.13)	5.92 (5.51)	11.60 (11.41)	25	10
$[Th(H_2L)_2(NO_3)_2](NO_3)_2$	$ThC_{40}H_{32}N_8O_{16}$ (yellow crystalline)	1127 (1112)	>250	20.95 (20.86)	43.60 (43.16)	2.34 (2.87)	10.50 (10.07)	—	335	125
$[Th(H_2L)_2(SCN)_4]$	$ThC_{44}H_{32}N_8O_4S_4$ (yellow crystalline)	1068 (1096)	>250	22.93 (21.16)	48.73 (48.18)	3.50 (2.92)	10.40 (10.22)	—	35	16

TABLE-2: KEY IR DATA (cm^{-1}) OF THE LIGAND AND OF METAL COMPLEXES

Compound	Anion vibrational modes	Uranyl modes		ν(OH) and ν(CH)	ν(C=N)	ν(C—O)	ν(C—N)	ν(C=O)
		$\nu_{sym}(UO)_2$	$\nu_{asym}(UO_2)$					
Ligand (H_2L)	—	—	—	3400 br	1638 s, 1605 s, 1590 m	1290 s	1207 s	—
$[UO_2(H_2L)(NO_3)_2]H_2O$, C_2H_5OH	1460 s, 1030 s, 920 s, 810 s, 1290 s, 730 s	818 s, 822 s	910 s	3140 s, 3120 s, 2980–2820 br, 2760 s, 2275 s	1622 s 1615 s	1282 s	1192 s	—
$[UO_2(H_2L)SO_4]$	1152 s, 1122 m, 1105 s, 1090 s, 1035 s, 985 m, 638 s, 605 m	820 s, 805 s, 760 s	910 s	2900 br, 2800 s, 2720 s, 2660 s	1620 s 1592 s	1285 s	1192 s	—
$[UO_2(H_2L)_2]Cl_2$	—	850 s, 825 s, 260 m	920 s	3100 br 2660 br	1618 s 1592 m	1310 s 1295 m	1200 s 1185 s 1165 s	—
$[UO_2(H_2L)_2]I_2$	—	855 s, 830 s, 260 s	915 s	3100 br 2660 br	1618 s 1592 s	1315 s 1290 s	—	—
$[UO_2(H_2L)CH_3COO{\cdot}H_2O]$	1730 m, 1690 s, 1620 s, 1385 s, 1030 m, 720 s	850 s, 820 s	915 s	3180 s 2980–2820 br 2720 br, 2660 s	1618 s 1590 s	1312 s	1198 s 1155 s	1735 s
$[UO_2(H_2L)(SCN)_2]$	2030 s, 825 m, 460 m	820 s	910 s	3100 br 2720 s	1630 s 1595 m	1290 s	1185 s 1160 m	1710 st
$[UO_2(HL)_2(CH_3COCH_3)_2$	—	850 s, 815 m	935 s 920 s	2900 s 2725 s 2675 m	1615 st 1595 s 1450 m	1305 s 1275 s	1155 s 1128 m 1105 m	1715 st
$[Th(H_2L)_2(NO_3)_2](NO_3)_2$	1578 s, 1470 s, 1300 br, 1380 st, 1245 st, 920 m 810 s, 745 st, 795 m	—	—	2980–2825 br 2720 s, 2660 s	1615 st 1570 s 1450 st	1325 s	1175 s 1160 s	1720 s
$[Th(H_2L)_2(SCN)_4]$	2035 s, 820 s, 460 m	—	—	2920 s 2820 br	1690 s, 1610 s 1600 s, 1580 w	1370 s	1160 s	1700 s

$[Th(H_2L)_2(NO_3)_2](NO_3)_2$: $Th(NO_3)_4{\cdot}6H_2O$ (0.5 g, 1 mmol) in ethanol (10 mL) was added dropwise to ligand (0.62 g, 2 mmol) solution in ethanol (50 mL) and refluxed for 1 h. The greyish precipitate obtained was filtered off and 5 drops of conc. HNO_3 was added to the filtrate and refluxed for 2 h. The resulting refluxed solution was concentrated to about 20 mL and cooled overnight. The bright yellow brittle compound formed was filtered, washed in ethanol and dried under reduced pressure.

$[Th(H_2L)_2(SCN)_4]$: $Th(SCN)_4$ was prepared metathetically by reacting hydrated $Th(NO_3)_4$ (0.59 g, 1 mmol) with KSCN (0.38 g, 4 mmol) in absolute ethanol (5 mL) and filtering off the insoluble white precipitate of KNO_3. This solution was added dropwise to the ligand (0.62 g, 2 mmol) in ethanol (50 mL) boiling condition. The mixture solution was refluxed for 2 h and concentrated, and on cooling overnight a yellow compound was formed which was filtered washed in ethanol and dried under reduced pressure.

RESULTS AND DISCUSSION

The analytical, conductivity measurement data and the IR absorptions of the complexes are given in Tables 1 and 2 respectively. Conductivity measurements indicated that uranyl complexes except the halide complexes are nonionic while in case of thorium complexes the nitrate complex is 1:2 electrolyte and the thiocyanate complex is non-electrolyte.

The presence of SO_4^{2-} in the inner sphere is indicated by the splitting of the ν_3 and ν_4 modes of bidentate SO_4^{2-} and appearance of the forbidden $\nu_1(SO_4)$ vibration at 985 cm^{-1} in the IR spectra. The bands at 1152, 1122, 1105, 1090, 1035, 638, 605 cm^{-1} confirm the bidentate nature of sulphate[17, 18].

In case of uranyl nitrate complex, absence of any absorption at 1380 cm^{-1} is indicative of a non-ionic NO_3^-. The ν_1 (1290 cm^{-1}), ν_2 (1030 cm^{-1}) and ν_3 (730 cm^{-1}) modes in the IR spectra confirmed monodentate nitrato in the complex[19–21]. The presence of water and ethanol in the outer sphere is indicated by a broad νH_2O absorption band at 3100 cm^{-1} in the IR spectra and loss of water at 270°C in the TG analysis, % loss 8.5 (calcd. 8.26). In the nitrato and sulphato complexes uranium is 8-coordinated. In the thorium nitrate complex a sharp band at 1380 cm^{-1} is indicative of ionic nitrate in the outer sphere of the complex[22–24]. Besides characteristic bands of bidentate nitrato group at 1520, 1470, 1300, 1030, 920, 810 cm^{-1} are observed in the IR spectra of the complex[24–27] Thus the coordination number of thorium is 12.

The conductivity measurement data and absence of IR absorption between 240–200 cm^{-1} of the uranyl halide complexes indicates that Cl^- and I^- are non-coordinated and are present in the ionisation sphere[13]

In the uranyl acetate complex the acetato group acts as a symmetrically bidentate chelating group coordinating through both the oxygen atoms. This information was obtained from conductance measurement and IR absorptions at 1620, 1385, 1030, and 720 cm^{-1} corresponding to $\nu_{asym}(COO)$, $\nu_{sym}(COO)$ and $\delta(COO)$ respectively[28, 29]. Presence of one molecule of water is indicated by the IR band at 3180 cm^{-1}. The loss of the water molecule at 350°C, known from TG analysis, confirmed it to be coordinated in nature [% loss 3.1 (calcd. 2.7)].

When uranyl acetate is allowed to react with the ligand in presence of sodium acetate, two anionic ligands formed by losing one proton each are bonded to the UO_2^{2+} group in the equatorial position. Two molecules of acetone are weakly bonded and are present outside the coordination sphere. TG analysis shows [% loss 11.6 (calcd. 11.4)] both the acetone molecules are removed below 150°C. A strong and sharp IR band at 1730 and 1720 cm^{-1} confirmed the presence of ketonic carbonyl group which is supported by the experimental molecular weight value.

In both the thiocynato complexes of uranium and thorium the IR bands around 2030, 825 and 460 cm^{-1} corresponding to ν(C—N), ν(C—S) and δ(NCS) respectively of a terminal thiocynato group coordinated through nitrogen atom[30, 31].

The IR bands around 920 and 810 cm^{-1} are observed due to the ν_{asym}(U—O) and ν_{sym}(U—O) modes[33] respectively and the band at 260 cm^{-1} corresponding to δ(O—U—O) bending vibration indicated the linearity of UO_2^{2+} group[32, 33]

The vibrational modes of the ligands in the complexes are in the range 1620–1590 cm^{-1} for ν_{sym}(C=N), 1400–1280 cm^{-1} for ν_{sym}(C—O) and 1210–1190 cm^{-1} for ν_{sym}(C—N) and the phenyl ring vibrations around 1550, 1020 cm^{-1}. The ligand ν(O—H) vibration appears as broad band between 2950 to 2870 cm^{-1} suggesting the coordination of a neutral ligand and not the anions of the ligand[34, 35]. The ν(C—H) are observed at 2720 and 2660 cm^{-1}.

The electronic spectra of the ligand and the complexes are recorded in the wavelength range 200 to 1600 nm in KBr and with organic solvents (MeOH and $PhNO_2$) of different polarity. The uranyl complexes in general exhibited absorption bands at 340 to 500 nm due to the vibronic structure and the effects of the equaitorial ligand on these absorptions are negligible[36, 37]. The shape and absorption maxima of all the complexes are found identical at 300 nm, 380 nm and at 480 nm were observed. However, the absorption band of the UO_2^{2+} between 390–450 nm is overlapped by the fairly strong ligand to metal charge transfer bands[38, 90]. This charge transfer transition occurs from the π-orbitals of the Schiff base to the 'f' orbitals of U and Th.

The thermal decompositions of the uranyl nitrate and thorium thiocyanate complexes were investigated to get more information about the stoichiometry of the complexes. The stoichiometry of thermal decomposition obtained is:

$$[UO_2(H_2L)(NO_3)_2]H_2O{\cdot}C_2H_5OH \xrightarrow{ca.\ 150^{\circ}C} UO_2(H_2L)(NO_3)_2$$

$$\xrightarrow{ca.\ 350^{\circ}C} UO_2(NO_3)_2 \xrightarrow{ca.\ 700^{\circ}C} U_3O_8$$

$$[Th(H_2L)_2(NCS)_4] \xrightarrow{ca.\ 330^{\circ}C} [Th(H_2L)(NCS)_4] \xrightarrow{ca.\ 360^{\circ}C} Th(NCS)_4$$

$$\xrightarrow{ca.\ 400^{\circ}C} ThO_2$$

It is significant to observe here that in case of uranyl complexes U_3O_8 and in case of thorium complexes ThO_2 is obtained as the end product.

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