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Synthesis and Studies of Thorium(IV) and Uranyl(VI) Complexes with Some Bidentate Schiff Bases

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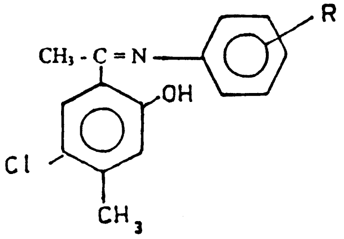
A series of complexes of bidentate Schiff bases, obtained from 5-chloro-4-methyl-2-hydroxy acetophenone and substituted anilines with UO_2^{2+} and Th^{4+} has been synthesised. The complexes have been isolated in solid state and characterised on the basis of elemental analysis, conductivity, UV, IR, TGA and magnetic susceptibility measurements. The complexes formed are of the types $[Th(L)_2(NO_3)_2]$ and $[UO_2(L)_2]$.

INTRODUCTION

The oxygen bridged mono-bidentate and tridentate complexes have attracted much attention due to their interesting spectral and magnetic properties and their use in biochemical processes and homogeneous catalysis[1–4]. In the present study we have prepared bidentate complexes directly by the reaction of Schiff bases derived from 5-chloro-4-methyl-2-hydroxy acetophenone-aniline and substituted anilines with thorium and uranyl nitrates. The complexes obtained are of the type $[Th(L)_2(NO_3)_2]$ and $[UO_2(L)_2]$ respectively, where L is a schiff base molecule as shown below.



where R = H, R = *o,m,p*-chloro or R = *o,m,p*-methyl

EXPERIMENTAL

All the chemicals used were of AR grade (BDH or Fluka); 5-chloro-4-methyl-2-hydroxy acetophenone was prepared by the Fries migration reaction of the acetate derivative of 4-chloro-3-methyl phenol.

The Schiff bases (ligands) were prepared by refluxing equimolar quantities of acetophenone and aromatic amines in ethanol with catalytic quantity of acetic acid for 3 h, solidification occurred after concentrating and cooling. The resulting crystals were filtered dried and purified by recrystallisation in ethanol and their purities checked by elemental analysis, m.p. etc. (Table-1). All the Schiff bases were yellowish in colour and crystalline in nature.

TABLE-1
ANALYTICAL DATA OF SCHIFF BASE LIGANDS

Ligand no.	Ligand (m.f.)	m.w.	m.p. (°C)	% Found (Calcd.)			
				C	H	N	Cl
L_1	$C_{15}H_{14}ONCl$	259.739	152	69.30 (69.36)	5.48 (5.43)	5.41 (5.39)	13.69 (13.65)
L_2	$C_{15}H_{13}ONCl_2$	294.180	115	61.30 (61.24)	4.48 (4.45)	4.79 (4.76)	24.22 (24.10)
L_3	$C_{15}H_{13}ONCl_2$	294.180	137	61.26 (61.24)	4.49 (4.45)	4.78 (4.76)	24.20 (24.10)
L_4	$C_{15}H_{18}ONCl_2$	294.180	146	61.28 (61.24)	4.47 (4.45)	4.79 (4.76)	24.18 (24.10)
L_5	$C_{16}H_{16}ONCl$	273.761	102	70.25 (70.20)	5.91 (5.89)	5.15 (5.12)	13.00 (12.95)
L_6	$C_{16}H_{16}ONCl$	273.761	122	70.24 (70.20)	5.93 (5.89)	5.15 (5.12)	13.02 (12.95)
L_7	$C_{16}H_{16}ONCl$	273.761	129	70.26 (70.20)	5.92 (5.89)	5.15 (5.12)	12.99 (12.95)

The complexes were prepared by refluxing ethanolic solutions of the metal nitrates and ligands in 1 : 2 ratio for 3 h. After cooling and adjusting the pH to 7.0 with dilute alcoholic ammonia solution the complex precipitated out was filtered and washed with hot ehtanol and dried in vacuum.

The thorium complexes were yellow while uranyl complexes were orange in colour. The complexes were analysed for metal ions by standard methods[5]. Carbon, hydrogen, nitrogen and chlorine were analysed microanalytically (Tables 2 and 3).

TABLE-2
ANALYTICAL DATA OF THORIUM(IV) COMPLEXES

Complex (m.w.)	Decomposition temp. (°C)	Conductivity ohm^{-1} cm^2 mol^{-1}	% Found (Calcd.)				
			C	H	N	Cl	Th
1. $[Th(L_1)_2(NO_3)_2]$ (873.54)	>300	12.25	41.32 (41.25)	3.12 (3.00)	6.55 (6.41)	8.18 (8.12)	26.66 (26.57)
2. $Th(L_2)_2(NO_3)_2]$ (942.41)	>250	6.27	38.30 (38.23)	2.61 (2.57)	6.02 (5.95)	15.13 (15.05)	24.73 (24.62)
3. $[Th(L_3)_2(NO_3)_2]$ (942.41)	>250	6.13	38.29 (38.23)	2.60 (2.57)	5.99 (5.95)	15.20 (15.05)	24.70 (24.62)
4. $[Th(L_4)_2(NO_3)_2]$ (942.41)	>250	6.30	38.32 (38.23)	2.62 (2.57)	6.08 (5.95)	15.12 (15.05)	24.75 (24.62)
5. $[Th(L_5)_2(NO_3)_2]$ (901.58)	>250	5.62	42.71 (42.63)	3.43 (3.35)	6.30 (6.21)	7.89 (7.87)	25.80 (25.74)
6. $[Th(L_6)_2(NO_3)_2]$ (901.58)	>250	5.58	42.73 (42.63)	3.44 (3.35)	6.33 (6.21)	7.95 (7.87)	25.83 (25.74)
7. $[Th(L_7)_2(NO_3)_2]$ (901.58)	>250	5.79	42.74 (42.63)	3.45 (3.35)	6.36 (6.21)	7.98 (7.87)	25.88 (25.74)

TABLE-3
ANALYTICAL DATA OF URANYL(VI) COMPLEXES

Complex (m.w.)	Decomposition temp. (°C)	Conductivity ohm^{-1} cm^2 mol^{-1}	% Found (calcd.)				
			C	H	N	Cl	U
1. $[UO_2(L_1)_2]$ (787.52)	>250	9.73	45.87 (45.76)	3.42 (3.33)	3.68 (3.56)	9.12 (9.00)	30.98 (30.23)
2. $[UO_2(L_2)_2]$ (856.38)	>300	5.32	42.20 (42.08)	2.98 (2.82)	3.40 (3.27)	16.71 (16.56)	27.95 (27.80)
3. $[UO_2(L_3)_2]$ (856.38)	>300	5.28	42.22 (42.08)	2.97 (2.82)	3.41 (3.27)	16.70 (16.56)	28.01 (27.80)
4. $[UO_2(L_4)_2]$ (856.38)	>300	5.40	42.19 (42.08)	2.99 (2.82)	3.39 (3.27)	16.72 (16.56)	28.01 (27.80)
5. $[UO_2(L_5)_2]$ (815.54)	>300	3.78	47.20 (47.13)	3.86 (3.71)	3.55 (3.43)	8.81 (8.69)	29.35 (29.20)
6. $[UO_2(L_6)_2]$ (815.54)	>300	3.69	47.19 (47.13)	3.85 (3.71)	3.58 (3.43)	8.80 (8.69)	29.36 (29.20)
7. $[UO_2(L_7)_2]$ (815.54)	>300	3.81	47.24 (47.13)	3.83 (3.71)	3.60 (3.43)	8.82 (8.69)	29.34 (29.20)

RESULTS AND DISCUSSION

All the complexes are very much stable and have high m.p. and are sparingly soluble in common organic solvents. The analytical data of the complexes are recorded in Tables 2 and 3. The elemental analyses indicate that the metal and ligand is in 1 : 2 stoichiometry. The thorium complexes are of the type $[Th(L)_2(NO_3)_2]$, while uranyl complexes are $[UO_2(L)_2]$ respectively. The conductance measurements were carried out at room temperature using an ELICO conductivity instrument. The electrical conductivity values of 10^{-3} M solutions in DMF (Tables 2 and 3) were in the range 3.0–12.0 ohm^{-1} cm^2 mol^{-1} indicating nonelectrolytic nature of the complexes[6, 7]. The electronic spectra of the ligand and complexes were measured by using Shimadzu UV-265 instrument. The ligand and the complexes exhibit bands at 265–330 nm due to the vibronic structure of the metal, which seems to be overlapped by the fairly strong ligand to metal charge transfer bands[8, 9]. The bands are obtained below 330 nm corresponding to the ligand π-π^* region and provide no assistance in determining the environment of the metal atom in the complexes.

The IR spectra of the ligands and complexes were recorded in KBr on Perkin-Elmer-781 IR spectrophotometer. In the IR spectra of the ligands, bands were obtained in the range 1650–1570 cm^{-1} for ν(C═N) at 1300, 1100 cm^{-1} for ν(C—O) and at about 2900, 2490 cm^{-1} for ν(C—H). The broad weak band in the region 3450–3400 cm^{-1} is due to the intramolecularly H bonded OH. This band totally disappeared in the complexes suggesting the involvement of OH group in coordination. The shift of lower to higher wave numbers of ν(C═N) or ν(C—O) respectively in the complexes indicates participiation of nitrogen atom of the azomethine group and phenolic (C—O) in coordination after deprotonation[10–12]. This was further supported by the disappearance of OH stretching vibration in the complexes. The uranyl complexes exhibiting a strong bands at 901–890 cm^{-1} are due to ν_{sym}(U=O), ν_{asym}(U=O) respectively of a linear O=U=O moiety[13]. The IR spectra of Th(IV) complexes exhibited bands around 1270–1220 cm^{-1} corresponding to unidentate nitrate group[14, 15]. The formation of the (M—N) and (M—O) bonds was further supported by the appearance of ν(M—N) and ν(M—O) in the regions 410, 430, 465 cm^{-1} and 520, 540, 560 cm^{-1} respectively in the spectra of the complexes[9]. The IR spectral data of the ligands and their metal complexes are summarised in Tables 4–6 respectively.

TABLE-4

SELECTED INFRARED FREQUENCIES (cm^{-1}) OF SCHIFF BASE LIGANDS

Ligand no.	ν(C—H)	ν(C=N)	ν(C=C)	ν(C—O)	ν(OH)	ν(C—Cl)
L_1	2490 w	1615 sh	1558 sh 1482 sh	1256 m 1208 sh	3414 s	695 sh
L_2	2900 w	1620 s	1490 sh 1460 sh	1180 sh	3400 s	780 sh
L_3	2885 w	1610 s	1490 sh 1460 m	1290 m	3420 s	770 sh
L_4	2910 w	1630 s	1500 sh 1450 m	1180 sh 1110 sh	3450 s	780 sh
L_5	2900 w	1640 s	1500 sh 1470 w	1290 sh 1250 sh	3420 s	770 sh
L_6	2910 w	1630 s	1490 w 1460 w	1190 sh	3410 s	780 sh
L_7	2900 w	1620 s	1460 w 1450 w	1220 sh	3400 s	785 sh

TABLE-5

SELECTED INFRARED FREQUENCIES (cm^{-1}) OF THORIUM(IV) COMPLEXES

Sl. No.	ν(C—H)	ν(C=N)	ν(C=C)	ν(C—O)	ν(M—O)	ν(M—N)
1.	2900 w	1620 s	1500 w 1490 w	1220 sh 1180 sh	540 m	465 m
2.	2800 w	1640 s	1520 w 1460 w	1300 sh 1240 sh	560 m	425 m
3.	2810 w	1630 s	1530 w 1460 w	1240 sh 1200 sh	565 m	415 m
4.	2900 w	1630 s	1520 w 1480 sh	1240 sh 1190 sh	550 m	410 m
5.	2800 w	1600 sh	1550 sh 1490 sh	1200 sh 1190 sh	570 sh	430 sh
6.	2920 w	1610 sh	1540 sh 1470 sh	1230 sh 1160 sh	520 sh	430 sh
7.	2910 w	1590 sh	1480 sh 1440 sh	1250 sh 1160 sh	520 sh	430 m

TABLE-6 SELECTED INFRARED FREQUENCIES OF URANYL(VI) COMPLEXES

Sl. No.	ν(C—H)	ν(C═N)	ν(C═C)	ν(C—O)	ν(M—O)	ν(M—N)	ν(O═U═O)
1.	2900 w	1620 s	1490 w	1300 sh 1240 sh	550 m	460 m	910 sh
2.	2880 w	1640 sh	1440 sh	1250 sh 1230 sh	590 m	570 s	890 sh
3.	2890 w	1640 sh	1430 sh	1240 sh 1220 sh	580 m	460 s	890 s
4.	2890 w	1630 sh	1440 sh	1260 sh 1220 sh	590 m	465 s	880 s
5.	2990 w	1610 s	1450 sh	1250 sh 1230 sh	550 m	430 m	900 s
6.	2980 w	1620 s	1460 sh	1270 sh 1240 sh	560 m	425 m	890 s
7.	2900 w	1620 s	1510 sh 1490 sh	1260 sh 1240 sh	570 m	480 m	900 s

The TGA analyses of thorium and uranyl complexes were carried out to get information about the decomposition trend and relative volatility, The thorium complexes are stable up to 250°C and uranyl complexes are stable up to 225°C. The complexes lose the ligands earlier than the anion and finally form the stable oxides at 500°C and 700°C. The thermoanalytical data for the complexes are summarised in Tables 7 and 8.

TABLE-7 THERMOANALYTICAL DATA OF THORIUM(IV) COMPLEXES

Sr. no.	Complex	Thermal effect (DTA) T_{max} (°C)	% Found (calcd.) weight loss	Loss due to
1.	$[Th(L_1)_2(NO_3)_2]$	255 (Exo)	29.00 (28.98)	$2[Cl + N—C_6H_5]$
		285 (Exo)	20.50 (20.39)	$2[C—CH_3 + NO_3]$
		450 (Exo)	20.50 (20.40)	$2[C_6H_2—CH_3]$
		500	30.50 (30.23)	ThO_2
2.	$[Th(L_2)_2(NO_3)_2]$	250 (Exo)	34.28 (34.17)	$2[Cl_2 + N—C_6H_4]$
3.	$[Th(L_3)_2(NO_3)_2]$	315 (Exo)	19.00 (18.90)	$2[NO_3 + C—CH_3]$
4.	$[Th(L_4)_2(NO_3)_2]$	450 (Exo)	19.15 (18.91)	$2[C_6H_2—CH_3]$
		500	27.85 (28.02)	ThO_2
5.	$[Th(L_5)_2(NO_3)_2]$	285 (Exo)	31.50 (31.19)	$2[Cl + N—C_6H_4—CH_3]$
6.	$[Th(L_6)_2(NO_3)_2$	315 (Exo)	20.00 (19.75)	$2[NO_3 + C—CH_3]$
7.	$[Th(L_7)_2(NO_3)_2]$	385 (Exo)	20.00 (19.77)	$2[C_6H_2—CH_3]$
		500	29.50 (29.29)	ThO_2

TABLE-8
THERMOANALYTICAL DATA OF URANYL(VI) COMPLEXES

Sr. no.	Complex	Thermal effect (DTA) (°C)	% Found (calcd.) weight loss	Loss due to
1.	$UO_2(L_1)_2$	270 (Exo)	39.20 (39.01)	$2[Cl + CH_3\text{—}C\text{—}N\text{—}C_6H_5]$
		450 (Exo)	26.80 (26.70)	$2[CH_3\text{—}C_6H_2]$
		700	34.10 (34.29)	UO_2
2.	$UO_2(L_2)_2$	225 (Exo)	16.70 (16.56)	$2[Cl_2]$
3.	$UO_2(L_3)_2$	380 (Exo)	21.10 (21.04)	$2[N\text{—}C_6H_4]$
4.	$UO_2(L_4)_2$	450–500 (Exo)	30.92 (30.86)	$2[CH_3\text{—}C\text{—}C_6H_2O\text{—}CH_3]$
		750	31.92 (31.54)	UO_2
5.	$UO_2(L_5)_2$	225 (Exo)	8.80 (8.89)	$2[Cl]$
6.	$UO_2(L_6)_2$	350 (Exo)	26.00 (25.79)	$2[N\text{—}C_6H_4\text{—}CH_3]$
7.	$UO_2(L_7)_2$	370 (Exo)	6.70 (6.63)	$2[CH_3\text{—}C\text{—}]$
		450–500 (Exo)	25.60 (25.57)	$2[CH_3\text{—}C_6H_2\text{—}O\text{—}]$
		750	33.20 (33.12)	UO_2

Magnetic susceptibilities of all the compounds were measured at room temperature (300 K) by Farday apparatus using CAHN balance and $Hg[CO(NCS)_4]$ was used as calibrating agent. The values of specific susceptibility (χ) and molar susceptibility (χ_m) of all the complexes were determined (Tables 9–10). The molar magnetic susceptibilities of the complexes were computed using Pascal's additivity law and the values of susceptibilities for thorium, uranyl nitrate ions, required for this purpose were taken from the literature. It is evident from the results that all the UO_2^{2-} and Th^{4+} complexes are diamagnetic[16–21] indicating that all are spin-paired. The magnetic moment values of thorium complexes lie in the range 0.927 to 1.008 B.M. and for uranyl complexes lie in the range 0.832 to 0.881 B.M. respectively.

TABLE-9
MAGNETIC SUSCEPTIBILITY DATA OF THORIUM(IV) COMPLEXES

Sl. No.	m.w.	χ_m (observed) -1×10^{-6} c.g.s. unit	χ'_m (computed) -1×10^{-6} c.g.s. unit	$\Delta\chi_m = \chi_m - \chi'_m = [\chi_p]$	% $\Delta\chi_m$	μ_{eff} computed (observed) B.M.
1.	873.54	414.32	368.34	+45.98	+11.09	0.950 (1.008)
2.	942.41	381.02	402.68	–21.66	–5.68	0.994 (0.967)
3.	942.41	382.71	402.68	–19.97	–5.22	0.994 (0.969)
4.	942.41	377.06	402.68	–25.62	–6.79	0.994 (0.962)
5.	901.58	350.08	384.86	–34.78	–9.93	0.971 (0.927)
6.	901.58	352.34	384.86	–32.52	–9.23	0.971 (0.929)
7.	901.58	357.21	384.86	–27.65	–7.74	0.971 (0.936)

TABLE-10
MAGNETIC SUSCEPTIBILITY DATA OF URANYL(VI) COMPLEXES

Sl. No.	m.w.	χ_m (observed) -1×10^{-6} c.g.s. unit	χ'_m (computed) -1×10^{-6} c.g.s. unit	$\Delta\chi_m = \chi_m - \chi'_m = [\chi_p]$	% $\Delta\chi_m$	μ_{eff} computed (observed) B.M.
1.	787.52	282.25	260.90	+21.35	+7.56	0.800 (0.832)
2.	856.41	322.34	283.04	+39.30	+12.19	0.833 (0.890)
3.	856.41	305.04	283.04	+22.00	+7.22	0.833 (0.866)
4.	856.41	306.93	283.04	+23.89	+7.78	0.833 (0.869)
5.	815.54	315.78	284.62	+31.16	+9.87	0.835 (0.880)
6.	815.54	306.32	284.62	+21.70	+7.08	0.835 (0.867)
7.	815.54	316.35	284.62	+31.73	+10.03	0.835 (0.881)

From the above studies the tentative structure proposed for the thorium(IV) and uranyl(VI) complexes is as shown in Figs. 1 and 2.

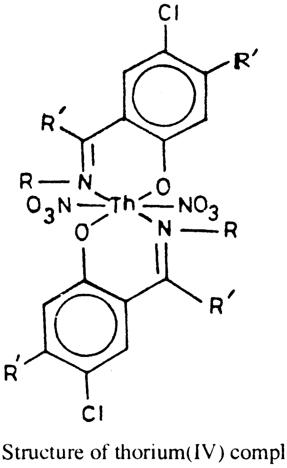


Fig. 1. Structure of thorium(IV) complexes
where R′ = CH_3, R = C_6H_5, C_6H_4Cl(*o,m,p*), $C_6H_4CH_3$(*o,m,p*)

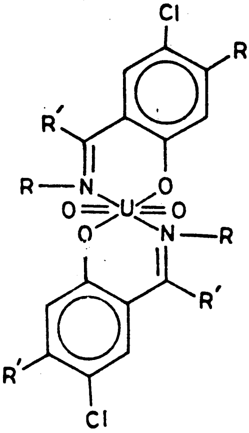


Fig. 2. Structure of Uranyl(VI) complexes
where R′ = CH_3, R = C_6H_5, $C_6H_4Cl^-$(*o,m,p*), $C_6H_4CH_3$(*o,m,p*)

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