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Preparation and Investigation of Ce(III), Th(IV) AND U(VI) Chelates with Some Schiff Bases Derived from 5,7-Dihydroxy-6-Formyl-2-Methylbenzopyran-4-One

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PREPARATION AND INVESTIGATION OF Ce(III), Th(IV) AND U(VI) CHELATES WITH SOME SCHIFF BASES DERIVED FROM 5,7-DIHYDROXY-6-FORMYL-2-METHYLBENZOPYRAN-4-ONE

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ABSTRACT

Schiff bases were prepared by condensation of equimolar amounts of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one and aniline, anthranilic acid, 2-aminophenol, 5-chloro-2-aminophenol or 4-amino-3-hydroxybenzenesulphonic acid. The molecular structure of the prepared Schiff bases was confirmed by mass and UV spectra. The chelates of Ce(III), Th(IV), and U(VI) with the above Schiff bases were prepared. All the prepared compounds were subjected to elemental analyses for C, H, N, Cl, S and metal (for the chelates), IR and ^{1}H NMR spectroscopy. The studies show that Ce(III) and Th(IV) give 1:1, 1:2 and 2:1 (M:L) metal chelates, while U(VI) gives only 1:1 and 1:2 (M:L) chelates. This may be attributed to the difficulty of coordinating two bulky uranyl ions to the same molecule because of their steric effect. The studies revealed that the Ce(III) and Th(IV) chelates exhibit octahedral structure with the coordination number 6 while U(VI) chelates exhibit dodecahedral structure with the coordination number 8. Thermogravimetric analysis data were obtained for some of the prepared chelates.

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INTRODUCTION

The condensation of primary amines with carbonyl compounds was first reported by Schiff[1] and the condensation products are often referred as Schiff bases. They are also known as anils, imines or azomethines[2]. These bases have the general structure R-CH=N-R′ where R and R′ are alkyl, cyclohexyl, aryl or heterocyclic groups which may be variously substituted.

Chromones are compounds that contain a pyrone nucleus fused to a benzene ring at the 5 and 6 positions. They are known as benzopyrone[3], pheno-γ-pyrone[4] or 4-H-benzopyran-4-one[5].

Little work has been done on Schiff bases derived from chromones. The chelates of some Schiff bases derived from chromone and some substituted amines with Cu(II) and U(VI)[6], Co(II), Ni(II), and Cu(II)[7,8] and with Cu(II), Co(II), Ni(II), Mn(II), and Zn(II)[9,10] were investigated and characterized earlier by several techniques. The studies proposed a possible structure for each of the metal chelates.

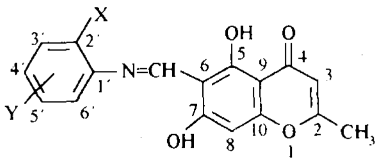
The suggested structure of the Schiff bases of this study is shown in Fig. 1.

The present investigation deals with the preparation and structure elucidation of the metal chelates formed between Ce(III), Th(IV) and U(VI) with some Schiff bases prepared by condensation of equimolar amounts of 5,7-dihydroxy-6-formyl-2-methyl-benzopyran-4-one with aniline, anthranilic acid, 2-aminophenol, 5-chloro-2-aminophenol or 4-amino-3-hydroxybenzenesulphonic acid[8]. The molecular structures of the prepared Schiff bases were confirmed by mass and UV spectra. All of the prepared compounds (chromones, Schiff bases, and chelates) were subjected to elemental analyses for C, H, N, Cl, S, and metal content (for the chelates), UV, IR, and ^{1}H NMR spectroscopy. Thermogravimetric analyses of some of the prepared chelates were studied and discussed.

EXPERIMENTAL

Materials and Instrumentation

All chemicals used in this investigation were chemically pure grade. All organic solvents used in this work were either purified by the recommended methods or obtained as spectroscopic grade solvents from BDH. Double-distilled water from glass equipment was used. The elemental analyses for C, H, N, Cl, S, and metal content



X	Y	
H	H	H_2L^1
COOH	H	H_3L^2
OH	H	H_3L^3
OH	5'-Cl	H_3L^4
OH	4'-SO_3H	H_4L^5

Fig. 1. Suggested Structure of the Investigated Schiff Bases

were performed at the microanalytical center, Cairo University, Cairo, Egypt. The mass spectra of the prepared Schiff bases were recorded with a Q1000 EXGC-MS Shimadzu spectrometer at 70 eV and 100 μA energy using a direct insertion probe at 90-110° C. The IR spectra were recorded in KBr discs using a Testscan Shimadzu FTIR spectrometer. The UV and visible absorption spectra were recorded using a Perkin Elmer Lambda 4B spectrophotometer. Electronic absorption measurements of the Schiff bases were carried out in ethanol. The ^1H NMR spectra of the Schiff bases and some of their chelates were recorded using a Varian-Gemini 200-200 MHz spectrometer. The solvent used was deuterated dimethyl sulphoxide (DMSO-d_6), and tetramethylsilane as an internal standard. The spectra extended from 0-17 ppm. Thermogravimetric analyses of some of the prepared chelates were performed using a Shimadzu 50 thermal analyzer (Japan). The weight loss was measured from ambient temperature up to 800° C in a heating rate of 10° C per minute under nitrogen atmosphere.

Preparation of Schiff Bases

6-Formyl-7-hydroxy-5-methoxy-2-methylchromone was synthesized by oxidation of visnagin (4-methoxy-5H-furo[3,2-g][1]-benzopyran-5-one) with chromic acid while 5,7-dihydroxy- 6-formyl-2-methylchromone was prepared by hydrolysis of the former with HCl[11]. The Schiff bases were prepared by condensation of 0.01 mole of 6-formyl-5,7-dihydroxy-2-methylchromone (2.2 g dissolved in 30 mL ethanol) with 0.01 mole of aniline (1 mL), 0.01 mole of anthranilic acid (1.37 g), 0.01 mole of 2-aminophenol (1.1 mL), 0.01 mole of 5-chloro-2-aminophenol (0.1435 g) and 0.01 mole of 4-amino-3-hydroxy-benzenesulphonic acid (0.189 g). The amines were dissolved in 20 mL ethanol except for the last one, which was dissolved in 20 mL 4% (W/W) NaOH-water solution because of its insolubility in ethanol. The molar ratio was 1:1 and the reaction mixture was refluxed for at least two hours. The obtained yellow-orange precipitates were filtered, washed with ethanol and recrystallized from ethanol (H_3L^3 and H_3L^4), toluene (H_2L^1) and DMF (H_3L^2 and H_4L^5).

Preparation of the Chelates

The chelates were prepared by mixing 20 mL hot ethanolic solutions containing 0.001 mole of the metal ions [$CeCl_3.6H_2O$ (0.354 g), $Th(NO_3)_4.6H_2O$ (0.548 g) or $UO_2(CH_3COO)_2.2H_2O$ (0.424 g)] with the requisite amount of Schiff base under investigation (dissolved in 30 mL ethanol) sufficient to form 1:1, 1:2 and 2:1 (M:L) chelates. The reaction mixture was stirred on a water bath at 100° C for at least 1 h.. If the solid chelates did not separate on standing at room temperature, ammonia solution was added until the pH 7-8 is reached. The solid chelates were filtered, washed several times with ethanol until the filtrate became colorless and kept in a vacuum desiccator. All the prepared compounds (chromones, Schiff bases, and chelates) were subjected to elemental analyses for C, H, N, Cl, and S. The metal contents of the chelates were determined after decomposition of the chelates using the method described by Macdonald[12].

RESULTS AND DISCUSSION

The calculated and found values of the microelemental analysis data of the investigated Schiff bases are listed in Table I. The results show good agreement with the suggested formula of such compounds.

Table 1. Physical Properties of the Prepared Schiff Bases and their Elemental Analyses

Comp.	Empirical Formula	F. W.	Color	Yield (%)	M. p (°C)	Elemental analyses Found / (Calculated)			
						%C	%H	%N	%X
H_2L^1	$C_{17}H_{13}NO_4$	295.28	Yellow	95	227	68.9 (69.15)	4.8 (4.41)	4.7 (4.74)	-
H_3L^2	$C_{18}H_{13}NO_6$	339.29	Orange	97	250	63.3 (63.72)	4.0 (3.83)	4.3 (4.13)	-
H_3L^3	$C_{17}H_{13}NO_5$	312.29	Orange	98	275	65.5 (65.59)	3.9 (4.18)	4.5 (4.50)	-
H_3L^4	$C_{17}H_{12}NO_5Cl$	345.72	Orange	95	285	59.3 (59.06)	3.6 (3.47)	4.3 (4.04)	10.7[a] (10.27)
H_4L^5	$C_{17}H_{13}NO_8S$	391.34	Orange	85	325	52.7 (52.17)	3.3 (3.32)	3.7 (3.58)	8.0[a] (8.18)

[a] X = Cl for H_3L^4 and S for H_4L^5.

Elemental Analysis of the Chelates.

The results of the elemental analyses for the chelates [Table II] indicate that Ce(III) and Th(IV) form 1:1, 1:2 and 2:1 (M:L) metal chelates while U(VI) forms only 1:1 and 1:2 (M:L) chelates. This can be attributed to the difficulty of coordinating two bulky uranyl ions to the same molecule because of their steric effect. The results are in good agreement with those calculated for the suggested formula. The chelation reactions may be summarized by the following equations.

For the 1:1 chelates:

$$H_aL + M^{n+} \longrightarrow [MH_bL]^{n-(a-b)} + (a-b)H^+$$

For the 1:2 chelates:

$$2H_aL + M^{n+} \longrightarrow [M(H_bL)_2]^{n-(a-b)} + (a-b)H^+$$

For the 2:1 chelates:

$$H_aL + 2M^{n+} \longrightarrow [M_2L]^{2n-a} + aH^+$$

Table II. Physical Properties and Elemental Analyses Data for Ce(III), Th(IV) and U(VI) Chelates with the Investigated Schiff Bases.

Chelate	Empirical Formula	M:L	F. W.	Yield (%)	Color	M. P. °C	Elemental analyses Found / (Calculated)					
							%C	%H	%N	%Cl	%S	%M
Ce(III) Chelates												
$[Ce(L^1)Cl(H_2O)_3].2H_2O$	$CeC_{17}H_{21}O_9NCl$	1:1	558.92	75	red	> 350	36.5 (36.50)	3.9 (3.76)	2.6 (2.50)	6.3 (6.35)	-	25.2 (25.07)
$[Ce(HL^1)_2Cl(H_2O)].H_2O$	$CeC_{34}H_{28}O_{10}N_2Cl$	1:2	800.15	80	brown	> 350	50.9 (50.99)	3.9 (3.50)	3.3 (3.50)	4.1 (4.44)	-	17.9 (17.51)
$[Ce_2(HL^1)(OH)_4(H_2O)_3(C_2H_5OH)]$	$Ce_2C_{19}H_{27}O_{12}N$	2:1	741.65	77	black	> 350	30.8 (30.74)	3.6 (3.64)	1.9 (1.89)	-	-	37.81 (37.79)
$[Ce(L^2)(H_2O)_2(C_2H_5OH)_2]$	$CeC_{22}H_{26}O_{10}N$	1:1	604.56	76	red	> 350	43.9 (43.69)	4.5 (4.3)	2.5 (2.32)	-	-	23.1 (23.18)
$[Ce(H_2L^2)_2Cl(H_2O)].2H_2O$	$CeC_{36}H_{30}O_{15}N_2Cl$	1:2	906.18	81	brown	> 350	47.6 (47.67)	3.1 (3.31)	3.0 (3.09)	3.8 (3.92)	-	15.7 (15.46)
$[Ce_2(L^2)(OH)_3(H_2O)_4].5H_2O$	$Ce_2C_{18}H_{31}O_{18}N$	2:1	829.68	80	black	> 350	26.1 (26.03)	3.9 (3.74)	1.6 (1.69)	-	-	33.5 (33.78)
$[Ce(L^3)(H_2O)_4]$	$CeC_{17}H_{18}O_9N$	1:1	520.44	74	red	> 350	39.4 (39.20)	3.4 (3.46)	2.8 (2.69)	-	-	26.7 (26.92)

$[Ce(H_2L^3)_2Cl(H_2O)]$	$CeC_{34}H_{26}O_{11}N_2Cl$	1:2	814.13	80	brown	> 350	50.4 (50.11)	3.2 (3.19)	3.6 (3.44)	4.5 (4.36)	-	17.5 (17.21)
$[Ce_2(L^3)(OH)Cl_2(H_2O)_2(C_2H_5OH)_2]\ 2H_2O$	$Ce_2C_{21}H_{31}O_{12}NCl_2$	2:1	840.61	72	black	> 350	30.1 (29.99)	3.9 (3.69)	1.9 (1.67)	8.1 (8.45)	-	33.5 (33.34)
$[Ce(L^4)(H_2O)_3(C_2H_5OH)]$	$CeC_{19}H_{21}O_9NCl$	1:1	582.94	76	red	> 350	38.9 (39.11)	3.6 (3.60)	2.6 (2.40)	6.2 (6.09)	-	24.5 (24.04)
$[Ce(H_2L^4)_2Cl(H_2O)].4H_2O$	$CeC_{34}H_{30}O_{15}N_2Cl_3$	1:2	953.06	78	brown	> 350	42.6 42.81	3.4 3.15	2.6 (2.93)	11.1 (11.17)	-	14.8 (14.70)
$[Ce_2(L^4)(OH)_3(H_2O)_4]$	$Ce_2C_{17}H_{20}O_{12}NCl$	2:1	746.03	80	black	> 350	27.1 (27.34)	2.9 (2.68)	2.0 (1.88)	4.6 (4.76)	-	37.8 (37.56)
$[Ce(HL^5)(H_2O)_4)].2H_2O$	$CeC_{17}H_{22}O_{14}NS$	1:1	636.53	74	red	> 350	32.1 (32.05)	3.4 (3.46)	2.3 (2.20)	-	4.9 (5.03)	22.0 (22.01)
$[Ce(H_3L^5)_2Cl(H_2O)].4H_2O$	$CeC_{34}H_{34}O_{21}N_2ClS_2$	1:2	1046.32	79	brown	> 350	38.9 (39.00)	3.2 (3.25)	2.9 (2.68)	3.40 (3.39)	6.3 (6.12)	13.4 (13.39)
$[Ce_2(L^5)Cl_2(H_2O)_3(C_2H_5OH)_2]$	$Ce_2C_{21}H_{27}O_{13}NCl_2S$	2:1	884.63	76	black	> 350	28.8 (28.49)	3.2 (3.05)	1.8 (1.58)	7.9 (8.03)	3.9 (3.62)	31.9 (31.68)

continued

Table II continued

Th(IV) Chelates											
$[Th(L^1)(OH)_2(H_2O)(C_2H_5OH)]$	$ThC_{19}H_{21}O_8N$	1:1	623.4	80	red	> 350	36.6 (36.57)	3.3 (3.37)	2.4 (2.25)	-	-	37.1 (37.24)
$[Th(L^1)_2(H_2O)_2].5H_2O$	$ThC_{34}H_{36}O_{15}N_2$	1:2	944.68	76	brown	> 350	43.5 (43.19)	3.8 (3.81)	3.1 2.97	-	-	24.8 (24.58)
$[Th_2(L^1)(OH)_6(C_2H_5OH)_2)]$	$Th_2C_{21}H_{29}O_{12}N$	2:1	719.49	75	black	> 350	26.8 26.48	3.2 3.05	1.6 1.47	-	-	48.6 (48.77)
$[Th(L^2)(OH)(H_2O)_3].2H_2O$	$ThC_{18}H_{21}O_{12}N$	1:1	443.36	74	red	> 350	32.2 31.97	3.2 3.11	2.2 2.07	-	-	34.2 (34.34)
$[Th(HL^2)_2(H_2O)_2].H_2O$	$ThC_{36}H_{28}O15N_2$	1:2	690.65	76	brown	> 350	44.9 44.97	3.2 2.92	3.1 2.92	-	-	23.9 (24.15)
$[Th_2(L^2)(NO_3)_5(H_2O)_2].2H_2O$	$Th_2C_{18}H_{18}O_{25}N_6$	2:1	1182.45	75	black	> 350	18.6 (18.27)	1.8 (1.52)	7.4 (7.11)	-	-	39.6 (39.26)
$[Th(L^3)(NO_3)(H_2O)_3].3H_2O$	$ThC_{17}H_{22}O_{14}N_2$	1:1	710.67	77	red	> 350	29.1 (28.71)	3.4 (3.10)	4.2 (3.94)	-	-	32.9 (32.65)
$Th(HL^3)_2(H_2O)_2].3H_2O$	$ThC_{34}H_{32}O_{15}N_2$	1:2	940.65	73	brown	> 350	43.6 (43.37)	3.7 (3.40)	3.2 (2.98)	-	-	24.5 (24.67)

$[Th_2(L^3)(OH)(NO_3)_4(H_2O)_2]$	$Th_2C_{17}H_{15}O_{20}N_5$	2:1	1073.41	80	black	> 350	19.1 (19.00)	1.6 (1.40)	6.5 (6.52)	-	-	43.5 (43.25)
$[Th(L^4)(OH)(H_2O)_2(C_2H_5OH)]$	$ThC_{19}H_{20}O_9NCl$	1:1	673.85	77	red	> 350	33.7 (33.84)	3.1 (2.97)	2.3 (2.08)	5.5 (5.27)	-	34.7 (34.43)
$[Th(HL^4)_2(H_2O)_2].5H_2O$	$ThC_{34}H_{34}O_5N_2Cl_2$	1:2	853.57	80	brown	> 350	47.6 (47.80)	3.8 (3.98)	4.5 (4.45)	8.5 (8.32)	-	27.4 (27.18)
$[Th_2(L^4)(OH)_3(NO_3)_2(H_2O)_2].2H_2O$	$Th_2C_{17}H_{20}O_5N_3Cl$	2:1	845.88	72	black	> 350	24.3 (24.12)	2.1 (2.36)	4.8 (4.96)	4.1 (4.43)	-	54.5 (54.86)
$[Th(L^5)(H_2O)_4].2H_2O$	$ThC_{17}H_{21}O_{14}NS$	1:1	727.45	81	red	> 350	27.9 (28.04)	3.0 (2.89)	2.2 (1.93)	-	4.6 (4.40)	31.7 (31.9)
$[Th(H_2L^5)_2(H_2O)_2].5H_2O$	$Th(C_{34}H_{36}O_{23}N_2S_2$	1:2	1136.8	75	brown	> 350	35.7 35.89	3.5 3.17	2.5 (2.46)	-	5.7 5.63	20.7 (20.41)
$[Th(L^5)(OH)(NO_3)_3(H_2O)_3].3H_2O$	$Th_2C_{17}H_{22}O_{24}N_4S$	2:1	1162.45	78	black	> 350	17.9 (17.55)	2.3 (1.89)	5.1 (4.82)	-	2.6 (2.75)	39.6 (39.92)
U(VI) Chelates												
$[UO_2(L^1)(H_2O)_3(C_2H_5OH)].H_2O$	$UC_{19}H_{25}O_{11}N$	1:1	681.44	80	Red	> 350	33.8 (33.46)	3.4 (3.67)	2.0 (2.06)	-	-	35.2 (34.93)

continued

Table II continued

$[UO_2(HL^1)_2(H_2O)_2].H_2O$	$UC_{34}H_{30}O_{13}N_2$	1:2	912.63	72	Black	> 350	45.0 (44.71)	3.1 (3.29)	3.3 (3.07)	-	-	25.9 (26.08)
$[(UO_2)(HL^2)(H_2O)_2(C_2H_5OH)_2].2H_2O$	$UC_{22}H_{31}O_{14}N$	1:1	771.51	76	Red	> 350	34.1 (34.22)	3.7 (4.02)	2.1 (1.82)	-	-	30.6 (30.85)
$[UO_2(H_2L^2)_2(H_2O)_2]$	$UC_{36}H_{28}O_{16}N_2$	1:2	982.64	79	Black	> 350	43.8 (43.96)	3.0 (2.85)	3.1 (2.85)	-	-	24.5 (24.22)
$[UO_2(HL^3)(H_2O)_2(C_2H_5OH)_2]$	$UC_{19}H_{27}O_{11}N$	1:1	683.45	83	Red	> 350	35.6 (35.36)	4.0 (3.95)	2.1 (2.05)	-	-	33.5 (34.83)
$[UO_2(H_2L^3)_2(H_2O)_2].3H_2O$	$UC_{34}H_{34}O_{17}N_2$	1:2	980.67	78	Black	> 350	41.9 (41.60)	3.7 (3.47)	2.9 (2.86)	-	-	24.4 (24.27)
$[UO_2(HL^4)(C_2H_5OH)_2(H_2O)_2].H_2O$	$UC_{19}H_{28}O_{12}NCl$	1:1	735.91	82	Red	> 350	30.9 (30.98)	3.8 (3.80)	2.1 (1.90)	4.9 (4.82)	-	32.5 (32.35)
$[UO_2(H_2L^4)_2(H_2O)_2].2H_2O$	$UC_{34}H_{30}O_{16}N_2Cl2$	1:2	1031.53	74	Black	> 350	39.5 (39.55)	2.9 (2.91)	2.9 (2.72)	7.0 (6.89)	-	22.9 (23.08)
$[UO_2(H_2L^5)(C_2H_5OH)(H_2O)_3].H_2O$	$UC_{19}H_{25}O_{15}NS$	1:1	777.5	76	Red	> 350	29.6 (29.32)	3.5 (3.22)	2.0 (1.80)	-	4.0 (4.12)	30.9 (30.62)
$[UO_2(H_3L^5)_2(H_2O)_2].5H_2O$	$UC_{34}H_{38}O_{19}N_2S_2$	1:2	1080.82	73	Black	> 350	34.5 (34.74)	3.4 (3.52)	2.5 (2.59)	-	5.6 (5.92)	20.5 (20.02)

M = Ce(III), Th(IV) and U(VI)

where M = Ce(III), Th(IV) and UO_2(VI); a = 2-5; n = 2-4; b = 0, 1 (for 1:1 chelates) and 1, 2 (for 1:2 chelates), and $L = L^{1-5}$ as described in Fig. 1.

Mass Spectra of the Schiff Bases

The mass spectra of the prepared Schiff bases show molecular ion peaks at M for the Schiff base H_2L^1 and (M+1) for Schiff bases H_3L^2 and H_3L^3. Because the molecularion peaks for the Schiff bases H_3L^4 and H_4L^5 are unstable, they could not bedetected. The peaks seen represent the most stable fragments; the Schiff base H_2L^4 loses a Cl atom giving an ionic fragment at m/z 311 and the Schiff base H_4L^5 loses the phenyl ring with its substituents to give an ionic fragment with m/z 218.

It is observed that the band appearing at m/z 218, which represents the chromone ring bonded to the C=N-ph group, is the most abundant fragment of all Schiff bases. This means that the fragmentation process starts by the loss of substituents X and Y on the phenyl ring followed by fragmentation of the ring itself. The fragmentation of the phenyl ring is followed by the loss of CN resulting in the parent chromone ring, m/z 192, which decomposes either by the loss of carbon monoxide giving the benzofuran ion, m/z 164[13], or undergoes retro-Diels-Alder fragmentation to give a quinoid ion fragment, m/z 120[3,14] [both pathways are observed in the spectrum of the Schiff base H_3L^4]. The quinoid ion undergoes further loss of carbon monoxide to give a cyclopentanone ionic fragment, m/z 65[15], that decomposes into smaller fragments with smaller molecular weights. The suggested fragmentation patterns are shown in Fig. 2.

The Infrared Spectra of the Schiff Bases and Chelates

The free Schiff bases show a broad band within the range 3700-3500 cm^{-1} which is assigned to the stretching vibration of the OH groups. This band in the chelates is replaced by the broad OH band extending from 3700-2500 cm^{-1} [Table III]. Such a broad band can be attributed to the stretching vibration of coordinated water, ethanol molecules[16] or OH ions attached to metal ions of the chelates to satisfy its coordination numbers or to neutralize their charges.

The band observed within the range 1666-1651 cm^{-1} in the spectra of the free Schiff bases is assigned to the stretching vibration for the C=O group in position 4 of

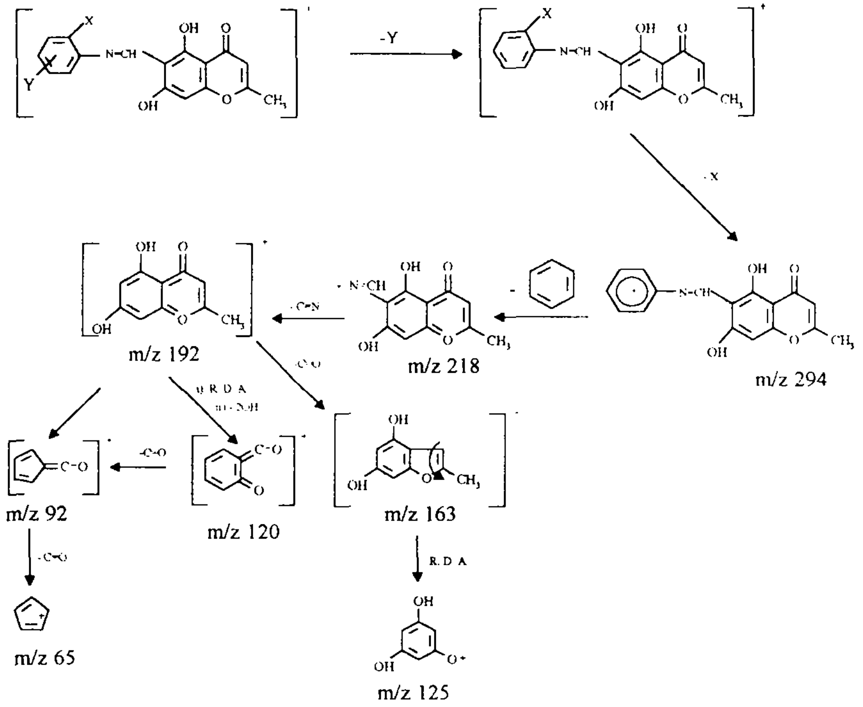


Fig. 2. General Route of Fragmentation of the Investigated Schiff Bases.

the chromone moiety. This band disappeared in the spectra of the chelates indicating that the C=O group participated in chelation. The stretching vibration for C=O of the COOH group of the free Schiff base H_3L^2 observed at 1775 cm^{-1}, was not affected in the spectra of the 1:1 and 1:2 chelates. In the spectra of the 2:1 chelates of the Schiff base H_3L^2, two new bands within the ranges 1552-1522 and 1440-1420 cm^{-1} were observed which may be assigned to asymmetrical and symmetrical COO$^-$ vibrations indicating its participation in chelation. The stretching vibration for the C=N group in the free Schiff bases was observed within the range 1625-1639 cm^{-1}. No significant change was observed in the position of the C=N band in the spectra of the 1:1 and 1:2 (M:L) metal chelates. On the other hand, this band disappeared in the case of 2:1 (M:L) chelates suggesting that both the azomethine and carbonyl groups are involved in chelation to give binuclear metal chelates.

In the spectra of the chelates, the O-H bending of coordinated water molecules[17] is found within the range 850-800 cm^{-1}. In addition, the O-H bending vibration is observed at 1600 cm^{-1}. In some Th(IV) chelates, the NO_3^- band appears within the range 1558-1520 cm^{-1}. Bands around 700 and 450 cm^{-1} may be assigned to the (M-O) stretching frequency and (M←O), respectively[18]. These bands are possibly due to the formation of covalent and coordinate bonds between the donor atom and central metal ion. The IR band assignments are listed in Table III.

Electronic Absorption Spectra of the Schiff Bases

The electronic absorption spectra of the Schiff bases under investigation show three absorption bands in the 207-370 nm region. The long wave length band (370 nm) is assigned to the intramolecular hydrogen bond between C=O in position 4 and OH in position 5 of the chromone ring. The medium wave length band (280-290 nm) can be attributed to the π-π^* transition for C=O and C=N groups overlapped with each others. The short wave length band (207-220 nm) is assigned to π-π^* transition in the phenyl ring of the aniline moiety[18]. The Schiff base H_2L^5 shows an additional absorption band at 241 nm corresponding to the n-σ^* transition in which an electron in the p-orbital of the sulfur atom is excited to the σ^* orbital of the molecule[19].

Proton ^{1}H NMR Spectra of the Schiff Bases and Their Chelates

The ^{1}H NMR spectra of all Schiff bases exhibit a resonance at 2.3 ppm assigned to the CH_3 protons of the solvent (DMSO) and a resonance in the 3-3.6 ppm region which is assigned to the aliphatic CH_3 group in position 2 of the chromone moiety[20]. The signal observed at 6.2-6.4 ppm may be assigned to the proton in position 3 of the chromone moiety while the multiplet observed at 7.2-7.5 ppm is assigned to the aromatic protons and the C-8 proton of the chromone moiety[21]. The azomethine CH=N proton is observed in the range 9.2-10.2 ppm.

Both OH groups in positions 5 and 7 of the chromone moiety are hydrogen-bonded to the C=O group in position 4[22] of the chromone ring and the CH=N group[23], respectively. Since the electronegativity of oxygen (3.5) is higher than that of nitrogen (3.1) and since the electronegativity of nitrogen is reduced by the positive mesomeric effect of the anilino ring, the strength and, hence, the deshielding effect of hydrogen

Table III. Assignment of IR Bands (cm^{-1}) of the Investigated Schiff Bases and the Ce(III), Th(IV) and U(VI) Chelates.

Compound	M:L	ν(OH)	δ(OH)	γ(OH)	M-O	M←O	M-X
H_2L^1	-	3325 s, b	1603 w	-	-	-	-
H_3L^2	-	3003 s, b	1596 m	-	-	-	-
H_3L^3	-	3300 s, b	1603 m	-	-	-	-
H_3L^4	-	3070 b	1593 s	-	-	-	-
H_4L^5	-	3250 s, b	1567 s	-	-	-	-
$[Ce(L^1)Cl(H_2O)_3].2H_2O$	1:1	3076 s, b	1595 m	823 s	761 s	469 m	560 m
$[Ce(HL^1)_2Cl(H_2O)].H_2O$	1:2	3122 s, b	1595 m	826 m	760 s	452 s	572 m
$[Ce_2(HL^1)(OH)_4(H_2O)_3(C_2H_5OH)]$	2:1	3387 s, b	1593 w	849 s	764 m	470 m	-
$[Ce(L^2)(H_2O)_2(C_2H_5OH)_2]$	1:1	3222 s, b	1595 w	844 s	741 m	430 w	-
$[Ce(H_2L^2)_2Cl(H_2O)].2H_2O$	1:2	3140 s, b	1600 m	847 m	735 m	458 m	552 m
$[Ce_2(L^2)(OH)_3(H_2O)_4].5H_2O$	2:1	3080 s, b	1600 w	844 w	760 s	452 m	-
$[Ce(L^3)(H_2O)_4]$	1:1	3063 s, b	1587 m	829 m	723 w	418m	-
$[Ce(H_2L^3)_2Cl(H_2O)]$	1:2	3079 s, b	1589 w	844 s	734 m	472 m	565 m
$[Ce_2(L^3)(OH)Cl_2(H_2O)_2(C_2H_5OH)_2].2H_2O$	2:1	3150 s, b	1589 w	843 s	760 m	462 s	572 m
$[Ce(L^4)(H_2O)_3(C_2H_5OH)]$	1:1	3072 s, b	1600 w	844 m	733 w	457 w	-
$[Ce(H_2L^4)_2Cl(H_2O)].4H_2O$	1:2	3377 s, b	1590 w	845 s	737 s	457 s	563 m
$[Ce_2(L^4)(OH)_3(H_2O)_4]$	2:1	3377 s, b	1601 w	843 m	725 s	458 s	-
$[Ce(HL^5)(H_2O)_4)].2H_2O$	1:1	3393 s, b	1601 w	828 s	734 m	457 s	-
$[Ce(H_3L^5)_2Cl(H_2O)].4H_2O$	1:2	3393 s, b	1601w	828 s	736 m	458 s	547 m
$[Ce_2(L^5)Cl_2(H_2O)_3(C_2H_5OH)_2]$	2:1	3390 s, b	1595 w	830 s	740 s	445 m	575 m
$[Th(L^1)(OH)_2(H_2O)(C_2H_5OH)]$	1:1	3136 s, b	1600 w	841 s	745 s	482 s	-
$[Th(L^1)_2(H_2O)_2].5H_2O$	1:2	3151 s, b	1593 w	849 m	744 s	420 s	-
$[Th_2(L^1)(OH)_6(C_2H_5OH)_2]$	2:1	3421 s, b	1600 w	-	745 s	440 s	-
$[Th(L^2)(OH)(H_2O)_3].2H_2O$	1:1	3074 s, b	1589 w	833 s	744 w	486 w	-
$[Th(HL^2)_2(H_2O)_2].H_2O$	1:2	3078 s, b	1589 w	833 s	744 s	482 s	-
$[Th_2(L^2)(NO_3)_5(H_2O)_2].2H_2O$	2:1	3213 s, b	1601 w	845 m	764 w	420 w	659 w

Table III continued

$[Th(L^3)(NO_3)(H_2O)_3].3H_2O$	1:1	3163 s, b	1595 w	841 m	744 s	432 m	648 m
$Th(HL^3)_2(H_2O)_2].3H_2O$	1:2	3136 s, b	1589 w	840 w	744 s	475 m	-
$[Th_2(L^3)(OH)(NO_3)_4(H_2O)_2]$	2:1	3147 s, b	1589 w	826 w	741 m	471 m	648 m
$[Th(L^4)(OH)(H_2O)_2(C_2H_5OH)]$	1:1	3078 s, b	1589 w	833 m	745 m	482 m	-
$[Th(HL^4)_2(H_2O)_2].5H_2O$	1:2	3167 s, b	1600w	822 s	745 m	432 m	-
$[Th_2(L^4)(OH)_3(NO_3)_2(H_2O)_2].2H_2O$	2:1	3143 s, b	1600 w	826 w	745 s	421 m	652 m
$[Th(L^5)(H_2O)_4].2H_2O$	1:1	3406 s, b	1593 w	837 s	720 m	474 m	-
$[Th(H_2L^5)_2(H_2O)_2].5H_2O$	1:2	3232 s, b	1590 w	829 s	745 m	432 w	-
$[Th(L^5)(OH)(NO_3)_3(H_2O)_3].3H_2O$	2:1	3078 s, b	1601 w	833 s	745 w	482 s	644 s
$[UO_2(L^1)(H_2O)_3(C_2H_5OH)].H_2O$	1:1	3449 s, b	1593 s	837 s	748 s	421 s	-
$[UO_2(HL^1)_2(H_2O)_2].H_2O$	1:2	3464 s, b	1595 s	825 m	748 s	421 s	-
$[(UO_2)(HL^2)(H_2O)_2(C_2H_5OH)_2].2H_2O$	1:1	3425 s, b	1593 w	841 s	748 s	436 m	-
$[UO_2(H_2L^2)_2(H_2O)_2]$	1:2	3448 s, b	1601 w	844 s	748 m	428 m	-
$[UO_2(HL^3)(H_2O)_2(C_2H_5OH)_2]$	1:1	3425 s, b	1601m	844 m	748 m	436 m	-
$[UO_2(H_2L^3)_2(H_2O)_2].3H_2O$	1:2	3082 s, b	1593 m	840 m	748 m	440 m	-
$[UO_2(HL^4)(C_2H_5OH)_2(H_2O)_2].H_2O$	1:1	3422 s, b	1593 w	841 s	748 s	440 s	-
$[UO_2(H_2L^4)_2(H_2O)_2].2H_2O$	1:2	3421 s, b	1593m	845 m	748 m	421 m	-
$[UO_2(H_2L^5)(C_2H_5OH)(H_2O)_3].H_2O$	1:1	3090 s, b	1596 m	844 s	748 s	440 s	-
$[UO_2(H_3L^5)_2(H_2O)_2].5H_2O$	1:2	3298 s, b	1600 s	814 m	748 s	444 s	-

M = Ce(III), Th(IV) or U(VI); X = Cl [for Ce(III) chelates] and N [for Th(IV) chelates]; b: broad, s: strong, m: medium, and w: weak.

bonding on the OH proton in position 7 is lower than that for the OH proton in position 5, thus the C-5 OH proton appears at the higher ppm value (14.5-16.3 ppm) and the C-7 OH proton appears at 12.1-14.8 ppm.

The evidence for the effect of the phenyl ring on the hydrogen bonding between CH=N and the OH group in position 7 is the variation of the position of the OH resonance with the variation of substituents on the phenyl ring as follows:

(1) Introducing COOH or OH groups in the ortho position to the azomethine group (Schiff bases H_3L^2 and H_3L^3) decreases the hydrogen bonding between CH=N

and the OH group in position 7, either by a steric effect (if the groups are on the same side) or by the formation of another hydrogen bond between the CH=N and the introduced COOH and OH groups (i.e. competition between the COOH and OH groups and the C-7 OH group for H-bond formation with CH=N). The OH proton in position 7 becomes more shielded and appears at 12.1 ppm, while the COOH proton is observed at 9 ppm and the phenolic proton is observed at 12.2 ppm and is superimposed with the OH proton in position 7, indicating that both protons have the same probability for hydrogen bonding with the azomethine group.

(2) Introducing a Cl group in the meta position relative to the CH=N group, in addition to the OH group in its ortho position (Schiff base H_2L^4), increases the electron density of the aromatic ring due to the +M effect of the Cl atom. This increase in the electron density is extended to the nitrogen atom of the azomethine group, thus increasing the extent of its hydrogen bonding with both the OH group in its ortho position and OH group in position 7. Such increase in hydrogen bonding gives rise to more shielded protons shifting their OH bands into the higher ppm region so that the OH proton in position 7 is observed at 14.8 ppm and the phenolic OH band signal is observed at 10.4 ppm.

(3) Introducing OH and SO_3H groups in the ortho and para positions to the CH=N group (Schiff base H_4L^5) results in a shielding effect on the OH proton in position 7. This can also be attributed to the -I effect of the SO_3H group which decreases the electron density in the anilino ring and, hence, around the azomethine group. The hydrogen bonding between CH=N and OH proton in position 7 decreases and the OH proton in position 7 band is observed at 14.6 ppm. The signals observed at 14.3 and 12.0 ppm can be attributed to phenolic OH and SO_3H protons, respectively. The disappearance of the signals of OH, COOH and SO_3H protons on deuteration confirms that they are ionizable protons.

The ^1H NMR spectra of some of the prepared chelates show the disappearance of the signal produced by the OH proton in position 5 which is observed in the free Schiff base. This means that chelation occurs through bonding to the metal ion with the C=O group in position 4 and the hydroxyl anion in position 5 of the chromone moiety (after ionization of the OH group) to give a stable six-membered chelate ring. The shift of the position of the CH=N and OH in position 5 may be attributed to the redistribution of electron density through the whole molecule as a result of chelation. The spectra of all chelates show the appearance of a new singlet at 3.5 ppm that represents coordinated and hydrated water molecules, alcoholic OH, and/or OH ions involved in chelation to satisfy the oxidation number of the metal ions. The signals observed at 2.0-2.5 ppm can be attributed to the aliphatic CH_3 proton in position 2 of the chromone moiety and/or alcoholic CH_2 and CH_3 of ethanol involved in chelation and CH_3 of the solvent (DMSO).

TG and DTA of Some Solid Chelates

The initial weight loss occurring in the 50-130° C temperature range is interpreted as a loss of moisture and hygroscopic water during the drying of the chelates, whereas that at 130-250° C is due to the loss of coordinated water in the chelate. After the loss of water of crystallization, the solid chelates show thermal stability within the temperature range 250-500° C. On further heating, the TG curves show decomposition of the organic part of the chelates till a constant weight and the metal oxide is formed as the final product. During the decomposition of the organic part of the chelate, additional inflections in the TG curves are observed which may be attributed to the formation of unstable intermediate products [e.g. 1:1 chelates, arylcarboxylates, carbonates, etc.][24]. The dehydration and water decoordination processes are represented by endothermic peaks in the DT curves while the decomposition of the organic part of the chelate is represented by a strong exothermic one. The residue of all samples is found to be the metal dioxide where Ce(III) is oxidized to Ce(IV) giving CeO_2, Th(IV) gives ThO_2 and U(VI) is reduced to U(IV) giving UO_2 as end products[25]. TG and DT analyses for some of Ce(III) chelates are represented in Fig. 3.

From the thermal analyses of the chelates, the following scheme of decomposition may be suggested:

$$[M_m(\text{ligand})_a(\text{water})_bX_c(\text{ethanol})_d].nH_2O \xrightarrow{50\text{-}130^\circ\,C} [M_m(\text{ligand})_a(\text{water})_bX_c(\text{ethanol})_d]$$

$$[M_m(\text{ligand})_a(\text{water})_bX_c(\text{ethanol})_d] \xrightarrow{130\text{-}250^\circ\,C} [M_m(\text{ligand})_aX_c(\text{ethanol})_d]$$

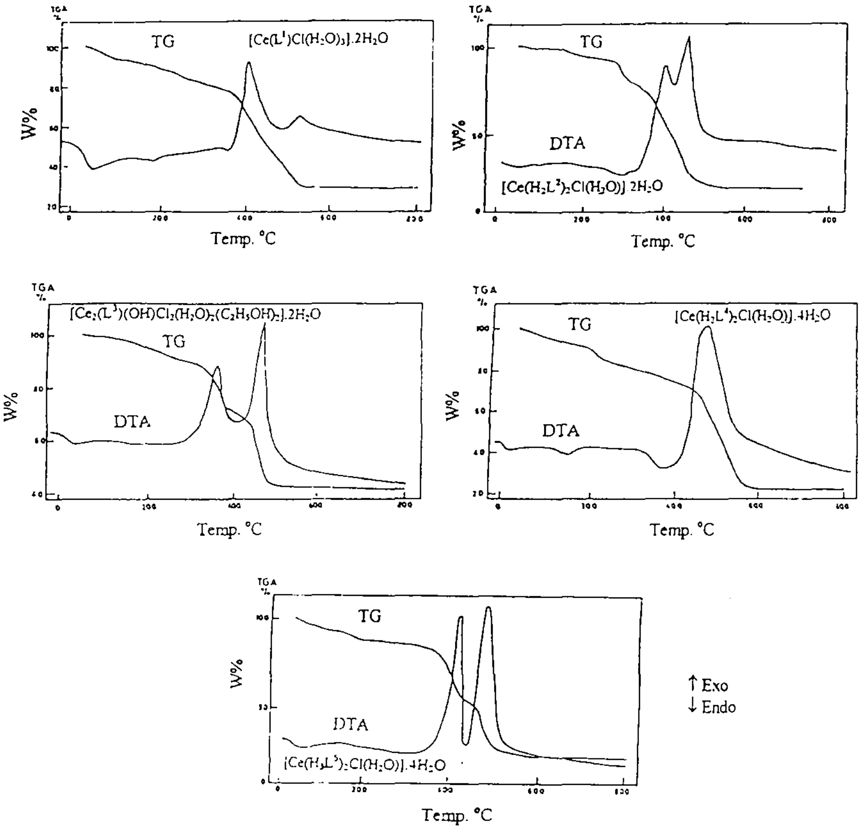
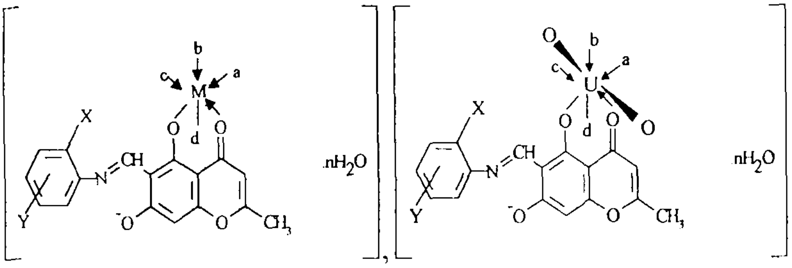


Fig. 3. Thermogravimetric and Differential Thermal Analyses Curves of Some Ce(III) Chelates.

$$[M_m(\text{ligand})_aX_c(\text{ethanol})_d] \xrightarrow{250\text{-}500^0\ C} \text{thermal stability}$$

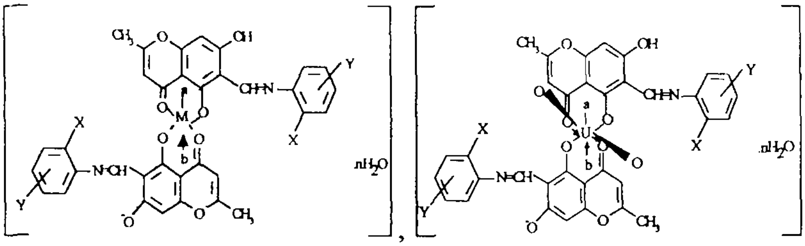
$$[M_m(\text{ligand})_aX_c(\text{ethanol})_d] \xrightarrow{500\text{-}750^0\ C} MO_2$$

where M in the complexes is Ce(III), Th(IV) and UO_2(VI) [for MO_2, M = Ce(IV), Th(IV) and U(IV)]; m = 1, 2; a = 1, 2; b – 1-5; X = OH^-, Cl^- or NO_3^-; c – 0-5; d = 0-2 and n = 0-5.



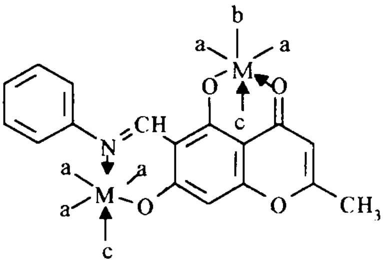
	a	b	c	d	n
M = Ce(III)	H_2O	H_2O	H_2O or EtOH	Cl^-, H_2O or EtOH	0, 2
M = Th(IV)	OH^- or NO_3^-	OH^- or H_2O	EtOH	H_2O or EtOH	0, 2, 3
U(VI)	H_2O	H_2O	H_2O	EtOH	0-2

Fig. 4. Suggested Structure of the 1:1 chelates



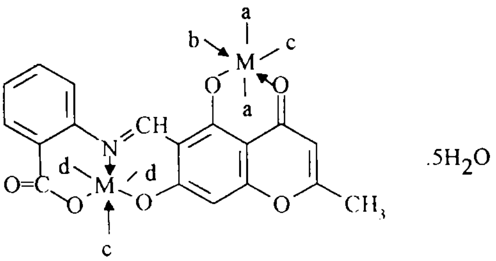
	a	b	n
M = Ce(III)	Cl^-	H_2O	0, 1, 2, 4
M = Th(IV)	H_2O	H_2O	1, 3, 5
U(VI)	H_2O	H_2O	0-3

Fig. 5. Suggested Structure of the 1:2 Chelates



M	a	b	c
Ce(III)	OH^-	H_2O	EtOH
Th(IV)	OH^-	OH^-	EtOH

Fig. 6. Suggested Structure of the H_2L^1 2:1 Chelates

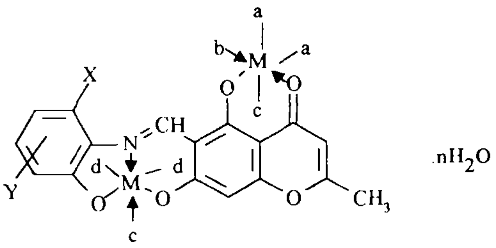


M	a	b	c	n
Ce(III)	OH^-	H_2O	H_2O	5
Th(IV)	NO_3^-	NO_3^-	H_2O	2

Fig. 7. Suggested Structure of the H_2L^2 2:1 Chelates

Conclusion

Based on the results of the elemental analyses, IR, ^{1}H NMR, and thermal analyses, it may be concluded that the Schiff base H_2L^1 acts as a dibasic bidentate ligand in all of its chelates except for the U(VI) 1:1 chelate where it acts as a monobasic bidentate ligand. The Schiff bases H_3L^2, H_3L^3 and H_3L^4 act as tribasic bidentate ligands on chelation with Ce(III) and Th(IV) to give 1:1 chelates and as



X	M	a	b	c	d	n
H (H_3L^3), m-Cl	Ce(III)	OH^- or Cl^-	H_2O or EtOH	H_2O	H_2O or EtOH	0, 2
(H_3L^4), SO_3^- (H_4L^5)	Th(IV)	NO_3^-	H_2O	H_2O	NO_3^-	0, 2, 3

Fig. 8. Suggested Structure of the H_3L^3, H_3L^4 and H_4L^5 2:1 Chelates

tribasic pentadentate ligands in case of 2:1 chelates. On complexation with the U(VI) ion, they act as dibasic bidentate ligands to give 1:1 chelates, and as monobasic bidentate ligands in case of 1:2 chelates. In all of its 2:1 chelates, the Schiff base H_4L^5 acts as a tetrabasic pentadentate ligand. However, in the 1:1 chelates, it acts as tribasic bidentate ligand with Ce(III), as tetrabasic bidentate ligand with Th(IV) and as a dibasic bidentate ligand with U(VI). In case of the 1:2 (M:L) chelates, the Schiff base H_4L^5 acts as monobasic bidentate ligand with Ce(III) and U(VI) and as dibasic bidentate ligand with Th(IV).

Structure of the Chelates.

The Ce(III), Th(IV) and U(VI) chelates with the Schiff bases under investigation may be formulated as shown below. The coordination numbers of the Ce(III) and Th(IV) ions in their metal chelates is six with ocahedral structures while that for U(VI) is 8 with a dodecahedral[26] structure.

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