

**SYNTHESIS AND STUDIES OF Th(IV) AND Ce(III)
COMPLEXES WITH SOME AZOPYRAZOLONE COMPOUNDS**

BY

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ABSTRACT

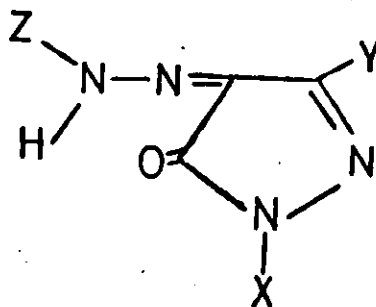
A number of chelate complexes of Th(IV) and Ce(III) with some heterocyclic azo-5-pyrazolones have been prepared. The stoichiometry and the structure of the complexes were studied using elemental analysis, conductivity measurements, electronic, IR and ^1H NMR spectra. TGA data confirms the hydrated nature of the complexes. The molar conductance measurements proved that all complexes behave as electrolytes in DMF. The apparent formation constants of the prepared complexes were determined and they support the use of these compounds for the microdetermination for Th(IV) and Ce(III) ions in their solutions. Also, all data of the compounds under studies confirm that the azostructure can exist beside the hydrazone structure.

INTRODUCTION

The interest in the azopyrazolones chelates was essentially based on the problem of the structure of both the organic compound and its chelates. Also, from

the possibility that the compounds are used as analytical reagents [1-3], which was ascribed to their tendency to form stable metal chelates of higher coordination numbers.

In continuation of our studies in this field [4] and in view of searches for new heterocyclic azopyrazolone complexes this work was carried out. The compounds used in the present study are :-



$X = H (L_1, L_2 ; C_6H_5 (L_3 - L_6) \quad Y = NH_2(L_1) ; CH_3(L_2-L_6)$

$Z = 3\text{-pyridine } (L_1-L_3) ; 6\text{-hydroxy-2-pyridine } (L_4) ; \text{thiazol } (L_5) ; \text{Benzthiazole } (L_6) ..$

EXPERIMENTAL

Materials :

4-substituted hydrazo-5-pyrazolones were synthesized using the method as described previously [5]. The dizonium chloride of the pure heterocyclic amine was coupled to pyrazolone using a sodium acetate buffer of $pH \approx 5.5$. The

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products were crystallized from ethanol. The purity of the compounds (ligands) was checked by thin layer chromatography and elemental analysis.

The 1:1 and 1:2 ($M^{n+} : L$) complexes of Th(IV) and Ce(III) were prepared by refluxing a mixture of the required amounts of ligand and metal salt in ethanol on a water bath for ~ 1 hr. The resulting product was concentrated by reducing the volume to the half. On cooling, the metal chelate separated, filtered, washed with ethanol and dried in vacuo over silica gell. The soild complexes were analysed for their C,H and N contents. The analytical data with the physicochemical properties are listed in Table 1.

Stock solutions (1×10^{-2} mol.l $^{-1}$) of the subject lig. ands and the metal salts $Th(NO_3)_4 \cdot 5H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ (A.R.) were prepared by dissolving the accurately weighed amount of each compound in ethanol.

Physical Measurements:

The physical measurements were obtained at 30°C. Ultraviolet and visible spectra were recorded on a Shimadzu 240 recording spectrophotometer using 1 cm matched silica cell. IR spectra were taken with the help of a Perkin-Elmer 599B spectrophotometer as KBr discs in the region 4000 - 200 cm $^{-1}$. Nuclear magnetic resonance spectra (NMR) were determined on a EM. 390-90 MHZ spectrometer. Chemical

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shifts values are reported in parts per million (δ)
downfield from internal TMS.

The conductance measurements were carried out on a Kink conductance bridge using conducting cell of a dipping type.

RESULTS AND DISCUSSION

The analytical data (Table 1) show that, on complexation the ligands L_2 , L_5 , L_6 act as monobasic, ligands L_1 , L_3 as neutral and L_4 acts as monobasic, bibasic or neutral ligand. The difference in chelating behaviour of these ligands can be explained on the basis of azo-hydrazone tautomeric structure which may exist in the compounds under investigation [6,7]. The molar conductance values for the solid complexes in DMF solution at a concentration $1 \times 10^{-3} \text{ mol.l}^{-1}$ (Table 1) are generally high values ($118.6 - 189.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) indicating the occurrence of two nitrate ions in DMF medium. However, three exceptional cases are recorded for Ce(III) chelate with L_2 and L_5 in 1:2 ratio and L_4 in 1:1 ratio where $58.2 - 61.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ values have been measured showing them to be 1:1 electrolytes [8].

The electronic absorption spectra of the ligands and their complexes in solution may add a further support

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to the tautomeric structure suggested. Thus, the spectra of the ligands exhibit a strong band in the range 235-250 nm(L_1 - L_3) and 300-310 nm(L_4 - L_6) assignable to $\Pi - \Pi^*$ transition in the pyrazolone ring. Other band located at longer wavelenghtes (350 - 380 nm) are assigned to Π - Π^* transition of electrons through the hydrazone group. These assignments are in agreement with the above reported structure of 4-aryl hydrazon-3-methyl-5-pyrazolones [9]. The addition of Th(IV) or Ce(III) to each ligand solution, causes a small bathochromic shift of the shorter wavelength band, while the longer wavelength band shows a clear red shift. This can be considered as an evidence for instantaneous complex formation. Thus, the lower energy shift observed can be ascribed to an easier intramolecular CT within the complexed ligand relative to that in the free one. This is due to the high acceptor character of the coordinating positive charge of the metal ions (Th(IV) , Ce(III)).

The stoichiometry of the different species formed in ethanolic solution are determined by applying the conventional spectrophotometric methods [10,11], using as blank the ligand solution of the same concentration as in the complex solution. The representative results are shown in Figs 1 & 2. The results reveal that complexes with composition of 1:1 and 1:2 ($M^{n+} : L$) could be detected in solution.

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The results of the conductometric titration confirm the above spectrophotometric results. The increase in conductance values observed during the titrations, can be ascribed to the possibility of the liberation of the hydrogen ion from the ligand and nitrate ion from the metal salt as a result of complex formation. This fact is in accordance with the results of the elemental analysis.

The results of the spectral studies can be utilized in calculating the apparent stability of the metal chelates under investigation [12]. It is evident from the results obtained (Table 2) that the stability constants of Th(IV) and Ce(III) complexes are higher relative to its previous complexes [13,14]. This fact encouraged us to study the validity of Beer's law for the chelates of the Th(IV) and Ce(III) ions with the ligands under investigation in ethanol medium at λ_{max} of each chelate. Straight lines passing through the origin at lower concentration of metal ions are obtained. Accordingly, the azopyrazolone compounds under studies can be used for micro-determination of Th(IV) and Ce(III) ions, the results obtained for the lower limit of the metal ion concentration with the extinction coefficient and λ_{max} are collected in Table 3.

The coordination sites of the ligands can be obtained from the comparison of important infrared frequencies

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and the proton NMR signals which are recorded in Table 4. For the free ligands and the complexes the observed broad band in the $3180 - 2090 \text{ cm}^{-1}$ region is assigned to ν_{NH} stretching [15]. The absence of ν_{NH} stretching from the spectra of some ligands and complexes can be interpreted on the basis that the band would be probably broad and weak or due to its obscure under the strong broad bands of coordinated water molecules which are located at $3380 - 3220 \text{ cm}^{-1}$ region. Moreover, additional coordination of the pyridine-OH group in the ligand L_4 is possible. The disappearance of this band (3450 cm^{-1}) from the spectra of L_4 complexes, denotes that the hydroxy group is probably taking part in coordination. A strong band at $1670-1665 \text{ cm}^{-1}$ region is observed in the spectra of the free ligands which is characteristic of $\nu_{\text{C=O}}$ [16]. Coordination of the carbonyl oxygen atom to the metal ion would be expected to reduce the electron density in the C=O link and thus lower the $\nu_{\text{C=O}}$ stretching. In all complexes studied the $\nu_{\text{C=O}}$ is shifted to lower values, showing the existence of a carbonyl coordinated bond.

The heterocyclic C=N (ring) vibration observed around 1590 cm^{-1} shows no change on complexation as compared to the free ligand, indicating that this center is not taking part in coordination. The band located in the region $1420 - 1400 \text{ cm}^{-1}$ corresponding to the stretching vibration

of $\text{N}=\text{N}$ moiety [16], is disappeared in the ir spectra of L_2 and its complexes which confirm their hydrazone structures. Bands at $512 - 439 \text{ cm}^{-1}$ and $405 - 250 \text{ cm}^{-1}$ regions can be tentatively assigned to $\text{M}-\text{N}$ and $\text{M}-\text{O}$ stretching, however, specific assignments are difficult [17].

The ^1H nmr spectra of Th(IV) and Ce(III) complexes (Table 4) reveal the presence of coordinated water molecules (except of L_5 complexes) $\delta = 3.5 \text{ ppm}$ [18]. The hydroxyl proton signal of L_4 ligand (5.93 ppm) is absent in the spectra of the complexes indicating the involvement of OH group in chelation. The methyl signal which appears as quartet centred at $\delta = 2.3 \text{ ppm}$ in the ligands spectra shifts to upfield indicating its shielding during chelation. The ^1H nmr spectra of L_1 , L_2 , L_5 and L_6 contained a broad weak signal at $\delta = 6.0, 5.25, 3.8$ and 3.8 ppm respectively. This resonance must be assigned to the hydrazone NH proton [19]. The signal due to the aromatic protons resonate downfield in the range $\delta = 7.1 - 9.1 \text{ ppm}$.

On the basis of diffuse reflectance spectral measurements of the solid complexes under investigation, a distorted octahedral geometry with lower symmetry can be suggested. The data show three bands around $39000, 23000$ and 16400 cm^{-1} . The uv. band may be ascribed to $\pi - \pi^*$ intraligands transition [20]. The second one might be CT

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L \rightarrow M processes. The visible spectra band may be due to the f-f transition in octahedral stereochemistry [21].

The thermogravimetric analysis of the complexes show endothermic peak at $\sim 160^\circ$ C which is related to the loss of water molecules. The solid complexes show four TGA peaks around 160 - 230, 345 - 435, 500 - 575 sh and 720 - 850°C, the stage being due to formation of stable metal oxide.

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Table 1: Characterisation data of the azopyrazolones (L₁-L₆) metal Chelates.

Formula	% Calc. (Found)			Colour	Decomp. Temp. (°C)	Molar Conductance ohm ⁻¹ cm ² mol. ⁻¹
	C	H	N			
<u>Chelates of C₈H₈N₅O (L₁):</u>						
[(C ₈ H ₈ N ₅ O) ₂ Ce(NO ₃) ₂ ·2H ₂ O] (NO ₃) ₂	24.9 (24.9)	2.6 (2.7)	27.3 (27.1)	Deep Brown	212	136.9
[C ₈ H ₈ N ₅ O Th(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	13.0 (13.2)	2.2 (2.4)	19.0 (18.0)	Pale Brown	206	148.2
[(C ₈ H ₈ N ₅ O) ₂ Th(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	20.0 (20.2)	2.4 (2.5)	23.3 (23.5)	Deep Brown	250	189.5
<u>Chelates of C₉H₈N₅O (L₂):</u>						
[C ₉ H ₈ N ₅ O Ce·4H ₂ O] (NO ₃) ₂	20.1 (20.0)	3.0 (3.2)	18.2 (18.0)	Yellow	182	139.8
[(C ₉ H ₈ N ₅ O) ₂ Ce·4H ₂ O] NO ₃	31.9 (31.7)	3.6 (3.5)	22.7 (22.5)	Yellow	212	61.9
[(C ₉ H ₈ N ₅ O) ₂ Th] (NO ₃) ₂	28.4 (28.5)	2.1 (2.3)	22.1 (22.0)	Deep Yellow	238	122.3
<u>Chelates of C₁₅H₁₃N₅O (L₃):</u>						
[C ₁₅ H ₁₃ N ₅ O Ce(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	26.6 (26.5)	3.1 (2.9)	16.5 (16.5)	Yellow-Orange	154	126.7
[(C ₁₅ H ₁₃ N ₅ O) ₂ Ce(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	37.7 (37.9)	3.6 (3.4)	19.0 (18.8)	Orange	160	150.5
[C ₁₅ H ₁₃ N ₅ O Th(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	21.7 (21.9)	2.6 (2.5)	15.2 (15.1)	Orange	186	154.3
[(C ₁₅ H ₁₃ N ₅ O) ₂ Th(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	32.4 (32.3)	3.1 (3.2)	17.7 (17.5)	Orange	198	150.6
<u>Chelates of C₁₅H₁₃N₅O₂ (L₄):</u>						
[C ₁₅ H ₁₃ N ₅ O ₂ Ce·H ₂ O] NO ₃	35.1 (35.0)	2.6 (2.5)	16.4 (16.6)	Orange	176	58.2
[(C ₁₅ H ₁₃ N ₅ O ₂) ₂ Ce(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	36.4 (36.5)	3.5 (3.3)	18.4 (18.6)	Brown	180	164.8
[(C ₁₅ H ₁₂ N ₅ O ₂) ₂ Th] (NO ₃) ₂	38.1 (38.0)	2.6 (2.5)	17.8 (17.7)	Deep Yellow	207	133.2
<u>Chelates of C₁₅H₁₁N₅O (L₅):</u>						
[C ₁₅ H ₁₀ N ₅ SO Ce] (NO ₃) ₂	28.5 (28.5)	1.8 (2.1)	17.9 (18.0)	Pale Brown	192	172.8
[(C ₁₅ H ₁₀ N ₅ SO) ₂ Ce] NO ₃	40.5 (40.4)	2.6 (2.4)	20.0 (20.2)	Deep Brown	220	77.1
[C ₁₅ H ₁₀ N ₅ SO Th(NO ₃) ₂] (NO ₃) ₂	22.2 (22.5)	1.4 (1.5)	16.0 (15.8)	Brown	200	118.6
[(C ₁₅ H ₁₀ N ₅ SO) ₂ Th] (NO ₃) ₂	33.8 (33.6)	2.2 (2.2)	18.2 (18.2)	Brown	244	152.0
<u>Chelates of C₁₇H₁₃N₅SO (L₆):</u>						
[C ₁₇ H ₁₂ N ₅ SO Ce·4H ₂ O] (NO ₃) ₂	30.5 (30.4)	3.0 (3.1)	14.6 (14.5)	Orange	198	169.0
[(C ₁₇ H ₁₂ N ₅ SO) ₂ Ce·4H ₂ O] NO ₃	43.3 (43.1)	3.4 (3.5)	16.3 (16.5)	Brown	195	174.4
[C ₁₇ H ₁₂ N ₅ SO Th(NO ₃) ₂ ·4H ₂ O] (NO ₃) ₂	24.5 (24.6)	2.5 (2.7)	13.6 (13.5)	Yellow	190	177.4
[(C ₁₇ H ₁₂ N ₅ SO) ₂ Th·4H ₂ O] (NO ₃) ₂	37.2 (37.0)	2.9 (2.8)	15.3 (15.5)	Orange	202	183.5

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Table 2. The Stability constant values K_f ($l.mol^{-1}$) and energy of formation $-\Delta G$ (k cal.mol $^{-1}$) for the Th(IV) and Ce(III) complexes.

	Ratio	Th(IV) Complexes		Ce(III) Complexes	
		K_f	$-\Delta G$	K_f	$-\Delta G$
L_1	1:1	$(1.15 \pm 0.06) \times 10^7$	9.76 ± 0.02	$(9.15 \pm 0.08) \times 10^6$	9.62 ± 0.01
	2:1	$(3.62 \pm 0.14) \times 10^{11}$	15.97 ± 0.03	$(6.86 \pm 0.15) \times 10^{10}$	14.97 ± 0.02
L_2	1:1	$(9.31 \pm 0.08) \times 10^6$	9.63 ± 0.02	$(2.48 \pm 0.05) \times 10^6$	8.83 ± 0.02
	2:1	$(1.13 \pm 0.15) \times 10^{11}$	15.27 ± 0.04	$(1.00 \pm 0.16) \times 10^{10}$	13.82 ± 0.04
L_3	1:1	$(7.76 \pm 0.05) \times 10^7$	10.90 ± 0.01	$(1.15 \pm 0.09) \times 10^7$	9.76 ± 0.03
	2:1	$(8.06 \pm 0.12) \times 10^{11}$	16.51 ± 0.03	$(2.24 \pm 0.18) \times 10^{11}$	15.68 ± 0.04
L_4	1:1	$(2.55 \pm 0.09) \times 10^7$	10.23 ± 0.04	$(8.22 \pm 0.07) \times 10^6$	9.55 ± 0.02
	2:1	$(5.00 \pm 0.19) \times 10^{11}$	16.16 ± 0.05	$(9.29 \pm 0.11) \times 10^{10}$	15.15 ± 0.05
L_6	1:1	$(8.99 \pm 0.07) \times 10^7$	10.99 ± 0.05	$(5.55 \pm 0.08) \times 10^7$	10.70 ± 0.04
	2:1	$(9.75 \pm 0.21) \times 10^{11}$	16.57 ± 0.07	$(4.85 \pm 0.12) \times 10^{11}$	16.15 ± 0.06

Table 3. Lower limit for micro-determination of Th(IV) and Ce(III) ions ($\mu g/ml$) at $\lambda_{max.}(nm)$ and $\epsilon_{max.}$ ($l.mole^{-1}cm^{-1}$) of each complex at 30°C.

Ligand Concentration	Th(IV) Complex			Ce(III) Complex		
	[Th(IV)]	$\lambda_{max.}$	$\epsilon_{max.}$	[Ce(III)]	$\lambda_{max.}$	$\epsilon_{max.}$
L_1 (4.0×10^{-4} mol.l $^{-1}$)	1.95	500	1650	2.56	507	1310
L_2 (6.0×10^{-4} mol.l $^{-1}$)	2.72	490	950	3.00	515	1040
L_3 (3.2×10^{-4} mol.l $^{-1}$)	0.83	495	2225	1.35	490	2050
L_4 (4.0×10^{-4} mol.l $^{-1}$)	1.00	510	1750	1.89	505	1800
L_6 (2.5×10^{-4} mol.l $^{-1}$)	0.75	485	2540	0.90	477	2370

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Table 4. Some IR(cm^{-1}) and ^1H NMR(PPM) band of the ligands(L_1 - L_6) and their Th(IV) and Ce(III) Complexes (1:1 ratio).

Compound	L_1	L_2	L_3	L_4	L_5	L_6	Assignment	
	<u>IR frequencies</u>							
Free ligand	3180w	3100b	-	-	3150	2988b	NH	stretching
	1670s	1667	1665s	1700m	1682m	1698	C=O	stretching
	1580w	1586	1593w	1590m	1590	1590m	C=N	stretching
	1424	-	1405	1405	1400	1420w	N=NZ	stretching
	1386m	1372	1364m	1372	1364	1366w	N-NH	stretching
Th(IV)-Complex	3380b	3350b	3350b	3352b	-	3250b	HCH	stretching
	2090w	2340w	2312w	2395	2903w	-	NH	stretching
	1655s	1640	1670	1670m	-	1642	C=O	stretching
	1564	1620m	1618	1600m	1595w	1598	C=N	stretching
	-	-	1410	1460w	-	-	N=N	stretching
	1380m	1380	1382	1382s	1370	1368m	N-NH	stretching
	454w	508w	488m	512w	460m	478m	M-N	stretching
	250s	382m	300s	405w	375m	340w	M-O	stretching
Ce(III)-Complex	3300b	3360b	3364b	3350b	-	3220b	HCH	stretching
	2390w	-	2315b	2360w	2680w	-	NH	stretching
	1660	1660s	1650	1660	1635	1630	C=O	stretching
	1580m	-	1610w	1600	1588	1610w	C=N	stretching
	1405	-	1407	1412w	-	-	N=NZ	stretching
	1380s	1380	1300	1380w	1378m	1370m	N-NH	stretching
	445s	464s	485m	439w	412m	464m	M-N	stretching
	380m	340m	260w	200s	313m	328s	H-O	stretching
	<u>^1HNMR signals</u>							
Free ligand	-	2.22	2.32	2.37	2.32	2.30	CH_3	protons
	6.00b	5.25b	-	-	3.80b	3.80b	NH	protons
	7.2-9.0	7.8-8.9	7.2-9.0	7.1-8.0	7.1-7.9	7.2-7.9	ring	protons
Th(IV)-Complex	-	2.15	2.28	2.32	2.20	2.25	CH_3	protons
	3.46	3.40	3.45	3.40	-	3.45	H_2O	protons
	5.80b	4.85b	-	-	3.80b	3.88b	NH	protons
	7.2-8.8	7.3-9.0	7.1-8.9	7.1-8.1	7.0-8.2	7.0-7.9	ring	protons
Ce(III)-Complex	-	2.18	2.25	2.05	2.20	2.25	CH_3	protons
	3.40b	3.30b	3.50b	3.75	-	3.41	H_2O	protons
	5.82b	4.25b	-	-	3.90b	3.85	NH	protons
	7.3-8.9	7.0-8.9	7.0-8.9	7.0-8.4	7.1-8.0	7.0-8.0	ring	protons

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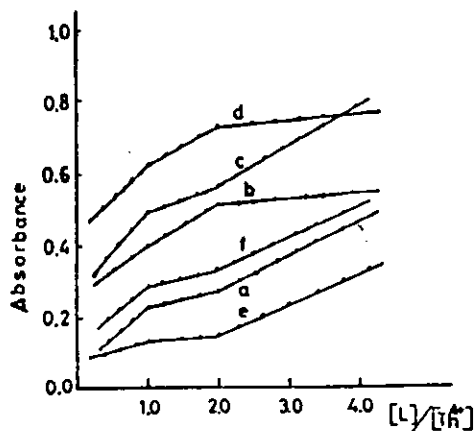


Figure 1. Molar ratio method for Th(IV)-L chelates;

- a- L_1 , $\lambda = 500$ nm, $[Th(IV)] = 1 \times 10^{-4}$ mol.l $^{-1}$
 b- L_2 , $\lambda = 490$ nm, $[Th(IV)] = 1 \times 10^{-4}$ mol.l $^{-1}$
 c- L_3 , $\lambda = 495$ nm, $[Th(IV)] = 1 \times 10^{-4}$ mol.l $^{-1}$
 d- L_4 , $\lambda = 510$ nm, $[Th(IV)] = 1 \times 10^{-4}$ mol.l $^{-1}$
 e- L_5 , $\lambda = 502$ nm, $[Th(IV)] = 5 \times 10^{-5}$ mol.l $^{-1}$
 f- L_6 , $\lambda = 485$ nm, $[Th(IV)] = 5 \times 10^{-5}$ mol.l $^{-1}$

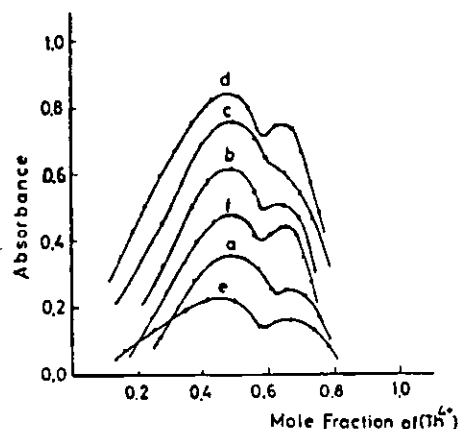


Figure 2. Continuous variation method for Th(IV)-L chelates;

- a- L_1 , $\lambda = 500$ nm, $[Th(IV) + L_1] = 8.6 \times 10^{-4}$ mol.l $^{-1}$
 b- L_2 , $\lambda = 490$ nm, $[Th(IV) + L_2] = 1.0 \times 10^{-3}$ mol.l $^{-1}$
 c- L_3 , $\lambda = 495$ nm, $[Th(IV) + L_3] = 7.2 \times 10^{-4}$ mol.l $^{-1}$
 d- L_4 , $\lambda = 510$ nm, $[Th(IV) + L_4] = 8.4 \times 10^{-4}$ mol.l $^{-1}$
 e- L_5 , $\lambda = 502$ nm, $[Th(IV) + L_5] = 1.0 \times 10^{-3}$ mol.l $^{-1}$
 f- L_6 , $\lambda = 485$ nm, $[Th(IV) + L_6] = 5.6 \times 10^{-4}$ mol.l $^{-1}$

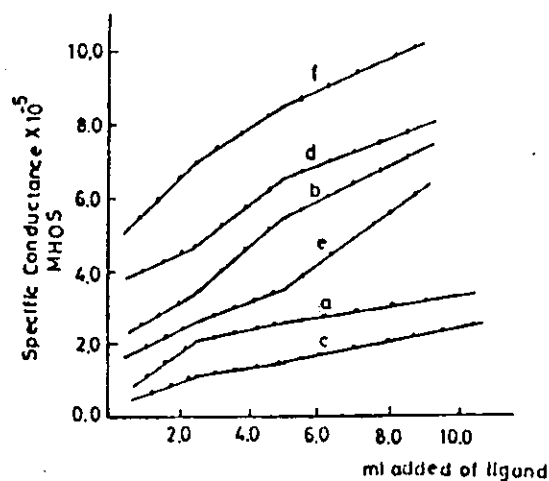


Figure 3. Conductometric titration of 25 ml (1×10^{-3} M) Th(IV) with: 1×10^{-2} M ligand L_1 (a) ; L_2 (b) ; L_3 (c) ; L_4 (d) ; L_5 (e) ; L_6 (f).

تخليق ودراسة بعض متراكبات الثوريوم والسيريوم

مع مركبات البيرازولون

فاروق عبد الكريم ، ومحمد توفيق الحاطى

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لقد تم تحضير بعض متركبات الثوريوم واليريوم الثلاثى مع مركبات البيرازولون وذلك لكثرة استخدامها الصناعية . وقد تم دراسة تركيب ونسب تكوين ودرجة ثبات هذه المتراكبات بناء على التحاليل الكمائية التى شملت التحليل الدقيق للعناصر وكذلك التحليل الطيفى فى مناطق الأشعة فوق البنفسجية وكذلك الأشعة تحت الحمراء وأطياف الرنين المغناطيس النووى والتحليل الحرارى .