Thermochimica Acta, 236 (1994) 149–164
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01559-L

Complexation of uranyl (UO_2^{2+}) and thorium (Th^{4+}) with arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)methanes

A.A.T. Ramadan *, S.L. Stefan, B.A. El-Shetary and F.M. Omar

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

(Received 6 August 1993; accepted 18 August 1993)

Abstract

The thermodynamic parameters of complexes of UO_2(II) and Th(IV) cations with arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)methanes and other derivatives have been measured in 75% (v/v) methanol–water and 0.10 M KNO_3 using potentiometry. Comparison of the experimental and calculated (using the modified Born equation) values of ΔG indicates the inner sphere nature of all the complex systems. The solid complexes were isolated and characterized by elemental analysis, conductance, infrared spectra, and by TG, DTG and DTA measurements. The ligands behave towards the metal ion as monobasic bidentate ligands.

INTRODUCTION

Previous studies [1] in this laboratory on a series of pyrazolone derivatives which resulted from the condensation of 3-methyl-1-phenylpyrazol-5-one with various substituted aldehydes yielding the novel bis-condensation products, arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)methanes have been carried out. The structure (tautomerism) and pK^H values of these compounds were studied by elemental analysis, IR spectroscopy, pH-metric titration and ^1H NMR analysis, in order to explain their metal-binding characteristics.

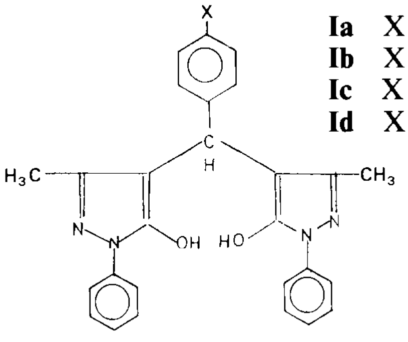
In the present study the metal-binding characteristics of four compounds (**Ia**, **Ib**, **Ic** and **Id**) with dioxouranium(II), thorium(IV), and Ln(III) ions are described.

EXPERIMENTAL

The preparation of the solid ligands and metal nitrates, the purification of methanol and the working procedures adopted were the same as described previously [1, 2].

---

* Corresponding author.



Ia X is $-NO_2$
Ib X is $-CH_3$
Ic X is $-OCH_3$
Id X is -H

Arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)methane (**Id**)

Preparation of the solid complexes

The UO_2(II) nitrate or Th(IV) nitrate and the solid ligand were mixed in 1:1 molar ratios and added to methanol as solvent. This mixture was refluxed for 12 h. The different solid complexes were obtained overnight. The solid complexes were collected, washed with methanol–water mixture and dried under vacuum. The analytical results are given in Table 1.

Procedures

The potentiometric titrations and experimental conditions were the same as described in ref. 3. The temperatures were 10, 20, 30 and 40°C and the ionic strength was maintained at 0.10 M with KNO_3. All measurements were taken in 75% (v/v) methanol–water solvent. The correction of pH values in 75% methanol–water was taken as −0.21 [3].

Physical measurements

The conductance and infrared measurements were the same as given in ref. 4.

The thermal stabilities of the solid complexes were studied using TG, DTG and DTA techniques. The measurements were made with an OD-102 Paulik–Erdey derivatograph (MOM, Hungary) with the following sensitivities: TG, 100 mg; DTG, 1/5; and DTA, 1/5. The samples were heated in platinum crucibles in static air atmosphere at a heating rate of 5 K min^{-1} up to 600°C, using Al_2O_3 as a reference compound.

RESULTS

Representative plots for the titration curves of ligands **Ia**, **Ib**, **Ic** and **Id**, in the absence and presence of UO_2(II) and Th(IV) ions, are shown in Figs.

TABLE 1

Elemental analysis and molar conductance data for UO_2(II)- and Th(IV)-arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)methane complexes

Aryl substituent	Complex	Calculated			Found			Λ [a]
		%C	%H	%M	%C	%H	%M	
H–	$[UO_2(C_{27}H_{23}N_4O_2)\cdot 3(MeOH)]NO_3\cdot 4H_2O$	38.50	4.59	25.45	38.60	4.40	25.01	100
4-CH_3–	$[UO_2(C_{28}H_{25}N_4O_2)\cdot 3(MeOH)]NO_3\cdot 4H_2O$	39.20	4.74	25.07	38.96	4.66	24.54	90
4-OCH_3–	$[UO_2(C_{28}H_{25}N_4O_3)\cdot 3(MeOH)]NO_3\cdot 4H_2O$	38.55	4.66	24.66	38.06	4.44	24.04	80
4-NO_2–	$[UO_2(C_{27}H_{22}N_5O_4)\cdot 3(MeOH)]NO_3\cdot H_2O$	38.88	3.88	25.70	39.70	3.70	25.09	80
H–	$[Th(C_{27}H_{23}N_4O_2)(NO_3)_2\cdot 4(MeOH)]NO_3\cdot 3H_2O$	35.94	4.34	22.47	36.57	4.17	22.53	100
4-CH_3–	$[Th(C_{28}H_{25}N_4O_2)(NO_3)_2\cdot 4(MeOH)]NO_3\cdot 3H_2O$	36.60	4.30	22.12	37.30	4.34	22.23	110
4-OCH_3–	$[Th(C_{28}H_{25}N_4O_3)(NO_3)_2\cdot 4(MeOH)]NO_3\cdot 3H_2O$	36.05	4.60	21.78	36.53	4.46	21.53	110

[a] In Ω^{-1} mol^{-1} cm^2 in DMF at 25°C.

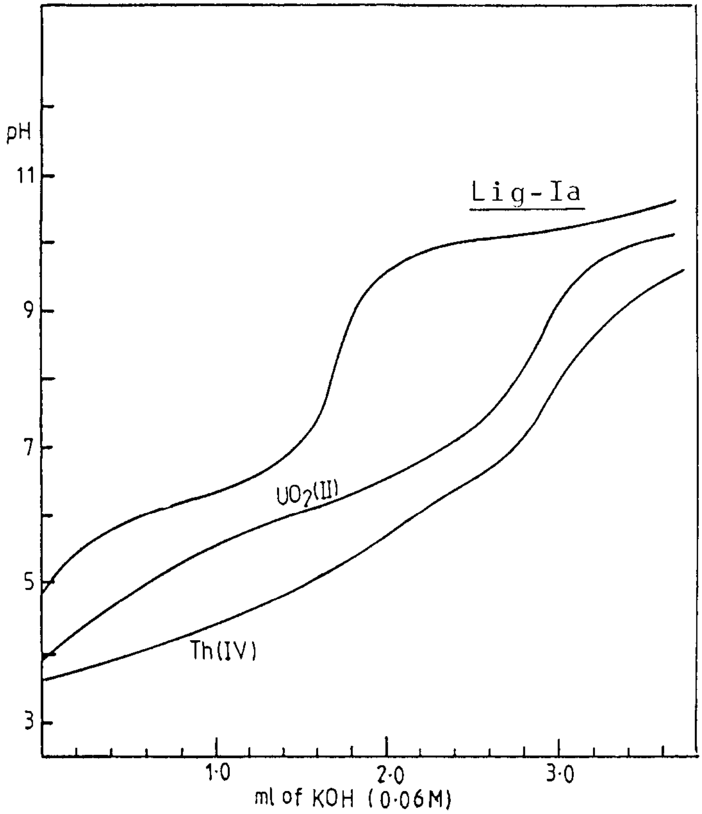


Fig. 1. Potentiometric titration curves of 30 ml Lig-**Ia** (0.0034 M) in the absence and presence of 0.001 M UO_2(II) and Th(IV) ions in 75% methanol–water ($t = 30$°C, $\mu = 0.1$).

1, 2, 3 and 4, respectively. These curves can be explained with reference to the diprotic nature (H_2L) of these ligands [1] and the formation of mononuclear 1:1 and 1:2 (M:L) complexes. The values of the protonation constants, stability constants and thermodynamic parameters (ΔG, ΔH, ΔS) were calculated as described previously [5]. The values obtained are given in Table 2.

DISCUSSION

Complexes in solution

The relationship $\log K = a\mathrm{p}K^{\mathrm{H}} + b$, first used by Bjerrum [6], has been found by some to hold for transition metal complexes for a series of closely related ligands. We have examined this relation for UO_2(II) and Th(IV) complexes with the ligands **Ia**–**Id**. If the changes in partial molar free energies of the metal–ligand and proton–ligand complexes compensate

TABLE 2

Stability constants[a] and thermodynamic parameters[b] for UO_2(II) and Th(IV) complexes with ligands **Ia**, **Ib**, **Ic** and **Id** in 75% (v/v) methanol–water solvent (ionic strength $\mu = 0.10$ M KNO_3)

Cation	$\log K_1$				$\log K_2$				$-\Delta G_1$	$-\Delta H_1$	ΔS_1	$-\Delta G_2$	$-\Delta H_2$	ΔS_2
	10°C	20°C	30°C	40°C	10°C	20°C	30°C	40°C						
Ligand–**Ia**														
H^+	6.58	6.30	6.03		10.28	9.85	9.48		35.02	45.10	−31.8	55.02	65.61	−35.2
UO_2^{2+}	9.21	8.93	8.31		7.40	6.21	4.94		48.24	73.85	−84.9			
Th^{4+}	11.92	11.45	10.60		8.61	7.83	7.30		61.51	107.82	−152.8	42.38	107.57	−215.1
Ligand–**Ib**														
H^+	7.42	6.99	6.74		10.80	10.23	9.81		39.12	40.06	−6.3	56.94	81.30	−80.3
UO_2^{2+}	9.01	8.47	8.13						47.20	72.30	−82.8			
Th^{4+}	12.42	11.82	11.56		6.72	6.46	6.10		67.11	70.79	−12.1	35.40	49.08	−45.19
Ligand–**Ic**														
H^+	7.23	7.06	6.87		10.72	10.22	10.08	9.68	39.87	23.18	55.2	58.16	54.56	2.6
UO_2^{2+}	9.73	9.54	8.99	8.73	7.39	7.21	6.85	6.55	52.01	80.75	−95.0	37.75	48.58	−29.3
Th^{4+}	12.63	12.19	11.94	11.62					69.29	55.65	45.2	35.19		
Ligand–**Id**														
H^+	7.32	6.85	6.70	6.65	10.98		10.19	9.66	38.95	37.24	7.5	59.16	67.87	−28.9
UO_2^{2+}	10.38	9.31	9.94	9.45	5.45	5.65	5.80	5.92	57.70	49.79	29.9	33.68	−26.49	198.7
Th^{4+}	13.32	12.00	12.44	11.76			7.98		17.25	20.37	−10.2	11.07		

[a] $\log K_1 \pm (0.01–0.16)$; $\log K_2 \pm (0.01–0.28)$. [b] $\Delta H_1 \pm (0.04–1.70)$; $\Delta H_2 \pm (0.04–0.58)$; $\Delta S_1 \pm (0.04–3.8)$; $\Delta S_2 \pm (0.04–0.9)$. ΔG in kJ mol^{-1}; ΔH in kJ mol^{-1}; ΔS in kJ mol^{-1} K^{-1}.

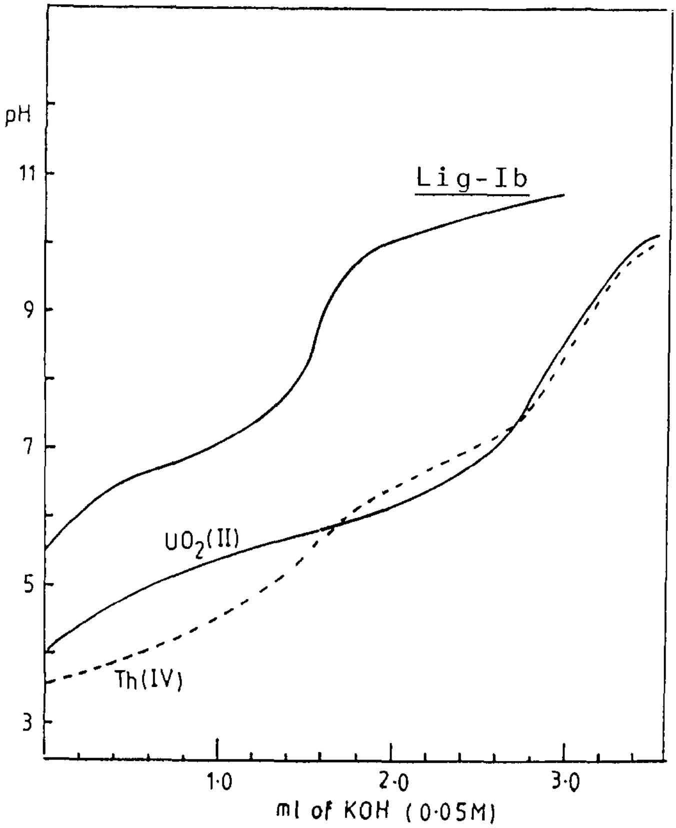


Fig. 2. Potentiometric titration curves of 30 ml Lig–**Ib** (0.0022 M) in the absence and presence of 0.001 M UO_2(II) and Th(IV) ions in 75% methanol–water ($t = 30°C$, $\mu = 0.1$).

each other, the log K^M versus ΣpK_i^H plot should give a straight line with a slope of unity. The slope values observed for the UO_2(II) and Th(VI) plots were 0.97 and 1.20, respectively (Fig. 5). According to Ernst and Menashi [7], the effect of substitution in the ligand on the stability of the metal–ligand complexes, compared to that of proton–ligand complexes will be: to a similar extent if the slope is 1; to a lesser extent if the slope is < 1; and to a greater extent if the slope is > 1.

Jones et al. [8] suggested that the metals act as acceptors, for a series of closely related ligands, the slope of the correlation plot should be less than unity for π-electron donors, and greater than unity for acceptors. The disagreement observed for UO_2^{2+} (slope < 1) and Th^{4+} (slope > 1) chelates suggests that the π-donating or π-accepting properties of the cation may not be the only factor influencing the slope values. Other factors, such as the ionization potential of the metal ion and donor atoms, and ligand field stablization effects, may influence the slope values.

Irving and Rossotti [9] have proposed two types of deviation from the theoretically predicted behaviour: major deviations in which log K_1 is always

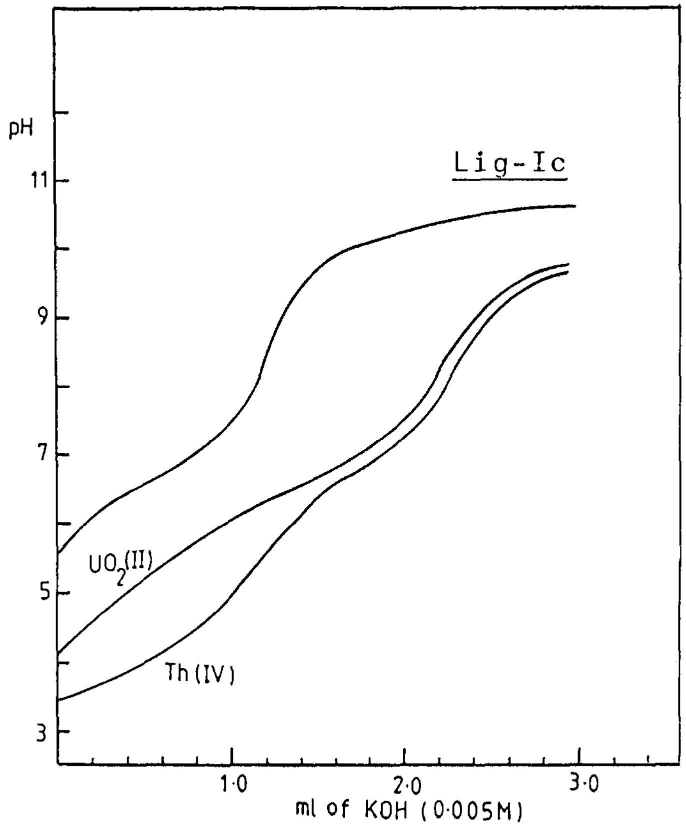


Fig. 3. Potentiometric titration curves of 30 ml Lig–**Ic** (0.0022 M) in the absence and presence of 0.001 M $UO_2(II)$ and Th(IV) ions in 75% methanol–water ($t = 30°C$, $\mu = 0.1$).

smaller than predicted; and minor deviations in which $\log K_1$ may be smaller or greater than predicted. In the present study, all the points for ligands **Ia**, **Ib**, **Ic** and **Id** of Th(IV) fall on a straight line. In the case of $UO_2(II)$ complex systems, only the point for **Ic** is divergent (Fig. 5). This suggests that in the formation of these chelates, steric factors do not play a significant role, which could be related to the fact that the substituent (X) in the ligands is deshielded from the coordination with different groups.

The thermodynamic parameters for the complexes of $UO_2(II)$ and Th(IV) with different ligands are given in Table 2. In general, the thermodynamic changes on complexation of actinide and lanthanide ions are associated with changes in the hydration of the cations and the ligands [10–14]. Complexation results in a decrease in the hydration of the ions. This provides a positive entropy contribution due to the increase in the randomness of the system and an endothermic (positive) enthalpy contribution as a result of the breakage of the ion–water and water–water bonds in the

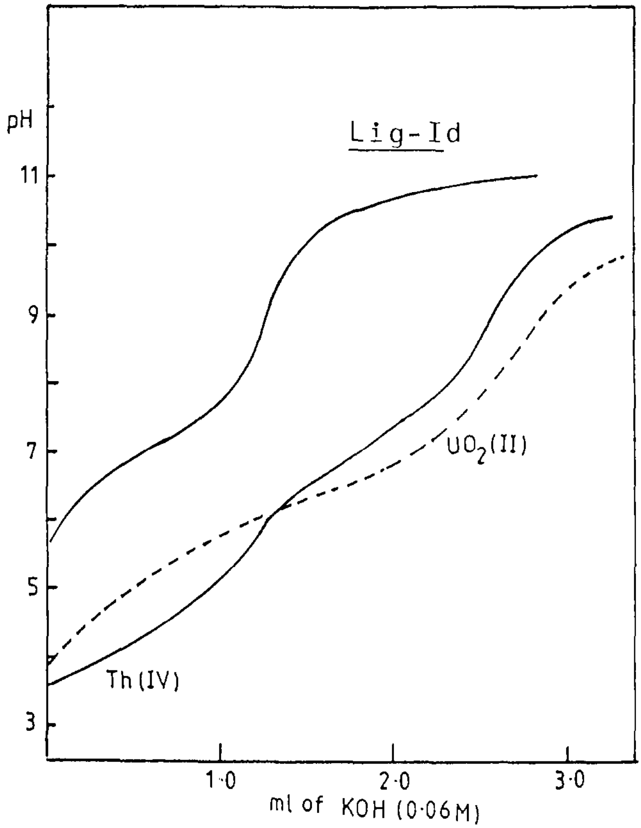


Fig. 4. Potentiometric titration curves of 30 ml Lig-**Id** (0.0026 M) in the absence and presence of 0.001 M UO_2(II) and Th(IV) ions in 75% methanol–water ($t = 30°C$, $\mu = 0.1$).

hydrated species. Generally, the combination of cation and ligand results in exothermic (enthalpy) and negative entropy contributions. The observed net changes, positive or negative, reflect the relative extent of these opposite contributions. For inner sphere complexation, the hydration sphere is sufficiently disrupted that the net entropy and enthalpy changes are normally positive. In outer-sphere complexes, the dehydration sphere appears to be only partially disrupted and the net enthalpy is usually near zero or slightly exothermic. The corresponding entropy change is also small and usually negative. With these principles in mind, we can discuss the thermodynamic data given in Table 2.

The sign and the values of the enthalpy and entropy of all the complex systems given in Table 2 indicate the outer-sphere nature of these complexes. These assignments are in agreement with earlier proposals [15, 16] for actinide and lanthanide complexes that ligands with pK^H values less than zero form predominantly outer-sphere complexes, while ligands with pK^H values greater than zero form predominantly inner-sphere complexes. According to this model, it is difficult to accept that the present complex

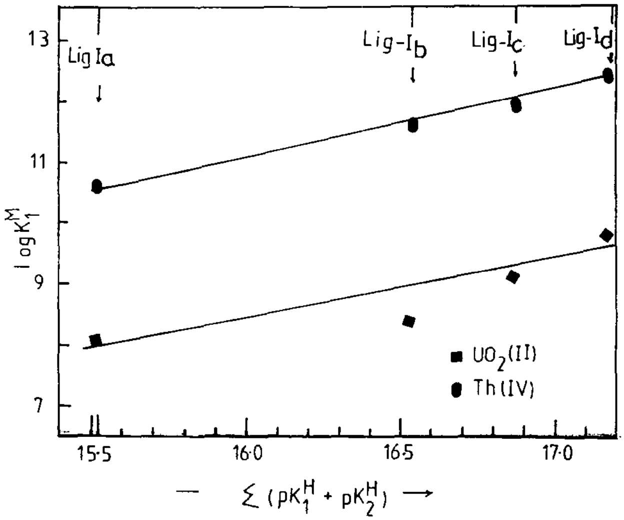


Fig. 5. Relationship between the values of log K_1^M of UO_2L and ThL^{2+} complexes and the ligand basicity $\Sigma(pK_1^H + pK_2^H)$.

systems are outer sphere, because the basicities of the ligands (ΣpK_i^H) are very high (15.50–17.14).

In order to substantiate the nature of all complex systems given in this study, i.e. outer sphere versus inner sphere, the equation developed by Munze [17] was used. The equation is basically the Born equation, eqn. (1), for the Coulombic term plus a cratic term to account for change in the number of particles during reaction $v(-1)$, and a term to estimate the activity coefficient at experimental ionic strength

$$\Delta G = \frac{Ne^2 Z_1 Z_2}{(4.187 \times 10^2) D_{\text{eff}} d_{12}} - RTv \ln 55.51 + RT \sum \ln f(\mu) \qquad (1)$$

where N is Avogadro's number, e is the unit charge (4.8×10^{-10}), Z_1 and Z_2 are the ionic charges of the metal and the ligand, respectively, D is the dielectric constant, d_{12} is the distance between charge centres and

$$\ln f(\mu) = -(\Delta Z^2) \frac{0.511 \mu^{1/2}}{(1 + Ba^0)\mu^{1/2}} - C\mu^{1/2} - E \qquad (2)$$

where $B = 0.33$, $C = 0.75$, $E = -0.15$ and $a^0 = 4.3$ Å.

It was found necessary to use the values of the effective dielectric constant $D_{\text{eff}} = 43.50$ [18], and $d_{12} = 1.80$ and 3.00 Å, in order to obtain agreement between calculated and experimental stability constants for UO_2(II)–**Id** and Th(IV)–**Id** complexes, respectively. The values of the outer-sphere stability constants were obtained from the relation

$$\beta^{\text{exp}} = \beta_o + \beta_i^{\text{calc}} \qquad (3)$$

where β^{exp} is the total experimental stability constant, β_{o} the outer-sphere stability constant, and $\beta_{\mathrm{i}}^{\mathrm{calc}}$ the inner sphere stability constant.

The values of $\Delta G_{\mathrm{i}}^{\mathrm{calc}}$ for UO_2(II)–**Id** and Th(IV)–**Id** complexes calculated using eqn. (1) are -59.17 and 73.33 kJ mol^{-1}, respectively. Then, an estimate of the relative amount of inner sphere nature yields 100% inner sphere for the two complexes. The same results (100% inner sphere) were obtained for other complex systems.

From the above, we cannot relate the signs of both the enthalpy and the entropy of all the complex systems in this study to the outer sphere nature of these species. Other factors could result from the use of methanol as a solvent.

The formation of 1:1 complexes of UO_2(II) or Th(IV) with ligands **Ia**, **Ib**, **Ic** and **Id** is accompanied by the dehydration of two moles of water in the first hydration sphere of the complex (the ligands are bidentate O,O-donors). The number of water molecules expelled from the whole coordination shell of the complex on introduction of one ligand molecule may be larger than 2, because dehydration of the ligand molecule and the second coordination sphere of the complex may be expected in the complex formation reaction. This dehydration will cause an increase in entropy. But in methanol the reverse is true, i.e. the entropy decreases. This is because when water molecules are liberated from the coordination sphere of UO_2(II) or Th(IV) ions by chelate formation with ligand molecules, the water molecules cannot behave freely in the bulk phase of methanol–water solvent. This is due to methanol forming hydrogen-bonded associations with water. Therefore, in the dehydrating process accompanying the chelate formation with the ligands, the entropy decreases. Also, a decrease in entropy is obtained due to combination of ligand molecule with the metal ion.

From visible [19, 20] and NMR [21] spectral studies on the solvation of certain transition metal ions in alcohol–water mixtures, it has been found that the alcohol molecules take part in the solvation of the metal ion. With an increase in the alcohol concentration of the solvent mixture, the water molecules can be replaced by alcohol molecules. Therefore, the water molecules are bound substantially more weakly than in aqueous ion, and this facilitates the encroachment of the ligand molecule (negative enthalpy). In addition, another weakening of the bond could arise from electron donation from the coordination sites of the ligand to the central metal ion, by which the fractional charge on the UO_2(II) or Th(IV) might decrease. Therefore the replacement of water molecules with the complexes needs less energy, i.e. the enthalpy becomes more negative.

In Fig. 6, the values of log K_1 for the rare earth complexes with ligand **Ia** are plotted against the atomic number z of the rare earth elements. Instead of the expected linearity, a curve is obtained. The first part of the curve shows a rapid increase from La to Sm chelates. Beyond Dy–Ho, the change

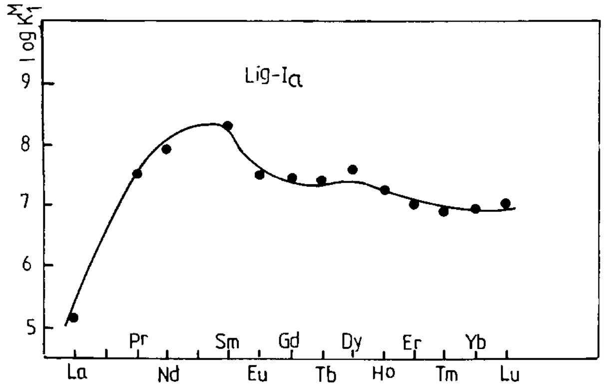


Fig. 6. Plots of $\log K_1^M$ for Lig-I–Ln(III) chelates as a function of atomic number of lanthanide elements.

in K values is very small. The complex nature of the region Gd–Dy is associated with the change in solvation properties of the cations [22, 23].

Complexes in the solid state

All the prepared complexes were subjected to elemental analysis; the data are listed in Table 1. The data reveal that the ligands behave as monobasic bidentate ligands towards UO_2(II) and Th(IV) ions. All the solid complexes are insoluble in most organic solvents but easily soluble in dimethylformamide (DMF). The values of the molar conductance, amounting to 80–110 Ω^{-1} mol^{-1} cm^2 (Table 1) for the solid complexes in DMF at room

TABLE 3

Peak maxima temperatures for UO_2(II) and Th(IV) complexes with ligands **Ia**, **Ib**, **Ic** and **Id**

Aryl substituent	Dehydration peak/°C	Loss of coordinated methanol molecules/°C	Loss of two (C_6H_5–) and ionic NO_3^- group/°C	Decomposition peak/°C
UO_2(II) complexes				
H–	80	235	420	520
4-CH_3–	85	247	430	540
4-OCH_3–	75	237	410	505
4-NO_2–	70	230	405	495
Th(IV) complexes				
H–	85	125	280	450
4-CH_3–	100	130	290	460
4-OCH_3–	70	115	275	446

TABLE 4

Thermogravimetric analyses for UO_2(II)-arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)methane complexes

Molar mass	Temp. range/°C	% Loss		Assignments
		Found	Calc.	
$[UO_2(C_{27}H_{23}N_4O_2)\cdot 3(MeOH)]NO_3\cdot 4H_2O$				
935	30–180	7.54	7.70	Loss of water of crystallization (four molecules)
	210–260	17.84	17.97	Loss of coordinated methanol (three molecules)
	280–430	40.21	41.07	Loss of two phenyl rings attached to the two pyrazolyl rings and elimination of the nitrato group
	430–560	69.86	71.12	Decomposition of the complex with the formation of UO_3
$[UO_2(C_{28}H_{25}N_4O_2)\cdot 3(MeOH)]NO_3\cdot 4H_2O$				
949	35–135	7.66	7.59	Loss of water of crystallization (four molecules)
	215–266	17.59	17.71	Loss of the coordinated methanol (three molecules)
	270–445	36.89	40.47	Loss of the two phenyl rings attached to the two pyrazolyl rings and elimination of the nitrato group
	445–600	70.38	71.56	Decomposition of the complex with the formation of UO_3
$[UO_2(C_{28}H_{25}N_4O_3)\cdot 3(MeOH)]NO_3\cdot 4H_2O$				
965	30–176	7.54	7.46	Loss of water of crystallization ($4H_2O$)
	210–279	17.42	17.41	Loss of the coordinated methanol (3MeOH)
	290–428	36.14	39.75	Loss of the two phenyl rings attached to the two pyrazolyl rings and elimination of the nitrato group
	428–575	70.98	72.02	Decomposition of the complex with the formation of UO_3
$[UO_2(C_{27}H_{22}N_5O_4)\cdot 3(MeOH)]NO_3\cdot H_2O$				
	35–97	1.89	1.94	Loss of water of crystallization (H_2O)
	216–255	12.16	12.31	Loss of the coordinated methanol (3MeOH)
	269–428	33.77	35.64	Loss of the two phenyl rings attached to the two pyrazolyl rings and elimination of the nitrato group
	428–530	69.71	70.85	Decomposition of the complex with the formation of UO_3

TABLE 5

Thermogravimetric analyses for Th(IV)-arylbis(5-hydroxy-3-methyl-1-phenylpyrazol-4-yl)-methane complexes

Molar mass	Temp. range/°C	% Loss		Assignments
		Found	Calc.	
$[Th(C_{27}H_{23}N_4O_2)(NO_3)_2 \cdot 4(MeOH)]NO_3 \cdot 3H_2O$				
1035	30–110	5.21	5.22	Loss of water of crystallization (three molecules)
	110–130	17.53	17.59	Loss of the coordinated methanol (four molecules)
	235–300	29.51	29.57	Loss of the coordinated nitrato group (two molecules)
	378–462	70.13	70.25	Decomposition of the complex with the formation of $ThOCO_3$
$[Th(C_{28}H_{25}N_4O_2)(NO_3)_2 \cdot 4(MeOH)]NO_3 \cdot 3H_2O$				
1049	30–105	5.14	5.15	Loss of water of crystallization (three molecules)
	105–135	17.28	17.35	Loss of the coordinated methanol (four molecules)
	242–310	28.96	29.19	Loss of the coordinated nitrato groups (two molecules)
	396–489	70.72	70.64	Decomposition of the complex with the formation of $ThOCO_3$
$[Th(C_{28}H_{25}N_4O_3)(NO_3)_2 \cdot 4(MeOH)]NO_3 \cdot 3H_2O$				
1065	33–94	5.06	5.07	Loss of water of crystallization (three molecules)
	94–163	17.04	17.09	Loss of the coordinated methanol (four molecules)
	245–313	28.75	28.73	Loss of the coordinated nitrato groups (two molecules)
	338–492	71.33	71.08	Decomposition of the complex with the formation of $ThOCO_3$

temperature (25°C), indicate that these complexes fall within the range expected for 1:1 electrolytes.

The data obtained from the thermograms for the solid complexes are shown in Tables 3, 4 and 5. On the basis of % loss in weight, the thermal decomposition for mononuclear UO_2(II) and Th(IV) complexes with ligand **Id** as a representative example (the other complex systems are similar and are described in Tables 4 and 5) can be formulated as follows.

$$[UO_2(C_{27}H_{23}N_4O_2)\cdot 3(MeOH)]NO_3\cdot 4H_2O \xrightarrow[30-180^\circ C]{-4H_2O}$$

$$[UO_2(C_{27}H_{23}N_4O_2)\cdot 3(MeOH)]NO_3 \xrightarrow[210-260^\circ C]{-3(MeOH)}$$

$$[UO_2(C_{27}H_{23}N_4O_2)]NO_3 \xrightarrow[280-430^\circ C]{-(2C_6H_5)+NO_3^-}$$

$$[UO_2(C_{15}H_{13}N_4O_2)] \xrightarrow[430-560^\circ C]{Decomp.} UO_3$$

$$[Th(C_{27}H_{23}N_4O_2)(NO_3)_2\cdot 4(MeOH)]NO_3\cdot 3H_2O \xrightarrow[30-110^\circ C]{-3H_2O}$$

$$[Th(C_{27}H_{23}N_4O_2(NO_3)_2\cdot 4(MeOH)]NO_3 \xrightarrow[110-130^\circ C]{-4MeOH}$$

$$[Th(C_{27}H_{23}N_4O_2)(NO_3)_2]NO_3 \xrightarrow[235-300^\circ C]{2(NO_3)^-}$$

$$[Th(C_{27}H_{23}N_4O_2)]^{2+}NO_3 \xrightarrow[378-462^\circ C]{Decomp.} ThOCO_3$$

The peak maximum temperatures taken from DTA curves for the UO_2(II) and Th(IV) complexes are summarized in Table 3. The uranyl chelates decompose to give a DTA curve containing a series of endothermic and exothermic peaks. The first endothermic process is registered in the temperature range 70–85°C and represents the loss of the molecules of crystalline water. The exothermic maxima in the DTA curves at 230–247°C are due to the loss of the coordinated methanol molecules. The next exothermic process at 405–430°C is related to the loss of the two phenyl rings attached to the pyrazolyl moieties and the ionic nitrato group. The final exothermic process with a maximum in the range 495–540°C corresponds to the loss of the rest of the ligand itself. This last process is accompanied by the bonding of oxygen atoms to the UO_2(II) ion. In this way, UO_3 is obtained as the final product of decomposition. The residue at the end of this process is in agreement with the calculated value of this oxide [24].

As is clear from the data given in Table 3, Th(IV) complexes show the first endothermic peak in the range 70–100°C, due to the loss of crystalline water [25]. The exothermic processes with DTA maxima, for all the complexes of thorium, at 115–130°C are attributed to the loss of coordinated methanol molecules. The next step is an exothermic process in the range 275–290°C which relates to the loss of coordinated nitrato groups [26]. The final exothermic process with a maximum at 446–460°C corresponds to ignition of the organic ligand yielding ThO_2 with the intermediate formation of $ThOCO_3$ [25].

In general, from peak maxima temperatures, Th(IV) complexes are less thermally stable than those of UO_2(II). The results show that the thermal decomposition of these UO_2(II) and Th(IV) complexes are similar to those of Th(IV)- and UO_2(II)-substituted 8-quinolines [27].

The bonding of the ligands to the metal ions was investigated by IR spectroscopy. The OH-form of the ligands was previously established on the basis of IR and ^{1}H NMR spectroscopy [1]. The broad band in the complexes observed at 3500–3300 cm^{-1} is due to either the water or methanol molecules. The bonding vibration band of the enolic OH group δ(OH) at 1300 cm^{-1} and the ν(C–OH) stretch band at 1040–1050 cm^{-1} in each of the spectra of ligands **Ia**, **Ib**, **Ic** and **Id** disappear in the spectra of the complexes. This indicates that the two enolic oxygen atoms of the two pyrazolyl rings are the coordination sites of the complex formation. Also, the absence of the band near 1587 cm^{-1} with a new broad band at 1540–1490 cm^{-1} which may have its origin in the vibration of the mode of the conjugated C=C–C=N system in the pyrazolyl ring, suggests destruction of the keto group through enolization and participation of the enolic oxygen in coordination.

The IR spectra of the Th(IV) complexes contain four additional bands at 1450, 1299, 1016 and 1375 cm^{-1} which are not present in the spectra of the free ligands. Of these, the first three are assigned to the ν_1, ν_4 and ν_2 modes of the coordinated nitrate ion, respectively. In fact, the ν_1 and ν_4 modes of the nitrate ion are the two split bands of the ν_3 mode of the uncoordinated nitrate ion. The magnitude of the splitting of the ν_1 and ν_4 modes is in the order of 151 cm^{-1} and this indicates that the nitrate ions are coordinated unidentately to the thorium ion in the present complexes. The fourth additional band at 1375 cm^{-1} is assigned to the non-coordinated nature of NO_3^-.

In the IR spectra of the UO_2(II) complexes, the sharp intense band near 900 cm^{-1} could be assigned to the asymmetric uranyl stretching frequency ν(U=O). The non-coordinated nature of NO_3 is supported by the appearance of strong split bands at 1380–1370 cm^{-1} in the spectra of the complexes.

From the data obtained by elemental analysis, IR spectroscopy, and conductance and thermogravimetric studies, we can conclude that the ligands under investigation act as monobasic bidentate ligands. In each case the coordination at uranium is pentagonal bipyramidal with short U–O bonds to the oxygen atoms in the axial positions. Four of the equatorial positions are occupied by oxygen atoms (two from the enolate ligands and two from the coordinated methanol molecules), and the fifth is occupied by an oxygen atom from the coordinated methanol.

In the case of Th(IV) complexes, the coordination atoms are four oxygen atoms (methanol molecules), two oxygen atoms (two enolate OH), and two nitrate oxygen atoms.

REFERENCES

1 S.L. Stefan, M. El-Behairy, A.A.T. Ramadan and S.H. Mahmoud, J. Chem. Res. (M), (1992) 1951.

2 A.A.T. Ramadan, S.M. Abu-El-Wafa, G.A. El-Inany and M.F. Eid, Acta Chim. Acad. Sci. Hung., 128 (1991) 53.

3 E.N. Rizkalla, A.A.T. Ramadan and M.H. Seada, Polyhedron, 2 (1983) 1155.

4 A.A.T. Ramadan, M.H. Seada, M.A. El-Behairy, A.I. Ismail and M.M. Mahmoud, Anal. Lett., 26 (1993) 745.

5 A.A.T. Ramadan, Thermochim. Acta, 186 (1991) 235.

6 J. Bjerrum, Chem. Rev., 46 (1952) 381.

7 Z.L. Ernst and J. Menashi, Trans. Faraday Soc., 59 (1963) 2838.

8 J.G. Jones, J.B. Poole, J.C. Tomkinson and R.J.P. Williams, J. Chem. Soc., (1958) 2001.

9 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2910.

10 G.R. Choppin and W.F. Strazik, Inorg. Chem., 4 (1965) 1250.

11 A.D. Jones and G.R. Choppin, Actinides Rev., 1 (1969) 311.

12 R.G. de Carvalho and G.R. Choppin, J. Inorg. Nucl. Chem., 29 (1967) 725.

13 G.R. Choppin and A.J. Graffeo, Inorg. Chem., 4 (1965) 1254.

14 J.B. Walker and G.R. Choppin, Lanthanide and Actinide Chemistry Series, Am. Chem. Soc., Washington D.C., No. 71 (1967) 127.

15 S. Ahrland, Coord. Chem. Rev., 8 (1921) 21.

16 G.R. Choppin and S.L. Bertha, J. Inorg. Nucl. Chem., 35 (1973) 1309.

17 R. Munze, J. Inorg. Nucl. Chem., 34 (1972) 661.

18 N. Kole and A.K. Chaudhury, J. Inorg. Nucl. Chem., 43 (1981) 2471.

19 N.J. Friedman and R.A. Plane, Inorg. Chem., 2 (1963) 11.

20 R.F. Pasternack and R.A. Plane, Inorg. Chem., 4 (1965) 1171.

21 Z. Luz and S. Meiboom, J. Chem. Phys., 40 (1964) 1066.

22 I. Grenthe, Acta Chem. Scand., 18 (1964) 293.

23 G. Degischer and G.R. Choppin, J. Inorg. Nucl. Chem., 34 (1972) 2823.

24 S. Sitrans and D. Fregona, J. Coord. Chem., 20 (1989) 193.

25 W. Brzyska and S. Karasinski, J. Therm. Anal., 34 (1988) 195.

26 P.V. Khadikav, D. Apte, B. Amma and P. Suri, Acta Chim. Acad. Sci. Hung., 126 (1989) 645.

27 W.W. Wendlandt and G.R. Horton, Anal. Chem., 34 (1962) 1098.