

## Studies of Uranyl (UO<sub>2</sub>)<sup>+2</sup> and Thorium (Th)<sup>4+</sup> Complexes with some Azo-β-diketone in Methanol-water Solvent

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**T**HE THERMODYNAMIC parameter of complexes of UO<sub>2</sub>(II) and Th(IV) cations with ortho substituted of some phenyl hydrazo compounds of di-bzoyl methane or acetoacetanilide was studied. The ortho-substitution involves carboxy or phenolic or thiol groups. The potentiometric titrations were carried out in 75% (v/v) methanol-water and 0.10 M KNO<sub>3</sub>. The thermodynamic parameters have been divided into electrostatic (el.) and non-electrostatic (non), which give some light upon the nature of the coordination between metal ions and ligands. Comparison of the experimental and calculated (using modified Born equation) values of  $\Delta G$  indicates the inner sphere nature of all the complex systems. Spectrophotometric studies were carried out between UO<sub>2</sub>(II) and o-hydroxy phenyl hydrazo acetoacetanilide. Also, conduct metric titration for both UO<sub>2</sub>(II) and Th(IV) with o-carboxy phenyl-hdrazo acetoacetanilide to confirm the stoichiometric structures of formed complexes was calculated. The solid complexes were isolated and characterized by elemental analysis, infrared and TG, DTG and DTA measurements. The results show that the ligands behave towards the metal ion as dibasic tridentate ligands.

**Keywords:** Azo-β-diketone complexes, Potentiometric titration, Thermodynamic parameter, TG, DTG and DTA and Solid complexes.

Hydrazones are compounds derived from the condensation of hydrazines with carbonyl compounds, namely aldehydes and ketones. Hydrazones are known to function as chelating agents. These compounds can display antitubercular effects, based on their tendency to form metal chelates with transition metal ions. The complexes of 2-substituted phenyl hydrazone ligands with divalent transition and tetravalent lanthanides metal ions in solution and in solid states have been extensively studied in our laboratory<sup>(1-3)</sup> as examples, but little are reported with UO<sub>2</sub> (II) and Th (IV) ions<sup>(4-6)</sup>.

The aim of the present study was to obtain more information about the stability constants of uranyl- or thorium- complexes in methanol-water mixture at different temperatures to distinguish the effect of substituent groups on the

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stabilities of these complexes. The nature of coordination bonds in both uranyl and thorium complexes was studied by dividing thermodynamic parameters into two parts electrostatic and non-electrostatic quantities. Stability constant values for uranyl ion calculated from the potentiometric studies are nearly equal to the obtained using spectrophotometric method for uranyl ion with one from organic ligand used in this manuscript as an example. Also, the conductometric titration studies for both uranyl (II) and thorium (IV) ions with another organic ligand confirm the stoichiometric of complexes formed in solution. Two solid complexes are isolated as an example and investigated in this paper.

### Experimental

The preparation of solid ligands and metal nitrates, the purification of methanol and the working procedures adopted were the same as described previously<sup>(1,2)</sup>. The abbreviations of six organic ligands can be written as; 2-carboxy-, 2-hydroxy- or thiophenyl- phenyl hydrazo dibenzoyl methane (2-CPHDBM, 2-HPHDBM or 2-TPHDBM) and also the second series as; 2-carboxy, 2-hydroxy or 2-thiophenyl- phenyl hydrazo acetoacetanilide (2-CPHAAA, 2-HPHAAA or 2-TPHAAA). All chemicals used are A. R. grade.

#### *Preparation of the solid complexes*

The UO<sub>2</sub>(II) nitrate or Th(IV) nitrates solution and 2-HPHAAA ligand in dioxane were mixed in 1:1 molar ratio. This mixture was refluxed for 12 hr. The different solid complexes were formed. The solid complexes were collected, washed with dioxane-water mixture and dried under vacuum. The elemental analysis of both the ligand and the complexes are given in Table 1.

#### *Procedures*

Potentiometric titrations and experimental conditions were described elsewhere<sup>(1,5)</sup>. The temperatures were 10, 16, 20 and 30°C and ionic strength was maintained at 0.1 M with KNO<sub>3</sub>. All measurements were taken in 75% (v/v) methanol-water solvent. The values of hydrogen ion concentration were derived from pH values after subtracting a correction of 0.205<sup>5</sup> in case of methanol-water solvent.

U.V. and visible spectra of the compounds investigated were obtained by using Shimadzu U. V. -visible Recording Spectrophotometer (UV- 240) with one centimeter quartz glass cells.

#### *Physical measurements*

The conductance and infrared measurements were described in the previous work<sup>(7)</sup>. The thermal stabilities of the solid complexes were studied using TG, DTG and DTA techniques. The measurements were made with 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°C. min<sup>-1</sup> up to 600°C, using Al<sub>2</sub>O<sub>3</sub> as a reference compound.

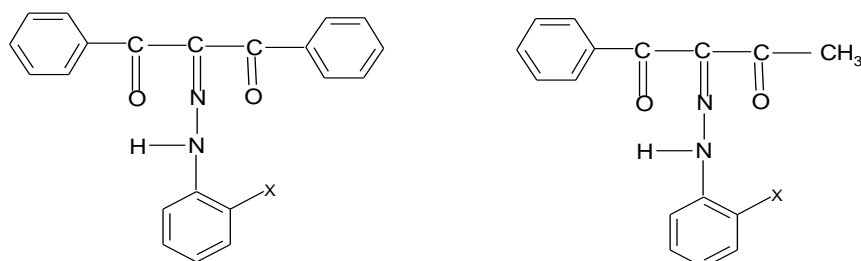
**TABLE 1. Elemental analysis of organic ligands and UO<sub>2</sub>(II)- and Th(IV)-2-HPHAAA complexes.**

Compound	%C	%H	%N	%S	%M	M. P.	Physical State
2-CPHAAA C <sub>17</sub> H <sub>15</sub> O <sub>4</sub> N <sub>3</sub> M.wt. 325	62.80 (63.02)	4.62 (4.85)	12.92 (12.78)	---	---	145°C	Yellow crystal
2-HPHAAA C <sub>16</sub> H <sub>17</sub> O <sub>3</sub> N <sub>3</sub> M.wt. 297	64.60 (64.89)	5.05 (5.21)	14.14 (14.46)	---	---	162°C	Brillion Brown crystal
2-TPHAAA C <sub>16</sub> H <sub>15</sub> O <sub>2</sub> N <sub>3</sub> S M.wt. 313	61.34 (61.56)	7.79 (7.39)	13.42 (13.64)	10.22 (10.40)	---	193°C	Deep brown crystal
2-CPHDBM C <sub>22</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> M.wt. 372	70.76 (70.98)	4.25 (4.41)	7.45 (7.59)	---	---	159°C	Yellow crystal
2-HPHDBM C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub> M.wt. 344	73.26 (73.44)	4.56 (4.71)	8.14 (8.23)	---	---	188°C	Reddish brown crystal
2-TPHDBM C <sub>21</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S M.wt. 344	70.00 (70.32)	4.44 (4.61)	7.78 (7.49)	8.89 (9.05)	---	208°C	Deep brown crystal
[UO <sub>2</sub> (C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> N <sub>3</sub> ) H <sub>2</sub> O] 2H <sub>2</sub> O M.wt. 619	31.62 (31.35)	3.07 (3.21)	6.79 (6.90)	---	38.45 (38.20)	---	Pale brown powder
[Th(C <sub>16</sub> H <sub>15</sub> O <sub>3</sub> N <sub>3</sub> )(NO <sub>3</sub> ) (H <sub>2</sub> O)]2H <sub>2</sub> O M.wt 705	27.23 (27.53)	2.70 (2.61)	9.39 (10.04)	---	32.91 (33.08)	---	Brown powder

% Calc. (% found)

### Results and Discussion

The two series of the 2-substituted  $\beta$ -diketones ligands used in this communication have the following chemical structures confirmed from elemental analysis as mentioned latter, where  $\beta$ -diketones, dibenzoyl methane (DBM) or acetoacetanilide (AAA) are represented in the following scheme.



2- Substituted phenyl hydrazo  
Dibenzoyl methane 2-XPHDBM

2- Substituted phenyl hydrazo  
acetoacetanilide 2-XPHAAA

(X = -COOH, -OH or -SH)

#### Complexes in solution

The titration curves of 2-thiophenol phenyl hydrazo acetoacetanilide (2-TPHAAA) and also 2-thiophenyl phenyl hydrazo dibenzoyl methane (2-TPHDBM) ligands at different temperatures in the absence and presence of  $\text{UO}_2(\text{II})$  and  $\text{Th}(\text{IV})$  at  $30^\circ\text{C}$ , are represented Fig. 1 & 2. The shapes of these curves clearly indicate the formation of 1:1 as well as 1:2 (M:L) complexes. Thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) were calculated as described previously<sup>(8)</sup>, the values obtained are given in Table 2.

The relationship  $\log K = APK^H + b$ , first used by Bjerrum and applied previously in our work<sup>(1)</sup>, has been found by some to hold for transition metal complexes for a series of closely related ligands. This relation for  $\text{UO}_2(\text{II})$  and  $\text{Th}(\text{IV})$  complexes with the ligands contain carboxylic or phenolic groups as substituent donating sites in these ligands was applied. If the changes in partial molar free energies of the metal-ligand and proton-ligand complexes compensate each other,  $\log k^M$  versus  $\sum pk_i^H$  plots should give a straight line with a slope of unity. The slope values observed for the  $\text{UO}_2(\text{II})$  and  $\text{Th}(\text{IV})$  plots were 0.92 and 1.24, respectively (Fig. 3). According to Ernst and Menasha<sup>(9)</sup>, the effect of substitution in the ligand on the stability of the metal-ligand complexes, compared to that of proton-ligand complexes will be:

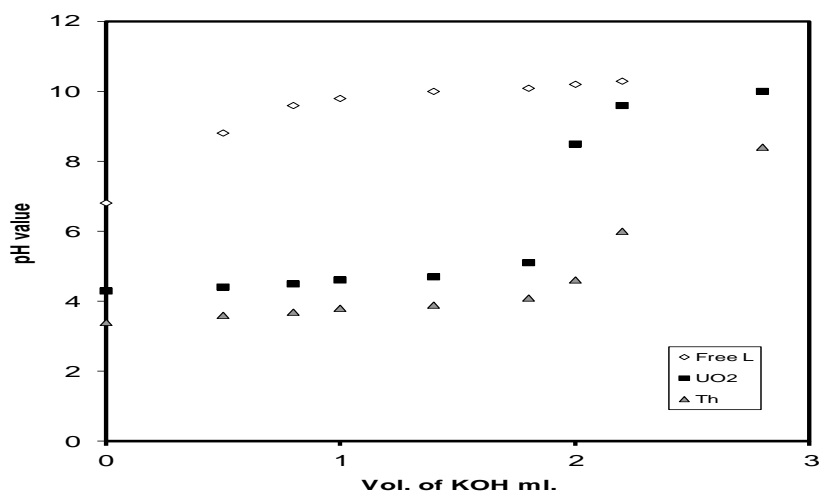
- To a similar extent if the slope is 1
- To a lesser extent if the slope is < 1
- To a greater extent if the slope is > 1

**TABLE 2. Stability constants and thermodynamic parameters for UO<sub>2</sub>(II) and Th(IV) complexes with ligands in 75% (v/v) methanol-water solvent (ionic strength  $\mu = 0.10\text{M KNO}_3$  at 30°C).**

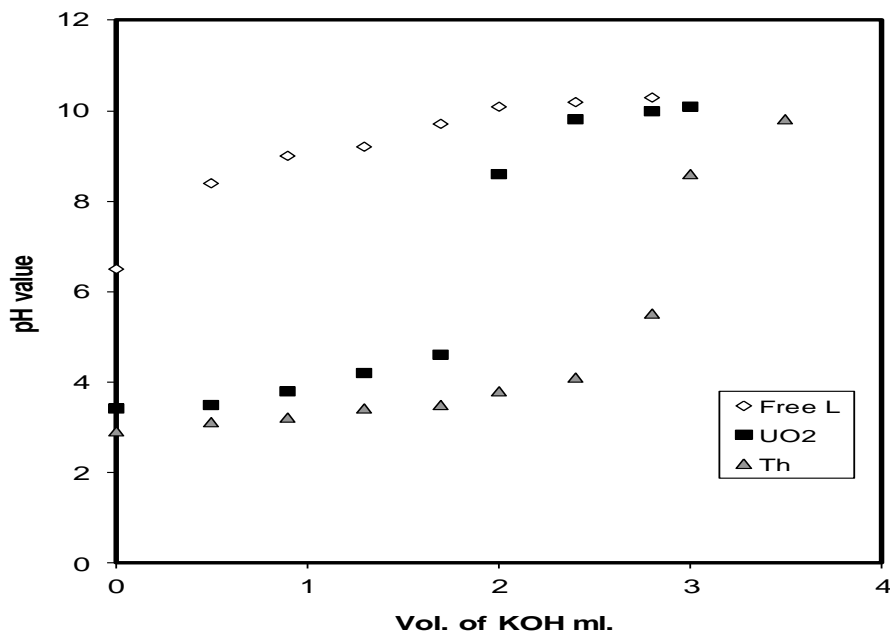
Cation	Log k <sub>1</sub>	Log k <sub>2</sub>	- $\Delta G_1$	- $\Delta H_1$	- $\Delta S_1$	- $\Delta G_2$	- $\Delta H_2$	- $\Delta S_2$
2-CPHAAA								
H <sup>+</sup>	5.42	9.14	- 7.505	-18.280	35.561	-13.335	-11.425	-6.303
(UO <sub>2</sub> ) <sup>2+</sup>	13.28	12.16	18.389	36.560	-59.900	16.838	21.621	-15.784
Th <sup>4+</sup>	16.35	14.43	22.640	27.420	15.776	21.086	24.702	-11.934
2-HPHAAA								
H <sup>+</sup>	9.60	10.42	-13.293	-11.425	-6.616	-14.429	-10.054	-14.438
(UO <sub>2</sub> ) <sup>2+</sup>	12.95	11.43	17.932	18.280	11.49	15.794	33.513	58.479
Th <sup>4+</sup>	16.18	15.70	22.405	25.909	11.565	19.981	17.138	-9.384
2-TPHAAA								
H <sup>+</sup> (UO <sub>2</sub> ) <sup>2+</sup>	9.80	11.81	-13.570	-9.140	-14.621	-14.429	-10.054	-14.438
Th <sup>4+</sup>	9.48	8.83	13.127	19.994	22.663	11.535	18.947	24.551
	11.05	10.01	15.301	20.311	16.535	13.044	15.233	7.266
2-CPHDBM								
H <sup>+</sup> (UO <sub>2</sub> ) <sup>2+</sup>	5.51	10.49	-7.630	-9.500	6.172	-15.038	-10.156	-16.114
Th <sup>4+</sup>	14.42	13.22	19.968	22.850	9.512	18.306	21.327	9.970
		14.43	22.959	18.818	-12.615	19.981	40.622	68.122
2-HPHDBM								
H <sup>+</sup> (UO <sub>2</sub> ) <sup>2+</sup>	8.51	9.78	-11.787	-6.093	-18.782	-13.543	-12.187	-4.474
Th <sup>4+</sup>	13.25	11.86	17.967	34.275	53.822	16.680	31.990	52.200
	16.29	15.88	22.557	15.233	-24.171	21.989	22.850	2.870
2-TPHDBM								
H <sup>+</sup>	9.15	10.40	-12.670	-17.366	15.498	-14.401	-9.140	-17.363
(UO <sub>2</sub> ) <sup>2+</sup>	11.66	10.42	16.063	22.850	22.401	14.429	27.420	42.875
Th <sup>4+</sup>	13.32	12.65	18.444	15.233	15.233	16.132	13.710	-2.422

Log k<sub>1</sub>  $\pm$  (0.01-1.0), log k<sub>2</sub>  $\pm$  (0.01-2.8),  $\Delta H_1$   $\pm$  (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)

$\Delta G$  in k.cal.mole<sup>-1</sup>,  $\Delta H$  in k.cal.mole<sup>-1</sup> and  $\Delta S$  in cal.mole<sup>-1</sup>K<sup>-1</sup>



**Fig. 1. Potentiometric titration curves for UO<sub>2</sub>(II)-2-TPHDBM and Th(IV)-2-TPHDBM in 75% (v/v) methanol-water.**

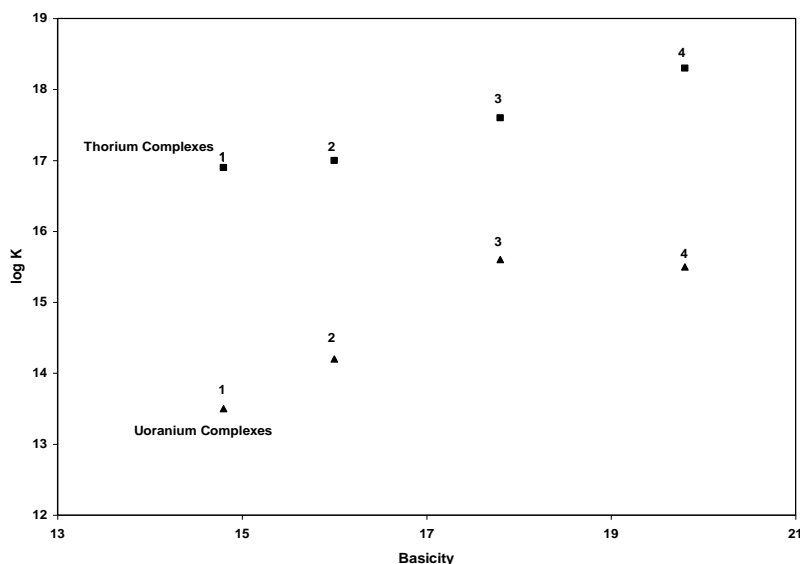


**Fig. 2.** Potentiometric titration curves for  $\text{UO}_2(\text{II})$ -2-TPHAAA and  $\text{Th}(\text{IV})$  2 TPHAAA in 75% (v/v) methanol-water .

Jones *et al.*<sup>(10)</sup> suggested that the metal acts as acceptor, for closely related ligands, the slope of the correlation plot should be less than unity for  $\pi$ -donating or  $\pi$ -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 stabilization effects may influence the slope values. Also, the deviation than the predicted (Fig. 2) is perhaps associated with a significant steric effects of the substituent adjacent to the chelating centers. Irving and Rossotti<sup>(11)</sup>, have proposed two types of deviation from the theoretically predicted behavior, the major deviation in which  $\log K_1$  is always smaller than predicted; and the minor deviation in which  $\log K_1$  may be smaller or greater than predicted. In the present study, the point of  $\text{Th}^{4+}$  falls on the straight line. In the case of  $\text{UO}_2(\text{II})$  complex system, only the point for 2-carboxy phenyl hydrazone acetoacetanilide (2-CPHAAA) is divergent (Fig. 2). 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<sup>(12)</sup>.

Thermodynamic parameters for the complexes of  $\text{UO}_2(\text{II})$  and  $\text{Th}(\text{IV})$  with different ligands are given in Table 2. In general, the thermodynamic changes on complexation of actinide and lanthanide ions are associated with change in the hydration of the cations and the ligands<sup>(1,5)</sup>. Complexation causes a decrease in

the hydration of the ions. The negative entropy changes ( $\Delta S$ ) for most complex systems (Table 2) can be attributed to the extensive solvation of the metal chelate in aqua-organic medium. On the other hand, water molecules liberated from coordination sphere of the metal upon complex formation can't behave freely in methanol-water mixture due to the hydrogen bond formation with methanol molecules<sup>(13)</sup>. As a result of this, the dehydrating water molecules from the metal ion will combine with those in bulk solvent molecules by the formation of hydrogen bonds leading to decrease in the entropy  $\Delta S$ . Therefore, the decrease in the entropy of any complex system in 75% (v/v) methanol-water is attributed to an entropy loss of water liberated. The positive entropy changes obtained in some cases of UO<sub>2</sub>(II) and Th(IV) complexes could be related to the higher tendencies of these metal cations toward the ligand molecules as indicated by their higher  $\Delta S$ , in some cases of UO<sub>2</sub>(II) and Th(IV) complex systems could be due to the small cationic radius compared to the divalent metal ions.



**Fig. 3. Relation between basicity of some ligands and formation constant .**

- |                    |                    |
|--------------------|--------------------|
| <b>1. 2-CPHAAA</b> | <b>2. 2-CPHDBM</b> |
| <b>3. 2-HPHDBM</b> | <b>4. HPHAAA</b>   |

The negative enthalpy  $\Delta H$  values obtained for all complex systems reported here (Table 2) could result from the covalent interaction of metal ion and oxygen of carboxylic, carbonyl or phenolic groups or sulfur from -SH group, or nitrogen of azomethane group. Thus, the thermodynamic parameters of all complex systems have been analyzed in terms of electrostatic (el) and non-electrostatic (non) parts, applied method of calculation mentioned before by Murakami<sup>(14)</sup>, and the results are given in Table 3, the (non) values of thermodynamic parameter are much higher than the corresponding (el) ones, this indicates the covalent nature of the formed complexes.

**TABLE 3. Non-electronic (non) and electronic (el.) thermodynamic quantities associated with reaction of metal ions with 2-HPHAAA and 2-HPHDBM ligands in 75% (v/v) methanol-water at 30°C.**

Complex	$\Delta G_{\text{non}}$ k.cal.mole <sup>-1</sup>	$\Delta G_{\text{el.}}$ k.cal.mole <sup>-1</sup>	$\Delta H_{\text{non}}$ k.cal.mole <sup>-1</sup>	$\Delta H_{\text{el.}}$ k.cal.mole <sup>-1</sup>	$\Delta S_{\text{el.}}$ Cal.mole <sup>-1</sup> K <sup>-1</sup>
(UO <sub>2</sub> ) <sup>2+</sup> -2-HPHAAA	-26.74	8.8	-29.15	10.87	6.81
Th <sup>4+</sup> -2-HPHAAA	-17.75	-4.66	-20.16	-5.75	-3.60
(UO <sub>2</sub> ) <sup>2+</sup> -2-HPHDBM	41.30	-59.26	38.89	-73.16	-45.86
Th <sup>4+</sup> -2-HPHDBM	-64.09	41.52	-66.50	51.26	32.13

Also, the heat change upon complex formation will be related to the difference between the strength of the metal-donor bonds and hydration bonds. The heat change on complexation must be determined from the electrostatic and covalent interactions, together with a structural contribution and ligand field stabilization. Therefore, this could indicate that the coordination between UO<sub>2</sub>(II) or Th(IV) ion with the ligands in the present work behave as covalent characters.

Also, we can remember that, the lower entropy values obtained in most chelates in Table 2, cause no usual effects within the chelates of a given reagents. It must be noted that the chelates of 2-TPHAAA and 2-TPHDBM take another behavior. It could be explained based on hard-soft concept, ligands contain a carboxylate or phenolate group (*i.e.* oxygen is donating atom) which is hard atom, while ligands, contain thiol group (*i.e.* sulfur is a donating atom) which is soft atom.

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 entropy and enthalpy changes are normally positive. In outer sphere complexes, the dehydration sphere appears to be only partial by 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 value 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 proposal<sup>(15)</sup> 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 systems are outer sphere, because the basicities of the ligands  $pK_i^H$  are very high (15.47-21.53). In order to substantiate the nature of all complex

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systems given in this study, *i.e.* outer sphere versus inner sphere, the equation developed by Munze<sup>(16)</sup> was used. The equation is basically the Born equation (1), for the coulombic term plus a citric term to account for change in the number of particles during reaction  $\gamma(-1)$ , and a term to estimate the activity coefficient at experimental ionic strength<sup>(17)</sup>.

$$\Delta G = \frac{Ne^2 z_1 z_2}{(4.187 * 10^2) D_{eff} d_{12}} - RT * \gamma \ln 55.51 + RT \ln f(\mu) \quad (1)$$

where, N is Avogadro's number, e is the unit charges, Z<sub>1</sub> and Z<sub>2</sub> are the ionic charges of the metal and the ligand, respectively, D is dielectric constant, d<sub>12</sub> is the distance between charge centers and:

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

where, B = 0.33, c = 0.75, E = -0.15 and a<sup>0</sup> = 4.3A<sup>o(17)</sup>

It was found necessary to use the values of the effective dielectric constant D<sub>eff</sub> = 43.50<sup>(18)</sup>, and d<sub>12</sub> = 1.80300A<sup>o</sup>, in order to obtain agreement between calculated and experimental stability constants for (UO<sub>2</sub>)<sup>2+</sup>-CPHAAA and Th<sup>4+</sup>-2-CPHAAA complexes, respectively. The values of the outer sphere stability constants were obtained from the relation:

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

where,  $\beta^{exp}$  is the total experimental stability constant,  $\beta_o$  the outer sphere stability constant, and  $\beta_i^{calc}$  the inner sphere stability constant. The values of  $\Delta G_i^{calc}$  for UO<sub>2</sub> (II)- and Th(IV)-2-CPHAAA complexes calculated using Equation (1) are 38.126 and 29.298 k.cal/mole, respectively. Then an estimate of the relative amount of inner sphere nature yields 100% inner sphere for the two complexes. 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. Also, the conduct metric titration for UO<sub>2</sub> (II) and Th(IV) ions against 2-CPHAAA as a titrant indicating the stepwise formation of MA and MA<sub>2</sub> (metal-ligand) ratio, which is in agreement with the above potentiometric studies. The electronic absorption spectra of 2-HPHAAA in 75% methanol-water solvent show three different bands; the first located at 375, the second appears as a shoulder one at 320 nm, while the third one is located at 250 nm. The band may be due to charge transfer (CT) transition. This charge transfer originates from a phenyl hydrazo ring as a source to the acetoacetanillide carbonyl groups as a sink. The two other bands can be assigned to  $\pi \rightarrow \pi^*$  transition of the benzenoid system of the compound<sup>(19)</sup>. The acid dissociated constant of the free ligand was calculated from the spectrum, using the modified limiting absorbance method<sup>(19)</sup>. A value of

$pK_1^H = 4.5$  was obtained well agrees with that of pH metric results. On addition of uranyl ion solution to the yellow solution of 2-HPHAAA in 50% (v/v) methanol-water a pale brown color was observed. The optimum pH to form stable complex is 5.0 for  $UO_2(II)$ -2-HPHAAA experimentally. The value of  $\lambda_{max}$  for this complex is located at 410 nm, with a free ligand as reference. The red shift in the visible band for metal complex than this of free ligand could be attributed to the complexation process. The complex of  $UO_2(II)$ -2-HPHAAA obeyed Beer's law in the concentration range; this permits the possible application of the spectrophotometric method for quantitative determination of uranyl ion.

Stoichiometric complex of  $UO_2(II)$ -2-HPHAAA can be examined by applying molar ratio, Job's and slope ratio methods<sup>(20)</sup>, which indicate the formation of  $MA_2$  complex between metal and ligand. Formation constants for 1:2 (metal: ligand) was calculated using Awadallah method<sup>(21)</sup>, from the data obtained of molar ratio and Job's methods applied the following relation:

$$\beta = \frac{(A / A_m)}{[1 - (A / A_m)^{n+1} n^2 (L^-)^n]} \quad (4)$$

where  $\beta$  is apparent formation constant, A and  $A_m$  are absorbance at given ligand concentration (L) at limiting absorbance value, also n is stoichiometric of complex formed. The value of  $(L^-)$  could be obtained from the relation described previously<sup>(2)</sup>

$$C_L = \frac{[L^{2-}](1 + [H^+])}{K_1^H} + \frac{[H^+]}{K_1^H K_2^H} \quad (5)$$

The detailed calculations for the value of  $\log \beta$  using molar ratio method as an example are given in Table 4. Also, the value of  $\log \beta$  obtained from Job's method is  $29.870 \pm 0.909$ . These above two values of  $\log \beta$  for  $UO_2(II)$  - and  $Th(IV)$ -2-HPHAAA are in good agreement with those obtained from pH-metric study.

#### *Complexes in the solid state*

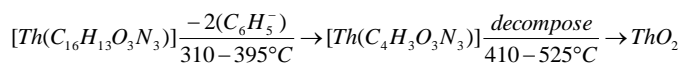
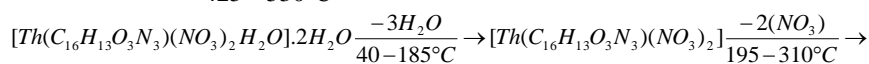
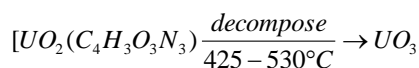
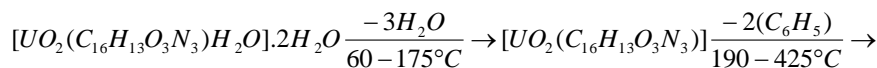
Two complexes were prepared which are  $UO_2(II)$ - and  $Th(IV)$ -2-HPHAAA as examples and subjected to elemental analysis. The data obtained are listed in Table 1. The data reveal that the ligand (2-HPHAAA) behaves as dibasic tridentate ligands towards  $UO_2(II)$  and  $Th(IV)$  ions. All the solid complexes are insoluble in most organic solvents but easily soluble in dimethyl formamide DMF. The values of the molar conductance, amounting 5.9 and 7.3  $\text{mol}^{-1} \text{cm}^2$  for the uranyl and thorium complexes, respectively in DMF at room temperature, indicate the non-electrolytic nature of these complexes.

**TABLE 4. Calculation of apparent formation constant for (UO<sub>2</sub>)<sup>2+</sup>-2-HPHAAA in 50% (v/v) methanol-water and pH 5±0.01, using molar ratio method.  $K_1^H = 2.5 \cdot 10^{-10}$ ;  $K_2^H = 3.8 \cdot 10^{-11}$  and  $A_m = 0.610$  at  $\lambda = 440$  nm .**

C <sub>L</sub> 10 <sup>5</sup>	[L <sup>-2</sup> ]10 <sup>16</sup>	A	A/A <sub>m</sub>	(1-A/A <sub>m</sub> )	Log β
0.2	1.9102	0.057	0.093	0.907	29.931
0.4	3.8204	0.107	0.175	0.825	29.72
0.5	4.7755	0.140	0.230	0.771	29.740
0.6	5.9306	0.163	0.267	0.733	29.740
0.8	7.6408	0.220	0.361	0.639	29.772
1.0	9.5510	0.260	0.426	0.574	29.790
1.2	11.4613	0.317	0.520	0.480	29.951
1.4	13.3715	0.373	0.612	0.388	30.370
1.5	14.3266	0.397	0.651	0.349	30.270
1.6	12.2817	0.044	0.721	0.279	30.550
1.8	17.1919	0.473	0.775	0.225	30.760
2.0	19.1012	0.550	0.902	0.098	31.817
2.5	23.877	0.575	0.943	0.0574	32.339
3.0	---	0.610	1.00	0	---

$\delta = 0.8401$  ;  $\log \beta \cdot X = 30.3673$  ;  $\log \beta = \log k_1 + \log k_2$

The data obtained from the thermo grams for solid complexes on the basis of loss in weight percent (Tables 5&6) the thermal decomposition of mononuclear UO<sub>2</sub>(II) and Th(IV) complexes with 2-HPHAAA ligand as an example can be formulated as follows:



**TABLE 5. Thermal analysis for UO<sub>2</sub><sup>+2</sup> - 2 - HPHAAA Complexes.**

Complex M. wt.	Temp. range °C	%loss		Assignment
		Found	Calc.	
[UO <sub>2</sub> (C <sub>16</sub> H <sub>13</sub> O <sub>3</sub> N <sub>3</sub> )H <sub>2</sub> O]·2H <sub>2</sub> O 473	60 to 175	11.30	11.42	Loss of 2 water moles. of crystallization and one coordinated water mol.
	190 to 425	36.81	36.75	Loss of two phenyl rings from ligand
	425 to 530	52.61	52.83	Decomposition of the complex with the formation of UO <sub>3</sub>

TABLE 6. Thermal analysis for  $\text{Th}^{4+} - 2 - \text{HPHAAA}$  Complexes .

Complex M. wt.	Temp. range °C	%loss		Assignment
		Found	Calc.	
$[\text{Th}(\text{C}_{16}\text{H}_{13}\text{O}_3\text{N}_3(\text{NO}_3)_2\cdot\text{H}_2\text{O})_2\text{H}_2\text{O}]$ 563	40 to 185	9.47	9.59	Loss of 2 water moles. of crystallization and one coordinated water mole.
	195 to 310	24.23	24.36	Loss of two coordinated nitro groups
	315 to 390	33.70	33.85	Loss of phenyl groups from ligand
	415 to 525	40.65	40.51	Decomposition of the complex with the formation of $\text{ThO}_3$

The peak maximum temperature taken from DTA curve for the uranyl chelate 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 crystalline water. The exothermic maxima in the DTA curves at 105-170°C is due to the loss of coordinated water molecules. The next exothermic process at 325-415°C is related to the loss of two phenyl rings attached to ligand moieties. The final exothermic process with a maximum range 415-520°C corresponds to the loss of the rest of the ligand itself. This last process is accompanied by the banding of oxygen atoms to the UO(II) ion. In this way,  $\text{UO}_3$  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<sup>(22)</sup>.

As clear, Th (IV) complex shows the first endothermic peak in the range 70-100°C, due to the loss of crystalline water<sup>(23)</sup>. The exothermic process with DTA maxima, at 120-140°C is due to the loss of coordinated water molecule<sup>(23)</sup>. The next step is an exothermic process at 275-290°C which relates to the loss of coordinated nitro groups<sup>(24)</sup>. The exothermic maxima curve at 305-320°C is attributed to loss of two phenyl groups from ligand itself. The final process with a maximum at 445-460°C corresponds to ignition of the residual organic ligand yielding  $\text{ThO}_2$  with the intermediate

formation ThOCO<sub>3</sub><sup>(23)</sup>. In general, from peak maxima temperatures, Th (IV) complexes are less thermally stable than those of UO<sub>2</sub>(II) and this agrees with the previous work<sup>(25)</sup>.

The infrared spectra of 2-HPHAAA exhibited bands which could be associated with both tautomeric isomers, azo (=C-N=N-) and hydrazo (-C=N-NH-) structures. The  $\gamma_{\text{NH}}$ ,  $\gamma_{\text{C=N}}$  and  $\gamma_{\text{C=O}}$  (hydrogen bounded) for hydrazo form were detected at 3200, 1590 and 1642 cm<sup>-1</sup>, respectively. Also, the I.R. spectrum of free ligand shows a medium band around 3350 cm<sup>-1</sup> and intermolecular hydrogen bonded stretch<sup>(5)</sup>, these completely, disappeared in the spectrum of uranyl and thorium complexes, showing the coordination of the hydroxyl group.

In addition, the infrared spectra of these two solid complexes are characterized by the presence of strong band between 3600-2900 cm<sup>-1</sup> attributed to the presence of coordinated water molecule. Also, the appearance of new medium band at 847 cm<sup>-1</sup> in both complexes spectra, is attributed to  $\pi_{\text{H}_2\text{O}}$  ( $\rho_x$ ) rocking modes of coordinated water<sup>(26)</sup>. The other coordination site is the hydrazone (-NH-N=) group. The strong evidence of sharing this group in complexation can be seen from the band at 1598 cm<sup>-1</sup> in the free ligand shifts to lower frequencies at 1587 and 1589 cm<sup>-1</sup> for uranyl and thorium complexes, respectively<sup>(27)</sup>.

The  $\gamma_{\text{C=O}}$  observed at 1642 cm<sup>-1</sup> in the spectrum of free ligand is shifted to lower frequencies at 1630 and 1625 cm<sup>-1</sup> for uranyl and thorium chelates, respectively, denoting the role of this group in coordination processes. Other evidence confirming this argument is the appearance of metal-oxygen vibration at 440 and 436 cm<sup>-1</sup> for uranyl and thorium complexes, respectively as given by Nokamoto<sup>(7)</sup>. A new band appears at 500-600 cm<sup>-1</sup> which is due to the presence of metal-nitrogen bands in both chelates<sup>(27)</sup>.

The I.R. spectra of Th(IV) complex contain three additional bands at 1450, 1349 and 1060 cm<sup>-1</sup> which are not present in the spectra of the  $\gamma_1$ ,  $\gamma_4$  and  $\gamma_2$  modes of the coordinated nitrate ion, respectively. The magnitude of the splitting of the  $\gamma_1$  and  $\gamma_4$  modes indicates that the nitrate ions are coordinated bidentate to the Th(IV) ion in the present complex<sup>(27)</sup>. In the I.R. spectra of the UO<sub>2</sub>(II) complexes the sharp intense band near 900 cm<sup>-1</sup> could be assigned to the asymmetric uranyl stretching frequency  $\gamma_{(\text{U=O})}$ . From studies carried out in the two solid complexes it can be indicated that the coordination number  $z = 8$  is to be expected for two metal ions.

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## دراسات علي متراكبات اليورانيوم والثوريوم مع بعض ليجاندات الأزو بيتا ثنائي الكيتون المتكونة في مخلوط من الميثانول- والماء

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تم دراسة ثرموديناميكية لمتراكبات كلا من اليورانيل  $UO_2(II)$  والثوريوم  $Th(IV)$  مع ليجندات مركبات اورثو فينيل هيدرازو داي بنزويل ميثان أو اسيتواسيتانيليد. حيث تتوافر مجموعة كربوكسيل أو فينول أو ثايو ناتجة من الوضع اورثو في الليجندات المستعملة في هذه الدراسة.

تمت الدراسة في المحلول باستخدام المعايرة الجهدية وأجريت التجارب في مذيب يتكون من الكحول الأيثيلي والماء بنسبة 75% مع الاحتفاظ بالقوة الأيونية ثابتة باستخدام محلول من نترات البوتاسيوم ذو تركيز 0.1 مولر. تمت الدراسة عند درجات حرارة مختلفة 10، 15، 20، 30 درجة مئوية حتي يمكن تعيين الدوال الثرموديناميكية  $\Delta H$  و  $\Delta G$  وكذلك  $\Delta S$  للأستدلال علي طبيعة الرابطة المتكونة بين العنصر والليجاند تحت الدراسة.

كذلك تم دراسة المتراكبات المتكونة بالطرق المختلفة مثل Spectrophotometric وأيضاً Conduct metric titration للتعرف علي المتراكب المتكون.

أيضاً تم فصل المتراكب الصلب ودراسته باستخدام تحليل دقيق للعناصر وطيف الأشعة تحت الحمراء IR وكذلك DTA , DTG , TGA للتعرف علي طبيعة المتراكب. وقد أوضحت النتائج ان الليجند يتفاعل مع العنصر كثنائي القاعدة ثلاثي الشعب Dibasic tridentate .