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# Dioxouranium(Vi) Mixed Ligand Complexes Containing 8-Hydroxyquinoline and Some Amino Acids

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### DIOXOURANIUM(VI) MIXED LIGAND COMPLEXES CONTAINING 8-HYDROXYQUINOLINE AND SOME AMINO ACIDS

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#### **ABSTRACT**

The formation equilibria of binary and ternary complexes of  $UO_2(VI)$ with 8-hydroxyquinoline (HL) and some amino acids (HL') in 40% EtOH-H<sub>2</sub>O solution have been investigated by a potentiometric technique. The stepwise formation constants of the complexes formed in solution were calculated using the non-linear, least-squares computer program MINIQUAD. The concentration distribution of the complex species was resolved. Mixed ligand complexes of the general formula  $[UO_2LL'-(H_2O)_n](NO_3)_m$ , where HL = 8-hydroxyquinoline; HL' = glycine, alanine, L-valine, proline, leucine,  $\beta$ -phenylalanine and H<sub>2</sub>L' = histidine or histamine, n = 0 or 2 and m = 0 or 1, have been synthesised and characterized by elemental analyses, electrolytic conductance, electronic spectra, IR, <sup>1</sup>H NMR spectra and thermogravemetric studies. The uranium atom in these complexes is 6- or 8-coordinate. Both HL

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and HL' are bidentate, bonding through N or O atoms (phenolate or ionized COO<sup>-</sup> groups).

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#### **INTRODUCTION**

An important aspect of the chemistry of the transuranic elements is the way in which they interact with environmentally important molecules, such as amino acids. The stability constants of a variety of amino acid complexes with dioxouranium(VI) have been measured<sup>1</sup> and the uranyl complexes of certain amino acids have been prepared and characterized<sup>2</sup>. Complexes of amino acids with the dioxouranium(VI) ion are, therefore, potentially model systems for the study of UO<sub>2</sub>protein interaction. Also, 8-hydroxyquinoline has found numerous applications in analytical chemistry as chromophoric and metalochromic indicators<sup>3,4</sup>.

In the present work we report the determination of the stability constants of binary and ternary complexes of  $UO_2(VI)$  with 8hydroxyquinoline (HL) as primary ligand and amino acids (HL') as secondary ligands using potentiometric techniques. The structure of the synthesised metal chelates was established by physico-chemical studies, including spectral, conductance and thermogravemetric determination.

#### **EXPERIMENTAL**

#### Materials and Reagents

8-Hydroxyquinoline (8-HQ) was supplied by Sigma Chem. Co., and was used as obtained. The amino acids investigated were glycine (gly), alanine (ala), L-valine (val), proline (prol), leucine (leuc),  $\beta$ phenylalanine (phenala), histidine (histi) and histamine (hista) and were

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provided by Fluka Chemical Company, the latter two as HCl salts. Uranyl nitrate,  $UO_2(NO_3)_2.6H_2O$ , was obtained from BDH. The solution of uranyl ion was standardized by conventional methods<sup>5</sup>. The 8-hydroxyquinoline solution (0.02 M) was prepared immediately before use by exact weighing of the substance and then dissolving in an equivalent amount of 0.02M HNO<sub>3</sub>. All solutions were prepared in deionized water. Carbonate-free NaOH (titrant) was prepared and standardized against potassium hydrogen phthalate solution.

#### Synthesis of the UO2(VI) Mixed-Ligand Complexes

Dioxouranium(VI) mixed-ligand complexes of the general formula  $[UO_2LL'(H_2O)_n](NO_3)_m$ , where HL = 8-hydroxyquinoline; HL' = amino acids, n = 0 or 2 and m = 0 or 1, were prepared by mixing 0.005 mole (2.51 g) of uranyl nitrat dissolved in 5 mL H<sub>2</sub>O with 0.005 mol (0.73 g) of 8-hydroxyquinoline dissolved in 10 mL ethanol. An equivalent amount of amino acid (0.005 mole), dissolved in 10 mL water, was added to this mixture to obtain the 1:1:1 mixed - ligand complex. The pH of the mixture was raised to 5-7 by dilute sodium hydroxide solution. The mixture was refluxed for 2 h. The complex precipitated after cooling and was filtered, washed thoroughly with ethanol-water (1:1) and finally with ether. The analytical results are given in Table I.

#### Measurements

Potentiometric measurements were made using a Metrohm 686 titroprocessor (Switzerland) equipped with a 665 Dosimat. The electrode and titroprocessor were calibrated with standard buffer solutions prepared according to NBS specifications<sup>6</sup>. The pH meter

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the UO2(VI) Mixed - Ligand Complexes. of Table I. Analytical Data and Physical Properties

Complex	Colour	Yield	Dec.	Anal	lyses %: Foi	und (Calcul	ated)	V
[Empirical formula and formula weight]		%	point oC	U	Н	V	D	mohs.cm <sup>2</sup> .mol <sup>-1</sup>
(1) UO <sub>2</sub> (gly)(8-Q)(H <sub>2</sub> O) <sub>2</sub>	Orange	06	242-247	25.0	2.7	5.1	45.1	25
[C <sub>11</sub> H <sub>14</sub> O <sub>5</sub> N <sub>2</sub> U] [523.81]				(25.2)	(2.7)	(5.3)	(45.4)	· · ·
(2) UO <sub>2</sub> (ala)(8-Q)	Orange	06	246-251	28.6	2.5	5.4	41.0	15
[C <sub>12</sub> H <sub>20</sub> O <sub>5</sub> N <sub>2</sub> U] [501.74]				(28.7)	(2.4)	(5.6)	(41.4)	
(3) UO <sub>2</sub> (val)(8-Q)(H <sub>2</sub> O) <sub>2</sub>	Orange	80	235-240	29.8	3.4	4.9	36.8	28
[C <sub>14</sub> H <sub>20</sub> O <sub>5</sub> N <sub>2</sub> U] [484.85]				(29.7)	(3.5)	(4.9)	(36.7)	
(4) UO <sub>2</sub> (pro)(8-Q)	Orange	70	240-245	31.8	2.5	5.2	39.8	16
[C <sub>14</sub> H <sub>13</sub> O <sub>5</sub> N <sub>2</sub> U] [451.41]				(31.9)	(2.5)	(5.3)	(39.5)	

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5) $UO_2(leuc)(8-Q)(H_2O)_2$	Orange	80	230-235	31.0	3.9	4.5	36.1	21	
c <sub>15</sub> H <sub>22</sub> O <sub>7</sub> N <sub>2</sub> U] [586.65]				(31.0)	(3.8)	(4.8)	(35.9)		
6) UO <sub>2</sub> (phenylala)(8-Q) C H O . N . UI 1577 541	Orange	06	250-255	37.5	3.0	5.0	36.2	18	
[1] [			k	(+., c)	(0.7)	(0.+)	(0.05)		
7) UO <sub>2</sub> (histi)(8-Q)	Orange	80	233-238	31.7	2.6	6.6	36.9	12	
C <sub>15</sub> H <sub>14</sub> O <sub>5</sub> N4U] [567.82]				(31.7)	(2.5)	(6.9)	(36.9)		
8) [UO <sub>2</sub> (hista)(8-Q)]NO3	Orange	606	248-253	28.5	2.7	11.7	35.3	120	
C <sub>14</sub> H <sub>15</sub> O <sub>6</sub> N <sub>5</sub> U] [587.41]				(28.6)	(2.6)	(11.9)	(35.4)		

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readings (B) recorded in EtOH-H<sub>2</sub>O solution were converted for hydrogen concentration  $[H^+]$  by means of the following widely used relation<sup>7</sup>.

$$-\log[H^+] = B + \log U_H$$

where  $\log U_{\rm H}$  is the correction factor for the solvent composition and ionic strength  $\mu$  for which B is read. The value of  $\log U_{\rm H}$  at ionic strength 0.1 M at 25±0.1°C was found to be -0.20. The electrolytic conductance was measured by means of a WTW conductivity bridge, model LBR. IR spectra were recorded (KBr) on a Perkin-Elmer 1430 spectrophotometer, electronic spectra were taken on a Shimadzu UV-160 A spectrophotometer. The NMR spectra were obtained using a Varian Gemini 200 spectrometer (200 MHz). Deuterated dimethyl sulphoxide (DMSO-d6) was used as solvent. The water content of the complexes was determined by thermogravimetric analysis by using a Perkin-Elmer TGA7 computerized system, with a scanning rate of 20°C min<sup>-1</sup> in nitrogen atmosphere.

#### Procedure and Technique

The following mixtures (A-E) were prepared for the equilibrium constant determination:

- (A) 0.01 M amino acid (10 mL) + 0.26 M KNO<sub>3</sub> (20 mL) + 20 mL ethanol.
- (B) 0.01 M (8-HQ) (10 mL) + 0.26 M KNO<sub>3</sub> (20 mL) + 20 mL ethanol.
- (C) 0.005 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (10 mL) + 0.01 M amino acid (10 mL) + 0.52 M KNO<sub>3</sub> (10 mL) + 20 mL ethanol.

#### DIOXOURANIUM MIXED-LIGAND COMPLEXES

- (D) 0.005 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (10 mL) + 0.01 M (8-HQ) (10 mL) + 0.52 M
   KNO<sub>3</sub> (10 mL) + 20 mL ethanol.
- (E) 0.02 M  $UO_2(NO_3)_2$  (5 mL) + 0.01 M (8-HQ) (10 mL) + 0.01 M amino acid (10 mL) + 0.52 M KNO<sub>3</sub> (5 mL) + 20 mL ethanol
- (F) 0.01 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (10 mL) + 0.01 M amino acid (10 mL) + 0.01 M (8-HQ) (10 mL) + 20 mL ethanol.

The mixture (F) was titrated conductometrically against 0.10 M NaOH. The 8-hydroxyquinoline (8-HQ) solution for the equilibrium constants determinations was prepared in one equivalent of  $HNO_3$  solution. The acid dissociation constants of the amino acids were determined by titrating mixture (A). The acid dissociation constant of 8-HQ was determined by titrating mixture (B). The stability constants of the binary complexes of  $UO_2(VI)$  ion with amino acid and 8-HQ, respectively, were determined by titrating mixtures C and D, respectively. The stability constants  $K_{UO_2LL'}^{UO_2L}$  of the ternary complexes were determined by titrating mixture (D). All titrations were performed in a purified N<sub>2</sub> atmosphere, using 0.10 M NaOH as titrant.

The equilibrium constants were evaluated from titration data. These are defined by eqs. (1) and (2)

$$l(M) + p(Q) + q(A) + rH \longrightarrow M_{l}(Q)_{p}(A)_{q}(H)_{r}$$
(1)  
$$\beta_{lpqr} = \frac{[M_{l}(Q)_{p}(A)_{q}(H)_{r}]}{[M]^{l}[Q]^{p}[A]^{q}[H]^{r}}$$
(2)

Where 1, p, q and r are the stoichiometric coefficients corresponding to  $UO_2(VI)$ , 8-HQ, amino acid and H<sup>+</sup>, respectively, and M, Q, A and H stand for  $UO_2(VI)$ , 8-hydroxyquinoline, amino acid and proton,

respectively. To calculate stability constants of binary complexes, UO<sub>2</sub>(VI) with 8-HQ or UO<sub>2</sub>(VI) with amino acid, set q(A) = 0 or p(Q) = 0 in eq. (1), respectively, and the stability constant in eq. (2) is modified to become (3) or (4), respectively.

$$\beta_{1pr} = \frac{[M_{I}(Q)_{p}(H)_{r}]}{[M]^{I}[Q]^{p}[H]^{r}}$$
(3)  
$$\beta_{1qr} = \frac{[M_{I}(A)_{q}(H)_{r}]}{[M]^{I}[A]^{q}[H]^{r}}$$
(4)

The values of these constants are found in Table II. For 8-HQ they equal 10.05, 8.77 [18.82-10.05] (with l, p, q and r being 1 1 0 0 or 1 2 0 0). Thus,  $UO_2(VI)$  forms with 8-HQ a binary complex in the mole ratio 1:1 and 1:2, respectively, while UO<sub>2</sub>(VI) and amino acid, e.g. glycine (with l, p, q and r being 1 0 1 0 or 1 0 1 -1) form [UO<sub>2</sub>(gly)] and [UO<sub>2</sub>(gly)OH] complexes, and their values equal 8.21, 3.79, respectively. It is clear that the binary complex between  $UO_2(VI)$ , 8-HQ is more stable than the  $UO_2(VI)$ , amino acid complexes. Calculations were made with the aid of the computer program<sup>8</sup> MINIQUAD-75 on an IBM-486 computer. The model selected that which gave the best statistical fit and proved consistent was chemically with the titration data without giving any systematic bias in residuals.

The calculations were restricted to data obtained at pH values below 9 or that before precipitation in order to avoid complications due to the hydrolysis of complex species at higher pH. The results obtained are presented in Table II.

#### **RESULTS AND DISCUSSION**

The acid dissociation constants of the amino acids in aqueous solutions have been reported previously<sup>9</sup>. We redetermined them under the experimental condition of a 40% EtOH-H<sub>2</sub>O mixture (T = 25°C,  $\mu$  = 0.1 M KNO<sub>3</sub>). 8-Hydroxyquinoline in acid medium behaves as a diprotic acid [H<sub>2</sub>L<sup>+</sup>], and the differential log protonation constants were found to be 9.42 and 13.95. In the potentiometric titration, the addition of base produces, as a first step, the deprotonation of the protonated ternary nitrogen atom, pKa<sub>1</sub> = 9.42, and yielding the neutral species [HL]; when the pH is increased further, the deprotonation of the OH group, pKa<sub>2</sub>= 13.95, occurs as shown in eq. (5).



A representative set of pH titration curves for the  $UO_2(VI)$ -8-HQ system is shown in Fig. 1. The  $UO_2(VI)$ -8-HQ (1:1) mixture titration curve starts at pH = 2.8 and has a long low pH buffer region followed by a sharp inflection at a = 2, (a = number of moles of base added per mole of  $UO_2(VI)$ ) corresponding to complete formation of the 1:1 complex. Beyond a = 2 at pH > 4 the titration curve shows an inflection at a = 3 due to the formation of the [ $UO_2(8-Q)OH$ ] complex.

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System	1	р	q	rª	logβb	Sc	∆logK
8-HQ	0	1	0	1	9.42(0.01)	1.5E-8	
	0	1	0	2	13.95(0.02)	1 ( 7 0	
	1	1	0	0	10.05(0.02) 18.82(0.03)	1.62-9	
	1.						
$UO_{2}(VI)(gIy)(8-Q)$	0	0	1	1	9.75(0.01)	1.4E-9	
	1	0	1	U,	8.21(0.01)	I.IE-8	
	1	0	1	- 1 0	3.79(0.02) 6.65(0.01)	1.4E-7	-1.56
				Ŧ			
UO,(VI)(ala)(8-Q)	0	0	1	1	9.79(0.01)	2.5E-6	
2.	1	0	1	0	7.21(0.02)	1.4E-8	
	1	0	1	- 1	3.20(0.01)		
1. A.	1	1	1	0	6.60(0.03)	2.4E-7	-0.61
UO <sub>2</sub> (VI)(val)(8-Q)	0	0	- 1	1 1	9.61(0.01)	2.4E-8	
-	1	0	1	0	8.31(0.02)	6.6E-9	
	1	0	- 1	- 1	3.92(0.01)		-1.40
	1	1	1	0	6.91(0.02)	1.4E-6	
UQ. (VI)(prol)(8-0)	0	0	1	1	10 79(0 02)	2 58-8	
UO <sub>2</sub> (VI)(prol)(8-Q)	1	õ	1	Ô	8 60(0 01)	3 1E-7	
	1	Ő	- 1	-1	4 93(0 02)	5,16-7	
	1	1	1	0	7.09(0.03)	1.8E-7	-1.51
UO <sub>2</sub> (VI)(leuc)(8-Q)	0	0	1	1	9.82(0.01)	2.4E-9	
	1	0	1	0	7.92(0.02)	2.5E-8	
	1	0	- 1	-1	5.33(0.01)		
	1	1	ł	U	7.01(0.03)	1.8E-7	-0.91
UO_(VI)(phenylala)-	0	0	1	1	9.35(0.01)	2.6E-8	
Z	1	0	1	0	8.93(0.02)	6.5E-7	
(8~Q)	1	0	1	- 1	3.56(0.03)		
	1	1	1	0	6.61(0.03)	1.5E-6	-2.32
			_				
UO <sub>2</sub> (VI)(histi)(8-Q)	0	0	1	1	9.35(0.01)	2.5E-9	
	0	0	1	2	15.35(0.02)	3 4 12 9	
	1	0	1	-1	0.00(U.U1) 2.27(0.03)	2.45-8	
	1	U 1	1	0	7.11(0.03)	5 9F-7	3 84
	1	1	1	1	13.45(0.03)	J, J 1 - 1	2.44
	-	-	-	-			

Table II. Formation Constants of the Binary and Ternary Complexes of UO<sub>2</sub>(VI).

Table II. Continued						- 4.5 <u>2</u>	
(UO,(VI)(hista)(8-	0	0	1	1	9.94(0.01)	3.5E-8	
· 2· · · ·	0	0	1	2	16.79(0.02)		
Q) NO3	1	0	1	- 1	9.88(0.01)	5.7E-7	
	1	0	1	0	3.25(0.03)		
	1	1	1	0	7.01(0.02)	3.2E-6	3.75

<sup>a</sup> 1, p,q and r are the stoichiometric coefficient corresponding to  $UO_2(VI)$ , 8-HQ, amino acid and H<sup>+</sup> respectively; <sup>b</sup> Standard deviations are given in parentheses <sup>c</sup> Sum of square of residuals.



Fig. 1. Potentiometric Titration Curves of the UO<sub>2</sub>(VI)-8-HQ-Alanine System; (1) alanine; (2) UO<sub>2</sub>(VI): 8-HQ=1:1; (3) UO<sub>2</sub>(VI) -8-HQ-Alanine and (4) Composite Curve.

The ternary complex formation could be considered in terms of stepwise equilibria, as shown in eqs. (6) and (7).

$$UO_2^{2^+} + HL \implies UO_2L^+ + H^+$$
 (6)

$$UO_2 L^+ + HL' \longrightarrow UO_2 LL' + H^+$$
 (7)

The formation of a ternary complex is ascertained by comparison of the mixed-ligand titration curve with the composite curve obtained by graphical addition of the amino acid (HL') titration curve and the  $UO_2(8-Q)$  titration curve. It is clear that the former curve deviates considerably from the latter, indicating the formation of a stable ternary complex species. The results show the formation of 1:1:1 complexes with all of the ligands studied. In the case of the histidine (H<sub>2</sub>L') system, MINIQUAD refined a model consisting of the species  $UO_2LL'$ .

The protonated complex  $UO_2LL'H$  has a dissociable proton. The dissociation may be represented by eq. (8)

$$UO_2LL'H^+ \implies UO_2LL' + H^+$$
 (8)

The acid dissociation constant of the protonated complex is given by eq. (9).

$$pK_{UO_{2}LL'H}^{H} = logK_{UO_{2}LL'H}^{UO_{2}} - logK_{UO_{2}LL'}^{UO_{2}}$$
(9)

The values of  $pK_H$  is 6.34 (13.45-7.11) [ for l, p, q and r being 1 1 1 0 or 1 1 1 1] for the histidine ternary complex in Table II. This value

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compares favourably with respect to the acid dissociation constant of the protonated imidazole residue, amounting to 6.0 (15.35-9.35) [ for l, p, q and r being 0 0 1 1, 0 0 1 2] in Table II, if the acidification of the (N-imidazole)  $H^+$  site caused by the bound  $UO_2L$  complex is considered. This indicates that histidine coordinates through the amino group of the amino acid moiety. The relative stabilities of the ternary and corresponding binary complexes can be expressed quantitatively in different ways. A review of the available methods<sup>10</sup> argues that the most suitable comparison is expressed in terms of  $\Delta \log K$  values designated by the relation of eq. (10).

$$\Delta \log K = \log K_{UO_2LL'}^{UO_2L} - \log K_{UO_2L'}^{UO_2L}$$
(10)

The conductometric titration curve of the ternary complex containing alanine, Fig. 2, shows an initial decrease and an inflection at a = 2. This probably corresponds to the neutralization of H<sup>+</sup> resulting from the formation of the UO<sub>2</sub>L complex. In the 3>a>2 range, the conductance increases slightly due to the formation of a ternary complex associated with the release of a proton from the alanine. Beyond a = 3, the conductance increases appreciably due to the presence of an excess of NaOH.

Based on the above finding and the fact that the  $UO_2$ -8hydroxyquinoline complex is more stable than that of the amino acid, the 8-hydroxyquinoline ligand is preferentially ligated first to the  $UO_2(VI)$ ion, then followed by ligation of the amino group of the amino acid to form the mixed-ligand complex.



Fig.2. Conductometric Titration of the UO<sub>2</sub>(VI)-8-HQ-Alanine System.

The concentration distribution of the various complex species formed in solution (formation %) is a function of pH. This provides a useful picture of metal ion binding towards the ligands. The distribution curves of the  $UO_2$ -8-HQ-alanine system, taken as a representative, are shown in Fig. 3.

#### **Characterization of Metal Complexes**

The analytical data for the mixed- ligand complexes are listed in Table I. The molar conductance values of  $1 \times 10^{-3}$  M solutions of the isolated complexes in DMF in Table I show that the complexes (1)-(7) are non-



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Fig. 3. Concentration Distribution of Various Species as a Function of pH in the U0<sub>2</sub>(VI)-8-HQ-Alanine System; (1)[U0<sub>2</sub>(VI)]<sup>2+</sup>;(2)[U0<sub>2</sub>L<sub>2</sub>];(3)[U0<sub>2</sub>LL'] and (4) [UO212 (AD].



(1),(3) and (5)



(2),(6) and (7)



Fig. 4, Proposed General Structural Formulas for the Dioxouranium(VI) Complexes; (1) R = H (glycine); (2) R = Me (alanine)

(3) R = CHMe<sub>2</sub> (L-valine) ; (4) (proline) ;

(5)  $R = CH_2CHMe_2$  (L-leucine); (6)  $R = CH_2Ph$  ( $\beta$ -phenykalanine)  $CH_2$ (7) R = -N

electrolytes and conductivity values are in the range 12-28 ohm<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup>. However, these values are higher than expected, probably due to partial replacement of coordinate water by DMF molecules<sup>11,12</sup>. The molar conductance of the histamine mixed ligand complex is 120 ohm<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup>. The histamine mixed-ligand complex is the only one which may be ionic due to unligated nitrate ion. Structural formulas for the complexes (1)-(8) are proposed in Fig 4.

#### **IR** Spectra

IR vibrational bands of the complexes are The fundamental sharp, medium intensity band in the included in Table III. The 3460-3250 cm<sup>-1</sup> region is attributed to v(R-NH<sub>3</sub><sup>+</sup>). Corresponding bands of the free amino acids occur at 3200-3180 cm<sup>-1</sup>; and the shift upon complexation is indicative of coordination via the amino group nitrogen<sup>13</sup>. The OH band of 8-HQ (very sharp at 3680 cm<sup>-1</sup>) disappears in the complex spectra, indicating hydroxyl coordination. The presence of coordinated water molecules in the complexes (1), (3) and (5) is indicated by the presence of a stronge broad band<sup>14-16</sup> in the region 3460-3330 cm<sup>-1</sup>, which is absent in the complexes (2), (4), (6), (7) and (8), in agreement with their elemental analysis and TG results. The proline band at 3100 cm<sup>-1</sup>, due to the NH-stretching vibration, is shifted upon complexation to 3080 cm<sup>-1</sup>. The v<sub>asym</sub> (COO<sup>-</sup>) modes of the amino acids coordinated to uranyl are likewise shifted to lower frequencies compared to the spectra of this free amino acid<sup>14</sup>. The IR spectrum of the histamine complex reveals a sharp band at 810 cm<sup>-1</sup>, indicating the bidentate chelating character of the nitro group<sup>17</sup>. The  $v_{asym}$  (UO<sub>2</sub>) bands are shifted to lower frequencies in the complexes compared to the  $v_{asym}$  (O=U=O) mode of uranyl nitrate at 965 cm<sup>-1</sup>. Hence, we deduce that the ligands form strong bonds with uranium, lowering the U=O bond order and, consequently, lowering the  $v_{asym.}(O=U=O)$  frequency. Weak bands at 270-260 cm<sup>-1</sup> (far IR) and 450-440 cm<sup>-1</sup> are assigned to  $v(U-N)^{18}$  and  $v(U-O)^{19}$ , indicating that the coordination number eight is attained by uranium in the complexes (1), (3), and (5) and  $six^{20}$  in the complexes (2), (4), (6), (7) and (8).

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Table III. IR Data (cm<sup>-1</sup>) for the Dioxouranium(VI) Mixed Ligand Complexes.

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#### **Electronic Spectra**

The electronic absorption spectra of  $10^{-3}$  M DMF solutions of the complexes in Table IV are very similar. Assignments were made by comparison with related species<sup>21</sup>. These complexes exhibit a new band at 540 nm and successive shoulders in the 410-475 nm range due to L-UO<sub>2</sub> charge transfer and to internal transitions in the UO<sub>2</sub> group.

#### <sup>1</sup><u>H NMR</u> Spectra

The <sup>1</sup>H NMR spectra of 8-HQ and its mixed ligand complexes in DMSO are shown in Table V. The 8-HQ spectrum exhibits a singlet signal at 10.8 ppm due to the hydroxyl proton. In the <sup>1</sup>H NMR spectra of the  $UO_2(VI)$ -mixed-ligand complexes the latter signal disappeared which is taken as evidence for its participation in coordination. The <sup>1</sup>H NMR spectra of the amino acids revealed<sup>22</sup> a broad signal due the amino group protons occurring at 2.3 ppm. In the spectra of the complexes the latter signal displays a downfield shift of 0.2-0.5 ppm. This shift may be due to a shielding effect<sup>23</sup> of the central  $UO_2$  ion on the NH<sub>2</sub> protons. All complexes give a broad multiplet in the region 6.8-7.2 ppm which is assigned to the aromatic ring protons<sup>24</sup>. The presence of water molecules in the complexes is confirmed by the appearance of a new signal around 3.8 ppm, attributed to coordinated H<sub>2</sub>O protons<sup>25,26</sup>.

#### **TG** Analysis

The thermograms showed the presence of two coordinated water molecules in the complexes (1), (3) and (5), which are lost in two steps<sup>27-29</sup>, initially at 162°C with a weight loss of 3% (theor., 3.4, 3.7, 3.1 for complexes (1), (3) and (5), respectively), followed by the second

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Table IV. Electronic Spectral Data for the Dioxouranium(VI) Mixed- Ligand Complexes.

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Complex	(λ <sub>max</sub> ) <sup>a</sup> U(f→ f)	(е <sub>тах</sub> ) <sup>0</sup> L-UO <sub>2</sub> -8нQ	Internal O=U=U Iransition	и - и
(1)	603 sh (840)	530(1090)	400 sh (7500), 419 sh (6050)	320 (14080)
(2)	603 sh (830)	525(1100)	420 sh (7400), 440 sh (6040)	318 (14030)
(3)	610 sh (820)	540(1120)	409 sh (7500), 420 sh (6060)	313 (14060)
(4)	613 sh (810)	550(1300)	420 sh (7300), 470 sh (6070)	325 (14030)
(5)	603 sh (810)	515(1200)	411 sh (7400), 422 sh (6040)	320 (14000)
(9)	605 sh (800)	510(1300)	429 sh (7300), 472 sh (6030)	313 (14050)
(1)	609 sh (800)	514(1200)	410 sh (7200), 470 sh (6040)	316 (14050)
(8)	613 sh (810)	520(1400)	420 sh (7250), 440 sh (6020)	312 (14040)

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coefficients in litre cm<sup>-1</sup> mol<sup>-1</sup>.

	Chemical Shifts, (δ ppm)	
System	(Assignment) <sup>a</sup>	
8-HQ	10.7 (s, 1H, OH), 6.5-7.0 (m, 6H, ArH)	
(1)	6.8-7.3 (m, 6H, ArH), 5.55 (s,2H, CH <sub>2</sub> ), 3.8 (s,4H, H <sub>2</sub> O), 2.7 (s, 2H, NH <sub>2</sub> )	
(2)	6.7-7.1 (m, 6H, ArH), 4.1 (m, 1H, CH), 2.6 (s, 2H, NH <sub>2</sub> ), 2.4 (d, 3H, CH <sub>3</sub> , $J = 8.1$ Hz)	
(3)	6.7-7.4 (m, 6H, ArH), 4.1 (d, 1H, CH, J = 9.1 Hz), 3.7 (s, 4H, H <sub>2</sub> O), 2.5 (s, 2H, NH <sub>2</sub> ), 2.4-2.6 (m, 7H, CHMe <sub>2</sub> )	
(4)	6.5-7.5 (m, 6H, ArH), 7.2 (m, 1H, NH), 4.2 (m, 1H, CH)	
(5)	6.6-7.4 (m, 6H, ArH), 4.1 (m, 1H, CH), 3.7 (s, 4H, H <sub>2</sub> O), 2.8 (s, 4H, H <sub>2</sub> O), 2.2-2.7 (m, 9H, CH <sub>2</sub> CHMe <sub>2</sub> )	
(6)	6.6-7.3 (m, 6H, ArH), 4.0 (t, 2H, CH), 2.7 (s, 2H, NH <sub>2</sub> ), 2.5 (d, 2H, CH <sub>2</sub> , J = 7.5 Hz)	
(7)	6.7-7.2 (m, 6H, ArH), 4.1 (s, 2H, CH <sub>2</sub> ), 3.5 (d, 2H, CH, $J = 7.5$ Hz), 2.6 (s, 2H, NH <sub>2</sub> )	
(8)	6.7-7.4 (m, 6H, ArH), 7.2 (s, 1H, NH), 3.0 (d, 2H, CH, J = 8.1 Hz), 2.8 (s, 2H, NH <sub>2</sub> ), 2.4-2.6 (m,4H,CH <sub>2</sub> )	

Table V. <sup>1</sup>H NMR Chemical Shifts of the 8-HQ and UO<sub>2</sub>(VI)-Mixed-Ligand Complexes.

a; s = singlet, d = doublet, m = multiplet, Ar = aromatic ring, Me = methyl groupand J = coupling constant. stage at 195°C with the weight loss data 6%, 7%, 6%, respectively (theor., 6.8, 7.4, 6.2 for complexes (1), (3) and (5), respectively). All complexes finally gave the oxide  $U_3O_6$  as a stable end product up to 750°C in agreement with the experimentally found uranium content.

#### **Conclusion**

The results of this study support the conclusion that formation of 1:1  $UO_2(VI)$ : 8-HQ complexes preceeds secondary complexation by the amino acids through the anticipated primary donor function of the ligand.

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