

Uranyl(II) and Thorium(IV) Complexes of N-(*o*-Hydroxy Substituted Benzyl) Alanines

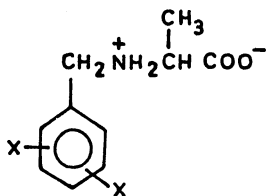
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Several uranyl(II) and thorium(IV) complexes of N-(*o*-hydroxy substituted benzyl) alanines have been isolated from 50% (v/v) aqueous-DMSO medium in 1 : 1 and 1 : 2 molar ratios which were characterized by elemental analysis and spectral measurements.

INTRODUCTION

Systematic work on the preparation of metallo-organic/organometallic derivatives of N-(*o*-hydroxy substituted benzyl)alanines(I) *via* the interaction of the corresponding metal isopropoxides with the latter has been reported from these laboratories earlier¹⁻⁹. The work described here relates to the preparation of 1 : 1 and 1 : 2 complexes of UO₂(II) and Th(IV) of I, *viz.*, (i) N-(2-hydroxy-3-methyl benzyl)alanine (H₂hmba-3), (ii) N-(2-hydroxy-6-methyl benzyl) alanine (H₂hmba-6) and (iii) N-(2-hydroxy-5-methyl benzyl) alanine (H₂hmba-5) which were obtained as coloured solids and characterized by elemental analysis, as well as by IR and PMR spectral measurements.



(Where X = -H or -CH₃)

(I)

EXPERIMENTAL

All the reagents used were of analytical grade. The metal contents in the complexes isolated were determined by usual methods¹⁰. The IR spectra were recorded on a Perkin-Elmer model 983 spectrometer in KBr pellets in the region 4000-400 cm⁻¹, while the PMR spectra were taken in DMSO-d₆ solution and recorded on a Varian EM-390, 90 MHz spectrometer. The m.p.s. were recorded on an electrothermal CAT no. 1A 8103 digital m.p. apparatus.

Preparation of 1 : 1 Th(IV)-H₂hmba-3 complex

A solution of H₂hmba-3 (0.4867 g; 2.3260 mmole in 5.0 mL DMSO + 5.0 mL water) was added dropwise to a solution of thorium nitrate (1.3262 g; 2.3260 mmole in 5.0 mL water + 5.0 mL DMSO). The reaction mixture was then refluxed on a water bath. After *ca.* 9 h of reflux, the product isolated as a light brown solid which was washed with 50% (v/v) aqueous-DMSO (2–3 times) followed by ethanol (2–3 times) and then air dried. The product was found to be sparingly soluble in dimethylsulphoxide but insoluble in other common organic solvents.

Similar procedures were adopted for the preparation and purification of other 1 : 1 complexes.

TABLE-1
ANALYTICAL DETAILS OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES
AND THEIR URANYL(II) AND THORIUM(IV) COMPLEXES

Compound (molar ratio)/colour	Reflux time (h)	m.p. (°C)	% Analysis, found (calcd.)			
			C	H	N	Metal
H ₂ hmba-3 (dull white)	—	110	62.96 (63.14)	7.20 (7.23)	6.67 (6.69)	—
H ₂ hmba-6 (light pink)	—	105	62.98 (63.14)	7.20 (7.23)	6.66 (6.69)	—
H ₂ hmba-5 (dull white)	—	95	62.85 (63.14)	7.21 (7.23)	6.69 (6.69)	—
UO ₂ (hmba-3)·3H ₂ O (1 : 1) (orange)	6	181	24.77 (24.87)	3.59 (3.60)	2.63 (2.64)	44.69 (44.80)
UO ₂ (hmba-6)·3H ₂ O (1 : 1) (orange)	10	170	24.75 (24.87)	3.61 (3.60)	2.65 (2.64)	44.60 (44.80)
UO ₂ (hmba-5)·3H ₂ O (1 : 1) (orange)	9	160	24.97 (24.87)	3.59 (3.60)	2.63 (2.64)	45.00 (44.80)
UO ₂ (Hhmba-3) ₂ ·2H ₂ O (1 : 2) (brick red)	6	136	36.40 (36.57)	4.44 (4.46)	3.87 (3.88)	32.80 (32.95)
UO ₂ (Hhmba-6) ₂ ·2H ₂ O (1 : 2) (orange)	5	138	36.46 (36.57)	4.47 (4.46)	3.89 (3.88)	32.87 (32.95)
UO ₂ (Hhmba-5) ₂ ·2H ₂ O (1 : 2) (orange)	6	140	36.62 (36.57)	4.45 (4.46)	3.87 (3.88)	32.88 (32.95)
Th(hmba-3)(NO ₃) ₂ ·3H ₂ O (1 : 1) (light brown)	9	175	21.30 (21.40)	3.09 (3.10)	6.83 (6.81)	37.47 (37.59)
Th(hmba-6)(NO ₃) ₂ ·3H ₂ O (1 : 1) (brown)	7	185	21.48 (21.40)	3.11 (3.10)	6.79 (6.81)	37.65 (37.59)
Th(hmba-5)(NO ₃) ₂ ·3H ₂ O (1 : 1) (light brown)	6	180	21.37 (21.40)	3.09 (3.10)	6.80 (6.81)	37.47 (37.59)
Th(hmba-3) ₂ ·2H ₂ O (1 : 2) (pinkish brown)	7	152	38.60 (38.71)	4.42 (4.43)	4.09 (4.10)	33.90 (34.00)
Th(hmba-6) ₂ ·2H ₂ O (1 : 2) (brown)	6	156	38.68 (38.71)	4.45 (4.43)	4.12 (4.10)	34.15 (34.00)
Th(hmba-5) ₂ ·2H ₂ O (1 : 2) (light brown)	10	160	38.75 (38.71)	4.41 (4.43)	4.08 (4.10)	33.85 (34.00)

Abbreviations: H₂hmba-3 (or -6 or -5) = CH₃C₆H₃(OH)CH₂⁺NH₂CH(CH₃)COO⁻

TABLE-2
 CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF N-(*o*-HYDROXY SUBSTITUTED BENZYL)ALANINES AND
 THEIR URANYL(II) COMPLEXES

Compound	$\nu(\text{OH})$ and aromatic $\nu(\text{C}-\text{H})$	$\nu(\text{N}-\text{H})$ and aromatic $\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{H})$ of $-\text{CH}_2-$ and $-\text{CH}_3$ groups	$\nu(\text{NH})$ of $>\text{NH}_2$ groups	$\nu_{\text{sym}}(\text{COO})$	$\delta(\text{H}_2\text{O})$	$\Delta\nu(\text{COO})$	$\nu(\text{C}-\text{N})$	$\nu(\text{U}-\text{O})$	$\nu(\text{U}-\text{N})$
H ₂ hmba-3	3680-3000 (vb)	—	2920 (m)	2395 (wb)	1625 (vsb)	—	1405 (mb)	—	1235 (s)	—
H ₂ hmba-6	3660-3000 (b)	—	2920 (m)	2340 (m)	1630 (vsb)	—	1405 (wb)	—	1250 (w)	—
H ₂ hmba-5	3690-3000 (b)	—	2920 (m)	2390 (wb)	1630 (vsb)	—	1390 (s)	—	1220 (m)	—
UO ₂ (hmba-3)·3H ₂ O	—	3455 (s)* 3200-3000 (b)	2920 (m)	—	1640 (s)	1620 (w)	1395 (m)	245 (s)	1260 (s)	500 (m) 385 (m)
UO ₂ (hmba-6)·3H ₂ O	—	3450 (m)* (mb)	2910 (w)	—	1635 (s)	1620 (m)	1380 (s)	255 (m)	1270 (m)	505 (m) 380 (m)
UO ₂ (hmba-5)·3H ₂ O	—	3455 (m)* (b)	2920 (w)	—	1635 (m)	1620 (m)	1380 (s)	255 (w)	1275 (w)	500 (m) 385 (m)
UO ₂ (Hhmba-3)·2H ₂ O	—	3500-3240 (mb)	2930-2410 (mb)	—	1630 (s)	1620- 1600 (m)	1390 (m)	240 (s)	1260 (s)	500 (m) 385 (m)
UO ₂ (Hhmba-6)·2H ₂ O	—	3500-3300 (mb)	2930-2490 (mb)	—	1635 (m)	1625- 1600 (b)	1390 (s)	245 (m)	1265 (m)	500 (m) 385 (m)
UO ₂ (Hhmba-5)·2H ₂ O	—	3450-3300 (sb)	2920-2450 (b)	—	1640 (m)	1625- 1600 (b)	1390 (s)	250 (m)	1260 (m)	500 (m) 380 (m)

*H₂O alone

Abbreviations: s = strong, b = broad, vb = very broad, sb = strong broad, vsb = very strong broad, m = medium, mb = medium broad, w = weak, wb = weak broad.

TABLE-3
CHARACTERISTIC INFRARED FREQUENCIES (cm⁻¹) OF THORIUM(IV) COMPLEXES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

Compound	$\nu(\text{H}_2\text{O})$	$\nu(\text{N-H})$ and aromatic $\nu(\text{C-H})$	$\nu(\text{C-H})$ of —CH ₂ — and —CH ₃	$\delta(\text{H}_2\text{O})$	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\Delta\nu(\text{COO})$	$\nu(\text{NO}_3)$	$\nu(\text{C-N})$	$\nu(\text{Th-N})$	$\nu(\text{Th-O})$
Th(hmba-3)(NO ₃) ₂ ·3H ₂ O	3340 (w)	3200-3020 (mb)	2900 (m) 2825 (w)	1685-1630 (wb)	1605 (s)	1395 (s)*	210	1290 (m)	1260 (s)	490 (s)	380 (m)
Th(hmba-6)(NO ₃) ₂ ·3H ₂ O	3445 (w)	3200-3070 (mb)	2910 (w) 2820 (s)	1680-1670 (wb)	1605 (s)	1390 (s)*	205	1290 (m)	1260 (s)	495 (m)	375 (w)
Th(hmba-5)(NO ₃) ₂ ·3H ₂ O	3445 (w)	3250-3000 (b)	2910 (w) 2820 (w)	1685-1650 (mb)	1600 (s)	1380 (w)*	220	1290 (m)	1260 (m)	490 (s)	380 (m)
Th(hmba-3) ₂ ·2H ₂ O	3455 (m)	3200-3000 (mb)	2910 (m) 2860 (w)	1680-1660 (b)	1625 (s)	1380 (m)	245	—	1265 (s)	490 (m)	375 (m)
Th(hmba-6) ₂ ·2H ₂ O	3450 (m)	3220-3090 (mb)	2930 (m) 2860 (w)	1680-1645 (mb)	1620 (s)	1380 (m)	240	—	1260 (s)	495 (m)	380 (m)
Th(hmba-5) ₂ ·2H ₂ O	3450 (m)	3200-3000 (b)	2940 (m) 2860 (m)	1660-1630 (wb)	1610 (s)	1380 (s)	230	—	1260 (s)	495 (s)	375 (m)

*Overlapping of $\nu_{\text{sym}}(\text{COO})$ and $\nu(\text{NO}_3)$

Abbreviation: s = strong, m = medium, mb = medium broad, b = broad, w = weak, wb = weak broad.

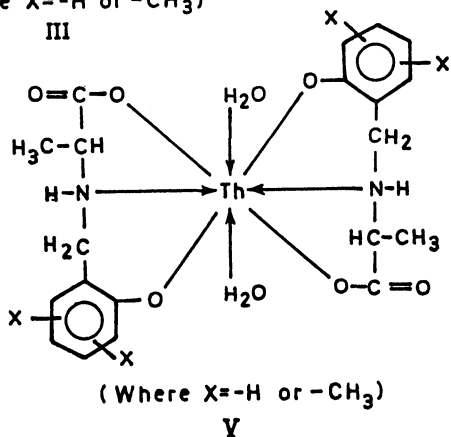
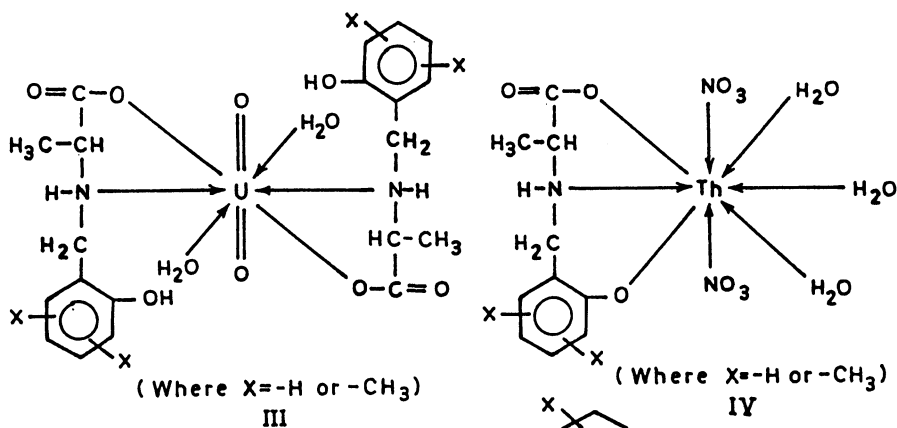
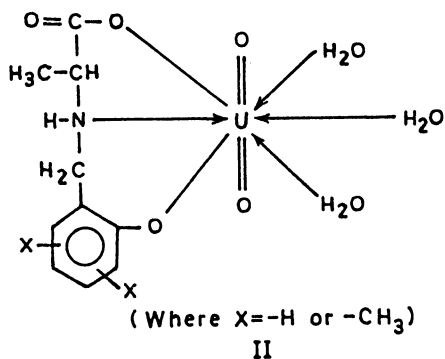
TABLE-4
 PROTON MAGNETIC RESONANCE SPECTRA (δ VALUES) OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES AND THEIR URANYL(II) AND THORIUM(IV) COMPLEXES

Compound	Aromatic ring	Phenolic (—OH) group	>CH—	H ₂ O	⁺ >NH ₂	>NH	—CH ₃ attached with benzene ring	—CH ₂ — attached with benzene ring	—CH ₃ of alanine part
H ₂ hmba-3	6.92 (d)	6.75 (s)	3.40-4.00 (bm)	—	3.20-3.40 (h)	—	2.22 (s)	2.05-2.10 (m)	1.35 (d)
	6.85 (d)								
	6.60-6.70 (m)								
H ₂ hmba-6	7.25 (t)	6.55 (s)	3.40-4.10 (bm)	—	3.00-3.30 (h)	—	2.15 (s)	2.00-2.10 (m)	1.20 (d)
	6.60 (d)								
	6.50 (d)								
H ₂ hmba-5	6.85 (s)	6.90 (s)	3.35-4.05 (bm)	—	3.20 (h)	—	2.15 (s)	2.00-2.10 (m)	1.22 (d)
	6.62 (d)								
	6.55 (d)								
UO ₂ (hmba-3)·3H ₂ O	6.25-7.20 (m)	—	3.50-3.85 (q)	3.35 (s)	—	3.15 (s)	2.25 (s)	2.10 (d)	1.30 (d)
UO ₂ (Hhmba-3)·2H ₂ O	6.75-7.20 (m)	6.70 (s)	3.50-3.00 (m)	3.40 (s)	—	3.15 (s)	2.25 (s)	2.05 (d)	1.30 (d)
Th(hmba-3)(NO ₃) ₂ ·3H ₂ O	6.60-7.00 (m)	—	3.40-3.80 (q)	3.25 (s)	—	3.05 (s)	2.25 (s)	2.05 (d)	1.35 (d)
Th(hmba-3)·2H ₂ O	6.40-7.00 (m)	—	3.50-3.85 (q)	3.30 (s)	—	3.10 (s)	2.25 (s)	2.05 (d)	1.30 (d)

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bm = broad multiplet, h = hump

Preparation of 1 : 2 Th(IV)-H₂hmba-3 complex

A solution of H₂hmba-3 (0.9749 g, 4.6590 mmole in 7.5 mL DMSO + 7.5 mL water) was added dropwise to a solution of thorium nitrate (1.3282 g; 2.3295 mmole in 7.5 mL water + 7.5 mL DMSO). The reaction mixture was then refluxed on a water bath. After *ca.* 8 h of reflux, the product isolated as a light brown solid which was washed with 50% (v/v) aqueous-DMSO (2–3 times) followed by



ethanol (2–3 times) and then air dried. The product was found to be sparingly soluble in dimethylsulphoxide but insoluble in other common organic solvents.

Similar procedure was adopted for the preparation and purification of other 1:2 complexes.

The relevant analytical details, characteristic IR frequencies and PMR data are recorded in Tables 1–4 respectively. It may be mentioned here that absorptions corresponding to $\nu_{as}(\text{O}=\text{U}=\text{O})$ and $\nu_s(\text{O}=\text{U}=\text{O})$ were observed to occur at appropriate places^{11, 12} in all the $\text{UO}_2(\text{II})$ complexes isolated, which have not been included in the IR tables.

RESULTS AND DISCUSSION

Based on analytical data, characteristic IR frequencies and NMR data the modes of bonding^{13–18} in 1:1 and 1:2 $\text{UO}_2(\text{II})$ -I complexes are shown in structures II and III respectively, while those in case of 1:1 and 1:2 $\text{Th}(\text{IV})$ -I complexes in Structures IV and V respectively.

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