Asian Journal of Chemistry Vol. 11, No. 2 (1999), 625–632

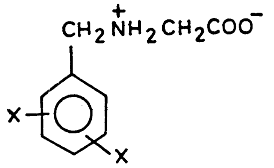
Uranyl(II) and Thorium(IV) Complexes of N-[*o*-Hydroxy Substituted (or H) Benzyl] Glycines

KANTI BALLABH KARNATAK, CHANDRA SHEKHAR PANT,
KESHAR SINGH DHAMI, KIRTI BALLABH MELKANI
and MADHUP CHANDRA*
Department of Chemistry
DSB Campus, Kumaun University
Nainital-263 002, India

Several uranyl (II) and thorium(IV) complexes of N-[*o*-hydroxy substituted (or H) benzyl]glycines have been isolated from 50% (v/v) aqueous-DMSO or DMF 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 (or H) benzyl] glycines (I) (Structure I) *via* the interaction of the corresponding metal isopropoxides with the latter has been reported earlier from these laboratories.[1, 2] The work described here relates to the preparation of 1 : 1 and 1 : 2 complexes of UO_2(II) and Th(IV) of I, *viz.*, (i) N-(2-hydroxy benzyl)glycine ((H_2hbg)), (ii) N-(2-hydroxy-3-methyl benzyl)-glycine (H_2 hmbg-3), (iii) N-(2-hydroxy-6-methyl benzyl)glycine (H_2hmbg-6) and (iv) N-(2-hydroxy-5-methyl benzyl)glycine (H_2hmbg-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 $-CH_3$)

I

EXPERIMENTAL

All the reagents used were of analytical grade. The metal contents in the complexes isolated were determined by usual methods.[3] 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-d_6 solution and recorded on a Varian EM-390, 90 MHz spectrometer. The m.p. were recorded on an electrothermal CAT no. 1A8103 digital melting point apparatus.

TABLE-1
ANALYTICAL DETAILS OF N-[*o*-HYDROXY SUBSTITUTED (or H) BENZYL] GLYCINES AND THEIR URANYL(II) AND THORIUM(IV) COMPLEXES

Compound (molar ratio)/(colour)	m.p. (°C)	% Analysis Found (Calcd.)			
		C	H	N	M
H_2hbg (off white)	50	59.40 (59.66)	6.10 (6.12)	7.70 (7.73)	—
H_2hmbg-3 (off white)	190	61.40 (61.52)	6.69 (6.71)	7.15 (7.18)	—
H_2hmbg-6 (off white)	88	61.30 (61.52)	6.68 (6.71)	7.16 (7.18)	—
H_2hmbg-5 (off white)	148	61.45 (61.52)	6.70 (6.71)	7.15 (7.18)	—
UO_2(hbg)·$3H_2O$ (1 : 1) (brick red)	138	21.40 (21.48)	3.00 (3.01)	2.79 (2.78)	47.50 (47.30)
UO_2(hmbg-3)·$3H_2O$ (1 : 1) (brown)	140	23.11 (23.21)	3.32 (3.31)	2.70 (2.71)	45.80 (46.02)
UO_2(hmbg-6)·$3H_2O$ (1 : 1) (brick red)	150	23.10 (23.21)	3.30 (3.31)	2.71 (2.71)	45.90 (46.02)
UO_2(hmbg-5)·$3H_2O$ (1 : 1) (brick red)	125	23.15 (23.21)	3.29 (3.31)	2.70 (2.71)	46.10 (46.02)
UO_2(Hhbg)$_2$·$2H_2O$ (1 : 2) (orange)	141	32.33 (32.44)	3.62 (3.63)	4.22 (4.20)	35.82 (35.72)
UO_2(Hhmbg-3)$_2$·$2H_2O$ (1 : 2) (brick red)	142	34.50 (34.59)	4.05 (4.06)	4.03 (4.03)	34.16 (34.28)
UO_2(Hhmbg-6)$_2$·$2H_2O$ (1 : 2) (orange)	145	34.51 (34.59)	4.07 (4.06)	4.02 (4.03)	34.20 (34.28)
UO_2 (Hhmbg-5)$_2$·$2H_2O$ (1 : 2) (brick red)	190	34.45 (34.59)	4.05 (4.06)	4.01 (4.03)	34.22 (34.28)
Th(hbg)$(NO_3)_2$·$3H_2O$ (1 : 1) (red)	182	18.38 (18.34)	2.57 (2.57)	7.15 (7.13)	39.25 (39.38)
Th(hmbg-3)$(NO_3)_2$·$3H_2O$ (1 : 1) (purple)	165	19.83 (19.91)	2.83 (2.84)	6.95 (6.97)	38.32 (38.46)
Th(hmbg-6)$(NO_3)_2$·$3H_2O$ (1 : 1) (yellow)	150	20.00 (19.91)	2.84 (2.84)	6.94 (6.97)	38.30 (38.46)
Th(hmbg-5)$(NO_3)_2$·$3H_2O$ (1 : 1) (brown)	130	19.81 (19.91)	2.84 (2.84)	6.96 (6.97)	38.35 (38.46)
Th(hbg)$_2$·$2H_2O$ (1 : 2) (orange)	140	34.49 (34.51)	3.55 (3.54)	4.48 (4.47)	36.90 (37.04)
Th(hmbg-3)$_2$·$2H_2O$ (1 : 2) (brown)	150	36.75 (36.70)	3.98 (4.00)	4.30 (4.28)	35.36 (35.46)
Th(hmbg–6)$_2$·$2H_2O$ (1 : 2) (orange)	159	36.67 (36.70)	4.01 (4.00)	4.26 (4.28)	35.50 (35.46)
Th(hmbg–5)$_2$·$2H_2O$ (1 : 2) (brown)	180	36.69 (36.70)	4.00 (4.00)	4.27 (4.28)	35.35 (35.46)

Abbreviationa: H_2hbg = $HOC_6H_4CH_2\overset{+}{N}H_2CH_2CO\bar{O}$ and H_2hmbg–3 (or –6 or –5) = $HOC_6H_3(CH_3)CH_2\overset{+}{N}H_2CH_2CO\bar{O}$.

TABLE-2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{1}) of N-[*o*-HYDROXY SUBSTITUTED (OR H)BENZYL]GLYCINES AND THEIR URANYL(II) COMPLEXES

Compound	ν(OH) and aromatic ν(C–H)	$\nu(H_2O)$ and ν(OH)	ν(N–H)and aromatic ν(C–H)	ν(C—H) of $-CH_2$ and $-CH_3$ groups	ν(NH) of $\overset{+}{N}H_2$ group	δH_2O	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C–N)	ν(U—O)	ν(U—N)
H_2hbg	3450–3000 (vb)	—	—	2940 (w) 2850 (w)	2600 (wb)	—	1630 (vsb)	1400 (s)	—	1230 (m)	—	—
H_2hmbg–3	3600–3000 (vb)	—	—	2950 (vb) 2855 (wb)	2390 (wb)	—	1635 (vsb)	1405 (m)	—	1230 (s)	—	—
H_2hmbg–6	3500–3000 (vb)	—	—	2910 (mb) 2860 (wb)	2375 (wb)	—	1640 (vsb)	1405 (m)	—	1225 (m)	—	—
H_2hmbg–5	3500–3000 (vb)	—	—	2910 (mb) 2870 (w)	2380 (w)	—	1635 (vsb)	1400 (s)	—	1220 (m)	—	—
UO_2(hbg)·$3H_2O$	—	3450 (w)*	3200–3100 (b)	2960 (w) 2930 (w)	—	1680–1645 (mb)	1640 (m)	1390 (m)	250	1260 (m)	500 (m)	380 (m)
UO_2(hmbg–3)·$3H_2O$	—	3450 (w)*	3200–3000 (mb)	2970 (w) 2920 (w)	—	1685–1650 (b)	1640 (s)	1385 (m)	255	1255 (m)	505 (m)	380 (w)

Compound	ν(OH) and aromatic ν(C–H)	ν(H_2O) and ν(OH)	ν(N–H)and aromatic ν(C–H)	ν(C—H) of –CH_2 and –CH_3 groups	ν(NH) of $\overset{+}{N}H_2$ group	·δH_2O	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C–N)	ν(U—O)	ν(U—N)
UO_2(hmbg–6)·$3H_2O$	—	3450 (m)*	3200– 3080 (b)	2960 (m) 2900(w)	—	1680– 1635 (b)	1630 (s)	1390 (m)	240	1265 (m)	505 (m)	380 (m)
UO_2(hmbg–5)$_2$·$3H_2O$	—	3455 (m)*	3180– 3000 (mb)	2970 (m) 2910 (w)	—	1675– 1640 (b)	1630 (s)	1395 (m)	235	1260 (m)	500 (m)	385 (m)
UO_2(Hhbg)$_2$·$2H_2O$	—	3400–3250 (b)	3240– 3170 (wb)	2930– 2400 (b)	—	1670– 1660 (wb)	1635 (s)	1390 (m)	245	1260 (m)	505 (s)	380 (m)
UO_2(Hhmbg–3)$_2$·$2H_2O$	—	3500–3300 (mb)	3250– 3150 (wb)	2940– 2400 (mb)	—	1680– 1645 (wb)	1630 (s)	1385 (m)	245	1255 (m)	500 (m)	385 (m)
UO_2(Hhmbg–6)$_2$·$2H_2O$		3500–3300 (b)	3240– 3140 (b)	2940– 2430 (mb)	—	1675– 1645 (mb)	1635 (s)	1395 (m)	240	1260 (m)	510 (m)	385 (m)
UO_2(Hhmbg–5)$_2$·$2H_2O$	—	3400–3350 (mb)	3200– 3100 (b)	2930– 2440 (mb)	—	1680– 1640 (b)	1630 (s)	1395 (m)	235	1265 (m)	510 (m)	385 (w)

*ν(H_2O) alone

Abbreviations: s = strong, b = broad, vb = very 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 (OR H) BENZYL] GLYCINES

Compound	ν(H_2O)	ν(N–H) and aromatic ν(C–H)	ν(C–H) of $-CH_2-$ and $-CH_3$ groups	δH_2O	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(NO_3)	ν(C–N)	ν(Th—N)	ν(Th—O)
Th(hbg)(NO_3)$_2$·3H_2O	3450 (s)	3250–3000 (mb)	2900 (w) 2820 (w)	1685–1630 (mb)	1635 (mb)	1385 (s)*	250	1290 (m)	1255 (s)	495 (m)	380 (m)
Th(hmbg–3)(NO_3)$_2$·3H_2O	3460 (m)	3200–3020 (mb)	2910 (w) 2820 (s)	1680–1640 (mb)	1630 (s)	1400 (m)*	230	1290 (w)	1270 (m)	490 (s)	375 (s)
Th(hmbg–6)(NO_3)$_2$·3H_2O	3455 (m)	3200–3000 (b)	2900 (w) 2830 (m)	1645–1620 (wb)	1615 (s)	1395 (w)*	220	1290 (w)	1270 (s)	490 (w)	380 (m,)
Th(hmbg–5)(NO_3)$_2$·3H_2O	3455 (m)	3250–3080 (b)	2910 (m) 2800 (w)	1680–1640 (mb)	1620 (s)	1395 (s)*	225	1290 (m)	1260 (s)	495 (m)	380 (m)
Th(hbg)$_2$·2H_2O	3455 (w)	3220–3080 (mb)	2900 (m) 2825 (w)	1680–1640 (mb)	1610 (s)	1395 (m)	215	—	1260 (s)	495 (s)	380 (s)
Th(hmbg–3)$_2$·2H_2O	3450 (m)	3250–3000 (mb)	2900 (m) 2810 (s)	1680–1640 (mb)	1610 (s)	1395 (m)	215	—	1265 (m)	490 (m)	380 (m)
Th(hmbg–6)$_2$·2H_2O	3455 (m)	3240–3090 (b)	2905 (m) 2820 (m)	1675–1650 (wb)	1605 (s)	1395 (m)	210	—	1270 (s)	495 (w)	375 (w)
Th(hmbg–5)$_2$·2H_2O	3460 (w)	3200–3000 (b)	2910 (m) 2800 (s)	1670–1630 (mb)	1605 (s)	1390 (m)	215	—	1260 (s)	490 (w)	385 (w)

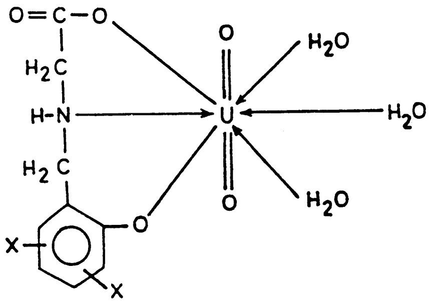
* Overlapping of ν_{sym}(COO) and ν(NO_3)

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

TABLE-4
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUES) OF N-[*o*-HYDROXY SUBSTITUTED (OR H) BENZYL]GLYCINES AND THEIR URANYL(II) AND THORIUM(IV) COMPLEXES

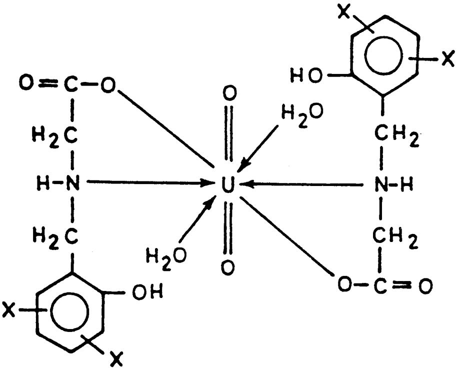
Compound	Aromatic ring	Phenolic OH	H_2O	$>\overset{+}{N}H_2$	>NH	$-CH_2-$		$-CH_3$ attached with benzene ring
						benzene ring	glycine part	
H_2hbg	6.50–7.30 (q)	4.50–5.90 (h)	—	3.60 (s)	—	3.25 (s)	2.45 (s)	—
H_2hmbg–3	6.50–7.10 (t)	4.50–5.70 (h)	—	3.55 (s)	—	3.15 (s)	2.50 (s)	2.15 (s)
H_2hmbg–6	6.40–7.10 (t)	4.40–5.60 (h)	—	3.65 (s)	—	3.20 (s)	2.45 (s)	2.15 (s)
H_2hmbg–5	6.50–7.00 (t)	4.50–5.50 (h)	—	3.70 (s)	—	3.25 (s)	2.45 (s)	2.15 (s)
$UO_2(hbg)\cdot 3H_2O$	6.50–7.00 (t)	—	3.40 (s)	—	3.10 (s)	3.20 (s)	2.40 (s)	—
$UO_2(Hhbg)_2\cdot 2H_2O$	6.40–7.20 (m)	4.50–5.90 (h)	3.40 (s)	—	3.15 (s)	3.25 (s)	2.40 (s)	—
$Th(hbg)(NO_3)_2\cdot 3H_2O$	6.50–10 (m)	—	3.40 (s)	—	3.10 (s)	3.20 (s)	2.40 (s)	—
$Th(hbg)_2\cdot 2H_2O$	6.55–7.15 (m)	—	3.40 (s)	—	3.10 (s)	3.25 (s)	2.40 (s)	—

Abbreviations: s = singlet, t = triplet, q = quartet, m = multiplet, h = hump.



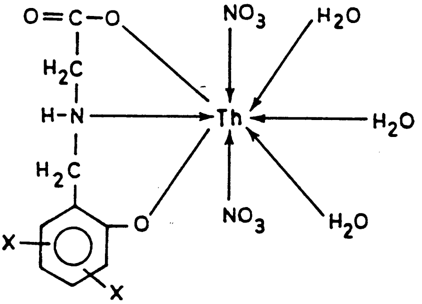
(Where $X = -H$ or $-CH_3$)

II



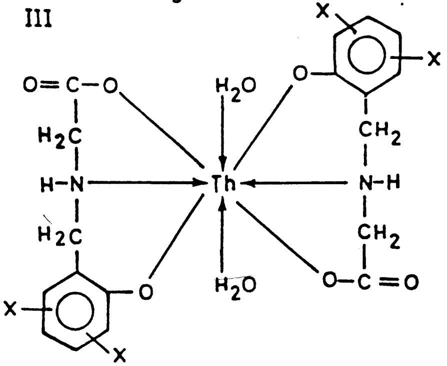
(Where $X = -H$ or $-CH_3$)

III



(Where $X = -H$ or $-CH_3$)

IV



(Where $X = -H$ or $-CH_3$)

V

Preparation of 1 : 1 UO_2(II)-H_2hbg Complex

A solution of H_2hbg (0.4292 g; 2.3687 mmole in 5.0 mL DMSO + 5.0 mL water) was added dropwise to a solution of uranyl acetate (1.0048 g; 2.3687 mmole in 5.0 mL water + 5.0 mL DMSO). The reaction mixture was then refluxed on a water bath. After *ca.* 5 h of reflux, the product isolated as a brick red solid which was filtered under suction and 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 Th(IV) and UO_2(II) 1 : 1 complexes. However, the reaction medium in case of isolation of H_2hmbg-5 complexes has been 50% (v/v) aqueous-DMF, instead of 50% (v/v) aqueous—DMSO.

Preparation of 1 : 2 UO_2(II)-H_2hbg Complex

A solution of H_2hbg (0.4530 g; 2.5000 mmole in 5.0 mL DMSO + 5.0 mL water) was added dropwise to a solution of uranyl acetate (0.5303 g; 1.2501 mmole in 5.0 mL water + 5.0 mL DMSO). The reaction mixture was then refluxed on a water bath. After *ca.* 6 h of reflux, the product isolated as a red solid which was filtered under suction and 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 DMSO but insoluble in other common organic solvents.

Similar procedure of preparation and purification was adopted in case of the other 1 : 2 complexes and the reaction medium for isolation of H_2hmbg-5 complexes has been 50% (v/v) aqueous-DMF, as before.

The relevant analytical details, characteristic IR frequencies and PMR data are summarized in Tables 1–4. It may be mentioned here that abosrptions corresponding to $\nu_{asym}(O{=}U{=}O)$ and $\nu_{sym}(O{=}U{=}O)$ were observed to occur at appropriate places[10, 11] in all the UO_2(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 (in several representative cases), the modes of bonding[4–8] in 1 : 1 and 1 : 2 UO_2(II)-I complexes are shown in Structures (II) and (III) respectively, while those in case of 1 : 1 and 1 : 2 Th(IV)-I complexes in Structures IV and V, respectively.

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(*Received*: 28 November 1998; *Accepted*: 17 December 1998) AJC-1665