

Dioxouranium(VI) Complexes Of Some Unsaturated β -diketones

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Abstract: UO₂(VI) complexes with the formula [UO₂L₂] of nine unsaturated β -diketones (HL) derived from acetylacetone and aromatic aldehydes (benzaldehyde, cinnamaldehyde, furfural, 2-hydroxy-1-naphthaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 3,4-dimethoxy benzaldehyde) have been synthesized. Analytical, IR, ¹H NMR and mass spectral data indicate monobasic bidentate coordination in which the intramolecularly hydrogen bonded enol proton is replaced by UO₂(VI) ion.

Key words: Unsaturated β -diketones; UO₂(VI) complexes; IR spectra; ¹H NMR spectra and mass spectra.

INTRODUCTION

β -diketones are found to be the most efficient for the extraction of uranyl and lanthanide ions from radioactive wastes [1]. Complexes of uranium with β -diketonates were extensively studied because of their importance in the processes of solvent extraction [2] and separation of uranium [3]. Uranyl(VI) complexes are active materials of the uranium redox-flow battery where high solubility in an aprotic solvent is required [4]. Many of the reported studies on uranyl β -diketonates are based on synthetic β -diketones in which the diketo function is directly linked to alkyl/aryl groups [5]. No report appeared on uranyl complexes of β -diketones in which the diketo group is linked to alkenyl function. Such unsaturated β -diketones possess many biological applications as in Curcuminoids [6,7], the active chemical constituent of the herbaceous Indian medicinal plant turmeric (*Curcuma longa*, Linn, *Zingiberaceae* family). In continuation of our studies on such unsaturated β -diketones and their metal complexes [7], we here report the synthesis and characterization of UO₂(VI) complexes of nine unsaturated β -diketones (HL¹-HL⁹) obtained by the condensation between acetylacetone and aromatic aldehydes.

EXPERIMENTAL

Materials and methods

Carbon, hydrogen and nitrogen contents were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The electronic spectra of the compounds in methanol (10^{-4} mol/L) were recorded on a 1601 Shimadzu UV-Vis. spectrophotometer, IR spectra (KBr discs) on an 8101 Shimadzu FTIR spectrophotometer, ^1H NMR spectra (CDCl_3 or DMSO-d_6) on a Varian 300 NMR spectrometer and mass spectra on a Jeol/SX-102 mass spectrometer (FAB using Argon and *meta*-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF ($\sim 10^{-3}$ mol/L) at $28 \pm 1^\circ\text{C}$. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance at room temperature ($28 \pm 1^\circ\text{C}$) using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard. All the chemicals and solvents were of

reagent grade (Merck, Fluka and Sigma-Aldrich) and were used without further purification.

Synthesis of unsaturated β -diketones

The unsaturated β -diketones were synthesized by the condensation between acetylacetone and aromatic aldehydes as reported earlier [7].

Synthesis of $\text{UO}_2(\text{VI})$ complexes

A methanolic solution of uranyl acetate (0.01 mol, 25 mL) was added slowly with stirring to a solution of the unsaturated β -diketone (0.02 mol, 25 mL methanol). The mixture was stirred well and refluxed gently for ~ 1 h and the volume was reduced half. The precipitated complex on cooling to room temperature was filtered, washed with 1:1 methanol-water mixture, dried and recrystallized from hot methanol to get chromatographically (TLC) pure compound.

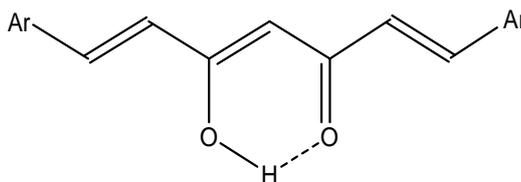


Figure 1. Structure of unsaturated β -diketones

Compound	Ar-
HL^1	Phenyl
HL^2	Styryl
HL^3	2-Furyl
HL^4	2-Hydroxy-1-naphthyl
HL^5	4-Methoxyphenyl
HL^6	4-Hydroxyphenyl
HL^7	4-Dimethylaminophenyl
HL^8	4-Hydroxy-3-methoxyphenyl
HL^9	3,4-dimethoxyphenyl

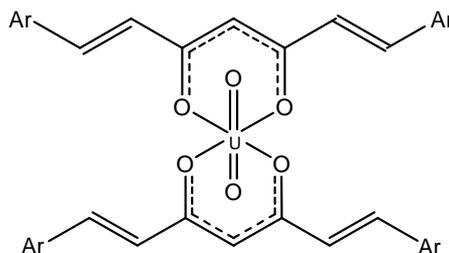


Figure 2. Structure of $\text{UO}_2(\text{VI})$ complexes of unsaturated β -diketones

Table 1. Physical and analytical data of the UO₂(VI) complexes

Complex/ Molecular formula	Yield %	m.p. °C	Elemental Analysis: Found (Calculated)%			
			C	H	N	M
[UO ₂ (L ¹) ₂] C ₃₈ H ₃₀ O ₆ U	70	238	55.40 (55.61)	3.60 (3.66)	-	29.05 (29.02)
[UO ₂ (L ²) ₂] C ₄₆ H ₃₈ O ₆ U	60	252	59.66 (59.74)	4.13 (4.11)	-	25.65 (25.76)
[UO ₂ (L ³) ₂] C ₃₀ H ₂₂ O ₁₀ U	65	242	46.20 (46.15)	2.90 (2.82)	-	30.54 (30.51)
[UO ₂ (L ⁴) ₂] C ₅₄ H ₃₈ O ₁₀ U	70	262	59.58 (59.78)	3.48 (3.50)	-	21.75 (21.96)
[UO ₂ (L ⁵) ₂] C ₄₂ H ₃₈ O ₁₀ U	70	268	53.56 (53.62)	3.99 (4.04)	-	25.25 (25.32)
[UO ₂ (L ⁶) ₂] C ₃₈ H ₃₀ O ₁₀ U	65	265	51.56 (51.58)	3.33 (3.39)	-	26.75 (26.92)
[UO ₂ (L ⁷) ₂] C ₄₆ H ₅₀ N ₄ O ₆ U	70	240	55.56 (55.65)	5.02 (5.04)	5.59 (5.65)	23.85 (23.99)
[UO ₂ (L ⁸) ₂] C ₄₂ H ₃₈ O ₁₄ U	80	293	50.26 (50.20)	3.83 (3.78)	-	23.75 (23.71)
[UO ₂ (L ⁹) ₂] C ₄₆ H ₄₆ O ₁₄ U	75	272	52.16 (52.08)	4.33 (4.33)	-	22.35 (22.45)

RESULTS AND DISCUSSION

All the unsaturated β -diketones (HL, **figure 1**) formed stable and well defined complexes with UO₂(VI) ion. They show sharp melting points and are soluble in common organic solvents. The analytical data (Table 1) together with non-electrolytic nature in DMF (specific conductance $<10\Omega^{-1}\text{cm}^{-1}$; 10^{-3} M solution) suggest [UO₂L₂] stoichiometry. Magnetic measurements indicate that all the complexes are diamagnetic in nature, as expected. The observed spectral data of the complexes are in conformity with **figure 2**.

Infrared spectra

The IR spectra of the unsaturated β -diketones show a strong band at $\sim 1625\text{ cm}^{-1}$ and a broad band in the range $2800\text{--}3500\text{ cm}^{-1}$ due to the stretching of the chelated carbonyl and the intramolecularly hydrogen bonded enol functions respectively. The absence of any band assignable to a normal, -unsaturated carbonyl group in the region $1640\text{--}1740\text{ cm}^{-1}$ indicates the existence of the compounds entirely in the enolic form [7,8] as in **figure 1**.

In the IR spectra of the UO₂(VI) complexes the band at $\sim 1625\text{ cm}^{-1}$ of the ligand due to the stretching of the chelated carbonyl is absent and, instead, a strong band assignable to the stretching of the coordinated carbonyl moiety appeared at $\sim 1580\text{ cm}^{-1}$. The broad band in the region $2800\text{--}3500\text{ cm}^{-1}$ cleared up in the spectra indicating the replacement of enolic proton by the uranyl cation during complexation [7,9]. However spectra of the complexes of HL⁴, HL⁶ and HL⁸ exhibited bands in the range $3200\text{--}3600\text{ cm}^{-1}$ due to the stretching of OH group in the phenyl ring. This suggests that only the enol proton is replaced by uranyl ion and the phenolic OH is excluded from coordination. A comparatively intense band at $\sim 920\text{ cm}^{-1}$ is assignable to UO₂ stretching vibration [9]. The prominent band at $\sim 975\text{ cm}^{-1}$ is typical of a *trans* -CH=CH- group which remained unaltered in the spectra of metal complexes [7]. That the carbonyl groups are involved in bonding with the metal ion is further supported by the appearance of two medium intensity bands at ~ 420 and $\sim 470\text{ cm}^{-1}$ assignable to $\nu_{\text{U-O}}$ [9]. Thus the IR spectral data strongly support **figure 2** of the uranyl complexes. Important bands that appeared in the spectra are given in Table 2.

Table 2. Characteristic IR stretching bands (cm⁻¹) of UO₂(VI) complexes

Complex	Chelate d C=O	CH=CH <i>trans</i>	UO ₂	U-O
[UO ₂ (L ¹) ₂]	1576 s	972 m	916 s	419 m, 473 m
[UO ₂ (L ²) ₂]	1580 s	976 m	926 s	419 m, 468 m
[UO ₂ (L ³) ₂]	1599 s	978 m	923 s	418 m, 472 m
[UO ₂ (L ⁴) ₂]	1595 s	968 m	920 s	418 m, 467 m
[UO ₂ (L ⁵) ₂]	1586 s	980 m	918 s	420 m, 469 m
[UO ₂ (L ⁶) ₂]	1572 s	972 m	922 s	419 m, 470 m
[UO ₂ (L ⁷) ₂]	1574 s	978 m	923 s	417 m, 471 m
[UO ₂ (L ⁸) ₂]	1597 s	976 m	922 s	419 m, 467 m
[UO ₂ (L ⁹) ₂]	1592 s	972 m	920 s	416 m, 473 m

s = strong, m = medium

Table 3. ¹H NMR spectral data (u, ppm) of UO₂(VI) complexes of HL² and HL⁴

Complex	Methine	CH=CH	Phenyl	Phenyl substituent
[UO ₂ (L ²) ₂]	6.32 s	7.61 d, 7.72 d	6.50-7.20 m	-
[UO ₂ (L ⁴) ₂]	6.38 s	7.59 d, 7.69 d	6.86-7.48 m	11.50 s

s = singlet, d = doublet, m = multiplet

¹H NMR spectra

The ¹H NMR spectra of the unsaturated β-diketones displayed a characteristic downfield singlet at ~δ16 ppm due to the intramolecularly hydrogen bonded enolic proton [7] as in Figure 1. The methine proton signal is located at ~δ5.8 ppm and olefinic protons at ~δ7.3 ppm.

In the ¹H NMR spectra of the diamagnetic UO₂(VI) complexes of HL² and HL⁴ the low field signal at ~δ16 ppm of the ligand is absent indicating its replacement by the uranyl ion during complexation [7,10]. The methine proton signal shifted appreciably to low field compared to the shift in the olefinic protons due to the aromatic character imparted to the C₃O₂U ring system of the chelates by the highly conjugated groups attached to the dicarbonyl moiety. The alkenyl proton signals with a *J* value of ~16 Hz suggest the *trans* nature of the alkene double bond, as it is in the free ligands [7]. Aryl protons appear in the range δ6.5-7.5 ppm as a complex multiplet. The integrated intensities of various signals agree well with the structure of the complexes as in figure 2. That the phenolic OH group is not involved in complex formation is clearly indicated [11] in the spectrum of the complex of HL⁴ from the presence of a signal at ~δ11.5 ppm. The integrated intensity of the signal corresponds to four protons there by confirming the presence of two ligands in the complex. The measured frequency of the signal reveals that it is a combination of at least three resonance signals at δ11.504, 11.434 and 11.409 ppm. This is due to steric factors which do

not permit the four -OH groups of the complex to lie in identical environments. The assignments of various proton signals observed are assembled in Table 3.

Mass spectra

Mass spectra of all the unsaturated β-diketones showed intense molecular ion peaks [7]. The FAB mass spectrum of the UO₂(VI) complex of HL⁸ displays a relatively intense (P+1) peak corresponding to [UO₂L₂]⁺ stoichiometry. The relative intensities of the peaks at 1003-1007 are in agreement with the natural abundance of various isotopes of uranium [11]. Other prominent peaks are due to the elimination of OCH₃, H₂O, phenyl groups, C₂H₂, etc from the molecular ion. An intense peak at *m/z* 637 is due to [UO₂L]⁺ fragment. The important peaks found in the spectrum are, *m/z* = 1005, 987, 820, 772, 687, 637, 531, 460, 422, 371, 221, 177, 107.

Electronic spectra

The UV spectra of the unsaturated β-diketones exhibited two absorption maxima at ~380 and ~260 nm assignable respectively to the various n→π* and π→π* transitions of the highly conjugated molecule [7]. The absorption maxima of the metal chelates bear close resemblance with the free ligands which indicates that no structural alteration of the ligand has occurred during complexation. However the values shifted slightly to longer wavelength (~10 nm) indicating the involvement of the carbonyl group in metal complexation [12].

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