

Synthesis and structure of bis(β -dibenzoyl methanato -O,O') (aquo-O) dioxouranium (VI) compound

S KANNAN^{a,*} and M G B DREW^b

^aFuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400 085 India

^bDepartment of Chemistry, University of Reading, Reading, UK

e-mail: skannan@barc.gov.in

MS received 30 April 2014; accepted 22 May 2014

Abstract. The compound $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$ was synthesized and characterized by IR, ¹H NMR and CHN analysis. Structure of the compound shows that the uranium atom is surrounded by seven oxygen atoms in a pentagonal bi-pyramidal geometry. The water molecule is hydrogen bonded to another molecule via the uranyl and β -diketonate oxygen atoms to give a linear zig-zag arrangement along the 'a' axis. The whole molecule is stabilized in solid state by various intermolecular hydrogen bonding interactions.

Keywords. β -diketonates; uranyl ion; adduct compound; crystal structure; hydrogen bonding.

1. Introduction

Structural studies on uranyl bis(β -diketonates) are very important to aid our understanding of the nature of species formed during the extraction of uranyl ion from nitric acid medium by using the β -diketones alone or a mixture of β -diketones and neutral donor ligand.¹ Enhancement in the extraction of uranyl ion from nitric acid medium by using a mixture of β -diketones and neutral donors rather than only β -diketones is due to the formation of uranyl bis(β -diketonate)–neutral donor complexes which are more soluble in organic media. It was proposed that the water molecule from the primary coordination sphere is replaced by the neutral ligands to make the complex more soluble.^{1,2} A large number of uranyl bis(β -diketonates)-neutral ligand complexes have been reported and for a select few,^{3–12} their crystal structures have also been reported. In continuation of our interest in structural studies on the complexes of uranyl bis (β -diketonates) with neutral ligands,^{3–8} we report herein the structure of the uranyl bis (β -dibenzoyl methanato) - water complex.

2. Experimental

2.1 Synthesis of $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$

To a hot methanolic solution (25 mL) of dibenzoyl methane (450 mg, 2.00 mmol), $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (425 mg, 1.00 mmol) solid was added slowly with

stirring and refluxed for 15 min. The orange coloured crystalline product obtained was filtered, washed with ether and dried. The crystal suitable for x-ray diffraction was obtained by the slow evaporation of CHCl_3 /toluene mixture.

2.2 Physical measurements

Yield: 93%. M. p.: 230°C (decom). IR: 3300 (br, H_2O), 2930–2850 (C_6H_5), 1590 (CO), 925 ($\text{O}=\text{U}=\text{O}$) cm^{-1} ; ¹H NMR: δ 7.24 (br, s, CH, CO-CH-CO), 7.5–8.4 (br, m, C_6H_5); Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{O}_7\text{U}$: C, 49.0%; H, 3.3%. Found: C, 48.8%; H 3.2%.

2.3 Crystal structure determination

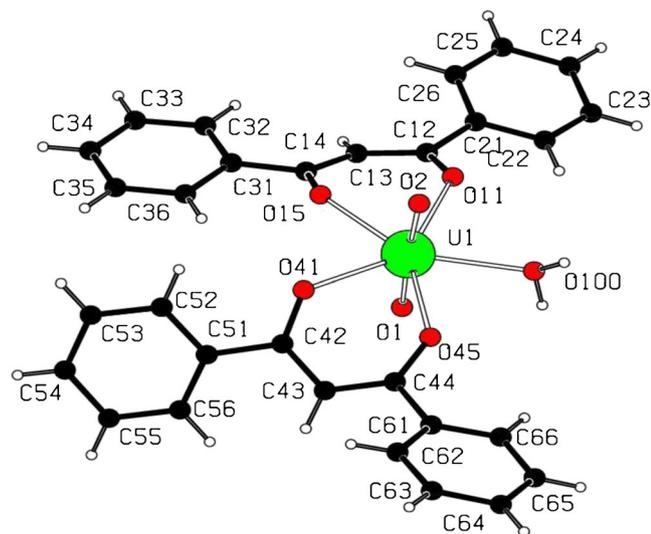
Crystal data for the title compound was measured on a Oxford Diffraction X-Calibur CCD System at 150(2)K with the MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was positioned at 50 mm from the CCD. 321frames were measured with a counting time of 10 s. Data analysis was carried out with the CrysAlis program.^{13a} The structure was solved using direct methods with the Shelxs97 program.^{13b} All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in the geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they attached. Empirical absorption correction was carried out using the ABSPACK program.^{13c} The structure was refined to convergence

*For correspondence

Table 1. Crystal and structural refinement details for $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$.

Empirical formula	$\text{C}_{30}\text{H}_{24}\text{O}_7\text{U}$
Formula weight	734.52
Crystal System	Triclinic
Space Group	P-1
a (Å)	7.5470(6)
b (Å)	12.6698(10)
c (Å)	13.3266(11)
α (°)	92.168(7)
β (°)	91.268(7)
γ (°)	91.970(7)
Volume (Å ³)	1272.26(2)
Z (formula unit)	2
Calculated density (g/cm ³)	1.917
Reflections collected/Unique	8996/7087
Data/restraints/ parameters	7087/9/349
Goodness of fit on F^2	0.987
Final R indices [$I > 2\sigma(I)$]	0.0480
R indices (all data)	0.0625

$$W = 1/[\sigma^2(\text{Fo}^2) + (0.0504\text{P})^2 + 0.0000\text{P}], \text{ where } \text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3.$$

**Figure 1.** Molecular Structure of $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$

on F^2 using Shelxl97.^{13b} Selected crystallographic data are summarized in table 1.

3. Results and discussion

3.1 Characterization

Reaction of dibenzoyl methane with uranyl acetate in methanol yielded the title compound in good yield. IR spectrum of the complex shows a broad peak at 3300 cm^{-1} , indicating the presence of water molecule in the compound. It shows further that a sharp peak at 1590 cm^{-1} is due to the presence of carbonyl group of the β -diketonate ion and at 925 cm^{-1} is due to $\text{O}=\text{U}=\text{O}$ (uranyl) group. ¹H NMR spectrum of the complex shows the expected peaks and multiplicities. The CO-CH-CO proton shows a sharp singlet at δ 7.24 ppm and the aromatic protons show a broad peak between δ 7.5 to 8.4 ppm. The CHN analysis revealed only one water molecule per formula unit in the crystal lattice.

3.2 Structure of $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$

The structure of $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$ with the atomic numbering scheme adopted is shown in figure 1 and important inter atomic bond distances and angles are given in table 2. The uranium atom is surrounded by seven oxygen atoms (four from two dibenzoyl methane ligands, two uranyl oxygen atoms and

Table 3. Hydrogen bonding geometry (Å,°).

D-H...A	D-H	H-A	D...A	\angle D-H...A
O(100)-H(1)...O(1) [#]	0.85(2)	2.08	2.932(6)	176
O(100)-H(2)...O(11) [*]	0.84(2)	1.95	2.7754(6)	165
C(34)-H(34)...O(1) [§]	0.93	2.58	3.261(7)	136
C(36)-H(36)...O(15) [§]	0.93	2.37	2.697(7)	100
C(56)-H(56)...O(2) ^{&}	0.93	2.53	3.419(8)	160

Symmetry Codes : [#] = $-x, -y, -z$; ^{*} = $1-x, 1-y, -z$; [§] = $-x, 1-y, 1-z$; [&] = $-1+x, -1+y, z$.

Table 2. Selected bond distances (Å) and angles (°) for $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$.

U(1) - O(1)	1.792 (4)	O(1) - U(1) - O(2)	176.58 (18)
U(1) - O(2)	1.784 (4)	O(11) - U(1) - O(15)	69.38 (13)
U(1) - O(11)	2.415 (4)	O(41) - U(1) - O(45)	70.78 (14)
U(1) - O(15)	2.298 (4)	O(11) - U(1) - O(100)	73.86 (13)
U(1) - O(41)	2.353 (4)	O(45) - U(1) - O(100)	74.52 (14)
U(1) - O(45)	2.356 (4)	O(11) - U(1) - O(45)	148.36 (14)
U(1) - O(100)	2.474 (4)	O(41) - U(1) - O(11)	140.86 (143)

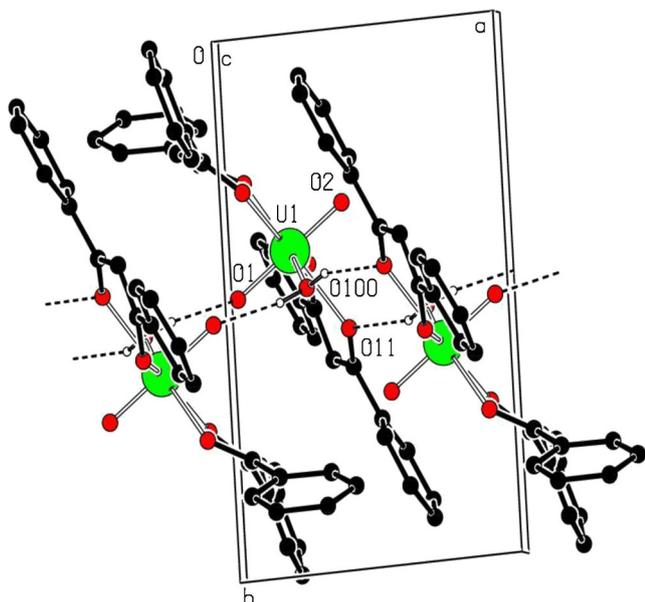


Figure 2. Hydrogen bonding in compound $[\text{UO}_2(\text{C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2 \cdot \text{H}_2\text{O}]$ along “a” axis direction (The hydrogen atoms not involved in hydrogen bonding were removed from the figure for clarity).

one water molecule) at the vertices of a distorted pentagonal bipyramid. Four oxygen atoms of dibenzoyl methane ligands and one oxygen atom from the water molecule form a planar pentagon with a r.m.s. deviation of 0.022 Å, the metal being 0.009(2)Å from the plane,

and the uranyl oxygen atoms are in the apical positions. The bond distances U-O (uranyl) [1.788(4)Å]^{3–12}, U-O (DBM) [2.355(4)Å]^{3–8} and U-O (H₂O) [2.474(4) Å]⁸ are within the accepted ranges reported for similar type of compounds.

It is interesting to note that the hydrogen atoms (H1 and H2) of the water molecule are hydrogen bonded to another molecule via O100-H1...O1 and O100-H2...O11 bonds (table 3) to give a zigzag polymeric arrangement along the “a” axis (figure 2). Two of these layers are stabilized in the solid state by various hydrogen bonding interactions (table 3) to give a three dimensional network (figure 3).

4. Conclusions

The crystal structure of the compound shows that the uranium (VI) ion is surrounded by seven oxygen atoms in a pentagonal bi-pyramidal geometry. The hydrogen atoms of the water molecule are hydrogen bonded to the oxygen atoms of other molecules along the “a” axis to give a zigzag polymeric arrangement.

Supplementary Information

The CIF file is deposited at the Cambridge Crystallographic Data Centre and the deposition number is CCDC-1000213.

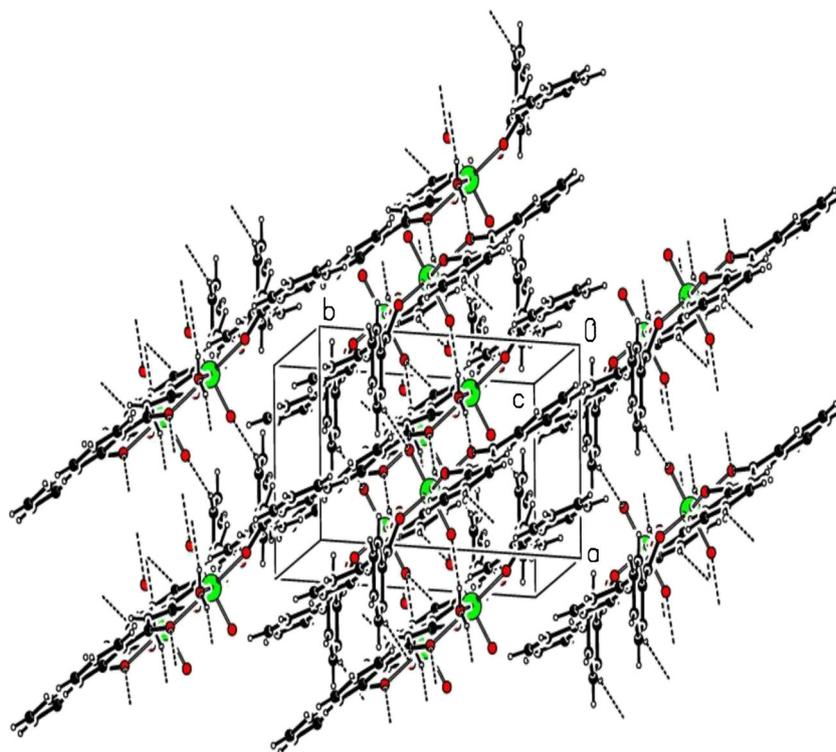


Figure 3. Three dimensional networks with all hydrogen bonding interactions.

Acknowledgements

S K wishes to thank, Dr. S K Aggarwal, Associate Director, Radiochemistry and Isotope group, and Head, Fuel Chemistry for his support. M G B D wishes to thank EPSRC (UK) and the University of Reading for funds for the diffractometer.

References

1. Ramakrishna V V and Patil S K 1984 *Structure and Bonding* **56** 35
2. Mathur J N and Choppin G R 1993 *Solvent. Extr. Ion Exch.* **11** 1
3. Kannan S and Venugopal V V 1995 *Polyhedron* **14** 2349
4. Kannan S, Venugopal V V, Pillai M R A, Droege P A and Barnes C L 1997 *Inorg. Chim. Acta* **254** 113
5. Kannan S 2000 *J. Chem. Soc. Chem. Res.(s)* 344
6. Rajgopal K, Krishnakumar R V, Subha Nanthini M, Kannan S and Natarajan S 2002 *Acta. Cryst. E* **58** m316
7. Kannan S, Deb S B, Gamare J S and Drew M G B 2008 *Polyhedron* **27** 2557
8. Das S, Kannan S, Maity D K and Drew M G B 2012 *Inorg. Chem.* **51** 4869
9. Mizuoka K and Ikeda Y 2004 *Radiochim. Acta* **92** 631
10. Tokao K and Ikeda Y 2008 *Acta Cryst. E* **64** m219
11. Zhu L M, Wang L Y, Jin J R, Li B L and Zhang Y 2008 *J. Coord. Chem.* **61** 917
12. Umeda K, Zukerman- Schpector J and Isolani P C 2006 *Polyhedron* **25** 2447
13. (a) CrysAlis 2006 Oxford Diffraction Ltd. Abingdon, UK; (b) Sheldrick G M Shelxs97 and Shelxl97, program for crystallographic solution and refinement, 2008 *Acta Crystallogr. A* **64** 112; (c) ABSPACK 2005 Oxford Diffraction Ltd., Oxford, UK