Crystal Structure of a Novel Polymer of Dioxo tetrakis(μ -dimethyl-phosphato) Dimethyl-sulfoxide Uranium(VI) Complex, $C_6H_{18}P_2O_{11}SU$

Masoud RAFIZADEH,[†] Fatemeh HOSEINZADEH, and Vahid AMANI

Department of chemistry, Teacher training University, 49 Mofateh Avenue, 15614 Tehran, Iran

The crystal structure of $[UO_2(\mu-DMP)_4(DMSO)]_n$, (DMP = dimethyl phosphate), (DMSO = dimethyl sulfoxide), has been determined by the X-ray diffraction method. This polymeric complex crystallizes in the orthorhombic system, space group $P2_12_12_1$, with four molecules per unit cell. The unit cell dimensions are $a = 8.8085(13)\text{\AA}$, $b = 11.8499(17)\text{\AA}$, $c = 15.359(2)\text{\AA}$, $V = 1603.2(4)\text{\AA}^3$. The final R value is 0.035 for 13322 measured reflections. In this complex, a distorted pentagonal bipyramidal coordination is located around the central U atom. There are two oxygens of uranyl at the axial position, four oxygen atoms of four bridging DMP ligands and one oxygen atom of DMSO are in the equatorial position. The phosphorous atom in the bridging DMP is arranged in a deformed tetrahedron skeleton with a simultaneously Z-in, Z-out distortion, and the phosphate methyl esters have gt conformer (gauche, trans).

(Received August 16, 2005; Accepted October 20, 2005; Published on web January 27, 2005)

A large number of metal complexes with a variety of central atoms, such as d-block transition metals and lanthanides,¹ incorporating various types of phosphate moieties, are applied to investigate cleavage of phosphate ester bonds in order to interpret the importance of these interactions in biological

systems. Polymeric heterometallic complexes have been reported in which the phosphate moieties adopt monodentate, chelating and bridging dispositions.² A group of polymeric powder compounds with the unit formula $[M^{x+}(DMP)_x]_n$ could be prepared (M is a lanthanid metal).³ Recently we studied the coordination chemistry of a novel polymeric UO_2 complex, in which each unit consists of one uranyl, where the U atom is connected to four bridging DMP ligands and one DMSO.

Preparation: The title compound was obtained from the reaction between a solution of $UO_2(NO_3)_2$ with trimethyl phosphate in a 1:2 molar ratio and dimethyl sulfoxide. Slow evaporation of this solution resulted in prismatic yellow crystals after three weeks.

The X-ray data were collected on a diffractometer (Mo K_α radiation, graphite monochromator) at 120(2)K. The crystal data and experimental parameters are given in Table 1.

The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located from sequent difference fourier

Table 1 Crystal and experimental data

Empirical formula: $C_6H_{18}P_2O_{11}SU$
Formula weight = 598.23
Crystal system: orthorhombic
Space group: $P2_12_12_1$
$Z = 4$
$a = 8.8085(13)\text{\AA}$
$b = 11.8499(17)\text{\AA}$
$c = 15.359(2)\text{\AA}$
$V = 1603.2(4)\text{\AA}^3$
$D_x = 2.479\text{ g/cm}^3$
Absorption coefficient = 10.502 mm^{-1}
$F(0\ 0\ 0) = 1120$
Crystal dimension (mm): $0.30 \times 0.28 \times 0.27$
$R1 = 0.035$
$wR2 = 0.093$
θ range for data collection: 2.17 to 25.00°
Goodness-of-fit = 1.024
No. of reflection used = 2704
No. of parameter = 196
Measurment: Bruker SMART 1000 CCD
Program system: SMART V 5.051 and SAINT V5.00
Largest diff. peak and hole: 2.956 and -1.665 e^{-3}
Structure determination: direct method
Refinement: full-matrix least-squares on F^2
CCDC 250659 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

[†] To whom correspondence should be addressed.
E-mail: rafizadeh@saba.tmu.ac.ir

Table 2 Selected bond distances ($\text{\AA}$), bond angles (deg) and torsion angles (deg) in Fig. 2

U(1)-O(1)	1.775(6)	P(1)-O(4)	1.492(7)
U(1)-O(2)	1.777(6)	P(1)-O(3)	1.507(6)
U(1)-O(3)	2.329(6)	P(1)-O(5)	1.583(7)
U(1)-O(7)	2.359(6)	P(1)-O(6)	1.567(7)
U(1)-O(11)	2.443(7)	O(11)-S(1)	1.515(7)
U(1)-O(8A)	2.359(6)	S(1)-C(2S)	1.795(9)
U(1)-O(4A)	2.347(7)	S(1)-C(1S)	1.782(10)
O(1)-U(1)-O(2)	178.7(4)	C(2S)-S(1)-C(1S)	97.8(5)
O(3)-U(1)-O(7)	75.0(2)	O(4)-P(1)-O(3)	117.8(4)
O(7)-U(1)-O(4A)	73.7(2)	O(4)-P(1)-O(5)	105.6(4)
O(4A)-U(1)-O(11)	71.4(2)	O(5)-P(1)-O(6)	101.3(4)
O(11)-U(1)-O(8A)	67.9(2)	O(6)-P(1)-O(3)	109.6(4)
O(8A)-U(1)-O(3)	72.1(2)	P(1)-O(3)-U(1)	177.1(4)
O(1)-U(1)-O(3)	91.7(3)	P(2)-O(7)-U(1)	148.2(4)
O(1)-U(1)-O(7)	88.2(3)	P(1)-O(6)-C(2P)	118.2(6)
O(1)-U(1)-O(4A)	89.0(3)	P(1)-O(5)-C(1P)	119.9(7)
O(1)-U(1)-O(11)	90.5(3)		
O(1)-U(1)-O(8A)	90.4(3)	C(2P)-O(6)-P(1)-O(5)	-169.6(7)
U(1)-O(11)-S(1)	134.1(4)	C(1P)-O(5)-P(1)-O(6)	65.6(10)
O(11)-S(1)-C(2S)	103.7(4)	C(3P)-O(9)-P(2)-O(10)	63.3(7)
O(11)-S(1)-C(1S)	104.4(5)	C(4P)-O(10)-P(2)-O(9)	-168.1(7)

Fig. 1 Chemical structure.

Fig. 2 Discrete fragment of the molecular structure in the $\text{UO}_2(\mu\text{-DMP})_4(\text{DMSO})$ chain with the atomic labeling scheme.

maps and refined with the riding model to final R indices (all data) of $R_1(0.0356)$, and $WR_2(0.0934)$. Selected bond lengths and angles are given in Table 2.

An X-ray structural analysis established that Fig. 1 consists of a discrete $[\text{UO}_2(\mu\text{-DMP})_4(\text{DMSO})]_n$ fragment. An ORTEP plot (Fig. 2) shows that the complex consists of one uranyl, which is linked to other fragments *via* four O-P-O bridges of four phosphate esters; also, one DMSO is linked to each uranyl *via* its oxygen atom. Figures 1 and 2 show discrete fragments of the molecular structure. Figure 3 shows the polymeric structure of the title complex, which the (O-P-O) moieties of the phosphate form doubly bridge between two uranyles. The DMSO molecule appears as a monodentate ligand in every single U atom, different from the behavior of DMSO in the $[\text{Cu}_2(\mu\text{-DMP})_4\text{DMSO}]_n$ complex.⁴ We also provided other compounds that included double bridges of alkylphosphates, their structures were determined by X-ray analyses such as $[\text{Cu}_2(\mu\text{-DMP})_4\text{DMSO}]_n$,⁴ $[\text{Ce}(\text{DMP})_6]_n$ and $[\text{Ce}_2(\text{DEP})_6\text{TEP}]_n$. Two of the latest will be published soon.

The phosphate groups in $\text{UO}_2(\mu\text{-DMP})_4\text{DMSO}$ are arranged as an abnormal distorted tetrahedron. The angles of O-P-O and MeO(5)-P(1)-O(6)Me are unequal. The angle of the MeO(5)-P(1)-O(6)Me moiety is $101.3(4)^\circ$, whereas that of O(4)-P(1)-O(3) is $117.8(4)^\circ$. According to a survey on a similar polymeric Cu complex,⁴ an acceptable reason are simultaneous Z-in and Z-out distortions for the DMP. In addition, the conformation of the DMP anion depends on the C-O-P-O angles. In this complex, we unexpectedly observed the gt conformation for DMP base on the dihedral angles. At this complex, for example, the dihedral angles of one of the DMP ligands are: $\text{C}(2\text{P})\text{-O}(6)\text{-P}(1)\text{-O}(5) = -169.6(7)^\circ$ and

Fig. 3 Polymeric structure of the title complex.

$\text{C}(1\text{P})\text{-O}(5)\text{-P}(1)\text{-O}(6) = 65.6(10)^\circ$. Each U center occupies an irregular pentagonal bipyramidal (pbp) geometry with the DMSO ligand and phosphate oxygens in the equatorial position and uranyl oxygens in the axial position. Such pentagonal bipyramidal coordination is rare in infinite solid uranate structures, apparently because an equatorial plane cannot be tiled exclusively with regular pentagons.⁵

Two U=O bonds are located in the axial position. Their lengths, as expected for 7-coordinate uranyl complexes.⁶ The axial U=O bond lengths are shorter than equatorial U-O bond lengths: $\text{U}(1)\text{-O}(3) = 2.329(6)\text{\AA}$, $\text{U}(1)\text{-O}(4) = 2.347(7)\text{\AA}$, $\text{U}(1)\text{-O}(7) = \text{U}(1)\text{-O}(8) = 2.359(6)\text{\AA}$, $\text{U}(1)\text{-O}(11) = 2.443(11)\text{\AA}$. A pentagonal bipyramidal coordinated central uranium atom having triple bonds to the two axial oxygens and single bonds to the five equatorial oxygens uses a total of $(2)(3) + (5)(1) = 11$ orbitals, corresponding to an sd^5f^6 manifold.

The related $\text{U}(1)\text{-O}(11)$ bond to DMSO is relatively longer than the other equatorial bonds. The uranyl angle $\text{O}(1)\text{-U}(1)\text{-O}(2)$ is $178.7(4)^\circ$, as would be expected ($178 - 180^\circ$). The bond angles $\text{P}(1)\text{-O}(3)\text{-U}(1)$ and $\text{P}(2)\text{-O}(7)\text{-U}(1)$ are $177.1(4)^\circ$ and $148.2(4)^\circ$, respectively. The angle of $\text{S}(1)\text{-O}(11)\text{-U}(1)$ is $134.1(4)^\circ$. The large mentioned angle may belong to a steric hindrance induced by the methyl groups of DMSO, and lone pairs on the oxygen of DMSO with the U atom environment. According to experimental geometry data for DMSO, the bond angles are $\text{CSC} = 96.6^\circ$ and $\text{CSO} = 106.5^\circ$. Therefore, we observe that they have almost not changed.

Acknowledgements

We are grateful from Teacher Training University for financial support.

References

1. R. Reichenbach-Klinke and B. König, *J. Chem. Soc. Dalton Trans.*, **2002**, 121.
2. M. Yamami, H. Furutachi, T. Yokoyama, and H. Okawa, *Inorg. Chem.*, **1998**, 37, 6832.
3. M. Rafizadeh, *Chem. Engin. Chem. Publ. Iran*, **1986**, 7, 16.
4. M. Rafizadeh, R. Tayebie, V. Amani, and M. Naseh, *Bull. Korean Chem. Soc.*, **2005**, 26, 4.
5. R. Bruce King, *J. Chem. Mater.*, **2002**, 14, 3628.
6. A. D. Sutton, G. H. John, M. J. Sarsfield, J. C. Renshaw, I. May, L. R. Martin, A. J. Selvage, D. Collison, and M. Helliwell, *Inorg. Chem.*, **2004**, 43, 5480.