ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 9, pp. 671–675. © Pleiades Publishing, Ltd., 2014.

Spectroscopy and X-ray Studies of {{6,6'-Dimethoxy-2,2'-[Ethane-1,2-diyl-bis-(Nitrilomethylidyne)]diphenolato}(aqua)-Dioxouranium(VI)} Dehydrate[1]

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Received January 23, 2014

Abstract—The $C_{18}H_{20}N_2O_7U \cdot 2H_2O$ (**I**) complex has been prepared and characterized by single crystal X-ray diffraction properties (CIF file CCDC no. 913243). The title compound crystallizes in the orthorhombic system, space group *Pbca* with $a = 19.542(5)$, $b = 9.916(5)$, $c = 21.940(5)$ Å, $V = 4252(3)$ Å^3 and $Z = 8$. In complex **I**, the U atom has a distorted pentagonal–bipyramidal geometry with a tetradentate Schiff base ligand and water molecule in the equatorial plane and oxo atoms in the axial positions. The crystal packing occurs intra-inter molecular hydrogen bonds.

DOI: 10.1134/S1070328414090139

INTRODUCTION

Many Schiff base complexes have potential biological interest in an attempt to mimic the structural and functional features of multimetal active sites. Schiff bases have also found useful applications in the synthesis of molecular and supramolecular polymetallic functional systems exhibiting specific optical or magnetic properties [1]. Schiff bases constitute an interesting class of chelating agents, capable of coordination with one or more metal ions to form mononuclear as well as polynuclear metal complexes [2, 3]. Some of their applications can be found in analytical chemistry and serve as biochemical models [4, 5]. Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic activities [6]; in particular, sulfur-containing Schiff bases are very effective.

In order to acquire more information on the properties uranium(VI) complex, we report synthesis, characterization and crystal structure of the $C_{18}H_{20}N_2O_7U \cdot 2H_2O$ (**I**) metal complex.

EXPERIMENTAL

Materials and measurement. The optical absorption spectra of title complex were recorded at room temperature in acetonitrile solution on a Unicam UV2 UV-Vis spectrometer working between 200 and 900 nm. The IR spectra were recorded on a Vertex 80v Bruker FTIR spectrophotometer in 4000–400 cm^{-1} using KBr pellets.

Synthesis of {{6,6'-dimethoxy-2,2'-[ethane-1,2-diyl-bis-(nitrilomethylidyne)]diphenolato}(aqua)-dioxouranium(VI)} dehydrate (I). In this study, we intended to synthesize heterodinuclear complex $[L(UO_2)AgNO_3]$ (L = *N*,*N*'-ethylene-bis(3-methoxysalicylideneimine), but heterodinuclear complex could not be obtained. An aqueous solution (10 mL) of $AgNO_3$ (0.11 g, 6.47×10^{-4} mol) was added to a solution of the UO_2(VI) complex of H_2L (0.42 g, 6.47×10^{-4} mol) [1], in tetrahydrofuran (20 mL). The mixture was refluxed for 24 h with stirring. The resulting solution was then cooled to room temperature and a dark pink powder was precipitated. The product was filtered and washed with tetrahydrofuran-water (1 : 1). The suitable for X-ray diffraction crystals were grown from an acetonitrile solution by slow evaporation over a period of 5 days (m.p. > 300°C and the yield was 81%).

IR data (KBr; ν, cm^{-1}): 3492 m, 3360 s ν(O–H), 1624 s ν(C=N), 1458 m ν(C–O), 1263 m ν($C–O_{CH_3}$), 910 s ν(O=U=O), 640 w ν(U–O), 478 w ν(U–N), 1510 m ν(C=C), 1469 m, 1370 w ν(C–H), 1180 m, 1072 m, 1032 w, 818 m, 694 w $\nu_{\text{benzene ring bone}}$. UV-Vis data ($CH_3CN$; 1.00×10^{-4} M): 236–272 ($\pi \to \pi^*$), 349 ($n \to \pi^*$), 418 nm (charge transfer transition).

X-ray crystallography. X-ray data collection was carried out an X-AREA diffractometer (Stoe & Cie, 2002); with a graphite monochromatized MoK_α radiation. Cell refinement: X-AREA (Stoe & Cie, 2002); data reduction: X-RED32 (Stoe & Cie, 2002) [7]; program(s) used to solve structure: SHELXS-97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL-97 (Sheldrick, 1997) [8]; molecular graph-

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Molecular weight	614.4
Temperature, K	296
Wavelength, Å	0.71073
Crystal system	Orthorhombic
Crystal size, mm	0.660 × 0.550 × 0.350
Space group	*Pbca*
a, Å	19.542(5)
b, Å	9.916(5)
c, Å	21.940(5)
Volume, Å^3	4252(3)
Z	8
T_{min}, T_{max}	0.5190, 1.0000
ρ, mg m^{-3}	1.92
F(000)	2319.5
θ Range, deg	3.5–25.0
Index ranges	$-13 \le h \le 23$, $-11 \le k \le 11$, $-23 \le l \le 26$
Measured reflections	10235
Independent reflections (R_{int})	3728 (0.0554)
Observed reflections, $I > 2\sigma(I)$	2616
Goodness–of–fit on F^2	1.045
R_1, wR_2 indice, $I > 2\sigma(I)$	0.040, 0.062
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.956/–0.823

Table 2. Selected bond distances (Å) and angles (deg) of **I**

Bond	*d*, Å	Bond	*d*, Å
U(1)–O(1)	2.290(6)	U(1)–O(5)	2.422(9)
U(1)–O(2)	2.262(6)	U(1)–N(1)	2.548(8)
U(1)–O(3)	1.759(6)	U(1)–N(2)	2.560(8)
U(1)–O(4)	1.765(6)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(2)U(1)O(1)	151.8(2)	O(3)U(1)O(5)	88.8(3)
O(4)U(1)O(3)	176.9(3)	O(4)U(1)O(5)	94.3(3)
O(2)U(1)O(3)	93.0(3)	O(2)U(1)N(2)	71.1(2)
O(2)U(1)O(4)	87.5(3)	O(1)U(1)N(1)	70.5(2)
O(1)U(1)O(3)	91.2(3)	N(1)U(1)N(2)	66.5(2)
O(1)U(1)O(4)	89.8(3)		

ics ORTEP-3 for Windows (Farrugia, 1997) [9]. Experimental conditions are given in Table 1. The positions of all H atoms, except for those attached to oxygen atoms, were calculated geometrically, and refined by using a riding model with C–H distances of 0.93–0.97 Å. The H atoms displacement parameters were restricted to 1.2 U_{eq} (1.5 U_{eq} for methyl atoms) of the parent atom. Selected bond lenghts and angles are summarized in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 913243; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The U(VI) atom has a distorted pentagonal-bipyramidal coordination geometry, with the Schiff base ligand and water molecule in the equatorial plane (Fig. 1). The phenoxide atoms O(1) and O(2) are displaced by 0.0445 (5) and 0.1124 (5) Å, respectively, from the plane defined by O(1)N(1)N(2)O(2)(1)O(5). The oxo atoms O(3) and O(4) occupy the axial positions. The U(1)–O(3) and U(1)–O(4) bond distances

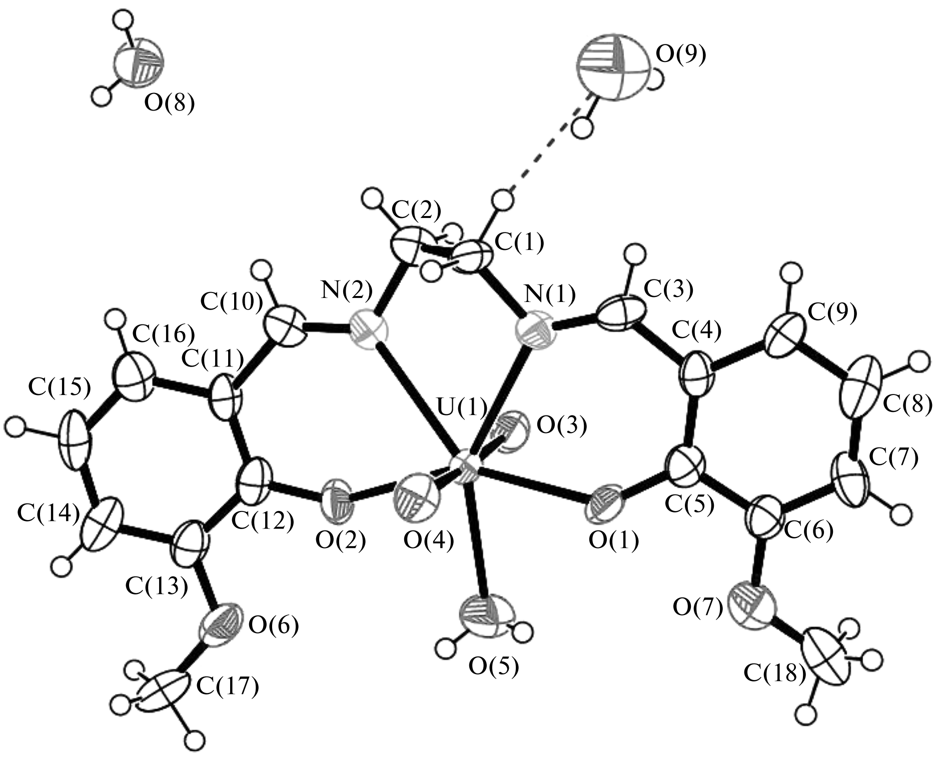

Fig. 1. ORTEP drawing of the molecular structure of **I**, showing the atom numbering scheme and 50% probability displacement ellipsoids with C–H···O intramolecular hydrogen bonding.

(Table 2) are typical for U=O double bonds, close to those reported previously (1.778 (4) and 1.794 (5) Å) [10]. The dihedral angles between five-six-membered chelate rings: A (UN_2C_2), B (U(1)O(1)N(1)C(3–5) and C (U(1)O(2)N(2)C(10–12), and phenyl rings D (C(4)–C(9)) and E (C(11)–C(16)) are A/B = 18.2(3)°, B/C = 3.4(3)°, C/D = 8.4(4)° and D/E = 3.6(5)°.

The crystal packing involves inter- and intramolecular hydrogen bonds with details of which are given in Table 3. The intra-molecular C–H···O hydrogen bonding is shown in Fig. 1. The intermolecular O–H···O hydrogen bondings is shown in Fig. 2. In these hydrogen bondings, the atom O(5) of the coordinated water molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor, via atoms H(5*A*) and H(5*B*) to the atoms O(9) and O(8) of the solvent water molecules at (1/2 + *x*, 1/2 – *y*, –*z*) and (1/2 + *x*, *y*, 1/2 – *z*), respectively. These hydrogen bonds are shown in Fig. 2a. As can be seen Fig. 2b, one of the solvent water molecules, the

Table 3. Geometric parameters of hydrogen bonds of structure **I***

	Distance, Å			Angle D–H···A, deg
D–H···A	D–H	H···A	D···A	
O(5)–H(5*A*)···O(9)^{i}	0.85(3)	1.99(8)	2.562(16)	124(8)
O(5)–H(5*B*)···O(8)^{ii}	0.82(9)	1.78(8)	2.596(12)	178(12)
O(82)–H(8*A*)···O(6)^{iii}	0.83(8)	2.38(15)	2.762(11)	109(12)
O(8)–H(8*B*)···O(1)^{iv}	0.82(6)	2.12(6)	2.823(10)	145(5)
C(1)–H(1*B*)···O(9)	0.97	2.52	3.465(14)	165

* Symmetry codes: ^{i} 1/2 + *x*, 1/2 – *y*, –*z*, ^{ii} 1/2 + *x*, *y*, 1/ 2 – *z*, ^{iii} –1/2 + *x*, *y*, 1/2 – *z*, ^{iv} 1/2 – *x*, 1 – *y*, 1/2 + *z*.

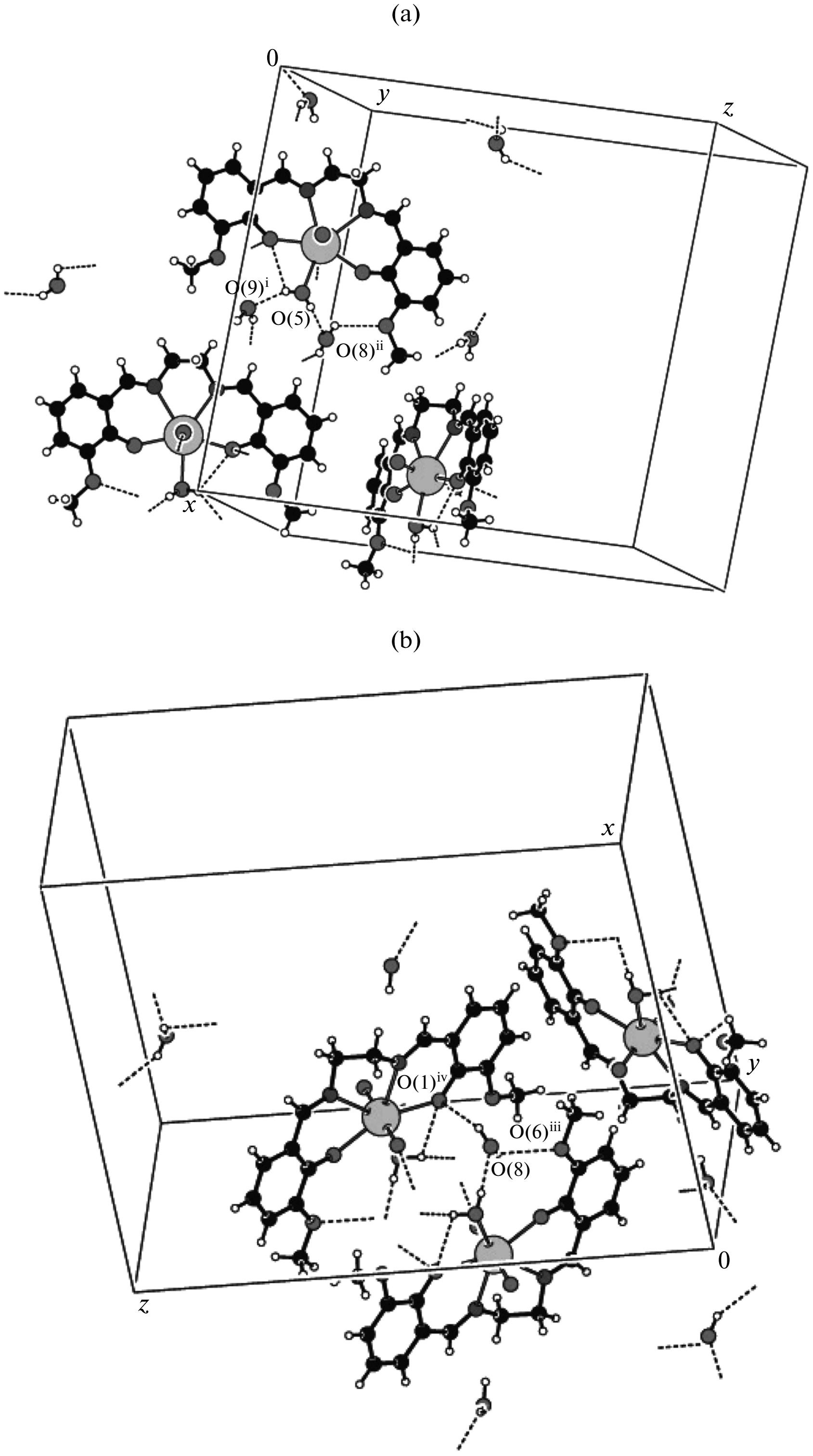

Fig. 2. PLATON drawing a partial packing diagram of complex **I**: symmetry codes: ^{i} $1/2 + x, 1/2 - y, -z$; ^{ii} $1/2 + x, y, 1/2 - z$ (a); ^{iii} $-1/2 + x, y, 1/2 - z$; ^{iv} $1/2 - x, 1 - y, 1/2 + z$ (b). O–H···O interactions has been shown as broken lines.

atom O(8) at (x, y, z) acts as hydrogen-bond donor, via atoms H(8*A*) and H(8*B*) to the atoms O(6) and O(1) at ($-1/2 + x, y, 1/2 - z$) and ($1/2 - x, 1 - y, 1/2 + z$), respectively. The hydrogen bonds with this water molecule to be done, connect two different molecules, together. The O(5)–H(5*B*)···O(8)^{ii} and O(8)–

$H(8A)\cdots O(6)^{iii}$ hydrogen bonds are characterized by an $R_2^2(9)$ motif.

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