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Bis(methanol-κ*O*)dioxido[3,3′-(1*H*-1,2,4-triazole-3,5-diyl)diphenolato-κ^3*O*,*N*^{4},*O*′]uranium(VI) methanol monosolvate

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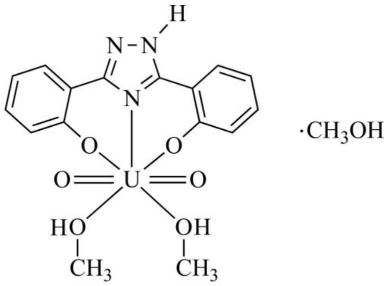
The structure of the title compound, $[U(C_{14}H_9N_3O_2)O_2(CH_3OH)_2]\cdot CH_3OH$, is the first to be reported for an actinide complex including triazole ligands. The U^{VI} atom exhibits a pentagonal–bipyramidal NO_6 coordination environment, involving two axial oxide ligands [U═O = 1.766 (3) and 1.789 (3) Å], four equatorial O atoms [U—O = 2.269 (3)–2.448 (3) Å] from the ligand and the two coordinated methanol molecules, and one equatorial N atom [U—N = 2.513 (4) Å] from the ligand. In the crystal structure, the complex molecules are linked *via* intermolecular N—H···O and O—H···O hydrogen bonds to form a two-dimensional structure.

Comment

The synthesis of coordination compounds containing *f*-block elements and, more specifically, those containing the uranyl cation (UO_2^{2+}) has undergone an important development in recent years. This interest is largely due to the increasing handling of uranium in the nuclear fuel cycle worldwide. In order to recover uranium, the development of new ligand systems suitable for the co-extraction of lanthanides and actinides from nuclear waste is most important. 1,2,4-Triazole and its derivatives are potentially useful for separating problematic metals from both ordinary and radioactive waste. Recently, the triazole ligands 2,6-bis(5-butyl-1,2,4-triazol-3-yl)pyridine (DBTZP) and 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine (DMTZP) have been found to have good extraction properties (Drew *et al.*, 1999).

The uranyl ion, being a hard Lewis acid, has a high affinity for hard donor groups. Equatorial pentacoordination generally results from five- and six-membered chelate rings with bidentate ligands, as in $[UO_2(acac)_2(H_2O)]$ (acac is acetylacetate; Frasson *et al.*, 1966), or with small monodentate ligands, as in $[UO_2(DMSO)_5]^{2+}$ (DMSO is dimethyl sulfoxide; Harrowfield *et al.*, 1983). To expand our studies concerning the coordination chemistry of 1,2,4-triazole, we were interested in investigating the behaviour of *O*,*N*,*O*′-chelating ligands with UO_2^{2+}. A substantial amount of research has been dedicated to *d*-block complexes which incorporate derivatives of 1,2,4-triazoles (Aromi *et al.*, 2011). These compounds are receiving growing interest due to their magnetic and luminescent properties. Previously, coordination compounds of vanadium and copper with 3,5-bis(2-hydroxyphenyl)-1,2,4-triazole (H_2L) have been synthesized. In the case of copper, the two-dimensional mixed-valence complex $[Cu^ICu^{II}(L)]_n$ was obtained (Fang *et al.*, 2011), while for vanadium the product was $[(VOL)_2(OMe)_2]\cdot H_2O$ (Browne *et al.*, 2006). We report here the structure of the title compound, $[(UO_2)(L)(MeO)(MeOH)]\cdot MeOH$, (I), which is the first reported crystal structure of a 1,2,4-triazole complex of UO_2^{2+}. The structure is important as a prototype for the construction of actinide and triazole coordination frameworks, which could be anticipated especially for the typical MO_2^{2+} cations and for a wide range of azole ligands, such as 1,2,3-triazole, 1,2,4-triazole and tetrazole.



(I)

In (I), the ligand is coordinated in a tridentate manner to the uranyl(VI) ion, together with two methanol molecules

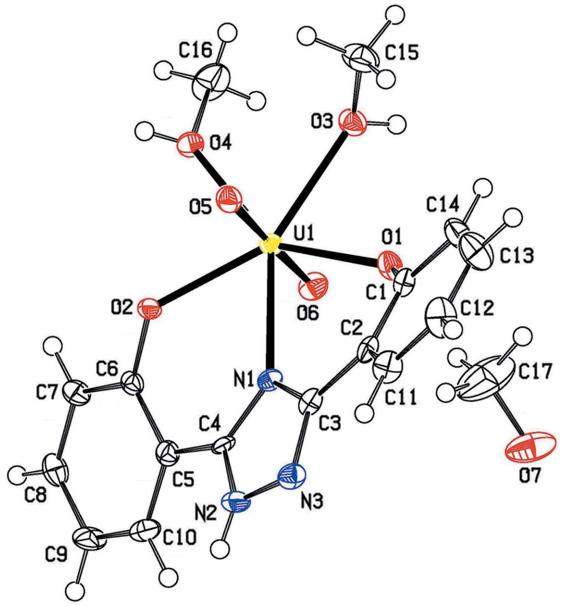


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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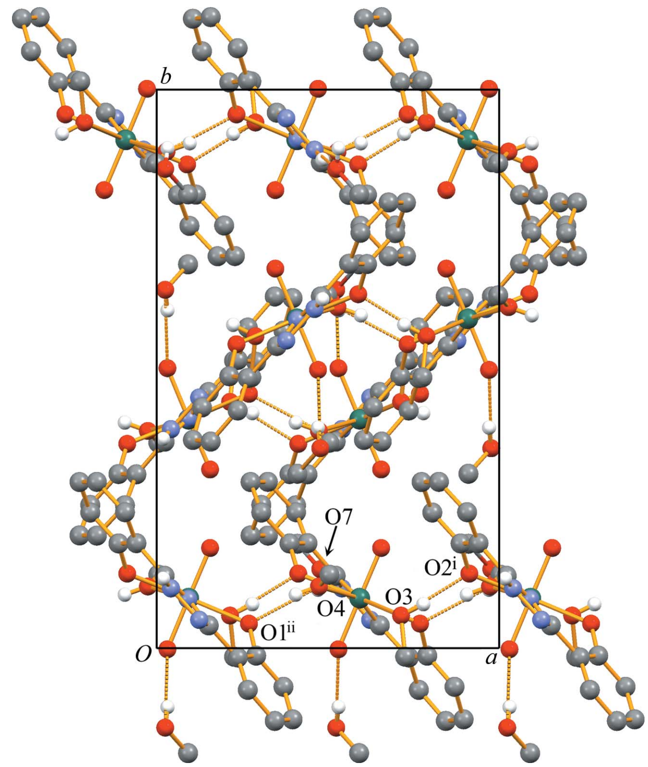

Figure 2
A projection of the structure of (I) along the *c* axis. Intermolecular hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$.]

(Fig. 1). This evokes a pentagonal–bipyramidal geometry around the metal centre. These kinds of monomeric neutral complexes of uranyl with tridentate ligands are very rare. There are only a few similar complexes containing ligands such as 2-pyridineformamide thiosemicarbazone (Santos & Abram, 2004), 2,2′:6′,2′′-terpyridine (Charushnikova & Auwer, 2004; Berthet *et al.*, 2004), bis(2-hydroxycyclohexyl) sulfide (Baracco *et al.*, 1975), *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamide (Duval *et al.*, 2006), aminobis(phenolate) (Sopo *et al.*, 2008), 2,6-bis[(dimethylamino)methyl]pyridine (Masci & Thuéry, 2004), diglycolamide ligands (Kannan *et al.*, 2008) and 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (Berthet *et al.*, 2008). Amongst these, only *N*,*N*,*N*′,*N*′-tetraalkylpyridine-2,6-dicarboxamide and aminobis(phenolate) are of the *O*,*N*,*O*′-chelating type. In (I), the 3,3′-(1*H*-1,2,4-triazole-3,5-diyl)diphenolate ligand (*L*) binds to UO_2^{2+} as a dianion *via* the two phenolate O atoms and triazole atom N1, while the labile H atom is located on atom N2. The U1—O1 bond length [2.269 (3) Å] is comparable with those reported for related six-membered chelate fragments involving phenolate and N-atom donors (Back *et al.*, 2010; Sopo *et al.*, 2008), while the coordination interaction with the second phenolate ring is slightly longer [U1—O2 = 2.281 (3) Å]. The U1—N1 distance of 2.513 (4) Å is notably shorter than the average for U—N bonds, but is consistent with the situation in other *O*,*N*,*O*′-bonded uranium complexes (Sopo *et al.*, 2008; Lam *et al.*, 2010). It is worth noting that the ligand is not planar: the torsion angles between the phenolate rings and the central triazole unit are C1—C2—C3—N1 = −19.4 (7)° and N1—C4—C5—C6 = −26.0 (7)°. The corresponding values are 14.0 and 19.6° for $[Al(L1)_2]^-$ {*L*1 is [3,5-bis(2-hydroxyphenyl)-1,2,4-triazol-1-yl]benzene}, and 19.2 and 24.0° for $[Cu(L1)(pyridine)]_2$ (Steinhauser *et al.*, 2004).

The O═U═O group is not exactly linear, as the O═U═O angle is 178.69 (15)°. Nonlinear O═U═O bonds are found generally in uranyl complexes with five nonsymmetrically bonding equatorial ligands, one of them being methanol (Back *et al.*, 2009). The reason for the bending of the O═U═O bonds is presumably due to uneven π-donation from the ligands to the UO_2^{2+} unit, which results from the asymmetrical location of the donor atoms around uranium caused by pentacoordination (Sonnenberg *et al.*, 2005).

The intermolecular interactions in (I) involve hydrogen bonding between the two coordinated methanol molecules and two phenolate O atoms in adjacent complex molecules (Table 1). The uncoordinated methanol molecule also links between complex molecules *via* N—H⋯O and O—H⋯O hydrogen bonds. The hydrogen bonds link the complex molecules into a two-dimensional structure parallel to the (010) plane (Fig. 2).

Experimental

For the preparation of (I), a mixture of 3,5-bis(2-hydroxyphenyl)-1*H*-1,2,4-triazole (0.2 mmol) and $UO_2(CH_3COO)_2 \cdot 2H_2O$ (0.2 mmol) in methanol (25 ml) was stirred for 20 min and then filtered. The filtrate was left to evaporate slowly at room temperature. Red single crystals of (I) suitable for X-ray analysis were obtained after 4 d.

Crystal data

$[U(C_{14}H_9N_3O_2)O_2(CH_4O)_2] \cdot CH_4O$
$M_r = 617.40$
Orthorhombic, *Pbca*
$a = 11.0737$ (11) Å
$b = 18.0705$ (17) Å
$c = 20.1156$ (19) Å
$V = 4025.3$ (7) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 8.11$ mm^{-1}
$T = 173$ K
0.45 × 0.18 × 0.12 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.121$, $T_{max} = 0.443$
12248 measured reflections
4019 independent reflections
3126 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.061$
$S = 1.04$
4019 reflections
272 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.94$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}

Atoms H3O, H4O, H7O and H2N were located in difference Fourier maps and their coordinates and isotropic displacement parameters were refined; the O—H distances were restrained to 0.82 (2) Å, while atom H2N was left unrestrained. The remaining H atoms were placed geometrically and treated as riding, with C—H = 0.95 (aromatic) or 0.98 Å (methyl), and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms or $1.2U_{eq}$(parent) otherwise. The methyl groups were

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O7	0.82 (5)	1.95 (5)	2.758 (6)	165 (5)
O3—H3O···O2^{i}	0.82 (2)	1.81 (2)	2.629 (5)	174 (6)
O4—H4O···O1^{ii}	0.81 (2)	1.80 (2)	2.594 (5)	168 (5)
O7—H7O···O5^{iii}	0.80 (2)	2.04 (2)	2.831 (6)	168 (7)

Symmetry codes: (i) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (ii) $x-\frac{1}{2}, y, -z+\frac{3}{2}$; (iii) $-x+1, -y, -z+1$.

also allowed to rotate about their local threefold axes. The maxima and minima in the residual electron density are associated with atom U1.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3033). Services for accessing these data are described at the back of the journal.

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