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# CRYSTAL STRUCTURE OF A HYDROXO-BRIDGED DIMERIC URANYL COMPLEX WITH A 2,2′:6′,2″-TERPYRIDINE LIGAND

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A new dimeric compound $[\{UO_2(\mu\text{-}OH)(terpy)\}_2](ClO_4)_2\cdot 0.67CH_3CN$, containing an uranyl cation and a tridentate 2,2′:6′,2″-terpyridine (terpy) ligand, is synthesized from an acetonitrile solution of uranyl perchlorate and terpy. The crystal structure of the compound is determined by single crystal X-ray diffraction. The crystal structure shows the formation of symmetric and asymmetric cationic hydroxo-bridged uranyl dimers. The uranium atoms adopt a distorted pentagonal bipyramidal configuration with a $UO_4N_3$ coordination environment formed by two uranyl O atoms, three N atoms from the terpy ligand, and two O atoms from the hydroxide anions.

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**Keywords:** uranyl complex, terpyridine, hydroxide bridge, crystal structure.

## INTRODUCTION

In the last two decades, much attention has been paid to studies on the synthesis and characterization of actinide(III) and lanthanide(III) complexes with poly-N-dentate ligands due to their application in the reprocessing of nuclear fuel [1]. Concurrently, the chemistry of An(IV) and An(VI) with the same type of N-donor ligands was less developed despite the fact that the main components of nuclear spent fuel are uranyl and plutonium(IV) ions. The complexation of uranyl ions with 2,2′:6′,2″-terpyridine has been studied recently [2-6]. This tridentate *N*-donor ligand, shorthanded here as terpy, can provide variously organized systems with the $UO_2^{2+}$ cation. The formation of some simple complexes, *e.g.*, $[UO_2(NO_3)_2(terpy)]$ [7], $[UO_2(OTf)_2(terpy)]$, and $[UO_2(terpy)_2](OTf)_2$ [8], is favored in anhydrous organic solvents and with weakly coordinating counterions. The formation of mono- or bis-terpy species can be observed with uranyl ions. In turn, in the presence of an aqueous acidic solution, terpyridinium salts $(H_2terpy)[UO_2Cl_4]\cdot H_2O$ and $(H_2terpy)_2[UO_2Cl_4]Cl_2$ with doubly protonated terpy molecules have been obtained [2]. The interesting fact is the formation of $[\{UO_2(OH)(terpy)\}_2](OTf)_2$ due to the hydrolysis [8]. In addition, a dimeric complex $[\{UO_2(NO_3)(terpy)\}_2(\mu\text{-}O_2)]$ with a bridging peroxide ion has been isolated [6]. Taking into account the important role of f-block elements and our interest in the characterization of actinide complexes containing poly-N-dentate ligands, we report here the synthesis and crystal structure of a new cationic hydroxo-bridged uranyl compound. Only three crystal structures containing the cationic complex $[\{UO_2(OH)(terpy)\}_2]^{2+}$ with triflate or mixed nitrate and tri(nitrato)-aqua-uranyl anions as counterions have been presented to date in the Cambridge Structural Database [8, 9].

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# EXPERIMENTAL

**Materials and methods.** All chemicals were used as purchased from commercial sources. Spectra in the range 400-4000 $cm^{-1}$ at a resolution of 2 $cm^{-1}$ were recorded with a Bruker Equinox 55 FT-IR spectrometer using KBr pellets.

**Synthesis of $[\{UO_2(\mu\text{-}OH)(terpy)\}_2](ClO_4)_2\cdot0.67CH_3CN$.** The stock solution of uranyl perchlorate in acetonitrile was obtained in the following manner: uranyl nitrate hexahydrate (0.10 g, 0.19 mmol) was dissolved in 10 ml of concentrated perchloric acid (~11 M) and evaporated to dryness 3 times with the addition of 2 ml of $HClO_4$. Next, this procedure was repeated 3 times with the similar successive volumes of diluted $HClO_4$ (~0.1 M). Finally, the remaining residue was dissolved in 10 ml of acetonitrile and the concentration of uranyl ions was determined with ARSENAZO(III) [10]. Acetonitrile solution (1 ml) of terpyridine (0.02 g, 0.086 mmol) was added dropwise to the solution of uranyl ions (0.04 M) in acetonitrile (1 ml). The clear solution was stored in the dark at room temperature. After a few months light greenish crystals suitable for X-ray crystallography were obtained. Yield: ~0.007 g (~14%). Selected IR bands (KBr pellet, $cm^{-1}$): ~3400(br), 3117, 3076(br) $\nu$(CH), 1599, 1574, 1555, 1541sh, 1484, 1451, 1437, 1371, 1311, 1235, 1142sh(br), 1120, 1108, 1089, 1015, 940, 775, 653, 637, 625. ***Warning:*** *Uranium compounds are radioactive and toxic and should be treated with great caution and suitable protection for handling such substances. Perchlorate salts are potentially explosive.*

**X-ray crystallography.** X-ray diffraction data were collected at 100 K on an Agilent Technologies SuperNova (dual source) diffractometer equipped with an Eos CCD detector. A suitable crystal was mounted within a nylon loop with a help of cryoprotectant oil (paratone-N). Mirror-monochromated Mo$K_\alpha$ radiation ($\lambda$ = 0.7107 Å) from a micro-focus Nova X-ray source was used for the measurement. Data collection and reduction and the multi-scan absorption correction were performed using the CrysAlis PRO software. The structure was solved by direct methods and refined by full matrix least-squares treatment on $F^2$ data. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. The H atoms bonded to the C atoms of the aromatic rings were located in their calculated positions with C–H set at 0.95 Å and refined isotropically using a riding model with $U_{\text{iso}}$(H) set to 1.5$U_{\text{eq}}$(C). In turn, the H atoms of the OH groups were placed in a difference map and their positions were freely refined with $U_{\text{iso}}$(H) set to 1.5$U_{\text{eq}}$(O). One of the perchlorate anions ($Cl(3)O_4^-$) was disordered over two positions with the occupancy ratio refined to 0.46:0.54. In addition, the acetonitrile molecule was also disordered over two possible orientations sharing the C atom of the methyl group, with partial occupancy refined to about 0.40. The H atoms associated with the solvent molecule were not located. All calculations were performed with the SHELXTL program package [11]. The MERCURY program [12] was applied for the crystal graphics. Selected crystallographic parameters and refinement details are as follows: $C_{94}H_{72}Cl_6N_{20}O_{42}U_6$, $M$ = 3794.60, crystal symmetry is monoclinic, space group $P2_1/c$, $a$ = 10.35172(12) Å, $b$ = 37.7278(5) Å, $c$ = 14.02251(18) Å, $\beta$ = 100.0118(11)°, $V$ = 5393.06(12) $Å^3$, $Z$ = 2, $D_{\text{calc}}$ = 2.337 $g/cm^3$, $\mu$ = 9.225 $mm^{-1}$, 67068 reflections collected ($\theta_{\max}$ = 27.514°), 9461 independent, 807 parameters refined, for $I > 2\sigma(I)$ $R_1$ = 0.0292, $wR_2$ = 0.0589, $S$ = 1.294, $\Delta\rho$(max/min) = 1.561/–1.110 e/$Å^3$.

CIF file containing complete information on the studied structure has been deposited with CCDC, deposition number 1482610, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

# RESULTS AND DISCUSSION

**Description of the molecular and crystal structure.** The structure consists of dimeric $[\{UO_2(OH)(terpy)\}_2]^{2+}$ cations, perchlorate anions, and acetonitrile molecules. There are two crystallographically different dimeric units in the crystal structure (Fig. 1). One of them contains two associated asymmetric $\{UO_2(OH)(terpy)\}$ moieties (for U1 and U2), while the other is formed by an element of symmetry (the twofold axis) relating such monomers (for U3). Each uranium atom is surrounded by seven donor atoms. Two of them belong to tightly bonded oxygen atoms of the uranyl cation. There are also three nitrogen atoms from the tridentate terpy ligand and two oxygen atoms from the hydroxyl groups. The U–N bond distances are in the range of 2.542-2.576(6) Å, with the mean value of 2.560(6) Å. In turn, the $U–O_{(OH)}$ bond lengths are a bit

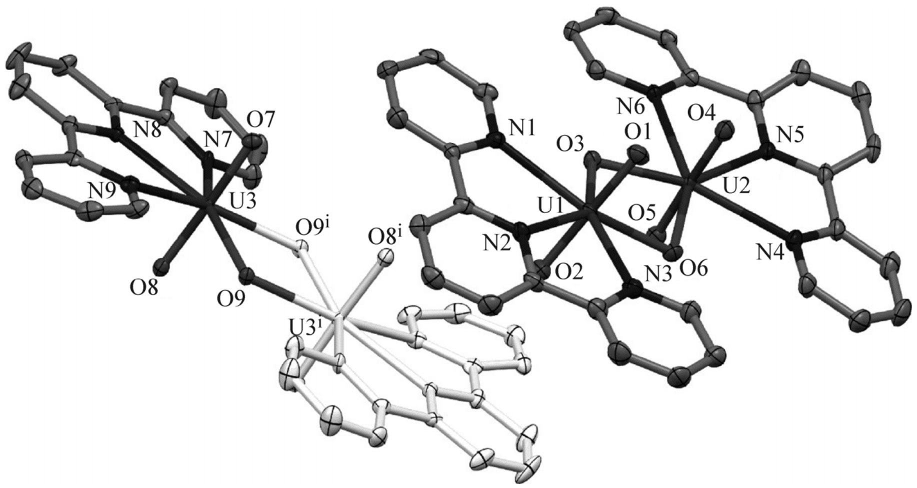

**Fig. 1.** Molecular structure of the uranyl complex with the asymmetric unit marked in dark [symmetry code: $^{i}$ $-x+2, -y+1, -z+1$]. Hydrogen atoms, perchlorate anions, and a solvent molecule are omitted for clarity. The atoms are shown as the 50% probability ellipsoids.

shorter, ranging from 2.330 Å to 2.349(5) Å (mean 2.336(5) Å). Two oxygen atoms in the $UO_2^{2+}$ units have short U=O distances with the mean value of 1.763(4) Å (range 1.756-1.769(4) Å). The geometry around the uranium atom can be described as a distorted pentagonal bipyramid (a $UO_4N_3$ motif) with the apex positions occupied by the uranyl oxygen atoms forming almost a linear O=U=O fragment (the mean angle 177.9(2)°). The remaining donor atoms lie in an almost planar pentagonal plane perpendicular to the $UO_2$ fragment. The OH anions act as bridging groups between two neighboring $UO_2$(terpy) moieties. The U–O–U angles and U···U distances within the $U_2(\mu_2\text{-OH})_2$ groups are 106.3(2)°, 107.0(2)°, and 108.3(2)°, and 3.755(1) Å and 3.788(1) Å, respectively. However, the quadrangle built up from U3, O9, U3$^i$, and O9$^i$ atoms is planar, while the one formed by U1, O3, U2, and O6 atoms is strongly distorted (U2 atom is 0.563(6) Å out of the plane formed by U1, O3 and O6 atoms). Both dimeric complex cations differ also in the O···O distances between the opposite uranyl oxygen atoms. In the first molecule, these distances are different and are 3.261(6) Å (O1···O4) and 4.360(6) Å (O2···O5), while in the second complex they are equidistant, 3.860(6) Å (O7···O8$^i$). The selected geometrical parameters are given in detail in Table 1.

All the interactions between the neighboring complex units $[\{UO_2(\mu\text{-OH})(\text{terpy})\}_2](ClO_4)$ are represented in Fig. 2. The crystal structure is stabilized by intermolecular O–H···O hydrogen bonds of 2.787(7) Å (O3–H3···O12$^{iii}$), 2.812(7) Å (O6–H6···O18$^{ii}$), and 2.915(6) Å (O9–H9A···O11$^{ii}$), involving perchlorate ions and hydroxyl groups [symmetry

**TABLE 1.** Selected Bond Lengths, Distances (Å), and Angles (deg.) According to the Labeling Scheme in Fig. 1 [Symmetry Code: $^{i}$ $-x+2, -y+1, -z+1$]

| 1st molecule | | | | 2nd molecule | |
|---|---|---|---|---|---|
| U1–O1 | 1.766(4) | U2–O4 | 1.758(4) | U3–O7 | 1.768(4) |
| U1–O2 | 1.756(4) | U2–O5 | 1.769(4) | U3–O8 | 1.761(4) |
| U1–O3 | 2.341(4) | U2–O3 | 2.330(4) | U3–O9 | 2.331(4) |
| U1–O6 | 2.349(4) | U2–O6 | 2.343(5) | U3···U3$^i$ | 3.7882(3) |
| U1–N1 | 2.552(5) | U2–N4 | 2.569(5) | O7–U3–O8 | 177.7(2) |
| U1–N2 | 2.561(5) | U2–N5 | 2.571(5) | U3–N7 | 2.565(4) |
| U1–N3 | 2.542(5) | U2–N6 | 2.576(5) | U3–N8 | 2.556(5) |
| U1···U2 | 3.7547(3) | O3···O6 | 2.737(6) | U3–N9 | 2.546(4) |
| O1–U1–O2 | 178.3(2) | O4–U2–O5 | 177.6(2) | O9···O9$^i$ | 2.736(6) |

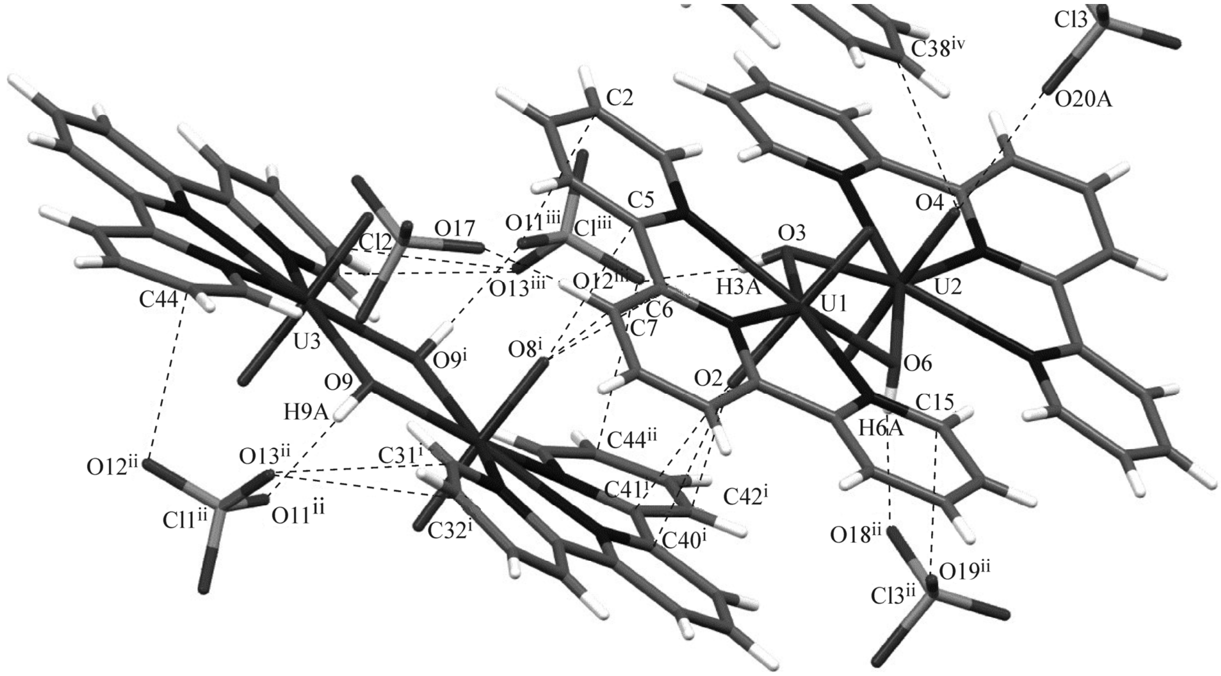

**Fig. 2.** Fragment of the crystal structure showing selected hydrogen bonds and intermolecular interactions [symmetry codes: $^{\text{i}}\,-x+2, -y+1, -z+1$; $^{\text{ii}}\,x+1, y, z$; $^{\text{iii}}\,-x+1, -y+1, -z+1$; $^{\text{iv}}\,x-1, y, z$].

codes: $^{\text{ii}}\,x+1, y, z$; $^{\text{iii}}\,-x+1, -y+1, -z+1$]. In addition, some weaker C—H···O hydrogen bonds are observed (e.g. 3.113(9) Å, C7–H7···O17 and 3.044(8) Å, C38–H38···O4). In the extended crystal lattice the molecules are held together by O···C interactions between O atoms of the uranyl moieties and aromatic rings of the adjacent molecules (3.095(7) Å, 2.953(6) Å, and 3.155(7) Å for O2···C40$^{\text{i}}$, O2···C41$^{\text{i}}$ and O2···C42$^{\text{i}}$, respectively and 2.949(6) Å, 2.958(7) Å, and 3.203(7) Å for O8$^{\text{i}}$···C5, O8$^{\text{i}}$···C6 and O8$^{\text{i}}$···C7, respectively) [symmetry code: $^{\text{i}}\,-x+2, -y+1, -z+1$]. Moreover, other O$_{(\text{ClO4})}$···C and O$_{(\text{ClO4})}$···O contacts can also be distinguished (3.00(2) Å for O19$^{\text{ii}}$···C15, 3.126(8) Å for O12$^{\text{ii}}$···C44, 3.175(7) Å for O11$^{\text{iii}}$···C2 and O13$^{\text{iii}}$···C32, 3.195(8) Å for O13$^{\text{iii}}$···C31 and 3.11(1) Å for O20A···O4).

**IR spectrum.** In the IR region the spectrum of the compound is dominated by the vibrations belonging to the terpyridine ligand. The broad band between 3100-3500 cm$^{-1}$ corresponds to the OH vibrations. The main vibrational modes

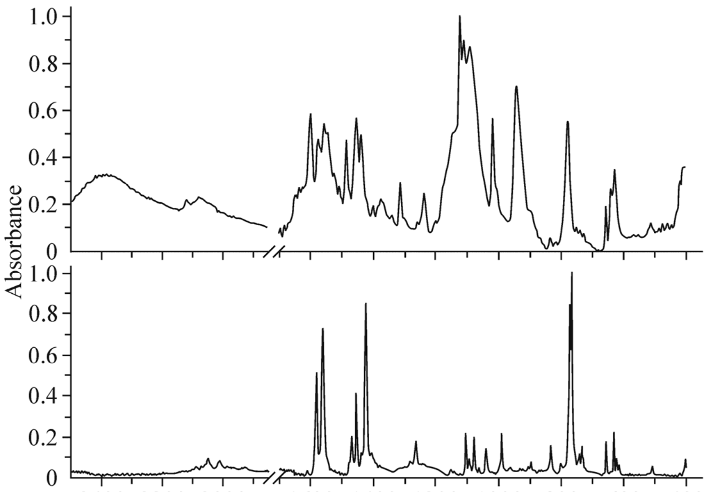

**Fig. 3.** FTIR spectra of the complex (top) and free 2,2′:6′,2″-terpyridine ligand (bottom).

derived from the $ClO_4^-$ ions are observed as overlapping bands located in the range 1030-1200 cm$^{-1}$ and a smaller band at 623 cm$^{-1}$ just as for other compounds containing this anion [13-15]. The O=U=O asymmetric stretching vibrations found at 940 cm$^{-1}$ appear at the frequencies similar to other uranyl complexes [16]. The position of this band is slightly shifted to lower frequencies in comparison to that of simple uranyl nitrates [12]. This tendency was previously found for uranyl ions in its hydro complexes and other coordination complexes [12, 17].

## CONCLUSIONS

A new compound containing $UO_2^{2+}$ cations and 2,2′:6′,2″-terpyridine has been synthesized from uranyl perchlorate and terpy in an acetonitrile solution. In this case, a hydroxo-bridged dimeric complex $[\{UO_2(OH)(terpy)\}_2]^{2+}$ has been found in the reaction mixture. The coordination polyhedron around metal centers is a distorted pentagonal bipyramid. The bond lengths around the uranium atoms increase in the order $U{=}O < U{-}O_{(OH)} < U{-}N$.

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