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Actinide Polyoxometalates: Incorporation of Uranyl–Peroxo in U-Shaped 36-Tungsto-8-Phosphate

Sib Sankar Mal, Michael H. Dickman, and Ulrich Kortz*[a]

Dedicated to Professor Michael T. Pope on the occasion of his 75th birthday

The synthesis and reactivity of polyoxometalates (POMs) are of current interest owing to their enormous range of shape, size, composition, acid–base, and redox properties, as well as potential applications in catalysis, medicine, photochemistry, and materials science.[1] One possible application involves the use of lanthanide and actinide complexes in the sequestration and storage of radioactive waste.[2] In addition, lanthanides and actinides are of interest in recent POM chemistry because of their larger flexible coordination numbers compared with 3d transition metals, including pentagonal-bipyramidal seven-coordination and hexagonal-bipyramidal eight-coordination.[3] Furthermore, uranium binds two axial oxygen atoms to form the linear uranyl species (UO_2^{2+}) in its +6 oxidation state. The uranyl ion exhibits good stability and forms complexes with various oxygen-donor, nitrogen-donor, and sulfur-donor ligands.[4] Finally, the uranyl ion has a rich structural chemistry and attractive magnetic and electrochemical properties, which could lead to the development of new functional compounds.

In 2003, O'Hare et al. reported uranyl phosphonate derivatives,[5] and in 2005 Evans et al. reported octa-uranium rings with alternating nitride and azide bridges $[\{(C_5Me_5)_2U(\mu\text{-}N)U(\mu\text{-}N_3)(C_5Me_5)_2\}_4]$.[6] In particular, Thuéry's group has been quite active in this area, reporting several reduced and mixed-valence organouranium compounds.[7]

We are currently investigating the structural and catalytic properties of peroxo complexes.[8] The uranium–peroxo system is also of interest for uranium separation chemistry.[9] Despite the importance of uranium–peroxide complexes, relatively little is known about their structure and stability. In the early 1960s, Gurevich and co-workers isolated uranium–peroxide compounds from alkaline solutions but structures were not reported for these materials.[10] Until recently the only inorganic uranium–peroxide reported was $Na_4[UO_2(O_2)_3]\cdot 9H_2O$,[11] but since 2005 Burns and co-workers have prepared several interesting examples.[12]

There are few well-characterized POMs containing uranium(VI) as an addenda element. In 1999, Pope and co-workers reported the first sandwich-type uranium–POM complex $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$[13] and subsequently, they have prepared several uranium-containing Keggin and Wells–Dawson polyanions: $[Na_2(UO_2)(GeW_9O_{34})_2]^{14-}$, $[\{Na(H_2O)\}_4(UO_2)_4(SiW_{10}O_{34})_4]^{22-}$, $[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]^{15-}$, $[(UO_2)_3(H_2O)_5As_3W_{29}O_{104}]^{19-}$, $[(UO_2)_{12}(\mu_3\text{-}O)_4(\mu_2\text{-}H_2O)_{12}(P_2W_{15}O_{56})_4]^{32-}$, $[(UO_2)_2(H_2O)_2(SbW_9O_{33})_2]^{14-}$, $[(UO_2)_2(H_2O)_2(TeW_9O_{33})_2]^{12-}$, and $[Na_2As_2W_{18}U_2O_{72}]^{12-}$.[14] Recently, Xiaohong Wang and co-workers reported the uranium-containing tungstogermanates $[A\text{-}\alpha\text{-}Na_2(UO_2)_2(GeW_9O_{34})_2]^{14-}$ and $[A\text{-}\beta\text{-}Na_2(UO_2)_2(GeW_9O_{34})_2]^{14-}$,[15] and in 2008 Alizadeh et al. reported the uranium-substituted tungstobismuthate(III) $[Na(UO_2)_2(H_2O)_4(BiW_9O_{33})_2]^{13-}$,[16] but none of these uranium-substituted POM complexes contain peroxo linkages.

Our group has been interested in the interaction of 3d and 4d transition-metal ions, lanthanides, and actinides with Tézé's lacunary, wheel-shaped 48-tungsto-8-phosphate $[H_7P_8W_{48}O_{184}]^{33-}$ (**P_8W_{48}**) and its half unit $[H_6P_4W_{24}O_{94}]^{18-}$ (**P_4W_{24}**) for some time.[17] Pope's group prepared the first lanthanide derivative $\{Ln_4(H_2O)_{28}[K\subset P_8W_{48}O_{184}(H_2O)_{28}[K\subset P_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}]^{13-}\}_x$ (Ln = La, Ce, Pr, Nd),[18] and our group reported the first transition-metal and organoruthenium derivatives, $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$,[19] $[\{K(H_2O)\}_3\{Ru(p\text{-cymene})(H_2O)\}_4P_8W_{49}O_{186}(H_2O)_2]^{27-}$,[20] and $[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{20-}$.[21] Mialane and co-workers isolated the Cu_{20}-azide derivative $[P_8W_{48}O_{184}Cu_{20}(N_3)_6(OH)_{18}]^{24-}$,[22] and Mül-

[a] S. S. Mal, Dr. M. H. Dickman, Prof. U. Kortz
Jacobs University, School of Engineering and Science
P.O. Box 750 561, 28725 Bremen (Germany)
Fax: (+49) 421-200-3229
Homepage: http://www.jacobs-university.de/schools/ses/ukortz/
E-mail: u.kortz@jacobs-university.de

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ler's group prepared the mixed-valence dodecavanadium cluster $[K_8\subset\{P_8W_{48}O_{184}\}\{V^V_4V^{IV}_2O_{12}(H_2O)_2\}_2]^{24-}$.[23]

Although the 24-tungsto-4-phosphate $\mathbf{P_4W_{24}}$ has been known since 1985,[17] its reactivity towards electrophiles in aqueous solution has remained pretty much unexplored. In 2006, our group reported the dimethyltin complex $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$ by using $\mathbf{P_4W_{24}}$ as a precursor.[24] This was the first structural evidence for the elusive $\mathbf{P_4W_{24}}$ and at the same time the first evidence for a lacunary Preyssler ion. To our knowledge, no other structural reports using the $\mathbf{P_4W_{24}}$ precursor have been reported.

Here we present the uranyl–peroxo containing 36-tungsto-8-phosphate $[Li(H_2O)K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6W_{36}O_{136}]^{25-}$ (**1**; Figure 1). In contrast with the various complexes mentioned above, only three "P_2W_{12}" units combine in **1** to form a gapped ring encircling the central U_8–peroxo moiety. This is the first time that such a U-shaped "$(P_2W_{12})_3$" assembly has been seen. Polyanion **1** was synthesized by reaction of the $[H_6P_4W_{24}O_{94}]^{18-}$ ($\mathbf{P_4W_{24}}$) precursor with UO_2^{2+} ions in a 1:3 ratio in aqueous medium at pH 4.0. The polyanion was crystallized as a mixed potassium–lithium salt in the monoclinic space group $P2_1/n$.[25] The compound $K_6Li_{19}[Li(H_2O)K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6W_{36}O_{136}]\cdot 74\,H_2O$ (**1a**) has been fully characterized in the solid state by single-crystal X-ray diffraction, thermogravimetric analysis/differential scanning colorimetry (TGA/DSC), IR spectroscopy, and elemental analysis, as well as in solution by ^{31}P NMR spectroscopy. Interestingly, **1** cannot be obtained by using $\mathbf{P_2W_{12}}$ as the reagent instead of $\mathbf{P_4W_{24}}$. Polyanion **1** is composed of three units of $\mathbf{P_2W_{12}}$ fused via the respective caps and two dangling phosphates, which hang outside of the polyanion where a fourth unit of $\mathbf{P_2W_{12}}$ would be placed in $\mathbf{P_8W_{48}}$ (see Figure 1). There are also four potassium ions inside the anion, which connect the two independent, neutral $[(UO_2)(O_2)]_4$ units. The third $\mathbf{P_2W_{12}}$ unit and two dangling phosphate groups are apparently formed in situ by decomposition of some $\mathbf{P_4W_{24}}$ precursor. The cavity of the newly generated polyanion "P_6W_{36}" is filled by two symmetrical uranium–peroxo clusters. This type of uranium cluster has been seen once before with the 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethnoanthacene organic ligand,[26] but this is the first report of a uranium–peroxo cluster coordinated with an inorganic nucleophile.

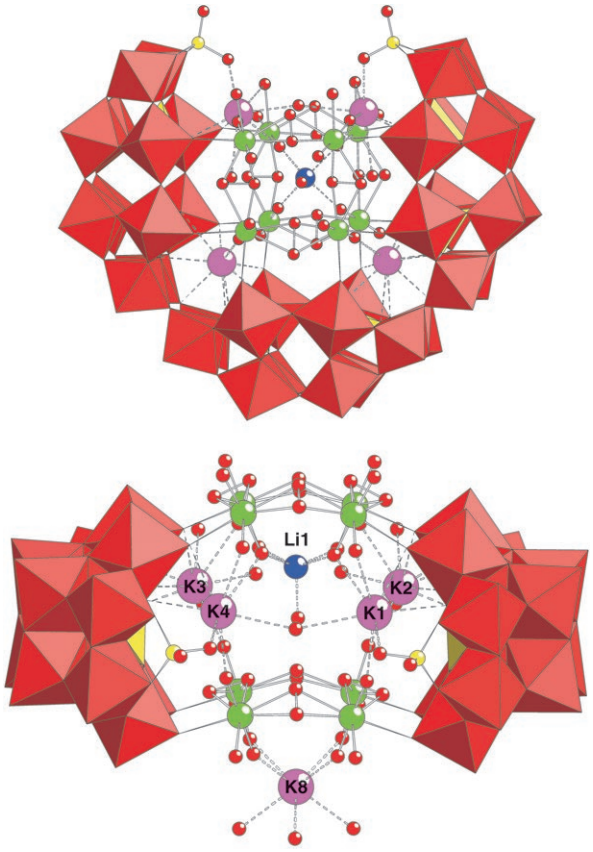

Figure 1. Combined polyhedral/ball-and-stick representations of **1**. The side view (top) shows the U-shaped "P_6W_{36}" POM ligand into which the two neutral $[(UO_2)(O_2)]_4$ units are incorporated. The top-down view (bottom) from the "open" side of **1** (with the central "P_2W_{12}" POM fragment in the back removed for clarity) highlights that the two uranyl–peroxo clusters are 1) connected via four potassium ions (K1, K2, K3, K4) and 2) displaced towards one side of the "P_6W_{36}" POM. The concave surface of the "outer" $[(UO_2)(O_2)]_4$ unit is capped by the square-pyramidal Li1, whereas the "inner" $[(UO_2)(O_2)]_4$ unit is capped by the seven-coordinate K8. Color code: WO_6 octahedra: red; PO_4 tetrahedra: yellow; U: green; P: yellow; K: pink; Li: blue; O: red.

The central coordination complex inside **1** comprises eight uranyl–peroxo units divided into two $[(UO_2)(O_2)]_4$ squares, the μ_2-peroxo ions being bound at right angles to each pair of uranium atoms. The uranium ions in **1** are all eight-coordinate. The two $[(UO_2)(O_2)]_4$ squares (U1, U3, U5, U7 and U2, U4, U6, U8) are displaced toward one end (the "top") of the $\mathbf{P_6W_{36}}$ unit (see Figures 1 and 2). The square composed of U1, U3, U5, and U7 is placed slightly above the ring at about 4.5 Å from the middle of the anion, and the other (U2, U4, U6, U8) square is inside the "bottom" of the anion at about 3.0 Å from the center (the mean plane of the eight P atoms). As a result, the two uranium–peroxo clusters encapsulated by the "P_6W_{36}" framework somewhat resemble satellite dishes that are 1) connected via four potassium ions (K1, K2, K3, K4) and 2) capped by a lithium ion (Li1) or a potassium ion (K8). The potassium ions K1 and K4 are connected via a bridging water ligand.

The four K^+ (K1, K2, K3, and K4) ions inside the anion are also displaced toward the top by about 1 Å from the mean plane of the eight P atoms. Each uranium atom has two *trans*-oxo atoms with bond lengths ranging from 1.73(2) to 1.83(2) Å. The four uranyl oxo atoms pointing into the anion from U1, U3, U5, and U7 are coordinated to an atom interpretable as a square-pyramidal Li (Li–O distances ranging from 1.95(6) to 2.20(6) Å) with an apical water pointing toward the center of the anion (see Figure 1). Finding a lithium atom in a polytungstate is unusual given that the electron density of the W atoms generally obscures them, but in this case the Li atom is held in the middle of the anion and the position is well defined compared with cations outside.

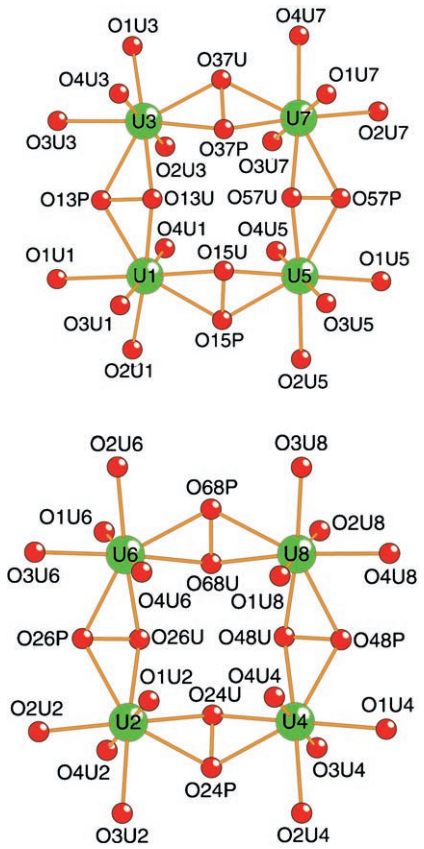

Figure 2. Ball-and-stick representation of the two uranium–peroxo squares in **1**. The upper $[(UO_2)(O_2)]_4$ is located at the "top" of **1** (i.e., capped by Li1), whereas the lower $[(UO_2)(O_2)]_4$ is located at the "bottom" of **1** (i.e., capped by K8). The color code is the same as in Figure 1.

The oxo atoms of U2, U4, U6, and U8, which point below the anion are coordinated to K8. Each uranium atom is also coordinated to four peroxo oxygen atoms. The U–O_2^{2-} bond lengths range from 2.28(4) to 2.42(3) Å. The bond lengths within the peroxo group, O–O, range from 1.44(2) to 1.53(2) Å. These values are virtually identical with the side-on peroxo bridges (O–O 1.50(3) to 1.55(3) Å) in our very recently reported Zr_6/Hf_6–peroxo polyanions.[12]

The two remaining oxygen atoms of U5 (O2U5, O1U5), U6 (O2U6, O3U6), U7 (O2U7, O4U7), and U8 (O3U8, O4U8) bridge to tungsten atoms. For U1, U2, U3, and U4, one remaining coordination site is occupied by a water molecule and the other oxygen bridges to the polyanion (see Figures 1 and 2). All four water molecules (O1U1, O3U2, O3U3, and O2U4) in **1** point towards the gap in the U-shaped structure. The width of the anion is about 24 Å using the van der Waals radii. The width of the $[(UO_2)(O_2)]_4$ cluster is about 11 Å, which is smaller than for the $\{Cu_{20}(OH)_{24}\}^{16+}$ cluster (16 Å) in $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$ and the $\{Fe_{16}(OH)_{28}(H_2O)_4\}^{20+}$ cluster (14 Å) in $[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{20-}$. Perhaps steric constraints allow only three units of $\mathbf{P_2W_{12}}$ to combine rather than the usual four units. The average distances between the U atoms within the $[(UO_2)(O_2)]_4$ units are 4.14(6) and 4.19(7) Å (and 7.329(2) Å between the squares). In contrast, for Thuery's complex the longest edge is 10.02 Å between the two $[(UO_2)(O_2)]_4$ squares, whereas the distances between the U atoms in the square for Thuery's complex are the same as in the present compound (4.14 Å).

To complement our solid-state X-ray diffraction results on **1** with solution studies, we performed room-temperature ^{183}W and ^{31}P NMR spectroscopy on **1a** redissolved in 1 M CH_3COOLi/CH_3COOH at pH 4.0. We were unable to obtain a decent ^{183}W spectrum, but the ^{31}P spectrum exhibited five signals ($\delta = 2.2$, 0.5, −6.4, −6.7, −7.9 ppm) with approximate relative intensities 1:1:2:2:2 (Figure 3), instead of

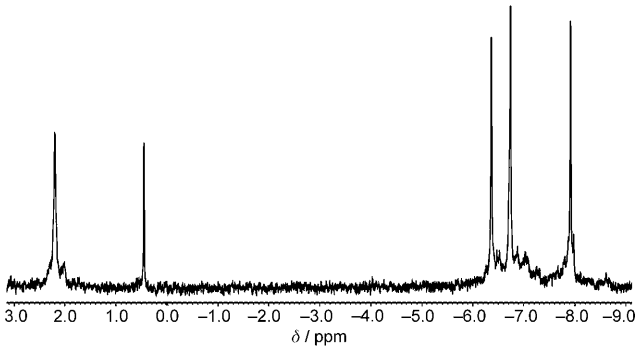

Figure 3. Room-temperature ^{31}P NMR spectrum of **1a** redissolved in 1 M CH_3COOLi/CH_3COOH at pH 4.0.

the expected four peaks with intensity ratios 1:1:1:1. The three upfield peaks at $\delta = -6.4$, −6.7, and −7.9 ppm are attributed to the three nonequivalent pairs of phosphate hetero groups. The peak at $\delta = 2.2$ ppm also exhibits poorly resolved, but visible satellites, indicating coupling (P–O(W)) to the two neighboring tungsten centers. Therefore, we assign this signal to the two dangling phosphate groups that actually appear to be in equilibrium with "free" phosphate as seen by the singlet (without any satellites) at $\delta = 0.5$ ppm. Indeed, addition of extra phosphate to the solution results in an increase of the signal at $\delta = 0.5$ ppm. The exchange of "free" and "bound" phosphate in **1** is slow on the NMR timescale.

The two phosphate caps in **1** are bound via only two P–O(W) bridges each to the "P_6W_{36}" fragment (P–O(W) 1.53–1.57(2) Å). The two remaining oxygen atoms are terminal, and bond valence sum (BVS) calculations[27] indicate that one of them (O1P7/O1P8) is actually a hydroxo group (P–O(H) 1.56-1.57(3) Å). This hydroxo group is stabilized by a long interaction to K1/K4 (~2.8 Å). The remaining terminal PO_4 oxygen atom is non-protonated (P–O 1.47(3) Å) and points away from the polyanion ligand.

We also performed TGA measurements on **1a** from room temperature to 900 °C to confirm the number of crystal waters derived from elemental analysis (see Figure S1 in the Supporting Information).

In summary, we have isolated a uranium–peroxo derivative of the hitherto unknown "P_6W_{36}" Wells–Dawson ion. The title POM $[Li(H_2O)K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2$-

$(PO_3OH)_2P_6W_{36}O_{136}]^{25-}$ (**1**) was synthesized by using the poorly investigated precursor $[H_6P_4W_{24}O_{94}]^{18-}$ ($\mathbf{P_4W_{24}}$). Hence this work demonstrates that novel lacunary polytungstate ligands can be stabilized by exotic coordination complex templates. In future work we plan to examine the acid–base and redox properties of **1** in more detail, including electrochemistry and homogeneous oxidation catalysis studies with the green oxidant H_2O_2.

Experimental Section

Preparation of $K_6Li_{19}[Li(H_2O)K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6W_{36}O_{136}]\cdot 74H_2O$ (1a): A sample of $UO_2(NO_3)_2\cdot 7H_2O$ (0.042 g. 0.083 mmol) was dissolved in 1 M CH_3COOLi/CH_3COOH buffer (20 mL) at pH 4.0, followed by addition of $K_{16}Li_2[H_6P_4W_{24}O_{94}]\cdot 33H_2O$ (0.181 g, 0.025 mmol; synthesized according to Contant and Tézé)[17] and, after complete dissolution, 4–6 drops of 30% H_2O_2 were added. This solution was heated to 50 °C for 1 h, and filtered hot. Then the filtrate was layered with 1 M NH_4Cl solution (ca. 1 mL), and allowed to evaporate in an open vial at room temperature. After about one week a yellow, crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the solid product, which was filtered off and air-dried. Yield: 0.044 g (32%, based on uranium). IR: $\tilde{\nu}$= 1138(s), 1089(s), 1025(s), 986(sh), 955(sh), 928(s), 870(sh), 843(w), 770(s), 667(w), 572(w), 530(w), 462(w) cm^{-1} (see also Figure S2 in the Supporting Information); elemental analysis calcd (%) for **1a**: K 2.9, Li 1.0, W 48.7, P 1.8, U 14.0; found: K 2.8, Li 1.1, W 47.0, P 1.7, U 13.8.

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Keywords: NMR spectroscopy · peroxo ligands · polyoxometalates · structure elucidation · tungsten · uranium

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[25] Crystal data for $K_6Li_{19}[Li(H_2O)K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6W_{36}O_{136}]\cdot 74H_2O$ (**1a**): A yellow rod of **1a** with dimensions $0.27\times0.03\times0.03\ mm^3$ was mounted in a Hampton cryoloop for indexing and intensity data collection at 173 K on a Bruker D8 APEX II CCD single-crystal diffractometer using $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). Of the 507786 reflections collected ($2\theta_{max}=49.78°$, 99.4% complete), 42978 were unique ($R_{int}=0.2858$) and 22961 reflections were considered observed ($I>2\sigma(I)$). Routine Lorentz and polarization corrections were applied and an absorption correction was performed by using the SADABS program (Sheldrick, G. M.; Siemens Analytical X-ray Instrument Division: Madison, WI, 1995). Direct methods were used to locate the tungsten and uranium atoms (SHELXS-97). Then the remaining atoms were found from successive Fourier maps (SHELXL-97). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (W, U, P, and K atoms) and isotropic thermal parameters (O and Li atoms) converged at $R=0.0806$ ($I>2\sigma(I)$) and $R_w=0.1966$ (all data). In the final difference map the deepest hole was $-3.61\ e\,Å^{-3}$ (1.03 Å from U6) and the highest peak $5.01\ e\,Å^{-3}$ (0.09 Å from U7). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-419629.

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