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$[Hg_5O_2(OH)_4][(UO_2)_2(AsO_4)_2]$: A complex mercury(II) uranyl arsenate

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ABSTRACT

Under mild hydrothermal conditions $UO_2(NO_3)_2 \cdot 6H_2O$, $Hg_2(NO_3)_2 \cdot 2H_2O$, and $Na_2HAsO_4 \cdot 7H_2O$ react to form $[Hg_5O_2(OH)_4][(UO_2)_2(AsO_4)_2]$ **(HgUAs-1)**. Single crystal X-ray diffraction experiments reveal that **HgUAs-1** possesses a pseudo-layered structure consisting of two types of layers: ${}^{2}_{\infty}[Hg_5O_2(OH)_4]^{2+}$ and ${}^{2}_{\infty}[(UO_2)_2(AsO_4)_2]^{2-}$. The ${}^{2}_{\infty}[Hg_5O_2(OH)_4]^{2+}$ layers are complex, and contain three crystallographically unique Hg centers. The coordination environments and bond–valence sum calculations indicate that the Hg centers are divalent. The ${}^{2}_{\infty}[(UO_2)_2(AsO_4)_2]^{2-}$ layers belong to the Johannite topological family. The ${}^{2}_{\infty}[Hg_5O_2(OH)_4]^{2+}$ and ${}^{2}_{\infty}[(UO_2)_2(AsO_4)_2]^{2-}$ layers are linked to each other through μ_2-O bridges that include $Hg \cdots O=U=O$ interactions.

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1. Introduction

Uranyl arsenates display remarkably rich crystal chemistry that can be attributed in part to the structural versatility of U(VI), which generally occurs as tetragonal, pentagonal, and hexagonal bipyramids [1–8]. The formation of extended structures containing uranyl polyhedra usually arises only through the equatorial positions owing to the terminal nature of the apical positions, which typically yields two-dimensional structures [9]. There are some recent examples of interactions between uranyl cations that make use of the apical oxygen atoms, but these are exceedingly rare [10,11].

Of late there has been interest in expanding structural diversity and physico-chemical properties of uranyl phosphates and arsenates through the incorporation of main group elements and transition metals [12–14]. One possibility is that the second metal center could display mixed-valence on a stoichiometric level, but this has yet to be observed in compounds in this class. However, the occurrence of this feature might lead to versatile functional materials with atypical magnetic behavior [15,16]. An unusual and understudied choice for a metal that might display this behavior is mercury. Only a few crystal structures of synthetic Hg(I) compounds have been reported (e.g. $(Hg_2)_2(OH)(NO_3)_3$ and $(Hg_2)_5(OH)_4(NO_3)_6$) [17,18], several Hg(I) minerals are also known [19,20]. The mixed-valence compounds $Hg_4O_2(NO_3)_2$, $Hg^{I}_2(OH)(NO_3) \cdot Hg^{II}O$, and $(Hg_2)Hg(OH)_2(ClO_4)_2$ have also been structurally characterized [21,22]. Hg^{I} compounds typically contain $[Hg_2]^{2+}$ units that possess a Hg–Hg single bond with a bong length of approximate 2.53 Å [23], which allows one to partially distinguish Hg(I) from Hg(II) compounds [23]. Some of these aforementioned structural features have been combined into a single compound, namely $[Hg_5O_2(OH)_4][(UO_2)_2(AsO_4)_2]$ (**HgUAs-1**), which is discussed in this work.

2. Experimental

Synthesis: $UO_2(NO_3)_2 \cdot 6H_2O$ (98%, Alfa Aesar), $Hg_2(NO_3)_2 \cdot 2H_2O$ (98.5%, Baker), $Na_2HAsO_4 \cdot 7H_2O$ (99.9%, Baker), and $(CH_3)_4NCl$ (97%, Aldrich), were used as received. Reactions were carried out in PTFE-lined Parr 4749 autoclaves with a 23 mL internal volume. Distilled and millipore filtered water with a resistance of 18.2 MΩ cm was used in the reactions. Standard precautions were performed for handling radioactive materials during work with $UO_2(NO_3)_2 \cdot 6H_2O$ and the products of the reactions. Semi-quantitative EDX analysis was performed using a JEOL 7000F.

$[Hg_5O_2(OH)_4][(UO_2)_2(AsO_4)_2]$ (**HgUAs-1**). $UO_2(NO_3)_2 \cdot 6H_2O$ (0.194 g, 0.388 mmol), $Na_2HAsO_4 \cdot 7H_2O$ (0.0612 g, 0.196 mmol), $Hg_2(NO_3)_2 \cdot 2H_2O$ (0.220 g, 0.695 mmol), $(CH_3)_4NCl$ (0.0215 g, 0.196 mmol), and 2 mL of water were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 200 °C in a box furnace for three days. The autoclave was then cooled at an average rate of 9 °C/h to 35 °C. Initial pH = 1.63 and ending pH = 1.95. Yellow blocks of **HgUAs-1** were recovered and thoroughly washed with water, then rinsed with methanol, and

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allowed to dry. Yield: 146 mg, 19.4% based on uranium. EDX analysis confirmed the presence of Hg, U, and As in the crystals.

Crystallographic studies: A single crystal of **HgUAs-1** was mounted on a thin glass fiber and optically aligned on a Bruker APEX CCD X-ray diffractometer using a digital camera. Initial intensity measurements were performed using graphite monochromated Mo*K*α ($\lambda = 0.71073$ Å) radiation from a sealed tube and monocapillary collimator. SMART (v 5.624) was used for preliminary determination of the cell constants and data collection control. The intensities of reflections of a sphere were collected by a combination of three sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 30 s.

For **HgUAs-1**, determination of integrated intensities and global refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame integration algorithm. A face-indexed numerical absorption correction was initially applied using XPREP, where individual shells of unmerged data were corrected [24]. The absorption coefficient of this compound is very large, and the moderate residuals are probably the result of a somewhat inadequate absorption correction. These files were subsequently treated with a semi-empirical absorption correction by SADABS [25]. The program suite SHELXTL (v 6.12) was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [24]. The final refinement included anisotropic displacement parameters for all atoms. Some crystallographic details are given in Table 1. Additional details can be found in the Supporting information.

Raman spectroscopy: The Raman spectrum of **HgUAs-1** was acquired from a single crystal using a Renishaw inVia Confocal Raman microscope with a 514 nm Ar$^+$ laser.

Fluorescence spectroscopy: The fluorescence spectrum of **HgUAs-1** was acquired using a PI Acton spectrometer (SpectraPro SP 2356, Acton, NJ) that is connected to the side port of an epi-fluorescence microscope (Nikon TE-2000U, Japan). The emission signal was recorded by a back-illuminated digital CCD camera (PI Acton PIXIS:400B, Acton, NJ) operated by a PC. For all the three compounds examined, the excitation was generated by a mercury lamp (X-Cite 120, EXFO, Ontario, Canada) filtered by a band-pass filter at 450–490 nm. The emission signal was filtered by a long-pass filter with a cutoff wavelength of 515 nm.

Table 1
Crystallographic data for $[\mathrm{Hg_5O_2(OH)_4}][(\mathrm{UO_2})_2(\mathrm{AsO_4})_2]$ (**HgUAs–1**).

Compound	$[\mathrm{Hg_5O_2(OH)_4}][(\mathrm{UO_2})_2(\mathrm{AsO_4})_2]$
Formula mass	1923
Color and habit	Yellow, block
Space group	$P\bar{1}$
a (Å)	6.8229(5)
b (Å)	6.8795(5)
c (Å)	9.5959(6)
α (deg)	109.456(1)
β (deg)	104.834(1)
γ (deg)	93.867(1)
V (Å^3)	404.74(5)
Z	1
T (K)	193
λ (Å)	0.71073
Maximum 2θ (deg)	28.30
ρ_{calcd} (g cm^{-3})	7.864
μ (Mo$K\alpha$) (cm^{-1})	713.12
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$$^{\mathrm{a}}$	0.0555
$R_w(F_o^2)$$^{\mathrm{b}}$	0.1349

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$.

3. Results and discussion

Structure of $[\mathrm{Hg_5O_2(OH)_4}][(\mathrm{UO_2})_2(\mathrm{AsO_4})_2]$ (HgUAs-1): **HgUAs-1** possesses a pseudo-layered structure with ${}^{2}_{\infty}[\mathrm{Hg_5O_2(OH)_4}]^{2+}$ and ${}^{2}_{\infty}[(\mathrm{UO_2})_2(\mathrm{AsO_4})_2]^{2-}$ layers. The latter layers consist of $\mathrm{UO_7}$ pentagonal bipyramids that are linked into edge-sharing dimers that are joined together by $\mathrm{AsO_4^{3-}}$ tetrahedra. The former layers formulated as ${}^{2}_{\infty}[\mathrm{Hg_5O_2(OH)_4}]^{2+}$ consists of three crystallographically unique mercury centers and a mixture of oxo and hydroxo groups. As shown in Fig. 1, the compact three-dimensional structure is constructed by the joining of these layers by bridging oxo atoms, which provide linkages for As(1)···Hg(3), Hg(2)···U(1), As(1)···Hg(3), and U(1)···Hg(3). Fig. 2 shows the interactions of the $\mathrm{UO_2^{2+}}$ cations and Hg(1) that provides one method for interconnecting the layers. Previous reports show that the apical (uranyl) vertices of the uranyl bipyramids can be shared with polyhedra containing higher-valence cations, even though this would over-bond the oxygen position [13]. However, long uranyl oxo interactions with interlayer cations are well

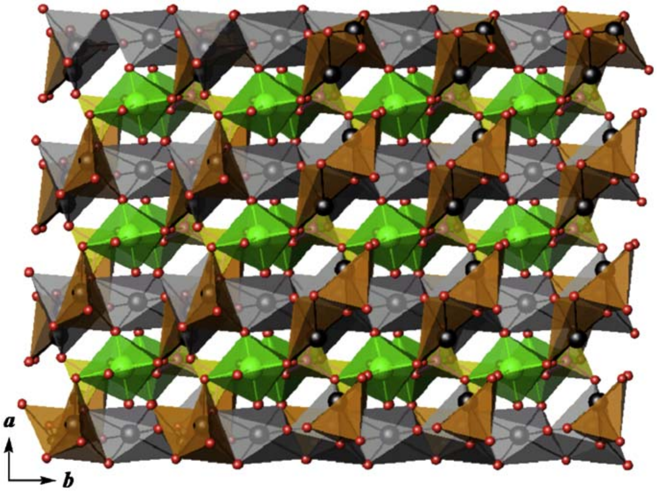

Fig. 1. A view of the three-dimensional structure of $[\mathrm{Hg_5O_2(OH)_4}][(\mathrm{UO_2})_2(\mathrm{AsO_4})_2]$ (**HgUAs-1**). $\mathrm{UO_7}$ pentagonal bipyramids are shown in green, Hg polyhedra are shown in gray and brown. $\mathrm{AsO_4}$ tetrahedra are shown in yellow. [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

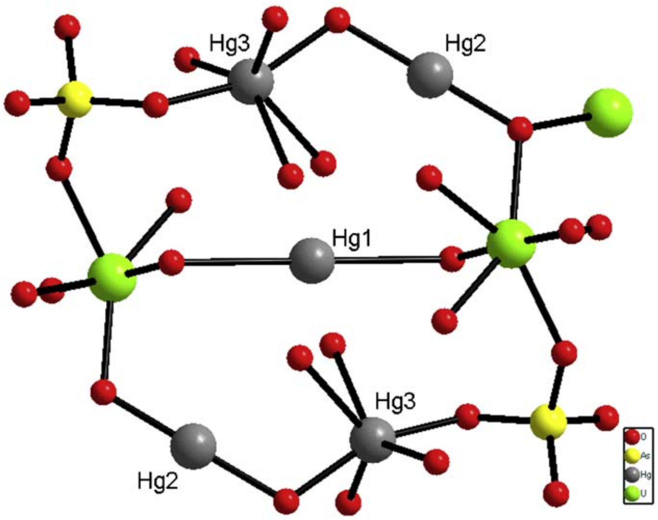

Fig. 2. A depiction of the coordination environments for mercury in $[\mathrm{Hg_5O_2(OH)_4}][(\mathrm{UO_2})_2(\mathrm{AsO_4})_2]$ (**HgUAs-1**).

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