

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Syntheses

**Caution!**  $^{239}\text{Pu}$  is a high specific activity  $\alpha$ -emitting radionuclide. Research with this radionuclide should only be undertaken in a radiological or nuclear facility with the appropriate implementation of controls for the safe handling and manipulation of radioactive materials.

Synthesis of  $\text{Na}_{8.5}\text{H}_{1.5}[\text{A-GeW}_9\text{O}_{34}]\cdot 20\text{H}_2\text{O}$  was undertaken in accordance with the literature method. Single crystal X-ray diffraction indicated that the sample would contain 10 %  $\alpha$  and 90 %  $\beta$  isomers.<sup>1</sup>

Preparation of a  $\text{Pu}^{\text{VI}}$  (Pu-239) stock in dilute HCl. In a typical preparation 0.468 mL of a 0.268 mol L<sup>-1</sup>  $\text{Pu}^{\text{IV}}$  stock in concentrated HCl was added to 0.5 mL of 2 mol L<sup>-1</sup> HCl (primarily to increase the solution volume). Ozone was then bubbled through the solution overnight resulting in a colour change from orange to brown.  $\text{NH}_4\text{OH}$  (conc. and 10 %) was then added to increase the pH to 7 yielding a brown suspension of residual  $\text{Pu}^{\text{IV}}$ , now present as hydroxides. Ozone was then bubbled through this suspension for 2 h to yield a clear orange/brown solution. An assay of this solution (10  $\mu\text{L}$  added to 1 mL 1 mol L<sup>-1</sup>  $\text{HClO}_4$ ) revealed the presence of peaks attributable only to  $\text{Pu}^{\text{VI}}$  in perchloric acid.<sup>2</sup> The pH was again raised to 7 through the addition of  $\text{NH}_4\text{OH}$  and then  $\text{CO}_2$  was bubbled through the pH neutral solution to yield a pale pink precipitate of hydrated  $\text{PuO}_2\text{CO}_3$ . The suspension was centrifuged and the supernatant removed. The pale pink pellet of  $\text{PuO}_2\text{CO}_3$  was then washed with  $2 \times 1$  mL  $\text{H}_2\text{O}$  before the solid product was dissolved in 6 mL of 0.1 mol L<sup>-1</sup> HCl to yield a pale orange/pink solution.

Preparation of Diffraction quality crystals of  $\text{K}_{11}[\text{K}_3(\text{PuO}_2)_3(\text{GeW}_9\text{O}_{34})_2]\cdot 12\text{H}_2\text{O}$ .

0.7 mL of  $\{\text{PuO}_2\}^{2+}$  stock (2.6 mg,  $1.1 \times 10^{-2}$  mmol Pu) in dilute HCl were added to solid  $\text{Na}_{8.5}\text{H}_{1.5}[\text{GeW}_9\text{O}_{34}]\cdot 20\text{H}_2\text{O}$  (55 mg,  $1.9 \times 10^{-2}$  mmol) to yield a cloudy yellow solution which was clarified through the addition of 30  $\mu\text{L}$  2 mol L<sup>-1</sup> HCl. The significantly clearer solution was then filtered to yield a pale yellow filtrate (pH 4.13). 20  $\mu\text{L}$  of 1 mol L<sup>-1</sup> NaOH was added to yield a pH 7.17 solution with a more intense lemon yellow colour. 32.7 mg of NaCl was then added to the solution which was left vapour diffuse with EtOH. After 4 days a light yellow microcrystalline precipitate had formed under a now colourless solution. Addition of HCl (0.1 and 2 mol L<sup>-1</sup>) led to the dissolution of this precipitate, yielding a slightly cloudy solution, which became more cloudy on the addition of a further portion of  $\text{Na}_{8.5}\text{H}_{1.5}[\text{GeW}_9\text{O}_{34}]\cdot 20\text{H}_2\text{O}$  (55 mg,  $1.9 \times 10^{-2}$  mmol) and KCl (41 mg). Addition of NaOH (0.1 and 1 mol L<sup>-1</sup>) above pH 7 led to the almost quantitative precipitation of a yellow solid. The supernatant, containing excess salt, was removed and the solid dissolved in the minimum amount of distilled  $\text{H}_2\text{O}$ . Vapour diffusion with MeCN yielded diffraction quality lemon yellow crystals of the title compound after a couple of days.

In the course of experimental refinement it was found that raising the pH above 8 aided complexation and that the addition of NaCl was not required. In addition, if proportionally less ligand and KCl are added then the reaction can proceed without any precipitation and redissolution of the product prior to crystallization. A yield of 45 % could be obtained (based on an initial mass of 7.9 mg Pu) but in practice the reaction is near quantitative, the low yield a result of both the small scale of reaction and added complexity of manipulations encountered when working with Pu-239.

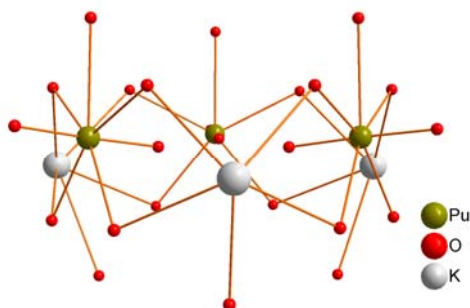
1. X. Cao, H. Naruke and T. Yamase, *Acta Cryst.*, 2003, **E59**, i116.
2. D. Cohen, *J. Inorg. Nucl. Chem.*, 1961, **18**, 211.

### Potential Additional Analysis

While single crystal X-ray diffraction is still the most definitive tool for structural determination in polyoxometalate chemistry there are additional spectroscopic and structural techniques that may be applied. In terms of plutonium coordination chemistry, the high specific radioactivity of the main isotopes renders synthetic chemistry and physical characterisation challenging. As well as structural characterisation of the hydrated salt of  $[\text{K}_3(\text{PuO}_2)_3(\text{GeW}_9\text{O}_{34})_2]^{11-}$  we have also undertaken a UV/vis/nIR study which provides a vital link between solution state and crystalline solid state structures, and yields definitive information with respect to plutonium oxidation state. As our plutonium coordination chemistry studies continue in this area we will seek to apply additional characterisation tools where appropriate, including vibration and NMR spectroscopic studies. The preliminary magnetisation data reported here is an example of the steps that we are taking to study transuranic polyoxometalate complexes in more detail.

### Further Structural Discussion

In  $[\text{K}_3(\text{PuO}_2)_3(\text{GeW}_9\text{O}_{34})_2]^{11-}$  the  $\text{W-O}_{\text{terminal}}$  oxygens are also coordinated to the three  $\text{K}^+$  cations, linking them with the  $\{\text{PuO}_2\}^{2+}$  moieties via bridging oxygens. The  $\text{K}^+$  cations are also associated with the  $\text{W-O}_{\text{bridging}}$  oxygens of the  $\text{GeW}_9$  ligand which does not form  $\text{W-O}_{\text{bridging}} - \text{Pu}$  bonds. Therefore, the  $\text{K}^+$  ions are more closely associated with one  $\text{GeW}_9$  anion and the  $\{\text{PuO}_2\}^{2+}$  cations with the other, rendering a crown shaped internal ring structure (see figure below).

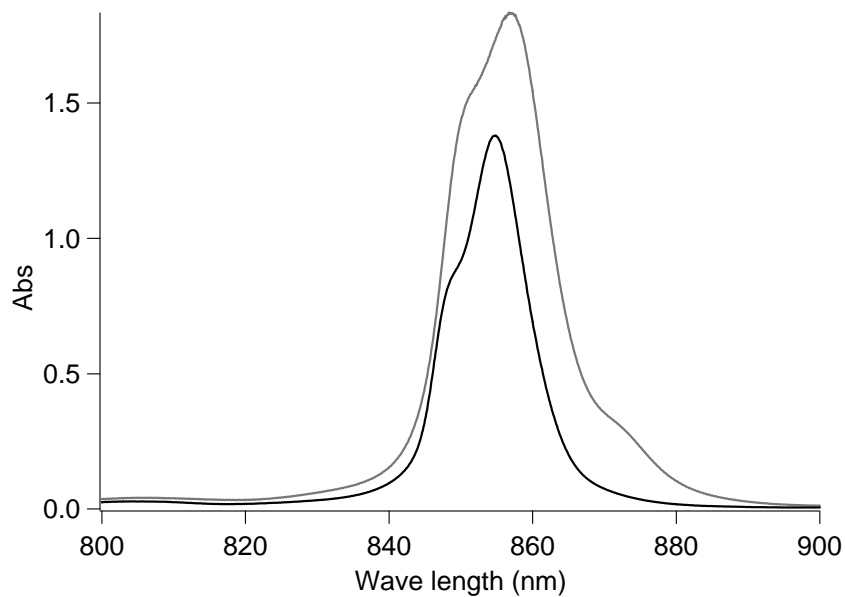
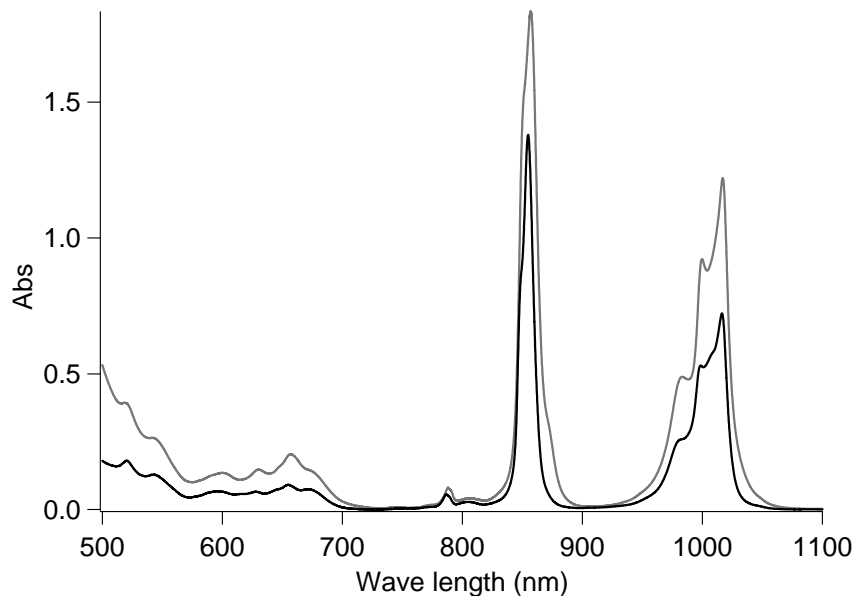


Ball and stick representation of the central  $3\text{K}^+$  and  $3\{\text{PuO}_2\}^{2+}$  cations and associated coordinated oxygens from the  $[\text{GeW}_9\text{O}_{34}]^{10-}$  anions in  $[\text{K}_3(\text{PuO}_2)_3(\text{GeW}_9\text{O}_{34})_2]^{11-}$ .

## Spectroscopic Data

In the presence of KCl there is a subtle change in solution state spectral features with the main *f-f* transition blue shifting slightly to 853 nm (from 856 nm prior to the addition of KCl). Assuming the 3:2 complex is the dominant solution species this can perhaps be attributed to the displacement of Na<sup>+</sup> with K<sup>+</sup> cations in the structure, with solution equilibria previously determined for  $[\text{Na}_2(\text{UO}_2)_2(\text{PW}_9\text{O}_{34})_2]^{12-} \rightleftharpoons [\text{M}_2(\text{UO}_2)_2(\text{PW}_9\text{O}_{34})_2]^{12-}$ , where M = K<sup>+</sup> or NH<sub>4</sub><sup>+</sup>.<sup>1</sup>

1. K.-C. Kim and M.T. Pope, *J. Am. Chem. Soc.*, 1999, **121**, 8512.



Absorption spectra of  $8.9 \text{ mM L}^{-1}$  Pu(VI) in the presence of one molar equivalent of  $[\text{A-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  at pH 7.77 (black trace) and  $14.8 \text{ mM L}^{-1}$  Pu(VI) in the presence of one molar equivalent  $[\text{A-}\beta\text{-SiW}_9\text{O}_{34}]^{10-}$  at pH 7.27 (grey trace). Note that both plots show the same spectra, just with different wave length ranges.