Glenn T. Seaborg Center Seminar

Utilising Polyoxometalate Ligands to Probe Structural Diversity and Investigate the Spectroscopic Properties of Actinyl Cation (U, Np and Pu) Bonds

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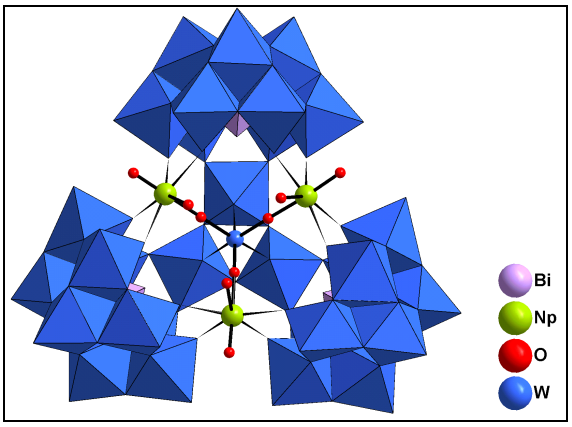
In recent years it has been shown that di-, and especially tri-, lacunary heteropolyoxotungstate anions will readily coordinate to the uranyl(VI) cation forming a large array of structurally diverse anionic clusters. The tri-lacunary ligands investigated fall into two general classes: - A-type, $[XW_9O_{34}]^{n-}$ (where X = P^V, As^V, Si^{IV} or Ge^{IV} and n = 9 or 10) or B-type, $[XW_9O_{33}]^{n-}$ (where X = Te^{IV}, As^{III}, Sb^{III} or Bi^{III}, and n = 8 or 9). The reaction between the uranyl cation and both the Dawson-Wells B-type tri-lacunary anion, $[P_2W_{15}O_{56}]^{12-}$, and di-lacunary anions $[\gamma\text{-}XW_{10}O_{36}]^{8-}$ (X= Ge^{IV} or Si^{IV}) have also been studied. Structural diversity is driven by ligand type, reaction conditions and additional ligand formation *in-situ*. Whilst undertaking initial studies with the uranyl cation our focus has always been on the transuranic actinyl cations and we have now studied the reaction of many of the above ligands with both the neptunyl(V and VI) and plutonyl(VI) cations. For the A-type ligands analogous 2:2 sandwich complexes are readily formed with $\{UO_2\}^{2+}$ and both $\{NpO_2\}^{2+}$ and $\{NpO_2\}^{+}$. However, preliminary structural and spectroscopic studies indicate that the $\{PuO_2\}^{2+}$ chemistry is subtly different. For B-type ligand reactions neptunyl(V) 'yl' oxygens are directly incorporated into the polyoxotungstate framework, in direct contrast to the An(VI) studies. As well as this structural diversity many of these complexes show unusual absorption and emission spectroscopic features through the visible and near-IR spectral regions, including ligand induced sensitization of uranyl(VI) and neptunyl(VI) luminescence. Finally, we have recently started a computational project, both to investigate the effect of polyoxometalate coordination on actinyl electronic structure (*vs.* other strong O-donor ligands, including hydroxide) and also to attempt to explain the observed spectroscopic features.



$Na_4[(Np_3W_4O_{15})(H_2O)_3(BiW_9O_{33})_3]^{14-}$

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