

Supporting Information

A versatile precursor for non aqueous neptunyl(V) chemistry

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General

Experiments were performed under an argon atmosphere using a Schlenk line contained within a regular atmosphere negative pressure radiological containment glovebox. Strict radiological control and safety practices were observed during the manipulation of highly radioactive neptunium-237 (half life 2.608×10^7 years). All solvents were anhydrous grade purchased from Sigma-Aldrich. UV/Vis/nIR were recorded on a Varian Cary and Infra-red spectra recorded on a Bruker Equinox.

Preparation and purification of acidic neptunium(V) stock solution

A nitric acid stock solution of neptunium-237 (750 mg ^{237}Np) was obtained from CEA Marcoule legacy stocks and contains both Np(V) and Np(VI) by absorption spectroscopy. To this solution NaOH (6 M, 1 ml) was added to precipitate a brown solid that was collected by centrifuge, the clear supernatant discarded and then washed five times with deionised water. The brown solid was dissolved in HCl (1 M, 15 ml) and confirmed to contain both $\text{NpO}_2(\text{V})$ and $\text{NpO}_2(\text{VI})$ by absorption spectroscopy. To the solution a NaNO_2 solution (2M) was added dropwise and agitated until no bubbling was apparent, a slight decrease in the green colouration of the solution is observed. The reduction of Np(VI) to Np(V) was confirmed by absorption spectroscopy (loss of the band at 1223 cm^{-1} and increase in band at 980 cm^{-1}). To the solution NaOH (6 M) was added dropwise and agitated until a very fine green precipitate was apparent and was removed by centrifuge. Alpha analysis of the resulting green solution revealed 695.2 mg ^{237}Np and complete removal of residual ^{239}Pu and ^{241}Am . To the solution NaOH (6 M) was added dropwise to precipitate a green solid of $\text{NpO}_2(\text{OH}) \cdot x\text{H}_2\text{O}$ that was collected by centrifuge and the colourless supernatant discarded. The green solid was washed five times with deionised water and then re-dissolved in 1 M HCl, the total volume of the solution was 22 ml ($31.6\text{ mgL}^{-1}\text{ }^{237}\text{Np}$).

Synthesis of $[\text{NpO}_2(\text{salophen-}^t\text{Bu}_2)(\text{py})]\text{K}$

$\{[\text{NpO}_2\text{Py}_5][\text{KI}_2\text{Py}_2]\}$ (0.0078 g, 7 μmol) was added to a solution of $\text{K}_2\text{salophen-}^t\text{Bu}_2$ (0.0048 g, 7

μmol) in pyridine (667 μl). The resulting reaction mixture was stirred for 2 hours producing a red coloured solution. The solution was evaporated under reduced pressure close to dryness and di-isopropylether (500 μl) added to afford an orange solid. The solid was washed with two portions of di-isopropyl ether (500 μl) and dried under vacuum (6 mg, 69 %).

Figure S1. IR Spectra (ATR) of **1** and complex with t-butylSalophen

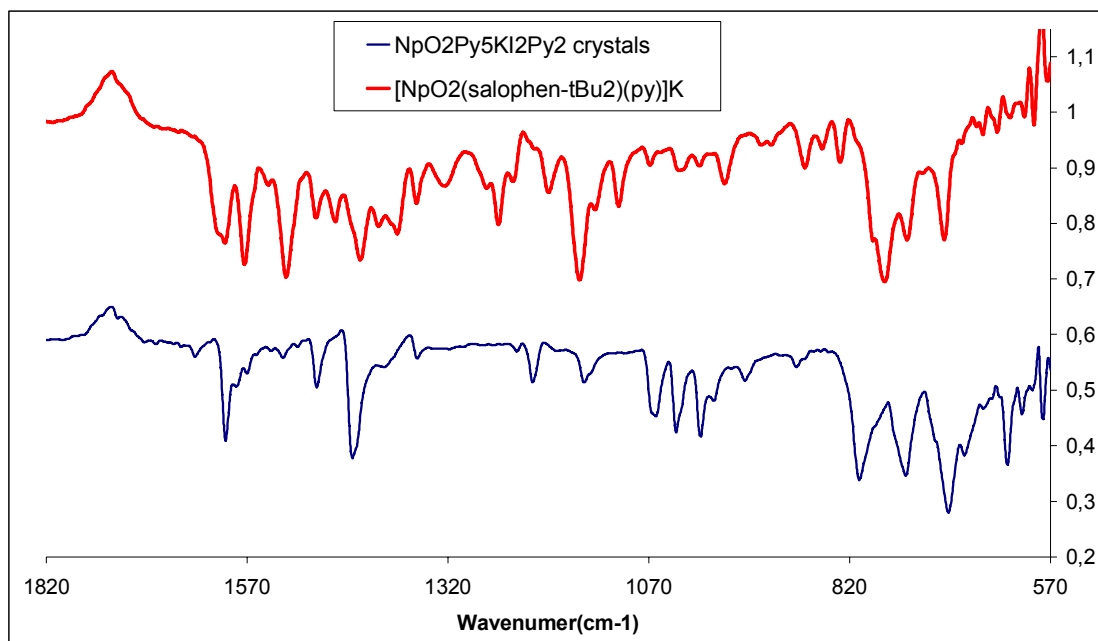


Figure S2. FTIR spectra, in KBr pellets, of NpO₂⁺(V) (blue line) and UO₂⁺(V) (red line).

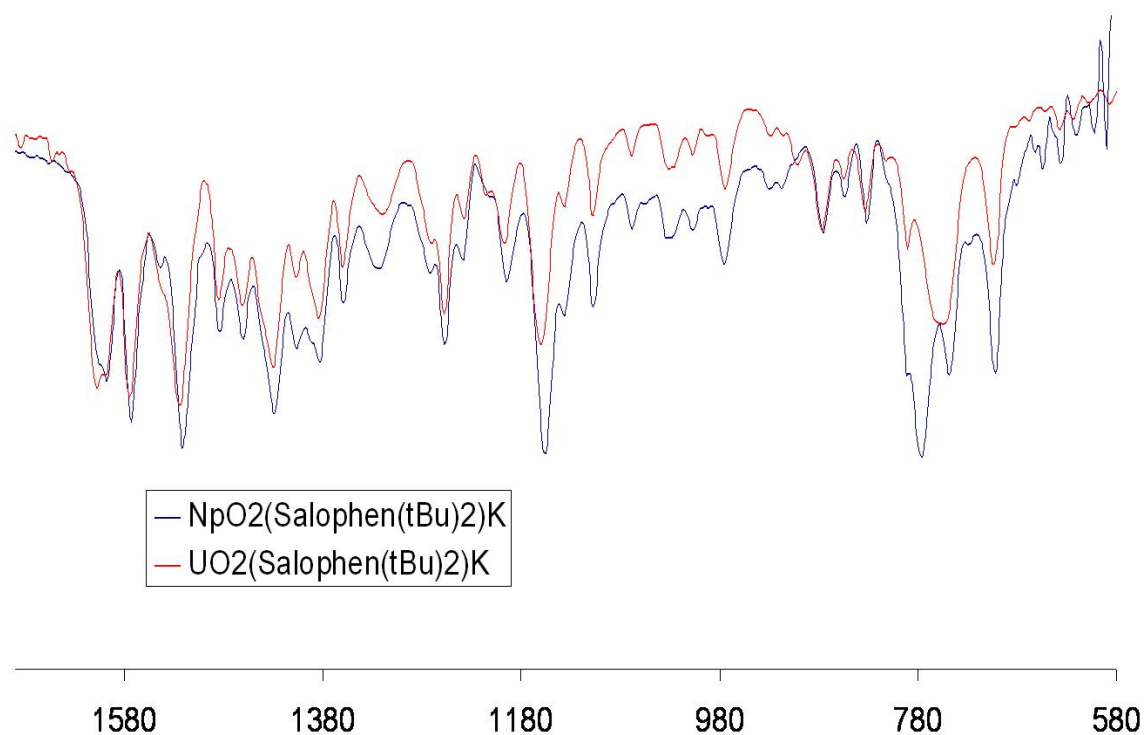


Figure S3. NIR of 0.44 mM pyridine solutions of **1** (green) and of $[\text{NpO}_2(\text{salophen-}^t\text{Bu}_2)(\text{py})]\text{K}$ (blue).

