Supporting Information

Structural characterization of environmentally relevant ternary uranyl citrate complexes present in aqueous solutions and solid state materials.

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Thermogravimetric Analysis

Thermogravimetric analysis of U_2Fe_4 displays a total water molecule depletion at 150 °C which comprises an 11.3% mass loss (Fig. S1). A large secondary mass loss of 33.2% occurs at 340 °C due to the breakdown of ethylenediamine and citrate molecules. Complete decomposition of U_2Fe_4 , at approximately 540 °C, reveals a residual product that is 43.6% of the original mass which corresponds exactly to the expected value for $U_3O_8 + Fe_2O_3$ of 43.6%.

 U_2Fe_2 exhibits a 10.3% mass loss at175 °C which is accredited to all of the interstitial water groups. A major mass loss from piperazine and citrate molecules at 360 °C accounts for 31.1% of the total mass. The calculated final product of 43.1% arises from the combination of $Fe_2O_3 + U_3O_8 + MgU_3O_{10} + MgO$ and agrees relatively well with the final residual mass of 44.6% occurring at 575 °C.

The analysis of U_2Al_2 displays a total water molecule loss at 190 °C and makes up 12.1% of the total mass. The breakdown of piperazine and citrate generates a final residual mass of 47.9% which completes the decomposition of U_2Al_2 at 475 °C. The expected value was derived from SrUO₄ + Al₂O₃ which yield a 48.5% final mass.



Figure S1. Thermogravimetric analysis was performed on U_2Fe_4 , U_2Fe_2 , and U_2Al_2 to parse the thermal stability of each compound and investigate the solvated water molecules. Powder XRD was utilized to confirm that the residual product was amorphous.

Mass Spectrometry

Mass Spectrometry was performed on the U_2Fe_4 , U_2Fe_2 , and U_2AI_2 complexes to determine fragmentation patterns. In all cases, the crystals were re-dissolved in aqueous solutions at 100 ppm U levels. In all cases, the 1:1:2 U:(Fe, Al):cit species dominated the spectra in solutions with pH values between 4 to 10. Representative spectra at pH 8-9 are given below for U_2AI_2 (Fig. S2), U_2Fe_2 (Fig. S3), and U_2Fe_4 (Fig. S4).



Figure S2. Mass spectra of the U_2Al_2 complex dissolved in aqueous solution at pH 9.



Figure S3. Mass spectra of the U_2Fe_2 complex dissolved in aqueous solution at pH 9.



Figure S4. Mass spectra of the U_2Fe_4 complex dissolved in aqueous solution at pH 8.