



# Thermochemical properties of U(VI) hybrid materials containing uranyl tetrachloride anions



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## ABSTRACT

The enthalpies of formation from simpler components of four hybrid materials bearing the  $[\text{UO}_2\text{Cl}_4]^{2-}$  anion have been measured and compared to that of  $\text{Cs}_2[(\text{UO}_2)\text{Cl}_4]$ . The hybrids contain protonated amines as charge balancing cations that form bifurcated H-bonding interactions with the chloro ligands of the anions. The structure of each material contains similar motifs and the driving force for the formation of the hybrids appears to be the enthalpy of organic cation formation (protonation). The hybrids are energetically much more stable than the corresponding cesium salt without a protonated organic cation.

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## 1. Introduction

Hybrid materials containing the uranyl cation and organic anions continue to draw attention owing to their rich structural diversity, their relevance to the nuclear fuel cycle and their potential as photocatalysts [1–7]. Much work has been done in the area of coordination polymers and related framework materials wherein hydrothermal syntheses give rise to a range of oligomeric hydrolysis products that manifest as building units in the solid state. Nevertheless, designed syntheses of desired topologies remain elusive as hydrolysis tends to be unpredictable and subject to a range of influences. An alternative approach to the formation of uranyl bearing hybrids is to crystallize materials from high chloride media in which the speciation profile is essentially restricted to the  $[\text{UO}_2\text{Cl}_4]^{2-}$  anion. Assembly of this single species thus relies on charge balancing cationic organic species and supramolecular interactions (or ‘synthons’) such as hydrogen and halogen bonding.

Cahill’s group has synthesized a number of families of materials utilizing these and related approaches. They have explored series of materials wherein hydrogen bonding is the sole type of supramolecular interaction, and have also explored combinations of hydrogen and halogen bonding motifs [8–13]. They (and others) [14–17] have also utilized alternative aqueous media for syntheses, such as high concentrations of  $\text{Br}^-$  or  $\text{NCS}^-$  to promote the

formation of  $[\text{UO}_2\text{Br}_4]^-$ ,  $[(\text{UO}_2)(\text{NCS})_4\text{H}_2\text{O}]^{2-}$ ,  $[(\text{UO}_2)(\text{NCS})_5]^{3-}$  or  $[(\text{UO}_2)(\text{NCSe})_5]^{3-}$  species which may then assemble through a variety of supramolecular interactions originating from the bromo or isothio(seleno)cyanate ligands, respectively.

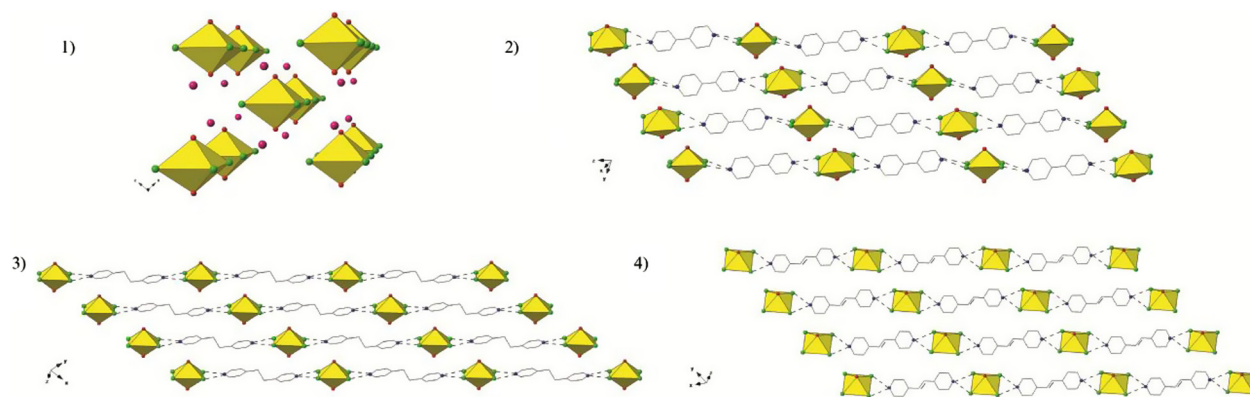
Despite this diversity of compositions and supramolecular interactions therein, little has been done to explore the stabilities and thermodynamic landscape of these materials. Moreover, the systematic nature of the structure types (that is, a fixed anion with a range of charge balancing organic cations), these  $[\text{UO}_2\text{Cl}_4]^{2-}$  materials provide an ideal forum for exploring energetics of formation and potentially ranking the strengths of supramolecular interactions. The latter remains an area of significant interest as we strive to develop assembly criteria within these materials, which may be useful in guiding future targeted synthetic efforts. Herein we report the heats of reaction for four compounds: (1)  $\text{Cs}_2[\text{UO}_2\text{Cl}_4]$ , (2)  $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ , (3)  $(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ , and (4)  $(\text{C}_{12}\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ . The syntheses and structures of each of these materials (Fig. 1) has been reported previously [13,18], and each (except for the Cs salt) contains a bifurcated hydrogen bonding relationship between the tetrachloride anion and the protonated organic cation.

## 2. Experimental methods

The enthalpies of solution,  $\Delta H_{\text{sol}}$ , of compounds 1–4 and their corresponding reference materials were measured using isothermal acid solution calorimetry. The method and calorimeter used

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**Fig. 1.** The structures of (1)  $\text{Cs}_2[\text{UO}_2\text{Cl}_4]$ , (2)  $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ , (3)  $(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ , and (4)  $(\text{C}_{12}\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ . The organic cations in 2, 3 and 4 are 4,4'-dipyridyl, 1,2-bis(4-pyridyl)ethane and trans-1,2-bis(4-pyridyl)ethylene, respectively. Yellow polyhedra are U(VI) centers axial oxygen (red) and equatorial chloride (green) ligands, with Hydrogen bonding interactions are represented as dashed lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**  
Summary of sample descriptions and purities used in this work.

Sample	Source	Mass fraction purity	Analysis Method
$\text{Cs}_2[\text{UO}_2\text{Cl}_4]$	Prepared in house <sup>b</sup>	>0.99	XRD <sup>c</sup>
$(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{UO}_2\text{Cl}_4]$	Prepared in house <sup>b</sup>	>0.99	XRD
$(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{UO}_2\text{Cl}_4]$	Prepared in house <sup>b</sup>	>0.99	XRD
$(\text{C}_{12}\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$	Prepared in house <sup>b</sup>	>0.99	XRD
$(\text{C}_{10}\text{H}_8\text{N}_2)$	Aldrich	0.98	Manufacturer Assay
$(\text{C}_{12}\text{H}_{12}\text{N}_2)$	Aldrich	0.99	Manufacturer Assay
$(\text{C}_{12}\text{H}_{10}\text{N}_2)$	Aldrich	0.97	Manufacturer Assay
Uranium Oxide, $\text{UO}_3$	International Bio-Analytical Industries Inc.	>0.99	Manufacturer Assay, PXRD <sup>a</sup>
Cesium Chloride, CsCl	Alfa Aesar	>0.99	Manufacturer ICP
Hydrochloric acid, HCl	Fisher Scientific	2.0 mol/dm <sup>3</sup> standardized solution (mass fraction of HCl is 0.071)	Manufacturer standardized against NIST potassium acid phthalate

<sup>a</sup> Annealed under oxygen then stored and prepared for measurement under nitrogen atmosphere in a glovebox. Identification and phase purity checked with powder X-ray diffraction.

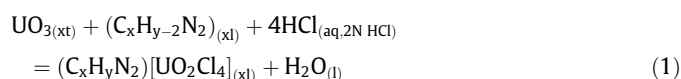
<sup>b</sup> Synthesis method reported in Deifel and Cahill (2009) [13]. Isotopic distribution for depleted uranium (from which these materials were prepared) is typically greater than 99.7 wt% U-238 and less than 0.3 wt% U-235.

<sup>c</sup> Identification and phase purity of compounds 1–4 was achieved via powder X-ray diffraction on bulk reaction products. Single crystals were then selected for calorimetric studies.

are described extensively elsewhere [19]. Briefly, a commercial CSC 4400 microcalorimeter was operated isothermally at  $T = 298$  K with constant mechanical stirring to aid in dissolution. Crystals of each sample (~10 mg) and reference material were carefully selected and dropped into the calorimeter containing hydrochloric acid ( $25.0 \pm 0.1$  g, 7.06 wt% aqueous solution) in a Teflon reaction container. The calorimeter was calibrated using the heat of solution of KCl, NIST standard reference material (SRM) 1655 in deionized water under the same experimental conditions. The uncertainties in calibrations (taken over a number of months) are on the order of 0.5% and, being much smaller than uncertainties in solution enthalpies, do not contribute significantly to the overall error (Table 1).

### 3. Results

The  $\Delta H_{\text{sol}}$  of the uranyl hybrid materials and cesium compounds are reported in Table 2. These measured values are used in the thermodynamic cycles, Tables 3 and 4, to calculate an enthalpy of the formation reaction,  $\Delta H_{\text{rxn}}$ , from the components (Eq. (1)).



### 4. Discussion

The  $\Delta H_{\text{rxn}}$  for the formation of compounds 1–4 from their constituent starting materials, as reported in Tables 2 and 3, indicate that the more easily protonated the cation, the more stable the resulting uranyl hybrid material. This is perhaps intuitive considering the structural similarities between compounds 1–4: each contains a  $[\text{UO}_2\text{Cl}_4]^{2-}$  anion and those with organic cations and 2–4 are assembled through similar H-bonding motifs. Indeed, the only variable, other than the enthalpy of solution of the hybrid, within the cycle for the calculation of  $\Delta H_{\text{rxn}}$  for compounds 2–4 (Table 2) is the enthalpy of protonation of the organic species, measured as  $\Delta H_3$ . Fig. 2 shows a strong linear correlation between  $\Delta H_{\text{rxn}}$  and  $\Delta H_3$ . Without organic cation protonation, the cesium salt ( $\text{Cs}_2[\text{UO}_2\text{Cl}_4]$ ) has a substantially less exothermic enthalpy of reaction than the hybrid materials.

In addition to a fundamental exploration of the thermodynamic landscape of uranyl hybrid materials, an additional goal of this study was to attempt to correlate reaction enthalpies with observed physical parameters such as strengths of supramolecular interactions or molar volumes as obtained via crystallographic data. Other than the correlation with protonation energy however, we could not find any systematic dependence of enthalpy of reaction on bond lengths, or lengths of non-covalent interactions. Nor is there any correlation of enthalpy with molar volume (Table 2),

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