A new uranyl tetrachloride salt with chemical formula, \((\text{NH}_4)_2[\text{UO}_2\text{Cl}_4]\cdot2\text{H}_2\text{O}\), namely, diammonium uranyl tetrachloride dihydrate, \(\text{I}\), was prepared and crystallized \textit{via} slow evaporation from a solution of 2 M hydrochloric acid. As confirmed by powder X-ray diffraction, the title compound crystallizes with an ammonium chloride impurity that formed as a result of the breakdown of a triazine precursor. The \((\text{UO}_2\text{Cl}_4)^{2-}\) dianion is charge balanced by ammonium cations, while an extensive hydrogen-bond network donated from structural water molecules stabilize the overall assembly. Compound \(\text{I}\) adds to the extensive collection of actinyl tetrachloride salts, but it represents the first without an alkali cation for purely inorganic compounds. Diffuse reflectance and luminescence spectra show typical absorption and emission behavior, respectively, of uranyl materials.

1. Chemical context

Hexavalent actinides such as uranium, neptunium, and plutonium exist in aqueous solution as the linear triatomic actinyl cation, with formula \((\text{AnO}_2)^{2+}\). The actinyl ion coordinates a variety of poly- and mono-atomic anions such that four to six atoms bond in the equatorial plane (Burns, 2005; Lussier \textit{et al.}, 2016). In part due to their ease of synthesis, structural simplicity, and high symmetry, the actinyl tetrachloride family of compounds has remained a relevant subclass of materials over several decades and has led to a deeper understanding of actinide electronic structure, bonding, and optical properties, among many others. The actinyl tetrachlorides have general formula \((\text{AnO}_2\text{X}_4)^{2-}\) (where \(\text{An} = \text{U}^{VI}, \text{Np}^{VI}, \text{and Pu}^{VI}\) and \(\text{X} = \text{Cl}^{-}\) and \(\text{Br}^{-}\)) and have been studied to investigate periodic trends in \(f\)-element chemistry. Of the numerous compounds that include this anionic complex, the Cs\(^+\) salt with formula \(\text{Cs}_2(\text{AnO}_2\text{Cl}_4)\) has been one of the most extensively characterized actinyl compounds. The uranyl structure was first reported in 1966 (Hall \textit{et al.}, 1966) with an improved model reported in 1991 (Watkin \textit{et al.}, 1991). In that time, it was used to quantitatively assign infrared (Ohwada, 1975) and Raman (Ohwada, 1980) active bands of the uranyl ion, which were found to be at 916 cm\(^{-1}\) and 831 cm\(^{-1}\), respectively. Improvements in analytical (\textit{i.e.} X-ray absorption spectroscopies) and computational techniques (\textit{i.e.} density functional theory calculations) over time have advanced our understanding in the electronic and molecular orbital energies of the uranyl ion in \(\text{Cs}_2(\text{UO}_2\text{Cl}_4)\), providing strong evidence that actinide atoms can bind with significant covalent character (Denning, 2007; Vitova \textit{et al.}, 2015). Luminescence
spectroscopy, Raman spectroscopy, and computational works have also been used to study bond-length changes of the uranyl ion with respect to different pressures in Cs2(UO2Cl4) (Osman et al., 2016; Warzecha et al., 2019). Beyond the Cs salt, systematic studies into actinyl bond strength changes as a function of metal center (i.e. An=U VI,NpVI and PuVI) have been reported for organic-based counter-cations (Schnaars & Wilson, 2013; Surbella III et al., 2017; Schnaars & Wilson, 2018). Quite recently, focus has been placed on the cationic influence on supramolecular assembly as well as actinyl bond-strength changes (Schnaars & Wilson, 2013; Surbella III et al., 2016; Carter et al., 2018; Pyrch et al., 2020; Augustine et al., 2023). Despite these numerous studies with actinyl tetrahalide species, we report a new inorganic uranyl tetrachloride not charge-balanced by an alkali cation, with formula (NH4)2(UO2Cl4)·2H2O (compound 1).

2. Structural commentary

Compound 1 crystallizes in the space group $P\bar{1}$. The uranyl tetrachloride dianion ($\text{UO}_2\text{Cl}_4^{2-}$) is composed of a $\text{U}^{\text{VI}}$ metal center that is coordinated to two terminal, axial oxygen atoms and four equatorial chlorine atoms as shown in Fig. 1. The ($\text{UO}_2\text{Cl}_4^{2-}$) dianion adopts a square-bipyramidal coordination geometry with $D_{4h}$ point group symmetry. The $\text{U}^{\text{VI}}$ atom sits on a center of inversion symmetry, resulting in a linear uranyl ($\text{UO}_2^{2+}$) cation with a $\text{U}1$—$\text{O}1$ bond distance of 1.7745 (14) Å and $\text{O}1$—$\text{U}1$—$\text{O}1$ angle of 180°. The $\text{U}^{\text{VI}}$ atom is also coordinated to two crystallographically unique chlorine atoms with $\text{U}1$—$\text{Cl}1$ and $\text{U}1$—$\text{Cl}2$ bond distances of 2.6752 (5) Å and 2.6623 (4) Å, respectively. The two $\text{Cl}1$—$\text{U}1$—$\text{Cl}2$ bond angles measure 88.855 (15)° and 91.145 (15)°, and $\text{O}1$—$\text{U}1$—$\text{Cl}1$, bond angles also slightly deviate from 90°. The $\text{U}1$—$\text{O}1$ bond lengths are typical for these compounds. The structure contains one crystallographically unique structural water molecule ($\text{O}1\text{w}$) with two $\text{O}1$—H covalent bonds with restrained bond lengths near 0.95 Å, and one crystallographically unique ammonium cation ($\text{N}1$) is present to provide charge balance to the overall structure. There are four $\text{N}$—$\text{H}$ covalent bonds with restrained bond lengths that are approximately 0.87 Å. The extended crystal structure is shown in Fig. 2.

3. Supramolecular features

A hydrogen-bond network consisting of seven unique interactions exists between ammonium cations, water molecules, and uranyl tetrachloride units as depicted in Fig. 3 and as

![Figure 1](image1.png)

*Figure 1*
The uranyl tetrachloride anionic unit along with a crystallographically unique water molecule and ammonium cation. Displacement ellipsoids for non-hydrogen atoms are shown at 50% probability.

![Figure 2](image2.png)

*Figure 2*
The crystal packing observed in compound 1 as viewed along the $a$-axis.

![Figure 3](image3.png)

*Figure 3*
The seven unique hydrogen-bond interactions shown with the hydrogen-bond distances from donor hydrogen atom to acceptor atom.
structures in the ICSD, Cs salts of the (AnO2Cl4)2− (Schnaars & Wilson, 2013). Other charge-balancing cations reported in the CSD include organic-functional groups (Di Sipio et al., 1974a,b; Bois et al., 1976a,b; Rogers et al., 1987; Gatto et al., 2004; Schnaars & Wilson, 2013; Biswas et al., 2017; Serezhkina et al., 2021). Compound I has ammonium with a water molecule, while one report has ammonium with crown ethers (Rogers et al., 1987). The other ammonium-based cations include organic-functional groups (Di Sipio et al., 1974a,b; Bois et al., 1976a,b; Gatto et al., 2004; Schnaars & Wilson, 2013; Biswas et al., 2017; Serezhkina et al., 2021). Other types of cations that charge-balance (UO2Cl4)2− in the CSD include pyridinium-based (Graziati et al., 1975; Bombieri et al., 1978; Marsh, 1988; Pospieszna et al., 2008; Deifel & Cahill, 2009; Baker et al., 2010; Andrews & Cahill, 2012; Lhoste et al., 2013; Hashem et al., 2013; Surbella III et al., 2016, 2017; Carter et al., 2018; Mishra et al., 2019; Pyrch et al., 2020), phenanthroline-based (Di Sipio et al., 1981), imidazolium-based (Zalkin et al., 1983; Qu et al., 2014; Kohlgruber, 2022), and phosphonium-based (Brown et al., 1996; Schnaars & Wilson, 2014) species. Other (UO2Cl4)2− complexes have crystallized in the presence of separate metal complexes (Moody & Ryan, 1979; Rogers et al., 1987, 1990; Pons y Moll et al., 2001; Hashem et al., 2014; Falaise et al., 2015; Zhang et al., 2017; Schöne et al., 2018), crown ethers (Wang et al., 1986; Rogers et al., 1987, 1991; Rogers & Benning, 1991; Evans et al., 2002) and porphyrins (Mishra et al., 2019). In total, there are over 60 known uranyl tetrachloride crystal structures in the CSD. Reference codes for these compounds can be found in the supporting information.

### 4. Database survey

Compound I is the first inorganic uranyl tetrachloride charge-balanced with a non-alkali metal in the Inorganic Crystal Structure Database (Zagorac et al., 2019). With respect to structures in the ICSD, Cs salts of the (AnO2Cl4)2− species have been reported for U (Hall et al., 1966; Watkin et al., 1991; Tutov et al., 1991; Schnaars & Wilson, 2013), Np (Wilker son et al., 2007), and Pu (Wilkinson & Scott, 2008; Schnaars & Wilson, 2013). Other charge-balancing cations reported in the ICSD for UVI and PuVI include Rb (Anson et al., 1996; Schnaars & Wilson, 2013) and tetramethylammonium (Schnaars & Wilson, 2013), while that of Np includes (UO2Cl4)2−-doped NpVI (Wilkinson & Berg, 2009) and a

### 5. Synthesis and crystallization

Concentrated hydrochloric acid, HCl, (Sigma-Aldrich, 37%) was diluted to 2 M. Then, 0.0366 g (0.44 mmol) of 1,3,5-triazine (Sigma-Aldrich, 97.0%) was dissolved into 1 mL of 2 M HCl in a 1-dram borosilicate glass reaction vial. Uranyl acetate dihydrate (0.10216 g; 2.4 mmol) was added to this solution and allowed to dissolve completely. The vial was placed uncapped in a 20 mL centrifuge tube on a bed of desiccant. The centrifuge tube was capped, and the reaction solution was allowed to evaporate for 3 weeks until large yellow crystals formed. It was noticed that compound I partially dissolves in ethanol, affecting the preparation for characterization beyond single-crystal X-ray diffraction. Powder-diffraction data was collected using a Rigaku Ultima IV Diffractometer with Cu Kα radiation and a linear position-sensitive detector. The analysis revealed an ammonium chloride, NH4Cl, impurity phase along with compound I. Diffuse reflectance and luminescence spectra were also collected for the mixed-phase material and can be found in the supporting information along with the powder-diffraction data.

---

Table 1

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Symmetry codes: (i) x, −y + 1, −z + 2; (ii) x, y, z + 1; (iii) x, y + 1, z; (iv) −x, −y + 1, −z + 1; (v) −x + 1, −y + 2, −z + 2.

Figure 4

The crystal packing along with the hydrogen-bond network observed in compound I as viewed slightly offset along the a-axis.
6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in Fourier difference maps, and their positions refined with positional restraints.

Acknowledgements

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References

Diammonium uranyl tetrachloride dihydrate

Crystal data
(NH₄)₂[UO₂Cl₄]·2H₂O  \(Z = 1\)
Mᵣ = 483.95  \(F(000) = 218\)
Triclinic, \(P\overline{1}\)  \(D_\lambda = 2.823 \text{ Mg m}^{-3}\)
\(a = 6.6574 (4) \text{ Å}\)  \(\text{Mo } K\alpha\) radiation, \(\lambda = 0.71073 \text{ Å}\)
\(b = 6.6954 (4) \text{ Å}\)  Cell parameters from 9764 reflections
\(c = 7.4018 (4) \text{ Å}\)  \(\theta = 3.5\text{–36.7}^\circ\)
\(\alpha = 99.827 (2)^\circ\)  \(\mu = 15.17 \text{ mm}^{-1}\)
\(\beta = 93.879 (2)^\circ\)  \(T = 100 \text{ K}\)
\(\gamma = 117.354 (1)^\circ\)  Block, yellow
\(V = 284.69 (3) \text{ Å}^3\)  \(0.10 \times 0.03 \times 0.03 \text{ mm}\)

Data collection
Bruker D8 Venture  2803 independent reflections
diffractometer  2803 reflections with \(I > 2\sigma(I)\)
Radiation source: microsource Diamond II  \(R_{\text{min}} = 0.042\)
\(\varphi\) and \(\omega\) scans  \(\theta_{\text{max}} = 36.8^\circ\), \(\theta_{\text{min}} = 3.5^\circ\)
Absorption correction: multi-scan  \(h = -11\rightarrow 11\)
(SADABS; Krause et al., 2015)  \(k = -11\rightarrow 11\)
\(T_{\text{min}} = 0.460, T_{\text{max}} = 0.747\)  \(l = -12\rightarrow 12\)
24049 measured reflections

Refinement
Refinement on \(F^2\)  Secondary atom site location: difference Fourier map
Least-squares matrix: full  Hydrogen site location: difference Fourier map
\(R[F^2 > 2\sigma(F^2)] = 0.017\)  All H-atom parameters refined
\(wR(F^2) = 0.041\)  \(w = 1/\{\sigma(F_o^2) + (0.0306P)^2\}\)
\(S = 1.09\)  where \(P = (F_o^2 + 2F_c^2)/3\)
2803 reflections  \((\Delta/\sigma)_{\text{max}} = 0.001\)
76 parameters  \(\Delta p_{\text{max}} = 2.94 \text{ e Å}^{-3}\)
12 restraints  \(\Delta p_{\text{min}} = -1.97 \text{ e Å}^{-3}\)
Primary atom site location: dual

(NH₄)₂[UO₂Cl₄]·2H₂O, a new uranyl tetrachloride with ammonium charge-balancing cations

Tsuyoshi A. Kohlgruber and Robert G. Surbella III

Computing details
Data collection: APEX4 (Bruker, 2014); cell refinement: SAINT (Bruker, 2014); data reduction: SAINT (Bruker, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: CrystalMaker (CrystalMaker, 2014); software used to prepare material for publication: publCIF (Westrip, 2010).
Special details

Geometry. All estimated standard deviations (esds), except those pertaining to the dihedral angle between two least squares (ls) planes, are estimated using the full covariance matrix.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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Hydrogen-bond geometry (Å, °)

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<th>D—H</th>
<th>H···A</th>
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<th>D—H···A</th>
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<td>O1w—H1A···Cl1ii</td>
<td>0.95 (6)</td>
<td>2.36 (7)</td>
<td>3.283 (2)</td>
<td>165 (7)</td>
</tr>
<tr>
<td>O1w—H1B···Cl2iii</td>
<td>0.95 (5)</td>
<td>2.35 (5)</td>
<td>3.268 (2)</td>
<td>163 (5)</td>
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<tr>
<td>N1—H2A···O1w</td>
<td>0.87 (3)</td>
<td>2.02 (3)</td>
<td>2.843 (2)</td>
<td>157 (3)</td>
</tr>
<tr>
<td>N1—H2B···Cl1iv</td>
<td>0.87 (4)</td>
<td>2.68 (4)</td>
<td>3.441 (2)</td>
<td>148 (3)</td>
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<tr>
<td>N1—H2C···O1</td>
<td>0.87 (2)</td>
<td>2.32 (4)</td>
<td>3.014 (3)</td>
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<tr>
<td>N1—H2C···Cl1v</td>
<td>0.87 (2)</td>
<td>2.77 (3)</td>
<td>3.4060 (17)</td>
<td>131 (4)</td>
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<tr>
<td>N1—H2D···O1wvi</td>
<td>0.87 (3)</td>
<td>2.03 (3)</td>
<td>2.887 (3)</td>
<td>169 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (ii) −x, −y +1, −z +2; (iii) x, y, z +1; (iv) x, y +1, z; (v) −x, −y +1, −z +1; (vi) −x +1, −y +2, −z +2.