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Bonding in Uranium(V) Hexafluoride Based on the Experimental Electron Density Distribution Measured at 20 K

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Supporting Information

ABSTRACT: The electron density distribution of [PPh₄][UF₆] was obtained from high-resolution X-ray diffraction data measured at 20 K. The electron density was modeled with an augmented Hansen–Coppens multipolar formalism. Topological analysis reveals that the U–F bond is of incipient covalent nature. Theoretical calculations add further support to the bonding description gleaned from the experimental model. The impact of the uranium anomalous dispersion terms on the refinement is also discussed.

Understanding chemical bonding to actinide elements has been of interest for decades^{1,2} and is of importance as the demand for nuclear power continues to increase. Among the extensively studied actinide systems is uranium hexafluoride, well-known for its use in uranium enrichment. While still a subject of debate, theoretical results indicate that the U–F bond is partially covalent and could even possess multiple bond character, resulting from F → U π interactions.^{2–4} We have previously demonstrated that the electron density distribution obtained from high-resolution X-ray diffraction at low temperature provides insight into chemical bonding, even in systems containing actinide elements.^{5,6} While the challenges in handling UF₆ make it a poor candidate for charge-density experiments, the singly reduced UF₆[−] anion is synthetically available and has also received considerable attention, including structural characterization with a variety of cations.^{7,8} Herein we report the first experimental electron density study of a uranium(V) system, as well as of U–F bonding, in the context of [PPh₄][UF₆] (**1**). The nature of the U–F bond(s) is discussed from the perspective of quantum theory of atoms in molecules (QTAIM).⁹ The topology of the experimental electron density is also compared to that obtained computationally.

A 0.17 × 0.14 × 0.09 mm crystal of **1**, grown by slow evaporation from dry acetonitrile under an argon atmosphere, was mounted on a Rigaku diffractometer with an ULTRAX-18 rotating anode (molybdenum; graphite monochromator; 50 kV, 300 mA) and a RAPID II image-plate detector. The crystal was cooled to 20 K,^{10,11} and 355 images were collected (5° oscillation width, ω scans, 120 s). The *HKL2000* software package¹² was

used for reflection indexing and unit-cell parameter refinement, while *VIIPP* was used for peak integration.^{13,14} An absorption correction was applied as described previously⁵ with the program *CCDABS*,¹⁵ and a decay correction was also applied. The data were then scaled and merged with *SORTAV*^{16,17} to give 9826 independent reflections for $0 < \sin \theta/\lambda < 1.3 \text{ \AA}^{-1}$ ($R_{\text{int}} = 0.017$; average multiplicity = 7.7). The structure and total electron density distribution were refined with a modified Hansen–Coppens multipolar formalism implemented in the *MoPro* program suite,¹⁸ using the Volkov and co-workers relativistic wave function data bank.¹⁹ Multipolar expansion was carried out up to $l = 6$ for uranium, and anomalous dispersion terms were also refined (see [Table 1](#) and the [Supporting Information](#) (SI) for further crystallographic details and refinement results). Details concerning the synthesis of **1** and theoretical calculations

Table 1. Experimental Details

formula	PPh ₄ UF ₆ (C ₂₄ H ₂₀ F ₆ PU)
M_r	410.875
temp of measurement (K)	20.0(1)
λ (Å)	0.71073
space group	$\bar{I}4$
unit-cell dimens (Å)	$a = b = 12.2518(1)$, $c = 7.2893(2)$
V (Å ³), Z	1094.17(3), 2
$T_{\text{min}}/T_{\text{max}}$, μ (mm ^{−1})	0.657/1, 7.551
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1}), d_{max} (Å)	1.30, 0.385
reflns integrated	75559
R_{int} /average multiplicity	0.017, 7.7
indep reflns, $I > 3\sigma$	9826, 9388
refined U , f''	−9.745, 9.830
reflns/param	23.12
param, restraints	406, 37
extinction coeff	0.07481
weighting scheme: ^a a , b	0.002, 0.002
final $R1(F)$, $wR2(F^2)$ (all data)	0.0066, 0.0095
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (all data; e Å ^{−3})	−0.787, 0.586
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ ($\sin \theta/\lambda < 1.0 \text{ \AA}^{-1}$)	−0.561, 0.295

$$^a w = 1/\{\sigma^2(F^2) + (ap)^2 + bp\}, p = 0.3333F_{\text{obs}}^2 + 0.6667F_{\text{calc}}^2$$

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(density functional theory/B3LYP) for the isolated UF_6^- ion can also be found in the SI.

Fluorination of $[\text{PPh}_4][\text{UCl}_6]$ with 48% HF provided **1** in 77% yield as large pale-blue crystals. Chlorine–fluorine exchange was confirmed by IR spectroscopy, which showed a strong absorption at 528.9 cm^{-1} , similar to the ν_3 stretch observed for the UF_6^- anion in $[\text{AsPh}_4][\text{UF}_6]$ (525 cm^{-1}).²⁰ Charge-density-quality crystals were grown by slow evaporation from acetonitrile. Compound **1** crystallizes in the space group $I\bar{4}$ with the U and P atoms on $\bar{4}$ special positions and one F atom (F2) on a 2-fold axis, while the remaining atoms are in general positions. The UF_6^- group exhibits axial elongation from a perfect octahedron with U–F distances of $2.0768(4)\text{ \AA}$ (U–F2) and $2.06503(19)\text{ \AA}$ (U–F1) for the axial and equatorial F atoms, respectively (see Figure 1). There is also deviation of the F1

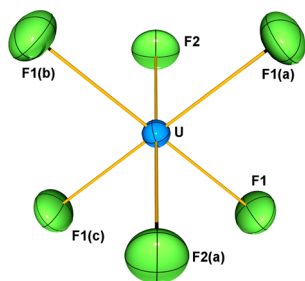


Figure 1. ORTEP diagram of the UF_6^- portion of **1**. Thermal ellipsoids are depicted at the 99% probability level. Symmetry operators: a, $y, 1 - x, -z$; b, $1 - x, 1 - y, z$; c, $1 - y, x, -z$.

atoms from the equatorial plane, arranged in turns slightly above and below it, with F1–U–F2 angles alternating between $89.93(2)^\circ$ and $90.07(2)^\circ$. We note that the observed S_4 point symmetry is consistent with previous electron paramagnetic resonance measurements on UF_6^- .⁷

The recent implementation of spherical harmonics up to $l = 6$ in the *MoPro* program suite¹⁸ allows for the proper treatment of *f*-electron systems and should improve the accuracy of multipolar models for heavy elements.^{21–23} Additionally, refinement of the uranium anomalous dispersion terms has been implemented in *MoPro* because these terms have been shown to vary depending on the chemical environment.²⁴

In a previous multipole refinement of the charge density in $\text{Cs}_2\text{UO}_2\text{Cl}_4$, we employed a “split”-atom model because we found that the standard approach was inadequate.^{5,6} Tradition-

ally, the radial term used to model the aspherical valence electron density in the Hansen–Coppens formalism involves the weighted averaging of participating valence functions yielding a single radial term. In the case of uranium, the valence functions correspond to the 5*f*, 6*d*, and 7*s* shells and the radial distributions are significantly different; accordingly, a single (averaged) radial function is inadequate to describe the electron density distribution around uranium. Thus, we treat the U atom as the superposition of several components with different radial terms: a core +6*s* “valence” and four “valence-only” components, each invoking a single radial term (namely, 6*p*, 5*f*, 6*d*, and 7*s*), allowing for modeling of both the aspherical valence electron density and core polarization. Thermal parameters and atomic coordinates were constrained to be identical for all split-atom components. Two restrained κ parameters were refined for each split component. Populations were initially refined freely for the 5*f* and 6*d* components before being restrained to contain a slight excess charge to prevent the total charge from drifting too positive. The populations of the 6*s* and 6*p* components were restrained to be nearly neutral, and the 7*s* population was restrained to stay below 0.1 e^- . Additionally, the uranium anomalous dispersion terms were refined. We note that the refined values of f' and f'' are less than 2% from the standard values, but despite this small difference, the impact on the multipole parameters is not negligible (see the SI).

Models were also explored that completely omitted the 7*s* term but were not stable. Multipoles on all components were refined according to the local $4/m$ symmetry (instead of $\bar{4}$; see the SI) and were subject to similarity restraints included as needed to dampen the effects of parameter correlation. Fluorine, phosphorus, carbon, and hydrogen were also lightly restrained (see the SI) but otherwise treated as usual. Unfortunately, parameter correlations were too significant to perform full least-squares refinement in the absence of restraints or constraints; accordingly, 37 restraints were employed to stabilize the model. We have chosen to employ restraints rather than constraints when possible.

Deformation density (DD) maps (the difference between the multipolar model electron density and a neutral spherical atom model density) are useful to confirm the presence of valence density features (e.g., covalent bonds, lone pairs).²⁵ The definition of the electronic configuration of the neutral spherical uranium, which is employed in the calculation of DD, is nontrivial.³ We have found that the $5f^4 6d^2 7s^0$ configuration provides a better description of the U proatom in the current

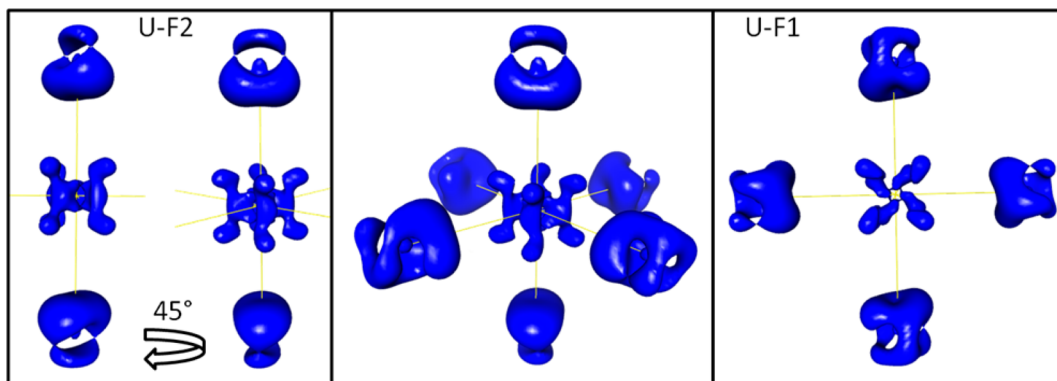


Figure 2. Static DD maps depicting charge concentrations (blue) for the entire UF_6^- ion (middle) and selected views depicting the contributions from U and F2 (left) and U and F1 (right). Isosurfaces are drawn at the 0.2 e^{-3} level.

experiment rather than the commonly used gas-phase-free atom ground-state configuration ($5f^3 6d^1 7s^2$). However, we are hesitant to make conclusions on the nature of the U–F bond(s) on the sole basis of DD maps because their appearance is so dependent on the definition of the U proatom. With this in mind, it is still worth considering the features of the DD.

Differences in the U–F interaction for F1 and F2 atoms are clear from the static DD (see Figure 2). Interestingly, the DD around the axial F2 atom resembles that of the oxo ligands in $\text{Cs}_2\text{UO}_2\text{Cl}_4$.^{5,6} In the present case, charge distributions around the axial ligand are significantly polarized and suggest $\text{F} \rightarrow \text{U} \pi$ character, while charge distributions around the equatorial ligands are nearly spherical (i.e., ionic). On the other hand, no regions of the charge concentration are directly shared between the U and F atoms, indicating ionic bonding. Because the UF_6^- ion is formally an f^1 system, we were intrigued by the possibility of mapping electrons in f orbitals. In this regard, we note (given the caveat above) that the areas of the charge concentration around the U nucleus are strongly reminiscent of the electron density expected for population of a nonbonding f orbital (specifically, the xyz orbital, which corresponds to the A symmetry representation in the point group S_4). It is tempting to attribute these charge concentrations to the formal population of f orbitals because maxima are at distances of $\sim 0.45\text{--}0.75$ Å from the U nucleus and the $5f$ radial term has a maximum around 0.43 Å from the nucleus, while the $6p$ term has a maximum around 0.75 Å from the nucleus, but as we stated above, the appearance of the DD (and therefore any resulting interpretation) is dependent on the definition of the proatom. Nevertheless, the xyz function of the A symmetry representation in the S_4 point group transforms as a_{2u} in the O_h point group (and as b_{1u} in D_{4h}) and agrees with theoretical calculations, indicating that the singly occupied molecular orbital in UF_6^- is of a_{2u} symmetry.^{2,26,27}

The differences observed in the U–F bond distances and DD are also manifest in the topological properties of the U–F bonds from the QTAIM⁹ perspective. The electron densities at the bond critical point (ρ_b) are $0.93 \text{ e } \text{Å}^{-3}$ (U–F1) and $0.90 \text{ e } \text{Å}^{-3}$ (U–F2), while the Laplacian values ($\nabla^2\rho_b$) are 7.68 and $6.30 \text{ e } \text{Å}^{-5}$, respectively. The experimental values compare favorably with those obtained from theory for a gas-phase, isolated UF_6^- ion calculated at the experimental bond distances ($\rho_b = 0.83 \text{ e } \text{Å}^{-3}$, U–F1; $0.81 \text{ e } \text{Å}^{-3}$, U–F2; $\nabla^2\rho_b = 11.88 \text{ e } \text{Å}^{-5}$, U–F1; $11.58 \text{ e } \text{Å}^{-5}$, U–F2). The direct interpretation of bonding using these values is difficult, with there being few other similar experimental charge density studies for comparison. However, the nature of the U–F bond(s) in **1** can also be considered using the scheme proposed by Espinosa et al. and Gatti,^{28,29} wherein interactions are classified on the basis of the bond-critical-point properties (ρ_b , $\nabla\rho_b$, and $\nabla^2\rho_b$) and energy densities (potential, V_b ; kinetic, G_b ; total electronic energy, H_b). While we have noted previously that such a classification of systems composed of elements with such different Z values should be made cautiously, a comparison can still be made across a series of similar compounds analyzed in the same manner. In the present case, both U–F1 and U–F2 interactions can be classified as incipient covalent bonds ($1 < |V_b|/G_b < 2$; $H_b < 0$; $\nabla^2\rho_b > 0$). This corresponds to a description in the transit region between covalent and ionic bonding. Generally, $H_b < 0$ indicates covalency, while $\nabla^2\rho_b > 0$ indicates ionic character. The U–F bonds have bond degrees (BD = H_b/ρ_b) of -0.57 and -0.59 for the U–F1 and U–F2 bonds, respectively. These values fall neatly between the BD values for U–Cl (-0.34) and U–O (-0.93), as observed in $\text{Cs}_2\text{UO}_2\text{Cl}_4$.^{5,6}

The predicted BD values are smaller (-0.38 and -0.37) because of the larger Laplacian values.

We describe an experimental charge density model, derived from X-ray diffraction data at 20 K, for **1** and report the properties of the U–F bond derived from the total electron density. Distortion of the UF_6^- group ideal O_h symmetry is slight but statistically significant. The bonding pictures derived from the experiment and theory are in good agreement and indicate that the U–F bond is very polar, but with some covalent contributions, and can be classified as an incipient covalent bond. We also note that there are limitations and subtleties in the modeling technique. For example, our model includes refinement of the anomalous dispersion terms for uranium but neglects to properly account for the resolution dependence of these terms.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02971.

X-ray crystallographic data in CIF format (CIF)

Details on refinement, synthesis, and gas-phase calculations, additional deformation and residual maps, and a table of bond critical point properties (PDF)

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This manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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