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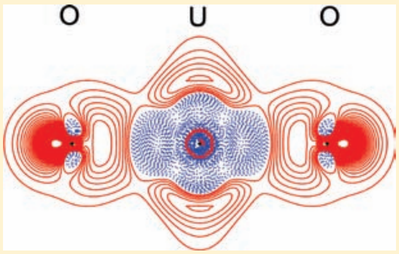
Chemical Bonding in Cesium Uranyl Chloride Based on the Experimental Electron Density Distribution

Vladimir V. Zhurov, Elizabeth A. Zhurova, and A. Alan Pinkerton*

Department of Chemistry, University of Toledo, Toledo, Ohio 43606, United States

Supporting Information

ABSTRACT: Details of the electron density distribution in $Cs_2UO_2Cl_4$ have been obtained from an accurate X-ray diffraction experiment at 20 K. The electron density was described with the Hansen−Coppens multipole model. Topological analysis of the electron density confirms that the U−O bond is probably a triple bond, the U−Cl bonds are incipient covalent interactions, and the Cs−Cl and Cs−O interactions are of the closed-shell type. The results obtained serve as a proof of principle that electron density features related to chemical bonding may be obtained from X-ray data for even the heaviest elements.



INTRODUCTION

With the renewed interest in the nuclear power industry, there has been a renaissance of interest in the characterization of the chemical bonds involving actinide elements. In particular, the uranyl dication $[UO_2]^{2+}$ has been extensively studied by means of quantum chemical methods and various spectroscopies (particularly photoelectron spectroscopy). A detailed and comprehensive review has been published by Denning.[1] Although calculations were performed for different surrounding ligands lying in the equatorial plane, most studies concentrate on the uranyl ion itself. Despite the large amount of theoretical and spectroscopic work performed, which defines energy levels and possible orbital interactions, there is a serious lack of experimental electron density studies for actinide compounds. To our knowledge, this type of X-ray study has only been applied to one other actinide compound, $Th(S_2PMe_2)_4$.[2] In this case, the dominant scattering of the thorium core electrons was absent in half of the Bragg reflections due to the special position of the thorium atom; hence, the electron density due to covalent bonding was accessible. With the recent developments in the X-ray experiment, as we show below, the electron density distribution due to covalent bonding is now available for elements as heavy as the actinides, even in the presence of the dominant core scattering.

EXPERIMENTAL SECTION

A crystal of $Cs_2UO_2Cl_4$ (40 × 70 × 100 μm), obtained from acidic, aqueous (HCl) solution, was mounted on a Rigaku diffractometer, equipped with an Ultrax-18 Mo rotating anode generator (50 kV, 300 mA) and a RAPID cylindrical image plate detector. The crystal was cooled to 20 K,[3] and 355 images (5°/360 s, oscillation width/time) were collected. Reflection indexing and cell parameter refinement were carried out with HKL2000.[4] Peak integration was performed with a modified version of VIIPP,[5] and intensities were corrected for absorption with CCDABS.[6] Data were merged with SORTAV,[7] to give 3555 independent reflections with $I/\sigma > 3$ for $0 < \sin\theta/\lambda < 1.24$ Å^{-1} ($R_{int} = 0.015$, average multiplicity 10.1). The structure[8] and the electron density distribution were refined using the Hansen−Coppens multipole model[9] as implemented in the XD2006 program,[10] using the Volkov and co-workers data bank containing STO relativistic wave functions obtained at the PBE/QZ4P level for ground state atoms.[10] Further crystallographic details and refinement results are reported in Table 1.

RESULTS AND DISCUSSION

Traditionally, in multipole model refinements, the electron density contributed by each atom is treated as the sum of a spherical core and a nonspherical valence part, where the valence radial function is averaged and combined from separate orbital radial functions with weights depending on each orbital population. This average radial function is insufficient to properly describe the situation for uranium, where terms of very different radial distributions must be included. Thus, we have chosen a model for uranium described by the superposition of four components: one atom comprised of a core with averaged 6s and 6p radial functions in the "valence shell" (thus allowing for deformation of the core) and three no-core atoms with only 7s, 6d, or 5f radial functions. As deformation of the cesium core was found, which could not be fit using a simple mixture of 5s, 5p, and 6s radial functions, a two-component model was chosen for Cs: the core with "valence" 5s and 5p electrons and a no-core atom plus a 6s part. The atomic coordinates, all thermal parameters, and κ values were constrained to be the same for "split" parts of a single atom, while the monopole and multipole populations were refined independently with the restriction that the total molecular charge be zero. Oxygen and chlorine atoms were treated as usual. Cesium

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Table 1. Experimental Details

empirical formula	$Cs_2UO_2Cl_4$
M_r	677.65
temp of measurement	20.0(1) K
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	$C2/m$
unit cell dimensions (Å, deg)	$a = 11.7882(3)$, $b = 7.6411(2)$, $c = 5.7686(2)$, $\beta = 100.438(3)$
V (Å^3), Z	511.01(3), 2
μ (mm^{-1})	23.89
T_{min}/T_{max}	0.153/0.427
d (g/cm^3)	4.404
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	1.240
reflns integrated	35939
R_{int}/average data multiplicity	0.015/10.1
independent reflns	3570
reflns used ($I > 3\sigma$)	3555
reflns/parameter	26.7
extinction coefficient	0.0178(2)[a]
weighting scheme: a, b[b]	0.004, 0.004
final $R(F)$, $R(F^2)$, GoF	0.0072, 0.0082, 1.1084
$\Delta\rho_{min/max}$, e Å^{-3} all data,	−0.715/0.708,
$\sin \theta/\lambda < 1.0$ Å^{-1}	−0.476/0.368

[a] Worst extinction 33.2% for reflection −2 2 1. [b] $w = 1/\{\sigma^2(F^2) + (ap)^2 + bp\}$, $p = 0.3333F_{obs}^2 + 0.6667F_{calc}^2$.

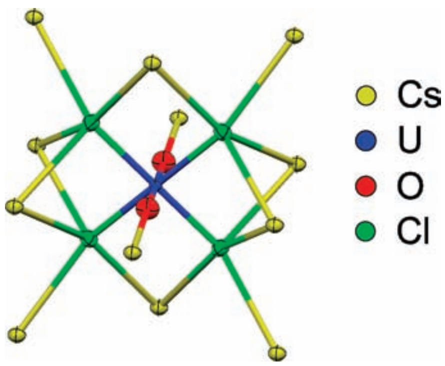

Figure 1. Structure of the $[UO_2Cl_4]^{2-}$ anion and the closest neighbor Cs^+ cations (Mercury[11]).

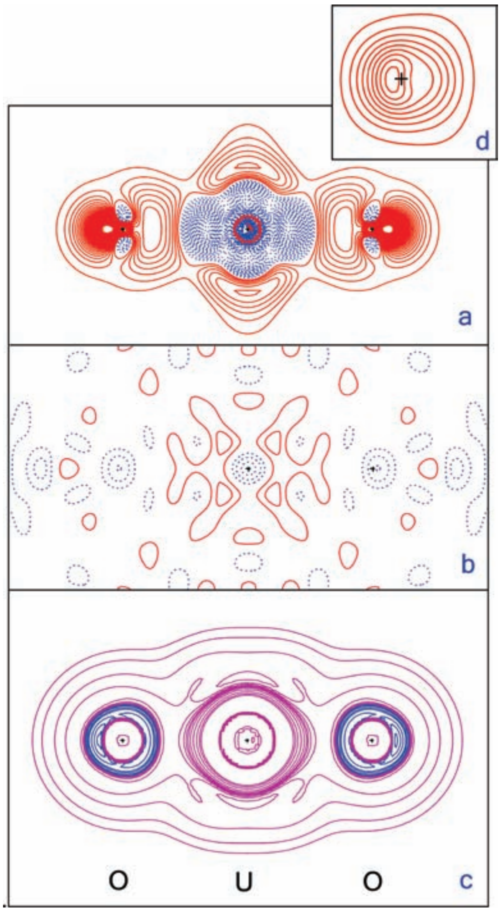

Figure 2. (a) The deformation density, (b) residual density, and (c) Laplacian maps for the uranyl ion in a plane through the 2-fold axis and the O−U−O line in $Cs_2UO_2Cl_4$, plus (d) the deformation density through the maximum and perpendicular to the U−O bond. Deformation density contour intervals are 0.05 e/Å^3. Residual contours are 0.1 e/Å^3. Positive values corresponding to an excess of electrons are red; negative ones are blue. The Laplacian contours vary—blue ones corresponding to a negative Laplacian (electron concentration).

and uranium components were refined up to hexadecupoles as allowed by symmetry. The chlorine atom was also refined up to hexadecapoles, whereas the expansion for the oxygen atom was truncated at the octupole level.

Refinement of anharmonic thermal parameters for cesium gave cleaner residual maps and improved reliability factors. However, no improvement was obtained from the anharmonic refinement of any other atoms; hence they were treated harmonically. We note that small adjustments of the anomalous scattering coefficients for uranium and cesium also improved the model.

On the basis of our refined model for the electron density distribution, we may now consider the most important bonding interactions, viz, the strong, multiple U−O bond, the weaker, equatorial U−Cl bonds, and the contribution of cesium via Cs−Cl and Cs−O interactions. These will be compared on the basis of their deformation density (the difference between the total electron density and a superposition of spherical atoms), the Laplacian of the total density, and the analysis of the topology of the total density using the Quantum Theory of Atoms in Molecules (QTAIM) approach.[12]

The structure of the $[UO_2Cl_4]^{2-}$ anion is shown in Figure 1, along with the nearest neighbor Cs^+ counterions. The features of the static deformation density distribution in $Cs_2UO_2Cl_4$ are shown in Figures 2 and 3. Figure 2 is drawn through the 2-fold axis of the unit cell and the O−U−O line. The picture also contains the Laplacian distribution and residual error maps. The residual map (Figure 2b) confirms the reliability of the model. Figure 3 is rotated by 45° about the O−U−O line and contains two U−Cl bonds. Both U−O and U−Cl bonds demonstrate positive deformation density values, but they differ in magnitude and shape. This is in agreement with a stronger bond to oxygen and a significant ionic contribution to the U−Cl bond. The magnitude of the U−O deformation density, and the observation of only one lone pair on the oxygen atom, suggests that this bond has triple bond character. This is reinforced by plotting the

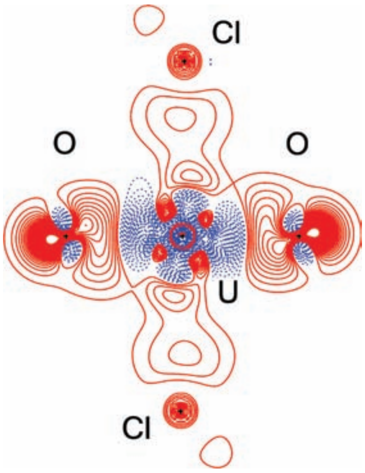

Figure 3. Deformation density map in the U−O−Cl plane of $Cs_2UO_2Cl_4$. Contours intervals are 0.05 e/Å^3. Positive values are red; negative ones are blue.

deformation density through the maximum and perpendicular to the U−O vector (Figure 2d), which shows the expected approximately axial symmetry of the bond. The valence shell charge concentrations (VSCC) obtained from the Laplacian of the total density, and observed on either side of the oxygen atom, confirm that there is only one lone pair on the oxygen, all other valence electrons being associated with the U−O bond. This is in agreement with recent theoretical studies.[1,13] It is noteworthy that the charge distribution around the oxygen atoms correlates with the reported ^{17}O chemical shift anisotropy.[14]

A critical point search[12] (WinXPro program[15]) of the total electron density revealed two identical U−O bonds (1.7762(12) Å), four identical U−Cl bonds (2.6699(1) Å), one Cs−O bond (3.259(1) Å), and four pairs of Cs−Cl bonds (3.5024(1)−3.6240(1) Å). Values of the total electron density (ρ_b) and its Laplacian ($\nabla^2\rho_b$) at the bond critical points were 1.695 e/Å^3 and 15.77 e/Å^5 (U−O), 0.486 e/Å^3 and 3.28 e/Å^5 (U−Cl), and 0.053 e/Å^3 and 0.72 e/Å^5 (Cs−O) and varied within the limits 0.067−0.076 e/Å^3 and 0.63−0.73 e/Å^5 for the Cs−Cl bonds. Espinosa et al.[16] and Gatti[17] have provided a discussion of the classification of bonds based on these critical point properties, as well as the corresponding potential (V_b), kinetic (G_b), and total electronic ($H_b = V_b + G_b$) energy densities as derived from ρ_b, $\nabla\rho_b$, and $\nabla^2\rho_b$.[18] Although we hesitate to use these classifications for bonds between atoms of such disparate atomic numbers, and for such strong interactions as in the present case, we have included them for completeness. Thus, both kinds of uranium bonds could be characterized as incipient covalent ($1 < |V_b|/G_b < 2$, $H_b < 0$, $\nabla^2\rho_b > 0$). The U−O bond has a significantly higher bond degree (BD) = $H_b/\rho_b = -0.93 \equiv$ covalence degree (CD) compared to −0.34 for the U−Cl bond. All interactions involving the cesium atom are the closed-shell type ($|V_b|/G_b < 1$, $H_b > 0$, $\nabla^2\rho_b > 0$) with low BD = $H_b/\rho_b = 0.2 \equiv$ softness degree (SD) for the Cs−O bond, and on average 0.1 for Cs−Cl bonds.

■ CONCLUSION

We have established that the extraction of highly accurate charge density details is possible even for very heavy elements such as uranium using a laboratory-based X-ray experiment. We have also provided experimental evidence that the U−O bond in uranyl compounds is most likely a triple bond, as predicted by theory, and that there is a significant covalent contribution to the weaker U−Cl bonds in $Cs_2UO_2Cl_4$, whereas all interactions with the cesium ion are of the closed-shell type.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic information in CIF format and additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: A.PINKERTON@utoledo.edu.

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