Inorganic Chemistry

Actinide 5f Occupations: The Case of PuO_2

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Cite This: https://doi.org/10.1021/acs.inorgchem.5c01709 **Read Online**

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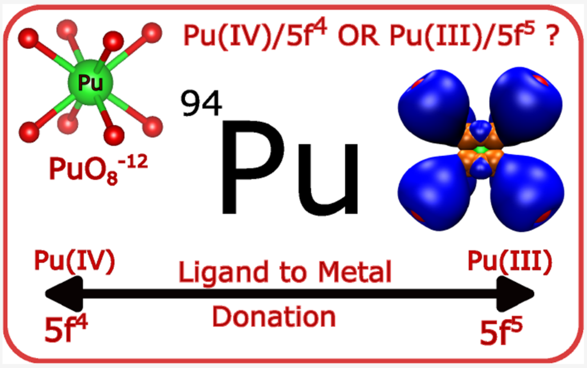
ABSTRACT: In actinide chemistry, the formal number of open-shell 5f electrons, n_{open}, is a well-defined quantity with an integer value. The *effective* 5f occupation, n_f, additionally takes donation and back-donation into account, generally has a non-integer value, and has varying numerical definitions. The present study explores the important distinction between n_f and n_{open} in actinide chemistry with the example of PuO_2, by using electronic structure methods with a relativistic Hamiltonian in combination with experimental Pu M_5-edge high-energy-resolution X-ray absorption and emission spectroscopic data. The total donation to the metal in PuO_2 is between 3.1 and 2.4 electrons, depending on the type of calculation, most of which is to the Pu 6d and 5f shells. The donation into 5f is sensitive to the approximations in the electronic structure model but likely amounts to 1.6/0.8 electrons when the diffuse regions of the 5f shell are included/excluded. Valence band resonant inelastic X-ray scattering experiments demonstrate that Pu 5f electron density is present in the valence band; thus, there is a clear experimental signature of covalent bonding in PuO_2. Pu M_5-edge and M_3-edge high-energy-resolution X-ray absorption near-edge structures for Pu^{3+} and Pu^{4+} in an aqueous solution are compared to PuO_2, showing that Pu in PuO_2 has an n_f closer to Pu^{4+}(aq).



1. INTRODUCTION

A major challenge in lanthanide (Ln) and actinide (An) chemistry is the characterization of the valence f-shell properties, in particular the identification and quantification of Ln 4f and An 5f covalency. Therefore, f-shell covalency is the focus of many ongoing experimental, theoretical, and joint efforts. This knowledge is of paramount importance for a wide range of applications, such as for the rational design of new f-element materials. The quantification of covalency is also directly associated with the assignment of the metal oxidation numbers, which are sometimes hotly contested in f-element chemistry. For example, the literature about the Ce oxidation number (ON) of cerocene (+III or +IV?) and other formal Ce(IV) complexes stretches over many decades.[1,2] Another example of an f-element system with contested metal ON is PuO_2, which is the subject of the present study.

PuO_2 is solid under ambient conditions. It crystallizes in the flourite (CaF_2) structure and features eight-coordinate plutonium with cubic site symmetry and four-coordinate oxygen sites. The local coordination of Pu in the solid is shown in Figure 1. PuO_2 would appear to be a straightforward case of assigning Pu^{4+} and O^{2-} formal ion charges, along with Pu(+IV) and O(−II) oxidation numbers (ONs) and an open-shell Pu $5f^4$ electron configuration. The number of open-shell electrons is therefore $n_{open} = 4$. The magnetic susceptibility of PuO_2 as a function of temperature is fully consistent with the assigned $5f^4$ configuration and a nonmagnetic ground state,[3,4] although it took several decades of theoretical

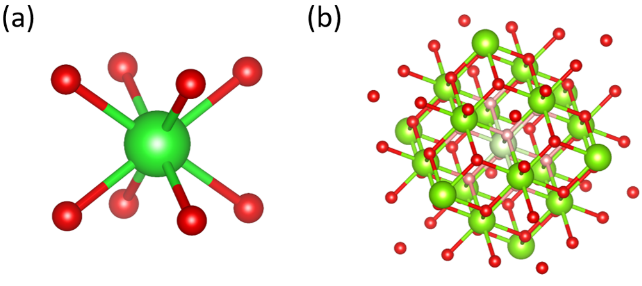


Figure 1. (a) 'Ball & stick' representation for the structure of the PuO_8^{12-} molecular cluster treated quantum mechanically. (b) First surrounding shell (boundary region) of the embedding model. The cluster from (a) is shown with lighter colors in the center.

Received: April 17, 2025
Revised: April 29, 2025
Accepted: May 6, 2025