



Schiff-base coordination complexes with Plutonium(IV) and Cerium(IV)

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Bonnie E. Klamm, Cory J. Windorff, Matthew L. Marsh, David S. Meeker, and Thomas E. Albrecht-Schmitt*

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PuL₂ and CeL₂ (L = *N,N'*-bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine) have been synthesized, and characterized by single crystal X-ray diffraction, UV/vis/NIR spectroscopy, and cyclic voltammetry. These studies reveal enhanced stabilization of Pu(IV) versus Ce(IV) with this Schiff base, and quasi-reversible redox behaviour only with the plutonium complex.

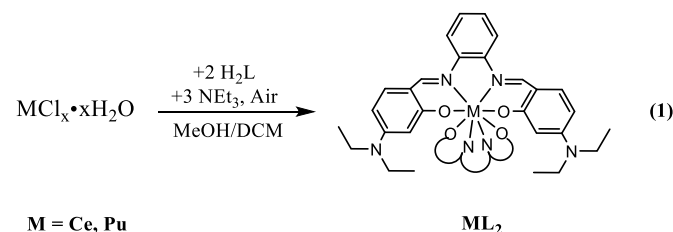
Understanding the complex chemistry of plutonium and other actinide elements has important applications to civilian nuclear fuel production, spent nuclear fuel processing, nuclear deterrents, waste disposal, and environmental monitoring.^{1,2} Current progress in plutonium studies lags behind contemporary knowledge of transition metals, lanthanides, and early actinide (Th, U) chemistry.¹ This provides an opportunity to increase our knowledge of the structural preferences, reactivity signatures, and bonding interactions in plutonium complexes. For example, the nature of the metal-based orbitals that interact with the ligand-based orbitals are active areas of research. By carefully selecting solvents, a wide variety of ligands can be utilized in order to understand the relative participation of actinide frontier orbitals (*6p*, *6d*, *5f*, *7s*, *7p*) in bonding. Additionally, the development of new types of plutonium compounds can aid in the separation and extraction of plutonium from organic solvent solutions.^{2,3}

Metal-salen, Schiff-base complexes and their derivatives are a prototypical ligands in inorganic chemistry and have been examined with elements across the periodic table, yet few homoleptic *f*-element complexes have been studied.^{4,6} The ligands feature flexible coordination modes and commonly coordinate through the oxygen atoms of the phenolic group and the backbone nitrogen atoms.⁴ This allows the ligand to coordinate to many different metals, stabilize them in various oxidation states, synthesize poly- and heterometallic complexes, and provide insight into the nature of bonding in complexes.^{4,7,8} The selectivity of certain soft-donor ligands for An^{III} and Ln^{III} ions is hypothesized to stem from enhancement of covalency in soft-donor bonding and differences in solvation.^{9,10} A number of salen and salen-

like lanthanide complexes with different compositions have been reported, however structural characterization of salen and/or salen-like lanthanide or actinide complexes are not as common.^{6, 11-15} Only a few complexes of tetravalent plutonium with salen ligands have been reported in extraction experiments, but none have been structurally characterized.^{16, 17}

Lanthanides often serve as analogs in actinide chemistry. Cerium is most often used as an analog for plutonium due to similarities in ionic radii, M^{III} → M^{IV} redox potential, coordination geometries, and these similarities often leads to isotopic series.^{3,18-20} The coordination pattern of salen ligands revealed by X-ray analysis provides valuable information for structural studies of other related lanthanide and actinide complexes.^{1,10,13,14, 21-23} In this study, we have utilized a phenylenediamine Schiff base, *N,N'*-bis[(4, 4'-diethylamino)salicylidene]-1,2-phenylenediamine (H₂L) ligand, and structurally characterize both the Pu^{IV} and Ce^{IV} complexes.

We began by synthesizing the protio ligand in a modified manner to that of the literature.^{9,15,23,20} Condensation of 1,2-phenylenediamine, *o*-C₆H₄(NH₂)₂, and two equivalents of 4-diethylaminosalicylaldehyde, HC(O)C₆H₃,2-OH,4-NEt₂ in refluxing methanol to form H₂L in high yield^{8,13,24} and characterized by ¹H and ¹³C, see ESI. Then, in air, MCl₃·xH₂O (M = Pu, Ce) was reacted with two equivalents of H₂L in methanol and in the presence of excess NEt₃ and layered with pentane. This method produced X-ray quality crystals overnight, Equation 1, Figure 1, and Figure 2.



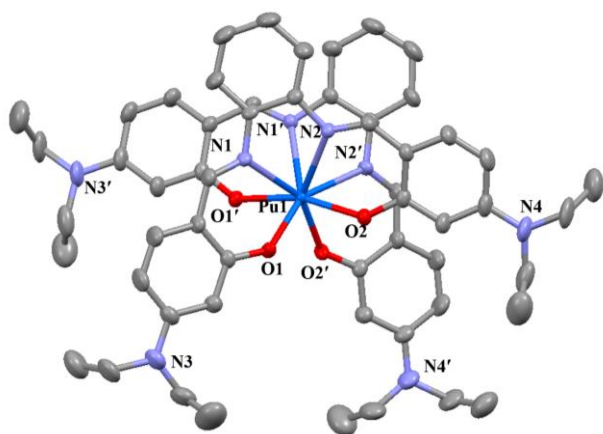


FIGURE 1. Molecular structure of PuL_2 ($L = N,N'$ -bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine) drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity. The Ce analog, CeL_2 is isomorphous.

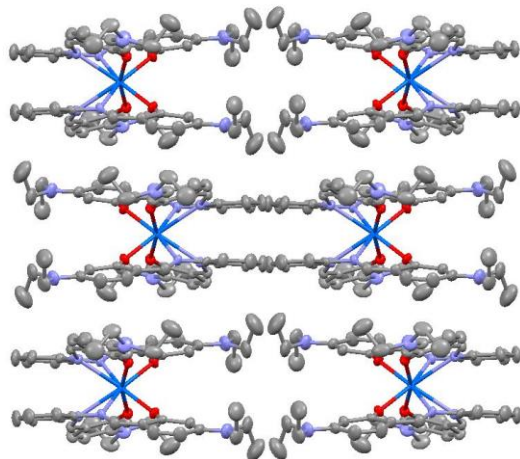


FIGURE 2. Packing diagram of PuL_2 ($L = N,N'$ -bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine) shown down the c axis. Drawn at the 50% probability level with hydrogen atoms and lattice solvent omitted for clarity. The Ce analog, CeL_2 is isomorphous.

Single crystal X-ray diffraction studies reveal that CeL_2 and PuL_2 are isomorphous, and crystallize in the monoclinic space group, $C2/c$. The metal is 8-coordinate forming a distorted square antiprism. The two ligands are skewed from one another and stack on top of each other (i.e. a sandwich-type structure), rather than a perpendicular geometry as exhibited by other CeSal_2 complexes.^{4,8,12,21,22} The sandwich structure is due to the rigidity of the phenylene moiety in the backbone of the ligand.^{4,11} The average M–O and M–N bond distances for Pu and Ce, respectively, are 2.225(3) and 2.2397(16) Å, and 2.555(3) and 2.5896(19) Å, respectively; with O(1)–M–O(2) and N(1)–M–N(2) angles for Pu and Ce, respectively, of 84.9(1)° and 85.82(6)°, and 61.6(1)° and 61.09(6)°. As expected, the Pu–L and Ce–L bond distances are not statistically different.

The solid-state, UV/vis/NIR spectra for both compounds reveal a broadband feature that begins in the high-energy region of the visible spectrum and extends into the UV. The λ_{max} for PuL_2 occurs at 529 nm, and at 411 nm for CeL_2 . This feature is consistent with a Laporte-allowed charge-transfer band and the intense dark-red/black coloring. In PuL_2 , the band is followed by much weaker peaks that have been assigned to $5f \rightarrow 5f$ transitions^{3,7,25}. Although weak, these absorption peaks are indicative of Pu^{IV} .²⁵

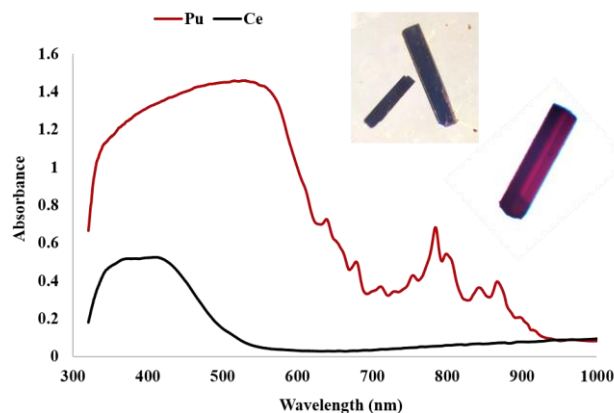


FIGURE 3. UV/vis/NIR absorption spectra and photographs of CeL_2 and PuL_2 ($L = N,N'$ -bis[(4,4'-diethylamino)salicylidene]-1,2-phenylenediamine).

To further investigate the redox potentials of PuL_2 and CeL_2 , both complexes were interrogated via cyclic voltammetry in non-aqueous solution as shown in Figure 4. While the ligand is redox active, its non-innocent behavior is altered by the onset of complexation by both Ce^{IV} and Pu^{IV} (0.45 V vs. Fc/Fc^+) for causing dearomatization.^{8,24} This oxidation was best observed at a slow (10 mV/sec) scan rate, but becomes significantly elongated at faster rates, while for the reduction (-1.29 V vs. Fc/Fc^+), re-aromatization is only observed at faster rates (>100 mV/sec). A full series of scan dependence and baseline corrections reveals that $I_{\text{pc}}/I_{\text{pa}}$ ratios increase substantially beyond 50 mV/sec, and this suggests that reoxidation is fast (Figure S7). Both hydroxylated positions on the ligand can be oxidized, but are unresolved in ligand exclusive experiments. When Ce^{IV} is bound, however, both sites become nonequivalent. Site 1 becomes easier to oxidize; while the second site becomes much more difficult to oxidize (Site 1 = 0.27 V and Site 2 = 0.80 V vs. Fc/Fc^+). Ce^{IV} is stabilized by complexation, yet shows irreversible behavior ($E_{\text{anode}} = 0.52$ V and $E_{\text{cathode}} = -1.75$ V vs. Fc/Fc^+). In contrast, Pu^{IV} appears to be stabilized by the ligand to a greater extent ($E_{1/2} = -1.75$ V vs. the Fc/Fc^+ couple) and displays quasi-reversible electrochemical behavior with a peak-to-peak separation value of 266 mV. Additionally, the greater itinerancy of the 6d and 5f shells likely serve to stabilize the redox transitions of the ligand, as all sites become more reversible overall (Site 1 = 0.23 V, Site 2 = 0.36 V, and $E_{\text{cathode}} = 0.028$ V vs. Fc/Fc^+).

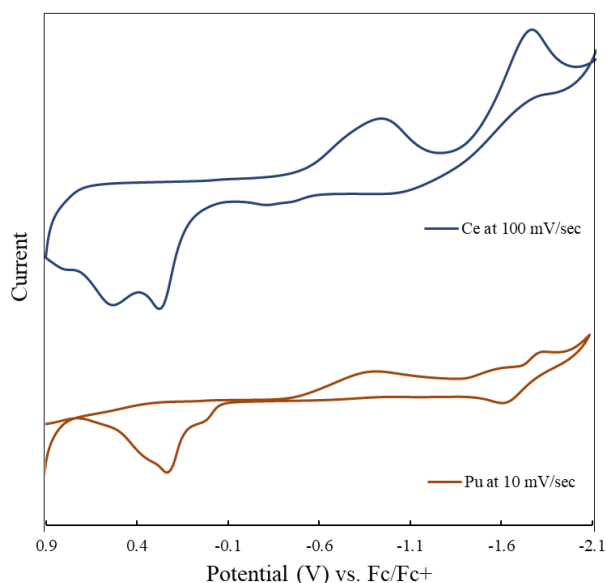


FIGURE 4. Cyclic voltammogram showing both CeL_2 at a concentration of 5×10^{-3} M and $v = 100$ mV/sec (above) and PuL_2 at $v = 10$ mV/sec (below). Both scans are taken at 25°C and with 0.1 M $[\text{N}^{\text{Bu}}_4][\text{PF}_6]$ in DCM.

Despite the wealth of previous use of salen ligands on f -elements for extraction purposes, there are few reports of single crystal structures or even homoleptic complexes. This study has focused on the synthesis of homoleptic Pu^{IV} and Ce^{IV} salen complexes by autooxidation of the M^{III} cation in air. The molecular structure and spectroscopic features of the ML_2 complexes have been characterized and confirm the M^{IV} oxidation state assignment. Both the lanthanide and actinide complexes adopt the same coordination and structure with only subtle differences. These observations provide insight to the nature of bonding and coordination of the heavy elements.

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Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, RM. 118 DLC, Tallahassee, Florida 32306, United States.

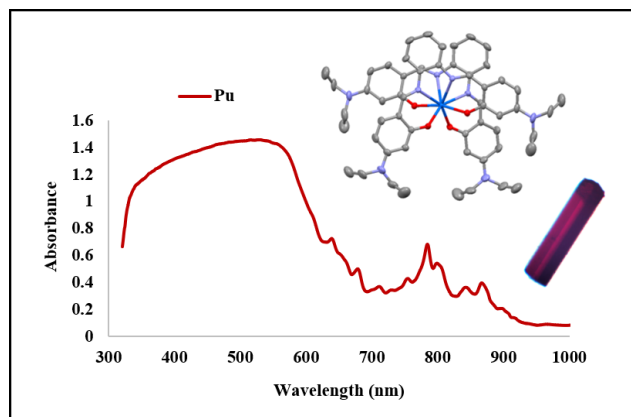
† Electronic supplementary information (ESI) available: Experimental details and crystallographic data (PDF and CIF) for compound names (CCDC numbers). For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/xxxxxxxxxx

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Synthesis and characterization of a Pu(IV) salen complex reveals stabilization the +4 oxidation state with respect to that observed with Ce(IV).