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Evidence of Alpha Radiolysis in the Formation of a Californium Nitrate Complex

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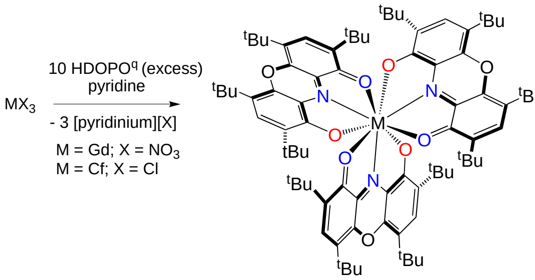
Abstract: Well-characterized complexes of transplutonium elements are scarce because of the experimental challenges of working with these elements and the rarity of the isotopes. This leads to a lack of structural and spectroscopic data needed to understand the nature of chemical bonds in these compounds. Herein we report the synthesis of $Cf(DOPO^q)_2(py)(NO_3)$ ($DOPO^q$ = 2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoxazin-9-olate; py = pyridine) where the nitrate anion is hypothesized to form via the α-radiolysis-induced reaction of pyridine and/or the ligand. Computational analysis of the electronic structure of the complex reveals that the Cf^{III}–ligand interactions are largely ionic.

In the last two decades, significant strides have been made in understanding the chemistry and physics of transuranium elements.[1] One indication of these advances is the rapid increase in compounds and complexes for which single crystal structures are known. Even elements as heavy as plutonium, have had several hundred of high-resolution structures and their accompanying properties have been reported.[2] These data are critical to understanding how electronic structure evolves in an area of the periodic table that has eluded simple descriptions because of heightened relativistic effects on electrons, high coordination numbers, a host of potential frontier orbitals that could be involved in bonding, and often ignored radiolytic effects on reactions.[3]

Despite significant progress in the chemistry of neptunium and plutonium, elements beyond Z = 94 remain poorly understood for a variety of reasons that include significant safety challenges from the evolving nuclear properties of the elements (i.e. intense γ-ray emission and neutron hazards from spontaneous fission need to be taken into account in experimental design). Moreover, the availability of isotopes is also problematic and reactions scales beyond a few milligrams are non-existent beyond californium. Thus, chemistry with elements from Z = 95 to 98 can only be conducted in a few labs in the world. To date, nine structurally-characterized californium complexes have been reported that range from simple binary compounds like $CfCl_3$ to complex molecules such as $Cf(Hdpa)_3$ (dpa = 2,6-pyridinedicarboxylate or dipicolinate).[4]

Recently, our team reported the synthesis and characterization of the californium dioxophenoxazine complex $Cf(DOPO^q)_3$ ($DOPO^q$ = 2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoxazin-9-olate).[5] The isolation of $Cf(DOPO^q)_3$ is an important indicator of progress in transuranium chemistry, as this includes the use of non-aqueous solvents under air-free conditions that has been expanded in scope to include recent reports of highly-reactive compounds such as $AmCl_3(thf)_3$ and $Am(Cp^‡)_3$ ($Cp^‡$ = tetramethylcyclopentadienyl).[6,7] Thus, with significant preparation and lanthanide modelling, chemistry that once stopped at uranium can now be extended to californium.

The most efficient synthesis for dark teal $Cf(DOPO^q)_3$ was found to be treating $^{249}CfCl_3$ with 10 equivalents of $HDOPO^q$ because this facilitated fast crystallization from pyridine (eq 1). Computational analysis of this complex determined that the bonding between the californium center and the ligands is more ionic than found in $Cf(Hdpa)_3$,[4] $Cf[B_6O_8(OH)_5]$,[8] $Cf_4[B_{16}O_{26}(OH)_4(H_2O)_3Cl_4]$,[9] and $Cf(IO_3)_3$[10] perhaps because interactions between bulky tert-butyl groups on neighboring $DOPO^q$ ligands prevent short enough interactions to significantly engage frontier orbitals on the californium center.



(1)

An important cautionary note was included in the synthesis of $Cf(DOPO^q)_3$ in that the dark teal solution of Cf^{3+} in pyridine became dark red in color within a few hours, likely due to radiolysis effects. ^{249}Cf presents among the most significant technical challenges for chemical studies because its most abundant γ emission is highly penetrating with an energy of 388 KeV, and its moderately-short half-life of 351 years is caused by α decay with energies of ~6 MeV. Radiolysis plays a role in all reactions involving short-lived isotopes, and reports even indicate that longer-lived ^{239}Pu ($t_{½}$ = 24,110 y) can radiolytically convert N_2 from air into nitrate in the presence of water.[11] While this conversion at first glance might seem astonishing, the energy of α particles from the nuclear decay of actinides is ~10^6 greater than the largest bond dissociation energy. It should be expected that the even higher energy decay of ^{249}Cf should also lead to radiolytic products.

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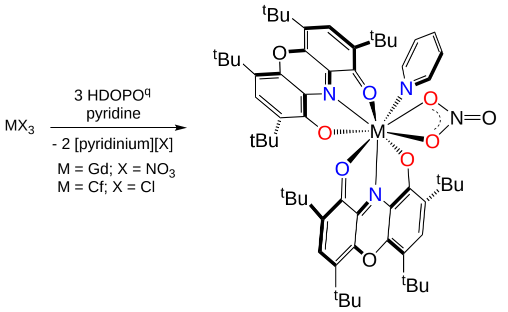
In efforts to reproduce this dark red material, stirring 3 equiv. of HDOPO^q with $^{249}CfCl_3$ resulted in slower formation of dark red crystals and the isolation of an unexpected californium complex containing a ligand that likely results from radiolysis,



(2)

$Cf(DOPO^q)_2(py)(NO_3)$ (eq 2). The structure of this molecule was confirmed by X-ray diffraction analysis of single crystals obtained from a concentrated pyridine solution.

In this case, two DOPO^q ligands, one pyridine molecule, and one κ^2-nitrate compose the coordination sphere, generating a nine-coordinate distorted tricapped trigonal prismatic Cf center. (Fig 1, right). Overall, the Cf–L bond distances are in accord with that expected for Cf^{3+}. The Cf–O bond lengths (Table 1), ranging from 2.380(2) to 2.455(3) Å, are similar to those reported for $Cf(Hdpa)_3$ (2.387(4) – 2.494(4) Å).[4] The Cf–N distances of 2.518(3) and 2.539(13) Å in $Cf(DOPO^q)_2(py)(NO_3)$ also correspond well to those in $Cf(Hdpa)_3$ of 2.508(4), 2.512(4), 2.545(4) Å. The intra-ligand distances for both DOPO ligands produce an average metrical oxidation state (MOS) value of -1.02(17), consistent with the quinone resonance form.[5,12] Repeated attempts at isolation of crystals of $Cf(DOPO^q)_3$ were unsuccessful with reaction stoichiometry of M:L = 1:3. Instead, crystals of $Cf(DOPO^q)_2(py)(NO_3)$ were obtained exclusively every time.

Degradation of the dark teal solution of $Cf(DOPO^q)_3$ is evident even on milligram scales, with the dark red color signifying formation of $Cf(DOPO^q)_2(py)(NO_3)$. It is proposed that the nitrate is likely formed from radiolysis of the pyridine or ligand in the presence of water, since the californium starting material exists as the hydrate, $^{249}CfCl_3{\cdot}nH_2O$. As the nitrate concentration increases, it competes with $(DOPO^q)^{1-}$ for californium binding and ultimately $Cf(DOPO^q)_2(py)(NO_3)$ crystallizes. A high-resolution mass spectrum of $^{249}CfCl_3{\cdot}nH_2O$ reveals no nitrate is present in the material. Furthermore, multiple fresh batches of $^{249}CfCl_3{\cdot}nH_2O$ from Oak Ridge National Lab as well as freshly recycled and re-purified material were tested and yielded the same result. Ultimately, nitrate is not present at detectable levels in the starting material and likely forms from radiolysis of pyridine or ligand and subsequent reactions of radiolytic products with water (or even radiolysis products of water). Generation of the californium nitrate in this case highlights that while non-aqueous chemistry can be performed with short-lived isotopes, crystallization conditions need to be optimized for rapid precipitation of crystals - preferably in minutes.

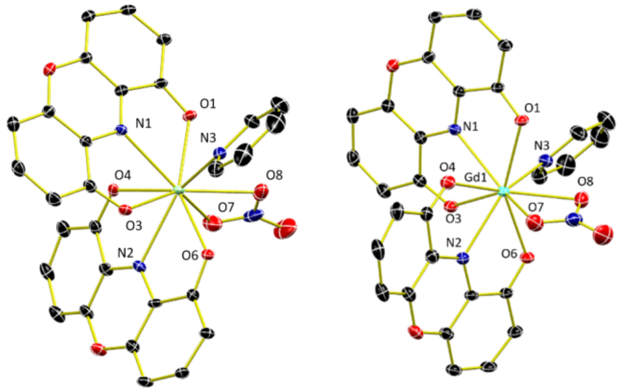


Figure 1. Molecular structures of $M(DOPO^q)_2(NO_3)(py)$ (M = Gd, Cf). For clarity, all hydrogen atoms, tert-butyl substituents, and solvent molecules have been omitted (displacement ellipsoids drawn at 30% probability).

Table 1. Selected bond lengths of $M(DOPO)_2(NO_3)(py)$ (M: Gd, Cf) in Å

	Gd	Cf
M-O1	2.386(2)	2.419(2)
M-O3	2.426(2)	2.411(2)
M-O4	2.434(2)	2.380(2)
M-O6	2.401(2)	2.455(13)
M-N1	2.493(3)	2.518(3)
M-N2	2.516(3)	2.539(13)
M-O7(	2.469(3)	2.475(3)
M-O8	2.500(3)	2.506(3)
M-N3(py)	2.528(3)	2.526(3)

In efforts to better understand the formation of $Cf(DOPO^q)_2(NO_3)(py)$, the synthesis of the Gd^{3+} analog was explored. Lanthanide congeners are often used as synthetic models for actinides because of their similar ionic radii and coordination environments. Our previous syntheses showed rapid formation of $Gd(DOPO^q)_3$ on a 5 mg scale from $GdCl_3$ (anhydrous). In this case, $Gd(NO_3)_3$ was suspended in pyridine and 3 equivalents of HDOPO^q were added, producing the recognizable vibrant teal coloration indicative of $Gd(DOPO^q)_3$. However, upon standing, dark blue crystals of $Gd(DOPO^q)_2(NO_3)(py)$ formed as was observed with Cf^{3+}, demonstrating that nitrate can replace the dioxophenoxazine ligand easily in solution. Increasing the gadolinium concentration in the same amount of pyridine or using excess ligand both resulted in the isolation of $Gd(DOPO^q)_3$, also confirmed by X-ray crystallography. ^1H NMR spectra of these gadolinium species were not useful for structural assignment due to the paramagnetism of the Gd^{3+}, a $4f^{\,7}$ ion.

The molecular structure of $Gd(DOPO^q)_2(NO_3)(py)$ is isomorphous with the Cf^{3+} analogue (Figure 1, left). The Gd–O (DOPO) bond distances range from 2.386(2) to 2.434(2) Å and compare well with $Gd(Hdpa)_3$; however, these distances are shorter than those observed for $Gd(DOPO^q)_3$. The Gd–N bond distances of 2.493(3) and 2.516(3) Å agree well with $Gd(Hdpa)_3$, but are still shorter than those in $Gd(DOPO^q)_3$. The intra-ligand distances for both DOPO ligands are consistent with a MOS value of -1.12(94), which is expected for the quinone resonance form.[12] The Gd-O(nitrate) bonds are 2.496(3) and 2.500(3) Å which are expected for these bonds.

The general structural trend that is evident for $M(DOPO^q)_2(NO_3)(py)$ (M = Cf, Gd) is that the metal-ligand distances are shorter in the bis(ligand) derivatives as compared to the tris(ligand) derivatives. This is likely due to the significant steric hindrance imparted by the *tert*-butyl groups on the DOPO^q ligand causing elongation of the M–O and M–N bonds for both M(DOPO^q)$_3$ (M = Cf, Gd) derivatives. From the space filling models (Figure S1), it is possible to see that the tert-butyl groups are crowded, which could be preventing closer access of the ligands to the metal center. Replacing the third ligand with the κ^2-nitrate and pyridine ligand provides a larger degree of freedom, allowing the ligands to more effectively bond with the metal resulting in shorter bonds.

Electronic absorption spectroscopic data was acquired for both M(DOPO^q)$_2$(NO$_3$)(py) (M = Cf, Gd) as solid crystals in the UV-visible-NIR regions (Figure S2). Both Cf(DOPO^q)$_2$(NO$_3$)(py) and Gd(DOPO^q)$_2$(NO$_3$)(py) have analogous absorbances, showing characteristic transitions at 426 and 598 nm. These absorbances are in the same range of those observed for Gd(DOPO^q)$_3$ and Cf(DOPO^q)$_3$, but are also broader than what was noted for those complexes.[5] These absorbances are assigned as the π to π^* transitions of the DOPO^q ligand. The intensities of these absorbances are characteristic of a transition into an empty DOPO^q -based π^* orbital. The energies of these transitions are consistent with those observed for KDOPO^q(THF) (λ_{max} = 735 nm) as well as the corresponding sodium salt (λ_{max} = 695 nm).[12,13]

A computational studybased on complete active space self consistent field calculations (CASSCF) of the electronic structure of the californium and gadolinium derivatives was performed to compare bonding between the lanthanides and actinides in trivalent DOPO complexes (see Computational Methods, section S1 for details). For trivalent Cf(DOPO^q)$_2$(py)(NO$_3$), there are 9 electrons to place on the seven 5*f* orbitals, generating three possible spin states, namely sextet, quartet and doublet. Therefore, the active space consists of nine electrons and seven orbitals, analyzed in a CASSCF(9,7) calculation (Table S2). Results show the sextet is the most stable spin state, with the quartet and doublet being higher in energy. The orbitals of the active space for the sextet spin state along, reported in Figure 3 with the respective occupation numbers are mainly 5*f* orbitals localized on Cf, with no significant contribution from the DOPO^q ligand orbitals. LoProp[14] charge and Mulliken spin density analyses confirm this outcome (Table S3), showing that the orbitals and spin density are completely localized on Cf (5*f* orbitals), with a LoProp charge for Cf of 2.41. In order to reveal possible ligand involvement, the active space was expanded by including two occupied (and the two corresponding virtual) orbitals on the DOPO ligands, corresponding to a CASSCF(13,11), namely 13 electrons in 11 orbitals. This calculation did not change the spin state energetics, the spin density, or the LoProp charge on Cf, suggesting no significant electron delocalization between the Cf 5*f* orbitals and ligand orbitals (Tables S4-S5 and Figure S3). Furthermore, the DOPO ligands are found as the quinone resonance form, consistent with experimental observations.

The electronic structure of Gd(DOPO^q)$_2$(py)(NO$_3$) was elucidated by performing a CASSCF(7,7) calculation. The results (Table S6-S7) show that the ground spin state is high spin, with all the spin density localized on Gd, consistent with a Gd(III) ion. Figure S4 shows that the unpaired electrons are localized in the 4*f* orbitals of Gd, with no ligand involvement whatsoever. Expanding the active space to (11,11) by adding two ligand based orbitals and the corresponding virtual orbitals did not change the result, as again, no spin density was found on the ligand orbitals (Tables S8-S9 and Figure S5).

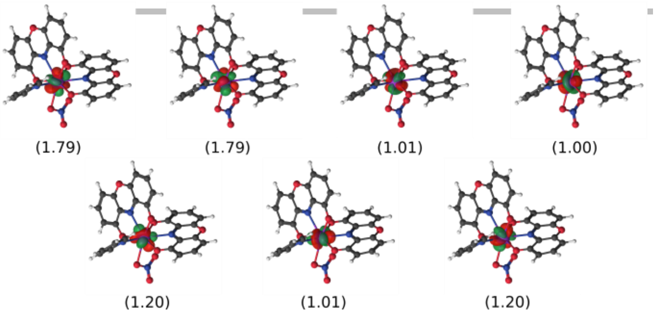


Figure 2. Active space orbitals (occupation numbers in brackets) for the ground state (sextet spin state) of Cf(DOPO^q)$_2$(py)(NO$_3$) complex.

Further computational studies of M(DOPO^q)$_2$(NO$_3$)(py) (M = Gd, Cf) were performed to see if the differences between the 4f and 5*f* orbitals might increase covalency in the Cf-DOPO bond with respect to the Gd-DOPO bond (see section S3 in the ESI). Covalency is small in both complexes, but a difference in bonding is noted using *Ab-initio* Ligand Field Theory (AILFT), which shows a pronounced ligand cloud expansion over the *f* shell for Cf-DOPO. Likewise, the Atoms in Molecules (AIM) approach shows an increased concentration of electron density and delocalization indices at Cf–DOPO bonds. While the bonding in these derivatives is best described as ionic, these results imply slightly better orbital overlap in Cf-DOPO over Gd-DOPO.

Conclusions. In summary, the formation of Cf(DOPO)$_2$(NO$_3$)(py) has been observed, and the characterization of this molecule has been reported. Based on modeling experiments with gadolinium, it is clear that metal concentration plays a key role in the formation of products on small scales. Comparison of Cf(DOPO)$_2$(NO$_3$)(py) as to the previously established Cf(DOPO^q)$_3$ shows shorter M-L bond distances. Computational analysis shows that both Cf and Gd are in a +3 oxidation state, with the DOPO ligands being in the quinone resonance form. The Cf-DOPO bond shows a slightly higher covalency than the Gd-DOPO bond.

This work demonstrates when modeling for the heavier, short lived transuranium elements, radiolytic effects cannot be neglected since the lanthanides do not model the nuclear properties of these elements. Despite well-choreographed experiments on the lanthanide series, translating onto heavier actinides may afford smaller yields, poorer crystal quality, and side products. Because relativistic effects dictate the chemistry of the transuranium elements, the study of the fundamental properties of these elements is essential to understand the trends that occur in this area of the periodic table

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Keywords: Californium • Radiolysis• f-element • Electronic Structure Analysis

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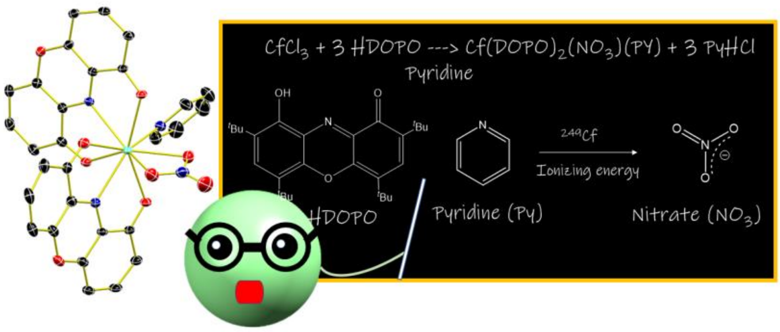

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Page No. – Page No.

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