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ARTICLE

A hydrolytically stable Ce(IV) complex of glutarimide-dioxime

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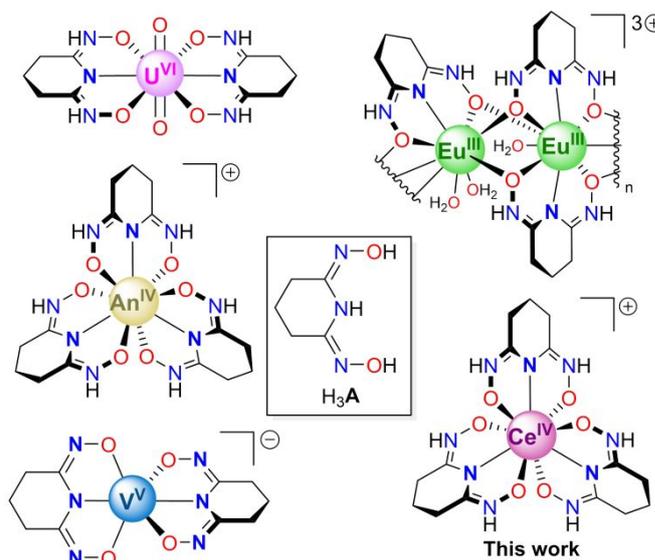
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The coordination chemistry of glutarimide-dioxime (H₃A) has been studied related to applications in uranyl sequestration from seawater and for the stabilization of early transition metals in high oxidation states. We report here that the H₂A⁻ anion is also suitable for stabilizing Ce(IV) and acts as a tridentate ligand to form the [Ce(H₂A)₃]⁺ cation. The metal complexes [Ce(H₂A)₃]Cl and [Ce(H₂A)₃][BPh₄]⁻ have been obtained by auto-oxidation of Ce^{III} in the presence of H₃A under aerobic conditions. UV-Vis spectroscopy and DFT calculations were performed to characterize the electronic structure and ligand-to-metal charge transfer (LMCT) bands of [Ce^{IV}(H₂A)₃]⁺. X-ray absorption spectroscopy (XAS) was also performed to verify the Ce(IV) oxidation state. Absent a clear electrochemical signal for cerium reduction in [Ce(H₂A)₃]Cl or [Ce(H₂A)₃][BPh₄]⁻ under a range of conditions, DFT calculations predicted a Ce(III/IV) redox couple of -1.22 V vs Fc/Fc⁺. These results further expand the coordination chemistry of glutarimide-dioxime to tetravalent cerium.

Introduction

Among the lanthanides, the element cerium (Ce) can exhibit the unusual characteristic of a relatively accessible +4 oxidation state.^{1,2} To stabilize this high oxidation state, it is necessary to employ an electron-donating ligand that is resistant towards oxidation.³⁻⁸ There are a variety of reported Ce(IV) complexes stabilized by different ligand frameworks, such as [NEt₄]₂[CeCl₆], [Ce(acac)₄], [CeX(TriNOx)] (TriNOx³⁻ = [(2-t BuNO)C₆H₄CH₂]₃N³⁻; X= F, Cl, Br), [Ce(pyNO)₄] (pyNO = 2-(^tBuNO)pyridine), and others.⁹⁻¹³ Glutarimide-dioxime (H₃A, C₅H₉N₃O₂), a compound reported to be useful for sequestering uranium from seawater, is considered here for stabilization of the cerium(IV) cation.

H₃A was originally known to extract uranyl (U^{VI}O₂²⁺) as [UO₂(HA)] and [UO₂(H₂A)(HA)]⁻ from seawater, while competing with other uranyl species, such as [UO₂(CO₃)₂]²⁻ and [UO₂(CO₃)₃]⁴⁻.¹⁴⁻¹⁸ H₃A was then developed to readily chelate simple metal ions, such as Ca(II),¹⁹ Mg(II),¹⁹ Cu(II),²⁰ Pb(II),²⁰ Ni(II),²⁰ Mn(II),²¹ Fe(III),²⁰ Eu(III),²² Nd(III),²² and metals of high oxidation states, such as Th(IV),²³ Np(IV),²³ Pu(IV),²⁴ Np(V),²⁵ and V(V).²⁶⁻²⁸ We reasoned it would similarly stabilize the Ce(IV) cation as in the high oxidation state metal complexes cases (Scheme 1).



Scheme 1 Glutarimide-dioxime (H₃A) and its complexes: [U^{VI}O₂(H₂A)₂], [Eu^{III}₂(H₂A)₃(H₂O)₃(ClO₄)₃], [An^{IV}(H₂A)₃]⁺ (An = Th, Np, Pu), [V^VA₂]⁻, and [Ce^{IV}(H₂A)₃]⁺ (this work).

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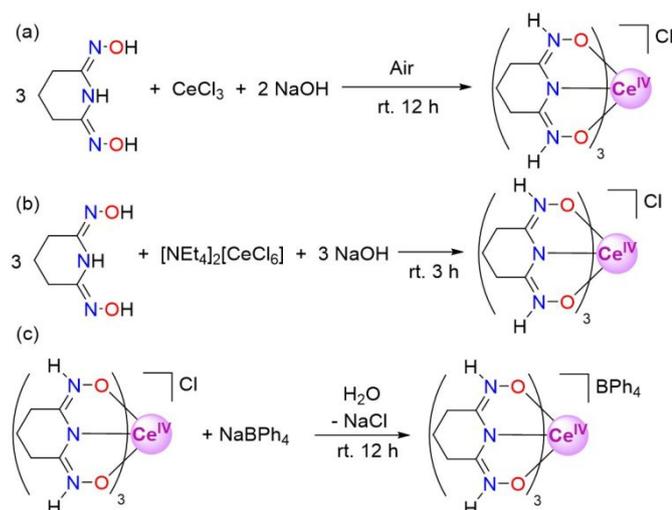
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Scheme 2 (a), (b) Synthesis of $[\text{Ce}^{\text{IV}}(\text{H}_2\text{A})_3]\text{Cl}$. (c) Synthesis of $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$.

Complexation of glutarimide-dioxime (H_3A) with tetravalent cerium is of potential interest from applied and fundamental chemistry perspectives. A tetravalent cerium cation is expected to have a higher binding affinity with H_3A than trivalent lanthanides, which could facilitate lanthanide separations. From a fundamental standpoint, obtaining structural data, UV-Vis spectroscopic, and X-ray absorption spectra of a $\text{Ln}^{\text{IV}}-\text{H}_3\text{A}$ complex would allow the better understanding of the valency and ligand-to-metal charge transfer (LMCT) bands for Ln^{IV} complexes, and would provide an opportunity for comparison with the previously reported $\text{An}^{\text{IV}}-\text{H}_3\text{A}$ complex ($\text{An} = \text{Th}, \text{Np}, \text{Pu}$).²³⁻²⁴

Results and discussion

Synthesis of $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ and $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$

Adding an aqueous solution of $\text{Ce}^{\text{III}}\text{Cl}_3$ to a prepared aqueous solution of 3 equiv H_3A and 2 equiv NaOH in aerobic condition, resulted in an immediate colour change from colourless to first maroon and then purple (Scheme 2a). Oxidation of $\text{Ce}(\text{III})$ to $\text{Ce}(\text{IV})$ was strongly indicated by the presence of a characteristic LMCT band at 505 nm (Figure S9).¹⁰ Using $(\text{NH}_4)_2[\text{CeCl}_6]$ as a $\text{Ce}(\text{IV})$ starting material with H_3A and NaOH in the proper stoichiometry, an identical purple solution was obtained and verified by ^1H NMR spectroscopy (Scheme 2b). ^1H NMR spectroscopy recorded on the purple solution in D_2O confirmed that the purple solution contained a new species, $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$.

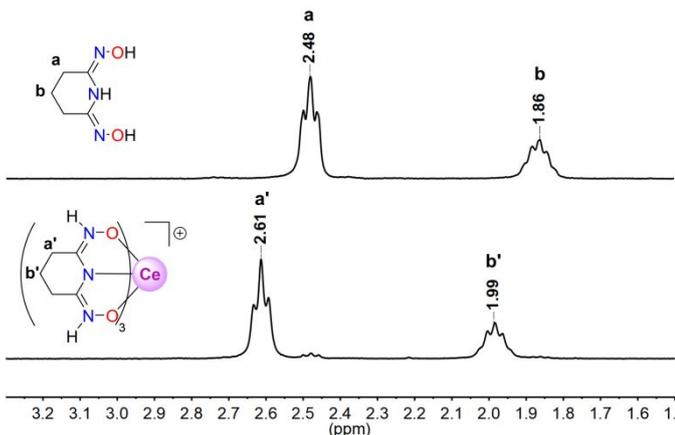


Figure 1 ^1H NMR of H_3A and $[\text{Ce}(\text{H}_2\text{A})_3]^+$ in D_2O (300 MHz, room temperature). H_3A has shown the peaks at 2.48 and 1.86 ppm, while $[\text{Ce}(\text{H}_2\text{A})_3]^+$ has shown peak at 2.61 and 1.99 ppm.

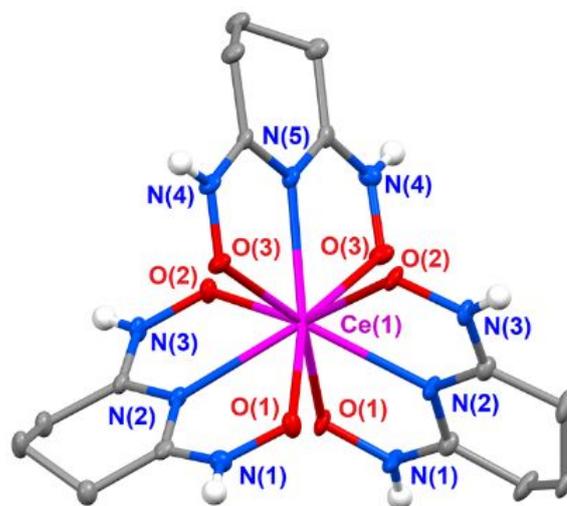


Figure 2 Thermal ellipsoid plot of $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ at 50% probability (Cl^- , aliphatic hydrogen atoms, and H_2O molecules are omitted for clarity).

The downfield chemical shift indicated a diamagnetic H_3A -based metal complex, consistent with previous reports (Figure 1).²² Noting that the chemical shift of water is pH sensitive, we added trace acetone or Et_2O to the ^1H NMR sample to act as an internal standard to obtain consistent results for H_3A and $[\text{Ce}(\text{H}_2\text{A})_3]^+$.

Purple needle-shaped crystals of $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ were obtained by slow evaporation of an aqueous solution of the cerium(IV) complex (Figure 2). The single crystal X-ray structure showed that $[\text{Ce}(\text{H}_2\text{A})_3]^+$ ions formed a 3-dimensional hydrogen bonding network with $=\text{N}(\text{O})\text{H}$ groups acting as proton donors and $\text{N}-\text{O}$ moieties functioning as proton acceptors, together with H_2O and Cl^- (See Figure S2).

Due to the low solubility of $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ in organic solvents, a salt metathesis reaction was performed by adding an aqueous solution of NaBPh_4 to obtain a more organic soluble species (Scheme 2, c). Chunks of purple crystals of $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$ were obtained by recrystallization. The crystal structure of $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$ showed that $[\text{Ce}(\text{H}_2\text{A})_3]^+$ ions formed a 2-dimensional hydrogen bonding network together with interstitial H_2O molecules. These 2-dimensional layers were separated by hydrophobic $[\text{BPh}_4]^-$ layers (See Figure S4).

Characterization and Computational analysis

UV-Visible absorption spectroscopy studies indicated that the purple colour of $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ was due to a LMCT band at 505 nm (Figure 3, a; $\epsilon = 2600 \text{ M}^{-1}\text{cm}^{-1}$). Gaussian fits to the absorption band data yielded 3 bands at 228 nm, 284 nm and 487 nm (see Figure S10). The 228 nm band was assigned as a ligand-based transition considering the 228 nm absorption peak of the proligand.²⁹ The bands centred at 487 nm were assigned as LMCT bands, consistent with previous reports on other $\text{Ce}(\text{IV})$ systems.⁹⁻¹⁰

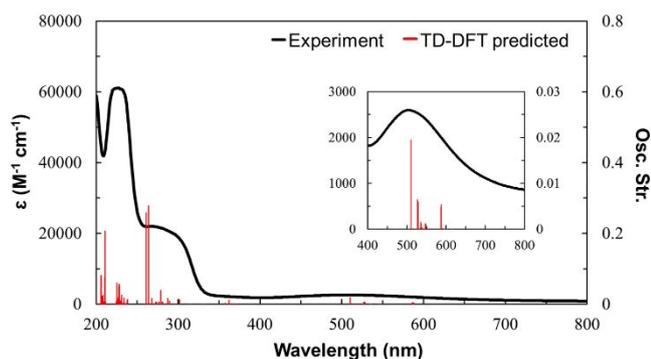


Figure 3 UV-Vis spectrum and TD-DFT predicted oscillator strength of the $[\text{Ce}(\text{H}_2\text{A})_3]^+$ cation in H_2O . The inset showed the transition at 505 nm by zooming in, and all axes units were identical.

To further understand the electronic transitions of the $[\text{Ce}(\text{H}_2\text{A})_3]^+$ cation, we have computed the electronic structure of $[\text{Ce}(\text{H}_2\text{A})_3]^+$ by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods, based on the coordinates from the crystal structure. Similar calculations involving Ce(IV) or H_3A have been reported previously.^{16,21,28,30-32} The optimized structure exhibited good overall agreement with crystallographic data. The major differences involved the Ce-N bonds, exhibiting deviations up to 0.05 Å between the computational and experimental results. The highest occupied molecular orbital (HOMO) has a primarily

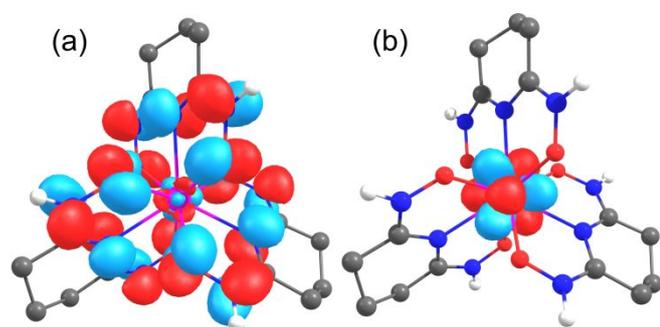


Figure 4 (a) HOMO and (b) LUMO of $[\text{Ce}(\text{H}_2\text{A})_3]^+$ (protons attached to carbons are omitted for clarity).

ligand character (>98%) while the lowest unoccupied molecular orbitals (LUMO) has mostly Ce character (>97%), consistent with a highly ionic bonding interaction (Figure 4).

TD-DFT calculations yielded vertical excitations within 3 major regions ~211, 261 and 510 nm. These corresponded to 3 transitions at 228 nm, 284 nm and 487 nm, obtained from a Gaussian fitting of the UV-Visible spectrum (Figure 3). As mentioned above, the first peak at 211 nm comprises transitions mostly from a C=N ($\pi \rightarrow \pi^*$) orbital, and transitions partially from a N-C-N π orbital to the Ce 4f orbitals. The second peak at 261 nm matches transitions from a C=N π orbital and a N-O π^* orbital to the C=N π^* orbital. The third transition at 510 nm denotes the transitions from a C=N π orbital and a N-O π^* orbital to the Ce 4f orbitals.

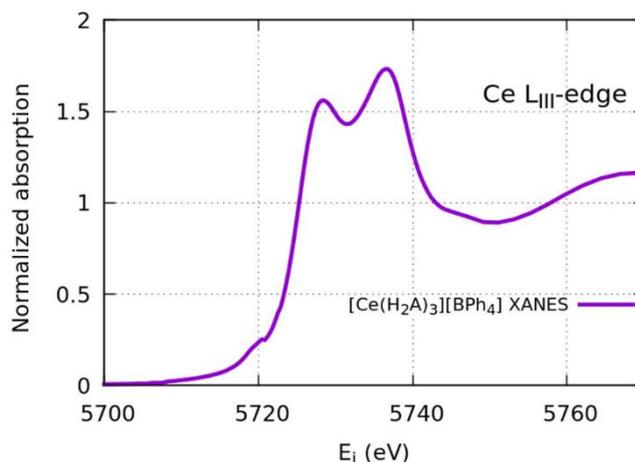


Figure 5 X-ray absorption spectrum for $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$.

The third region of transitions was assigned between donors and acceptors: donors from HOMO-2 to HOMO of the ligand-based orbitals (>95%), and acceptors from LUMO to LUMO+6 of the Ce 4f based orbitals (>92%) (See Supporting Information Table S4). Thus, the calculated transition at 510 nm can be assigned as a LMCT band.

Cerium (IV) compounds are known to exhibit valence instability and multi-configuration ground states.³³ Thus, an X-ray absorption spectroscopic (XAS) experiment on the Ce L^{III} -absorption edge was performed to confirm the 4+ oxidation state without valence instability and emphasize the ligand stabilizing ability. The spectrum showed 2 peaks indicative of the core hole excitation from a Ce(IV) ion of $2p_{3/2}4f^1\bar{L}5d^0$ and $2p_{3/2}4f^05d^0$ to the final states of $2p_{3/2}4f^1\bar{L}5d^1$ and $2p_{3/2}4f^05d^1$, where the bar indicates a hole (vacancy) and L indicates the ligand (Figure 5). These data confirmed the expected 4+ oxidation state of cerium within the complex. XANES fitting (see Supporting Information) revealed a fractional f occupancy (n_f) of 0.54(3), typical of formal Ce(IV) compounds.

To further evaluate the ligand stabilization of Ce(IV), we attempted to measure the redox potential of the Ce(III/IV) couple for the $[\text{Ce}(\text{H}_2\text{A})_3]^+$ cation. Solution cyclic voltammetry experiments were carried out for $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ in H_2O using NaCl as supporting electrolyte and for $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$ in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (4:1 v/v) or propylene carbonate, both using $[\text{N}^n\text{Bu}_4]\text{PF}_6$ as supporting electrolyte. Notably, $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ and $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$ exhibited no obvious redox waves for Ce(III/IV) redox couple under these conditions. H_3A is known to lack electrochemical signals in its neutral state.²¹ The absence of a Ce(III/IV) redox wave in either case is somewhat unexpected, but self-consistent between the two different anions and sets of measurements conditions. The absence of Ce(III/IV) waves has been noted for other cerium complexes previously, including $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$.³⁴ This phenomenon is tentatively attributed to slow kinetics of electron transfer from the sterically saturated Ce(III) complexes.^{34, 35} Oxidation of Ce(III) complexes is typically accompanied by a reduction in cerium-ligand bonds of ~0.1 Å.³⁶ The slow electron transfer rate is thus

attributed to a large inner sphere reorganization energy, as described by some of us previously.³⁵ Indeed, the only wave observed in the cyclic voltammetry experiments was an irreversible, BPh₄⁻ oxidation peak (See Supporting Information). Although no wave corresponding to Ce(IV) reduction was detected in multiple trials in different solvents, DFT computation was used for a rough estimation of the cerium(III/IV) redox couple. This calculation method was used previously by us and shown to give good agreement with experimental values.^{30, 31} Calculations for both [Ce^{IV}(H₂A)₃]⁺ and [Ce^{III}(H₂A)₃] were carried out using DCM as CPCM, B3LYP as the functional, ECP28MWB and 6-31G* as basis sets following previous reports.^{30, 31} According to the total energy difference of [Ce^{IV}(H₂A)₃]⁺ and [Ce^{III}(H₂A)₃], the predicted redox potential was about -1.22 V vs Fc/Fc⁺ after calibration, which is relatively low compared with some cerium(IV) complexes, such as [NⁿBu₄][Ce(NO₃)₆] (0.62 V), Ce(acac)₂ (-0.38 V, acac = acetylacetonate), Ce(OAr)₄ (-0.50 V, OR = 2,6-diphenylphenol), Ce(OQ)₂ (-0.61 V, OQ = 8-hydroxyquinolate) and Ce(OEP)₂ (-1.06 V, OEP = octaethylporphyrin).^{30, 31} This estimation indicates that H₂A⁻ is a good electron-donating ligand for stabilizing Ce(IV).

Attempts to obtain another redox isomer: [Ce^{III}(H₂A)₃], including mixing aqueous CeCl₃, H₃A, and base under anaerobic condition, or reacting Ce[N(SiMe₃)₂]₃ with H₃A in organic solvents under an inert environment were attempted. While these reaction conditions have produced colorless or yellow solids respectively, as yet, no [Ce^{III}(H₂A)₃] complexes have been successfully isolated.

Experimental Details

Materials and Methods

1,6-heptadiyne was purchased from Fisher Scientific. Deuterated water or acetonitrile were purchased from Cambridge Isotope Laboratories, Inc. CeCl₃ (>99.9% purity) was purchased from Strem. Glutarimide-dioxime (H₃A) was prepared and recrystallized using a known procedure.¹² Benchtop reactions were carried out under aerobic conditions. Anaerobic conditions were carried out using Schlenk techniques under N₂ atmosphere or in glovebox under N₂ atmosphere in attempts to prepare Ce(III) complexes.

Preparation of [Ce(H₂A)₃]Cl•3 H₂O

A H₂O (20 mL) solution of NaOH (27 mg, 0.67 mmol, 2 equiv) was added into a H₂O (80 mL) solution of H₃A (143.2 mg, 1.00 mmol, 3 equiv) in a round bottom flask with stirring. When all of the H₃A was dissolved, a 20 mL H₂O solution of CeCl₃•7 H₂O (124.1 mg, 0.33 mmol, 1 equiv) was added dropwise into the flask, and a purple solution appeared immediately. The reaction was allowed to react under aerobic conditions for 12 h. Anal. Calcd for C₁₅H₂₄O₆N₉CeCl: C, 29.93; H, 4.02; N, 20.94. Found: C, 29.98; H, 4.10; N, 20.57. ¹H NMR (300 MHz, D₂O, room temperature) showed a yield of 81.3 %,

compared to [NMe₄]I that was added as an internal standard. A solid yield was not obtained due to difficulties in crystallization, but the pure crystal suitable for X-ray analysis was determined to be about 3% yield (6 mg) from slow evaporation of a saturated aqueous solution, with addition of several drops of saturated NaCl solution. ¹H NMR (300 MHz, D₂O, room temperature) δ: 1.98 (2H, -CH₂-CH₂-CH₂-), 2.61 (4H, -CH₂-CH₂-CH₂-). ¹³C NMR (126 MHz, D₂O) δ: 17.45 (-CH₂-CH₂-CH₂-), 21.28 (-CH₂-CH₂-CH₂-), 157.81 (-C=N=OH). MS (ESI): m/z= 423.1 [Ce(H₂A)(HA)]⁺, 143.1 [H₄A]⁺.

Preparation of [Ce(H₂A)₃][BPh₄]

An identical procedure was followed here for the preparation of [Ce(H₂A)₃]Cl•3 H₂O. After the H₂O solution of [Ce(H₂A)₃]Cl was prepared according to procedure above, a H₂O (20 mL) solution of NaBPh₄ (114.1 mg, 0.33 mmol, 1 equiv) was added into the flask. Black solid precipitated out of solution immediately and was collected by filtration over a medium frit after reaction for 12 hours. The collected solid was redissolved in acetone:H₂O (2:1) mixture and then filtered through a medium frit. The filtrate was collected and evaporated to obtain X-ray quality crystals, yielding [Ce(H₂A)₃][BPh₄]•4 H₂O in 53% yield for the whole reaction (180 mg). Anal. Calcd for C₃₉H₅₂O₁₀N₉B₄Ce: C, 48.91; H, 5.47; N, 13.16. Found: C, 48.89; H, 5.26; N, 12.80. Upon dissolution of [Ce(H₂A)₃][BPh₄] in CD₃CN-D₂O (2:1) free proligand was always evident, indicating partial dissociation of H₂A⁻ from the complex (See Supporting Information). ¹H NMR (300 MHz, CD₃CN:D₂O=2:1, room temperature) δ: 1.99 (-CH₂-CH₂-CH₂-); 2.49 (-CH₂-CH₂-CH₂-); 2.62 (-CH₂-CH₂-CH₂-); 6.93, 7.08, 7.35 (BPh₄⁻). ¹³C NMR (126 MHz, CD₃CN:D₂O=2:1) δ: 18.64 (-CH₂-CH₂-CH₂-); 22.30 (-CH₂-CH₂-CH₂-); 158.21 (-C=N=OH); 122.85, 126.63, 126.65, 164.66 (BPh₄⁻). MS (ESI): m/z= 423.1 [Ce(H₂A)(HA)]⁺, 143.1 [H₄A]⁺.

Characterization and Computational analysis

¹H NMR spectra were obtained on a Bruker AM-500 or a Bruker UNI-300 Fourier transform NMR spectrometer at 500 or 300 MHz, respectively. ¹³C{¹H} NMR spectra were recorded on a Bruker AM-500 Fourier transform NMR spectrometer at 126 MHz. Elemental analyses were obtained on a Costech ECS 4010 instrument at the Earth and Environmental Science department of the University of Pennsylvania. X-ray intensity data were collected on a Bruker APEXII CCD area detector or a Bruker APEXIII D8QUEST CMOS area detector, both employing graphite-monochromated MoK α radiation (λ= 0.71073 Å) at 100(1) K. UV-Visible spectra were collected on a Perkin Elmer 950 UV Vis/NIR spectrophotometer. Ce L_{III}-edge XANES data were collected at beamline 11-2 at the Stanford Synchrotron Radiation Lightsource. DFT and TD-DFT calculations were carried out in Gaussian 09 Rev. A.02. In the DFT and TD-DFT calculation, we have employed cam-B3LYP-D3BJ as the functional in a H₂O CPCM as solvent continuum, ECP28MWB as an ECP for cerium and 6-311+G* as a general basis set. A second calculation employing B3LYP as the functional was also carried

out for comparison and Ce(IV/III) redox couple prediction (See Supporting Information).

Conclusions

We have reported the cerium(IV) glutarimide dioxime complexes: $[\text{Ce}(\text{H}_2\text{A})_3]\text{Cl}$ and $[\text{Ce}(\text{H}_2\text{A})_3][\text{BPh}_4]$. The compounds have been characterized by X-ray crystallography, NMR spectroscopy, UV-Vis spectroscopy and XANES. Solution electrochemical experiments did not reveal metal-based waves in either case. DFT calculations were used to assign the electronic structure and LMCT bands, and to estimate the Ce(IV) reduction potential -1.22 V versus Fc/Fc^+ . These studies expand the coordination chemistry of the glutarimide-dioxime compound amongst f-elements and expand cerium(IV) coordination chemistry to a new type of strongly-stabilized ligand environment.

Conflicts of interest

There are no conflicts to declare.

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