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

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The coordination chemistry of glutarimide-dioxime (H_3A) 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 H_2A^- anion is also suitable for stabilizing Ce(IV) and acts as a tridentate ligand to form the $[Ce(H_2A)_3]^+$ cation. The metal complexes $[Ce(H_2A)_3]Cl$ and $[Ce(H_2A)_3][BPh_4]$ have been obtained by oxidation of Ce^{III} in the presence of H_3A 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 $[Ce^{IV}(H_2A)_3]^+$. X-ray absorption spectroscopy (XAS) was also performed to verify the Ce(IV) oxidation state. Absent a clear electrochemical signal for cerium reduction in $[Ce(H_2A)_3]Cl$ or $[Ce(H_2A)_3][BPh_4]$ 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 $[NEt_4]_2[CeCl_6]$, $[Ce(acac)_4]$, $[CeX(TriNOx)]$ ($TriNO_x^{3-}$ = $[((2\text{-}^t BuNO)C_6H_4CH_2)_3N]^{3-}$; X = F, Cl, Br), $[Ce(pyNO)_4]$ (pyNO = 2-(^{t}BuNO)pyridine), and others.[9–13] Glutarimide-dioxime (H_3A, $C_5H_9N_3O_2$), a compound reported to be useful for sequestering uranium from seawater, is considered here for stabilization of the cerium(IV) cation.

H_3A was originally known to extract uranyl ($U^{VI}O_2^{2+}$) as $[UO_2(HA)]$ and $[UO_2(H_2A)(HA)]^-$ from seawater, while competing with other uranyl species, such as $[UO_2(CO_3)_2]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$.[14–18] H_3A 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).

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 Ln^{IV}-H_3A 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 An^{IV}-H_3A complex (An = Th, Np, Pu).[23,24]

Results and discussion

Synthesis of $[Ce(H_2A)_3]Cl$ and $[Ce(H_2A)_3][BPh_4]$

Adding an aqueous solution of $Ce^{III}Cl_3$ to a prepared aqueous solution of 3 equiv. H_3A and 2 equiv. NaOH in aerobic condition, resulted in an immediate colour change from colour-

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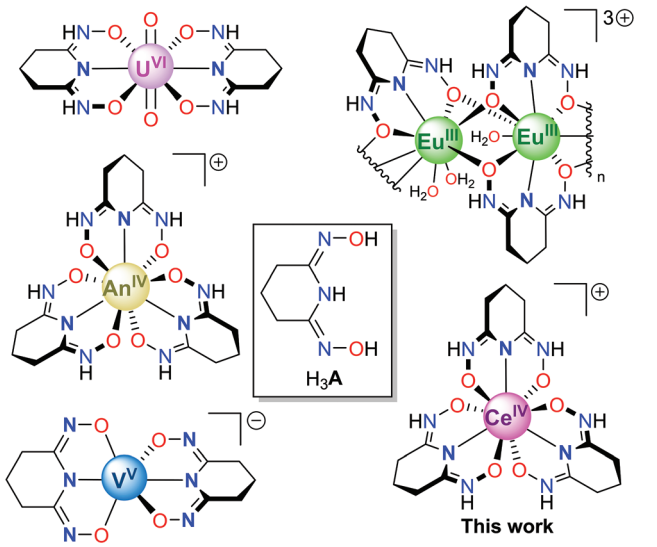
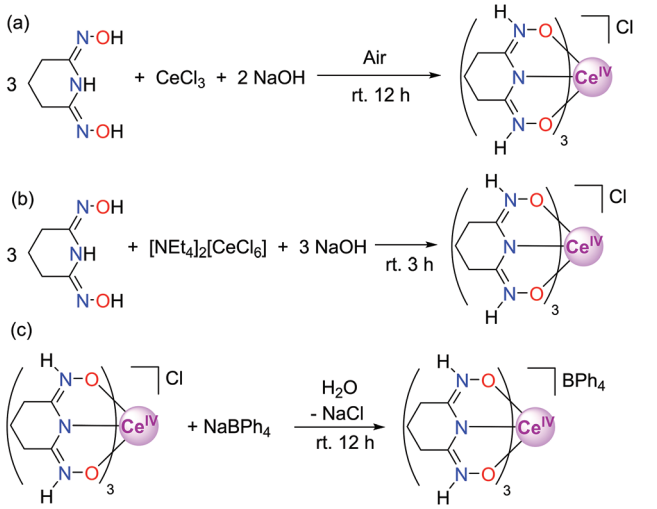


Scheme 1 Glutarimide-dioxime (H_3A) and its complexes: $[U^{VI}O_2(H_2A)_2]$, $[Eu^{III}_2(H_2A)_3(H_2O)_3(ClO_4)_3]$, $[An^{IV}(H_2A)_3]^+$ (An = Th, Np, Pu), $[V^{V}A_2]^-$, and $[Ce^{IV}(H_2A)_3]^+$ (this work).



Scheme 2 (a), (b) Synthesis of $[Ce^{IV}(H_2A)_3]$ Cl. (c) Synthesis of $[Ce(H_2A)_3]$ $[BPh_4]$.

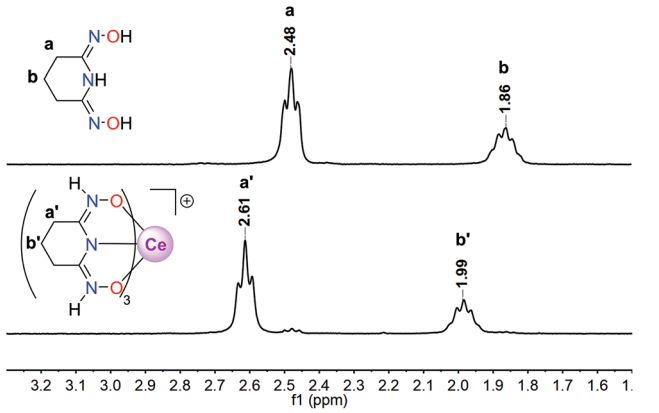


Fig. 1 ^{1}H NMR of H_3A and $[Ce(H_2A)_3]^+$ in D_2O (300 MHz, room temperature). H_3A has shown the peaks at 2.48 and 1.86 ppm, while $[Ce(H_2A)_3]^+$ has shown peak at 2.61 and 1.99 ppm.

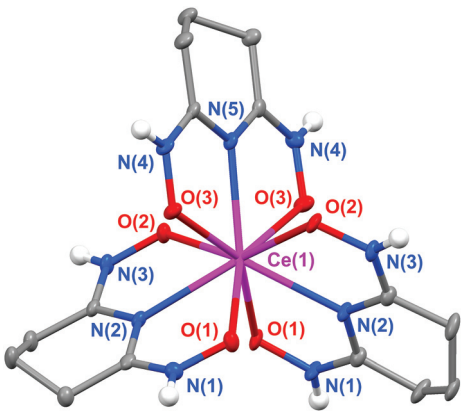


Fig. 2 Thermal ellipsoid plot of $[Ce(H_2A)_3]Cl$ at 50% probability (Cl–, aliphatic hydrogen atoms, and H_2O molecules are omitted for clarity).

less to first maroon and then purple (Scheme 2a). Oxidation of Ce(III) to Ce(IV) was strongly indicated by the presence of a characteristic LMCT band at 505 nm (Fig. S9†).[10] Using $(NEt_4)_2(CeCl_6)$ as a Ce(IV) starting material with H_3A and NaOH in the proper stoichiometry, an identical purple solution was obtained and verified by ^{1}H NMR spectroscopy (Scheme 2b). ^{1}H NMR spectroscopy recorded on the purple solution in D_2O confirmed that the purple solution contained a new species, $[Ce(H_2A)_3]Cl$.

The downfield chemical shift indicated a diamagnetic H_3A-based metal complex, consistent with previous reports (Fig. 1).[22] Noting that the chemical shift of water is pH sensitive, we added trace acetone or Et_2O to the ^{1}H NMR sample to act as an internal standard to obtain consistent results for H_3A and $[Ce(H_2A)_3]^+$.

Purple needle-shaped crystals of $[Ce(H_2A)_3]Cl$ were obtained by slow evaporation of an aqueous solution of the cerium(IV) complex (Fig. 2). The single crystal X-ray structure showed that $[Ce(H_2A)_3]^+$ ions formed a 3-dimensional hydrogen bonding network with =N(O)**H** groups acting as proton donors and N–**O** moieties functioning as proton acceptors, together with H_2O and Cl^- (see Fig. S2†).

Due to the low solubility of $[Ce(H_2A)_3]Cl$ 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 2c). Chunks of purple crystals of $[Ce(H_2A)_3][BPh_4]$ were obtained by recrystallization. The crystal structure of $[Ce(H_2A)_3][BPh_4]$ showed that $[Ce(H_2A)_3]^+$ ions formed a 2-dimensional hydrogen bonding network together with interstitial H_2O molecules. These 2-dimensional layers were separated by hydrophobic $[BPh_4]^-$ layers (see Fig. S4†).

Characterization and computational analysis

UV-visible absorption spectroscopy studies indicated that the purple colour of $[Ce(H_2A)_3]Cl$ was due to a LMCT band at 505 nm (Fig. 3, a; ε = 2600 M^{-1} cm^{-1}). Gaussian fits to the absorption band data yielded 3 bands at 228 nm, 284 nm and 487 nm (see Fig. 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 Ce(IV) systems.[9,10]

To further understand the electronic transitions of the $[Ce(H_2A)_3]^+$ cation, we have computed the electronic structure of $[Ce(H_2A)_3]^+$ 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 ligand character (>98%) while the lowest unoccupied molecular orbitals (LUMO) has mostly Ce character (>97%), consistent with a highly ionic bonding interaction (Fig. 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 (Fig. 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.

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 ESI Table S4†). Thus, the calculated transition at 510 nm can be assigned as a LMCT band.

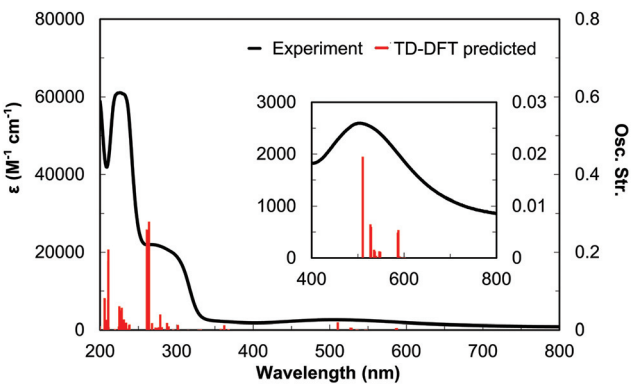


Fig. 3 UV-Vis spectrum and TD-DFT predicted oscillator strength of the $[Ce(H_2A)_3]^+$ cation in H_2O. The inset showed the transition at 505 nm by zooming in, and all axes units were identical.

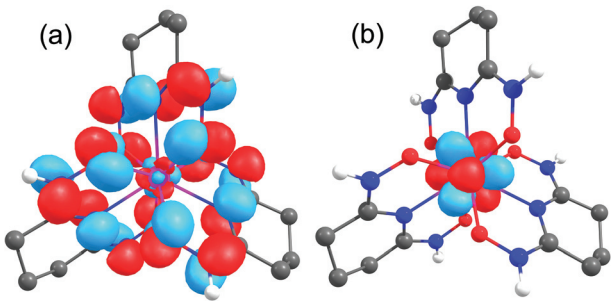


Fig. 4 (a) HOMO and (b) LUMO of $[Ce(H_2A)_3]^+$ (protons attached to carbons are omitted for clarity).

Cerium(IV) compounds are known to exhibit valence instability and multiconfigurational ground state.[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 $\overline{2p_{3/2}}$ $4f^1\bar{L}5d^1$ and $\overline{2p_{3/2}}$ $4f^05d^1$, where the bar indicates a hole (vacancy) and L indicates the ligand (Fig. 5). These data confirmed the expected +4 oxidation state of cerium within the complex. XANES fitting (see ESI†) 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 $[Ce(H_2A)_3]^+$ cation. Solution cyclic voltammetry experiments were carried out for $[Ce(H_2A)_3]Cl$ in H_2O using NaCl as supporting electrolyte and for $[Ce(H_2A)_3][BPh_4]$ in $CH_3CN:H_2O$ (4 : 1 v/v) or propylene carbonate, both using $[N^nBu_4]PF_6$ as supporting electrolyte. Notably, $[Ce(H_2A)_3]Cl$ and $[Ce(H_2A)_3][BPh_4]$ 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

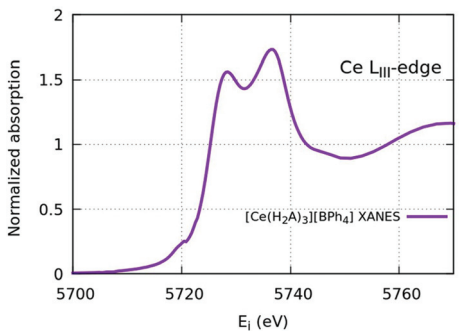


Fig. 5 X-ray absorption spectrum for $[Ce(H_2A)_3][BPh_4]$.

of measurement conditions. The absence of Ce(III/IV) waves has been noted for other cerium complexes previously, including $Ce[N(SiMe_3)_2]_3$.[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, BPh_4^- oxidation peak (see ESI†).

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 $[Ce^{IV}(H_2A)_3]^+$ and $[Ce^{III}(H_2A)_3]$ 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 $[Ce^{IV}(H_2A)_3]^+$ and $[Ce^{III}(H_2A)_3]$, 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 $[N^nBu_4][Ce(NO_3)_6]$ (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-hydroxyquinolinate) and $Ce(OEP)_2$ (−1.06 V, OEP = octaethylporphyrin).[30,31] This estimation indicates that H_2A^- is a good electron-donating ligand for stabilizing Ce(IV).

Attempts to obtain another redox isomer: $[Ce^{III}(H_2A)_3]$, including mixing aqueous $CeCl_3$, H_3A, and base under anaerobic condition, or reacting $Ce[N(SiMe_3)_2]_3$ with H_3A in organic solvents under an inert environment were attempted. While these reaction conditions have produced colorless or yellow solids respectively, as yet, no $[Ce^{III}(H_2A)_3]$ 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. $CeCl_3$ (>99.9% purity) was purchased from Strem. Glutarimide-dioxime (H_3A) was prepared and recrystallized using a known procedure.[12] Benchtop reactions were carried out under aerobic conditions. Reactions in anaerobic conditions were carried out using Schlenk techniques under N_2 atmosphere or in glovebox under N_2 atmosphere in attempts to prepare Ce(III) complexes.

Preparation of $[Ce(H_2A)_3]Cl{\cdot}3H_2O$

A H_2O (20 mL) solution of NaOH (27 mg, 0.67 mmol, 2 equiv.) was added into a H_2O (80 mL) solution of H_3A (143.2 mg, 1.00 mmol, 3 equiv.) in a round bottom flask with stirring. When all of the H_3A was dissolved, a 20 mL H_2O solution of $CeCl_3{\cdot}7H_2O$ (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 $C_{15}H_{24}O_6N_9CeCl$: C, 29.93; H, 4.02; N, 20.94. Found: C, 29.98; H, 4.10; N, 20.57. ^{1}H NMR (300 MHz, D_2O, room temperature) showed a yield of 81.3%, compared to $[NMe_4]I$ that was added as an internal standard. A solid yield was not obtained due to difficulties in crystallization, but the single crystals of X-ray quality were 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. ^{1}H NMR (300 MHz, D_2O, room temperature) δ: 1.98 (2H, $-CH_2-\mathbf{CH_2}-CH_2-$), 2.61 (4H, $-\mathbf{CH_2}-CH_2-\mathbf{CH_2}-$). ^{13}C NMR (126 MHz, D_2O) δ: 17.45 ($-CH_2-\mathbf{CH_2}-CH_2-$), 21.28 ($-\mathbf{CH_2}-CH_2-\mathbf{CH_2}-$), 157.81 ($-\mathbf{C}{=}N{=}OH$). MS (ESI): m/z = 423.1 $[Ce(H_2A)(HA)]^+$, 143.1 $[H_4A]^+$.

Preparation of $[Ce(H_2A)_3][BPh_4]$

An identical procedure was followed here for the preparation of $[Ce(H_2A)_3]Cl{\cdot}3H_2O$. After the H_2O solution of $[Ce(H_2A)_3]Cl$ was prepared according to procedure above, a H_2O (20 mL) solution of $NaBPh_4$ (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 : H_2O (2 : 1) mixture and then filtered through a medium frit. The filtrate was collected and evaporated to obtain X-ray quality crystals, yielding $[Ce(H_2A)_3][BPh_4]{\cdot}4H_2O$ in 53% yield for the whole reaction (180 mg). Anal. calcd for $C_{39}H_{52}O_{10}N_9BCe$: C, 48.91; H, 5.47; N, 13.16. Found: C, 48.89; H, 5.26; N, 12.80. Upon dissolution of $[Ce(H_2A)_3][BPh_4]$ in $CD_3CN–D_2O$ (2 : 1) free proligand was always evident, indicating partial dissociation of H_2A^- from the complex (see ESI†).^{1}H NMR (300 MHz, $CD_3CN : D_2O$ = 2 : 1, room temperature) δ: 1.99 ($-CH_2-\mathbf{CH_2}-CH_2-$); 2.49 ($-\mathbf{CH_2}-CH_2-\mathbf{CH_2}-$); 2.62 ($-\mathbf{CH_2}-CH_2-\mathbf{CH_2}-$); 6.93, 7.08, 7.35 ($BPh_4^-$). ^{13}C NMR (126 MHz, $CD_3CN : D_2O$ = 2 : 1) δ: 18.64 ($-CH_2-\mathbf{CH_2}-CH_2-$); 22.30 ($-\mathbf{CH_2}-CH_2-\mathbf{CH_2}-$); 158.21 ($-\mathbf{C}{=}N{=}OH$); 122.85, 126.63, 126.65, 164.66 (BPh_4^-). MS (ESI): m/z = 423.1 $[Ce(H_2A)(HA)]^+$, 143.1 $[H_4A]^+$.

Characterization and computational analysis

^{1}H NMR spectra were obtained on a Brüker AM-500 or a Brüker UNI-300 Fourier transform NMR spectrometer at 500 or 300 MHz, respectively. $^{13}C\{^1H\}$ NMR spectra were recorded on a Brüker 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 MoKα radiation (λ = 0.71073 Å) at 100(1) K. UV-visible spectra were collected on a PerkinElmer 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 H_2O 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 ESI†).

Conclusions

We have reported the cerium(IV) glutarimide dioxime complexes: $[Ce(H_2A)_3]Cl$ and $[Ce(H_2A)_3][BPh_4]$. 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 cerium(IV) coordination chemistry to a new type of strongly-stabilized ligand environment.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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