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## Structural and electrochemical characterization of a cerium(IV) hydroxamate complex: implications for the beneficiation of light rare earth ores<sup>†</sup>

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Reaction of *N*-phenyl-pivalohydroxamic acid with Ce<sup>III</sup> precursors leads to a homoleptic hydroxamate complex: Ce<sup>IV</sup>[<sup>f</sup>BuC(O)N(O)Ph]<sub>4</sub>. Electrochemical experiments indicate a significant stabilization of the Ce<sup>IV</sup> cation at  $E_{\rm p,c} = -1.20$  V *versus* SCE in the hydroxamate ligand framework. The spontaneous oxidation of Ce<sup>III</sup> in a hydroxamate ligand field is discussed in the context of beneficiation of the light rare earths from the fluorocarbonate mineral bastnäsite.

Due to their unique physical properties, rare earth metals have become increasingly useful and irreplaceable components of many materials, especially in hard magnets and optical materials, among many others.<sup>1</sup> To be used in such applications, mixed rare earth containing minerals are beneficiated and ultimately purified through a liquid-liquid separations process to attain the required high purities.<sup>2</sup> Depending on the ore type, the beneficiation of mixed rare earth minerals is accomplished by gravity-, magnetic-, or electrostatic separation, or by froth flotation.<sup>2</sup> In the critical froth flotation unit operation, hydroxamates are used as collectors to separate rare earth bearing minerals from barite and calcite gangue materials.<sup>3</sup> The froth flotation process has been applied to beneficiate the light rare earth fluorocarbonate minerals, bastnäsite, e.g. (Ce, La, Y)CO<sub>3</sub>F, from the key global ore bodies at Mountain Pass, CA, U.S.A. and the Bayan Obo Mining District in the Inner Mongolia Region of the P.R.C.<sup>3a,4</sup>

In models of the froth flotation beneficiation process, hydroxamate collectors are proposed to chemisorb selectively to the rare earth metal cations at the ore particle surface, and/or extract the ions, creating multi-layers of lipophilic rare earth complexes that render the ore particles hydrophobic.<sup>5</sup> Since cerium constitutes a major component of bastnäsite with up to 50% content in given ores, a better understanding

of cerium-hydroxamate chemistry is crucial for rationalizing the models of collector-surface interactions and improving beneficiation.<sup>6</sup>

Early studies on the coordination chemistry of cerium with hydroxamates, especially that of Agrawal and co-workers,<sup>7</sup> included the spectrophotometic determination of cerium and selective precipitation of rare earths. Notably, Alimarin reported extraction of Ce<sup>III</sup> hydroxamate complexes into organic phases concomitant with oxidation.<sup>8</sup> However, none of the products were structurally characterized and the nature of the cerium oxidation chemistry remains somewhat ambiguous.

Recent results from our group have established the unprecedented stability of the Ce<sup>IV</sup> cation endowed by a pyridyl nitroxide framework.9 We reasoned that the oxidation of cerium might play an important role in the froth flotation process that had not been explicitly considered in models of bastnäsite beneficiation. In this respect, the chemistry of related lanthanide catecholates illustrates the importance of cerium redox chemistry. Notably, the reaction of insoluble Ce<sup>III</sup>PO<sub>4</sub> and aqueous catechol results in a stoichiometric release of CeIII cations under anaerobic conditions while oxidation of cerium is observed under aerobic conditions.<sup>10</sup> The aerobic oxidation of Ce<sup>III</sup>PO<sub>4</sub> is driven by a strong thermodynamic preference for the 4+ state of  $Ce^{IV}[O_2C_6H_4]_4^{-4-}$ ; the reduction potential of  $Ce^{IV}[O_2C_6H_4]_4^{4-}$  was determined at -0.69 V versus SCE by Raymond and co-workers indicating a startling 1036-fold difference in formation constants for the tetravalent versus trivalent forms of the tetrakis(catecholate) complex.11

Herein, we report the first crystal structure of a simple homoleptic  $Ce^{IV}$  hydroxamate complex and its spectroscopic and electrochemical characterization; the structure is reminiscent of reported lanthanide and actinide complexes of bidentate hydroxypyridinonates.<sup>12</sup> Our findings suggest that cerium hydroxamate complexes exhibit a strong thermodynamic preference for the 4+ oxidation state. Extrapolating these results, we expect that redox chemistry plays an important role in the superior beneficiation of bastnäsite using alkyl hydroxamic acids over other flotation collectors such as tall oil-derived fatty acids.

The synthesis of *N*-phenyl-pivalohydroxamic acid (**HL**) was accomplished conveniently from *N*-phenyl-hydroxylamine and pivaloyl chloride (see ESI†). Reaction of 3 or 4 equiv. of **HL** with

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Full experimental details, electrochemistry data, NMR data, UV-vis data, shape parameters and computational details. CCDC 952851. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc46486e



Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> under anaerobic conditions invariably produced the neutral, 1:4 cerium complex (Scheme 1). Complex 1 was synthesized reliably in 50% yield by adding four equiv. of HL to a solution of Ce<sup>III</sup>[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> in diethyl ether, though the identity of the oxidant in this reaction is not currently known. Addition of TEMPO, 2,2,6,6-tetramethylpiperidine-N-oxyl, or exposure to dioxygen decreased the reaction time and increased the isolated yield to 75% and 84% respectively. In each case,  $\sim 3$  equiv. of H[N(SiMe\_3)\_2] were also formed in addition to 1 as observed by <sup>1</sup>H NMR spectroscopy. In the reaction with TEMPO, TEMPO-H/TEMPO-D was also observed as a byproduct. In addition to the oxidations of Ce<sup>III</sup>[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> observed in the presence of HL, reaction of the Ce<sup>III</sup> precursors CeCl<sub>3</sub> or Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O with HL and LiO<sup>t</sup>Bu in CH<sub>2</sub>Cl<sub>2</sub> under aerobic conditions resulted in spontaneous formation of 1. Using  $Ce(NO_3)_3 \cdot 6H_2O$ , our favoured synthesis, a nearly quantitative yield of 1 was obtained.

The active role of the hydroxylamine moiety in the redox chemistry of metal complexes is precedented in f-block chemistry. Reaction of Pu<sup>III</sup> precursors with the iron siderophore desferriox-amine E (DFE) resulted in the isolation of only a Pu<sup>IV</sup>(DFE) complex.<sup>13</sup> Tetrakis(hydroxamate) uranium complexes undergo oxygen transfer reactions to give uranyl bis(hydroxamate) complexes.<sup>14</sup> A similar reactivity is observed in the syntheses of the structurally related tetrakis( $\beta$ -diketonato) cerium(v) complexes, which undergo auto-oxidation under aerobic conditions.<sup>15</sup>

The structure of **1** was determined using X-ray crystallography (Fig. 1). The coordination polyhedron formed by the hydroxamate framework around the cerium cation is best described as a distorted square antiprism; shape parameters for **1** are provided in Table S2 (ESI $\dagger$ ). A comparison with previously reported structures of homoleptic, tetravalent metal hydroxamate complexes show that the structure is consistent with a Ce<sup>IV</sup> cation coordinated by four fully

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Compound	М- $O_C$ (Å)	М- $O_N$ (Å)	N-O (Å)	Radius <sup><i>a</i></sup> (Å)	Ref.
$Zr[MeC(O)N(O)Me]_4$	2.198(13)	2.188(11)	1.340(11)	0.84	16
Hf[PhC(O)N(O)Ph] <sub>4</sub>	2.258(10)	2.116(10)	1.375(1)	0.83	17
1	2.430(8)	2.265(3)	1.379(3)	0.97	—
$Th[^{t}BuC(O)N(O)^{i}Pr]_{4}$	2.492(3)	2.357(3)	1.376(4)	1.05	14
<sup><i>a</i></sup> Ionic radii based on a coordination number of eight. <sup>18</sup>					

reduced hydroxamate anions (Table 1). The average N–O distance in 1 was determined to be 1.379(3) Å. The average Ce–O<sub>C</sub> distance is noticeably longer than the average Ce–O<sub>N</sub> distance, consistent with the data for the group 4 hydroxamate complexes (Table 1). The difference in the Ce–O bond lengths is best explained by a higher charge density on the nitrogen oxygen. The slightly long average C=O bond length (1.265(5) Å), the slightly short average C<sub>acyl</sub>–N bond length (1.324(4) Å), and the planarity of the hydroxamate ligand are attributed to the participation of the charge-separated resonance structure of the hydroxamate ligand in 1.<sup>14</sup>

Solution phase cyclic voltammetry experiments were performed on **1** in order to assess the stability of the Ce<sup>IV</sup> cation (see ESI<sup>†</sup>). The cyclic voltammogram of 1 exhibited a quasi-reversible redox couple for the cerium metal centre and a chemically irreversible oxidation couple for the hydroxamate ligands. Given the experimental rest potential of -0.18 V versus SCE, we assigned the cathodic current at  $E_{\rm p,c}$  = -1.20 V and the anodic current at  $E_{\rm p,a}$  = -0.48 V to the reduction and the oxidation of the cerium metal centre respectively. The scan rate dependence of this isolated Ce<sup>III/IV</sup> redox event is shown in Fig. 2. Following the method used by Raymond in the study of  $Ce^{IV}[O_2C_6H_4]_4^{-1}$  using a reference potential of  $E^{\circ\prime} = 1.02 \text{ V}$ measured for  $[{}^{n}Bu_{4}N]_{2}$  [Ce(NO<sub>3</sub>)<sub>6</sub>] in CH<sub>3</sub>CN,<sup>19</sup> the relative stability of the tetravalent form of **1** can be estimated. Approximating the  $E_{1/2}$  = -0.84 V for 1, a  $10^{31}$ -fold difference in formation constants is calculated between the neutral and anionic forms of 1. This large, negative reduction potential and overwhelming thermodynamic preference of the 4+ state in 1 highlight the ability of the hydroxamate framework to stabilize the Ce<sup>IV</sup> cation. In comparison, the reduction potential of the related compound Ce<sup>IV</sup>(acac)<sub>4</sub> appears at  $E_{1/2} = -0.04$  V versus SCE.<sup>20</sup> The striking difference in the reduction potentials of 1 and Ce(acac)<sub>4</sub> prompted us to investigate the electronic structure of 1 in more detail using DFT calculations.



(ng) 0.4 -0.1 -0.6 -1.1 -1.6 -2.1 V(V vs. SCE)

-1000mV/s -800mV/s -500mV/s -250mV/s -50mV/s

Fig. 1 Thermal ellipsoid plot of 1 at 30% probability with hydrogen atoms omitted for clarity. Selected bond distances (Å) Ce(1)-O(1) 2.259(3), Ce(1)-O(2) 2.439(3), N(1)-O(1) 1.369(5), C(1)-N(1) 1.324(7), C(1)-O(2) 1.279(6).

Fig. 2 Cyclic voltammogram of complex **1** measured in 0.1 M  $[^{n}Pr_{4}N][BAr^{F}_{4}]$  in CH<sub>2</sub>Cl<sub>2</sub> versus SCE.



Fig. 3 Calculated HOMO and LUMO of complex 1.

DFT calculations on 1 were performed at the B3LYP level of theory, with the ECP28MWB pseudopotential<sup>21</sup> for the cerium cation. The geometry optimized bond distances and angles for 1 agree well with the experimental values. The resulting molecular orbital depiction shows that the HOMO comprises primarily hydroxamate  $\pi^*$  orbital character with an ~6% contribution from the cerium  $4f_{z(x^2-y^2)}$  orbital (Fig. 3). The hydroxamate ligands are oriented at the cerium cation to allow for a symmetry-matched bonding interaction between the N–O  $\pi^*$  orbitals and a 4f orbital of cerium, though the overlap is small. The LUMO is calculated to be 2.95 eV above the HOMO and consists of the corresponding antibonding interaction. Furthermore, the natural population analysis shows a high degree of charge donation into the central metal cation as indicated by a low natural charge of the cerium metal centre of 1.41. A similar electronic structure was observed in the homoleptic Ce[2-(<sup>t</sup>BuNO)py]<sub>4</sub> complex reported recently by our group,<sup>9</sup> providing further evidence that there is an electronic preference for the pseudo-cubic  $D_{2d}$  symmetry observed in the 8-coordinate  $\kappa^2$ -nitroxide complexes.

Evidence in support of the calculated electronic structure and electrochemistry of **1** was determined using UV-visible electronic absorption spectroscopy (Fig. S9, ESI†). A broad transition at 2.93 eV was assigned to a LMCT from the hydroxamate ligand field to a metal 4f orbital. The energy of this transition is in good agreement with the calculated energy gap between the HOMO and the LUMO of 2.95 eV. The broadness of this transition can be attributed to partial mixing of the ligand-based orbitals with the metal-based 4f orbitals (Fig. 3). A similar spectroscopic interpretation has been advanced for tetrakis( $\beta$ -diketonato) cerium complexes.<sup>22</sup>

In total, our results suggest that the thermodynamics of cerium hydroxamate complexes strongly favour oxidation to the cerium(v) state. Given the typical  $pK_a$  range for hydroxamic acids of ~ 8.0–8.5, we expect that the aerated (aerobic) and basic (pH = 9.5) conditions of froth flotation<sup>3b</sup> strongly favour binding and oxidation of cerium at bastnäsite ore surfaces. Mono- and multi-layers of rare earth complexes proposed to generate hydrophobic foams would be expected to comprise tetravalent cerium complexes in this context. These observations are consistent with the recently reported superior performance of alkyl hydroxamic acids over fatty acids in the beneficiation of Mountain Pass bastnäsite.<sup>4</sup>

The results also suggest that future models of light rare earth metal ore beneficiation should take into account cerium redox chemistry. Further, collectors that increase the tendency for the cerium redox reaction to occur, namely through electron donating groups that further stabilize the Ce<sup>IV</sup> cation, could further improve hydroxamic acid performance. Exploration of the effect of hydroxamic acid substituents on the redox properties of the resulting cerium complexes is currently underway in our laboratories.

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