

Oxidative Dissolution of Lanthanide Metals Ce and Ho in Molten GaCl₃

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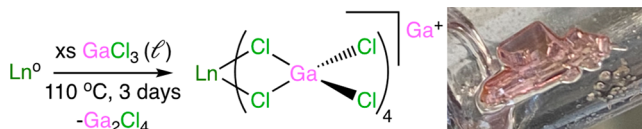
ABSTRACT: Gallium trichloride (GaCl₃) was used as a solvent for the oxidative dissolution of the lanthanide (Ln) metals cerium (Ce) and holmium (Ho). Reactions were performed at temperatures above 100 °C in sealed vessels to maintain the liquid phase for GaCl₃ during the oxidizing reactions. The best results were obtained from reactions using 8 equiv of GaCl₃ to metal where the inorganic complexes [Ga][Ln(GaCl₄)₄] [Ln = Ce (1), Ho (2)] could be isolated. Recrystallization of 1 and 2 employing fluorobenzene (C₆H₅F) produced [Ga(η⁶-C₆H₅F)₂][Ln(GaCl₄)₄] [Ln = Ce (3), Ho (4)] where reversible η⁶ coordination of C₆H₅F to [Ga]⁺ was observed. All complexes were characterized through elemental analysis (F and Cl), IR and UV–vis–near-IR spectroscopies, and both solution and solid-state NMR techniques.

Oxidative dissolution is a nascent field of metal recycling and purification with a high potential impact.^{1–3} Outside of aqueous acid solutions, many of the reaction media used in these transformations bear trihalide counterions that perform two-halide oxidation reactions, concomitantly oxidizing and dissolving metals.^{4,5} Both ionic liquid and molten salt matrixes offer variation with liquid temperatures, redox stability, and polarity, all of which could benefit lanthanide recycling. Employing ionic liquid and molten salt matrixes with 4f metals allows for unique transformations,^{6–11} separations,^{12–21} and redox behaviors^{22–24} that encourage further development to expand inorganic reaction chemistry. Continued investigations into lanthanide recycling may also expose untapped sources of these critical materials.

The oxidative dissolution of lanthanide metals using gallium trichloride (GaCl₃) may provide new avenues for recycling while generating novel molecular motifs. With an accessible melting point of 77.9 °C, GaCl₃ has properties that exist between ionic liquids and molten salts, making it an unconventional solvent to investigate oxidative chemical transformations. Reports have detailed investigations of GaCl₃ as a solvent matrix for chalcogen oxidative dissolution^{25,26} and as a Lewis acidic solvent for the dissolution of the elements bismuth^{27–29} and antimony.³⁰ Our prior work demonstrated the potential of GaCl₃ as a chlorine-transfer reagent for uranium and plutonium,³¹ furthering our interests in exploring GaCl₃ as a solvent in metal dissolution chemistry. No prior reports detail its use as a solvent for f-block metals. Here, a mild-temperature, molten binary-salt flux of GaCl₃ was explored as a nonclassical solvent for the oxidative dissolution of Ln metals (Scheme 1). The reaction provided us access to rare coordination motifs that standard reaction solvents would be unlikely to provide.

The metals cerium (Ce) and holmium (Ho) were selected for this study. Ce was chosen for its prominence in lanthanide chemistry as a plutonium surrogate and its accessible 3⁺/4⁺

Scheme 1. Reaction Scheme Depicting the Oxidative Dissolution of Ce and Ho in GaCl₃ and Picture of the Resultant Crystal of [Ga][Ho(GaCl₄)₄]



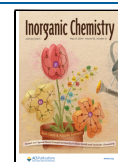
redox couple.^{32–34} The accessibility of Ce⁴⁺ is a useful probe to study potential overoxidation under these reaction conditions. Ho represents a middle-to-late lanthanide with an inherently high magnetic moment. Additionally, Ho³⁺ complexes can adopt a pink coloration, which is valuable for monitoring the reaction progress and facilitating the technically challenging purification. This report describes the oxidative dissolution of Ce and Ho and the product isolation and characterization via solid-state and solution NMR spectroscopy, elemental analysis, UV–vis–near-IR (NIR) and IR techniques, and single-crystal X-ray diffraction (SC-XRD).

The synthetic investigation was performed in sealed gas chromatography vials or vacuum-sealed ampules containing Ce or Ho metal with excess GaCl₃. The reactions were heated to temperatures above the melting point of GaCl₃ (ca. 110 °C) for 3–5 days. Over this time, the metals dissolved and were oxidized by GaCl₃. The reaction of Ce remained colorless, while the Ho reaction acquired a pink hue (Figure S1). No evidence of Ce⁴⁺ formation was observed during this study.

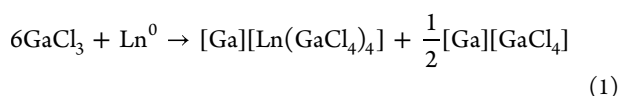
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Slow cooling of the reactions led to the formation of large crystals interspersed with a fine white powder. Rinsing the material with pentane removed the excess GaCl_3 and resulted in a crude purification where small amounts of Ga_2Cl_4 , found as $[\text{Ga}][\text{GaCl}_4]$, were observed along with the desired products, as determined by ^{71}Ga NMR. The large crystals were physically separated, analyzed by SC-XRD, and assigned as $[\text{Ga}][\text{Ln}(\text{GaCl}_4)_4]$ [$\text{Ln} = \text{Ce}$ (1), Ho (2)]. The formation of $[\text{Ga}][\text{GaCl}_4]$ was confirmed through a comparison of the solid-state ^{71}Ga NMR spectra of the crude products to reference samples of $[\text{Ga}][\text{GaCl}_4]$ (Figure S4). The reaction stoichiometry proposed for these observations is found in eq 1.



SC-XRD studies of the crystalline product revealed salt pairs of $[\text{Ga}]^+$ and $[\text{Ln}(\text{GaCl}_4)_4]^-$. The Ce and Ho structures were isomorphous, crystallizing in the monoclinic space group $P2_1/c$. The asymmetric unit cell comprises half of the $[\text{Ln}(\text{GaCl}_4)_4]^-$ anion and half of the $[\text{Ga}]^+$ cation. The Ln in the anionic fragment was found in a distorted square-antiprismatic geometry (Figure 1a). The average Ga–Cl distances of

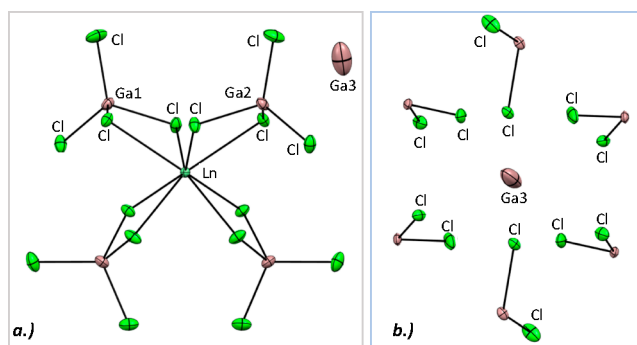


Figure 1. (a) Grown unit cell of 2 presented at 50% probability ellipsoids. 1 is isostructural. (b) Expansion of the chloride environment around $[\text{Ga}]^+$.

$[\text{GaCl}_4]^-$ were found to be 2.1818(2) and 2.1820(7) Å for the Ce and Ho complexes, respectively, similar to that of other $[\text{Ga}][\text{GaCl}_4]$ main-group salts [$\text{Ga}-\text{Cl}_{\text{avg}} = 2.1721(4)$ Å].^{35–38} The bridging Ga–Cl values are longer, with an average of 2.2285(4) Å compared to that of the terminal chlorides, at 2.1360(6) Å. The Ln–Cl bond also contracts with a decreasing ionic radius from 2.8774(10) Å (Ce) to 2.7728(7) Å (Ho).

A coordination sphere of eight chlorine atoms is rare in f-metal chemistry. One example, published by Schwotzer and co-workers, detailed a trimeric U^{4+} complex, $[\eta^6\text{-C}_6\text{Me}_6]\text{UCl}_2(\mu\text{-Cl})_3\text{UCl}_2(\eta^6\text{-C}_6\text{Me}_6)]$, where the central uranium atom displays similar chloride saturation.³⁹ A few examples are also reported of f-metals bound directly to tetrachlorogallate $[\text{GaCl}_4]^-$ anions, where the lanthanide metal (La, Ce, or Yb) is bound to three $[\text{GaCl}_4]^-$ anions and an η^6 -arene ligand.^{40,41} The $[\text{Ga}]^+$ cation is found to be unbound in 1 and 2 but is surrounded by chloride atoms in the extended salt lattice (Figure 1b). The average Ga3–Cl bond distances [3.4382(11) Å (Ce); 3.4332(8) Å (Ho)] are significantly longer than the average Ga–Cl bond lengths of the GaCl_4 fragments by approximately 1.2 Å, indicating minimal interaction and the presence of a free $[\text{Ga}]^+$.

The generation of noncoordinated $[\text{Ga}]^+$ under the reaction conditions is a notable result. An exciting trend in monovalent gallium began in 2010 when a report detailed an accessible synthesis of $[(\eta^6\text{-arene})\text{Ga}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ using the non-coordinating tetrakis(perfluoro-*tert*-butoxide)aluminate anion.⁴² This and related $[\text{Ga}]^+$ materials have most commonly been synthesized by the oxidation of Ga metal with silver salts or through the reductive elimination of gallium hydride materials.^{42–52} The results obtained from this study can be explained by the presence of $[\text{Ga}][\text{GaCl}_4]$ in the reaction mixture. These products can be considered to be a “true” salt pair $[\text{Ga}]^+[\text{Ln}(\text{GaCl}_4)_4]^-$ or, alternatively, an adduct of $[\text{Ga}][\text{GaCl}_4]$ and $\text{Ln}(\text{GaCl}_4)_3$.

The further purification and removal of residual $[\text{Ga}][\text{GaCl}_4]$ was achieved through recrystallization of 1 and 2 from fluorobenzene ($\text{C}_6\text{H}_5\text{F}$). Dissolution of 1 and 2 in $\text{C}_6\text{H}_5\text{F}$ allowed for filtration of the poorly soluble $[\text{Ga}][\text{GaCl}_4]$, where crystallization produced a bis(η^6 -arene)-coordinated $[\text{Ga}]^+$ derivative that was identified as $[\text{Ga}(\eta^6\text{-C}_6\text{H}_5\text{F})_2][\text{Ln}(\text{GaCl}_4)_4]$ [$\text{Ln} = \text{Ce}$ (3), Ho (4)]. Elemental analysis of the material confirmed complete conversion, with the expected F^- and Cl^- content consistent with the calculated values. Holding complexes 3 and 4 under reduced pressure induced $\text{C}_6\text{H}_5\text{F}$ loss and the regeneration of 1 and 2, respectively. This reversible coordination of the arene ring was leveraged to purify 1 and 2.

SC-XRD experiments performed on 3 and 4 confirmed their assignment (Figure 2). The crystals of the two homologues

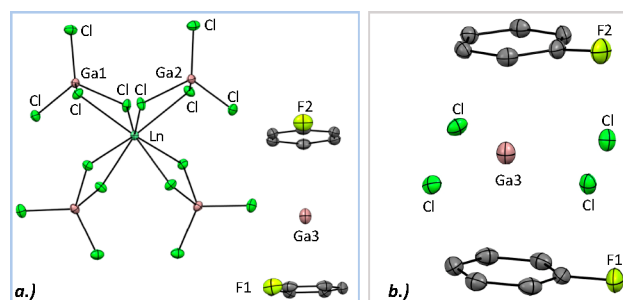


Figure 2. (a) Grown unit cell of 4 presented at 50% probability ellipsoids, with hydrogen and disordered fluorine atoms removed for clarity. 3 is isostructural. (b) Expansion of the arene and chloride environments of $[\text{Ga}]^+$.

were solved in the orthorhombic space group $Pbca$, with the asymmetric unit cell comprising half of the $[\text{Ln}(\text{GaCl}_4)_4]^-$ fragment and with an outer-sphere $[\text{Ga}]^+$ sandwiched by two half $\text{C}_6\text{H}_5\text{F}$ molecules. The observed arene–centroid distances to $[\text{Ga}]^+$ were fairly long [3, 2.8990(13) and 3.0807(14) Å; 4, 2.905(2) and 3.117(2) Å] and on the order of previously reported arene–centroid distances between 3.145(3) and 2.536(2) Å.^{42–48} The centroid– $[\text{Ga}]^+$ –centroid angle was nearly linear at 175.15(4)° for 3 and 174.68(6)° for 4 (Figure 2b). The nearest chloride distances to the free $[\text{Ga}]^+$ were contracted significantly to 3.1558(6) and 3.2138(6) Å (3) and 3.1448(12) and 3.2020(11) Å (4). The Ln–Cl distances of the $[\text{Ln}(\text{GaCl}_4)_4]^-$ anion for 3 and 4 showed a similar decrease of 0.1047(9) Å, with a decreasing ionic radius of the Ln^{3+} ion from Ce to Ho.

UV–vis–NIR and IR spectroscopies were performed. The expected transitions in the UV–vis–NIR spectrum for 3 were hidden under the solvent absorbance at $\sim 300\text{ nm}^{-1}$, while the spectrum of 4 contained the expected $f \rightarrow d$ and $f \rightarrow f$

transitions (Figures S6 and S7). The IR spectra for complexes 1 and 2 show large broad bands at approximately 3440 and 3420 cm^{-1} , which are shifted from a similar feature of $[\text{Ga}][\text{GaCl}_4]$ found at 3316 cm^{-1} . The other bands are broad and large, also reminiscent of those of $[\text{Ga}][\text{GaCl}_4]$. The $\text{C}_6\text{H}_5\text{F}$ adducts 3 and 4 reveal that these prominent features are replaced with small sharp bands for each complex found around 2975 cm^{-1} for the C–H bonds of the arene (Figures S8 and S9).

A series of ^{71}Ga NMR experiments were performed to further characterize 1–4. The coordinated $[\text{GaCl}_4]^-$ fragments were unobserved due to their proximity to the paramagnetic metal center. Being further removed from the paramagnetic center, $[\text{Ga}]^+$ appeared as a sharp resonance observed at $\delta = -594.6$ ppm (1) and $\delta = -603.7$ ppm (2) in dichloromethane (CH_2Cl_2). The ^{71}Ga NMR resonances attributed to $[\text{Ga}]^+$ for compounds 3 and 4 were observed at $\delta = -700.9$ ppm (3) and $\delta = -690.9$ ppm (4) in $\text{C}_6\text{H}_5\text{F}$; purified 3 and 4 were observed at $\delta = -629.9$ and -644.9 ppm in CH_2Cl_2 . These complexes were unstable in CH_2Cl_2 ; the solution turned dark brown in color, and the sharp $[\text{Ga}]^+$ resonance diminished over the course of minutes. The use of solid-state NMR techniques provided a more complete characterization.

The ^{71}Ga magic-angle-spinning (MAS) NMR spectra of 1–4 were collected, and the observed resonances were assigned as $[\text{Ga}]^+$ (Figure 3). Variation of the spin rate up to 12 kHz was

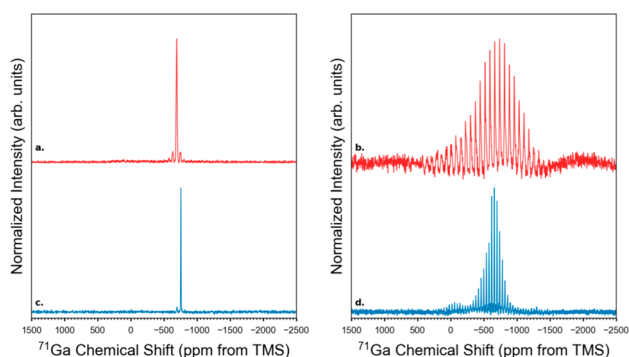


Figure 3. Solid-state ^{71}Ga NMR spectra presented for the Ce complexes 1 (a) and 3 (c) and the Ho complexes 2 (b) and 4 (d).

performed to identify the peak arising from the isotropic shift from the spinning side bands. The low magnetic moment of the Ce^{3+} center did not affect the observed $[\text{Ga}]^+$ resonance in 1 and 3. Compared to $[\text{Ga}][\text{GaCl}_4]$, the MAS spectra contained no observed resonances attributable to the Ln-coordinated $[\text{GaCl}_4]^-$ units. The spectrum of purified 1 consisted of a resonance centered at $\delta = -693.6$ ppm, which shifted to $\delta = -756.2$ ppm upon coordination to $\text{C}_6\text{H}_5\text{F}$. The ^{71}Ga MAS NMR spectra of 2 and 4 appeared to be much more complex due to the paramagnetic Ho^{3+} . This complexity arose from increased shift anisotropy from hyperfine interactions with the Ho metal center.^{53–56} The results of the ^{71}Ga NMR experiments are summarized in Table S1. To characterize the $[\text{GaCl}_4]^-$ units, a series of static ^{71}Ga NMR spectra were collected (Figure S5). The signal from these units appeared as a broad signal underlying the sharper peak for the $[\text{Ga}]^+$ species. Again, the line widths of the spectra for compounds 2 and 4 were substantially broader than those of compounds 1 and 3 due to the larger hyperfine interactions with Ho^{3+} . Spectral deconvolutions revealed the relative contributions to

the line shapes from quadrupolar coupling and the paramagnetic chemical shift (Table S2). We observed a significantly larger shift contribution to the $[\text{GaCl}_4]^-$ line shape compared to $[\text{Ga}]^+$ due to their proximity to the lanthanide center. The $[\text{GaCl}_4]^-$ units also had a large contribution from quadrupole coupling, but in 2 and 4, this contribution was minor compared with that from the paramagnetic chemical shift. The quadrupole coupling constant (C_Q) for $[\text{Ga}]^+$ showed a substantial increase upon removal of $\text{C}_6\text{H}_5\text{F}$, which was attributed to a change in the relative motion of $[\text{Ga}]^+$ that results in an averaging of the quadrupole coupling.

By exploring the reactivity of molten GaCl_3 as an oxidizing solvent for Ce and Ho, this work incorporates several impactful facets of chemistry, including oxidative dissolution with nonclassical solvents, lanthanide reactivity and bonding, and low-valent gallium chemistry. The reactions of Ce and Ho in a molten GaCl_3 matrix were successful and the products were high yielding, generating coordination motifs previously unobserved for lanthanide metals. The solid-state NMR experiments provided characterization of complexes 1–4 without the solvent effects or undesired reactivity that was observed using solution-phase NMR. We will continue to explore the oxidative dissolution of f-block metals using GaCl_3 , focusing on uranium and plutonium, and pursue further characterization and reactivity of the resultant products.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c02774>.

Experimental conditions, crystallographic tables and correlated CCDC deposition numbers, and spectroscopic characterization of all compounds synthesized (PDF)

Accession Codes

CCDC 2245656–2245659 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

This work was conceived by N.H.A. and A.M.T. and executed at Los Alamos National Laboratory.

Notes

The authors declare no competing financial interest.

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