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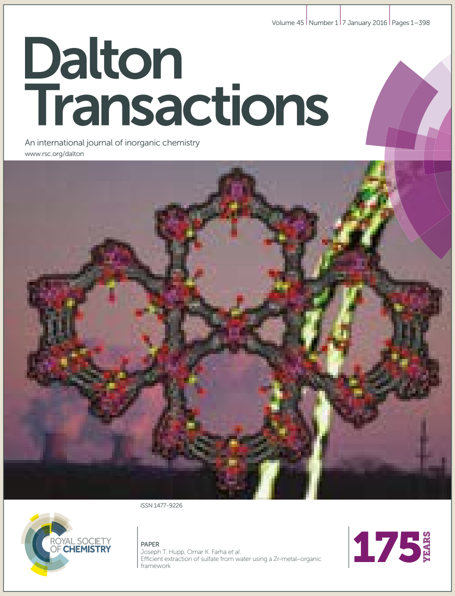

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Diethyl Ether Adducts of Trivalent Lanthanide Iodides

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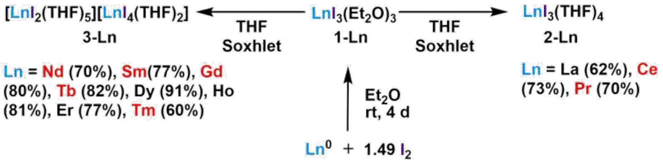
The synthesis and structural characterization of the first molecular complexes of lanthanide iodides supported by the weak-base, diethyl ether, are reported. Single-crystal diffraction studies reveal a conserved [LnI_3(*mer*-Et_2O)$_3$] structure (Ln = Ce, Pr, Nd, Sm, Gd, Tb, and Tm). These precursors are for all lanthanides La to Tm (excluding Pm and Eu) from lanthanide metal and iodine in diethyl ether and provide the THF adducts in good to excellent (60–91%) yield in a two-step process.



Scheme 1. Two-step reaction scheme for synthesis of **2-Ln** and **3-Ln** through diethyl ether adduct, **1-Ln**. Yields are shown for the two-step process and metals depicted in red are structurally characterized as **1-Ln**.

Starting material development and characterization remains an important technical issue facilitating discoveries across the *f*-block including the development of single-molecule magnets[1-8] and low-valent transuranic complexes.[9-12] These studies are facilitated by anhydrous, hydrocarbon-soluble starting materials that are well-defined and supported by weakly-coordinating supporting ligands, often solvent adducts. Numerous methods have been reported for the preparation of trivalent lanthanide and actinide halides starting from other metal halides,[13-20] metal oxides,[21] or bulk metal[22-32] and an appropriate oxidant.

In order to access divergent properties of low-coordinate and low-valent lanthanide and actinide complexes, precursor complexes prepared in low-polarity solvents, including diethyl ether, have been developed.[23-24, 33] These materials are typically isolated as partial solvates [$MI_3(Et_2O)_x$], where the amount of diethyl ether remaining is dependent on isolation conditions and is variable from batch-to-batch and no structural information has been reported to-date. In our application of these methods, it was discovered that the lanthanide triodides exhibited noticeable, albeit sparing, solubility in diethyl ether. Herein we report a bulk synthetic method for the preparation of diethyl ether supported lanthanide triiodides, their crystallographic characterization, and their conversion to more stable precursors.

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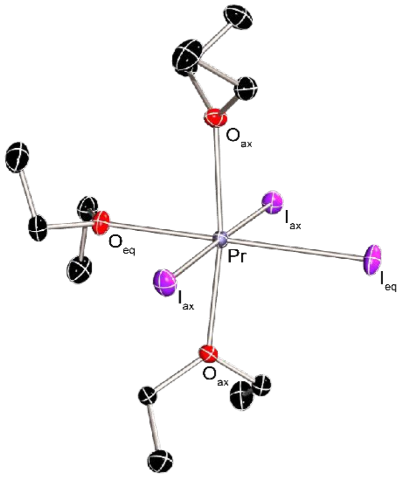

Figure 1. Molecular structure of **1-Pr** with thermal ellipsoids shown at 50% probability and H atoms are omitted for clarity.

The diethyl ether complexes of the lanthanide iodides are prepared by treating lanthanide metal turnings (up to 1 gram) slurried in diethyl ether with a slightly substoichiometric amount of iodine (< 1.5 equivalents) dissolved in diethyl ether (Scheme 1). A substoichiometic amount of iodine is essential to avoid the formation of red-brown $[I_3]^{1-}$. Due to the use of substoichiometric iodine, it is crucial that high-quality metal turnings are used to avoid incorporation of Ln_2O_3 in the product. After 4 days, the complex, $[LnI_3(Et_2O)_x]$, **1-Ln**, is isolated on a frit. This material can be used directly in further reactions but must be characterized by elemental analysis to determine amount of coordinated diethyl ether for reactions that require careful control of stoichiometry and have any residual metal removed mechanically. In our laboratory, ether content after exposure to vacuum depended on the surface area, absolute vacuum, and metal identity and varied between 1.9 and 0.6 ethers per metal ion (see SI for details of methodology). In practice, well-defined *solvento-* complexes are obtained by tetrahydrofuran Soxhlet extraction of the $[LnI_3(Et_2O)_x]$ residue to afford the THF adducts of the lanthanide iodides, $[LnI_3(THF)_4]$, **2-Ln**, or $[LnI_2(THF)_5][LnI_4(THF)_2]$, **3-Ln**. The residual metal and metal oxide remain on the frit. The yield for this two-step process is good to excellent (60-91%). The neutral, **2-Ln**, or charge-separated form, **3-Ln**, was established by comparison of lattice parameters with known structures or full structural characterization (See Fig. S8).[18, 22, 34] There is, however, flexibility in this dichotomy of structures as it has been demonstrated that recrystallization from toluene will lead to the isolation of all lanthanides in the charge-separated system.[24] Bulk phase purity was established by complexometric titration (see SI).[35] The isolation of the trivalent lanthanide, diethyl ether adducts proved to be unsuitable for metals with accessible divalent oxidation states – namely Eu and Yb. Oxidation of the lanthanide metal in diethyl ether resulted in the formation in a mixture of divalent and trivalent products. This product mixture suggests that the divalent intermediate is only slowly oxidized to the trivalent state. Instead, a direct route to **3-Ln** in tetrahydrofuran is used for these two elements (see SI).

In the case of Pr, Nd, and Sm, the final reaction mixtures of the iodine oxidation in diethyl ether were definitively colored (pale green, pale blue, and yellow, respectively), indicating partial solubility of the trivalent iodide complex in diethyl ether. UV/vis spectra for these compounds were obtained to accurately determine molar absorptivity of the observed features (see SI). Figure 2 shows the UV/vis spectra for saturated solutions of **1-Sm** and **1-Nd** in diethyl ether. The saturated solution concentrations obtained by this method for **1-Sm** and **1-Nd** were 6.65 mM and 29.1 mM, respectively. Due to the low solubility and low molar absorptivity of the f-f transitions for **1-Pr**, accurate determination of concentration is difficult. However, the saturated solution concentration can be estimated at around 3 mM. This observed solubility suggested that the etherate complexes could be isolated and structurally characterized. For **1-Ln** (Ln = Ce, Pr, Nd, Sm, Gd, Tb, and Tm), X-ray diffraction quality single crystals are grown by cooling saturated diethyl ether solutions to -35°C. Each of the lanthanide iodide ether adduct complexes adopt a pseudo-octahedral geometry and with a meridional orientation of the iodides and diethyl ether ligands (Figure 1). The complexes, **1-Ln** (Ln = Ce, Pr, Sm, Gd, and Tb), crystallize in the Pbcn space group, giving isomorphic structures. Complexes, **1-Nd** and **1-Tm** diverge. Complex **1-Nd** is isolated in Pna21, while **1-Tm** crystallizes in P-1 and does not yield a satisfactory refinement (however, connectivity was confirmed: a representation of connectivity and initial lattice parameters are included in the SI). These divergent crystal systems demonstrate the relatively soft potential the complexes have for crystallization and the sensitivity to diethyl ether loss.

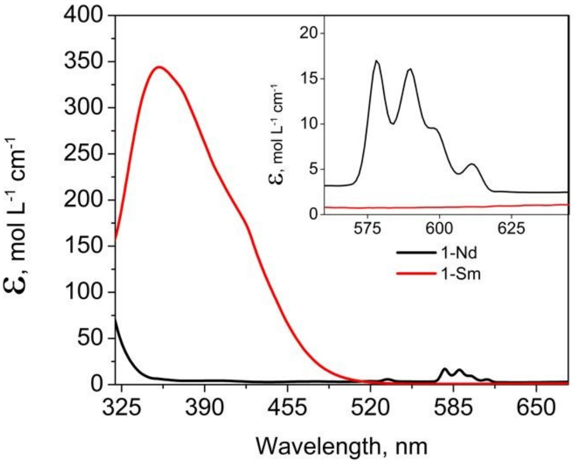

Figure 2. UV-vis spectra of **1-Nd** and **1-Sm in diethyl ether**.

The crystal structure of **1-Pr**, $[PrI_3(mer\text{-}Et_2O)_3]$, is shown in Figure 1. This complex is isostructural with the other **1-Ln** complexes and is representative for the series. The praseodymium atom is coordinated by the three iodides and three diethyl ether molecules, forming a pseudo-octahedral coordination sphere. The $I_{ax}–Pr–I_{eq}$ bond angles are both 89.124(6)° and the $I_{ax}–Pr–I_{ax}$ bond angle is 178.248(12)°. The

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Pr–I$_{ax}$ bond lengths are 3.0812(3) Å while the Pr–I$_{eq}$ bond length is 3.0441(4) Å, giving an average length of 3.069(3) Å. There is similar variation in the Pr–O distances which span 2.406(2) to 2.522(4) Å and average 2.445(3) Å. The average Ln–I bond length for each structurally characterized complex is consistent with lanthanide ion contraction as atomic number increases. Figure 3 demonstrates the linear decrease in bond length of analogous equatorial iodide of the crystallographically characterized **1-Ln** complexes in the Pbcn space group (Ln = Ce, Pr, Sm, Gd, Tb). A linear fit to the data (with an R^2 value of 0.9908) gives a slope of 1.0776. The y-intercept is 1.974, slightly shorter than the iodide ionic radii.[36] This model is consistent with structural indications of ionic bonding.[37]

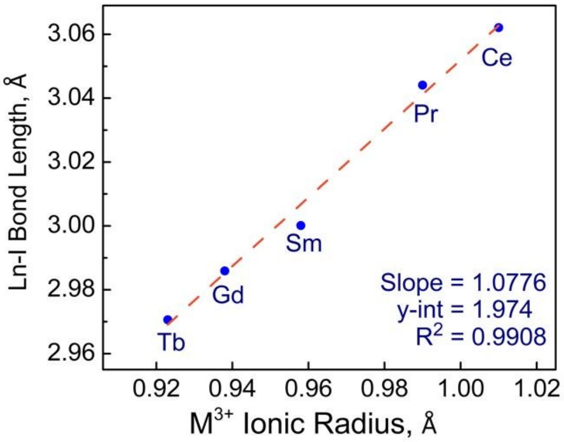

Figure 3. Plot of the equatorial Ln–I bond distance relative to trivalent metal ionic radii in structurally characterized **1-Ln** compounds in the Pbcn space group. Error bars are smaller than the point size.

In these complexes, the Ln ion was six coordinate and the correct space group was Pbcn (or its chiral enantiomer Pna2$_1$, except for 1-Tm) with the Ln atom located at a special position with point symmetry 2. Thus, the coordination polyhedron has C$_2$ symmetry. The coordination geometry is severely distorted from a regular octahedron because of the very different donor properties of the diethyl ether and iodide ligands. Not surprisingly, the ether molecules (and the I atoms) bind to the Ln atom with substantially different Ln-O distances (and Ln-I distances) despite having identical donor characteristics because the trans pair of Ln-O bonds will form substantially stronger bonds than the ether trans to the Ln-I bond. For example, the Ce-O distance is 2.3518(11) for the trans ethers and 2.4480(15) Å for the third ether. There is a correlation between the asymmetric binding of the ether molecules and the binding of the iodine atoms. The distortion of the geometry of the octahedra from regularity was measured by the quadratic elongation (λ_{oct}) and the bond angle variance (σ^2_{oct}). The distortions are presented in Table S39 in the SI.

A useful method of quantifying the size and distortion of the coordination geometry is by analyzing the Voronoi–Dirichlet polyhedron (the dual of the coordination polyhedron). The values of solid angles of corresponding Dirichlet domain faces characterize the lanthanide interactions in the complexes. They correlate well with the bond valences of the bonds. The volumes of Dirichlet domains (V, Å^3) and the corresponding radii of spherical domains (Rsd, Å) are characteristic for the atoms in a given oxidation state.[38] There is a systematic reduction in the polyhedral volumes, average bond lengths, VDP's and Rsd's across the series. The solid angles for the same atom types stays relatively constant across the series. The significant result is that the VDP's and Rsd's reflects the atomic sizes of the lanthanide atom in these compounds. The solid angle is proportional to the portion of the valence electron density from the lanthanide atom which is taking part in the formation of bonds. This relationship has been interpreted as an analogue of valence-electron density in the volume between the interacting atoms.[39] Since the sum of the bond valences is equal to the oxidation state of the metal atom (+3 in all these compounds), the valences to the same atom types and the solid angles are expected to be constant for all these compounds.

After Soxhlet extraction, **2-Ln** or **3-Ln** can be utilized to produce synthetically useful quantities of standard lanthanide complexes. The *tris*-benzyl complex, [Ce(C$_7$H$_7$)$_3$(THF)$_3$], is produced in comparable yields as reported with similar starting reagents,[40] while increased yields are reported for materials such as [Ce[N{Si(Me)$_3$}$_2$]$_3$],[41] see SI. These reactions are accomplished by reacting **2-Ln** or **3-Ln** with an alkali metal salt of the ligand, *i.e.* potassium benzyl or potassium *bis*(trimethylsilyl)amide in appropriate stoichiometries.

In summary, a standard methodology to produce lanthanide triiodide etherate complexes is established for early- and late-lanthanides, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm. This method offers a consistent route for the production of trivalent lanthanide iodide precursors on reasonable scales for bulk synthesis (~1 g). Crystallographic investigation of the **1-Ln** complexes reveal that these solvated lanthanide triiodides are isostructural with three weakly bound diethyl ethers to each lanthanide metal center.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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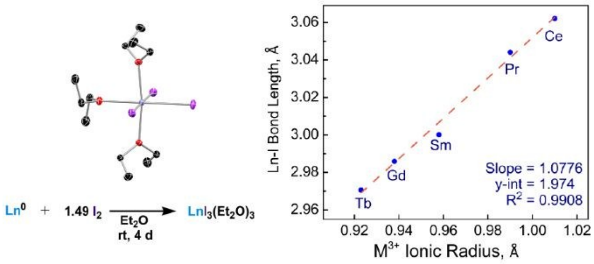

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