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Article

Heterometallic Lanthanide Group 12 Metal Iodides

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Neodymium tri-iodide reacts with Group 12 metal (M; M = Zn, Cd, Hg) iodides to form heterometallic compounds. These Lewis acidic M cleave Nd–I bonds to give either ionic {$[(THF)_5NdI_2][MI_3THF]$; M = Zn, Cd} or charge-neutral {$(THF)_5NdI(\mu_2I)HgI_3$} compounds. Differences in structure are interpreted primarily in terms of M–L bond strengths, rather than Nd–L bond strengths. Experiments with Yb indicate that if there is any excess iodide present in these syntheses then the most readily isolated product is a triiodide salt, i.e., $[(THF)_5YbI_2][I_3]$. In conventional solvents the presence of Lewis acid is not required for iodide displacement—from pyridine, "YbI_3" crystallizes as $[(py)_5YbI_2][I]$. These compounds are potentially useful as heterometallic sources of lanthanide-doped iodide matrixes, they illustrate the ease with which iodides are displaced from lanthanide coordination spheres, and they underscore the complexity associated with using lanthanide iodides as Lewis acid catalysts.

Introduction

Heterometallic compounds containing lanthanides (Ln) and transition metals (M) continue to be investigated as potentially useful electronic materials with readily tailored electronic or magnetic properties.[1−7] This chemistry is complicated by the disparate natures of the ionic Ln and covalent M, i.e., finding ligand systems that coordinate to both metals, or solvent systems that can be used to recrystallize ionic/covalent combinations rather than deliver mixtures of monometallic products, is often frustrating.

Multifunctional ligand systems have been developed[1] extensively to deliver a large family of heterometallic compounds with specific physical properties. Much of this work focuses on the preparation of materials with controlled electronic structure, but other efforts have been devoted to enhancing or optimizing Lewis acid reactivity.[1c]

There is extensive literature describing the use of pseudohalide ligands (CN,[2] SCN,[3] SPh,[4] SePh[5]) to connect Ln with M. These heterometallic materials, representing the earliest heterometallic chemistry containing Ln ions,[2a] often exhibit thought-provoking magnetic and electronic properties. Within this molecular class, both charge-neutral and ionic species have been generated by careful balance of relative M−L and Ln−L bond strengths. A recent extension of this work to chalcogenido clusters[6] led to the preparation of cluster salts, with separate cationic LnE and anionic ME cluster cores.

Of the molecular heterometallic compounds in the literature, all but two contain M and Ln bridged either by organic or oxo ligands. The exceptions are poly-Mn compounds with Cl, oxo, and catecholate bridges linking Mn with La.[7] Oddly

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enough, simple homoleptic halides have never been used as starting materials in heterometallic syntheses. Such an uncomplicated approach to heterometallic chemistry could present an entry to new optoelectronic materials, as metal halide lattices have relatively low phonon energies,[8] and so Ln-doped halide matrixes have potentially useful transmission windows.[9]

In this work we outline our first attempts to prepare heterometallic iodide compounds containing both Ln and the group 12 metals Zn, Cd, and Hg. Difficulties associated with producing heterometallic iodides are identified, and the various structures of isolated heterometallic compounds are discussed in terms of relative M−I bond strengths.

Experimental Section

General Methods. All syntheses were carried out under high-purity nitrogen (Airgas), using conventional drybox or Schlenk techniques. Solvents (Aldrich) were either refluxed continuously over molten alkali metals or K/benzophenone and collected immediately prior to use, or purified with a dual column Solv-Tek Solvent Purification System. Lanthanides were purchased from Strem. Melting points were taken in sealed capillaries and are uncorrected. IR spectra were taken on a Thermo Nicolet Avatar 360 FTIR spectrometer, and recorded from 4000 to 600 cm^{-1} as a Nujol mull on NaCl plates. Electronic spectra were recorded on a Varian DMS 100S spectrometer with the samples in a 0.10-mm quartz cell attached to a Teflon stopcock. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ).

Synthesis of $(THF)_5NdI(\mu_2\text{-}I)HgI_3$ (1). Nd (0.29 g, 2.0 mmol) and I_2 (0.76 g, 3.0 mmol) were combined in THF (35 mL). The mixture was stirred until most of the metal was consumed (2 days) to give a translucent brick red solution. Hg (0.40 g, 2.0 mmol) and more I_2 (0.51 g, 2.0 mmol) were added to the mixture and stirred for 2 days. The solution was allowed to settle and a tan solid precipitated. The rust solution was filtered (30 mL) and layered with hexanes (8 mL) to give colorless rods (0.39 g, 15%) that turn black at 95 °C and decompose at 310 °C. Anal. Calcd for $C_{20}H_{40}O_5NdHgI_5$: C, 17.9; H, 3.01. Found: C, 17.5; H, 3.15. The compound does not show an optical absorption maximum from 300 to 800 nm in pyridine or THF. IR: 2964 (w), 2843 (w), 2729 (s), 1459 (m), 1377 (m), 1260 (s), 1096 (s), 1020 (s), 804 (s), 722 (s) cm^{-1}.

Synthesis of $[(THF)_5NdI_2][(THF)ZnI_3]$ (2). Nd (0.29 g, 2.0 mmol) and I_2 (0.76 g, 3.0 mmol) were combined in THF (25 mL). The mixture was stirred until the metal was consumed (5 days) to give a translucent pale brown solution. Zn (0.13 g, 2.0 mmol) and more I_2 (0.51 g, 2.0 mmol) were added to the mixture and stirred for 4 days. The mixture was allowed to settle and the tan precipitate was separated from the golden yellow solution by filtration. The solution (22 mL) was layered with hexanes (13 mL) to give colorless rods (0.56 g, 22%) that turn black at 140 °C and melt at 195 °C. Anal. Calcd for $C_{24}H_{48}O_6NdZnI_5$: C, 22.6; H, 3.79. Found: C, 22.6; H, 4.10. The compound is colorless, but exposure to air produces an optical absorption maximum at 368 nm in THF. IR: 3769 (s), 3704 (s), 2958 (w), 2920 (w), 2856 (w), 1937 (s), 1598 (s), 1459 (m), 1410 (m), 1378 (m), 1265 (w), 1104 (w), 1018 (w), 862 (m), 808 (s), 706 (m), 658 (m) cm^{-1}.

Synthesis of $[(THF)_5NdI_2][(THF)CdI_3]$ (3). As for **2**, Nd (0.29 g, 2.0 mmol), I_2 (0.76 g, 3.0 mmol), THF (25 mL), Cd (0.23 g, 2.0 mmol), and more I_2 (0.51 g, 2.0 mmol) gave colorless lathes (0.40 g, 19%) that turn black at 150 °C and melt at 255 °C. Anal. Calcd for $C_{24}H_{48}O_6NdCdI_5$: C, 21.8; H, 3.65. Found: C, 20.8; H, 3.86. The compound is colorless, but exposure to air produces an optical absorption maximum at 368 nm in THF. IR: 2958 (w), 2921 (w), 2852 (w), 2357 (s), 2337 (s), 1941 (s), 1605 (s), 1454 (m), 1409 (m), 1377 (m), 1262 (w), 1099 (w), 1021 (w), 866 (m), 805 (s), 6946 (m), 670 (m) cm^{-1}. Cell data from single-crystal X-ray diffraction (87 reflections with $2° < \theta < 21°$): $a = 8.582(4)$ Å, $b = 9.065(4)$ Å, $c = 24.691(13)$ Å, $\beta = 82.76(2)°$, $V = 1905.7(16)$ Å^3.

Synthesis of $[(py)_5YbI_2][I]\cdot 1/2(py)$ (4). Yb (0.35 g, 2.0 mmol) and I_2 (0.72 g, 2.9 mmol) were combined in THF (40 mL). The mixture was stirred until all the metal was consumed (3 days) to give a transparent pale yellow solution and a salmon pink precipitate. The precipitate was isolated by filtration, dried under vacuum, and dissolved in pyridine (25 mL) to give a transparent rust solution. After a day the solution was filtered to remove trace black precipitate, and layered with hexanes (20 mL) to give yellow needles (1.10 g, 50%) that turn black and melt at 375 °C. Anal. Calcd for $C_{27.5}H_{27.5}N_{5.5}YbI_3$: C, 33.4; H, 2.80; N, 7.79. Found: C, 33.2; H, 3.05; N, 7.65. The compound does not show an optical absorption maximum from 300 to 800 nm in pyridine and was insoluble in THF. IR: 2922 (w), 2854 (w), 2366 (s), 1634 (s), 1596 (m), 1580 (m), 1521 (s), 1457 (w), 1437 (m), 1377 (m), 1260 (s), 1215 (s), 1144 (s), 1069 (s), 1029 (s), 990 (s), 884 (m), 805 (m), 743 (m), 700 (w), 668 (s) cm^{-1}.

Synthesis of $[(THF)_5YbI_2][I_3]$ (5). Yb (0.35 g, 2.0 mmol) and I_2 (0.76 g, 3.0 mmol) were combined in THF (50 mL). The mixture was stirred for 3 days to give pink powder and a light yellow solution. The solution was filtered, concentrated to 38 mL, and layered with hexanes (25 mL) to give long yellow needles (0.59 mg, 25%) that turned brown at 201 °C but did not melt below 296 °C. Anal. Calc. for $C_{20}H_{40}O_5I_5Yb$: C, 20.6; H, 3.45. Found: C, 20.0; H, 3.31. IR: 3658 (s), 3583 (s), 2923 (w), 2727 (s), 2670 (s), 2362 (s), 1654 (s), 1461 (w), 1377 (m), 1305 (s), 1261 (s), 1154 (s), 1091 (s), 1018 (s), 800 (s), 722 (s) cm^{-1}.

X-ray Structure Determination of 1, 2, 4, and **5.** Data for **1**, **2**, **4**, and **5** were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$Å) at 100 K. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a multiscan (SADABS)[10] method. The structures were solved by Patterson or direct methods (SHELXS86).[11] All non-hydrogen atoms were refined (SHELXL97)[12] based upon F_{obs}^2. All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (f_o, f', f'') are as described in SHELXL97. Crystallographic data and final R indices for **1**, **2**, **4**, and **5** are given in Table 1. ORTEP diagrams[13] for **1**, **2**, **4**, and **5** are shown in Figures 1, 2, 3, and 4, respectively. Significant bond geometries for **1**, **2**, **4**, and **5** are given in the figure captions. Complete crystallographic details for **1**, **2**, **4**, and **5** are given in the Supporting Information.

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Table 1. Crystallographic Data and Final R Indices for **1**, **2**, **4**, and **5**

compound	**1**	**2**	**4**	**5**
empirical formula	$C_{20}H_{40}HgI_5NdO_5$	$C_{24}H_{48}I_5NdO_6Zn$	$C_{27.5}H_{27.5}I_3N_{5.5}Yb$	$C_{20}H_{40}I_5O_5Yb$
fw	1339.85	1276.73	988.79	1168.06
space group	$P2_12_12_1$	Pn	$P2_1/c$	$Pbcn$
cryst syst	orthorhombic	monoclinic	monoclinic	orthorhombic
a (Å)	12.5824(9)	8.5245(7)	25.950(1)	12.3056(1)
b (Å)	13.0371(9)	9.0424(7)	15.8012(7)	21.741(2)
c (Å)	20.411(1)	24.515(2)	16.0894(8)	11.896(1)
α (deg)	90	90	90	90
β (deg)	90	96.641(1)	106.302(1)	90
γ (deg)	90	90	90	90
V (Å$^{3)}$	3348.1(4)	1877.0(3)	6332.0(5)	3182.7(6)
Z	4	2	8	4
D (calcd) (g/cm^{-3})	2.658	2.259	2.074	2.438
temperature (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
abs coeff (mm^{-1})	10.748	6.149	5.904	7.813
R(F)^a [$I > 2\sigma(I)$]	0.032	0.050	0.033	0.037
R$_w$(F^2)^a [$I > 2\sigma(I)$]	0.064	0.097	0.057	0.075

^{a} $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. Additional crystallographic details are given in the Supporting Information.

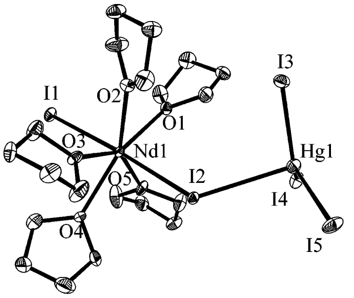

Figure 1. Molecular structure of $(THF)_5NdI(\mu_2\text{-}I)HgI_3$. Thermal ellipsoids are drawn at the 50% probability level. Significant bond distances (Å) and angles (°): Nd(1)−O(1), 2.445(5); Nd(1)−O(5), 2.451(5); Nd(1)−O(3), 2.453(5); Nd(1)−O(2), 2.454(4); Nd(1)−O(4), 2.463(5); Nd(1)−I(1), 3.0543(6); Nd(1)−I(2), 3.1086(6); I(2)−Hg(1), 3.2452(5); Hg(1)−I(4), 2.7146(6); Hg(1)−I(5), 2.7206(6); Hg(1)−I(3), 2.7250(5); Nd(1)−I(2)−Hg(1), 126.71(2); I(4)−Hg(1)−I(5), 122.05(2); I(4)−Hg(1)−I(3), 119.78(2); I(5)−Hg(1)−I(3), 114.43(2); I(4)−Hg(1)−I(2), 93.14(2); I(5)−Hg(1)−I(2), 98.66(2); I(3)−Hg(1)−I(2), 97.74(2); I(1)−Nd(1)−I(2), 176.72(2).

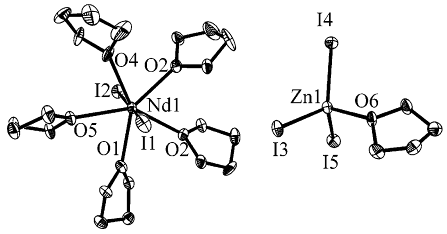

Figure 2. Molecular structure of $[(THF)_5NdI_2][(THF)ZnI_3]$. Thermal ellipsoids are drawn at the 50% probability level. Significant bond distances (Å) and angles (°): Nd(1)−O(1), 2.441(6); Nd(1)−O(4) 2.453(6); Nd(1)−O(3), 2.458(6); Nd(1)−O(2), 2.463(6); Nd(1)−O(5), 2.484(6); Nd(1)−I(1), 3.0496(7); Nd(1)−I(2), 3.0522(7); Zn(1)−O(6), 2.068(6); Zn(1)−I(3), 2.5633(11); Zn(1)−I(4), 2.5764(12); Zn(1)−I(5), 2.5783(11); O(1)−Nd(1)−O(4), 145.4(2); O(1)−Nd(1)−O(3), 143.1(2); O(4)−Nd(1)−O(3), 71.0(2); O(1)−Nd(1)−O(2), 71.6(2); O(4)−Nd(1)−O(2), 142.6(2); O(3)−Nd(1)−O(2), 71.6(2); O(1)−Nd(1)−O(5), 71.5(2); O(4)−Nd(1)−O(5), 74.6(2); O(3)−Nd(1)−O(5), 145.4(2); O(2)−Nd(1)−O(5), 142.9(2); O(1)−Nd(1)−I(1), 87.94(14); O(4)−Nd(1)−I(1), 85.27(17); O(3)−Nd(1)−I(1), 91.06(16); O(2)−Nd(1)−I(1), 93.03(14); O(5)−Nd(1)−I(1), 89.18(15); O(1)−Nd(1)−I(2), 93.81(14); O(4)−Nd(1)−I(2), 91.07(17); O(3)−Nd(1)−I(2), 89.91(16); O(2)−Nd(1)−I(2), 91.27(14); O(5)−Nd(1)−I(2), 87.64(15); I(1)−Nd(1)−I(2), 175.68(2); O(6)−Zn(1)−I(3), 101.9(2); O(6)−Zn(1)−I(4), 102.6(2); I(3)−Zn(1)−I(4), 114.83(4); O(6)−Zn(1)−I(5), 104.6(2); I(3)−Zn(1)−I(5), 114.28(4); I(4)−Zn(1)−I(5), 116.00(4).

Results

The group 12 metal iodides MI_2 (M = Zn, Cd, Hg) react with LnI_3 to form heterometallic compounds with a transfer of iodide from Ln to M. Saturation of a THF solution of HgI_2/NdI_3 results in the isolation of $(THF)_5NdI(\mu\text{-}I)HgI_3$ (**1**). A low-temperature single-crystal X-ray diffraction analysis of this product revealed a structure with pentagonal bipyramidal geometry about the Nd, having two axial I^- and five equatorial THF ligands. Figure 1 gives an ORTEP diagram of **1**, with significant bond lengths and angles in the figure caption. In the structure of **1**, an I^- has been extracted from the Nd(III) coordination sphere, and this I^- coordinates the Hg(II) ion. One of the Nd bound I^- also coordinates to the Hg(II) ion, and while there are four I^- about the Hg, the geometry is better described as trigonal planar HgI_3^- with a relatively weak, e.g. dative, interaction between Hg and I(2). The three terminal iodides on Hg have similar bonding geometries, both in terms of bond lengths [Hg(1)−I(4), 2.7146(6) Å; Hg(1)−I(5), 2.7206(6) Å; Hg(1)−I(3), 2.7250(5) Å] and angles [I(4)−Hg(1)−I(5), 122.05(2)°; I(4)−Hg(1)−I(3), 119.78(2)°; I(5)−Hg(1)−I(3), 114.43(2)°]. In contrast, the distance between Nd and I(2) is 3.2542(3) Å, and the average I(2)Hg−I angle is 96.5°. The mutual effects of each metal on the others M−iodide bond length is apparent not only in the Hg−I bond but also, in a less dramatic way, in the bonds to Nd, where the Nd−I(1) bond length is 3.0543(6) Å and Nd−I(2) bond length is longer at 3.1086(6) Å.

The more acidic MI_2 compounds also extract I^- from LnI_3, but the bridging $Ln-I^--M$ interaction present in **1** has been disrupted by THF coordinated to both Ln and M to give the ionic compounds $[(THF)_5NdI_2][(THF)MI_3]$ [M = Zn(**2**), Cd(**3**)]. Figure 2 gives an ORTEP diagram of **2**, with significant bond lengths and angles in the figure caption. The unit cell data for the Cd compound **3** indicated that it is isostructural with **2**. The cationic Nd fragment has considerable precedence in the literature,[14] while the overall geometries of the main group anions are similar to those of other M(II) anions.

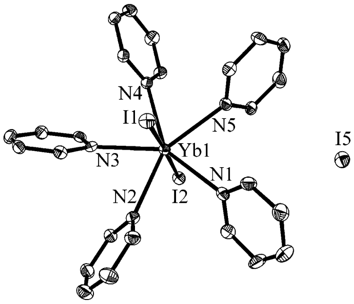

Figure 3. Molecular structure of $[(py)_5YbI_2][I]$. Thermal ellipsoids are drawn at the 50% probability level. Significant bond distances (Å) and angles (°): Yb(1)−N(3), 2.454(4); Yb(1)−N(1), 2.474(4); Yb(1)−N(4), 2.474(3); Yb(1)−N(2), 2.474(4); Yb(1)−N(5), 2.482(3); Yb(1)−I(2), 2.9645(3); Yb(1)−I(1), 2.9729(3); N(3)−Yb(1)−N(1), 144.64(11); N(3)−Yb(1)−N(4), 70.67(11); N(3)−Yb(1)−N(2), 70.88(11); N(1)−Yb(1)−N(2), 73.79(11); N(1)−Yb(1)−N(5), 74.97(11); N(4)−Yb(1)−N(5), 69.75(11). The second independent $(py)_5YbI_2$ cation has nearly the same bond distances and angles, but several torsion angles are quite different (e.g., as a rotational isomer).

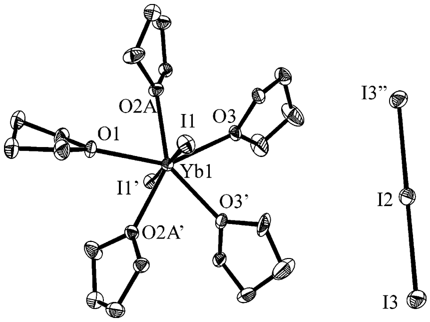

Figure 4. Molecular structure of $[(THF)_5YbI_2][I_3]$. Thermal ellipsoids are drawn at the 50% probability level. Significant bond distances (Å) and angles (°): Yb(1)−O(2A)′, 2.341(4); Yb(1)−O(2A), 2.341(4); Yb(1)−O(1), 2.349(6); Yb(1)−O(3)′, 2.351(4); Yb(1)−O(3), 2.351(4); Yb(1)−I(1)′, 2.9505(5); Yb(1)−I(1), 2.9505(5); I(2)−I(3), 2.9058(5); I(2)−I(3)″, 2.9058(5); O(2A)′−Yb(1)−O(1), 72.1(1); O(2A)−Yb(1)−O(1), 72.1(1); O(2A)′−Yb(1)−O(3)′, 71.99(14); O(2A)−Yb(1)−O(3), 71.99(14); O(3)′−Yb(1)−O(3), 71.9(2); I(1)′−Yb(1)−I(1), 179.57(2); I(3)−I(2)−I(3)″, 180. Atom C5 is modeled as disordered 55:45 about two sites (site A shown here). Symmetry operations used: $' = -x, y, -z + {}^{1}/_{2}$, and $'' = -x, -y, -z + 1$.

Solvent selection is crucial to the isolation of heterometallic iodides. In pyridine, analogous reactions did not yield a crystalline product with Nd. However, saturation of solution containingYbI_3 in pyridine results in the crystallization of $[(py)_5YbI_2][I]$ (**4**) an ionic compound with a pentagonal bipyramidal Yb ion having two axial iodides, five equatorial pyridine ligands, and the monoanion I^-. Figure 3 gives an ORTEP drawing of the molecule, with significant bond lengths and angles given in the figure caption. Both Yb−I and Yb−N bond lengths are consistent with previously reported trivalent Yb compounds.[15] The deep yellow color of this compound presumably originates from an iodide to ytterbium charge-transfer absorption that tails from the UV into the visible spectrum.

Similarly, when an excess of iodine is added toYbI_3 in THF the resultant deep red solution can be saturated to give $[(THF)_5YbI_2][I_3]$ (**5**), a salt that can be prepared in 25% yield. These yellow-orange crystals routinely grow to >1 cm long. Structural characterization of **5** revealed a cationic structure similar to that found in **4**, with a pentagonal bipyramidal Yb(III) ion containing two axial I^- and five equatorial THF ligands. The counterion in this case was the well-known triiodide, I_3^-. Figure 4 gives an ORTEP diagram of **5**, with significant bond lengths and angles included in the figure caption. Tri-iodides were always noted as minor cocrystallized products in the synthesis of **1**−**4** if an excess of I_2 was present, or if solutions of these compounds were exposed to air.

Discussion

Of the three heterometallic products described herein, only the mercury compound **1** crystallizes as a molecular product, with the Zn and Cd analogues **2** and **3**, as well as the pyridine complex **4** and triiodide compound **5**, crystallizing as salts. All compounds serve to illustrate the particular ease with which iodides are removed from lanthanide coordination spheres. Variations in the Group 12 compounds reflect the relatively covalent nature of Hg, compared with Cd or Zn. Precedence for MI_3^- and MI_4^{2-} anions is noted[16] for all three of the group 12 metals.

Iodide chemistry of the Group 12 metals has been thoroughly examined. Mercuric iodide is certainly the most complicated of the group. A light-sensitive material,[17] solid-state HgI_2 is complex, with a remarkable range of Hg−I interactions: there is a red form containing Hg in a distorted tetrahedral geometry [four 2.783 Å Hg−I bonds, I−Hg−I = 103.1° and 112.7°], and a yellow form that contains essentially linear HgI_2 molecules (I−Hg−I = 178.3°) with two short (2.615 and 2.620 Å) and four long (2 × 3.507 Å and 2 × 3.510 Å) Hg−I bonds.[18] HgI_2 has often incorporated additional I^- within the primary Hg(II) coordination sphere, resulting in a multitude of Hg coordination geometries. Compound **1**, with three well-defined Hg−I bonds (bond lengths range from 2.7146(4) to 2.7250(5) Å and average 2.720(1) Å) can be described either as a grossly distorted tetrahedron or a trigonal planar Hg with an additional weak Hg−I (3.2452(3) Å) interaction. Precedence for each type of geometry already exists.[16,19] It should be noted that in the absence of Lewis base solvents, there appears to be no reaction of HgI_2 with LnI_3.[20]

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Introduction of Lewis bases leads to a rich HgI_2 coordination chemistry, with an even more complicated range of Hg coordination geometries.[19] In addition to the plethora of regular and distorted T_d structures, there are compounds such as R_3PHgI_2,[19b] a trigonal bipyramidal molecule with three strong bonds to Hg (P, I, I) and two weak HgI interactions between neighboring molecules. In this class of materials, structures often appear to be influenced by lattice requirements, brought to prominence because bonds to Hg are generally less than robust and form more open complexes with lower coordination numbers, particularly when the ligands are relatively electropositive.

In **2** and **3**, the more acidic MI_2 (M = Zn, Cd) moieties coordinate an additional THF ligand rather than the terminal I bound to Nd. Similar reactivity has been noted in chloride systems, for example where $LaCl_3$ reacts with $FeCl_3$ in the presence of $OPPh_3$ to give $[(OPPh_3)_5LaCl][FeCl_4]_2$,[21] in the preparation of $[(THF)_5YbCl_2][(THF)W(O)Cl_4]$,[14a] or in Cu chemistry, i.e., $[GdCl_2(OPPh_3)_4][CuCl_3]$.[22] In these cases, the stronger chloride ligands are removed from Ln(III) in the presence of highly charged (Fe(III), W(V), Cu(II)) Lewis acids. The Cd product **3** could, conceivably, find use as a Ln-doping source in the synthesis of cadmium halide glasses.[23]

Iodide extraction has often been noted in lanthanide chemistry, and can be achieved by interaction with either acids or bases. While it was long known that the strongest Lewis bases would displace I^- to form ionic materials,[24] the diversity of reagents that cleave Ln−I bonds, as revealed in the present study, is surprising. Early work examining the coordination chemistry of LnI documented the formation of conducting solutions with a variety of Lewis bases, including urea,[24a] dimethylacetamide,[24b] ethylenediamine,[24c] DMSO, DMF,[24d] and bipyrimidine.[24e] The number of displaced iodides paralleled the donor strength, i.e., DMSO formed a 1:3 electrolyte whereas bipyrimidine displaced only a single I^-.

The shift away from synthetic methodologies using these strong donor solvents, toward preparative inorganic/organometallic chemistry involving less polar solvents (i.e., THF, DME, pyridine) will certainly benefit from analyses of simple coordination chemistry, particularly if lanthanide iodides are to be developed as catalysts.[25] In the present work, it is clear that even a monodentate nitrogen-containing donor such as pyridine is sufficiently basic so as to displace I^- from Ln(III) coordination spheres. This reactivity does not necessarily apply to the larger, early lanthanides, given that in the chemically similar actinide series, UI_3, which has an ionic radius slightly larger than Nd, crystallizes from pyridine as molecular $(py)_4UI_3$.[26]

Displacement of I^- by pyridine is important when examining the catalytic behavior of lanthanide iodides, because it suggests that even in the conventional monodentate solvents currently used in synthetic chemistry, both neutral and charged species are possible. For example, in the reported polymerization of butyl-4-vinylbenzoate with SmI_2, the presence of SmI_3 had a dramatic impact on molecular weight distribution.[27] Clearly, the possibility that $((THF)_6SmI)^+$, $Sm(THF)_7{}^{2+}$, or polynuclear species are the superior catalysts must be considered. Related examples of I^- extraction by a Lewis acid can be found in reports describing the self-ionization of LnI_3 to give $LnI_2{}^+/LnI_4{}^-$.[14b,c,d]

Extraction of I^- from YbI_3 by I_2, as evidenced by the structure of **5**, again serves as a reminder that catalysis with lanthanide iodides can be complicated by an abundance of neutral and ionic species in solution. Surprisingly, this compound is isostructural with the analogous La derivative,[28] making this formulation one of the rare instances in which all the lanthanides can form an isostructural series of compounds. In the La and Yb crystal structures, the I−I−I anions have inversion symmetry requiring equivalent I−I (e.g., 2.508 Å in **5**) bond lengths. It has often been noted that a slight excess of Ln enhances the yield of **1**−**3**, presumably because any adventitious oxygen/water does not result in the generation of excess I_2, which would otherwise react with LnI_3 to form particularly insoluble $(THF)_5LnI_2(I_3)$.

This iodide chemistry has frequent parallels with pseudohalide ligand systems. With respect to cyanide ligands, there exist structures with CN linking ionic/covalent combinations[2] such as Sm/Ni or Yb/Fe. There is also a thiocyanate bridge linking La and Hg where, as expected, N coordinates to La and S coordinates to Hg.[3] In recently described chalcogenolate reactivity group 12 $M(EPh)_2$ compounds were used to stabilize $Ln(EPh)_x$ compounds. Selenolates were often extracted from Ln(II) by Hg(II) ions, while more acidic metals such as Zn(II) or Fe(III) were necessary to effect SePh extraction from Ln(III).[4] Thiolates have been displaced from

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Ln coordination spheres, but only in the presence of multidentate Lewis bases.[29]

Conclusion

Discrete complexes comprised of LnI_3 with the group 12 metal iodides MI_2 can be prepared and isolated either as ionic or molecular products. A common feature to all three products, the extraction of I^- by M from the Ln coordination sphere, is also noted in the extraction of I^- by I_2 and the displacement of I^- by pyridine. All of these compounds illustrate the facility with which iodide is removed from Ln coordination spheres.

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Supporting Information Available: X-ray crystallographic files in CIF format for the crystal structures of **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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