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# Large Scale Synthesis of Dysprosium and Neodymium Diiodides

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$DyI_2$ and $NdI_2$, which may become useful reagents in organic synthesis, can be prepared in up to 50 g quantities in a few hours without using welded tantalum tubes or temperatures over 1000 °C by direct reaction of the metal and iodine.

## Introduction

Samarium diiodide, $SmI_2$, has found widespread use as a one-electron reductant in organic synthesis[1−5] and as a starting material for the preparation of divalent samarium inorganic and organometallic complexes.[6−10] It is available commercially and widely used. Recently, the existence of soluble molecular diiodide complexes of the more reducing divalent lanthanides, Tm(II), Dy(II), and Nd(II), has been established: $TmI_2(DME)_3$,[11] $DyI_2(DME)_3$,[12] $NdI_2(THF)_5$.[13] Preliminary reactivity studies with these diiodides show that they will not only be useful in organic[12,14] and organometallic[15,16] synthesis, as is $SmI_2$, but they will also provide new levels of divalent lanthanide reactivity beyond that possible with Sm(II).[14,16−20] This reactivity is consistent with the relative reduction potentials of the divalent ions (V vs NHE): Sm, −1.55; Tm, −2.3; Dy, −2.5; Nd, −2.6.[21]

To utilize the high reactivity of the divalent Tm(II), Dy(II), and Nd(II) ions, convenient preparations of the diiodide complexes of these metals must be available. The divalent lanthanide diiodides of europium, ytterbium, samarium, and thulium can be prepared by the reaction of the metal with iodine in THF or DME under an inert atmosphere.[10,14,22] However, this method has not been successful for dysprosium and neodymium, since solutions of $DyI_2$ and $NdI_2$ in THF and DME quickly decompose at 25 °C. Until methods are found to selectively form the diiodides in solution at a reasonable rate at low temperatures, other routes must be used.

To avoid solution synthesis of $DyI_2$ and $NdI_2$, solid-state methods can be used. In the past, divalent halides of most of the lanthanides have been made either by $Ln/LnX_3$ reductions (X = halide) in welded tantalum vessels at temperatures ranging from 600 to 1100 °C[23−28] or by alkali

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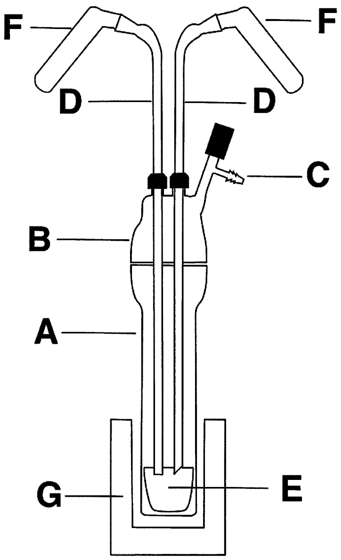

**Figure 1.** Diagram of the solid-state apparatus: (A) quartz tube, (B) top O-ring joint, (C) valve to vacuum line, (D) quartz addition tubes, (E) quartz crucible, (F) Schlenk addition funnel, and (G) furnace.

metal reductions of $LnX_3$ under similar conditions.[29] Although these methods are successful, the necessary apparatus is usually found only in solid-state laboratories.

Recently, Bochkarev and co-workers reported that $DyI_2$ and $NdI_2$ could be made in glass vessels from the metal and iodine at temperatures estimated to be 1500 °C.[30] The reactions are reported to occur with a spectacular burst of light and heat but were sufficiently fast that the glass vessels neither cracked nor melted when the reactions were run on a 1 g scale. We report here a modification of that procedure in which solvent free $DyI_2$ and $NdI_2$ can be made in a more controlled fashion in quantities up to 50 g.

## Experimental Section

Samples of Dy and Nd were obtained as 40 mesh metal powders from Strem Chemicals at 99.5% purity or were filed from metal ingots obtained from Stanford Materials (Aliso Viejo, CA). Iodine was obtained from Acros Chemical and used without further purification.

**Apparatus.** $DyI_2$ and $NdI_2$ were prepared in a quartz crucible (30 mL) in an apparatus of the following design. The bottom of the apparatus, A in Figure 1, consists of a quartz vessel (50 mm × 270 mm) with a graded seal connecting it to an O-ring joint. The O-ring joint connects to another, B, fitted with a greaseless high vacuum valve, C, and two small O-ring tube fittings. Quartz tubes, D, (8 mm × 400 mm) topped with 14/20 standard joints at a 45° angle, are placed through the O-ring fittings in B. A quartz crucible, E, is placed inside the quartz vessel, A, such that the tubes, D, empty into it. These tubes direct the addition of material to the crucible from addition funnels or Schlenk addition flasks, F. The tube used for metal additions is scalloped in the last 12 mm to avoid plugging during the reaction. The apparatus is placed in a furnace, G, such that the entire crucible can be heated. The temperature is monitored with a thermocouple placed between the furnace and quartz vessel A.

**Operation.** In air, one of the addition flasks, F, is charged with powdered Dy or Nd metal (−40 mesh); the second is charged with powdered iodine. A and B are clamped together, and an inert atmosphere is then established through valve C by repeatedly evacuating and slowly refilling with argon. This valve is closed at the beginning of the reaction such that a static vacuum is present in the apparatus. After the temperature of the furnace is raised to approximately 450 °C, a small amount of lanthanide metal is added to the crucible through the quartz tube. A small amount of iodine (approximately 200 mg) is subsequently added which reacts vigorously emitting a bright light. After the light subsides, the furnace temperature is raised to slightly above the melting point of the lanthanide diiodide being produced (659 °C for Dy, 562 °C for Nd)[10] to run the reaction in a diiodide melt. Reactions in the melt allow shorter reaction times and lower temperatures than solid-state reactions. $LnI_2$ melts are preferable to $LnI_3$ melts since they are accessible at lower temperature and are less viscous.[31]

Small amounts of metal are subsequently added, each followed by iodine addition. Addition of iodine is always accompanied by an orange glow and an increase in temperature. The iodine should not be added too quickly to avoid large temperature increases that will cause material to sublime onto the walls of the apparatus. The alternating addition of metal and iodine is continued over a period of up to 2 h until all the reagents are consumed. During these additions, valve C is occasionally opened to the vacuum system for short periods. After all the reagents have been added, the furnace is removed, and the apparatus is allowed to cool to room temperature. Excess iodine is removed under vacuum through valve C. The system is then filled with argon, section A is separated from B, and the crucible is promptly placed in a recirculating glovebox containing argon. In the glovebox, the dark solid product is removed from the crucible with a spatula and crushed to a powder with a mortar and pestle. When powdered, the product attains a color distinctive of the solvate-free lanthanide diiodide: violet for $DyI_2$ and black for $NdI_2$. If any pieces of unreacted metal are present, they are generally at the bottom of the sample and can be removed manually.

**Quantities and Usage of $LnI_2$.** The reactor is designed to provide up to 50 g of product. For example, the reaction of Dy (18.0 g, 0.11 mol) with $I_2$ (30.0 g, 0.12 mol) generated 46.3 g of dark solid product. The products are stored as solids under an inert atmosphere until used. At that time, the amount needed (see later) is weighed and dissolved in THF or DME. The exact concentration can be determined by the complexometric titration procedure described in the next section. Concentrations of 0.06 M for $DyI_2$ (0 °C) and 0.05 M for $NdI_2$ (−15 °C) have been obtained in THF. Examination of the molarities of a series of THF solutions of $DyI_2$ made from a single batch of solid $DyI_2$ stored over several months at ambient temperature in a glovebox showed negligible decomposition of the solid.

**Purity.** The purity of the samples was examined by elemental analysis. Analysis of solid samples before extraction with solvent showed 1.73 I/Dy (Anal. Dy, 42.09; I, 57.02) and 1.74 I/Nd ratios (Anal. Nd, 39.01; I, 59.71). This deviation from 2 expected for $LnI_2$ can be explained by the presence of metallic Dy and Nd. If no $LnI_3$ contaminant is present, this would amount to 0.16 Dy per $DyI_2$ and 0.15 Nd per $NdI_2$. If $LnI_3$ is present, the amounts of Ln would be higher. In comparison, $Ln/I_2$ reactions conducted at 1500 °C are reported to give I/Ln ratios of 1.8−2.4.[32]

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Since the solubility of $LnI_2$ in ether solvents is much greater than that of Ln and $LnI_3$, the latter contaminants can be removed by extraction. Any LnOI formed by reaction with the quartz vessel[33] can also be separated in this manner. Material obtained by extraction of the product from the apparatus in Figure 1 with THF at −15 °C followed by removal of the solvent under vacuum gives materials with 2.02 I/Dy (Anal. Dy, 28.79; I, 45.30) and 2.00 I/Nd ratios (Anal. Nd, 28.05; I, 49.50).

Analysis of samples is routinely done in house via complexometric titration according to the following procedure. Deionized water is added to a 2.0 mL aliquot of $DyI_2$ or $NdI_2$ solution (in THF or DME) removed from a stock solution via syringe. The resulting mixture is titrated directly for lanthanide content with a 3.0 mM $Na_2$EDTA solution with xylenol orange as indicator and hexamethylenetetramine as a buffer.[34] The purity of the solids obtained has ranged from 84% to 98% on the basis of these titrations, which is consistent with the elemental analysis of the solid products.

## Results and Discussion

$DyI_2$ and $NdI_2$ compounds can be synthesized directly from the metal and iodine in a quartz system that does not require the use of a sealed tantalum container or extremely high temperatures. Although the I/Ln ratio of the crude product does not match $LnI_2$ as well as samples prepared in sealed tantalum vessels, the procedure avoids the need for tantalum welding. The purity of the samples is comparable to those made at 1500 °C, but much larger amounts can be prepared. As in the 1500 °C reactions, the Ln and $LnI_3$ contaminants can be removed by solvent extraction. Since the compounds are used in solution, this step would be done in any case. The purity of the solutions obtained in this way has proven to be sufficient for both organic synthesis applications[12,14] as well as for inorganic[20] and organometallic synthesis.[16]

## Conclusion

$DyI_2$ and $NdI_2$ can be conveniently made in a few hours in up to 50 g quantities. The solids can be stored for months until they are ready for use in solution at low temperature for organic synthesis or preparative synthetic inorganic and organometallic chemistry.

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