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Synthesis and some properties of neodymium(III) and dysprosium(III) iodide hydrides LnI_2H

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The iodide hydrides NdI_2H (**1**) and DyI_2H (**2**) were obtained by the reactions of diiodides NdI_2 (**3**) and DyI_2 (**4**) with hydrogen at atmospheric pressure and temperature of 120—200 °C. Hydrolysis of products **1** and **2** gives hydrogen in a high yield. The reactions of **1** with phenol and of **2** with isopropyl alcohol in THF afford the iodide phenoxide $NdI_2(OPh)(THF)_4$ and iodide isopropoxide $DyI_2(OPr^i)(Pr^iOH)_3$, respectively. The reaction of **2** with cyclopentadiene is accompanied by disproportionation and gives, besides dihydrogen, $Cp_2DyI(THF)_2$ and $DyI_3(THF)_3$.

Key words: diiodides, hydrides, dysprosium, neodymium, isopropoxide, cyclopentadienide.

The reactivities of divalent neodymium and dysprosium diiodides LnI_2 are similar to those of alkali and rare earth metals.[1] The latter easily react with H_2 to form hydride phases with a composition close to LnH_3 or, at elevated temperature, to LnH_2 (see Ref. 2). To our knowledge, the reactions of the diiodides LnI_2 with hydrogen have not been studied earlier, and the chemical properties of the probable products such as LnI_2H have not been studied either. Meanwhile, such hydrides can be of considerable interest as synthons and catalysts of hydrogenation of organic and organometallic compounds. So far, only rare earth metal organic hydrides, *i.e.*, molecular complexes containing organic ligands bound to the metal atom, apart from the Ln—H group, have been used in the synthetic practice.[3] This study deals with the reactions of diiodides **3** and **4** with hydrogen and some properties of the iodide hydrides **1** and **2** thus formed.

Results and Discussion

Heating of powders **3** and **4** under atmospheric pressure of H_2 to a temperature of 120 °C was found to induce slow gas absorption, which is considerably accelerated at higher temperatures. During the reaction, the color of NdI_2 does not change, while the color of the DyI_2 powder gradually changes from dark violet to black. Despite the higher reduction potential of Nd^{II} (−2.62 V) compared to Dy^{II} (−2.45 V),[4] iodide **3** reacts more slowly than dysprosium salt **4**. At 200 °C, hydrogen absorption stopped after 10 h in the case of **3**, whereas in the case of iodide **4**, the reaction was almost completed after 2 h. The amounts of absorbed hydrogen in reactions with compounds **3** and **4** were 52 and 80%, respectively, relative to the value calculated from the equation

$$\underset{\mathbf{3},\,\mathbf{4}}{2\,LnI_2} + H_2 \xrightarrow{120—200\,°C} \underset{\mathbf{1},\,\mathbf{2}}{LnI_2H}, \qquad (1)$$

Ln = Nd (**1**, **3**), Dy (**2**, **4**).

Thulium(II) diiodide, whose reduction potential (−2.3 V)[4] is considerably lower than the potentials of neodymium(II) and dysprosium(II), does not react with hydrogen under comparable conditions.

The considerable difference between the calculated and absorbed amounts of hydrogen in reaction (1) is probably due to shielding of the particle surface of diiodides **3** and **4** by the iodide hydrides **1** and **2** formed. Presumably, the density of the layer of product **1** is higher, which is reflected in the reaction rate and degree of conversion. The rate of reaction (1) and the amount of absorbed hydrogen depend appreciably on the degree of dispersion of the initial iodide powders. Compounds with particle size of 0.01—0.05 mm were used in the work.

Products **1** and **2** are rapidly hydrolyzed in air; however, they are quite stable in dry inert atmosphere. Heating to 150 °C *in vacuo* does not induce visible changes or hydrogen evolution. The IR spectra of compounds **1** and **2** in the 400—4000 cm^{-1} range contain a broad band with peaks at 930 (Nd) and 950 cm^{-1} (Dy), which may be assigned to Ln—H vibrations. In the spectra of the complexes $LnH_2(THF)_3$ (Ln = Sm, Eu, Yb), the bands for hydride groups occur at 1250 cm^{-1} (see Refs 5 and 6).

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Lanthanide cyclopentadienyl hydrides have typically two absorption regions for the Ln—H groups: 650—900 cm^{-1} and 1100—1350 cm^{-1} (see Ref. 7).

Hydrides **1**, **2** are insoluble in hexane, toluene, and ether; they are slowly dissolved in pyridine and acetonitrile, but dissolution is accompanied by chemical transformations, which are currently under study. The powders of **1** and **2** are insoluble in THF; however, the solution acquires violet (**1**) or green (**2**) color due to dissolution of the impurities of initial iodides **3** and **4** present in the sample. These can be isolated from solutions by low-temperature crystallization as the complexes $LnI_2(THF)_5$ (see Ref. 8). After treatment with tetrahydrofuran and drying *in vacuo* at 40 °C for 4 h, the hydrides contain no THF, as indicated by the absence of new bands in the IR spectrum of the powders and good agreement of the metal and iodine contents with the formulas NdI_2H and DyI_2H. Since products **1** and **2** are insoluble in THF and do not retain it in the coordinated state, one can conclude that THF molecules do not destroy the crystal lattice of LnI_2H. The magnetic moment of hydride **1** (3.8 μ_B) is markedly higher than the μ_{eff} value of the initial iodide **3** (2.7 μ_B) and corresponds to trivalent neodymium,[9] which thus confirms the redox nature of reaction (1) and the salt-like nature of products **1** and **2**.

Hydrolysis of the iodide hydrides with water proceeds vigorously and is accompanied by hydrogen evolution. The yield of the gas (98% for **1** and 85% for **2**) is somewhat lower than the stoichiometric yield, because of the presence of triiodide LnI_3 impurity in diiodides **3** and **4**.

The reaction of compound **2** with isopropyl alcohol is very slow; however, in the presence of THF, the reaction is nearly as vigorous as that with water. As the metal-containing product, the isopropoxide $DyI_2(OPr^i)(Pr^iOH)_3$ was isolated as colorless crystals.

$$DyI_2H + 4\ Pr^iOH \xrightarrow{THF} I_2Dy(OPr^i)(Pr^iOH)_3 + H_2. \quad (2)$$

Hydride **1** showed a lower reactivity toward compounds containing an active hydrogen atom. Deprotonation of isopropyl alcohol even in a THF solution at room temperature proceeds during 7 days and gives an intractable mixture of products. The reaction of **1** with phenol, which was accelerated by sonication of the mixture, gave the phenoxide $PhONdI_2(THF)_4$ (yield 83%).

$$\underset{\mathbf{1}}{NdI_2H} + PhOH \xrightarrow{THF} PhONdI_2(THF)_4 + H_2. \quad (3)$$

An equally pronounced difference between the reactivities of hydrides **1** and **2** was manifested in the reaction with cyclopentadiene. Whereas hydride **1** is absolutely inert toward CpH, hydride **2** readily reacts with it at room temperature. The reaction is accompanied by hydrogen evolution and precipitation of $DyI_3(THF)_3$. After separation of the precipitate, the complex $Cp_2DyI(THF)_2$ was isolated from the solution by low-temperature crystallization.

$$2\ DyI_2H + 2\ CpH \xrightarrow{THF}$$

$$\longrightarrow Cp_2DyI(THF)_2 + DyI_3(THF)_3 + 2\ H_2. \quad (4)$$

The formation of dysprosium triiodide in 46% yield and the dicyclopentadienyl complex attest to disproportionation of the monocyclopentadienyl product $CpDyI_2$, which must have formed in the initial stage. Substituent redistribution processes of this type are usual for rare earth metal cyclopentadienyl halides.[7] No disproportionation was noted in the homogeneous reaction of diiodides **3** and **4** with cyclopentadiene in a THF solution, resulting in the complexes $CpLnI_2(THF)_3$.[10]

Thus, divalent neodymium and dysprosium iodides **3** and **4** add hydrogen under relatively mild conditions to give iodide hydrides **1** and **2**. The metal is simultaneously oxidized to the trivalent state. Hydrogen within compounds **1** and **2** is highly reactive, thus making these compounds promising as hydrogenating agents.

Experimental

The syntheses were carried out under conditions excluding contact with oxygen or air moisture using Schlenk type glassware. Tetrahydrofuran was distilled from NaOH, deaerated, dried by adding NdI_2 (THF, 500 mL; NdI_2,2 g; 20 °C, 30 min), and condensed into the reaction vessel directly prior to use. Isopropyl alcohol was dried by a standard procedure. The diiodides NdI_2 and DyI_2 were prepared by a previously developed procedure.[8,11] The IR spectra were recorded on a FSM-1201 FT IR spectrometer in the 4000—400 cm^{-1} range. The samples were prepared as mineral oil mulls. The lanthanide content in the obtained compounds was determined by complexometry and the iodine content, by back titration. Magnetic measurements were carried out by a known procedure.[12]

Synthesis of diiodide hydride NdI_2H (1). A tube containing a powder of **3** (4.52 g, 11.35 mmol) was connected to a hydrogen-filled gas burette and heated at 200 °C. Hydrogen was gradually absorbed. The reaction stopped after 10 h after absorption of 66 mL (52%; standard conditions) of H_2. The resulting powder was washed with tetrahydrofuran (6×25 mL) at room temperature and dried for 4 h *in vacuo* at 40 °C to give 2.16 g (56%) of hydride **1**. Found (%): I, 62.50; Nd, 36.78. HI_2Nd. Calculated (%): I, 63.60; Nd, 36.15. IR (mineral oil, KBr, ν/cm^{-1}): 930. μ_{eff} (293 K) = 3.8 μ_B.

Synthesis of diiodide hydride DyI_2H (2). Compound **4** (2.97 g, 7.13 mmol) was kept under hydrogen for 2 h under conditions of the previous experiment. The color of the powder of **4** changed from dark violet to black; 63 mL (79%; standard conditions) of H_2 was absorbed. The product was washed with THF (6×25 mL) at room temperature and dried for 4 h *in vacuo* at 40 °C to give 2.4 g (80%) of hydride **2**. Found (%): Dy, 38.65; I, 59.81. $HDyI_2$. Calculated (%): Dy, 38.92; I, 60.83. IR (mineral oil, KBr, ν/cm^{-1}): 950.

Hydrolysis of complexes 1 and 2. Water (10 mL) was added at room temperature to a powder of **1** (0.18 g, 0.45 mmol). Vigorous gas evolution was observed. After 1 min, the reaction was completed; 9.9 mL (98%; standard conditions) of hydrogen was evolved.

Under similar conditions hydride **2** (0.47 g, 1.13 mmol) gave 21.2 mL (85%; standard conditions) of hydrogen.

Reaction of 1 with phenol. A solution of PhOH (0.18 g, 1.91 mmol) in THF (15 mL) was added at room temperature to a tube containing compound **1** (0.59 g, 1.48 mmol). The tube was placed into an ultrasonic bath and kept for 8 h at 40 °C until the black powder of **1** completely dissolved and a pale blue finely crystalline precipitate formed. THF (20 mL) was added to the reaction mixture and the resulting solution was filtered through a glass filter. Slow removal of THF resulted in the precipitation of pale-blue crystals of $PhONdI_2(THF)_4$, which were separated by decantation, washed with cold THF, and dried *in vacuo*. The product yield was 0.95 g (83%); m.p. 145—147 °C (decomp.). Found (%): I, 33.10; Nd, 19.00. $C_{22}H_{37}I_2NdO_5$. Calculated (%): I, 32.56; Nd, 18.50. IR (mineral oil, KBr, ν/cm^{-1}): 1585 m, 1500 s, 1344 s, 1280 m, 1219 m, 1065 s, 1019 s, 921 w, 860 s, 772 m, 699 m, 596 m, 560 m.

Reaction of 2 with isopropyl alcohol. Isopropyl alcohol (5 mL) and THF (0.5 mL) were added *in vacuo* to hydride **2** (0.34 g, 0.82 mmol). Gas evolution and gradual dissolution of **2** were observed. The mixture was stirred for 1.5 h until hydrogen evolution ceased. The solution thus formed was centrifuged, decanted from the precipitate, and concentrated *in vacuo*. The finely crystalline precipitate formed was separated by decantation, washed with cold THF, and dried *in vacuo* at room temperature to give 0.40 g (75%) of the compound $I_2Dy(OPr^i)(Pr^iOH)_3$ as colorless crystals. Found (%): Dy, 24.40; I, 40.11. $C_{12}H_{31}DyI_2O_4$. Calculated (%): Dy, 24.79; I, 38.80. IR (mineral oil, KBr, ν/cm^{-1}): 1285 m, 1159 m, 1142 m, 1112 m, 1080 s, 942 s, 917 s, 797 s, 743 w, 533 m.

Reaction of 2 with cyclopentadiene. A solution of CpH (1 mL) and THF (5 mL) were added *in vacuo* to hydride **2** (0.44 g, 1.05 mmol). Hydrogen evolution and gradual dissolution of **2** were observed. The mixture was centrifuged, decanted from the precipitate, and concentrated by slow removal of the solvent. The resulting colorless needle crystals were separated by decantation, washed with cold THF, and dried *in vacuo* to give 0.17 g (30%) $Cp_2DyI(THF)_2$; m.p. 180 °C. Found (%): Dy, 29.30; I, 30.11. $C_{18}H_{26}DyIO_2$. Calculated (%): Dy, 28.84; I, 23.50. IR (mineral oil, KBr, ν/cm^{-1}): 1343 w, 1293 w, 1260 w, 1176 w, 1038 m, 1010 s, 953 w, 913 m, 851 s, 784 s, 670 m.

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