A New Route to Neodymium(II) and Dysprosium(II) Iodides

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Abstract: Microcrystalline molecular iodides of neodymium(II) and dysprosium(II), $LnI_2(THF)_5$ and $LnI_2(DME)_3$ (Ln = Dy, Nd) have been obtained by heating a mixture of the appropriate metal with iodine, subsequently dissolving the products in THF or DME, and crystallization at low temperature. Prolonged drying of $DyI_2(THF)_5$ in vacuum yielded a violet powder of composition $DyI_2(THF)_3$. These crystalline complexes are thermally stable, but in the solution their stability is lower. Both NdI_2 and DyI_2, as well as TmI_2, dissolve in liquid NH_3 to give unstable blue solutions.

Keywords: dysprosium · lanthanides · neodymium

Introduction

Neodymium and dysprosium belong to the family of the so-called trivalent lanthanoids (Ln), that is rare-earth metals which only form stable molecular complexes in the +3 oxidation state.[1] However, compounds containing these metals in the +2 state are known including the dihalides LnX_2, halide–hydrides LnHX, and ternary halides MLn_2X_5.[1] Not one of these substances has been isolated as a molecular compound and their reactivity has not been studied, although diiodides of Tm, Dy, and Nd dissolve in THF to give unstable malachite-green (Tm), brown (Dy), or cherry-red (Nd) solutions.[2] One of the reasons, hampering their study is that they are difficult to prepare. The only preparative route to dihalides of Tm, Nd, and Dy is by heating of a mixture of the appropriate LnX_3 and rare-earth metal Ln in a welded tantalum container at about 1000 °C for several days or weeks. The synthesis of the neodymium(II) chloride, $NdCl_2(THF)_2$, containing 2.5 % of LiCl has been claimed.[3] It was obtained by the poorly reproducible reaction of $NdCl_3$ with lithium and naphthalene. Later this compound was used as a precursor for the preparation of organometallic complexes $[K(THF)_n]_2[(\eta^5\text{-}C_5Me_5)_2NdCl_2]$[4] and (CHPhCHPhCHPhCHPh)Nd$(THF)_n$.[5]. The evidence for Nd^{II} for the former complex was based on elemental analysis and some chemical properties. For the latter, the oxidation state of the metal was not considered, but the cited formula corresponds to Nd^{II}. However, reinvestigation of the aforementioned dichloride $NdCl_2(THF)_2$ and the ate-complex $[K(THF)_n]_2[(\eta^5\text{-}C_5Me_5)_2NdCl_2]$ has shown these were Nd^{III} compounds.[6] It is likely that the above metallacycle is also a Nd^{III} derivative since it was derived from the same precursor. Transient intermediate Ce^{II} and Nd^{II} species were postulated to have been formed in the reactions of Cp'_3Ln ($Cp' = \eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$; Ln = Ce or Nd) with Li or K in DME at room temperature, which yielded $[\{LnCp'_2(\mu\text{-}OMe)\}_2]$ or $[NdCp'_2(\mu\text{-}OMe)Li(DME)]$.[7] The related reduction of Cp'_3La by potassium in DME at −30°C afforded a dark blue solution, containing the La^{II} compounds $Cp'_2La(DME)_x$ and $[K(DME)_y][Cp'_3La]$, as established by ESR spectroscopy.[8] A Ce^{II} compound of formula $[K(DME)]_2[(C_8H_8)_2Ce]$ was claimed to have been formed in the reaction of $(C_8H_8)_2Ce$ with potassium in DME.[9] The Sc^{II} complex, $[C_6H_3(tBu)_3]Sc(H)[C_6H_3(tBu)_2CH_2]$, has been identified by ESR spectroscopy in a mixture formed by co-condensation of Sc metal vapor and 1,3,5-$tBu_3C_6H_3$ at −79°C.[10] Finally, a crystalline X-ray-authenticated La^{II} compound $[K([18]crown\text{-}6)(\eta^2\text{-}C_6H_6)_2][(LaCp^t_2)_2(\mu\text{-}C_6H_6)]$ ($Cp^t = \eta^5\text{-}C_5H_3(tBu)_2\text{-}1,3$), containing $[C_6H_6]^-$ as a bridging anion, was obtained from $[LaCp^t_3]$, K, and [18]crown-6 in benzene.[11]

Recently we have found that thulium, also belonging to the block of „trivalent“ lanthanoids, may be obtained in the form of the molecular Tm^{II} complex $TmI_2(DME)_3$ or $TmI_2(THF)_5$ by the reaction of TmI_3 with thulium metal in the appropriate solvent at 70 °C.[12] In this paper we report on the synthesis of the molecular iodides of Nd^{II} and Dy^{II}.[13]

Results and Discussion

In contrast to the above Tm experiments,[12] metallic neodymium or dysprosium did not reduce NdI_3 or DyI_3 even at 80 °C and ultrasonic treatment. Hence, for preparation of NdI_2 and DyI_2 the metals were allowed to react directly with iodine [Eq. (1); Ln = Nd, Dy]. This procedure does not require any

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special equipment. A mixture of the appropriate Ln metal shavings and iodine in molar ratio 1.1 (Nd) or 1.3 (Dy) was heated in an evacuated glass tube. In the reaction zone a temperature greater than 1500 °C developed judging by the fact that the metal melts (dysprosium melts at ca. 1400°C). After completion of the reaction unreacted metal freezes as the drops. Since the reaction zone moves quickly along the tube and the walls of it are cooled by ambient air, the glass of reaction flask did not melt. The high temperature of the reaction and the stoichiometry of the reactants employed is appropriate for the formation of phases of LnI_2 composition. The triiodides LnI_3, which were also formed in 10–15% yield as side products, were deposited mainly on the cold walls of the tube as tight white coatings and remained in the reaction flask when the black ingot of LnI_2 was transferred into another tube. The magnetic moment of NdI_2, 2.9 μ_B, is close to the value 2.83 μ_B predicted for divalent neodymium in $4f^4$ configuration, and is markedly different from that of Nd^{III}, 3.68 μ_B.[14] In the case of Dy, magnetic measurements do not allow the oxidation state of the metal to be determined because Dy^{2+} and Dy^{3+} have practically identical values of $\mu_{eff} = 10.6\,\mu_B$.

$$Ln + I_2 \rightarrow LnI_2 \quad (1)$$

Addition of THF to the resulting iodides at −50 °C afforded deeply colored solutions; violet for NdI_2 and khaki-green for DyI_2. After separation of undissolved salts and unreacted metal, the microcrystalline precipitates of $NdI_2(THF)_5$ (**1a**) and $DyI_2(THF)_5$ (**2a**) were isolated from the solutions by evaporation of the solvent under vacuum, or by addition of hexane to these solutions at low temperature. The DME analogues, $NdI_2(DME)_3$ (**1b**) and $DyI_2(DME)_3$ (**2b**), were obtained when 1,2-dimethoxyethane was used as solvent. Both the THF and DME complexes of neodymium are violet, but the dysprosium derivatives are green. Their solubility at room temperature in both THF and DME is about 0.02–0.04 mol L^{-1}. The compound **2a** readily looses two molecules of THF under drying in vacuum, leading to a lilac powder of the composition $DyI_2(THF)_3$ (**3**). The magnetic moments of **1a**, 2.7 μ_B, and **1b**, 2.8 μ_B, confirmed them to be Nd^{II} complexes.

Each of the above solid complexes was reasonably robust in vacuum. The change of color (decolorization) for **1a** and **2a** due to intramolecular oxidation became noticeable in about 3 hours at room temperature, although the increase of μ_{eff} was less than 0.1 μ_B. In three days crystals of **1a** acquired the typical pale blue color of a Nd^{III} derivative and the magnetic moment rose to 3.3 μ_B. The completely oxidized sample (in a week) had μ_{eff} 3.6 μ_B. In the case of the DME complex **2a**, even in a week the substance partially retained its violet color and μ_{eff} did not exceed 3.2 μ_B. Rapid heating of the crystals of **1a** or **1b** led to decolorization above 50 °C. The stability of the dysprosium iodides **2a**, **2b**, and **3** was similar, but somewhat higher than that of the Nd analogues. The crystals of these compounds lost their green color and became light yellow-brown after more than four days. A change of a color upon heating was observed at about 70 °C. The decomposition of all the complexes was accelerated by exposure to daylight.

In THF or DME, complexes **1a**, **1b**, **2a**, and **2b** were less stable. The violet or green color disappeared in 2–3 h at room temperature to give pale blue solutions for Nd derivatives and pale yellow for the Dy analogues. Evolution of gaseous products was invariably observed. We suggest that the decomposition proceeded in a manner characteristic for other organolanthanoid compounds[15] or $TmI_2(DME)_3$,[12] that is by scission of C–O bonds of the solvents by LnI_2 species and formation of transient products such as $I_2LnOCH{=}CH_2(THF)$ or $I_2LnOMe(DME)$. It should be noted that dissolving one of these complexes in THF or DME containing even a trace amount of an aromatic compound gave dark brown solutions from which the Nd^{II} or Dy^{II} derivatives could not be isolated. Dark brown solutions were also formed if the violet or green solutions were set aside without separating them from the initial solid containing the unreacted metal, LnI_3, and undissolved residual LnI_2. The appearance of the brown color upon decomposition of NdI_2 or DyI_2 solutions in THF mentioned in the work[16] is probably caused by the same reasons.

The thulium diiodide phase TmI_2, and related complexes $TmI_2(DME)_3$ and $TmI_2(THF)_5$, may be obtained in a similar fashion as these neodymium or dysprosium analogues but the reaction of TmI_3 with thulium metal[12] is the more convenient pathway. The characterization of $TmI_2(DME)_3$ samples obtained by both these methods suggests the same molecular structure of this compound which has been determined before as pentagonal bipyramid with Tm atom in the center surrounded by oxygen atoms at equatorial sites (one of DME is monodentate) and the iodide ligands in the axial positions.[12] High reactivity and low stability in solutions prevent the preparation of **1a**, **1b**, **2a**, and **2b** in the form of good crystals suitable for X-ray analysis or determination of their molecular weight. However taking into account the similarity of coordinating ability of Nd, Dy, Tm, and Sm it seems reasonable to suppose that the structure of neodymium(II) and dysprosium(II) iodides is close to that of thulium analogue and related samarium halides $SmI_2(THF)_5$, $SmI_2(DME)(THF)_3$, and $SmI_2(DME)_2(THF)$.[17]

The IR spectra of **1a**, **2a**, and **3** revealed a set of bands in the regions 800–890, 910–925, and 1040 cm^{-1} characteristic for coordinated THF, whereas the spectra of compounds **1b** and **2b** showed an absorption of coordinated DME at 1060 cm^{-1}. The UV/Vis spectra of the THF and DME complexes in THF or DME, respectively, were identical for each metal and correspond to the spectra recorded previously for the solutions of NdI_2 and DyI_2 in THF.[16]

The obtained diiodide phases LnI_2 (Ln = Nd, Dy, Tm) easily dissolved in liquid NH_3 to give deep blue solutions from which a white solid gradually precipitated with concomitant dihydrogen evolution, evidently due to the ammonolysis of the salts. It is known that the blue solution of Na in liquid ammonia reveals an ESR signal of the solvated electron; however, the solutions of all three LnI_2 were ESR-silent. This may be due to the substantial broadening of the signal under the influence of the highly paramagnetic Ln cations.

A preliminary study of reactivity of **1a** and **2b** has shown that they are more powerful reducing agents than $TmI_2(DME)_3$. In solutions in THF or DME at −30°C they reacted with anthracene, naphthalene, benzene, cyclopentadiene, and dihydrogen. The reactivity studies will be reported elsewhere.

Conclusion

A convenient route to the iodides NdI_2 and DyI_2 is reported, froom which the first molecular iodides of Nd^{II} and Dy^{II} were prepared as complexes with THF or DME. In the solid state, each of these complexes has limited stability at room temperature. The complexes may be used as novel powerful single-electron reducing agents in various organic and organometallic syntheses. Taking into account the recent data on $TmI_2(DME)_3$,[12] it is evident that the group of „divalent“ lanthanoids is not limited to Sm, Eu, and Yb. At least Nd, Dy, and Tm can now be included in this family. The relative stability of these Ln^{II} iodides decreases in the sequence Eu > Yb > Sm > Tm > Dy > Nd, consistent with cyclic voltammetry data in aqueous solutions.

Experimental Section

The synthesis, isolation, and study of the products were all performed in vacuum using standard Schlenk techniques. THF and DME were dried and freed of oxygen by refluxing over sodium hydroxide/sodium metal immediately prior to their use in reactions with NdI_2 or DyI_2. The IR spectra were obtained by using a „Specord M80“ infrared spectrometer with the samples as Nujol mulls between CsI discs. UV/Vis spectra were recorded with a Specord M40 spectrometer. Magnetic measurements were carried out at room temperature, as described previously.[18]

Synthesis of NdI_2: A mixture of thin (115–170 mesh) shavings of neodymium metal (0.55 g, 3.81 mmol) and powdered iodine (0.87 g, 3.43 mmol) was placed in a glass tube (10 × 80 mm) connected to a vacuum line by rubber tube. After evacuating, the rubber tube was clamped with a clip, and the mixture was heated at the point closest to the edge of mixture, up to the beginning of burning (ca. 200 °C). A front of fast burning smoothly spread along the mixture and reached the end of the reaction tube within 2–3 seconds. If the burning proceeds too vigorously the pressure of iodine vapor may lacerate the rubber tube; therefore, the synthesis should be carried out behind a safety shield. Immediately after completion of the reaction, the tube was evacuated to remove the remaining negligible amount of free iodine. The formed black ingot was crushed by shaking the tube. The contents were transferred to another tube. It should be noted that the pretty high stability of the resulting iodide in air allows the reaction tube to be opened for a few seconds and the ingot to be quickly crushed with metal stick. Most of the NdI_3 formed in the reaction remained in the first tube as a white cover on the walls. The yield of NdI_2 was 1.04 g (73 %). $\mu_{eff} = 2.9\,\mu_B$. I_2Nd (398.1): calcd I 63.76, Nd 36.24; found I 63.23, Nd 36.77. The product contained unconverted neodymium metal (0.1 g, 18 %) as frozen drops, which were readily separated and a small amount of NdI_3. These impurities do not prevent the use of the obtained NdI_2 for the preparation of its molecular complexes with THF and DME.

Synthesis of DyI_2: **DyI_2** was synthesized similarly to **NdI_2** from Dy metal (0.55 g, 3.38 mmol) and iodine (0.54 g, 2.12 mmol). The yield of DyI_2 was 0.67 g (76 %). $\mu_{eff} = 10.6\,\mu_B$. DyI_2 (416.3): calcd Dy 39.03, I 60.97; found Dy 40.20, I 60.69.

$NdI_2(THF)_5$ (1a): A sample of the above NdI_2 (0.21 g, 0.28 mmol) was placed in a 30 mL tube and THF (25 mL) was added at −50 °C. The mixture was stirred for 15 min. Partial dissolution of the precipitate and formation of a dark violet solution was observed. The mixture was allowed to settle and the solution was separated from the precipitate of excess of metal, formed NdI_3, and undissolved NdI_2 by decantation. The solvent was removed from the solution in vacuo at −30 °C. This portion of the solvent was used again for the next extraction of the precipitate under the same conditions. The extraction was repeated three times. Each time the extract was decanted into the same tube. After the final evaporation of THF, the residual microcrystalline violet solid **1** was dried in vacuo for 15 min at −20 °C. The yield of **1** was 0.16 g (40 %). M.p. > 50 °C (decomp); IR (Nujol): $\tilde{\nu} = 650$, 830 sh, 860, 1005 cm^{-1}; $\mu_{eff} = 2.7\,\mu_B$. $C_{20}H_{40}I_2NdO_5$ (758.6): calcd I 33.46, Nd 19.01; found I 37.01, Nd 18.83.

$NdI_2(DME)_3$ (1b): Compound **1b** was obtained under the conditions used for the preparation of **1a** except DME was used as solvent instead of THF. The yield of small violet crystals of **1b** was 43 %. M.p. > 50 °C (decomp); IR (Nujol): $\tilde{\nu} = 548$, 860, 1035, 1060, 1095, 1189 cm^{-1}; UV/Vis (DME): λ (ε) = 383 (100), 413 (140), 515 (420), 585 (290), 633 (200), 1190 (210) nm; $\mu_{eff} = 2.8\,\mu_B$. $C_{12}H_{30}I_2NdO_6$ (668.4): calcd I 37.97, Nd 21.58; found I 38.07, Nd 21.00.

$DyI_2(THF)_5$ (2a): Compound **2a** was synthesized and isolated as its neodymium analogue, and dried in vacuo but for no longer than 5 min. From 0.14 g of DyI_2, 0.13 g (49.8 %) of **2a** was obtained as a microcrystalline green solid. M.p. > 70 °C (decomp); IR (Nujol): $\tilde{\nu} = 655$, 825 sh, 860, 1010 cm^{-1}; $\mu_{eff} = 10.6\,\mu_B$. $C_{20}H_{40}DyI_2O_5$ (776.9): cald Dy 20.95, I 32.67; found Dy 20.16, I 33.24.

$DyI_2(THF)_3$ (3): Compound **2a** (0.1 g, 0.16 mmol) was dried under dynamic vacuum at −30 °C. The green crystals transformed into a lilac powder. In 20 min 0.08 g (100 %) of **3** was obtained. M.p. > 70 °C (decomp); IR (Nujol): $\tilde{\nu} = 660$, 800, 840 sh., 910, 1010, 1090 cm^{-1}. $C_{12}H_{24}DyI_2O_3$ (632.6): cald Dy 25.65, I 40.12; found Dy 26.02, I 37.10.

$DyI_2(DME)_3$ (2b): The complex was synthesized as described for **1b**, by dissolving DyI_2 (0.15 g, 0.22 mmol) in DME (20 mL) at −40 °C. Subsequently, green microcrystals of **2b** (0.146 g, 59 %) were isolated. M.p. > 70 °C (decomp); IR (Nujol): $\tilde{\nu} = 715$, 800, 850, 1010, 1060, 1200, 1230 cm^{-1}; UV/Vis (DME): λ (ε) = 515 (325), 473 (575), 567 (225), 714 (429) nm; $\mu_{eff} = 10.7\,\mu_B$. $C_{12}H_{30}DyI_2O_6$ (686.7): cald Dy 23.66, I 36.96; found Dy 22.80, I 37.36.

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