# Synthesis and characterization of mixed iodide—naphthalene complexes of lanthanides

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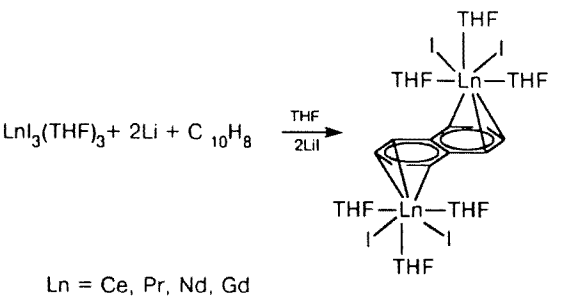
The $[LnI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$ complexes were obtained by reactions of $LnI_3(THF)_3$ (Ln = Ce, Pr, Nd, or Gd) with lithium and excess naphthalene. The magnetic moments of these complexes correspond to the oxidation state +3 of the metal atoms. The $Yb^{II}$ complex, $[YbI(DME)_2]_2(\mu\text{-}C_{10}H_8)$, was synthesized by the reaction of $YbI_2(DME)_2$ with an equimolar amount of naphthalenelithium.

**Key words**: lanthanides, naphthalene, iodine; magnetic moment, stability.

Previously, it was demonstrated[1,2] that reactions of anhydrous rare-earth element halides with alkali-metal naphthalenides yield noncrystalline products, which makes it impossible to use X-ray structural analysis for establishing their structures. However, we have found recently[3] that when the reducing agent is deficient, lanthanum(III) and europium(II) iodides form crystalline complexes $[LaI_2(THF)_3]_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-}C_{10}H_8)$ and $[EuI(DME)_2]_2(\mu_2\text{-}\eta^4\text{:}\eta^4\text{-}C_{10}H_8)$. These compounds are precursors of completely reduced naphthalenelanthanides and, apparently, have similar geometries of $C_{10}H_8$—Ln fragments. The X-ray structural analysis of these complexes has demonstrated that they have reversed-sandwich structures such that the metal atoms are coordinated to different rings of the naphthalene dianion. With the aim of elucidating the possibility of preparing analogous complexes with other 4f metals in oxidation states +3 or +2, we carried out reactions with iodides of trivalent Ce, Pr, Nd, Gd, Tb, and Ho and divalent Sm, Tm, and Yb.

It was found that reactions of stoichiometric amounts of $LnI_3(THF)_3$ (Ln = Ce, Pr, Nd, or Gd) with lithium in the presence of an excess of naphthalene in THF yielded the $[LnI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$ complexes, which were isolated in good yields as air-unstable finely crystalline dark-blue powders. When heated above 100 °C, the solid products decompose. These products are insoluble in hexane, benzene, and dimethoxyethane and moderately soluble in THF. The complexes are substantially less stable in solutions, and the stability decreases substantially in going from light to heavy lanthanides. For example, the Ce, Pr, and Nd derivatives in THF solutions slowly decompose at room temperature, whereas the gadolinium complex decomposes even at −25 °C. The stability of solutions of the Tb and Ho compounds is so low that these compounds cannot be isolated even when the synthesis is carried out at −30 °C.




The magnetic moments of the Ce, Pr, Nd, and Gd complexes (2.53, 3.22, 3.52, and 7.55 $\mu_B$, respectively) are in the range of the values typical of organic compounds of the corresponding trivalent metals (Ce, 1.8—2.5 $\mu_B$; Pr, 2.8—3.6 $\mu_B$; Nd, 2.98—3.7 $\mu_B$; and Gd, 7.7—8.9 $\mu_B$).[4]

The products were not studied by X-ray structural analysis. However, the method, which was used for the preparation of these compounds, the lanthanide content, and the IR spectra are analogous to those of the lanthanum complex discussed above.[3] This suggests that the molecules of the Ce, Pr, Nd, and Gd derivatives have, similar to the lanthanum complex, the reversed-sandwich structure in which two $LnI_2(THF)_3$ fragments form $\eta^4$-bonds with the naphthalene dianion. It is interesting to note that the mixed cyclopentadienyl—naphthalene complexes of rare-earth elements ($CpLnC_{10}H_8(DME)$, where Ln = Y, Gd, Er, Tm, or Lu) exhibit an alternative coordination mode of the naphthalene dianion to the lanthanide atom.[5] In this

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case, the metal—naphthalene bond corresponds to the $2\eta^1 : \eta^2$ type and is interpreted as the $(2\sigma,\pi)$ interaction. Derivatives of heavy lanthanides are the most stable.

Reactions of equimolar amounts of $C_{10}H_8Li$ with iodides of divalent lanthanides $LnI_2(DME)_3$ (Ln = Sm, Tm, or Yb) yield the desired compound only in the case of ytterbium. In the latter case, the $[YbI(DME)_2]_2(\mu\text{-}C_{10}H_8)$ complex was obtained, which was isolated as a finely crystalline dark-violet powder. This complex is weakly paramagnetic, soluble in THF, and insoluble in DME. The IR spectrum and the composition of this complex (except for the metal) are identical to those of the europium complex $[EuI(DME)_2]_2(\mu^2\text{-}\eta^4\text{:}\eta^4\text{-}C_{10}H_8)$, which was obtained and structurally characterized previously.[3] This fact indicates that their structures are similar. Under the same conditions, samarium(II) and thulium(II) iodides give dark-colored waxy mixtures from which we failed to isolate individual products.

## Experimental

Because all the products obtained are characterized by a very high sensitivity with respect to oxygen and moisture, all operations associated with the syntheses and isolation of the compounds were carried out using the standard Schlenk technique under conditions precluding exposure to the atmosphere. The solvents were distilled *in vacuo* from benzophenone ketyl. The lanthanide content was determined chelatometrically. The IR spectra were recorded on a Specord-M80 instrument. The samples were prepared as Nujol mulls. Iodides of $Ce^{III}$, $Pr^{III}$, $Nd^{III}$, $Sm^{II}$, and $Yb^{II}$ were prepared by the reaction of lanthanide metals with diiodomethane in THF and recrystallized from THF. The synthesis and the structure of the previously unknown molecular iodide of divalent thulium $TmI_2(DME)_3$ will be reported elsewhere.

**Synthesis of $[CeI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$.** THF (30 mL) was added to an ampule containing $CeI_3(THF)_3$ (2.06 g, 2.79 mmol), lithium (19.5 mg, 2.78 g-at.), and naphthalene (1.79 g, 13.98 mmol). Lithium was gradually dissolved with intense stirring over a period of 3 h. A pearly-blue finely crystalline precipitate formed. The precipitate was filtered off (Schott filter No. 2), washed with cold THF (2×15 mL), and dried *in vacuo* at room temperature. The $[CeI_2(THF)_3]_2(\mu\text{-}C_{10}H_8)$ compound was obtained in a yield of 1.77 g (81%) as a disperse blue powder. When heated in an evacuated sealed capillary above 100 °C, the compound decomposed. The product obtained under the above-described conditions contains three THF molecules of crystallization per mole of the complex. Found (%): Ce, 17.8. $C_{46}H_{80}Ce_2I_4O_9$. Calculated (%): Ce, 17.91. IR, $\nu/cm^{-1}$: 1500, 1400, 1330, 1300, 1280, 1225, 1150, 1165, 1060, 1020, 1000, 945, 910, 850, 830, 785, 775, 760, 735, 660, 455. Magnetic moment (293 K): $\mu_{eff} = 2.53\ \mu_B$.

**Synthesis of $[YbI(DME)_2]_2(C_{10}H_8)$.** $YbI_2(THF)_3$ (1.51 g, 2.64 mmol), lithium (18.5 mg, 2.64 g-at.), and naphthalene (0.65 g, 5.07 mmol) were placed in an ampule, and then DME (35 mL) was added. Lithium completely dissolved with intense stirring over a period of 5 h, and a finely crystalline brown-red precipitate formed. The precipitate was filtered off (Schott filter No. 2), washed with DME (2×10 mL), and dried *in vacuo* at room temperature for 30 min. The $[YbI(DME)_2]_2(C_{10}H_8)$ complex was obtained in a yield of 1.2 g (84%) as a finely disperse dark-violet powder, which decomposed upon heating above 100 °C. Found (%): Yb, 31.0. $C_{26}H_{48}I_2O_8Yb_2$. Calculated (%): Yb, 31.03. IR, $\nu/cm^{-1}$: 1490, 1385, 1270, 1230, 1185, 1100, 1050, 1015, 1000, 965, 850, 825, 770, 755, 695, 460. Magnetic susceptibility: $\chi(293\ K) = 270.7 \cdot 10^{-6}$ SGS.

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