Reactions of neodymium(II), dysprosium(II), and thulium(II) diiodides with cyclopentadiene. Molecular structures of complexes $CpTmI_2(THF)_3$ and $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$

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The reactions of LnI_2 (Ln = Nd (**1**) or Dy (**2**)) with cyclopentadiene (CpH) in THF at 0 °C afforded the $CpLnI_2(THF)_3$ complexes in 65—67% yields. The reaction of thulium diiodide (**3**) with an excess of CpH at 60 °C produced $CpTmI_2(THF)_3$, $Cp_2TmI(THF)_2$, and $TmI_3(THF)_3$ in 21, 58, and 63% yields, respectively. The reactions of **1** and **2** with pentamethylcyclopentadiene (Cp*H) in THF were accompanied by disproportionation giving rise to the $Cp^*{}_2LnI(THF)_2$ and $LnI_3(THF)_x$ complexes. Neodymium triiodide was isolated in the ionic form $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$. Its structure and the structure of $CpTmI_2(THF)_3$ were established by X-ray diffraction analysis.

Key words: dysprosium(II), neodymium(II), thulium(II), cyclopentadiene, complexes, synthesis, structure, X-ray diffraction analysis.

Investigations of the reactivities of neodymium(II),[1] dysprosium(II),[1] and thulium(II)[1,2] diiodides with respect to THF, 1,2-dimethoxyethane (DME),[1b] ketones, alkyl halides,[3a,b] alcohols,[3c] fused aromatic compounds,[3b] and pyridine[3d] demonstrated that these salts are strong reducing agents. In the presence of benzene, their reducing ability (judging from the fact that THF and DME readily decomposed) is even higher than that of alkali metals.[4] By contrast, all three diiodides in THF do not react with aliphatic hydrocarbons, diethyl ether, and hexamethyldisilazane in spite of the presence of the labile N—H hydrogen atom in the latter compound. In the present study, we examined the reactions of NdI_2 (**1**), DyI_2 (**2**), and TmI_2 (**3**) with cyclopentadiene (CpH) and pentamethylcyclopentadiene (Cp*H) and established the structures of the resulting complexes $Cp_2TmI(THF)_2$ (**4**) and $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$ (**5**).

Results and Discussion

The reactions of **1** and **2** with equimolar amounts of CpH in THF readily proceeded at −5—0 °C. The reactions were accompanied by liberation of H_2 and gradual decoloration of the reaction solutions. After 15—20 min, these solutions turned pale-blue or pale-yellow, which is characteristic of Ln^{III}. Cooling of the solutions afforded the expected $CpNdI_2(THF)_3$ and $CpDyI_2(THF)_3$ products as blue (Nd) or colorless (Dy) crystals in 65 and 67% yields, respectively.

$$\underset{\mathbf{1,\,2}}{LnI_2} + CpH \xrightarrow[-H_2]{THF,\ 0\ ^\circ C} CpLnI_2(THF)_3$$

Ln = Nd (**1**), Dy (**2**)

Taking into account the simplicity of the procedure and satisfactory yields of the products, this method can be recommended for the preparative synthesis. This approach is of particular importance for the neodymium complex, because standard methods for its synthesis with the use of CpNa are of little use.[5]

Unlike compounds **1** and **2**, thulium diiodide (**3**) is a weaker reducing agent and it reacts with CpH only upon heating to 60 °C and when the latter is used in a large excess. In this case, the reaction gave rise to $TmI_3(THF)_3$ (63%) and $Cp_2TmI(THF)_2$ (58%) as the major products, whereas the yield of the $CpTmI_2(THF)_3$ complex (**4**) was at most 21%. Apparently, the first two products were generated due to disproportionation of the initially formed

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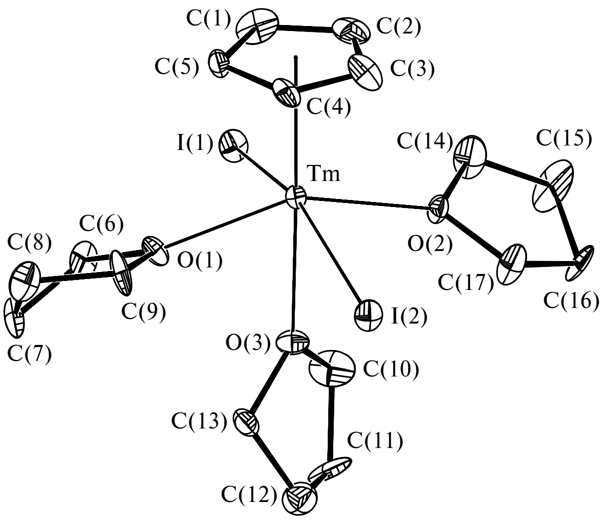


Fig. 1. ORTEP plot of the $CpTmI_2(THF)_3$ molecule. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms are omitted.

complex **4**. Analogous processes are typical of cyclopentadienyl halide derivatives of rare-earth metals and are often used for the preparation of the $CpLnX_2$ complexes from Cp_3Ln and LnX_3 under comparable conditions.[5]

$$\underset{\mathbf{3}}{TmI_2} + CpH \xrightarrow[-H_2]{\text{THF, 60 °C}} \underset{\mathbf{4}}{CpTmI_2(THF)_3} \longrightarrow$$

$$\longrightarrow TmI_3(THF)_3 + Cp_2TmI(THF)_2$$

The formation of all three compounds was confirmed by elemental analysis data and IR spectroscopic characteristics. The IR spectrum of $TmI_3(THF)_3$ has only bands of coordinated THF, whereas the spectra of $Cp_2TmI(THF)_2$ and **4** show also absorption bands of the Cp ligands. In addition, the structure of **4** was established by X-ray diffraction analysis. In molecule **4** (Fig. 1), the thulium atom is located in the center of a distorted octahedron, whose equatorial plane is formed by two iodine atoms and two oxygen atoms of the THF ligands. The Cp ligand and the oxygen atom of the third THF molecule occupy the axial positions. This complex is isomorphous with the samarium analog $CpSmI_2(THF)_3$.[6] The differences in the interatomic distances are consistent with the difference in the ionic radii of Sm^{III} and Tm^{III} (0.078 Å)[7] (Cp—Ln: Ln = Sm, 2.444 Å; Tm, 2.347 Å; Ln—I: Ln = Sm, 3.143 and 3.168 Å; Tm, 3.066 and 3.107 Å; Ln—O: Ln = Sm, 2.416—2.506 Å; Tm, 2.323—2.395 Å).

Pentamethylcyclopentadiene did not react with thulium iodide (**3**) even when an excess of the former was used and the reaction mixture was heated to 70 °C. By contrast, the addition of Cp*H to solutions of **1** or **2** in THF at 0 °C led to an immediate change in the color of the solutions. In both cases, the mixtures turned brown and triiodide $LnI_3(THF)_x$ precipitated out from the solution in a yield of up to 90—95%. Neodymium triiodide crystallized from THF in the ionic form $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$ (**5**). The structure of this complex was confirmed by the results of X-ray diffraction analysis. The molecule consists of the $[NdI_2(THF)_5]^+$ cation and the $[NdI_4(THF)_2]^-$ anion (Fig. 2), which do not form short contacts with each other. In the seven-coordinate neodymium cation, the crystallographic twofold rotation axis passes through the Nd(1) and O(3) atoms and the midpoint of the C(10)—C(10′) bond. The oxygen atoms of the THF molecules occupy the equatorial positions and the iodine atoms are located in the axial posi-

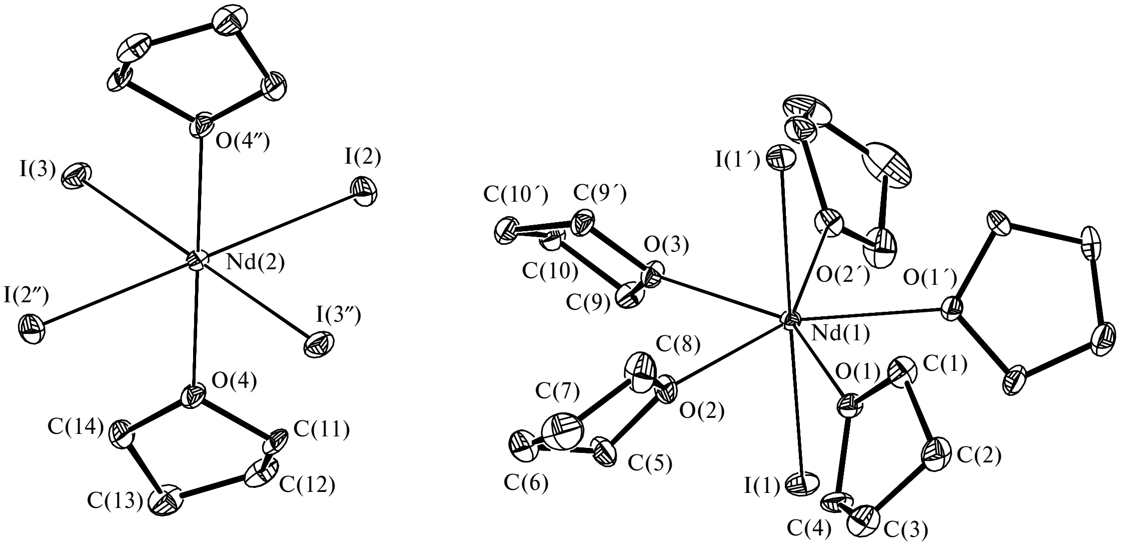


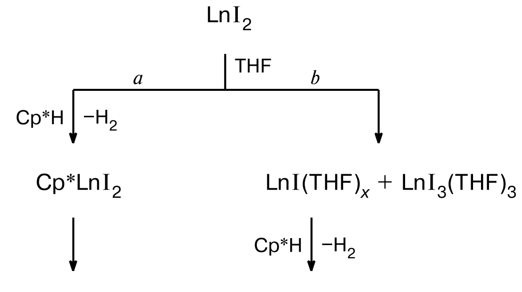
Fig. 2. ORTEP plot of the $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$ molecule (**5**). Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms are omitted.

tions of the pentagonal bipyramid. The coordination geometry of the centrosymmetrical $[\mathrm{NdI_4(THF)_2}]^-$ anion corresponds to a virtually regular octahedron. Complex **5** is isomorphous with the samarium and ytterbium analogs $[\mathrm{LnI_2(THF)_5}][\mathrm{LnI_4(THF)_2}]$.[8,9] The observed differences in the Ln—I distances in the $\mathrm{LnI_2(THF)_5}^+$ cation (Ln = Nd, 3.044 Å; Sm, 3.028 Å; Yb, 2.937 Å) and the $\mathrm{LnI_4(THF)_2}^-$ anion (Ln = Nd, 3.076 and 3.092 Å; Sm, 3.051 and 3.071 Å; Yb, 2.964 and 2.986 Å) for the corresponding lanthanides are comparable to the differences in the ionic radii of $\mathrm{Ln^{III}}$ (Nd—Sm: 0.025 Å, Nd—Yb: 0.115 Å)[10]. The same is true for the Ln—O bond lengths, except for the $\mathrm{Ln(THF)_2}$ fragment in the $\mathrm{LnI_4(THF)_2}^-$ anions of the neodymium and samarium complexes, in which these distances are almost equal (Ln = Nd, 2.385 Å; Sm, 2.386 Å; Yb, 2.279 Å), and these distances are similar in the $\mathrm{LnI_2(THF)_5}^+$ cations (Ln = Nd, 2.467 and 2.478 Å; Sm, 2.441 and 2.455 Å; Yb, 2.340 and 2.365 Å).

In addition to the above-described triiodides, finely crystalline compounds (pale-blue and colorless for Nd and Dy, respectively) were isolated from the reaction mixtures. According to the IR spectroscopic data, these compounds contain the Cp* groups and coordinated THF molecules. These products are characterized by similar metal and iodine contents, but these contents are not in precise agreement with the formulas $\mathrm{Cp^*{}_2NdI(THF)_2}$ and $\mathrm{Cp^*{}_2DyI(THF)_2}$. The I : Ln ratio is substantially larger than unity due, apparently, to the presence of impurities of the diiodide derivatives $\mathrm{Cp^*LnI_2(THF)}_x$. We failed to isolate these compounds in individual form and obtain their crystals suitable for X-ray diffraction study.

In our opinion, the compositions of these reaction products as well as of those synthesized by the reaction of **3** with cyclopentadiene are indicative of disproportionation of the initially formed monocyclopentadienyl derivatives $\mathrm{Cp^*LnI_2(THF)}_x$ (Scheme 1, path *a*). However, another pathway involving disproportionation of the starting diiodides into $\mathrm{LnI_3}$ and LnI followed by oxidation of LnI by cyclopentadiene is also possible (see Scheme 1, path *b*).

Scheme 1



Ln = Nd, Dy

Earlier, we have proposed disproportionation of **1** and **2** into triiodide and monoiodide as an explanation of the transformations observed upon the addition of unfused aromatic compounds to solutions of these salts in THF and DME.[4] It is not inconceivable that Cp*H, like benzene, serves as a promoter of generation of the exceptionally active LnI molecules, which not only cause decomposition of the solvent molecules (to give, like in reactions with aromatic compounds, brown products of the LnIRR´ type) but also partially react with Cp*H to form the $\mathrm{Cp^*{}_2LnI(THF)}_x$ complexes. The observed brown color of the reaction mixture and the moderate yield of $\mathrm{Cp^*{}_2LnI(THF)}_x$ due to the competitive character of the above-mentioned processes is evidence in favor of the path *b*.

To summarize, we developed a new convenient procedure for the preparation of the neodymium and dysprosium cyclopentadienyl iodide complexes $\mathrm{CpLnI_2(THF)_3}$ by the direct reactions of cyclopentadiene with diiodides **1** or **2**. The reactions of **1** and **2** with pentamethylcyclopentadiene were accompanied by disproportionation to give the $\mathrm{LnI_3(THF)}_x$, $\mathrm{Cp^*{}_2LnI(THF)}_x$, and $\mathrm{Cp^*LnI_2(THF)}_x$ complexes. Neodymium triiodide was isolated from the reaction in the ionic form $[\mathrm{NdI_2(THF)_5}]^+[\mathrm{NdI_4(THF)_2}]^-$ (**5**). Less active thulium iodide (**3**) can be used only for the synthesis of complexes with unsubstituted cyclopentadiene.

Experimental

All operations associated with the synthesis and isolation of the products were carried out *in vacuo* using the standard Schlenk technique. Tetrahydrofuran was purified from oxygen and moisture by refluxing over alkali and distillation over sodium. A small amount of $\mathrm{NdI_2}$ or $\mathrm{DyI_2}$ was added to THF immediately before use. The resulting solution was kept for 10 min and then the solvent was condensed into a reaction vessel. Cyclopentadiene, which was distilled from dicyclopentadiene, and pentamethylcyclopentadiene (Aldrich) were dried over sodium. The IR spectra were recorded on Specord M80 and Perkin—Elmer 577 spectrometers in Nujol mulls. Diiodides **1**—**3** were prepared according to a procedure developed earlier.[1] The amounts of $\mathrm{LnI_2}$ involved in the reactions and the yields of the products were calculated as described earlier.[4]

Reaction of neodymium(II) diiodide (1) with cyclopentadiene. A solution of cyclopentadiene (0.12 g, 1.81 mmol) in THF (10 mL) was added with stirring and cooling (0 °C) to $\mathrm{NdI_2}$ (0.674 g, 1.7 mmol) partially dissolved in THF (30 mL). The reaction was accompanied by liberation of hydrogen. After 10 min, the precipitate of **1** was completely dissolved and the color of the solution changed from dark-violet to pale-blue. The solvent was removed from the reaction mixture by condensation to 1/3 of the initial volume and the resulting solution was kept at −12 °C for 12 h. The pale-blue crystals of $\mathrm{CpNdI_2(THF)_3}$ that formed were separated by centrifugation followed by decantation, washed with cold THF (10 mL), and dried *in vacuo* at ~20 °C. The yield was 0.518 g (65%), m.p. 151—153 °C.

Found (%): I, 36.85; Nd, 21.22. $C_{17}H_{29}I_2NdO_3$. Calculated (%): I, 37.76; Nd, 21.23. IR (Nujol), ν/cm^{-1}: 1000 s, 920 m, 860 m, 850 s, 840 sh, 790 s, 660 m.

Reaction of dysprosium(II) diiodide (2) with cyclopentadiene. A solution of cyclopentadiene (0.10 g, 1.52 mmol) in THF (1 mL) was added to a solution of DyI_2 (0.60 g, 1.44 mmol) in THF (25 mL) under the conditions described above. The resulting pale-yellow solution was concentrated to 5 mL and kept at −15 °C for 10 h. The colorless crystals that precipitated were washed with THF and dried *in vacuo*. The yield of $CpDyI_2(THF)_3$ was 0.73 g (67%), m.p. 137—139 °C (decomp.). Found (%): Dy, 23.90; I, 40.84. $C_{17}H_{30}DyI_2O_3$. Calculated (%): Dy, 23.29; I, 41.38. IR (Nujol), ν/cm^{-1}: 1020 w, 1010 s, 910 m, 850 s, 840 sh, 790 s, 660 m.

Reaction of thulium(II) diiodide (3) with cyclopentadiene. Cyclopentadiene (4.1 g, 62.1 mmol) was added to a green solution of $TmI_2(THF)_5$ (1.23 g, 1.57 mmol) in THF (30 mL). The reaction mixture was heated at 60 °C for 3 h. The gas evolved was removed at intervals by evacuation. The reaction mixture gradually turned colorless and $TmI_3(THF)_3$ precipitated. The reaction mixture was kept at ~20 °C for 12 h, after which the precipitate of $TmI_3(THF)_3$ (0.38 g, 63%) was separated by decantation. The solvent and excess cyclopentadiene were removed from the solution by vacuum condensation. After recrystallization of the solid residue from THF, $CpTmI_2(THF)_3$ (**4**) was obtained in a yield of 0.23 g (21%) as greenish needle-like crystals, m.p. 145—147 °C. Found (%): I, 35.97; Tm, 23.02. $C_{17}H_{29}I_2O_3Tm$. Calculated (%): I, 36.04; Tm, 23.99. IR (Nujol), ν/cm^{-1}: 1030 m, 1005 s, 920 m, 860 sh, 850 s, 790 s, 660 w. The mother liquor was concentrated to 5 mL and then hexane (10 mL) was added, which gave rise to a colorless precipitate. The mixture was centrifuged, the solution was separated from the precipitate by decantation, and the precipitate was dried *in vacuo* at 80 °C for 1 h. The colorless finely crystalline compound $Cp_2TmI(THF)_2$ was obtained in a yield of 0.26 g (58%), m.p. 202—204 °C. Found (%): I, 23.00; Tm, 29.85. $C_{18}H_{26}IO_2Tm$. Calculated (%): I, 22.26; Tm, 29.63. The IR spectrum of the product was analogous to that of **4**.

Reaction of neodymium(II) diiodide (1) with pentamethylcyclopentadiene. A solution of pentamethylcyclopentadiene (0.205 g, 1.5 mmol) in THF (5 mL) was added to a violet solution of NdI_2 (0.6 g, 1.5 mmol) in THF (30 mL) at 0 °C. The solution immediately turned brown and $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$ (**5**) precipitated in a yield of 0.27 g. The precipitate was separated by filtration. An additional amount of the triiodide (0.29 g) was obtained as pale-blue cubic crystals by keeping the filtrate in a refrigerator at −5 °C for 10 h. This portion of the product was used for X-ray diffraction study. The total yield of $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$ (**5**) was 0.56 g (92%). The solvent was partially removed (25 mL) from the mother liquor by condensation and then pentane (30 mL) was added to the residue. The pale-blue finely crystalline precipitate (0.52 g) that formed was separated by decantation and dried *in vacuo* at ~20 °C to obtain the $Cp^*_2NdI(THF)_2$ complex. Found (%): I, 20.04; Nd, 21.27. $C_{28}H_{46}IO_2Nd$. Calculated (%): I, 18.50; Nd, 21.03. IR (Nujol), ν/cm^{-1}: 1340 m, 1250 m, 1170 w, 1085 w, 1030 m, 1000 s, 950 w, 910 m, 850 s, 830 s, 800 sh, 720 m, 660 m.

Reaction of dysprosium(II) diiodides (2) with pentamethylcyclopentadiene. Under the conditions of the above-described experiment, pentamethylcyclopentadiene (0.2 g, 1.47 mmol) was added to a green solution of DyI_2 (0.57 g, 1.369 mmol) in THF (30 mL). The color of the solution changed to brown and $DyI_3(THF)_3$ precipitated in a yield of 0.537 g (83%). The solution was decanted from the precipitate. The solvent and an excess of Cp*H were removed by vacuum condensation. The residue was extracted with toluene (10 mL). The extract was concentrated to 2 mL and then pentane (10 mL) was added. The colorless white solid compound that precipitated (0.11 g) was washed with cold pentane and dried *in vacuo* at ~20 °C. The $Cp^*_2DyI(THF)_2$ complex was obtained. Found (%): Dy, 22.20; I, 21.66. $C_{28}H_{46}DyIO_2$. Calculated (%): Dy, 23.08; I, 18.02. The IR spectrum of the product is analogous to the above-mentioned spectrum of the neodymium analog.

Table 1. Crystallographic data for $CpTmI_2(THF)_3$ (**4**) and $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$ (**5**)

Parameter	4	5
Molecular formula	$C_{17}H_{29}I_2O_3Tm$	$C_{20}H_{40}I_2NdO_5^+ \cdot$ $\cdot C_8H_{16}I_4NdO_2^-$
Crystal system	Orthorhombic	Monoclinic
Space group	*Pna*2$_1$	*C*2/*c*
a/Å	19.0517(4)	12.8714(2)
b/Å	13.5014(1)	12.1521(2)
c/Å	8.1805(2)	28.9133(4)
β/deg	90.0	98.307(1)
V/Å^3	2104.23(7)	4475.01(12)
Z	4	4
d_{calc}/g cm^3	2.223	2.307
Final *R* factors		
R	0.0485	0.0475
R_w	0.0700	0.0847
S	1.007	1.101
Number of reflections with $I > 2\sigma(I)$	3328	5128

Table 2. Selected bond lengths (*d*) in molecule **4** (Cg is the center of the Cp ring C(1)—C(5))

Bond	*d*/Å
Tm—Cg	2.347(5)
Tm—I(1)	3.0655(11)
Tm—I(2)	3.1072(11)
Tm—O(1)	2.323(9)
Tm—O(2)	2.366(9)
Tm—O(3)	2.395(9)

Table 3. Selected bond angles (ω) in molecule **4** (Cg is the center of the Cp ring C(1)—C(5))

Angle	ω/deg
Cg—Tm—I(1)	101.42(12)
Cg—Tm—I(2)	99.66(12)
Cg—Tm—O(1)	102.9(3)
Cg—Tm—O(2)	104.8(3)
Cg—Tm—O(3)	177.4(2)
I(1)—Tm—I(2)	158.76(3)
I(1)—Tm—O(1)	88.5(2)
I(1)—Tm—O(2)	86.0(2)
I(1)—Tm—O(3)	80.4(2)
I(2)—Tm—O(1)	89.4(2)
I(2)—Tm—O(2)	86.2(2)
I(2)—Tm—O(3)	78.7(2)
O(1)—Tm—O(2)	152.3(3)
O(1)—Tm—O(3)	75.1(3)
O(2)—Tm—O(3)	77.3(3)

Table 4. Selected bond lengths (*d*) in molecule **5**

Bond	*d*/Å	Bond	*d*/Å
Nd(1)—I(1)	3.0436(4)	Nd(1)—O(2)	2.474(4)
Nd(2)—I(2)	3.0922(4)	Nd(1)—O(3)	2.478(6)
Nd(2)—I(3)	3.0760(5)	Nd(2)—O(4)	2.385(5)
Nd(1)—O(1)	2.467(4)		

Table 5. Selected bond angles (ω) in molecule **5**

Angle	ω/deg
I(1)—Nd(1)—I(1´)	179.04(3)
I(1)—Nd(1)—O(1)	90.68(10)
I(1)—Nd(1)—O(2)	89.74(11)
I(1)—Nd(1)—O(3)	90.479(13)
I(1)—Nd(1)—O(1´)	88.55(10)
I(1)—Nd(1)—O(2´)	90.56(11)
O(1)—Nd(1)—O(2)	71.89(15)
O(1)—Nd(1)—O(1´)	72.5(2)
O(2)—Nd(1)—O(3)	71.87(11)
O(1´)—Nd(1)—O(2´)	71.90(15)
O(1)—Nd(1)—O(3)	143.74(10)
O(1)—Nd(1)—O(2´)	144.35(15)
O(2)—Nd(1)—O(2´)	143.7(2)
I(2)—Nd(2)—I(2″)	180.0
I(3)—Nd(2)—I(3″)	180.0
O(4)—Nd(2)—O(4″)	180.0
I(2)—Nd(2)—I(3)	91.788(13)
I(2)—Nd(2)—I(3″)	88.213(13)
O(4)—Nd(2)—I(2)	93.45(12)
O(4)—Nd(2)—I(3)	88.52(12)
O(4)—Nd(2)—I(2″)	86.55(12)
O(4)—Nd(2)—I(3″)	91.48(12)

X-ray diffraction study of the crystals of complexes **4** and **5** was carried out on a Siemens SMART CCD diffractometer (Mo-Kα radiation, λ = 0.71073 Å). The structures of complexes **4** and **5** were solved by direct methods using all reflections and refined by the full-matrix least-squares method with anisotropic thermal parameters for all nonhydrogen atoms. All calculations were carried out using the SHELX-97 program packages.[11]

The crystallographic data for compounds **4** and **5** are given in Table 1. The selected bond lengths and bond angles in molecules **4** and **5** are listed in Tables 2—5. The atomic coordinates were deposited with the Cambridge Structural Database.

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References

1. (a) M. N. Bochkarev and A. A. Fagin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1200 [*Russ. Chem. Bull.*, 1999, **48**, 1187 (Engl. Transl.)]; (b) M. N. Bochkarev and A. A. Fagin, *Chem. Eur. J.*, 1999, **5**, 2990.
2. M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, T. V. Petrovskaya, J. W. Ziller, R. N. R. Broomhall-Dillard, and W. J. Evans, *Angew. Chem., Int. Ed.*, 1997, **35**, 133.
3. (a) W. J. Evans and N. T. Allen, *J. Am. Chem. Soc.*, 2000, **122**, 2118; (b) W. J. Evans, N. T. Allen, and J. W. Ziller, *J. Am. Chem. Soc.*, 2000, **122**, 11749; (c) M. N. Bochkarev, A. A. Fagin, I. L. Fedushkin, T. V. Petrovskaya, W. J. Evans, M. A. Greci, and J. W. Ziller, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1804 [*Russ. Chem. Bull.*, 1999, **48**, 1782 (Engl. Transl.)]; (d) I. L. Fedushkin, V. I. Nevodchikov, M. N. Bochkarev, S. Dechert, and H. Schumann, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 145 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 154].
4. M. N. Bochkarev, A. A. Fagin, and G. V. Khoroshen´kov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1757 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1909].
5. (a) H. Schumann, J. A. Meese-Marktscheffer, and L. Esser, *Chem. Rev.*, 1995, **95**, 865; (b) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953.
6. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1970, **26**, 1046.
7. D. Stellfeldt, G. Meyer, and G. B. Deacon, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1252.
8. Z. Xie, K.-Y. Chiu, B. Wu, and T. C. W. Mak, *Inorg. Chem.*, 1996, **35**, 5957.
9. M. Niemeyer, *Acta Crystallogr.*, 2001, **E57**, m363.
10. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1970, **26**, 1046.
11. G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Determination*, Göttingen University, Göttingen (Germany), 1997.

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