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Complexes of neodymium and dysprosium triiodides with amines. Molecular structures of the $\{Dy[Me_2N(CH_2)_3NH_2]_8\}I_3$, $NdI_3(Pr^iNH_2)_4$, and $NdI_3(Pr^iNH_2)_5$ complexes*

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The dissolution of DyI_2 in diamine $Me_2N(CH_2)_3NH_2$ (DMDA) is accompanied by the disproportionation of the salt, hydrogen evolution, and oxidation of Dy^{II} to Dy^{III}. The $[Dy(DMDA)_8]I_3$ complex (**1**) was isolated from the solution. The neodymium amide amine complex $(Pr^iNH)NdI_2(IPA)_4$ was produced by the reaction of NdI_2 with isopropylamine (IPA). The recrystallization of this complex from IPA afforded the $NdI_3(IPA)_4$ complex (**2**). The recrystallization of $(Pr^iNH)NdI_2(IPA)_4$ from a toluene—IPA mixture gave the complex with five amine ligands, $NdI_3(IPA)_5$ (**3**). The structures of compounds **1**, **2**, and **3** were established by X-ray diffraction.

Key words: isopropylamine, *N*,*N*-dimethyltrimethylenediamine, diiodide, dysprosium, complexes, neodymium, triiodide.

Anhydrous rare-earth halides serve as the main starting materials in the synthesis of their organometallic and coordination derivatives. The most readily available chlorides $LnCl_3$ or bromides $LnBr_3$ are most commonly used for this purpose.[1] However, in many cases, the use of iodides LnI_3 allows a substantial increase in the yield of the products or the synthesis of compounds, which cannot be prepared by the reactions with chlorides or bromides.[2] Numerous structural studies of trihalide complexes with coordinating solvents showed that there are two main types of molecules, *viz.*, the neutral molecules $LnHal_3(B)_x$ (B is a Lewis base)[3] and the ionic molecules $\{[LnHal_2(B)_y][LnHal_4(B)_z]\}$.[4] As a rule, the compounds differ in the reactivity and catalytic activity. The formation of a particular type of complexes depends on the method employed for their synthesis, the procedure for the isolation of the reaction products, and the nature of the coordinated ligand. Most of the structurally characterized complexes contain THF or DME molecules. Complexes with alcohols, hexamethylphosphoric triamide, and ethers were described. Rare-earth trihalides coordinated to amine molecules are unknown.

Recently, we have found[5] that the dissolution of diiodides LnI_2 (Ln = Nd, Sm, Eu, Dy, Tm, or Yb) in isopropylamine (IPA) affords stable (Sm, Eu, Tm, or Yb) or relatively stable (Nd or Dy) $LnI_2(IPA)_x$ complexes (x = 4 or 5). Other primary amines, such as $MeNH_2$, Pr^nNH_2, Bu^tNH_2, or $PhNH_2$, also dissolve neodymium, dysprosium, and thulium diiodides but they actively react with the latter compounds, which hinders the synthesis of the corresponding amine complexes. An interesting attempt was made to use *N*,*N*-dimethyltrimethylenediamine (DMDA), which can form η^2-coordinated complexes, as the solvent and ligand for diiodides LnI_2. In the present study, we determined the molecular structure of the complex isolated from a solution of DyI_2 in DMDA as well as the structures of the neodymium complexes produced by oxidation of NdI_2 with isopropylamine.

Results and Discussion

Upon the addition of $Me_2N(CH_2)_3NH_2$ (DMDA) to dysprosium diiodide at −20 °C, the solution turned violet, which is characteristic of solutions of divalent dysprosium in amines. The dissolution of the salt was accompanied by the vigorous hydrogen evolution, which is indicative of the rapid oxidation of dysprosium. After 3—5 min, the gas evolution ceased and the solution turned colorless. The slow removal of the amine from the reaction mixture afforded pale-yellow crystals of triiodide DyI_3 coordinated by eight DMDA molecules (**1**). The high yield of this complex (83%) and the hydrogen evolution are evidence for the disproportionation of the starting diiodide and the rapid oxidation of DyI species. This oxidation most probably gives the monoiodide derivative

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$DyI(HNCH_2CH_2NMe_2)_2$ (**A**), *i.e.*, the reaction can be described by the following equation:

$$2\ DyI_2 \xrightarrow{DMDA}$$

$$\longrightarrow \underset{\mathbf{1}}{[Dy(DMDA)_8]I_3} + \underset{\mathbf{A}}{DyI[HN(CH_2)_3NMe_2]_2} + H_2$$

Attempts to isolate compound **A** in the individual state failed. After the separation of triiodide **1** from the reaction mixture and the removal of DMDA *in vacuo*, a product was obtained as a turbid viscous pale-brown liquid. The dysprosium and iodide contents in this product are similar but not equal to those calculated for compound **A**. The IR spectrum of the compound shows stretching bands of C—H (2970, 2940, 2858, 2815 cm^{-1}), NC—H (2769 cm^{-1}), N—H (3304, 3154, 1588 cm^{-1}), and N—C (1261 cm^{-1}) groups.

According to the X-ray diffraction study, the metal cation in triiodide molecule **1** is surrounded by eight DMDA molecules η^1-coordinated through the nitrogen atoms of the NH_2 groups (Fig. 1, Table 1). As a result, the coordination polyhedron of the Dy atom can be described as a distorted square antiprism. The Dy(1)—N distances vary in a wide range (2.510(3)—2.570(3) Å). Seven DMDA molecules adopt a bent conformation, and only one DMDA molecule is linear. The N(5)C(11)C(12)C(13), C(11)C(12)C(13)N(6), C(12)C(13)N(6)C(14), and C(12)C(13)N(6)C(14) torsion angles in the linear DMDA molecule are 173.1, 166.6, −171.3, and 67.7°, respectively, whereas the analogous angles in the molecules adopting a bent conformation, for example, N(13)C(31—33)N(14)C(34,35), are −77.3, 56.2, 77.8, and −160.5. The C—C (1.511(5)—1.577(6) Å) and C—N (1.454(6)—1.501(5) Å) bond lengths and the bond angles in the coordinated diamine molecules are similar to the corresponding parameters in amines.[6] Apparently, compound **1** is the first example of complexes containing a monodentate diamine ligand.

The fact that the Dy(1)—N distances vary in a wide range, the η^1 coordination of the DMDA molecules, and the linear conformation of one of these molecules provide indirect evidence for a high degree of space filling of the coordination sphere of the Dy atom. Consequently, the structure of complex **1** is determined by nonbonding ligand—ligand interactions (steric repulsion) in the coor-

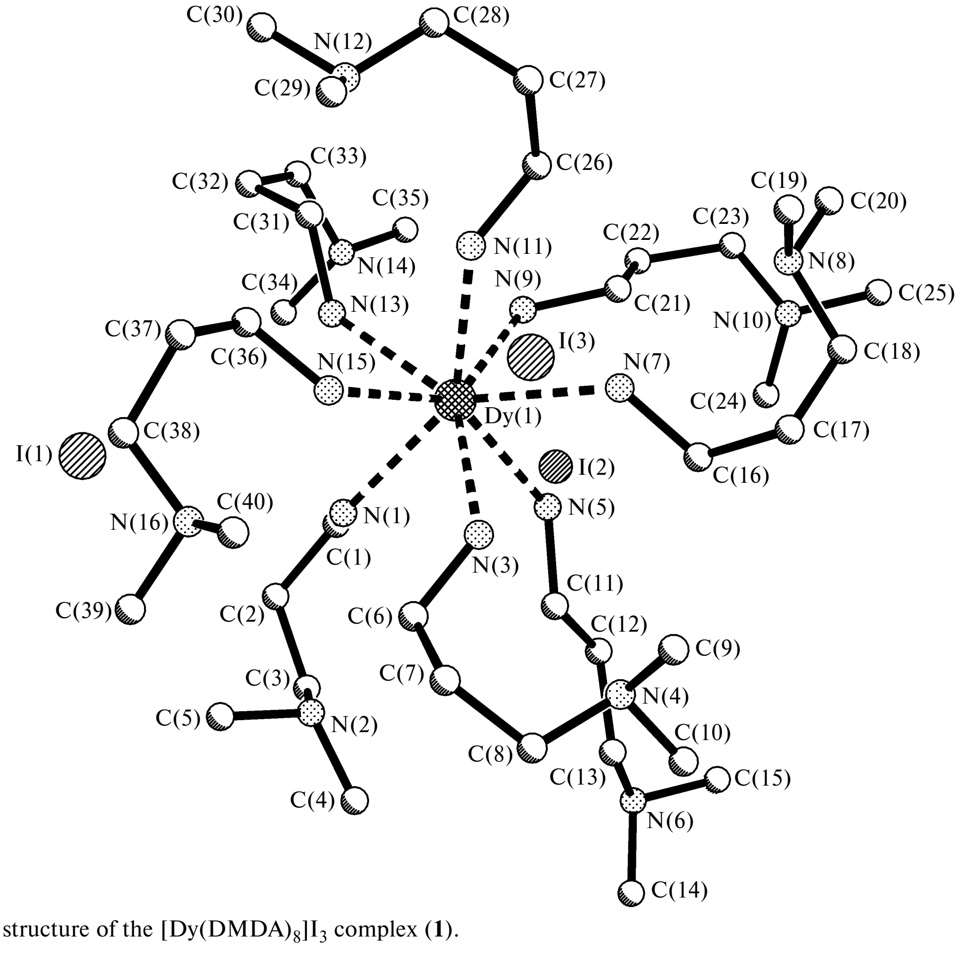

Fig. 1. Molecular structure of the $[Dy(DMDA)_8]I_3$ complex (**1**).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **1**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Dy(1)—N(1)	2.510(3)	N(1)—Dy(1)—N(13)	72.60(9)	N(3)—Dy(1)—N(15)	69.22(9)
Dy(1)—N(13)	2.522(3)	N(1)—Dy(1)—N(11)	143.67(10)	N(1)—Dy(1)—N(5)	75.20(10)
Dy(1)—N(11)	2.523(3)	N(13)—Dy(1)—N(11)	81.51(9)	N(13)—Dy(1)—N(5)	117.01(9)
Dy(1)—N(7)	2.547(3)	N(1)—Dy(1)—N(7)	142.07(9)	N(11)—Dy(1)—N(5)	140.59(10)
Dy(1)—N(3	2.548(3)	N(13)—Dy(1)—N(7)	144.27(9)	N(7)—Dy(1)—N(5)	76.91(9)
Dy(1)—N(15)	2.561(3)	N(11)—Dy(1)—N(7)	70.16(9)	N(3)—Dy(1)—N(5)	81.08(10)
Dy(1)—N(5)	2.567(3)	N(1)—Dy(1)—N(3)	80.01(9)	N(15)—Dy(1)—N(5)	144.38(10)
Dy(1)—N(9)	2.570(3)	N(13)—Dy(1)—N(3)	140.77(9)	N(1)—Dy(1)—N(9)	111.01(9)
		N(11)—Dy(1)—N(3)	106.89(9)	N(13)—Dy(1)—N(9)	71.10(10)
		N(7)—Dy(1)—N(3)	70.66(9)	N(11)—Dy(1)—N(9)	83.04(9)
		N(1)—Dy(1)—N(15)	80.54(9)	N(7)—Dy(1)—N(9)	83.95(9)
		N(13)—Dy(1)—N(15)	78.86(9)	N(3)—Dy(1)—N(9)	146.77(9)
		N(11)—Dy(1)—N(15)	69.60(9)	N(15)—Dy(1)—N(9)	141.91(9)
		N(7)—Dy(1)—N(15)	109.54(9)	N(5)—Dy(1)—N(9)	72.35(10)

dination sphere of the Dy atom. The absence of a free coordination site near the Dy atom is confirmed by the fact that the iodide cations are located at nonbonding distances from Dy^{3+} (4.621—5.280 Å). Earlier,[7] an analogous organization of molecular rare-earth halides has been observed only in the bis(ethylimine)ethylamine complexes $\{[(MeC=NH)_2CMeNH_2]Ln(MeCN)_6\}I_3$ (Ln = Dy or Tm).[7]

An analogous transformation of the lanthanide diiodide derivative into the triiodide was observed in the reaction of NdI_2 with isopropylamine. In this case, the initially formed dark-violet solution containing the $NdI_2(IPA)_5$ complex turned colorless upon storage at room temperature for 1 h as a result of oxidation of neodymium(II) with amine.[5] The reaction is accompanied by the hydrogen evolution and produces the amide amine complex $(Pr^iNH)NdI_2(IPA)_4$. The composition of the latter was confirmed by elemental analysis and IR spectroscopy. With the aim of growing crystals suitable for X-ray diffraction, the complex was recrystallized from IPA under mild conditions. However, the product appeared to be the amino complex of triiodide **2**. Analogous compound **3**, which contains a larger number of coordinated amine molecules, was isolated by recrystallization of $(Pr^iNH)NdI_2(IPA)_4$ from an IPA—toluene mixture. These results provide additional evidence that neodymium and dysprosium diiodide complexes are highly prone to disproportionation.

The X-ray diffraction study showed that, as opposed to complex **1**, all I^- anions in compound **2** are directly bound to the metal cation (Fig. 2).

The coordination environment of the Nd^{3+} cation formed by three iodine atoms and the nitrogen atoms of the amine ligands can be described as a distorted pentagonal bipyramid, in which all equatorial positions are occupied by organic molecules and the I(3) atom, and the apical positions are occupied by the I(1) and I(2) atoms.

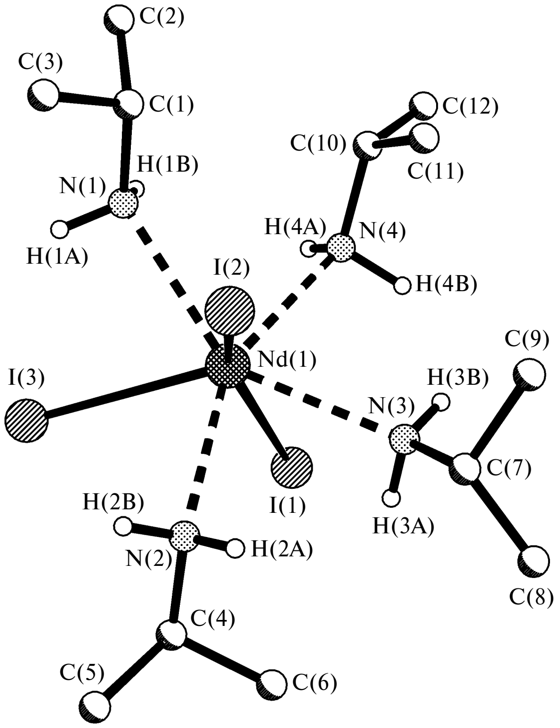

Fig. 2. Molecular structure of complex **2**.

The Nd—I distances in molecule **2** (Table 2) have similar values but noticeably exceed than the corresponding bond lengths in the tetrahydrofuran analog $NdI_3(THF)_4$ (3.0714(4), 3.0894(4), and 3.1468(4) Å),[8] in which the Nd atom is also in a pentagonal-bipyramidal coordination. According to the calculated degree of space filling of the coordination environment of the Nd atoms (G parameter[9]), the coordination sphere in **2** is filled by 79.1(2)%, and this value is comparable with that found for the $NdI_3(THF)_4$ complex (81.6(2)%). Assuming that the Nd—I distances in complex **2** are equal to those in the

Table 2. Selected bond lengths (*d*) and bond angles (ω) in compound **2**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Nd(1)—N(1)	2.627(2)	N(2)—Nd(1)—N(3)	77.19(7)	N(4)—Nd(1)—I(2)	108.56(5)
Nd(1)—N(2)	2.607(2)	N(2)—Nd(1)—N(4)	154.08(7)	N(1)—Nd(1)—I(2)	80.11(5)
Nd(1)—N(3)	2.618(2)	N(3)—Nd(1)—N(4)	77.54(7)	N(2)—Nd(1)—I(3)	76.65(5)
Nd(1)—N(4)	2.620(2)	N(2)—Nd(1)—N(1)	126.91(7)	N(3)—Nd(1)—I(3)	142.61(5)
Nd(1)—I(1)	3.1711(2)	N(3)—Nd(1)—N(1)	143.81(7)	N(4)—Nd(1)—I(3)	122.22(5)
Nd(1)—I(2)	3.1130(2)	N(4)—Nd(1)—N(1)	78.11(7)	I(2)—Nd(1)—I(3)	114.525(6)
Nd(1)—I(3)	3.1558(2)	N(2)—Nd(1)—I(2)	73.78(5)	I(2)—Nd(1)—I(1)	155.349(6)
N(1)—C(1)	1.503(3)	N(3)—Nd(1)—I(2)	82.74(5)	I(3)—Nd(1)—I(1)	81.373(6)

tetrahydrofuran analog and the geometry of the IPA ligands remains unchanged, the G parameter is 89.3(2)%. Based on this fact, it can be concluded that the nonbonding ligand—ligand interactions in the coordination sphere of the metal atom in complex **2** are minimized compared to those in $NdI_3(THF)_4$, due to an elongation of the Nd—I distances.

In complex **3** (Fig. 3), the coordination number of neodymium increases to 8 due to the coordination of the fifth IPA ligand. The coordination polyhedron of the Nd(1) atom can be described as a distorted bicapped trigonal prism. The Nd—I and Nd—N bond lengths (Table 3) are slightly larger than those in molecule **2**. This is associated with an increase in the number of ligands in the coordination sphere of Nd^{3+} in **3** and, correspondingly, with a strengthening of the nonbonded ligand—ligand interactions, which are minimized by increasing the Nd—I and Nd—N distances. The geometric characteristics of the IPA ligands in triiodides **2** and **3** are virtually equal to the corresponding parameters in the amine molecules in the $LnI_2(IPA)_4$ complexes (Ln = Tm or Eu).[5]

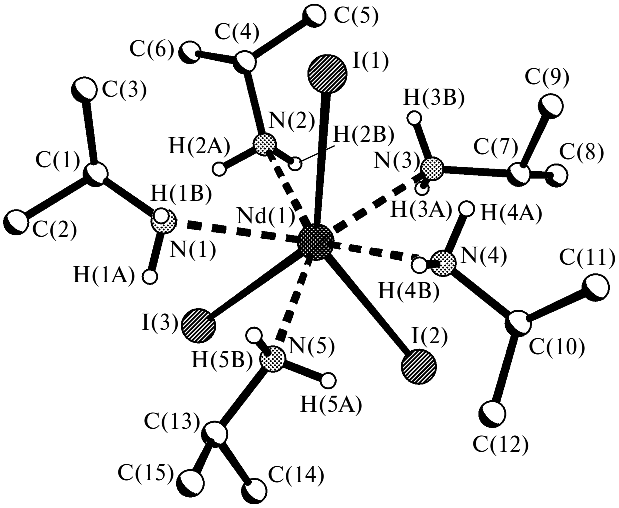

Fig. 3. Molecular structure of complex **3**.

The present study showed that the neodymium and dysprosium amide iodide complexes LnI_2(amide) undergo rapid disproportionation even under mild conditions to give the corresponding triiodides coordinated by neutral amine, $LnI_3(\text{amine})_x$. The structural analysis of the complexes revealed that the Ln...I distance changes from that

Table 3. Selected bond lengths (*d*) and bond angles (ω) in compound **3**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Nd(1)—N(1)	2.6424(19)	N(1)—Nd(1)—N(2)	79.88(6)	N(2)—Nd(1)—I(1)	82.16(4)
Nd(1)—N(2)	2.6481(19)	N(1)—Nd(1)—N(3)	142.84(6)	N(3)—Nd(1)—I(1)	78.99(4)
Nd(1)—N(3)	2.6539(19)	N(2)—Nd(1)—N(3)	69.78(6)	N(5)—Nd(1)—I(1)	101.38(4)
Nd(1)—N(5)	2.6569(18)	N(1)—Nd(1)—N(5)	67.85(6)	N(4)—Nd(1)—I(1)	71.76(4)
Nd(1)—N(4)	2.687(2)	N(2)—Nd(1)—N(5)	145.28(6)	I(2)—Nd(1)—I(1)	141.891(6)
Nd(1)—I(1)	3.1957(2)	N(3)—Nd(1)—N(5)	144.94(6)	N(1)—Nd(1)—I(3)	70.73(4)
Nd(1)—I(2)	3.1645(2)	N(1)—Nd(1)—N(4)	119.08(6)	N(2)—Nd(1)—I(3)	70.27(4)
Nd(1)—I(3)	3.2863(2)	N(2)—Nd(1)—N(4)	141.26(6)	N(3)—Nd(1)—I(3)	115.90(4)
N(1)—C(1)	1.501(3)	N(3)—Nd(1)—N(4)	77.35(6)	N(5)—Nd(1)—I(3)	86.74(4)
N(2)—C(4)	1.500(3)	N(5)—Nd(1)—N(4)	69.80(6)	N(4)—Nd(1)—I(3)	145.59(4)
		N(1)—Nd(1)—I(2)	140.35(4)	I(2)—Nd(1)—I(3)	76.969(5)
		N(2)—Nd(1)—I(2)	110.32(4)	I(1)—Nd(1)—I(3)	139.668(6)
		N(3)—Nd(1)—I(2)	72.67(4)	I(2)—Nd(1)—I(1)	141.891(6)
		N(5)—Nd(1)—I(2)	88.29(4)	C(1)—N(1)—Nd(1)	132.63(13)
		N(4)—Nd(1)—I(2)	77.50(4)	C(1)—N(1)—H(1A)	105.4(9)
		N(1)—Nd(1)—I(1)	76.00(4)	Nd(1)—N(1)—H(1A)	94.0(10)

nearly equal to the sum of the ionic radii of Ln^{3+} and I^- to the nonbonding distance with increasing number of coordinated amine molecules. This is evidence of both the role of nonbonding ligand—ligand interactions in the structure formation of these compounds and the nonrigidity of the Ln—I bond, which, apparently, determine the high reactivity and catalytic activity of lanthanide iodides compared to the related chlorides and bromides.

Experimental

All reactions and operations associated with the isolation of the reaction products were carried out *in vacuo* using the standard Schlenk technique. Isopropylamine and DMDA (Aldrich) were treated with a small amount of NdI_2 for 5 min immediately before use and then condensed into a reaction vessel. The IR spectra were recorded on Specord M-75 spectrometers in the 4000—450 cm^{-1} region as Nujol mulls. Diiodides NdI_2 and DyI_2 were prepared according to a procedure developed earlier.[10]

Reaction of DyI_2 with *N*,*N*-dimethyltrimethylenediamine (DMDA). Diamine DMDA (6 mL) was added by condensation into a tube containing a DyI_2 powder (0.41 g, 0.98 mmol) at −20 °C. Heating of the reaction mixture to room temperature led to the dissolution of the diiodide powder, the formation of a violet solution, and the gas evolution. After 5 min, the solution became completely colorless. Then the solution was separated from the precipitate by decantation and concentrated to 4 mL by the slow removal of the diamine *in vacuo*. The pale-yellow crystals of compound **1** that precipitated were separated by decantation, washed with cold DMDA, and dried *in vacuo*. The yield was 0.56 g (83%); m.p. 51—53 °C. Found (%): Dy, 11.60. $C_{40}H_{112}I_3N_{16}Dy$. Calculated (%): Dy, 11.95. IR (Nujol mulls, KBr), ν/cm^{-1}: 3304, 3154, 2765, 1588, 1261, 1218, 1041, 820, 798. One crystal was used for the X-ray diffraction study. The diamine was completely removed from the mother liquor by vacuum condensation. A viscous pale-yellow liquid was obtained in a yield of 0.14 g. The metal content (32.00%) and the iodine content (24.10%) in this liquid correspond to the formula $DyI(HNCH_2CH_2NMe_2)_2$ (Dy, 33.07%; I, 25.8%). The IR spectrum of the product is identical to the spectrum of compound **1**.

Reaction of NdI_2 with isopropylamine (IPA). A solution of NdI_2 (0.46 g, 1.15 mmol) in IPA (11 mL) was stirred at room temperature for 50 min. The color of the solution changed from violet to pale-blue. Then the solution was filtered, and the solvent was removed *in vacuo*. The resulting pale-blue oily compound was washed with hexane and dried *in vacuo* at 30—40 °C.

Table 4. Crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **1**, **2**, and **3**

Parameter	1	2	3
Molecular formula	$C_{40}H_{112}DyI_3N_{16}$	$C_{12}H_{36}I_3N_4Nd$	$C_{15}H_{45}I_3N_5Nd$
Molecular weight	1360.66	761.39	820.50
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*P*2(1)2(1)2(1)	*Pbca*	$P\bar{1}$
Unit cell parameters			
a/Å	14.5690(8)	16.9469(8)	6.9378(3)
b/Å	18.8309(10)	14.3566(7)	10.7341(5)
c/Å	22.5478(12)	19.6296(9)	18.6971(9)
α/deg	90	90	94.5820(10)
β/deg	90	90	96.9860(10)
φ/deg	90	90	95.9800(10)
$V/Å^3$	6185.9(6)	4775.9(4)	1368.48(11)
Z	4	8	2
$\rho/g\ cm^{-3}$	1.461	2.118	1.991
μ/mm^{-1}	2.744	6.052	5.289
Transmission coefficient, T_{min}/T_{max}	0.6679/0.5033	0.6767/0.2476	0.8163/0.5694
F(000)	2756	2840	778
Crystal dimensions/mm	0.29×0.16×0.16	0.32×0.22×0.07	0.12x0.08x0.04
θ-Scan range, deg	1.77—27.00	2.07—27.50	1.92—27.50
Indices of measured reflections	$-18 \leq h \leq 17$ $-24 \leq k \leq 23$ $-28 \leq l \leq 25$	$-22 \leq h \leq 22$ $-18 \leq k \leq 18$ $-25 \leq l \leq 25$	$-9 \leq h \leq 9$ $-13 \leq k \leq 13$ $-24 \leq l \leq 24$
Number of observed reflections	40605	43527	13226
Number of independent reflections (R_{int})	13503 (0.0338)	5482 (0.0365)	6201 (0.0250)
Goodness-of-fit on F^2	0.992	1.057	1.043
R_1/wR_2 ($I > 2\sigma(I)$)	0.0260/0.0549	0.0233/0.0570	0.0270/0.0548
R_1/wR_2 (based on all reflections)	0.0303/0.0559	0.0280/0.0584	0.0342/0.0566
Absolute structure factor	0.011(6)		
Residual electron density, $(\rho_{max}/\rho_{min})/e\ Å^{-3}$	1.096/−0.502	1.524/−0.952	1.432/−0.584

The $(Pr^iNH)NdI_2(Pr^iNH_2)_4$ compound was obtained as a pale-blue powder in a yield of 0.76 g (95%), m.p. 55 °C (decomp.). Found (%): Nd, 21.03. $C_{15}H_{44}I_2N_5Nd$. Calculated (%): Nd, 20.83. IR (Nujol mulls, KBr, ν/cm^{-1}): 3280, 3217, 1562, 1245, 1160, 1030, 940, 807, 525, 478. The $(Pr^iNH)NdI_2(Pr^iNH_2)_4$ powder was dissolved in IPA (5 mL). The solution was concentrated to the viscous liquid state. Upon cooling of the concentrated solution to 5 °C, pale-blue crystals of compound **2** precipitated (0.39 g, 93%). Found (%): Nd, 19.50. $C_{12}H_{36}I_3N_4Nd$. Calculated (%): Nd, 18.95. IR (Nujol mulls, KBr, ν/cm^{-1}): 3280, 3217, 1562, 1245, 1160, 1030, 940, 807, 525, 478.

Compound **3** was synthesized analogously with the difference that an IPA—toluene mixture (1 : 5) was used for the recrystallization of the $(Pr^iNH)NdI_2(Pr^iNH_2)_4$ powder. Found (%): Nd, 18.10. $C_{15}H_{45}I_3N_5Nd$. Calculated (%): Nd, 17.58. The IR spectrum of compound **3** is identical to the spectrum of complex **2**. Crystals of **2** and **3** were used for X-ray diffraction.

The X-ray diffraction studies of complexes **1**, **2**, and **3** were carried out on a Smart Apex diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω—φ scanning technique) at 100 K. The structures of complexes **1—3** were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with the use of the SHELXTL program package.[11] Absorption corrections were applied with the SADABS program.[12] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms in complex **1** were positioned geometrically and refined isotropically using a riding model. The hydrogen atoms in complexes **2** and **3** were located in difference electron density maps and refined isotropically. The crystallographic parameters and the X-ray diffraction data collection and refinement statistics for compounds **1—3** are given in Table 4. Selected bond lengths and bond angles for compounds **1—3** are listed in Tables 1—3, respectively.

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