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Synthesis and characterization of isopropylamine complexes of lanthanide(II) diiodides: Molecular structure of $TmI_2(Pr^iNH_2)_4$ and $EuI_2(Pr^iNH_2)_4$

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Dedicated to Professor Glen Deacon on the occasion of his 70th birthday.

Abstract

It was found that the lanthanide diiodides LnI_2 (**1**) (Ln = Nd, Sm, Eu, Dy, Tm, Yb) are dissolved in isopropylamine (IPA) without redox transformations. Stability of the formed solutions decreases in a row Eu ≈ Yb > Sm > Tm > Dy > Nd. Removing of a solvent in vacuum leaves complexes $LnI_2(IPA)_x$ (**2**) (Nd, $x = 5$; Sm, Eu, Dy, Tm, Yb, $x = 4$) as crystalline colored solids. Stability of **2-Nd**,**Dy**,**Tm** is higher than that of known THF or DME coordinated salts. Divalent state of metal in the products is confirmed by data of UV–Vis spectroscopy, magnetic measurements and their chemical behavior. Structure of **2-Eu** and **2-Tm** was established by X-ray diffraction analysis. Oxidation of **2-Nd**,**Dy** in IPA affords amine-amides $(Pr^iNH)Ln(IPA)_y$ (**3**) (Nd, $y = 4$; Dy, $x = 3$). *n*-Propylamine also dissolves the iodides **1-Sm**,**Eu**,**Dy**,**Tm**,**Yb** but stability of the solutions is significantly lower. **1-Nd** vigorously reacts with Pr^nNH_2 even at −30 °C which hampers the formation of the solution.

Keywords: Primary amines; Complexes; Divalent lanthanides; Diiodides; Isopropylamine

1. Introduction

Complexes of subvalent, in particular divalent lanthanides always attracted significant attention of investigators because of their unusual properties and promising synthetic ability. In the latter decade, numerous works were concerned with the complexes of divalent thulium, dysprosium and neodymium, which before remained entirely unstudied [1]. All known to date complexes of these metals, most of which are thulium derivatives $TmI_2(DME)_3$ [2a,2b], $TmI_2(THF)_x$ ($x = 2, 3, 5$) [2a,2b,2c,2d,2e], $TmI_2(DME)_2(THF)$ [2f], $[(Me_3Si)_2C_5H_3]_2Tm(THF)$ [2g], $[Me_2(Me_3Si)_2C_4E]_2Tm(THF)$ (E = P, As) [2h], $[(Me_3Si)_2C_4H_2P]_2Tm(THF)$, $[Bu^t_2C_4H_2P]_2Tm(THF)$, $(C_5H_3Bu^t_2)_2Tm(THF)$ [2i] and only four – $LnI_2(THF)_5$, $LnI_2(DME)_3$ (Ln = Nd [2b,2f], Dy [2b,3]) – are compounds of neodymium and dysprosium, contain THF or DME molecules as coordinating ligands. Attempts to synthesize new complexes with other Lewis bases such as NH_3 [2b], HMFA [4], pyridine [5], acetonitrile [6] or benzonitrile [7] failed due to the readily proceeding oxidation of the divalent metals by these compounds.

In this paper we report on our efforts to utilize primary amines as solvents for diiodides **1** and as coordinating ligands for novel molecular complexes of divalent lanthanides. The amines RNH_2 as a medium are related by nature to liquid ammonia, which is known to be a fine solvent for various chemicals including rare earth metal derivatives.

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The iodides **1-Nd**,**Dy**,**Tm** are also soluble in liquid NH_3 but the formed solutions immediately decompose because of amidation. Electronic and steric effects of R radicals in amines essentially decrease reactivity of the remaining N–H groups which gives a chance to prepare stable complexes of the amines with such a strong reductant as **1**. Another attractive feature of the amines is their reduced donating ability [8] as compared with THF or DME and consequently reduced stability of the metal–ligand bond which provides new synthetic capacity to lanthanide complexes. Previously, primary amine was repeatedly used as a component of the reaction mixture in the hydroamination reactions with organolanthanide catalysts (see, for example [9]) but to the best of our knowledge, as a solvent in lanthanide chemistry they were applied only once. Evans and coworkers dissolved $Cp^*_2Sm(THF)_x$ in Bu^tNH_2 and obtained presumably complex $Cp^*_2Sm(Bu^tNH_2)_2$ [10]. There are very few other lanthanide compounds containing coordinately bonded primary amines or similar ligands. Amine-amides of lanthanum and neodymium $Cp^*_2LaNHR(RNH_2)$-(R = Me, Et), $Cp^*_2NdNHEt(EtNH_2)$ were synthesized by reaction of $Cp^*_2LnCH(TMS)_2$ with excess amine RNH_2 in pentane [11]. A similar way was used for the preparation of $Cp^*_2ScNHCH_2C_6H_4OMe(H_2NCH_2C_6H_4OMe)$ [12] and $Cp^*_2CeNH^tBu(H_2N^tBu)$ [13]. Samarium amine-ketimido derivative $Cp^*_2SmN{=}CPh_2(H_2NCHPh_2)$ was obtained from $Cp^*_2Sm(THF)_2$ and benzophenone imine in THF [14]. Perchlorate [15] and triflate [16] lanthanum complexes of composition $LaX_3(H_2NCH_2CH_2NH_2)(MeCN)$ ($X = ClO_4$, CF_3SO_3) were synthesized by treatment of LaX_3 with ethylenediamine in acetonitrile solution. Complexes of lanthanum and ytterbium $Ln(CF_3SO_3)(L)(MeCN)$ with macrocyclic 1,9-bis(2-aminoethyl)-1,4,6,9,12,14-hexaazacyclohexadecane (L) were obtained by refluxing of $Ln(CF_3SO_3)_3$ and $N(CH_2CH_2NH_2)_3$ in MeCN [16].

2. Experimental

2.1. Methods and materials

All manipulations were performed in vacuum using standard Schlenk technique. In the experiments with **1-Nd** and **1-Dy**, any contacts of solvents and reaction mixtures with rubber tubes were excluded because of extremely high sensitivity of formed solutions to admixtures. The diiodies **2** were synthesized by burning of mixtures of shavings of respective lanthanide and iodine powder as described in [17]. All amines (Aldrich) to dry were treated with NdI_2 for 10 min before use and collected in a reaction vessel by condensation in vacuum. Magnetic moments were measured by Faraday method as described previously [18]. IR spectra were obtained on a Specord M-75 and recorded from 4000 to 450 cm^{-1} as a Nujol mull on KBr plates. UV–Vis spectra were recorded with a Perkin–Elmer Lambda 25 spectrometer in a region from 380 to 1100 nm.

2.2. Syntheses

2.2.1. Synthesis of $NdI_2(IPA)_5$(**2-Nd**)

Ten milliliters of IPA was condensed to 0.15 g (0.38 mmol) of **1-Nd** at the temperature of liquid nitrogen and the mixture was allowed to warm to room temperature with stirring. At about −30 °C, the solution acquired blue-violet color and evolution of gas bubbles begun. In a few minutes, visible gas evolution stopped. The mixture was filtered through a glass filter and concentrated to 3 ml. The formed dark violet crystals were separated by decantation and dried in vacuum at ambient temperature for 5 min to yield 0.11 g (42%) of **2-Nd**. Heating of the product in sealed capillary led to its decomposition at 68–74 °C. *Anal.* Calc. for $C_{15}H_{45}I_2N_5Nd$: Nd, 20.83; I 34.80. Found: Nd, 20.79; I, 34.58%. IR: 3464 m, 3166 sh, 3084 sh, 1569 m, 1488 sh, 1395 sh, 1208 w, 1156 m, 794 w, 460 w cm^{-1}; μ_{eff} (293 K) 2.7 μ_B.

2.2.2. Synthesis of $DyI_2(IPA)_4$ (**2-Dy**)

To an ampoule containing 0.42 g (1.01 mmol) of **1-Dy** was condensed 10 ml of IPA at the temperature of liquid nitrogen and the mixture was allowed to warm to room temperature. Beginning from about 0 °C, slow evolution of dihydrogen was observed. In 5 min at room temperature, evolution of gas bubbles stopped. The formed violet solution was stirred for 5 min, filtered through glass filter and IPA was removed from the filtrate by condensation in vacuum to leave 0.17 g (26%) of **2-Dy** as dark violet microcrystalline solid with m.p. 125–127 °C (dec.). *Anal.* Calc. for $C_{12}H_{36}DyI_2N_4$: Dy, 24.89; I, 38.88. Found: Dy, 24.33; I, 38.18%. IR (ν, cm^{-1}): 3470 m, 3170 sh, 3085 sh, 1584 m, 1569 m, 1206 w, 1016 m, 939 m, 809 m, 461 w cm^{-1}.

2.2.3. Synthesis of $TmI_2(IPA)_4$ (**2-Tm**)

Ten milliliters of IPA was added to 0.99 g (2.33 mmol) of **1-Tm** at room temperature and the mixture was stirred for 10 min. The formed dark emerald green solution was filtered and IPA was removed from the filtrate by condensation to leave 1.015 g (80%) dark green crystals of **2-Tm** with m.p. > 115 °C (dec.). *Anal.* Calc. for $C_{12}H_{36}I_2N_4Tm$: Tm, 25.55; I, 38.39. Found: Tm, 25.09; I, 38.78%. IR: 3465 m, 3161 sh, 3073 sh, 1587 m, 1569 m, 1488 sh, 1394 sh, 1261 w, 1207 w, 1155 m, 1031 m, 938 m, 807 m, 460 w cm^{-1}; μ_{eff} (293 K) 4.1 μ_B.

2.2.4. Synthesis of $SmI_2(IPA)_4$ (**2-Sm**)

Stirring of **1-Sm** (1.24 g, 3.07 mmol) in 5 ml of IPA for 20 min resulted in formation of a green solution which was filtered and the solvent was removed in vacuum to give dark green powder of **2-Sm** (0.21 g, 11%); m.p. 131–132 °C (dec.). *Anal.* Calc. for $C_{12}H_{36}I_2N_4Sm$: Sm, 23.47; I, 39.62. Found: Sm, 23.15; I, 39.81%. IR: 3477 m, 3165 sh, 3073 sh, 1585 m, 1567 m, 1487 sh, 1394 sh, 1206 m, 1156 m, 1010 m, 978 w, 940 w, 808 m, 795 w, 460 m cm^{-1}; μ_{eff} (293 K) 3.4 μ_B.

2.2.5. Synthesis of $YbI_2(IPA)_4$ (**2-Yb**)

A greenish-yellow solution obtained after stirring of **1-Yb** (0.412 g, 0.972 mmol) in 7 ml IPA for 20 min was filtered and the solvent evaporated to give **2-Yb** as a greenish-yellow crystalline solid, which was washed with cold IPA and dried in vacuum at ambient temperature for 5 min; yield 0.24 g (37%). Heating of the product to 90 °C in sealed capillary resulted in contraction of the sample, at 200 °C its color changed to yellow. *Anal.* Calc. for $C_{12}H_{36}I_2N_4Yb$: Yb, 26.09. Found: Yb, 26.12%. IR: 3473 m, 3161 sh, 3073 sh, 1584 sh, 1570 m, 1488 sh, 1394 sh, 1208 w, 1158 m, 1015 m, 938 m, 809 w, 462 w cm^{-1}. ^1H NMR (C_6D_6, 200 MHz, 20 °C): δ 1.00 (d, 24H, CH_3, $J = 6.3$), 1.38 (s, 8H, NH_2), 2.97 (sept, 4H, $CHMe_2$, $J = 6.3$).

2.2.6. Synthesis of $EuI_2(IPA)_4$ (**2-Eu**)

Stirring of 0.35 g (0.86 mmol) of **1-Eu** in 15 ml of IPA for 20 min resulted in the formation of a pale yellow-green fluorescent solution which was centrifuged, separated from precipitate and IPA was removed in vacuum. Remaining pale yellow-green crystals were washed with cold IPA and dried at room temperature to give 0.46 g (83%) of **2-Eu**; m.p. 90–95 °C (dec). *Anal.* Calc. for $C_{12}H_{36}EuI_2N_4$: Eu, 23.66; I, 39.52. Found: Eu, 23.60; I, 38.99%. IR: 3477 m, 3161 sh, 3074 sh, 1585 sh, 1569 s, 1488 sh, 1394 sh, 1261 m, 1205 m, 1156 m, 1048 m, 1022 m, 979 w, 941 w, 802 m, 458 w cm^{-1}; μ_{eff} (293 K) 7.4 μ_B.

2.2.7. Synthesis of $(Pr^iNH)DyI_2(IPA)_3$ (**3-Dy**)

A solution of **1-Dy** (0.29 g, 0.7 mmol) in 9 ml of IPA was left for 2 days at room temperature. Gradual decolorization of the initial dark violet solutions was observed. The solution was filtered through glass filter and the solvent was removed in vacuum to leave a colorless precipitate of **3-Dy** which was dried for 5 min at room temperature; yield 0.34 g (75%), m.p. 132–136 °C (dec.). *Anal.* Calc. for $C_{12}H_{35}DyI_2N_4$: Dy, 24.93. Found: Dy, 25.09%. IR: 3281 w, 3219 w, 1562 m, 1160 s, 1030 s, 940 m, 811 m, 530 w, 478 w cm^{-1}.

2.2.8. Synthesis of $(Pr^iNH)NdI_2(IPA)_4$ (**3-Nd**)

A solution of 0.19 g (0.48 mmol) of **1-Nd** in 11 ml IPA was stirred for 50 min at ambient temperature until the initial violet color turned pale blue. Following filtration and removing the solvent, left pale blue oil which was dried in vacuum for 10 min at 30–40 °C and washed with hexane. A formed powder was dried in vacuum at room temperature for 10 min. to give 0.24 g (73%) of **3-Nd**; m.p. 55 °C (dec.). *Anal.* Calc. for $C_{15}H_{44}I_2N_5Nd$: Nd 20.83. Found: Nd, 21.03%. IR: 3280 w, 3217 w, 1562 m, 1245 w, 1160 m, 1030 m, 940 m, 807 m, 525 w, 478 w cm^{-1}; μ_{eff} (293 K) 3.6 μ_B.

2.3. X-ray structural study

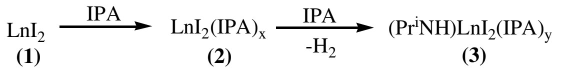
Crystals of **2-Tm** and **2-Eu** were grown from solutions of these salts in IPA by slow removal of the solvent in vacuum at room temperature. Intensity data were collected on a Smart Apex diffractometer (graphite monochromator, Mo Kα radiation, $\varphi - \omega$ scan mode ($\omega = 0.3°$, 10 s on each frame)) Absorption corrections were made by SADABS program [19]. The structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL [20]. All non-hydrogen atoms were refined anisotropically. The H atoms in all complexes were placed in calculated positions and refined in the "riding-model".

Table 3 summarizes the crystal data and some details of the data collection and refinement for **2-Tm** and **2-Eu**.

3. Results and discussion

Studying the chemical behavior of **1-Nd**,**Dy**,**Tm** in various solvents, we have found quite unexpectedly that isopropylamine (IPA) readily dissolves these salts as well as europium, samarium, and ytterbium diiodides. Despite the presence of reactive N–H groups in the amine, stability of the formed solutions is comparable with that in THF. It decreases in a row Eu ⩾ Yb > Sm > Tm > Dy > Nd (Table 1) which corresponds to increasing of reductive potentials of the Ln(II). Solubility of **1** in IPA is somewhat lower than that in THF (0.02–0.03 mol/l). Color of the solutions in IPA mimics the color of THF solutions for all diiodides except **1-Dy** which is khaki-green in THF but violet in IPA. Evaporation of amine from the solutions under vacuum leaves amine complexes of respective diiodide $LnI_2(IPA)_x$ (**2**) (Nd, $x = 5$; Sm, Eu, Dy, Tm, Yb, $x = 4$) as crystalline solids (Table 2). Surprisingly, even less stable Nd and Dy complexes in crystalline state do not change noticeably their color at room temperature over a day. Magnetic measurements indicate that in 24 h only about 10% of neodymium is oxidized to trivalent state. Solid **2-Eu** and **2-Yb** upon heating in sealed capillary, slightly change their appearance at ~90 °C but magnetic measurements reveal that even after 1 h at 100 °C, more than 90% of europium and 50% of ytterbium remain divalent.

Elemental analysis of all obtained compounds and their IR spectra are in good agreement with the formula $LnI_2(IPA)_x$ ($x = 4, 5$). Divalent state of the metals in these products is confirmed by UV/Vis spectra which contain the sets of bends characteristic for responded Ln^{2+} ions [21], magnetic moments and graduate oxidation of **2-Nd**,**Dy** in solutions at room temperature to amides $(Pr^iNH)Ln(IPA)_x$ (**3**) which is manifested as their decolorization (indicated in Table 1 as decomposition).


$$\underset{\mathbf{(1)}}{LnI_2} \xrightarrow{IPA} \underset{\mathbf{(2)}}{LnI_2(IPA)_x} \xrightarrow[-H_2]{IPA} \underset{\mathbf{(3)}}{(Pr^iNH)LnI_2(IPA)_y}$$

2, Ln = Nd, x = 5 ; Sm, Eu, Dy, Tm, Yb, x = 4
3, Ln = Nd, y = 4; Dy, y = 3

Prolonged drying of the complexes **2** in vacuum at ambient temperature leads to reduction of the number of

Table 1
Properties of solutions of LnI_2 (**1**) in IPA

	Nd	Sm	Eu	Dy	Tm	Yb
Color	bluish-violet	emerald green	salad green	violet	emerald green	greenish-yellow
Decomposition time at r.t.	~0.5 h	>4 d	>1 week	~1 d	>3 d	>1 week
UV/Vis (IPA), λ_{max} (ε)	432(19) 530(22) 586(28)	363(7) 437(8) 608(9) 648(10)	355(19)	425(2) 521(9) 650(2) 807(12)	459(12) 525(1.5) 633(6) 737(5)	371(15) 415(31)

Table 2
Properties of crystalline complexes $LnI_2(IPA)_x$ (**2**)

	Nd	Sm	Eu	Dy	Tm	Yb
Color	dark violet	green	pale green	dark violet	dark green	yellow
M.p. (dec.) (°C)	68–74	131–132	90–95	125–127	>115	>90
μ_{eff} (293 K, μ_B)	2.7	3.4	7.4		4.1	diamagnetic

Table 3
Crystallographic data and structure refinement details for **2-Tm** and **2-Eu**

Identification code	**2-Tm**	**2-Eu**
Empirical formula	$C_{12}H_{36}I_2N_4Tm$	$C_{12}H_{36}EuI_2N_4$
Formula weight	659.18	642.21
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	6.9397(6)	12.4537(6)
b (Å)	15.925(1)	12.7147(6)
c (Å)	10.0311(8)	14.3394(7)
β (°)	93.783(2)	
Volume (Å^3)	1106.2(2)	2270.6(2)
Z	2	4
Density$_{calc}$ (Mg/m^3)	1.979	1.879
Absorption coefficient (mm^{-1})	6.798	5.479
$F(000)$	622	1220
Crystal size (mm)	0.24 × 0.12 × 0.08	0.27 × 0.18 × 0.14
θ Range (°)	2.40–24.00	2.14–23.99
Index ranges	$-7 \leqslant h \leqslant 7$, $-16 \leqslant k \leqslant 18$, $-7 \leqslant l \leqslant 11$	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
Reflections collected	5463	16393
Independent reflections [R_{int}]	1732 [0.0249]	3555 [0.0219]
Completeness to theta (%)	99.8	99.8
Absorption correction	SADABS	
Refinement method	full-matrix least-squares on F^2	
Data/restraints/parameters	1732/23/161	3555/3/172
Goodness-of-fit on F	1.063	1.092
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0266$, $wR_2 = 0.0713$	$R_1 = 0.0142$, $wR_2 = 0.0339$
R indices (all data)	$R_1 = 0.0291$, $wR_2 = 0.0729$	$R_1 = 0.0146$, $wR_2 = 0.0340$
Absolute structure parameter		0.005(10)
Largest difference in peak and hole (e Å^{-3})	1.533 and −1.117	0.630 and −0.378

coordinated IPA molecules, however complete removing of it does not occur even at 100 °C.

Attempts to prepare crystals of complexes **2** and **3** suitable for X-ray diffraction analysis were successful in the cases of **2-Tm** and **2-Eu**. The molecule of thulium complex has a structure close to that of regular tetragonal bipyramid with apical iodine atoms and four N atoms in equatorial plane (Fig. 1).

The Tm–N distances (2.532(4)–2.575(3) Å) are close to Tm…N contacts in $[(PhSe)_2Tm(py)_3]_2(\mu\text{-}PhSe)_2$ (2.428–2.489 Å) [22] but essentially longer than valent Tm–N bonds in $\{[(Me_3Si)_2N]_2Tm(THF)\}_2(N_2)$ (2.211–2.295 Å) [23]. Unlike the bent shape of I–Tm–I fragments in the known DME and THF coordinated thulium diiodides $TmI_2(DME)_3$ [2a] and $TmI_2(DME)_2(THF)$ [2b] in the compound **2**(Tm), this grouping is linear: I–Tm–I angle is 180.000(10)°.

Molecular structure of europium iodide **2-Eu** (Fig. 2) also can be described as tetragonal bipyramid but essentially distorted. The atoms of N(4) and I(1) occupy apical

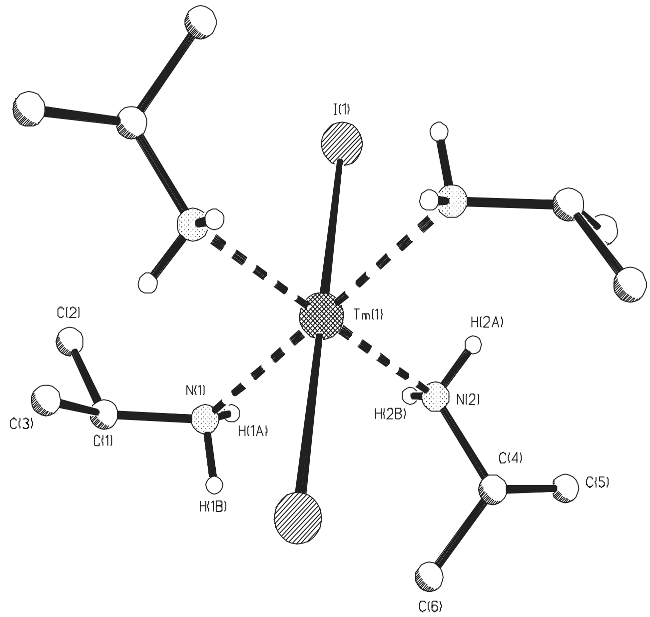


Fig. 1. Molecular structure of complex **2-Tm**; selected bond lengths (Å) and angles (°): Tm(1)–I(1) 3.1325(3), Tm(1)–I(2) 3.1325(3), Tm(1)–N(1) 2.575(3), Tm(1)–N(1′) 2.532(4), Tm(1)–N(2) 2.547(2), N(1)–Tm(1)–N(2) 180.0(4), N(1)–Tm(1)–N(3) 91.84(16), N(1)–Tm(1)–N(4) 88.16(16), N(1′)–Tm(1)–I(1) 72.20(14), N(2)–Tm(1)–I(1) 81.87(5).

positions in this case. The N(4)–Eu(1)–I(1) angle, which is the biggest angle in coordination sphere of Eu atom, is 169.99(7)° whereas the I(1)–Eu–I(2) angle is 101.377(8)°.

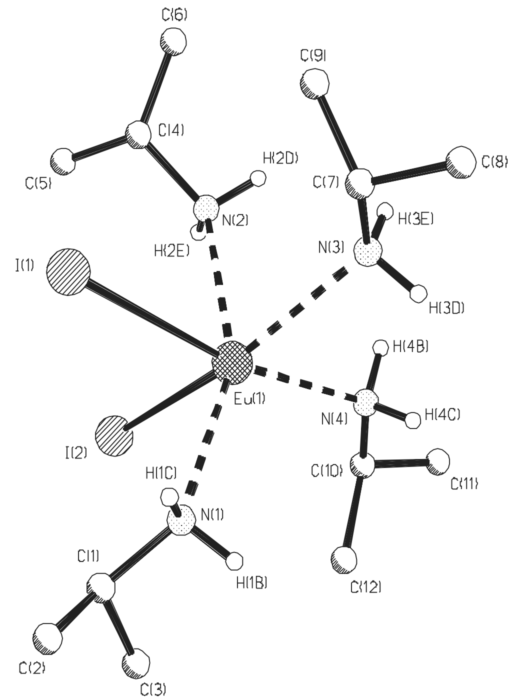


Fig. 2. Molecular structure of complex **2-Eu**; selected bond lengths (Å) and angles (°): Eu(1)–N(4) 2.651(3), Eu(1)–N(3) 2.678(3), Eu(1)–N(1) 2.682(3), Eu(1)–N(2) 2.697(3), Eu(1)–I(1) 3.2850(3), Eu(1)–I(2) 3.2860(3); N(3)–Eu(1)–I(1) 92.09(6), N(1)–Eu(1)–I(1) 74.08(7), N(2)–Eu(1)–I(1), 86.59(7), N(3)–Eu(1)–I(2) 155.24(6)°, N(4)–Eu(1)–I(2) 86.43(8), N(1)–Eu(1)–I(2) 91.37(7), N(2)–Eu(1)–I(2) 77.61(7), N(4)–Eu(1)–N(2) 89.02(11).

The Eu–I bonds 3.2850(3) and 3.2860(3) Å are somewhat longer than the same distances in the known complex $EuI_2(THF)_5$ [24] (3.230, 3.231 Å) but shorter than in the other analogue $EuI_2(DME)_3$ [25] (3.343, 3.370 Å). Note, the molecules of both these diiodides have bipyramidal shape with I atoms in apical positions. The Eu–N contacts in **2-Eu** from 2.651(3) to 2.697(3) Å are noticeably longer than the coordination Eu–N bonds in the dimer $[EuI(\mu\text{-}I)(N\text{-}MeIm)_3]_2$ [26] (*N*-MeIm – *N*-methylimidazole) (2.582, 2.610, 2.614 Å) which probably indicates weaker Eu...N interaction in the IPA complex.

Behavior of the iodides **1** solutions in IPA is similar to that in THF or DME including the most unusual property: sensitivity of the solutions of **1**(Nd, Dy), but not other iodides **1**, towards aromatic compounds which dramatically accelerate their decompositions [27]. *n*-Propylamine like IPA dissolves the diiodides **1-Sm**,**Eu**,**Dy**,**Tm**,**Yb** to give solutions of appropriate color but essentially less stable. Neodymium salt **1-Nd** vigorously reacts with Pr^nNH_2 even at −30 °C which hampers the formation of the solution. It should be noted that dissolving of **1-Dy** in Pr^nNH_2 as well as dissolving of **1-Nd**,**Dy** in IPA is also accompanied by dihydrogen evolution but these reactions proceed pretty slowly. The solutions of **1-Nd**,**Dy**,**Tm**,**Sm** in $MeNH_2$, Bu^tNH_2, and $PhNH_2$ cannot be obtained because of fast amidation reactions. Weaker reductant **1-Eu,Yb** are inert towards Bu^tNH_2 and are not dissolved in it. Secondary amines Et_2NH, $(Me_3Si)_2NH$ and tertiary amine Et_3N do not dissolve and do not interact with the **1-Nd**,**Dy**,**Tm**. Reducing solubility of **1**, on going from liquid NH_3 to amines does not seem surprising since hydrocarbon radicals in the latter formally decrease in the medium concentration of donating N atoms stipulating solubility of the salts. On the contrary, dependence of reactivity of amines towards reductants **1** on the radicals R in RNH_2 is not so clear. Taking into account steady increase of positive inductive and steric effects of R groups and basic capacity of the amines [8] in a row $R = H > Me > Pr^n > Pr^i > Bu^t$ one can expect that the less reactive would be Bu^tNH_2. However this amine revealed higher reactivity than IPA and even Pr^nNH_2. The only possible explanation of the phenomena would be specific coordination interaction of Bu^tNH_2 with the surface of solid **1**. The bulky Bu^t groups do not allow to form close Ln–N contacts and consequently generation of the complexes of $LnI_2(Bu^tNH_2)_n$ type but they do not prevent from the redox reaction between NH_2 groups and Ln(II) atoms in the crystalline lattice of diiodide **1**.

4. Summary remarks

The found capability of IPA to dissolve diiodides **1** has shown that the homogeneous reactions with participation of these salts can be conducted not only in etheric solvents. With example of DyI_3, Cp_3Nd, Cp_2DyI, Cp_2M (M = V, Cr, Fe, Ni) we have found as well that IPA is a suitable solvent for triiodides LnI_3, cyclopentadienyl complexes of lanthanides and d-transition metals. Of cause, the presence of active N–H groups in IPA superimpose some restrictions on application of the amine as reaction medium, however isolation of divalent complexes **2-Nd** and **2-Dy** reveals that even strong reductants could be used in these reactions. Furthermore, enhanced stability of complexes **2** in solid sate as compared with their THF and DME analogues allow to suppose that IPA can be applied as coordinating ligand for preparation of other highly reactive lanthanide complexes. It should be noted that preliminary investigations revealed that **2-Nd**,**Dy** are effective precatalysts of hydroamination of acetonitrile by IPA leading to mono-N-substituted amidine $\mathrm{MeC(NHPr}^i) = \mathrm{NH}$ in contrast to most other catalysts which afford disubstituted products [28]. Further investigations of chemical properties of the complexes **2** are under progress.

5. Supplementary material

CCDC-288178 (**2-Tm**) and 299176 (**2-Eu**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK, fax: (internat.) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk.

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