

Syntheses and Crystal Structures of Anionic Lanthanide Chloride Complexes $[(\text{CH}_3)_2\text{NH}_2][\text{LnCl}_4(\text{HMPA})_2]$ ($\text{Ln} = \text{La}, \text{Nd}$) and $[(\text{CH}_3)_2\text{NH}_2]_4[\text{LnCl}_6]\text{Cl}$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}$)

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Abstract

Reactions of lanthanide oxides, hexamethylphosphoramide (HMPA), chlorotrimethylsilane and water in tetrahydrofuran (THF) afforded new complexes $[(\text{CH}_3)_2\text{NH}_2][\text{LnCl}_4(\text{HMPA})_2]$ ($\text{Ln} = \text{La}$ (1), Nd (2)) and $[(\text{CH}_3)_2\text{NH}_2]_4[\text{LnCl}_6]\text{Cl}$ ($\text{Ln} = \text{Nd}$ (3), Sm (4), Eu (5)). Lanthanide oxides react with *in situ* formed HCl, while the cations $[(\text{CH}_3)_2\text{NH}_2]^+$ are formed by the hydrolysis of HMPA with the cleavage of P–N bonds. The X-ray crystal structures of the complexes 1–5 are reported. The complexes 1 and 2 are the first known compounds with HMPA coordinated to a lanthanide in an anion.

Key words: crystal structure, lanthanide chloride complexes, P–N bond cleavage, anionic complexes

Introduction

Complexes of lanthanide halides with HMPA were well investigated in the past due to the catalytic activity of lanthanide(II) complexes with HMPA in reduction of organic functional groups. Addition of HMPA to SmI_2 accelerates rate of reduction of organic halides by SmI_2 and provides increased diastereoselectivities in wide range of reactions.¹ The reactivity of species depends upon redox potential and substrate access to the metal center. Determination of crystal structures of lanthanide complexes with HMPA, their stability and possibility of ligand displacement is crucial for a better understanding of these processes.²

Molecules of HMPA and anionic ligands are coordinated to lanthanide ion achieving mononuclear molecules or cations in the known complexes. Crystal structures of the complexes depend upon basicity of anions coordinated to a lanthanide and reaction conditions. Strong coordination bonds formed with chloride or isocyanate ligands favour formation of the molecular complexes $[\text{LnCl}_3(\text{HMPA})_3]$,^{3–6} $[\text{La}(\text{NCS})_3(\text{HMPA})_4]$ ⁷ and $[\text{CeCl}_4(\text{HMPA})_2]$.⁸ Cationic complexes are usually formed with weaker ligands as bromide, iodide or trifluoromethanesulfonate (OTf): $[\text{LnBr}_2(\text{HMPA})_4]\text{Br}\cdot 0.5\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Sm}$),⁹ $[\text{SmBr}_2(\text{HMPA})_4]\text{Br}\cdot \text{THF}$,¹⁰ $[\text{SmI}_2(\text{HMPA})_4]\text{I}\cdot (\text{CHCl}_3)_2$,¹¹ $[\text{Sm}(\text{HMPA})_3(\text{H}_2\text{O})_4]\text{I}_3$, $[\text{Sm}(\text{HMPA})_2(\text{H}_2\text{O})_5]\text{I}_3$

$\cdot(\text{HMPA})_2$,¹² and $[\text{Ln}(\text{OTf})_2(\text{HMPA})_4]\text{OTf}\cdot \text{CHCl}_3$.¹³ Reaction conditions have also an important influence on the structure of products. Reactions in the presence of air moisture resulted in cationic complexes even if strong anions as chloride are used: $[\text{SmCl}(\text{HMPA})_2(\text{H}_2\text{O})_4]\text{Cl}_2\cdot \text{THF}$ and $[\text{Yb}(\text{HMPA})_2(\text{H}_2\text{O})_5]\text{Cl}_3\cdot \text{HMPA}\cdot \text{H}_2\text{O}$.⁵ Medium strong anion, such as bromide, form the molecular complex $[\text{SmBr}_3(\text{HMPA})_2(\text{THF})]^{10}$ at the appropriate molar ratio of samarium to HMPA. Molecular complexes can be prepared also with weak anions like OTf[–], if appropriate starting compounds are used. For example, $[\text{Sm}(\text{OTf})_3(\text{HMPA})_3(\text{H}_2\text{O})]\cdot \text{C}\cdot \text{HCl}_3$ could be prepared from HMPA and anhydrous $\text{Sm}(\text{OTf})_3$.¹⁴

There is no evidence of lanthanide complexes with HMPA coordinated to a lanthanide in an anion in the literature despite an extensive research of these systems. Preparation and characterisation of anionic lanthanide chloride complexes $[\text{LnCl}_4(\text{HMPA})_2]^-$ are presented in this article.

Isolated anions $[\text{LnCl}_6]^{3-}$ are characteristic for many complexes of smaller, heavier lanthanides like $[(\text{CH}_3)_2\text{NH}_2]_4[\text{LnCl}_6]\text{Cl}$ ($\text{Ln} = \text{Ho}, \text{Er}, \text{Tm},^{15} \text{Yb}$)¹⁶ or $[(\text{CH}_3)\text{Py}]_3[\text{LnCl}_6]$ ($\text{Ln} = \text{Dy},^{17} \text{Tb}$),¹⁸ while larger, lighter lanthanides tend to form dimers or chains to achieve a coordination number higher than six. For example, six chlorides and two waters are coordinated to each praseodymium in the anions $[\text{PrCl}_4(\text{H}_2\text{O})_2]^-$, which

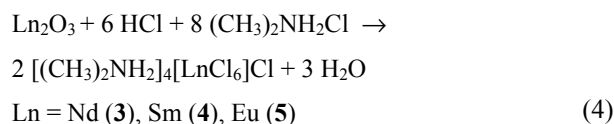
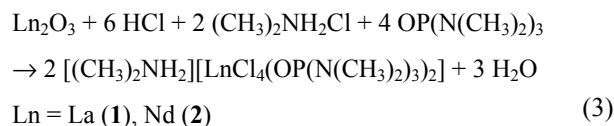
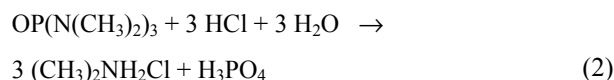
are connected by chlorine bridges into chains.¹⁹ Isolated $[\text{LnCl}_6]^{3-}$ anions of lighter lanthanides are known in $[(\text{C}_6\text{H}_5)_3\text{PH}]_3[\text{PrCl}_6]^{20}$ and $[\text{Nd}(\text{EO}_4)_2]_4[\text{NdCl}_6]\text{Cl}_9$ (EO_4 = tetraethylene glycol).²¹ A combination of isolated $[\text{NdCl}_6]^{3-}$ ions and $[\text{NdCl}_4(\text{H}_2\text{O})_2]^-$ chains bridged by chlorides was observed in $[\text{CH}_3\text{NH}_3]_8[\text{NdCl}_4(\text{H}_2\text{O})_2]_2[\text{NdCl}_6]\text{Cl}_3$.²²

Syntheses and crystal structures of neodymium, samarium or europium compounds isotopic to $[(\text{CH}_3)_2\text{NH}_2]_4[\text{LnCl}_6]\text{Cl}$ ($\text{Ln} = \text{Ho}, \text{Er}, \text{Tm}, ^{15} \text{Yb}$)¹⁶ are described in this article.

Results

Syntheses

Products **1**, **2**, **3**, **4**, **5** and $[\text{HOP}(\text{N}(\text{CH}_3)_2)_3]\text{Cl}$ were isolated in the one pot synthesis from Ln_2O_3 , HMPA (written as $\text{OP}(\text{N}(\text{CH}_3)_2)_3$ in the reactions), $(\text{CH}_3)_3\text{SiCl}$ and water in THF. The proposed reactions in the suspension are:



The excess of $(\text{CH}_3)_3\text{SiCl}$ guarantees a complete consumption of water and *in situ* formation of HCl (Reaction 1). $[(\text{CH}_3)_2\text{NH}_2]^+$ is a product of P–N bond cleavage in HMPA in a presence of HCl (Reaction 2), as hydrogen halides are known to cleave P–N bonds in phosphoryl amino derivatives.²³ Ln_2O_3 reacts with HCl and $[(\text{CH}_3)_2\text{NH}_2]\text{Cl}$ according to the reactions 3 and 4 resulting in the precipitated complexes **1**, **2** and in the soluble compounds **3**, **4** and **5**. The complexes **1** and **2** were recrystallized from THF. In the cooled reaction solutions grew big crystals of $[\text{HOP}(\text{N}(\text{CH}_3)_2)_3]\text{Cl}$ (Reaction 5), which were filtered off and later at room temperature the compounds **3**, **4** and **5** crystallized from these solutions during a slow evaporation. The unit cell

determined for a selected crystal of $[\text{HOP}(\text{N}(\text{CH}_3)_2)_3]\text{Cl}$ was the same as reported in the literature.²⁴

Molecules of HMPA are involved in three processes in the reaction system: coordination of the molecules to a lanthanide, protonation resulting in $[\text{HOP}(\text{N}(\text{CH}_3)_2)_3]^+$ and hydrolysis. The hydrolysis of HMPA affording dimethylammonium chloride provides free chloride ions contributing to the formation of the ionic complexes **1** and **2** instead of molecular ones. The complexes **1** and **2** are the first known compounds with HMPA coordinated to a lanthanide in an anion. In the products **1** and **2** are four chloride ions coordinated to the lanthanide ion on contrary to three in the molecular complexes $[\text{LnCl}_3(\text{HMPA})_3]$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$), which were prepared from HMPA and $[\text{LnCl}_3(\text{DME})_x]^{6,25}$ or LnCl_3 .³

Crystal structures of the compounds **1** and **2**

The complexes **1** and **2** (Figure 1) are isomorphous, consisting of cation $[(\text{CH}_3)_2\text{NH}_2]^+$ and anion $[\text{LnCl}_4(\text{HMPA})_2]^-$. Four chlorides and two oxygen atoms from HMPA molecules are octahedrally coordinated to a lanthanum or a neodymium ion in $[\text{LnCl}_4(\text{HMPA})_2]^-$. It is interesting that HMPA ligands are in *cis* configuration on contrary to *trans* configuration of less bulky THF ligands in similar coordination anions $[\text{LnCl}_4(\text{THF})_2]^-$ ($\text{Ln} = \text{Er}, ^{26} \text{Dy}$).²⁷

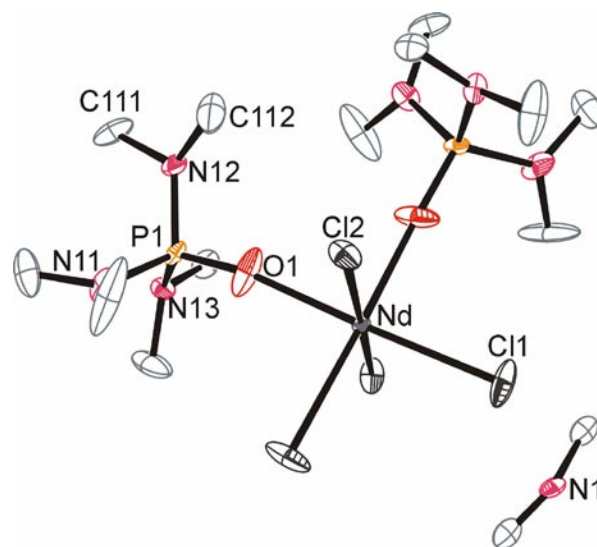


Figure 1. $[(\text{CH}_3)_2\text{NH}_2]^+$ and $[\text{NdCl}_4(\text{HMPA})_2]^-$ ions in the complex **2** with the numbering scheme adopted also in the complex **1**. Hydrogen atoms are omitted for clarity.

The interatomic distances in **1** and **2** listed in Table 1 vary as expected for the lanthanide contraction from lanthanum to neodymium.²⁸

Table 1. Selected bond distances (Å) and interatomic angles (°) in the complexes **1** and **2**.

| bond | La - 1 | Nd - 2 |
|------------------|---------------|---------------|
| Ln – Cl1 | 2.779(2) | 2.715(2) |
| Ln – Cl2 | 2.814(1) | 2.755(1) |
| Ln – Cl aver. | 2.79(2) | 2.73(2) |
| Ln – O1 | 2.351(4) | 2.300(5) |
| P1 – O1 | 1.498(5) | 1.493(5) |
| P1 – N11 | 1.624(4) | 1.628(5) |
| P1 – N12 | 1.631(4) | 1.629(5) |
| P1 – N13 | 1.641(4) | 1.641(5) |
| angle | | |
| Cl1 – Ln – Cl2 | 91.82(4) | 91.89(5) |
| Cl1 – Ln – O1 | 90.1(1) | 89.9(1) |
| Cl1 – Ln – Cl1_a | 92.29(5) | 92.15(6) |
| Cl1 – Ln – O1_a | 177.4(2) | 177.7(1) |
| Cl2 – Ln – O1 | 90.1(1) | 89.7(1) |
| Cl2 – Ln – Cl2_a | 176.09(5) | 175.55(6) |
| Cl2 – Ln – O1_a | 87.0(1) | 87.1(1) |
| O1 – Ln – O1_a | 87.5(2) | 88.1(2) |

The average Ln–Cl distances in the anions of **1**, **2** are longer than expected according to Pr–Cl distances in the molecular *mer*-[PrCl₃(HMPA)₃] (2.72(1) Å),³ if only ionic radii of the lanthanides are considered. The observed increase in Ln–Cl distances in the anionic complexes comparing to the molecular one could be explained by a negative partial charge on the lanthanides. The La–O distance in compound **1** is only slightly shorter than in the anion of [LaBr₂(HMPA)₄][−] (2.364(4)–2.380(4) Å).⁹ Anions [LnCl₄(HMPA)₂][−] and dimethylammonium cations are connected into chains by Cl1...H–N1 and Cl2...H–N1 hydrogen bonds.

Crystal structures of the compounds **3**, **4** and **5**

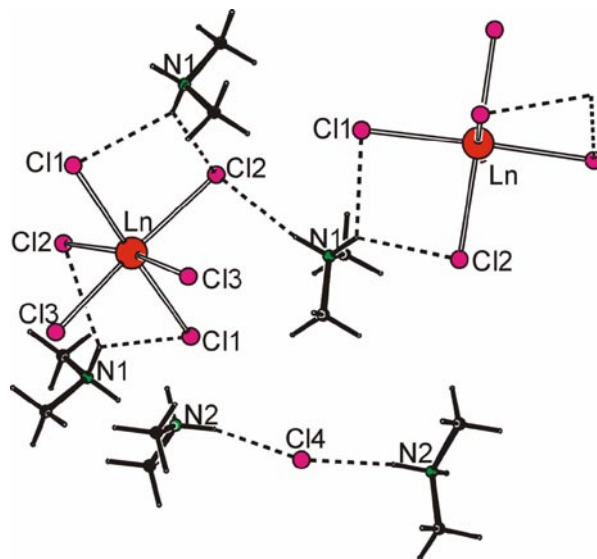
The X-ray crystal structures of the compounds **3**, **4** and **5** confirm the presence of [(CH₃)₂NH₂]⁺, [LnCl₆]^{3−} (Ln = Nd, Sm, Eu) and Cl[−] ions, similar as in compounds [(CH₃)₂NH₂]₄[MCl₆]Cl reported in the literature for some trivalent transition metals (M = Cr, Rh,²⁹ Mo)³⁰ and some heavier lanthanides (M = Ho, Er, Tm).¹⁵ Six chlorides are coordinated to a neodymium, samarium or europium ion in these compounds in a form of slightly distorted octahedron as shown by Cl–Ln–Cl angles in Table 2.

Table 2. Selected bond distances (Å) and interatomic angles (°) in the complexes **3**, **4** and **5**.

| bond | Nd - 3 | Sm - 4 | Eu - 5 |
|--------------------|---------------|---------------|---------------|
| Ln – Cl1 | 2.7157(4) | 2.6888(6) | 2.6756(4) |
| Ln – Cl2 | 2.7229(4) | 2.6922(7) | 2.6799(5) |
| Ln – Cl3 | 2.7067(5) | 2.6806(8) | 2.6681(6) |
| angle | | | |
| Cl – Ln – Cl min. | 83.35(2) | 84.12(2) | 84.24(2) |
| Cl – Ln – Cl max.* | 101.56(1) | 100.76(2) | 100.19(2) |

* The maximal interatomic angle involving two neighbouring chlorides.

Nd–Cl interatomic distances in the complex **3** (Table 2) are in the same range as the shortest Nd–Cl distances in the complex **2** (Table 1). The longer distance from neodymium to the chloride Cl2 in the complex **2** reflect the greater bulkiness of HMPA in comparison to chlorides.³¹ Similar Nd–Cl interatomic distances as in **3** are reported for [NdCl₆]^{3−} ions in [CH₃NH₃]₈[NdCl₄(H₂O)₂]₂[NdCl₆]Cl₃ (2.706(2)–2.716(2) Å)²² and [Nd(EO₄)₂]₄[NdCl₆]Cl₉ (2.73(1) Å).²¹ Ln–Cl bond distances in **4** (Table 2) are similar as in *fac*-[SmCl₃(HMPA)₃] (2.657(8)–2.680(7) Å)⁶ and in **5** in the same range as in [HPy]₂[EuCl₃Py] (2.650(2)–2.672(2) Å),³³ while longer average Ln–Cl distances were reported for anions [LnCl₆]^{3−} in [2,4,6-Trimethylpyridinium]₃[LnCl₆] (Sm–Cl 2.759 and Eu–Cl 2.693 Å).³² Hydrogen bonds in the complexes **3**, **4** and **5** are shown in Figure 2, while distances between nitrogen and chlorides participating in these bonds are listed in Table 3. Hydrogen atoms bonded to N1 are involved in N1–H...Cl1 and N1–H...Cl2 hydrogen bonds connecting [LnCl₆]^{3−} octahedrons and [(CH₃)₂NH₂]⁺ to anionic layers [(CH₃)₂NH₂]₂[LnCl₆][−]. Hydrogen atoms bonded to N2 are involved in N2–H...Cl4 hydrogen bonds connecting isolated chloride Cl4 and [(CH₃)₂NH₂]⁺ to [(CH₃)₂NH₂]₂Cl⁺ units, which are between the anionic layers.

**Figure 2.** Hydrogen bonds in the complexes **3**, **4** and **5**. The same numbering scheme is adopted in all complexes.**Table 3.** Distances (Å) between nitrogen and chlorides participating in hydrogen bonds in the compounds of **3**, **4** and **5**.

| | Ln = Nd | Ln = Sm | Ln = Eu |
|--------------|----------|----------|----------|
| N1 – H...Cl1 | 3.267(2) | 3.264(3) | 3.263(2) |
| N1 – H...Cl2 | 3.291(2) | 3.288(3) | 3.288(2) |
| N1 – H...Cl2 | 3.342(2) | 3.343(3) | 3.343(2) |
| N2 – H...Cl4 | 3.045(2) | 3.047(3) | 3.047(2) |

Conclusions

The reactions in the suspension of lanthanide oxides in THF, HMPA, trichlorotrimethylsilane and water afforded new anionic complexes of lanthanide chlorides. HCl formed *in situ* from trichlorotrimethylsilane and water causes a cleavage of P–N bonds in HMPA and the formation of $[(\text{CH}_3)_2\text{NH}_2]\text{Cl}$. The suspended lanthanide oxides react with hydrogen chloride, resulted predominately in precipitated $[(\text{CH}_3)_2\text{NH}_2][\text{LnCl}_4(\text{HMPA})_2]$ and partly in soluble $[\text{LnCl}_6]^{3-}$. In the HMPA complexes obtained in investigated systems four chloride ions and two molecules of HMPA are coordinated to the central lanthanide ion instead of only three chlorides in molecular $[\text{LnCl}_3(\text{HMPA})_3]$. The molecular complexes $[\text{LnCl}_3(\text{HMPA})_3]$ were prepared from anhydrous lanthanide chlorides³ or $[\text{LnCl}_3(\text{DME})_2]$ ⁶ by addition of HMPA to the solvent. The formation of anionic complexes $[\text{LnCl}_4(\text{HMPA})_2]^-$ could be explained by an excess of free chloride ions provided by the hydrolysis of HMPA which resulted in dimethylammonium chloride.

Isolated anions $[\text{LnCl}_6]^{3-}$ of lighter lanthanides were crystallized as $[(\text{CH}_3)_2\text{NH}_2]_4[\text{LnCl}_6]\text{Cl}$ (Ln = Nd, Sm, Eu), which are isotopic to the compounds of some heavier lanthanides (Ln = Ho, Er, Tm¹⁵ and Yb).¹⁶

Experimental

General

All the manipulations were carried out under an atmosphere of purified argon. Lanthanide oxides (Aldrich, 99.99%), chlorotrimethylsilane (Aldrich, 97%), HMPA (Aldrich, 99%) were used as received, THF was dried over Na/K alloy. The solvents were distilled before use.

The suspensions of ground samples in nujol were prepared in a dry box. IR spectra were recorded on a Perkin Elmer 1720X instrument between 400 and 4000 cm^{-1} .

The lanthanide content was determined by a gravimetric analysis. The complexes were dissolved, precipitated as oxalates, which decompose at higher temperatures to lanthanide oxides. Elemental analyses were obtained by a Perkin-Elmer 2400 CHN analyser at University of Ljubljana (Department of Organic Chemistry).

The ¹H NMR spectra were recorded on a Bruker DPX 300 spectrometer.

Syntheses

$[(\text{CH}_3)_2\text{NH}_2][\text{LaCl}_4(\text{HMPA})_2] - 1$

30 mL of THF, 1.97 g (11.0 mmol) of HMPA, 13.99 g (129 mmol) of $(\text{CH}_3)_3\text{SiCl}$ and 0.090 g (5.0 mmol) of water were added to 0.330 g (1.01 mmol) of La_2O_3 . The suspension was stirred for one day, the solution was

decanted and the solid residual dried in vacuo. 1.11 g (80% yield) of the complex **1** was gained. Anal. Calcd for $\text{C}_{14}\text{H}_{44}\text{Cl}_4\text{N}_7\text{LaO}_2\text{P}_2$: H 6.47, C 24.54, N 14.31, La 20.3. Found: H 6.42, C 24.32, N 14.20, La 20.1. IR (Nujol): 1298 s, 1186 m, 1143 m, 1119 s, 1071 w, 987 vs, 874 w, 802 w, 758 s, 482 m cm^{-1} . ¹H NMR, (300 MHz, CDCl_3) δ 9.00 (s, 2H, $(\text{CH}_3)_2\text{NH}_2^+$), 2.79 (t, 6H, $(\text{CH}_3)_2\text{NH}_2^+$), 2.72, J(PH) 9 Hz (d, 36H, HMPA).

Colourless crystals of the complex **1** grew out of the THF solution during a slow evaporation of the solvent.

$[(\text{CH}_3)_2\text{NH}_2][\text{NdCl}_4(\text{HMPA})_2] - 2$

25 mL of THF, 1.07 g (5.98 mmol) of HMPA, 12.17 g (112 mmol) of $(\text{CH}_3)_3\text{SiCl}$ and 0.090 g (5.0 mmol) of water were added to 0.340 g (1.01 mmol) of Nd_2O_3 . The suspension was stirred for one day, the solution was decanted and the solid residual dried in vacuo 1.13 g (81% yield) of the complex **2** was gained. Anal. Calcd For $\text{C}_{14}\text{H}_{44}\text{Cl}_4\text{N}_7\text{NdO}_2\text{P}_2$: H 6.42, C 24.35, N 14.20, Nd 20.9. Found: H 6.23, C 24.22, N 14.00, Nd 21.0. IR (Nujol): 1301 s, 1191 s, 1167 m, 1123 vs, 1065 m, 1013 s, 987 vs, 870 w, 802 w, 753 m, 613 w, 483 m, 454 w cm^{-1} .

Bright, pale blue crystals grew out of the THF solution during a slow evaporation of the solvent.

$[(\text{CH}_3)_2\text{NH}_2]_4[\text{NdCl}_6]\text{Cl} - 3$

18 mL of THF, 2.29 g (12.8 mmol) of HMPA, 12.34 g (114 mmol) of $(\text{CH}_3)_3\text{SiCl}$ and 0.090 g (5.0 mmol) of water were added to 0.340 g (1.01 mmol) of Nd_2O_3 . The suspension was stirred for one day, then the blue solution was filtered off. A lot of white crystals of $[\text{HOP}(\text{N}(\text{CH}_3)_2)\text{Cl}]$ grew out of the solution at 4 °C, but the solution was still coloured. The blue solution was separated from the white crystals. Pale blue crystals of the complex **3** (yield less than 10%) grew during a slow evaporation of the solution at room temperature. Anal. Calcd for $\text{C}_8\text{H}_{32}\text{Cl}_7\text{N}_4\text{Nd}$: H 5.59, C 16.66, N 9.71. Found: H 5.51, C 16.61, N 9.72. IR (Nujol): 3166 m, 1569 w, 1154 w, 1013 m, 888 w, 836 w, 810 w cm^{-1} .

$[(\text{CH}_3)_2\text{NH}_2]_4[\text{SmCl}_6]\text{Cl} - 4$

30 mL of THF, 1.17 g (6.53 mmol) of HMPA, 14.07 g (130 mmol) of $(\text{CH}_3)_3\text{SiCl}$ and 0.120 g (6.67 mmol) of water were added to 0.440 g (1.26 mmol) of Sm_2O_3 . The suspension was stirred for one day, then the solution was filtered off. A lot of large white crystals of $[\text{HOP}(\text{N}(\text{CH}_3)_2)\text{Cl}]$ grew out of the solution at 4 °C. After removal of the white crystals of $[\text{HOP}(\text{N}(\text{CH}_3)_2)\text{Cl}]$ colourless crystals of the complex **4** (yield less than 10%) grew during a slow evaporation of the solution at room temperature. Anal. Calcd for $\text{C}_8\text{H}_{32}\text{Cl}_7\text{N}_4\text{Sm}$: H 5.53, C 16.48, N 9.61. Found: H 5.36, C 16.69, N 9.47. IR (Nujol): 3160 w, 1570 w, 1028 m, 889 w, 810 w cm^{-1} .

$[(CH_3)_2NH_2]_4[EuCl_6]Cl - 5$

35 mL of THF, 0.988 g (5.51 mmol) of HMPA, 11.63 g (107 mmol) of $(CH_3)_3SiCl$ and 0.080 g (4.44 mmol) of water were added to 0.310 g (0.88 mmol) of Eu_2O_3 . The suspension was stirred for one day, then the solution was filtered off. A lot of large white crystals of $[HOP(N(CH_3)_2)Cl]$ grew out of the solution at 4 °C. After removal of the white crystals of $[HOP(N(CH_3)_2)Cl]$ colourless crystals of the complex **5** (yield less than 10%) grew during a slow evaporation of the solution at room temperature. Anal. Calcd for $C_8H_{32}Cl_7EuN_4$: H 5.52, C 16.44, N 9.59. Found: H 5.46, C 16.40, N 9.41.

Crystal structure determination

The details of the crystal data collections and refinement parameters are listed in Table 4 (compounds **1**, **2**) and Table 5 (compounds **3**, **4**, **5**). All studied compounds were hygroscopic. The crystals were greased on a glass thread. Diffraction data were collected on a Nonius Kappa CCD diffractometer with a CCD area detector at 150(2) K. A graphite monochromatic $Mo K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) was employed in all measurements. The structures were solved by direct methods implemented in SHELXS-97³⁴ and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97)³⁵ included to WinGX v1.70.01.³⁶ All non-hydrogen atoms were refined anisotropically, while all the hydrogen atoms in compounds **2**, **3**, **4** and **5** were included in the model at geometrically calculated positions and refined using a riding model. Only the two hydrogen atoms bonded to nitrogen in $[NH_2(CH_3)_2]^+$ in the compound **1** were located from a ΔF synthesis

and included in the refinement at calculated positions with the isotropic displacement parameters of 1.2 times the U_{eq} value of the respective nitrogen atom. Nitrogen atoms in $[NH_2(CH_3)_2]^+$ ions of the compounds **1** and **2** are in two disordered positions, each site occupied by a half. The absolute structures were determined for the compounds **3** and **4**, while racemic twinning (Flack parameter 0.288(6)) was considered in the refinement of the compound **5**.

Table 4. Crystallographic data, data collection and structure refinement data of the compounds **1** and **2**.

| | 1 | 2 |
|---|--|--|
| Chemical formula | $C_{14}H_{44}Cl_4N_7LaO_2P_2$ | $C_{14}H_{44}Cl_4N_7NdO_2P_2$ |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $C2/c$ (No. 15) | $C2/c$ (No. 15) |
| <i>a</i> , <i>b</i> , <i>c</i> [Å] | 17.5692(2) 10.8556(2) 16.1248(2) | 17.5464(5) 10.7820(3) 16.0462(5) |
| α , β , γ [°] | 90, 98.761(1), 90 | 90, 99.105(2), 90 |
| <i>V</i> [Å ³] | 3039.51(8) | 2997.46(15) |
| <i>Z</i> | 4 | 4 |
| <i>D</i> _{calc} [g/cm ³] | 1.497 | 1.530 |
| μ (MoK α) [mm ⁻¹] | 1.885 | 2.2 |
| Crystal colour | colourless | light blue |
| Crystal Size [mm] | 0.18 × 0.14 × 0.14 | 0.08 × 0.05 × 0.05 |
| θ range [°] | 3.24, 27.45 | 3.26, 27.47 |
| Data meas., unique | 6519, 3462 | 6140, 3420 |
| Data used, threshold | 3090, [$I > 2.0\sigma(I)$] | 2446, [$I > 2.0\sigma(I)$] |
| <i>R</i> _{int} | 0.0179 | 0.0489 |
| Number of parameters | 154 | 152 |
| <i>R</i> ^a (observed), <i>R</i> _w ^b , <i>S</i> | 0.0379, 0.0832, 1.083 | 0.0462, 0.0782, 1.054 |
| Max./min. res. el. | 1.14, -1.06 | 0.85, -0.70 |
| dens.[e/Å ³] | | |

$$^a R = (|F_o| - |F_c|) / |F_o|, \quad ^b wR_2 = ((w(F_o^2 - F_c^2)^2) / (wF_o^2)^2)^{1/2}.$$

Table 5. Crystallographic data, data collection and structure refinement data of the compounds **3**, **4** and **5**.

| | 3 | 4 | 5 |
|--|---------------------------------------|---------------------------------------|---------------------------------------|
| Chemical formula | $C_8H_{32}Cl_7N_4Nd$ | $C_8H_{32}Cl_7N_4Sm$ | $C_8H_{32}Cl_7EuN_4$ |
| Crystal System | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12$ (No. 18) | $P2_12_12$ (No. 18) | $P2_12_12$ (No. 18) |
| <i>a</i> , <i>b</i> , <i>c</i> [Å] | 8.6883(1) 10.3508(2) 13.3495(2) | 8.6909(1) 10.3378(2) 13.2640(2) | 8.6965(1) 10.3204(1) 13.2304(2) |
| <i>V</i> [Å ³] | 1200.53(3) | 1191.70(3) | 1187.45(3) |
| <i>Z</i> (space group/ formula) | 4/2 | 4/2 | 4/2 |
| <i>D</i> _{calc} [g/cm ³] | 1.596 | 1.624 | 1.635 |
| μ (MoK α) [mm ⁻¹] | 2.9 | 3.2 | 3.4 |
| Crystal colour | light blue | colourless | colourless |
| Crystal Size [mm] | 0.25 × 0.23 × 0.17 | 0.1 × 0.1 × 0.08 | 0.11 × 0.10 × 0.09 |
| θ range [°] | 1.02, 27.9 | 1.02, 27.5 | 1.02, 27.5 |
| Data meas., used | 2803, 2785, | 2741, 2620 | 2731, 2682 |
| Unique refl. + Fr.rel. | 1658 + 1145 | 1592 + 1149 | 1587 + 1144 |
| Threshold | [$I > 2.0\sigma(I)$] | [$I > 2.0\sigma(I)$] | [$I > 2.0\sigma(I)$] |
| Number of param. | 96 | 96 | 97 |
| <i>R</i> ^a (observed), <i>R</i> _w ^b | 0.0136, 0.0330 | 0.0218, 0.0408 | 0.0142, 0.0304 |
| <i>S</i> | 1.14 | 1.06 | 1.06 |
| Flack parameter | 0.013(7) | 0.013(10) | 0.288(6) |
| Max./min. res. el. dens.[e/Å ³] | 0.33, -0.52 | 0.83, -0.63 | 0.46, -0.46 |

$$^a R = (|F_o| - |F_c|) / |F_o|, \quad ^b wR_2 = ((w(F_o^2 - F_c^2)^2) / (wF_o^2)^2)^{1/2}.$$

Supplementary material

CCDC 278818 (1), CCDC 278817 (2), CCDC 278814 (3), CCDC 278815 (4) and CCDC 278816 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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References

1. A. Molander, *Chem. Rev.* **1996**, *96*, 307–338.
2. E. Prasad, B. W. Kettle, R. A. Flowers, *J. Am. Chem. Soc.* **2004**, *126*, 6891–6894.
3. L. J. Radonovich, M. D. Glick, *J. Inorg. Nucl. Chem.* **1973**, *35*, 2745–2752.
4. X. W. Zhang, X. F. Li, F. Benetollo, G. Bombieri, *Inorg. Chim. Acta* **1987**, *139*, 103–104.
5. Z. Hou, K. Kobayashi, H. Yamazaki, *Chem. Lett.* **1991**, 268, 265–268.
6. S. Petriček, A. Demšar, L. Golič, J. Košmrlj, *Polyhedron* **2000**, *19*, 199–204.
7. D. Barr, A. T. Brooker, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith, D. S. Wright, *Angew. Chem.* **1990**, *102*, 300–301.
8. J. G. H. du Preez, H. E. Rohwer, J. F. de Wet, M. R. Caira, *Inorg. Chim. Acta* **1978**, *26*, 59–60.
9. S. Petriček, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1947–1952.
10. K. Asakura, T. Imamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 731–732.
11. A. Cabrera, M. Salmon, N. Rosas, J. Perez-Flores, L. Velasco, G. Espinoza-Perez, J. L. Arias, *Polyhedron* **1998**, *17*, 193–197.
12. T. Imamoto, Y. Yamanoi, H. Tsuruta, K. Yamaguchi, M. Yamazaki, J. Inanaga, *Chem. Lett.* **1995**, 949–950.
13. T. Imamoto, M. Nishiura, Y. Yamanoi, H. Tsuruta, K. Yamaguchi, *Chem. Lett.* **1996**, 875–876.
14. M. Nishiura, Y. Yamanoi, H. Tsuruta, K. Yamaguchi, T. Imamoto, *Bull. Soc. Chim. Fr.* **1997**, *134*, 411–420.
15. A. Becker, W. Urland, *J. Alloys Com.* **1998**, 275–277, 62–66.
16. M. Czjzek, H. Fuess, I. Pabst, *Z. Anorg. Allg. Chem.* **1992**, *617*, 105–109.
17. J. Hallfeldt, W. Urland, *Z. Anorg. Allg. Chem.* **2001**, 627, 545–548.
18. W. Urland, J. Hallfeldt, *Z. Anorg. Allg. Chem.* **2000**, 626, 2569–2573.
19. A. Becker, W. Urland, *Z. Anorg. Allg. Chem.* **1999**, 625, 1033–1036.
20. R. J. Majeste, D. Chriss, L. M. Trefonas, *Inorg. Chem.* **1977**, *16*, 188–191.
21. R. D. Rogers, A. N. Rollins, R. F. Henry, J. S. Murdoch, R. D. Etzenhouser, S. E. Huggins, L. Nunez, *Inorg. Chem.* **1991**, *30*, 4946–4954.
22. P. Runge, M. Schulze, W. Urland, *Z. Anorg. Allg. Chem.* **1991**, 592, 115–120.
23. R. H. Neilson, *Encyclopedia of Inorganic Chemistry*, edited by R. B. King, Wiley, Chichester, UK, 1994, 6, 3183.
24. X. D. Liu, J. G. Verkade, *Inorg. Chem.* **1998**, *37*, 5189–5197.
25. S. Petriček, A. Demšar, L. Golič, *Polyhedron* **1999**, *18*, 529–532.
26. S. Anfang, M. Karl, N. Faza, W. Massa, J. Magull, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1997**, 623, 1425–1432.
27. G. R. Willey, P. R. Meehan, T. J. Woodman, M. G. B. Drew, *Polyhedron* **1997**, *16*, 623–627.
28. R. D. Shanon, *Acta Cryst.* **1976**, *A32*, 751–767.
29. O. S. Filipenko, D. D. Makitova, O. N. Krasočka, V. I. Ponomarev, L. O. Atovmal, *Coord. Chimia* **1987**, *13*, 669–672.
30. I. Leban, P. Šegedin, *Z. Kristallographie* **1993**, *206*, 69–75.
31. J. Marçalo, A. P. Matos, *Polyhedron* **1989**, *8*, 2431–2437.
32. Crystallographic data obtained through the Cambridge Crystallographic Data Centre, [2,4,6-Trimethylpyridinium]₃[LnCl₆], Ln = Sm (refcode: UNEREK), Eu (refcode: UNEQAF), J. Hallfeldt, Contribution from the thesis of J. Hallfeldt, University of Hannover, Germany 2003.
33. J. S. Li, B. Neumuller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **2002**, 628, 2785–2789.
34. G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen, Germany, 1997.
35. G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1997.
36. L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837–838.

Povzetek

Po reakciji med lantanoidnimi oksidi, heksametilfosforamidom (HMPA), klorotrimetilsilanom in vodo v tetrahidrofuranu (THF) nastanejo novi kompleksi, oborita se $[(\text{CH}_3)_2\text{NH}_2][\text{LnCl}_4(\text{HMPA})_2]$ (Ln = La (1), Nd (2)), iz raztopine pa izkristalizirajo $[(\text{CH}_3)_2\text{NH}_2][\text{LnCl}_4]\text{Cl}$ (Ln = Nd (3), Sm (4), Eu (5)). Lantanoidni oksidi reagirajo s HCl, ki nastane *in situ*, kationi $[(\text{CH}_3)_2\text{NH}_2]^+$ pa nastanejo po hidrolizi HMPA s cepitvijo P–N vezi. Poročamo o kristalnih strukturah spojin 1–5. Kompleksa 1 in 2, sta prvi znani spojini v katerih je ligand HMPA koordiniran v anionu.