

Scientific paper

# Synthesis and Structural Similarities of Yttrium and Lanthanide Chloride Complexes with Diglyme and Tetrahydrofuran

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Dedicated to the memory of Professor Ljubo Golič

## Abstract

Mononuclear molecular complexes,  $[\text{YCl}_3(\text{diglyme})(\text{THF})]$  (**1**) and  $[\text{LuCl}_3(\text{diglyme})(\text{H}_2\text{O})]$  (**2**),  $[\text{ErBr}_3(\text{diglyme})(\text{H}_2\text{O})]$  (**3**), and binuclear molecular complexes  $[\text{MCl}_3(\text{diglyme})]_2$  ( $\text{M} = \text{Y}$  (**4**),  $\text{Lu}$  (**5**)) were synthesized by the reactions of corresponding halide hydrates,  $(\text{CH}_3)_3\text{SiX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and diethylen glycol dimethyl ether (diglyme) in tetrahydrofuran (THF). The complex **1** crystallized from a reaction solution, while the complexes **2**, **3** and the binuclear complexes **4**, **5** were obtained by recrystallizations of reaction products from dichloromethane. The complexes **2** and **3** were obtained if some water was present during crystallization. The central ions  $\text{M}$  ( $\text{M} = \text{Y}, \text{Er}, \text{Lu}$ ) in the complexes **1–5** are seven-coordinate in a distorted pentagonal bipyramidal fashion. Four oxygen atoms and three halide ions are coordinated to the central ions in  $[\text{MX}_3(\text{diglyme})(\text{L})]$  (**1**, **2**, **3**), while two bridging and two nonbridging chloride ions and three oxygen atoms are coordinated to yttrium or lutetium in  $[\text{MCl}_3(\text{diglyme})]_2$ , **4** and **5**, respectively. A reaction of  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{CH}_3)_3\text{SiCl}$  in THF resulted in an ionic complex  $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$  (**6**).

**Keywords:** Lanthanide chloride; Lanthanide bromide; Diglyme; Crystal structure; Binuclear complexes; Bridging chlorides

## 1 Introduction

Scandium, yttrium and lanthanides are generally grouped together in the Group 3 of the periodic table. Yttrium bears a close chemical resemblance to the late lanthanides, which are of similar size due to the lanthanide contraction.<sup>1</sup>

Many yttrium chloride complexes with O-donor ligands reported in literature have a similar stereochemistry as complexes of lanthanides. A variety of coordination numbers of the lanthanides in the complexes with a particular ligand is expected across the lanthanide series due to the lanthanide contraction. Yttrium, with ionic radius very similar to holmium, usually adopts same coordination number and geometry as the late lanthanides in chloride complexes of THF, dimethoxyethane (DME) and triethylene glycol (treg). The complexes of yttrium and the late lanthanides  $[\text{MCl}_2(\text{THF})_5][\text{MCl}_4(\text{THF})_2]$  ( $\text{M} = \text{Y}, \text{Gd–Lu}$ ),<sup>2–6</sup>  $[\text{MCl}_3(\text{DME})_2]$  ( $\text{M} = \text{Y}, \text{Nd–Lu}$ )<sup>7,8</sup> and

$[\text{MCl}_3(\text{treg})] \cdot 18\text{-crown-6}$  ( $\text{M} = \text{Y}, \text{Dy}$ )<sup>9</sup> are isostructural. On contrary,  $[\text{YCl}_3(\text{THF})_2]_n$  displays a different crystal structure from the complexes of the late lanthanides, the polymeric yttrium complex resembles a structure of the early lanthanides,  $[\text{LnCl}_3(\text{THF})_2]_n$  ( $\text{Ln} = \text{Ce–Nd}$ ).<sup>2,4,5</sup>

Glymes  $(\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3)$  as flexible polyether ligands are able to coordinate to a whole range of lanthanides. We have continued our studies of lanthanide halide complexes with diglyme to compare reactivity of yttrium oxide and yttrium chloride hydrate and to explore structural relations of yttrium and lanthanide chloride complexes with diglyme.<sup>10–13</sup> We have also prepared a new binuclear compound  $[\text{LuCl}_3(\text{diglyme})]_2$  and the first complex of erbium bromide with solely O-donor organic ligands. On the contrary to ionic complexes  $[\text{LnBr}_2(\text{diglyme})_2][\text{LnBr}_4(\text{diglyme})]$  ( $\text{Ln} = \text{La}, \text{Sm}, \text{Eu}$ ),<sup>11, 14</sup> the complex of erbium achieves the mononuclear molecular compound  $[\text{ErBr}_3(\text{diglyme})(\text{H}_2\text{O})]$ .

## 2. Experimental Section

### 2.1. General

All manipulations were carried out under an atmosphere of purified argon. Yttrium oxide (Aldrich, 99.999%), yttrium and lutetium chloride hexahydrate (Aldrich, 99.99%), erbium bromide hydrate (Aldrich, 99.999%), diglyme (Fluka, 99.5%), chlorotrimethylsilane (Aldrich, 97.0%) and bromotrimethylsilane (Aldrich, 97.0%) were used as delivered. THF and pentane were dried over Na/K and  $\text{CH}_2\text{Cl}_2$  over calcium hydride. The solvents were distilled before use.

Suspensions of ground samples in Nujol were prepared in a dry box. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer from 400 to  $4000\text{ cm}^{-1}$ .

Yttrium and erbium content were determined by gravimetric analysis and the chlorine content by potentiometric titration of chloride ions with silver nitrate. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyzer at the University of Ljubljana (Department of Organic Chemistry).

### 2.2. Synthesis of $[\text{YCl}_3(\text{diglyme})(\text{THF})]$ (1) and $[\text{YCl}_3(\text{diglyme})]_2$ (4)

30 mL of THF, 0.46 g (3.43 mmol) of diglyme and 14.79 g (136 mmol) of  $(\text{CH}_3)_3\text{SiCl}$  were added to 0.563 g (1.86 mmol) of  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ . A suspension was stirred for six days at room temperature and then left to settle. Approximately one half of the solution above the precipitate was filtered and crystals of **1** grew out of the solution during slow evaporation at reduced pressure at room temperature. The remaining suspension was dried *in vacuo*, 0.523 g of  $[\text{YCl}_3(\text{diglyme})(\text{THF})_x]$  (80.5% yield) was gained. The formula  $[\text{YCl}_3(\text{diglyme})(\text{THF})_x]$  ( $x \sim 0.3$ ) was calculated according to elemental analyses. Anal. Calcd for  $\text{C}_{7.2}\text{H}_{16.4}\text{Cl}_3\text{O}_{3.3}\text{Y}$ : Y 25.3, Cl 30.3. Found: Y 25.2, Cl 30.1. IR (in Nujol), 1305 w, 1261 m, 1245 m, 1208 w, 1153 w, 1098 m, 1080 s, 1056 w, 1040 s, 1025 m, 956 m, 919 w, 879 m, 867 m, 834 w,  $800\text{ m cm}^{-1}$ . Recrystallization of  $[\text{YCl}_3(\text{diglyme})(\text{THF})_x]$  from  $\text{CH}_2\text{Cl}_2$  resulted in crystals of binuclear complex **4**.

Complex **1** was obtained also in the reaction of  $\text{Y}_2\text{O}_3$ ,  $(\text{CH}_3)_3\text{SiCl}$  and diglyme in THF which took place at  $80^\circ\text{C}$  for 23 hours. On the contrary to  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Y}_2\text{O}_3$  does not react completely as shown by a characteristic peak of  $\text{Y}_2\text{O}_3$  at  $560\text{ cm}^{-1}$  in the IR spectrum of a resulting mixture.

### 2.3. Synthesis of $[\text{LuCl}_3(\text{diglyme})(\text{H}_2\text{O})]$ (2) and $[\text{LuCl}_3(\text{diglyme})]_2$ (5)

30 mL of THF, 0.31 g (2.31 mmol) of diglyme and 14.25 g (131 mmol) of  $(\text{CH}_3)_3\text{SiCl}$  were added to 0.445 g of  $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  (1.14 mmol). A suspension was stirred at room temperature and after four days dried *in vacuo*.

Recrystallization of the powder product from  $\text{CH}_2\text{Cl}_2$  was repeated several times and resulted in crystals of mononuclear complex **2** or binuclear complex **5**. IR (**2** in Nujol) 3381 m, 1621 m, 1261 m, 1105 s, 1070 s, 1057 m, 1032 s, 978 m, 875 m, 832 w,  $801\text{ m cm}^{-1}$ . IR (**5** in Nujol) 1261 m, 1240 w, 1095 s, 1071 vs, 1026 s, 1010 s, 1000 m, 960 w, 872 m,  $800\text{ m cm}^{-1}$ .

### 2.4. Synthesis of $[\text{ErBr}_3(\text{diglyme})(\text{H}_2\text{O})]$ (3)

30 mL of THF, 0.260 g (1.94 mmol) of diglyme and 17.12 g (112 mmol) of  $(\text{CH}_3)_3\text{SiBr}$  were added to 0.404 g ( $n(\text{Er}) = 0.716\text{ mmol}$ ) of  $\text{ErBr}_3 \cdot x\text{H}_2\text{O}$ . The suspension was stirred for four days at room temperature. 0.412 g (93.8% yield)  $[\text{ErBr}_3(\text{diglyme})(\text{THF})]$  was gained after drying *in vacuo* and washing with pentane. Anal. Calcd for  $\text{C}_{10}\text{H}_{22}\text{Br}_3\text{ErO}_4$ : C 19.59, H 3.62, Er 27.3. Found: C 19.00, H 3.71, Er 26.9. IR ( $[\text{ErBr}_3(\text{diglyme})(\text{THF})]$  in Nujol) 1293 w, 1275 w, 1257 m, 1246 w, 1232 w, 1201 w, 1100 s, 1069 s, 1054 s, 1023 vs, 981 m, 950 w, 921 w, 887 w, 871 s, 829 m,  $803\text{ m cm}^{-1}$ . Recrystallization of  $[\text{ErBr}_3(\text{diglyme})(\text{THF})]$  from  $\text{CH}_2\text{Cl}_2$  was repeated several times and resulted in low quality crystals with proposed formula  $[\text{ErBr}_3(\text{diglyme})(\text{THF})]$  or in the complex **3**.

### 2.5. Synthesis of $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$ (6)

30 mL of THF, and 18.39 g (169 mmol) of  $(\text{CH}_3)_3\text{SiCl}$  were added to 0.550 g of  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  (1.15 mmol). The suspension was stirred for seven days at room temperature. Complex **6** was gained after drying *in vacuo* and washing with pentane. The product was recrystallized from THF. Anal. Calcd for  $\text{C}_{28}\text{H}_{56}\text{Cl}_6\text{Ho}_2\text{O}_7$ : C 32.11, H 5.39. Found: C 31.09, H 5.30. IR ( $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$  in Nujol) 1014 s,  $862\text{ s cm}^{-1}$ .

### 2.6. Crystal structure determination

Details of the crystal data collections and the refinement parameters of the complexes **1–6** are listed in Table 1. All studied compounds are hygroscopic. The crystals were greased on a glass fiber. Diffraction data were collected on a Nonius Kappa CCD diffractometer with a CCD area detector at 150(2) K. Graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) was employed for all measurements. The data were processed using the program DENZO.<sup>15</sup> The crystal structures were solved by direct methods implemented in SHELXS-97 and refined by a full-matrix least-squares procedure based on  $F^2$  (SHELXL-97).<sup>16,17</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the models at geometrically calculated positions and refined using a riding model. The positions of two hydrogen atoms bonded to oxygen in a water molecule of the complexes **2** and **3** were located by difference Fourier maps.

**Table 1.** Crystallographic data, data collection and structure refinement data for the compounds  $[MX_3(\text{diglyme})(L)]$ , **1**, **2** and **3**,  $[MCl_3(\text{diglyme})]_n$ , **4**, **5**, and  $[\text{HoCl}_2(\text{THF})_3][\text{HoCl}_4(\text{THF})_2]$ , **6**

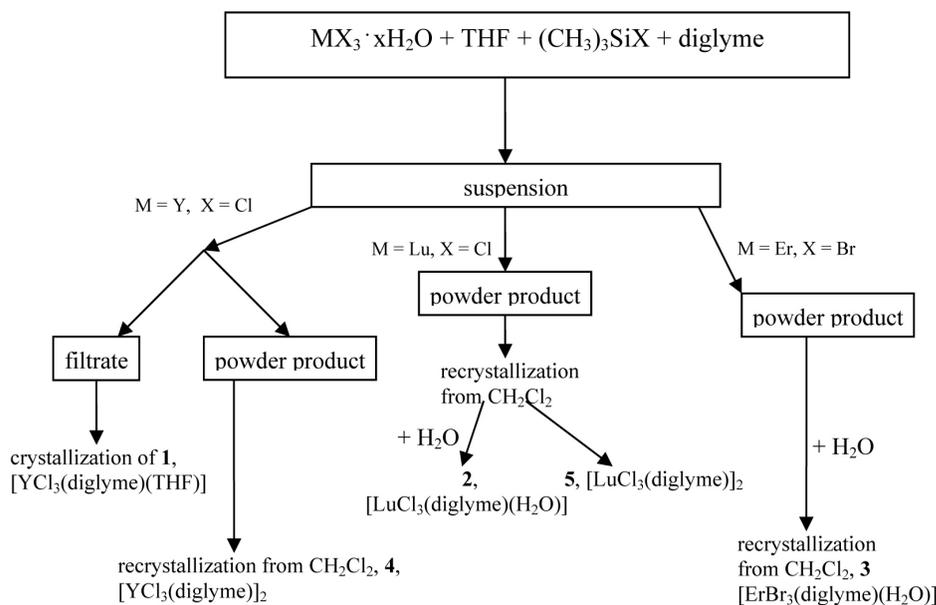
	1	2	3	4	5	6
chemical formula	$[\text{YCl}_3(\text{O}_4\text{C}_{10}\text{H}_{22})][\text{LuCl}_3(\text{O}_4\text{C}_6\text{H}_{16})][\text{ErBr}_3(\text{O}_4\text{C}_6\text{H}_{16})][\text{YCl}_3(\text{O}_3\text{C}_6\text{H}_{14})]_2[\text{LuCl}_3(\text{O}_3\text{C}_6\text{H}_{14})]_2[\text{HoCl}_2(\text{O}_5\text{C}_{20}\text{H}_{40})][\text{HoCl}_4(\text{O}_2\text{C}_8\text{H}_{16})]$					
color	colorless	colorless	colorless	colorless	colorless	pale pink
for. mass/ g mol <sup>-1</sup>	401.54	433.51	559.18	658.86	830.98	1047.29
cryst. syst.	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space gr.	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
$a / \text{\AA}$	9.6088(2)	9.8057(2)	9.9779(4)	7.8035(2)	7.7838(2)	12.5686(2)
$b / \text{\AA}$	11.5544(3)	9.4084(2)	9.8579(4)	14.3400(3)	14.2897(3)	11.3637(1)
$c / \text{\AA}$	14.6195(3)	14.6608(4)	15.0948(5)	11.1223(2)	10.9897(3)	26.7891(3)
$\beta / ^\circ$	98.925(2)	105.550(1)	106.891(2)	98.069(1)	99.147(1)	93.346(1)
$V / \text{\AA}^3$	1603.46(6)	1303.04(5)	1420.69(9)	1232.29(5)	1206.82(5)	3819.65(8)
Z (form.)	4	4	4	2	2	4
$D_{\text{cal.}} / \text{g cm}^{-3}$	1.663	2.210	2.614	1.776	2.287	1.821
$\mu / \text{mm}^{-1}$	4.139	8.179	14.33	5.359	8.82	4.571
crystal size / mm	0.24 0.23 0.22	0.09 0.08 0.07	0.05 0.05 0.04	0.22 0.20 0.18	0.06 0.06 0.05	0.18 0.12 0.12
$\theta$ Range/ $^\circ$	3.31–27.47	3.61–27.48	3.50–27.51	3.32–27.46	3.76–27.68	3.25–28.69
Tot.no.coll reflns.	6929	5534	5988	5346	5336	9176
No.unique reflns.	3667	2966	3250	2813	2777	4924
$R_{\text{int}}$	0.021	0.020	0.051	0.0240	0.031	0.023
No. reflns. used	3157	2796	2319	2448	2299	4134
Threshold	$[I > 2.0 \sigma(I)]$	$[I > 2.0 \sigma(I)]$	$[I > 2.0 \sigma(I)]$	$[I > 2.0 \sigma(I)]$	$[I > 2.0 \sigma(I)]$	$[I > 2.0 \sigma(I)]$
No.param.	165	135	135	120	120	197
$R^a$ (obs.)	0.025	0.018	0.039	0.023	0.024	0.025
$wR_2^b$	0.051	0.041	0.065	0.048	0.042	0.052
S	1.050	1.045	1.021	1.033	1.046	1.026
max/min res.elec.	0.283	0.684	1.622	0.307	1.175	1.729
$d. / e \text{\AA}^{-3}$	-0.391	-1.444	-1.215	-0.451	-0.770	-0.792

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

Crystallographic data for the structures **1** (CCDC 719087), **2** (CCDC 719085), **3** (CCDC 719083), **4** (CCDC 719086), **5** (CCDC 719084) and **6** (CCDC 719082) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+ (1223 336033; e-mail for inquiry).

## 2. 7. Syntheses

The reactions between lanthanide halide hydrates and complexes **1–5** at room temperature as presented in halotrimethylsilanes<sup>12,13</sup> were used to prepare the new Scheme 1.



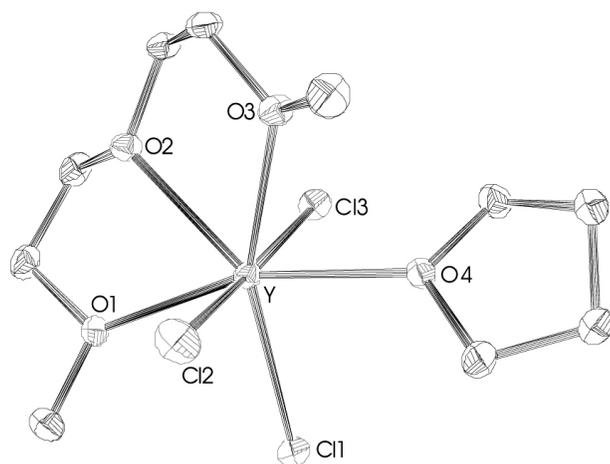
Scheme 1

Yttrium oxide hardly reacts with  $(\text{CH}_3)_3\text{SiCl}$  and diglyme in THF even at elevated temperatures, but the reaction of  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  with the same reactants resulted in a complex of yttrium chloride with diglyme in a high yield (Scheme 1). A low reactivity of oxides in similar reactions was already described for the late lanthanides ( $\text{Ln} = \text{Gd-Lu}$ ) and explained by a declining basicity of  $\text{Ln}_2\text{O}_3$  across the lanthanide series.<sup>12</sup> Full dehydration of yttrium or lanthanide halide hydrates by reactions with halotrimethylsilane and diglyme in THF resulted in water-free lanthanide halide complexes with diglyme as shown by IR spectra of the products. Recrystallization of the water-free complexes of yttrium, lutetium and erbium from dichloromethane achieved binuclear complexes **4**, **5**,  $[\text{MCl}_3(\text{diglyme})]_2$  ( $\text{M} = \text{Y, Lu}$ ), or aqua mononuclear complexes **2**, **3**,  $[\text{MX}_3(\text{diglyme})(\text{H}_2\text{O})]$  ( $\text{M} = \text{Lu, Er, X} = \text{Cl, Br}$ ). The aqua complexes **2** and **3** are obtained only if some water is present during crystallization.

The synthesis of **6**,  $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$ , is the first example of the reaction of lanthanide chloride hydrate and chlorotrimethylsilane without a polyether ligand.

## 2. 8. Crystal structures of **1**, **2**, and **3**

The metal ions in the complexes **1**, (Figure 1), **2**, and **3** are coordinated by three halide ions, three oxygen atoms from a diglyme molecule and one oxygen atom from a molecule of THF (**1**) or water (**2**, **3**) in a distorted pentagonal bipyramidal fashion with two halides in axial positions. Selected interatomic distances and angles are listed for the compounds **1**, **2**, and **3** in Table 2.

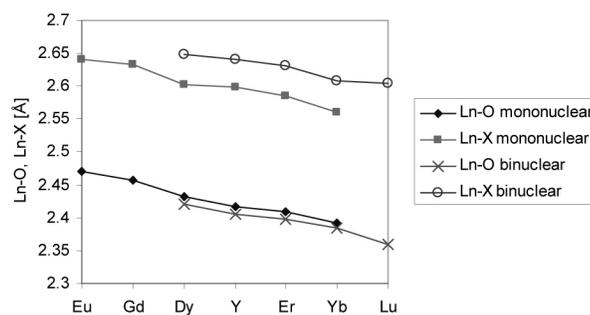


**Figure 1.** Seven-coordinate yttrium ions in the mononuclear molecular compound **1**,  $[\text{YCl}_3(\text{diglyme})(\text{THF})]$ . The same numbering scheme is adopted for the complexes **2** and **3** with a water molecule coordinated by O4 to lutetium or erbium instead of THF in the complex **1**. Bromides in the complex **3** are coordinated to erbium in the same way as chlorides to yttrium in **1**. Hydrogen atoms are omitted for clarity.

**Table 2.** Comparison of selected interatomic distances/Å and angles/° in  $[\text{MX}_3(\text{diglyme})(\text{L})]$ , **1**, **2**, and **3**

M, X	<b>1</b> (Y, Cl)	<b>2</b> (Lu, Cl)	<b>3</b> (Er, Br)
M1–X1	2.6038(5)	2.5852(7)	2.7626(8)
M1–X2	2.5969(5)	2.5863(7)	2.7728(8)
M1–X3	2.5950(5)	2.5319(7)	2.7191(8)
M1–X <sub>av</sub>	2.599(1)	2.568(2)	2.752(2)
M1–O1	2.428(1)	2.405(2)	2.414(5)
M1–O2	2.418(1)	2.358(2)	2.368(5)
M1–O3	2.464(1)	2.371(2)	2.382(5)
M1–O(diglyme) <sub>av</sub>	2.437(3)	2.378(6)	2.39(2)
M1–O4	2.3586(13)	2.294(2)	2.322(5)
X2–M1–X3	173.58(2)	166.98(2)	169.17(3)
X2–M1–X1	92.78(2)	90.30(2)	90.03(3)
X2–M1–O1	87.37(3)	90.39(5)	91.17(13)
X2–M1–O2	97.66(3)	82.77(5)	84.09(13)
X2–M1–O3	81.07(3)	83.17(5)	83.13(12)
X2–M1–O4	92.54(3)	104.95(6)	103.28(15)
X1–M1–O3	153.50(3)	142.58(5)	142.41(11)
X1–M1–O4	82.22(3)	77.51(6)	76.96(14)
O1–M1–O2	64.79(4)	67.48(7)	67.02(16)
O2–M1–O3	64.87(4)	67.80(6)	67.53(16)
O1–M1–O4	161.20(4)	153.75(8)	154.57(18)

The complex **1** is isostructural to the series of  $[\text{LnCl}_3(\text{diglyme})(\text{THF})]$  described for complexes of the late lanthanides ( $\text{Ln} = \text{Eu, Gd, Dy, Er, Yb}$ ).<sup>13</sup> The aqua complexes of **2** and **3** are isostructural to  $[\text{ErCl}_3(\text{diglyme})(\text{H}_2\text{O})]$  and  $[\text{GdBr}_3(\text{diglyme})(\text{H}_2\text{O})]$  respectively.<sup>12, 13</sup> All average M–X ( $\text{M} = \text{Y, Lu, Er; X} = \text{Cl, Br}$ ) and M–O interatomic distances in **1**, **2**, and **3** fit well to the trend of interatomic distances in the isostructural series corresponding to differences in  $\text{Y}^{3+}$  and  $\text{Ln}^{3+}$  radii.<sup>18</sup>



**Figure 2.** Decreasing average Ln–O and Ln–Cl interatomic distances with the decreasing ionic radii across the lanthanide series in isostructural mononuclear  $[\text{LnCl}_3(\text{diglyme})(\text{THF})]$  ( $\text{Ln} = \text{Eu, Gd, Dy, Er, Yb}$ )<sup>13</sup> and binuclear  $[\text{LnCl}_3(\text{diglyme})]_2$  ( $\text{Ln} = \text{Dy, Er, Yb}$ )<sup>13</sup> or **5**). Y–O and Y–Cl interatomic distances in **1** and **4** are included in the figure according to ionic radii of the late lanthanides and  $\text{Y}^{3+}$ .

The decreasing ionic radii across the lanthanide series resulted in shortening of the average Ln–O and Ln–Cl in-

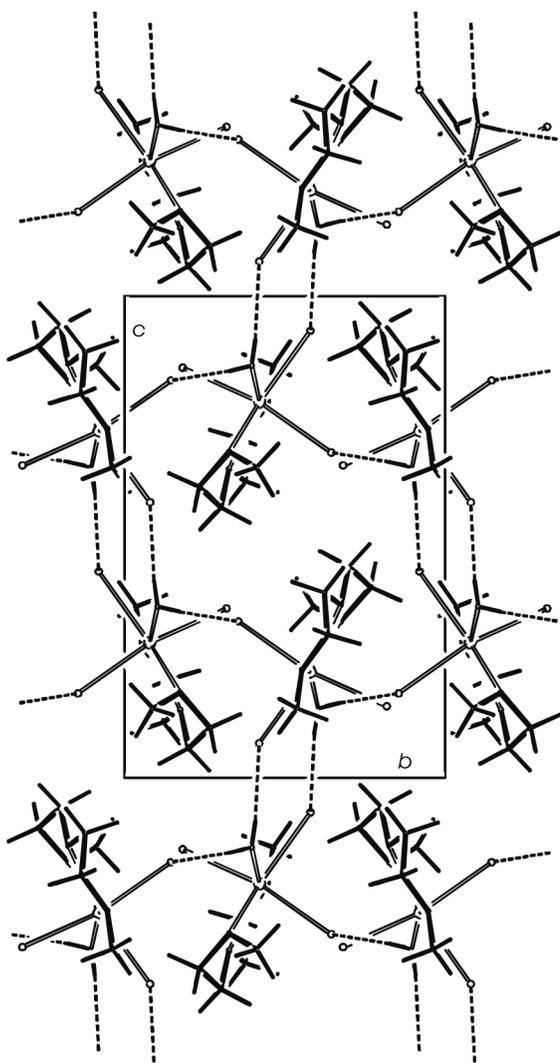
teratomic distances in  $[\text{LnCl}_3(\text{diglyme})(\text{THF})]$  ( $\text{Ln} = \text{Eu}, \text{Gd}, \text{Dy}, \text{Er}, \text{Yb}$ )<sup>13</sup> (Figure 2). Y–O and Y–Cl interatomic distances in **1** are between Ln–O and Ln–Cl interatomic distances for dysprosium and erbium. In the complexes **1**, **2**, and **3** are the interatomic distances M – O4(THF or H<sub>2</sub>O) ( $\text{M} = \text{Y}, \text{Lu}, \text{Er}$ ) approximately 0.08 Å shorter than the M–O(diglyme) distances.

The geometry of the complexes **1** with four oxygen atoms and three chlorides coordinated to yttrium in a distorted pentagonal bipyramidal fashion is similar to the geometry of  $[\text{YCl}_3(\text{deg})(\text{THF})]\text{THF}$  (deg = diethylene glycol).<sup>19</sup> Some differences of interatomic distances in these two complexes are due to hydroxyl groups of the ligand deg and formation of hydrogen bonds in  $[\text{YCl}_3(\text{deg})(\text{THF})]\text{THF}$ . Y–O(diglyme) interatomic distances in the complex **1** (Table 2) are longer than average Y–O(hydroxyl) in  $[\text{YCl}_3(\text{deg})(\text{THF})]\text{THF}$  (Y–O 2.37(1) Å). One chloride in the deg complex is involved in a hy-

drogen bond, resulting in a longer interatomic distance Y–Cl (2.643(2) Å) than in **1**.

A comparison of the complex **2** (Table 2) to  $[\text{LuCl}_3(\text{diglyme})(\text{THF})]$  shows longer Lu–Cl<sub>1,2</sub> and shorter Lu–O(diglyme) interatomic distances in **2** than in  $[\text{LuCl}_3(\text{diglyme})(\text{THF})]$  (average Lu–Cl 2.553(2) Å, Lu–O(diglyme) 2.414(6) Å).<sup>12</sup> Two chlorides, Cl<sub>1</sub>, Cl<sub>2</sub>, in the complex **2** are involved in hydrogen bonds (Figure 3), resulting in an elongation of the Lu–Cl interatomic distances.

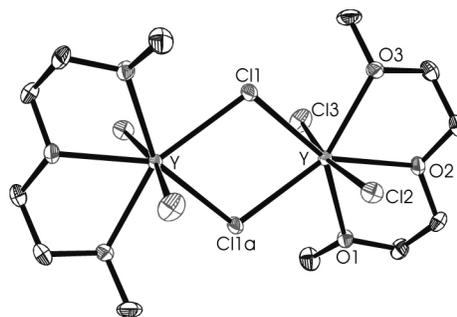
The complex **3**,  $[\text{ErBr}_3(\text{diglyme})(\text{H}_2\text{O})]$ , is the first complex of erbium bromide with O-donor organic ligands. Only two erbium bromide complexes, both organometallic compounds with bridging bromides, were structurally characterized by now according to CSD.<sup>20–22</sup> Two out of three Er–Br interatomic distances in **3** are longer (Table 2) due to weak hydrogen bonds (Figure 3). All interatomic distances Er–O(diglyme or H<sub>2</sub>O) in the complex **3** are in the same range as in  $[\text{ErCl}_3(\text{diglyme})(\text{H}_2\text{O})]$  (2.325(2)–2.428(1) Å).<sup>12</sup>



**Figure 3.** Hydrogen bonds (dashed lines) in the complexes **2** and **3** connect halides and water molecules.

## 2. 9. Crystal structures of **4** and **5**

The X-ray crystal structures of the complexes **4** (Figure 4) and **5** confirm the presence of binuclear molecules of  $[\text{MCl}_3(\text{diglyme})_2]$  ( $\text{M} = \text{Y}, \text{Lu}$ ) in which two metal ions are connected by two bridging chloride ions. Three oxygen atoms from a diglyme molecule, two bridging and two nonbridging chloride ions are coordinated to each yttrium or lutetium in the complexes **4** and **5** in a distorted pentagonal bipyramidal fashion. Selected interatomic distances and angles for the compounds **4** and **5** are listed in Table 3.



**Figure 4.** Two yttrium ions in **4**,  $[\text{YCl}_3(\text{diglyme})_2]$  are connected by bridging chloride ions to a binuclear molecule. Hydrogen atoms are omitted for clarity. The same numbering scheme is also adopted in the complex **5**.

Crystal structures of the complexes **4** and **5** are isostructural to the complexes of  $[\text{LnCl}_3(\text{diglyme})_2]$  ( $\text{Ln} = \text{Dy}, \text{Er}, \text{Yb}$ ).<sup>13</sup> A binuclear molecule of two lanthanides connected by two bridging chlorides was identified also in  $[\text{YbCl}_3(\text{THF})_2]_2$ .<sup>23</sup> The similar structural motif could be explained by steric coordination numbers which are al-

**Table 3.** Comparison of selected interatomic distances/Å and angles/° in,  $[\text{MCl}_3(\text{diglyme})]_2$ , **4** and **5**

M	Y - <b>4</b>	Lu - <b>5</b>
M1–Cl3	2.5627(6)	2.531(1)
M1–Cl2	2.5966(5)	2.562(1)
M1–Cl1	2.7104(5)	2.680(1)
M1–Cl1a	2.7139(5)	2.647(1)
M1–Cl <sub>av</sub>	2.646(2)	2.605(4)
M1–O1	2.426(1)	2.395(3)
M1–O2	2.372(1)	2.327(3)
M1–O3	2.420(1)	2.356(3)
M1–O <sub>av</sub>	2.406(3)	2.36(1)
Cl2–M1–Cl3	169.22(2)	170.47(4)
Cl1–M1–Cl1a	74.81(2)	74.11(3)
Cl1–M1–Cl2	90.74(2)	89.91(4)
Cl1a–M1–Cl2	89.05(2)	88.71(4)
Cl1a–M1–O1	78.26(3)	78.54(7)
Cl1–M1–O3	75.76(3)	75.30(7)
Cl2–M1–O1	89.60(3)	90.48(7)
Cl2–M1–O2	80.23(4)	80.64(8)
Cl2–M1–O3	96.66(4)	96.80(7)
O1–M1–O2	67.54(5)	67.51(10)
O2–M1–O3	65.76(5)	66.83(10)

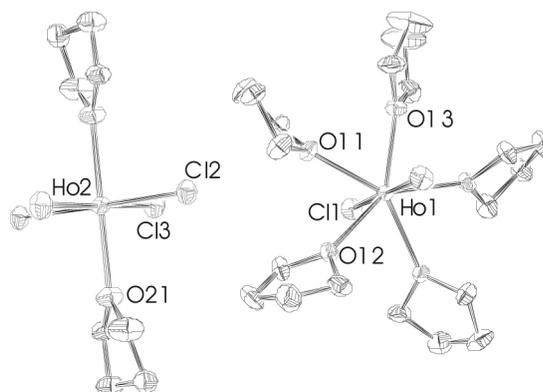
most the same for one diglyme and two THF molecules.<sup>24</sup> Interatomic distances from central ions to ligands (Figure 2) and unit cell volumes of all isostructural complexes  $[\text{LnCl}_3(\text{diglyme})]_2$  decrease across the lanthanide series strictly following decreasing ionic radii. As expected, the volume of yttrium complex (Table 1) is between the volumes of dysprosium and erbium complexes according to similar ionic radii of  $\text{Y}^{3+}$ ,  $\text{Dy}^{3+}$  and  $\text{Er}^{3+}$ .<sup>13,18</sup> All nonbridging M–Cl (M = Y, Lu) interatomic distances in the complexes **4** and **5** are at least 0.09 Å shorter than the bridging ones. A comparison of interatomic distances in binuclear compounds **4** and **5** to those in mononuclear **1** and **2** reveals longer average M–Cl and shorter M–O(diglyme) interatomic distances in the binuclear complexes **4** and **5** (Figure 2, Table 2 and 3). Bridging and nonbridging Y–Cl interatomic distances in the complex **4** are in the same range as corresponding distances in the polymeric complex of  $[\text{YCl}_3(\text{THF})_2]_n$  (2.541(3)–2.739(2) Å).<sup>2</sup>

The compound **5** is the first lutetium complex with bridging chlorides and O-donor organic ligands. Bridging chloride ions were observed by now only in organometallic and N-donor complexes of lutetium according to the CSD.<sup>22</sup>

## 2. 10. Crystal structure of **6**

The X-ray crystal structure of the complex **6** (Figure 5) consists of discrete ion pairs, holmium ions are seven-coordinate in cations  $[\text{trans-HoCl}_2(\text{THF})_5]^+$  and six-coordinate in anions  $[\text{trans-HoCl}_4(\text{THF})_2]^-$ . The holmium in the cation displays pentagonal bipyramidal geometry with two apical chloride ions and five equatorial THF mole-

cules while the anion has octahedral stereochemistry with *trans* THF molecules. Selected interatomic distances and angles for the compound **6** are listed in Table 4.

**Figure 5.** The crystal structure of **6** with the numbering scheme adopted. Hydrogen atoms are omitted for clarity.**Table 4.** Selected interatomic distances/Å and angles/° in  $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$ , **6**

cation - C.N.=7		anion - C.N. = 6	
Ho1–O11	2.372(2)	Ho2–O21	2.319(2)
Ho1–O12	2.374(2)	Ho2–Cl2	2.5992(8)
Ho1–O13	2.382(3)	Ho2–Cl3	2.6206(7)
Ho1–Cl1	2.5703(7)	Ho2–Cl <sub>av</sub>	2.610(3)
Ho1–O <sub>av</sub>	2.375(11)		
Cl1–Ho1–Cl1a	178.81(4)	O21–Ho2–O21	180.00(11)
O11–Ho1–Cl1	94.27(5)	Cl2–Ho2–Cl3	92.03(3)
O12–Ho1–Cl1	85.69(6)	O21–Ho2–Cl2	90.05(6)
O13–Ho1–Cl1	90.59(2)	O21–Ho2–Cl3	90.86(6)
O11–Ho1–O12	72.66(7)		
O11–Ho1–O13	71.86(5)		
O12–Ho1–O12a	72.15(10)		
O12–Ho1–O13	143.92(5)		

Crystal structure of the complex **6** is the missing one in the isostructural series of  $[\text{LnCl}_2(\text{THF})_5][\text{LnCl}_4(\text{THF})_2]$  (Ln = Gd–Yb)<sup>3–6</sup> and  $[\text{YCl}_2(\text{THF})_5][\text{YCl}_4(\text{THF})_2]$ .<sup>2</sup> The ionic structure of **6** was expected due to similar ionic radii of holmium and these late lanthanides.<sup>18</sup> The differences of interatomic distances Ln–Cl and Ln–O among the isostructural complexes  $[\text{LnCl}_2(\text{THF})_5][\text{LnCl}_4(\text{THF})_2]$  are small, corresponding to those expected from differences in Ln<sup>3+</sup> radii and various temperatures of X-ray measurements.<sup>18</sup> Interatomic distances Ho1–Cl in the cation are by 0.04 Å shorter than Ho2–Cl interatomic distances in the anion in spite of a higher coordination number in the cation (Table 4). On the contrary to Ho–Cl, Ho–O interatomic distances are not influenced by ion charge and are longer in seven-coordinate cation than in six-coordinate anion of the complex **6**.

The comparison of the interatomic distances in the complex **6** to those in  $[\text{HoCl}_3(\text{diglyme})(\text{THF})]$  also show the influence of ion charge on Ho–Cl distances.<sup>12</sup> Ho–Cl<sub>av</sub> interatomic distances in six-coordinate anion of **6** (Table 4) are longer than in seven-coordinate molecular complex  $[\text{HoCl}_3(\text{diglyme})(\text{THF})]$  (2.593(2) Å).<sup>12</sup>

### 3. Conclusions

Yttrium oxide hardly reacts with  $(\text{CH}_3)_3\text{SiCl}$  and diglyme in THF even at elevated temperatures, similar to  $\text{Ln}_2\text{O}_3$  of the late lanthanides (Ln = Gd–Lu).<sup>12</sup> Therefore  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  was used instead of  $\text{Y}_2\text{O}_3$  to prepare **1** and **4**, yttrium chloride complexes with diglyme. **1** and **4** are isostructural to the complexes of the late lanthanides:  $[\text{LnCl}_3(\text{diglyme})(\text{THF})]$  (Ln = Eu, Gd, Dy, Er, Yb) and  $[\text{LnCl}_3(\text{diglyme})]_2$  (Ln = Dy, Er, Yb, Lu(5)) respectively.<sup>12, 13</sup> The relation of average interatomic distances Y–O and Y–Cl in **1** and **4** to average interatomic distances Ln–O and Ln–Cl in isostructural complexes is the same as the relation of ionic radii of  $\text{Y}^{3+}$  to the late lanthanides. Yttrium is seven coordinated in both isolated complexes, mononuclear **1**,  $[\text{YCl}_3(\text{diglyme})(\text{THF})]$ , and binuclear **4**,  $[\text{YCl}_3(\text{diglyme})]_2$ . A close chemical resemblance of yttrium and the late lanthanides is obvious also from a comparison of the complex **6**,  $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$ , to  $[\text{YCl}_2(\text{THF})_5][\text{YCl}_4(\text{THF})_2]$ .<sup>2</sup>

A full dehydration of yttrium or lanthanide halide hydrates could be achieved by reactions with chloro- or bromo-trimethylsilane as shown by water-free products of reactions between  $\text{MCl}_3 \cdot 6\text{H}_2\text{O}$  (M = Y, Lu) or  $\text{ErBr}_3 \cdot x\text{H}_2\text{O}$ ,  $(\text{CH}_3)_3\text{SiX}$  (X = Cl, Br) and diglyme in THF. The binuclear complexes **4**, **5**,  $[\text{MCl}_3(\text{diglyme})]_2$  (M = Y, Lu), and aqua complexes **2**, **3**,  $[\text{MX}_3(\text{diglyme})(\text{H}_2\text{O})]$  (M = Lu, Er, X = Cl, Br), were obtained by recrystallization of the water-free products from dichloromethane, either in a water-free system (**4**, **5**) or in the presence of water (**2**, **3**).

The complex **3**,  $[\text{ErBr}_3(\text{diglyme})(\text{H}_2\text{O})]$ , is the first complex of erbium bromide with O-donor ligands.

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## Povzetek

Monojedrne molekulske komplekse  $[\text{YCl}_3(\text{diglyme})(\text{THF})]$  (**1**) in  $[\text{LuCl}_3(\text{diglyme})(\text{H}_2\text{O})]$  (**2**),  $[\text{ErBr}_3(\text{diglyme})(\text{H}_2\text{O})]$  (**3**), ter dvojedrna molekulska kompleksa  $[\text{MCl}_3(\text{diglyme})_2]$  ( $\text{M} = \text{Y}$  (**4**),  $\text{Lu}$  (**5**)) smo pripravili po reakciji med izbranimi halogenidi hidrati,  $(\text{CH}_3)_3\text{SiX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in dietilenglikol dimetil etrom (diglyme) v tetrahidrofuranu (THF). Kristali spojine **1** so zrasli iz raztopine, ki je vsebovala vse produkte reakcije, ostale spojine, **2**, **3**, **4** in **5** pa smo prekristalizirali iz diklorometana. Med kristalizacijo spojin **2** in **3** je bila v sistemu prisotna voda. V kompleksih **1–5** je na vsak centralni ioni  $\text{M}$  ( $\text{M} = \text{Y}, \text{Er}, \text{Lu}$ ) koordiniranih sedem ligandov v obliki popačene pentagonalne bipiramide. Na centralni ion so v kompleksih  $[\text{MX}_3(\text{diglyme})(\text{L})]$  (**1**, **2**, **3**) koordinirani štiri kisiki in trije halogenidi, v kompleksih  $[\text{MCl}_3(\text{diglyme})_2]$  (**4**, **5**) pa trije kisiki ter dva mostovna in dva terminalna klorida. Po reakciji med  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  in  $(\text{CH}_3)_3\text{SiCl}$  v THF nastane ionski kompleks  $[\text{HoCl}_2(\text{THF})_5][\text{HoCl}_4(\text{THF})_2]$  (**6**).