Synthesis, crystal structure, and chirality of divalent lanthanide reagents containing tri- and tetraglyme

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Abstract

Six new divalent lanthanide complexes using triglyme (trigly) and tetraglyme (tetgly) as achiral ligands have been prepared, using a facile synthetic method, in search for enantioselective solid-state reagents. The crystal structures of *cis*-[SmI$_2$(trigly)thf] (**1**), *trans*-[YbI$_2$(trigly)thf] (**2**), *trans*-[SmI$_2$(trigly)dme] (**3**), *trans*-[YbI$_2$(tetgly)] (**4**), *trans*-[EuI$_2$(tetgly)thf] (**5**), and [Sm(tetgly)$_2$][SmI$_3$(tetgly)]I (**6**) have been determined. All complexes, except **5**, are chiral. The 10-coordinate cation in **6** displays a helical chirality since the two tetraglyme ligands are wrapped around the samarium ion. Since *trans*-[YbI$_2$(tetgly)] (**4**), which has a chiral arrangement of terminal methyl groups, crystallizes as a conglomerate, preferential crystallization and consequent enantioselective reduction of acetophenone was attempted, but resulted in racemic products, possibly on account of racemic twinning in **4**.
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1. Introduction

Divalent lanthanide complexes can function as one-electron reductants, and especially samarium(II) complexes such as [SmI$_2$(thf)$_5$] [1], [SmI$_2$(hmpa)$_4$] [2], and [Sm(hmpa)$_6$]I$_2$ [3] have found extensive use as mild and selective reducing agents [4–13]. With the long-term goal of mastering the design and synthesis of enantioselective reducing agents, we have embarked on an exploratory synthesis project. Primarily, the prepared lanthanide complexes are intended to be used as solid state reagents, which means that properties such as selectivity and reduction potential may be correlated to the crystal structure. It is also likely that (if appropriate stabilizing ligands can be identified) handling, transportation and storage of solid reagents will be more convenient as compared to the delicate handling that is usually necessary with the oxygen-sensitive solutions of lanthanide(II) complexes. The final, and

perhaps most important, advantage with solid-state reagents is that labile chiral reagents, which would racemize in solution, are stereochemically inert in the solid state. In fact, even achiral reagents which crystallize in chiral crystals (due to conformation, aggregation, or packing) may be effective in stereoselective reactions.

A common strategy for inducing enantioselectivity into a reaction is to use a metal reagent or catalyst that coordinates a chiral ligand. The stereochemical information can then, hopefully, be transferred to the substrate. In this work, however, we have used only achiral ligands with the intention of obtaining reagents exhibiting chirality via stereogenic metal centers, aggregation (e.g., helix formation) or conformational chirality. In this context, the lanthanides are a good choice since they display a rich structural chemistry, often with high coordination numbers and a multitude of potential coordination figures. On account of their lability, such complexes are candidates for total spontaneous resolution if they crystallize as conglomerates (i.e., if they crystallize in a chiral space group with only one molecule in the asymmetric unit), which means that such

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solid state reagents may be prepared (theoretically) in 100% yield and enantiomeric excess.

We have recently reported the preparation and crystal structure of [SmI$_2$(dme)$_3$] [14], which has stereogenic samarium atoms and indeed crystallizes as a conglomerate in space group $P2_12_12_1$. However, we have experienced problems with racemic twinning during large-scale synthesis of this potential reagent. Labile reagents that crystallize as conglomerates can be used in absolute asymmetric synthesis [15–17], and the relative robustness of [SmI$_2$(dme)$_3$] (compared to e.g., [SmI$_2$(thf)$_5$]) encouraged us to continue our search for conglomerates among new divalent lanthanide reagents, using polydentate glyme ligands, and we now report on complexes of tri- and tetraglyme with samarium(II), ytterbium(II), and europium(II) iodide.

2. Experimental

2.1. General

All operations were carried out under nitrogen or argon using Schlenk or low temperature [18] techniques. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone shortly prior to use. Neutral polydentate ligands such as triglyme (trigly) and tetraglyme (tetgly) were deoxygenated and dried with 4 Å molecular sieves. Commercial 1,2-diiodoethane was recrystallized from ethanol. Samarium, ytterbium, and europium chips (99.9%) from Apollo Scientific Ltd. were dried under vacuum prior to use.

2.2. Preparation of cis-[SmI$_2$(trigly)thf] (1)

1,2-Diiodoethane (2.88 g, 10.2 mmol) and 50 ml THF were added, at ambient temperature, to an argonfilled centrifuge tube containing samarium chips (1.85 g, 12.3 mmol). The resulting yellow solution was sonicated for 3 h at 50 °C, during which time the solution turned dark-blue, indicating the formation of Sm(II) complexes. The reaction mixture was centrifuged and the solution was transferred to a Schlenk flask. Triglyme (1.9 ml, 10.5 mmol) was added slowly from a syringe and dark blue crystals of 1, suitable for X-ray analysis, started to form after a few hours. After 24 h, the solution was removed and the crystals were washed with cold hexane and dried under vacuum. Yield: 5.39 g, 81%. Crystals of 1 are air-sensitive and start to decompose visibly after a few minutes at ambient temperature.

2.3. Preparation of trans-[YbI$_2$(trigly)thf] (2)

1,2-Diiodoethane (1.00 g, 3.6 mmol) and 50 ml THF were added, at ambient temperature, to a Schlenk flask containing ytterbium chips (1.73 g, 10 mmol). The resulting yellow solution was stirred for 3 h at ambient temperature and then sonicated for 12 h at 50 °C, during which time the solution turned greenish yellow. The solution was withdrawn with a syringe and triglyme (1.0 ml, 5.5 mmol) was added slowly. Crystals of 2, suitable for X-ray analysis, formed after a few days. The solution was removed and the crystals were washed with cold hexane and dried under vacuum. Yield: 1.54 g, 63%. Crystals of 2 are air-sensitive and start to decompose visibly after a few minutes at ambient temperature.

2.4. Preparation of trans-[SmI$_2$(trigly)dme] (3)

1,2-Diiodoethane (0.30 g, 1.06 mmol), triglyme (1 ml, 5.53 mmol), and DME (10 ml) were added, at ambient temperature, to Schlenk tube containing samarium chips (0.23 g, 1.52 mmol). The resulting yellow solution was stirred for 12 h, at ambient temperature, during which time the solution turned dark-purple. The reaction was completed by sonication at 50 °C for 8 h. Dark-blue crystals of 3 formed when the solution was kept at ambient temperature. After 24 h, the solution was removed and the crystals (and the remaining samarium chips) were washed with cold hexane and dried under vacuum. Approximate yield: 0.36 g, 51%. Crystals of 3 are moderately air-sensitive.

2.5. Preparation of trans-[YbI$_2$(tetgly)] (4)

1,2-Diiodoethane (1.00 g, 3.6 mmol) and 50 ml THF were added, at ambient temperature, to a Schlenk flask containing ytterbium chips (1.73 g, 10 mmol). The resulting yellow solution was stirred for 3 h at ambient temperature and then sonicated for 12 h at 50 °C, during which time the solution turned greenish yellow. The solution was withdrawn with a syringe and tetraglyme (1.0 ml, 4.5 mmol) was added slowly. Crystals of 4, suitable for X-ray analysis, formed after a few days. The solution was removed and the crystals were washed with cold hexane and dried under vacuum. Yield: 1.36 g, 58%. Crystals of 4 are moderately air-sensitive.

2.6. Preparation of trans-[EuI$_2$(tetgly)thf] (5)

1,2-Diiodoethane (0.66 g, 2.34 mmol) and 50 ml THF were added, at ambient temperature, to an argonfilled centrifuge tube containing europium chips (0.42 g, 2.76 mmol). The resulting yellow suspension was sonicated for 3 h at 50 °C, whereafter the reaction mixture was centrifuged and the solution was transferred to a Schlenk flask. Tetraglyme (1.0 ml, 4.5 mmol) was added slowly from a syringe and yellow crystals of 5, suitable for X-ray analysis, started to form after a few hours. After 24 h, the solution was removed and the crystals were washed with cold hexane and dried under vacuum.

Yield: 0.84 g, 51%. Crystals of **5** are air-sensitive and turn red within a few seconds of air-exposure.

2.7. Preparation of [Sm(tetgly)$_2$][SmI$_3$(tetgly)]I (**6**)

1,2-Diiodoethane (0.50 g, 1.8 mmol) and 15 ml tetraglyme were added, at ambient temperature, to a Schlenk tube containing samarium chips (0.31 g, 2.0 mmol). The suspension was sonicated for 12 h at 50 °C, whereafter, at ambient temperature, dark blue crystals of **6**, suitable for X-ray analysis, started to form. After 24 h, the solution was removed and the crystals were washed with cold hexane and dried under vacuum. Approximate yield: 0.89 g, 67%. Crystals of **6** are air-sensitive and start to decompose visibly after a couple of minutes at ambient temperature.

2.8. Reduction with trans-[YbI$_2$(tetgly)] (**4**)

A supersaturated solution of YbI$_2$ in THF (see Section 2.5) was seeded with a single crystal of **4**. After completed crystallization, the solvent was withdrawn and acetophenone was added at −78 °C. The solids were mixed and a stoichiometric amount of methanol was added. The mixture was slowly allowed to reach ambient temperature. After 12 h, work-up was initiated and

the ratio of 1-phenylethanol enantiomers (coupling products were not considered) was measured on a Varian Star 3400 CX gas chromatograph using a chiral stationary phase GC column (CP-Chirasil-DEX CB, 25 m 0.32 mm) from Chrompack. All analyses were performed at 100 °C (injector: 225 °C, detector: 250 °C) with helium as carrier gas (t_R (*R*)-1-phenylethanol = 14.5 min and t_R (*S*)-1-phenylethanol = 16.3 min).

2.9. X-ray crystallography

All crystals were selected and mounted under nitrogen in a glass capillary at low temperature [18] and transferred in liquid nitrogen to a Rigaku AFC6 diffractometer. Diffracted intensities were measured at −120 °C, using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation from a RU200 rotating anode operated at 50 kV and 180 mA. Stationary background counts were recorded on each side of a reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability during the diffraction experiment. Cell constants were obtained by

Table 1
Crystal and refinement data for **1**, **2** and **3**

	1	**2**	**3**
Compound	*cis*-[SmI$_2$(trigly)thf]	*trans*-[YbI$_2$(trigly)thf]	*trans*-[SmI$_2$(trigly)dme]
Empirical formula	C$_{12}$H$_{26}$SmI$_2$O$_5$	C$_{12}$H$_{26}$YbI$_2$O$_5$	C$_{12}$H$_{28}$SmI$_2$O$_6$
Formula weight	654.48	677.17	672.49
Temperature (K)	153(2)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	$Pna2_1$	$Pca2_1$	$P\bar{1}$
Unit cell dimensions			
a (Å)	15.650(4)	25.849(5)	15.662(4)
b (Å)	11.629(3)	8.3955(15)	16.504(5)
c (Å)	11.129(6)	9.151(2)	8.387(2)
α (°)	90	90	98.01(2)
β (°)	90	90	97.51(2)
γ (°)	90	90	89.13(2)
Volume (Å^3)	2025.4(13)	1985.9(7)	2128.4(10)
Z	4	4	4
Density (calculated) (Mg/m^3)	2.146	2.265	2.099
Absorption coefficient (mm^{-1})	5.960	7.831	5.678
Crystal size (mm^3)	0.20×0.20×0.20	0.2×0.2×0.2	0.2×0.2×0.2
θ range for data collection (°)	2.18–24.99	2.43–24.99	2.47–25.00
Reflections collected	1878	1853	7703
Independent reflections (R_{int})	1878	1853	7413 (0.0500)
Completeness to $\theta = 25°$ (%)	99.8	99.5	99.1
Absorption correction	Empirical	Empirical	Empirical
Data/restraints/parameters	1878/1/181	1853/1/181	7413/0/380
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0342$, $wR_2 = 0.0724$	$R_1 = 0.0282$, $wR_2 = 0.0572$	$R_1 = 0.0455$, $wR_2 = 0.1084$
R indices (all data)	$R_1 = 0.0811$, $wR_2 = 0.0843$	$R_1 = 0.0550$, $wR_2 = 0.0642$	$R_1 = 0.0992$, $wR_2 = 0.1329$
Absolute structure parameter	0.05(4)	0.073(18)	Centrosymmetric
Largest difference peak and hole (e Å^{-3})	0.997 and −1.049	0.982 and −0.881	1.426 and −1.996

Table 2
Crystal and refinement data for **4**, **5** and **6**

	4	5	6
Compound	*trans*-[YbI$_2$(tetgly)]	*trans*-[EuI$_2$(tetgly)thf]	[Sm(tetgly)$_2$][SmI$_3$(tetgly)]I
Empirical formula	C$_{10}$H$_{22}$YbI$_2$O$_5$	C$_{14}$H$_{30}$EuI$_2$O$_6$	C$_{30}$H$_{66}$Sm$_2$I$_4$O$_{15}$
Formula weight	649.12	700.14	1475.13
Temperature (K)	153(2)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1$	$Pnma$	$P\bar{1}$
Unit cell dimensions			
a (Å)	7.7492(15)	20.757(5)	17.244(6)
b (Å)	10.413(2)	12.701(4)	17.249(6)
c (Å)	10.9187(14)	8.644(6)	17.165(6)
α (°)	90	90	98.92(3)
β (°)	100.259(12)	90	99.59(3)
γ (°)	90	90	78.94(3)
Volume (Å^3)	867.0(3)	2278.8(19)	4900(3)
Z	2	4	4
Density (calculated) (Mg/m^3)	2.487	2.041	1.999
Absorption coefficient (mm^{-1})	8.962	5.483	4.946
Crystal size (mm^3)	0.2×0.15×0.15	0.2×0.1×0.1	0.2×0.2×0.2
θ range for data collection (°)	2.67–25.00	2.53–25.01	2.17–25.00
Reflections collected	1724	2094	17814
Independent reflections (R_{int})	1603 (0.0524)	2094	17187 (0.0800)
Completeness to $\theta = 25°$ (%)	99.2	99.2	99.4
Absorption correction	Empirical	Empirical	Empirical
Data/restraints/parameters	1603/1/114	2094/0/112	17187/0/909
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0357$, $wR_2 = 0.0916$	$R_1 = 0.0484$, $wR_2 = 0.1200$	$R_1 = 0.0512$, $wR_2 = 0.1158$
R indices (all data)	$R_1 = 0.0645$, $wR_2 = 0.1052$	$R_1 = 0.1348$, $wR_2 = 0.1524$	$R_1 = 0.2323$, $wR_2 = 0.1720$
Absolute structure parameter	0.31(9)	Centrosymmetric	Centrosymmetric
Largest difference peak and hole (e Å^{-3})	1.358 and −1.611	1.370 and −1.468	1.022 and −1.852

least-squares refinement from the setting angles of 20 reflections. An empirical correction for the effects of absorption was made based on several ψ-scans. Crystal and refinement data for compounds **1**–**6** are summarized in Tables 1 and 2. All structures were solved using SHELXS-97 [19] and refined using full-matrix least-squares calculations on F^2 (SHELXL-97) [19] operating in the WinGX program package [20]. Anisotropic thermal displacement parameters were refined for all the non-hydrogen atoms, except in **4** where the carbon atoms are slightly disordered due to racemic twinning. Hydrogen atoms were placed in calculated positions and refined using a riding model. Structural illustrations have been drawn with ORTEP-3 [21] for Windows and PLUTON [22] under WinGX.

3. Results and discussion

3.1. Synthesis

Divalent lanthanide complexes are inherently sensitive towards oxidation and although solutions of SmI$_2$ in THF are commercially available, it is advantageous to prepare them (directly prior to use) in the laboratory by sonication of samarium chips and 1,2-diiodoethane

in THF. If the reaction is performed in a centrifuge tube, it is easy to withdraw the clear dark-blue solution with a cannula after centrifugation. Should the solution not be used directly, one can add a few chips of samarium metal, which will prohibit high concentrations of Sm(III). It is not easy to judge the Sm(III) content by the color of the solution, since Sm(II) complexes are very dark blue (almost black) while the corresponding Sm(III) complexes are light-yellow. We have discovered that freshly prepared THF solutions of SmI$_2$ are excellent precursors for the preparation of new divalent samarium complexes containing neutral polydentate ligands. Moreover, if the new ligand is introduced slowly along the sides of the Schlenk flask, the product will exclusively consist of large, X-ray quality single crystals. This preparative method can be extended to ytterbium and europium, but the solvent volume must be increased since the solubility of YbI$_2$ in THF is approximately ten times lower as compared to SmI$_2$. An alternative synthetic method is to use the polydentate ligand as solvent and sonicate the metal, 1,2-diiodoethane, and the ligand for an extended period of time in order to ensure that the reaction is completed. The product, in this case, will contain lanthanide metal (since it must be added in excess) residues and the crystal quality will generally be lower. Work-up of this crude material is not trivial due
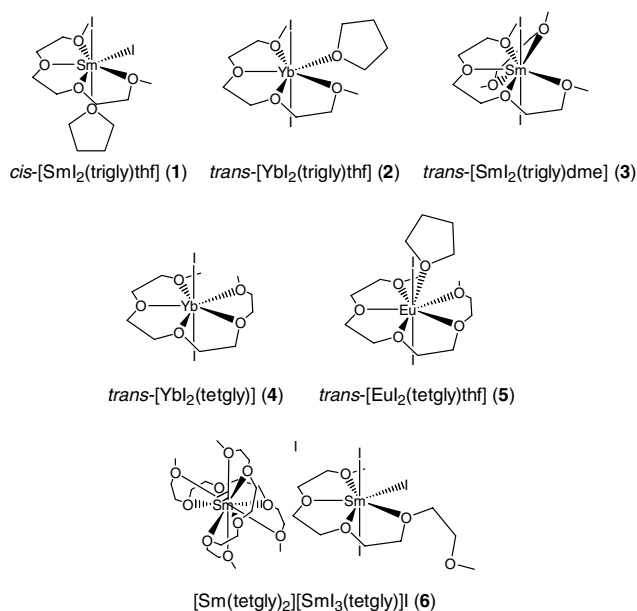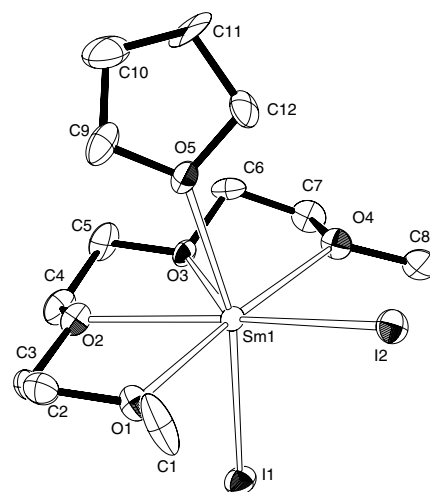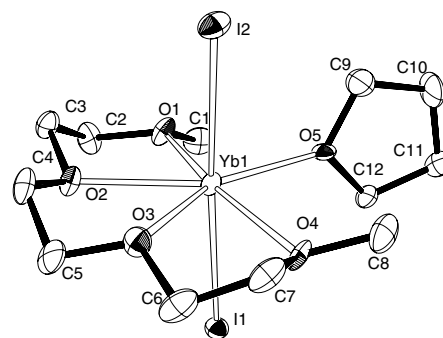
cis-[SmI₂(trigly)thf] (**1**)   *trans*-[YbI₂(trigly)thf] (**2**)   *trans*-[SmI₂(trigly)dme] (**3**)

trans-[YbI₂(tetgly)] (**4**)   *trans*-[EuI₂(tetgly)thf] (**5**)

[Sm(tetgly)₂][SmI₃(tetgly)]I (**6**)

Fig. 1. Complexes synthesized in this work.

to the low solubility and high air-sensitivity of the complexes in question.

3.2. Crystal structures

Schematic drawings of the six complexes (**1**–**6**) prepared in this work are presented in Fig. 1. The molecular structures of **1** and **2** are shown in Figs. 2 and 3, respectively, and selected intramolecular bond distances and angles are listed in Tables 3 and 4. It is interesting to note that while [SmI₂(trigly)thf] (**1**) has the iodide ligands in a *cisoid* arrangement, the ytterbium analogue is

Fig. 2. ORTEP drawing of **1**.

Fig. 3. ORTEP drawing of **2**.

isolated as *trans*-[YbI₂(trigly)thf] (**2**). This reminds of the first isolation of eight-coordinate stereoisomers, which was reported in 1987 by Sen et al. [23]. They could

Table 3
Selected bond lengths (Å) and angles (°) in **1**

Bond lengths			
Sm(1)–O(5)	2.581(11)	Sm(1)–O(3)	2.609(13)
Sm(1)–O(2)	2.624(14)	Sm(1)–O(4)	2.634(13)
Sm(1)–O(1)	2.653(13)	Sm(1)–I(1)	3.2070(14)
Sm(1)–I(2)	3.2569(13)	O(1)–C(1)	1.40(2)
O(1)–C(2)	1.46(2)	O(2)–C(4)	1.45(2)
O(2)–C(3)	1.46(2)	O(3)–C(5)	1.43(2)
O(3)–C(6)	1.45(2)	O(4)–C(7)	1.44(2)
O(4)–C(8)	1.46(2)	O(5)–C(9)	1.42(2)
Bond angles			
O(5)–Sm(1)–O(3)	82.5(4)	O(5)–Sm(1)–O(2)	77.2(4)
O(3)–Sm(1)–O(2)	63.3(4)	O(5)–Sm(1)–O(4)	90.3(5)
O(3)–Sm(1)–O(4)	62.3(4)	O(2)–Sm(1)–O(4)	125.3(4)
O(5)–Sm(1)–O(1)	89.2(5)	O(3)–Sm(1)–O(1)	126.0(4)
O(2)–Sm(1)–O(1)	62.9(4)	O(4)–Sm(1)–O(1)	171.5(4)
O(5)–Sm(1)–I(1)	164.5(3)	O(3)–Sm(1)–I(1)	88.1(3)
O(2)–Sm(1)–I(1)	87.6(3)	O(4)–Sm(1)–I(1)	96.2(4)
O(1)–Sm(1)–I(1)	86.4(3)	O(5)–Sm(1)–I(2)	88.5(2)
O(3)–Sm(1)–I(2)	144.7(3)	O(2)–Sm(1)–I(2)	147.0(3)
O(4)–Sm(1)–I(2)	83.8(4)	O(1)–Sm(1)–I(2)	87.7(3)
I(1)–Sm(1)–I(2)	106.11(4)	C(1)–O(1)–C(2)	112.9(16)

Table 4
Selected bond lengths (Å) and angles (°) in **2**

Bond lengths			
Yb(1)–O(5)	2.432(10)	Yb(1)–O(2)	2.508(9)
Yb(1)–O(3)	2.510(9)	Yb(1)–O(1)	2.515(9)
Yb(1)–O(4)	2.525(8)	Yb(1)–I(1)	3.1034(13)
Yb(1)–I(2)	3.1196(12)	O(1)–C(1)	1.435(16)
O(1)–C(2)	1.462(16)	O(2)–C(3)	1.437(15)
O(2)–C(4)	1.439(16)	O(3)–C(6)	1.419(16)
O(3)–C(5)	1.441(18)	O(4)–C(7)	1.429(16)
O(4)–C(8)	1.431(17)	O(5)–C(9)	1.445(18)
O(5)–C(12)	1.447(16)	C(2)–C(3)	1.520(18)
Bond angles			
O(5)–Yb(1)–O(2)	146.8(3)	O(5)–Yb(1)–O(3)	149.2(3)
O(2)–Yb(1)–O(3)	63.9(3)	O(5)–Yb(1)–O(1)	80.8(3)
O(2)–Yb(1)–O(1)	66.1(3)	O(3)–Yb(1)–O(1)	130.0(3)
O(5)–Yb(1)–O(4)	84.9(3)	O(2)–Yb(1)–O(4)	128.1(3)
O(3)–Yb(1)–O(4)	64.8(3)	O(1)–Yb(1)–O(4)	163.4(3)
O(5)–Yb(1)–I(1)	88.1(2)	O(2)–Yb(1)–I(1)	91.8(2)
O(3)–Yb(1)–I(1)	94.0(3)	O(1)–Yb(1)–I(1)	87.5(2)
O(4)–Yb(1)–I(1)	83.8(2)	O(5)–Yb(1)–I(2)	91.2(2)
O(2)–Yb(1)–I(2)	91.3(2)	O(3)–Yb(1)–I(2)	84.3(3)
O(1)–Yb(1)–I(2)	97.0(2)	O(4)–Yb(1)–I(2)	91.5(2)
I(1)–Yb(1)–I(2)	175.31(3)	C(1)–O(1)–C(2)	109.5(11)

isolate both *cis*-[SmI$_2$(digly)$_2$] and *trans*-[SmI$_2$(digly)$_2$], digly = diglyme, from the same solution. Concerning complexes **1** and **2**, it is possible that the smaller ytterbium ion prefers to have the iodide ligands in *trans* position. That Yb(II) is smaller than Sm(II) is reflected in shorter Ln–O and Ln–I distances in **2**. Both **1** and **2** are seven-coordinate complexes and may be described as having pentagonal bipyramidal coordination geometry [24], although the O5–Sm1–I1 axis is bent in **1**.

If the thf ligand in **1** is replaced by a 1,2-dimethoxy (dme) ligand, eight-coordinate *trans*-[SmI$_2$(trigly)dme] (**3**) is obtained. There are two molecules in the asymmetric unit of **3** (see Figs. 4 and 5), which is chemically reasonable since the molecules are enantiomers. Selected
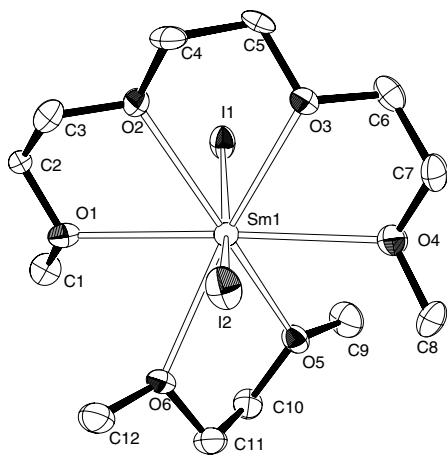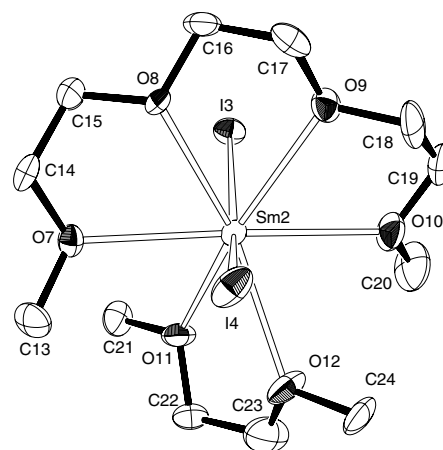

Fig. 5. ORTEP drawing of the Sm2 enantiomer in the asymmetric unit of **3**.

intramolecular bond distances and angles are given in Table 5. In contrast to **1**, the iodide ligands are now in *trans* position, and although the dme ligand is tilted with respect to the equatorial plane, the most appropriate coordination figure is a distorted hexagonal bipyramid. Sm–O and Sm–I bond distances are somewhat longer in **3** (compared to **1**), which reflects the higher coordination number.

The molecular structures of *trans*-[YbI$_2$(tetgly)] (**4**) and *trans*-[EuI$_2$(tetgly)thf] (**5**) are shown in Figs. 6 and 7, respectively, and selected intramolecular bond distances and angles are given in Tables 6 and 7. The pentadentate tetraglyme ligand leaves little room for a sixth ligand in the equatorial plane and the ytterbium

Fig. 4. ORTEP drawing of the Sm1 enantiomer in the asymmetric unit of **3**.

Table 5
Selected bond lengths (Å) and angles (°) in **3**

| Bond lengths			
Sm(1)–O(3)	2.645(9)	Sm(1)–O(2)	2.649(9)
Sm(1)–O(6)	2.653(9)	Sm(1)–O(5)	2.682(9)
Sm(1)–O(4)	2.715(9)	Sm(1)–O(1)	2.743(9)
Sm(1)–I(1)	3.2833(14)	Sm(1)–I(2)	3.2923(14)
Sm(2)–O(8)	2.639(8)	Sm(2)–O(9)	2.646(9)
Sm(2)–O(10)	2.684(10)	Sm(2)–O(7)	2.685(8)
Sm(2)–I(3)	3.2752(14)	Sm(2)–I(4)	3.3042(15)
O(1)–C(1)	1.404(16)	O(1)–C(2)	1.421(14)
O(2)–C(3)	1.420(16)	O(2)–C(4)	1.429(16)
O(3)–C(6)	1.414(15)	O(3)–C(5)	1.445(16)
Bond angles			
O(3)–Sm(1)–O(2)	61.3(3)	O(3)–Sm(1)–O(6)	159.2(3)
O(2)–Sm(1)–O(6)	121.2(3)	O(3)–Sm(1)–O(5)	123.7(3)
O(2)–Sm(1)–O(5)	158.9(3)	O(6)–Sm(1)–O(5)	62.4(3)
O(3)–Sm(1)–O(4)	60.9(3)	O(2)–Sm(1)–O(4)	122.2(3)
O(6)–Sm(1)–O(4)	112.1(3)	O(5)–Sm(1)–O(4)	67.4(3)
O(4)–Sm(1)–O(1)	176.9(3)	O(3)–Sm(1)–I(1)	86.5(2)
O(2)–Sm(1)–I(1)	79.1(2)	O(6)–Sm(1)–I(1)	114.2(2)
O(5)–Sm(1)–I(1)	80.79(19)	O(4)–Sm(1)–I(1)	99.0(2)
O(1)–Sm(1)–I(1)	80.49(19)	O(3)–Sm(1)–I(2)	79.8(2)
O(2)–Sm(1)–I(2)	86.1(2)	O(6)–Sm(1)–I(2)	79.8(2)
O(5)–Sm(1)–I(2)	114.60(19)	O(4)–Sm(1)–I(2)	82.6(2)
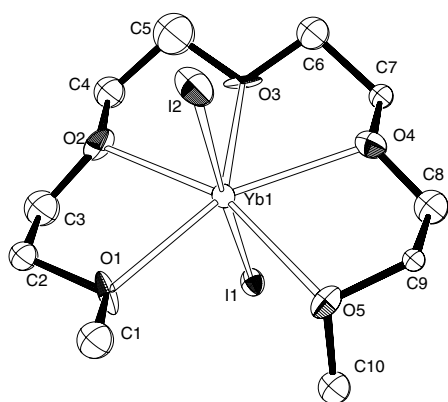
Fig. 6. ORTEP drawing of **4**.
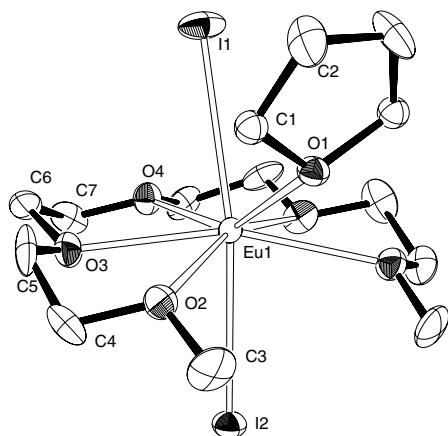
Fig. 7. ORTEP drawing of **5**.

complex crystallizes without any thf ligand even though THF is used as solvent. Taking the high oxophilicity of lanthanide ions into consideration, this should mean that Yb(II) is coordinatively saturated. But when the slightly larger Eu(II) is used, eight-coordinate *trans*-[EuI₂(tetgly)thf] (**5**) is formed. As can be seen in Fig. 7, the thf ligand is coordinated distinctly out of the equatorial plane, which results in bending of the I1–Eu1–I2 axis. The Eu–O and Eu–I distances in **5** are comparable to those in eight-coordinate *trans*-[SmI₂(trigly)dme] (**3**).

While attempting to prepare a samarium analogue of **4**, we were instead able to isolate ionic [Sm(tetgly)₂][SmI₃(tetgly)]I (**6**). The molecular structure of the cation in **6** is shown in Fig. 8, and the complex anion in **6** is displayed in Fig. 9. Selected intramolecular bond distances and angles are listed in Table 8. The Sm(II) ion can apparently accommodate two tetraglyme ligands and thus form a 10-coordinate cationic complex. A similar cesium cation has been previously reported [25]. Two anions, seven-coordinate [SmI₃(tetgly)]⁻ and a iodide ion, balance the charge.

3.3. Chirality

All three triglyme complexes (**1**–**3**) are, by necessity, conformationally chiral in the solid state, since the triglyme ligand forms an odd number (three) of five-membered rings upon coordination to the metal. These rings have chiral conformations, denoted δ and λ (to distinguish chelate ring helicity from configurational helicity, lower case symbols are used), usually in an

Table 6
Selected bond lengths (Å) and angles (°) in **4**

| Bond lengths			
Yb(1)–O(2)	2.367(15)	Yb(1)–O(3)	2.385(12)
Yb(1)–O(1)	2.450(9)	Yb(1)–O(4)	2.507(15)
Yb(1)–O(5)	2.522(16)	Yb(1)–I(2)	3.0782(13)
Yb(1)–I(1)	3.1283(12)	C(6)–C(7)	1.56(3)
O(1)–C(1)	1.38(3)	O(1)–C(2)	1.53(3)
O(2)–C(4)	1.40(2)	O(2)–C(3)	1.45(2)
O(3)–C(6)	1.44(3)	O(3)–C(5)	1.45(4)
O(4)–C(8)	1.39(2)	O(4)–C(7)	1.39(2)
O(5)–C(10)	1.42(2)	O(5)–C(9)	1.48(3)
C(2)–C(3)	1.47(3)	C(4)–C(5)	1.51(4)
Bond angles			
O(2)–Yb(1)–O(3)	68.6(6)	O(2)–Yb(1)–O(1)	70.7(7)
O(3)–Yb(1)–O(1)	138.9(8)	O(2)–Yb(1)–O(4)	134.0(6)
O(1)–Yb(1)–O(4)	155.2(8)	O(2)–Yb(1)–O(5)	157.4(6)
O(3)–Yb(1)–O(5)	133.6(5)	O(1)–Yb(1)–O(5)	86.8(7)
O(4)–Yb(1)–O(5)	68.6(5)	O(2)–Yb(1)–I(2)	89.4(4)
O(3)–Yb(1)–I(2)	95.8(3)	O(1)–Yb(1)–I(2)	89.0(2)
O(4)–Yb(1)–I(2)	89.1(4)	O(5)–Yb(1)–I(2)	91.7(3)
O(2)–Yb(1)–I(1)	91.6(3)	O(3)–Yb(1)–I(1)	83.1(3)
O(1)–Yb(1)–I(1)	92.9(2)	O(4)–Yb(1)–I(1)	89.0(4)
O(5)–Yb(1)–I(1)	87.9(3)	I(2)–Yb(1)–I(1)	178.05(5)

Table 7
Selected bond lengths (Å) and angles (°) in **5**

Bond lengths			
Eu(1)–O(3)	2.618(9)	Eu(1)–O(1)	2.628(12)
Eu(1)–O(2)	2.655(10)	Eu(1)–O(4)	2.656(13)
Eu(1)–I(2)	3.2940(19)	Eu(1)–I(1)	3.326(2)
O(1)–C(1A)	1.53(3)	O(4)–C(7)	1.406(16)
O(2)–C(3)	1.419(16)	O(2)–C(4)	1.428(17)
O(3)–C(5)	1.408(18)	O(3)–C(6)	1.416(15)
C(1A)–C(2)	1.49(3)	C(2)–C(2)*	1.52(3)
Bond angles			
O(3)–Eu(1)–O(3)*	120.5(5)	O(3)–Eu(1)–O(1)	118.2(2)
O(3)–Eu(1)–O(2)	62.2(3)	O(3)*–Eu(1)–O(2)	161.2(3)
O(1)–Eu(1)–O(2)	68.7(3)	O(2)*–Eu(1)–O(2)	108.9(4)
O(3)–Eu(1)–O(4)	61.2(2)	O(3)*–Eu(1)–O(4)	61.2(2)
O(1)–Eu(1)–O(4)	148.4(4)	O(2)–Eu(1)–O(4)	123.2(2)
O(3)–Eu(1)–I(2)	83.5(2)	O(1)–Eu(1)–I(2)	120.9(3)
O(2)–Eu(1)–I(2)	78.3(2)	O(4)–Eu(1)–I(2)	90.7(3)
O(3)–Eu(1)–I(1)	89.0(2)	O(1)–Eu(1)–I(1)	74.3(3)
O(2)–Eu(1)–I(1)	109.8(2)	C(1A)–O(1)–Eu(1)	114.3(16)
O(4)–Eu(1)–I(1)	74.1(3)	I(2)–Eu(1)–I(1)	164.80(5)
C(1A)–O(1)–C(1A)*	113(2)	C(3)–O(2)–C(4)	112.1(12)

Symmetry transformation used to generate equivalent atoms: *$x, -y + 1/2, z$.

alternating pattern. The isomer of **1** shown in Fig. 10 is thus named δλδ, with respect to the triglyme ring conformations. Likewise, the isomer of **2** shown in Fig. 11, and the isomer of **3** shown in Fig. 12, should also be labelled δλδ. However, since none of compounds **1**–**3** crystallize in chiral space groups, the λδλ enantiomer also exists in equal quantity in crystals of **1**–**3**. Another element of chirality is the orientation of the terminal methyl groups in the triglyme ligand. As can be seen in Figs. 10–12, the left methyl group is located below the ligand plane while the right methyl group is situated

above the triglyme plane in the δλδ isomer. The opposite situation is obviously at hand in the λδλ isomer. Finally, a third element of chirality can be found, see Fig. 12, in complex **3**: the orientation of the dme ligand (and the ring helicity). As can be seen from Figs. 4 and 5, both orientations are present in the asymmetric unit of **3**.

The tetraglyme ligand (in complexes **4**–**6**, Figs. 13–15) can form centrosymmetric complexes since it yields an even number of chelate rings on metal coordination. This is very obvious in **5**, where a crystallographic mirror plane runs through I1, I2, Eu1, O1, and O4 (Figs.
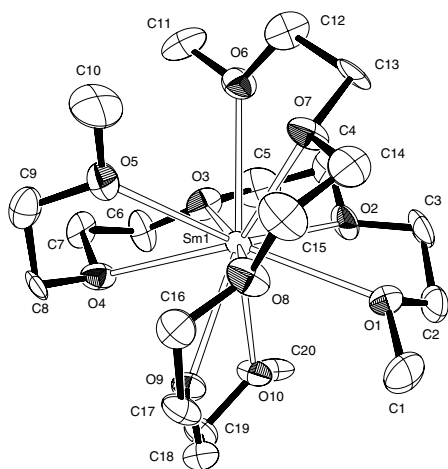
Fig. 8. ORTEP drawing of the cation in **6**.
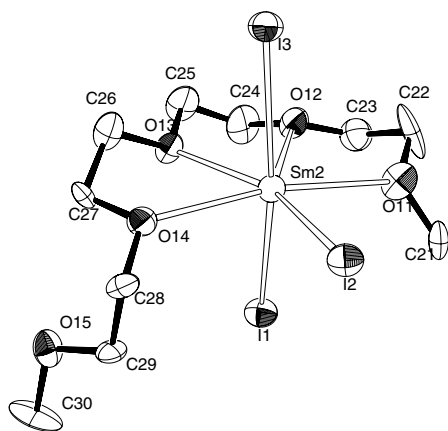
Fig. 9. ORTEP drawing of the complex anion in **6**.

7 and 14), resulting in alternating (δλδλ or δλδλ) ring helicities. However, also in **4** the same pattern can be discerned, even though the crystallographic symmetry is absent. In the cation of complex **6**, two tetraglyme ligands are coordinated (Fig. 15). One of these displays the alternating chelate ring helicity pattern, while the other has a λλδλ (or δδλδ) pattern.

As can be seen from Fig. 15, the cation of **6** exhibits another element of chirality: the tetraglyme ligands are wrapped around the samarium metal in a helical manner. Unfortunately, both enantiomers are present in equal amounts in **6**, since it crystallizes in a centrosymmetric space group. It might, however, be possible to resolve the cations with an enantiopure anion.

The only complex in this work which crystallizes as a conglomerate, and thus has potential as an enantioselective reagent, is *trans*-[YbI₂(tetgly)] (**4**). The chirality in molecules of **4** stems from the arrangement of the terminal methyl groups in the tetraglyme ligand. The two enantiomers are depicted in Fig. 13. Since these enantiomers crystallize in separate crystals, they can be subjected to preferential crystallization.

3.4. Reactivity

Since complex **4** crystallizes as a conglomerate, it should be possible to obtain a bulk sample that is enantiomerically enriched, utilizing the secondary nuclei that are spawned from an enantiopure seed crystal. A problem is that there seems to be substantial racemic twinning in crystals of **4**. As can be seen from the refinement results (the Flack parameter was refined separately and found to

Table 8
Selected bond lengths (Å) and angles (°) in **6**

Bond lengths			
Sm(1)–O(2)	2.667(12)	Sm(1)–O(3)	2.669(13)
Sm(1)–O(9)	2.706(12)	Sm(1)–O(1)	2.707(14)
Sm(1)–O(4)	2.712(14)	Sm(1)–O(10)	2.715(13)
Sm(1)–O(8)	2.717(14)	Sm(1)–O(5)	2.735(14)
Sm(1)–O(7)	2.751(13)	Sm(1)–O(6)	2.822(14)
Sm(2)–O(11)	2.604(13)	Sm(2)–O(13)	2.616(11)
Sm(2)–O(12)	2.639(12)	Sm(2)–O(14)	2.655(12)
Sm(2)–I(2)	3.260(2)	Sm(2)–I(3)	3.2622(19)
Sm(2)–I(1)	3.2823(19)	O(1)–C(2)	1.42(3)
O(1)–C(1)	1.49(2)	O(2)–C(3)	1.40(2)
O(2)–C(4)	1.43(2)	O(3)–C(6)	1.43(2)
O(3)–C(5)	1.44(3)	O(4)–C(8)	1.41(2)
Bond angles			
O(2)–Sm(1)–O(3)	60.1(4)	O(2)–Sm(1)–O(9)	127.2(4)
O(3)–Sm(1)–O(9)	121.4(4)	O(2)–Sm(1)–O(1)	60.7(4)
O(3)–Sm(1)–O(1)	118.8(5)	O(9)–Sm(1)–O(1)	84.5(4)
O(13)–Sm(2)–I(2)	151.4(3)	O(12)–Sm(2)–I(2)	146.2(3)
O(14)–Sm(2)–I(2)	89.2(3)	O(11)–Sm(2)–I(3)	95.7(3)
O(13)–Sm(2)–I(3)	85.1(3)	O(12)–Sm(2)–I(3)	84.0(3)
O(14)–Sm(2)–I(3)	92.1(3)	I(2)–Sm(2)–I(3)	90.89(5)
O(11)–Sm(2)–I(1)	85.8(3)	O(13)–Sm(2)–I(1)	81.2(3)
O(12)–Sm(2)–I(1)	82.5(3)	O(14)–Sm(2)–I(1)	88.8(3)
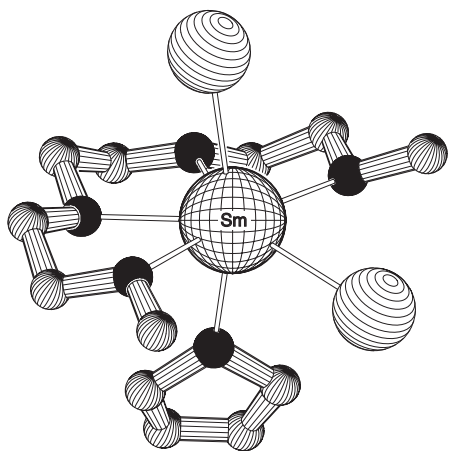
Fig. 10. Showing the chelate ring helicity in **1**.
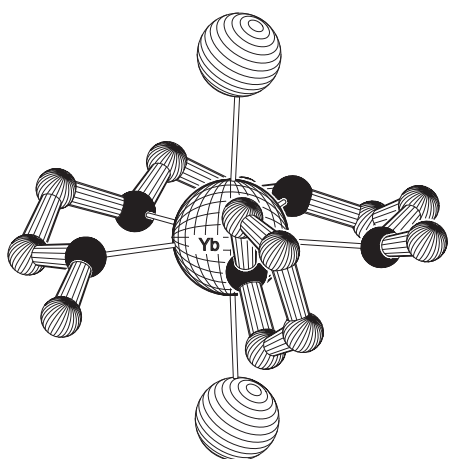
Fig. 11. Showing the ligand conformation in **2**.
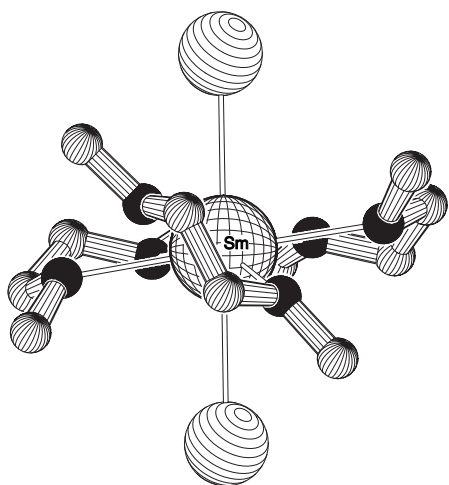
Fig. 12. Coordination of the dme ligand in **3** adds an element of chirality to the molecule.
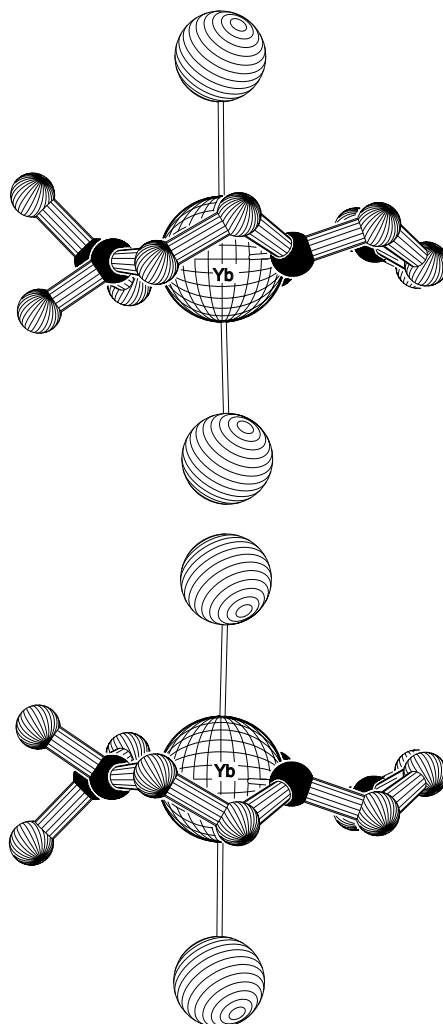
Fig. 13. The two enantiomers in **4** crystallize separately.
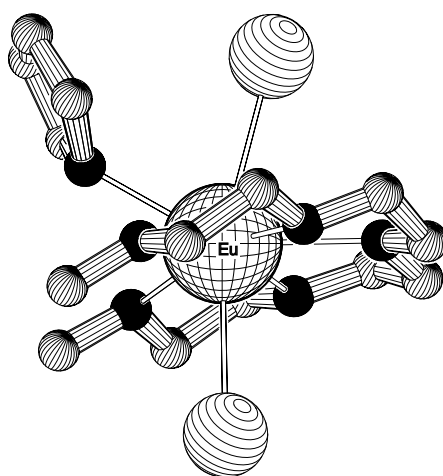
Fig. 14. A thf ligand can be coordinated in **5** by adjustment of the tetraglyme ligand conformation.

be 0.31) of the diffraction data of **4** in Table 2, this crystal consisted of 31% of one enantiomer and, consequently, 69% of the other. In our experience, if one crystal exhibits
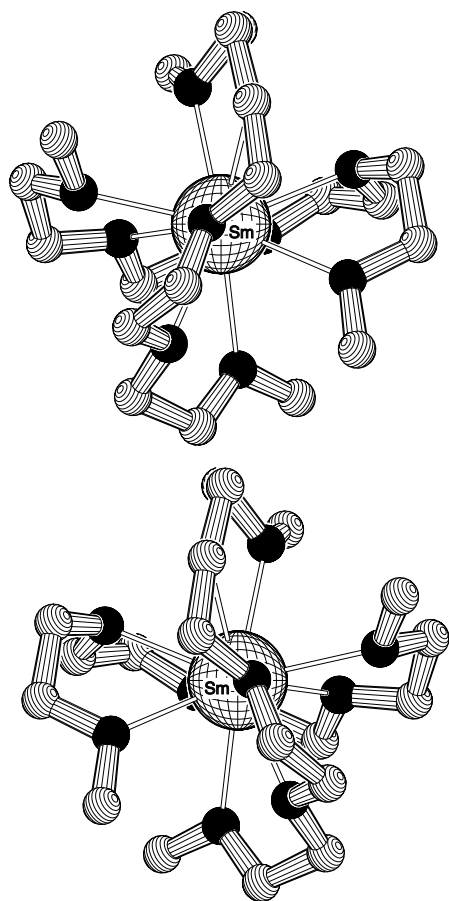
Fig. 15. The cations in **6** display helical chirality.

racemic twinning, it is very likely that all crystals are twinned. However, despite partial twinning, it is still possible that the bulk is enantiomerically enriched. To prevent racemization, reactions must be heterogeneous or/and performed at low temperature. In an attempt to test the enantioselectivity, acetophenone was added to a suspension of the chiral ytterbium complex **4** at low temperature, using methanol as proton donor. However, the obtained 1-phenylethanol was racemic. It must be concluded that either the reagent sample was racemic (from twinning) or else the enantioselectivity (using this solid ytterbium reagent, which is only conformationally chiral) in carbonyl reductions is very low.

An important piece of information regarding possible transition states may be present in the molecular structures of *trans*-[YbI$_2$(tetgly)] (**4**) and *trans*-[EuI$_2$(tetgly)thf] (**5**), see Figs. 13 and 14. It is apparently possible for a monomeric seven-coordinate ytterbium (or samarium) complex like **4** to accommodate an incoming substrate, modelled by the thf ligand in **5**, without having to expel a iodide ion (or reduce the denticity of the tetraglyme ligand) first. Of course, depending on the ligands that carry the stereochemical information, aggregation may have to be considered as well.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 223690 for compound **1**, CCDC 223691 for compound **2**, CCDC 223692 for compound **3**, CCDC 223693 for compound **4**, CCDC 223694 for compound **5**, and CCDC 222695 for compound **6**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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