

## The Heterometallic Clusters of Trivalent Rare Earth Metals of [Ln(OPh)<sub>6</sub>{Li(dme)}<sub>3</sub>], with Ln = Eu and Sm

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Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

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Two new heterobimetallic phenoxide Ln<sup>III</sup>-Li complexes of formula [Ln( $\mu_2$ -OPh)<sub>6</sub>{Li(dme)}<sub>3</sub>] (Ln = Sm, Eu) have been synthesized and characterized using single-crystal X-ray diffraction. These two compounds are isostructural.

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**Introduction.** – The use of the bis(cyclopentadienyl) ligand sets ((C<sub>5</sub>R<sub>5</sub>)<sub>2</sub>, R = H, Me) as stabilizing and solubilizing moieties has for a long time been a crucial factor in the development of organolanthanide chemistry (for reviews, see [1]). Later, in an attempt to extend lanthanide chemistry, alternative ligands such as alkoxides and aryl oxides have been employed. Alkoxides (aryl oxides) are attractive ligands for lanthanides, since they induce strong metal–ligand bonds and can be sterically easily tuned. Lanthanide alkoxides and aryl oxides have been extensively studied due to the applicability of these complexes as precursors to high purity oxides [2] and catalysts for organic reactions [3]. However, in order to form monomers or aggregates with a small degree of polymerization such as dimers or trimers, encumbered aryolate anions are usually employed. So far, little is known about the less sterically hindered, simple phenolate anion. In a recent paper [4], we described the similar behavior observed for lanthanide(II) (Sm<sup>2+</sup> and Eu<sup>2+</sup>) and heavy alkaline earth metal ions (Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>) in weak polar, aprotic solvents using the unhindered ligands PhO<sup>−</sup>. We showed that due to similar ionic radii and chemical behavior, Ln<sup>2+</sup> (Ln = Sm, Eu) and Sr<sup>2+</sup> aryloxide complexes adopt similar structural arrangements in the presence of LiOPh and THF, yielding cluster compounds of the general composition [M<sup>2+</sup>Li<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>]. We also studied the impact of the recrystallization solvent using the bidentate Lewis-base ligand DME (DME = 1,2-dimethoxyethane) [4][5]. However, divalent lanthanide complexes are inherently sensitive towards oxidation and during attempts of crystallization of compounds [LnLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (Ln = Sm, Eu) in DME solution, two isostructural Ln<sup>III</sup> complexes have been produced, namely [Sm( $\mu$ -OPh)<sub>6</sub>{Li(dme)}<sub>3</sub>], **1**, and [Eu( $\mu$ -OPh)<sub>6</sub>{Li(dme)}<sub>3</sub>], **2**. We report herein the synthesis and structural characterization of these new complexes.

**Results and Discussion.** – The two [Ln( $\mu_2$ -OPh)<sub>6</sub>{Li(dme)}<sub>3</sub>] clusters (Ln = Sm and Eu, **1** and **2**, resp.) crystallize in the trigonal space group *R*-3 (Nr. 148) with six

molecules per unit cell. Their crystal structures are presented in *Figs. 1* and *2*, respectively.

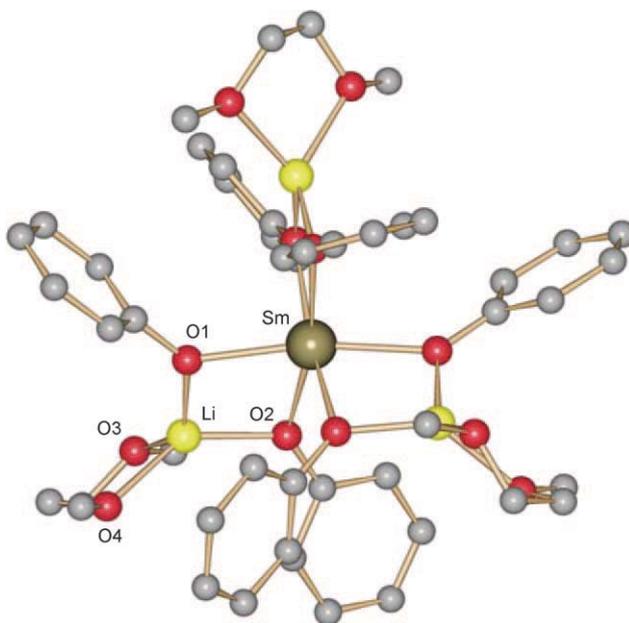


Fig. 1. Partially labeled molecular structure of **1**, H-atoms have been omitted for clarity

In both complexes, **1** and **2**, the  $\text{Ln}^{3+}$  cation lies on a three-fold axis ( $\text{Ln}^{3+}$ :  $1/3, 2/3, z$  (c)). The coordination geometry of each cation can be considered as a trigonal antiprism derived by trigonal compression of an octahedron. Indeed, the distortion from octahedral geometry is induced by the presence of three bridging Li-atoms between pairs of phenolate ligands. The most important bond lengths and angles in **1** and **2** are summarized in *Tables 1* and *2*. For instance, the bite angles  $\text{O1}-\text{Ln}^{3+}-\text{O2}$  are  $73.29(2)^\circ$  in **1**, and  $74.01(5)^\circ$  in **2**, respectively. In **1** and **2**, the rhombic  $\text{LnLiO}_2$  are very similar in distances and angles.

The  $\text{Ln}^{3+}-\mu_2\text{-OPh}$  distances are slightly longer in **1** compared to **2** probably due the smaller ionic radius of  $\text{Eu}^{3+}$  and thus the  $\text{O1}-\text{Ln}^{3+}-\text{O2}$  angle is smaller in **1**. For **2**, the  $\text{Eu}^{3+}-\mu_2\text{-OPh}$  bond lengths average is  $2.285(5) \text{ \AA}$  and with an average distance of  $2.306(4) \text{ \AA}$  in **1**, the  $\text{Sm}^{3+}-\mu_2\text{-OPh}$  bond lengths in **1** are longer than the only  $\text{Sm}-\text{OPh}$  distance found in the literature for  $[\text{Sm}(\text{Cp}^*)_2(\text{OPh})(\text{thf})]$  ( $2.1645(14) \text{ \AA}$ ) [6] ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ), the latter being terminal. Thus, as expected, they are also longer than other terminal  $\text{Sm}^{3+}-\text{OR}$  bonds [7], even with a very bulky alkyl-group such as either  $^i\text{Pr}$ - or  $^t\text{Bu}$ -groups in *ortho* positions of the Ph ring as found in  $[\text{Sm}(\text{Cp}^*)(2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3\text{O})_3\text{-Li}(\text{thf})]$  ( $2.144(6) \text{ \AA}$ ) or  $[\text{Sm}(\text{Cp}^*)(2,6\text{-}^t\text{Bu}_2\text{-C}_6\text{H}_3\text{O})_2(\text{thf})]$  (average  $2.160(5) \text{ \AA}$ ) [7a][7b]. This is an effect of the loss of electron density at the O-atom upon forming the  $\text{Sm}-\text{O}-\text{Li}$  bridges.

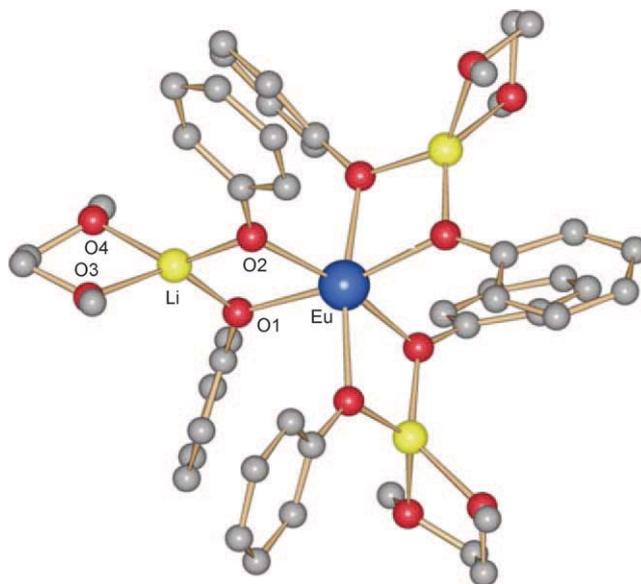


Fig. 2. Partially labelled molecular structure of **2**, H-atoms have been omitted for clarity

Table 1. Most Important Bond Lengths and Angles in **1**

Bond	Bond Length [ $\text{\AA}$ ]	Angle	Angle [ $^\circ$ ]
Sm–O1(OPh)	2.318(4)	O1–Sm–O2 (bridge)	73.29(2)
Sm–O2(OPh)	2.294(4)	O1–Sm–O2 (same plane)	88.67(2)
Li–O1(OPh)	1.907(2)	O1–Sm–O1	102.21(2)
Li–O2(OPh)	1.874(2)	O2–Sm–O2 (same plane)	96.32(2)
Li–O3(dme)	2.015(2)	O1–Sm–O2 ( <i>trans</i> )	168.97(2)
Li–O4(dme)	2.020(2)	O3–Li–O4	81.9(4)
Sm $\cdots$ Li	3.145(1)	Li $\cdots$ Sm $\cdots$ Li	119.63(5)

Table 2. Most Important Bond Lengths and Angles in **2**

Bond	Bond Length [ $\text{\AA}$ ]	Angle	Angle [ $^\circ$ ]
Eu–O1(OPh)	2.294(1)	O1–Eu–O2 (bridge)	74.01(5)
Eu–O2(OPh)	2.279(7)	O1–Eu–O2 (same plane)	89.56(6)
Li–O1(OPh)	1.909(4)	O1–Eu–O1	101.32(5)
Li–O2(OPh)	1.875(4)	O2–Eu–O2 (same plane)	95.67(5)
Li–O3(dme)	2.024(4)	O1–Eu–O2 ( <i>trans</i> )	168.89(5)
Li–O4(dme)	2.029(4)	O3–Li–O4	81.75(2)
Eu $\cdots$ Li	3.124(4)	Li $\cdots$ Eu $\cdots$ Li	119.66(4)

However, bond lengths slightly shorter than the rare Sm<sup>3+</sup>– $\mu_2$ -OAr are found in the literature. In [Li(thf)<sub>2</sub>][Sm(2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] [**7b**] and [Sm(Cp\*)(2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>Li(thf)] [**7a**], the two phenolate anions also bridge a Sm<sup>III</sup> metal ion to a Li<sup>+</sup>

cation with relatively shorter  $\mu_2$ -OAr bonds lengths (average 2.265(7) Å in the former, 2.248(5) Å in the latter) than found in **1**. Nevertheless, this can be understood with the lower coordination number of the samarium cation in both complexes. The Li- $\mu_2$ -OPh bond lengths in **1** and **2** are similar with 1.890(5) Å in **1**, respectively 1.892(4) Å in **2**. As expected they are shorter than the Li- $\mu_3$ -OPh observed in the parent THF-clusters and due to the bridging mode of the PhO-anions. They correspond well with those found in [Sm(Cp\*)(2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>Li(thf)] (Li-OAr = 1.910(5) Å) [7a] or [Li(thf)]<sub>2</sub>[Sm(2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (average 1.874(5) Å) [7b], although the lithium cation possesses the lower coordination number 3 in both complexes, but the aryloxy groups are bulkier. As cited above, on the one hand due to longer Ln-OPh distances in **1** compared to **2**, the O1-Sm-O2 angle is with 73.29(16)° in **1** slightly smaller than the one observed in **2** (O1-Eu-O2 = 74.01(6)°), on the other hand, the Ln-O(Ar)-Li angles are similar (96.6(4)° in **1**, 96.29(5)° in **2**) which are in the same range of values as found in [Li(thf)]<sub>2</sub>[Sm(2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (average ArO-Sm-OAr = 73.81(22)°, Sm-OAr-Li = 96.2(6)°) [7b] and [Sm(Cp\*)(2,6-<sup>i</sup>Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>Li(thf)] (average ArO-Sm-OAr = 76.9(2)°, Ln-O(Ar)-Li = 94.6(6)°) [7a].

In both complexes **1** and **2**, the Li-atoms complete their traditional tetrahedral coordination sphere with a coordinating DME molecule with average Li-O(dme) distances of 2.017(5) Å in **1** and of 2.026(5) Å in **2**. The Li-O(dme) bonds are slightly longer in **2** due to the shorter Eu- $\mu_2$ -OPh distances. These values are common, as well as the O(dme)-Li-O(dme) angles with 81.9(4)° in **1**, respectively 81.75(2)° in **2** [8].

These two complexes join the group of the few structurally characterized homoleptic six-coordinated phenolate complexes which are usually obtained with early-transition metals. For instance for W<sup>V</sup>, two compounds are reported: [W(OPh)<sub>6</sub>][N(Et)<sub>4</sub>] and [W(OPh)<sub>6</sub>][Li(thf)<sub>2</sub>] [9] and for W<sup>VI</sup>, only the compound [W(OPh)<sub>6</sub>] [10] is known. From the literature, only one isostructural complex has been characterized with V<sup>III</sup>, namely [V( $\mu_2$ -OPh)<sub>6</sub>Li(dme)]<sub>3</sub> [8a].

If the two bridging phenolate-groups are replaced by a binaphtholate (binaphthol = (C<sub>10</sub>H<sub>6</sub>OH)<sub>2</sub>) or catecholate group (catechol = C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>), a rich structural database for trivalent lanthanide as well as transition metals complexes, with general formula M'<sub>3</sub>[M(X)<sub>3</sub>] (M' = alkali metal, M = lanthanide or transition metals, X = binaphthol [11] or catecholate [12]) is reported. In the binaphtholate complexes, the two naphtholate-groups can rotate around the C-C bond, and thus, chirality is induced. The M<sub>3</sub>[Ln(binol)<sub>3</sub>] (M = alkali metal, Ln = lanthanide) complexes are very efficient catalysts in enantioselective organic reactions following a Lewis-acid mechanism, such as alkyl additions to aldehydes. Unfortunately, **1** and **2** have not shown any catalytic activity for such organic reactions. Recently, Wooten *et al.* have discussed the possible issues of why the binolate complexes do show catalytic activity [11j][11k]. One prerequisite is the capability of binding of a substrate. It was shown that the complexes of the type M<sub>3</sub>[Ln(binol)<sub>3</sub>] described in Literature ([11]) are asymmetric with respect to the view along the C<sub>3</sub>-axis, if seen from above or below (Fig. 3). This asymmetry is due to the fact that the three alkali metal ions form a mean plane from which the lanthanide cation is more or less offset, leading to one 'triangular' face which is more open and exposes partially the lanthanide ion, so that a guest molecule is able to bind. This was shown by NMR studies as well as by single crystal structures [11j][11k]. The lanthanide ion increases then its coordination number from six to seven. The deviation

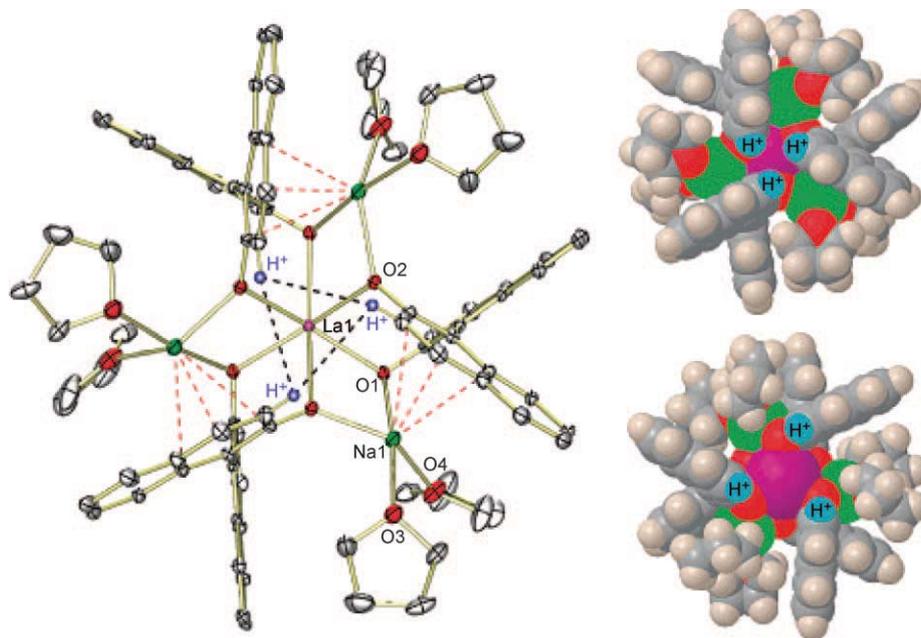


Fig. 3. Example of a  $M_3[Ln(binol)_3]$  with  $M = Na$ ,  $Ln = La$  and the two sights onto the  $C_3$ -axis [ $x$ ] ([11a])

of the lanthanide cation from the mean plane formed by the alkali metal cations varies in the literature examples between 0 and 0.5 Å, and depends on the size of the lanthanide ion when the binol and alkali metal ion are identical [11g].

Figs. 4 and 5 show that compounds **1** and **2** also possess an asymmetric arrangement compared to the mean plane of lithium cations in each structure. On one side of this triangle, the Ph moieties of the PhO groups arrange such that three H-atoms point towards each forming a triangle as indicated in Figs. 4 and 5, left. This side is the one which is widest open for potential guest molecules, but compared to other literature examples, the cavity is tiny (see Fig. 3). On the opposite side of the triangle, a denser packing of the Ph rings is observed, together with interactions of the H-atoms from a Me group of DME with the neighbor Ph rings. However, the asymmetry between the two sides is not very strong, and the lanthanide cation is out of plane only by 0.193(2) Å, and 0.182(4) Å for **1** and **2**, respectively. None of the small cavities formed is large enough for substrate molecules to enter and coordinate to the  $Ln^{III}$  cation. This explains why our compounds do not have catalytic properties.

The packing of both compounds **1** and **2** is such that *via* H-bonds, a three-dimensional network of cluster compounds is formed.

**Conclusions.** – Simple, sterically unhindered phenolates are capable of forming similar  $C_3$ -symmetrical cluster compounds as the well-known binolates. A slight asymmetry is observed for the binding of the phenolate anions, when their arrangement below and above the mean plane through the alkali metal ions is considered. This does however not allow the binding of a substrate molecule, and thus, no catalytic activity is observed.

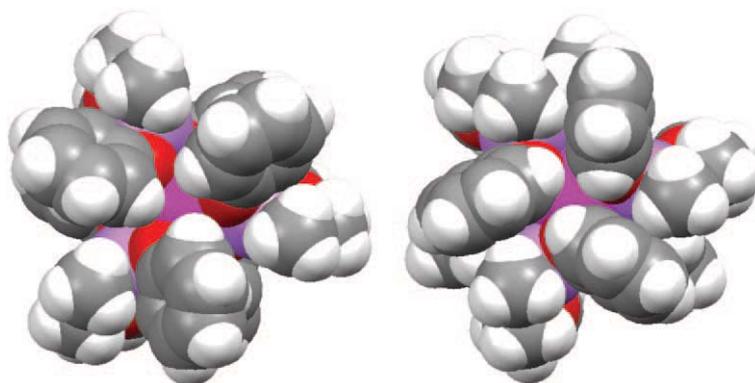


Fig. 4. Space-filling model of **1** seen along the  $C_3$ -axis from above and below

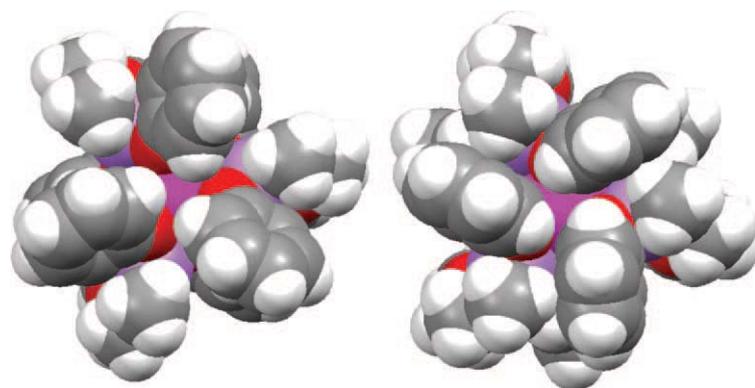


Fig. 5. Space-filling model of **2** seen along the  $C_3$ -axis from above and below

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#### Experimental Part

*General.* All experiments were carried out under an inert  $N_2$  or Ar atmosphere, using *Schlenk* techniques. THF and 1,2-dimethoxyethane (DME) solvents were dried over Na/benzophenone ketyl and distilled under  $N_2$  prior to use. Further investigations other than single-crystal structure analysis were difficult or impossible due to air and water sensitivity of the compounds.

$[Sm(OPh)_6\{Li(dme)\}_3]$ . In the labmaster glovebox, a 1M soln. of LiOPh in THF (10 equiv., 10.0 ml) was added dropwise under  $N_2$  to a 0.1M soln. of  $SmI_2$  in THF (10 ml, 1.00 mmol). The blue-purple soln. turned yellow within 2 h after getting out of the labmaster glovebox. The yellow soln. was left at r.t. under magnetic stirring during 1 d. Afterwards the soln. was evaporated to dryness yielding a yellow-brown solid which was partially dissolved in 15 ml of DME. The mixture was left at r.t. under magnetic stirring one night and then filtered. Colorless single crystals of **1** suitable for X-ray analysis were grown in a yield of 35% with respect to  $SmI_2$  at  $-25^\circ$  within 3 d. Anal. calc. for  $C_{48}H_{60}Li_3O_{12}Sm$  (1000.13): calc. C 57.59, H 6.02; found: C 57.07, H 5.87.

$[Eu(OPh)_6\{Li(dme)\}_3]$ . In the labmaster glovebox, to  $EuI_2$  (0.402 g, 0.99 mmol) a 1M soln. of LiOPh in THF (10 equiv., 10.0 ml) was added dropwise under  $N_2$ . The slight yellow soln. turned yellow within

1 h after getting out of the labmaster glovebox. The yellow soln. was left at r.t. under magnetic stirring during 1 d. Afterwards, the soln. was evaporated to dryness yielding a yellow-brown solid, which was partially dissolved in 15 ml of DME. The mixture was left at r.t. under magnetic stirring one night and then filtered. Colorless single crystals of **2** suitable for X-ray analysis were grown in a yield of 23% with respect to  $\text{EuI}_2$  at  $-25^\circ$  within 3 d. Anal. calc. for  $\text{C}_{48}\text{H}_{60}\text{EuLi}_3\text{O}_{12}$  (1001.74): calc. C 57.51, H 6.01; found: C 56.95, H 5.87.

*Crystallographic Analysis.* Single crystals were mounted on a glass fiber and all geometric and intensity data were taken from this crystal. Data collection using  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was performed at the University of Basel, on a *STOE IPDS-II* diffractometer equipped with an *Oxford Cryosystem* open flow cryostat [13]. Absorption corrections were partially integrated in the data reduction procedure [14]. The structures were solved by direct methods (SHELXS) and refined using full-matrix leastsquares on  $F^2$  (SHELXL-97 [15] or SHELXL-99 [16]). All heavy atoms could be refined anisotropically. H-Atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions. Crystallographic data for the structures **1** and **2** have been deposited with the *Cambridge Crystallographic Data Center* with the CCDC No. 730163 and 730164, resp. Copies of the data can be obtained free of charge on application to *CCDC*, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

*Crystal Data and Structure Refinement for  $[\text{Sm}(\text{OPh})_6[\text{Li}(\text{dme})_3]$  (**1**).* See Table 3.

*Crystal Data and Structure Refinement for  $[\text{Eu}(\text{OPh})_6[\text{Li}(\text{dme})_3]$  (**2**).* See Table 3.

Table 3. *Crystal Data and Structure Refinement for **1** and **2***

	$[\text{Sm}(\text{OPh})_6[\text{Li}(\text{dme})_3]$ ( <b>1</b> )	$[\text{Eu}(\text{OPh})_6[\text{Li}(\text{dme})_3]$ ( <b>2</b> )
Empirical formula	$\text{C}_{48}\text{H}_{60}\text{Li}_3\text{O}_{12}\text{Sm}$	$\text{C}_{48}\text{H}_{60}\text{EuLi}_3\text{O}_{12}$
$M_r$	1000.13	1001.74
$T$	203(2) K	203(2) K
$\lambda$	0.71073 $\text{\AA}$	0.71073 $\text{\AA}$
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}$
Unit cell dimensions	$a = 20.456(3) \text{ \AA}$ $c = 20.519(4) \text{ \AA}$	$a = 20.4556(11) \text{ \AA}$ $c = 20.5558(14) \text{ \AA}$
Volume	$7436(2) \text{ \AA}^3$	$7448.9(8) \text{ \AA}^3$
$Z$	6	6
$\rho_{\text{calc}}$	$1.340 \text{ Mg/m}^3$	$1.340 \text{ Mg/m}^3$
Abs. coefficient	$1.242 \text{ mm}^{-1}$	$1.320 \text{ mm}^{-1}$
$F(000)$	3090	3096
$\theta$ range	$1.99 - 27.04^\circ$	$2.50 - 26.99^\circ$
Index ranges	$-23 \leq h \leq 26$ , $-19 \leq k \leq 26$ $-18 \leq l \leq 26$	$-25 \leq h \leq 25$ $-25 \leq k \leq 25$ $-26 \leq l \leq 26$
Reflections coll.	4873	19017
Indep. reflections	3205 [ $R(\text{int}) = 0.1007$ ] (2468 observed)	3543 [ $R(\text{int}) = 0.2260$ ] (3437 observed)
Completeness	88.3 %	98.1 %
Ref. method	Full-matrix least-squares	Full-matrix least-squares
Parameters refined	195	196
GooF	1.051	1.131
Final $R$ [ $I > 2\sigma(I)$ ]	$R^1 = \Sigma  F_o - F_c  / \Sigma F_o = 0.0663$ $wR^2 = 0.1586$	$R^1 = \Sigma  F_o - F_c  / \Sigma F_o = 0.0456$ $wR^2 = 0.1186$
$R$ indices (all data)	$R^1 = 0.0880$ $wR^2 = 0.1720$	$R^1 = 0.0463$ $wR^2 = 0.1198$

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