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Crystal structure of chiral binaphthol lanthanide complexes and their catalysis in asymmetric transfer hydrogenation of acetophenone

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Heterometallic [$(THF)_2Na]_3[Ln(R\text{-Binolate})_3(H_2O)]$ [Ln = Sm (1) and Gd (2)] has been synthesized by the reactions of either $LnCl_3$ or $LnBr_3$ with 3 equiv. Na(*R*-HBinolate) and characterized by X-ray crystallographic analysis. Structural analyses proposed that 1 and 2 are isomorphous complexes, crystallizing in the hexagonal space group P6$_3$ with C_3 symmetry. The coordination geometry of the lanthanide ions in 1 and 2 can be best approximated as a mono-capped triangle antiprism. When complexes 1 and 2 were employed as catalysts in the Meerwein–Ponndorf–Verley (MPV) reactions of acetophenone, the *S*-phenylethanol was separated in 94 and 85% enantiomeric excess (e.e.) for 1 and 2, respectively. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: synthesis; structure; chiral binaphthol lanthanide; catalysis; asymmetric transfer hydrogenation

INTRODUCTION

Heterometallic alkali metal lanthanide binaphtholates of the general formula $M_3[Ln(Binolate)_3(H_2O)]$ [M = alkali metal, Ln = lanthanide metal, H_2Binolate = Binaphthol] were first applied[1–3] as catalysts and structurally characterized by Shibasaki and Aspinall.[4–8] $M_3[Ln(Binolate)_3(H_2O)]$ exhibits the unique feature that it can act as a bifunctional catalyst, e.g. lanthanide metals work as Lewis acids and binaphthol ligands can act as Brønsted bases. This bifunctional behavior has been identified as the same as that of enzymes. In the past decade, this group of catalysts has played an essential role in asymmetric catalytic reactions,[9–11] e.g. $Li_3[La(Binolate)_3]$ efficiently catalyzes the asymmetric nitroaldol reactions by reducing catalyst loading (1 mol%);[12] $Na_3[La(Binolate)_3]$ is an effective catalyst for Michael addition reactions;[5,13,14] and $K_3[Ln(Binolate)_3]$ is a successful catalyst for hydrophosphonylation of imines.[15–17] However, this series of complexes has not been applied as catalysts for the Meerwein–Ponndorf–Verley (MPV) reduction of ketones. It is known that MPV reactions are catalyzed successfully by small quantities of lanthanide alkoxides, in which a highly enantioselective product of this reaction has been reported by Evans.[18] However, the catalyst formed *in situ* was not isolated and characterized in this case. To our knowledge, among the heterometallic sodium lanthanide chiral binaphtholates of the general formula $[Na(THF)_2]_3[Ln(Binolate)_3(H_2O)]$, only a few complexes (Ln = La, Pr, Nd and Eu) have been structurally studied. In addition, the catalytically important lanthanide metal samarium has not been studied. In this paper, complexes $\{[(THF)_2Na]_3[Ln(R\text{-Binolate})_3(H_2O)]\}$ [Ln = Sm (**1**) and Gd (**2**)] were synthesized by the reactions of either anhydrous $LnCl_3$ or $LnBr_3$ with chiral Na_2(*R*-Binolate) and characterized by X-ray crystallographic analyses. When **1** and **2** were applied as catalysts in the MPV reactions of acetophenone, a highly enantioselective product (up to 94% e.e.) of asymmetric hydrogen transfer reduction was isolated.

RESULTS AND DISCUSSION

Synthesis

From previous descriptions of a large variety of aryloxide lanthanide complexes, the most popular synthetic

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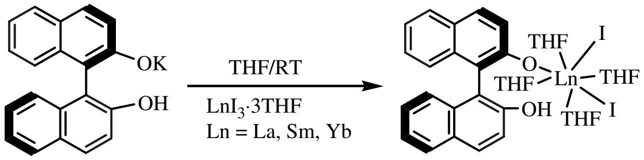
routes have been halide metathesis or protonolytic exchange with trisilylamides or with trialkyllanthanides.[10] Shibasaki[5] developed a synthesis of $[(\mathrm{THF})_2\mathrm{Na}]_3[\mathrm{Ln}(R\text{-Binolate})_3(\mathrm{H_2O})]$ (Ln = La, Pr, Nd and Eu) by the reactions of $\mathrm{Ln(O\text{-}}i\text{-}\mathrm{Pr)_3}$ and $\mathrm{Na_2}(R\text{-Binolate})$ [equation (1)]. However, the complexes prepared from $\mathrm{LnCl_3}$ could not be crystallized. A preliminary structure (not fully refined) of $[(\mathrm{THF})_2\mathrm{Li}]_3[\mathrm{Sm}(R\text{-Binolate})_3(\mathrm{H_2O})]$ has also been reported.[19]

$$\mathrm{Ln(O\text{-}}i\text{-}\mathrm{Pr)_3} + \mathrm{Na_2}(R\text{-Binolate}) \xrightarrow[\text{-Na(O-}i\text{-Pr)}]{\text{THF/RT}} [(\mathrm{THF})_2\mathrm{Na}]_3[\mathrm{Ln}(R\text{-Binolate})_3(\mathrm{H_2O})] \tag{1}$$

Aspinall[6] synthesized anhydrous $\mathrm{M_3[Ln(Binolate)_3]}$ (M = Li, Ln = Y, Eu and Yb; M = Na, Ln = Y and Yb) from lanthanide trisilylamides $[\mathrm{Ln\{N(SiMe_3)_2\}_3}]$, which are extremely reactive with protic reagents. The only byproduct is $\mathrm{H[N(SiMe_3)_2]}$ [equation (2)].

$$\mathrm{Ln[N(SiMe_3)_2]_3} + \mathrm{Na_2}(R\text{-Binolate}) \xrightarrow[\text{-3H[N(SiMe}_3)_2]]{\text{THF/0 °C}} [(\mathrm{THF})_2\mathrm{Na}]_3[\mathrm{Ln}(R\text{-Binolate})_3] \tag{2}$$

In contrast, Collin[20] reported the synthesis and characterization of the first mono-R-binaphthoxide diiodo lanthanide complexes by the reactions of $\mathrm{LnI_3{\cdot}3THF}$ (Ln = La, Sm and Yb) and $\mathrm{K}(R\text{-HBinolate})$ [equation (3)].



(3)

In this paper, we developed a straightforward synthesis of **1** and **2** starting from anhydrous $\mathrm{LnCl_3}$ and $\mathrm{LnBr_3}$ [equation (4)]. Recrystallization of **1** and **2** from THF–hexane gave single crystals suitable for X-ray diffraction analysis. One molecular aqua from the complex was unexpectedly produced because this complex was reluctant to crystallize. Ingress of sufficient atmospheric moisture into the Schlenk tube to form this mixture was expected to be a slow process, which also occurred in a previous report.[6] Nevertheless, an attempt to synthesize mono- or di-R-Binaphthoxy bromide lanthanide complexes, with regard to the mono-R-Binaphthoxide diiodo lanthanide complexes, was not successful starting with either $\mathrm{LnBr_3}$ or $\mathrm{LnCl_3}$. Both Ln–Cl and Ln–Br bonds were cleaved during the reactions. This may be attributed to the size of chloride and bromide atoms, which are less bulky than the iodine atom and cannot stabilize the lanthanide ions forming the expected complexes:

$$\mathrm{LnX_3}\ (\mathrm{X = Cl, Br}) + \mathrm{Na_2}(R\text{-Binolate}) \xrightarrow[\text{-3HX}]{\text{THF/RT}} [(\mathrm{THF})_2\mathrm{Na}]_3[\mathrm{Ln}(R\text{-Binolate})_3(\mathrm{H_2O})] \tag{4}$$

Spectroscopic analysis

Infrared spectra for binaphthol, **1** and **2** have been examined, and the results (Table 1) showed that infrared absorption peaks of ν_S(O–H) and δ(O–H) in binaphthol disappeared while the peaks of ν_m(C–O–C) and ν_m(Ln–O) were newly generated in complexes **1** and **2.** The coexistence of all other peaks in both uncoordinated binaphthol and complexes suggested a tendency for red shift from an uncoordinated binaphthol to a coordinated one. Thus, infrared spectra proposed the cleavage of the O–H bonds and the formation of the Ln–O bonds.

Thermal analysis of **1** and **2** showed that no complex has a clear melting point, but instead lost an approximate 30% in weight for both **1** and **2** when heated to 300 °C. These results suggested the presence of six THF and one $\mathrm{H_2O}$ molecule in the crystals.

Crystal structure

X-ray crystallographic analysis showed in Table 2 that **1** and **2** are isomorphous with the stoichiometry $[(\mathrm{THF})_2\mathrm{Na}]_3[\mathrm{Ln}(R\text{-Binolate})_3(\mathrm{H_2O})]$ [Ln = Sm (**1**) and Gd (**2**)], crystallizing in the hexagonal space group $P6_3$ with C_3 symmetry. The molecule structures (Figs 1 and 2) indicated that the three alkali–metals are located on the top of a triangle and the lanthanide metal nearly shares the plane of the triangle; however, the lanthanide atoms slightly distort the planarity. Each lanthanide(III) ion is seven-coordinated by six bridging oxygen atoms from three binaphthol and an oxygen atom from $\mathrm{H_2O}$. The coordination geometry of the lanthanide ions in **1** and **2** can best be approximated as a mono-capped triangle antiprism (Fig. 3). The two opposite triangle planes are defined by O(1)O(2)O(2B) and O(1A)O(2A)O(1B), respectively. The O(5W) atom caps the triangle plane defined by

Table 1. Infrared spectra data for binaphthol, **1** and **2**

Chemical bonds	Binaphthol	**1**	**2**
ν_S(O–H)	3486, 3402	—	—
ν_w(ArC–H)	3045	3045, 2955, 2925	3045, 2978, 2871
ν_S(ArC–C)	1618, 1597	1611, 1584	1611, 1590
δ(O–H)	1381, 1322, 1216	—	—
ν_S(ArC–O)	1175, 1146, 1125	1363, 1342, 1280	1362, 1345, 1275
ν_m(C–O–C)	—	1070, 866	1055, 859
ν_m(Ln–O)	—	452	461

Table 2. Asymmetric transfer hydrogenation reaction of acetophenone

Entry	Catalyst	Substrate/catalyst/ $KOBu^t$	Temperature (°C)	*T* (h)	Yield (%)[a]	e.e. (%)[b]	Configuration[c]
1	**1**	100 : 2 : 16	20	24	6	58	*S*
2	**1**	100 : 2 : 16	80	24	11	3.3	*S*
3	**1**	100 : 5 : 16	20	24	20	94	*S*
4	**1**	100 : 5 : 16	80	24	23	37	*S*
5	**2**	100 : 2 : 16	20	24	4	29	*S*
6	**2**	100 : 5 : 16	20	24	20	85	*S*

[a] Determined by GLC analysis. [b] Determined by HPLC analysis (CHIRALCEL OD-H; 5% of *i*-PrOH in hexane; 0.5 ml/min). [c] The absolute configuration was determined by comparison of the retention time of the enantiomers on the HPLC analysis with literature values[27].

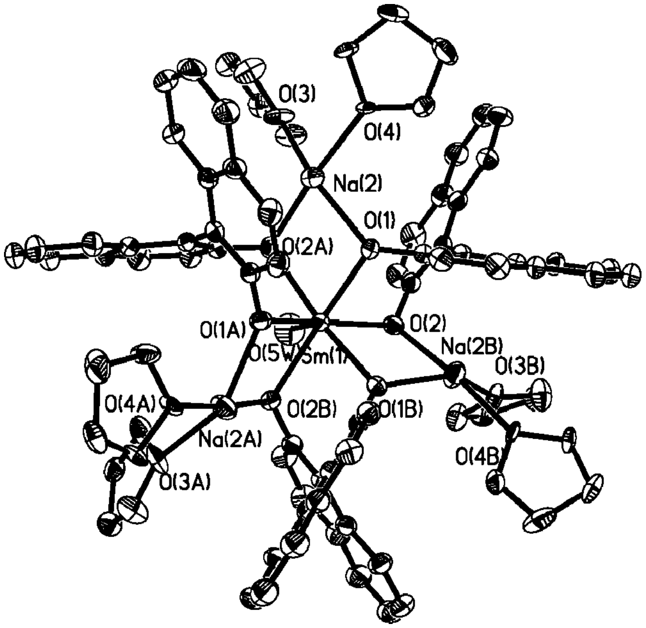


Figure 1. Plot of the molecular structure of {[(THF)$_2$Na]$_3$[Sm (*R*-Binolate)$_3$(H$_2$O)]} (**1**) (30% thermal ellipsoids and hydrogen atoms removed for clarity). Selected bond distances (Å): Sm(1)–O(2A) 2.328(3); Sm(1)–O(1) 2.334(3); Sm(1)–O(5W) 2.692(15); O(1)–Na(2) 2.247(3); O(2B)–Na(2) 2.358(4); O(3)–Na(2) 2.348(7); O(4)–Na(2) 2.371(5); Sm(1)–Na(2) 3.617(2); selected bond angles (°): O(2A)–Sm(1)–O(2B) 110.95(8); O(2A)–Sm(1)–O(1B) 163.54(12); O(2A)–Sm(1)–O(1) 75.72(11); O(2)–Sm(1)–O(1) 78.94(11); O(1)–Sm(1)–O(1A) 91.39(12).

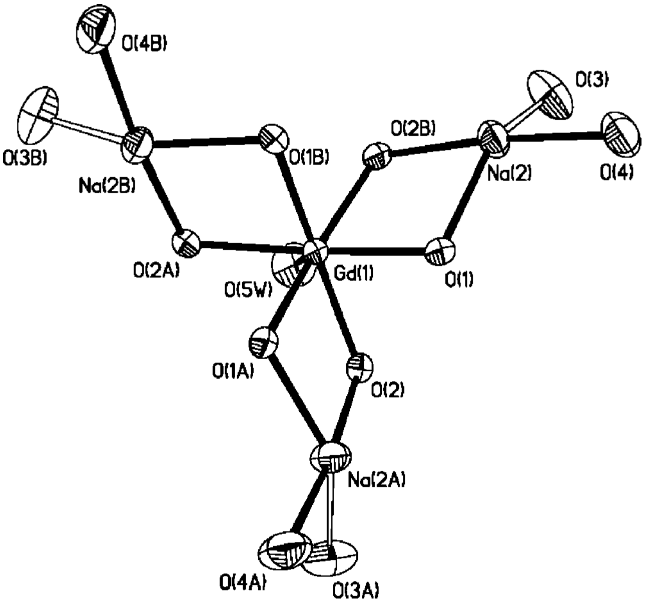


Figure 2. Plot of the molecular structure of {[(THF)$_2$Na]$_3$[Gd (*R*-Binolate)$_3$(H$_2$O)]} (**2**) (30% thermal ellipsoids and hydrogen atoms removed for clarity). Selected bond distances (Å): Gd(1)–O(2A) 2.293(3); Gd(1)–O(1B) 2.297(3); Gd(1)–O(5W) 2.76(4); Na(2)–O(1) 2.239(3); Na(2)–O(3) 2.341(7); Na(2)–O(2B) 2.366(4); Na(2)–O(4) 2.372(5); Gd(1)–Na(2A) 3.5783(19); selected bond angles (°): O(2A)–Gd(1)–O(2B) 109.16(8); O(2A)–Gd(1)–O(1B) 165.75(12); O(2B)–Gd(1)–O(1B) 79.88(10); O(2)–Gd(1)–O(1A) 76.87(10); O(1)–Gd(1)–O(1B) 91.91(11).

O(2)O(2A)O(2B). The bond distances of Sm–O and Gd–O are 2.328(3), 2.334(3) and 2.692(15) Å for **1** (Fig. 1) and 2.293(3), 2.297(3) and 2.76(4) Å for **2** (Fig. 2). It should be noticed that not all Ln–O bonds are even. The bond distances of Ln–O (H_2O) are significantly longer than those of the bridged Ln–O (binaphthol) bonds, disclosing that the bond of Ln–O (H_2O) is essentially weaker than the Ln–O (binaphthol) bonds. The bond distances of Na–O are 2.247(3), 2.358(4), 2.348(7) and 2.371(5) Å for **1** and 2.239(3), 2.341(7), 2.366(4) and 2.372(5) Å for **2**. However, bond discrimination between Na–O (binaphthol) and Na–O (THF) has not been proposed. The bond angles of O(binaphthol)–Ln–O(binaphthol) are 75.72(11), 78.94(11), 91.39(12), 110.95(8) and 163.54(12)° for **1** and 76.87(10), 79.88(10), 91.91(11), 109.16(8) and 165.75(12)° for **2**. This is in accord with the reported Pr, Nd and Eu analogs.[4–8]

Catalysis

Chiral binaphthol has already been used to generate enantioselective lanthanide catalysts, the most spectacularly

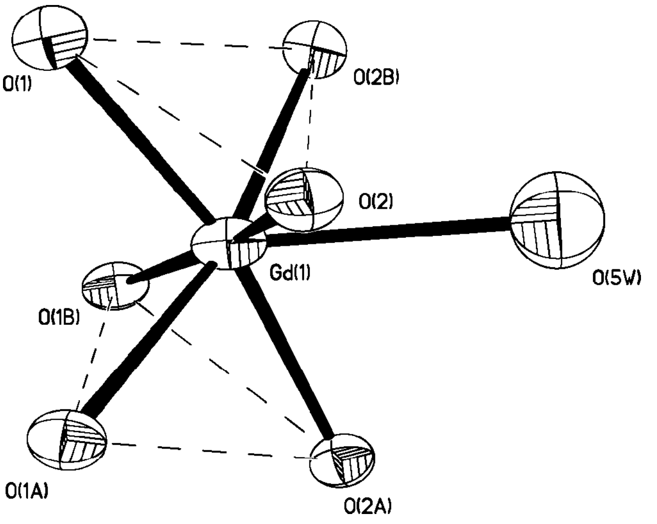
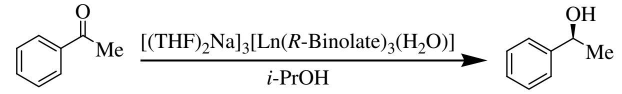


Figure 3. Perspective view for the core in compound **2**.

successful of which are Shibasaki's heterometallic complexes {[(THF)$_2$Na]$_3$[Ln(R-Binolate)$_3$(H$_2$O)]} (Ln = La, Pr and Eu). These complexes act as both Brönsted base and Lewis acid catalysts for a series of organic transformations.[3,8,11,21–23] However, complexes {[(THF)$_2$Na]$_3$[Ln(R-Binolate)$_3$(H$_2$O)]} have never been used as catalysts in the MPV reduction of ketones. Notably, a highly enantioselective version of this reaction has only been reported by Evans.[18,24] In this preliminary catalytic study, complexes **1** and **2** were employed as catalysts in MPV reactions of acetophenone. The catalytic reactions were conducted as in equation (5).



(5)

The catalytic results in Table 3 suggested that the amount of the catalysts, the ratios of the catalyst to the substrate, the temperature of the reactions and the central lanthanide metals of the complexes affect enantioselectivity of the MPV reactions. They suggest that complex **1** leads to a better selectivity than complex **2**; 5 mmol% of the catalyst to the substrate yields a better enantioselectivity than 2 mmol%.

Table 3. Crystal data and structure refinement for **1** and **2**

Crystal data	1	2
Empirical formula	$C_{72}H_{48}Na_3O_{9.53}Sm$	$C_{72}H_{48}GdNa_3O_{9.53}$
Formula weight	1284.98	1291.80
Temperature	293(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	hexagonal	hexagonal
Space group	P6$_3$	P6$_3$
Unit cell dimensions	$a = 15.312(2)$ Å $\alpha = 90°$	$a = 15.271(2)$ Å $\alpha = 90°$
	$b = 15.312(2)$ Å $\beta = 90°$	$b = 15.271(2)$ Å $\beta = 90°$
	$c = 18.477(4)$ Å $\gamma = 120°$	$c = 18.500(4)$ Å $\gamma = 120°$
Volume, Z	3751.9(11) Å^3, 2	3736.2(11) A^3, 2
Calculated density	1.137 mg/m^3	1.148 mg/m^3
Absorption coefficient	0.848 mm^{-1}	0.954 mm^{-1}
F(000)	1303	1306
Crystal size	0.36 × 0.36 × 0.32 mm^3	0.35 × 0.35 × 0.30 mm^3
θ range (deg)	3.07–27.47°	3.08–27.47°
Limiting indices	$-19 <= h <= 19$	$-19 <= h <= 19$
	$-19 <= k <= 19$	$-19 <= k <= 19$
	$-22 <= l <= 23$	$-23 <= l <= 22$
Reflections collected	36 409	35 105
Unique reflections	5596 [R(int) = 0.0576]	5583 [R(int) = 0.0211]
Completeness to $\theta = 27.47$	99.8%	99.7%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5596/25/323	5583/457/323
Goodness-of-fit on F^2	1.129	1.118
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0475$, $wR_2 = 0.1424$	$R_1 = 0.0445$, $wR_2 = 0.1413$
R indices (all data)	$R_1 = 0.0564$, $wR_2 = 0.1497$	$R_1 = 0.0512$, $wR_2 = 0.1487$
Absolute structure parameter	0.02(3)	0.04(3)
Largest difference peak and hole	0.768 and −0.386 e. Å^{-3}	0.835 and −0.595 e. A^{-3}

The higher the temperature of the reactions, the lower the e.e. values of the products. In contrast, the higher the temperature of the reactions, the higher the chemical yield of the product. When complexes **1** and **2** were employed as catalysts in the reduction of acetophenone in 2-propanol at ambient temperatures over 24 h, the *S*-phenylethanol was separated in 94 and 85% e.e. for **1** and **2**, respectively, notwithstanding that the chemical yields were low in this preliminary study. On the basis of the comparison with the known lanthanide catalysts for the MPV reaction of acetophenone, 94% e.e. is among the few highly enantioselective lanthanide catalysts, e.g. 96% e.e. was gained using a catalyst consisting of tridentate ligand and samarium complex,[18] and 95% e.e. was harvested using a catalyst consisting of a chiral multidentate ligand and samarium complex.[26] It is worth noting that only the lanthanide catalysts applied in this study for the MPV reductions were isolated and structurally characterized. Other lanthanide catalysts used for the MPV reduction of ketones were generated and applied *in situ*. Therefore, this series of chiral lanthanide complexes has been demonstrated to effectively catalyze the asymmetric MPV reduction of acetophenone, which may be a potential catalyst for industry.

CONCLUSION

Two new heterometallic sodium lanthanide binapthol complexes were synthesized using a straightforward method and characterized by X-ray crystallographic analysis. For the first time, catalytic data demonstrated that two newly synthesized complexes were able to efficiently catalyze the MPV reduction of acetophenone with high enantioselectivity. These results further enriched the structural and catalytic chemistry of heterometallic alkali metal lanthanide binaphtholates. We believe that this series of catalysts can make possible MPV reduction with high e.e. and chemical yield at ambient temperature. Further studies on this concept are currently in progress in our laboratory.

EXPERIMENTAL

General procedures

Unless otherwise stated, all experiments were carried out in a nitrogen atmosphere with standard Schlenk and syringe technique. Binaphthol was purchased from J&K Chemical Ltd. All solvents were distilled from sodium–benzophenone ketyl and stored under nitrogen prior to use. Microanalysis was conducted using Perkin-Elmer-2400. Infrared spectra were recorded on a Perkin-Elmer 60000 spectrophotometer. Thermal analyses were conducted on a DTA-1700 with a heating rate of 10 °C/min in the temperature range of from room temperature to 700 °C.

The MPV reductions were carried out on a scale of 2 mmol for the substrate and the products were isolated by flash chromatography. Column chromatography was carried out on silica gel (Merck, 230–400 mesh) eluted by petroleum ether–ethyl acetate (9 : 1). The conversion was determined using GC with a PEG-20M column. The enantiomeric excess was determined using HPLC analysis with a Chiralcel OD-H column (Daicel Chemical Industry).

Synthesis of [(THF)$_2$Na]$_3$[Ln(*R*-Binolate)$_3$(H$_2$O)] [Ln = Sm (1) and Gd (2)]

The preparations of **1** and **2** were carried out in a similar manner. The preparations of {[(THF)$_2$Na]$_3$[Sm(*R*-Binolate)$_3$ (H$_2$O)]} (**1**) for a typical example is described as follows: Na$_2$[*R*-Binolate] was prepared by addition of NaH (0.144 g, 3.0 mmol) to a solution of binaphthol (0.429 g, 1.5 mmol) in THF (10 ml) at 0 °C. The reactants were then stirred for 40–50 min. To this solution was added a suspension of SmBr$_3$. 4THF (0.302 g, 0.5 mmol) in THF (10 ml). The mixture was allowed to warm up to the ambient temperature and stirred for an additional 20 h. Solvent was then removed *in vacuo*, and the resulting solid was recrystallized from THF/hexane to yield products as crystals.

*[(THF)$_2$Na]$_3$[Sm(R-Binolate)$_3$(H$_2$O)] (**1**)*

Light yellow prisms. Yield: 0.227 g (30%). Anal. C$_{84}$H$_{84}$Na$_3$O$_{13}$Sm requires: C, 66.33%; H, 5.57%; Found: C, 66.26%; H, 5.35%. IR (cm^{-1}, KBr pellet): 3400 s, 3044 w, 2955 w, 2925 w, 1610 m, 1583 m, 1494 m, 1450 m, 1363 s, 1342 s, 1280 s, 1265 m, 1238 m, 1069 w, 982 m, 932 m, 824 m, 752 m, 452 m. TG-DTA: 27.8% loss in weight (158.8 °C).

*[(THF)$_2$Na]$_3$[Gd(R-Binolate)$_3$(H$_2$O)] (**2**)*

Light yellow prisms. Yield: 0.157 g (21%). Anal. C$_{84}$H$_{84}$GdNa$_3$O$_{13}$ requires: C, 66.03%; H, 5.54%; Found: C, 65.86%; H, 5.38%. IR (cm^{-1}, KBr pellet): 3411 w, 3044 w, 2977 w, 2870 w, 1610 m, 1589 m, 1499 m, 1461 m, 1362 s, 1345 s, 1274 s, 1248 m, 1054 m, 956 m, 827 m, 750 m, 460 m. TG-DTA: 28.3% loss in weight (210.5 °C).

X-ray crystallographic analysis

Suitable single crystals were coated and glued on the top of a glass fiber with epoxy resin. Crystal data collections for **1** and **2** were performed at 293 K using a Rigaku Raxis–Rapid single X-ray diffractometer (Mo Kα, graphite monochromator, $k = 0.71073$ Å) in the φ rotation scan mode. The structures were solved by direct methods with the SHELXS-97 package[25] and refined by full-matrix least squares on F^2 (SHELXL-97).[26] X-ray crystallographic data for **1** and **2** are summarized in Table 3.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Centre, CCDC nos 287158 and 287159 for complexes **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Acknowledgments

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