# Synthesis and Structure of Lanthanide Sandwich Complexes with Mixed Cyclooctatetraenyl and Chelating Substituted-indenyl Ligands

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**Two types of sandwich complexes ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Ln($\eta^8$-$C_8H_8$)(THF)$_n$ [Ln = La (1), Nd (2), $n$ = 0; Sm (3), Dy (4) and Er (5), $n$ = 1] and ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Ln($\eta^8$-$C_8H_8$)(THF) [Ln = La (6), Nd (7), Sm (8), Dy (9) and Er (10)] were synthesized by the reactions of $LnCl_3$ with equivalent mole of $K_2C_8H_8$, followed by treatment with correspnding potassium salt of ether-substituted indenide. The molecular structures of 3 and 8 were determined by single crystal X-ray diffraction. ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Sm($\eta^8$-$C_8H_8$)(THF) (3) monoclinic, $p2_1/c$, $a$ = 1.4793(3) nm, $b$ = 0.8716(2) nm, $c$ = 1.6149(3) nm, $\beta$ = 98.17(3), $V$ = 2.0612(7) nm$^3$, $Z$ = 4, $R$(F) = 0.0362. ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Sm($\eta^8$-$C_8H_8$)(THF) (8) orthorhombic, $p2_12_12_1$, $a$ = 0.8754(2) nm, $b$ = 1.1000(2) nm, $c$ = 2.3117(5) nm, $V$ = 2.2260(8) nm$^3$, $Z$ = 4, $R$(F) = 0.0497.**

**Keywords** Organolanthanide complexes, cyclooctatetraenyl, methoxyethyl indenyl, tetrahydrofurfuryl indenyl, crystal structure

## Introduction

The cyclooctatetraenyl ligand is ubiquitous in lanthanide chemistry, and due to its stability, it is often referred to as a stabilizing backbone of organolanthanide complexes.[1,2] The chemistry of rare earth cyclooctatetracnyl is currently receiving renewed interest.[3-4]

In recent years, cyclopentadienyl ligands with an additional donor functionality have attracted increasing interest in the organometallic chemistry of transition metals and rare earth metals.[5-11] Such bidentate ligands can coordinate to the metal with the cyclopentadienyl ring and the intramolecular donor atom, increasing the stability of highly reactive complexes. Using chiral substitutents at the cyclopentadienyl ring, Marks and coworkers synthesized the chiral organolanthanocene complexes.[12-14] In this paper, we present chiral lanthanocene complexes containing the rare earth metal as the asymmetric center.

## Results and discussion

Scheme 1 shows the general synthetic route used to prepare our sandwich organolanthanide complexes from $K_2C_8H_8$ and the ether-substituted indenyl ligands, which can be either methoxyethyl indenyl or tetrahydrofurfuryl indenyl.

All ten compounds were successfully synthesized, and finally purified by recrystallization. In all cases, the total yield was respectable.

X-ray structure determination was performed upon compounds **3** and **8** (see Tables 1—7). Suitable crystals

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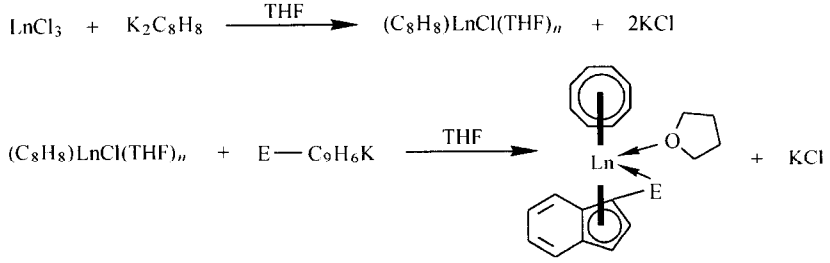
for X-ray diffraction study were grown from THF solution. The structures show expected features. The samarium is coordinated in a distorted tetrahedral configuration with the eight-membered cyclooctatetraenyl ring, the five-membered indenyl ring, two oxygens from THF and side chain group of indenyl ligand. The intramolecular coordination between oxygen atom of ligand and samarium can satisfy the co-ordination requirement of the lanthanide center. There is one THF molecule in crystal and here the co-ordination number of samarium is ten.

Mass spectra were recorded for all complexes and they are all very similar, showing a fragment ion ($M^+$ − THF), relative fragments and no parent molecular ion. These indicate that the coordinations between lanthanide center and the solvent THF are not very strong. Elemental analyses showed that complexes had one molecule of THF, which was confirmed by the X-ray diffraction studies of **3** and **8**. Elemental analysis, mass spectra and X-ray determination prove the proposed structure shown in Scheme 1.

**Scheme 1**




E=methoxyethyl, Ln=La (**1**), Nd (**2**), Sm (**3**), Dy (**4**), Er (**5**)
E= tetrahydrofurfuryl, Ln=La (**6**), Nd (**7**), Sm (**8**), Dy (**9**), Er (**10**)

The crystal structures of complex **3** and complex **8** are shown in Fig. 1 and Fig. 2 respectively.

The bond lengths of Sm—C ($\eta^8$) in (Fig. 2) range from 0.2633 to 0.2685 nm (average 0.2660 nm), similar to that in (COT)Sm($C_5H_4PPh_2$)(THF) 0.2683 nm[15] and (COT)Sm(2,4-$C_7H_{11}$)(THF) 0.2660 nm.[16] The distance of Sm—C ($\eta^5$) ranges from 0.2741 to 0.2928 nm (average 0.2822 nm) shorter than that in (COT)Sm(2,4-$C_7H_{11}$)(THF) 0.2880 nm, similar to that in (COT)Sm($C_5H_4PPh_2$)(THF) 0.2792 nm,

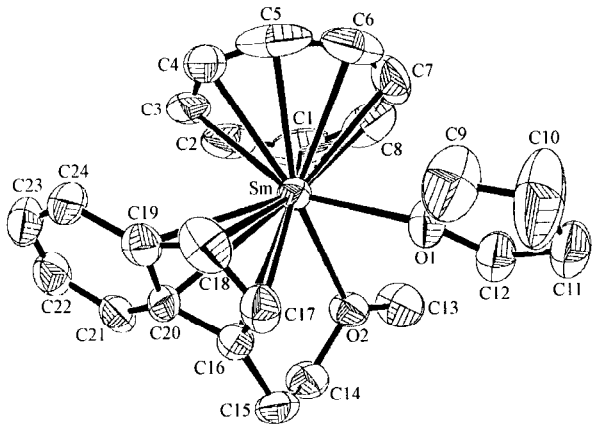



**Fig. 1** Molecular structure of **3**.

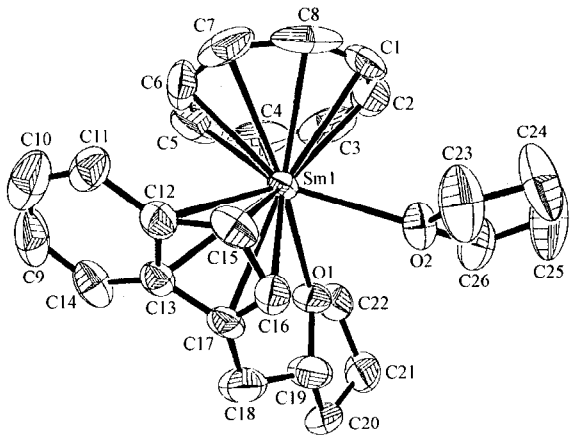



**Fig. 2** Molecular structure of **8**.

longer than that in Sm($C_9H_7$)$_3$0.275 nm.[17] The Sm—O1($\eta^5$) bond distance is 0.2542 nm which is shorter than Sm—O2 (THF) bond 0.2616 nm. The Sm—O (THF) bond length is 0.250 nm in (COT)Sm(2,4-$C_7H_{11}$)(THF).

The bond lengths of Sm—C ($\eta^8$) in complex **3** (Fig. 1) range from 0.2629 to 0.2689 nm (average 0.2659 nm), similar to 0.2660 nm in complex **8**. The distance of Sm—C($\eta^5$) ranges from 0.2735 to 0.2940 nm (average 0.2822 nm) which is in agreement with

0.2822 nm in complex **8**. The Sm—O2($\eta^5$) bond distance is 0.2579 nm lightly longer than 0.2542 nm in complex **8**, and the Sm—O1 (THF) bond length is 0.2568 nm lightly short than 0.2616 nm in complex **8**.

From above data we can see that similar substituent at indenyl has no significant effect on the bond length. From Table 4 and Table 5 it can be seen that owing to the steric effect, Sm—C12 in complex **8** and Sm—C19 in complex **3** are the longest [Sm—C($\eta^5$)] bond in respective compound.

The distance Sm—C($\eta^8$) is evidently smaller than that of Sm—C($\eta^5$), which is due to that $C_8H_8$ has two negative charges while substituted indenyl only has one.

## Experamental

All operations were carried out under purified argon using standard Schlenk techniques. All solvents were freshly refluxed and distilled over blue sodium-benzophenone ketyl under argon prior to use. Indene and cyclooctatetraene (Fluka) were purified by vacuum distillation from calcium hydride. Anhydrous lanthanide chloride was prepared according to the published procedure.[18] 2-Methoxyethyl indene and 2-tetrahydrofurfuryl indene were prepared as our previously reported method and reacted with potassium to obtain the salts.[19] Cyclooctatetraene potassium salt was prepared in a manner similar to the literature.[20]

Electron impact mass spectra were obtained at 70 eV on an HP 5989A mass spectrometer at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, where elemental analyses were performed.

*Preparation of* ($\eta^5$-$MeOCH_2CH_2C_9H_6$)La($\eta^8$-$C_8H_8$) (**1**)

To a suspension of $LaCl_3$(0.90 g, 3.67 mmol) in THF (30 mL) was added $K_2C_8H_8$(3.66 mmol) in THF (6.0 mL) at room temperature and stirred for 30 min, then the solution of potassium salt of methoxyethyl indene (3.68 mmol) in THF (5.0 mL) was added at ambient temperature. The mixture was stirred for 24 h. The suspension was centrifuged and the solution was transferred to another flask, the residue was washed with THF (2 × 20 mL), removal of solvent of the combined solution provided crude product, which was purified by recrystallization in THF at −18℃. The obtained product was pale-yellow solid (yield = 53%). In this compound there is no THF to coordinate to the metal center. Anal. $C_{20}H_{21}OLa$. Calcd: C, 57.70; H, 5.09; Found: C, 57.88; H, 5.19. *m/z* (%): 416($M^+$ − THF, 86.8), 312 (La($MeOCH_2CH_2C_9H_6$), 14.2), 243 (La(COT), 91.1).

*Preparation of* ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Nd($\eta^8$-$C_8H_8$) (**2**)

A procedure similar to that for **1** was adopted with $NdCl_3$(0.85 g, 3.39 mmol), $K_2C_8H_8$(5.6 mL, 3.40 mmol) and potassium salt of methoxyethyl indene (5.7 mL, 3.39 mmol). It provided a green crystal (yield = 65%). In this compound there is no THF to coordinate to the metal center. Anal. $C_{20}H_{21}ONd$. Calcd: C, 56.97; H, 5.02. Found: C, 56.75; H, 5.37. *m/z* (%): 419($M^+$, 1.1), 315(Nd($MeOCH_2CH_2C_9H_6$), 57.6), 246 (Nd(COT), 38.1).

*Preparation of* ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Sm($\eta^8$-$C_8H_8$)-(THF) (**3**)

The same procedure was followed as for the preparation of ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Sm($\eta^8$-$C_8H_8$)(THF). Black-crystal was obtained in 62% yield. Anal. $C_{24}H_{29}O_2Sm$. Calcd: C, 57.67; H, 5.85. Found: C, 57.45; H, 5.70. *m/z* (%): 429($M^+$ − THF, 11.8), 325 (Sm($MeOCH_2CH_2C_9H_6$), 84.2), 256 (Dy(COT), 1.7).

*Preparation of* ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Dy($\eta^8$-$C_8H_8$)-(THF) (**4**)

The procedure for **1** was again followed for preparation of ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Dy($\eta^8$-$C_8H_8$)(THF). Yellow crystal was got in 57% yield. Anal. $C_{24}H_{29}O_2Dy$. Calcd: C, 56.30; H, 5.71. Found: C, 56.35; H, 5.76. *m/z* (%): 441($M^+$ − THF, 100), 337 (Dy($MeOCH_2CH_2C_9H_6$), 4.7), 268 (Dy(COT), 42.7).

*Preparation of* ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Er($\eta^8$-$C_8H_8$)-(THF) (**5**)

The same procedure was used as for the preparation

of ($\eta^5$-$MeOCH_2CH_2C_9H_6$)Er($\eta^8$-$C_8H_8$)(THF). Pale-red solid was obtained in 42% yield. Anal. $C_{24}H_{29}O_2Er$. Calcd: C, 55.78; H, 5.66. Found: C,55.40; H,5.60. *m/z* (%): 443 ($M^+$ - THF, 100), 339 (Er($MeOCH_2CH_2C_9H_6$), 7.4), 270 (Er(COT), 48.4).

*Preparation of* ($\eta^5$-$C_4H_7OCH_2C_9H_6$)La($\eta^8$-$C_8H_8$)-(THF) (**6**)

$LaCl_3$ (1.15 g, 4.69 mmol) was suspended in THF (30 mL) and stirred 30 min, the solution of $K_2C_8H_8$ (7.9 mL, 4.70 mmol) was added by syringe at room temperature and stirred 20 min, then the solution of potassium salt of tetrahydrofurfuryl indene (10.2 mL, 4.69 mmol) was added at room temperature. The suspension solution was stirred for 24 h, then centrifuged. The residue was washed with THF (2 × 20 mL), and the combined solution was transferred to another flask and about half volume of solvent was removed. A yield of 58% pale-yellow crystals was obtained after several days at −18℃. Anal. $C_{26}H_{31}O_2La$. Calcd: C, 60.70; H, 6.07. Found: C, 60.49; H, 5.97. *m/z* (%): 442 ($M^+$ - THF, 14.5), 338(La($C_4H_7OCH_2C_9H_6$),2.4), 243 (La(COT), 23.1).

*Preparation of* ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Nd($\eta^8$-$C_8H_8$)-(THF) (**7**)

The procedure for **6** was followed for preparation of ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Nd($\eta^8$-$C_8H_8$)(THF). Green crystal was got in 47% yield. Anal. $C_{26}H_{31}O_2Nd$. Calcd: C, 60.08; H, 6.01. Found: C, 59.66; H, 5.96. *m/z* (%): 445 ($M^+$ - THF, 3.1), 341(Nd-($C_4H_7OCH_2C_9H_6$),4.4), 246 (Nd(COT), 3.0).

*Preparation of* ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Sm($\eta^8$-$C_8H_8$)-(THF) (**8**)

The same procedure was used as for the preparation of ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Sm($\eta^8$-$C_8H_8$)(THF). Black crystal was obtained in a good yield. Anal. $C_{26}H_{31}O_2Sm$. Calcd: C, 59.38; H, 5.94. Found: C,59.31; H,5.86. *m/z* (%): 455($M^+$ - THF, 6.5), 351(Sm-($C_4H_7OCH_2C_9H_6$),28.1), 256 (Sm(COT), 18.7).

*Preparation of* ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Dy($\eta^8$-$C_8H_8$)-(THF) (**9**)

The same procedure was again followed as for the preparation of ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Dy($\eta^8$-$C_8H_8$)-(THF). Yellow-crystal was obtained in 57% yield. Anal. $C_{26}H_{31}O_2Dy$. Calcd: C, 58.04. H, 5.81. Found: C,57.73; H,5.79. *m/z* (%): 467($M^+$ - THF, 3.7), 363(Dy($C_4H_7OCH_2C_9H_6$),1.1), 268 (Dy(COT), 3.4).

*Preparation of* ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Er($\eta^8$-$C_8H_8$)-(THF) (**10**)

The target product ($\eta^5$-$C_4H_7OCH_2C_9H_6$)Er($\eta^8$-$C_8H_8$)(THF) was obtained as pale-red solid (40%) by a procedure similar to that for **6**. Anal. $C_{26}H_{31}O_2Er$. Calcd: C, 57.53; H, 5.76. Found: C,56.99; H, 5.80. *m/z* (%): 469($M^+$ - THF, 78.6), 365(Er($C_4H_7OCH_2C_9H_6$),9.0), 270 (Er(COT), 32.0).

*X-ray structural determination of the complexes* **3** *and* **8**

Suitable crystals were selected and mounted in glass capillaries under argon and investigated on a Siemens P4 diffractometer using Mo $K_\alpha$ ($\lambda$ = 0.071069 nm) radiation. The data were corrected for Lorentz and polarization and empirical absorption. The structure was solved by heavy-atom Patterson methods[21] and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated position. The crystal data and structure refinement for complexes **3** and **8** are given in Table 1. Coordinates of non-hydrogen atoms are given in Table 2 and 3, selected bond lengths and angles are summarized in Tables 4, 5, 6 and 7, respectively.

**Table 1** Crystal data and structure refinement for **3** and **8**

| complex | **3** | **8** |
|---|---|---|
| Empirical formul | $C_{24}H_{29}O_2Sm$ | $C_{26}H_{31}O_2Sm$ |
| Formula weight (g/mol) | 499.82 | 525.86 |

Continued

| complex | **3** | **8** |
|---|---|---|
| Space group | $P2_1/c$ | $P2_12_12_1$ |
| $a$ (nm) | 1.4794(3) | 0.8754(2) |
| $b$ (nm) | 0.8716(2) | 1.1000(2) |
| $c$ (nm) | 1.6149(3) | 2.3117(5) |
| α (°) | 90 | 90 |
| β (°) | 98.17(3) | 90 |
| γ (°) | 90 | 90 |
| $V$ (nm$^3$) | 2.0612(7) | 2.2260(8) |
| $Z$ | 4 | 4 |
| $D_c$ (g/cm$^3$) | 1.611 | 1.569 |
| Absorption coefficient (mm$^{-1}$) | 2.864 | 2.656 |
| $F$ (000) | 1004 | 1060 |
| θ range (°) | 2.72—24.99 | 1.76—25.01 |
| Unique reflections | 8373 | 5681 |
| Observed reflections ($I > 3\sigma(I)$) | 3627 | 3918 |
| Data/parameters | 3627/244 | 3918/262 |
| Goodness-of-fit indicator | 1.001 | 1.130 |
| $R$ indices (all data) | 0.0596 | 0.0530 |
| Final $R$ indices ($I > 3.00\sigma(I)$) | 0.0362 | 0.0497 |
| Largest diff. peak and hole (e10$^{-3}$nm$^{-3}$) | 1.465, −1.032 | 0.855 , −1.309 |

**Table 2** Atomic coordinates and isotropic displacement coefficients for **3**

| Atom | $x$ | $y$ | $z$ | $U$eq (10$^{-2}$ nm$^2$) |
|---|---|---|---|---|
| Sm | 0.7455(1) | 0.0871(1) | 0.9822(1) | 35(1) |
| O1 | 0.6298(3) | 0.2898(6) | 0.9190(2) | 54(1) |
| O2 | 0.8420(3) | 0.3300(6) | 0.9695(2) | 49(1) |
| C1 | 0.8684(6) | −0.0220(12) | 0.8936(6) | 83(3) |
| C2 | 0.8752(6) | −0.1116(10) | 0.9649(6) | 76(3) |
| C3 | 0.8153(8) | −0.1924(9) | 1.0045(5) | 86(3) |
| C4 | 0.7245(8) | −0.2187(10) | 0.9915(4) | 92(3) |
| C5 | 0.6506(7) | −0.1647(11) | 0.9378(6) | 95(4) |
| C6 | 0.6426(6) | −0.0792(11) | 0.8671(6) | 84(3) |
| C7 | 0.6994(8) | −0.0012(12) | 0.8222(4) | 92(3) |
| C8 | 0.7956(9) | 0.02900(11) | 0.8332(5) | 94(4) |
| C9 | 0.5329(5) | 0.2648(13) | 0.9156(6) | 103(3) |
| C10 | 0.4897(7) | 0.3760(15) | 0.8643(8) | 147(6) |
| C11 | 0.5525(6) | 0.4806(11) | 0.8345(6) | 89(3) |
| C12 | 0.6434(5) | 0.4138(9) | 0.8660(5) | 72(2) |
| C13 | 0.8809(5) | 0.3789(10) | 0.8969(4) | 74(2) |
| C14 | 0.8923(5) | 0.3992(8) | 1.1043(4) | 59(2) |
| C15 | 0.8291(5) | 0.4120(8) | 1.1089(4) | 60(2) |
| C16 | 0.7793(4) | 0.2668(8) | 1.1219(3) | 43(2) |
| C17 | 0.6835(4) | 0.2516(10) | 1.1081(3) | 52(2) |
| C18 | 0.6586(4) | 0.1047(10) | 1.1269(3) | 61(2) |
| C19 | 0.7390(4) | 0.0243(9) | 1.1602(3) | 50(2) |
| C20 | 0.8138(4) | 0.1257(8) | 1.1555(3) | 40(1) |
| C21 | 0.9041(4) | 0.0775(8) | 1.1840(3) | 48(2) |
| C22 | 0.9172(5) | −0.0647(9) | 1.2189(4) | 64(2) |
| C23 | 0.8442(6) | −0.1602(10) | 1.2279(4) | 71(2) |
| C24 | 0.7566(6) | −0.1190(9) | 1.1990(4) | 66(2) |

**Table 3** Atomic coordinates and isotropic displacement coefficients for **8**

| Atom | $x$ | $y$ | $z$ | $U$eq ($10^{-2}$ nm$^2$) |
|---|---|---|---|---|
| Sm | 0.6436(1) | 0.5695(1) | 0.1307(1) | 33(1) |
| O1 | 0.6001(8) | 0.7903(6) | 0.1029(3) | 44(2) |
| O2 | 0.8150(9) | 0.7006(8) | 0.1993(3) | 53(2) |
| C1 | 0.5905(25) | 0.4859(20) | 0.2355(6) | 84(6) |
| C2 | 0.4882(24) | 0.5714(20) | 0.2308(6) | 82(5) |
| C3 | 0.3865(22) | 0.6076(13) | 0.1914(10) | 93(7) |
| C4 | 0.3395(13) | 0.5700(15) | 0.1381(9) | 82(5) |
| C5 | 0.3759(21) | 0.4745(22) | 0.1009(8) | 97(7) |
| C6 | 0.4770(24) | 0.3749(19) | 0.1076(7) | 93(7) |
| C7 | 0.5818(24) | 0.3359(13) | 0.1503(9) | 92(6) |
| C8 | 0.6359(21) | 0.3847(16) | 0.2036(9) | 90(6) |
| C9 | 0.6134(15) | 0.4144(17) | -0.0501(6) | 78(5) |
| C10 | 0.6848(17) | 0.3143(16) | -0.0240(8) | 82(5) |
| C11 | 0.7843(15) | 0.3272(11) | 0.0194(6) | 53(3) |
| C12 | 0.8192(12) | 0.4463(11) | 0.0403(4) | 44(2) |
| C13 | 0.7489(11) | 0.5503(10) | 0.0139(4) | 40(2) |
| C14 | 0.6442(15) | 0.5304(13) | -0.0318(4) | 58(3) |
| C15 | 0.9223(14) | 0.4901(12) | 0.0832(5) | 51(3) |
| C16 | 0.9197(13) | 0.6180(11) | 0.0798(5) | 46(3) |
| C17 | 0.8146(11) | 0.6558(10) | 0.0389(4) | 42(2) |
| C18 | 0.7722(18) | 0.7839(13) | 0.0218(6) | 63(3) |
| C19 | 0.7166(16) | 0.8581(12) | 0.0696(5) | 60(3) |
| C20 | 0.6463(18) | 0.9815(10) | 0.0576(5) | 57(3) |
| C21 | 0.5348(17) | 0.9992(11) | 0.1053(6) | 63(3) |
| C22 | 0.4771(14) | 0.8727(10) | 0.1172(5) | 52(3) |
| C23 | 0.9465(19) | 0.6546(20) | 0.2282(7) | 98(6) |
| C24 | 0.9439(30) | 0.7019(25) | 0.2863(7) | 132(9) |
| C25 | 0.8457(26) | 0.8067(21) | 0.2860(8) | 121(8) |
| C26 | 0.7661(18) | 0.8064(13) | 0.2324(6) | 69(4) |

**Table 4** Selected bond lengths of complex **3** ($10^{-1}$ nm)

| Bonds | Distance | Bonds | Distance |
|---|---|---|---|
| Sm—O1 | 2.569(4) | Sm—O2 | 2.578(4) |
| Sm—C1 | 2.645(7) | Sm—C3 | 2.651(8) |
| Sm—C2 | 2.629(7) | Sm—C4 | 2.690(9) |
| Sm—C5 | 2.648(8) | Sm—C6 | 2.658(7) |
| Sm—C7 | 2.689(7) | Sm—C8 | 2.665(6) |
| Sm—C16 | 2.735(5) | Sm—C17 | 2.750(6) |
| Sm—C18 | 2.827(7) | Sm—C19 | 2.940(8) |
| Sm—C20 | 2.857(7) | O1—C9 | 1.443(8) |
| O1—C12 | 1.410(8) | O2—C13 | 1.442(7) |
| O2—C14 | 1.442(7) | | |

**Table 5** Selected bond lengths of complex **8** ($10^{-1}$ nm)

| Bonds | Distance | Bonds | Distance |
|---|---|---|---|
| Sm—O1 | 2.542(7) | Sm—O2 | 2.615(8) |
| Sm—C1 | 2.633(12) | Sm—C3 | 2.685(13) |
| Sm—C2 | 2.683(13) | Sm—C4 | 2.668(12) |
| Sm—C5 | 2.658(14) | Sm—C6 | 2.645(13) |
| Sm—C7 | 2.664(13) | Sm—C8 | 2.641(11) |
| Sm—C12 | 2.928(12) | Sm—C13 | 2.861(11) |
| Sm—C15 | 2.814(10) | Sm—C16 | 2.741(10) |
| Sm— C17 | 2.766(9) | O1—C19 | 1.480(13) |
| O1—C22 | 1.446(12) | O2—C23 | 1.420(2) |
| O2—C26 | 1.458(14) | | |

**Table 6** Selected bond angles (°) for complex **3**

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| O1-Sm-O2 | 75.46(14) | O1-Sm-C2 | 150.0(2) |
| O2-Sm-C2 | 96.3(2) | O1-Sm-C1 | 120.2(3) |
| O2-Sm-C1 | 79.7(2) | O2-Sm-C5 | 159.6(2) |
| O1-Sm-C5 | 99.5(3) | O2-Sm-C3 | 123.7(3) |
| O1-Sm-C3 | 155.7(2) | O1-Sm-C6 | 79.3(2) |
| O2-Sm-C6 | 131.3(3) | O1-Sm-C8 | 91.6(3) |
| O2-Sm-C8 | 81.7(2) | O2-Sm-C7 | 103.1(3) |
| O1-Sm-C7 | 75.6(2) | O2-Sm-C4 | 152.6(3) |
| O1-Sm-C4 | 128.9(2) | O1-Sm-C16 | 88.1(2) |
| O2-Sm-C16 | 63.69(15) | C2-Sm-C16 | 114.5(2) |
| C1-Sm-C16 | 126.4(2) | C5-Sm-C16 | 136.5(2) |
| C3-Sm-C16 | 113.1(2) | C6-Sm-C16 | 155.3(2) |
| C8-Sm-C16 | 144.3(3) | C7-Sm-C16 | 161.5(2) |
| C4-Sm-C16 | 122.0(2) | O1-Sm-C17 | 70.2(2) |
| O2-Sm-C17 | 83.0(2) | C2-Sm-C17 | 138.4(2) |
| C1-Sm-C17 | 156.1(2) | C5-Sm-C17 | 114.4(2) |
| C3-Sm-C17 | 122.9(3) | C6-Sm-C17 | 125.7(2) |
| C8-Sm-C17 | 158.7(3) | C7-Sm-C17 | 142.6(3) |
| C4-Sm-C17 | 114.9(2) | C14-O2-Sm | 120.3(3) |
| C13-O2-Sm | 126.6(4) | | |

**Table 7** Selected bond angles (°) for complex **8**

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| O1-Sm-O2 | 73.3(2) | O1-Sm-C1 | 122.7(6) |
| O2-Sm-C1 | 74.7(4) | O1-Sm-C8 | 153.3(5) |
| O2-Sm-C8 | 93.0(5) | O2-Sm-C6 | 152.3(5) |
| O1-Sm-C6 | 129.7(6) | O2-Sm-C5 | 151.6(6) |
| O1-Sm-C5 | 100.2(5) | O1-Sm-C7 | 159.1(5) |
| O2-Sm-C7 | 123.0(6) | O1-Sm-C4 | 82.2(3) |
| O2-Sm-C4 | 122.2(5) | O2-Sm-C2 | 76.4(4) |
| O1-Sm-C2 | 97.7(5) | O2-Sm-C3 | 94.5(5) |
| O1-Sm-C3 | 81.8(4) | O1-Sm-C16 | 80.6(3) |
| O2-Sm-C16 | 69.3(3) | C1-Sm-C16 | 128.3(5) |
| C8-Sm-C16 | 116.5(5) | C6-Sm-C16 | 123.8(5) |
| C5-Sm-C16 | 138.0(5) | C7-Sm-C16 | 116.1(4) |
| C4-Sm-C16 | 155.1(4) | C2-Sm-C16 | 144.7(5) |
| C3-Sm-C16 | 158.9(4) | O1-Sm-C17 | 63.8(3) |
| O2-Sm-C17 | 88.0(3) | C1-Sm-C17 | 157.2(5) |
| C8-Sm-C17 | 140.2(5) | C6-Sm-C17 | 114.9(4) |
| C5-Sm-C17 | 114.4(4) | C7-Sm-C17 | 124.9(4) |
| C4-Sm-C17 | 126.0(4) | C2-Sm-C17 | 158.9(5) |
| C3-Sm-C17 | 143.2(5) | C16-Sm-C17 | 29.1(3) |
| C22-O1-C19 | 108.5(9) | C22-O1-Sm | 130.7(6) |
| C19-O1-Sm | 120.7(6) | C23-O2-C26 | 105.9(10) |
| C23-O2-Sm | 123.5(10) | C26-O2-Sm | 126.2(7) |

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