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# Is there a continuum from organosamarium hydroxo to oxo compounds? Crystal structures of $[\{(Me_3Si)_2C_5H_3\}_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ and three distinct crystalline forms of $[\{(Me_3Si)_2C_5H_3\}_2Sm(\mu\text{-}OH)]_2$

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**Abstract**

Partial hydrolysis of cationic organolanthanide compounds $[Cp''_2Sm][B(C_6H_5)_4]$ and $[Cp''_2Sm][CB_{11}H_6Br_6]$ ($Cp'' = (Me_3Si)_2C_5H_3$) in toluene at −30°C gave $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ and two distinct crystalline forms of $[Cp''_2Sm(\mu\text{-}OH)]_2$, respectively. The two crystalline forms are not crystallographically convertible, and they are clearly distinguishable from one another. These new observations together with the reported crystalline form of $[Cp''_2Sm(\mu\text{-}OH)]_2$ imply that there may be a continuous process from organosamarium hydroxo to oxo compounds. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Continuum; Hydroxo; Oxo; Samarium; Structure

## 1. Introduction

Organolanthanide compounds are extremely sensitive towards moisture and air [1,2]. Hydrolysis cannot always be avoided and is sometimes a problem in dealing with such types of compounds, since glassware and solvents may not be absolutely dry, but from another point of view this is the most common route to generate organolanthanide hydroxo compounds. All known compounds of the type $[Cp^0_2Ln(\mu\text{-}OH)]_2$ ($Cp^0 = C_5H_5$, Ln = Y [3]; $Cp^0_2 = O(CH_2CH_2C_5H_4)_2$, Ln = Y [4]; $Cp^0 = (Me_3Si)_2C_5H_3$, Ln = Sm [5]; $Cp^0 = (Me_3Si)C_5H_4$, Ln = Yb [5]; $Cp^0 = {}^tBuC_5H_4$, Ln = Nd, Dy [6]; $Cp^0 = MeOCH_2CH_2C_5H_4$, Ln = Er [7], Ho [8]) were obtained by careful hydrolysis of the corresponding organolanthanide compounds. Sometimes, hydrolysis can also lead to the formation of μ-oxo compounds, for example, $[(C_5H_5)_2Lu(THF)]_2O$ [9,10]. Most hydrolysis process of organolanthanides are very difficult to be fully control. Many of the hydroxo compounds formed adventitiously and there are big gaps in our chemical understanding. A mechanism for such hydrolysis reactions was proposed after successful isolation and structural characterization of the first water coordinated compound, $(CH_3C_5H_4)_3Ho{\cdot}OH_2$ [4]. It is, however, still not understood if this process is continuous and why a μ-oxo derivative can sometime be isolated instead of a μ-hydroxo one. During the course of the recrystallization of cationic organolanthanide compounds [11] from toluene, $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ ($Cp'' = (Me_3Si)_2C_5H_3$) and another two distinct crystalline forms of $[Cp''_2Sm(\mu\text{-}OH)]_2$, which differ from the reported one [5], were unexpectedly isolated and subsequently structurally characterized. We report here our new observations on the above reactions. After careful examination of the crystal structures of three unique crystalline forms and related μ-oxo compounds, a continuum in the transformation at least from organolanthanide hydroxo to oxo is proposed for the hydrolysis of such types of compounds.

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Table 1
Crystal data and details of data collection and structure refinement for $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ and $[Cp''_2Sm(\mu\text{-}OH)]_2$

| Compound | $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ | $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **B**) | $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **A**) |
|---|---|---|---|
| Empirical formula | $C_{44}H_{86}O_2Si_8Sm_2$ | $C_{44}H_{86}O_2Si_8Sm_2$ | $C_{44}H_{86}O_2Si_8Sm_2$ |
| $M$ | 1172.5 | 1172.5 | 1172.5 |
| Crystal class | Triclinic | Monoclinic | Triclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 11.632(1) | 11.445(1) | 11.618(1) |
| $b$ (Å) | 12.051(1) | 13.132(1) | 12.042(1) |
| $c$ (Å) | 22.398(1) | 20.908(1) | 12.885(1) |
| $\alpha$ (°) | 88.44(1) | 90.00 | 63.39(1) |
| $\beta$ (°) | 78.63(1) | 104.07(1) | 73.49(1) |
| $\gamma$ (°) | 89.45(1) | 90.00 | 89.50(1) |
| $U$ (Å$^3$) | 3077(1) | 3048(2) | 1530.4(8) |
| $Z$ | 2 | 2 | 1 |
| $D_{calc}$ (g cm$^{-3}$) | 1.266 | 1.278 | 1.270 |
| $\mu$ (mm$^{-1}$) | 2.074 | 2.093 | 2.085 |
| $F$(000) | 1204 | 1204 | 602 |
| No. of observed reflections | 5785 | 5152 | 5507 |
| No. of parameters refined | 510 | 255 | 310 |
| Data-to-parameters ratio | 11.3:1 | 20.2:1 | 17.8:1 |
| Goodness of fit | 1.84 | 2.34 | 2.58 |
| $R_F$ (%) | 4.87 | 5.06 | 3.60 |
| $R_w$ (%) | 4.86 | 5.86 | 4.62 |

## 2. Results and discussion

Organolanthanide cations are extremely oxophilic and very strong Lewis acids [11]. Recrystallization of these cations from toluene at −30°C gave partial hydrolysis products. A few yellow block and prism crystals were collected from a toluene solution of $[Cp''_2Sm][B(C_6H_5)_4]$ [11], which were identified as $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ and $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **A**), respectively. Partial hydrolysis of $[Cp''_2Sm][CB_{11}H_6Br_6]$ [11] in toluene afforded some yellow prism crystals that were characterized as $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **B**). Elemental analyses show that all three compounds have the same composition. The solid-state IR spectrum of $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ displays a broad band at 3300 cm$^{-1}$ attributable to the O–H stretching band of the coordinated $H_2O$ molecule, while those of the two forms of $[Cp''_2Sm(\mu\text{-}OH)]_2$ exhibit one sharp band at about 3668 cm$^{-1}$ that is usually assigned to the O–H stretching mode of the Ln(μ-OH)Ln unit [12]. The MS spectrum of $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ shows ions with a maximum $m/z$ of 945 ($[M - Cp'' - H_2O]^+$) along with a series of fragments containing one or two Sm atoms. The MS spectra of two forms of $[Cp''_2Sm(\mu\text{-}OH)]_2$ are essentially identical showing the ions with a maximum $m/z$ of 962 ($[M - Cp'']^+$) along with a series of fragments containing one or two Sm atoms. The data on IR and MS spectra indicate that $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$ can be well distinguished from the different crystalline forms of $[Cp''_2Sm(\mu\text{-}OH)]_2$.

The solid-state structures of two crystalline forms of $[Cp''_2Sm(\mu\text{-}OH)]_2$ as derived from single-crystal X-ray diffraction studies reveal that they are centrosymmetric hydroxo-bridging dimers with pseudo-tetrahedral geometry around the Sm atoms, similar to the molecular structure of the reported one (form **C**) [5]. They are isostructural, but only crystalline forms **A** and **C** are isomorphous (Table 1). Fig. 1 represents the typical structure of crystalline form **A**. Careful examination shows that the three structures of the different crystalline forms are not crystallographically convertible, and they are clearly distinguishable from one another. Table 2 lists their bond distances and angles. A summary of some key structural parameters for

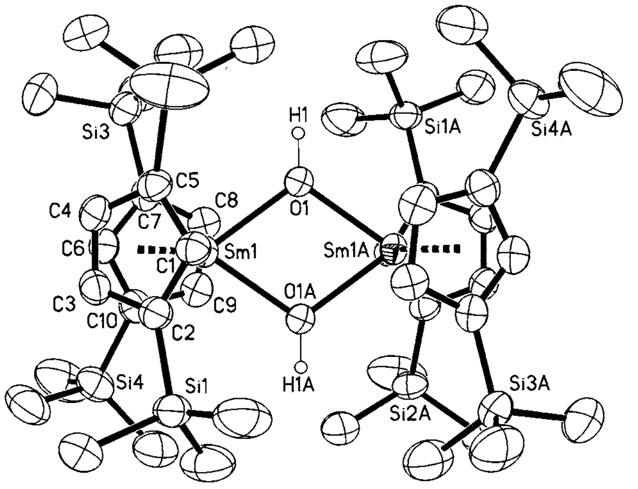

Fig. 1. Perspective view of the molecular structure of $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **A**). The thermal ellipsoids are drawn at the 35% probability level.

Table 2
Selected bond distances (Å) and angles (°) for $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ and $[Cp''_2Sm(\mu\text{-OH})]_2$ (forms **A** and **B**)

| | | | |
|---|---|---|---|
| Compound $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ | | | |
| *Bond lengths* (Å) | | | |
| Sm(1)–O(1) | 2.332 (7) | Sm(2)–O(1) | 2.235 (8) |
| Sm(1)–O(2) | 2.742 (12) | Sm(2)–O(2) | 2.657 (9) |
| Sm(1)–O(1′) | 2.305 (8) | Sm(2)–O(1′) | 2.261 (7) |
| Sm(1)–O(2′) | 2.511 (11) | Sm(2)–O(2′) | 2.566 (15) |
| Sm(1)–C(1) | 2.772 (8) | Sm(2)–C(11) | 2.755 (9) |
| Sm(1)–C(2) | 2.681 (9) | Sm(2)–C(12) | 2.829 (9) |
| Sm(1)–C(3) | 2.690 (10) | Sm(2)–C(13) | 2.657 (9) |
| Sm(1)–C(4) | 2.761 (10) | Sm(2)–C(14) | 2.815 (9) |
| Sm(1)–C(5) | 2.905 (10) | Sm(2)–C(15) | 2.802 (9) |
| Sm(1)–C(6) | 2.783 (8) | Sm(2)–C(16) | 2.708 (8) |
| Sm(1)–C(7) | 2.677 (9) | Sm(2)–C(17) | 2.864 (9) |
| Sm(1)–C(8) | 2.760 (10) | Sm(2)–C(18) | 2.767 (8) |
| Sm(1)–C(9) | 2.662 (8) | Sm(2)–C(19) | 2.678 (9) |
| Sm(1)–C(10) | 2.823 (8) | Sm(2)–C(20) | 2.629 (7) |
| *Bond angles* (°) | | | |
| O(1)–Sm(1)–O(2) | 78.1 (3) | O(1)–Sm(2)–O(2) | 81.6 (3) |
| O(1′)–Sm(1)–O(2′) | 76.1 (4) | O(1′)–Sm(2)–O(2′) | 75.7 (3) |
| Sm(1)–O(1)–Sm(2) | 111.5 (3) | Sm(1)–O(2)–Sm(2) | 88.7 (3) |
| Sm(1)–O(1′)–Sm(2) | 111.6 (3) | Sm(1)–O(2′)–Sm(2) | 96.1 (4) |
| $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **A**) | | | |
| *Bond lengths* (Å) | | | |
| Sm(1)–O(1) | 2.313 (2) | Sm(1)–C(6) | 2.769 (3) |
| Sm(1)–C(1) | 2.749 (2) | Sm(1)–C(7) | 2.792 (3) |
| Sm(1)–C(2) | 2.739 (2) | Sm(1)–C(8) | 2.752 (2) |
| Sm(1)–C(3) | 2.715 (2) | Sm(1)–C(9) | 2.718 (2) |
| Sm(1)–C(4) | 2.757 (2) | Sm(1)–C(10) | 2.743 (2) |
| Sm(1)–C(5) | 2.773 (2) | Sm(1)–O(1A) | 2.314 (1) |
| *Bond angles* (°) | | | |
| Sm(1)–O(1)–Sm(1A) | 107.7 (1) | O(1)–Sm(1)–O(1A) | 72.3(1) |
| $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **B**) | | | |
| *Bond lengths* (Å) | | | |
| Sm(1)–C(6) | 2.757 (6) | Sm(1)–C(9) | 2.738 (7) |
| Sm(1)–C(7) | 2.741 (5) | Sm(1)–C(10) | 2.780 (6) |
| Sm(1)–C(8) | 2.721 (6) | Sm(1)–O(1A) | 2.308 (3) |
| *Bond angles* (°) | | | |
| Sm(1)–O(1)–Sm(1A) | 107.9 (2) | O(1)–Sm(1)–O(1A) | 72.1(2) |

$[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ and three crystalline forms of $[Cp''_2Sm(\mu\text{-OH})]_2$ is given in Table 3. Overall, the structural parameters (bond distances and angles) of forms **A** and **B** are almost identical although they are not isomorphous. It is possible to argue that forms **A** and **C** may be the same. Comparison of structural parameters of form **A** with those of form **C**, however, suggests that they should be two different crystalline forms. For example, the average Sm–O(H) distance is 2.314(2) Å in form **A**, and 2.41(2) Å in form **C**. The Sm–O(H)–Sm angle is 107.7(1)° in form **A**, and 103.4(5)° in form **C**. These differences should be considered to be significant for the same compound.

Fig. 2 shows the solid-state structure of $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$. As far as we are aware, this is the first organolanthanide compound containing two doubly bridging oxo and aqua ligands to be reported. Each Sm atom is $\eta^5$-bound to two cyclopentadienyl rings and $\sigma$-bound to two oxygen atoms in a pseudo-tetrahedral arrangement. The average Sm–C and Sm–Cent (Cent: the centroid of the cyclopentadienyl ring) distances and the Cent(1)–Sm–Cent(2) angle are almost identical with those in forms **A** and **B** of $[Cp''_2Sm(\mu\text{-OH})]_2$. However, the Sm–O distances differ significantly from those in $[Cp''_2Sm(\mu\text{-OH})]_2$. The Sm–O(1) and Sm–O(2) distances in $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ are also quite different from each other, indicating that they are oxo and aqua ligands, respectively, which is supported by both IR and MS spectra. Anisotropic refinement of these two oxygen atoms led to greatly elongated thermal ellipsoids, which is suggestive of 2-fold orientational disorder. In the model used for refinement, two sets of oxygen atoms (O1, O2 and O1′, O2′) related by a pseudo inversion center were assigned half site occupancy and varied isotropically.

The average Sm–O2($H_2O$) distances of 2.61(1) and 2.63(1) Å are longer than the average Sm–O($H_2O$) distance of 2.525(8) Å in $[Cu_{12}Sm_6(\mu\text{-OH})_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-ClO}_4)][ClO_4]_{17}$ [13] and the Ho–O($H_2O$) distance of 2.31(2) Å in the 10-coordinate holmium compound $(CH_3C_5H_4)_3Ho\cdot OH_2$ [4] if the Shannon's ionic radii [14] are taken into account, which is expected for the bridging ligand. The average Sm–O1(oxo) distances of 2.248(8) and 2.318(8) Å are significantly shorter than the average Sm–O2($H_2O$) distances, but are longer than that of 2.094(1) Å in $[(C_5Me_5)_2Sm]_2(\mu\text{-O})$ [10a] and 2.109(7) Å in $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-O})$ [10c]. The relatively longer Sm–O1(oxo) distances may result from the very small Sm(1)–O(1)–Sm(2) angle of 111.6(3)° that prevents any possible π-interactions between metal and oxygen atom [10a,15]. This small Sm–O–Sm angle can

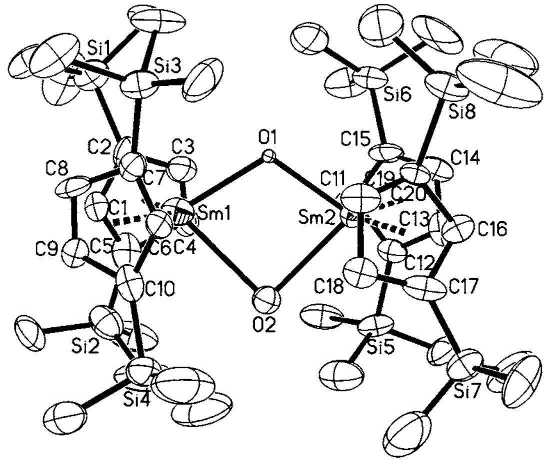

Fig. 2. Perspective view of the molecular structure of $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ (only one set of oxygen atoms is shown). The thermal ellipsoids are drawn at the 35% probability level.

Table 3
Some key structural parameters for $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ and three crystalline forms of $[Cp''_2Sm(\mu\text{-OH})]_2$

| Compound | $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **A**) | $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **B**) | $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **C**) [a] | $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ |
|---|---|---|---|---|
| Av. Sm–C (Å) | 2.751(3) | 2.752(6) | 2.72(3) | 2.751(9) |
| Sm–O (Å) | 2.313(2), 2.314(1) | 2.309(4), 2.308(3) | 2.40(2), 2.41(1) | 2.248(8), 2.318(8), 2.61(1), 2.63(1) |
| Av. Sm–Cent (Å) | 2.473 | 2.474 | 2.45 | 2.470 |
| Sm···Sm (Å) | 3.777 | 3.733(1) | 3.777 | 3.775(1) |
| O–Sm–O (°) | 72.3(1) | 72.1(2) | 76.6(6) | 74.3(3), 77.4(3) |
| Cent(1)–Sm–Cent(2) (°) | 127.9 | 127.3 | 129.5 | 127.4, 129.0 |
| Sm–O–Sm (°) | 107.7(1) | 107.9(2) | 103.4 | 111.6(3), 92.4(4) |

[a] See Ref. [5].

be compared with the Ti–O–Ti angle of 115.3(4)° in $[\{H_3CC(CH_2N^iPr)_2(CH_2NH^iPr)\}Ti(\mu\text{-Cl})]_2(\mu\text{-O})$ [16], which is to be seen as a consequence of geometry imposed by the $\mu\text{-OH}_2$ bridge.

The isolation and structural characterization of the first organolanthanide compound containing both doubly bridging oxo and aqua ligands offers additional information about the hydrolysis reactions of organolanthanide compounds. $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ may serve as an intermediate in the transformation from $[Cp''_2Sm(\mu\text{-OH})]_2$ to $[Cp''_2Sm]_2(\mu\text{-O})$ [17]. Since both $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ and $[Cp''_2Sm(\mu\text{-OH})]_2$ were isolated from the same solution, it is not unreasonable to propose that some of these species such as μ-oxo, μ-hydroxo, μ-aqua, and (μ-oxo)(μ-aqua) organolanthanide compounds may coexist in certain hydrolysis reactions. This hypothesis could explain why one or more of these compounds can sometime be adventitiously isolated from the same solution as mentioned in the introduction [3–9]. Different crystalline forms of $[Cp''_2Sm(\mu\text{-OH})]_2$ may indicate that the transformation from μ-hydroxo to μ-oxo is probably a continuous process. It may be argued that these different crystalline forms are perhaps due to the crystallization conditions. This possibility can not be ruled out at this moment although the crystalline forms were all isolated from toluene solution at −30°C.

## 3. Experimental

### 3.1. General procedure

All experiments were performed under an atmosphere of dry nitrogen using standard Schlenk or cannula techniques. Toluene was freshly distilled from sodium benzophenone ketyl prior to use. Compounds $[Cp''_2Sm][B(C_6H_5)_4]$ and $[Cp''_2Sm][CB_{11}H_6Br_6]$ were prepared according to the literature methods [11]. IR spectra were obtained from KBr pellets prepared inside the glove-box on a Nicolet Magna 550 Fourier transform spectrometer. MS spectra were recorded on a Bruker APEX FTMS spectrometer.

### 3.2. Isolation of $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ and $[Cp''_2Sm(\mu\text{-OH})]_2$ (form *A*)

Recrystallization of $[Cp''_2Sm][B(C_6H_5)_4]$ from toluene at −30°C gave $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$ as yellow block crystals and $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **A**) as yellow prism crystals, respectively. Two types of crystals were separated using Pasteur's method. For $[Cp''_2Sm]_2(\mu\text{-O})(\mu\text{-OH}_2)$. IR (KBr, $cm^{-1}$): $\mu_{OH}$ 3300m. MS (EI) *m/z* (%): 945 (15) $[M-Cp''-H_2O]^+$, 736 (9) $[M-2Cp''-H_2O]^+$, 568 (20) $[Cp''_2Sm]^+$. Anal. Found: C, 44.78; H, 7.11. $C_{44}H_{86}O_2Si_8Sm_2$ Calc.: C, 45.06; H, 7.39%. For $[Cp''_2Sm(\mu\text{-OH})]_2$ (form **A**). IR (KBr, $cm^{-1}$): $\mu_{OH}$ 3669m. MS (EI) *m/z* (%): 962 (80) $[M-Cp'']^+$, 752 (33) $[M-2Cp'']^+$, 567 (15) $[Cp''_2Sm]^+$. Anal. Found: C, 44.92; H, 7.31. $C_{44}H_{86}O_2Si_8Sm_2$ Calc.: C, 45.06; H, 7.39%.

### 3.3. Isolation of $[Cp''_2Sm(\mu\text{-OH})]_2$ (form *B*)

Recrystallization of $[Cp''_2Sm][CB_{11}H_6Br_6]$ from toluene at −30°C gave crystalline form **B** as yellow prism crystals. IR (KBr, $cm^{-1}$): $\mu_{OH}$ 3668m; MS (EI) *m/z* (%): 962 (65) $[M-Cp'']^+$, 752 (28) $[M-2Cp'']^+$, 570 (11) $[Cp''_2Sm]^+$. Anal. Found: C, 45.20; H, 7.45. $C_{44}H_{86}O_2Si_8Sm_2$ Calc.: C, 45.06; H, 7.39%.

### 3.4. X-ray structure determination

All single crystals were sealed under $N_2$ in thin-walled glass capillaries. Data were collected at 294 K on a MSC/Rigaku RAXIS-IIC imaging plate using Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. All structures were solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically for all non-hydrogen atoms by full-matrix least squares, on *F* using the Siemens SHELXTL V 4.1 program package (PC version) [18]. All hydrogen atoms were geometrically fixed using the riding model.

Crystal data and details of data collection and structure refinement are given in Table 1.

## 4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 118590 for $[Cp''_2Sm]_2(\mu\text{-}O)(\mu\text{-}OH_2)$, CCDC 118591 for $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **A**) and CCDC 118592 for $[Cp''_2Sm(\mu\text{-}OH)]_2$ (form **B**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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