Synthesis and Structural Characterisation of a Hexanuclear Gd^{III} Compound $Gd_6(\mu_3\text{-}OH)_6(acac)_{12}\cdot 1.25\ CHCl_3$ as a Potential Precursor for Gd_2O_3 Nanomaterials

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While aging the reaction mixture of gadolinium tri-isopropoxide with acetylacetone (pentane-2,4-dione, acacH) in a 1 : 2 molar ratio in toluene for crystalisation, crystals of $Gd_6(\mu_3\text{-}OH)_6(acac)_{12}\cdot 1.25$ $CHCl_3$ (**1**) were obtained in high yield. The crystal structure analysis reveals that **1** has a M_6O_{12} core which is constituted of two distorted, tricapped, face-sharing cubane units (each with one missing edge) wherein the metal atoms are octacoordinated with a distorted square-antiprismatic geometry. In a sol-gel treatment the amorphous xerogel obtained from **1** was transformed into a nano-crystalline product at 600 °C while the xerogel of $Gd(OPr^i)_3$ under similar conditions required a heat treatment up to 900 °C for the same development.

Key words: Gadolinium, *iso*-Propoxy, Hydroxo Ligands, Acetylacetonato, Gd_2O_3

Introduction

The synthesis and characterisation of suitable molecular precursors for sol-gel/hydrothermal processes is of great importance for the preparation of industrially significant materials [1 – 4] in various forms such as thin films, fibres, nanopowders *etc*. In fact, small changes in the molecular architecture of the precursors can alter their volatility, solubility and oligomerisation and hence the characteristics of the final material. For example, the BET surface area of silica particles was found to be doubled [5] when, instead of $Si(OCH_3)_4$, its hydrolysed product $Si_8O_8(OCH_3)_{12}$ was used as precursor in the sol-gel process under the same set of conditions. Similarly, condensation of titanium tetra-isopropoxide generated 10 – 20 nm TiO_2 particles while the modified precursors $Ti(OPr^i)_3(acac)$ and $Ti(OPr^i)_2(acac)_2$ resulted in spherical [6] 5 nm particles and polymeric chains, respectively.

Gadolinium oxide is an important constituent of many commercially important materials such as in garnets ($Gd_3Ga_5O_{12}$), magnetic thin films ($CoFeGdO_4$), electrolytes in solid oxide fuel cells ($Ce_{0.9}Gd_{0.1}O_{1.95}$) and rare earth ion-doped nanophosphors [3, 4, 7, 8]. Although there are some reports on the synthesis of Gd_2O_3 material by employing different precursors including gadolinium isopropoxide, the structural data for suitable metallo-organic precursors are still scarce. Some gadolinium carboxylates [9 – 11] have been characterised for this purpose, however, the number of corresponding β-diketonate compounds is relatively smaller. β-Diketones, which are a typical class of chelating ligands, are anticipated to result in stable molecular architectures. Reaction of $GdCl_3$ with hfpd-H (1,1,1,5,5,5-hexafluoropentane-2,4-dione) generated tetranuclear $Gd_4(OH)_4(hfpd)_8$-$(H_2O)_6$ in aqueous medium while in acetone/water the mononuclear compound $Gd(hfpd)_3(Me_2CO)(H_2O)$ was obtained [12]. The structure of the former consists of a distorted bicapped cubane made by four gadolinium atoms (all having coordination number nine as tricapped trigonal prisms) and four triply bridging hydroxy ligands, while in the latter there is only one eight-coordinated Gd atom with square-antiprismatic arrangement. Furthermore, novel alkoxy compounds of gadolinium have also been synthesised as precursors for sol-gel/MOCVD applications [13]. To the best of our knowledge $Gd_6(\mu_4\text{-}O)(OC_2H_4OMe)_{16}$ is the only [14] hexanuclear alkoxy gadolinium compound which has been structurally characterised for this purpose. It contains one μ_4-oxo ligand along with both hepta- and octa-coordinated metal centres which have capped octahedral and square-antiprismatic geometry around them, respectively. We wanted to make Eu^{III}-doped nano-dimensional Gd_2O_3 phosphors by the sol-gel process for bioconjugation [15]. In this connection, the commercially available precursor gadolinium isopropoxide was chosen to be modified by acetyl acetone (acacH). We present here the synthesis and single crystal X-ray structure of $Gd_6(\mu_3\text{-}OH)_6(acac)_{12}\cdot 1.25\ CHCl_3$ (**1**) which is a unique hexanuclear hydroxo acetylacetonato complex. Gadolinium isopropoxide and **1** as precursor in a typical sol-gel transformation are compared.

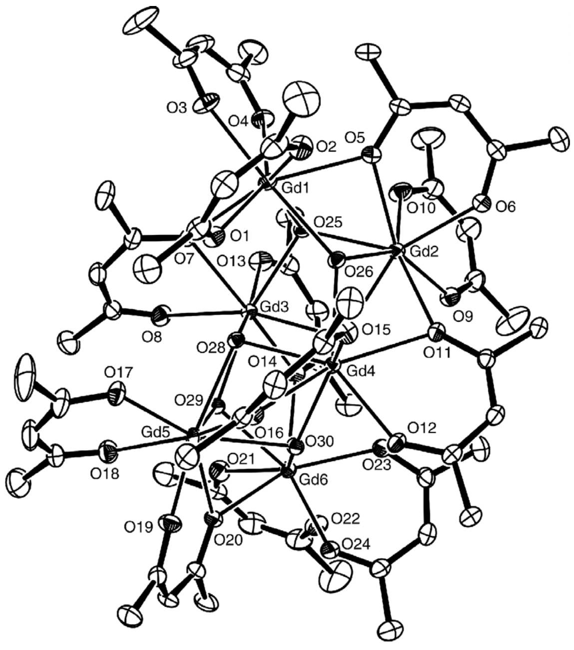

Fig. 1. ORTEP representation of the molecular structure of **1** in the crystal (displacement ellipsoids at the 50 % probability level; hydrogen atoms omitted for clarity).

Results and Discussion

Gadolinium tri-isopropoxide was reacted with acetylacetone in a 1 : 1 molar ratio at ambient temperature in chloroform, and the reaction mixture was stirred for eight hours. After evaporation of the solvent, a product (as a pasty mass) with analytical and spectroscopic composition $Gd(OPr^i)_2(acac)$ was obtained in quantitative yield. When acetylacetone was added to $Gd(OPr^i)_3$ in a 1 : 2 molar ratio under the same conditions, another product corresponding analytically to $Gd(OPr^i)(acac)_2$ was obtained as a viscous liquid in quantitative yield. The physical state of both compounds prevented their further characterisation by X-ray diffraction analysis.

In another experiment, acetylacetone was again added to $Gd(OPr^i)_3$ in a 2 : 1 stoichiometric ratio, and stirring was continued for eight h. Instead of removing all of the solvent, the reaction mixture was concentrated to half of the initial volume and left at −20 °C for crystallisation. Colourless crystals of a product analytically and spectroscopically corresponding to the formula $Gd(OH)(acac)_2$ were obtained after 45 h. One of these crystals proved to be $Gd_6(\mu_3\text{-}OH)_6(acac)_{12}\cdot 1.25\ CHCl_3$ (**1**) by X-ray analysis.

$$\begin{aligned} &Gd(OPr^i)(acac)_2 + Pr^iOH \\ &\quad \rightarrow Gd(OH)(acac)_2 + Pr^iOPr^i \end{aligned} \tag{1}$$

It appears that the initially formed bis-acetyl acetonato product $Gd(OPr^i)(acac)_2$ during aging in solution condenses with iso-propanol (present as a by-product of the reaction) to yield **1** by liberating di-isopropyl ether (Eq. 1). The presence of ether has been confirmed by the IR spectrum of the volatiles of the reaction. Ether elimination from alkoxy species leading to the generation of oxo ligands have also been reported previously [16], and viewed as an outcome of the propensity of metal atoms to enhance their coordination number.

Crystal structure

Compound **1** crystallises in the triclinic space group $P\bar{1}$. The molecular structure (Fig. 1) consists of a hexanuclear unit of $Gd_6(\mu_3\text{-}OH)_6(acac)_{12}\cdot 1.25\ CHCl_3$. In the structure of this unit, there are two distorted tricapped, face-sharing cubanes (each with one missing edge) constructed by six gadolinium atoms and six triply bridging hydroxy ligands resulting in a Gd_6O_{12} core (Fig. 2 shows the structure with only metal-oxygen bonds). The important bond lengths and bond angles are given in Tables 1 and 2, respectively. The distortion in the two incomplete cubanes is also evident from an examination of the bond angles (Table 2) around the μ_3-OH groups (which range from 97.7

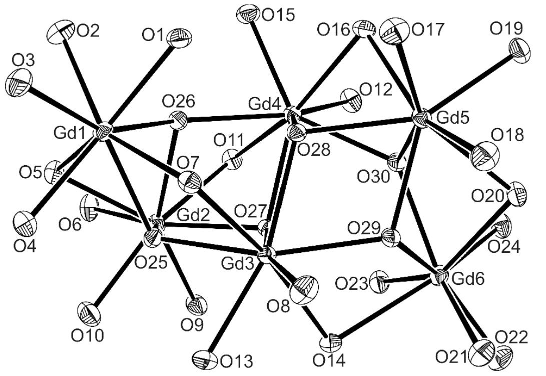

Fig. 2. Molecular structure of complex **1** showing only the metal and oxygen atoms.

to 135.4°). Similarly, the bond angles around the Gd atoms range from 68.7 to 157.6° for the bonds connecting with the hydroxy groups. The capping positions for the first cubane are O5, O7 and O11 while the oxygen atoms O14, O16 and O20 are capping the second cubane. The faces made by the Gd1, O26, Gd2, O25 and Gd5, O29, Gd6, O30 atoms for the two cubanes, respectively, are highly distorted. This may be due to the different coordination environments of the metal atoms. For example, although all the gadolinium atoms are eight-coordinated with an approximate square-antiprismatic geometry, coordination of Gd2 and Gd5 is completed by three μ_3-hydroxy ligands, one chelating acac moiety, one doubly bridging (with Gd1 and Gd6, respectively) chelating acac group and one μ-acac ligand (with Gd4 for both), while Gd3 and Gd4 have no attachment of any chelating acac group, and their coordination sphere is completed by four μ_3-OH groups and two bridging (with Gd1 and Gd6 for Gd3 and with Gd2 and Gd5 for Gd4) chelating acetylacetonate ligands. The face which is common between the two incomplete cubanes is constituted of the atoms Gd3, Gd4 along with the triply bridging hydroxy groups O27 and O28.

Furthermore, unlike the other four gadolinium centres, Gd1 and Gd6 are not directly connected to each other, but their coordination environment is similar. It features two chelating acac groups, two bridging (with Gd2, Gd3 for Gd1 and with Gd3, Gd5 for Gd6) acac groups and two μ_3-OH groups.

Compound **1** is the first structurally characterised hexanuclear β-diketonate Gd complex with a highly asymmetrical molecular core structure constituted of a distorted bis-cubane arrangement. Asymmetry is also evident by an examination of the bonding behaviour of the various acac ligands. One of the acac ligands is symmetrically chelating Gd1 (average bond lengths 2.344 Å) while the other is asymmetric (Gd1–O3 2.313(5), Gd1–O4 2.362(4) Å), but on Gd6 both chelating ligands are bonded asymmetrically (Gd6–O21 2.373(5), Gd6–O22 2.327(5), Gd6–O23 2.321(5) Gd6–O24 2.367(4) Å). Similarly, although Gd2 and Gd5 have a similar coordination environment, the former has a symmetrically chelating acac group (average bond length 2.332 Å) while the latter has an unsymmetrical attachment (Gd5–O17 2.328(5), Gd5–O18 2.351(5) Å).

Table 1. Selected bond lengths (Å) for **1**.

Gd1–O1	2.342(4)	Gd1–O2	2.345(4)
Gd1–O4	2.362(4)	Gd1–O26	2.443(4)
Gd2–O5	2.483(4)	Gd2–O6	2.320(5)
Gd2–O9	2.333(5)	Gd2–O11	2.557(4)
Gd3–O14	2.483(4)	Gd3–O27	2.420(4)
Gd3–O29	2.378(3)	Gd3–O8	2.323(5)
Gd4–O11	2.541(4)	Gd4–O12	2.322(4)
Gd4–O15	2.325(4)	Gd4–O16	2.480(4)
Gd5–O17	2.328(5)	Gd5–O16	2.577(3)
Gd5–O20	2.491(4)	Gd5–O28	2.412(3)
Gd6–O20	2.449(4)	Gd6–O21	2.373(5)
Gd6–O22	2.327(5)	Gd6–O24	2.367(4)

Table 2. Selected bond angles (deg) for **1**.

O1–Gd1–O2	73.48(16)	O5–Gd1–O26	66.82(12)
O3–Gd1–O4	71.13(15)	O3–Gd1–O7	93.63(15)
O5–Gd2–O26	67.71(12)	O10–Gd2–O27	117.84(14)
O6–Gd2–O27	150.53(15)	O25–Gd2–O26	69.66(13)
O26–Gd2–O27	72.26(12)	O7–Gd3–O8	72.46(14)
O7–Gd3–O27	121.30(11)	O8–Gd3–O27	162.94(14)
O8–Gd3–O14	97.41(14)	O11–Gd4–O28	136.30(12)
O1–Gd4–O12	71.98(14)	O11–Gd4–O27	68.68(13)
O11–Gd4–O16	154.50(12)	O16–Gd5–O17	81.97(15)
O16–Gd5–O29	126.74(12)	O17–Gd5–O20	141.31(15)
O19–Gd5–O30	102.39(14)	O14–Gd6–O21	76.32(13)
O14–Gd6–O20	134.56(14)	O14–Gd6–O22	100.73(13)
O14–Gd6–O24	150.54(15)		

In case of the acetylacetonate ligands the metal-oxygen distances (average 2.484 Å) for the bridging oxygen atoms are expectedly longer than for the non-bridging atoms (average bond distance 2.316 Å). However, for one such ligand present on both Gd3 and Gd4 this difference is surprisingly more pronounced (Gd3–O7 2.527(4), Gd3–O8 2.323(5), Gd4–O11 2.541(4) and Gd4–O12 2.322(4) Å). Most of the Gd–μ_3-OH distances in complex **1** can be averaged out to be 2.402 Å which is in accordance with a previous report [12]. However, the bond lengths for Gd1–O25, Gd2–O25, Gd5–O29 and Gd6–O29 (average 2.346 Å) are comparatively shorter.

*Comparison of $Gd(OPr^i)_3$ vs. compound **1** as precursors in sol-gel processes*

Compound **1** was found to be fairly soluble in common organic solvents and also in mixtures with isopropanol. Since our aim was to make potential precursors for rare earth ion-doped Gd_2O_3 nanomaterials, we compared the performance of complex **1** with the commercially available precursor compound gadolinium tri-isopropoxide. Eu^{III}-incorporating, amorphous xerogels were prepared by separate hydrolyses of sols of compound **1** and $Gd(OPr^i)_3$ by a similar method as reported previously by us for Eu^{III}/Y_2O_3 nanopowders [17]. The molar ratio of the dopant ion (Eu^{III}) with the host matrix (Gd_2O_3) was kept at 0.2 M : 1 M in both experiments. In general, the sol-gel derived xerogels obtained by using metal alkoxides as precursors are initially formed as amorphous powders which have to be annealed at higher temperatures to generate crystallites. While the europium-incorporating xerogel obtained with gadolinium isopropoxide developed a crystalline phase (Fig. 3) at 900 °C annealing temperature, the xerogel obtained from complex **1** turned crystalline (Fig. 4) at only 600 °C, as evidenced by the corresponding XRD patterns. The average particle sizes of the powders derived from gadolinium isopropoxide and complex **1** as calculated from XRD was found to be 34 nm and 57 nm, respectively. The photoluminescence spectra of xerogels obtained from **1** and gadolinium isopropoxide are shown in Figs. 5 and 6, respectively, which clearly show the characteristic $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions of europium. It is noteworthy that when $GdCl_3$ was employed [18] as precursor in a typical sol-gel process to produce Eu^{III}-doped Gd_2O_3, the xerogel was required to be heated to 800 °C to obtain a crystalline phase. Therefore, compound **1** described in the present investigation is not only interesting for its novel structural parameters but is also a potential precursor for Gd_2O_3-based materials.

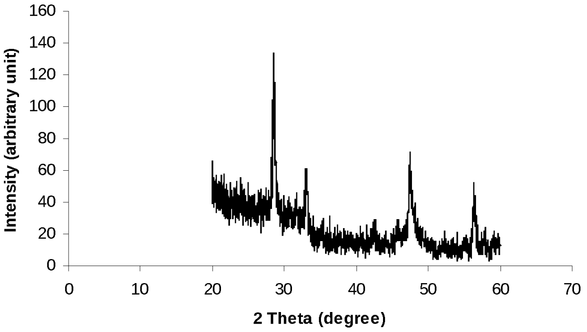

Fig. 3. XRD pattern of the xerogel obtained from $Gd(OPr^i)_3$ heated to 900 °C.

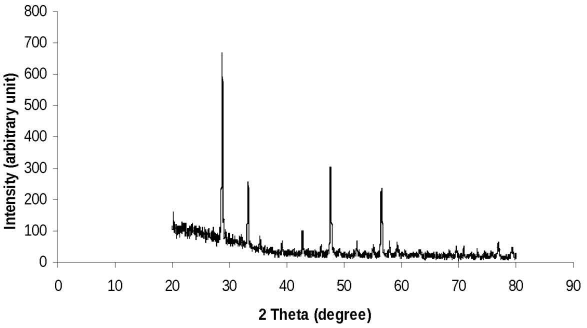

Fig. 4. XRD pattern of the xerogel obtained from complex **1** heated to 600 °C.

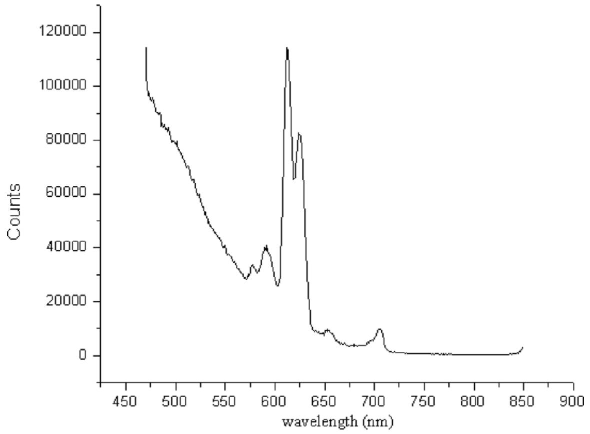

Fig. 5. Eu^{III} photoluminescence spectrum (at 440 nm excitation wavelength) of the xerogel obtained from complex **1** which was heated to 600 °C.

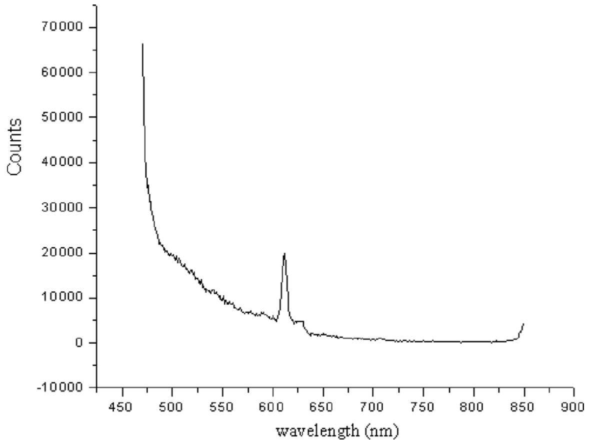

Fig. 6. Eu^{III} photoluminescence spectrum (at 440 nm excitation wavelength) of the xerogel obtained from $Gd(OPr^i)_3$ and heated to 900 °C.

Experimental Section

All the reactions were carried out under stringently anhydrous conditions using glove box and Schlenck techniques under dry argon. Gd(OPr^i)$_3$ (Strem Chemicals) was used as such for carrying out the reactions. Chloroform and $CDCl_3$ were dried by standard procedures. A JASCO FT-IR-5300 spectrometer was used for recording the infrared spectra of the compounds as Nujol mulls between NaCl plates. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker Biospin ARX 300 spectrometer with tetramethylsilane as internal reference. The photoluminescence spectra were recorded on an Ocean Optics system with range 200 to 1800 nm. Gadolinium was determined by titration with standard ethylenediaminetetraacetic acid (EDTA), using xylenol orange as an indicator [19], and isopropoxy analysis was done by the method of Bradley *et al.* [20].

Syntheses

Synthesis of Gd(OPr^i)$_2$(acac)

A solution of acacH (0.574 g, 5.74 mmol) in chloroform (20 mL) was added dropwise to a stirred solution of Gd(OPr^i)$_3$ (1.923 g, 5.74 mmol) in $CHCl_3$ (30 mL) over 30 min at r. t. (25 °C). After complete addition stirring of the reaction mixture was continued for 8 h. Then all the solvent was removed in vacuum to give a reddish brown pasty mass (2.139 g, 99.4 %). – Analysis for $GdC_{11}H_{21}O_4$ (374.21): calcd. Gd 42.02, OPr^i 31.52; found Gd 41.96, OPr^i 31.33. – ^{1}H NMR (25 °C): δ = 1.32 (d, gem-Me$_2$ of OPr^i, 4.33 (sept. CH of OPr^i), 1.88, 2.08 (s, CH_3 of acac), 5.38, 5.53 (s, CH of acac). – FT-IR (Nujol): ν = 1604 ν(C–O), 1541 ν(C–C), 1115 (terminal OPr^i), 1015 (bridging OPr^i) cm^{-1}.

Synthesis of Gd(OPr^i)(acac)$_2$

A solution of acacH (1.148 g, 11.48 mmol) in chloroform (25 mL) was added dropwise to a stirred solution of Gd(OPr^i)$_3$ (1.923 g, 5.74 mmol) in $CHCl_3$ (30 mL) over 30 min at r. t. (25 °C). After complete addition stirring of the reaction mixture was continued for 8 h. Then all the solvent was removed in vacuum to give a light brown viscous liquid. (2.362 g, 99.1 %). – Analysis for $GdC_{13}H_{21}O_5$ (414.20): calcd. Gd 37.96, OPr^i 14.24; found Gd 37.99, OPr^i 14.21. – ^{1}H NMR (25 °C): δ = 1.22 (d, gem-Me$_2$ of OPr^i), 4.55 (sept. CH of OPr^i), 1.97 (s, CH_3 of acac), 5.51 (s, CH of acac). – FT-IR (Nujol): ν = 1599 ν(C–O), 1501 ν(C–C), 1090 (terminal OPr^i), 1010 (bridging OPr^i) cm^{-1}.

*Synthesis of $Gd_6(\mu_3\text{-}OH)_6(acac)_{12}\cdot 1.25\ CHCl_3$ (**1**)*

A solution of acacH (1.148 g, 11.48 mmol) in chloroform (25 mL) was added dropwise to a stirred solution of Gd(OPr^i)$_3$ (1.923 g, 5.74 mmol) in $CHCl_3$ (30 mL) over 30 min at r. t. (25 °C). After complete addition stirring of the reaction mixture was continued for 8 h. The solvent was evaporated in vacuum reducing the solution to half of the original volume. Then the reaction mixture was kept at −20 °C, and after 45 h the crystalline product **1** was obtained. (0.679 g, 67.4 %). Analysis for $GdC_{10}H_{15}O_5$ (372.00): calcd. Gd 42.27; found Gd 42.33. – ^{1}H NMR (25 °C): δ = 1.98, 2.01, 2.05, 2.09 (s, CH_3 of acac), 5.45, 5.50 (s, CH of acac). – FT-IR (Nujol): ν = 1599 ν(C–O), 1501 ν(C–C), 3350 ν(O–H) cm^{-1}.

Table 3. Crystallographic data for complex **1**.

Formula	$C_{61.25}H_{91.25}Cl_{3.75}Gd_6O_{30}$
M_r, g mol^{-1}	2384.03
Crystal size, mm	0.14 × 0.11 × 0.09
T, K	200(2)
Radiation; wavelength, Å	MoK_α; 0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	13.8230(2)
b, Å	16.6541(2)
c, Å	21.3555(3)
α, deg	98.5072(8)
β, deg	98.2696(8)
γ, deg	112.3465(7)
V, Å^3	4388.11(10)
Z	2
Density (calcd.), g cm^{-3}	1.80
μ(MoK_α), mm^{-1}	4.7
Absorption correction; $T_{\min}/T_{\max}$	multi-scan; 0.562/0.658
θ range, deg	3.20 – 26.11
Refls. measured/unique/R_{int}	77679/17209/0.0405
mean $\sigma(I)/I$	0.0332
Observed reflections [$I \geq 2\sigma(I)$]	14659
Hydrogen refinement	mixed
Refined parameters	937
$R1(F)^a$ [$I \geq 2\sigma(I)$]	0.033
$wR2(F^2)^a$ (all reflections)	0.085
x/y (weighting scheme)	0.0346/14.4415
S (GoF)^a	1.072
shift/error$_{\max}$	0.002
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	1.18/−1.04

[a] $R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (xP)^2 + yP]^{-1}$, where $P = (\text{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$, $S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Photoluminescence spectra of the xerogels

Photoluminescence spectrum of Gd_2O_3 powder obtained from **1**: $^5D_0$–$^7F_1$ transitions: 580 and 590 nm, $^5D_0$–$^7F_2$ transitions: 625 and 627 nm.

Photoluminescence spectrum of Gd_2O_3 powder obtained from Gd(OPr^i)$_3$: $^5D_0$–$^7F_2$ transition: 614 nm.

*Crystal structure determination and refinement of **1***

A crystal suitable for X-ray crystallography was selected by means of a polaris microscope, mounted on the tip of a glass fiber, and investigated on a Nonius Kappa CCD diffractometer using MoK_α radiation (graded multilayer X-ray optics). Crystal data for compound **1** are given in Table 3. The measurement temperature was 200 K. A multi-scan absorption correction was performed with SADABS [21]. The structure was solved by Direct Methods with the programme SIR97 [22] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97 [23]). Anisotropic displacement parameters were refined for all non-hydrogen atoms. The latter were isotropically refined with the C-bound hydrogen atoms riding on their parent atoms while the O-bound hydrogen atoms have not been considered in the refinement.

CCDC 626316 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.Cam.ac.uk/data_request/cif.

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