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Synthesis and structure of a tris-chelate Gd^{III} complex with tridentate 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinone ligands

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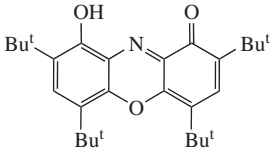
A new Gd^{III} complex with the tridentate chelating redox ligand 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinone was synthesized and studied by X-ray crystallography, ESR spectroscopy and magnetic measurements. The rigid tricyclic framework of the ligands ensures the formation of a nine-coordinate environment of Gd^{III} surrounded by three nitrogen and six oxygen atoms in the form of a tricapped trigonal prism.

Due to their exciting magnetic, spectral and photophysical properties, rare earth element complexes have found versatile biomedical and technical applications as MRI agents, luminescent bioprobes and laser materials.[1] Because of the high metal reactivity and the proneness to easily extend the metal coordination sphere, the lanthanide complexes are usually prepared and isolated as solvates or adducts with other salts. This trend initiates interest in monomeric solvent- and salt-free complexes with rare-earth-centered coordination sites available to further purposeful coordination. To prevent the association, the ligands of lanthanide complexes can be functionalized with sterically bulky or intramolecularly coordinating substituents.[2] Here, we report on the synthesis of a new Gd^{III} complex based on a tridentate ligand, 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinone **1**,[3] whose structure integrates both of the above features: the bulky 2,8-*tert*-butyl groups providing for the steric shielding of a metal center and ONO chelating triad of the properly arranged donor atoms. It is well known[4] that the complexation of trivalent metal ions with another structurally similar but conformationally flexible tridentate redox-active ligand **2** generally results in the formation of complexes with only two coordinated chelating ligands. The only exclusions are represented by the nine-coordinate complexes of Sr^{III} and Sm^{III} with **2**.[4,5] By contrast, the rigid tricyclic framework of **1** secures the ONO donor centers in the position suitable for coordination to the ions with appropriately large ionic radii and is expected to ensure the formation of M(ONO)$_3$ metal chelates.



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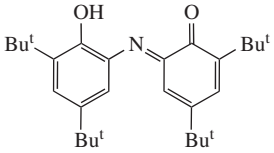
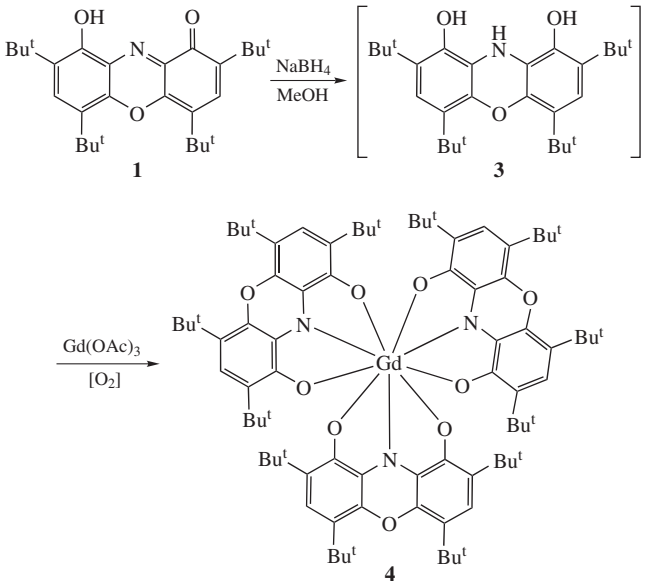


2

We have previously developed a convenient method for the synthesis of a series of bis-chelate 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinonate complexes with divalent metal ions M^{II} (M = Mn, Fe, Co, Ni, Cu and Zn) based on the reaction of metal acetates with **1** in methanol solution.[6] This approach has been recently applied to the preparation of Pb^{II} complexes.[7] However, attempts to extend this approach to the preparation of tris-chelate complexes of trivalent metal ions M^{III} failed primarily because the insufficiently large ionic radii of the transition metal ions block coordination with three spacious chelating ligands **1**. This problem was expected to be overcome in the case of trivalent lanthanide ions, *e.g.* Gd^{III}, whose ionic radii (0.938 Å) are sufficient for the formation of the coordination site of a tris-chelate complex of **1**. Because of the relatively low reactivity of **1**, its direct reaction with gadolinium acetates or chlorides yielded no target tris-chelate Gd^{III} complex **4** (Scheme 1). This compound was prepared in a high yield by the reaction of a highly reactive reduced form of **3** with Gd^{III} acetate.[†]



1 **3** **4**

Scheme 1

[†] *Tris[2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinonate] gadolinium(III)* **4**. $NaBH_4$ (5 mmol) was added to a solution of 2,4,6,8-tetrakis-(*tert*-butyl)-9-hydroxyphenoxazinone **1** (3 mmol) in 25 ml of methanol. After the total decoloration of the solution, Gd^{III} acetate (1 mmol) in 5 ml of methanol was added; the solution was stirred and allowed to stand at room temperature for 24 h. The solvent was then evaporated, and the residue was washed with 10 ml of hexane and filtered off. Careful evaporation of the hexane solution (at room temperature) resulted in the blue crystals of **4**, which were crystallized from methanol. The yield of

Table 1 Selected bond lengths (Å) and angles (deg) in GdL_3 **4**.

L		L^a		L^b	
Bond	*d*	Bond	*d*	Bond	*d*
Gd(1)–O(1)	2.398(4)	Gd(1)–O(1a)	2.458(3)	Gd(1)–O(1b)	2.448(3)
Gd(1)–O(29)	2.418(3)	Gd(1)–O(29a)	2.433(3)	Gd(1)–O(29b)	2.424(4)
Gd(1)–N(31)	2.537(4)	Gd(1)–N(31a)	2.537(4)	Gd(1)–N(31b)	2.543(4)
O(1)–C(2)	1.277(6)	O(1a)–C(2a)	1.245(5)	O(1b)–C(2b)	1.258(5)
C(28)–O(29)	1.270(5)	C(28a)–O(29a)	1.274(5)	C(28b)–O(29b)	1.274(6)
Angle	*ω*	Angle	*ω*	Angle	*ω*
C(2)–O(1)–Gd(1)	124.1(3)	C(2a)–O(1a)–Gd(1)	123.9(3)	C(2b)–O(1b)–Gd(1)	122.6(3)
C(28)–O(29)–Gd(1)	122.2(3)	C(28a)–O(29a)–Gd(1)	123.9(3)	C(28b)–O(29b)–Gd(1)	123.2(3)
Angle	*α*	Angle	*α*	Angle	*α*
OGdO–L	20.4	OGdO–L^a	6.6	OGdO–L^b	17.5

The structure of the Gd^{III} complex was determined by single crystal XRD analysis (Figure 1).‡ The coordination environment of the Gd atom is formed by three N atoms [Gd–N distances are 2.537(4)–2.543(4) Å] and six O atoms [Gd–O 2.398(4)–2.458(3) Å], and it can be described as a tricapped trigonal prism. Table 1 summarizes selected bond lengths and angles. Note that the Gd–O and Gd–N distances of the ligands L, L^a and L^b lie in a narrow interval, but dihedral angles between the O–Gd–O plane and the plane of a corresponding tricyclic system (OGdO–L) are remarkably different (Table 1).

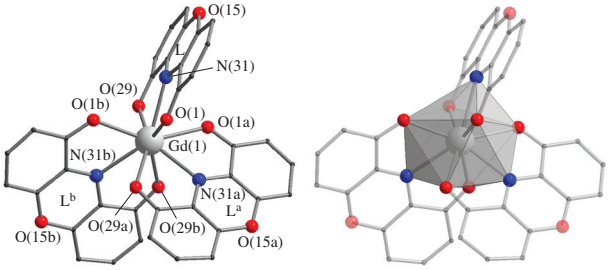


Figure 1 Molecular structure of Gd^{III} tris[2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinonate] **4**. H atoms and Bu^t groups are omitted for clarity.

4 was 76%, mp > 300 °C. IR (ν/cm^{-1}): 2955 (w), 2909 (w), 2869 (w), 1611 (w), 1590 (w), 1541 (w), 1503 (m), 1482 (w), 1459 (w), 1451 (w), 1440 (w), 1394 (m), 1351 (s), 1322 (s), 1283 (m), 1243 (m), 1233 (m), 1195 (m), 1163 (m), 1117 (w), 1087 (w), 1073 (w), 1033 (m), 1022 (w), 997 (s), 928 (w), 908 (w), 898 (w), 877 (m), 821 (w), 802 (w), 779 (w), 739 (m), 693 (m), 673 (w), 614 (w), 599 (w), 568 (w). UV-VIS spectra were recorded on an Agilent HP-8453 spectrophotometer in hexane; concentration, 1.40×10^{-7} mol dm^{-3}, [λ_{max} (ε/mol^{-1} cm^{-1})]: 247 (7971428), 293 (2735714), 399 (4064285), 764 (2907142). Found (%): C, 68.81; H, 7.91; N, 2.88; Gd, 10.75. Calc. for $C_{84}H_{114}N_3O_9Gd$ (%): C, 68.77; H, 7.83; N, 2.86; Gd, 10.72.

‡ *Crystal data for complex* **4**. The array of reflections from a single crystal of **4** was obtained on an AXS automated diffractometer (Bruker) using a standard procedure. The structure was solved by direct methods and refined by the full-matrix least-squares procedure anisotropically for nonhydrogen atoms. The H atoms were calculated geometrically and included in the refinement as riding groups. All calculations were fulfilled with the SHELXTL 6.14 program package.

Cell parameters: a = 38.663(9), b = 14.522(3) and c = 34.157(8) Å, β = = 92.128(15)°, V = 19165(8) Å^3, $C2/c$, Z = 8, d_{calc} = 1.017 g cm^{-3}, μ = = 0.783 mm^{-1}, 3.126 < θ < 29.270°, 96 803 I_{hkl} measured, 25684 unique (R_{int} = 0.1885), 11 820 I_{hkl} observed [$I > 2\sigma(I)$], 864 parameters; GOF = = 0.864; R_1 = 0.0630, wR_2 = 0.1492 for $I > 2\sigma(I)$; R_1 = 0.1449, wR_2 = 0.1775 for all I_{hkl}; residue electron density max/min 1.034/–2.128 eÅ^{-3}.

CCDC 1401462 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

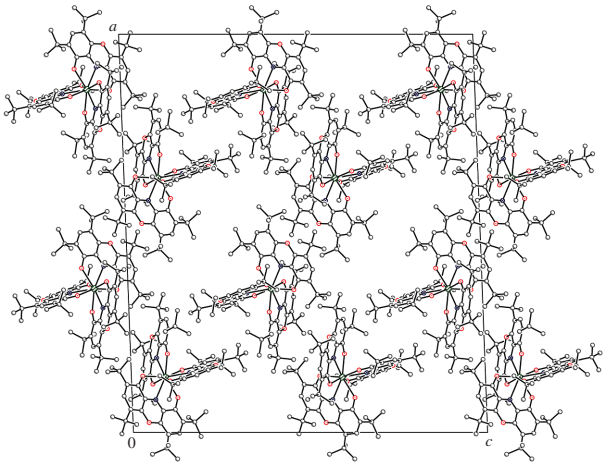


Figure 2 Crystal packing of Gd^{III} tris[2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinonate] **4**.

Figure 2 shows the crystal packing of complex **4**. A comparison of the structures of the Gd(**1**)$_3$ and Sm(**2**)$_3$[5] complexes reveals a redistribution in the M–N and M–O bond lengths of the complexes. Whereas the former ones in Sm(**2**)$_3$ are longer than those in Gd(**1**)$_3$, the reverse order takes place for the M–O bonds. This trend cannot be assigned to a small difference in the ionic radii of Gd (1.247 Å) and Sm (1.272 Å) and relates to the rigidness of the tricyclic framework of **1**.

The solvate $GdL_3\cdot C_7H_{16}\cdot CH_2Cl_2$ was obtained by the crystallization of complex **4** in dichloromethane. The effective magnetic moment of this solvate (7.85μ_B) is independent of temperature (Figure 3). This value is close to the theoretical one expected for seven unpaired electrons.

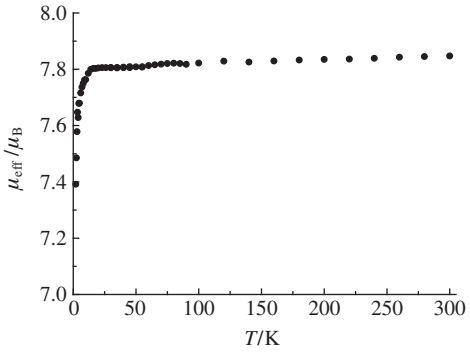


Figure 3 Experimental temperature dependence of the effective magnetic moment $\mu_{eff}(T)$ of $GdL_3\cdot C_7H_{16}\cdot CH_2Cl_2$ [L = 2,4,6,8-tetrakis(*tert*-butyl)-9-hydroxyphenoxazinonate].

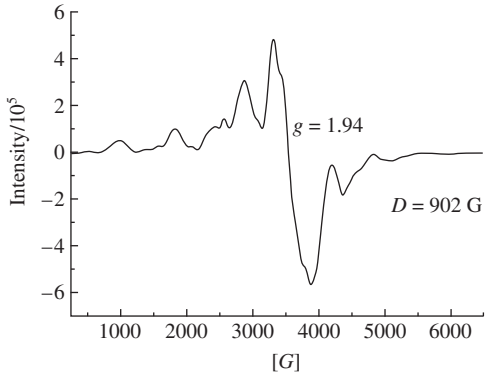


Figure 4 ESR spectrum of crystalline complex **4** (T = 120 K).

The ESR spectrum of complex **4** is displayed in Figure 4. The measured g and D parameters of the crystalline sample are close to those typical of Gd^{III} complexes.[8]

In conclusion, by an example of the synthesis of a stable Gd^{III} complex, we have demonstrated that it is possible to prepare monomeric solvent- and solvent-free lanthanide complexes by the appropriate adjustment of the ionic radius of a central trivalent ion and the size of a chelating moiety of a tridentate ligand. The application of the developed procedure to the synthesis of other rare earth metal complexes is underway now.

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