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Synthesis and X-ray Structure of the Mononuclear Nine-Coordinate Gadolinium(III) Hydrogen Oxydiacetate $[Gd(C_4H_5O_5)_3]\cdot C_4H_6O_5\cdot H_2O$

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Introduction

Current interest in new gadolinium(III) compounds derives in part from their potential applications as magnetic[1] and/or optical[2] probes. Studies of the interactions of trivalent lanthanides with the oxydiacetate dianion (oda $= {}^{-}O_2CCH_2OCH_2CO_2{}^{-}$) have shown that complexes with 1:1, 1:2, and 1:3 metal-to-ligand ratios can occur in solution.[3,4] X-ray structural data are available for a number of lanthanide oxydiacetates with additional sodium−metal−ligand units. These studies showed the mononuclear nine-coordinate $Ln(oda)_3{}^{3-}$ complex anion with Ln = Ce,[5−7] Nd,[8] Eu,[9,10] Gd,[11] and Yb.[8] The complexes have tris-tridentate chelate structures in which each oda ligand is coordinated to the Ln^{3+} ion via two carboxylate oxygen atoms and an ether oxygen atom.

On the other hand, two salt-free oxydiacetate complexes $[Er_2(oda)_3(H_2O)_4\cdot 2H_2O]_n$ and $[La_2(oda)_3(H_2O)_3\cdot 5H_2O]_n$ have been structurally characterized showing the ability of the oda ligand to form polymeric species via bridging modes. The former is composed of two-dimensional sheets with the oda ligands linking eight- and nine-coordinate Er^{3+} ions,[12] and the latter is a three-dimensional polymeric structure containing two nonequivalent nine-coordinate La^{3+} ions.[13]

The binding of lanthanide cations to protonated oxydiacetate to give neutral complexes of composition $Ln(Hoda)_3$ remains, however, unexplored. The behavior of the Hoda anion as a ligand has been structurally investigated for alkali-metal cations only,[14] and tridentate chelation has been found for cations larger than Na^+. We report herein the synthesis and structure of the mononuclear nine-coordinate $[Gd(Hoda)_3]\cdot H_2oda\cdot H_2O$ complex, isolated from the reaction of Gd_2O_3 and oxydiacetic acid in aqueous media.

Table 1. Crystallographic Data for **1**

formula: $C_{16}H_{23}GdO_{21}$
fw = 708.6
$a = 6.566(3)$ Å
$b = 25.171(13)$ Å
$c = 14.710(7)$ Å
$\beta = 92.90(1)°$
$V = 2428(2)$ Å^3
$Z = 4$
space group: $P2_1/n$ (No.14)
$T = 22$ °C
$\lambda = 0.71073$ Å
$\rho_{calcd} = 1.94$ g cm^{-3}
$\mu = 2.83$ mm^{-1}
R1^a[$F^2 > 2\sigma(F^2)$] = 0.047
wR2^b[$F^2 > 2\sigma(F^2)$] = 0.112

^{a} R1: $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2: $[\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$.

Experimental Section

All commercially available reagents and chemicals were of analytical or reagent grade purity and were used as received. Water was purified by a Millipore Milli-Q system, yielding 18 MΩ cm water. Elemental analyses (C, H) were performed at INQUIMAE (Instituto de Química de Materiales, Medio Ambiente y Energía) with a Carlo Erba EA 1108 analyzer. Infrared spectra were recorded as KBr disks or as a mull in Nujol with a Nicolet 510P FT-IR spectrophotometer. Thermogravimetric analyses were recorded on a Mettler TG-50 thermal analyzer in a dynamic atmosphere of oxygen at a heating rate of 5 °C min^{-1}. Powder X-ray diffraction (XRD) data were collected using monochromated Cu Kα radiation on a Phillips X'Pert diffractometer.

Preparation of $[Gd(Hoda)_3]\cdot H_2oda\cdot H_2O$. To a solution of oxydiacetic acid (1.340 g, 10.0 mmol) in water (150 mL) was added a suspension of Gd_2O_3 (0.365 g, 1.0 mmol). After 4 h of stirring at 80 °C the resulting solution was concentrated to ca. 100 mL on a rotary evaporator and passed through a glass filter. The filtrate at pH 2.5−3.0 was stored in a stoppered flask at room temperature for 1 month, whereupon colorless crystals of the product suitable for X-ray analysis were collected by filtration and dried under vacuum for 4 h. Upon slow evaporation of water over a period of several days, a second crystal phase precipitated along with the former, but crystals were not of adequate size and quality for X-ray studies. Yield: 0.65 g, 45%. Anal. Calcd (found) for $C_{16}H_{23}O_{21}Gd$: C, 27.10 (26.55); H, 3.20 (3.22). FTIR (KBr; cm^{-1}): 3472 (br, vs), 2930 (m), 1738 (m), 1719 (m), 1683 (m), 1641 (m), 1597 (br, vs), 1474 (w), 1445 (vs), 1426 (s), 1364 (m), 1314 (m), 1279 (m), 1246 (m), 1119 (s), 1061 (s), 945 (m), 910 (m), 694 (m), 571 (m).

X-ray Crystallography. Crystal parameters and details of the data collection and refinement are summarized in Table 1 (for full details see the Supporting Information). A colorless crystal of good diffracting power was mounted in a glass fiber on a Siemens R3m diffractometer equipped with a graphite monochromator and using Mo Kα (λ = 0.710 73 Å) radiation. The unit cell parameters were determined by least-squares refinement of 25 reflections. Intensity data were collected in the range $3.20° \le 2\theta \le 50.04°$ by the $\omega/2\theta$ scan technique. Within index ranges ($0 \le h \le 7$, $0 \le k \le 29$, $-17 \le l \le 17$), 4275 unique reflections were collected. Intensities were corrected for Lorentz and polarization effects, and a semiempirical absorption correction (ψ scan) was also applied. Two standard reflections were monitored every 98, and showed no systematic changes. The structure was solved by a combination of direct methods and difference Fourier syntheses. Refinement of the structure was done by full-matrix least-squares procedures based on F^2, with anisotropic thermal parameters for the non-hydrogen atoms.

The methylene hydrogen atoms were placed in their ideal positions (d(C−H) = 0.96 Å) and allowed to ride on their corresponding carbon

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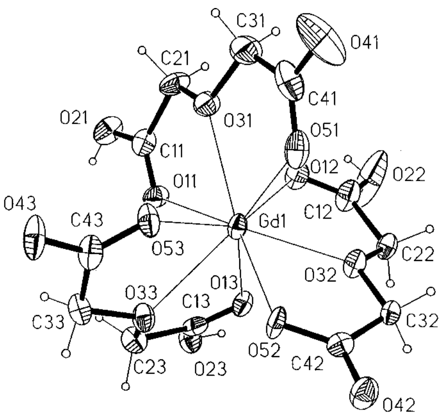

Figure 1. Structure of the Gd(Hoda)$_3$ unit of **1** with atom labels (50% thermal ellipsoids).

atoms. All the water and carboxylic hydrogen atoms were located in successive difference Fourier maps, and their positions were refined in the latest stages with a restrained geometry and an isotropic displacement parameter riding on the corresponding host atom multiplied by 1.3. Computer programs used in this study were SHELXL 93 and SHELXLTL/PC software packages[15,16] and PARST.[17]

Results and Discussion

Reaction of Gd_2O_3 with oxydiacetic acid in a 1:10 ratio in water and subsequent workup gave colorless crystals of $[Gd(Hoda)_3]\cdot H_2oda\cdot H_2O$ (**1**). The IR spectrum showed the characteristic absorptions corresponding to the presence of acid carbonyl groups (1738−1683 cm^{-1}), carboxylate anions (1597 and 1445 cm^{-1}), and water molecules (~1641 and ~3550−3400 cm^{-1}).[18] Complex **1** is a stable colorless crystalline solid and can be stored in a dry atmosphere at room temperature for extended periods of time. Thermal gravimetric analysis (TGA) of **1** was carried out under an oxygen atmosphere. Degradation occurred in a stepwise manner, and the final white residue was examined by XRD. No attempt was made to identify the intermediate products formed during this thermolysis. The mass of the final product at ~800 °C corresponds to the complete combustion of **1** to cubic Gd_2O_3 as shown by the X-ray powder diffraction pattern.[19]

Crystal Structure. The crystals of **1** contain Gd(Hoda)$_3$ discrete entities, oxydiacetic acid, and water crystallization molecules. The gadolinium ion is surrounded by an O_9 donor set with a geometry that is best approximated as a tricapped trigonal prism (TCTP) formed by the stacking of three triangular layers. Atoms O11, O12, O13 and O51, O52, O53 form the two outer triangular faces, and the capping positions are occupied by the ether oxygens O31, O32, and O33. A schematic drawing of the Gd(Hoda)$_3$ unit of **1** and the labeling of atoms are shown in Figure 1. Selected bond lengths of **1** are listed in Table 2.

Table 2. Selected Bond Lengths (Å) for **1**

Gd1−O53	2.320(6)	Gd1−O11	2.360(5)
Gd1−O51	2.367(7)	Gd1−O12	2.404(6)
Gd1−O52	2.416(5)	Gd1−O13	2.428(6)
Gd1−O32	2.458(5)	Gd1−O31	2.487(6)
Gd1−O33	2.584(6)	C11−O11	1.224(10)
C11−O21	1.279(10)	C11−C21	1.499(13)
C21−O31	1.412(10)	C31−O31	1.427(11)
C31−C41	1.486(15)	C41−O41	1.222(12)
C41−O51	1.283(13)	C12−O12	1.222(11)
C12−O22	1.275(11)	C12−C22	1.487(12)
C22−O32	1.414(9)	C32−O32	1.409(9)
C32−C42	1.522(11)	C42−O42	1.227(10)
C42−O52	1.267(10)	C13−O13	1.216(10)
C13−O23	1.303(10)	C13−C23	1.507(12)
C23−O33	1.431(10)	C33−O33	1.448(10)
C33−C43	1.501(12)	C43−O53	1.229(10)
C43−O43	1.277(10)	C14−O14	1.186(11)
C14−O24	1.326(12)	C14−C24	1.507(12)
C24−O34	1.415(11)	C34−O34	1.431(12)
C34−C44	1.494(14)	C44−O54	1.182(12)
C44−O44	1.324(13)		

Gadolinium(III) is coordinated to three tridentate Hoda ligands, coordinating one carboxylate oxygen (**O**−C−O)$^-$, one carbonyl oxygen (**O**=C−OH), and the ether oxygen of each ligand. One carboxylate oxygen and the carbonyl oxygen of each ligand are attached to the top and bottom vertices of the prism, while the middle ether oxygen occupies a capping position. The three oxygens are thus attached diagonally in a meridional conformation. The two outer triangular faces are rotated by 15.33°. The metal ion is close to the center of the trigonal prism shifted down by 0.15 Å from the equatorial plane defined by the capping ether oxygens toward the triangular face containing the oxygens of the negatively charged carboxylate groups. As a result, the gadolinium ion has a coordination number of 9 and an irregular polyhedral geometry, as has frequently been observed in the Ln(III) compounds.[20]

The six Gd−O prismatic bond distances, ranging from 2.320(6) to 2.428(6) Å, with an average value of 2.382(17) Å, agree well with the Gd−O$_{carboxylate}$ bond lengths in Gd(III)−polyamino polycarboxylate complexes.[21] The Gd−O capping bonds of the neutral ether oxygens are slightly longer than the former with a range and average value of 2.458(5)−2.584(6) and 2.510(38) Å, respectively, and demonstrate the comparative weakness of the less polar Gd−O$_{ether}$ bonds. These distances are comparable to the corresponding prismatic and capping distances in the related Gd(oda)$_3^{3-}$ complex (D_3 point-group symmetry), 2.41(1) and 2.49(3) Å, respectively.[11]

The C−O bonds in the carboxylate ends of the ligands are not equivalent. In ligands 1 and 2, the bonded C−O are longer than the outer C−O bonds, with average values of 1.275(8) and 1.224(2) Å, respectively. In ligand 3, the opposite occurs, and the bonded and outer C−O bonds are 1.229(10) and 1.277(10) Å, respectively, which might be the result of the strong interaction between the outer carboxylate oxygen atom O43 with the proton H21 of the corresponding COOH group (vide infra). In the carboxylic ends of the ligands the C−O bonds of the O-coordinated carbonyls are shorter than those in the C−OH groups, with average values of 1.221(2) and 1.286(9) Å, respectively, similar to those reported for carboxylic acids.[22] This is in accordance with the positions for the hydrogens on the COOH groups located in the difference map. It also reveals that the carboxylic groups of the Hoda ligands remain virtually unaffected by coordination to the gadolinium cation.

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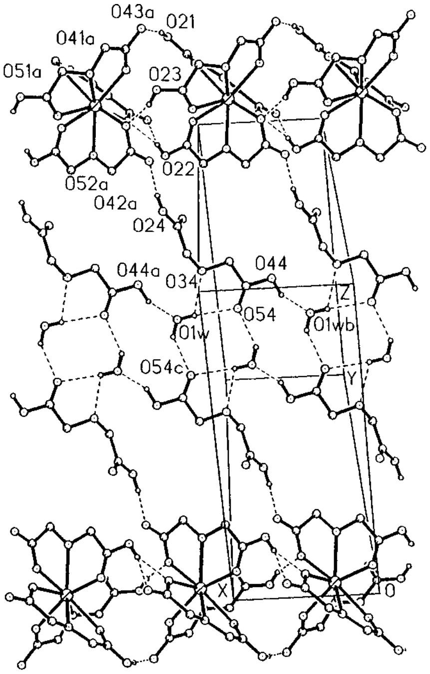

Figure 2. Packing diagram of **1** along the *a* axis. Atom labels and symmetry codes are as in Table 3.

The two five-membered chelate rings, with a common Gd−O bond for each Hoda ligand, are relatively planar, forming dihedral angles of 3.9(2), 5.2(2), and 14.8(2)° for ligands 1−3, respectively. The largest deviation from planarity is observed for C23 at 0.36 Å. The COO groups of the carboxylate and the carboxylic ends are further rotated about their C−C bonds by 16.0, 2.6, and 2.7° and by 10.1, 1.1, and 3.7° for ligands 1−3, respectively.

The crystal structure of **1** consists of ribbons parallel to the *a* axis. These are formed from two chains of neutral Gd(Hoda)$_3$ complexes separated by a middle chain containing the H$_2$oda and water molecules in an extended hydrogen-bonding network (Figure 2). A summary of bond distances and angles involving hydrogen-bonding contacts is given in Table 3. The Gd(Hoda)$_3$ molecules are connected by strong simple H-bonds (O21−H21···O43^a and O23−H23···O52^a) and an asymmetrical bifurcated H-bond around H22 (O22−H22···O41^a and O22−H22···O51^a). The H$_2$oda and water molecules in the middle chain are connected via a strong H-bond between a protonated carboxylic group and the water oxygen acceptor O1W (O44−H44···O1W^b). Furthermore, the water molecule also acts as a simple H-donor atom through H1WA to the carbonyl oxygen O54^c and as a bifurcated H-bond around H1WB to the carbonyl oxygen O54 and to the ether oxygen O34 of the H$_2$oda molecule. The molecular chains are further linked into ribbons along the *a* axis through strong H-bonds between protonated carboxylic units of H$_2$oda and outer carboxylate acceptors O42 (O24−H24···O42^a). Finally, weak hydrogen bonds of the type C−H···O participate in chain interlinking and in the packing of the ribbons in the solid. The shortest metal−metal separation is Gd···Gd ($x + 1, y, z$) = 6.566(3) Å and hence precludes any significant intermolecular interaction.

Table 3. Hydrogen-Bonding Contacts in **1**^{a}

O−H···O	O···O (Å)	O−H (Å)	H···O^b (Å)	O−H···O^b (deg)
O1W−H1WB···O34	3.000(10)	0.88(8)	2.46	117
O1W−H1WB···O54	3.075(11)	0.88(8)	2.14	172
O22−H22···O41^a	3.014(16)	0.90(8)	2.28	135
O22−H22···O51^a	2.613(12)	0.90(8)	1.74	153
O23−H23···O52^a	2.606(08)	0.89(5)	1.73	155
O24−H24···O42^a	2.616(10)	0.90(6)	1.68	178
O21−H21···O43^a	2.500(10)	0.90(7)	1.58	167
O44−H44···O1W^b	2.606(12)	0.90(6)	1.68	168
O1W−H1WA···O54^c	2.895(11)	0.88(9)	2.08	144

[a] Symmetry codes: (a) $x + 1,+y, +z$; (b) $x - 1, +y, +z$; (c) $-x + 1, -y, -z+2$. [b] Idealized distances and angles (for O−H = 0.94 Å) calculated according to ref 23.

In summary, the protonated (hydrogen oxydiacetato)gadolinium(III) complex [Gd(Hoda)$_3$]·H$_2$oda·H$_2$O has been isolated and structurally characterized. This is the first example of a neutral mononuclear Ln(III) derivative in a complex ligand environment created by tridentate chelation to three monoanionic Hoda ligands. Also, complex **1** has been shown to serve as an inorganic precursor to cubic Gd$_2$O$_3$.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the title compound is available on the Internet only. Access information is given on any current masthead page.

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