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Triaquaformatobis(4-formyl-2-methoxyphenolato)-gadolinium(III)

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In the title complex, $[Gd(L)_2(CHO_2)(H_2O)_3]$ (L^- = 4-formyl-2-methoxyphenolate anion, $C_8H_7O_3$), the Gd^{III} ion occupies a site with mirror symmetry and assumes a bicapped triangular prismatic coordination environment defined by four O atoms from two L^- ligands, three O atoms from three coordinated water molecules and one O atom from a formate group. The formate group and one water molecule lie on a mirror plane. A three-dimensional network is formed by O—H···O hydrogen-bond interactions.

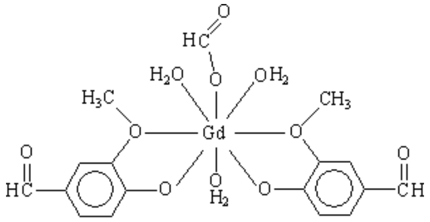
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.017
wR factor = 0.044
Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

4-Hydroxy-3-methoxybenzaldehyde (HL), which is better known as the flavoring material vanillin (Walton *et al.*, 2003), is a potential bidentate ligand with versatile binding modes. However, the reported crystal structures of metal complexes with HL are rare and mainly focus on mononuclear copper^{II} complexes (Greenhough & Ladd, 1978*a*,*b*; Hobson *et al.*, 1973). Recently, we isolated a new rare earth complex, $[Gd(L)_2(CHO_2)(H_2O)_3]$, (I), by the reaction of HL and gadolinium formate hexahydrate in an aqueous ethanol solution and its crystal structure is described here.


(I)

As shown in Fig. 1, the 4-hydroxy-3-methoxybenzaldehyde ligand bears a formal charge of −1, being deprotonated at the phenol atom O2. The Gd^{III} ion, the C9/H9/O4/O5 formate group and the O2W/H2W1/H2W2 water molecule occupy a mirror plane. The Gd^{III} ion is in an eight-coordinate environment, defined by four O atoms from two L^- ligands, one O atom from the formate group and three coordinated water molecules, and the Gd-atom geometry can best be described as bicapped trigonal prismatic (see Fig. 2). The two basal planes of the triangular prism are formed by atoms O4/O1W/O1W^i and O2W/O2/O2^i [symmetry code: (i) $x, \frac{1}{2}-y, z$], respectively, and the two planes are nearly parallel with a dihedral angle of 5.5 (3)°. The capping atom O1 extends 1.836 (2) Å beyond the plane defined by O4/O2W/O2/O1W [r.m.s. deviation = 0.013 (3)°]. The capped Gd—O1 distance of 2.617 (2) Å is the longest Gd—O bond distance (Table 1). The five-membered O1/C2/C3/O2/Gd chelate ring is roughly planar, with an r.m.s. deviation of 0.11 (3) Å. The

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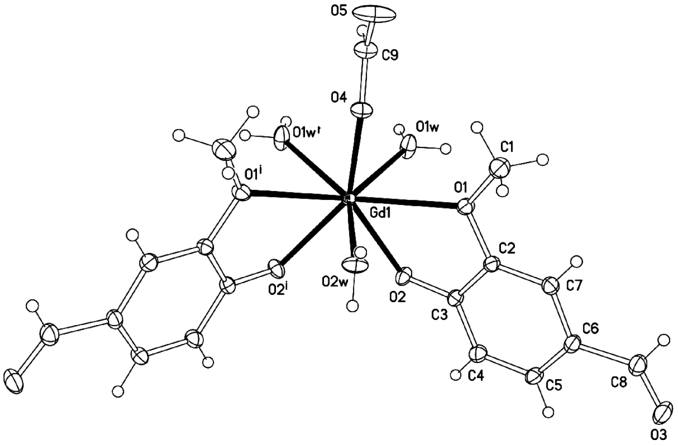

Figure 1
View of (I), shown with 30% probability displacement ellipsoids and arbitrary spheres for the H atoms. The symmetry code is as in Table 1.

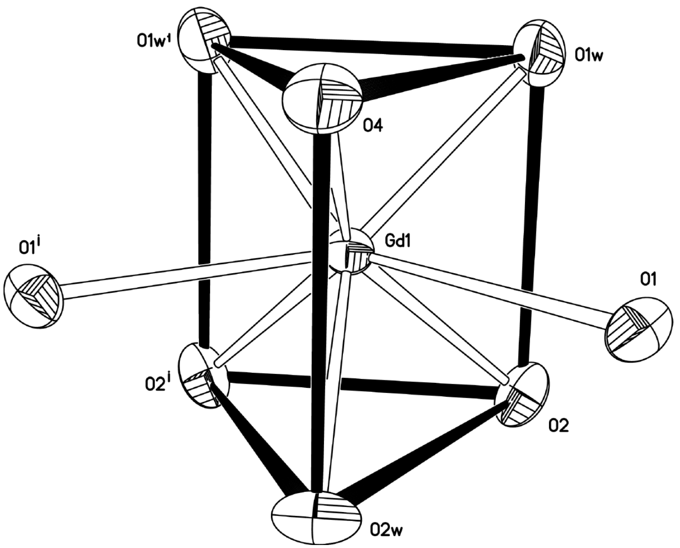

Figure 2
Detail of (I), showing the GdO_8 polyhedron. The symmetry code is as in Table 1.

bidentate chelating L^- ligand is essentially planar, with an overall r.m.s. deviation 0.04 (2) Å, and it makes a dihedral angle of 56.9 (3)° with the C9/O4/O5 fragment.

It should be noted that the C9—O4 distance of the formate group is longer than the C9—O5 distance, which is appropriate for a monodentate coordination mode of a carboxyl group. The coordinated water molecules form intermolecular hydrogen bonds (Table 2) with uncoordinated carboxyl atom O5, formyl atom O3 and coordinated phenolate O2 acceptors. The O···O distances range from 2.669 (2) to 2.820 (3) Å and the O—H···O angles range from 168 (3) to 177 (3)°, hence consolidating the crystal structure and leading to a three-dimensional network (Fig. 3).

Experimental

The title compound was prepared by the addition of gadolinium formate hexahydrate (2 mmol) to an aqueous ethanol solution of 4-hydroxy-3-methoxybenzaldehyde (H*L*, 4 mmol). The mixed solution was allowed to evaporate at room temperature and pale-yellow single crystals were isolated from the solution after 10 d. Analysis calculated for $C_{17}H_{21}GdO_{11}$: C 36.55, H 3.79; found: C 36.61, H 3.87%.

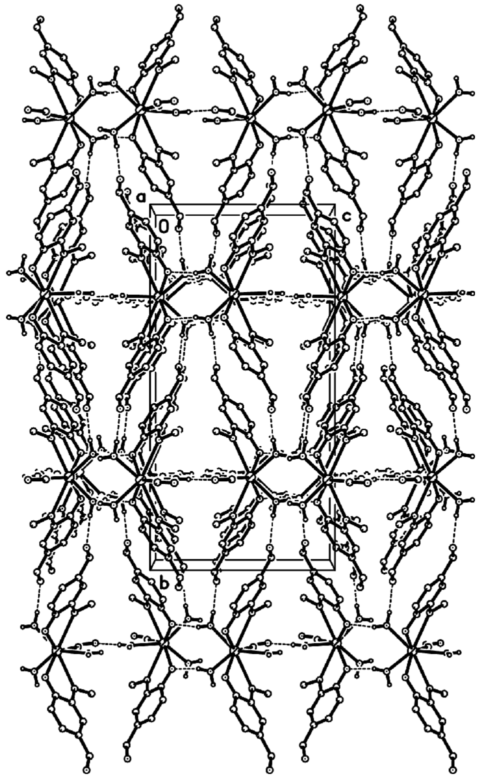

Figure 3
The packing of (I), with the O—H···O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Crystal data

$[Gd(C_8H_7O_3)_2(CHO_2)(H_2O)_3]$
$M_r = 558.59$
Orthorhombic, *Pnma*
$a = 7.7843$ (16) Å
$b = 21.977$ (4) Å
$c = 11.129$ (2) Å
$V = 1903.9$ (6) Å^3
$Z = 4$
$D_x = 1.949$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 17301 reflections
$\theta = 3.3$–27.5°
$\mu = 3.54$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.39 × 0.25 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.359$, $T_{max} = 0.510$
17409 measured reflections

2237 independent reflections
2159 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -28 \rightarrow 28$
$l = -13 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.044$
$S = 1.03$
2237 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 2.2018P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Gd1—O4	2.284 (2)	Gd1—O1	2.6174 (17)
Gd1—O2	2.3053 (15)	C9—O4	1.255 (4)
Gd1—O2*W*	2.364 (2)	C9—O5	1.220 (4)
Gd1—O1*W*	2.3986 (16)		
O1—Gd1—O1^{i}	130.86 (7)	O2—Gd1—O1*W*^{i}	124.39 (6)
O1*W*^{i}—Gd1—O1	143.13 (5)	O2^{i}—Gd1—O1*W*^{i}	79.49 (6)
O1*W*—Gd1—O1	72.69 (6)	O2*W*—Gd1—O1*W*^{i}	142.39 (4)
O1*W*^{i}—Gd1—O1*W*	74.23 (8)	O2*W*—Gd1—O1	69.87 (4)
O2—Gd1—O1	64.16 (5)	O4—Gd1—O1	76.24 (4)
O2^{i}—Gd1—O1	133.67 (5)	O4—Gd1—O1*W*^{i}	85.34 (7)
O2—Gd1—O2^{i}	76.53 (8)	O4—Gd1—O2	140.19 (4)
O2—Gd1—O2*W*	81.23 (6)	O4—Gd1—O2*W*	89.27 (8)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O2^{ii}	0.85 (3)	1.84 (3)	2.677 (2)	168 (3)
O1*W*—H1*W*2···O3^{iii}	0.85 (3)	1.97 (2)	2.820 (2)	175 (3)
O2*W*—H2*W*1···O5^{iv}	0.84 (3)	1.83 (3)	2.673 (4)	177 (3)
O2*W*—H2*W*2···O5^{v}	0.84 (2)	1.82 (2)	2.669 (3)	176 (3)

Symmetry code: (ii) $x - \frac{1}{2}, y, \frac{1}{2} - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (v) $1 + x, y, z$.

Carbon-bound H atoms were placed in calculated positions and were allowed to ride on their parent C atoms [C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic H atoms, and C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms]. Aqua H atoms were located in difference Fourier maps and refined with an O—H distance restraint of 0.85 (1) Å and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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References

Greenhough, T. J. & Ladd, M. F. C. (1978*a*). *Acta Cryst.* B**34**, 2619–2621.
Greenhough, T. J. & Ladd, M. F. C. (1978*b*). *Acta Cryst.* B**34**, 2744–2752.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Hobson, R. J., Ladd, M. F. C. & Povey, D. C. (1973). *J. Cryst. Mol. Struct.* **3**, 377–388.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC Inc., 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Walton, N. J., Mayer, M. J. & Narbad, A. (2003). *Phytochemistry*, **63**, 505–515.

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