

Aqua[5,17-dihydroxy-11,23-dimethylbicyclo-[18.3.1.1^{9,13}]hexacosa-1(25),2,7,9,11,13(26),21,23-octaene-25,26-diolato]dinitrato- κ^2O,O' ; κO -gadolinium nitrate–methanol–water (1/0.5/1.75)

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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C)$ = 0.007 Å
 Disorder in solvent or counterion
 R factor = 0.043
 wR factor = 0.118
 Data-to-parameter ratio = 15.4

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

The title complex, $[Gd((C_{24}H_{28}N_4O_4)(NO_3)_2(H_2O))(NO_3) \cdot 0.5CH_3OH \cdot 1.75H_2O]$, contains a gadolinium ion with a distorted monocapped square antiprismatic coordination.

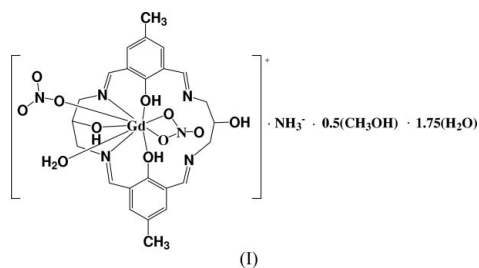
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Comment

The design and synthesis of macrocyclic ligands and their lanthanide complexes are an interesting area of research, due to their importance in basic and applied chemistry (Alexander, 1995). The ability of macrocyclic ligands to recognize lanthanide(III) ions makes them valuable for the development of applications such as selective separation of metals (Zhu & Izatt, 1990), luminescence probes in biological systems (Faulkner *et al.*, 2001) and supramolecular devices (Chen *et al.*, 2002). Gadolinium macrocyclic complexes have been extensively investigated, owing to their potential application in magnetic resonance imaging (Caravan *et al.*, 1999). 18- and 20-membered macrocycles, derived from [2 + 2]-condensation of 2,6-diformylphenol and diamines, have good complexing properties for lanthanide ions (Alexander, 1995), but only a few gadolinium complexes have been reported (Drew *et al.*, 1995).



We report here the crystal structure of a new gadolinium complex, $[Gd(H_4L)(NO_3)_2(H_2O)](NO_3) \cdot 0.5MeOH \cdot 1.75H_2O$, (I), with the neutral Schiff base ligand H_4L derived from 4-methyl-2,6-diformylphenol and 1,3-diaminopropanol. The same complex as a dihydrate, $[Gd(H_4L)(NO_3)_2(H_2O)](NO_3) \cdot 2H_2O$, has been reported previously (Spodine *et al.*, 2000), but (I) is a different solvate, belonging to a different crystal system (monoclinic, space group $C2/c$, compared with orthorhombic, $Pbca$).

In (I), atom Gd1 is coordinated by a monodentate nitrate ion, a bidentate nitrate ion, a water molecule, and the neutral Schiff base macrocycle H_4L , namely 5,17-dihydroxy-11,23-dimethylbicyclo[18.3.1.1^{9,13}]hexacosa-1(25),2,7,9,11,13(26),21,23-octaene-25,26-diol, which provides an N_2O_3 donor set to encapsulate only one gadolinium ion. The coordination polyhedron can be described as a distorted monocapped square antiprism, in which atoms N1, N2, O1 and O3 of H_4L form the lower plane [mean deviation = 0.0595 (2) Å], the

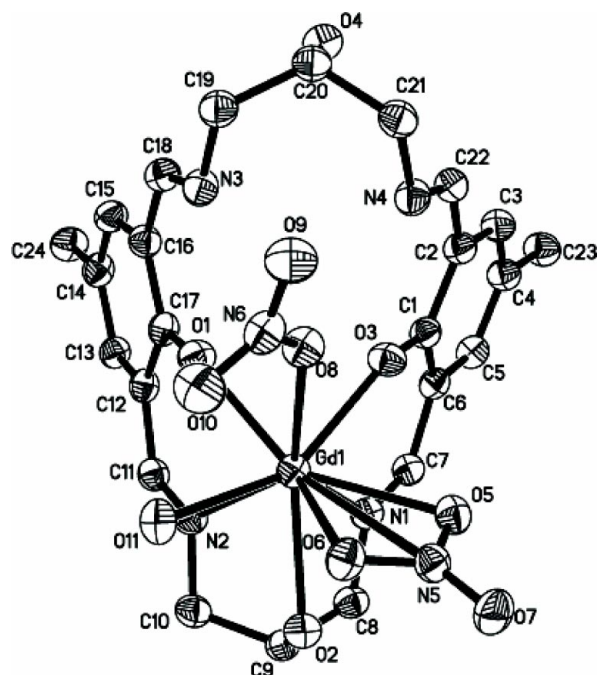


Figure 1
A view of the complex cation of (I), showing the labeling of the non-H atoms and 30% probability ellipsoids. H atoms have been omitted.

upper plane consists of O2, O11 (water molecule), O8 (from monodentate nitrate) and O5 (from bidentate nitrate) [mean deviation = 0.2160 (2) Å], and another O atom (O6) from the bidentate nitrate occupies the capping position.

The coordination distance is 2.418 (3) Å for the alcohol atom O2, slightly longer than those for the phenol atoms O1 [2.321 (3) Å] and O3 [2.296 (4) Å]. The Gd–O distances for the three-coordinate O atoms from the monodentate and the bidentate nitrate ions are in the range 2.509 (4)–2.545 (3) Å, and for O11 from the water molecule it is 2.403 (4) Å. Of the nine coordination distances, the longest are those for the two imino atoms N1 [2.549 (3) Å] and N2 [2.556 (4) Å]. Among all the nine coordination distances, only two (for water atom O11 and the phenol atom O1) are shorter than those of the previously reported complex (Spondine *et al.*, 2000), while the others show no significant differences. The two crystal structures belong to different crystal systems (monoclinic and orthorhombic, with space groups *C2/c* and *Pbca*, respectively), and have different solvent content. There is a larger dihedral angle between the two aromatic rings of 55.5 (2)° in the macrocyclic ligand of our complex, compared to 41.6° for the previous complex. The crystal structure of (I) is stabilized by intramolecular and intermolecular hydrogen bonds of the types O–H···O and C–H···O, where O atoms belong to water molecules, nitrate ions or the macrocyclic ligand (Table 1).

Experimental

To a methanol solution of 4-methyl-2,6-diformylphenol (0.01 mmol) and Gd(NO₃)₃(H₂O)₆ (0.005 mmol) was added a methanol solution

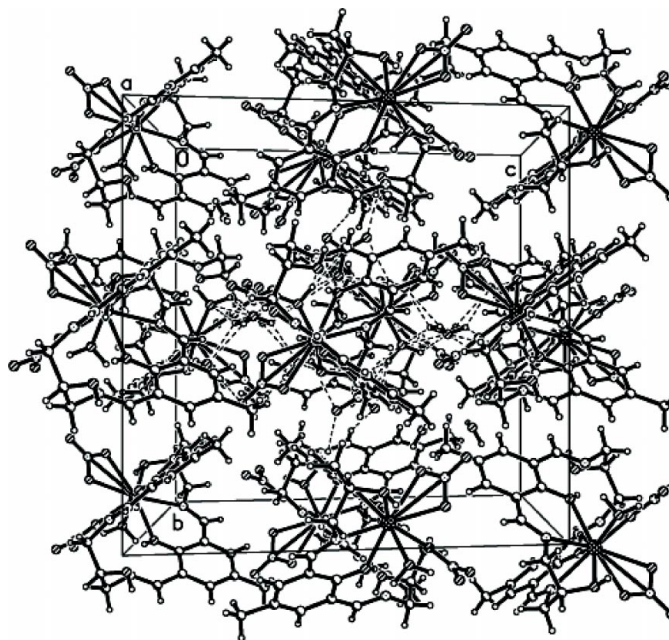


Figure 2
A view of the crystal packing, along the *a* axis. Hydrogen bonds are shown as dashed lines.

of 1,3-diaminopropanol (0.01 mmol). After the reaction mixture was refluxed for 10 h, the solvent was removed. The resulting yellow solid was recrystallized from acetonitrile, giving yellow prismatic crystals of (I) suitable for X-ray analysis.

Crystal data

[Gd(H₂O)(NO₃)₂(C₂₄H₂₈N₄O₄)]·
(NO₃)·0.5CH₄O·1.75H₂O
M_r = 845.35
Monoclinic, *C2/c*
a = 24.281 (3) Å
b = 17.339 (2) Å
c = 17.715 (2) Å
β = 103.63 (1)°
V = 7248.1 (15) Å³
Z = 8

D_x = 1.549 Mg m⁻³
Mo *Kα* radiation
Cell parameters from 966
reflections
θ = 2.3–19.6°
μ = 1.91 mm⁻¹
T = 293 (2) K
Prism, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-
detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2000)
T_{min} = 0.72, *T_{max}* = 0.83
19 353 measured reflections

7082 independent reflections
5746 reflections with *I* > 2σ(*I*)
R_{int} = 0.042
θ_{max} = 26.0°
h = –29 → 27
k = –20 → 21
l = –21 → 21

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.043
wR(*F*²) = 0.118
S = 1.08
7082 reflections
460 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 1.99P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
 $\Delta\rho_{max} = 0.77 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.66 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W–H1WB \cdots O12 ⁱ	0.85	2.35	3.000 (6)	133
O1W–H1WB \cdots O14 ⁱ	0.85	2.40	3.207 (6)	159
O2W–H2WA \cdots O6 ⁱⁱ	0.85	2.60	3.232 (6)	132
O2W–H2WC \cdots O1W ⁱⁱⁱ	0.85	2.28	2.990 (7)	141
O2W–H2WC \cdots O11 ⁱⁱ	0.85	2.39	2.765 (4)	108
O1W–H1WC \cdots O7 ⁱⁱ	0.85	2.56	3.154 (6)	128
O11–H11A \cdots O13 ⁱⁱⁱ	0.96	2.28	3.177 (6)	155
O11–H11A \cdots O14 ⁱⁱⁱ	0.96	2.11	2.794 (5)	127
O4–H4 \cdots O12 ^{iv}	0.82	1.96	2.771 (5)	171
C18–H18 \cdots O13 ^{iv}	0.93	2.28	3.172 (7)	161
C20–H20 \cdots O7 ^v	0.98	2.59	3.309 (6)	130
C19–H19A \cdots O9	0.97	2.57	3.390 (7)	142
C21–H21B \cdots O9	0.97	2.55	3.391 (7)	145
O11–H11B \cdots O10	0.96	2.00	2.852 (6)	147
O2W–H2WA \cdots O1W	0.85	2.37	2.990 (7)	130
O2–H2B \cdots O1W	0.97	1.77	2.649 (5)	148
O1–H1A \cdots N3	0.85	1.91	2.646 (5)	144
O3–H3B \cdots N4	0.85	2.06	2.643 (5)	125

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

All H atoms were positioned geometrically and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2$ (1.5 for methyl groups) times U_{eq} of the parent atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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