

A dicationic gallium–oxo–hydroxide cage compound

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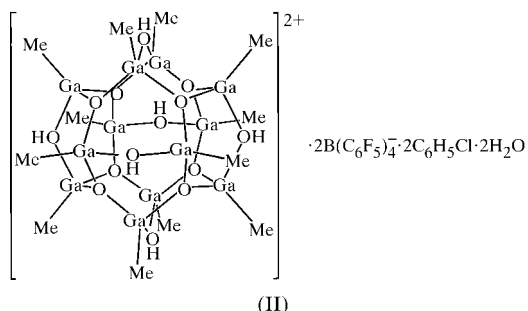
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The crystal structure of hexa- μ -hydroxo-dodecamethylocta- μ_3 -oxo-dodecagallium(III) bis[tetrakis(pentafluorophenyl)borate(III)] chlorobenzene disolvate dihydrate, $[\text{Ga}_{12}(\text{CH}_3)_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6](\text{C}_{24}\text{F}_{20}\text{B})_2 \cdot 2\text{C}_6\text{H}_5\text{Cl} \cdot 2\text{H}_2\text{O}$, is reported. The gallium–oxo–hydroxide dication is located on an inversion center and adopts a cage structure composed of 12 fused Ga_3O_3 rings and is associated with the hydrate molecules and the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions through hydrogen bonds and one $\text{O} \cdots \text{H} \cdots \pi$ -ring interaction. Disordered chlorobenzene solvent molecules are also present in the crystal structure.

Comment

In recent reports, we have described the chemistry of novel cationic group 13 alkyl complexes, some of which polymerize ethylene (Coles & Jordan, 1997; Ihara *et al.*, 1998; Radzewich *et al.*, 1998, 1999; Korolev *et al.*, 1999; Dagorne *et al.*, 2000). In the course of these studies, we found that the dinuclear cationic Ga–amidinate complex $[\text{Pr}_2\text{C}(\text{N}^i\text{Pr})_2]_2\text{GaMe}_2 \cdot \text{Pr}_2\text{C}(\text{N}^i\text{Pr})_2\text{GaMe}][\text{B}(\text{C}_6\text{F}_5)_4]$, (I), is hydrolyzed to the unexpected dicationic gallium–oxo–hydroxide cage compound $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6][\text{B}(\text{C}_6\text{F}_5)_4]_2 \cdot 2\text{C}_6\text{H}_5\text{Cl} \cdot 2\text{H}_2\text{O}$, (II), the structure of which is reported here.



Compound (II) crystallizes as $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ dications (Fig. 1), which are associated with the hydrate

molecules and the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions by hydrogen bonds and one $\text{O} \cdots \text{H} \cdots \pi$ -ring interaction. Two chlorobenzene solvate molecules are also present in the crystal structure. The dication of (II) adopts a cage structure that is composed of 12 fused six-membered Ga_3O_3 rings and is positioned on a center of symmetry. Each Ga–Me unit is coordinated to two $\mu_3\text{-O}$ atoms and one $\mu\text{-OH}$ group. The cage structure of the $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ dication is very similar to that of the neutral gallium–oxo–hydroxide complex $[\text{Ga}_{12}\text{Bu}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$ (Barron *et al.*, 1995), which is a doubly deprotonated analog of (II). The Ga centers in (II) exhibit slightly distorted tetrahedral geometries. The $\text{O} \cdots \text{Ga} \cdots \text{O}$ bond angles [average $100(3)^\circ$] are smaller than the ideal tetrahedral value, which is compensated for by an opening of the $\text{O} \cdots \text{Ga} \cdots \text{C}$ bond angles [average $118(3)^\circ$]. The Ga–($\mu_3\text{-O}$) bond distances [average $1.87(2) \text{ \AA}$] are comparable to the Ga–O bond distances in gallium oxide ($1.87\text{--}1.89 \text{ \AA}$; Barron *et al.*, 1995) and to the Ga–($\mu_3\text{-O}$) distances in $[\text{Ga}_{12}\text{Bu}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$ ($1.878\text{--}1.915 \text{ \AA}$; Barron *et al.*, 1995) and $[\text{Ga}_6\text{Mes}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4] \cdot 6\text{THF}$ (Mes is mesityl; $1.855\text{--}1.896 \text{ \AA}$; Roesky *et al.*, 1994). The $\mu_3\text{-O}$ centers exhibit trigonal-planar geometry. The Ga–($\mu\text{-OH}$) bond distances [average $1.92(2) \text{ \AA}$] are similar to those in the dinuclear Ga cation $[\text{Pr}_2\text{ATI}]\text{GaMe}_2(\mu\text{-OH})^+$ [$1.941(3) \text{ \AA}$; Guzei *et al.*, 2000] and the neutral Ga dimer $[\text{CH}(\text{SiMe}_3)_2]_2\text{Ga}(\mu\text{-OH})_2$ [average $1.96(1) \text{ \AA}$; Uhl *et al.*, 1996]. The Ga–($\mu\text{-OH}$)–Ga bond angles [average $128.4(8)^\circ$] are nearly identical to those in $[\text{Ga}_{12}\text{Bu}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$ [average $129.1(1) \text{ \AA}$; Barron *et al.*, 1995]. The Ga–C bond distances [average $1.92(2) \text{ \AA}$] in (II) are significantly shorter than those in $[\text{Ga}_{12}\text{Bu}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$ [average $1.98(1) \text{ \AA}$] due to the difference in cluster charge (dication *versus* neutral) and alkyl group size (Me *versus* Bu). The Ga–C distances in (II) are also shorter than those in $[\text{Pr}_2\text{ATI}]\text{GaMe}_2(\mu\text{-OH})^+$

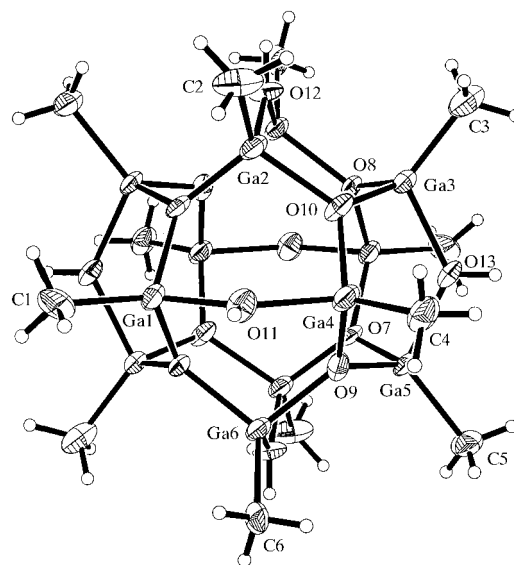


Figure 1

The $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ dication of (II). Displacement ellipsoids are shown at the 35% probability level.

[1.941 (3) Å; Guzei *et al.*, 2000] and (I) [average 1.950 (3) Å; Dagonne *et al.*, 2000]. The hydrate molecules and the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions of (II) are hydrogen bonded to the $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ dication through the Ga($\mu\text{-OH}$) groups. There are four unique hydrogen bonds (Table 2) and one O—H $\cdots\pi$ -ring interaction. The strongest interaction is between the O11—H11 group and the O90 water molecule, and can be considered as a moderately strong hydrogen bond (Jeffrey, 1997). Similar hydrogen bonds are present in $[\text{Ga}_6\text{Mes}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]\cdot 6\text{THF}$, in which the tetrahydrofuran molecules are hydrogen bonded to the $\mu_3\text{-OH}$ group, and in $[\text{Me}_2\text{Ga}(\mu\text{-OH})(\mu\text{-Me}_2\text{pz})\text{GaMe}_2]\cdot\text{HOCH}_2\text{Me}_2\text{pz}$ (pz is pyrazolyl), in which the OH group of the $\text{HOCH}_2\text{Me}_2\text{pz}$ molecule is hydrogen bonded to the $\mu\text{-OH}$ group (Roesky *et al.*, 1994; Trotter *et al.*, 1988). The second hydrogen bond in (II) is the O12—H12 \cdots F22 interaction which is longer than that in 2-fluoro-1,1,2-triphenylethanol $[\text{F}\cdots\text{O} 2.73 (4) \text{ \AA}$; Desmarteau *et al.*, 1992]. The other two hydrogen bonds are from the O90 water H atoms to F atoms of the anion. Hydrogen bonds from O—H donors to organic C—F groups are not common and may be ascribed, in the present case, to the electrostatic attraction between the $[\text{Ga}_{12}\text{Me}_{12}(\mu_3\text{-O})_8(\mu\text{-OH})_6]^{2+}$ dication and the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anions (Desiraju & Steiner, 1999). Additionally, an O—H $\cdots\pi$ -ring interaction is present between the O13 H atom and the (C11—C16)ⁱ phenyl ring: H13 $\cdots\pi$ -ring 3.11 Å and O13—H13 $\cdots\pi$ -ring centroid 159° [the coordinates for the ring centroid are 0.30717, 0.56226, 0.14106; symmetry code: (i) 1 + x, y, z].

The $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion in (II) adopts a slightly distorted tetrahedral structure. The C22—F22 bond distance is slightly longer than the other C—F bond distances and may be due to the O12—H12 \cdots F22 hydrogen bond.

Experimental

A mixture of $[\text{BuC}(\text{N}^i\text{Pr})_2]\text{GaMe}_2$ (200 mg, 0.706 mmol) and $(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]$ (326 mg, 0.353 mmol) in benzene (1 ml) was stirred for 1 h at 296 K. The benzene was removed under vacuum and the resulting yellow oil was analyzed by ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$), which established that (I) had formed quantitatively along with 0.5 equivalents of Ph_3CMe (Dagonne *et al.*, 2000). The solvent was removed under vacuum and the resulting oil was taken up in a 1:9 $\text{C}_6\text{H}_5\text{Cl}$ —pentane solvent mixture (1 ml). The solution was stored at 243 K for 2 d, after which time, pale-yellow crystals of (II) had formed.

Crystal data

$[\text{Ga}_{12}(\text{CH}_3)_{12}\text{O}_8(\text{OH})_6](\text{C}_{24}\text{F}_{20}\text{B})_2\cdot 2\text{C}_6\text{H}_5\text{Cl}\cdot 2\text{H}_2\text{O}$	$Z = 1$
$M_r = 2866.32$	$D_x = 1.938 \text{ Mg m}^{-3}$
Triclinic, $\overline{P}1$	Mo $K\alpha$ radiation
$a = 13.532 (3) \text{ \AA}$	Cell parameters from 40 reflections
$b = 15.223 (5) \text{ \AA}$	$\theta = 11.2\text{--}14.9^\circ$
$c = 12.755 (3) \text{ \AA}$	$\mu = 3.421 \text{ mm}^{-1}$
$\alpha = 101.98 (2)^\circ$	$T = 210 (2) \text{ K}$
$\beta = 106.91 (2)^\circ$	Prism, pale yellow
$\gamma = 83.71 (2)^\circ$	$0.34 \times 0.28 \times 0.18 \text{ mm}$
$V = 2455.7 (11) \text{ \AA}^3$	

Table 1
Selected geometric parameters (Å, °).

Ga1—O8 ⁱ	1.879 (6)	Ga4—O9	1.868 (6)
Ga1—O7 ⁱ	1.898 (5)	Ga4—O10	1.884 (5)
Ga1—O11	1.901 (6)	Ga4—O11	1.925 (5)
Ga1—C1	1.915 (9)	Ga4—C4	1.945 (8)
Ga2—O7 ⁱ	1.843 (6)	Ga5—O7	1.875 (5)
Ga2—O10	1.898 (5)	Ga5—O9	1.881 (5)
Ga2—C2	1.910 (9)	Ga5—C5	1.917 (8)
Ga2—O12	1.950 (5)	Ga5—O13	1.920 (6)
Ga3—O10	1.842 (5)	Ga6—O9	1.863 (5)
Ga3—O8	1.868 (6)	Ga6—O8 ⁱ	1.876 (5)
Ga3—C3	1.879 (10)	Ga6—O12 ⁱ	1.916 (6)
Ga3—O13	1.929 (5)	Ga6—C6	1.934 (8)
O8 ⁱ —Ga1—O7 ⁱ	102.2 (2)	O9—Ga5—C5	120.1 (3)
O8 ⁱ —Ga1—O11	98.5 (2)	O7—Ga5—O13	98.1 (2)
O7 ⁱ —Ga1—O11	97.5 (2)	O9—Ga5—O13	98.0 (2)
O8 ⁱ —Ga1—C1	122.3 (3)	C5—Ga5—O13	116.7 (3)
O7 ⁱ —Ga1—C1	118.9 (3)	O9—Ga6—O8 ⁱ	104.4 (2)
O11—Ga1—C1	113.1 (4)	O9—Ga6—O12 ⁱ	98.9 (3)
O7 ⁱ —Ga2—O10	104.3 (2)	O8 ⁱ —Ga6—O12 ⁱ	97.2 (2)
O7 ⁱ —Ga2—C2	119.2 (4)	O9—Ga6—C6	115.5 (3)
O10—Ga2—C2	121.4 (4)	O8 ⁱ —Ga6—C6	123.1 (3)
O7 ⁱ —Ga2—O12	97.8 (2)	O12 ⁱ —Ga6—C6	113.6 (3)
O10—Ga2—O12	96.9 (2)	Ga2 ⁱ —O7—Ga5	120.9 (3)
C2—Ga2—O12	112.7 (3)	Ga2 ⁱ —O7—Ga1 ⁱ	119.4 (3)
O10—Ga3—O8	104.1 (2)	Ga5—O7—Ga1 ⁱ	119.7 (3)
O10—Ga3—C3	119.8 (4)	Ga3—O8—Ga6 ⁱ	120.1 (3)
O8—Ga3—C3	117.9 (3)	Ga3—O8—Ga1 ⁱ	120.7 (2)
O10—Ga3—O13	96.1 (2)	Ga6 ⁱ —O8—Ga1 ⁱ	118.9 (3)
O8—Ga3—O13	97.8 (2)	Ga6—O9—Ga4	120.0 (3)
C3—Ga3—O13	117.0 (3)	Ga6—O9—Ga5	119.4 (3)
O9—Ga4—O10	101.8 (2)	Ga4—O9—Ga5	120.5 (3)
O9—Ga4—O11	97.7 (2)	Ga3—O10—Ga4	123.5 (3)
O10—Ga4—O11	99.6 (2)	Ga3—O10—Ga2	119.8 (3)
O9—Ga4—C4	119.8 (3)	Ga4—O10—Ga2	116.6 (3)
O10—Ga4—C4	121.7 (3)	Ga1—O11—Ga4	129.0 (3)
O11—Ga4—C4	112.0 (3)	Ga6 ⁱ —O12—Ga2	127.7 (3)
O7—Ga5—O9	103.2 (2)	Ga5—O13—Ga3	128.5 (3)
O7—Ga5—C5	117.0 (3)		

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.073$
θ – 2θ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scans (MolEN; Fair, 1990)	$h = -16 \rightarrow 16$
$T_{\text{min}} = 0.329, T_{\text{max}} = 0.540$	$k = -18 \rightarrow 18$
10 851 measured reflections	$l = -15 \rightarrow 6$
8067 independent reflections	4 standard reflections
4561 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 15.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.122$	$(\Delta\rho)_{\text{max}} = 0.009$
$S = 1.110$	$\Delta\rho_{\text{max}} = 0.55 \text{ e \AA}^{-3}$
8067 reflections	$\Delta\rho_{\text{min}} = -0.76 \text{ e \AA}^{-3}$
620 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0029 (3)

The chlorobenzene solvent molecule was disordered over two sites, with occupancies of 0.648 and 0.352 for the Cl atom. A rotation of approximately 120° about an axis through the center and perpendicular to the plane of the benzene ring produces the second Cl-atom site from the first. Due to apparent high thermal motion, each site was modeled with two rigid groups (C—C = 1.4 Å, C—Cl =

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O11–H11 \cdots O90	0.84	1.85	2.686 (10)	179
O12–H12 \cdots F22	0.84	2.13	2.924 (7)	157
O90–H90A \cdots F44 ⁱ	0.84	2.33	3.090 (10)	150
O90–H90B \cdots F26 ⁱⁱ	0.84	2.36	2.955 (10)	129

Symmetry codes: (i) $-1-x, 2-y, 1-z$; (ii) $1+x, y, 1+z$.

1.74 Å, C–H = 0.95 Å and all angles = 120°) of partial and equal occupancy. Two group isotropic displacement parameters were used for the C atoms, one for each site. Anisotropic displacement parameters were used for the Cl atoms, with those in close proximity (*i.e.* of the same site) constrained to be the same. The O–H bonds of the water molecule were restrained to be 0.84 Å and the H \cdots H intramolecular distance was restrained to be 1.33 Å. The hydroxyl and water H-atom locations were supported by difference-map peaks from *SHELXL* 'omit' maps.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1603). Services for accessing these data are described at the back of the journal.

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