inorganic compounds

$Ga_2(TeO_3)_3(H_2O)_3$

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The title compound, digallium(III) tris[tellurate(IV)] trihydrate, was obtained under hydrothermal conditions. It is isotypic with the analogous selenates(IV) of formula type $M^{III}_2(SeO_3)_3(H_2O)_3$ (M^{III} = Al, Cr, Fe, Sc, Ga) and comprises isolated GaO_6 and $GaO_3(H_2O)_3$ octahedra as well as TeO_3 trigonal pyramids as single building units. These polyhedra share corners and thereby establish a network structure. Additional hydrogen bonding between the water molecules and O atoms helps to stabilize this arrangement. Both crystallographically independent Ga atoms are located on threefold rotation axes. The crystal used was an inversion twin.

Related literature

For isotypic structures $M_2(SeO_3)_3(H_2O)_3$, see: M = Al (Harrison, Stucky, Morris & Cheetham, 1992), Cr (Harrison, Stucky & Cheetham, 1992), Fe (Giester & Pertlik, 1994), Sc (Johnston & Harrison, 2004), Ga (Rastsvetaeva et al., 1986). A review of the crystal chemistry of tellurates(IV) is given by Dolgikh (1991). For other tellurate compounds obtained under hydrothermal conditions, see: Weil (2005, 2007).

Experimental

Crystal data

$Ga_2(TeO_3)_3(H_2O)_3$
M_r = 720.29
Hexagonal, $R3c$
a = 9.5404 (13) Å
c = 20.3472 (19) Å
V = 1603.9 (3) Å^3

Z = 6
Mo $K\alpha$ radiation
μ = 13.12 mm^{-1}
T = 295 (2) K
$0.24 \times 0.23 \times 0.21$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: numerical (HABITUS; Herrendorf, 1997)
T_{min} = 0.106, T_{max} = 0.197
8621 measured reflections

1569 independent reflections
1563 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
3 standard reflections
every 180 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.040

S = 1.16
1569 reflections

61 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{max}$ = 1.47 e Å^{-3}
$\Delta\rho_{min}$ = −1.31 e Å^{-3}
Absolute structure: Flack (1983), 780 Friedel pairs
Flack parameter: 0.542 (16)

Table 1
Selected geometric parameters (Å, °).

Ga1—O1	1.966 (2)	Te—O2^{ii}	1.865 (2)
Ga1—O2	1.984 (2)	Te—O3	1.871 (2)
Ga2—O3^i	1.973 (2)	Te—O1	1.877 (2)
Ga2—O4	2.065 (3)		
O2^{ii}—Te—O3	94.37 (10)	O3—Te—O1	100.80 (11)
O2^{ii}—Te—O1	91.62 (10)		

Symmetry codes: (i) $-y + \frac{2}{3}, -x + \frac{4}{3}, z - \frac{1}{6}$; (ii) $-y + \frac{2}{3}, -x + \frac{1}{3}, z - \frac{1}{6}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H1$\cdots$O2	0.94 (3)	2.62 (4)	3.226 (4)	123 (3)
O4—H1$\cdots$O1^{iii}	0.94 (3)	2.14 (3)	3.060 (3)	170 (4)
O4—H2$\cdots$O1^{iv}	0.97 (3)	2.01 (4)	2.915 (4)	154 (4)

Symmetry codes: (iii) $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$; (iv) $-y, x - y, z$.

Data collection: CAD-4 Software (Enraf–Nonius, 1989); cell refinement: CAD-4 Software; data reduction: HELENA implemented in PLATON (Spek, 2003); method used to solve structure: coordinates taken from an isotypic structure (Giester & Pertlik, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 2006); software used to prepare material for publication: SHELXL97 (Sheldrick, 1997).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2042).

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supplementary materials

$Ga_2(TeO_3)_3(H_2O)_3$

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Comment

In continuation of our studies concerning synthesis and crystal chemistry of tellurate(IV) compounds formed under hydrothermal conditions (*e.g.* Weil, 2005; 2007)), we report here on crystallization and the structure of $Ga_2(TeO_3)_3(H_2O)_3$, (I). Compound (I) is the first tellurate(IV) crystallizing in the $M_2(SeO_3)_3(H_2O)_3$ structure type (M = Al (Harrison, Stucky, Morris & Cheetham, 1992), Cr (Harrison, Stucky & Cheetham, 1992), Fe (Giester & Pertlik, 1994), Sc (Johnston & Harrison, 2004), Ga (Rastsvetaeva *et al.*, 1986)).

(I) contains two Ga, one Te, four O and two H atoms in the asymmetric unit. The single building units are rather regular GaO_6 and $GaO_3(H_2O)_3$ octahedra and a trigonal–pyramidal TeO_3 group (Fig. 1). The average Ga—O bond length of 1.975 Å for the GaO_6 octahedron is slightly smaller than that of 2.019 Å for the $GaO_3(H_2O)_3$ octahedron which is caused by the longer Ga—OH_2 distance in comparison with the Ga—O distances (see Table). Whereas the Ga—O bond lengths in (I) are nearly the same as in the isotypic $Ga_2(SeO_3)_3(H_2O)_3$ structure, the average Te—O bond lengths are significantly longer than the corresponding average bond length in the selenate(IV), *viz*. 1.871 Å *versus* 1.708 Å. However, the Te—O bond lengths as well as the O—Te—O angles (average 95.5 °) are in the typical ranges as observed for the structures of other tellurate(IV) compounds (Dolgikh, 1991).

The two types of isolated octahedra are stacked along [001], forming an hexagonal array of rods. The TeO_3 units bridge the octahedra within one rod and cross-link adjacent rods which leads to the formation of a 3-D network (Fig. 2). Hydrogen bonding between water molecules and neighbouring O atoms stabilizes the structure both along the stacking direction [d(O···O) = 3.060 (3) Å] and between adjacent moieties (see Hydrogen bonding Table).

Experimental

All chemicals used were of analytical grade (Merck) and employed without further purification. 159.6 mg TeO_2 and 400 mg $Ga_2(SO_4)_3$.$x$$H_2O$ were placed in a Teflon inlay with 5 ml capacity. The inlay was charged with two-thirds of a 20%$_{wt}$ NH_4OH solution, sealed, placed in a steel autoclave and heated at 493 K for 6 d. The obtained material consisted of colourless crystals with unspecific habit. X-ray powder diffraction of the bulk revealed (I) as the main product, TeO_2 (paratellurite) as a minor product, and a few additional reflections which could not be assigned to any known phase.

Refinement

The coordinates of all non-H atoms of the isotypic compound $Fe_2(SeO_3)_3(H_2O)_3$ (Giester & Pertlik, 1994) were used as starting parameters. Both H positions were found in difference Fourier maps. Their positions were refined freely with a common U_{iso} parameter. The measured crystal was racemically twinned, with an approximate twin ratio of 1:1 (Flack parameter 0.542 (16)). The highest remaining peak in the final difference Fourier map is 0.03 away from Te and the deepest hole is 0.59 Å away from the same atom.
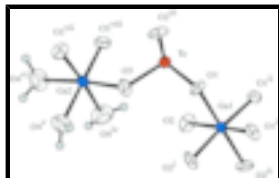
Figures

Fig. 1. The linkage between two GaO_6 and $GaO_3(H_2)_3$ octahedra *via* a TeO_3 unit. Displacement ellipsoids are displayed at the 90% probability level; H atoms are given as spheres of arbitrary radius. [Symmetry codes: (i) $-x + y$, $-x$, z; (ii) $-y$, x-y, z; (iii) $-x + y+2/3$, $y + 1/3$, $z - 1/6$; (iv) $x + 1/3$, x-$y + 2/3$, $z + 1/6$; (v) y-$x + 1/3$, $y - 1/3$, $z + 1/6$; (vi) $-y + 4/3$, $-x + 2/3$, $z + 1/6$; (vii) $1 - y$, x-y, z; (viii) $1 - x + y$, $1 - x$, z.]
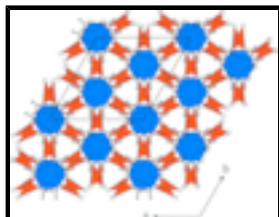

Fig. 2. The hexagonal rod packing of the GaO_6 octahedra in the crystal structure of (I). GaO_6 octahedra are blue and trigonal pyramidal TeO_3 units are red.

digallium(III) tris[tellurate(IV)] trihydrate

Crystal data

$Ga_2(TeO_3)_3(H_2O)_3$	$Z = 6$
$M_r = 720.29$	$F_{000} = 1920$
Hexagonal, $R3c$	$D_x = 4.474$ Mg m^{-3}
Hall symbol: R 3 -2"c	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.5404$ (13) Å	Cell parameters from 25 reflections
$b = 9.5404$ (13) Å	$\theta = 10.0$–$17.1°$
$c = 20.3472$ (19) Å	$\mu = 13.12$ mm^{-1}
$\alpha = 90°$	$T = 295$ (2) K
$\beta = 90°$	Fragment, colourless
$\gamma = 120°$	$0.24 \times 0.23 \times 0.21$ mm
$V = 1603.9$ (3) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.069$
Radiation source: fine-focus sealed tube	$\theta_{max} = 35.0°$
Monochromator: graphite	$\theta_{min} = 3.2°$
$T = 293(2)$ K	$h = -15 \rightarrow 15$
$\omega/2\theta$ scans	$k = -15 \rightarrow 15$
Absorption correction: numerical (HABITUS; Herrendorf, 1997)	$l = -32 \rightarrow 32$
$T_{min} = 0.106$, $T_{max} = 0.197$	3 standard reflections
8621 measured reflections	every 180 reflections
1569 independent reflections	intensity decay: none
1563 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0129P)^2 + 4.6051P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.020$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.040$	$\Delta\rho_{max} = 1.47$ e Å^{-3}
$S = 1.16$	$\Delta\rho_{min} = -1.31$ e Å^{-3}
1569 reflections	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
61 parameters	Extinction coefficient: 0.00111 (4)
4 restraints	Absolute structure: Flack (1983), 780 Friedel pairs
Primary atom site location: isomorphous structure methods	Flack parameter: 0.542 (16)
Hydrogen site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Ga1	0.0000	0.0000	0.09638 (2)	0.00750 (10)
Ga2	0.3333	0.6667	0.00547 (2)	0.00893 (10)
Te	0.38972 (2)	0.23787 (2)	0.053606 (9)	0.00860 (5)
O1	0.1896 (3)	0.0480 (3)	0.04221 (10)	0.0117 (4)
O2	0.1524 (3)	0.1845 (3)	0.15207 (11)	0.0146 (4)
O3	0.4808 (3)	0.1732 (3)	0.12004 (11)	0.0138 (4)
O4	0.1786 (4)	0.4827 (4)	0.06755 (13)	0.0238 (5)
H1	0.208 (5)	0.467 (5)	0.1097 (16)	0.017 (6)*
H2	0.118 (5)	0.378 (4)	0.0461 (19)	0.017 (6)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ga1	0.00780 (14)	0.00780 (14)	0.00689 (18)	0.00390 (7)	0.000	0.000
Ga2	0.00992 (15)	0.00992 (15)	0.00694 (17)	0.00496 (7)	0.000	0.000

Te	0.00799 (9)	0.00895 (9)	0.00906 (6)	0.00439 (7)	0.00024 (5)	0.00030 (5)
O1	0.0065 (8)	0.0117 (10)	0.0117 (8)	0.0005 (7)	0.0016 (7)	−0.0044 (7)
O2	0.0122 (10)	0.0144 (10)	0.0140 (8)	0.0042 (8)	−0.0016 (7)	−0.0091 (8)
O3	0.0148 (10)	0.0122 (10)	0.0135 (8)	0.0061 (9)	−0.0060 (8)	−0.0016 (7)
O4	0.0221 (13)	0.0249 (14)	0.0206 (11)	0.0088 (11)	0.0053 (10)	0.0078 (10)

Geometric parameters (Å, °)

Ga1—O1^{i}	1.966 (2)	Ga2—O4^{vi}	2.065 (3)
Ga1—O1	1.966 (2)	Ga2—O4	2.065 (3)
Ga1—O1^{ii}	1.966 (2)	Ga2—O4^{vii}	2.065 (3)
Ga1—O2	1.984 (2)	Te—O2^{viii}	1.865 (2)
Ga1—O2^{ii}	1.984 (2)	Te—O3	1.871 (2)
Ga1—O2^{i}	1.984 (2)	Te—O1	1.877 (2)
Ga2—O3^{iii}	1.973 (2)	O4—H1	0.94 (3)
Ga2—O3^{iv}	1.973 (2)	O4—H2	0.97 (3)
Ga2—O3^{v}	1.973 (2)		
O1^{i}—Ga1—O1	91.65 (9)	O3^{v}—Ga2—O4^{vi}	89.04 (12)
O1^{i}—Ga1—O1^{ii}	91.65 (9)	O3^{iii}—Ga2—O4	89.04 (12)
O1—Ga1—O1^{ii}	91.65 (9)	O3^{iv}—Ga2—O4	174.70 (11)
O1^{i}—Ga1—O2	176.01 (11)	O3^{v}—Ga2—O4	90.39 (12)
O1—Ga1—O2	86.13 (9)	O4^{vi}—Ga2—O4	86.49 (12)
O1^{ii}—Ga1—O2	91.73 (11)	O3^{iii}—Ga2—O4^{vii}	90.39 (12)
O1^{i}—Ga1—O2^{ii}	91.73 (11)	O3^{iv}—Ga2—O4^{vii}	89.04 (12)
O1—Ga1—O2^{ii}	176.01 (11)	O3^{v}—Ga2—O4^{vii}	174.70 (11)
O1^{ii}—Ga1—O2^{ii}	86.13 (9)	O4^{vi}—Ga2—O4^{vii}	86.49 (12)
O2—Ga1—O2^{ii}	90.61 (10)	O4—Ga2—O4^{vii}	86.49 (12)
O1^{i}—Ga1—O2^{i}	86.13 (9)	O2^{viii}—Te—O3	94.37 (10)
O1—Ga1—O2^{i}	91.73 (11)	O2^{viii}—Te—O1	91.62 (10)
O1^{ii}—Ga1—O2^{i}	176.01 (11)	O3—Te—O1	100.80 (11)
O2—Ga1—O2^{i}	90.61 (10)	Te—O1—Ga1	121.95 (11)
O2^{ii}—Ga1—O2^{i}	90.61 (10)	Te^{ix}—O2—Ga1	125.93 (14)
O3^{iii}—Ga2—O3^{iv}	93.85 (10)	Te—O3—Ga2^{x}	121.25 (13)
O3^{iii}—Ga2—O3^{v}	93.85 (10)	Ga2—O4—H1	124 (3)
O3^{iv}—Ga2—O3^{v}	93.85 (10)	Ga2—O4—H2	114 (3)
O3^{iii}—Ga2—O4^{vi}	174.70 (11)	H1—O4—H2	109 (3)
O3^{iv}—Ga2—O4^{vi}	90.39 (12)		

Symmetry codes: (i) −x+y, −x, z; (ii) −y, x−y, z; (iii) −x+y+2/3, y+1/3, z−1/6; (iv) −y+2/3, −x+4/3, z−1/6; (v) x−1/3, x−y+1/3, z−1/6; (vi) −x+y, −x+1, z; (vii) −y+1, x−y+1, z; (viii) −y+2/3, −x+1/3, z−1/6; (ix) −y+1/3, −x+2/3, z+1/6; (x) −y+4/3, −x+2/3, z+1/6.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O4—H1⋯O2	0.94 (3)	2.62 (4)	3.226 (4)	123 (3)

O4—H1···O1^{ix}	0.94 (3)	2.14 (3)	3.060 (3)	170 (4)
O4—H2···O1^{ii}	0.97 (3)	2.01 (4)	2.915 (4)	154 (4)

Symmetry codes: (ix) $-y+1/3$, $-x+2/3$, $z+1/6$; (ii) $-y$, $x-y$, z.

Fig. 1

Fig. 2