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Methylammonium Tris(galliophosphate)-hydroxide

Fredrik P. Glasser, R. Alan Howie and
Qiubin Kan

*Department of Chemistry, University of Aberdeen,
Meston Walk, Aberdeen AB9 2UE, Scotland*

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Abstract

The title compound, methylammonium trigallium triphosphate hydroxide, $[CH_3NH_3][Ga_3(PO_4)_3OH]$, exists as methylammonium cations in cavities within a zeolite-like hydroxygalliophosphate framework. The framework has the overall formula $[Ga_3P_3O_{13}H]^-$ and contains Ga in tetrahedral and fivefold coordination and PO_4 as tetrahedra.

Comment

The structural analysis of this compound was undertaken in order to confirm its chemical composition and to establish the connectivity of the galliophosphate component. Suitable crystals were obtained as products of the reaction at 453 K of a mixture of GaO(OH), H_3PO_4 (85%), methylamine and ethylene glycol in the molar ratio 1:1.8:1:22. Further preparative details are given by Wilson, Lok, Messina, Cannon & Flanigen (1982), Parise (1985), Huo & Xu (1990), and Estermann, McCusker, Baerlocher, Merrouche & Kessler (1991).

The hydroxygalliophosphate framework of this structure (Fig. 1) is composed of three each of Ga and P atoms and 13 O atoms in the asymmetric unit. All O atoms are bridging with *M*—O—*M′* angles in the range 129.6 (2)–142.0 (1)°. *M* and *M′* are both Ga only in the case of O10. All other O atoms bridge between Ga and P. The PO_4 tetrahedra display distances and angles in the ranges 1.516 (3)–1.551 (3) Å and 105.6 (2)–113.1 (1)°, respectively, and are, therefore, as expected. The main feature is the coordination of Ga (Table 2) where Ga1 is in a tetrahedral environment whereas both Ga2 and Ga3 are in trigonal bipyramidal sites with O10, O1, O3 and O9 in axial positions. It has not proved possible to locate the H atom required for charge balance and it is assumed to be associated with one or other of the framework O atoms. Indeed, it is possible that a second H atom is associated with the framework

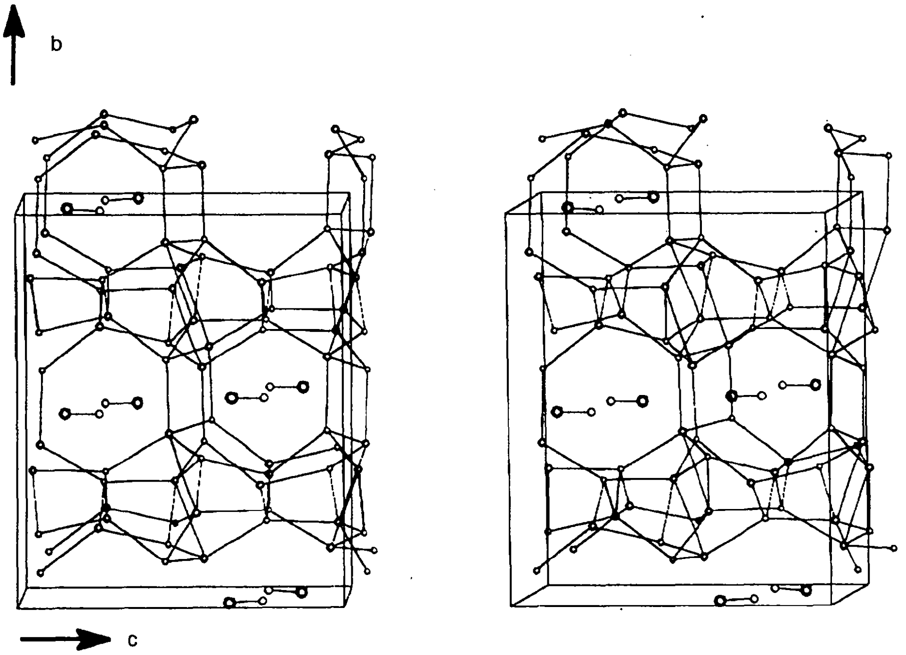

Fig. 1. Stereoscopic view of the cell of the title compound. The direction of view is more or less along **a** (down into the page) with **b** and **c** oriented as shown. The framework 'bonds' are vectors joining pairs of Ga—Ga and Ga—P which are, in fact, connected by bridging O atoms. Thus, O atoms, although not actually shown, can be considered to lie approximately at the midpoints of the 'bonds'. Ga and P are drawn as circles, Ga being the larger darker circles. C and N are also represented by circles, darker for N.

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rather than with the methylamine. The compound would then be regarded as an uncharged aquagalliophosphate framework of formula $Ga_3P_3O_{13}H_2$ with methylamine solvate molecules.

Fig. 1 was prepared using atomic coordinates generated with *STRUPLO*82 (Fischer, 1982).

Experimental

Crystal data

$[CH_3NH_3][Ga_3(PO_4)_3OH]$
M_r = 543.15
Orthorhombic
Pbca
a = 10.257 (3) Å
b = 16.941 (7) Å
c = 14.130 (7) Å
V = 2455 (2) $Å^3$
Z = 8
D_x = 2.938 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 14 reflections
θ = 11.8–14.2°
μ = 6.98 mm^{-1}
T = 293 K
Needle
0.9 × 0.2 × 0.1 mm
Colourless

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: empirical
T_{min} = 0.140, T_{max} = 0.222
4040 measured reflections
3495 independent reflections
3087 observed reflections [$F > 6\sigma(F)$]

R_{int} = 0.007
θ_{max} = 30°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 19$
2 standard reflections monitored every 50 reflections intensity variation: <2%

Refinement

Refinement on F
R = 0.031
wR = 0.057
S = 1.0561
3087 reflections
123 parameters
$w = 1/[\sigma^2(F) + 0.002181F^2]$
$(\Delta/\sigma)_{max}$ = 0.435
$\Delta\rho_{max}$ = 1.38 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.02 e $Å^{-3}$

Extinction correction: $[1-0.0001P(F_o^2/\sin\theta)]$ applied to F_o
Extinction coefficient: P = 0.00019 (5)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ga1	0.11691 (4)	0.19553 (2)	0.24287 (3)	0.0112 (1)
Ga2	0.88036 (3)	0.10519 (2)	0.93934 (2)	0.0098 (1)
Ga3	0.33912 (4)	0.30410 (2)	0.47472 (3)	0.0103 (1)
P1	0.36524 (9)	0.29995 (5)	0.25332 (6)	0.0104 (2)
P2	0.13090 (8)	0.08428 (5)	0.06691 (6)	0.0096 (2)
P3	0.13169 (8)	0.34507 (5)	−0.04649 (6)	0.0108 (2)
O1	0.1464 (2)	0.0015 (2)	0.1064 (2)	0.0136 (5)
O2	0.0956 (3)	0.1357 (2)	0.3494 (2)	0.0194 (5)
O3	0.1748 (3)	0.2591 (2)	−0.0378 (2)	0.0169 (5)
O4	0.2674 (3)	0.1168 (2)	0.0471 (2)	0.0151 (5)
O5	0.2617 (3)	−0.0963 (2)	−0.0187 (2)	0.0156 (5)
O6	0.3308 (3)	0.1655 (2)	−0.1508 (2)	0.0171 (5)
O7	0.3324 (3)	0.1364 (2)	−0.3182 (2)	0.0182 (5)
O8	0.0629 (2)	0.1367 (2)	0.1420 (2)	0.0155 (5)
O9	0.5117 (3)	0.1403 (2)	−0.0142 (2)	0.0169 (5)
O10	0.0826 (3)	−0.2149 (2)	0.0241 (2)	0.0153 (5)
O11	−0.0505 (3)	−0.0835 (2)	0.0234 (2)	0.0137 (5)
O12	0.2882 (3)	0.2759 (2)	−0.2659 (2)	0.0190 (5)
O13	0.5111 (3)	0.2188 (2)	−0.2513 (2)	0.0182 (5)
C	0.1063 (7)	0.4880 (4)	0.2475 (5)	0.052 (2)
N	0.0672 (5)	0.4908 (3)	0.1465 (3)	0.039 (1)

Table 2. *Selected coordination parameters* (Å, °)

Ga1—O2	1.826 (2)	Ga2—O1^{iii}	1.939 (3)
Ga1—O8	1.824 (3)	Ga2—O7^{iv}	1.858 (3)
Ga1—O13^{i}	1.818 (3)	Ga3—O3^{ii}	2.005 (3)
Ga1—O12^{ii}	1.827 (3)	Ga3—O6^{ii}	1.849 (3)
Ga2—O10^{iii}	1.966 (3)	Ga3—O9^{ii}	2.011 (3)
Ga2—O11^{iii}	1.859 (3)	Ga3—O4^{ii}	1.840 (3)
Ga2—O5^{iii}	1.845 (3)	Ga3—O10^{v}	1.848 (3)
O2—Ga1—O8	107.9 (1)	O8—Ga1—O13^{i}	107.7 (1)
O2—Ga1—O13^{i}	108.5 (1)	O8—Ga1—O12^{ii}	112.6 (1)
O2—Ga1—O12^{ii}	108.6 (1)	O13^{i}—Ga1—O12^{ii}	111.4 (1)
O10^{iii}—Ga2—O11^{iii}	86.0 (1)	O11^{iii}—Ga2—O1^{iii}	92.5 (1)
O10^{iii}—Ga2—O5^{iii}	94.0 (1)	O11^{iii}—Ga2—O7^{iv}	124.5 (1)
O10^{iii}—Ga2—O1^{iii}	174.9 (1)	O5^{iii}—Ga2—O1^{iii}	90.9 (1)
O10^{iii}—Ga2—O7^{iv}	91.4 (1)	O5^{iii}—Ga2—O7^{iv}	112.0 (1)
O11^{ii}—Ga2—O5^{iii}	123.6 (1)	O1^{iii}—Ga2—O7^{iv}	85.4 (1)
O3^{ii}—Ga3—O6^{ii}	91.5 (1)	O6^{ii}—Ga3—O4^{ii}	108.2 (1)
O3^{ii}—Ga3—O9^{ii}	175.6 (1)	O6^{ii}—Ga3—O10^{v}	127.6 (1)
O3^{ii}—Ga3—O4^{ii}	95.8 (1)	O9^{ii}—Ga3—O4^{ii}	88.1 (1)
O3^{ii}—Ga3—O10^{v}	87.8 (1)	O9^{ii}—Ga3—O10^{v}	88.4 (1)
O6^{ii}—Ga3—O9^{i}	89.1 (1)	O4^{ii}—Ga3—O10^{v}	124.0 (1)

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

The ω-scan width was 0.6° with scan rates in the range 1.0 to 29.3° min^{-1} dependent upon the pre-scan intensity of the reflection. Backgrounds were measured at 1.0° in ω on either side of the Bragg peak position. Cell refinement and data collection: Nicolet *P*3 software. Data reduction: *RDNIC* (Howie, 1980). Refinement was by full-matrix least squares. Methylammonium H atoms were placed in calculated positions (X—H = 0.95 Å) and methyl and NH_3 groups were refined as rigid bodies. High Δ/σ values are associated with the rotational parameters of these groups (up to 0.94 and 4.5 for methyl and NH_3, respectively). C and N atoms were identified as such solely from consideration of thermal vibration parameters. Structure solution and refinement software: *SHELXS*86 (Sheldrick, 1990) and *SHELX*76 (Sheldrick, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71740 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1069]

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Dipotassium Bis(oxalato)oxotitanate(IV) Dihydrate

A. Fester, W. Bensch and M. Trömel

Institut für Anorganische Chemie der Universität Frankfurt am Main, W 6000 Frankfurt/Main 50, Niederurseler Hang, Germany

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Abstract

The anions of the title compound, $K_2[TiO(C_2O_4)_2]$.$2H_2O$, form eight-membered rings of four Ti and four O atoms. Each Ti atom is in a distorted octahedral environment. Distances between Ti and O in the non-planar ring system, possessing an inversion centre, range from 1.789 (3) to 2.138 (3) Å. The K ions exhibit eight- or tenfold coordination with typical distances between 2.649 (17) and 3.158 (5) Å. Some of the K ions and the water molecules are disordered.

Comment

In contrast to well known ions like VO^{2+} and VO^{3+}, the corresponding titanium(IV) ions with a Ti=O double bond have not been found until now. The only well characterized compound with a rather short (1.619 Å) Ti—O bond is a titanyl porphyrine (Dwyer, Puppe, Buchler & Scheidt, 1975). In contrast to the chain structures found in *e.g.* $TiOSO_4$ (Lundgren, 1956) or $KTiOPO_4$ (Tordjman, Masse & Guitel, 1974), previous investigation of alkali or ammonium titanyl oxalates showed that these compounds exhibit ring systems (Van de Velde, Harkema & Gellings, 1974; Fester, 1990; Fester, Bensch & Trömel, 1991). Potassium bis(oxalato)oxotitanate(IV) hydrate was prepared in order to gain more information about the disorder phenomena found in the lithium and sodium compounds (Fester, Bensch & Trömel, 1991, 1992*a*).

Important bond angles and distances are summarized in Table 2. The atom numbering corresponds to that shown in Fig. 1. Like the other alkali oxoxalato titanates, $K_2[TiO(C_2O_4)_2]$.$2H_2O$ shows eight-membered ring systems with Ti—O bond lengths of ~ 1.80 Å. Fig. 1 shows this ring system and Fig. 2 presents a view of the unit cell (cations and water of crystallization omitted for clarity). Each Ti atom has a distorted octahedral environment; bond angles and distances in the octahedra are given in Table 2 as well as distances and angles for the four different oxalate groups. The bond lengths between the terminal O and C atoms are typical of C=O double bonds.

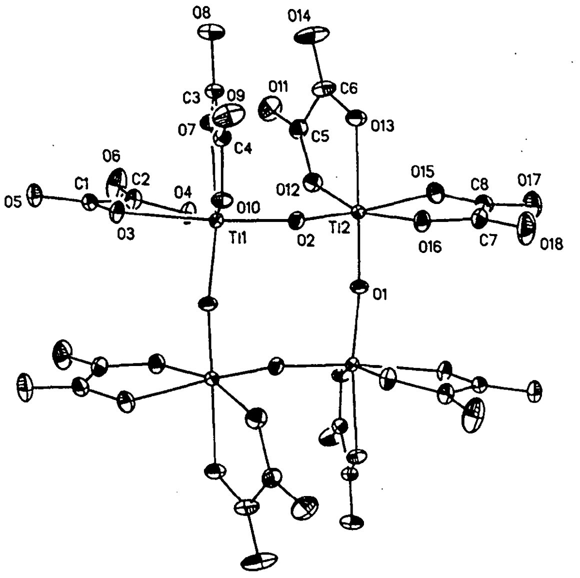

Fig. 1. View of the eight-membered ring system. Elliposids are drawn at the 25% probability level.

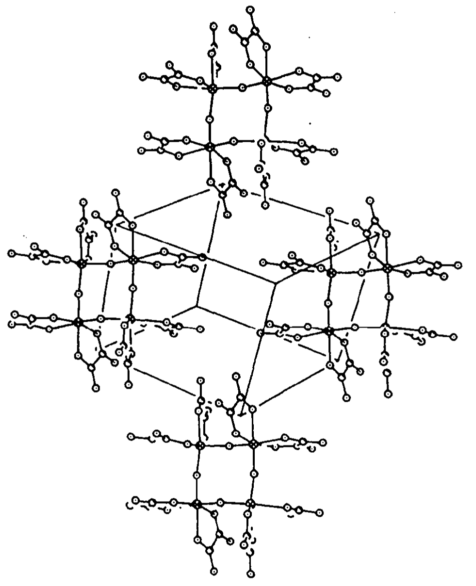

Fig. 2. View of the unit cell, drawn without cations and water of crystallization for clarity.

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