# Crystal structure of caesium diaquamanganese(II) gallium phosphate, $Cs[MnGa_2(PO_4)_3(H_2O)_2]$

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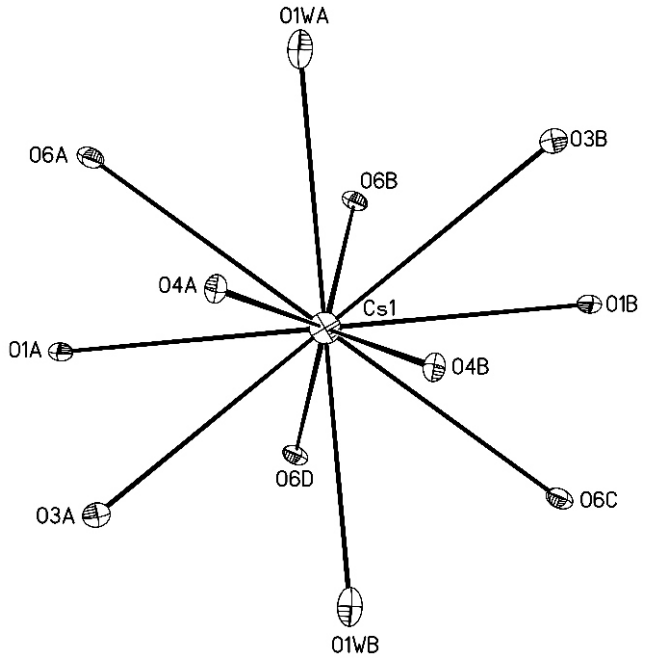


**Abstract**

$CsGa_2H_4MnO_{14}P_3$, monoclinic, *C*12/*c*1 (no. 15), $a = 13.482(5)$ Å, $b = 10.407(3)$ Å, $c = 8.913(3)$ Å, $\beta = 109.125(5)°$, $V = 1181.5$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.017$, $wR_{ref}(F^2) = 0.047$, $T = 296$ K.

**Source of material**

The title compound was synthesized from a mixture of 1.3001 g of $Cs_2CO_3$, 0.0937 g of $Ga_2O_3$, 0.4240 g of $Na_2CO_3$, 0.3065 g of $H_3BO_3$, 0.3451 g of $MnCO_3$, 3 mL of $H_3PO_4$, and 4 mL of $H_2O$ in the molar ratio of 8:1:10:6:8:100:44. This mixture was sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 180 °C for about 8 days under autogenous pressure, then cooled to room temperature. The resulting block-shaped colorless crystals were collected and dried in air at ambient temperature.
FT-IR data are available in the CIF file.

**Discussion**

Since the discovery of the microporous aluminum phosphates, the hydrothermal synthesis and structural characterization of new open-framework solids templated by organic molecules have attracted considerable attention. In the past several decades, many metal and nonmetal phosphates with open-framework structures have been synthesized owing to their rich structural chemistry and the potential applications in ion exchange, adsorption, separation and catalysis [1]. To date, a number of $MeGaPO_4$ (Me = V, Mn, Fe, Co and Zn) have been prepared, the majority of which contain $MO_4$ (M = Me or Ga) and $PO_4$ units. To our knowledge, however, only four examples of manganese (II)-substituted gallium phosphate compounds have been reported, such as $(C_3N_2H_5)_8$ $[Mn_8Ga_{16}P_{24}O_{96}]$ [2], $[C_6N_2H_{14}][MnGa(HPO_4)_2(PO_4)]$ [3], $NH_4[MnGa_2(PO_4)_3(H_2O)_2]$ [4], and $K[MnGa_2(PO_4)_3(H_2O)_2]$ [5].
The title crystal structure is similar to that of $NH_4[CoGa_2(PO_4)_3(H_2O)_2]$ [6], $K[NiGa_2(PO_4)_3(H_2O)_2]$ [7], and $NH_4[MeGa_2(PO_4)_3(H_2O)_2]$ (Me=Mn, Fe, Ni) [8] in the asymmetric unit. It consists of one $Cs^+$ cation and one $[MnGa_2(PO_4)_3(H_2O)_2]^-$ anion. In the anion, there are two crystallographically distinct phosphorus sites, both of which have approximately regular tetrahedral coordination. The Ga atoms occur in $GaO_5$ units with distorted trigonal bipyramidal shape and the Mn atoms are located in distorted octahedra $MnO_4(OH_2)_2$. The $GaO_5$, $MnO_6$ and $PO_4$ units are linked together through edge- and vertex-sharing to give a manganese-gallophosphate framework of composition $[MnGa_2(PO_4)_3(H_2O)_2]^-$. The Ga—O distances are from 1.854(2) Å to 2.009(2) Å (average 1.909 Å) and the O–Ga–O angles are between 87.9(1)° and 176.46(9)°. The Mn—O distances are from 2.072(2) Å to 2.263(2) Å (average 2.18 Å) and the O–Mn–O angles are between 64.0(1)° and 169.1(2)°. The $[MnGa_2(PO_4)_3(H_2O)_2]^-$ anions are also connected together through oxygen atoms shared by both gallium and phosphorus atoms to neighboring units forming a 3D open framework with 8-membered rings channels along *c* axis, in which the $Cs^+$ cations are located. The $Cs^+$ atom lies in a very distorted coordination with twelve near oxygen atoms and Cs1—O distances from 3.093(2) - 3.514(3) Å. $H_2O$ is also involved in hydrogen bonding to Ga–O–P bridging oxygen atoms with O···O distances of 2.925 Å and 3.120 Å.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colorless block, size 0.08 × 0.11 × 0.15 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 91.02 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II CCD, $\varphi/\omega$ |
| $2\theta_{max}$: | 50° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 2993, 104 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 994 |
| $N(param)_{refined}$: | 106 |
| Programs: | SHELXS-97, SHELXL-87, SHELXTL [9] |

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**Table 2.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(2) | 8*f* | 0.152(4) | –0.359(4) | 0.000(5) | 0.02(1) |
| H(1) | 8*f* | 0.159(4) | –0.251(5) | 0.034(6) | 0.04(2) |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cs(1) | 4*e* | 0 | 0.63967(3) | ¼ | 0.0244(2) | 0.0142(2) | 0.0252(2) | 0 | 0.0080(1) | 0 |
| Ga(1) | 8*f* | –0.17122(3) | –0.07529(3) | –0.07591(4) | 0.0103(2) | 0.0087(2) | 0.0083(2) | –0.0004(1) | 0.0032(1) | 0.0002(1) |
| Mn(1) | 4*e* | 0 | –0.28166(7) | –¼ | 0.0131(4) | 0.0108(4) | 0.0155(4) | 0 | 0.0073(3) | 0 |
| P(1) | 8*f* | –0.29044(6) | 0.12834(8) | –0.3295(1) | 0.0104(4) | 0.0093(4) | 0.0098(4) | 0.0012(3) | 0.0049(3) | 0.0008(3) |
| P(2) | 4*e* | 0 | 0.0039(1) | ¼ | 0.0097(5) | 0.0094(6) | 0.0076(5) | 0 | 0.0035(4) | 0 |
| O(1) | 8*f* | –0.2725(2) | –0.0501(2) | 0.0354(3) | 0.014(1) | 0.014(1) | 0.014(1) | 0.0000(9) | 0.008(1) | 0.0009(9) |
| O(2) | 8*f* | –0.2097(2) | 0.0856(2) | –0.1679(3) | 0.018(1) | 0.011(1) | 0.011(1) | 0.0023(9) | 0.005(1) | 0.0036(9) |
| O(3) | 8*f* | –0.2362(2) | –0.2285(2) | –0.1597(3) | 0.017(1) | 0.008(1) | 0.015(1) | –0.0020(9) | 0.0065(9) | –0.0030(9) |
| O(4) | 8*f* | –0.0576(2) | –0.0850(2) | 0.1126(3) | 0.013(1) | 0.013(1) | 0.011(1) | 0.0009(9) | 0.0009(9) | –0.0002(9) |
| O(5) | 8*f* | –0.0737(2) | –0.0972(2) | –0.2028(3) | 0.016(1) | 0.011(1) | 0.016(1) | –0.0004(9) | 0.011(1) | –0.0002(9) |
| O(6) | 8*f* | –0.0977(2) | –0.3927(2) | –0.1652(3) | 0.012(1) | 0.017(1) | 0.021(1) | 0.001(1) | 0.009(1) | 0.004(1) |
| O(1W) | 8*f* | 0.1199(2) | –0.3019(3) | –0.0120(3) | 0.021(2) | 0.022(2) | 0.021(1) | 0.001(1) | –0.002(1) | –0.002(1) |

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