Crystal structure of potassium manganese(II) gallium phosphate hydrate, $K[MnGa_2(PO_4)_3(H_2O)_2]$

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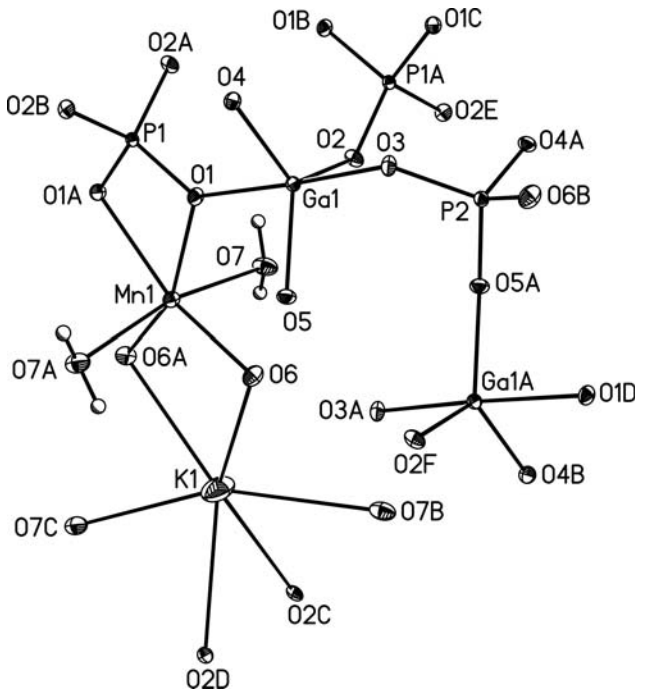

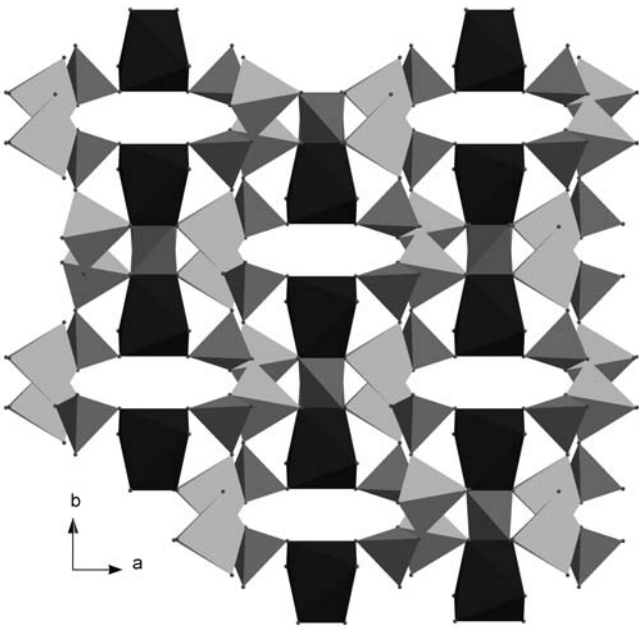

Abstract

$Ga_2H_4KMnO_{14}P_3$, monoclinic, *C*12/*c*1 (no. 15), a = 13.534(1) Å, b = 10.179(1) Å, c = 8.8703(7) Å, β = 107.948(1)°, V = 1162.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.021, $wR_{ref}(F^2)$ = 0.056, T = 298 K.

Source of material

The title compound was synthesized from a mixture of $K_2B_4O_7 \cdot 4H_2O$ (0.1528 g), Ga_2O_3 (0.0941 g), KOH (0.2954 g), $MnCO_3$ (0.2312 g), H_3PO_4 (0.5 mL) and H_2O (5 mL) in the molar ratio of 5 : 5 : 5 : 20 : 8 : 280. This mixture was sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 200 °C for about 10 days under autogenous pressure, then cooled to room temperature. The resulting colorless columnar crystals were collected and dried in air at ambient temperature. The TG analysis shows that the title compound has one step of mass loss between 81 °C and 600 °C. The total weight loss is 6.53 %, which corresponds to the loss of two water molecules, and can be compared with a calculated value of 6.24 %. FT-IR data are available in the CIF.

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 non-metal 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 compounds $MeGaPO_4$ (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 three examples of manganese(II)-substituted gallium phosphates have been reported: $(C_3N_2H_5)_8[Mn_8Ga_{16}P_{24}O_{96}]$ [2], $[C_6N_2H_{14}][MnGa(HPO_4)_2(PO_4)]$ [3], $NH_4[MnGa_2(PO_4)_3(H_2O)_2]$ [4].

The crystal structure of the title compound is similar to that of $NH_4[CoGa_2(PO_4)_3(H_2O)_2]$ [5], $K[NiGa_2(PO_4)_3(H_2O)_2]$ [6], and $NH_4[MeGa_2(PO_4)_3(H_2O)_2]$ (Me = Mn, Fe, Ni) [7]. It consists of K^+ cations and $[MnGa_2(PO_4)_3(H_2O)_2]^-$ anions in a 1 : 1 ratio. In the anion, there are two crystallographically distinct phosphorus sites, both of which have approximately regular tetrahedral environment. The Ga atoms occur in GaO_5 units with distorted trigonal bipyramidal shape and the Mn atoms in $MnO_4(OH_2)_2$ distorted octahedra. The GaO_5, MnO_6 and PO_4 units are linked together through common edges and vertexes to give a manganese-gallophosphate framework of the composition $[MnGa_2(PO_4)_3(H_2O)_2]^-$ (figure, top). The Ga—O bond lengthes are from 1.840(2) Å to 2.010(2) Å (average 1.905 Å) and the

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angles ∠O–Ga–O are between 87.75(9)° and 175.68(9)°. The Mn—O bond lengthes are from 2.067(2) Å to 2.259(2) Å (average 2.19 Å) and the ∠O–Mn–O are between 63.6(1)° and 167.3(1)°. 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 ring channels along [001] (figure, bottom), in which the templeted K^+ cations are located. The K^+ atom lie in a very distorted coordination environment with six near oxygen atoms with *d*(K1—O) = 2.918 (3) - 3.047 (3) Å). H_2O is also involved in hydrogen bonding to Ga–O–P bridging oxygen atoms with O···O distances of 2.776 and 2.918 Å.

Table 1. Data collection and handling.

Crystal:	colorless column, size 0.11 × 0.17 × 0.80 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	65.23 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2961, 102
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 953
$N(param)_{refined}$:	97
Programs:	SHELXS-97, SHELXL-97, SHELXTL [8]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7A)	8*f*	–0.1410	0.2645	–0.0255	0.030
H(7B)	8*f*	–0.1474	0.1325	0.0000	0.030

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}
Ga(1)	8*f*	0.17021(3)	0.42530(3)	0.06951(4)	0.0093(2)	0.0102(2)	0.0078(2)	0.0003(1)	0.0011(2)	–0.0002(1)
Mn(1)	4*e*	0	0.21915(7)	¼	0.0125(4)	0.0125(3)	0.0155(4)	0	0.0054(3)	0
K(1)	4*e*	0	–0.1373(1)	¼	0.068(1)	0.0229(7)	0.079(1)	0	0.040(1)	0
P(1)	4*e*	0	0.5037(1)	¼	0.0080(5)	0.0101(6)	0.0075(5)	0	0.0017(4)	0
P(2)	8*f*	0.28960(6)	0.37398(8)	–0.17819(9)	0.0098(4)	0.0114(4)	0.0089(4)	0.0016(3)	0.0029(3)	0.0007(3)
O(1)	8*f*	0.0695(2)	0.4078(2)	0.1942(3)	0.013(1)	0.014(1)	0.016(1)	–0.0006(9)	0.009(1)	–0.0011(9)
O(2)	8*f*	0.0603(2)	0.4046(2)	–0.1172(3)	0.012(1)	0.016(1)	0.009(1)	–0.0011(9)	–0.0029(9)	0.0020(9)
O(3)	8*f*	0.2726(2)	0.4535(2)	–0.0413(3)	0.016(1)	0.016(1)	0.012(1)	–0.0021(9)	0.0071(9)	–0.0030(9)
O(4)	8*f*	0.2070(2)	0.5884(2)	0.1634(3)	0.016(1)	0.012(1)	0.010(1)	–0.0013(9)	0.0019(9)	–0.0023(9)
O(5)	8*f*	0.2332(2)	0.2724(2)	0.1614(3)	0.015(1)	0.012(1)	0.014(1)	0.0030(9)	0.0027(9)	0.0028(9)
O(6)	8*f*	0.1020(2)	0.0983(2)	0.1832(3)	0.013(1)	0.020(1)	0.025(1)	0.001(1)	0.008(1)	–0.003(1)
O(7)	8*f*	–0.1054(2)	0.1947(2)	0.0009(3)	0.025(1)	0.018(1)	0.024(1)	–0.002(1)	–0.003(1)	0.003(1)

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