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The first mixed-valence $Mn^{II,III}$ gallium phosphate: synthesis and structural characterization of $(C_4H_{12}N_2)_2Mn_2Ga_5(H_2O)(PO_4)_8$†

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The synthesis and characterization of a novel mixed-valence MnGaPO phase is described; the 3D open-framework consists of discrete bioctahedra of $Ga_2O_{10}(H_2O)$ and GaO_5 trigonal bipyramids, connected *via* $Mn^{III}O_4$, $Mn^{II}O_4$ and PO_4 tetrahedra to generate intersecting tunnels within which piperazinium cations reside.

Substitution of first-row transition metal (TM) ions for Al^{3+} in the frameworks of aluminium phosphates is of particular interest for the enhancement of catalytic activity and the design of novel catalysts,[1,2] exemplified by MnAlPO-31 for the isomerization of but-1-ene,[3] and MnAlPO-5 which demonstrates reversible oxidation and reduction cycles.[4] The location and environment of the TM ion site is of considerable importance for understanding the catalytic and adsorptive properties of molecular sieves. As few single-crystal data are available for MAlPO-*n* samples,[5] evidence for incorporation of TM ions into the tetrahedral frameworks is difficult to establish.[1] Owing to the similarity in framework topology and the presence of even wider pores, in *e.g.* cloverite,[6] the search for gallium phosphates adopting microporous structures has attracted much attention. In contrast to MAlPOs, only a limited number of MGaPO compounds (M = V^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+})[7–12] have been synthesized. Up to now, only three Mn-substituted gallium phosphates have been reported.[10–12] None of these MAlPOs and MGaPOs contain the same TM ions in mixed oxidation states, which would offer more possibility in understanding and designing redox-catalytic or magnetic molecular sieves.[13] By employing hydrothermal crystallization, we have synthesized the first mixed-valence manganese gallium phosphate phase, $(pipz)_2Mn_2Ga_5(H_2O)(PO_4)_8$ (pipz = $C_4H_{12}N_2^{2+}$), denoted MnGaPO-4. A reaction mixture of piperazine (0.258 g, 3 mmol), $Ga(NO_3)_3\cdot xH_2O$ (0.307 g, 1.2 mmol), $MnCl_2\cdot 2H_2O$ (0.065 g, 0.4 mmol), H_3PO_4(aq) (85%, 6 mmol), ethylene glycol (5.8 mL) and H_2O (5.8 mL), was placed in a Teflon-lined digestion bomb (internal volume = 23 mL) and heated at 180 °C under autogenous pressure for 72 h. The final product contained a lot of light-brown tabular crystals mixed with a small amount of uncharacterized powder. A single-crystal structure analysis‡ indicated the tabular crystals to be $(pipz)_2Mn_2Ga_5(H_2O)(PO_4)_8$. The Mn:Ga:P ratios determined from single-crystal data (2 : 5 : 8) were corroborated by EMPA data (2.09 : 5.18 : 8.00). Elemental analysis also confirmed the organic content (Observed: C, 6.71; N, 4.19; H, 2.42%. Calc: C, 6.80; N, 3.97; H, 1.84%). Thermogravimetric analysis (N_2 atmosphere, heating rate 10 °C min^{-1}) on selected crystats showed a two-stage weight loss from *ca.* 200 to 1100 °C, with a total loss of 19.7%, corresponding to the removal of three water, two piperazine molecules and 1/5 P_4O_{10}.[9] It is also noted that another new Mn^{II}GaPO phase[14] results when piperazine is replaced by the bulkier 4,4′-trimethylenedipiperidine in the reaction mixture.

The three-dimensional anionic framework of MnGaPO-4 consists of GaO_6 octahedra and GaO_5 trigonal bipyramids, connected *via* MnO_4 and PO_4 tetrahedra (Fig. 1) to form intersecting tunnels along all three axial directions (Fig. 2). The pipz cations are located at the tunnel intersections, and four unique types of cages with different Mn content are found (Fig. 3). The open-framework nature of the structure is emphasized by a PLATON analysis[15] of the accessible solvent volume not occupied by the framework Ga, Mn, P and O atoms. The result showed that 457.5 Å^3 (*ca.* 28% of a unit cell volume) is 'solvent accessible'.

One remarkable feature of the structure is that the two distinct sites of the Mn ions adopt different charges, *i.e.* 2+ for Mn(1) and 3+ for Mn(2) based on bond-valence sum calculations.[16] The mixed-valence character is also evidenced by the color of the crystals of MnGaPO-4. According to a literature search, only three mixed-valence manganese phosphates have been previously structurally characterized *i.e.* $Cs_3Mn_4(P_6O_{18})_2$,

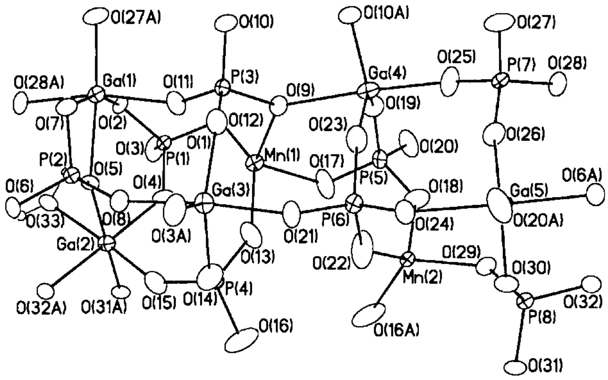

Fig. 1 ORTEP drawing of the building unit in MnGaPO-4. Average bond lengths (Å): Mn(1)–O 2.044(6), Mn(2)–O 1.888(6), Ga(1)–O 1.988(5), Ga(2)–O 1.974(5), Ga(3)–O 1.911(5), Ga(4)–O 1.909(5), Ga(5)–O 1.895(5), P–O 1.526(5) Å.

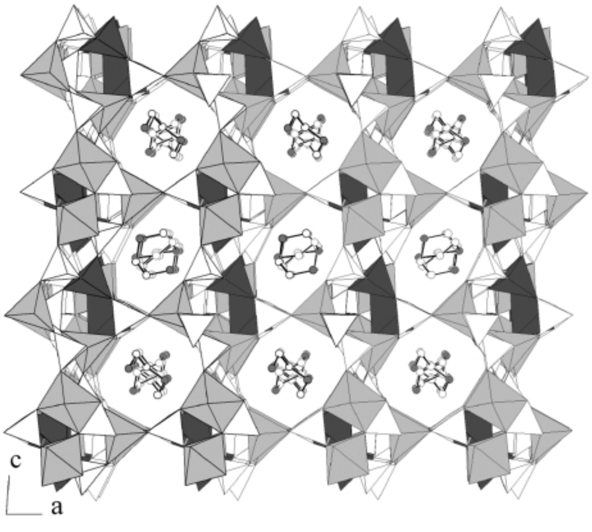

Fig. 2 View of the frameowork along [010], showing tunnels enclosed by eight-membered rings of diameter *ca.* 8 Å. The darker polyhedra are MnO_4, the lighter ones are GaO_5 and GaO_6, and the open tetrahedra are PO_4.

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† Electronic supplementary information (ESI) available: thermal analysis and magnetic susceptibility data for $(C_4H_{12}N_2)Mn_2Ga_5(H_2O)(PO_4)_8$. See http://www.rsc.org/suppdata/cc/a9/a908334k/

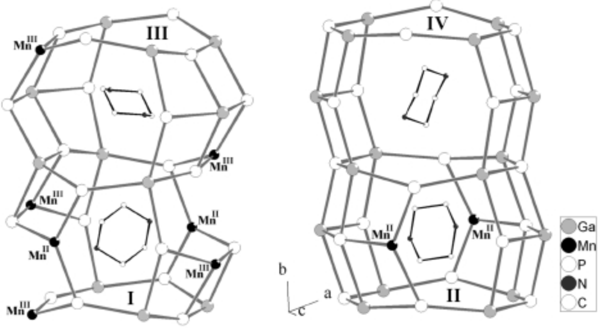

Fig. 3 Cages located at the interactions of three-dimensional tunnels. The pipz cations are located on inversion centers. Cages I show 8-ring windows and II, III and IV 4-ring windows when viewed along the *a*-axis direction.

$CsMn_2(P_6O_{18})$[17] and $Mn(H_2O)_4[Mn_2(OH)_2(PO_4)_2]$.[18] Unlike these, both Mn^{2+} and Mn^{3+} ions are tetrahedrally coordinated in our compound, having a distance to the fifth contact O atom at 2.61 and 3.06 Å, respectively. The four-coordinate Mn^{3+} ion in MnGaPO-4 is unprecedented for manganese phosphates where all of the Mn^{3+} ions are six-coordinate, typical of d^4 high-spin transition-metal ions. Furthermore, the charge distribution of the Mn centers varies in the enclosing structure of the cages; cage I has both Mn^{2+} and Mn^{3+} centers whilst cage II has Mn^{2+}, and cage III Mn^{3+} centers only (Fig. 3). This feature offers considerable possibilities in selective redox-catalytic applications. From the structural point of view, it may be anticipated that the Mn atoms have substituted for Ga rather than P atoms since the parent structure is an orthophosphate instead of a polyphosphate framework. The magnetic susceptibility data in the temperature range 50–300 K can be fitted to a Curie–Weiss law with $\theta = -17.2$ K and $C = 4.8$ emu, which corresponds to an effective magnetic moment per manganese ion of 6.2 μ_B, as expected, lower than that observed for pure Mn^{2+} ions in MnGaPO-2.[11]

Another interesting feature of the compound is in that an isolated $Ga_2O_{10}(H_2O)$ unit, built of corner-shared $Ga(1)O_6$ and $Ga(2)O_5(H_2O)$ octahedra, exists in the framework. Relative to gallium oxides, discrete gallium–oxygen cluster-containing phosphates are rare. The only example, $GaPO_4$-21,[19] was found to contain a dimer of corner-shared GaO_5 trigonal bipyramids. In the dimeric $Ga_2O_{10}(H_2O)$ cluster, a significant repulsion between the two Ga centers may arise since the distance between atoms Ga(1) and Ga(2) at 3.699 Å, is longer than that for two corresponding octahedral centers, 3.473 Å. As compared with $Ga(2)O_5(H_2O)$, the octahedron $Ga(1)O_6$ is much more distorted since it also shares a common edge with the $P(2)O_4$ tetrahedron. Atom O(5) bridges the Ga(1), Ga(2) and P(2) centers with the Ga(1)–O(5)–P(2) angle of 92.8°, deviating significantly from 120°, characteristic of trigonal planar geometry typical of a μ_3-O atom. In addition, the bridging Mn–O–P angles between corner-shared MnO_4 and PO_4 tetrahedra, ranging from 123.1 to 147.6°, span a rather wider range than those found in MnGaPOs and MnAlPOs.

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Notes and references

‡ *Crystal data* for $(C_4H_{12}N_2)_2Mn_2Ga_5(H_2O)(PO_4)_8$: triclinic, space group $P\bar{1}$; $a = 9.1314(2)$, $b = 12.7496(1)$, $c = 14.7479(3)$ Å, $\alpha = 89.480(1)$, $\beta = 86.249(1)$, $\gamma = 72.419(1)°$, $U = 1633.17(5)$ Å^3, $Z = 2$, $M_r = 1412.57$, $D_c = 2.872$ g cm^{-3}, μ(Mo-Kα) = 53.37 cm^{-1}, $\lambda = 0.71073$ Å. A crystal of dimensions 0.30 × 0.13 × 0.03 mm was selected for indexing and intensity data collection at 296 K. Total number of measured and observed independent reflections ($I_{obs} > 2\sigma_I$) are 7814 and 5536 and $R_{int} = 0.0516$. Least-squares refinements were based on F^2 and converged at $R1 = 0.0567$ and $wR2 = 0.1386$. CCDC 182/1502. See http://www.rsc.org/suppdata/cc/a9/a908334k/ for crystallographic files in .cif format.

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