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Novel Transition Metal Oxalatophosphates with a Two-Dimensional Honeycomb Structure: $(H_3TREN)[M_2(HPO_4)(C_2O_4)_{2.5}]\cdot 3H_2O$ ($M = Mn^{II}$ and Fe^{II}, TREN = Tris(2-aminoethyl)amine)[†]

Yau-Chen Jiang,[‡] Sue-Lein Wang,[*,‡] Shang-Fan Lee,[§] and Kwang-Hwa Lii[*,||,⊥]

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, R.O.C., Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C., Department of Chemistry, National Central University, Chungli, Taiwan, R.O.C., and Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C.

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Two new layered transition metal oxalatophosphates, $(H_3TREN)[M_2(HPO_4)(C_2O_4)_{2.5}]\cdot 3H_2O$ ($M = Mn^{II}$ and Fe^{II}), have been synthesized by hydrothermal methods in the presence of a structure-directing organic amine, tris(2-aminoethyl)amine, and characterized by single-crystal X-ray diffraction and magnetic susceptibility. They are the first metal oxalatophosphates which adopt a two-dimensional honeycomb structure with the organic cations and water molecules intercalated in between. Within a layer, there are 12-membered pores made from 6 Mn, 1 phosphate, and 5 oxalate units. Measurements of field dependence of magnetization and variable-temperature susceptibilities under different fields were performed on a polycrystalline sample of the manganese compound. The results indicate a phase transition from a paramagnetic to an antiferromagnetic coupled state at about 12 K. Crystal data for the manganese compound follow: triclinic, space group $P\bar{1}$ (No. 2), $a = 8.8385(6)$ Å, $b = 9.0586(6)$ Å, $c = 16.020(1)$ Å, $\alpha = 77.616(1)°$, $\beta = 83.359(1)°$, $\gamma = 68.251(1)°$, and $Z = 2$. Crystal data for the iron compound are the same as those for the manganese compound except $a = 8.7776(9)$ Å, $b = 8.9257(9)$ Å, $c = 15.884(2)$ Å, $\alpha = 78.630(2)°$, $\beta = 84.018(2)°$, and $\gamma = 67.372(2)°$.

Phosphate-based networks exhibiting open architectures have been prepared and studied with great intensity during the past two decades.[1] Open-framework structures can also be prepared by exploiting appropriate metal centers linked through suitable multidentate organic ligands.[2] This approach makes possible the rational design and synthesis of coordination polymers with potentially interesting properties. In recent years, a large number of hybrid compounds have been synthesized by incorporating multidentate organic ligands such as bipyridines and oxalate in the structures of metal phosphates. The underlying idea is to combine the robustness of inorganic phosphate frameworks with the versatility and chemical flexibility of organic ligands. In the former category, the use of 4,4′-bipyridine and 2,2′-bipyridine has led to a number of hybrid compounds.[3] In the latter category, a large number of oxalate−phosphates of V, Mn, Fe, Co, Zn, Mo, Al, Ga, In, and Sn have been synthesized.[4] Measurements of variable-temperature magnetic susceptibilities on the V, Mn, Fe, and Co compounds showed antiferromagnetic interactions at low temperatures. Three different

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[*] Authors to whom correspondence should be addressed. E-mail: liikh@cc.ncu.edu.tw (K.-H.L.); slwang@mx.nthu.edu.tw (S.-L.W.).

[†] Dedicated to Professor Kwang-Ting Liu on the occasion of his 65th birthday.

[‡] National Tsing Hua University.

[§] Institute of Physics, Academia Sinica.

[||] National Central University.

[⊥] Institute of Chemistry, Academia Sinica.

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types of oxalate coordination are observed in their structures, namely, bisbidentate, monobidentate, and bismono- and bisbidentate. In most cases, the 3D framework structures are formed of metal phosphate layers connected by bisbidentate oxalate bridges. The oxalate units are out-of-plane with respect to the inorganic layer. In contrast, the incorporation of oxalate ligands within the layers (in-plane) has been observed in a few cases only. We report herein a new Mn^{II} oxalatophosphate, $(H_3TREN)[Mn_2(HPO_4)(C_2O_4)_{2.5}]\cdot 3H_2O$ (H_3-TREN = $[NH_3(CH_2)_2]_3N$, TREN = tris(2-aminoethyl)amine) (denoted as **1**), and the iron analogue, $(H_3TREN)[Fe_2(HPO_4)(C_2O_4)_{2.5}]\cdot 3H_2O$ (denoted as **2**), that have a 2D layer structure built of in-plane oxalate units, in addition to $M^{II}O_6$ and HPO_4. They are the first examples where new metal oxalatophosphates are formed by partial replacement of oxalate units in the 2D honeycomb structure of tris(oxalato)metalate by phosphate groups.

Colorless columnar crystals of **1** were obtained in a yield of 74% by heating a mixture of $MnCl_2\cdot 4H_2O$ (1.50 mmol), H_3PO_4 (11.5 mmol), TREN (6.0 mmol), oxalic acid (3.0 mmol), and H_2O (11.0 mL) in a Teflon-lined acid digestion bomb at 120 °C for 3 days followed by slow cooling at 5 °C h^{-1} to room temperature. The powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern on the basis of the results from single-crystal X-ray diffraction. Elemental analysis of the bulk product confirmed the stoichiometry of **1** (Found: C, 21.01; H, 4.78; N, 8.83. Calcd for $C_{11}H_{28}Mn_2N_4O_{17}P$: C, 20.99; H, 4.49; N, 8.90). Red crystals of **2** were obtained along with a small amount of unidentified dark solid under similar reaction conditions. Elemental analysis of a sample of manually selected red crystals was also performed (Found: C, 21.10; H, 4.44; N, 8.85. Calcd for $C_{11}Fe_2H_{28}N_4O_{17}P$: C, 20.94; H, 4.47; N, 8.88). A room-temperature ^{57}Fe Mössbauer spectrum, which was recorded on a powdered sample of the red crystals, showed the presence of two Fe^{II} sites with equal intensity and a third site which is Fe^{III} in an estimated amount of 18%. It is yet unclear whether the small amount of Fe^{III} should be attributed to impurity or mixed valence.

As revealed by single-crystal X-ray crystallography,[5] the structure of **1** consists of macroanionic planar sheets of formula $[Mn_2(HPO_4)(C_2O_4)_{2.5}]^{3-}$ in the (110) plane which are interleaved by the templating triprotonated tris(2-aminoethyl)amine cations (Figure 1). The interlayer separation is 7.26 Å. Within a sheet there are 12-membered pores made from 6 Mn, 1 phosphate, and 5 oxalate units. The organic cations and water molecules sit in the middle of the pore (Figure 2). The organic cation penetrates into the sheet. The sheets are stacked in the sequence ···ABAB···. The structure motif is reminiscent of the honeycomb networks of bimetallic transition metal oxalates of the general formula $[A^+][MM'(ox)_3]$, where A^+ is a templating inorganic or organic countercation, and M and M′ are divalent and trivalent 3d metal ions, respectively.[6] These compounds have been extensively researched because of their interesting structural chemistry and magnetic properties. A pure zinc oxalate templated with 1,3-diaminopropane, $[H_3N(CH_2)_3NH_3][Zn_2(ox)_3]\cdot 3H_2O$, also adopts the honeycomb oxalato-bridged network structure.[7] Each metal atom is cross-linked to three oxalate units. One of the three oxalates is replaced by two HPO_4^{2-} units for every other metal atom, forming a honeycomb network of **1** as shown in Figure 2. To balance charge one can substitute $(H_3TREN)^{3+}$ for A^+ or $[H_3N(CH_2)_3NH_3]^{2+}$. Bond-valence calculation indicates that the manganese atoms in **1** are divalent. Both Mn(1) and Mn(2) are

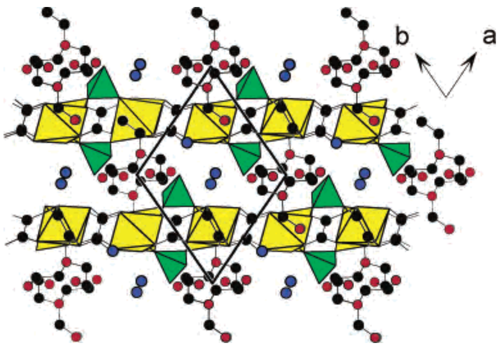

Figure 1. Structure of **1** viewed along the [001] direction. The MnO_6 octahedra are shown in yellow and PO_4 tetrahedra in green. Black circles, C atoms; red circles, N atoms; blue circles, water oxygen atoms. H atoms are not shown.

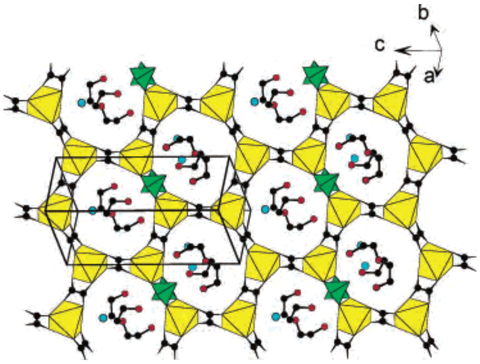

Figure 2. Section of a sheet in **1** viewed perpendicular to the (110) plane.

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(5) Crystal data for **1**: $C_{11}H_{28}Mn_2N_4O_{17}P$, colorless crystal of dimensions $0.14 \times 0.08 \times 0.06$ mm^3, $T = 295$ K, triclinic, space group $P\bar{1}$ (No. 2); $a = 8.8385(6)$ Å, $b = 9.0586(6)$ Å, $c = 16.020(1)$ Å, $\alpha = 77.616(1)°$, $\beta = 83.359(1)°$, $\gamma = 68.251(1)°$, $V = 1162.7(1)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.797$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 12.4$ cm^{-1}, 4265 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.6°$, R(int) = 0.0352), GOF = 1.048, R1 = 0.0390, wR2 = 0.1164. The H atoms in HPO_4 and the ammonium groups were located from difference Fourier maps and refined with fixed atomic coordinates and isotropic thermal parameters. The H atoms on the methylene groups were positioned geometrically and refined using a riding model. The H atoms associated with the water molecules were not located. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Crystal data for **2**: the same as those for **1** except $C_{11}H_{28}Fe_2N_4O_{17}P$, red crystal of dimensions $0.16 \times 0.14 \times 0.10$ mm^3; $a = 8.7776(9)$ Å, $b = 8.9257(9)$ Å, $c = 15.884(2)$ Å, $\alpha = 78.630(2)°$, $\beta = 84.018(2)°$, $\gamma = 67.372(2)°$, $V = 1125.6(2)$ Å^3; $\rho_{calcd} = 1.864$ g cm^{-3}, $\mu = 14.5$ cm^{-1}, 3945 unique reflections ($2\theta_{max} = 56.3°$, R(int) = 0.0277), GOF = 1.096, R1 = 0.0409, wR2 = 0.1257.

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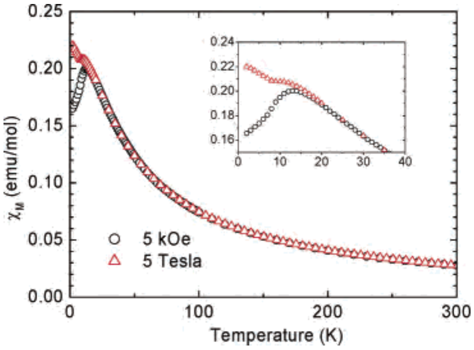

Figure 3. χ_M versus T under 5 kOe (○) and 5 T (△) for **1**.

six-coordinate, but they do not display the same coordination environment. Mn(1) is coordinated by two bidentate oxalate and two phosphate units, while Mn(2) is coordinated by three bidentate oxalate units. All oxalate units are bis-bidentate ligands to two Mn atoms. There are four independent oxalate ligands in the structure: $C(1)C(2)O_4^{2-}$ is at general position, whereas the other three oxalates have C_i symmetry. The HPO_4^{2-} units are linked through two oxygen atoms to two Mn(1) atoms, with one terminal P═O and one P─OH group. The two phosphate units that coordinate to Mn(1) are related by an inversion center. The organic cations and water molecules in **1** are well ordered, which can be attributed to the formation of extensive hydrogen bonds with the oxalate and phosphate oxygen atoms. Compound **2** is isostructural with **1** except that one of the aminoethyl groups in **2** is disordered.

Most of the magnetic properties of tris(oxalato)metalate based networks have been established on 2D bimetallic compounds prepared from the combination of $[M^{III}(ox)_3]^{3-}$ (M^{III} = Cr, Fe, Ru) with divalent transition metal ions (Mn^{2+}, Ni^{2+}, Fe^{2+}, etc.).[6] Some of these compounds show long-range magnetic order at low temperatures leading to ferromagnets, ferrimagnets, and canted antiferromagnets. Their magnetic properties are sensitive to small changes in the countercations situated quite far away in the lattice from magnetic centers. The synthesis of these bimetallic complexes is a strategy for inducing finite zero-field magnetization. To the best of our knowledge, a pure Mn oxalate with the 2D honeycomb structure is unknown yet. $[Fe^{II}(bpy)_3][Mn^{II}_2(ox)_3]$ adopts a chiral, 3D network structure.[8] It is therefore of interest to study the magnetic properties of the Mn oxalatophosphate, **1**. Measurements of field dependence of magnetization and variable-temperature susceptibilities under different fields were performed on a polycrystalline sample of **1**. The susceptibility showed paramagnetic $1/T$ dependence behavior at high temperature. At low temperature, deviation to lower value and external field dependence were clearly seen, as shown in Figure 3. Low field measurement showed a sharp peak around 12 K. These results suggested a phase transition from a paramagnetic to an antiferromagnetic coupled state. The inverse magnetic susceptibility, shown in Figure 4, follows the Curie−Weiss law, and a linear fit for $T > 50$ K data gave a Weiss temperature $\theta = -21.2$ K. The negative value is consistent with antiferromagnetic interactions. The Curie constant (4.45) obtained from the linear fit is in good agreement with the value (4.36) based on spin-only Mn^{2+} ions, which thus confirmed the oxidation state of Mn. The $\chi_M T$ value decreases with decreasing temperature, indicating again that the main magnetic interactions between Mn atoms are antiferromagnetic. At 300 K, $\chi_M = 0.0278$ emu/mol and $\chi_M T = 8.34$ emu·K/mol. Thus, the effective magnetic moment per Mn in sample **1** is calculated to be 5.80 μ_B/Mn, which differs by only 2% from the spin-only value of 5.92 μ_B for Mn^{2+}. The field dependence of magnetization below 12 K deviates from paramagnetic behavior only slightly up to the maximum field (5 T) available to us. There is a small hysteresis above 3.5 T, but there is no hysteresis at smaller field, nor at any field above 12 K. These results give a hint of a metamagnetic behavior. Unfortunately, we could only observe small minor loops close to 5 T. An M versus H curve at 10 K is included in the Supporting Information. A pure Mn oxalate with the 2D honeycomb structure has to be synthesized in order to know the effect of phosphate bridging ligand on the magnetic properties.

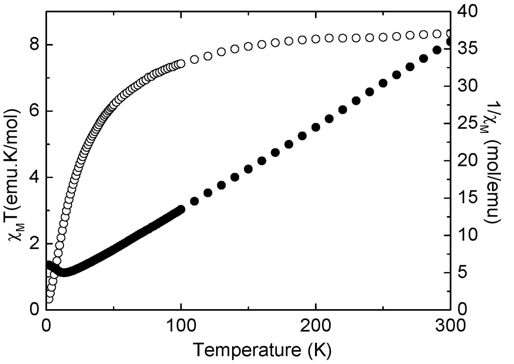

Figure 4. $\chi_M T$ versus T (○) and $1/\chi_M$ versus T (●) for **1**.

To our knowledge, the title compounds are the first examples of a honeycomb structure for oxalatophosphate materials. The structure is formed by partial replacement of oxalate units in 2D honeycomb networks of a metal oxalato complex by phosphate groups. The structure may be largely due to the use of the organic trication, $(H_3TREN)^{3+}$, in the synthesis; as such, a trication is needed for neutralizing the charge on the trianionic oxalatophosphate sheets. Compounds with other possible compositions of anionic sublattice and different organic countercations can be envisaged. Bimetallic networks are also highly interesting. We are now actively searching for synthetic conditions and appropriate structure-directing agents to prepare new oxalatophosphates of transition metals with the honeycomb structure.

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Supporting Information Available: Crystallographic data for **1** and **2** in CIF format and an M versus H curve for **1** at 10 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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