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Chirality and Magnetism in a Novel Series of Isotypic Borophosphates: $M^{II}[BPO_4(OH)_2]$ (M^{II} = Mn, Fe, Co)

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Three novel isotypic borophosphates $M^{II}[BPO_4(OH)_2]$ (M^{II} = Mn, Fe, Co) have been hydrothermally synthesized and structurally characterized. The isotypic compounds crystallize in the chiral space group $P3_121$ or $P3_221$. Their crystal structures are characterized by edge-sharing helical $M^{II}O_6$-octahedral chains wound around 3_1 or 3_2 screw axes (along [001]) interconnected by borophosphate single chains of alternating $BO_2(OH)_2$ and PO_4 tetrahedra perpendicular to [001], resulting in three-dimensional framework structures. The helical $M^{II}O_6$-octahedral chains lead to low-dimensional magnetic properties.

During the recent research on borophosphates, a series of compounds were found that crystallize in space group $P6_1$ ($P6_122$) or $P6_5$ ($P6_522$) with the general chemical formula $M^IM^{II}(H_2O)_2[BP_2O_8]\cdot yH_2O$ (M^I = Li, Na, K, NH_4; M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd; $y = 0.5-1.0$)[1-5] or $M^{III}(H_2O)_2[BP_2O_8]\cdot H_2O$ (M^{III} = Sc, Fe, In).[6-8] The helical borophosphate chains arranged around 6_1 or 6_5 screw axes are interconnected by metal coordination polyhedra to form a three-dimensional open-framework structure related to the CZP topology.[9] Excited by the phenomenon of chirality in this family of borophosphates, we put our effort into searching for other borophosphates also with the characteristics of chirality. In this paper, we report on three new isotypic compounds $M^{II}[BPO_4(OH)_2]$ (M^{II} = Mn, Fe, Co), designated as **Mn**, **Fe**, and **Co**, respectively, which crystallize in the chiral space group $P3_221$ or $P3_121$. The exciting points of the new compounds lie in the metal−oxygen partial structures that form helical $M^{II}O_6$-octahedral chains running along [001] and in the *vierer* borophosphate single chains extended perpendicular to [001].

The isotypic borophosphates were synthesized under hydrothermal conditions.[10] The crystal structures were determined by single-crystal X-ray diffraction,[11] and the compositions were confirmed by elemental analyses.

The crystal structure of the isotypic compounds contains one-dimensional infinite helices, which are built from $M^{II}O_4(OH)_2$ octahedra by sharing common edges, wound around 3_1 or 3_2 screw axes (Figure 1a). Each helix is, because of symmetry, surrounded by six adjacent chains at equal distance; thus, the resulting arrangement can be illustrated as a hexagonal rod stacking (Figure 1b,d). The two crystallographically independent metal(II) sites are both in a distorted octahedral coordination by oxygen with bond lengths and angles within the typical range.[1,2] The shortest intrachain distances of $M^{II}\cdots M^{II}$ are 3.32 Å (**Mn**), 3.27 Å

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(10) Three isotypic compounds were synthesized under mild hydrothermal conditions (443 K). The starting materials (see follow) were heated at 333 K in deionized water (5 mL) under stirring for 2 h. Meanwhile, HCl (37%) was added to adjust the pH value to 1.5. The clear solution was transferred into a Teflon autoclave (V = 20 mL; filling degree ≈ 40%) and treated at 443 K for 3 days. Crystals were separated from the mother liquor by vacuum, washed with deionized water, and dried at 333 K in air. **Mn**: 0.76 g of $MnCl_2$ 2.97 g of H_3BO_3, 2.69 g of DABCO (1,4-diazobicyclo[2.2.2]octane, $C_6H_{12}N_2$), 2.52 g of H_3PO_4 (85%). **Fe**: 1.18 g of $FeCl_2\cdot 4H_2O$, 2.97 g of H_3BO_3, 2.69 g of DABCO, 2.52 g of H_3PO_4 (85%). **Co**: 0.78 g of $CoCl_2$, 2.97 g of H_3BO_3, 2.69 g of DABCO, 2.52 g of H_3PO_4 (85%). The single crystals with trigonal-prismatic shape were prepared only in the presence of DABCO, although it does not appear in the product. Here, it may act as an acid buffer and control the shape of the crystals because they grow in a spherical aggregate without the addition of DABCO. **Mn** and **Co** could also be synthesized from $M^{II}O$, B_2O_3, P_2O_5, and H_2O. Elemental analyses results of **Mn** (found: Mn, 27.70(6); B, 5.43(1); P, 16.08; $Mn[BP_2O_4(OH)_2]$ requires Mn, 28.21; B, 5.55; P, 15.91%), **Fe** (found: Fe, 27.81(11); B, 5.37(1); P, 15.52(6); $Fe[BP_2O_4(OH)_2]$ requires Fe, 28.54; B, 5.53; P, 15.83%), and **Co** (found: Co, 29.81(15); B, 5.25(2); P, 15.56(4); $Co[BP_2O_4(OH)_2]$ requires Co, 29.65; B, 5.44; P, 15.59%). IR spectroscopic studies in the range of 4000−400 cm^{-1} show two sharp and strong absorption peaks, which are assigned to hydroxyl groups. **Mn**: 3515 and 3390 cm^{-1}. **Fe**: 3546 and 3384 cm^{-1}, **Co**: 3555 and 3374 cm^{-1}.

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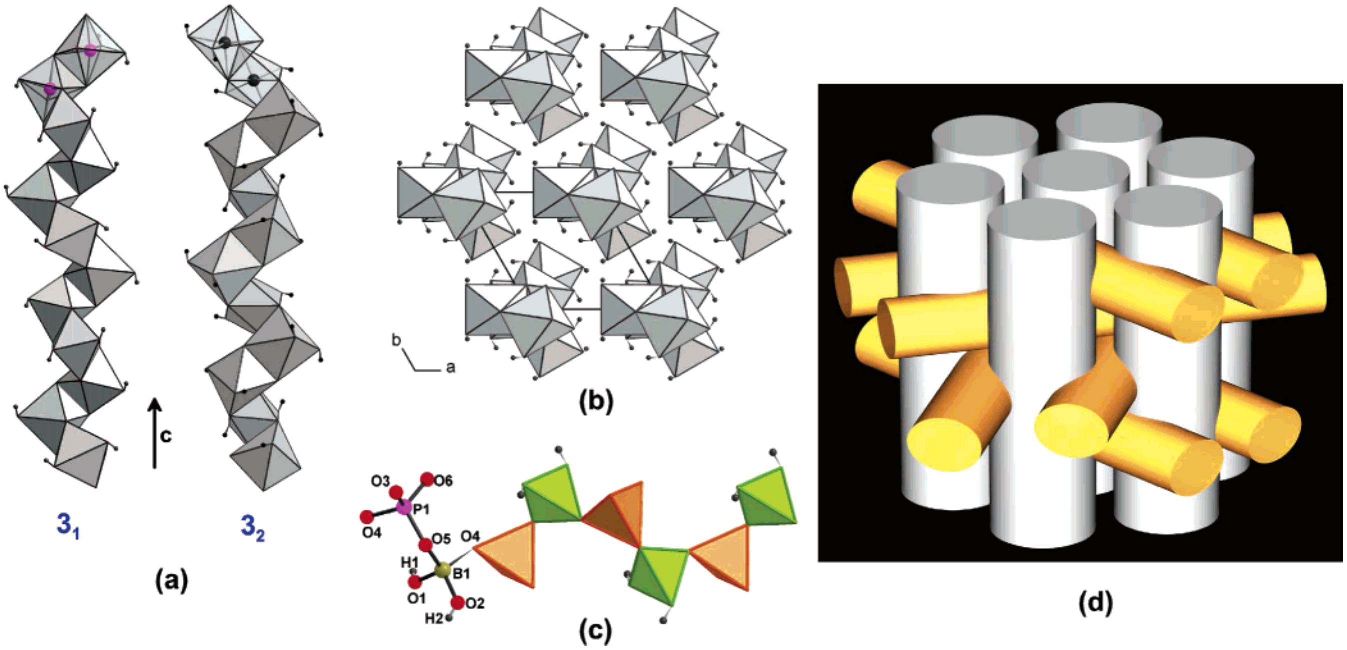

Figure 1. (a) Helical $M^{II}O_6$-octahedral chains wound around 3_1 or 3_2 screw axes extending parallel to [001] which are built from $M^{II}O_4(OH)_2$ octahedra by sharing common edges. (b) The arrangement of helical $M^{II}O_6$-octahedral chains exhibiting the motif of a hexagonal rod stacking. (c) The unbranched *vierer* single chain built from alternating $BO_2(OH)_2$ and PO_4 tetrahedra linked via common corners. (d) Cylinder representation of the three-dimensional crystal structures of the isotypic compounds. Gray cylinders: helical $M^{II}O_6$-octahedral chains. Yellow cylinders: borophosphate single chains.

(**Fe**), and 3.24 Å (**Co**), respectively. Phosphorus is 4-fold-coordinated by oxygen, whereas boron comprises a coordination sphere with two oxygen atoms and two OH groups. The resulting regular $BO_2(OH)_2$ and PO_4 tetrahedra are connected in an alternating manner, forming into an unbranched *vierer* single chain, $^{1}_{\infty}\{[BPO_4(OH)_2]^{2-}\}$, extending along the 2-fold axes perpendicular to [001]. Because of symmetry, unbranched *vierer* single chains with alternating orientation (layerwise rotated by 60°) are stacked at different heights ($z \approx {}^1/_6$, ${}^3/_6$, and ${}^5/_6$, respectively). A similar unbranched *vierer* borophosphate single chain, $^{1}_{\infty}\{[B_2P_2O_7(OH)_5]^{3-}\}$, was found in the crystal structure of $Fe[B_2P_2O_7(OH)_5]$,[12] which only differs in the degree of protonation. Interatomic distances and angles of the anionic partial structure are within the regular range for borophosphates.[1,2] The unbranched *vierer* borophosphate single chains interconnect the helical $M^{II}O_6$-octahedral chains, resulting in a three-dimensional framework structure (Figure 1d).

Thermal analyses of the isotypic compounds **Mn** and **Co** (in static air) and **Fe** (in a N_2 atomosphere) show a one-step weight loss corresponding to the removal of one H_2O per formula unit. Weight loss (H_2O). Found for **Mn**: 10.00% (obsd)/9.25% (calcd). Found for **Fe**: 9.57% (obsd)/9.21% (calcd). Found for **Co**: 9.64% (obsd)/9.07% (calcd). The results of the thermal analyses reveal that the isotypic compounds are thermally stable at least up to 732 K (**Mn**), 734 K (**Fe**), and 765 K (**Co**), respectively. The dehydration reaction is finished at maximum temperatures of 752 K (**Mn**), 753 K (**Fe**), and 799 K (**Co**), respectively. Reaction products immediately after dehydration were identified by X-ray powder diffraction as mixtures of BPO_4 and the respective pyrophosphates.

The magnetic susceptibilities $\chi = M(T)/H$ (Figure 2; carried out on powder samples) follow a Curie−Weiss law at temperatures above 50 K. The effective magnetic moments μ_{eff}/M atom and the Weiss temperatures Θ are as follows: **Mn**, 5.91 μ_B, −13.5 K; **Fe**, 5.47 μ_B, +5.0 K; **Co**, 4.92 μ_B, −6.8 K. The values of μ_{eff} are quite typical for pure (high-spin) M^{II} compounds. At lower temperatures, the $\chi(T)$ curves display broad maxima (**Mn**, at 7.4 K; **Fe**, 3.7 K; **Co**, 2.4 K; Figure 2, inset), indicating low-dimensional antiferromagnetic correlations of the M^{II} ions, probably from dominant exchange interactions within the one-dimensional octahedral chain structure. Specific heat measurements conducted on the Mn and Co compounds also display broad maxima (**Mn**, 4.5 K; **Co**, 2.5 K). Entropy data obtained from specific heat

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(11) Crystal structure determinations: Rigaku AFC7 four-circle diffractometer, equipped with a Mercury CCD detector (Mo Kα radiation, graphite monochromator, scan types ϕ and ω). X-ray data were collected at 295 K and corrected for Lorentz and polarization effects. A multiscan absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares methods by using *SHELXS*[13] and *SHELXL*[14] programs included in the WinGX package (Farrugia, L. J., Department of Chemistry, University of Glasgow, Glasgow, Scotland). After anisotropic refinement of the heavier atoms, all hydrogen atoms were located from the difference Fourier maps and refined without applying any restraints. Crystal data for **Mn**: $M = 194.74$ g/mol, trigonal, $P3_221$ (No. 154), $a = 7.5750(4)$ Å, $c = 12.9268(11)$ Å, $V = 642.37(7)$ Å^3, $Z = 6$, μ(Mo Kα) = 3.393 mm^{-1}, 5668 measured reflections, 1504 independent reflections, R1 = 0.030, wR2 = 0.056 for all data. Crystal data for **Fe**: $M = 195.65$ g/mol, trigonal, $P3_221$ (No. 154), $a = 7.4844(4)$ Å, $c = 12.844(11)$ Å, $V = 623.06(7)$ Å^3, $Z = 6$, μ(Mo Kα) = 3.951 mm^{-1}, 5122 measured reflections, 1235 independent reflections, R1 = 0.032, wR2 = 0.064 for all data. Crystal data for **Co**: $M = 198.73$ g/mol, trigonal, $P3_121$ (No. 152), $a = 7.4554(2)$ Å, $c = 12.7397(10)$ Å, $V = 613.24(5)$ Å^3, $Z = 6$, μ(Mo Kα) = 4.523 mm^{-1}, 5062 measured reflections, 1280 independent reflections, R1 = 0.033, final wR2 = 0.057 for all data.

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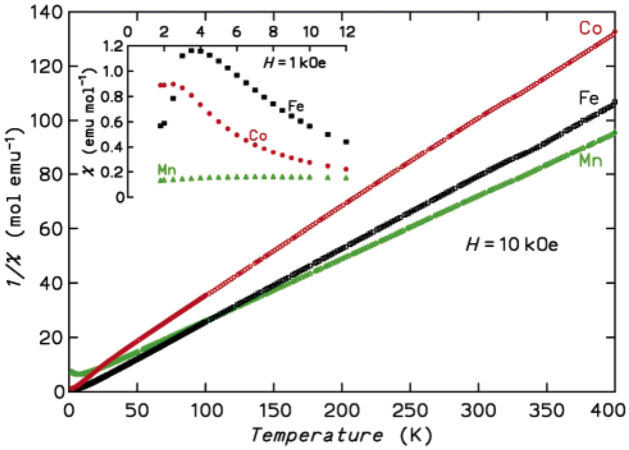

Figure 2. Inverse molar magnetic susceptibility (1/χ) vs temperature for compounds $M^{II}[BPO_4(OH)_2]$ (M^{II} = Mn, Fe, Co). Inset: $\chi(T)$ data at low fields show broad maxima, which indicate dominant one-dimensional magnetic correlations.

measurements in magnetic fields confirm the degeneracy of the magnetic ground states of the M^{II} ions. No clear signs for long-range ordering of the magnetic moments are found above 2.0 K.

First measurements of piezoelectricity (the Piezo effect) failed because of the insufficient size of the crystals. We are still interested in the material properties and will extend the investigations to nonlinear optics and the pressure dependence of magnetism.

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Supporting Information Available: Crystallographic data in CIF format, tables of atomic coordinates as well as bond length and bond angles, IR spectra, and thermogravimetric/differential thermal analysis curves for $M^{II}[BPO_4(OH)_2]$ (M^{II} = Mn, Fe, Co). This material is available free of charge via the Internet at http://pubs.acs.org.

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