Detailed magnetic study on the formate-bridged MOFs with anion-tunable magnetic properties

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Abstract: Detailed studies of the structures, magnetic properties and photodimerization of a series of formate-bridged MOFs with the general formula $M_2(\text{HCOO})_3(4,4'\text{-bpe})_3(\text{H}_2\text{O})_3(\text{X})$ (4,4'-bpe = 4,4'-bipyridylethylene, $M = \text{Mn}$ (**1-X**⁻), $\text{X}^- = \text{ClO}_4^-$, NO_3^- , BF_4^- , I^- , Br^- ; $M = \text{Co}$ (**2-X**⁻), $\text{X}^- = \text{ClO}_4^-$, NO_3^- ; $M = \text{Zn}$ (**3-X**⁻), $\text{X}^- = \text{NO}_3^-$) were reported. Careful magnetic measurements on an oriented single crystal of **1-ClO**₄⁻ determined the spin-flop magnetic phase diagram and some intrinsic parameters, such as the intralayer coupling J , the anisotropy field H_A and the exchange field H_E . Different anions can remarkably tune the magnetic properties of **1-X**⁻, especially the critical fields of the spin-flop transition. Compound **2-ClO**₄⁻ remained paramagnetic down to 2 K.

Keywords: metal formate, spin-flop, magnetic phase diagram, photodimerization

(a) The 2D herringbone layer of **1-ClO**₄⁻ with Mn^{2+} bridged by HCOO^- ; (b) the pillared framework, the yellow ball represents the anions; (c) the schematic A and B sites in the framework; (d) the 4,4'-bpe column along b axis.

Angular dependent susceptibility for 1-ClO_4^- under 1 kOe at different temperatures when the crystal is rotated along c axis and along ab plane ($\theta = 0^\circ$, $H \parallel c$).

Temperature dependence of χ for 1-ClO_4^- . Inset: (a) Expansion of χ below 10 K; (b) field dependent magnetization at 2 K. The data are for a single crystal ($H \parallel c$ and $H \perp c$) and a powder sample. The green line is the best-fit using HTS model.

(a) The field dependent magnetization at different temperatures and (b) the temperature dependent susceptibility under different fields of 1-ClO_4^- with $H \parallel c$.

(a) The temperature dependent ac susceptibility ($H_{ac} = 2$ Oe, $H_{dc} = 0$ Oe) and FC ($H = 200$ Oe, inset) for 1-X^- ; (b) the field dependent ac susceptibility at 1.8 K for the powder samples of 1-X^- up to 70 kOe.