



Magnetic materials based on 3d metal phosphonates

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ABSTRACT

Metal phosphonate chemistry has witnessed a rapid development during the past two decades. Numerous compounds have been synthesized which show new architectures and interesting physical or chemical properties. In this article, we focus on the 3d transition metal phosphonate clusters with single molecule magnet behavior; chain compounds with single chain magnet behavior; and layer or three-dimensional compounds with ferromagnetism, ferrimagnetism, canted antiferromagnetism, and metamagnetism. Finally, magnetic 3d metal phosphonates with multifunctions are also discussed.

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Abbreviations: ahbdpH₄, 4-amino-1-hydroxybutane-1,1-diphosphonic acid; 5-Brsalcy, N,N'-(1,2-cyclohexanediolethylene)bis(5-bromosalicylideneiminato) dianion; 5-Brsalen, N,N'-ethylenebis(5-bromosalicylideneiminato) dianion; BTPH₂, 4-(3-bromothieryl)phosphonic acid; Hchp, 6-chloro-2-hydroxypyridine; 2-cppH₃, 2-carboxyphenylphosphonic acid; cyampH₂, ((1-cyclohexylethyl)amino)methylphosphonic acid; H₄L¹, p-xylylenediphosphonic acid; H₂L², 2,3,5,6-(Me)₄C₆H₂CH₂PO₃H₂; H₄L³, 4-Me-C₆H₄CH₂N(CH₂PO₃H₂)₂; H₄L⁴, (benzylazanediy)bis(methylene)diphosphonic acid; H₃L⁵, 4-[(phosphonomethylamino)methyl]benzoic acid; hedpH₄, 1-hydroxyethylidenediphosphonic acid; hpyedpH₄, 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid; lmhedpH₄, 2-(1-imidazole)-1-hydroxyl-1,1'-ethylidenediphosphonic acid; 2-mmpme, monoethyl(pyridin-2-ylmethyl) phosphonate; napPO₃H₂, naphthylphosphonic acid; NDI-BP, N,N'-bis(2-phosphonoethyl)naphthalene-1,4:5,8-tetracarboximide; nempH₂, [1-(1-naphthyl)ethylamino]methylphosphonic acid; PDI-BP, 3,4:9,10-perylene-diimide bis-phosphonate; 4-piH₄, 4-phosphonoisophthalic acid; pinH₃, 2-phosphonic isonicotinic acid; 2-pmbH₃, 2-(phosphonomethyl)benzoic acid; pmbpH₂, 1-phosphonomethyl-2-benzimidazol-pyrrolidine; 2-pmpH₂, 2-pyridylmethylphosphonic acid; pnaH₃, 6-phosphonic nicotinic acid; 2-ppH₂, 2-pyridylphosphonic acid; ppapH₃, 3-phenyl-2-((phosphonomethyl)amino) propanoic acid; salen, N,N'-bis(salicylidene)ethylenediamine.

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1. Introduction

As an important class of inorganic–organic hybrid materials, metal phosphonates have received growing attention during the past three decades, owing to their potential applications in catalysis [1–3], absorption and separation [4–7], proton conductivity [8–10], photochemistry [11,12], and biotechnology [13–15], etc. Phosphonate (RPO_3^{2-}) ligands can show multiple coordination modes (Scheme 1), and this combined with the different geometries of the metal sites lead to a large number of compounds with versatile structures [16,17]. Most of them display layered or pillared layered structures with different layer topologies and the organic groups filling in the interlayer spaces. By introducing additional functional groups and organic templates or co-ligands, low dimensional metal phosphonates such as chains and clusters can be obtained.

Compared with the traditional inorganic materials, metal phosphonates can be prepared under mild conditions and their functions may be designed for specific purpose. These materials also possess advantages over many other metal–organic hybrids such as carboxylates because of their high thermal and chemical stabilities. It is noted, however, that the majority of work reported so far has centered on the syntheses and structural characterization of new metal phosphonate compounds, as summarized in a few reviews and books [16–19]. With regard to the functions, efforts have been devoted to porous or open-framework metal phosphonate materials which show appealing potentials in catalysis and adsorption [20,21], and also to those with interesting physical properties. Bellitto and Rabu and Drillon reviewed the magnetism of metal phosphonates, with the main focus on the layered compounds $\text{M}(\text{RPO}_3)(\text{H}_2\text{O})$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cr}$; $\text{R} = \text{Alkyl}, \text{Ph}$) [22–25]. The magnetic properties of cobalt phosphonates were summarized by us in 2012 [26].

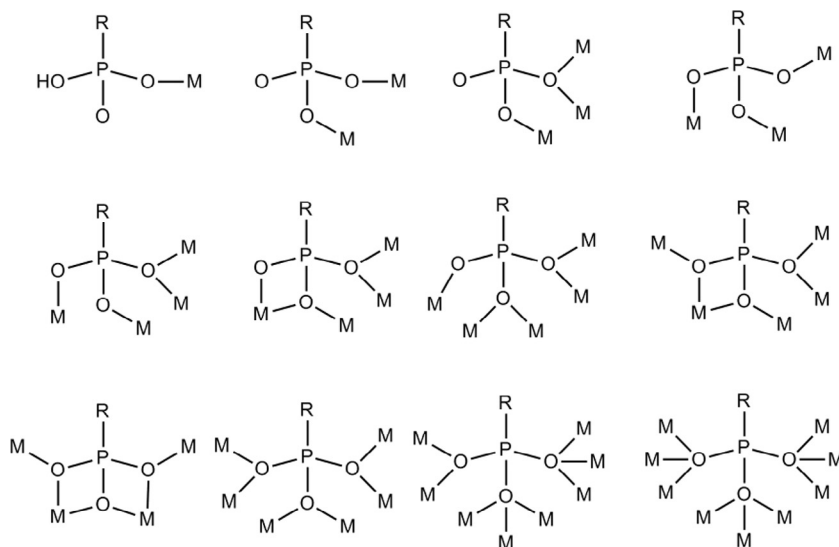
Herein, we shall concentrate on the magnetic materials based on the 3d transition metal phosphonates including low-dimensional magnets such as the single-molecule magnets (SMMs) and single-chain magnets (SCMs), as well as long-range ordered magnetic materials. The lanthanide (4f) or 3d-4f phosphonates are not included in this review, although they could show interesting magnetic behavior. Some phosphonate ligands mentioned in this article are listed in Scheme 2.

2. Nature of exchange coupling over O–P–O bridges

The phosphonate group can display versatile coordination modes, some of which are given in Scheme 1. However, one question has remained for a long period of time about the nature of the magnetic exchange coupling through the flexible O–P–O bridges. In most cases, the three-atom bridge mediates very weak antiferromagnetic interactions between metal centers ($|J| < 5 \text{ cm}^{-1}$) [27–30]. But exceptions also exist where a stronger antiferromagnetic or even the ferromagnetic interaction is observed [31–33]. To figure out the main structural parameters which determine the nature and magnitude of the exchange coupling, a few copper phosphonates were selected for a detailed investigation because the Cu^{II} ion is isotropic and possesses a single unpaired electron.

It is well known that the Jahn–Teller effect leads to the axial elongation of the Cu^{II} ion, and the magnetic orbital of Cu^{II} is located in the basal plane. Only a very small spin delocalization on the apical position is predicted, and hence very weak magnetic exchange coupling is expected when one or both interacting metal ions are connected to the bridging ligand through this apical position. When the bridging ligand occupies equatorial positions at both Cu^{II} ions, weak to moderate magnetic coupling is anticipated [34]. Since the phosphonate group can adopt *anti-anti*, *anti-syn* and *syn-syn* coordination modes in connecting the Cu^{II} ions (Scheme 3), the nature and magnitude of the exchange coupling are strongly dependent on the specific bridging mode of the phosphonate ligand. The difference in the bridging modes can be qualitatively recognized by the torsion angles of $\text{M}-\text{O}\dots\text{O}-\text{M}$ or $\text{M}-\text{O}-\text{P}-\text{O}$ over the O–P–O bridge, which is larger in the case of *anti-syn* mode.

The isomeric systems can provide unique opportunities to investigate the structure–property relationships in order to understand the fundamental phenomena [35,36]. By using 1-phosphonomethyl-2-benzimidazol-pyrrolidine (pmbpH_2 , Scheme 2), we have successfully isolated three isomeric copper(II) compounds under slightly different reaction conditions, namely, $\text{Cu}(\text{pmbp})\cdot 2.5\text{H}_2\text{O}$ (**Cu-1**), $\text{Cu}(\text{pmbp})\cdot 2\text{H}_2\text{O}$ (**Cu-2**), and $\text{Cu}(\text{pmbp})(\text{H}_2\text{O})\cdot x\text{H}_2\text{O}$ (**Cu-3**) [37]. All show chain structures in which the Cu^{II} ions are linked purely by O–P–O units, and the bridging phosphonate groups occupy equatorial positions at both Cu^{II} ions (Fig. 1).



Scheme 1. Coordination modes of phosphonate ligands.

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