

## Anhydrous manganese hypophosphite dense framework solid: Synthesis, structure and magnetic studies



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### ABSTRACT

Anhydrous manganese hypophosphite,  $[\text{Mn}(\text{H}_2\text{PO}_2)_2]_n \cdot (\text{DMF})_{0.11}$  (**1**) has been isolated under solvothermal conditions from the reaction of hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ) and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  in a mixture of DMF/EtOH/ $\text{H}_2\text{O}$  (8:1:1; v/v) in 60% yield. The compound is characterized by FT-IR spectroscopy, thermogravimetric analysis, PXRD, single crystal X-ray diffraction data and magnetic measurements. The ligand occupies all the octahedral coordination sites around Mn(II) ions and forms a dense 3-D coordination polymer with hexagonal 1-D channels along [001] direction. The Mn(II) ions in the framework exhibit weak antiferromagnetic interactions.

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Metal formate frameworks, templated by mono-ammonium cations have attracted a lot of interest in recent years for their order–disorder multiferroic properties [1–3]. Within this class of compounds, especially attractive are the  $\text{ABX}_3$  (where A = mono-ammonium cations, B = divalent metal ions such as Mn, Co, Ni, Fe, Cu and X = formate ion) compounds built up of  $\text{MO}_6$  octahedra connected by the formate groups while mono-ammonium cations reside in the voids [4,5]. Such complexes exhibit relatively short distance between metal centres, and therefore display magnetic order at low temperature. In order to enhance the properties of formate dependent frameworks, various mono-ammonium cations (such as ammonium, dimethyl ammonium, azetidin, hydrazinium and guanidinium) have been employed as templating agents [6–9]. On the contrary, formate ligand has invariably been used for linking metal centres. In the search of new materials, it would be of interest to investigate the possibility of other ligand systems which are structurally similar to formate ion such as hypophosphite,  $[\text{H}_2\text{PO}_2]^-$  (Chart 1). Metal hypophosphites have been proven to be useful as antioxidants [10], food supplements [11], flame retardants [12,13], reducing agents [14,15], and catalysts [12,16]. Also at high temperature, hypophosphites undergo thermal decomposition to yield magnetically and catalytically promising pyrophosphates [17]. Hypophosphito ligand can bind with two, three and four metal

ions to produce thermally and chemically stable complexes of various dimensionalities [18]. Weakley and co-workers isolated  $\text{Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ , and  $\text{Zn}(\text{H}_2\text{PO}_2)_2 \cdot n\text{H}_2\text{O}$  ( $n = 0, 1$ ) solids and determined the crystal structures [19]. Subsequently, Marcos and co-workers reported three different hydrates of Mn(II) hypophosphite monohydrate exhibiting polymorphism and one of the forms (i.e.,  $\alpha\text{-Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$ ) was found to be isostructural with the previously reported Zn(II) hypophosphite monohydrate [20,21]. In this article, we report a dense 3-D Mn(II) hypophosphite,  $[\text{Mn}(\text{H}_2\text{PO}_2)_2]_n \cdot (\text{DMF})_{0.11}$  (**1**) where all the coordination sites are occupied by the ligand through bridging modes with DMF molecules in the channels. The complex was obtained as colourless crystals by solvothermal reaction of  $\text{H}_3\text{PO}_2$  with  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  for 48 h in a mixture of DMF/ $\text{H}_2\text{O}$ /EtOH (8:1:1; v/v).

Formation of the complex **1** was confirmed by FT-IR spectrum. The strong band at  $2368 \text{ cm}^{-1}$  is attributed to the P–H stretching vibrations of the  $\text{PH}_2$  groups of the hypophosphito ligand (Fig. 1a). The peaks at 1168 and  $1055 \text{ cm}^{-1}$  are assigned to the H–P–H scissoring and deformation bending vibrations, respectively [22,23]. Two peaks around 2925 and  $2855 \text{ cm}^{-1}$  correspond to the asymmetric and symmetric C–H stretching vibrations of methyl groups of the guest DMF molecules present within the framework which is further supported by carbonyl stretching vibrations at  $1670 \text{ cm}^{-1}$ . The FT-IR spectrum of calcined sample **1** at  $500 \text{ }^\circ\text{C}$  differs significantly from that of the as-synthesised sample (Fig. 1b). The  $-\text{PO}_2$  asymmetric and symmetric stretching vibrations occur at 1315 and  $1045 \text{ cm}^{-1}$ . The broad band at  $1045 \text{ cm}^{-1}$  indicates merging of P–O–P asymmetric vibrational band with the symmetric stretching of  $-\text{PO}_2$  group while P–O–P symmetric

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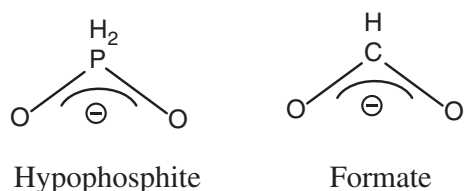


Chart 1. Structures of hypophosphite and formate ligands.

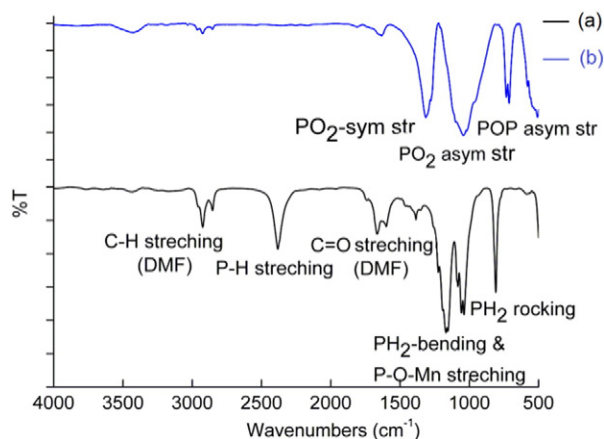


Fig. 1. FT-IR spectra of **1** (a) as-synthesised and (b) sample calcined at 500 °C.

stretching band is found at 730  $\text{cm}^{-1}$  [24]. Thermo gravimetric analysis indicates that initial weight loss (~3.5%) is because of the elimination of DMF guest molecules (Fig. 2). The hypophosphito ligand decomposes in the temperature range of 280–580 °C, corresponding to two consecutive weight losses (5.5 and 15.5%) due to the loss of water and phosphine, respectively (Scheme 1) (calcd: 5.13 and 18.3%, respectively) [24]. The TGA curve of calcined (at 500 °C) bulk sample of **1** shows no significant weight loss up to 1000 °C which supports the formation of thermally stable  $\text{Mn}_2\text{P}_2\text{O}_7$ .

The title compound **1** crystallizes in the trigonal  $R\bar{3}$  space group with one Mn(II) and two monoanionic hypophosphito ligands i.e.,  $[\text{H}_2\text{PO}_2]^-$  in the asymmetric unit. The Mn(II) centre exhibits a slightly distorted octahedral geometry where all the six coordination sites are occupied by the oxygen atoms of six different  $[\text{H}_2\text{PO}_2]^-$  ligands. The ligand binds with [3.21] mode of coordination according to Harris notation

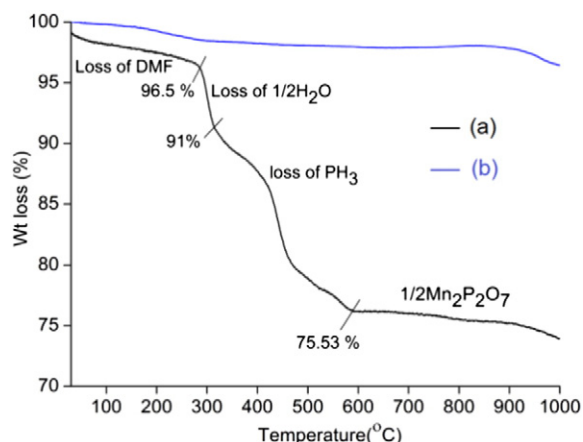
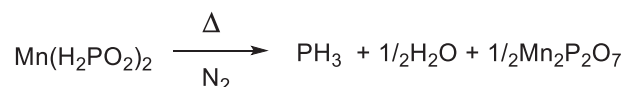


Fig. 2. TGA profiles of **1**, (a) as synthesized and (b) sample calcined at 500 °C.



Scheme 1. Thermal decomposition of Mn(II)-hypophosphite.

(Fig. S1) [25]. Each ligand molecule coordinates with three Mn(II) ions and forms two types of bridges, i.e. Mn–O–Mn and Mn–O–P–O–Mn as depicted in Fig. 3. A view down the crystallographic [001] direction reveals simultaneous presence of both the bridges which form infinite 1-D Mn–O–Mn chain.

Several of such chains are interconnected by Mn–O–P–O–Mn linkages which lead into the formation of a polymeric three-dimensional network containing hexagonal 1-D channels (Fig. 4). The earlier reported  $\alpha\text{-Mn}(\text{H}_2\text{PO}_2)_2 \cdot \text{H}_2\text{O}$  [20] compound consists of  $\text{Mn}_2\text{O}_{10}$  dimeric entities where each  $\text{MnO}_6$  octahedron is connected with the neighbouring one by edge sharing. The hypophosphito ligands provide Mn–O–P–O–Mn linkages between the dimeric units to form a 3-D network.

The Mn–O and P–O bond distances are in the range of 2.106(4)–2.269(4) and 1.480(4)–1.517(4) Å, respectively, that are in agreement with those found in the analogous compounds [19,26]. All the P–O bonds are approximately of similar distance which reveals that both the O atoms of  $[\text{H}_2\text{PO}_2]^-$  are coordinated and there are no terminal P–O or P–OH groups present in the structure. The P–H bond lengths of pseudotetrahedral  $\text{H}_2\text{PO}_2^-$  fall in the range of 1.27(5)–1.45(5) Å which is comparable to those reported metal hypophosphites [16]. The final Fourier map revealed that the channels may contain diffused electron density, which could not be modelled reliably. Hence, SQUEEZE routine implemented in PLATON was used to squeeze such electrons [27]. The electron count in the void corresponding to 74.1 is approximately equal to two DMF molecules per unit cell ( $Z = 18$ ). Hence, the chemical composition of the framework is determined to be  $[\text{Mn}(\text{H}_2\text{PO}_2)_2]_n \cdot (\text{DMF})_{0.11}$ . The presence of guest DMF molecules also renders the framework non-porous as determined by BET surface area measurements which were found to be zero ( $0.08 \text{ m}^2 \text{ g}^{-1}$ ). The phase purity of **1** at room temperature was

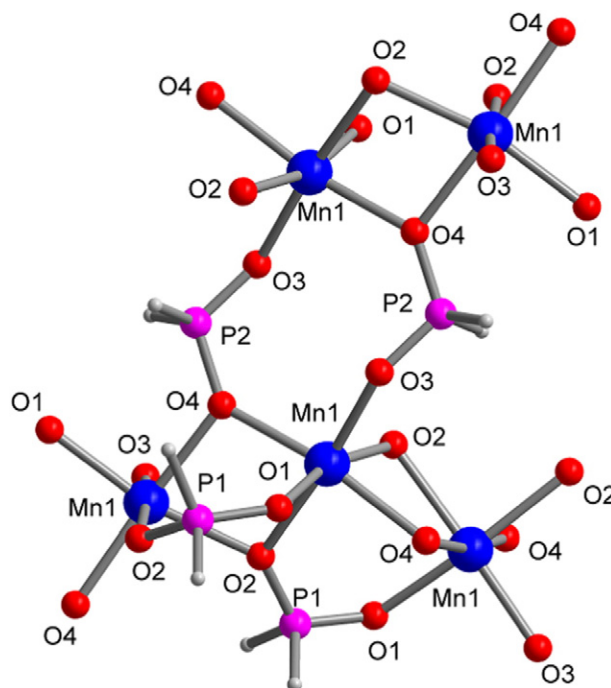


Fig. 3. Coordination environment of Mn(II) in **1**.

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