



## Ionothermal synthesis of a new open-framework manganese(II) diphosphate



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### ABSTRACT

A novel open-framework manganese diphosphate compound,  $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{MnP}_2\text{O}_7]$ , denoted as **JIS-13** (Jilin Ionothermal Synthesis-13), has been ionothermally synthesized by using a eutectic mixture of tetramethylammonium chloride and 2-imidazolidone as the solvent and template-delivery agent, which *in situ* yields ethylene diammonium cations ( $\text{en}^{2+}$ ) as the template. The structure of **JIS-13** is determined by single-crystal X-ray diffraction and further characterized by powder X-ray diffraction (PXRD), inductively coupled plasma (ICP), thermogravimetric (TG), elemental analyses, X-ray photoelectron spectroscopy (XPS) and magnetic measurements. The alternation of  $\text{MnO}_5$  trigonal bipyramids and  $\text{P}_2\text{O}_7$  units linking through their vertices forms the three-dimensional (3-D) open framework of **JIS-13**, which comprises 12-ring channels along the [100] direction. Protonated  $\text{en}^{2+}$  cations act as the templates to compensate the negative charges of the inorganic framework. Magnetic measurements reveal that weak antiferromagnetic interaction exists in **JIS-13**.

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Since the first discovery of microporous aluminophosphates in 1982 (designated as  $\text{AlPO}_4\text{-}n$ ,  $n$  denotes the structure type) by Wilson et al. [1], open-framework phosphate materials have been extensively studied in the past thirty years, due to their rich structural chemistry and widespread applications in catalysis, adsorption, separation and so on [2–4]. Subsequently, the constituent elements of the inorganic skeleton of these materials have been expanded from the main group to transition metal, and some transition metal phosphates have exhibited the unique features introduced by the transition metals, such as optical, electric and magnetic properties [5,6]. Among the family of transition metal phosphates, many phosphates of zirconium, iron, zinc, and nickel were investigated [7–9]. However, although several manganese phosphates have exhibited rich structures and interesting magnetic properties [5b,10], 3-D open-framework manganese phosphate materials are rarely reported. The family of organically templated manganese phosphates is dominated by 2-D sheet structures. To date, there is only one example of a 3-D structure with 6-ring and 7-ring channels being reported [6d].

Up to now, the organically templated manganese phosphates with rich structures and interesting magnetic properties have been synthesized by using hydrothermal or solvothermal methods [5b,10]. The employment of new synthetic methods has opened up many new opportunities in the exploration of previously unseen materials. Ionothermal synthesis, using ionic liquids or deep eutectic solvents (DESs) as the solvent in the preparation of aluminophosphate molecular sieves, was developed by Morris and co-workers in 2004 [11]. This

new method has interesting features and potential advantages over the traditional methods. For example, not only the ionic liquids act as solvent, but also they can provide organic cations as templates or structure directing agents (SDAs) in the formation of crystalline solids, and the synthesis can take place at ambient pressure, eliminating safety concerns associated with high solvent pressures [11,12]. Recent researches demonstrate that ionothermal synthesis has become a promising technique in the synthesis of crystalline solids, for example,  $5\text{H}_2\text{O} \cdot [\text{Ni}_8(\text{HPO}_3)_9\text{Cl}_3] \cdot 1.5\text{H}_2\text{O}$  (JIS-3), an open-framework nickel phosphite with extra-large 18-ring channels [13]; DNL-1 (-CLO framework type), the first AlPO molecular sieve with 20-ring pore openings [14]; and  $[\text{NH}_4]_2[\text{Ge}(\text{NH}_3)_2(\text{PO}_4)_2] \cdot 0.38\text{H}_2\text{O}$ , a novel germanium phosphate with a chain-like framework [15]. To date, many novel metal phosphates such as aluminophosphates, metal aluminophosphates, gallium phosphates, zinc phosphates, zirconium phosphates, nickel phosphate, metal borophosphates and germanium phosphate, have been achieved by using the ionothermal method from ionic liquids or ionic eutectic mixtures [8b,11,14–17]. However, ionothermal synthesis of open-framework manganese phosphates is rarely reported.

Herein, we report the first use of ionothermal synthesis approach in the preparation of a novel open-framework manganese diphosphate  $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3][\text{MnP}_2\text{O}_7]$ , denoted as **JIS-13** (Jilin Ionothermal Synthesis-13). **JIS-13** was synthesized by the ionothermal reaction of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{BPO}_4$ ,  $\text{H}_3\text{PO}_4$ , tetramethylammonium chloride and 2-imidazolidone at 180 °C for 9 days [18]. The mixture of tetramethylammonium chloride and 2-imidazolidone acted as the solvent and template-delivery agent in the ionothermal system. It is noted that ethylene diammonium was not added directly to the

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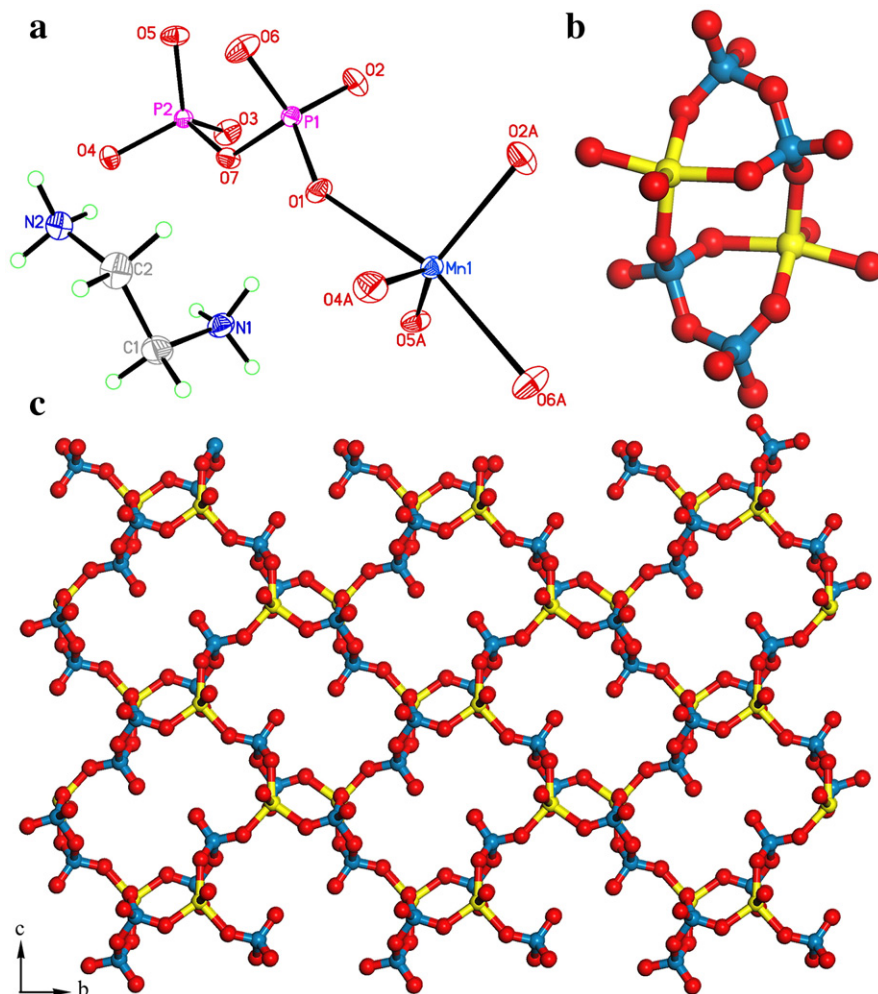
reaction mixture, but was *in situ* generated by the decomposition of 2-imidazolidone. **JIS-13** cannot be obtained in the existence of ethylene diammonium under hydrothermal or solvothermal conditions. The synthetic strategy by using unstable deep eutectic solvents (DESs) as template-delivery agents has been found in the ionothermal synthesis of  $\text{AlPO}_4$  and  $\text{ZnPO}_4$ -EU1 [19]. The successful synthesis of **JIS-13** further extends the possibility of application of this synthetic strategy for the synthesis of novel inorganic open-framework materials. The phase purity of **JIS-13** was confirmed by the agreement between the experimental powder X-ray diffraction (PXRD) pattern (Fig. S1).

Structural analysis [20] shows that **JIS-13** crystallizes in the monoclinic space group  $P2_1/c$  (No. 14), and the cell parameters are  $a = 6.5841(8) \text{ \AA}$ ,  $b = 13.6509(16) \text{ \AA}$ ,  $c = 9.9997(12) \text{ \AA}$ ,  $\beta = 104.131(2)^\circ$ , and  $V = 871.57(18) \text{ \AA}^3$ . Its structure is based on the alternation of  $\text{MnO}_5$  trigonal bipyramids and  $\text{P}_2\text{O}_7$  units to form an anionic framework. Charge neutrality is achieved by extra-framework protonated  $\text{en}^{2+}$  cations. Fig. 1a shows the thermal ellipsoids of **JIS-13**. There are two crystallographically distinct P sites and one Mn site in the framework. The Mn1 atom is connected with five bridging oxygen atoms, three of which link P1, and two of which link P2. The Mn–O bond lengths are in the range of 2.0769(14)  $\text{ \AA}$  to 2.1702(15)  $\text{ \AA}$  (Table S1), and the O–Mn–O angles are lying between 85.95(5)° and 164.96(6)° (Table S1). Each P atom is tetrahedrally coordinated with four O atoms with P–O bond lengths in the range of 1.4997(14)  $\text{ \AA}$ –1.6237(13)  $\text{ \AA}$  and the angles of O–P–O lying between 101.85(7)° and

115.49(9)° (Table S1). Two  $\text{PO}_4$  tetrahedra form one  $\text{P}_2\text{O}_7$  unit by corner-sharing, so one longer and three short P–O bonds are formed in each  $\text{PO}_4$  tetrahedron. The  $\text{P}_2\text{O}_7$  unit has one terminal P=O group, so the P2–O3 bond length (1.4997  $\text{ \AA}$ ) is shorter than the other P–O bond length. The P1–O7–P2 angle is 128.04(8)°, which is in the range of those found in other diphosphates [21].

The framework structure of **JIS-13** is built up from alternating  $\text{MnO}_5$  trigonal bipyramids and  $\text{P}_2\text{O}_7$  units, which are linked through their vertices, giving rise to a three-dimensional framework with 12-ring channels along the [100] direction. Interestingly, the 3-D framework can be conceptually considered to be built up from a composite building unit (CBU) denoted as  $\text{Mn}_2\text{P}_4\text{O}_{18}$ , featuring a twisted double three-ring (Fig. 1b). Each  $\text{Mn}_2\text{P}_4\text{O}_{18}$  building block is linked to four neighboring units to form a two-dimensional network with 12-rings parallel to the *bc* plane (Fig. 1c), and two adjacent layers are further linked by sharing O atoms to generate a 3-D open framework (Fig. 2a). Therefore, the elliptical 12-ring channels exist along the [100] direction (Fig. 2b). The guest  $\text{en}^{2+}$  cations are found perfectly arranged in the middle region of the 12-ring channels (Fig. S2), as the counterions to balance the overall negative charges of the 3-D open framework. There are strong hydrogen bonds among the framework oxygen atoms and the amine groups of the organic molecule (Table S2).

The valence sum calculations [22] show that the empirical valence of crystallographically distinct Mn atom is +2, which is consistent with the result of XPS analysis (Fig. S3). Thermogravimetric (TG) analysis of



**Fig. 1.** (a) Thermal ellipsoids given at 50% probability, showing the atomic labeling scheme of **JIS-13**. (b) View of the CBU in **JIS-13**. Color code: yellow, Mn; blue, P; red, O. (c) View of the inorganic layer along the [100] direction showing the 12-ring channels. Color code: yellow, Mn; blue, P; red, O.

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