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Ionothermal Synthesis of Chiral Metal Phosphite Open Frameworks with In Situ Generated Organic Templates

Li-Ming Li, Kai Cheng, Fei Wang, and Jian Zhang*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

Ⓢ *Supporting Information*

ABSTRACT: Two novel three-dimensional chiral metal phosphite open frameworks with 4-connected quartz topology, $[Me_2\text{-DABCO}][M_2(HPO_3)_3]$ [M = Co (**1**), Zn (**2**); Me_2-DABCO = *N*,*N*′-dimethyl-1,4-diazabicyclo[2.2.2]octane], have been ionothermally synthesized in deep eutectic solvents (choline chloride/1,3-dimethylurea). It is interesting that the organic template, Me_2-DABCO, is in situ generated from the alkylation reaction of 1,4-diazabicyclo[2.2.2]octane and dimethyl phosphites.

Syntheses of crystalline materials with open frameworks have attracted much attention in recent years.[1] The ionothermal method has been demonstrated as an effective approach toward the synthesis of porous materials.[2] Compared with other traditional solvents, ionic liquids have some special features, such as low vapor pressure, pollution-free for the environment, and excellent solvating properties.[3] So far, the ionothermal method has been used to synthesize inorganic zeolites, transition-metal phosphates and phosphites, oxides, or coordination polymers.[3c,4] Four achiral metal phosphite open frameworks synthesized by the ionothermal method have been reported previously,[5] in which only the compound NIS-3 prepared using 1-ethyl-3-methylimidazolium bromide as the solvent was organically templated.[5a] However, chiral metal phosphites are rarely synthesized using the ionothermal method. As we know, chiral open frameworks are particularly effective in enantioselective separation and catalysis, which is important for the chemical field.[6] Therefore, the synthesis of new chiral metal phosphites with three-dimensional (3D) structures is of great significance.

As a new type of ionic liquid, deep-eutectic solvents (DESs) including mixtures of quaternary ammonium salts (e.g., choline chloride) with neutral organic hydrogen-bonding donors (such as amides, amines, and carboxylic acids) are also desirable for applications in the large-scale synthesis of new functional materials.[3c,7] Because a DES contains an ionic compound and a molecular compound, it has multiple roles in directing the framework structures.[4a] As far as we know, no organically templated metal phosphites have been prepared using DES as the solvent to date.

Owing to the Co^{II} ion's catalytic and redox properties, the research for cobalt phosphites has been a subject of concern.[8] However, its development process is very slow. After Marcos et al. reported a 3D structure, $Co_{11}(HPO_3)_8(OH)_6$, in 1993,[9] several 3D cobalt phosphite structures were obtained through solvothermal or hydrothermal methods, and only one of them had the chiral characteristic.[10]

In this work, we first report two chiral organically templated metal phosphites, $(Me_2\text{-DABCO})[M_2(HPO_3)_3]$ [M = Co (**1**), Zn (**2**); Me_2-DABCO = *N*,*N*′-dimethyl-1,4-diazabicyclo[2.2.2]octane], which are ionothermally synthesized in DESs, respectively. Both compounds are isostructural and show intrinsic chiral quartz (denoted as qtz) topology by considering the dinuclear metal unit as the 4-connected node. It is also notable that the guest $Me_2\text{-DABCO}^{2+}$ cations in both frameworks are in situ generated via an alkylation reaction of 1,4-diazabicyclo[2.2.2]octane (DABCO) and dimethyl phosphites.

Crystals of **1** and **2** were prepared by the ionothermal reaction of $CoCl_2 \cdot 6H_2O$ or $Zn(NO_3)_2 \cdot 6H_2O$, DABCO, and dimethyl phosphite in the melting choline chloride/1,3-dimethylurea (molar ratio: 1:2) eutectic mixture, respectively.[11] Single-crystal X-ray diffraction reveals that both compounds crystallized in the chiral space group $P3_121$.[12] Because they are isostructural, only the structure of compound **1** is described as a representative sample. The asymmetric unit of **1** contains one crystallographically independent Co^{II} atom, which is tetrahedrally coordinated to four O atoms. The average Co−O distance is 1.94 Å, and the O−Co−O angles are in the range from 99.3(2) to 114.9(4)°. Each Co^{II} atom is connected to four P^{3+} centers via Co−O−P linkers, with the angles in the range from 126.3(4) to 145.7(5)°. There are two different P^{3+} centers in the asymmetric unit of **1**. The P1 site is half-occupied and shows disorder in two positions. P1 bridges only two Co atoms, leaving two terminal sites bonding to O and H atoms, while P2 links to three Co atoms via bridging O atoms (Figure 1). The existence of a P−H bond is

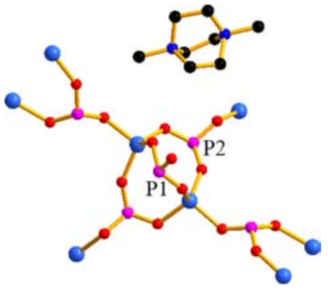

Figure 1. Coordination environment in **1** (Co, light blue; C, black; O, red; N, blue; P, pink).

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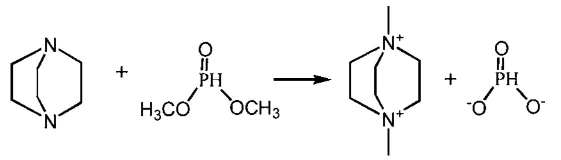
confirmed by the characteristic bands ($\tilde{\nu}$ = 2340 cm^{-1}; for **2**, $\tilde{\nu}$ = 2348 cm^{-1}) in the IR spectrum. Two identical Co atoms are bridged by three phosphites to form a $Co_2(HPO_2)_2(HPO_3)$ unit with a Co···Co distance of 3.5062 Å. The organic Me_2-DABCO cation acts as a template to balance the charge. It is interesting to note that this organic template, Me_2-DABCO, is in situ generated from the alkylation reaction of DABCO and dimethyl phosphite (Scheme 1). Two CH_3 groups in dimethyl phosphite transfer to two N ends of DABCO, which leads to the formation of Me_2-DABCO cations and HPO_3^{2-} anions. To the best of our knowledge, such an alkylation reaction has never been known previously.

Scheme 1



The structure of compound **1** consists of strictly alternating CoO_4 tetrahedral and HPO_3 pseudopyramidal units, which are linked through their vertexes to form a 3D open framework. Viewed along the *a* axis, the structure features two types of channels (Figure 2a). All small channels seem to be left-handed $[Co(HPO_3)]_n$ helices (Figure 2b); thus, the whole framework exhibits chirality. The Me_2-DABCO cations reside in the free voids of the channels as template molecules and interact with the framework O atoms through hydrogen bonds (Figure 3a,b). The length of the H···O hydrogen bond ranges from 2.48 to 2.90 Å. It is not easy to replace these Me_2-DABCO cations through ion-exchange methods. Thermogravimetric analysis (TGA) indicated that these organic Me_2-DABCO cations may be removed from the host framework after heating from 300 to 500 °C under a nitrogen atmosphere (Figure S4 in the Supporting Information); meanwhile, the host framework tends to collapse.

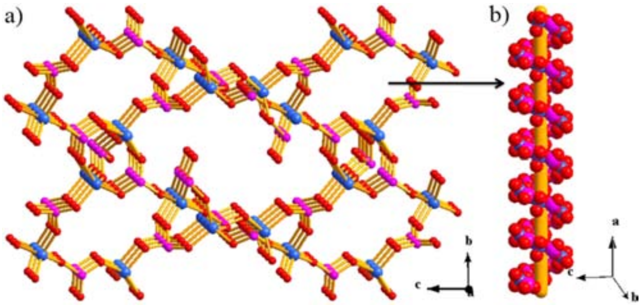


Figure 2. View of the left-handed helix (b) in the framework of **1** (a).

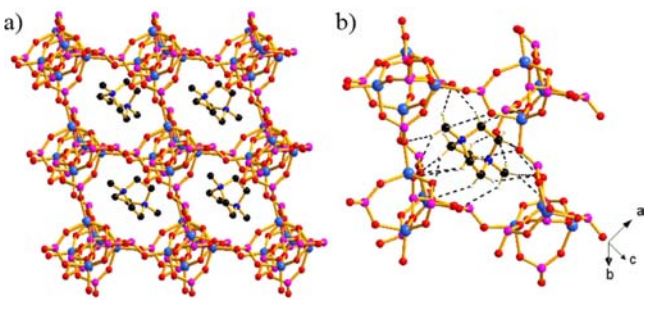


Figure 3. (a) View of the Me_2-DABCO cations in the free voids of the channels. (b) View of the Me_2-DABCO cations interacting with the framework O atoms through hydrogen bonds.

The structural topology of the framework of **1** is also of interest. Considering the μ_2-bridging nature of one HPO_2 group, it is better to reduce the dinuclear $Co_2(\mu_3\text{-}HPO_2)_2(\mu_2\text{-}HPO_3)$ unit into a 4-connected node (Figure 4a). Thus, the whole framework of **1** can be topologically represented as a chiral 4-connected qtz net with the Schläfli symbol of $(6^4.8^2)$ (Figure 4b). As we all know, the qtz net is intrinsic chiral,[13] which corresponds well with the chiral nature of this framework.

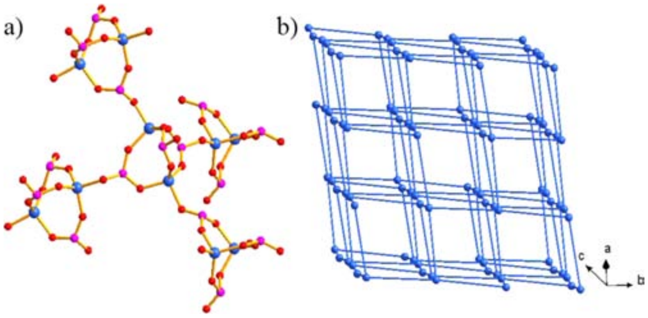


Figure 4. (a) Uninodal 4-connected node represented by the dinuclear unit. (b) 4-connected qtz net of compound **1**.

Magnetic susceptibility studies of compound **1** were carried out on the crystal sample at 1 kOe in the temperature range 2–300 K (Figure 5). Above 50 K, the magnetic susceptibility data well obey the Curie–Weiss law [$\chi_m = C/(T - \theta)$] with a Curie constant *C* of 2.65 cm^3 K mol^{-1} and a negative Weiss constant θ of −43.04 K. The effective magnetic moment of Co^{II} in this system is calculated as 4.66 μ_B, while the value of Co^{II} ($S = {}^3/_2$) ions for the spin-only magnetic moment is 3.87 μ_B. The higher value may be due to the orbital moment contribution of Co^{II} in an oxygen tetrahedral environment. At 300 K, the $\chi_m T$ value is 4.77 cm^3 mol^{-1} K and decreases smoothly to 3.78 cm^3 mol^{-1} K at 100 K. As the temperature continues to decrease, it begins to decrease more steeply to the lowest value of 0.32 cm^3 mol^{-1} K at 2 K. The negative Weiss constant θ and the curve trend of $\chi_m T$ versus *T* might indicate both antiferromagnetic interaction between the Co^{II} centers and spin–orbit coupling effects of the Co^{II} ions.

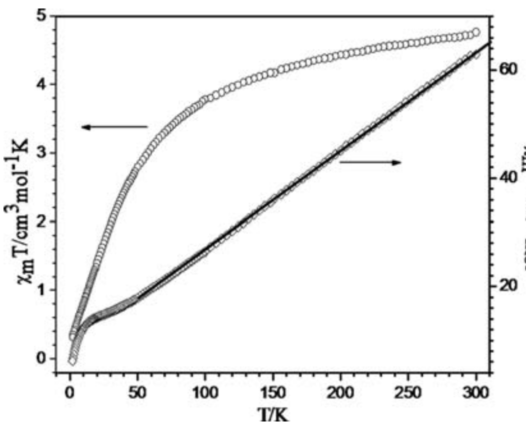


Figure 5. Plot of χ_m and $1/\chi_m$ vs *T* of compound **1** in an applied field of 1 kOe.

In summary, we presented here two chiral metal phosphite open frameworks that were prepared ionothermally in DES. These metal phosphites possess 4-connected qtz nets and contain in situ generated organic templates. An interesting alkylation reaction was also observed. The results further demonstrated that ionothermal synthesis is a powerful method for the synthesis of new functional materials.

■ ASSOCIATED CONTENT

Supporting Information

TGA, powder X-ray diffraction patterns, IR spectra, selected bond lengths and angles, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: zhj@fjirsm.ac.cn.

Notes

The authors declare no competing financial interest.

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(11) (a) Synthesis of **1**: A mixture of DABCO (0.224 g, 2 mmol), $CoCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), dimethyl phosphite (0.5 mL), and the melting choline chloride/1,3-dimethylurea (molar ratio: 1:2) eutectic mixture (2 mL) was added to a 20 mL vial and heated at 120 °C for 2 days. Before solidification, it was washed with ethanol, and dark-purple crystals were obtained (yield: 68%). Elem anal. Calcd for $C_8H_{21}Co_2N_2O_9P_3$: C, 19.22; H, 4.23; N, 5.60. Found: C, 19.10; H, 4.63; N, 5.58. (b) Synthesis of **2**: A mixture of DABCO (0.224 g, 2 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol), dimethyl phosphite (0.5 mL), and the melting choline chloride/1,3-dimethylurea (molar ratio: 1:2) eutectic mixture (2 mL) was added to a 20 mL vial and heated at 120 °C for 2 days. Before solidification, it was washed with ethanol, and colorless crystals were obtained (yield: 42.8%). Elem anal. Calcd for $C_8H_{21}Zn_2N_2O_9P_3$: C, 18.73; H, 4.13; N, 5.46. Found: C, 18.66; H, 4.27; N, 5.45.

(12) Crystal data for **1**: $C_8H_{21}Co_2N_2O_9P_3$, $M = 500.03$, trigonal, space group $P3_121$, $a = 9.8556(5)$ Å, $b = 9.8556(5)$ Å, $c = 15.7233(3)$ Å, $V = 1322.64(10)$ Å^3, $Z = 3$, 2579 reflections measured, 1553 independent reflections ($R_{int} = 0.0185$). The final R1 value was 0.0581 [$I > 2\sigma(I)$]. The final wR2(F^2) value was 0.1880 [$I > 2\sigma(I)$]. The GOF on F^2 was 1.058. Crystal data for **2**: $C_8H_{18}Zn_2N_2O_9P_3$, $M = 513$, trigonal, space group $P3_121$, $a = 9.8355(5)$ Å, $b = 9.8355(5)$ Å, $c = 15.6659(4)$ Å, $V = 1312.44(10)$ Å^3, $Z = 3$, 2472 reflections measured, 1520 independent reflections ($R_{int} = 0.0264$). The final R1 value was 0.0334 [$I > 2\sigma(I)$]. The final wR2(F^2) value was 0.0760 [$I > 2\sigma(I)$]. The GOF on F^2 was 1.038. The structures were solved by direct methods and refined on F^2 full-matrix least squares using the *SHELXTL-97* program package.

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