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# Hydrothermal synthesis and crystal structure of alkaline earth metal (Mg, Ca) based on 2,5-Dimethylbenzene-1,4-diylbis(methylene) diphosphonic acid

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New magnesium phosphonates $Mg(H_2L)_3$ **1** ($H_4L$ = 2,5-dimethylbenzene-1,4 -diylbis(methylene) diphosphonic acid) and $Ca(H_2L)\cdot 2H_2O$ **2** have been hydrothermally synthesized from $H_4L$ and the corresponding metal salts. Complex **1** and **2** have been characterized by IR, powder and single-crystal X-ray diffraction methods. Complex **1** crystallizes in trigonal space group R-3c and complex **2** belongs to the triclinic space group. The complexes both form two-dimensional (2D) network structure and show three-dimensional (3D) network through hydrogen bonds. Thermal stability of complex **1** and **2** have also been investigated. CCDC: 1534599 for **1**; 1536423 for **2**.

## 1. Introduction

Organic and inorganic hybrid materials as a new material combine the excellent properties of organic materials and inorganic materials, and metal phosphonates are a class of compounds with great potential in the field of inorganic-organic hybrid materials. These materials have good thermal stability and acid or alkali resistance, and the synthesis conditions are mild, their skeleton of organic groups will not easily be destroyed. At the same time, it is possible to predict the structure of many metal phosphonate coordination polymers, and the orientation of the target compound can be achieved. Metal phosphonates have attracted wide attention from scientists due to their excellent properties and potential applications in gas adsorption [1], photocatalysis [2], solar cells [3], ion selective materials [4,5], anticorrosion properties [6,7] and many other fields [8–11]. Currently, many functional groups, such as pyridyl [3], carboxyl [12], thiophene [13], amino [14], macrocyclic [15,16] and so on [17–20], are utilized to modify the acid ligands. In this way, one can synthesize the desired directional properties of the metal phosphonates, but their structure is very difficult to control. The choice and design of suitable phosphonic acid bridged ligands can effectively control the structure of the metal phosphonate.

Recently, the diphosphate ligand $H_2O_3P\text{-}R\text{-}PO_3H_2$ has aroused widespread concern. Diphosphonic acid has more coordination sites than monophosphonates. There are three oxygen atoms at both ends of the bisphosphonic acid and thus become hexa-coordinated organic ligands. The theoretical coordination pattern should be three-coordinated at both ends, but the study shows that coordinatied patterns of both ends are two-coordinated [21] single-coordinated [22] or other fashion [23–26]. A variety of coordination modes allow to obtain novel structures and properties of this kind of materials. At the same time, the organic part has the role of spacer, and the pore size of coordination polymers can be easily controlled using different organic groups of bisphosphonic acid. Dibenzoyl as bridges, $-PO_3H_2$ and metal ions can form a variety of structural coordination polymers, such as one-dimensional [27], two-dimensional [28] and three-dimensional structure [29,30]. Although many important results have been achieved in this field, the reports about such complexes are still relatively rare. 2,5-Dimethylbenzene-1,4-diylbis(methylene)diphosphonic acid($H_4L$) containing phosphoryl and hydroxyl groups can be used as diversified coordination points and hydrogen bond receptors, so it is

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**Table 1**
Summary of crystallographic data and structure refinement for complex **1** and **2**.

| Formula | $C_{30}H_{42}MgO_{18}P_6$ (1) | $C_{10}H_{18}CaO_8P_2$ (2) |
|---|---|---|
| Formula weight | 900.76 | 368.26 |
| Crystal size | 0.23 × 0.17 × 0 08 | 0.18 × 0.06 × 0 04 |
| Crystal system | trigonal | triclinic |
| Space group | R-3c | P-1 |
| a, b, c (Å) | 11.0212(5). 11.0212(5), 160.639(7) | 6.9392(6), 9.0237(7), 12.1952(9) |
| $\alpha/^o$ | 90 | 77.961(2) |
| $\beta/^o$ | 90 | 83.718(3) |
| $\gamma/^o$ | 120 | 77.595(3) |
| $V$/Å$^3$ | 16898.2(17) | 727.73(10) |
| Z | 18 | 2 |
| $D_{calcd}$/g cm$^{-3}$ | 1.593 | 1.681 |
| Absorption coefficient | 0.381 | 0.686 |
| F(000) | 8424.0 | 384 |
| θrange($^o$) | 2.776–24.999 | 3.013–25.000 |
| Dataset (h; k; l) | −12 to 10, -11 to 13, -190 to 126 | −8 to 8, -10 to 10, -14 to 14 |
| Total, unique date, $R_{(int)}$ | 3267, 2097, 0.1208 | 2540, 1780, 0.0934 |
| Goodness-of-fit on $F^2$ | 0.983 | 0.990 |
| $R_{1,}$ w$R_2$ | 0.0746, 0.1956 | 0.0542, 0.1040 |

easier to form a variety of frame structures. Under the guidance of the above ideas, we synthesized two new magnesium and calcium phosphonates by hydrothermal synthesis using 2,5-dimethylbenzene-1,4-diylbis(methylene)- diphosphonic acid as ligand, and the crystal structure and thermal stability will be reported in the following content.

## 2. Experimental

### 2.1. Materials and instruments

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

IR spectra were obtained at room temperature using KBr pellets in the range of 4000–400 cm$^{-1}$ on a VECTOR 22 spectrometer. The structures of single crystals of **1**–**2** were determined at 173 K using single-crystal X-ray diffraction measurements. The measurements were performed on a Bruker Smart CCD area-detector diffractometer with graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) in ω-scan mode. The collected data were reduced using the software package SAINT, 25 and semi-empirical absorption correction was applied to the intensity data using the SADABS program. The structure was solved using direct methods, and all nonhydrogen atoms were refined anisotropically by least squares on F2 using the SHELXTL-2014 program. Power X-ray diffraction (PXRD) measurements of the compounds were recorded on a Bruker AXS D8-Focus X-ray diffraction using Cu Kα radiation ($\lambda = 1.540598$ nm), and the X-ray tube was operated at 40 kV and 40 mA. Thermogravimetric analysis (TGA) was performed on a STA 409 PC thermal analyzer under nitrogen at a heating rate of 10 °C·min$^{-1}$ from room temperature to 1000 °C.

### 2.2. Synthesis of ligand ($H_4L$)

1,4-bis(bromothyl)-2,5-dimethylbenzene was prepared according to the reported procedure [31,32].

To a solution of triethyl phosphite (0.52 mL, 6.13 mmol) in a round-bottomed flask (50 mL) were added 1,4-bis(bromothyl)-2,5-dimethylbenzene (0.402 g, 1.38 mmol), refluxed at 125 °C for 24 h, then unreacted triethyl phosphite was removed under reduced pressure. The residue was hydrolyzed by excess concentrated hydrochloric acid. Mixture was filtered to get a white precipitate. Wash the cake three times with dimethylformamide and two times with water, vacuum drying 1 day under the condition of 100 °C, and white solid is obtained. $^1$H NMR (600 MHz, DMSO-$d_6$, ppm): δ6.78 (s, 2H, Ar–H); 2.99 (d, 2H, $J = 18$ Hz, Ar–$CH_2$); 2.71 (s, 2H, Ar–$CH_2$); 2.68 (s, 2H, Ar–$CH_2$); 2.03 (s, 6H, Ar–$CH_3$). IR (KBr pellet,-cm$^{-1}$):3428(m), 2916.70(m), 2264.61(m), 1637.78(m), 1510.68(m), 1462.05(w), 1408.32(m), 1259.88(m), 1198.80(m), 1091.26(m), 1045.66(m), 996.95(m), 952.14(m), 900.29(m), 852.30(w), 763.68(w), 737.72(m),606.86(m), 499.20(w), 473.08(m), 453.97(w)).

### 2.3. Synthesis of complexes

#### 2.3.1. Synthesis of $Mg(H_2L)_3$ (**1**)

A 0.073 g portion (0.25 mmol) of $H_4L$ was mixed with 0.043 g of $MgSO_4$(0.375 mmol) in 10 mL of deionized distilled water, adjust pH to 0.5 with 1 mol/L hydrochloric acid, and then the solution was transferred into a 25 mL Teflon-lined stainless autoclave and heated at 160 °C for three days under autogenous pressure. The vessel was cooled to room temperature in cooling rate 2 °C/h to obtain the colorless hexagonal flaky crystal. IR (KBr pellet, cm$^{-1}$): 3423.27(m), 2918.38(m), 2267.40(m), 1511.53(m), 1407.98(m), 1261.85(m), 1200.90(m), 1091.40(m), 1047.53(s), 991.32(s), 950.62(m), 901.39(w), 763.72(m), 608.07(m), 500.42(w), 470.88(w), 453.92(m).

#### 2.3.2. Synthesis of $Ca(H_2L)\cdot 2H_2O$ (**2**)

Same method was employed to synthesize complex **2**. A 0.0292 g portion (0.10 mmol) of $H_4L$ was mixed with 0.0162 g of $CaCl_2$(0.15 mmol) in 10 mL of deionized distilled water, adjust pH to 3.5 with triethylamine and the mixture was heated in Teflon-lined steel vessel (Volume 25 mL) at 160 °C for three days. The vessel was cooled to room temperature in cooling rate 2 °C/h, and X-ray-diffraction-quality colorless needle single crystals were collected from the Teflon liner by filtration. IR (KBr pellet, cm$^{-1}$): 3517.51(m), 2917.99(m), 2346.42(w), 1637.22(m), 1508.74(m), 1409.30(m), 1264.32(m), 1202.09(w), 1143.88(m), 1121.07(w), 1094.95(m),

**Table 2**
Selected bond distances (Å) for complex **1** and **2**.

| | | | | | |
|---|---|---|---|---|---|
| complex **1** | | | | | |
| Mg(1)–O(4) | 1.887(4) | Mg(1)–O(3) | 1.893(4) | Mg(2)–O(9) | 1.892(4) |
| complex **2** | | | | | |
| Ca(1)–O(2) | 2.329(3) | Ca(1)–O(3) | 2.546(3) | Ca(1)–O(4) | 2.365(3) |
| Ca(1)–O(5A) | 2.359(3) | Ca(1)–O(5) | 2.591(3) | Ca(1)–O(8) | 2.380(3) |
| Ca(1)–O(7) | 2.409(3) | | | | |