

SYNTHESIS AND CHARACTERIZATION OF A NEW METAL ORGANIC FRAMEWORK

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ABSTRACT

The synthesis of a new metal-phosphonate is described in this paper. Mg²⁺ vinylphosphonate has been synthesized by using an equimolecular ratio of reagents in hydrothermal conditions. The compound has been characterized by X-Ray and IR spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetry (TG) and quantum chemical calculations. Last method have been used to establish supramolecular pores size and to predict synthesized compound ability to filter hydrogen, methane, carbon dioxide, carbon monoxide, sulphur dioxide and benzene gases.

INTRODUCTION

Most recent technologies require materials with combined properties, which are not offered by conventional materials. Metal organic frameworks (MOFs) are one of most important synthetic material class because their wide variety of chemical compositions with improved or unusual properties are useful in fields like optics, electronics, mechanics, biology and medicine. Typical applications are smart membranes, new generations of photovoltaic cells, fuel cells, photocatalysts, temperature and humidity resistive sensors and smart microelectronic components [1-3].

Introduction of the organic group into the structure by using phosphorus compounds can be done in various ways, depending on the desired material [4,5].

Metal-phosphonate complexes are MOFs resulted from phosphonic acids reaction with metal salts in hydrothermal conditions. Metal-phosphonates are characterized by organic part being linked to inorganic part into a regular repetitive structure, into a crystalline network [6-8].

MOFs structures are suitable for gas adsorption and storage, competing with other microporous materials such as polymers, zeolites or carbon materials, all presenting channels and pores in the size range of 2.5 to 20 Å [9].

MATERIALS and METHODS

A 100 mL round-bottomed flask was charged with Mg(NO₃)₂·6H₂O (50.0 mmol), vinylphosphonic acid (50.0 mmol), urea (50.0 mmol), and distilled water (50 mL). The pH was adjusted to 2.8-3.1 with an aqueous solution of NaOH (0.10 M). The solution was heated in an oil-bath at 65-80^oC for 75-80 hours. The resulting crystals were collected by filtration and dried in air (yield: 70%). White solid Mg²⁺ vinylphosphonate compound has been obtained.

RESULTS

The synthesized compound has been characterized by X-Ray and IR spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetry (TG) and quantum chemical calculations.

X-Ray powder diffractogram has been performed by using BRUKER D8 Advance diffractometer at characteristic radiation K_{α} of copper, with generator mode 40 kV x 30 mA, and into the secondary beam path having inserted a graphite monochromator for copper characteristic radiation. Goniometer geometry was Bragg–Brentano ($\theta/2\theta$) with divergent incident beam. For the primary beam it have been used a Soller slit and a vertical rectangular diaphragm, and for the secondary (diffracted) beam two vertical slits.

The elementary cell was found to be orthorhombic, and the reticular parameter a representing the distance between crystalline layers of the structure vary by vinyl group nature. Vinyl groups are oriented into interlamellar space, and weak Van der Waals forces keep the layers linked (Figure 1). Magnesium ions are hexacoordinated, and arranged into a distorted tetragonal bipyramid with O-Co-O angles between 58° and 100° [8].

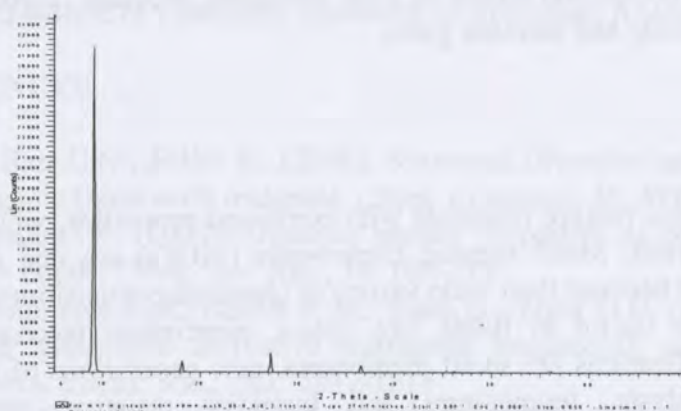


Figure 1. X-Ray powder diffractogram for Mg^{2+} vinylphosphonate

IR recorded spectra of Mg^{2+} vinylphosphonate by using Jasco-FT/IR-4200 reveals two intense absorption bands at 1110 and 1001 cm^{-1} attributed to $-PO_3$ and one weak band at 756 cm^{-1} corresponding to monosubstituted vinyl group. A strong absorption is observed around the 3495 cm^{-1} corresponding to hydroxyl group. The absence of any band in $2700\text{--}2560\text{ cm}^{-1}$, range where P-O and P-OH groups absorption should appear, confirm the Mg^{2+} vinylphosphonate formation.

Morphology analysis of the Mg^{2+} vinylphosphonate have been performed by SEM, with an Inspect S device. Lamellar structure of the compound was observed when magnified to $100\text{ }\mu\text{m}$ scale.

Lamellar structure of the compound has been revealed also by AFM using Nanosurf1 Easy-Scan 2 Advanced Research. Surface morphology is compact, and each layer has at its surface the vinyl phosphonic groups and water that will interfere with neighbor layer, leading to long distance regular arrangement.

Compound decomposition was register by a Perkin Elmer Diamond. thermoscale and plotted in figure 2. Thermal decomposition of the Mg^{2+} vinylphosphonate evolve in 3 clear steps: first in $80\text{--}160^{\circ}\text{C}$ range where 0.3 mg mass loss is attributed to water molecule, second in $160\text{--}245^{\circ}\text{C}$ range where 0.2 mg mass loss is attributed to second water molecule, and third over 420°C where one vinyl group loss occur. First two process are endothermic and last one is exothermic.

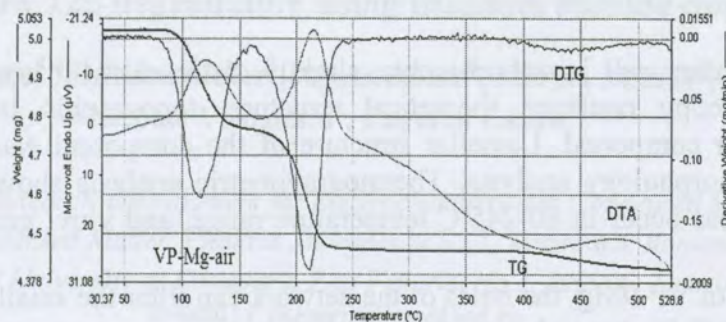


Figure 2. Thermogravimetric curves for Mg^{2+} vinylphosphonate at $20^{\circ}C/min$ heating speed

Gas phase equilibrium geometry of conformers was obtained by semi-empirical PM3-RHF calculations using the Polak-Ribiere conjugate gradient algorithm for geometry optimization. Stop criteria were: SCF convergence of 10^{-5} and RMS gradient of 10^{-2} kcal/A·mol. For the structures with $\frac{1}{2}$ spin number we used half electron approximation. Calculations have been performed with HyperChem7.52 package [10].

To predict the gas filtration property of Mg^{2+} vinylphosphonate metal organic framework, PM3 semi-empirical analysis was performed. The channels of Mg^{2+} vinylphosphonate metal organic framework are $5.14 \times 4.93 \text{ \AA}$ in diameter (Figure 3). The gases used for this study are hydrogen, methane, carbon dioxide, carbon monoxide, sulphur dioxide and benzene (Table 1).

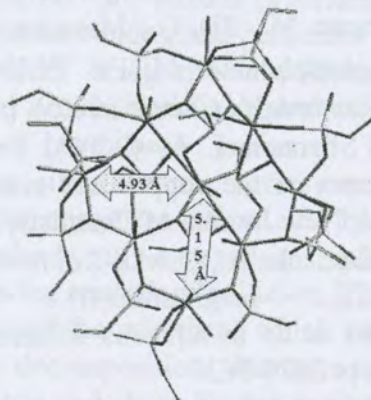


Figure 3. The channels of Mg^{2+} vinylphosphonate metal organic framework

Table 1. The gases used for this study

Gases	Surface area Aprox \AA^2	Surface area Grid \AA^2	Volume \AA^3	Refractivity \AA^3	Polarizability \AA^3	Mass (amu)
H ₂	102.36	91.89	86.43	1.60	0.77	2.02
N ₂	126.56	128.53	138.63	5.4	1.91	28.01
SO ₂	180.11	154.97	179.99	10.68	1.14	64.06
CO ₂	191.89	143.21	164.86	6.38	2.42	44.01
CO	109.16	133.95	147.36	1.95	0.57	28.01
C ₆ H ₆	211.86	241.06	300.89	26.06	10.43	78.11

CONCLUSIONS

- The elementary cell is orthorhombic, slightly distorted, with hexacoordinated Mg^{2+} ions. IR spectroscopy confirms theoretical structure, topographic images revealing a crystalline lamellar compound. Lamellar structure of the compound was indicated also by SEM and AFM morphology analysis. Thermogravimetric analysis shows Mg^{2+} coordinated water molecules loss occur in 80-245°C temperature range, and vinyl group loss occur over 400°C.
- In the case of VP-9Mg, the holes of the network can filter the small molecules (N_2 , H_2 , CO , CO_2 and SO_2). C_6H_6 due to high volume and steric hindrance can not be filter by the test compound. Further investigations will be made for this preliminary study and future applications of this metal organic network will be identified.

Acknowledgments: Research was partially supported by Program no 2, Project no. 2.4 from Institute of Chemistry Timisoara of Romanian Academy.

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