

Inorganic–organic hybrid materials of *p,p'*-diphenylmethylenediphosphinic acid (H_2pcp) with magnesium and calcium ions: Synthesis and characterization of $[Mg(Hpcp)_2]$, $[Mg(Hpcp)_2(H_2O)_4]$, $[Mg(pcp)(H_2O)_3](H_2O)$, $[Ca(Hpcp)_2]$ and $[Ca(pcp)(H_2O)]$ complexes

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Abstract

The *p,p'*-diphenylmethylenediphosphinic acid (H_2pcp) reacts with $Mg(SO_4)$ or $CaCl_2 \cdot 6H_2O$ to give the anhydrous hybrid material $[Mg(Hpcp)_2]$ or $[Ca(Hpcp)_2]$. Both the Mg and Ca derivatives, which are isomorphous, present polymeric 1D structural arrays, where the metal ions are doubly bridged by two $Hpcp^-$ ligands. When the reaction is carried out with $Mg(OH)_2$ (or $Ca(OH)_2$), hydrate metal complexes of the aprotic form pcp^{2-} are obtained, namely the hybrids $[Mg(pcp)(H_2O)_3] \cdot (H_2O)$ and $[Ca(pcp)(H_2O)]$. The magnesium compound presents a hydrogen bonding 2D layered structure, where the water molecules play the important role of cementing together the 1D chains of metal ions bridged by phosphinate ligands. Differently a 2D layered architecture of the calcium derivative is built up by dimeric units of calcium metals bridged by pcp^{2-} ligands, without the action of the water molecule, whose role is limited to stabilize the layer itself. From the mother solution affording the anhydrous $[Mg(Hpcp)_2]$ complex, the hydrate $[Mg(Hpcp)_2(H_2O)_4]$ can be isolated, which is a monomeric complex trapped in a closed 2D net of hydrogen bondings. The solid compounds were characterized by X-ray studies and thermogravimetric analysis.

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1. Introduction

Recently, we have studied the reactions of the bifunctional *p,p'*-diphenylmethylenediphosphinic acid, H_2pcp , with various metal(II) ions. In particular, the anion pcp^{2-} can form hybrid inorganic–organic materials with a variety of structural arrangements according to its proticity and to the metal ion nature [1–7]. Polymeric 1D-chains, 2D-layered structures and 3D-frameworks have been found, where the phosphinate ligand utilizes all of its four oxygen donors,

either chelating one metal in mono or bidentate fashion, or bridging two or more metal ions. Often the overall architecture is thickened by the presence of solvent or coordinated water molecules, which through hydrogen bonds with phosphinate oxygens play a double role, either of increasing the structure dimensionality or stabilizing the structure itself. An additional stabilizing factor in these types of compounds is provided by the arrangement adopted by the organic part of the ligand, namely the phenyl rings, which tend to pack in the lattice as stacked pillars [8].

Now we have considered the interactions of *p,p'*-diphenylmethylenediphosphinic acid (H_2pcp) with magnesium and calcium metal ions. Both anhydrous and hydrate

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hybrid materials, containing Hpcp^- or pcp^{2-} anions have been synthesized and structurally characterized. A great interest concerns the alkaline earth metal phosphates and phosphonates complexes [9–15], owing to their potential for chemical applications in the biomedical research. In particular, methylenebisphosphonates, which contain a stable P–C–P bridge against enzymatic hydrolysis, are commonly used as a therapy for bone formation and resorption disorders [16,17].

2. Experimental

2.1. Materials and methods

All reagents were analytical-grade commercial products and were used without further purification. The *p,p'*-diphenylmethylenediphosphinic acid (H_2pcp) was prepared as previously described [18]. Elemental analyses (C, H) were performed with an EA 1108 CHNS-O automatic analyzer. Thermal analyses (TG/DTG-DTA) were carried out on a Perkin–Elmer Diamond TG-DTA system (SEGAI Service of the University of La Laguna), under a nitrogen atmosphere (flow rate: $80 \text{ cm}^3 \text{ min}^{-1}$) in the range from room temperature to $550 \text{ }^\circ\text{C}$. The crystals of the samples (between 4.755 and 2.707 mg) were heated in an aluminium crucible ($45 \mu\text{L}$) at a rate of $5 \text{ }^\circ\text{C min}^{-1}$. The TG curves were analyzed as weight loss (%) as a function of temperature. The numbers of decomposition steps were identified using the derivative thermogravimetric curve (DTG). The DTA curves were analyzed as differential thermal analysis (DT (μV)).

2.2. Synthesis of $[\text{Mg}(\text{Hpcp})_2]$ (**1**)

A solution of $\text{Mg}(\text{SO}_4)$ (8.5 mg, 0.07 mmol) in water (10 ml) was added to a boiling solution of H_2pcp (40 mg, 0.135 mmol) in 60 ml of water. The resulting solution was boiled till colorless needles started separating. Then the mixture was held at ca. $80 \text{ }^\circ\text{C}$ to complete the precipitation of the complex. The compound was filtered, washed with water and dried in air, at room temperature. Yield, 26.5 mg, 62% based on magnesium.

Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{MgO}_8\text{P}_4$: C, 50.80; H, 4.26. Found: C, 50.65; H, 4.18%.

2.3. Synthesis of $[\text{Mg}(\text{Hpcp})_2(\text{H}_2\text{O})_4]$ (**2**)

The mother solution from the above synthesis was evaporated in air at room temperature affording colorless crystals. Yield, 12 mg, 25% based on magnesium.

Anal. Calc. for $\text{C}_{26}\text{H}_{34}\text{MgO}_{12}\text{P}_4$: C, 45.50; H, 4.99. Found: C, 45.62; H, 5.02%.

2.4. Synthesis of $[\text{Mg}(\text{pcp})(\text{H}_2\text{O})_3]\text{H}_2\text{O}$ (**3**)

A solution of $\text{Mg}(\text{OH})_2$ (8 mg, 0.135 mmol) in 20 ml of water was added to a boiling solution of H_2pcp (40 mg, 0.135 mmol) in 75 ml of water. The resulting solution was

evaporated in air at $80 \text{ }^\circ\text{C}$ till colorless crystals precipitated. Yield, 30 mg, 56.6% based on magnesium.

Anal. Calc. for $\text{C}_{13}\text{H}_{20}\text{MgO}_8\text{P}_2$: C, 40.0; H, 5.16. Found: C, 39.85; H, 5.20%.

2.5. Synthesis of $[\text{Ca}(\text{Hpcp})_2]$ (**4**)

Colorless needles of the complex were obtained with the same method used for the analogous Mg derivative, by using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in the place of $\text{Mg}(\text{SO}_4)$. Yield, 68% based on calcium.

Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{CaO}_8\text{P}_4$: C, 49.53; H, 4.16. Found: C, 49.60; H, 4.22%.

2.6. Synthesis of $[\text{Ca}(\text{pcp})(\text{H}_2\text{O})]$ (**5**)

Colorless platelet like crystals of the complex were obtained with the same method used to prepare $[\text{Mg}(\text{pcp})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, by reacting $\text{Ca}(\text{OH})_2$ in the place of $\text{Mg}(\text{OH})_2$. Yield, 64%, based on calcium.

Anal. Calc. for $\text{C}_{13}\text{H}_{14}\text{CaO}_5\text{P}_2$: C, 44.32; H, 4.01. Found: C, 44.23; H, 4.08%.

2.7. Crystallography

Diffraction data of **2** were collected at room temperature on an Enraf Nonius CAD4 and those of **1** and **5** on a Philips PW 1100 automatic diffractometer, respectively. Unit cell parameters of all the structures were determined from a least-squares refinement of the setting angles of 25 carefully centered reflections. Crystal data and data collection details are given in Table 1. The intensities were rescaled and assigned a standard deviation $\sigma(I)$ calculated using the value of 0.03 for the instability factor k [19]. Lorentz polarization and absorption correction were applied [20]. Atomic scattering factors were taken from Ref. [21] and an anomalous dispersion correction, real and imaginary part, was applied [22]. The structures were solved by direct methods and refined by full-matrix F^2 refinement, with anisotropic thermal parameters assigned to all non-hydrogen atoms in **1** and **2**, while in **5** the anisotropic refinement was limited to calcium, phosphorus and oxygen atoms, owing to the poor data/parameters ratio. The hydrogen atoms, when not detected by a difference Fourier map, were introduced in calculated positions with thermal factors 20% larger than those of the respective carbon atom. The function minimized during the refinement was $\sum w(F_o^2 - F_c^2)^2$, where w is defined as $1/[\sigma^2(F_o^2) + (0.0278P)^2 + 10.83P]$, $1/[\sigma^2(F_o^2) + (0.0947P)^2 + 0.62P]$ and $1/[\sigma^2(F_o^2) + (0.0970P)^2]$ in **1**, **2** and **5**, respectively, [$P = (\max(F_o^2, 0) + 2F_c^2)/3$]. All the calculations were performed on a PC using the WINGX package [23] with SIR-97 [24], SHELX-97 [25] and ORTEP-III [26] programs.

3. Discussion

By reaction of the *p,p'*-diphenylmethylenediphosphinic acid in boiling water solution with magnesium sulfate or

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