# Structural similarities in 1D coordination polymers of alkaline earth diphosphinates

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ABSTRACT

The coordination polymers $[Sr(Hpcp)_2(H_2O)]_n$, **1**, and $[Ba(Hpcp)_2(H_2O)]_n$, **2**, ($H_2pcp = p,p'$-diphenylmethylenediphosphinic acid) are isomorphous and consist of 1D chains. The solid compounds were characterized by X-ray diffraction, solid state NMR spectroscopy and thermogravimetric analysis. The photophysical properties of **1** and **2** were also investigated. The refinement of the crystal structures was based on laboratory X-ray powder diffraction data using the Rietveld method. An analysis of the effect of the size of the alkaline earth cation on the network dimensionality was based on a series of coordination polymers bearing ligands comparable to pcp in shape. We found that, as expected, the size of the metal atoms has a minor role in determining the dimensionality of the network, whereas other factors such as steric requirements of the ancillary groups bonded to the phosphorus atoms or the strong tendency of this type of ligand to chelate metal atoms revealed to be important.

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## 1. Introduction

Networks built up by using metal ion nodes bridged by organic ligands have attracted a great deal of interest in the last decade, due to their potential applications in various fields like gas sorption and separation, ion exchange and catalysis to mention a few [1]. Most of the applied ligands for the network construction are carboxylate- and/or phosphonate-based. In this context, phosphinate anions are valuable alternative ligands for the synthesis of coordination polymers. Polymeric metal mono-phosphinates were well studied in the sixties and seventies of the 20th century [2], finding their main application as flame-retardant reagents [3] or as components in electronic devices [4], replacing thus bromined polymers, which were banned by the European Union. Phosphinates bearing two oxygen atoms are similar either to carboxylates or phosphonates, as highlighted in Scheme 1. On the other hand, the two organic residues $R^1$ and $R^2$ of phosphinates still offer unexplored synthetic possibilities to chemists, which consist in fine-tuning the electronic and steric properties of the ligands.

As far as $p,p'$-diphenylmethylenediphosphinic acid ($H_2pcp$) (Scheme 2) is concerned, we have obtained in conjunction with bi-positive-charged metal atoms several 0D [5–7], as well as 1D or 2D coordination polymers [7–17]. The most encountered characteristics of these latter compounds are: (i) the supramolecular interaction of phenyl rings; (ii) the formation of hydrogen bonds, which are pH- and solvent-dependent; (iii) the effect of the metal coordination geometry on the solid state structure.

Given the increase of the atomic radius (see Table 1) [18], the alkaline earth metals can be used to explore correlations between the size of the cation and the solid state structure, applying the same type of ligand. A clear correlation between network-dimensionality and metal radius was found by Cote and Shimizu [19] in case of group II metal ions. In other cases [20], a common structural type is maintained at the expenses of the coordination number around the metal atom.

In spite of the importance of the economically favorable alkaline earth metal coordination polymers for different fields of applications, the synthetic approaches to vary their solid state properties are far from being exhausted [21]. Magnesium and calcium are important in life sciences [22], while recently barium phosphonate revealed to be a promising candidate to protect steel surfaces from corrosion [23–29]. On the other hand, there is a growing interest in finding new ligands capable of coordinating $^{90}Sr$ and hence removing it from nuclear wastes [30].

In this work, we report the synthesis and solid state structure of two novel coordination polymer of formula $[Sr(Hpcp)_2(H_2O)]_n$, **1**, and $[Ba(Hpcp)_2(H_2O)]_n$, **2**, based on powder diffraction data. Both compounds were compared with the solid state structure of the derivative $[Mg(Hpcp)_2]_n$, **3** [12]. The CP-MAS $^{31}P$ NMR spectra of **1–3** were registered. In case of **1** and **2** the solid state structure obtained from X-ray diffraction experiments was confirmed, while for **3** a new X-ray data collection at low temperature was necessary
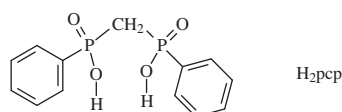
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[1] Passed away on January 15th 2012.

**Scheme 1.**

**Scheme 2.**

H$_2$pcp
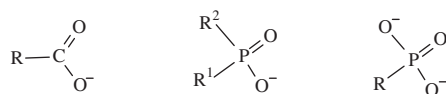
**Table 1**
Empirical atomic radius in Å for alkaline earth metals.

| Be | Mg | Ca | Sr | Ba |
|------|------|------|------|------|
| 1.05 | 1.25 | 1.80 | 2.00 | 2.15 |

to fully rationalize the unexpected $^{31}$P NMR pattern. The fluorescence spectra and the thermal behavior of **1** and **2**, studied by coupling thermogravimetric TG-analysis and temperature dependent X-ray diffraction (TDXD), were also shown. Finally we analyzed a series of alkaline earth complexes and coordination polymers bearing ligands comparable to pcp in shape in order to find relationships between structure and dimensionality of the network with factors such as the size of the cations or the steric hindrance of the ligands.

## 2. Results and discussion

### 2.1. Synthesis and description of the solid structure

The reaction between H$_2$pcp and strontium nitrate or barium nitrate in boiling water gave the corresponding coordination polymers of the formula [M(Hpcp)$_2$·(H$_2$O)]$_n$ M = Sr(II) (**1**), Ba(II) (**2**), as white crystalline material. The two compounds share the ligand as monoprotic acid. The presence of a water molecule in the crystal lattice was confirmed by IR spectroscopy and TG analysis. These complexes are isomorphous forming an 1D coordination polymer. As a consequence, only the solid state structure of **1** is described in details. Fig. 1 shows the metal coordination modes of the ligand in compound **1**.

The Sr atom coordinates to eight oxygen atoms, which stem from four different Hpcp$^-$ ligands and one water molecule (see Fig. 1a). The Sr–O distance in the case of the coordinated water molecule is 2.45(3) Å, while the other Sr–O distances are in the range of 2.38(1)–2.89(1) Å. Two independent Hpcp$^-$ ligands are present in the unit cell, one coordinates to three metal atoms, with two oxygen atoms in bridging position between two different metal centers (see Fig. 1b), while the other Hpcp$^-$ ligand chelates one metal center with two oxygen atoms (Fig. 1c). The latter ligand coordination mode is often encountered in the pcp-based coordination polymers [8].

The ligand showed two different P–O distances of ca. 1.45 and 1.50 Å. The latter P–O distance was assigned to oxygen atoms involved in hydrogen bonding or in the η$^2$-coordination to the Sr metal atom. The oxygen atoms O2 and O6 showed short contacts to the oxygen atoms O4 and O8, respectively (O2–O4 2.56 Å, O6–O8 2.60 Å), which is indicative for the presence of strong hydrogen bond interactions. The overall structure consists of 1D polymer
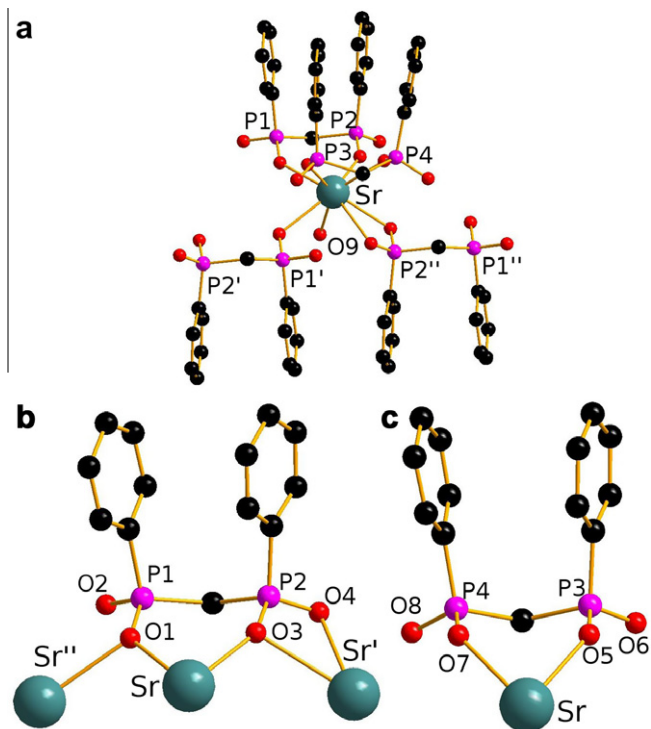


**Fig. 1.** Selected views of the solid state structure of **1**, without hydrogen atoms, showing: (a) the coordination environment of Sr; (b and c) the coordination mode of Hpcp$^-$ to Sr. Color code: O, red; H, white; C, black; P, pink; Mg, gray; Sr, cyan. Selected bond lengths (Å0 for **1**: Sr–O1 = 2.644(17); Sr–O1′ = 2.665(14); Sr–O3 = 2.375(14); Sr–O3′ = 2.867(17); Sr–O4 = 2.890(17); Sr–O5 = 2.557(13); Sr–O7 = 2.676(12); Sr–O9, 2.454(27). Symmetry transformations used to generate equivalent atoms: #′ (−x, 1 − y, −z), #″ (1 − x, 1 − y, −z). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

chains running along the *a* crystallographic direction (see Fig. 2a and b). The inorganic layer is somewhat included in the organic part of the polymer, namely the phenyl rings of the pcp ligand and reinforced by hydrogen bonds that extend along the axis of the chain.

The 1D coordination polymer of **1** and **2** was compared with that of the Mg-analogue of the formula [Mg(Hpcp)$_2$]$_n$ (**3**) [12]. A new structure determination of **3** based on X-ray data collected at 150 K was necessary to expain the CP-MAS $^{31}$P NMR pattern of **3** (*vide infra*) and in the discussion we use this new data. The magnesium atoms lie on a inversion center and are coordinated by six oxygen atoms of four different Hpcp (see Fig. 3). In the asymmetric unit cell only one Hpcp$^-$ ligand is present and all the non-protonated oxygen atoms are engaged in the metal coordination. There is a strong hydrogen bond between O3 and O2′ (symmetry transformation used to generate equivalent atoms: #′ (1/2 − x, 1/2 − y, 1 − z). For **1** and **2** the hydrogen bonds between the Hpcp$^-$ ligands were at the exterior part of the polymer chain and they have a well defined structural role in the overall architecture, while in **3** the hydrogen bond seems to assist the supramolecular architecture that is dictated by the metal coordination and by the arrangements of the phenyl rings. In particular the phenyl group bonded to P2 is disordered over two position with an occupancy factor of almost 50%. The latter structural feature was ignored in the precedent refinement but it becomes evident in the $^{31}$P MAS NMR spectra.

The differences between the 1D chain in **1** and **2** versus **3** are visualized in Fig. 2. A single chain of the two types and the packing of the chains perpendicular to the elongation direction is shown. In **1** the pcp ligands are parallel along the elongation axis of the 1D