How the Organic Moiety Drives the Coordination Chemistry of Metal Phosphonates: The First Enantiomerically Pure Zinc Phosphonate

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The first enantiomerically pure metallophosphonate, (*R*)-$Zn[O_3PCH_2P(O)(CH_3)(C_6H_5)]\cdot H_2O$ has been prepared. The layered arrangement in this compound is drastically different from that observed in the racemic series; this observation gives clear evidence of the critical role played by the organic moiety that fully drives the coordination chemistry of phosphonic acids with transition metals.

Metal phosphonate chemistry is undergoing rapid expansion, with applications in various areas such as ion exchange, catalysis, sensors, proton conductors, magnetism, or photochemically active materials.[1] Furthermore, an attractive feature is their potential for supramolecular assembly, provided that the structure of the phosphonate framework can be finely tuned by the suitable design of the RPO_3H_2 phosphonic acid precursor. For that purpose, it is essential to know, for a given metal, the role played by the organic moiety R attached to the phosphorus atom [via its shape, its rigidity, and the number and nature of its functional groups], on the structure and dimensionality of the resulting metal phosphonates. In this context, we have recently reported the coordination chemistry of phosphonic acids bearing functionalities of various bulks, showing that a control of the dimensionality of zinc phosphonates could be achieved.[2] Another aspect that has never been studied is the possibility to get enantiomerically pure phosphonate networks using chiral precursors. In this paper, we report the synthesis and structural characterization of the first enantiomerically pure metal phosphonate: (*R*)-$Zn[O_3PCH_2P(O)(CH_3)(C_6H_5)]\cdot H_2O$ (compound **A**), based on mixed phosphonic acid−phosphane oxide chiral building blocks.

The phosphonic acid $H_2O_3PCH_2P(O)(CH_3)(C_6H_5)$ racemate was prepared as previously described[2c] and the optical resolution was performed using quinine to give a 1:1 complex [quinine:$H_2O_3PCH_2P(O)(CH_3)(C_6H_5)\cdot 2\,H_2O$] in 81% yield (based on one of the enantiomer). The complex was treated with two equivalents of aqueous sodium hydroxide, and after extraction with dichloromethane to remove quinine, the pure enantiomeric (*R*)-form of the acid was quantitatively recovered by evaporation of the aqueous phase ($[\alpha]_D^{20} = -18$ ($c = 1.0$ in 1 M HCl)); reaction with zinc nitrate in water, under neutral-pH conditions, then yielded compound **A** in 85% yield. To ensure that all the crystals of the preparation corresponded to the same enantiomeric form, the specific rotation of compound **A** (after dissolution in 1 M HCl) was measured and found to be identical to that of the isolated resolved phosphonic acid precursor.

The structure consists of layers (*ab* plane; Figure 1) in which the zinc atoms are tetrahedrally coordinated with three oxygen atoms from the phosphonate groups [Zn−O: 1.891(6)−1.918(7) Å] and one oxygen atom from the phosphane oxide moiety [Zn−O: 1.993(5) Å]. In each layer, the zinc atoms are arranged in 12-membered rings, constructed by corner-sharing of alternating ZnO_4 and PO_3C tetrahedra. The phenyl groups are oriented toward the interlayer space, with a basal spacing ($c/2$ = 12.65 Å) shorter than the usual 15−16 Å value observed for layered metal phenylphosphonates, due to a close-packing of the sheets caused by the interdigitation of the aromatic rings from neighbouring slabs (Figure 2). The lattice water molecules are present

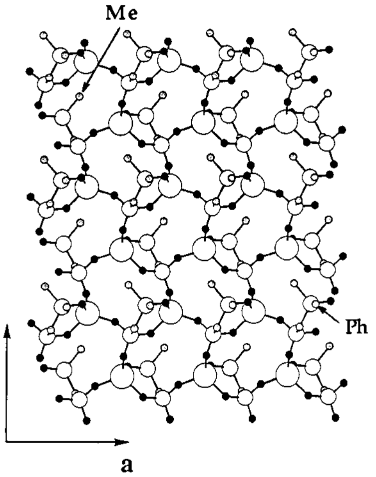

Figure 1. Schematic representation of a (*R*)-[$Zn(O_3PCH_2$-$P(O)(CH_3)(C_6H_5)]\cdot H_2O$ layer viewed down the *c* axis. The water molecule O(5) and the carbon atoms that are not directly bonded to the phosphorus atoms have been omitted for clarity (Me = methyl, Ph = phenyl)

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between the layers, presumably weakly hydrogen-bonded to phosphonate oxygen atoms [dO(H_2O)−O(phosphonate) = 3.06(1), 3.17(1), and 3.34(1) Å], thus explaining the low temperature (55°C) at which the dehydration takes place.

One important feature of this compound is the configuration of the phosphorus atom of the phosphane oxide that was unambiguously determined to be (*R*) (see Figure 2). Moreover, in a previous study, we had prepared from the phosphonic acid racemic precursor, in similar pH conditions, a layered zinc phosphonate (**B**) of composition $Zn[O_3PCH_2P(O)(CH_3)(C_6H_5)] \cdot 0.67\,H_2O$, in which the phosphane oxide is similarly bonded to zinc. It is important to note that the metal−PO_3 arrangement within the layers in this latter product (Figure 3) is different from that described for **A**; for example we can notice the presence of 16-membered rings forming at their junction smaller rings (see detail in Figure 3), in which the $O_3PCH_2P(O)(CH_3)(C_6H_5)$ units are arranged in pairs of opposite configurations, leading to a racemic zinc phosphonate. This observation clearly demonstrates that the inorganic framework has to adapt itself even to the presence of chiral atoms on the organic backbone, according to its racemic or optically pure character.

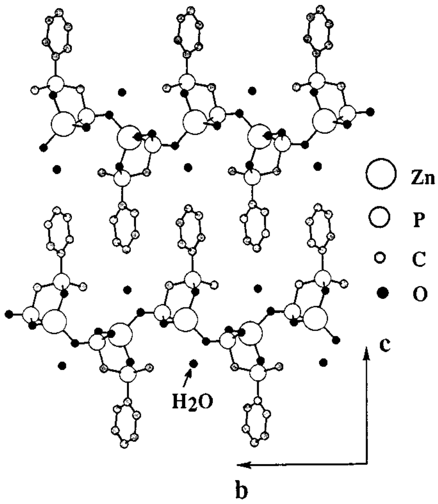

Figure 2. Schematic representation of (*R*)-$Zn[O_3PCH_2P(O)(CH_3)(C_6H_5)] \cdot H_2O$ (**A**) as seen perpendicular to the *a* axis; the (*R*)-configuration of the phosphorus atom of the phosphane oxide is clearly apparent

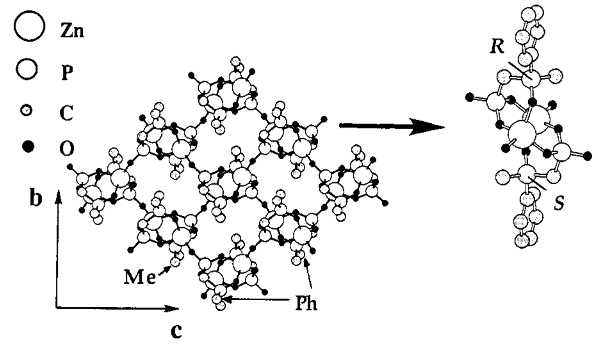

Figure 3. Schematic representation of a (*R*/*S*)-$Zn[O_3PCH_2P(O)(CH_3)(C_6H_5)] \cdot 0.67\,H_2O$ (**B**) layer as seen perpendicular to the *a* axis, according to ref.[2c] The water molecule O(5) and the carbon atoms that are not directly bonded to the phosphorus atoms have been omitted for clarity (Me = methyl, Ph = phenyl). A detail of the structure showing the pairs of $O_3PCH_2P(O)(CH_3)(C_6H_5)$ blocks of opposite configuration (*R*) and (*S*) is given.

In summary, this study nicely gives an additional evidence for the critical role played by the organic moiety that fully drives the coordination chemistry of phosphonic acids with transition metals. Furthermore, when the chiral organic precursor is enatiomerically pure, no racemization occurs during the preparation of the corresponding metal phosphonate, leading to an enantiomerically pure product.

Experimental Section

Synthesis of (*R*)-$Zn[O_3PCH_2P(O)(CH_3)(C_6H_5)] \cdot H_2O$ (A): A solution of 500 mg of racemic $H_2O_3PCH_2P(O)(CH_3)(C_6H_5)$ [2.13 mmol] in 30 mL of hot ethanol was added to a solution of 1.039 g of quinine [3.2 mmol] in 15 mL of ethanol. The mixture was allowed to stand for 5 days at room temperature, after which the crystals that gradually appeared were isolated by filtration, corresponding to a 1:1 dihydrate complex (81% yield. Elemental analysis: found: P 9.97, C 56.29, H 6.76, N 4.72; calcd. for $C_{28}P_2O_8N_2H_{40}$: P 10.42, C 56.56, H 6.78, N 4.71. $[\alpha]_D^{20} = -153$ (c = 1.0 in 1 M HCl). The complex (150 mg) was then suspended in 45 mL of water; 2 equivalents of sodium hydroxide were then added and the mixture was stirred for 1 hour. The reaction medium was then extracted 2 times with dichloromethane, allowing to recover quinine in the organic phase. The pure enantiomeric (*R*)-form of the acid was then quantitatively recovered by evaporation of the aqueous phase ($[\alpha]_D^{20} = -18$ (c = 1.0 in 1 M HCl)). The same result was obtained using cinchonidine as the resolving agent. Then a mixture of zinc nitrate (0.3 mmol) and the resolved phosphonic acid described above (0.2 mmol) in 20 mL water was placed in the PTFE cell of an autoclave, that was sealed and kept at 110°C in a drying oven for 3 days. Compound **A** was obtained as white crystals, used for the X-ray structure determination, in 85% yield.

Structure Determination: Data were collected from a single crystal (0.2 × 0.04 × 0.006 mm) on an STOE image plate system (ω scan, $\sin(\theta)/\lambda \leq 0.57$) and a Nonius CAD-4F diffractometer (ω/2θ scan, $\sin(\theta)/\lambda \leq 0.68$) at room temperature. After the usual Lorentz-polarization and decay (< 2%) corrections, the 8233 reflections from the IPDS and the 4234 reflections from the CAD4 were merged based upon the intensities of 218 common reflections with $I/\sigma(I) > 10$. Since the data set was consistent with the $P2_12_12_1$ space group, the reflections were then averaged according to the point group 222 (internal (R) value of 7.5%). Data processing and structure refinements were carried out with the JANA98 program.[3] Direct methods (using SHELXTL V5.0 package)[4] revealed the positions of all Zn and P and some C and O atoms. Subsequent full-matrix, least-squares refinements on F followed by difference Fourier syntheses revealed the position of the remaining O and C atoms. All hydrogen atoms were refined, but those of the water molecule were placed at their theoretical positions. The CH_3 group was refined as a rigid body. The refinement of the zinc, phosphorus, oxygen, and carbon atoms with independent anisotropic displacement parameters (ADP) converged with $R/wR = 0.0309/0.0312$ for 1071 independent reflections with $I/\sigma(I) > 3$ and 148 parameters. The hydrogen ADPs were restrained to those of the atom the hydrogen atom was attached to.

Crystal data: $ZnP_2O_4C_8H_{10} \cdot H_2O$; orthorhombic $P2_12_12_1$; a = 5.5378(11), b = 8.4143(12), c = 25.270(8) Å, V = 1177.5(5) Å^3

from the centering of 25 high angle reflections (CAD4) and monochromated Mo-K-$L_{2,3}$ radiation; $Z = 4$; $M = 315.5$; $\rho_{\text{calcd.}} = 1.779\ \text{g.cm}^{-3}$; $\mu = 23.5\ \text{cm}^{-1}$; residual electron density [−0.49, +0.39] e/Å^3. The absolute configuration was determined by refining the inversion twin ratio. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112086. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223/ 336-033; E-mail: deposit@ccdc.cam.ac.uk].

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