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Coordination chemistry of phosphonic acids with special relevance to rare earths

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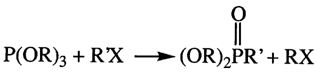
Abstract

The use of phosphonic acids as ligands for metal coordination and design of extended structures is described. The number and type of structures that can be designed is limited only by our ability to synthesize the desired phosphonic acid. The synthesis of metal phosphonates, open framework structures, self-assembled hydrogen bonded structures and rigid highly porous materials will be described. A number of these materials are natural nanoparticles as small as 4 nm with active functionalities. Special attention will be paid to rare earth phosphonates. The great range of coordination compounds that can be designed stems from the tetrahedral nature of the phosphonate group and the large number of protons that can be replaced in polyphosphonic acids.

Keywords: Phosphonic acid coordination compounds; Nanostructures; X-ray diffraction; Chemical synthesis; Lanthanide separations

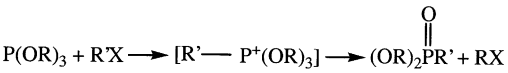
1. Phosphonic acids

We may represent a simple monophosphonic acid as RPO_3H_2, where R is an organic group and the defining characteristic is a P–C bond. An important example is phenylphosphonic acid [(1) in Scheme 1]. There are also bis- and trisphosphonic acids, Scheme 1 (2 and 3). As a variation one or two of the phosphonic acids may be replaced by carboxylic acids. Another class of important ligands are those containing amino or iminogroups, (4), (5). These ligands are invariably present in solution as zwitterions as illustrated in Scheme 1 for nitrilotris(phosphonic acid). The number and types of ligands are endless because of the ease of attaching a phosphonic acid group to the organic moiety. The most common synthetic route utilizes bromo or iodo derivatives in an Arbuzov type reaction.



$$P(OR)_3 + R'X \longrightarrow (OR)_2\overset{\overset{O}{\|}}{P}R' + RX \qquad (1)$$

This reaction was discovered by Michaelis and Kaehne [1] and later was explored extensively by Arbuzov [2]. Temperatures of 150–200 °C are required depending on the R' group. It is reasonably well established that the Michaelis–Arbuzov reaction occurs in two stages via an ionic phosphonium intermediate accompanied by valency expansion of the phosphorus, Eq. (2).



$$P(OR)_3 + R'X \longrightarrow [R'\text{—}P^+(OR)_3] \longrightarrow (OR)_2\overset{\overset{O}{\|}}{P}R' + RX \qquad (2)$$

The ester is then hydrolyzed in strong hydrochloric acid. In the event that R' is an aryl group, then a catalyst, $NiCl_2$ or $PdCl_2$, is required to promote the reaction.

In order to prepare iminophosphonic acids a Mannich type reaction is used [3] with formaldehyde and diethylphosphite.

$$RNH_2 + 2CH_2O + HP(OC_2H_5)_2 \xrightarrow[8\,h]{60\text{–}70\,^{\circ}C} RNHCH_2PO(OC_2H_5)_2 + CH_3OH$$

The type of complex one wishes to make can be designed through the choice of ligand and metal. Many buzz-words have been coined to describe different modern synthetic procedures, procedures that can be described by one or more of them, namely crystal engineering, self-assembly, nanochemistry, supramolecular, *chimie douce* (soft chemistry). However, phosphonic acid chemistry identifies with all of them. We shall illustrate all of these procedures in turn.

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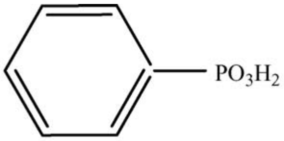
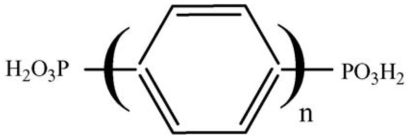


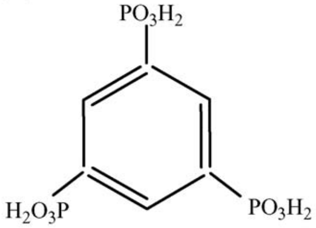
(1)



(2a)

$H_2O_3P(CH_2)_nPO_3H_2$

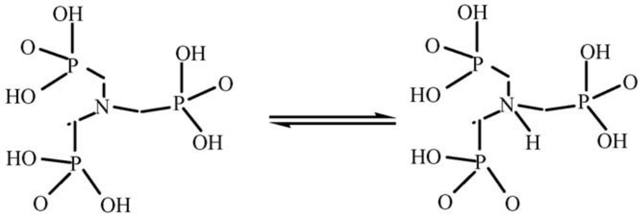
(2b)



(3)

$H_2O_3PCH_2HNCH_2CH_2NHCH_2PO_3H_2$

(4)



(5)

Scheme 1.

2. Monophosphonic acid derivatives

Simple monophosphonic acids readily form layered compounds with many four, three and two valent cations. The prototype is the zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, first reported by Alberti et.al. [4]. The crystal structure was determined from its X-ray powder pattern [5] which required 30 days of hydrothermal treatment at 180 °C to produce a sufficiently well crystallized product. The crystals belong to space group C^2/c with $a = 9.0985(5)$, $b = 5.4154(3)$, $c = 30.235$ Å, $\beta = 101.333(5)^\circ$. The in-plane a and b dimensions are very close to those corresponding dimensions in α-zirconium phosphate, $Zr(O_3POH)_2{\cdot}H_2O$ [6]. The layer structures are very similar except that the phenyl groups are tilted relative to the layers by 30° whereas the hydroxyl groups in the phosphate are essentially perpendicular to the layers. This tilt arises from the fact that in the C^2/c space group the Zr atoms are constrained to lie in the plane, whereas in α-zirconium phosphate, these atoms are slightly above and below a mean plane through the layer. The interlayer distance of this compound is 14.82 Å (Fig. 1).

The phenylphosphonate may be considered as the prototype compound of the phosphonate derivatives of the Group (IVB) metals. All of the layered alkyl and aryl derivatives of this group, prepared by direct precipitation, have the α-layered structure. The in-layer dimensions of the parent α-ZrP are approximately 9.06 Å × 5.3 Å, or about 48 Å^2. Within this area are two phosphate groups bonded to the layers. Any alkyl or aryl group whose lateral area does not exceed 24 Å^2 can fit onto an α-ZrP type layer.

Lanthanides and some divalent metals also form layered compounds similar to that of zirconium. They are able to do this by retaining one and two protons, respectively to obtain the required two to one phosphonic acid to metal ratio.

Formula	Ionic radius (Å)	Coordination number
$Zr(O_3PC_6H_5)_2$	0.72 Zr^{4+}	6
$Ca(HOPC_6H_5)_2$	1.00 Ca^{2+}	7
$La(O_3PC_6H_5)(HO_3PC_6H_5)$	1.18 La^{3+}	8

The lattice dimensions in the layers are shown in Fig. 2 according to Cao et al. [7]. Ligands with alkyl chains form similar layered compounds with the size of the interlayer spacing a function of the length of the chain.

It is instructive to examine the way that eight coordination is achieved with the same number of oxygen atoms available as in the six coordinate zirconium compounds [8]. Both phosphonate groups chelate the lanthanide (La, Ce, Sm) ion and the oxygen of each chelate ring donates a lone pair to an adjacent lanthanide ion. This arrangement forms chains as shown in Fig. 3. The third oxygen of each phosphonate group then connects the chains by bridging to metal ions in adjacent chains supplying the remaining two oxygens.

The proton was not found in the difference map. However, consideration of the P–O interatomic distances showed that two of the P–O bonds were found to be longer than the others. P1-01, 1.57(1) Å and P2-04, 1.55(1) Å and they are separated by a distance of 2.41 Å. The oxygens are two coordinate so they could be protonated. Thus, either the proton bonds to either of these oxygens or it is shared equally between them. A ^{31}P MAS NMR gave a single peak so either the H is equidistant between them or randomly distributed between these P–O groups.

A second type of lanthanium complex of composition $La_2(O_3PC_6H_5)_3{\cdot}3H_2O$ was synthesized at pH values above 8 [8]. Its X-ray powder pattern was insufficiently developed to effect a structure solution. However, the interlayer spacing was 15.2 Å compared to 15.9 Å for the proton containing derivative indicating its layered nature. Phosphites have been shown to form similar layered compounds with lanthanides [9]. Therefore, a series of mixed phosphite-phosphonate derivatives was prepared [10]. Table 1 provides the composition of the several derivatives and their interlayer spacings. The derivative with the smallest interlayer spacing contains the least amount of phenyl phosphonate. This decrease indicates that the layers are interdig-