



Mono and dinuclear group 12 phosphonates derived from a sterically encumbered phosphonic acid: Observation of esterification



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ABSTRACT

Metal phosphonates $[\text{Zn}_2(\text{dtbhp})_2(\text{TMEDA})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{CH}_3\text{CN}$ (**1**), $[\text{Cd}_2(\text{dtbhp})_2(\text{TMEDA})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{CH}_3\text{CN}$ (**2**), $[\text{Cd}_2(\text{mdtbp})_2(1,10\text{-phenanthroline})_4] \cdot (\text{ClO}_4)_2(\text{CH}_3\text{OH})_2$ (**3**), and $[\text{Cd}(\text{dtbhp-H})_2(2,2'\text{-bipyridine})_2] \cdot (\text{dtbhp-H})_2$ (**4**) have been synthesized at room temperature from a reaction between a suitable metal precursor, 3,5-di-tert-butyl-2-hydroxybenzylphosphonic acid (dtbhp-H₂) and an ancillary ligand, tetramethylenediamine (TMEDA), 1,10-phenanthroline and 2,2'-bipyridine; Single crystal X-ray structure determination reveals that compound **1** crystallizes in the orthorhombic *Fdd2* space group, while compounds **3** and **4** crystallize in the triclinic *P1̄* space group. A rare P–O–H bond esterification is observed in compound **3**, presumably catalyzed by perchloric acid formed in the reaction. Compounds **1–3** are discrete dinuclear complexes while monomeric complex **4** forms a 1D polymeric chain through extended intermolecular hydrogen bonding, aided by free P–OH and P=O groups of the coordinated as well as the lattice phosphonic acid.

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1. Introduction

Organic–inorganic hybrid materials constitute an important class of compounds within the area of materials chemistry. Mixed organic–inorganic materials, where the organic and inorganic components complement each other in structure and function, lead to solid-state materials with composite or even new properties [1–4]. Metal phosphonates are amongst the most suited candidates for the design of organic–inorganic hybrid materials [5–8]. In recent years, increased attention has been paid to the exploration of novel metal phosphonate compounds because such materials potentially have applications as sorbents and catalysts as seen in traditional zeotype materials, with the added benefit that the nature of the internal surface of phosphonate materials may be altered by changing the organic functional group of the starting phosphonic acid [5]. It has often been observed that the phosphonate materials containing divalent transition metal cations form lamellar structures, where the metal ions are bridged by the phosphonate groups, and the remaining organic part of the acid is hanging in the interlayer region [5,9–11]. The divalent transition metal phosphonates are of particular interest because they are soluble in acid solution and, therefore, are more easily crystallized compared to those containing tetravalent metal ions [12]. Among the transition metal phosphonates a number of zinc phosphonate compounds have been prepared, most of which have been structurally

characterized by single-crystal diffraction techniques or by ab initio structure solution from X-ray powder diffraction data. These include monophosphonates [13,14], diphosphonates [14–16], and functionalized phosphonates [16–20]. Structures of these compounds range from one-dimensional chain, two dimensional layer to three-dimensional pillared layers or open framework solids. Very recently Zheng and co-workers has reported a number of functionalized phosphonates $[\text{Zn}_2(4\text{-cppH})_2(\text{L}_1)]$, $[\text{Zn}_3(4\text{-cpp})_2(\text{L}_2)] \cdot 2.5\text{H}_2\text{O}$, and $[\text{Zn}_3(4\text{-cpp})_2(\text{L}_3)] \cdot \text{sH}_2\text{O}$ where $\text{L}_1 = 1,4\text{-bis}(\text{imidazol-1-ylmethyl})\text{benzene}$, $\text{L}_2 = 1,3\text{-bis}(\text{imidazol-1-ylmethyl})\text{benzene}$, $\text{L}_3 = 1,2\text{-bis}(\text{imidazol-1-ylmethyl})\text{benzene}$ and $4\text{-cppH}_3 = 4\text{-carboxyphenylphosphonic acid}$ [21]. In contrast to zinc phosphonate compounds, those involving cadmium phosphonates are relatively few, albeit exhibiting similar structural features to those of zinc phosphonates. The recently structurally characterized cadmium phosphonates includes $[\text{Cd}(3\text{-pyridylphosphonate})_2]\text{DMSO}$, $\text{Cd}(4\text{-pyridylphosphonate})_2$, $\text{Cd}(\text{ethyl-4-pyridylphosphonate})_2$ [22], $\text{Na}_2[\text{Cd}_2(\text{H}_2\text{O})_3(\text{O}_3\text{PCH}(\text{OH})\text{CO}_2)_2] \cdot 2\text{H}_2\text{O}$ [23], $[\text{Cd}(\mu\text{-Cl})_2(2\text{pypp})]_n$ [24], and $[\text{Cd}_3(\text{H}_2\text{O})_3((\text{O}_3\text{PCH}_2)_2\text{NH}-\text{CH}_2\text{C}_6\text{H}_4-\text{COOH})_2] \cdot 11\text{H}_2\text{O}$ [25]. Recently our group has reported on the alkali metal derivative of a bis-functionalized phosphonic acid forming a 3D network structure [26].

The use of sterically hindered and lipophilic phosphonic acids possessing additional functional groups has led to the isolation of soluble functional metal phosphonates. Another strategy that has also been successful in synthesizing discrete phosphonate clusters is the use of an ancillary N-donor ligands in conjunction with a phosphonic acid. Our group has recently focused on a variety of

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coordination modes leading to the formation of a number of metal cluster compounds especially in the presence of a secondary N-donor and/or O-donor auxiliary ligands such as TMEDA, 2,2'-bipy and 1,10-phenanthroline. Building up on our studies on phosphonic acids and phosphate esters as ligands [27–43], we have explored the coordination chemistry of a benzyl phosphonic acid with phenol side group towards zinc and cadmium ions in the presence of N-donor ligands with that objective to generate metalphosphonates that possess phenolic –OH functionalities. The results of this investigation, reporting the isolation of mono and dinuclear metal phosphonates, are described herein.

2. Results and discussion

2.1. Synthesis of 3,5-di-tert-butyl-2-hydroxybenzylphosphonic acid (L)

The phosphonic acid ligand [44] used in this work has been prepared in three steps using the Michaelis–Arbuzov's reaction starting from 2,4-di-tertbutyl phenol as shown in Scheme 1.

2.2. Synthesis and characterization of

$[M_2(dtbhp)_2(TMEDA)_2(H_2O)_2] \cdot 0.5CH_3CN$ ($M = Zn$ (**1**); Cd (**2**))

Compound **1** has been prepared from the reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with dtbhp- H_2 in presence of N-donor ancillary ligand, TMEDA in 1:1:1 stoichiometric ratio using CH_3CN-H_2O mixture (1:1) as solvent at room temperature (Scheme 2). Analytical and spectroscopic purity of the compound has been established by elemental analysis, FT-IR and NMR (1H and ^{31}P) spectroscopic studies (Table 1). The obtained elemental percentages are supportive to the formulation of **1** (Table 1). In the IR spectrum, the presence of broad ν_{O-H} absorption at 3424 cm^{-1} indicates the presence of water molecule, either in the coordination sphere of the metal or in the lattice. The characteristic absorptions for $\nu_{asy(C-H)}$, $\nu_{(P-O-O)}$ and ν_{M-O-P} vibrations are observed at 2953, 1118 and 1065 cm^{-1} respectively. In the 1H NMR spectrum, the methyl protons of the two $C(CH_3)_3$ groups on the aromatic ring and the $N(Me)_2$ group appear as three well resolved singlets in the range of δ 1.23–1.35 ppm while the methylene protons of $-N(CH_2)_2N-$ are observed as multiplets in the range δ 2.00–2.40 ppm. A doublet is observed at 3.01 ppm for the $Ar-CH_2$ protons ($^2J_{P-H} = 18\text{ Hz}$). Aromatic protons resonate in the range δ 6.95–7.01 ppm. For the phenolic O–H protons, two singlets are observed at δ 8.50 and 8.60 ppm. The ^{31}P NMR spectrum of compound **1** shows two peaks indicating the presence of two kinds of phosphorus in the compound which resonate at δ 28.6 and 26.6 ppm, probably indicating a different solution structure from that of the solid state (vide infra).

The TG-DTA trace of compound **1** shows the first weight loss of 17% in the temperature range from 25 to $125\text{ }^\circ\text{C}$ corresponding to the loss of acetonitrile and water molecules. The second major weight loss occurs in the range $150\text{--}530\text{ }^\circ\text{C}$ corresponding to the loss of two TMEDA and the organic part of the ligand.

Compound **2** has been prepared from the reaction of $Cd(ClO_4)_2 \cdot H_2O$ with dtbhp- H_2 in presence of N-donor ancillary ligand, TMEDA in 1:1:1 stoichiometric ratio using CH_3CN-H_2O mixture (1:1) as solvent at room temperature (Scheme 2) and has been characterized

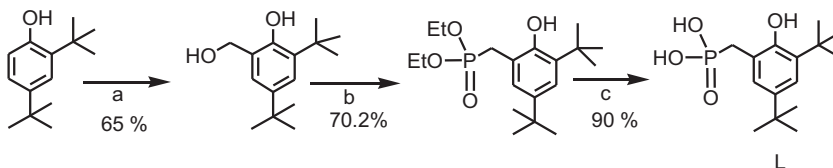
by elemental analysis, FT-IR and ^{31}P NMR spectroscopy. The obtained elemental percentages are supportive of the fact that compound **2** is similar in composition to **1**. In the IR spectrum, the presence of broad ν_{O-H} absorption at 3424 cm^{-1} indicates the presence of water molecule and unreacted phenolic –OH group on the ligand. The characteristic absorptions for $\nu_{asy(C-H)}$, $\nu_{(P-O-O)}$ and ν_{M-O-P} vibration are observed at 2953, 1131 and 1034 cm^{-1} , respectively. The ^{31}P NMR spectrum of compound **2** shows two peaks (as in **1**) indicating the presence two phosphorus centres (δ 28.8 and δ 25.9 ppm) in the molecule in solution.

2.3. Synthesis and characterization of $[Cd_2(mdtbhp)_2(1,10\text{-phenanthroline})_4](ClO_4)_2(CH_3OH)_2$ (**3**)

Compound **3** has been obtained as X-ray quality single crystals by the slow evaporation of methanol from a 1:2:2 reaction mixture of $Cd(ClO_4)_2 \cdot H_2O$, dtbhp- H_2 and 1,10-phenanthroline (Scheme 3). Complex **3**, soluble in solvents like methanol, chloroform, acetonitrile, etc. has been characterized by elemental analysis, FT-IR and multinuclear (1H and ^{31}P) NMR spectroscopy. The obtained elemental percentages are supportive to the chemical composition of **3**. In the IR spectrum, the presence of broad ν_{O-H} absorption at 3430 cm^{-1} indicates the presence unreacted phenolic O–H group. The characteristic peaks for $\nu_{asy(C-H)}$, $\nu_{asy(P-O-O)}$, ν_{M-O-P} , $\nu_{asy(Cl-O)}$, ν_{asy} bending(Cl–O), are observed at 2957, 1143, 1103, 1091, and 624 cm^{-1} , respectively. In the 1H NMR spectrum, the methyl protons of the two $C(CH_3)_3$ groups in the aromatic ring appear as two well resolved singlets of equal intensity at δ 0.92 and 1.14 ppm while the methylene protons are observed as a doublet at δ 3.16 ppm. The –OMe protons on phosphorus resonate at δ 3.49 ppm. Aromatic protons along with py-H proton are found to be resonating in the range δ 6.75–9.50 ppm. The ^{31}P NMR of compound **3** shows a single peak indicating the presence of one type phosphorus in the compound which resonates at δ 25.50 ppm.

2.4. Synthesis and characterization of $[Cd(dtbhp-H)_2(2,2'\text{-bipy})_2](dtbhp-H)_2$ (**4**)

As shown in Scheme 4, compound **4** has been obtained in a good yield at room temperature by slow evaporation of methanol from a 1:2:2 reaction mixture of $Cd(ClO_4)_2 \cdot H_2O$, dtbhp- H_2 and 2,2'-bipyridine respectively and characterized by elemental analysis, FT-IR and multinuclear (1H and ^{31}P) NMR spectroscopy. The methyl protons of the two $C(CH_3)_3$ group on the aromatic ring appear as single peaks at δ 1.3 ppm and δ 1.34 ppm. The characteristic peaks in FT-IR spectrum, for $\nu_{asy(C-H)}$, $\nu_{asy(P-O-O)}$ and ν_{M-O-P} are observed at 2956, 1128 and 1059 cm^{-1} , respectively. The broad peak observed at 2318 cm^{-1} is due to the presence of unreacted P–O–H bond of the lattice dtbhp- H_2 moiety. In the 1H NMR spectrum, the methylene protons appear as two doublets at δ 3.00 and 3.45 ppm. Aromatic protons along with 2,2'-bpy protons are found to be resonating in the range between δ 6.95–8.61 ppm. The ^{31}P NMR spectrum of compound **4** shows two peaks indicating the presence of two type phosphorus in the compound which resonates at δ 27.4 and 28.3 ppm, corresponding to the dtbhp-H unit and free dtbhp- H_2 .



Scheme 1. Synthesis of ligand L. (a) LiOH, HCHO, MeOH, $65\text{ }^\circ\text{C}$; (b) $P(OEt)_3$, Xylene, $110\text{ }^\circ\text{C}$; (c) HCl/H_2O , $100\text{ }^\circ\text{C}$.

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