Formation of a layered framework structure based upon 4-methyl-2,6-bis(methylphosphonic acid) phenol

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The trifunctional ligands, $[(HO)_2P(O)CH_2]_2C_6H_2(R)OH$, (5-H₄) (R = CH₃, Br) were prepared in good yield *via* an Arbusov reaction between P(OEt)₃ and the respective 4-R-2,6-bis(chloromethyl)phenols followed by acidic aqueous hydrolysis and they were spectroscopically characterized by IR and NMR techniques. The ligand 5-H₄–CH₃ readily dissolves lanthanide hydroxide residues and it forms a crystalline complex from aqueous LaCl₃ solutions. This complex was characterized by single crystal X-ray diffraction methods and found to adopt a complex 2-D lamellar network in the *bc* plane. The La(III) inner coordination sphere is seven coordinate formed by oxygen atoms from two water molecules and five phosphonate oxygen atoms from three different ligands. The phenolic oxygen atom is not involved in the ligand binding to La(III).

Introduction

Neutral organophosphonates, RP(O)(OR')2, and organophosphine oxides, R_3PO , typically behave as modest to weak ligands toward many transition metal cations while they display moderate to strong attractions toward harder lanthanide (Ln) and actinide (An) cations.¹ This distinction is accentuated when the phosphonate or phosphine oxide groups are part of a multifunctional ligand that can adopt stable chelate structures on the larger, less orbitally restrictive f-block ions. Such chelating ligands, e.g. carbamoylmethylphosphonates, $(RO)_2P(O)CH_2C(O)NR_2$, find utility in biphasic extractive separations of Ln and An ions present in acidic aqueous nuclear process waste solutions that contain a great variety of other cations.² Unfortunately, most organophosphonates undergo hydrolytic degradation in aqueous acid solutions with formation of phosphonic acids, RP(O)(OH)2.3 These species, even in small amounts, dramatically alter the extraction selectivity and phase separation behavior of the neutral organophosphonates. This no doubt results from less discriminate binding of phosphonate anions, RPO₃²⁻, toward all hard cations. It is known that organophosphonate anions form a wide variety of stable complexes with transition metal cations and much of that chemistry has been thoroughly reviewed by Clearfield.⁴ Many of these complexes are relatively insoluble and poorly crystalline, but where crystalline complexes are obtained, single crystal Xray diffraction analyses reveal intricate extended 1-D chain, 2-D layered and 3-D network structures. Far fewer complexes with lanthanide cations have been structurally characterized, but where data are available it is clear that extended structures are also produced.5-19

In support of the characterization of the extraction performance of a new family of phosphinomethyl pyridine N-oxide ligands,²⁰⁻²³ we have prepared and examined the ligation behavior of the previously unknown phosphonic acids $1-H_2$,²⁴ $2-H_2$ ²⁵ and $3-H_4$ ²⁶ that form under extended exposure of the parent organophosphonates

to strong acid solutions. Interestingly, 1-H₂ in the presence of lanthanide hydroxide or aged oxide-hydroxide precipitates produces water soluble complexes.²⁴ The crystal structure determination for one complex, $Er(1-H^{-})_{3}(1-H_{2})$, reveals a symmetrical eight coordinate structure having four Er-O-NVVPO seven-membered chelate ring interactions.24 Extended ligand donor atom-metal bridge bonding is absent from the structure; however, extensive hydrogen bonding involving N-O, P-O and P-OH groups is present. Ligand 2-H₂, with its longer exo-ethyl phosphonic acid arm does not form chelate interactions. Instead, as reported for $Nd(2-H^{-})_{3}$,²⁵ the 2-H-anions bridge bond between Nd(III) cations resulting in a chain structure that does not involve the N-oxide in the six coordinate Nd(III) inner sphere. However, the N-oxide is involved in the secondary hydrogen bonding structure. Finally, the tetra-acid, 3-H₄, forms complexes $Ln(3-H^{2})(3-H^{-})$ where both ligand types act as tridentate chelates and Ln(III) ions are bridged by Ln–O–P connections forming an extended chain structure.26



Much remains to be revealed about the range of structural chemistry displayed by the pyridyl N-oxide phosphonic acids **1-H**₂, **2-H**₂ and **3-H**₄ and work continues with these ligands in our group. We have also prepared related ligands on a phenol backbone and some aspects of the coordination chemistry of the neutral phosphine oxide derivatives $[Ph_2P(O)CH_2)]_2C_6H_2$ -(R)OH (R = Me, 'Bu) (4) have been reported.²⁷ These compounds act as neutral, tridentate chelating ligands forming complexes

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of the general type $Ln(L)(NO_3)_3$. Unlike the neutral pyridine N-oxide,²⁸ [Ph₂P(O)CH₂]₂C₆H₃NO, the bis(diphenylphosphinomethyl)phenols do not appear to form 2:1 ligand:Ln complexes, [Ln L₂(NO₃)](NO₃)₂. Since solvent extraction studies for the phenol derivatives are planned, it is appropriate to determine if these ligands form phosphonic acids **5-H**₄ and, if formed, evaluate how they behave as coordinating ligands. We report here the direct synthesis of two tetra-acids, [(HO)₂P(O)CH₂]₂C₆H₂(R)(OH) (R = Me, Br), and the formation and structural characterization of one complex formed with La(III).

Results and discussion

The phosphonic acids 5-H₄-CH₃ and 5-H₄-Br were prepared in high yield by the two step reaction sequence outlined in Scheme 1. The Arbusov reactions are rapid and proceed with complete conversion to the phosphonate esters 6-CH₃ and 6-Br that were characterized by ¹H, ¹³C and ³¹P NMR spectroscopy. The ³¹P chemical shifts δ 26.8 and 25.8 for R = CH₃ and Br, respectively, are comparable to the shift observed for the pyridine N-oxide analog [(EtO)₂P(O)CH₂]₂C₅H₃NO, δ 23.7.²⁹ Since our only interest in examples of 6 is as intermediates, no effort was made to isolate these compounds in analytically pure form. Instead, they were briefly heated in concentrated HCl (37%, 1-2 h), which induced hydrolysis of the ester groups and complete conversion to the phosphonic acids 5-H₄-CH₃ and 5-H₄-Br. The rates of hydrolyses for 6 are notably faster than that observed in the hydrolysis of [(EtO)₂P(O)CH₂]₂C₅H₃NO.²⁶ The new phosphonic acids were isolated as analytically pure, white crystalline solids that are soluble in water, slightly soluble in DMSO and insoluble in common organic solvents. Mass spectra obtained for both compounds show intense parent, (M^+) and $(M + H^+)$, ions and fragment ions that would be expected for substituted phenols. The ³¹P{¹H} NMR spectra show a sharp singlet at δ 25.4 (R = CH_3) and 24.6 (R = Br). These shifts are downfield of the shift observed for the pyridine N-oxide analog 3-H₄, δ 17.9, when recorded in D₂O solutions or δ 19.3 when recorded in DMSO.²⁷ The shifts are slightly upfield of the shifts of the respective phosphonate esters, 6-CH₃ and 6-Br. The shifts for the phosphonic acids are also upfield of the resonances for the phosphine oxide derivatives $[R_2P(O)CH_2]_2C_6H_2(R)OH$.²⁶ This allows for the use of ³¹P NMR analysis for monitoring hydrolysis of the phosphonate or phosphine oxide ligands when exposed to strong acids and/or radiation fields. It is noteworthy that short-term (7 day) acid exposures of the phosphine oxides shows no evidence of hydrolysis.

The behavior of the phosphonic acids, $5-H_4$, as ligands was evaluated in two ways. Initially, since we are interested in potential uses of the acids as decontamination agents, we qualitatively examined the lanthanide hydroxide dissolution behavior of 5-H₄-CH₃. Lanthanum hydroxide, La(OH)₃, precipitates were prepared by addition of aqueous NaOH to $La(NO_3)_3$ solution: (0.1 M). Colloids or precipitates form rapidly, depending upon the specific conditions used. Addition of sufficient (1 : 1) 5-H₄-CH₃ rapidly dissolves these precipitates and suspended colloids resulting in completely clarified solutions. In addition, when the La(OH)₃ solid was heated to 80 °C in water for several days then isolated, dried and stored for one week, the resulting solid easily redissolves when exposed to an aqueous solution containing 5- H_4 -CH₃. These initial tests support further evaluation of 5-H₄ as a decontamination agent for surfaces coated with hydroxide waste residues. Dissolution studies using actinide bearing materials are planned for the near future.

The solution coordination chemistry of **5-H**₄–**CH**₃ has also been examined. Initially, we attempted to isolate the complexes formed from the dissolution of La(OH)₃ precipitates as described above. Simple evaporation of the aqueous solutions produced solids with slightly variable elemental compositions that probably result from variable hydration of the solids. Attempts to obtain X-ray quality single crystals in this fashion were unsuccessful. However, when LaCl₃ and **5-H₄–CH**₃ were combined in a 1 : 1 ratio in dilute (0.02 M) HCl and the solution heated in a sealed tube at 125 °C for two days, the hydrothermal conditions provided X-ray diffraction quality crystals formed as colorless platelets.

The compound crystallizes in the centric monoclinic space group $P2_1/c$. There is one molecule, La $(5-H_1-CH_3)(H_2O)_2$ in the asymmetric unit and four molecules per unit cell. A view of the asymmetric unit is shown in Fig. 1. The two water molecules are directly coordinated to the La(III) cation with La–O(8) 2.646(2) Å and La–O(9) 2.608(2) Å. The $5-H_4-CH_3$ ligand has lost three of four available protons and the resulting trianionic ligand, $5-H_1-CH_3^{3-}$, is bonded in a bidentate fashion to the La(III) through



Scheme 1



Fig. 1 Asymmetric unit for $La(5-H_1-CH_3)(H_2O)_2$.

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the phosphonate oxygen atoms O(4) and O(7): La–O(4)P(1), 2.393(2) Å and La–O(7)P(2), 2.448(2) Å. The shorter distance results from bonding of the fully ionized phosphonate arm, $CH_2PO_3^{2-}$ while the longer distance appears with the partially ionized phosphonate arm, $CH_2PO_2(OH)^{-1}$. The phenol oxygen atom remains protonated under the synthetic conditions utilized. The phenol oxygen points in the general direction of the La(III) cation, but the separation distance, 3.165 Å, indicates that a La···O(1) interaction is, at the most, very weak.

Inspection of the unit cell (Fig. 2) reveals that the remainder of the La seven vertex inner coordination sphere is completed with phosphonate oxygen atoms from three neighboring asymmetric units containing La(1), La(2) and La(3). Two of the interactions result from bridge bonding with $-CH_2PO_3^{2-}$ fragments, La-O(31)2.421(2) Å and La-O(22) 2.490(2) Å, while the third occurs with the partially ionized -CH₂PO₂(OH) fragment, La-O(53) 2.552(2) Å. These seven nearest neighbor oxygen atoms provide a monocapped trigonal prismatic coordination polyhedron. An additional oxygen atom, O(73), on the $-CH_2PO_2(OH)$ arm, with La · · · O(73) 2.971(2) Å, is not considered to be part of the inner sphere coordination environment. From the perspective of the ligand $5-H_1$ - CH^{-3}_{3} , the exo $-C(7)H_2P(1)O(2)O(3)O(4)^{-2}$ arm forms three P-O-La bridge bonds to three different La(III) ions while the second exo -C(8)P(2)O(5)O(7)O(6)H⁻¹ arm forms P-O-La bridge bonds with two La(III) ions. The third oxygen atom remains protonated.

The resulting La–O–P interactions, along with extensive hydrogen bonding, produce a lamellar network in the bc plane, and a view of the network is shown in Fig. 3. The gap between the sheets of carbon atoms formed by the pyridine rings is 3.6(5) Å.

The P–O bond lengths involving the $-CH_2PO_3^{2-}$ arm are P(1)– O(2) 1.535(2) Å, P(1)–O(3) 1.512(2) Å and P(1)–O(4) 1.515(2) Å. The elongation in P(1)–O(2) is a consequence of a strong hydrogen bond interaction between O(2) and the P(2)O(6)-H group in a neighboring molecular unit: $P(2)O(6)H(6) \cdots O(2)$ [x, 1.5 - y, z - 0.5] 1.677 Å, O(6) · · · O(2) 2.575 Å O(6)–H(6) · · · O(2) 171.3° . Correspondingly, the P(2)–O(6) bond length 1.557(2) Å is significantly longer than the bond lengths P(2)-O(5), 1.517(2) Å and the P(2)–O(7) 1.509(2) Å in the $-CH_2PO_2(OH)^{-1}$ arm. There is also a short intramolecular hydrogen bond involving a coordinated water molecule and the phenol group: $O(1)H(1) \cdots O(9)$ 1.94 Å, $O(1) \cdots O(9)$ 2.650 Å, $O(1)-H(1) \cdots O(9)$ 138°. There is also a short inter-asymmetric unit hydrogen bond involving the same water molecule and O(5) [x, 1 + y, z] in another unit: $O(9)H(9) \cdots O(5)$ 1.88 Å, $O(9) \cdots O(5) [x, 1 + y, z]$ 2.712 Å, O(9)- $H(9) \cdots O(5) [x, 1 + y, z] 155.8^{\circ}.$

In summary, it is observed that the 4-methyl-2,6-bis(methyl-phosphonic acid) phenol, $5-H_4-CH_3$ readily dissolves lanthanide hydroxide precipitates and it forms a crystalline lamellar solid under hydrothermal synthesis conditions with a 1 : 1 ligand/ metal stoichiometry. The solid state structure is distinctly



Fig. 2 Extended bc-plane structure for La(5-H₁-CH₃)(H₂O)₂.



Fig. 3 Lamellar network in the bc plane: La polyhedra (green), phosphate tetrahedral (magenta), phenol O atom (red) and carbon atoms (grey).

different from that produced by the related phosphonic acid 2,6bis(methylphosphonic acid)pyridine N-oxide. That ligand, even with 1 : 1 reactant mixtures, forms 2 : 1 complexes, $Ln(3-H^{2-}_{2})(3-H^{1-}_{3})$, in which the lanthanide ion is seven coordinate and the ligands act as tridentate chelates. The seventh coordination site is occupied by a bridging phosphate interaction that produces a unique chain structure. Further studies with these and related phosphonic acid ligands are in progress that may lead to a systematic understanding of the structural and electronic factors operating in the assembly of these complex structures with lanthanide ions.

Experimental

The organic reagents were purchased from Aldrich Chemical Co. Organic solvents were purchased from VWR and dried by standard methods. The lanthanum nitrate was purchased from Ventron. All reactions were performed under dry nitrogen atmosphere unless noted otherwise. Infrared spectra were recorded on a Mattson 2020 FTIR and NMR spectra were obtained from Bruker FX-250 and JEOL-GSX-400 spectrometers using $Me_4Si(^{1}H, ^{13}C)$ and $H_3PO_4(^{31}P)$ as shift standards. Mass spectra were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska. Elemental analyses were obtained from Galbraith Laboratories.

Liquid syntheses

4-Methyl-2,6-bis(methylphosphonic acid)phenol (5-H₄–CH₃). Under dry nitrogen, 4-methyl-2,6-bis(chloromethyl)phenol (6.0 g, 0.03 mol),²⁷ was added with stirring at 23 °C to triethylphosphite (20.0 g, 0.12 mol). The temperature of the mixture rose during the addition and when addition was complete the mixture was briefly heated (10 min) at 150 °C. The excess (EtO)₃P was removed by vacuum evaporation leaving a colorless liquid, 4-methyl-2,6bis(diethylphosphonomethyl)phenol **6-CH**₃ (11.6 g, 95%). NMR (23 °C, CDCl₃): ³¹P{¹H} δ 26.8; ¹H δ 1.16 (t, *J* = 7.0 Hz, OCH₂CH₃) 2.14 (s, 4-CH₃); 3.11 (d, *J* = 21.4 Hz, -CH₂P); 3.95 (m, OCH₂), 6.82 (s, C₃-*H*); 8.40 (s, O*H*); ¹³C{¹H} δ 16.1 (d, *J* = 3.0 Hz, CH₃), 20.2 (s, 4-CH₃), 28.4 (d, *J* = 137.6 Hz, -CH₂P), 62.3 (d, *J* = 7.0 Hz, OCH₂), 120.2 (t, *J* = 6.0 Hz), 129.8 (s), 130.8 (t, *J* = 5.0 Hz), 151.1 (t, *J* = 5.9 Hz).

A sample of 6-CH₃ (10.0 g, 0.025 mol) was added to concentrated hydrochloric acid (37%, 60 mL) and the mixture refluxed (1 h). The resulting solution was evaporated to dryness under vacuum and the residue treated with acetone (100 mL). The resulting suspension was stirred at 23 °C (1 h), the solid collected by filtration, washed with fresh acetone (2 \times 40 mL) and dried in vacuum (7.0 g, 96%). The product, 4-methyl-2,6bis(methylphosphonic acid)phenol, 5-H₄-CH₃, is a white solid that is recrystallized from H₂O/acetone mixtures: mp 205–206°. Soluble in H₂O, sl. Sol in DMSO, insol in common organic solvents. Found: C, 36.27; H, 4.45. C₉H₁₄O₇P₂ requires C, 36.50; H, 4.77. Mass spectrum (FAB m/z): 297 (100%, M + H⁺), 296 (90%, M⁺), 279 (50%, M–OH⁺). IR (KBr, cm⁻¹): 3502 (m), 2922 (m), 1487 (m), 1215 (m), 1120 (s), 1022 (sh), 960 (s), 935 (s), 879 (sh), 841 (m), 727 (m), 497 (w). NMR (23 °C, D₂O): ${}^{31}P{}^{1}H{}\delta 25.4$; ${}^{1}H\delta 2.15$ (s, 4-CH₃), 2.95 (d, J = 21.1 Hz, $-CH_2P$), 6.87 (s, C₃-H), 10.43 (br, OH); ${}^{13}C{}^{1}H{}\delta 20.2$ (s, 4-CH₃), 30.3 (d, J = 133.9 Hz, CH₂P); 121.7 (t, J = 5.1 Hz), 127.8 (s), 130.0 (s), 151.5 (t, J = 6.1 Hz).

4-Bromo-2,6-bis(methylphosphonic acid)phenol (5-H₄Br). Under dry nitrogen, 4-bromo-2,6-bis(chloromethyl)phenol²⁷ (5.0 g, 0.18 mol) in benzene (30 mL) was added dropwise to (EtO)₃P (13.0 g, 0.078 mol) held at 114 °C. Following addition, the mixture was stirred and held at 114 °C (20 min) and then excess (EtO)₃P removed *in vacuo* leaving a colorless oil, 4-bromo-2,6-bis(diethylphosphonomethyl)phenol **6-Br** (8.5 g, 97%). NMR (23 °C, CDCl₃): ³¹P{¹H} δ 25.8; ¹H δ 1.20 (t, J = 7.0 Hz, OCH₂CH₃), 3.13 (d, J = 21.5 Hz, -CH₂P), 3.99 (m, OCH₂), 7.16 (s, C₃-H) 8.83 (s, OH); ¹³C{¹H} δ 16.2 (d, J = 3.1 Hz, CH₃), 28.4 (d, 136.2 Hz, CH₂P), 62.6 (d, J = 7.0 Hz, -OCH₂), 112.4 (s), 122.9 (t, J = 6.0 Hz); 132.7 (t, J = 5.0 Hz), 152.8 (t, J = 5.8 Hz).

A sample of 6-Br (7.7 g, 0.016 mol) was added to concentrated HCl (37%, 40 mL), the mixture stirred (60 °C, 1.5 h) and then evaporated to dryness at 23 °C. The residue was washed with Et₂O (30 mL) and then CHCl₃ (30 mL), collected by filtration and then washed again with acetone (2×30 mL). The remaining solid 4-bromo-2,6-bis(methylphosphonic acid)phenol, 5-H₄-Br, was recrystallized from H₂O/acetone mixtures: mp > 250 °C. Soluble in H₂O, sl. sol in DMSO. Found: C, 26.32; H, 2.96 $C_8H_{11}O_7P_2Br$ requires C, 26.62; H, 3.07. Mass spectrum (FAB, m/z): 362 (90%, M + H⁺), 361 (100%, M⁺), 344 (15%, M–OH⁺). IR (KBr, cm⁻¹): 3408 (m), 2920 (m), 1467 (m), 1367 (w), 1258 (m), 1207 (s), 1141 (s), 1016 (s), 927 (s), 875 (w), 727 (m), 509 (m). NMR (23 °C, D₂O); ³¹P{¹H} δ 24.6; ¹H δ 3.00 (d, J = 21.2 Hz, CH₂P), 7.24 (s, C₃-H), 9.74 (br, OH); ${}^{13}C{}^{1}H{}\delta$ 29.9 (d, J = 133.2 Hz, $-CH_2P$), 110.6 (s), 124.7 (d, J = 9.9 Hz), 131.5 (s), 153.3 (t, J =6.3 Hz).

Preparation of the complex

A sample of LaCl₃· $6H_2O$ (17.7 mg, 0.05 mmol) and **5-H₄-CH₃** (14.8 mg, 0.05 mmol) was dissolved in 0.02 M HCl (40 mL)

Table 1Selected bond lengths (Å) for $La(5-H_1-CH_3)(H_2O)_2$

La- $O(9)$ 2.608(2) La···O(73)#4 2.971(2)	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	89(2) 20(2) 52(2) 71(2)
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" The numbers, #n, refer to the three other molecules in the unit cell.

and stirred briefly. The solution was then transferred to a Pyrex tube and sealed. The tube was heated to 125 °C (2 d). Colorless platelets deposited that were suitable for X-ray diffraction analysis. IR (KBr, cm⁻¹): 3541 (m), 3495 (m), 3427 (m), 3115 (m), 2920 (m), 1650 (w), 1602 (m), 1483 (m), 1313 (w), 1203 (m), 1161 (s), 1111 (s), 1078 (vs), 1028 (s), 966 (s), 864 (w), 738 (w), 538 (m), 470 (m).

X-Ray diffraction analysis

A single crystal ($0.7 \times 0.37 \times 0.07$ mm) was mounted on a glass fiber and data were collected on a Siemans R3m/V diffractometer equipped with a graphite monochromator and using Mo Ka radiation ($\lambda = 0.71073$ Å). Crystal data: C₉H₁₅LaO₉P₂, M =468.06, monoclinic space group $P2_1/c$, a = 12.012(1), b = 8.605(1), c = 13.538(1) Å, $\beta = 98.29(1)^{\circ}$; V = 1384.7(2) Å³, Z = 4, $\mu = 3.358 \text{ mm}^{-1}, T = 20 \text{ }^{\circ}\text{C}, 5108 \text{ reflections collected}, 2440$ independent reflections, ($R_{int} = 0.0189$). The final refinement indices were R1 = 0.0194, wR2 = 0.0534 $[I \ge 2\sigma (I)]$, R1 (all data) = 0.0206, wR2 = 0.0538. All calculations were performed with SHELX-9730 and a face indexed absorption correction was applied. The structure was solved by Patterson map interpretation. The refinement was well behaved and the non-hydrogen atoms were refined anisotropically. The H atoms on the oxygen atoms and C(9) were located in difference maps and the H-atoms on the remaining C-atoms were placed in idealized positions (Riding model) (Table 1).

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603987a

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