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Hydrogen Bonded Framework Structures Constructed from 2-(Pyridyl *N*-oxide) Methylphosphonic Acid Ligands and Erbium(III)

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Syntheses for 2-(pyridyl *N*-oxide) methylphosphonic acid, **1-H**, and 2-(pyridyl *N*-oxide) hydroxymethylphosphonic acid, **4-H**, are described, and the crystal structures of both ligands are presented. Combination of these ligands with freshly prepared erbium hydroxide results in the formation of the isostructural complexes $Er(L^-)_3(LH)\cdot 8H_2O$. The crystal structure determinations of the complexes show that extensive hydrogen bonding links the individual eight coordinate $Er(L^-)_3(LH)$ molecular units into a 3-D structure.

Introduction

Combinations of organophosphonic acids, $RP(O)(OH)_2$, with metal ions under a variety of conditions have been found to produce structurally diverse collections of molecular compounds, amorphous microporous materials, and ordered 1-D, 2-D, and 3-D solid state materials.[1] These interesting substances are finding uses as ion exchangers, proton conductors, sensors, catalysts, and nonlinear optical materials. Such applications encourage continued evolution of the field. It appears that new compositions and structures can be designed through seemingly unlimited variations of the organic R group which may serve a space filling roll or may add chemical functionality in the solids. Further, a wide range of p-block and d-block metals in 2+, 3+, and 4+ oxidation states have been employed to construct the solid state framework structures, and a few reports of the use of lanthanide ions, Ln(III), have also appeared.[2−6] The last chemistry turns out to be relevant to ongoing research in our group.

We have been exploring the systematic design of multifunctional, neutral organophosphine oxide and organophosphonate ligands as potential chelators for Ln(III) and actinide, An(III), ions and the application of these ligands in liquid−liquid extraction separations of Ln(III) and/or An(III) ions in highly acidic nuclear materials solutions.[7,8] In some cases, the neutral organophosphonates, $RP(O)(OR'_2)$, have the tendency to undergo hydrolysis forming the corresponding organophosphonic acids, $RP(O)(OH)_2$. Although unfavorable for traditional LLE separations, some of the functionalized acids may be useful for dissolution and chelation of intractable Ln(III)/An(III) oxide−hydroxide precipitates while others may be employed for scrubbing trace quantities of metal ions from process solutions.[9] In an effort to alter and control the performance of some of these acidic ligands, we have examined reactions of selected organo-functionalized phosphonic acids with Er(III), and we report here the extended, hydrogen bonded structures formed with pyridine *N*-oxide deriviatized methylphosphonic acids: $2\text{-}(C_5H_4NO)\text{-}CH(R)P(O)(OH)_2$ (R = H, **1-H**; and R= OH, **4-H)**.

Experimental Section

General Information. 2-Picolyl chloride hydrochloride, triethyl phosphite, diethyl phosphite, and 2-pyridinecarboxaldehyde were purchased from Aldrich Chemical Co. Hydrogen peroxide, 3-chloroperbenzoic acid, and solvents were purchased from Fischer Scientific. Erbium nitrate was purchased from Alpha Ventron. Mass spectra were obtained from the Midwest Center for Mass Spectrometry, University of Nebraska, and elemental analyses were determined by Galbraith Laboratories. NMR spectra were obtained on JEOL GSX-400 and Bruker FX-250 spectrometers, and common standards (85% H_3PO_4 and Me_4Si) were employed.

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(1) Clearfield, A. *Prog. Inorg. Chem.* **1998**, *47*, 371 and references therein.
(2) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112.
(3) Wang, R. C.; Zhang, Y.; Hu, H.; Frausto, R. R.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 864.
(4) Serpaggi, F.; Ferey, G. *J. Mater. Chem.* **1998**, *8*, 2737.
(5) Fanucci, G. E.; Talham, D. R. *Langmuir* **1999**, *15*, 3289.
(6) Evans, O. R.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2001**, *123*, 10395.
(7) Bond, E. M.; Gan, X.; FitzPatrick, J. R.; Paine, R. T. *J. Alloys Compd.* **1998**, *271−273*, 172.
(8) Paine, R. T. In *Separations of f-Elements*; Nash, K. L., Choppin, G. R., Eds.; Plenum: New York, 1995; p 63.
(9) Gan, X.; Paine, R. T. Unpublished results.

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Ligand Syntheses. (2-Pyridyl *N*-Oxide) Methylphosphonic Acid (1-H). A sample of 2-picolyl chloride hydrochloride (15 g, 0.091 mol) was dissolved in water (40 mL), CH_2Cl_2 (70 mL) was added, and the mixture was stirred. Saturated aqueous $NaHCO_3$ solution was added dropwise to give a pH = 8 solution. The phases were separated, and the aqueous phase was washed with CH_2Cl_2 (2 × 50 mL). The combined organic phases were dried over Na_2SO_4, the solvent was evaporated, and the remaining red oil distilled (40 °C/0.01 Torr). The colorless oil, 2-(chloromethylpyridine) (8.8 g, 6.9 mmol, 75% yield), that was obtained was used immediately.[10] Triethyl phosphite (21 mL) was added under a dry nitrogen atmosphere to the oil contained in a Schlenk vessel (250 mL). The resulting mixture was heated under nitrogen (150 °C, 4 h), and a brown solution resulted. The volatile byproducts were removed by distillation leaving 2-[(diethylphosphono)methyl]pyridine *P*-oxide **2** as a dark brown oil: yield 15.0 g (95%). Anal. Calcd for $C_{10}H_{16}NO_3P$: C, 52.40; H, 7.04; N, 6.11. Found: C, 52.09; H, 7.23; N, 6.11. NMR spectra ($CDCl_3$): $^{31}P\{^1H\}$ δ 25.7; ^1H δ 1.2 (t, J = 7 Hz), 3.36 (d, J = 22 Hz), 4.03 (q, J = 7.2 Hz), 7.12 (t, J = 5.4 Hz), 7.35 (d, J = 7.4 Hz), 7.59 (t, J = 7.5 Hz), 8.49 (d, J = 4.2 Hz).

The 2-[(diethylphosphono)methyl]pyridine was converted by two methods to the target diacid **1-H**.

Method 1. A sample of 2-[(diethylphosphono)methyl]pyridine *P*-oxide, **2**, (7.9 g, 34 mmol) in $CHCl_3$ (60 mL) was treated with 3-chloroperoxybenzoic acid (7.8 g, 70−75%) in portions. The solvent began to reflux during the addition, and reflux was continued (18 h, bath temperature 55 °C). An additional portion of 3-chloroperoxy benzoic acid (2.8 g, 70−75%) was added and the mixture heated (1 h) to complete the reaction. The organic solution was cooled, and silica gel (70−230 mesh, 40 g) was added. The solvent was evaporated, and one-half of the solid was loaded onto a silica gel column (70−230 mesh, 50 cm × 4 cm). The column was eluted with CH_2Cl_2/MeOH (100:4) to remove impurities. The polarity of the eluant was then increased, CH_2Cl_2/MeOH (100:7), and the product eluted through the column. Two columns gave a yellow oil, **3**: yield 4.2 g (50%). NMR spectra ($CDCl_3$):$^{31}P\{^1H\}$ δ 23.6; ^1H δ 1.14 (t, J = 7 Hz), 3.55 (d, J = 22 Hz), 4.01 (q, J = 7 Hz), 7.07 (d of d, J = 7 Hz), 7.37 (m), 8.12 (m); $^{13}C\{^1H\}$ δ 16.72 (d, J = 6.1 Hz), 28.17 (d, J = 138.9 Hz), 28.36, 62.9 (d, J = 6.4 Hz), 125.7 (d, J = 2.9 Hz), 126.0 (d, J = 3.1 Hz), 127.7 (d, J = 5.3 Hz), 139.8 (d, J = 2.2 Hz), 144.4 (d, J = 7.5 Hz).

A sample of 2-[(diethylphosphono)methyl]pyridine *N*,*P*-dioxide, **3**, (4.0 g, 16 mmol) was dissolved in glacial acetic acid (20 mL), and H_2O_2 solution (3.6 mL, 30%) was added. The mixture was heated (70 °C, 18 h) and then evaporated to dryness leaving a white solid. A ^{31}P NMR spectrum revealed two resonances, δ 18.1 and 13.4. The latter is due to an impurity (∼11%). The solid was recrystallized from a minimum of hot water with slow cooling to 23 °C (5 h). The white solid, 2-(pyridyl *N*-oxide) methyl phosphonic acid, **1-H**, was recovered by filtration: yield 1.7 g (53%). Mp: 221−222 °C. Anal. Calcd for $C_6H_8NO_4P$: C, 38.11; H, 4.26; N, 7.41. Found: C, 38.17; H, 4.47; N, 7.32. NMR spectrum: $^{31}P\{^1H\}$ (D_2O) δ 18.1.

Method 2. A sample of 2-[(diethylphosphono)methyl]pyridine *P*-oxide, **2**, (15.0 g, 65 mmol) in acetic acid (40 mL) was treated with aqueous H_2O_2 (30%, 8 mL) and heated (16 h, 90 °C). The mixture was cooled, an additional portion of H_2O_2 (8 mL) was added, and heating continued (1 h). A clear orange solution formed. The solvent was removed by vacuum evaporation, and the resulting yellow powder was dried. The dry powder was dissolved in a minimum of hot water and poured into well stirred acetone (500 mL). The acid precipitated, and the mixture was held overnight at −20 °C. The cold mixture was filtered and the solid washed with acetone and dried leaving **1-H** as a white microcrystalline solid: yield 28 g (23%). NMR spectra: $^{31}P\{^1H\}$ (D_2O) δ 18.1, (DMSO) δ 19.7; ^1H (D_2O) δ 3.63 (d, J = 21.0 Hz), 7.67 (t, J = 7.0 Hz), 7.80 (d, J = 8.0 Hz), 8.0 (t, J = 7.8 Hz), 8.55 (d, J = 6.5 Hz); (DMSO-d_6) δ 3.55 (d, J = 21.0 Hz), 7.60 (m), 7.76 (m), 8.57 (d, J = 6.2 Hz); $^{13}C\{^1H\}$ (DMSO-d_6) δ 36.4 (d, J = 23 Hz), 130.2 (d, J = 2.6 Hz), 133.3 (d, J = 5.6 Hz), 135.2, 144.7 (d, J = 2.7 Hz), 151.1 (d, J = 9.4 Hz). A single impurity is present (∼7%) with $^{31}P\{^1H\}$ δ 13.4.

2-(Pyridyl *N*-Oxide) Hydroxymethylphosphonic Acid (4-H). 2-Pyridinecarboxaldehyde (3.0 g, 28 mmol) and diethyl phosphite (3.87 g, 28 mmol) were combined, and $NaOCH_3$/MeOH solution (15 drps) was added to catalyze the reaction. The temperature rose immediately, and the resulting warm solution was heated with an oil bath (100 °C, 10 min). The resulting mixture was distilled (80−90 °C, 200 mTorr) to remove unreacted starting materials leaving an oily residue, 2-[(diethylphosphono)hydroxymethyl]pyridine *P*-oxide, **5**: yield 6.77 g (98%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.4. The recovered intermediate was dissolved in acetic acid (15 mL), and 30% H_2O_2 (3.0 mL, 27 mmol) was added. The mixture was heated (68 °C, 17 h), and additional H_2O_2 (3.0 mL, 30%) was added and heating continued (1 h). During the reaction, white solid precipitated. The mixture was cooled to 23 °C and the solid collected by filtration and washed with acetone (2 × 25 mL). 2-(Pyridine *N*-oxide) hydroxymethylphosphonic acid **4-H** was recovered as a white solid: yield 5.0 g (88%). The material is soluble in H_2O (∼4 × 10^{-2} M) and slightly soluble in DMSO. Anal. Calcd for $C_6H_8NO_5P$: C, 35.14; H, 3.93; N, 6.83. Found: C, 34.60; H, 4.01; N, 6.67. Mass spectrum (FAB) (*m*/*e*, fragment, rel inten): 206 ($M + 1^+$) 40%, 205 (M^+) 3%, 190 ($M + 1 - O^+$) 15%. NMR spectra (DMSO-d_6): $^{31}P\{^1H\}$ δ 18.2; ^1H δ 5.31 (d, J = 15.3 Hz), 7.59−7.53 (m), 7.80−7.78 (m), 8.51 (d, J = 5.9 Hz), $^{13}C\{^1H\}$ δ 64.27 (d, J = 149.0 Hz), 125.12 (d, J = 4.5 Hz); 131.56, 139.54, 151.49, 166.95.

Synthesis of Complexes. The complexes were obtained by combination of freshly prepared erbium hydroxide (from $Er(NO_3)_3$ and KOH) (0.2 mmol) and **1-H** or **4-H** (0.8 mmol) in water (15 mL). The pink solutions were allowed to slowly evaporate at 23 °C, and blocky pink crystals, suitable for X-ray diffraction analysis, deposited.

X-ray Diffraction Analysis. A colorless platelet of **1-H** (0.46 × 0.23 × 0.09 mm^3), a colorless prism of **4-H** (0.46 × 0.29 × 0.25 mm^3), a colorless prism of Er(**1**$^-$)$_3$(**1-H**)·8H_2O (0.54 × 0.34 × 0.25 mm^3), and a light pink prism of Er(**4**$^-$)$_3$(**4-H**)·8H_2O (0.34 × 0.34 × 0.05 mm^3) were each mounted in glass capillaries and centered on the diffractometer. Data were collected at 20 °C by variable speed ω scans on a Siemens R3m/V diffractometer equipped with a graphite monochromator and using Mo Kα radiation. Lattice and data collection parameters are summarized in Table 1. All calculations were performed with SHELXL97.[11] The structures were solved by direct methods, and full-matrix least-squares refinements were employed.[12] The refinement for **1-H** was well behaved. All non-hydrogen atoms were refined anisotropically, and all H-atoms bonded to C-atoms were included in idealized positions. The H-atoms on O-atoms were allowed to vary in

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(10) Characterization data for 2-(chloromethyl) pyridine have been summarized in a previous report: Engelhardt, U.; Rapko, B. M.; Duesler, E. N.; Frutos, D.; Paine, R. T. *Polyhedron* **1995**, *14*, 2361.

(11) Sheldrick, G. M. *SHELXL 97*; Bruker Instruments: Madison, WI, 1999.

(12) The least squares refinements minimize $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F)^2 + gF^2]$.

Table 1. Crystallographic Data

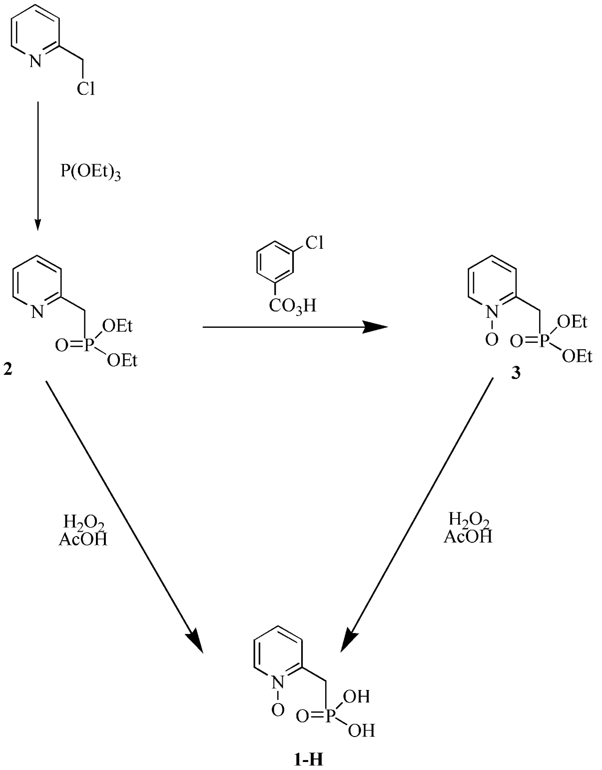
	1-H	**4-H**	**$Er(1^-)_3 1 \cdot 8H_2O$**	**$Er(4^-)_3 4 \cdot 8H_2O$**
empirical formula	$C_6H_8NO_4P$	$C_6H_8NO_5P$	$C_{24}H_{45}ErN_4O_{24}P_4$	$C_{24}H_{45}ErN_4O_{28}P_4$
fw	189.10	205.10	1064.78	1128.78
a, Å	4.5478(4)	4.8848(3)	17.589(4)	17.667(3)
b, Å	8.214(1)	8.0205(7)	9.487(2)	9.485(2)
c, Å	20.204(1)	19.558(1)	24.73(1)	25.051(5)
α, deg	90	90	90	90
β, deg	92.06(1)	90	110.03(3)	106.25(3)
γ, deg	90	90	90	90
V, Å^3	754.3(1)	766.3(1)	3877(2)	4030(1)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$C2/c$	$C2/c$
Z	4	4	4	4
D_{calcd}, g/cm^3	1.665	1.778	1.824	1.860
μ, mm^{-1}	0.336	0.348	2.425	2.346
R1, wR2 [$I \geq 2\sigma(I)$]	0.0330, 0.0738	0.0224, 0.0661	0.0252, 0.0601	0.0249, 0.0592

position, and all H-atoms were set with $U_{iso} = 1.25U_{eq}$ of the parent atom. The refinement for **4-H** also was well behaved. After all non-hydrogen atoms were refined anisotropically, it appeared that there were H atoms bonded to O(1), O(2), O(4), and O(5). Those on O(1) and O(2) were located in the difference maps; however, atom H(1) was disordered over O(4) and O(5) with 50% occupancy at each site. The positions were optimized with the O−H distance 0.85 Å and fixed in position. H atoms on the carbon atoms were included using the riding model. The refinements for the two isostructural Er(III) complexes were well behaved. For Er(**1**$^-$)$_3$(**1**-H), all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to the carbon atoms were treated by the riding model with U_{iso} set to $1.25U_{eq}$ of the parent atom. There were two disordered hydrogen atom sites: H(3a) (half occupancy) and H(12d)/H(12e) (half occupancy). The remaining H atoms were fixed in positions found in the difference maps with $U_{iso} = 1.25U_{eq}$ of the parent atom. For Er(**4**$^-$)$_3$(**4-H**), all non-hydrogen atoms were refined anisotropically, and the H atoms attached to carbon atoms were treated by the riding model with $U_{iso} = 1.25U_{eq}$ of the parent atom. The H atoms on the P−O and C−O groups and water molecules were located in the difference maps. Atom O(12) has three H atom positions, one fully occupied and two half occupied. The H atom position on O(8) is half occupied. The O−H bond distances were optimized at 0.85 Å, and all H atoms were fixed with $U_{iso} = 1.25U_{eq}$ of the parent atom.

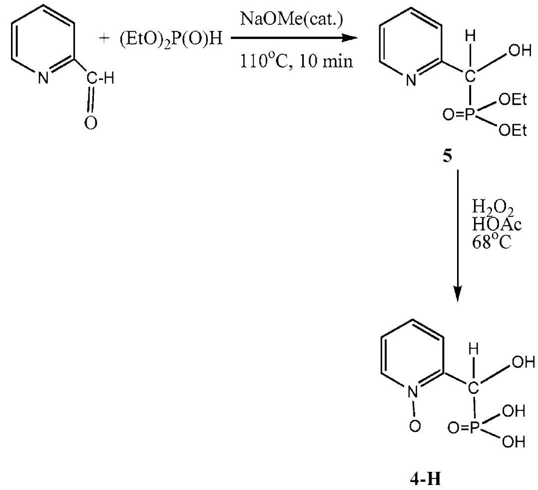
Results and Discussion

The syntheses derived for the 2-(pyridyl *N*-oxide) methylphosphonic acids, **1-H** and **4-H**, are summarized in Schemes 1 and 2, respectively. For **1-H**, the first step employed an Arbusov phosphonation of 2-chloromethylpyridine that gave 2-[(diethylphosphono)methyl]pyridine *P*-oxide, **2**, in high yield (95%) as a dark brown oil with a single ^{31}P NMR resonance at δ 25.7. This intermediate was converted to the target acid **1-H** by two methods. In the first, **2** was treated with *m*-chloroperbenzoic acid in $CHCl_3$ under reflux conditions. Following purification by column chromotography, 2-[(diethylphosphono)methyl]pyridine *N*,*P*-dioxide, **3**, was isolated as a yellow oil in 50% yield (^{31}P NMR, δ 23.6). This compound was then treated with H_2O_2/glacial acetic acid at 70 °C which produced a slightly impure white solid. The solid was recrystallized from a minimum of hot water giving **1-H** in 53% yield as an analytically pure white, crystalline solid. Alternatively, **2** was treated directly with H_2O_2/glacial acetic acid at 90 °C. Following workup, a yellow powder was obtained that was recrystallized from a minimum of hot water which was poured into acetone and cooled (−20 °C). The yield of **1-H** was 23%, and it displays a single ^{31}P NMR resonance at δ 18.1 (D_2O) or δ 19.7 (DMSO). The methyl carbon atom provides a diagnostic doublet resonance in the ^1H NMR spectrum, δ 3.63 (D_2O) or 3.55 (DMSO), and a doublet resonance in the $^{13}C\{^1H\}$ NMR spectrum, δ 36.4 (DMSO).

Scheme 1



Scheme 2



The acid **4-H** was obtained from a two step synthesis. In the first step, 2-pyridine carboxaldehyde was combined with diethyl phosphite and a catalytic amount of sodium methoxide. This gave 2-[(diethylphosphono)hydroxymethyl]pyridine *P*-oxide, **5**, as a clear oil in 98% yield. This intermediate shows a ^{31}P NMR resonance at δ 20.4. Subsequent oxidation and hydrolysis was accomplished in

Table 2. Selected Bond Lengths (Å)

	1-H		**4-H**		Er(1^-)$_3$(**1-H**)·8H_2O		Er(4^-)$_3$(**4-H**)·8H_2O	
Er−O					Er−O(1)	2.421(2)	Er−O(1)	2.408(2)
					Er−O(2)	2.267(2)	Er−O(2)	2.268(2)
					Er−O(5)	2.434(2)	Er−O(6)	2.496(2)
					Er−O(6)	2.262(2)	Er−O(7)	2.234(2)
P−O	P−O(2)	1.493(2)	P−O(2)	1.558(1)	P(1)−O(2)	1.489(2)	P(1)−O(2)	1.499(2)
	P−O(3)	1.523(2)	P−O(3)	1.498(1)	P(1)−O(3)	1.515(3)	P(1)−O(3)	1.578(3)
	P−O(4)	1.554(2)	P−O(4)	1.511(1)	P(1)−O(4)	1.554(3)	P(1)−O(4)	1.505(3)
					P(2)−O(6)	1.490(2)	P(2)−O(7)	1.498(2)
					P(2)−O(7)	1.505(3)	P(2)−O(8)	1.503(3)
					P(2)−O(8)	1.571(2)	P(2)−O(9)	1.568(3)
N−O	N−O(1)	1.352(2)	N−O(1)	1.363(2)	N(1)−O(1)	1.338(3)	N(1)−O(1)	1.346(4)
					N(2)−O(5)	1.338(3)	N(2)−O(6)	1.341(4)
P−C	P−C(6)	1.814(2)	P−C(6)	1.852(2)	P(1)−C(6)	1.813(4)	P(1)−C(6)	1.844(4)
					P(2)−C(12)	1.812(3)	P(2)−C(12)	1.839(4)
C−C	C(1)−C(6)	1.489(3)	C(5)−C(6)	1.498(3)				

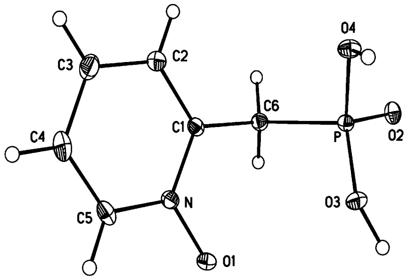


Figure 1. Molecular structure and atom numbering scheme for [(HO)$_2$P(O)CH$_2$]C$_5$H$_4$NO **1-H**.

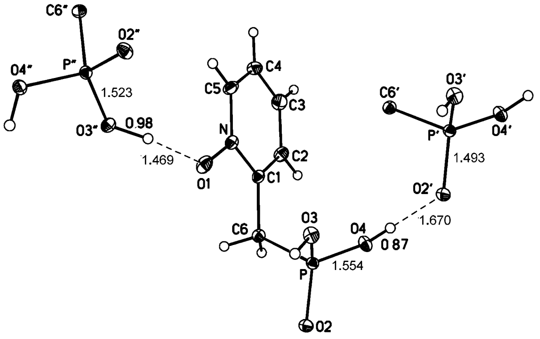


Figure 2. Hydrogen bond interactions in **1-H**.

H_2O_2/acetic acid solution, and **4-H** was recovered as an analytically pure white crystalline solid in 88% yield. A FAB-MS shows the presence of (M + H^+) and (M^+) ions. The ^{31}P NMR spectrum contains a single resonance at δ 18.2 (DMSO). The methyl carbon atom gives rise to a resonance at δ 5.31 in the ^{1}H NMR spectrum and a resonance at δ 64.27 in the ^{13}C{^{1}H} NMR spectrum. The downfield shifts, relative to **1-H**, are consistent with the presence of the electron withdrawing −OH substituent in **4-H**.

The molecular structure of **1-H** was determined by single crystal X-ray diffraction methods, and a view of the molecule is shown in Figure 1. Selected bond lengths are summarized in Table 2. The H-atoms bonded to the O-atoms are clearly located in the difference maps, and there is no disorder present. The most striking feature of the structure is the extensive hydrogen bonding between molecules in the unit cell. Hydrogen bond interactions O(3)″−H···O(1)−N and O(4)−H···O(2)′−P, as shown in Figure 2, result in a sheet structure in the *ab* plane, and the sheets stack along the *c* axis of the unit cell. There are three distinctly different P−O bond lengths. The shortest, P−O(2) 1.493(2) Å, corresponds to the localized P═O group. The bond length is slightly longer than the P═O bond lengths in the neutral phosphine oxides [Ph$_2$P(O)CH$_2$]$_2$C$_6$H$_4$, 1.485(2) Å (av),[13] and [Ph$_2$P(O)CH$_2$]$_2$ C$_5$H$_3$NO, 1.480(3) Å.[10] It is also noteworthy that the two P═O groups in [Ph$_2$P(O)CH$_2$]$_2$C$_6$H$_4$ are each hydrogen bonded to a water molecule. In all three structures, the P═O groups or the P═O and N−O groups are rotated away from each other due to strong dipole repulsions. For **1-H** this can be seen in both Figures 1 and 2. The two P−O−H groups display longer P−O bond lengths, P−O(3) 1.523(2) Å and P−O(4) 1.554(2) Å, and these in turn are hydrogen bonded to second and third molecules of **1-H**. It is interesting that the shorter of these two bond lengths, P−O(3), has the longer PO(3)−H bond length, 0.98 Å, and shorter PO(3)H···O(1) hydrogen bond distance. This suggests that, in the free ligand, the *N*-oxide oxygen atom is acting as a stronger base than the phosphoryl oxygen atom. Consistent with this conclusion, the N−O(1) bond length, 1.353(2) Å, is much longer than the N−O bond lengths in the neutral phosphine oxide [Ph$_2$P(O)CH$_2$]$_2$C$_5$H$_3$NO, 1.315(6) Å. This contrasts with observations made with neutral ligands such as [Ph$_2$P(O)CH$_2$]C$_5$H$_4$NO[14] and [Ph$_2$P(O)CH$_2$]$_2$C$_5$H$_3$NO[10,14] when they are chelated with Ln(III) ions. In the metal chelate structures, the P═O groups appear to be the stronger base site on the basis of bond length arguments.

The molecular structure of **4-H** was also determined, and a view of the molecule showing key hydrogen bonding interactions is shown in Figure 3. Selected bond lengths are summarized in Table 2. Acidic hydrogen atom positions were located in difference maps for P−O(2)−H(2A)···O(3B) and C(6)−O(5)−H(5A)···O(3C) while a third H-atom was found disordered over two sites N−O(1)−H(1A)···O(4A) (50%) and P−O(4)···H(4A)···O(1D) (50%). The H-atom positions on the oxygen atoms were optimized with an equivalent O−H distance, 0.85 Å, and fixed in position in the final refinements. The P−O bond lengths once more appear with three values: P−O(3) 1.498(1) Å, P−O(2) 1.558(1) Å, and

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(13) Tan, Y.; Gan, X.; Stanchfield, J. L.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **2001**, *40*, 2910.

(14) Rapko, B. M.; Duesler, E. N.; Smith, P. H.; Paine, R. T.; Ryan, R. R. *Inorg. Chem.* **1993**, *32*, 2164.

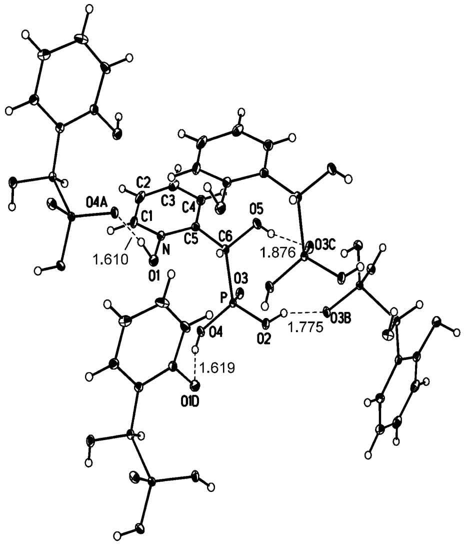

Figure 3. Molecular structure and atom numbering scheme of $[(HO)_2P(O)C(H)(OH)]C_5H_4NO$ **4-H**, with atom labeling scheme showing primary hydrogen bonding interactions.

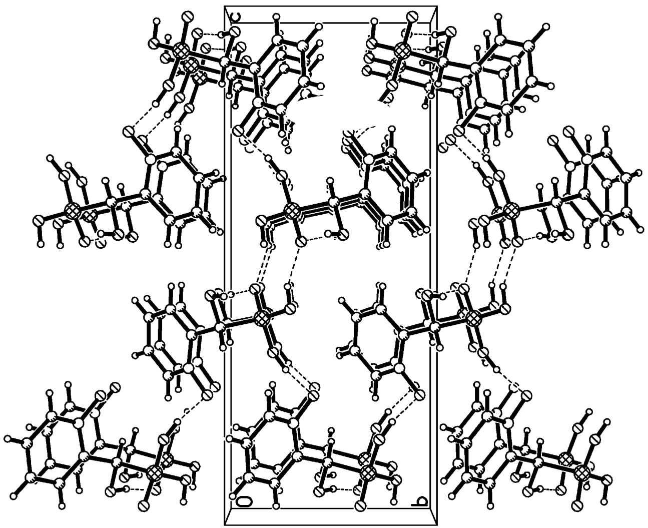

Figure 4. Unit cell contents for $[(OH)_2P(O)C(H)(OH)]C_5H_4NO$ **4-H** showing hydrogen bonded packing interactions.

P−O(4) 1.511(1) Å, and the P−O(3) interaction is considered to be the localized P═O phosphoryl bond. As in **1-H**, this bond length is slightly longer than those found in the related neutral phosphine oxide derivatives $[Ph_2P(O)CH_2]_2C_6H_4$ and $[Ph_2P(O)CH_2]_2C_5H_3NO$ probably due to the strong hydrogen bonding by the acidic POH groups. As shown in Figure 4, the hydrogen bonding network extends throughout the unit cell of **4-H** and the network is more complex than in **1-H** due to the additional C−OH group. The P−O(2)−H(2A) interacts with the P═O(3B) phosphoryl group in a second ligand molecule, the C(6)−O(5)−H(5A) interacts with the P═O(3C) phosphoryl group in the third ligand molecule, the N−O(1)−H(1A) hydrogen bonds (half occupancy) with P−O(4A) in a fourth ligand molecule, and P−O(4)−H(4A) hydrogen bonds (half occupancy) with the P═O(1D) phosphoryl group in a fifth ligand molecule.[15] The N−O bond distance in **4-H**, 1.363(2) Å, is also significantly longer than in $[Ph_2P(O)CH_2]_2C_5H_3NO$, 1.315(6) Å, in agreement with its involvement in the H-bonding scheme and with the NO group serving as the strongest base site.

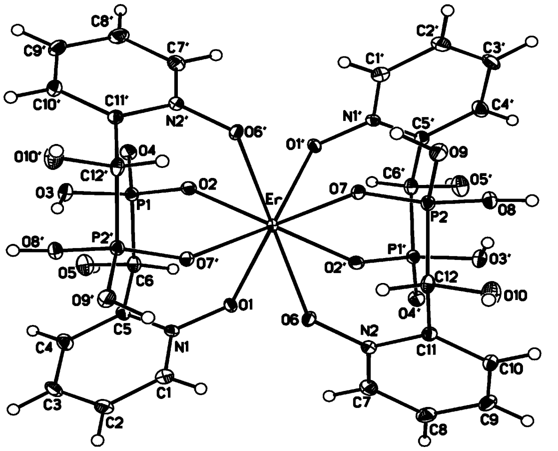

Figure 5. Molecular structure and atom numbering scheme for $Er\{[(HO)(O)P(O)C(H)(OH)]\ C_5H_4NO^-\}_3\{[(HO)_2P(O)C(H)(OH)]C_5H_4NO\} \cdot 8H_2O$, $Er(\mathbf{4}^-)_3(\mathbf{4\text{-}H}) \cdot 8H_2O$.

Both **1-H** and **4-H** are soluble in water, and these aqueous solutions readily dissolve lanthanide hydroxides including aged oxide−hydroxide precipitates. For the purposes of studying the resulting coordination chemistry, 1 equiv of freshly prepared $Er(OH)_3$ was treated with 4 equiv of **1-H** or **4-H** in water. The precipitate readily dissolves giving pale pink solutions from which single crystals deposit after slow evaporation of the water. The single crystal X-ray structure determinations for the complexes show that the complexes are isostructural and have the compositions $Er(\mathbf{L}^-)_3(\mathbf{L}{-}\mathbf{H})\cdot 8H_2O$. Metrical parameters for both complexes appear in Table 2; however, for the most part, discussion is limited to the $Er(\mathbf{4}^-)_3(\mathbf{4\text{-}H})\cdot 8H_2O$ complex. A view of the molecular structure of $Er(\mathbf{4}^-)_3(\mathbf{4\text{-}H})\cdot 8H_2O$ is shown in Figure 5.

The molecule $Er(\mathbf{4}^-)_3(\mathbf{4\text{-}H})$ has a 2-fold axis passing through the Er atom so that the asymmetric unit contains one-half Er, two $\mathbf{4}^-$ ligands, one-half (**4-H**) ligand, and four water molecules. The $\mathbf{4}^-$ ligands have lost one of the two protons from each of the parent phosphonic acid molecules. Therefore, each Er(III) is bonded to three anionic ligands $\mathbf{4}^-$ and one neutral acid ligand, **4-H**.[16] All ligands are bonded with a bidentate coordination mode through the *N*-oxide and phosphoryl oxygen atoms. These eight oxygen atoms generate a square antiprismatic inner sphere coordination polyhedron. The Er−O(P) bond lengths are Er−O(2) 2.268(2) Å, which belongs to the formally anionic ligand $\mathbf{4}^-$, and Er−O(7) 2.234(2) Å, which is associated with the $-^1/_2$ charged

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(15) The calculated hydrogen bond interaction parameters in **4-H** include the following: P−O(2)−H(2A)···O(3B) 1.775 Å, O(2)···O(3B) 2.579 Å, O(2)−H−O(3B) 157.1°; N−O(1)−H(1A)···O(4A) 1.610 Å, O(1)···O(4A) 2.453 Å, O(1)−H(1A)−O(4A) 170.6°; C(6)−O(5)−H(5A)···O(3C) 1.876 Å, O(5)···O(3C) 2.716, O(5)−H(5A)−O(3C) 168.9°; P−O(4)−H(4A)···O(1D) 1.619 Å, O(4)···O(1D) 2.543 Å, O(4)−H(4A)−O(1D) 166.5°.

(16) Since the Er(III) sits on a 2-fold rotation axis bound to four ligands, two ligands are unique and the other two are generated by the symmetry element $-x, y, ^1/_2 - z$. The $\mathbf{4}^-$ ligand containing P(1) is ordered with a H-atom on O(3) and O(4) carrying the formal minus charge. The ligand containing P(2) is disordered so that the H-atom on P(2)−O(8) is only present 50% of the time while the H on P(2)−O(9) is present all of the time. Relative to the asymmetric unit, the ligand containing P(2) has a $-^1/_2$ charge on the average.

ligand. These distances are significantly shorter than the Er−O(N) distances, Er−O(1) 2.408(2) Å and Er−O(6) 2.496(2) Å (2.457 Å av), which is consistent with the general coordinate bond length and relative base strength trends observed previously for (phosphinomethyl)pyridine *N*,*P*-oxide ligands chelated to metal cations.[10,14,17] It is also notable that the Er−O(P) distances are significantly shorter than the Tb−O(P) distances found in the square antiprismatic complex Tb{$[Ph_2P(O)CH_2]C_5H_4NO\}_4$ $(NO_3)_3$, 2.363 Å, even after accounting for the slightly larger Tb(III) effective ionic radius.[18] In the latter complex, all four organophosphinomethylpyridine *N*-oxide ligands are electronically neutral. The bond shortening in the Er(III) complex is, therefore, consistent with the −1 and $-^1/_2$ formal charges on the phosphonic acid ligands. The P−O bonds fall into four types. The P(1)−O(2) and P(2)−O(7) bonds are short, 1.499(2) Å and 1.498(2) Å, respectively, and they can be considered to be formally the P═O groups since they are comparable to the free ligand **4-H** phosphoryl P═O group bond lengths. The P(1)−O(3), 1.578(3) Å, and P(2)−O(9), 1.568(3) Å, bond lengths are long and associated with the oxygen atoms that are protonated. These distances are similar to one of the P−OH bond lengths in the free ligand **4-H**, 1.558(1) Å. The P(1)−O(4) unit (1.505(3) Å) is not directly involved with coordination to the Er(III). Last, the P(2)−O(8) distance, which involves the half occupied site, is 1.503(3) Å.

There are also four unique water molecules in the structure, and these participate in a complex hydrogen bonded network with the N−O, P−O, and P−OH functionalities in the coordinated ligands. The network structure is complicated by disorder involving O(12) on a water molecule and O(8) on a phosphoryl group.

Conclusion

The syntheses for the new phosphonic acids **1-H** and **4-H** described here are relatively efficient and potentially useful for large scale production. The acids are chemically robust toward strong acids and bases, and they show no signs of chemical degradation with time. The acids in water solution readily attack fresh and aged lanthanide oxide−hydroxide precipitates that are otherwise typically inert to most chemical dissolution reagents. The resulting anions form aqueous soluble complexes with Ln(III) cations, and the X-ray crystallographic data presented here reveal the nature of the anion chelation in complexes in the solid state. Although the solution structures have not yet been determined, it is likely that the anions also form related bidentate chelate structures in aqueous solutions. These results encourage further practical development of these and related ligands as dissolution/decontamination agents for lanthanide and actinide materials. Additional progress in this area will be described in future reports.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Gan, X.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **2002**, *41*, 5849.

(18) Effective ionic radii for Er(III) (CN = 8) and Tb(III) (CN = 8) are 1.00 Å and 1.04 Å, respectively. Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, *B26*, 1076.