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Article

A Three-Dimensional Framework Structure Constructed from 2-(2-Pyridyl-*N*-oxide) Ethylphosphonic Acid and Nd(III)

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A multistep synthesis for 2-(2-pyridyl-*N*-oxide) ethylphosphonic acid **6-H**$_2$ is described along with its spectroscopic (IR, NMR) data and a single-crystal X-ray diffraction structure analysis. Combination of the ligand with Nd(OH)$_3$ results in the formation of a complex Nd(**6-H**)$_3$. Single-crystal X-ray diffraction analysis reveals a three-dimensional crystal network generated by hydrogen-bonded chains along the crystallographic *c* axis. The hydrogen bonds are formed between phosphonic acid anion (**6-H**)$^{-1}$ protons on one chain and pyridyl *N*-oxide oxygen atoms in neighboring chains. The asymmetric unit contains 1/3[Nd(**6-H**)$_3$] and there are two unique Nd(III) atoms, each with $\bar{3}$ point symmetry. As a result, each Nd(III) ion is bound to six (**6-H**)$^{-1}$ ligands and the symmetry about the Nd(III) ion is octahedral with each vertex occupied by a phosphonate oxygen atom. The Nd–O bond lengths are essentially identical: Nd(1)–O(3), 2.336 (1) Å; Nd(2)–O(4), 2.340 (1) Å. The monoanionic ligand (**6-H**)$^{-1}$, therefore, serves to bridge the unique Nd(III) centers.

Introduction

Reactions between transition metal ions and organophosphonic acids are recognized to generate a wide array of interesting amorphorus microporous materials, as well as 1D, 2D, and 3D crystalline solid-state compounds, and this chemistry has been thoroughly reviewed in 1998 by Clearfield.[1] At that time, largely due to the insolubility of complexes prepared from commonly available phosphonic acids, there were relatively few reported examples of well-characterized lanthanide organophosphonate complexes.[2−6] Since then, a greater variety of phosphonic acids functionalized with hydrophobic and hydrophilic organic fragments have been prepared and used for solid-state framework construction chemistry.[2,7−16] Pertinent to the present study, Lin and co-workers[17,18] have reported 1D, 2D, and 3D structures based on pyridyl-derivatized phosphonic acids coordinated with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions. In these compounds, the pyridyl N-donor center and phosphonite oxygen atom together generate the inner-sphere coordination environment for the transition metal. In addition, Kong and Clearfield[19] have reported formation of 2D and 3D hydrogen-bonded framework structures from hydrothermal syntheses with Cu(II), Ni(II), and Co(II) and the trifunctional ligand 6-phosphonopyridine-2-carboxylic acid, **L-H**$_3$. In these complexes, the inner-sphere coordination

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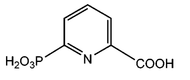
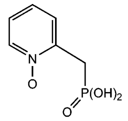
environment is derived from tridentate chelation of the **L-H**$_1^{2-}$ or **L**$^{3-}$ ligand.

Much of the interest in these compounds derives from the fundamental novelty and diversity displayed in the structural frameworks formed. In addition, there are practical interests in the materials as ion exchangers, proton conductors, and catalyst or catalyst supports.[1] In our own case, interest in donor-functionalized phosphonic acids results from a broader interest in the ligation behavior of related organophosphine oxides and organophosphonates. Multifunctional, neutral organophosphine oxides and organophosphonates act as strong chelating ligands toward lanthanide (Ln) and actinide (An) ions, and a few examples are very useful for biphasic separations of these ions.[20] In this context, we have recently described syntheses for 2-(organophosphinomethyl)pyridine P,N-dioxides and 2,6-bis(organophosphinomethyl)pyridine P,P,N-trioxides that act as unusually strong chelating ligands[21,22] and display selective biphasic extraction performance for Ln(III) and An(III)[23] ions in strongly acidic aqueous solutions. In some cases, neutral organophosphonates and phosphine oxides undergo hydrolytic degradation that produces the corresponding organophosphonic acids, RP(O)(OH)$_2$. This behavior, in solvent extraction systems, is undesireable since the phosphonic acids often form interactable solids and they typically offset extraction selectivity. On the other hand, in some instances, the acids may be employed to dissolve f-element oxide−hydroxide species and thereby serve as decontamination reagents. Therefore, we are interested in the basic chemistry of phosphonic acids that are functionally related to the neutral organophosphine oxides and phosphonates under development in our group as extractants. In this regard, we have recently reported[24] the synthesis of (2-pyridyl-*N*-oxide) methylphosphonic acid, **1-H**$_2$, and (2-pyridyl-*N*-oxide) hydroxymethylphosphonic acid, **1′-H**$_2$, that form isostructural complexes, Er(**1-H**)$_3$(**1-H**$_2$)·8H$_2$O and Er(**1′-H**$^-$)$_3$(**1′-H**$_2$)·8H$_2$O. In these complexes, both the anionic and neutral ligands bind in a bidentate fashion, resulting in an eight-coordinate inner-sphere environment on the Er(III) ion. Extensive hydrogen bonding results in a 3D framework structure.



L-H$_3$



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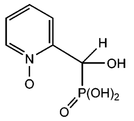
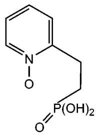


1'-H$_2$



6-H$_2$

In the present study, the ligand architecture of **1-H**$_2$ has been modified by addition of another $-CH_2-$ group in the pendent phosphonic acid arm, giving **6-H**$_2$. It was anticipated that this modification will alter the bidentate chelation characteristics of the ligand and thereby produce alternative metal−ligand inner-sphere and framework structures.

Experimental Section

General Information 2-(2-Hydroxyethyl)pyridine, triethyl phosphite, thionyl chloride, trimethylsilyl bromide (Aldrich), 3-chloroperoxybenzoic acid (Fischer), and Nd(NO$_3$)$_3$·5H$_2$O (Alpha Ventron) were purchased and used as received. Organic solvents were dried by standard methods as required in specific reaction steps. Mass spectra were obtained from the Midwest Center for Mass Spectrometry, University of Nebraska, and elemental analyses were determined at Galbraith Laboratories. NMR spectra were measured on JEOL GSX-400 and Bruker FX-250 spectrometers using external standards (85% H$_3$PO$_4$ and Me$_4$Si).

Synthesis of 2-(2-Pyridyl-*N*-oxide) Ethylphosphonic Acid (6-H$_2$). A sample of 2-(2-hydroxyethyl)pyridine (30 g, 0.24 mol) was added dropwise under nitrogen to thionyl chloride (70 mL, 0.96 mol) held at 0°C. After the addition was complete, the mixture was refluxed (45 min) using an oil bath held at 80°C. The mixture was cooled to 23 °C, and the excess thionyl chloride removed under reduced pressure. The residue was treated with water (30 mL), and the pH adjusted to 9 by addition of KOH (25 g) in water (60 mL). The aqueous solution was extracted with CH$_2$Cl$_2$ (3 × 50 mL), and the combined organic phases were dried over anhydrous Na$_2$SO$_4$. The CH$_2$Cl$_2$ was vacuum-evaporated leaving 2-(2-chloroethyl)pyridine (**2**) as a dark orange oil: yield, 32.2 g (93%). NMR (CDCl$_3$): ^{1}H δ 3.19 (t, $J = 6.9$ Hz), 3.89 (t, $J = 6.8$ Hz), 7.10−7.18 (m), 7.55−7.62 (m), 8.51−8.53 (m).

The sample of 2-(2-chloroethyl)pyridine, **2**, (32.2 g, 0.23 mol) was combined with triethyl phosphite (42 g, 0.25 mol), stirred, and heated (182°C, 3h). The unreacted starting materials were vacuum-evaporated (80°C/100 mTorr), leaving 2-[(2-diethylphosphono)-ethyl]pyridine (**3**) as a colorless oil: yield, 56 g (74%). NMR (CDCl$_3$): ^{31}P{^{1}H} δ 32.0; ^{1}H δ 1.26 (t, $J = 7.1$ Hz), 2.13−2.27 (m), 2.99−3.10 (m), 3.99−4.15 (m), 7.07−7.16 (m), 7.53−7.60 (m), 8.45−8.51 (m); ^{13}C{^{1}H} δ 16.0 (d, $J = 6.0$ Hz), 24.6 (d, $J = 141.2$ Hz), 30.4 (d, $J = 3.7$ Hz), 61.0 (d, $J = 6.3$ Hz), 121.0, 122.3, 136.0, 148.9, 159.7 (d, $J = 16.0$ Hz).

A sample of **3** (10 g, 41 mmol) and 3-chloroperoxybenzoic acid (12.7 g, 57−86%) were mixed in CHCl$_3$ (100 mL) and stirred (23°C, 2 h). The mixture was then extracted with aqueous NaHCO$_3$ solution (1 M, 120 mL), and the aqueous phase extracted with CH$_2$Cl$_2$ (8 × 60 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, and the solvent removed by vacuum evaporation leaving 2-[(2-diethylphosphono)ethyl]pyridine *N*-oxide (**4**) as an orange oil: yield, 6.8 g (64%). NMR (CDCl$_3$): ^{31}P{^{1}H} δ 31.1; ^{1}H δ 1.25 (t, $J = 7.0$ Hz), 2.19−2.32 (m), 3.09−3.21 (m), 3.99−4.10 (m), 7.17−7.22 (m), 7.28−7.32 (m), 8.22−8.25 (m); ^{13}C{^{1}H} δ 15.2 (d, $J = 6.0$ Hz), 20.2 (d, $J = 141.1$ Hz), 23.8 (d, $J = 3.7$ Hz), 60.4 (d, $J = 6.4$ Hz), 123.3, 124.9, 125.3, 138.4, 149.1 (d, $J = 14.4$ Hz).

A sample of **4** (2.0 g, 7.7 mmol) was combined dropwise with Me$_3$SiBr (2.54 g, 17.0 mmol) and stirred (23 °C, 3 h). The excess Me$_3$SiBr was vacuum-evaporated leaving 2-[2-bis((trimethylsilyl)-phosphono)ethyl]pyridine *N*-oxide (**5**) as an orange oil: yield, 2.6 g (98%). NMR (CDCl$_3$): ^{31}P{^{1}H} δ 11.8; ^{1}H δ 0.21, 2.11−2.18 (m), 3.24−3.30 (m), 7.56−7.79 (m), 8.77 (d, $J = 5.4$ Hz); ^{13}C {^{1}H} δ 0.2, 24.4 (d, $J = 148.4$ Hz), 24.7 (d, $J = 3.6$ Hz), 124.5, 126.4, 130.4, 139.3, 150.6 (d, $J = 16.3$ Hz).

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Table 1. Crystallographic Data

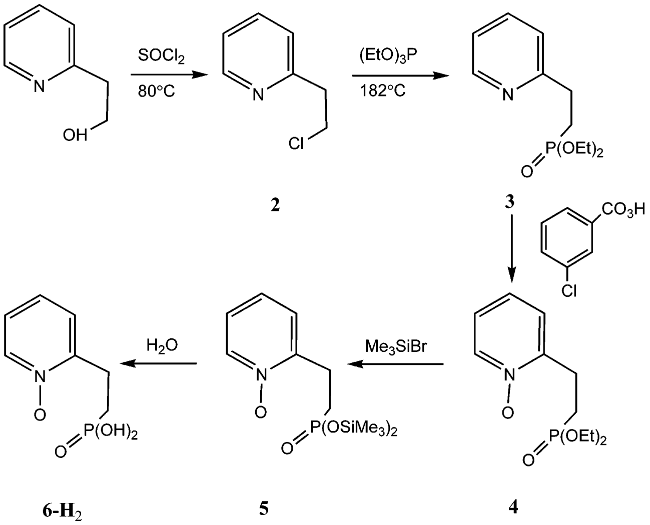
	6-H$_2$	Nd(**6-H**)$_3$
empirical formula	$C_7H_{10}NO_4P$	$C_{21}H_{27}N_3NdO_{12}P_3$
fw	203.13	750.61
a, Å	7.245 (3)	21.081 (3)
b, Å	8.766 (3)	21.081 (3)
e, Å	13.899 (3)	10.495 (2)
α, deg	94.88 (2)	90
β, deg	94.85 (2)	90
δ, deg	96.83 (2)	120
V, Å^3	869.3 (6)	4039.5 (10)
cryst syst	triclinic	rhombohedral, hexagonal
space group	$P\bar{1}$	$R\bar{3}$
Z	4	6
D_{calcd}, g/cm^3	1.552	1.851
μ, mm^{-1}	0.297	2.174
R1, wR2 [$I \geq 2\sigma(I)$]	0.0412, 0.1039	0.0165, 0.0410

A large sample of **5** (28.8 g, 83 mmol) was added to water (100 mL), and the mixture stirred (1 h). The resulting mixture was extracted with $CHCl_3$ (3 × 50 mL). The aqueous phase was filtered to remove insoluble impurities, and the filtrate evaporated, leaving a residue that was treated with dimethylformamide (60 mL) and stirred (23°C, 2h). The undissolved 2-(2-pyridyl *N*-oxide)ethylphosphonic acid was collected by filtration, washed with DMF (3 × 20 mL), and the solid dried under vacuum: yield, 11 g (66%). mp: 204−205 °C (dec). Anal. Calcd for $C_7H_{10}NO_4P$: C, 41.39; H, 4.96; N, 6.90. Found: C, 41.19; H, 5.37; N, 6.83. MS (FAB) (*m*/*e*, fragment, rel inten.): 204 ($[M + H]^+$, 40%), 203 (M^+, 5%), 188.1 ($[M + H - O]^+$, 5%). IR (KBr, cm^{-1}): 3470 (w), 3124 (w), 3084 (w), 2335 (m), 1641 (m), 1568 (m), 1492 (s), 1437 (s), 1280 (m), 1190 (s), 1167 (s), 1093 (s), 1047 (s), 993 (s), 954 (s), 841 (s), 767 (s), 738 (m), 580 (m), 553 (m), 474 (m), 430 (m). NMR (DMSO-d_6): $^{31}P\{^1H\}$ δ 26.1; ^1H δ 1.84−1.98 (m), 2.92−3.02 (m), 7.29−7.32 (m), 7.45−7.49 (m), 8.24−8.27 (m); $^{13}C\{^1H\}$ δ 24.1 (d, J = 136.4 Hz), 24.5 (d, J = 3.1 Hz), 124.4, 125.6, 126.0, 139.0, 150.7 (d, J = 16.9 Hz). Single crystals of **6-H**$_2$ were obtained by slow cooling of a saturated hot aqueous solution.

Synthesis of Complex. Freshly prepared $Nd(OH)_3$ (0.5 mmol) and **6-H**$_2$ (0.8 mmol) were mixed in water (20 mL) and heated (1 h). The resulting purple solution was filtered to remove unreacted $Nd(OH)_3$, and the filtrate allowed to slowly evaporate. Purple crystals of Nd(**6-H**)$_3$ suitable for single-crystal X-ray diffraction analysis were obtained. IR (KBr, cm^{-1}): 3088 (m), 2654 (br), 1728 (m), 1604 (m), 1492 (s), 1435 (s), 1367 (w), 1284 (w), 1194 (s), 1114 (s), 1047 (s), 954 (s), 927 (s), 850 (m), 812 (m), 779 (s), 761 (s), 713 (m), 613 (m), 542 (s), 486 (s), 441 (s).

X-ray Diffraction Analysis. A light brown prism of **6-H**$_2$ (0.62 × 0.34 × 0.08 mm^3) and a faint purple rod of Nd(**6-H**)$_3$ 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 (λ = 0.71073Å). Lattice and data collection parameters are summarized in Table 1. All calculations were performed by using SHELXL97.[25] The structures were solved by direct methods, and full-matrix least-squares refinements based upon F^2 were employed.[26] The refinement of **6-H**$_2$ was well behaved. All non-hydrogen atoms were refined anisotropically, and all H-atoms were located in difference maps. In the final cycles of refinement, the H-atoms were allowed to vary in position. The refinement for Nd(**6-H**)$_3$ was also well behaved with all non-hydrogen atoms refined anisotropically. The H-atoms were located in difference maps and were allowed to vary in position with $U_{\mathrm{iso}} = 1.25U_{\mathrm{eq}}$ of the parent atom.

Scheme 1



Results and Discussion

The synthesis developed for the target ligand **6-H**$_2$ is summarized in Scheme 1. Commercially available 2-(2-hydroxyethyl)pyridine was chlorinated with thionyl chloride and the resulting **2** was isolated as an orange oil in 93% yield. This known compound was directly converted without further purification to **3** via an Arbusov reaction with $(EtO)_3P$. The phosphonate was obtained as a colorless oil in 74% yield following standard reaction workup, and it was 98% pure based upon ^{31}P and ^1H NMR spectra. Compound **3** displays a single ^{31}P NMR resonance at δ 32.0 that is closely comparable to the chemical shifts of other organophosphonates and, in particular, pyridyl phosphonates.[21,27,28] This compound was N-oxidized with *m*-chloroperbenzoic acid giving **4** as an orange oil in 64% yield. Compound **4** is identified by a single $^{31}P\{^1H\}$ NMR resonance at δ 31.1. The conversion of **3** to **4** is nearly quantitative, as indicated by ^{31}P NMR; however, the isolated yield is reduced due to the partial aqueous solubility of **4** during reaction mixture workup. Several attempts were made to hydrolyze **4** directly to give **6-H**$_2$; however, low conversion was observed even when **4** was exposed to strong acids (HCl, HNO_3) and heat. In addition, it was difficult to purify the **6-H**$_2$ formed in aqueous hydrolysis reactions. Therefore, **4** was treated with Me_3SiBr, giving the silyl derivative **5** in high yield (98%) as an orange oil: $^{31}P\{^1H\}$ NMR, δ 11.8. This compound, without further purification, was treated with water, giving the phosphonic acid **6-H**$_2$ with good yields.[29,30] Compound **6-H**$_2$ is obtained in analytically pure form as a light tan, crystalline solid. A FAB-mass spectrum shows the presence

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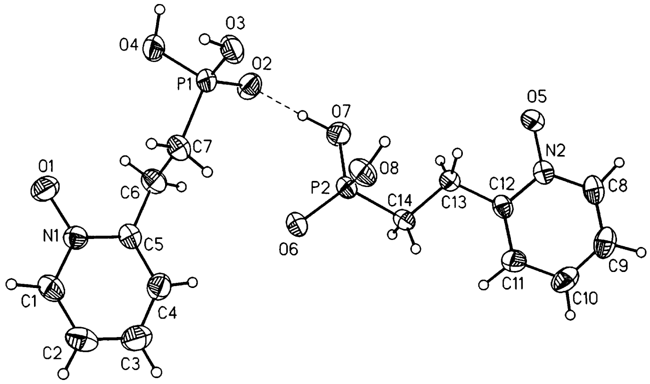

Figure 1. Molecular structure and atom labeling scheme for $[(HO)_2P(O)CH_2CH_2]C_5H_4NO$, **6-H$_2$**, showing the hydrogen-bonded dimer in the asymmetric unit (50% thermal ellipsoids).

of $(M + H^+)$ and (M^+) ions. The $^{31}P\{^1H\}$ NMR spectrum for **6-H$_2$** shows a single resonance δ 26.1 (d_6-DMSO) that is downfield of the resonance observed for **1-H$_2$** (δ 19.7), and **1′-H$_2$** (δ 18.2).

The molecular structure of **6-H$_2$** was determined by single-crystal X-ray diffraction methods, and a view of the molecule is shown in Figure 1. The asymmetric unit contains two molecules hydrogen-bonded through O(2)···H(7)−O(7) and O(4)−H(4)···O(6) [$x - 1, y, z$] interactions. The two unique molecules, **I** [containing P(1)] and **II** [containing P(2)], are also hydrogen-bonded to like molecules forming dimers through centers of symmetry: **I** to **I′** [$-x, 2 - y, 1 - z$] and **II** to **II′** [$1 - x, 1 - y, 2 - z$]. These dimers are stacked in the *a* direction. The **I** and **II** dimers are also hydrogen-bonded to each other: O(4)−H(4a)···O(6), O(7)−H(7c)···O(2). The P−OH bond lengths can be sorted into two slightly different groups: P−OH (short), P(1)−O(4) 1.537(2) Å and P(2)−O(7) 1.543(2) Å; P−OH (long), P(1)−O(3) 1.549(2) Å and P(2)−O(8) 1.552(2) Å. The differences correspond with the hydrogen-bonding interaction types: P−OH (short)···O−P (phosphine oxide) and P−OH (long)···O−N (pyridine *N*-oxide). The main difference between molecules **I** and **II** resides in the orientation of the pyridine *N*-oxide ring relative to the exo $-CH_2CH_2P(O)(OH)_2$ arm. In molecule **I**, the $-CH_2CH_2$ arm is almost perpendicular to the ring, while in molecule **II**, the arm is nearly in the plane of the ring. The phosphoryl P═O bond lengths (av 1.486(2) Å), as expected, are shorter than the P−OH bond lengths, and they are comparable to those in **1-H$_2$** (1.493(2) Å) and **1′-H$_2$** (1.498(1) Å). The N−O bond lengths (av 1.331(3) Å) are shorter than those found in **1-H$_2$** (1.352(2) Å) and **1′-H$_2$** (1.363(2) Å).

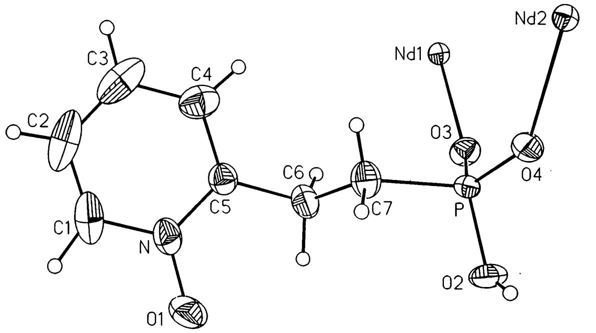

Figure 2. Molecular structure and atom labeling scheme for the asymmetric unit $1/3Nd\{[(HO)PO_2CH_2CH_2]C_5H_4NO\}_3$.

Table 2. Selected Bond Lengths (Å)

		6-H$_2$	Nd(**6-H**)$_3$
P−O	P(1)−O(2)	1.484(2)	P−O(2) 1.559(2)
	P(1)−O(3)	1.549(2)	P−O(3) 1.5093(14)
	P(1)−O(4)	1.537(2)	P−O(4) 1.5058(13)
	P(2)−O(6)	1.489(2)	
	P(2)−O(7)	1.543(2)	
	P(2)−O(8)	1.552(2)	
N−O	N(1)−O(1)	1.330(3)	N−O(1) 1.326(2)
	N(2)−O(5)	1.332(3)	
Nd−O			Nd(1)−O(3) 2.3360(13)
			Nd(2)−O(4) 2.3395(15)

Aqueous solutions of **6-H$_2$** readily dissolve lanthanide hydroxides suspended in rapidly stirred warm water.[31] In the present case, a purple complex with the same composition was obtained from Nd/**6-H$_2$** mixtures using mole ratios 0.7:0.3. Single crystals of the complex were obtained by slow evaporation of the solutions over several weeks. Single-crystal X-ray diffraction analysis shows that the complex has the composition Nd(**6-H**)$_3$. A view of the molecule is shown in Figure 2, and selected bond lengths are listed in Table 2. The compound crystallizes in the centric space group $R\bar{3}$ with six molecules in the unit cell. The asymmetric unit contains $1/3\{Nd[(HO)PO_2CH_2CH_2]C_5H_4NO\}_3$. There are two unique Nd(III) ions occupying *a* and *b* positions [*a*: 0, 0, 0; *b*: 0, 0, $^1/_2$]. These positions have $\bar{3}$ point symmetry; therefore, the Nd(III) ions are octahedrally coordinated to six (**6-H**)$^{-1}$ ligands. Each (**6-H**)$^{-1}$ ligand is bonded to both kinds of Nd(III) ions forming a chain along 0, 0, *z*.

The oxygen atoms in the two P−O bonds, P−O(3) and P−O(4), each bond to a different Nd(III) ion: Nd(1)[0, 0, 0]−O(3) and Nd(2)[0, 0, $^1/_2$]−O(4) with Nd(1)−O(3) 2.3360(13) Å, Nd(2)−O(4) 2.3395(13) Å and P−O(3) 1.5093(14) Å, P−O(4) 1.5058 (13) Å. The unique P−O(2)H group, P−O(2) 1.559(2) Å, is not involved in coordination with Nd(III); however, it is involved with hydrogen bonding to an *N*-oxide in a neighboring chain. The *N*-oxide oxygen atom does not bond to a Nd(III) ion. This makes the chelation behavior of (**6-H**$^{-1}$) uniquely different from the chelation type shown by (**1-H**)$^{-1}$ and (**1′-H**)$^{-1}$.

The coordination environment about each Nd(III) ion is octahedral, as shown in Figure 3. Looking down the *c* axis, with Nd(1) at [0, 0, 0] and Nd(2) at [0, 0, $^1/_2$], there are

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(30) **6-H$_2$** is soluble in water ($\sim 1 \times 10^{-1}$ M), partially soluble in DMSO, and insoluble in other common organic solvents. Due to the partial solubility in DMSO, some ligand is lost to the DMSO wash phase. These phases can be collected from several syntheses, evaporated, and the residue treated again by aqueous/DMSO workup. This provides for recovery of additional pure acid.

(31) As part of a broader study of the use of phosphonic acids as decontamination agents, we observe that aqueous solutions (0.1−1 M) of phosphonomethylpyridine *N*-oxides in their acid forms readily dissolve freshly prepared $Ln(OH)_3$ (Ln = La, Nd, Eu, Er) colloids and precipitates, as well as thermally aged (100 °C, 7 days) hydroxide precipitates.

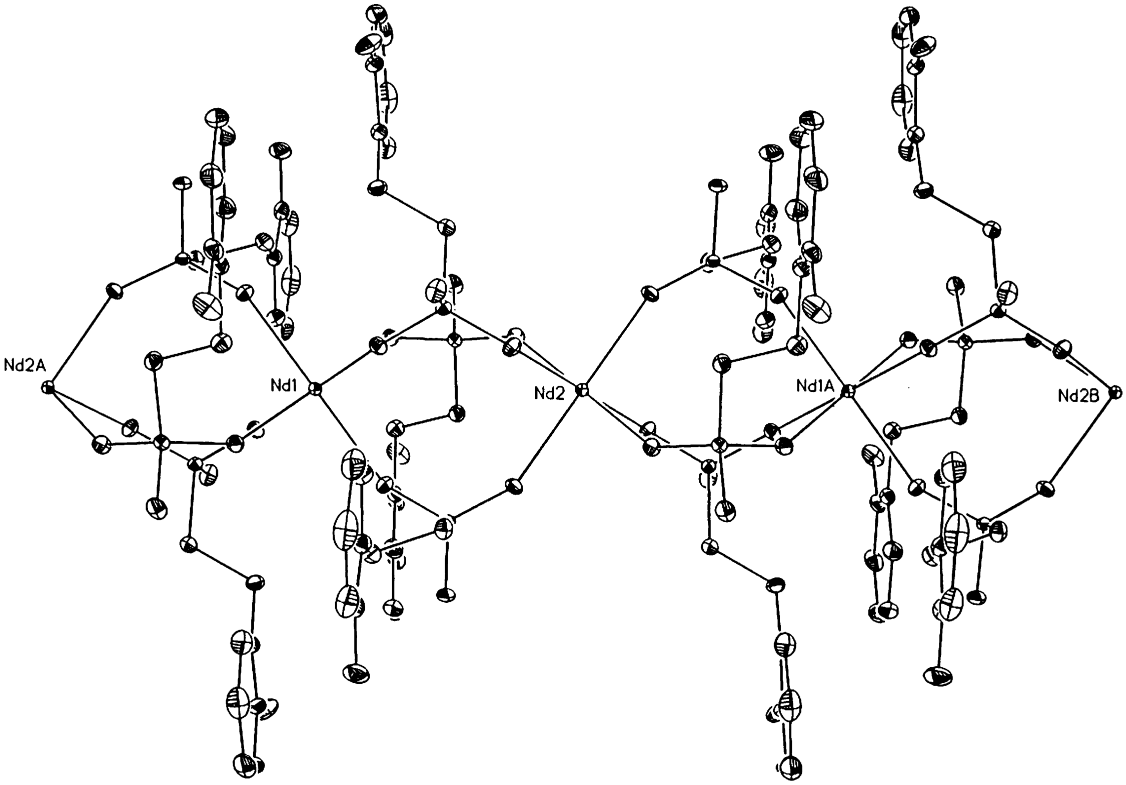

Figure 3. Chain structure of $\{Nd\{[(HO)PO_2CH_2CH_2]C_5H_4NO\}_3\}_n$ along 0, 0, *z*.

three ligands between Nd(1) and Nd(2) related by a 3-fold axis. Each Nd resides on a center of symmetry, so the three ligands project to the opposite side creating the octahedral symmetry. The chains formed are linked to each other by the hydrogen bonds mentioned above: N−O(1)···H (2a), 1.91 Å. There may also be very weak C−H···O(1) (2.39 Å) and C−H···O(2) (2.54 Å) hydrogen-bond interactions between chains although these distances are more likely a result of packing forces as the pyridine *N*-oxide rings are positioned to fit between O(1)···O(2) gaps.

Conclusion

As found with the pyridyl *N*-oxide functionalized phosphonic acids **1-H**$_2$ and **1′-H**$_2$, the compound **6-H**$_2$ is obtained efficiently from a multistep synthesis scheme. The acid is stable toward strong acids and bases, and water solutions dissolve neodyminium hydroxide with ease, forming a well-defined crystalline complex. In the solid state, the complex Nd (**6-H**)$_3$ displays an infinite chain structure in which each anionic phosphonate ligand (**6-H**)$^{-1}$ forms bridging connections between two Nd(III) ions in the chain and the *N*-oxide groups do not participate in forming the Nd(III) coordination environment. This contrasts with the coordination behavior displayed by (**1-H**)$^{-1}$ and (**1′-H**)$^{-1}$ which form bidentate chelate N−O, P−O interactions with Ln(III) ions. The difference very likely is a response to the need to produce an eight-membered chelate ring interaction with (**6-H**)$^{-1}$ if N−O, P−O binding is adopted.

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

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