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Formation of a 1-D chain structure from Nd(III) and 2,6-bis(methylphosphonic acid)pyridine *N*-oxide

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Abstract

The combination of $Nd(NO_3)_3 \cdot 6H_2O$ with 2,6-bis(methylphosphonic acid)pyridine *N*-oxide (**3-H$_4$**) in water under hydrothermal conditions results in the formation of a complex $Nd(\mathbf{3\text{-}H_2}^{2-})(\mathbf{3\text{-}H_3}^{1-})(H_2O)_{4/3}$ and the molecular structure of the 1-D chain has been determined by single crystal X-ray diffraction methods.

Keywords: Hydrothermal synthesis; Neodymium; Phosphonic acid derivatives; Pyridine *N*-oxide derivatives

1. Introduction

Combinations of organophosphonic acids with transition metal ions produce, in some cases, intractable amorphous solids while in other cases crystalline compounds with complex 1D, 2D or 3D structures are obtained. Much of this chemistry was thoroughly reviewed by Clearfield [1] in 1998 and the field has continued to grow since that time especially for compounds formed with late transition metal ions. Pertinent to our present study, Lin and co-workers [2,3] have reported the formation of crystalline complexes of several bifunctional pyridyl derivatized phosphonic acids coordinated to Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions. In these complexes, both the pyridyl N-donor center and a phosphonate oxygen atom form the inner sphere coordination environment. Recently Kong and Clearfield [4] have reported the synthesis of 2D and 3D framework structures by using trifunctional 6-phosphono pyridine-2-carboxylic acid in combination with Cu(II), Ni(II) and Co(II). The inner sphere coordination environments in these complexes result from tridentate chelation interactions by the anionic species $L\text{-}H_1^{2-}$ and L^{3-}.

Interest in these compounds derives not only from the novel extended solid state structures adopted but also from potential solid state materials applications as ion exchangers, ion conductors, proton conductors and catalyst supports. In our group, we are investigating the coordination chemistry of neutral multifunctional organophosphonate and organophosphine oxide ligands toward lanthanide [5–9] and actinide ions [10,11]. In these systems, the neutral ligand/f-element coordination chemistry is of fundamental interest and in some examples the ligands act as useful selective liquid–liquid extractants for f-element ions present in highly acidic aqueous solutions [12–14]. Because of this practical interest, it is important to determine the stability of these ligands toward hydrolysis or decomposition. If neutral organophosphonate ligands undergo hydrolysis, even slowly, it then becomes important to determine if hydrolysis products coordinate with f-element ions and influence separation selectivity. In this regard, some phosphonate esters, $RP(O)(OR)_2$ are known to undergo hydrolysis producing phosphonic acids, $RP(O)(OH)_2$ [15]. We have recently reported the direct synthesis of the

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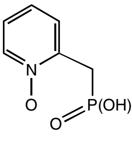
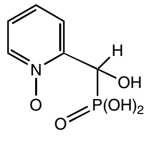
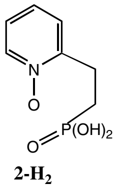
bifunctional 2-(methylphosphonic acid) pyridine *N*-oxides **1-H$_2$** [16], **1′-H$_2$** [16] and **2-H$_2$** [17] and their coordination chemistry toward selected lanthanide ions. For example, **1-H$_2$** and **1′-H$_2$** form complexes Er(**1-H**$^-$)$_3$(**1-H$_2$**) · 8H$_2$O in which all four ligands act as bidentate chelates producing an eight-coordinate metal center [16]. The P–O and N–O groups also participate in the formation of an extensive 3D hydrogen bonding network. The ligand **2-H$_2$**, with its longer *exo*-ethyl phosphonic acid arm, forms a complex Nd(**2-H**$^{-1}$)$_3$. The solid-state structure contains chains along the *c*-axis in which the *N*-oxide does not participate in chelate formation on Er(III), but is involved in hydrogen bond interactions with phosphonic acid hydrogen atoms [17]. The differences between these ligands and their coordination properties has led us to explore the directed synthesis of the trifunctional ligand, 2,6-bis(methylphosphonic acid)pyridine *N*-oxide **3-H$_4$**, and its coordination chemistry with Nd(III). The results of that study are reported here.



1-H$_2$



1′-H$_2$



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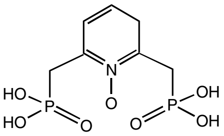
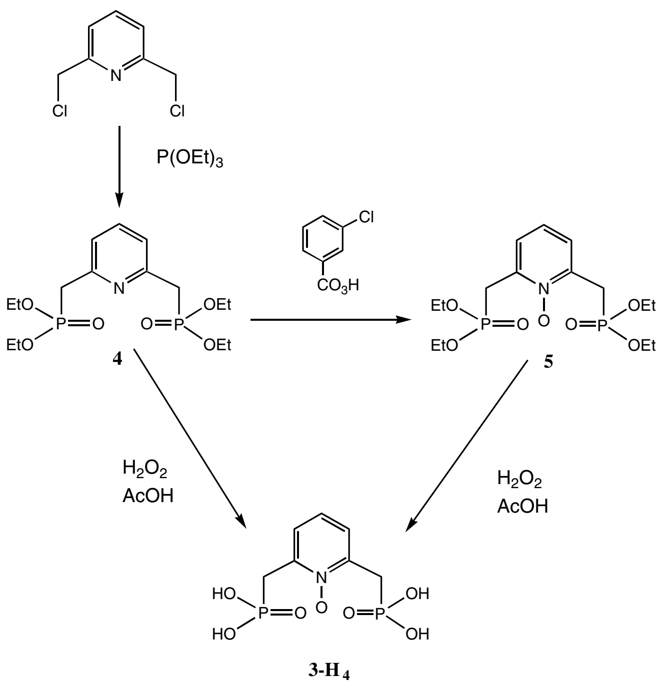


3-H$_4$

2. Results and discussion

2.1. Synthesis and characterization of ligand

The target ligand, 2,6-bis(methylphosphonic acid)pyridine *N*-oxide, **3-H$_4$**, was prepared in good to fair overall yields by two related approaches that differ in the method of oxidation of the intermediate, 2,6-bis(diethylphosphonomethyl)pyridine (**4**) (Scheme 1). We have previously reported the synthesis of **4** from an Arbusov reaction between P(OEt)$_3$ and 2,6-bis(chloromethyl)pyridine [6] and under the conditions described there (140–150 °C, 4 h), **4** was obtained in 88% yield. We note here that performing the reaction at 150 °C for 7 h results in essentially quantitative formation of **4** with a single ^{31}P NMR resonance at δ 25.6. This ^{31}P NMR shift appears in the region expected for alkyl phosphonates, RP(O)(OR)$_2$ [18]. The direct oxidative hydrolysis of the ester **4** to the acid **3-H$_4$** (Method 1) was examined by use of mixtures of glacial acetic acid and hydrogen peroxide. By this route, the oxidative conversion is only partially effective. Under the conditions described, about 65% of **4** remains unconverted after a typical reaction. Following extractive work up, the solid product is a mixture that contains ~93% **3-H$_4$** and ~7% of the pyridine compound [(HO)$_2$P(O)CH$_2$]$_2$C$_5$H$_3$N, that is identified by its ^{31}P NMR resonance, δ 14. This mixture is difficult to separate, and this fact together with the unsatisfactory overall conversion led us to seek an alternate synthesis approach.



Scheme 1.

In our previous report [6], in which a synthesis for compound **5** was sought, we noted that when the oxidation of **4** with 3-chloroperbenzoic acid (70 °C, 16 h) was not carefully controlled, variable quantities of **3-H$_4$** would also appear in samples of **5**. With the temperature sensitivity in mind, we performed here the N-oxidation of **4** with 3-chloroperbenzoic acid in CHCl$_3$ solution at 23 °C for 18 h (Method 2). This results in formation of **5** in 91% yield, which is a much improved yield compared to 47% obtained when the reaction is performed at elevated temperature. Characterization data obtained here for **5** are consistent with the data reported earlier. The subsequent hydrolysis of **5** with acetic acid/H$_2$O$_2$ solution is completed at 70 °C after ~17 h. The hydrogen peroxide is added to assist in the N-oxidation of any small quantities of **4** that remain in **5**. Simple work up normally provides pure **3-H$_4$** in 90% yield. However, if small amounts of **4** or **5** are carried through, recrystallization from acetone/water or Et$_2$O/pentane solutions removes these impurities. The product is an analytically pure, white, crystalline solid obtained as a monohydrate. The NMR spectra are solvent dependent and ^{31}P and spectral data are provided for D$_2$O and d_6-DMSO solutions.

2.2. Synthesis of the complex

The 2:1 combinations of **3-H$_4$** and Nd(NO$_3$)$_3$ in MeOH or Nd(OH)$_3$ in water produce clear solutions that deposit amorphous solids upon evaporation of the volatiles or addition of CHCl$_3$ to the reaction mixtures. Elemental analyses suggest formation of 2:1 ligand:metal complexes with varying degrees of solvation. However, when 2:1