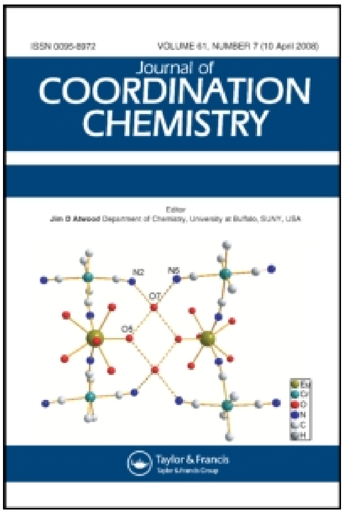

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Two new nickel phosphonate compounds: different supramolecule structures constructed by 1-aminoethylidenediphosphonic acid and ammonium counterions

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To cite this Article Liu, Qiao-Yun , Xiao, Yong , Li, Ming , Chen, Shuo-Ping and Yuan, Liang-Jie(2009) 'Two new nickel phosphonate compounds: different supramolecule structures constructed by 1-aminoethylidenediphosphonic acid and ammonium counterions', Journal of Coordination Chemistry, 62: 2, 205 — 215

To link to this Article: DOI: 10.1080/00958970802233144

URL: http://dx.doi.org/10.1080/00958970802233144

Journal of Coordination Chemistry
Vol. 62, No. 2, 20 January 2009, 205–215

Two new nickel phosphonate compounds: different supramolecule structures constructed by 1-aminoethylidenediphosphonic acid and ammonium counterions

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(*Received 12 March 2008; in final form 3 April 2008*)

Hydrothermal reactions of 1-aminoethylidenediphosphonic acid ($AEDPH_4$), $Ni(OH)_2$ and ammonium counterions afforded two nickel phosphonate compounds, $(enH_2)_3[Ni(AEDP)_2] \cdot 6H_2O$ (**1**) and $(NH_4)_6[Ni(AEDP)_2] \cdot 4H_2O$ (**2**) (en = ethylenediamine). Compounds **1** and **2** both contain $[Ni(AEDP)_2]^{6-}$ while having different three-dimensional (3-D) supramolecular structures. In **1**, the $[Ni(AEDP)_2]^{6-}$ anion and enH_2^{2+}cations interconnected via various hydrogen bonds and form a 3-D porous supramolecular network with extended one-dimensional channels, in which an interesting T4(2)6(2) water tape penetrates. Compared to **1**, the $[Ni(AEDP)_2]^{6-}$ anion and NH_4^+ cations in **2** constitute an enclosed 3-D supramolecular framework without obvious channels; two water-ammonium clusters with different structural motifs are observed. The magnetism of **1** exhibits weak antiferromagnetic interaction via the hydrogen bonds. The effect of protonated ammonium counterions on the structural types of the final products is also discussed.

Keywords: Nickel phosphonate compound; Water tape; Water-ammonium clusters; 1-Aminoethylidenediphosphonic acid

1. Introduction

Supramolecular chemistry based on hydrogen-bonded assembly has attracted considerable attention due to exquisite architectures and potential functions [1–7]. As an important part of supramolecular chemistry, metal-phosphonate compounds [8] have been constructed from a series of organophosphonic acids [9–13]. However, there is still a challenge to obtain the desired supramolecular structures of metal phosphonates since the crystal structures are strongly influenced by many factors. For example, counterions can readily affect the structural motif.

Among the diverse organophosphonic acids, 1-aminoethylidenediphosphonic acid ($AEDPH_4$) is chosen to extend the crystal design of novel supramolecules.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802233144

Some metal-AEDP supramolecular compounds have been reported in our previous work and display interesting structures [14–19]. Herein, we investigate the effect of protonated ammonium counterions on the structures of metal-phosphonate compounds using protonated ethylenediamine and ammonia as counterions. By hydrothermal reactions of 1-aminoethylidenediphosphonic acid ($AEDPH_4$), $Ni(OH)_2$ and ethylenediamine or ammonia, two nickel phosphonate compounds, i.e. $(enH_2)_3[Ni(AEDP)_2] \cdot 6H_2O$ (**1**) and $(NH_4)_6[Ni(AEDP)_2] \cdot 4H_2O$ (**2**) were synthesized and characterized by X-ray single-crystal diffraction, elemental analysis, infrared spectra (IR) and thermal gravimetric analysis (TGA). Both compounds contain $[Ni(AEDP)_2]^{6-}$ but different 3-D supramolecular structures, depending on the protonated ammonium counterions. Furthermore, the magnetism of **1** is also investigated.

2. Experimental

2.1. *Materials and measurements*

The 1-aminoethylidenediphosphonic acid ($AEDPH_4$) was prepared according to US Patent 4239695 [20]. The other starting materials were purchased from commercial sources and used without further purification. IR spectra were recorded from KBr pellets from 400–4000 cm^{-1} on a Nicolet 5700 FTIR spectrometer with spectral resolution of 4.00 cm^{-1}. Thermogravimetric studies were carried out with a NETZSCH STA 449C at a heating rate of 20 K/min under air. The elemental analysis data were obtained from a Perkin-Elmer 240B elemental analyzer.

2.2. *Synthesis*

Compound **1** was prepared from $Ni(Ac)_2 \cdot 4H_2O$ (0.0622 g, 0.25 mmol) and $AEDPH_4$ (0.1025 g, 0.5 mmol) in 2.0 ml H_2O, with 1 drop of ethylenediamine added to adjust pH to 8–9. The mixture was sealed in a Teflon reactor and then heated at 80°C for 2 days; blue needle-like crystals for single crystal diffraction analysis were obtained. Elemental analysis: Calcd for $(enH_2)_3[Ni(AEDP)_2] \cdot 6H_2O$: C, 15.90; H, 6.94; N, 14.84. Found: C, 15.80; H, 6.88; N, 14.65.

Compound **2** was synthesized by a method similar to **1** using twice the amount of $NH_3 \cdot H_2O$ instead of ethylenediamine. The mixture was sealed in a Teflon reactor and then heated for 2 days. Blue block-like crystals for single crystal diffraction analysis were obtained. Elemental analysis: Calcd $(NH_4)_6[Ni(AEDP)_2] \cdot 4H_2O$: C, 7.49; H, 6.56; N, 17.48. Found: C, 7.36; H, 6.41; N, 17.40.

2.3. *X-ray crystallography*

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer at room temperature (293 K) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were corrected for absorption using SADABS. The structures were solved by direct methods using SHELXS-97 [21]. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix

Table 1. Crystallographic data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{10}H_{52}N_8O_{18}P_4Ni$	$C_4H_{42}N_8O_{16}P_4Ni$
Formula weight	755.19	641.05
Temperature	293(2) K	293(2) K
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pnma*
Unit cell dimensions (Å, °)		
a	6.4342(7)	18.9539(17)
b	9.0106(9)	14.8905(13)
c	13.3307(13)	8.5160(7)
a	98.626(2)	90
β	96.859(2)	90
γ	91.543(2)	90
V (Å^3)	757.86(13)	2403.5(4)
Z, D_{Calcd} (g cm^{-3})	1, 1.655	4, 1.772
μ (mm^{-1})	0.937	1.158
F (000)	400	1352
Crystal size (mm^3)	$0.92 \times 0.09 \times 0.09$	$0.41 \times 0.35 \times 0.30$
θ range for data collection (°)	2.29 to 27.50	2.15 to 28.00
Index ranges	$-8 \le h \le 7$, $-10 \le k \le 11$, $-16 \le l \le 17$	$-24 \le h \le 25$, $-19 \le k \le 19$, $-7 \le l \le 11$
Reflections collected	4936	15292
Independent reflections		
Reflections observed (>2σ)	3385 [$R_{\text{int}} = 0.0146$]	3013 [$R_{\text{int}} = 0.0244$]
Data completeness	0.970	1.000
Data/restraints/parameters	3385/3/292	3013/0/254
Goodness-of-fit on F_2	1.073	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0330$[a], $wR_2 = 0.0872$[b]	$R_1 = 0.0370$, $wR_2 = 0.1056$
R indices (all data)	$R_1 = 0.0374$, $wR_2 = 0.0911$	$R_1 = 0.0396$, $wR_2 = 0.1079$
Largest diff. peak and hole (e Å^{-3})	1.328 and −0.427	1.256 and −0.485

[a] $R_1 = [\Sigma(|F_o| - |F_o|)/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[w(|F_o|^2 - |F_o|^2)^2]/\Sigma[w(|F_o|_2)_2]1/2$, $w = 1/[\sigma^2|F_o|^2 + (xp)^2 + yp]$, where $p = [|F_o|^2 + 2|F_o|^2]/3$.

least-squares calculations on F^2 using SHELXL-97. Hydrogen atoms were directly obtained from difference fourier maps. Crystallographic data and structure refinement parameters are listed in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2. Hydrogen bond details for **1** and **2** (Å and °) are listed in tables 3 and 4. Crystallographic data have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication No. CCDC 287017 (**1**) and 299672 (**2**). Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) (1223) 336033; E-mail for inquiry: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Crystal structure of 1*

As shown in figure 1, there is a half of $[Ni(AEDP)_2]^{6-}$, one and a half ethylenediamine cations and three free water molecules in the asymmetric unit of **1**. The $AEDPH_4$ in **1** is completely deprotonated to $AEDP^{4-}$ and each Ni(II) ion is chelated by two $AEDP^{4-}$ anions, exhibiting a distorted octahedral geometry. The bond lengths are 2.071(2) Å, 2.101(2) Å (Ni–O) and 2.161(2) Å (Ni–N). There are two different enH_2^{2+} cations in the

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
Ni(1)–O(1)#1	2.0706(15)	Ni(1)–O(4)#2	2.0872(16)
Ni(1)–O(1)	2.0706(15)	Ni(1)–O(4)	2.0872(16)
Ni(1)–O(4)#1	2.1013(16)	Ni(1)–O(1)	2.0998(16)
Ni(1)–O(4)	2.1013(16)	Ni(1)–O(1)#2	2.0998(16)
Ni(1)–N(1)	2.1608(19)	Ni(1)–N(1)	2.108(3)
Ni(1)–N(1)#1	2.161(2)	Ni(1)–N(2)	2.112(2)
O(1)#1–Ni(1)–O(1)	180.000(1)	O(4)#2–Ni(1)–O(4)	91.33(11)
O(1)#1–Ni(1)–O(4)#1	85.77(6)	O(4)#2–Ni(1)–O(1)	177.94(7)
O(1)–Ni(1)–O(4)#1	94.23(6)	O(4)–Ni(1)–O(1)	90.72(8)
O(1)#1–Ni(1)–O(4)	94.23(6)	O(4)#2–Ni(1)–O(1)#2	90.72(8)
O(1)–Ni(1)–O(4)	85.77(6)	O(4)–Ni(1)–O(1)#2	177.94(7)
O(4)#1–Ni(1)–O(4)	180.000(1)	O(1)–Ni(1)–O(1)#2	87.22(11)
O(1)#1–Ni(1)–N(1)	85.06(6)	O(4)#2–Ni(1)–N(1)	95.87(6)
O(1)–Ni(1)–N(1)	94.94(6)	O(4)–Ni(1)–N(1)	95.87(6)
O(4)#1–Ni(1)–N(1)	84.24(7)	O(1)–Ni(1)–N(1)	83.87(6)
O(4)–Ni(1)–N(1)	95.76(7)	O(1)#2–Ni(1)–N(1)	83.87(6)
O(1)#1–Ni(1)–N(1)#1	94.94(6)	O(4)#2–Ni(1)–N(2)	82.79(6)
O(1)–Ni(1)–N(1)#1	85.06(6)	O(4)–Ni(1)–N(2)	82.79(6)
O(4)#1–Ni(1)–N(1)#1	95.76(7)	O(1)–Ni(1)–N(2)	97.52(6)
O(4)–Ni(1)–N(1)#1	84.24(7)	O(1)#2–Ni(1)–N(2)	97.52(6)
N(1)–Ni(1)–N(1)#1	180.00(8)	N(1)–Ni(1)–N(2)	178.07(8)

Symmetry code: #1: $-x+1$, $-y+2$, $-z+1$; #2: x, $-y+1/2$, z.

Table 3. Hydrogen bonds for **1** [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)–H(1W1)···O(3)	0.897(11)	1.91(2)	2.752(3)	155(4)
N(2)–H(3)···O(3)#3	0.89(4)	1.78(4)	2.631(3)	159(3)
O(3W)–H(2W3)···O(2W)#4	0.89(6)	1.94(6)	2.758(3)	152(5)
O(3W)–H(1W3)···O(2W)#5	0.74(5)	2.07(5)	2.792(3)	168(5)
O(2W)–H(2W2)···O(5)#3	0.80(4)	1.91(5)	2.708(3)	172(4)
O(2W)–H(1W2)···O(1W)	0.80(6)	1.92(6)	2.718(4)	178(6)
N(3)–H(17)···O(4)#5	0.88(3)	2.52(3)	3.103(3)	124(2)
N(3)–H(17)···O(1)#5	0.88(3)	2.07(3)	2.916(3)	159(3)
N(3)–H(16)···O(2)#6	0.85(4)	1.87(4)	2.715(3)	170(3)
N(3)–H(15)···O(4)#3	0.87(4)	1.82(4)	2.694(3)	173(3)
N(4)–H(10)···O(6)#1	0.93(3)	1.94(3)	2.850(3)	164(3)
N(4)–H(9)···O(1)#6	0.92(3)	1.83(3)	2.746(3)	172(3)
N(4)–H(8)···O(6)#3	0.90(4)	1.82(4)	2.705(3)	165(3)
N(2)–H(5)···O(3W)#7	0.79(3)	2.11(4)	2.881(3)	165(3)
N(2)–H(4)···O(2)#8	0.87(4)	1.84(4)	2.687(3)	161(4)
N(1)–H(2)···O(5)#9	0.90(4)	2.33(4)	3.168(3)	154(3)
N(1)–H(1)···O(6)#1	0.88(3)	2.48(3)	2.959(3)	115(2)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+2$, $-z+1$; #2: $-x$, $-y$, $-z+2$; #3: x, $y-1$, z; #4: x, y, $z-1$; #5: $-x$, $-y+1$, $-z+1$; #6: $-x+1$, $-y+1$, $-z+1$; #7: x, y, $z+1$; #8: $x-1$, $y-1$, z; #9: $-x$, $-y+2$, $-z+1$.

unit, one is antiperiplanar (the torsion angle of N2–C3–C3a–N2a is 180°) and the other is synclinal (N3–C4–C5–N4 is 60°).

Neighboring $[\mathrm{Ni(AEDP)_2}]^{6-}$ anions are bridged by the antiperiplanar $\mathrm{enH_2^{2+}}$ cations via hydrogen bonds N4–H10···O6#1 (2.850(3) Å), N4–H9···O1#6 (2.746(3) Å) and N4–H8···O6#3 (2.705(3) Å), generating a 1-D ladder-like supramolecular chain along the *b* axis. The remaining N3 forms four N–H···O hydrogen bonds to the neighboring

Table 4. Hydrogen bonds for **2** (Å) and (°).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(1)–H(1)···O(1W)	0.89(3)	2.48(3)	3.218(3)	141(2)
N(2)–H(4)···O(2W)	0.88(3)	2.46(3)	3.201(3)	142(2)
N(3)–H(9)···O(6)	0.65(11)	2.34(8)	2.844(3)	136(3)
N(4)–H(10)···O(6)	0.95(4)	1.84(4)	2.785(3)	174(4)
N(5)–H(14)···O(6)	0.90(5)	2.63(4)	3.361(4)	139.0(16)
N(5)–H(16)···O(1W)	0.90(4)	1.96(4)	2.847(3)	169(3)
O(1W)–H(22)···O(4)	0.78(4)	1.86(4)	2.630(3)	170(4)
O(2W)–H(23)···O(1)	0.87(4)	1.81(4)	2.663(3)	169(4)
N(3)–H(7)···O(3)#2	0.97(9)	2.52(7)	3.286(4)	136(3)
N(3)–H(8)···O(2W)#2	0.87(5)	2.19(5)	3.039(4)	167(4)
N(3)–H(7)···O(3)#3	0.97(9)	2.52(7)	3.286(4)	136(3)
N(5)–H(14)···O(6)#1	0.90(5)	2.63(4)	3.361(4)	139.0(16)
N(3)–H(9)···O(6)#1	0.65(11)	2.34(8)	2.844(3)	136(3)
N(4)–H(11)···O(5)#4	0.92(4)	2.24(5)	3.151(4)	174(4)
N(4)–H(11)···O(4)#4	0.92(4)	2.51(5)	3.102(3)	123(3)
N(4)–H(13)···O(1)#4	0.83(6)	2.32(6)	2.998(3)	140(5)
N(4)–H(13)···O(2)#4	0.83(6)	2.47(5)	3.249(4)	157(5)
N(4)–H(12)···O(3)#5	0.99(6)	2.37(6)	3.257(3)	149(4)
N(4)–H(12)···O(2)#5	0.99(6)	2.51(6)	3.377(4)	146(4)
N(5)–H(15)···O(3)#5	0.78(8)	2.31(6)	2.907(3)	134(2)
N(5)–H(15)···O(3)#6	0.78(8)	2.31(6)	2.907(3)	134(2)
N(6)–H(17)···O(6)#7	0.93(6)	2.48(6)	3.368(4)	158(5)
N(6)–H(17)···O(5)#7	0.93(6)	2.52(6)	3.295(4)	141(5)
N(6)–H(18)···O(2)#8	0.91(4)	1.99(4)	2.898(3)	171(3)
N(6)–H(19)···O(3)#9	0.92(4)	1.86(4)	2.774(3)	176(3)
N(6)–H(20)···O(5)#10	0.88(5)	2.10(5)	2.921(3)	155(4)
O(2W)–H(24)···O(2)#11	0.76(4)	1.95(4)	2.702(3)	167(4)

Symmetry transformations used to generate equivalent atoms: #1: x, $-y+1/2$, z; #2: $x+1/2$, y, $-z+1/2$; #3: $x+1/2$, $-y+1/2$, $-z+1/2$; #4: $-x+1$, $-y$, $-z+1$; #5: $x+1/2$, y, $-z+3/2$; #6: $x+1/2$, $-y+1/2$, $-z+3/2$; #7: $-x+1$, $-y+1$, $-z+1$; #8: x, $y+1$, z; #9: $-x+1/2$, $-y+1$, $z+1/2$; #10: x, $y+1$, $z+1$; #11 $-x+1/2$, $-y$, $z-1/2$.

phosphonate group, extending the 1-D supramolecular chains to a 2-D supramolecular layer. The antiperiplanar enH$_2^{2+}$ also plays an important role in constructing the supramolecular network, generating strong hydrogen bonds N2–H3···O3#3 (2.631(3) Å) and N2–H4···O2#8 (2.687(3) Å), connecting the 2-D supramolecular layers to a 3-D porous supramolecular network [see figure 2(a)].

The supramolecular network contains 1-D channels with apertures of *ca.* 5 × 8 Å [see figure 2(b)]. Water molecules located in the 1-D channel are interconnected to form an ice-like T4(2)6(2) water tape along the *a* axis. In the T4(2)6(2) water tape, the cyclic water hexamer and the cyclic water tetramer are alternately connected by sharing two water molecules. The O···O distances within the water chain range from 2.718(4) to 2.792(3) Å. The average O···O distance is 2.756 Å, close to that in ice I$_c$ (2.75 Å) and I$_h$ (2.759 Å) [23]. The water tape connects to the host with strong hydrogen bonds O1W–H1W1···O3 (2.752(3) Å), O2W–H2W2···O5#3 (2.708(3) Å) and N2–H5···O3W#7 (2.881(3) Å) (see figure 3).

3.2. *Crystal structure of 2*

Compound **2** contains one [Ni(AEDP)$_2$]$^{6-}$, three NH$_4^+$ cations and two water molecules in the asymmetric unit (see figure 4). Combined with strong hydrogen bonds between

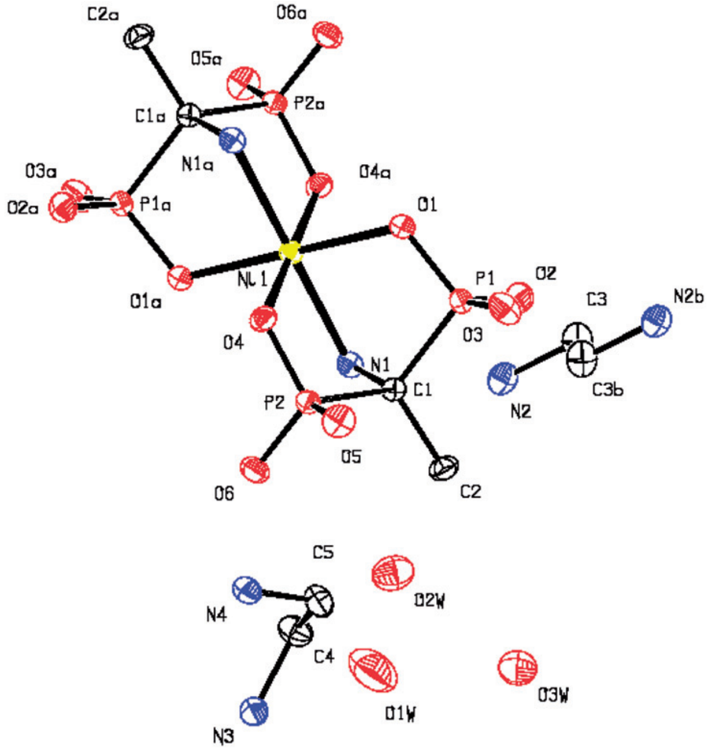

Figure 1. The ORTEP drawing of **1** with the thermal ellipsoids at 50% probability. All of the H atoms are omitted for clarity.

NH_4^+ cations and phosphate ions, each $[Ni(AEDP)_2]^{6-}$ anion is linked to eighteen NH_4^+ cations and each NH_4^+ cation also bonds to four $[Ni(AEDP)_2]^{6-}$ anions, forming an enclosed 3-D supramolecular network.

Different from **1**, the 3-D supramolecular framework in **2** has no obvious channels; water molecules located in the aperture of the network form two kinds of ammonium-water clusters with neighboring NH_4^+. One is O1W $\cdots$ N5 $\cdots$ O1W′ and the other is O2W $\cdots$ N3 $\cdots$ O2W′. Both ammonium-water clusters are V-shaped, in which the NH_4^+ cation serves as the center. In the O1W $\cdots$ N5 $\cdots$ O1W′ cluster, the N $\cdots$ O distance is 2.847(3) Å and the O $\cdots$ N $\cdots$ O angle is 104.69°, while in O2W $\cdots$ N3 $\cdots$ O2W′ cluster, the N $\cdots$ O distance is 3.039(4) Å and the O $\cdots$ N $\cdots$ O angle is 98.77°. The ammonium-water clusters are fixed by various hydrogen bonds to the $[Ni(AEDP)_2]^{6-}$ anions (see figure 5).

3.3. *FT-IR spectra and TG analysis*

The IR spectra of **1** and **2** are similar (Supplementary Material). Broad peaks centered at 3420 cm^{-1} suggest water molecules in the two compounds. The corresponding bending H–O–H (δ_{HOH}) vibration bands of the lattice water molecules are located at 1630 cm^{-1}. The P–O stretching vibrations from 1070–1170 cm^{-1} and O–P–O bending vibrations from 428–590 cm^{-1} are the common features.

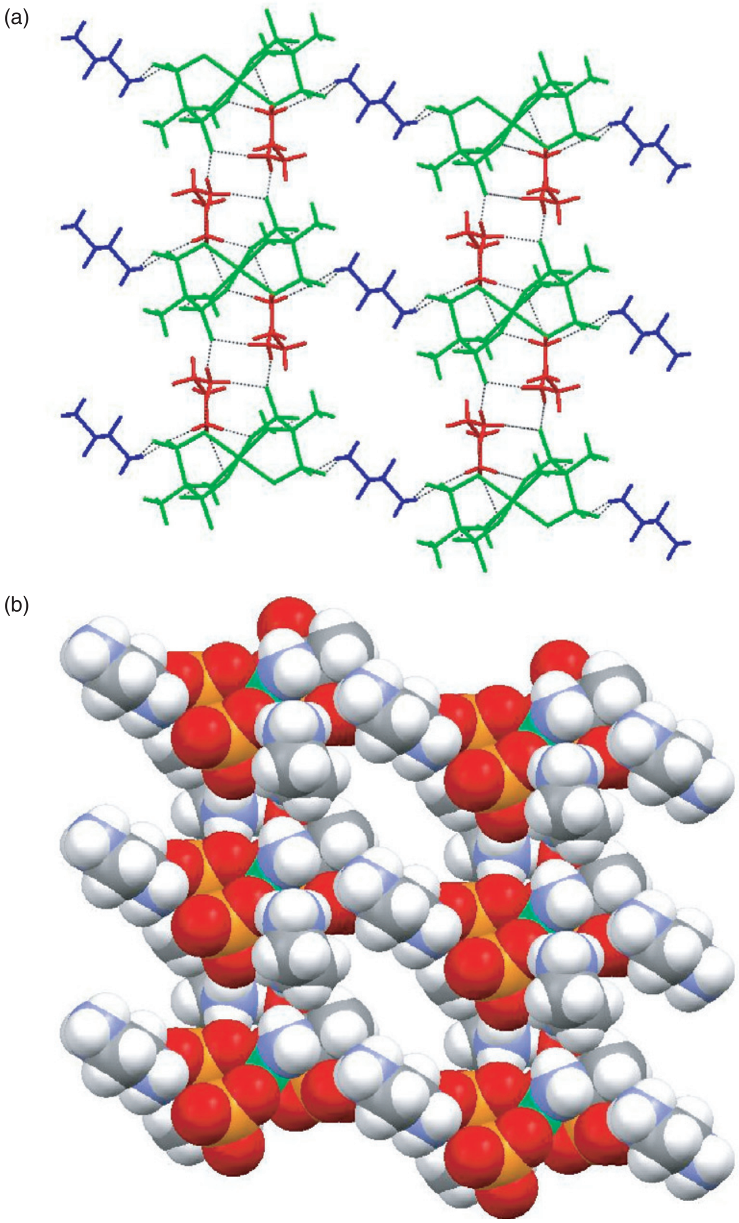

Figure 2. (a) Schematic view of the 3-D porous supramolecular network of **1**. [Ni(AEDP)2]$^{6-}$, green; antiperiplanar enH$_2^{2+}$, blue; synclinal enH$_2^{2+}$, red; dashed lines represent hydrogen bonds (color online only). (b) The space filling view of the supramolecular network which contains 1-D channel with apertures of *ca.* 5 × 8 Å.

The TG curves for **1** and **2** are shown in Supplementary Material. The thermal analysis of **1** shows that dehydration takes place beginning at 80°C. The weight loss is 5.12%, slightly larger than the calculated value (4.77%), corresponding to the loss of two water molecules. Weight loss between 90°C and 180°C is 14.16%, corresponding to the release of four residual water molecules (Calcd 14.30%). The weight loss of **2** before

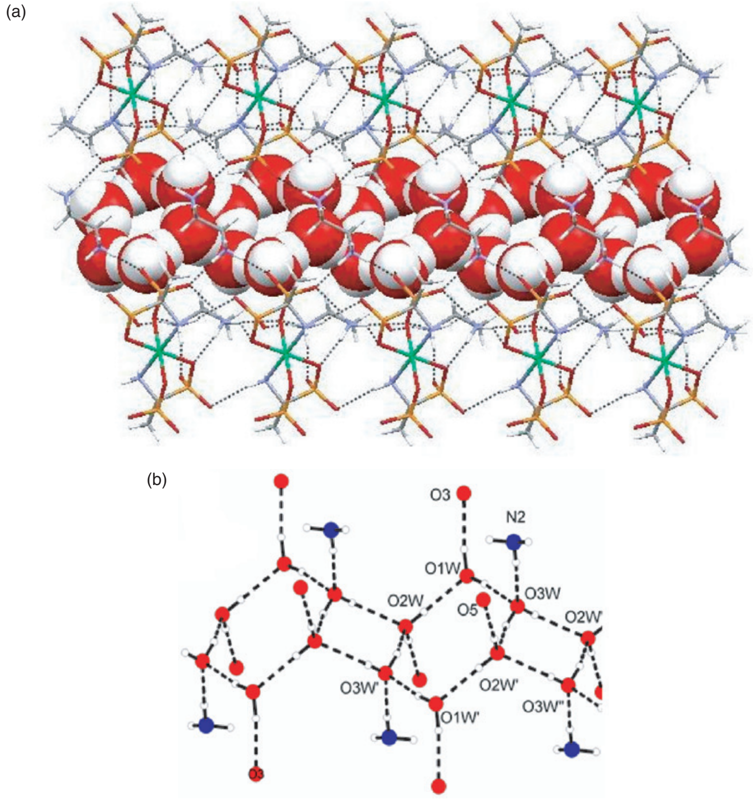

Figure 3. (a) The space filling 1-D T4(2)6(2) water tape which is connected to the host via hydrogen bonds. (b) Hydrogen bonding motif within the water tape.

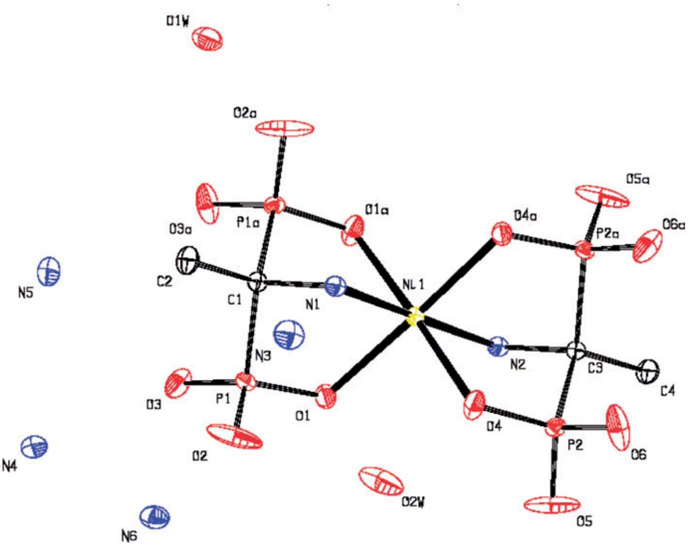

Figure 4. The ORTEP drawing of **2** with the thermal ellipsoids at 30% probability. All of the H atoms are omitted for clarity.

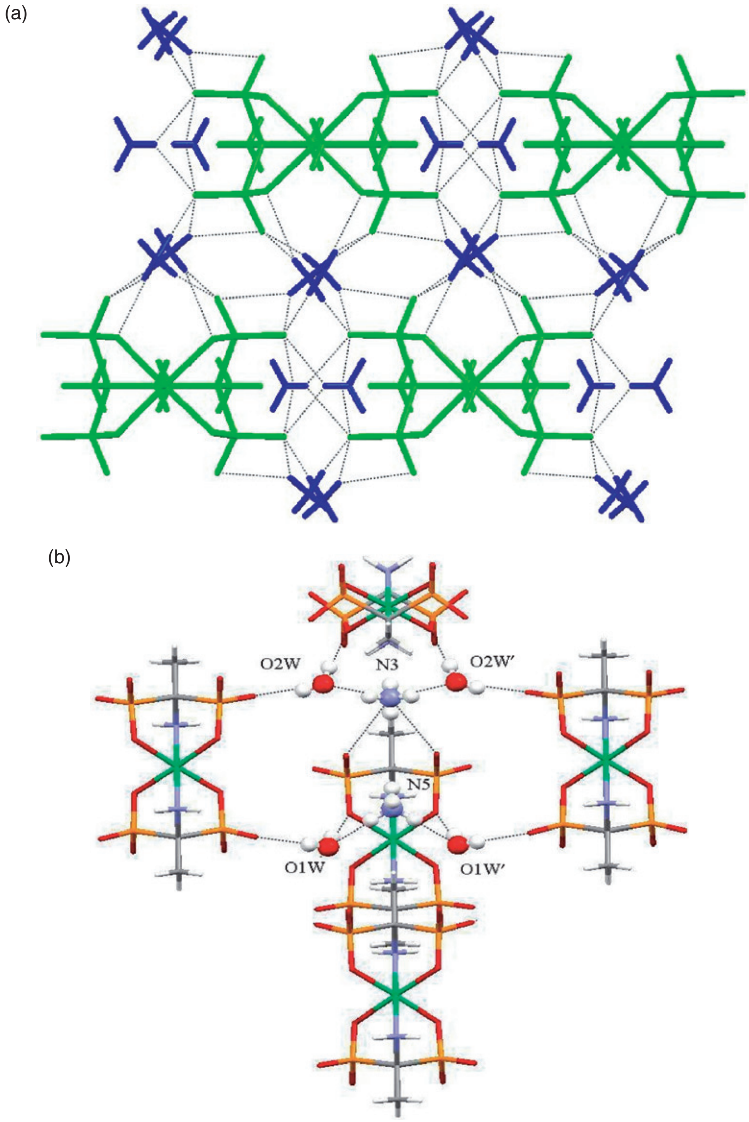

Figure 5. (a) Schematic view of the supramolecular network of **2**. $[Ni(AEDP)_2]^{6-}$, green; NH_4^+, blue; dashed lines represent hydrogen bonds (color online only). (b) Two kinds of water-ammonium clusters (ball and stick) connected to $[Ni(AEDP)_2]^{6-}$ via hydrogen bonds.

130°C is attributed to the absorption water, and **2** is stable to 130°C in air. From 130°C to 200°C, indicates loss of four water molecules and six NH_4^+ cations (24.93%), close to the calculated value (25.27%).

3.4. *Magnetic properties*

The magnetic properties of **1** were investigated using a PPMS-9T magnetometer at a field of 5000 Oe in the temperature range 2–300 K. The temperature dependence of χ_M^{-1}

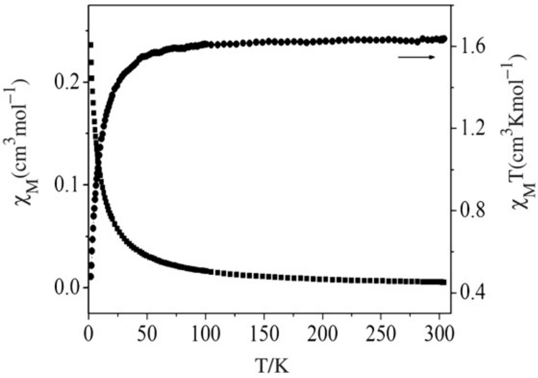

Figure 6. χ_M and χ_MT vs. T plots for **1**.

and χ_MT are shown in figure 6. The χ_MT at 300 K is 1.63 $cm^3\,K\,mol^{-1}$, higher than the spin only value for spin $S = 3/2$ centers (1.00 $cm^3\,K\,mol^{-1}$). This can be attributed to the significant orbital contribution of Ni(II) ions. Cooling from room temperature, χ_MT is steady at 100 K, and then decreases continuously, indicating weak antiferromagnetic interactions between the Ni(II) centers, also confirmed by a negative Weiss constant ($\theta = -4.123$ K) determined by the Curie–Weiss law $\chi_M = C/(T - \theta)$. From the structure described above, the observed weak antiferromagnetic interaction may be attributed to superexchange coupling between Ni(II) centers through the hydrogen bond interactions.

3.5. *Discussion*

Compounds **1** and **2** are both synthesized in similar conditions and contain $[Ni(AEDP)_2]^{6-}$, but different structural types, showing how protonated ammonium counterions can cause structural differences. Compared with NH_4^+ in **2**, the enH_2^{2+} in **1** tends to form a less compact supramoleuclar network, including a 1-D channel with a T4(2)6(2) water tape structure. In **2**, NH_4^+ forms an enclosed supramoleuclar network with $[Ni(AEDP)_2]^{6-}$, forming water-ammonium clusters but no channel.

4. Conclusions

In this article, two nickel phosphonate compounds, $(enH_2)_3[Ni(AEDP)_2] \cdot 6H_2O$ (**1**) and $(NH_4)_6[Ni(AEDP)_2] \cdot 4H_2O$ (**2**) (en = ethylenediamine), have been synthesized and characterized. Both contain $[Ni(AEDP)_2]^{6-}$ with different 3-D supramolecular structures. Compound **1** contains a T4(2)6(2) water tape while **2** has two water-ammonium clusters.

Acknowledgement

This work was supported by grants of the National Nature Science Foundation of China (No. 20671074).

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