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Complexes Formed between Nitrilotris(methylenephosphonic acid) and M^{2+} Transition Metals: Isostructural Organic–Inorganic Hybrids

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Nitrilotris(methylenephosphonic acid) (NTP, $[N(CH_2PO_3H_2)_3]$) recently has been found to form three-dimensional porous structures with encapulation of templates as well as layered and linear structures with template intercalation. It was, therefore, of interest to examine the type of organic–inorganic hybrids that would form with metal cations. Mn(II) was found to replace two of the six acid protons, while a third proton bonds to the nitrilo nitrogen, forming a zwitter ion. Two types of compounds were obtained. When the ratio of acid to Mn(II) was less than 10, a trihydrate, $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ (**2**) formed. Compound **2** is monoclinic $P2_1/c$, with $a = 9.283(2)$ Å, $b = 16.027(3)$ Å, $c = 9.7742(2)$ Å, $\beta = 115.209(3)°$, $V = 1315.0(5)$ Å^3, and $Z = 4$. The Mn atoms form zigzag chains bridged by two of the three phosphonate groups. The third phosphonate group is only involved in hydrogen bonding. The metal atoms are octahedrally coordinated with three of the sites occupied by water molecules. Adjacent chains are hydrogen-bonded to each other through POH and HN donors, and the additional participation of all the water hydrogens in H-bonding results in a corrugated sheetlike structure. Use of excess NTP at a ratio to metal of 10 to 1 yields an anhydrous compound $Mn[HN(CH_2PO_3H)_3]$ (**1**), $P2_1/n$, $a = 9.129(1)$ Å, $b = 8.408(1)$ Å, $c = 13.453(1)$ Å, $\beta = 97.830(2)°$, $V = 1023.0(2)$ Å^3, and $Z = 4$. Manganese is five coordinate forming a distorted square pyramid with oxygens from five different phosphonate groups. The sixth oxygen is 2.85 Å from an adjacent Mn, preventing octahedral coordination. All the protonated atoms, three phosphonate oxygens and N, form moderately strong hydrogen bonds in a compact three-dimensional structure. The open-structured trihydrate forms a series of isostructural compounds with other divalent transition metal ions as well as with mixed-metal compositions. This is indicative that the hydrogen bonding controls the type of structure formed irrespective of the cation.

Introduction

Phosphonic acids are interesting ligands for several reasons. They can complex metal atoms in several ways by loss of one or both protons and in addition can have their complexing ability modified by choice of organic functional groups.[1] The choice of phosphonic acid may also be utilized to dictate the dimensionality of the resultant metal complex. Dimensionality may also be mediated by the choice of experimental conditions. Our recent studies[2] involving phosphonic acids demonstrated that deprotonation of the organophosphonic acid results in very strong and predictable structural aggregates through symmetrical O···H···O hydrogen bonds (a) or hydrogen-bonded dimers (b) as in Chart 1.

Subsequently we have begun to examine the chemical behavior of nitrilotris(methylenephosphonic acid), NTP. This acid exists as a zwitterion in its pure form as in Scheme 1 and reveals a complex three-dimensional structure involving five of its acidic protons.[3]

To explore the behavior of NTP, several metal complexes have been prepared. Addition of NaOH to NTP in the ratio

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(1) Clearfield, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley: New York, 1988; Vol. 47, pp 371–510.

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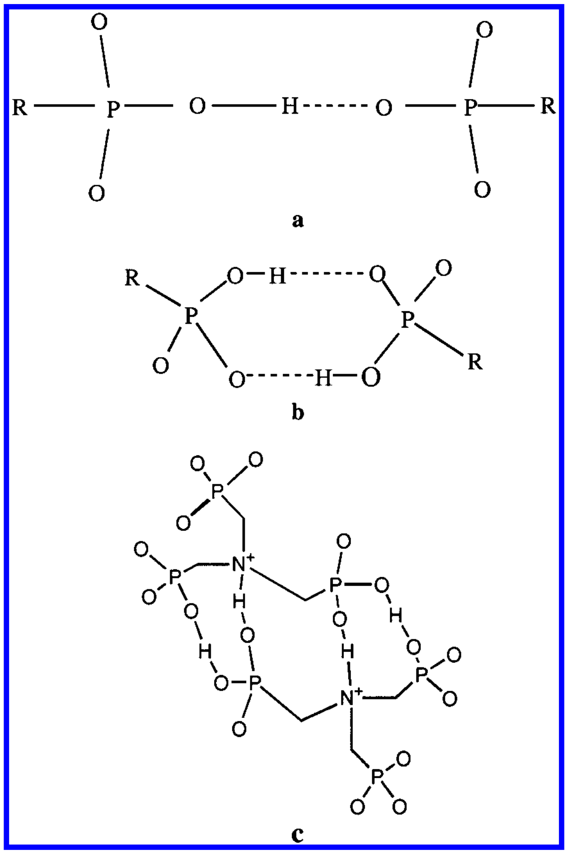
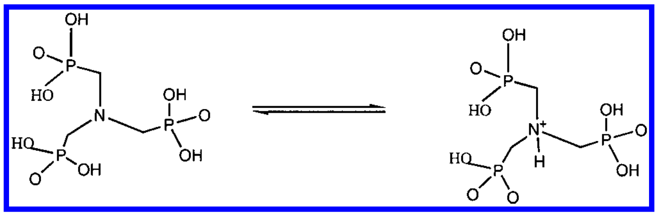
Chart 1



Scheme 1



2.6−2.7:1 followed by refluxing or hydrothermal treatment (130 °C) yielded $Na_2[(HO_3PCH_2)_3NH]\cdot 1.5H_2O$.[4] The structure contains Na_4O_{16} tetramers with each sodium in octahedral coordination. Each nitrilotris(methylenephosphonate acid) group forms seven tetrahedral groups, three phosphonates, three about the methylene carbons, and one HNC_3 group. The isolated tetramers are linked by phosphonate bridging to create small channels parallel to the *a*-axis direction. One water molecule is bonded to Na while the other at half-occupancy resides in the channels and is hydrogen bonded to P−OH groups.

Two lead compounds of NTP have been synthesized.[5] $Pb[(H_2O_3PCH_2)N(CH_2PO_3H)_2]$ is triclinic and was prepared by refluxing a mixture of NTP and $Pb(CH_3COO)_2$ in a molar ratio of 8:1. The lead ion is coordinated to five phosphonate oxygens, and the coordination sphere contains an open space where presumably the lone pair of the lead ion is located. There are six tetrahedra formed by the phosphonate groups, as the coordination about the nitrogen is pyramidal rather than tetrahedral. The compound is layered, the layers being formed by bridging of lead atoms at a distance of two full phosphonate groups apart. This bridging results in oval-shaped 16-atom rings or layered cavities.

The second compound, $Pb_2[(H_2O_3PCH_2)N(CH_2PO_3)_2]\cdot H_2O$, was prepared by refluxing a solution in which the Pb:NTP ratio was 1.5:1. This compound is also layered, but the metal coordination is quite different. One lead atom is 6-coordinate with distortion of the octahedral arrangement to provide space for the lone pair. The second lead atom is 4-coordinate, also highly distorted from tetrahedral. The two lead atoms are close together being bridged by two single oxygen atoms forming a parallelogram. There are six nonbonding oxygens at distances of 2.88−3.07 Å from the 4-coordinate lead atom and two oxygens at 3.03 and 3.37 Å from the 6-coordinate Pb. Thus, the layers are compactly built in contrast to the monolead layers that contain open cavities.

A salt of NTP with Al^{3+} has also been reported, $Al[HO_3PCH_2)_3N]\cdot H_2O$. The crystal structure is built up by a close packing of inorganic chains covalently interconnected by the organic groups.[6] All attempts to obtain a NTP derivative with Cu^{2+} were fruitless. The phosphonic acid undergoes a bond-breaking H_2 addition, yielding a nitrilobis(methylenephosphonic acid) (NDP, $[(H_2O_3PCH_2)_2NH]$). So, a new salt with stiochiometry $Cu_3[(O_3PCH_2)_2NH_2]$ was isolated.[6]

The structures described, to this point, are relatively compact, but we were able to construct open-framework structures[7] by transfer of half the protons to amino templates and form hydrogen bonds as shown in Chart 2. Additional H-bonds perpendicular to the plane of the open hexagons resulted in three-dimensional structures in which the phenanthroline templates reside in the tunnels. Prior to this work, we had prepared[8] amorphous insoluble tin(IV) nitrilotris(methylenephosphonates) of variable composition that behaved as ion exchangers.

We have now synthesized a series of complexes by reaction of NTP with divalent transition metals in which neutral complexes are formed. We have found that it is possible to form open structures with H-bonding such as shown in Chart 1c. Alternatively, dense 3-D structures were also found to form. In this paper, we describe these compounds in detail, using Mn(II) as the cation. A preliminary account of the more open compounds had been presented earlier.[9]

Experimental Section

Synthesis. The sources of nitrilotris(methylenephosphonic acid) were a 50% solution (Aldrich) and a solid, 97% pure (Fluka). Although the solution contains other phosphonic acids, the products obtained using both sources were the same.[4] All other chemicals were of reagent grade quality.

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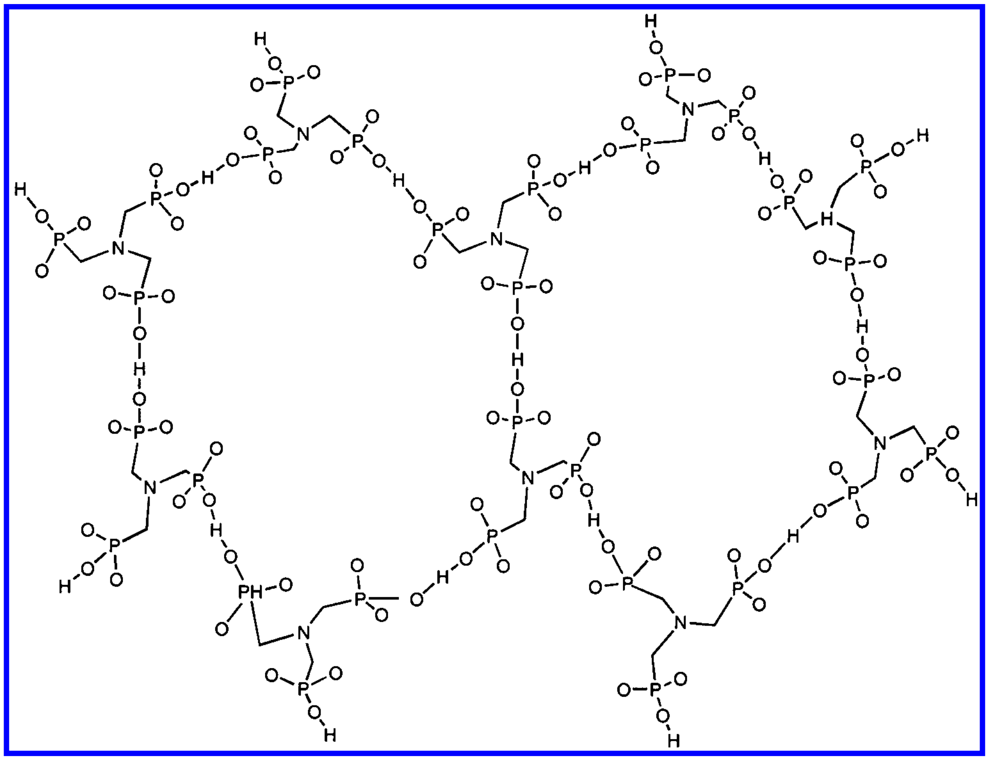
Chart 2



Mn[HN(CH$_2$PO$_3$H)$_3$] (1). A 2 g sample of the solid NTP was dissolved in 20 mL of distilled deionized water (ddi), and a second solution consisting of 0.87 mmol of Mn(CH$_3$COO)$_2$·2H$_2$O (Aldrich) in 20 mL of water was added to it. The ratio Mn:NTP was 1:10. At this ratio, the pH was 1.2, which was low enough to prevent precipitation. The mixture was added to a Teflon-lined pressure vessel and heated at 200 °C for 3 days. The precipitated solid was isolated by filtration and washed with ddi H$_2$O and finally with acetone. It was dried under vacuum at ambient temperature. Anal. Found: C, 10.40; N, 4.01; H, 3.10; C/N = 3.02. Calcd for Mn[HN(CH$_2$PO$_3$H)$_3$]: C, 10.34; N, 3.98; H, 2.86.

Mn[HN(CH$_2$PO$_3$H)$_3$(H$_2$O)$_3$] (2). To 13.1 mL of a NTP solution (50% w/w, 28.26 mmol) was added a solution containing 5.65 mmol of manganese(II) acetate dihydrate dissolved in 10 mL of distilled water. The resulting Mn:TPA molar ratio in the mixture was 1:5, and the final pH = 0.6. A white precipitate was immediately formed. The suspension was heated in a Teflon-lined autoclave at 200 °C for 3 days. A single phase was isolated by filtration, washed with water and with acetone, and dried. Anal. Found: C, 9.04; N, 3.44; H, 4.05; C:N ratio 3.06. Calcd: C, 8.50; N, 3.30; H, 4.24%; C/N ratio 3.00. This phase was also obtained in micropowder form by refluxing similar mixtures with Mn:NTP ratios of 1, 5, and 10. Single crystals could also be obtained by the layering technique described earlier.[9]

Instrumental Methods. Thermal analysis was carried out with either a Rigaku Thermoflex 8110 unit or a DuPont Thermal Analyst 950 unit at a heating rate of 10 °C/min in an air atmosphere. Infrared spectra were recorded with a Perkin-Elmer 883 spectrometer by the KBr disk method. C, H, and N contents were determined by elemental chemical analysis on a Perkin-Elmer 240 Analyzer.

Crystallography. Data collection for compounds **1** and **2** were carried out on a Bruker SMART 1000 CCD platform diffractometer equipped with monochromated Mo Kα radiation. Data collection and reduction were performed with SMART 5.4 and SAINT+ 6.0 from Bruker AXS.[10] Crystallographic computing was performed on a Pentium 450 MHz personal workstation using the SHELXTL 5.10 package.[11]

Compound 1, Mn[HN(CH$_2$PO$_3$H)$_3$]. A colorless crystal of compound **1** of appropriate dimensions, 0.12 × 0.10 × 0.10 mm^3, was mounted on a Bruker AXS CCD platform diffractometer with Mo Kα (λ = 0.710 73 Å) radiation at room temperature. A hemisphere of data with 1321 frames was collected with a scan width of 0.3° in ω and an exposure time of 20 s. Laue crystal symmetry restraints were used during data integration with the SAINT+ package.[10] Final cell parameters were obtained by refining the *xyz* centroids of 3851 strong reflections with $I/\sigma > 10$ to yield $a = 9.129(1)$ Å, $b = 8.408(1)$ Å, $c = 13.453(1)$ Å, $\beta = 97.830(2)°$, and $V = 1023.0(2)$ Å^3. An absorption correction was performed with SADABS[11] and led to a transmission parameter between 1 and 0.86. Of the 5859 reflections collected, 2080 are unique (R_{int} = 0.0174). A summary of crystallographic data is given in Table 1.

Structure Solution and Refinement. Structure solution was performed with XL[11] in space group $P2_1/n$ (No. 14). The positions of the non-hydrogen atoms were located by direct methods and refined by full-matrix lest squares on F^2 using the XS.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from a difference Fourier map and refined isotropically and their bond length restrained to 0.84 Å for O−H and 0.93 Å for C−H.

Compound 2, Mn[HN(CH$_2$PO$_3$H)$_3$(H$_2$O)$_3$]. A colorless crystal of compound **2** of approximate dimensions 0.21 × 0.11 × 0.07 mm^3 was mounted on a Bruker AXS CCD platform diffractometer with Mo Kα (λ = 0.710 73 Å) radiation equipped with an Oxford low-temperature controller. A full sphere of data with 2471 frames

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(10) SMART version 5.0 and SAINT+ version 6.01 area detector instrument control, data acquisition, and area detector data integration software, Bruker AXS, Inc., Madison, WI.

(11) Sheldrick, G. M. *SHEXTL (Xprep, SADABS, XS, XL) Crystallographic Software Package, Version 5.1*; Bruker-AXS: Madison,WI, 1998.

Table 1. Crystallographic Data for Mn[HN(CH_2PO_3H)$_3$] (**1**) and Mn[HN(CH_2PO_3H)$_3$(H_2O)$_3$] (**2**)

param	**1**	**2**
empirical formula	$MnC_3H_{10}P_3O_9N$	$MnC_3H_{16}P_3O_{12}N$
fw	351.97	406.02
temp (K)	295(2)	110(2)
wavelength (Mo Kα) (Å)	0.710 73	0.710 73
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.1292(10)	9.283(2)
b (Å)	8.4084(9)	16.027(3)
c (Å)	13.4528(14)	9.7742(2)
β (deg)	97.830(2)	115.209(3)
V (Å^3)	1023.04(19)	1315.0(5)
Z	4	4
d_{calc} (g/cm^3)	2.285	2.050
μ (cm^{-1})	18.00	14.36
GOF (F^2)	1.076	1.025
R^a [F^2, $I > 2\sigma(I)$]	R1 = 0.0237, wR2 = 0.0670	R1 = 0.0266, wR2 = 0.0607

[a] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

was collected with a scan width of 0.3° in ω and an exposure time of 20 s at −110 K. Laue crystal symmetry restraints were used in data integration with the SAINT+[10] package. Final cell parameters were obtained by refining the xyz centroids of 1024 strong reflections with 2 Å between 5.48 and 56.48°. The refined unit cell parameters are $a = 9.283(1)$ Å, $b = 16.027(3)$ Å, $c = 9.774(2)$ Å, $\beta = 115.209(3)$°, and $V = 1315.7(4)$ Å^3. A face-indexing absorption correction was performed with Xprep[11] and led to a transmission parameter between 0.776 and 0.905. Of the 15 981 reflections collected, 3238 are unique ($R_{int} = 0.039$).

Structure solution for compound **2** was performed with the SHELXTL[11] package in space group $P2_1/c$ (No. 14). The positions of the non-hydrogen atoms were located by direct methods and refined by full-matrix least squares on F^2 as for compound **1**. All non-hydrogen atoms were refined anistropically. Hydrogen atoms were located from difference Fourier maps and refined isotropically, and their bond lengths were restrained to 0.84 Å for O−H and 0.93 Å for C−H. Crystallographic data for **2** are summarized in Table 1.

Results

We have explored the possible compounds that can be obtained by the reaction of a Mn(II) salt and nitrilotris(methylenephosphonic acid). The variables examined were the NTP acid source, the Mn:NTP molar ratio (between 1:1 and 1:10), and the heating conditions (reflux or hydrothermal). Only two compounds were obtained under the experimental conditions tested that could be isolated as single phases. A fixed stoichiometry, Mn[HN(CH_2PO_3H)$_3$], is always obtained but with different hydration degrees: either three-hydrated or anhydrous.

Crystal Structure of Mn[HN(CH_2PO_3H)$_3$] (1). The positional parameters and U_{eq} values are listed in the Supporting Information Table S2. An ORTEP representation of part of the structure is shown in Figure 1, illustrating the conformation of the nitrilotris(methylenephosphonate) grouping and its bonding to manganese. The angles about the nitrogen average 109.4°, confirming that it is protonated. One oxygen of each of the three phosphonate groups is also protonated, and the other two bond to Mn atoms. Each Mn is coordinated by 5 oxygen atoms from five different phosphonate groups, two of the P1 type, two of the P2 type, and one from a P3 group. These oxygens form a distorted square pyramid with bond distances ranging from 2.094(2) to 2.174(2) Å (Table 2 and Figure 2). The Mn atom is slightly above or below the plane of the pyramid base as shown by the fact that all the O_{ax}−Mn−O_{eq} bond angles are greater than 90°. The axial Mn−O bond is the longest of the five at 2.174(2) Å, but the oxygen is also close to an adjacent Mn atom at 2.852(2) Å. This oxygen is in the position to fill the sixth site of an octahedron but at a distance too great to be bonded to the second manganese atom. However, it has the effect of blocking the axial sixth coordination site, preventing the formation of MnO_6 octahedra. This long interatomic distance is indicated by a thick dash line from O7 to Mn in Figure 2 and Figure 1. Only O9 of the nonprotonated phosphonate oxygens does not bond to manganese.

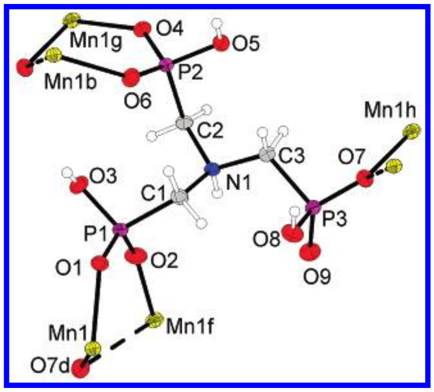

Figure 1. ORTEP representation of Mn[HN(CH_2PO_3H)$_3$] (**1**), showing the nitrilotris(methylenephosphonate) ligand conformation and its bonding to Mn atoms. The ellipsoids are at the 50% probability level.

In the phosphonate groups, the oxygens bonded to a proton exhibit significantly longer P−O bond lengths (average 1.568(3) Å) than the others (average 1.502(4) Å). The final difference map did reveal regions of weak, positive density at 0.82−0.90 Å from these oxygen atoms. A similar region of positive density was found near the nitrogen atom. There are no water molecules in the structure.

Figure 3 presents a view of the structure looking down the a axis. There are rows of Mn atoms bridged by O−P−O phosphonate groups running parallel to the b-axis direction at roughly $c = {}^1/_4$ and ${}^3/_4$ and b close to 0 and ${}^1/_2$. There are two sets of phosphonate bridges across Mn atoms. One group is alternately above and below the row of Mn atoms in the

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\mathrm{Mn[HN(CH_2PO_3H)_3]}$ (**1**)[a]

Bonds			
Mn1−O2a	2.094(2)	P1−O2	1.496(2)
Mn1−O6b	2.137(2)	P1−O1	1.508(2)
Mn1−O1	2.160(2)	P1−O3	1.571(2)
Mn1−O4c	2.163(2)	P1−C1	1.823(2)
Mn1−O7d	2.174(2)	N1−C1	1.505(3)
P2−O6	1.494(2)	P3−O9	1.495(2)
P2−O4	1.511(2)	P3−O7	1.506(2)
P2−O5	1.570(2)	P3−O8	1.564(2)
P2−C2	1.822(2)	P3−C3	1.823(2)
N1−C2	1.502(3)	N1−C3	1.509(3)
Angles			
O2a−Mn1−O6b	98.61(6)	O4c−Mn1−O1	82.75(6)
O2a−Mn1−O4c	92.25(6)	O4c−Mn1−O6b	158.55(6)
O2a−Mn1−O1	166.96(6)	O6b−Mn1−O1	80.87(6)
O2a−Mn1−O7d	94.61(6)	O6b−Mn1−O7d	104.23(6)
O4c−Mn1−O7d	91.71(6)	O7d−Mn1−O1	98.15(6)
O2−P1−O1	119.36(9)	P1−O2−Mn1f	155.37(11)
O6−P2−O4	115.68(9)	P1−O1−Mn1	131.29(9)
O9−P3−O7	120.00(10)	P2−O4−Mn1g	141.09(9)
C1−N−C2	113.3(2)	P2−O6−Mn1b	137.24(10)
C1−N−C3	113.1(2)	P3−O7−Mn1h	130.14(10)
C2−N−C3	111.4(2)	N1−C2−P2	120.4(1)
N1−C1−P1	114.1(2)	N1−C3−P3	117.3(1)

[a] Symmetry transformations used to generate equivalent atoms: a, $-x + {}^1/_2, y + {}^1/_2, -z + 3/2$; b, $-x, -y, -z + 1$; c, $x + {}^1/_2, -y - {}^1/_2, z + {}^1/_2$; d, $x - {}^1/_2, -y - {}^1/_2, z + {}^1/_2$; e, $-x + {}^1/_2, y - {}^1/_2, -z + 3/2$; f, $x + {}^1/_2, -y - {}^1/_2, z - {}^1/_2$; g, $x - {}^1/_2, -y - {}^1/_2, z - {}^1/_2$; h, $-x + 1, -y - 1, -z + 1$; i, $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$.

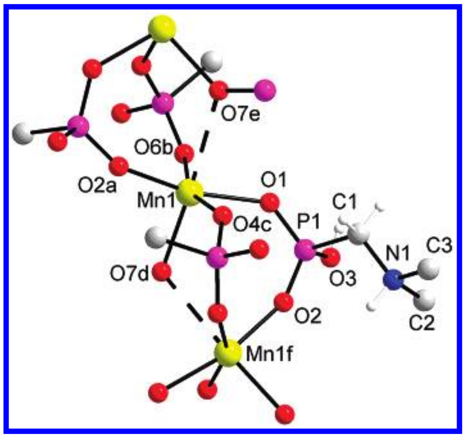

Figure 2. Ball-and-stick representation of the bridging mode of the phosphonate groups across adjacent Mn atoms in $\mathrm{Mn[HN(CH_2PO_3H)_3]}$ (**1**), showing how the 5-fold square pyramidal coordination arises. The thick dash line connecting O7 to Mn represents the long 2.85 Å nonbonded interatomic distance.

a-axis direction (O4−P2−O6). The other group is nearly at right angles to the first, alternately in the plus and minus *b*-axis direction (O1−P1−O2). This connectivity results in the formation of eight-membered rings, which are partially folded back on themselves (Mn−O1−P1−O2−Mn−O6−P2−O4). The fifth Mn coordination site is filled by O7 originating from P3 and occupies the apex of the square pyramid. At the same time, this oxygen atom is 2.85 Å away from an adjacent Mn in the chain and is situated opposite to the O7 bonded to this neighboring Mn atom. As a result, it blocks the sixth coordination site at the metal atoms. The Mn−Mn distance within a chain is 4.243(1) Å, close enough to exhibit some magnetic interaction. The interchain distance is 7.469(7) Å as can be seen in Figure 4.

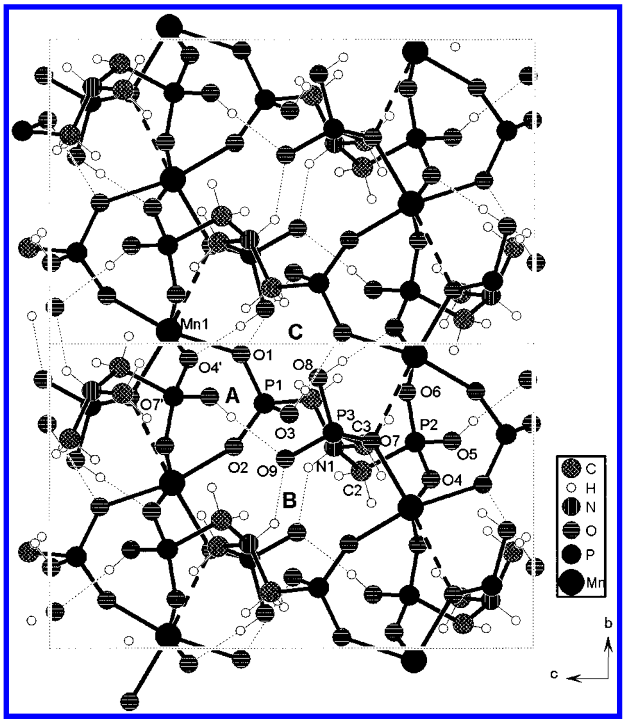

Figure 3. Packing diagram of $\mathrm{Mn[HN(CH_2PO_3H)_3]}$ (**1**) as viewed down the *a* axis. Two unit cells are shown for emphasis of the interchain connections and ring systems. Hydrogen bonds are depicted by thin dashed lines, and the O7−Mn nonbonded position is depicted by thick dashed lines. The 8-, 16-, and 24-member rings are indicated by letters A−C.

The chains of manganese phosphonate are connected to each other by covalent bonds, arising from the tetrahedral conformation of the nitrilotris(phosphonate) groups. The bridging phosphonate group, exemplified by O1−P1−O2, in Figure 4, extends through C1, N1, C3, P3, and O7 to bond to a metal atom in the chain at $c = {}^1/_4$ and through C2, P2, O4, and O6 bridges to a second chain. The chain at $c = {}^1/_4$ in the lower corner of the unit cell is also connected to the upper chain at $c = {}^3/_4$ through the NTP group whose nitrogen atom is designated by N1″. In fact, the two NTP groups connecting these two chains are related by a center of symmetry and together with the two Mn atoms, form a 16-membered ring B. This ring consists of 2 Mn, 2 N, 4 P, 4 C, and 4 O and is flanked by the eight-membered rings. Within this circle of the two 8-membered rings and one 16-membered ring, there are four hydrogen bonds, two N1−H···O9 type at 2.687(2) Å (see Table 3) and two O5−H···O9, 2.697(2) Å (perhaps more clearly seen in Figure 3).

There is yet another ring system C formed by the nitrilotris(phosphonate) groups. It is sandwiched between the two 8- and one 16-membered rings spread over two unit cells. It appears as a long, narrow 24-membered ring, half in the upper unit cell and half in the bottom one, consisting of 4 Mn, 2 N, 6 P, 4 C, and 8 O. Within its confines are two Mn···O7 weak interactions at 2.85 Å and two additional types of hydrogen bonds O3−H···O1, 2.780(2) Å, and O8−H···O4, 2.524(2) Å (Figure 3).

Figure 4 presents a view down the *b* axis. The Mn atoms anchoring the chains running parallel to the *b*-axis direction now appear in projection as slightly displaced although they

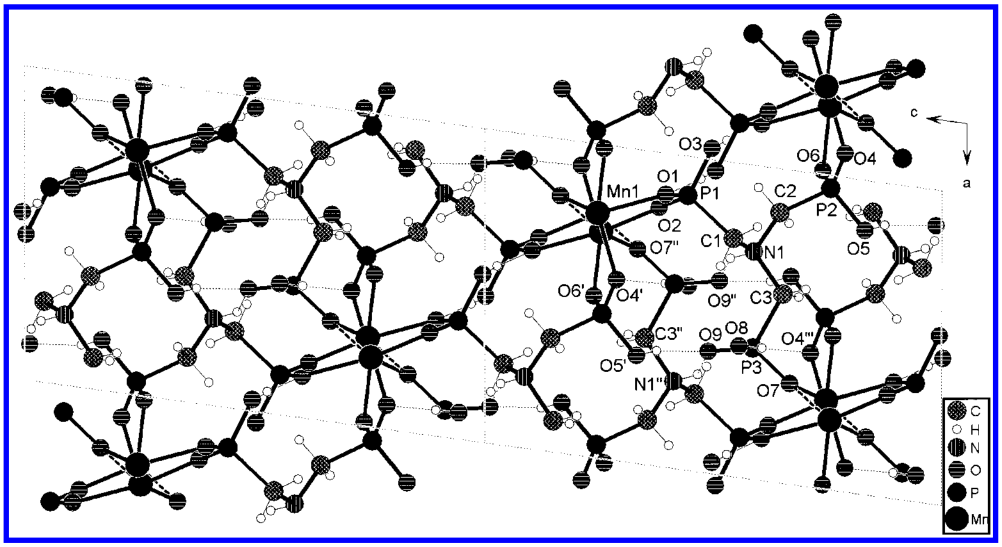

Figure 4. Packing diagram of Mn[HN(CH_2PO_3H)$_3$] (**1**) as viewed down the *b* axis. The NTP ligand is shown directly bonding to five Mn atoms by its three phosphonate groups. Hydrogen bonds are shown by thin dashed lines.

Table 3. Hydrogen Bonds for [Mn(HN(CH_2PO_3H)$_3$] (**1**) (Å and deg)[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
O3−H3C···O1b	0.82	1.96	2.779(2)	173.1
N1−H1C···O9h	0.91	1.93	2.687(2)	139.4
O8−H8A···O4i	0.82	1.70	2.524(2)	172.3
O5−H5A···O9g	0.82	1.89	2.696(2)	168.1

[a] Symmetry transformations used to generate equivalent atoms: a, $-x + 1/2, y + 1/2, -z + 3/2$; b, $-x, -y, -z + 1$; c, $x + 1/2, -y - 1/2, z + 1/2$; d, $x - 1/2, -y - 1/2, z + 1/2$; e, $-x + 1/2, y - 1/2, -z + 3/2$; f, $x + 1/2, -y - 1/2, z - 1/2$; g, $x - 1/2, -y - 1/2, z - 1/2$; h, $-x + 1, -y - 1, -z + 1$; I, $-x + 1/2, y + 1/2, -z + 1/2$.

are $1/2b$ apart. The O1, P1, and O2 phosphonate group of the N1 nitrilo nitrogen bridges across two adjacent Mn atoms at $c = 3/4$ and $a \cong 1/4$ and connects through N1 to an adjacent chain by an O7−Mn bond at approximately $1/2a$, $1/2c$ away.

The 3D network is further reinforced by an elaborate system of hydrogen bonds as indicated in Table 3. The hydrogen bonds in Figures 3 and 4 are indicated by thin dashed lines. Oxygen atoms 3, 5, and 8 are protonated and act as donors to O1, O4, and O9. O9 is bonded only to phosphorus and is therefore able to accept a second H-bond from the HN group.

Crystal Structure of Mn[HN(CH_2PO_3H)$_3$(H_2O)$_3$] (2). In compound **2**, the manganese displaces two protons, leaving one proton on each acid group and one on the nitrogen as for compound **1**. However, in this case, there are three water molecules bonded to each metal atom. An ORTEP presentation in Figure 5 shows the conformation of the nitrilotris(methylenephosphonate) together with the coordination of the Mn atoms. The Mn−O bond distances range from 2.118 to 2.202 Å, and the bond angles are close to those for an octahedral geometry. An interesting aspect of this structure is that the metal atoms form an eight-membered ring with two phosphonate groups of the same NTP molecule; i.e., only one Mn is present in the ring. The P3 oxygens, O7, O8, and O9, are only involved in hydrogen bonding.

The manganese atoms form a zigzig chain parallel to the *c*-axis direction, as shown in Figure 6. The metal atoms are connected by O4−P2−O6 phosphonate bridges to form the chains. The O4−P2 portion of this bridge also forms part of the eight-membered chelate ring. Only three of the nine phosphonate oxygens (O1, O4, O6) are utilized in bonding to the metal atoms, three additional oxygen atoms (O2, O5, O9) are protonated, and the remaining three oxygen atoms serve as hydrogen bond acceptors.

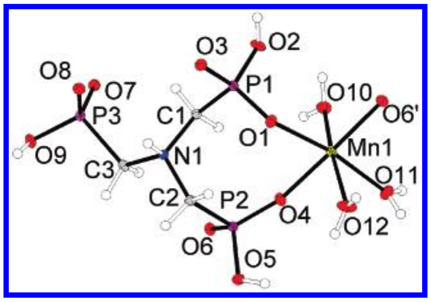

Figure 5. ORTEP drawing of Mn[HN(CH_2PO_3H)$_3$(H_2O)$_3$] (**2**), showing the octahedral coordination of Mn by three water molecules and three phosphonate oxygens. Two phosphonate groups of the same nitrilotris(methylenephosphonate) bond to the same Mn forming an eight-membered ring through chelation.

The chains have a corrugated appearance as described earlier.[9] The chains are connected to each other through hydrogen bonds as depicted in Figures 6 and 7. In Figure 6, there are two types of hydrogen bonds between adjacent chains, O9−H···O3, 2.586(2) Å, and N−H···O8, 2.725(2) Å. There is also an intrachain hydrogen bond O2−H···O7, 2.619(2) Å. In Figure 7, the chains parallel to the *c*-axis direction are represented by two yellow spheres showing the zigzag arrangement of the metal atoms. The three water molecules form six hydrogen bonds (Table 4), mostly in the *a*-axis direction, whereas the HN···O8 and O9−H···O3 hydrogen bonds connect with adjacent chains in the *b*-axis direction. As a result, the hydrogen bonds create a three-dimensional network of hydrogen-bonded linear chains. The overall effect is to create what appears to be two-dimensional corrugated sheets that nest within each other running along the *ab* diagonal. However, these sheets are made up of individual chains where the nonbonding P3, O7, O8, and O9 phosphonate groups overlap, as shown in Figure 7.

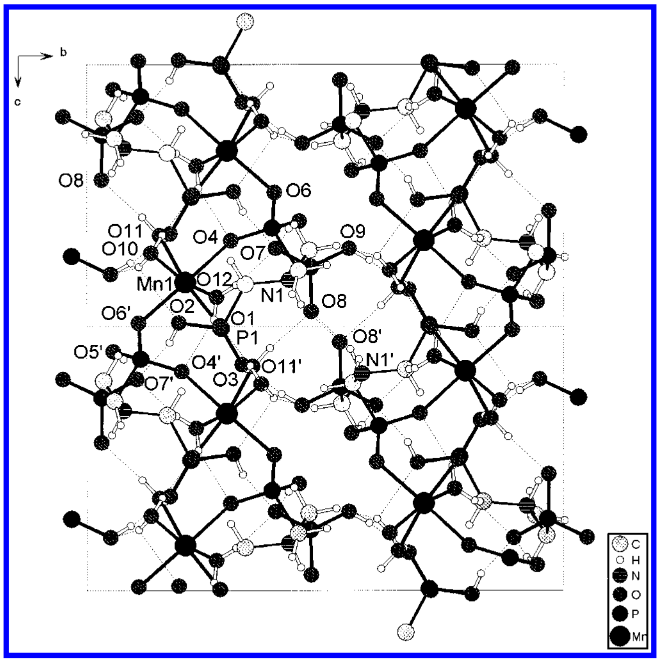

Figure 6. Packing diagram of $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ (**2**) as viewed down the *a* axis, depicting the complex chains running parallel to the *c* axis. Hydrogen bonds are represented by dashed lines.

Table 4. Hydrogen Bonds for $[Mn(HN(CH_2PO_3H)_3(H_2O)_3]$ (**2**) (Å and deg)[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
N1−H1···O8c	0.93	1.87	2.725(2)	151.6
O2−H2···O7a	0.832(17)	1.808(19)	2.619(2)	164(3)
O5−H5···O7d	0.825(18)	1.872(19)	2.686(2)	169(3)
O9−H9···O3c	0.817(17)	1.773(17)	2.586(2)	173(3)
O10−H10B···O1b	0.833(17)	2.051(17)	2.881(2)	174(3)
O10−H10A···O9e	0.823(17)	2.43(2)	3.160(2)	148(3)
O10−H10A···O2	0.823(17)	2.57(3)	3.008(2)	115(2)
O11−H11A···O3f	0.838(17)	1.907(19)	2.728(2)	166(3)
O11−H11B···O8f	0.846(17)	1.880(18)	2.711(2)	167(3)
O12−H12A···O7d	0.825(17)	1.951(18)	2.766(2)	169(3)
O12−H12B···O4a	0.811(17	2.13(2)	2.774(2)	137(3)

[a] Symmetry transformations used to generate equivalent atoms: a, x, $-y + 1/2$, $z + 1/2$; b, x, $-y + 1/2$, $z - 1/2$; c, $-x + 3$, $-y + 1$, $z + 2$; d, $x - 1$, y, z; e, $-x + 3$, $y - 1/2$, $-z + 3/2$; f, $x - 1$, $-y + 1/2$, $z - 1/2$.

We note in Table 4 that there are three hydrogen bonds to O7 as acceptor atom. This high participation in hydrogen bonding is unusual and rare. The effect is to lengthen the P3−O7 bond. In the P3 phosphonate group the bond lengths are P3−O7, 1.522(2), P3−O8, 1.504(2), and P3−O9−H, 1.566(2) Å. In the other two phosphonate groups, the protonated oxygen atoms have similarly longer P−O bonds, but the remaining shorter P−O bonds range from 1.502(2) to 1.509(2) Å. Thus, the P3−O7 bond is significantly longer than the P−O bonds of the nonprotonated oxygens. This suggests that this O7 finds itself in a more positive force field, resulting from the close approach of three hydrogen atoms. The consequence is the lengthening of the P−O bond.

Thermal Analysis. The combined TGA−DTA curves for $Mn[HN(CH_2PO_3H)_3]$ are shown in Figure 8a. Since the compound is anhydrous, there is no recorded weight loss until decomposition sets in. There are three exotherms at 340, 368, and 463 °C resulting from the destruction of the organic material and the formation of $Mn_2P_4O_{12}$ above 700 °C. Because the end product contains less phosphorus than the original manganese phosphonate, 0.5 mol of P_2O_5 is lost. There is a very broad endotherm above 500 °C that may be due to this final loss. The overall reaction can be represented as follows:

$$2Mn[HN(CH_2PO_3H)_3](s) + {}^{25}/_{2}O_2(g) \rightarrow Mn_2P_4O_{12}(s) + P_2O_5(g) + 6CO_2(g) + 2NO_2(g) + 10H_2O(g)$$

The total observed weight loss was 39.1% compared to a theoretical value of 39.51%.

TGA−DTA curves for $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ are shown in Figure 8b. The DTA curve shows an endothermic and three exothermic effects. The strong endotherm, centered at 200 °C, is due to the loss of hydration water molecules. The calculated weight loss for this process is 13.5%, and the observed loss is the ≈15.5%. However, it is difficult to determine this weight loss accurately as this process is slightly overlapped with the weight loss due to the combustion of the organic fraction. This process starts to take place at 385 °C, as a strong exothermic effect. Two other weak exotherms centered at 450 and 580 °C can be observed. The

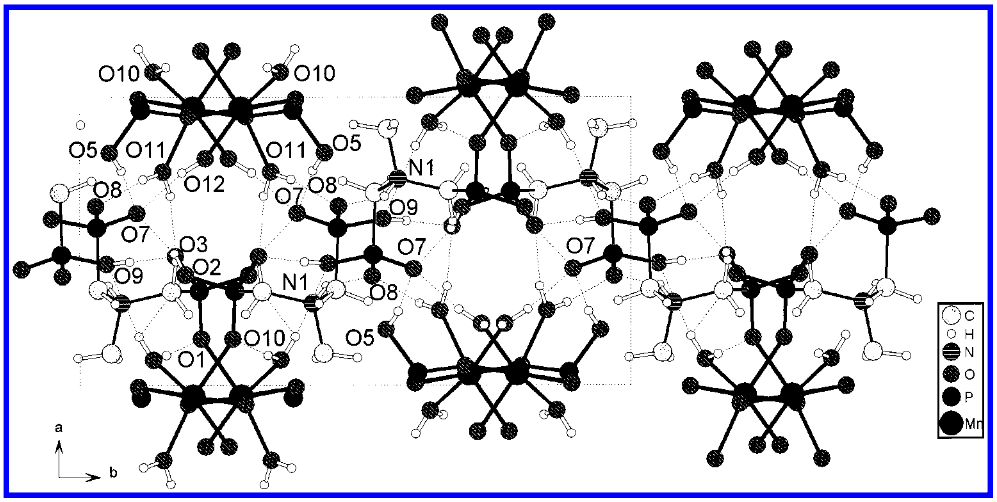

Figure 7. Packing diagram of $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ (**2**) as viewed down the *c* axis, which emphasizes the hydrogen bonding that knits the chains into corrugated layers. Oxygens O7, O8, and O9 participate in hydrogen bonding to other chains but do not bond to metal atoms.

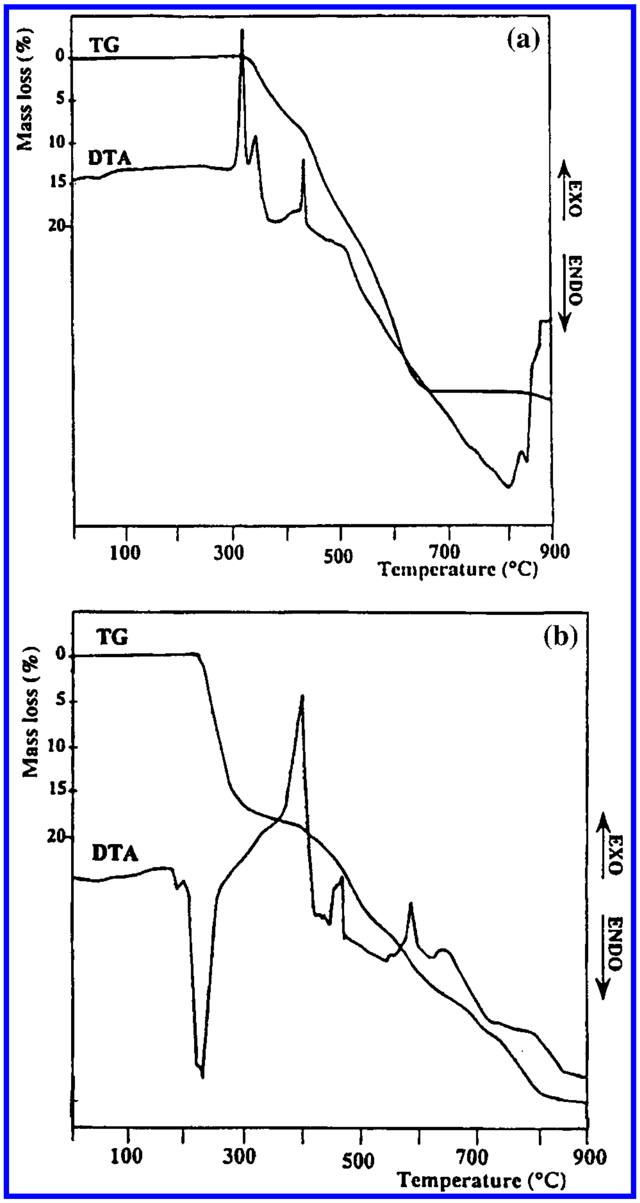

Figure 8. Thermogravimetric (TGA) and differential thermal analysis (DTA) curves for (a) $Mn[HN(CH_2PO_3H)_3]$ (**1**) and (b) $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ (**2**).

TG curve shows a continuous weight loss in this region. The final thermal decomposition product at 1000 °C has a powder diffraction pattern that matches that of $Mn_2P_4O_{12}$ (PDF database No. 36-0210), and no other peaks are present in the pattern. The proposed thermal decomposition reaction for the bulk material heated at 1000 °C is

$$2Mn[HN(CH_2PO_3H)_3(H_2O)_3](s) + {}^{25}/_{2}O_2(g) \rightarrow Mn_2P_4O_{12}(s) + P_2O_5(g) + 6CO_2(g) + 2NO_2(g) + 16H_2O(g)$$

A thermodiffractometric study of $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ was carried out to determine if it is transformed into crystalline $Mn[HN(CH_2PO_3H)_3]$ before thermal combustion. The data showed that the water loss is accompanied by the formation of an amorphous compound between 150 and 200 °C. Although the difference in the chemical formula is only the water content, crystalline $Mn[HN(CH_2PO_3H)_3]$ is not obtained by gentle heating of $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$. This is due to the very different crystal structures of the two compounds discussed below. The relatively high temperature at which the water molecules are lost is also understood on the basis of its crystal structure.

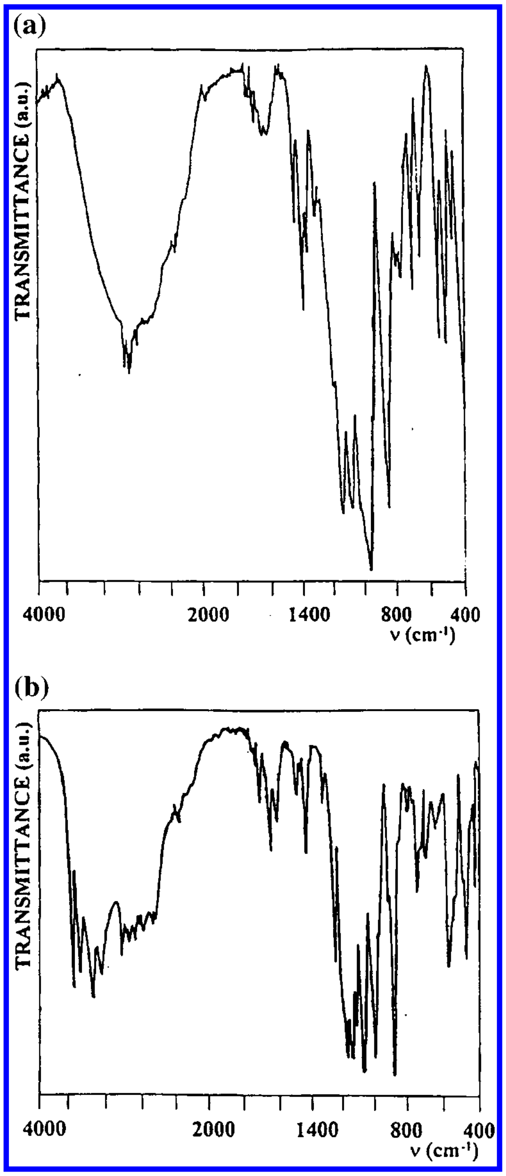

Figure 9. Infrared spectra of (a) $Mn[HN(CH_2PO_3H)_3]$ (**1**) and (b) $Mn[HN(CH_2PO_3H)_3(H_2O)_3]$ (**2**).

Infrared Spectra. The infrared spectrum of $Mn[HN(CH_2PO_3H)_3]$ is given in Figure 9a. The very broad band centered at 2900 cm^{-1} is attributed to the O−H and N−H stretching vibrations. The broadness of the band is due to the range of hydrogen bond strengths as shown by the *d*(donor−acceptor) values. The CH_2 stretching vibrations appear as weak, but sharp bands near 3000 cm^{-1} superimposed on the broad band. The multiple bands in the region of 900−1200 cm^{-1} are phosphonate P−O vibrations and are similar to bands for $Na_2[(HO_3PCH_2)_3NH]\cdot 1.5H_2O$.[4] The band at 1650 cm^{-1} is normally due to the water bending vibration. However, the compound is anhydrous. A similar band occurs in the anhydrous lead compounds.[5] This band may be a combination band or overtone from the strong bands observed at low wavelengths.

The IR spectrum of the trihydrate was recorded between 4000 and 400 cm^{-1} and is shown in Figure 9b. There are two intense doublets at 3580 and 3510 cm^{-1} and 3370 and 3265 cm^{-1}, respectively. These bands are due to the H−OH stretching vibration of the water molecules. The very broad band centered at ∼2900 cm^{-1} is due to the N−H stretching, and the shoulder at ∼2300 cm^{-1} is related to the hydrogen phosphonate, PO−H, groups. The C−H stretching vibrations are observed as sharp, weak bands close to 3000 cm^{-1}. Three sharp bands centered at 1690, 1640, and 1600 are due to the bending H−O−H vibration of the hydration water. The remaining vibration bands are typical of the nitrilotris(methylenetriphosphonate) salts.

Discussion

Recently, we found that monodeprotonation of nitrilotris(methylenephosphonic acid) with amines results in formation of three-dimensional hexagonal structures with encapsulation of the amine[7] as indicated in Scheme 1 of the Introduction. These structures are held together by very strong hydrogen bonds. Double deprotonation of NTP by amines led to layered compounds with the amines intercalated between the layers. Double deprotonation of NTP by NaOH yielded a tetramer,[4] while use of Pb^{2+} to doubly deprotonate NTP yielded two layered compounds.[5] In this study, it was found that divalent transition metal cations, as well as Zn^{2+} and Cd^{2+}, displaced two protons while protonation of the central nitrogen, through zwitterion formation, left only one hydrogen on each phosphonate group. This arrangement of protons and negatively charged phosphonate oxygens allows for a maximum level of hydrogen bonding.

In the case of the anhydrous compound **1**, all four protonated atoms form hydrogen bonds with one acceptor oxygen in each of the three phosphonate branches of NTP. Oxygen atom O9, which does not bond to Mn, accepts two H-bonds, one from the nitrilo nitrogen and one from O5. The other two acceptor atoms, O1 and O4, are also covalently bonded to a manganese atom.

The anhydrous compound was obtained only when the ratio of NTP to Mn was 10 or greater. Otherwise, the trihydrate forms and was found to yield an isomorphous series of complexes $M[HN(CH_2PO_3H)_3(H_2O)_3]$, M = Mn, Co, Ni, Cu, Cd, and even mixed derivatives of the type Zn and Cd.[9] These results indicate that it is the hydrogen bonding that dictates the final structure. While the ligand utilized five oxygens in covalent bonding to Mn in the anhydrous compound, only three oxygens, O1, O4, and O6, are utilized for this purpose in the trihydrate. Three oxygens, O2, O5, and O9, retain their protons and, together with NH, form moderately strong hydrogen bonds (D···A, 2.59−2.73 Å) to the three nonbonding oxygens, O3, O7, and O8. The O9−H···O3 and NH···O8 hydrogen bonds occur across adjacent chains as shown in Figure 6. Each water molecule utilizes both of its hydrogens to achieve a maximum level of hydrogen bonding. For this reason, no water is lost to slightly above 200 °C.

In summary, we have shown in this and other publications[7,9] that nitrilotris(methylenephosphonic acid) can form hexagonal porous three-dimensional structures encapsulating a template, layered structures with intercalated templates, linear polymers, dense structures,[4,5] and the isomorphous open-structured hydrates by proper manipulation of the protons. Phosphonic acids in general form very strong hydrogen bonds[2] and therefore can serve as a family of synthons for crystal-engineered structures as we will demonstrate in future publications.

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Supporting Information Available: X-ray crystallographic tables for structures **1** and **2**, including atomic coordinates, bonds and angles, anisotropic thermal factors, and hydrogen atom positions. This material is available free of charge via the Internet at http://pubs.acs.org.

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