Inorg. Chem. **2007**, *46*, 278–284

Inorganic Chemistry
Article

Inorganic–Organic Framework Structures; M(II) Ethylenediphosphonates ($M = Co$, Ni, Mn) and a Mn(II) Ethylenediphosphonato-phenanthroline

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Received September 26, 2006

The reaction of nickel, cobalt, and manganese with 1,2-ethylenediphosphonic acid or 1,2-ethylenediphosphonic acid and 1,10-phenanthroline under hydrothermal conditions resulted in the pillared layered structures $Co_2(H_2O)_2(O_3PC_2H_4PO_3)$ (**I**) and $Ni_2(H_2O)_2(O_3PC_2H_4PO_3)$ (**II**), which are isostructural to a zinc phase that has previously been characterized by X-ray powder methods. In addition, a 1D chain structure, $Mn(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$ (**III**), and a pillared layered structure, $Mn(HO_3P(CH_2)_2PO_3H)$ (**IV**), were obtained. The structures of these phases were solved by single-crystal X-ray diffraction methods. The crystallographic data are as follows: compound **I** $P2_1/n$ (No. 14), $a = 5.6500(11)$ Å, $b = 4.7800(10)$ Å, $c = 15.330(3)$ Å, $\beta = 98.50(3)°$, $V = 409.47(14)$ Å^3, $Z = 2$; compound **II** $P2_1/n$ (No. 14), $a = 5.5807(11)$ Å, $b = 4.7205(9)$ Å, $c = 15.250(3)$ Å, $\beta = 98.55(3)°$, $V = 397.28(13)$ Å^3, $Z = 2$; compound **III** $C2/c$ (No. 15), $a = 12.109(2)$ Å, $b = 15.328(3)$ Å, $c = 9.848(2)$ Å, $\beta = 108.88(3)°$, $V = 1729.5(6)$ Å^3, $Z = 4$; compound **IV** $P\bar{1}$ (No. 2), $a = 5.498(5)$ Å, $b = 7.715(6)$ Å, $c = 8.093(7)$ Å, $\alpha = 82.986(12)°$, $\beta = 75.565(12)°$, $\gamma = 80.582(12)°$, $V = 326.7(5)$ Å^3, $Z = 2$. Magnetic measurements show antiferromagnetic behavior below $T_N = 7$ K for **I** and 13 K for **II**.

Introduction

Current interest in the area of hybrid inorganic−organic framework materials focuses largely on two important classes: carboxylates[1] and phosphonates.[2] Although the carboxylates are currently more fashionable, the phosphonates have a much longer history, starting with the work of Alberti et al. and Dines et al.[3] on zirconium phosphonate layered materials that are related to the zirconium phosphate structure.[4] Diphosphonate ligands are often more versatile than monophosphonates because pillared layered structures and other architectures can be created. Mixtures of bifunctional diphosphonates and short monophosphonate spacers have been used to synthesize porous materials, although these generally lack pore ordering.[5]

There is extensive literature on metal diphosphonates. Zubieta et al. have worked extensively on the early transition-metal diphosphonates, focusing on vanadium- and molybdenum-related systems, as well as some tin-containing materials.[6,15 a,b] Clearfield et al. and Bujoli et al. are also major contributors to the area of transition-metal diphosphonate structures,[7] while Sevov et al. have reported cobalt and oxomolybdenum methylenediphosphonates.[8] Férey et al. have done much work on nickel, vanadium, titanium, and iron diphosphonates,[9] and Zheng et al. have used a hydroxyl-functionalized diphosphonate (etidronic acid) to make some copper, zinc, iron, and nickel phases.[10] Attfield et al. have worked on group 13 diphosphonate systems,[11] and Bellito

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10.1021/ic0618302 CCC: $37.00

et al. have branched out from their work on monophosphonates to include some Cr diphosphonate structures.[12] Stock et al. have synthesized several materials, including a number of M(II) *p*-xylenediphosphonates, M = Mn, Ni, Cd, Pb, and Sn,[13] and Cheetham et al. have contributed with work on tin, antimony, iron, aluminum, and gallium diphosphonates.[14]

In addition to systems with diphosphonate alone, there has been increasing interest in phosphonates combined with other ligands. Zubieta et al. and Fu et al. have introduced the use of 1,10-phenanthroline as a decorating ligand in addition to the ethylenediphosphonate bridging ligand.[15] Many of those structures are either coordination polymers with 0-D metal−oxygen−metal connectivity[15c,f] or are bimetallic.[15a,b,d,e] In addition to systems containing the 1,10-phenanthroline ligand,[16] there are several ethylenediphosphonates with pyridyl-type groups as framework ligands, most of which are also bimetallic.[17] Mixed phosphonate oxalates are also known,[18] and several groups have used phosphonates containing other functions, such as carboxyphosphonates[19] or pyridylphosphonates.[20] In the present work, we describe the synthesis and structure of three compounds based on the M(II)/1,2-ethylenediphosphonic acid system and one based

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Table 1. Crystal Data and Structure Refinement Parameters for **I**, $Co_2(H_2O)_2(HO_3P(CH_2)_2PO_3H)$, **II**, $Ni_2(H_2O)_2(O_3P(CH_2)_2PO_3)$, **III**, $Mn(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$, and **IV**, $Mn(HO_3P(CH_2)_2PO_3H)$

	I	II	III	IV
chemical formula	$Co_2(H_2O)_2(O_3P(CH_2)_2PO_3)$	$Ni_2(H_2O)_2(O_3P(CH_2)_2PO_3)$	$Mn(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$	$Mn(HO_3P(CH_2)_2PO_3H)$
formula mass	339.89	339.44	459.2	242.9
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$C2/c$	$P\bar{1}$
T (K)	293	293	293	293
a (Å)	5.6500(11)	5.5807(11)	12.173(2)	5.498(5)
b (Å)	4.7800(10)	4.7205(9)	15.393(3)	7.715(6)
c (Å)	15.330(3)	15.250(3)	9.867(2)	8.093(7)
α (deg)	90	90	90	82.986(12)
β (deg)	98.50(3)	98.55(3)	108.78(3)	75.565(12)
γ (deg)	90	90	90	80.582(12)
V (Å^3)	409.47(14)	397.28(13)	1750.5(6)	326.7(5)
Z	2	2	4	2
μ (mm^{-1})	4.458	5.159	0.995	2.486
2θ range (deg)	2.69−23.28	2.70−23.35	2.21−23.37	2.61−28.24
total data collected	2195	2280	5276	2719
unique data	591	568	1266	1436
obsd data ($\sigma > 2\sigma(I)$)	572	545	1149	1385
R_{int}	0.0274	0.0419	0.0323	0.0216
R1, wR2 [$I > 2\sigma(I)$]	0.0548, 0.1447	0.0719, 0.1905	0.0265, 0.0712	0.0251, 0.0666
R (all data)	0.0577, 0.1452	0.0730, 0.1912	0.0303, 0.07033	0.0259, 0.0671

on the M(II)/1,10-phenanthroline/1,2-ethylenediphosphonic acid system.

Experimental Section

Materials. All reagents were used as purchased: 1,2-ethylenediphosphonic acid from Lancaster Synthesis, $CoCl_2{\cdot}6H_2O$ and $MnCl_2{\cdot}4H_2O$ from Aldrich Chemical Co., $NiCl_2{\cdot}6H_2O$ and 1,10-phenanthroline from Alfa Aesar, and tetrahydrofuran from Fisher Scientific. The hydrothermal reactions were carried out in 23 mL Teflon-lined stainless-steel autoclaves under autogenous pressure.

Synthesis of $Co_2(H_2O)_2(O_3PC_2H_4PO_3)$, I. A mixture of $CoCl_2{\cdot}6H_2O$ (1 mmol) and 1,2-ethylenediphosphonic acid (1 mmol) in 5 mL of deionized (DI) water was placed into an autoclave. The autoclave was then sealed and heated for 6 days at 180 °C (initial and final pH 1 and 2, respectively). Pink powder containing crystals suitable for structure determination were obtained. Elemental analysis (C, H, N) was carried out by the Marine Sciences Institute Analytical Laboratory at UCSB. Found (wt %): H, 2.19; C, 7.23. Calcd (wt %): H, 2.37; C, 7.07. FTIR measurements were carried out on a Nicolet Magna 850 IR Spectrometer. FTIR frequencies (KBr) above 1400 cm^{-1}: 3467 vs, 3425 vs, 2962 m, 2920 m, 1616 s, 1412 s.

Synthesis of $Ni_2(H_2O)_2(O_3PC_2H_4PO_3)$, II. $NiCl_2{\cdot}6H_2O$, 1,2-ethylenediphosphonic acid, and DI water were placed into an autoclave in a ratio of 1.00 mmol/1.00 mmol/5 mL. The sealed autoclave was heated at 200 °C for 4 days (initial and final pH $<$ 1). Light green clusters of square platelet crystals were formed, washed with water, and dried in a 60 °C oven. A suitable crystal was broken off of the clusters for structure determination. Anal. Found (wt %): H, 2.20; C, 7.19. Calcd (wt %): H, 2.38; C, 7.08. FTIR frequencies (KBr) above 1400 cm^{-1}: 3444 s, 3410 s, 2966 m, 2920 m, 1647 s, 1412 s.

Synthesis of $Mn^{II}(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$, III. An autoclave containing 1.00 mmol of $MnCl_2{\cdot}4H_2O$ with 0.50 mmol each of 1,2-ethylenediphosphonic acid and 1,10-phenanthroline in 5 mL of DI water was heated for 2 days at 180 °C (initial and final pH $<$ 1). Colorless rhombohedral crystals were obtained and used in the structure determination. Anal. Found (wt %): H, 4.25; C, 36.45; N, 6.05. Calcd (wt %): H, 4.37; C, 36.46; N, 6.07. FTIR frequencies (KBr) above 1400 cm^{-1}: 3471 mbr, 1516 m, 1419 m.

Synthesis of $Mn^{II}(HO_3P(CH_2)_2PO_3H)$, IV. A mixture of $MnCl_2{\cdot}4H_2O$ (1.00 mmol) with 1,2-ethylenediphosphonic acid (0.50 mmol) and 1,10-phenanthroline (0.50 mmol) in 1 mL of DI water and 4 mL of tetrahydrofuran was placed into an autoclave, which was heated at 180° for 2 days (initial and final pH $<$ 1). Colorless rhombohedral crystals of $Mn^{II}(HO_3P(CH_2)_2PO_3H)$ were obtained within a field of colorless rhombohedral crystals of **III**, and they were used for structure determination. Elemental analysis and FTIR not available as a phase-pure sample of **IV** was not synthesized.

Structure Determination of $Co_2(H_2O)_2(O_3PC_2H_4PO_3)$, $Ni_2(H_2O)_2(O_3PC_2H_4PO_3)$, $Mn(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$, and $Mn(HO_3P(CH_2)_2PO_3H)$. Suitable single crystals of $Co^{II}_2(H_2O)_2(O_3P(CH_2)_2PO_3)$, $Ni^{II}_2(H_2O)_2(O_3P(CH_2)_2PO_3)$, $Mn^{II}(HO_3P(CH_2)_2PO_3H)$ $(H_2O)_2(C_{12}H_8N_2)$, and $Mn^{II}(HO_3P(CH_2)_2PO_3H)$ were carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate adhesive. Crystal structure determination by single-crystal XRD was performed on a Bruker SMART-CCD diffractometer equipped with a normal-focus 2.4 kW sealed-tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature. An empirical correction on the basis of symmetry-equivalent reflections was applied using the SADABS program.[21] The structure was solved by direct methods using the SHELXTL package of programs.[22] The relevant details of structure determination are presented in Table 1. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL package of programs. The hydrogen atoms were found in the Fourier difference map; any protons remaining on the acid were restrained to chemically relevant bond lengths for **I**, **II**, and **III** but were not restrained for **IV**. None of the O−H distances in the structures are less than the shortest O−H distance in the ethylenediphosphonic acid ligand.[23] The last cycles of refinement included atomic positions and anisotropic thermal parameters for all of the atoms

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(21) Sheldrick, G. M. *SADABS User Guide*; University of Göttingen: Göttingen, Germany, 1995.

(22) Sheldrick, G. M. *SHELXTL-97, A Program for Crystal Structure Solution and Refinement*, version 5.1; University of Göttingen: Göttingen, Germany, 1997.

(23) Peterson, S. W.; Gerbert, E.; Reis, A. H., Jr.; Druyan, M. E.; Mason, G. W.; Peppard, D. F. *J. Phys. Chem.* **1977**, *81*, 466.

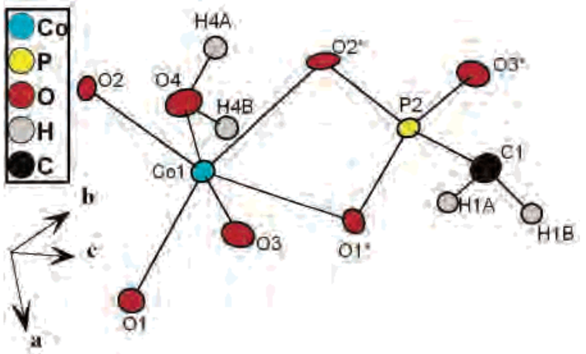

Figure 1. Asymmetric unit of **I**, with starred oxygens shown to complete the MO_6 octahedron. Thermal ellipsoids are given at 50% probability (hydrogen at 20% probability).

except hydrogen, which used isotropic thermal parameters. The bond valence sums obtained by using the program VALIST[24] confirm the assignment of the Ni, Co, and Mn as divalent. The program PLATON[25] determined that no obvious space group changes were needed or suggested.

Thermal Analysis and Magnetic Measurement Conditions. Thermogravimetric analyses were carried out with a heating rate of 10° min^{-1} in air on a Mettler 851eTG/sDTA. X-ray thermodiffractometry (Cu Kα radiation, λ=1.5418 Å) was performed under static air in a Bruker D8 Advance diffractometer outfitted with an M. Braun position-sensitive detector and an Anton Paar HTK 16 high-temperature stage. Patterns were scanned at room temperature, 100°, and every 50° thereafter until 1000°, with a temperature ramp of 0.5° min^{-1} for **I** and **III**, and they were scanned at room temperature, 300°, and every 50° thereafter until 850° for **II**. Magnetic measurements were carried out with a 1 kOe field from 5 to 400 K at a ramping rate of 5° min^{-1} using a Quantum Design MPMS 5XL SQUID magnetometer.

Results and Discussion

Structure of $Co_2(H_2O)_2(O_3PC_2H_4PO_3)$, I, and $Ni_2(H_2O)_2(O_3PC_2H_4PO_3)$, II. $Co^{II}_2(H_2O)_2(O_3P(CH_2)_2PO_3)$ and $Ni^{II}_2(H_2O)_2(O_3P(CH_2)_2PO_3)$ are isostructural to a zinc ethylenediphosphonate first synthesized by Poojary and Clearfield[7b] and characterized by powder methods and are new members of the transition-metal ethylenediphosphonate family. Relative unit cell lengths and volumes are consistent with the ionic radii. The asymmetric unit (Figure 1), shows that the M^{2+} is six-coordinate with a distorted $M^{II}O_5(H_2O)$ octahedron, that the phosphonate group (bonded to the M^{2+}) is fully deprotonated, and that all of the oxygens of the phosphonate group are involved in M^{2+}-O bonds.

This structure type is made of inorganic layers perpendicular to the *c* axis which are composed of corner-sharing $M^{II}O_5(H_2O)$ octahedra, similar to the cuprate layers in lanthanum cuprates (Figure 2). The layers themselves are pillared by the diphosphonate group. There are small channels between the pillars running parallel to the *b* axis in this structure (Figure 3).

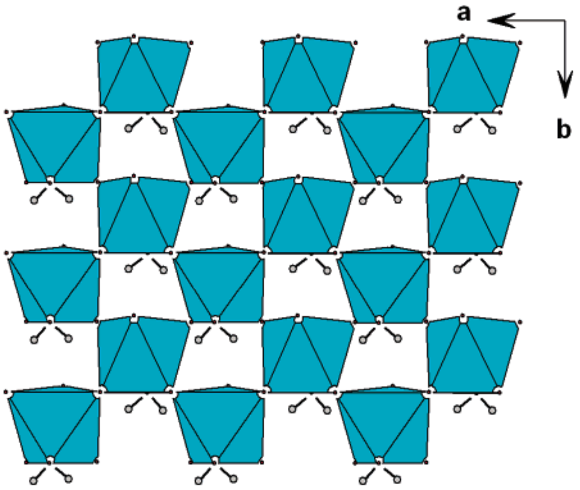

Figure 2. View of inorganic layer of **I** and **II** down the *c* axis.

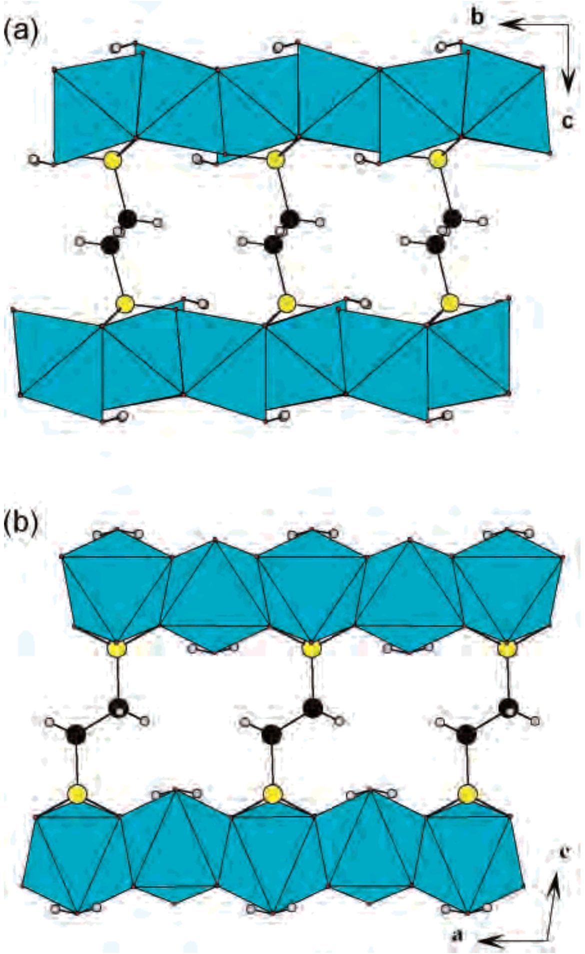

Figure 3. View of diphosphonate linkage of **I** and **II** (a) down the *a* axis and (b) down the *b* axis.

The large variation in bond distances and angles show the distortion of the CoO_6 and NiO_6 octahedra. The Co−O distances lie in the range of 2.051−2.219 Å ($(Co-O)_{av}$ = 2.123 Å), and the O−Co−O bond angles lie in the range of 67.1−102.9°. The Ni−O distances lie in the range of 2.048−2.158 Å ($(Ni-O)_{av}$ = 2.084), and the O−Ni−O bond angles lie in the range of 69.1−100.4°. The MO_6 octahedra are most distorted by the $M-O(2)^{\#2}$ and $M-O(1)^{\#1}$ bonds, which are

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[24] (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192−197.

[25] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, *C34*. (b) Spek, A. L. *PLATON*, *A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2005.

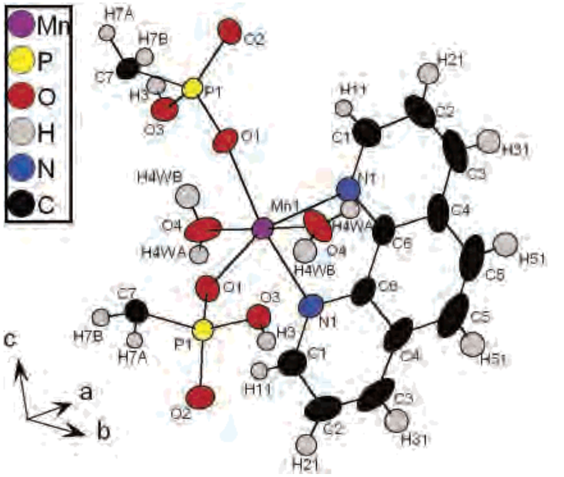

Figure 4. Formula unit of **III**. Thermal ellipsoids are given at 50% probability (hydrogen at 20% probability).

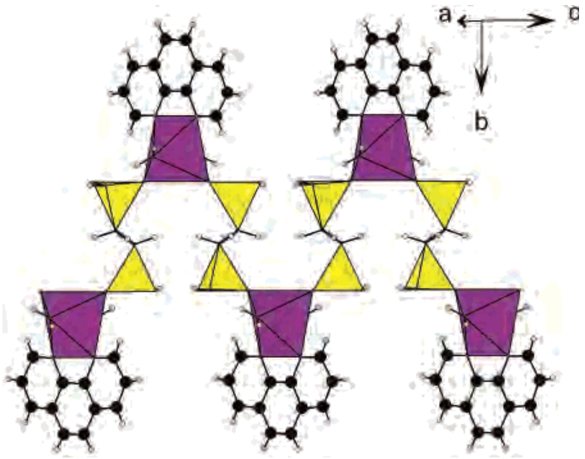

Figure 5. Individual pleated chain of **III**.

the longest bonds in the octahedron and have the smallest O−M−O angle because these oxygens belong to the same phosphonate group; the phosphonate tetrahedra are elongated along the P−C bond. The phosphonate bond angles and distances are consistent with similar phosphonate structures.

Structure of $Mn^{II}(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$, III. $Mn^{II}(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$ is made of $MnO_2(H_2O)_2N_2$ octahedra, with waters at the octahedron apexes, oxygens from phosphonates at adjacent corners, and *cis*-nitrogens belonging to a decorating 1,10-phenanthroline (Figure 4). The ethylenediphosphonate has one proton per phosphonate group. A pleated chain parallel to the *c* axis is formed through the Mn octahedron−ethylenediphosphonate−Mn octahedron connection (Figure 5). The chains assemble by interleaving the decorating phenanthrolines and stack such that phenanthroline sections alternate with diphosphonate groups in the *a* direction (Figure 6). This is a similar structure to a Cu phenanthroline ethylenediphosphonate which is primitive instead of *C* centered and whose *b* axis is twice the length because there are two Cu sites to allow for an off-planar angle between the coordinated phenanthrolines.[15f]

The six-coordinate manganese possesses a distorted octahedral geometry. The Mn−O distances lie in the range of 2.110−2.198 Å; the Mn−N distance is 2.289 Å, and the O(N)−Mn−O(N) angles lie in the range of 72.02−98.52°. The large variation in bond distances and angles show the distortion of the MnO_4N_2 octahedron from the constraint of the bidentate phenanthroline. The phenanthroline remains planar, but the water atoms are situated such that the Mn-(OH_2) bonds are not quite perpendicular to the phenanthroline plane. The Mn octahedra are distorted to accommodate the constraint induced by the bidentate phenanthroline, with the Mn−N distance being longer than the Mn−O distances and the N−Mn−N angle being the smallest octahedral angle. The phosphonate bond angles and distances are consistent with similar phosphonate structures. All phenanthroline bonds lengths are in good agreement with the bond length range reported for 1,10-phenanthroline monohydrate and for the Cu ethylenediphosphonato-phenanthroline.[15f,26]

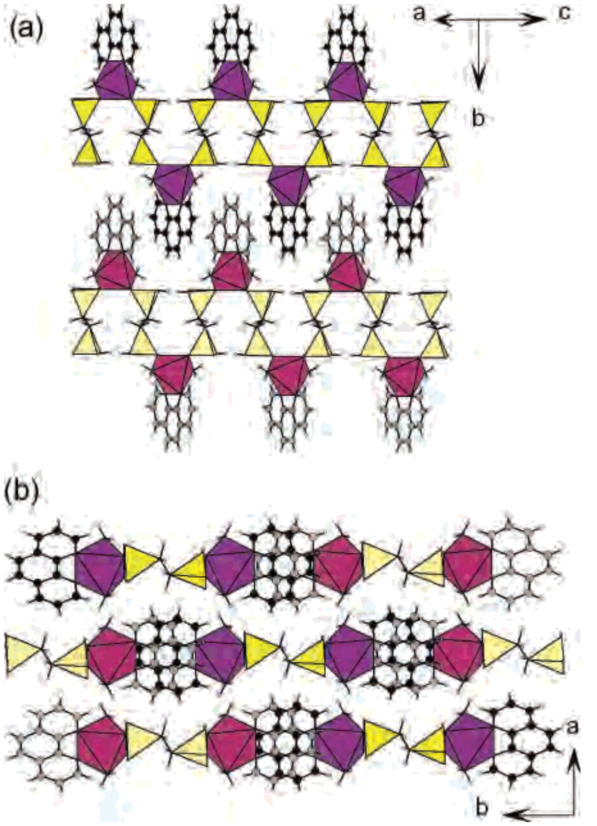

Figure 6. (a) Interleaving of two chains in **III** and the (b) layering of the interleaved chains; the layers are perpendicular to the *c* axis. Alternate chains are shaded differently to emphasize the separation of the chains.

Structure of $Mn^{II}(HO_3P(CH_2)_2PO_3H)$, IV. In spite of extensive research on transition-metal diphosphonates, we have found an entirely new structure type in the manganese(II) ethylenediphosphonate system. $Mn^{II}(HO_3P(CH_2)_2PO_3H)$, Figure 7, is made of an inorganic layer perpendicular to the *c* axis which is composed of edge-sharing octahedral dimers of $Mn_2^{II}O_{10}$ (two MnO_6 octahedra which share two O31 oxygens) connected to each other through PO_3C tetrahedra (Figure 8). Unlike the previous structures, there are no water molecules coordinated to the metal ions; all coordinating oxygens are supplied by the diphosphonate groups. The

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(26) Tian, Y. P.; Duan, C. Y.; Xu, X. X.; You, X. Z. *Acta Crystallogr.* **1995**, *C51*, 2309−2312.

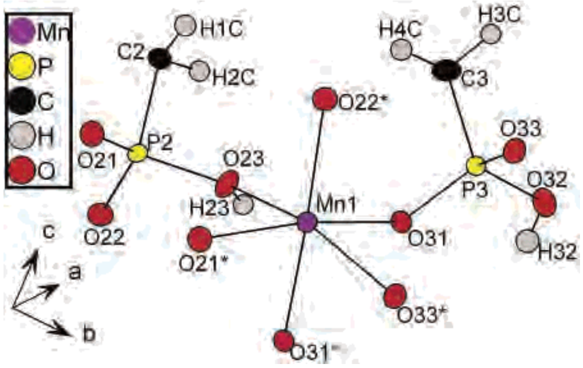

Figure 7. Asymmetric unit of **IV** with starred oxygens shown to complete the MnO_6 octahedron. Thermal ellipsoids are given at 50% probability (hydrogen at 20% probability).

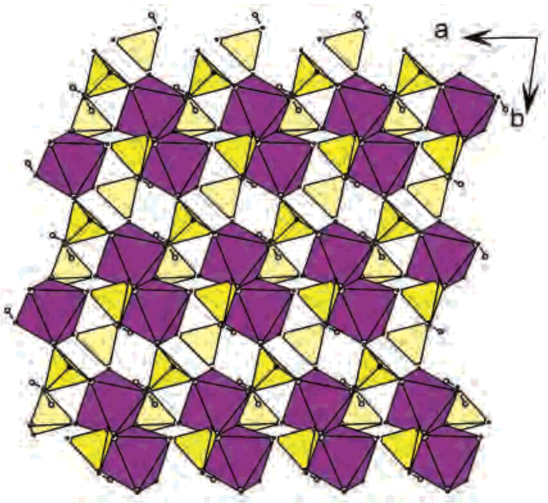

Figure 8. Inorganic layer of **IV** viewed down the *c* axis; the phosphonate groups behind the Mn_2O_{10} dimer plane are shaded lighter than those in front.

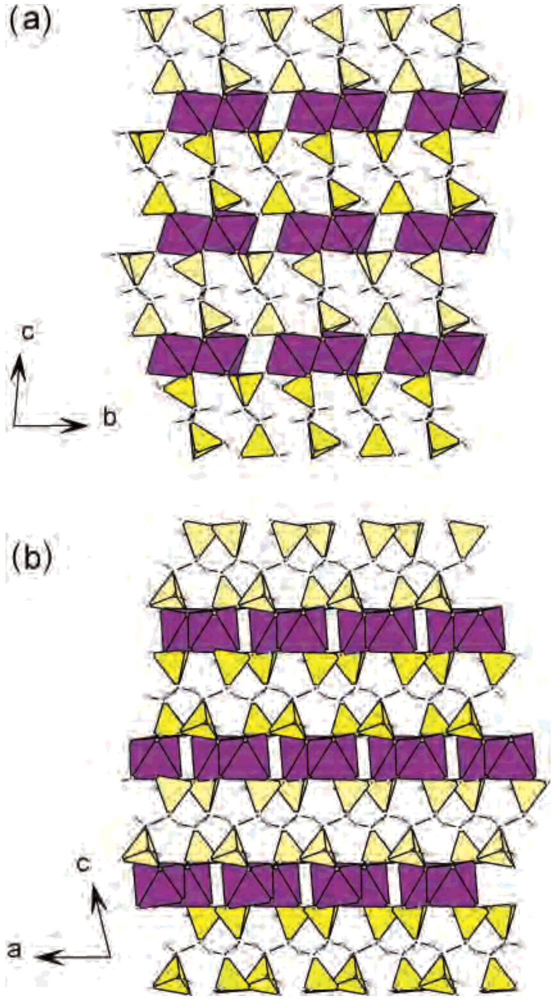

Figure 9. View of the diphosphonate linkage of **IV** (a) down the *a* axis and (b) down the *b* axis. Phosphonates in alternating layers shown in different shades, as in Figure 8.

layers themselves are pillared by the alkyl part of the diphosphonate group, Figure 9. There are no accessible pores in this structure.

The manganese is six-coordinated and possesses a distorted octahedral geometry. The Mn−O distances lie in the range of 2.092−2.328 Å, and the O−Mn−O bond angles are in the range of 75.37−108.82°. The large variation in bond distances and angles show the distortion of the MnO_6 octahedra. The phosphonate bond angles and distances are consistent with similar phosphonate structures. The P(2) phosphonate group is the more distorted tetrahedron, possibly because of the hydrogen bonded to O23 (the hydrogen in the P(3) phosphonate group is pendent).

Thermal Behavior of I, $Co_2(H_2O)_2(O_3PC_2H_4PO_3)$, and II, $Ni_2(H_2O)_2(O_3PC_2H_4PO_3)$. Compound I is stable to ∼225 °C, at which point it begins to lose coordinated water and a structural change begins. These changes, which are complete by 350 °C, are accompanied by a color change from magenta to deep blue. The dehydrated phase is stable to 550°, at which point the structure begins to evolve some organics and transform into cobalt pyrophosphate. The sample fraction of $Co_2P_2O_7$ grows and the remaining organic is removed from the structure between 650 and 850°.

In contrast to **I**, **II** is stable to ∼425 °C. Then loss of coordinated water and the corresponding structural change begins and is complete by 500 °C. In this temperature range, the color of **II** changes from bright green to light muddy green. The dehydrated phase of **II** is stable to 600°, when it starts to transform into nickel pyrophosphate. The change is complete between 750 and 800°. We believe that the greater stability of **II** may be caused by the enhanced ligand-field stabilization energy of Ni^{II} compared with Co^{II}.

Thermal Behavior of III, $Mn(HO_3P(CH_2)_2PO_3H)(H_2O)_2(C_{12}H_8N_2)$. Loss of coordinated water from the structure of **III** starts slightly prior to 150° and is complete just after 200°, and a dehydrated crystalline form of the compound exists up to 250°. The sample then begins to lose weight and crystallinity in the range 250−400°, at which point an amorphous phases is present. Manganese phosphate ($Mn(PO_3)_2$) starts to form between 750 and 800°, with increasing crystallinity and sample fraction as the temperature increases.

Magnetic Behavior of I, $Co_2(H_2O)_2(O_3PC_2H_4PO_3)$, and II, $Ni_2(H_2O)_2(O_3PC_2H_4PO_3)$. In the inverse susceptibility versus temperature curves for **I** and **II**, the zero-field-cooled and field-cooled curves appear to be almost the same. Both structures show evidence of antiferromagnetic ordering at low temperatures: below ∼7 K for **I** and below ∼13 K for **II**. In the paramagnetic region, the curves are fitted to the Curie−Weiss law above 150 K, and the experimental magnetic moment for **I** is estimated at $\mu_{\text{exp}} = 3.68\ \mu$B, which is close to the spin-only value of 3.87 μB for Co^{2+}. For **II**, $\mu_{\text{exp}} = 2.37\ \mu$B, which is rather lower than the spin-only value of 2.83 μB for Ni^{2+}. The Curie−Weiss temperatures, θ_p, are estimated to be −36 K for **I** and −35 K for **II**. The magnetic-ordering temperatures are much lower than that found in La_2CuO_4 (∼28−40 K), probably because of the puckering of the $M^{II}O_4$ sheets which reduces the M−O−M angle that controls the superexchange interactions to between ∼120 and 125°.

Acknowledgment. We thank Unilever plc for financial support. This work made use of MRL Central Facilities supported by the MRSEC Program of the NSF under award DMR05-20415. Ram Seshadri is thanked for helping with the magnetic measurements, and Srinivasan Natarajan and Kinson Kam are thanked for useful discussions.

Supporting Information Available: Thermogravimetric and thermodiffractograms are available for **I**, **II**, and **III**, inverse susceptibility vs temperature curves for **I** and **II**, IR spectra for compounds **I**, **II**, and **III**, tables of atomic coordinates and bond distances and angles for **I**−**IV**, and crystallographic data files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0618302