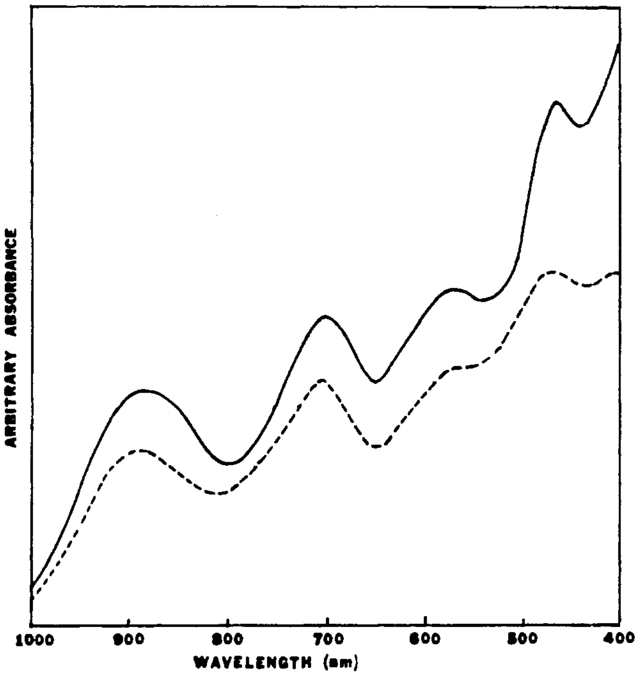

Figure 4. Reflectance electronic spectra for $W_2HCl_5(Etpy)_4$ (upper curve) and $W_2HCl_5(py)_4$ (lower curve).

these assignments for the terminal chlorines are tentative, especially since the terminal chlorine bond distances have a considerable amount of uncertainty associated with them as discussed earlier. When the chlorine ratios are allowed to vary, slight improvements in the fits are seen (lower χ^2's), and the ratios vary somewhat from the ideal 1:2:2, especially for $W_2HCl_5(py)_4$; however, the binding energies change insignificantly.

UV-Visible Spectra. Acquisition of UV-visible spectra was hampered by insolubility and/or decomposition of the pyridine and the 4-ethylpyridine compounds in most common organic solvents. Reflectance spectra were obtained for both compounds and are shown in Figure 4. The spectra are essentially identical. They are also quite similar to the spectra recorded by Wentworth and co-workers for the compounds $W_2Cl_6L_4$ (L = pyridine, 4-picoline, and 4-isopropylpyridine)[32] and by Walton and coworkers for $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(dppm)_2$ and $W_2(\mu\text{-}Cl)_2Cl_4(dppm)_2$.[6]

Conclusions

The preparation of $W_2HCl_5(py)_4$ can be viewed as the product of the oxidative addition of HCl to a quadruple bond, as previously described in the formation of $Mo_2Cl_8H^{3-}$,[24] $MoWCl_8H^{3-}$,[26] $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(O_2CPh)_2(P\text{-}n\text{-}Bu_3)_2$,[17] and $W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_4(dppm)_2$.[6] The reaction, however, is not straightforward in that the HCl generated would exist almost entirely as pyridinium chloride unless it reacted immediately with the ditungsten species in solution. Also, without the generation of HCl, numerous products with incomplete mhp replacement are obtained,[33] indicating the need for HCl in order to completely replace all mhp ligands. Because of these complications, it is not possible at present to formulate a simple reaction scheme for the formation of $W_2HCl_5(py)_4$.

Acknowledgment. We thank the National Science Foundation for a grant to the Department of Chemistry for the purchase of the photoelectron spectrometer used in this study. We also wish to thank Dr. R. A. Jacobson and his research group for their assistance in the X-ray structure determination.

Supplementary Material Available: Tables IS-IIIS, listing crystallographic data, anisotropic thermal parameters, and bond distances and angles for the 4-ethylpyridine ligands (3 pages); Table IVS, listing calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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(32) Saillant, R.; Hayden, J. L.; Wentworth, R. A. D. *Inorg. Chem.* **1967**, *6*, 1497.

(33) Carlin, R. T.; McCarley, R. E. Unpublished results.

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Synthesis and Characterization of a New Series of Zinc Phosphites

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Several new zinc phosphites have been synthesized in aqueous solution by reactions of Zn^{2+} with H_3PO_3 and either Na^+, K^+, or Ba^{2+}. The structures were determined by single-crystal X-ray diffraction techniques. $Zn(H_2PO_3)_2\cdot 3H_2O$: $R\bar{3}$, $a = 21.128$ (2) Å, $c = 7.769$ (6) Å, $V = 3003$ (2) Å^3, $Z = 18$, $R(F) = 0.073$ for 494 observations ($I > 3\sigma(I)$), 82 variables. $Zn_2(HPO_3)_2(H_2O)_4\cdot H_2O$: $P\bar{1}$, $a = 7.670$ (2) Å, $b = 9.454$ (1) Å, $c = 7.554$ (1) Å, $\alpha = 90.83$ (1)°, $\beta = 92.90$ (1)°, $\gamma = 88.54$ (2)°, $V = 546.9$ (2) Å^3, $Z = 2$, $R(F) = 0.022$ for 1430 observations ($I > 3\sigma(I)$), 175 variables. $Zn_3Na_2(HPO_3)_4$: *Pnma*, $a = 8.331$ (2) Å, $b = 12.243$ (2) Å, $c = 12.669$ (1) Å, $V = 1292.2$ (6) Å^3, $Z = 4$, $R(F) = 0.038$ for 704 observations ($I > 3\sigma(I)$), 103 variables. $Zn_3K_2(HPO_3)_4$: $P2_1/c$, $a = 12.373$ (2) Å, $b = 13.635$ (2) Å, $c = 8.571$ (2) Å, $\beta = 90.24$ (1)°, $V = 1445.9$ (4) Å^3, $Z = 4$, $R(F) = 0.037$ for 1525 observations ($I > 3\sigma(I)$), 206 variables. $Zn_3Ba(HPO_3)_4(H_2O)_6$: $C2/c$, $a = 22.707$ (2) Å, $b = 5.302$ (3) Å, $c = 15.029$ (1) Å, $\beta = 105.28$ (1)°, $V = 1745$ (1) Å^3, $Z = 4$, $R(F) = 0.054$ for 1530 observations ($I > 3\sigma(I)$), 141 variables. Each of the five structures is a new type with the Zn atoms in either octahedral or tetrahedral coordination bridged by phosphite groups to produce a framework of zinc and phosphorus-centered oxygen polyhedra. Several of the frameworks have open channels lined with phosphite H atoms or coordinated water molecules. In some cases, these polyhedra are bridged by alkali-metal or alkaline-earth-metal ions to produce different frameworks. The exact nature of each structure is highly dependent on the identity of the second metal as each adopts a different coordination environment. The coordination numbers of the Na^+, K^+, and Ba^{2+} ions are 6, 7, and 12, respectively. The role of the alkali and alkaline-earth metals in the structures is discussed, and the phosphite structures are compared with similar known phosphates.

Introduction

Transition-metal phosphates are of interest because of their ion exchange and conduction properties.[1] A particularly well-studied family of such compounds are the metal phosphates of groups 4 and 14 as represented by the formula $\alpha\text{-}M(HPO_4)_2\cdot H_2O$ (M = Ti, Zr, Hf, Ge, Sn, Pb).[2] These compounds have a layered structure in which the metal atoms are octahedrally coordinated by oxygen atoms from six different tetrahedral phosphate groups.[3]

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(1) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125-148 and references therein.

(2) *Inorganic Ion Exchange Materials*; Clearfield, A., Ed., CRC Press: Boca Raton, FL, 1982.

0020-1669/89/1328-2608$01.50/0 © 1989 American Chemical Society

The fourth phosphate oxygen points into the interlamellar space and bonds to a proton that is easily exchanged for cations. Recent work has also focused on the intercalation of organic amines, with the intention of using the size of the organic group to control the size of the interlayer region. The motivation is to produce host materials for catalytic reactions by propping the layers open with large inorganic cations.[4] In a similar vein, it is possible to functionalize the terminal phosphate oxygen to produce layered phosphonates in which the organic groups, now bound to the layers, are arranged in the interlamellar space. Examples include zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$,[5] whose structure, though still unknown, is believed[5,6] to be closely related to the α-$Zr(HPO_4)_2 \cdot H_2O$ structure. This would be in keeping with recent work by Mallouk et al.[7] and by us[8] on divalent transition-metal phosphonates in which the compounds $M(O_3PC_6H_5) \cdot H_2O$ (M = Mn, Mg, Ni, Cu, Zn) were prepared. These compounds were found to contain metal–"phosphate" layers that are essentially isomorphous with those found in the purely inorganic phases $(NH_4)MO_3PO \cdot H_2O$ (M = Fe, Cd, Mn).[9-11] In these divalent metal phosphates and phosphonates, the metal atoms are octahedrally coordinated, but the 1:1 $M:PO_4(PO_3R)$ ratio necessitates a chelating arrangement of the phosphate group as well as oxygen bridging of metal atoms and the incorporation of a water molecule to complete the 6-fold coordination. In contrast to this work, the area of phosphite chemistry has received relatively little attention. As the phosphite ion, HPO_3^{2-}, is structurally similar to phosphate, PO_4^{3-}, both having tetrahedral geometry, we might anticipate that transition-metal phosphites would exhibit a similar structural chemistry, but with important differences due to the lesser charge and smaller number of oxygens on the phosphite group. For example, zirconium phosphite has the same layer structure as α-zirconium phosphate.[5,12] Given the recent successes in synthesizing several new phosphonates and organic phosphates of zinc,[7,8,13,14] we have undertaken a study of first-row transition-metal phosphite systems. Our results described here reveal a new and diverse structural chemistry which contrasts with that of the phosphates.

Experimental Section

Synthesis. $Zn(H_2PO_3)_2 \cdot 3H_2O$. A 25-mL aliquot of 1 M H_3PO_3 (Aldrich, 99%) was added to a solution of 1.36 g of $ZnCl_2$ (Mallinckrodt, used as received) in 25 mL of water. The resulting clear solution was refluxed for 2 days and then concentrated down to approximately 5 mL on a rotavap. The concentrated solution was allowed to stand at room temperature for 2 weeks in a sealed flask. The colorless, very thin, needle-shaped crystals were filtered off and washed with an aqueous 80% ethanol solution until the pH of the filtrate was about 5. A thermogravimetric analysis of the sample was performed on a Cahn R.H. electrobalance. The observed weight loss of 20.51% (onset = 75 °C; completion = 170 °C) is consistent with a formula of $Zn(H_2PO_3)_2 \cdot 3H_2O$ (calculated value of 19.21%), assuming the entire loss to be due to water of crystallization.

$Zn_2(HPO_3)_2(H_2O)_4 \cdot H_2O$. A 1-g sample of ZnO (MCB reagents) and 50 mL of 2 M H_3PO_3 were refluxed for 15 h. The solution was then filtered to remove unreacted oxide, and the filtrate was placed in a constant-temperature bath at 50 °C for 5 days. The large, colorless, block-shaped crystals were recovered by filtration and washed with water. A TGA weight loss curve showed a continuous weight loss between 60 and 200 °C of 23.07% (calculated value for $Zn_2(HPO_3)_2(H_2O)_4 \cdot H_2O$ based on H_2O loss only of 23.65%).

$Zn_3Na_2(HPO_3)_4$. This compound was prepared by two routes. A 0.200-g sample of $Zn(H_2PO_3)_2 \cdot 3H_2O$, prepared as described above, was suspended in 40 mL of absolute ethanol (in which it is fairly insoluble). Ten milliliters of 0.10 N ethanolic NaOH solution was added, and the resultant mixture was allowed to react at room temperature for 10 days. The solid product, a white fibrous material, was filtered and washed with absolute ethanol. An alternative procedure involved the use of sodium hydrogen phosphite. To 20 mL of aqueous 1 M H_3PO_3 was added 2.52 g (0.0117 mol) of $Na_2HPO_3 \cdot 5H_2O$ (prepared as described in ref 15), followed by addition of 1.36 g (0.01 mol) of $ZnCl_2$. The solution was stirred overnight at room temperature and then concentrated down on a hot plate to give an oily residue. This oily residue was redissolved in 10 mL of water and 5 mL of ethanol added. The cloudy solution was left at room temperature for several days. The resultant product, a microcrystalline white powder, was recovered by filtration and washed with water. An X-ray powder diffraction pattern was in excellent agreement with a calculated pattern[16] based on the single-crystal X-ray structure of $Zn_3Na_2(HPO_3)_4$ (vide infra).

$Zn_3K_2(HPO_3)_4$. A 1.36-g (0.01-mol) sample of $ZnCl_2$ was added to a solution of 3.16 g (0.018 mol) of $K_2HPO_3 \cdot 0.67H_2O$ (prepared as in ref 15) in 20 mL of aqueous 1 M H_3PO_3. A precipitate developed immediately. The mixture was stirred for 1 h at room temperature, after which time the precipitate was filtered and washed with 75% $EtOH/H_2O$, yielding 0.40 g of $Zn_3K_2(HPO_3)_4$. As with the sodium compound, identification of the potassium phase was based on comparison of the X-ray powder diffraction pattern with the pattern calculated by using the structural data obtained in the single-crystal X-ray study. Large, colorless, rod-shaped crystals suitable for the X-ray experiment were grown from the filtrate, which was allowed to stand overnight at room temperature.

$Zn_3Ba(HPO_3)_4(H_2O)_6$. A 4.34-g sample of $BaHPO_3$ (prepared by reaction of H_3PO_3 and $Ba(OH)_2$) was dissolved in 27 mL of aqueous 1 M H_3PO_3, to which was added 1.36 g of $ZnCl_2$ in 5 mL of 1 M H_3PO_3. The clear, colorless solution was stirred for 1 h, after which time no precipitate was observed. Upon addition of 2 mL of EtOH, an as yet unidentified solid formed and was filtered out of the solution. The filtrate was allowed to stand at room temperature for 2 days, during which time many large, colorless rod-shaped crystals of $Zn_3Ba(HPO_3)_4(H_2O)_6$ formed as the solvent evaporated. TGA of the crystals revealed a weight loss of 14.86% between 40 and 265 °C (calculated value for $Zn_3Ba(HPO_3)_4(H_2O)_6$ based on H_2O of 14.19%).

Crystallographic Studies. All the single-crystal X-ray diffraction experiments were performed at room temperature on a Rigaku AFC5R four-circle diffractometer equipped with a 12-kW rotating anode Mo X-ray source ($\lambda(K\alpha) = 0.71069$ Å). In each case, a suitable single crystal was mounted on a glass fiber with silicone cement. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 high-angle reflections ($20° < 2\theta(\text{Mo } K\alpha) < 40°$) in which the appropriate cell angles were constrained to their ideal values (i.e., for monoclinic, $\alpha = \gamma = 90°$, etc.). Intensity data were collected by using standard scan techniques (ω or ω–2θ), except for $Zn(H_2PO_3)_2 \cdot 3H_2O$. This crystal was so small that the data were collected in an ω-step scan mode and processed with the Lehmann–Larsen profile analysis algorithm[17] to yield usable intensities. In all cases the intensities of 3 standard reflections, monitored at 150 reflection intervals throughout data collection, remained constant within experimental error. Space groups were selected on the basis of systematic absences and intensity statistics which in all cases led to satisfactory refinements. Crystallographic computations were performed on a DEC MicroVAX II computer with the TEXSAN[18] series of programs. Each of the structures was solved by direct methods. The heavy atoms (Zn or Ba) were located from an *E* map calculated by the program MITHRIL.[19] The remaining non-hydrogen atoms were found by direct-methods phase-refinement techniques (DIR-

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(3) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311–3314.

(4) Clearfield, A.; Roberts, B. D. *Inorg. Chem.* **1988**, *27*, 3237–3240.

(5) Alberti, G.; Allulli, S.; Costantino, U.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113–1117.

(6) Prout, K.; Frausto, R.; Clearfield, A. Unpublished results.

(7) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781–2785.

(8) Martin, K. J.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *155*, 7–9.

(9) Ivanov, Y. A.; Egorov-Tismenko, Y. K.; Simonov, M. A.; Belov, N. V. *Sov. Phys.—Crystallogr.* (*Engl. Transl.*) **1975**, *19*, 665–666; **1977**, *22*, 97–98.

(10) Durif, A.; Averbuch-Pouchot, M. T. *Bull. Soc. Fr. Mineral. Cristallogr.* **1968**, *91*, 495–496.

(11) Tranqui, D.; Durif, A.; Guitel, J. C.; Averbuch-Pouchot, M. T. *Bull. Soc. Fr. Mineral. Cristallogr.* **1968**, *91*, 10–12.

(12) Dines, M. B.; Digiacomo, P. *Inorg. Chem.* **1981**, *20*, 92–97.

(13) Ortiz-Avila, Y.; Rudolf, P. R.; Clearfield, A. *Inorg. Chem.*, in press.

(14) Frausto, R.; Martin, K. J.; Squattrito, P. J.; Clearfield, A. Unpublished results.

(15) *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Wiley: New York, 1971; Vol. III, Suppl. III, p 641 and references therein.

(16) Yvon, K.; Jeitschko, W.; Parthe, E. *J. Appl. Crystallogr.* **1977**, *10*, 73–74.

(17) MSC/AFC Diffractometer Control Software, Molecular Structure Corp.: The Woodlands, TX, 1988 (revised).

(18) "TEXSAN, Texray Structural Analysis Package"; Molecular Structure Corp.: The Woodlands, TX, 1987 (revised).

(19) Gilmore, G. J. "MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data"; University of Glasgow, Scotland, 1983.

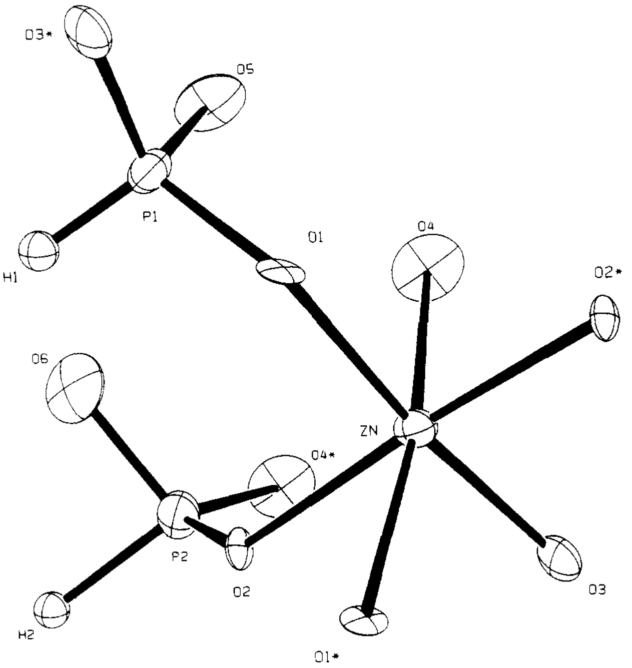

Figure 1. Octahedral coordination about zinc and the corner-sharing connectivity to the HPO_3 tetrahedra in $Zn(H_2PO_3)_2{\cdot}3H_2O$ are shown. Thermal ellipsoids in this and succeeding figures are drawn at the 50% probability level except as noted.

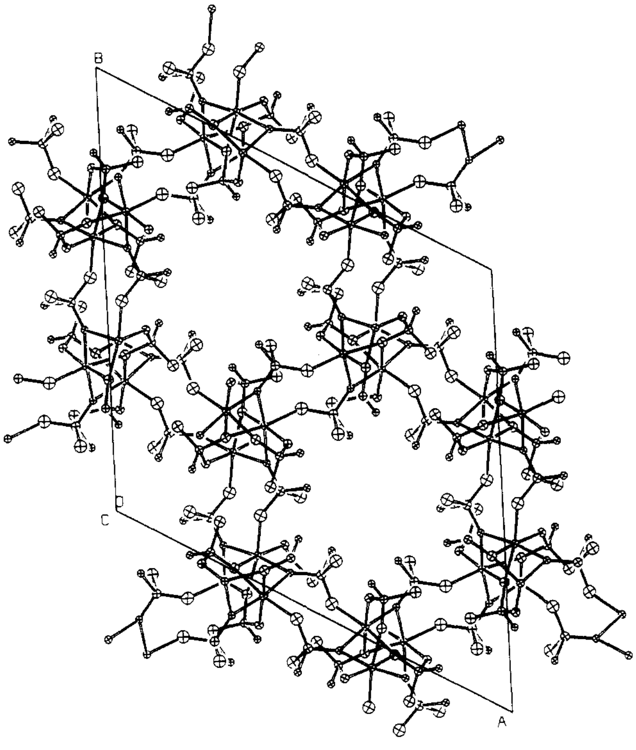

Figure 2. Extended view of the $Zn(H_2PO_3)_2{\cdot}3H_2O$ structure in the *a–b* plane. Atoms are shown with isotropic thermal parameters. Note the large channels running parallel to the *c* axis.

DIF).[20] Difference electron density maps revealed the location of at least some of the H atoms in each of the structures except $Zn_3Na_2(HPO_3)_4$. Final refinements for all the structures were performed on those data having $I > 3\sigma(I)$ and included anisotropic thermal parameters for all non-hydrogen atoms. Analyses of F_o versus F_c as a function of $(\sin\theta)/\lambda$, Miller indices, and F_o revealed no unusual trends. Final difference Fourier maps displayed no peaks with height greater than ca. 3% that of the heaviest atom in any of the structures except for $Zn(H_2PO_3)_2{\cdot}3H_2O$, in which several peaks of 2–3 e/Å^3 were located on special positions in the center of the large channels in the structure (see Figure 2). As the TGA data indicates water to be present in the structure, we attempted to refine some of these peaks as oxygen atoms, without success. These water molecules of hydration are probably disordered over a number of sites in the channels.

Table I. Crystallographic Data for New Zinc Phosphites

$Zn(H_2PO_3)_2{\cdot}3H_2O$	
$a = 21.128\ (2)$ Å	$T = 23$ °C
$c = 7.769\ (6)$ Å	$\lambda = 0.71069$ Å
$V = 3003\ (2)$ Å^3	$\rho_{calcd} = 2.80$ g·cm^{-3}
$Z = 18$	$\mu = 42.61$ cm^{-1}
fw = 281.40	$R(F_o) = 0.073$
space group: $R\bar{3}$ (No. 148)	$R_w(F_o) = 0.087$
$Zn_2(HPO_3)_2(H_2O)_4{\cdot}H_2O$	
$a = 7.670\ (2)$ Å	space group: $P\bar{1}$ (No. 2)
$b = 9.454\ (2)$ Å	$T = 23$ °C
$c = 7.554\ (1)$ Å	$\lambda = 0.71069$ Å
$\alpha = 90.83\ (1)$°	$\rho_{calcd} = 2.31$ g·cm^{-3}
$\beta = 92.90\ (1)$°	$\mu = 48.25$ cm^{-1}
$\gamma = 88.54\ (2)$°	transmn coeff = 0.674–1.0
$V = 546.9\ (2)$ Å^3	$R(F_o) = 0.022$
$Z = 2$	$R_w(F_o) = 0.033$
fw = 380.80	
$Zn_3Na_2(HPO_3)_4$	
$a = 8.331\ (2)$ Å	$T = 23$ °C
$b = 12.243\ (2)$ Å	$\lambda = 0.71069$ Å
$c = 12.669\ (1)$ Å	$\rho_{calcd} = 2.89$ g·cm^{-3}
$V = 1292.2\ (6)$ Å^3	$\mu = 62.75$ cm^{-1}
$Z = 4$	$R(F_o) = 0.038$
fw = 562.04	$R_w(F_o) = 0.049$
space group: *Pnma* (No. 62)	
$Zn_3K_2(HPO_3)_4$	
$a = 12.373\ (2)$ Å	$T = 23$ °C
$b = 13.635\ (2)$ Å	$\lambda = 0.71069$ Å
$c = 8.571\ (2)$ Å	$\rho_{calcd} = 2.73$ g·cm^{-3}
$\beta = 90.24\ (2)$°	$\mu = 61.28$ cm^{-1}
$V = 1445.9\ (4)$ Å^3	transmn coeff = 0.757–1.0
$Z = 4$	$R(F_o) = 0.037$
fw = 594.26	$R_w(F_o) = 0.045$
space group: $P2_1/c$ (No. 14)	
$Zn_3Ba(HPO_3)_4(H_2O)_6$	
$a = 22.707\ (2)$ Å	$T = 23$ °C
$b = 5.302\ (3)$ Å	$\lambda = 0.71069$ Å
$c = 15.029\ (1)$ Å	$\rho_{calcd} = 2.90$ g·cm^{-3}
$\beta = 105.278\ (6)$°	$\mu = 68.53$ cm^{-1}
$V = 1745\ (1)$ Å^3	transmn coeff = 0.832–1.0
$Z = 4$	$R(F_o) = 0.054$
fw = 761.48	$R_w(F_o) = 0.044$
space group: *C*2/*c* (No. 15)	

Details of the X-ray experiments and crystal data for the five compounds are summarized in Table I. Final positional and equivalent isotropic thermal parameters are contained in Table II, while selected bond distances and angles appear in Table III. Tables of crystallographic details and anisotropic thermal parameters (Table SI) and structure amplitudes ($10F_o$ vs $10F_c$) (Table SII) are provided as supplementary material.

Results and Discussion

$Zn(H_2PO_3)_2{\cdot}3H_2O$. The structure is shown in Figures 1 and 2. Each Zn atom is octahedrally coordinated to oxygen atoms from six different phosphite groups. The Zn–O distances, ranging from 2.03 (1) to 2.16 (1) Å, are similar to those observed for Zn in an octahedral environment in Zn phosphates.[21-23] The bond angles show the octahedron to be fairly regular, but with some distortions. The two independent phosphite groups have regular

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(20) Beurskens, P. T. "DIRDIF: Direct Methods for Difference Structures – An Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors"; Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, The Netherlands.

(21) Whitaker, A. *Acta Crystallogr., Sect. B* **1975**, *31*, 2026–2035.

(22) Averbuch-Pouchot, M. T.; Guitel, J. C. *Acta Crystallogr., Sect. B* **1977**, *33*, 1427–1431.

(23) Seethanen, D.; Durif, A.; Averbuch-Pouchot, M. T. *Acta Crystallogr., Sect. B* **1978**, *34*, 14–17.

Table II. Final Positional and Equivalent Isotropic Thermal Parameters

atom	*x*	*y*	*z*	B_{eq}, Å^2	atom	*x*	*y*	*z*	B_{eq}, Å^2
$Zn(H_2PO_3)_2 \cdot 3H_2O$									
Zn	0.3585 (1)	0.0615 (1)	0.7250 (3)	1.12 (7)	O(4)	0.3722 (8)	0.1590 (7)	0.833 (2)	2.4 (6)
P(1)	0.2380 (3)	0.0153 (3)	1.0256 (8)	1.3 (2)	O(5)	0.2661 (8)	0.0972 (7)	1.052 (2)	2.3 (6)
P(2)	0.2401 (3)	0.0942 (3)	0.5270 (8)	1.6 (2)	O(6)	0.1893 (8)	0.0838 (7)	0.682 (2)	2.8 (7)
O(1)	0.2966 (7)	0.0054 (7)	0.937 (2)	1.3 (5)	H(1)	0.1844	−0.0164	0.9430	4.0
O(2)	0.2721 (6)	0.0472 (6)	0.553 (2)	0.8 (5)	H(2)	0.1714	0.0555	0.4114	4.0
O(3)	0.4299 (7)	0.1187 (6)	0.534 (2)	1.1 (5)					
$Zn_2(HPO_3)_2(H_2O)_4 \cdot H_2O$									
Zn(1)	0	0	0	1.59 (3)	O(10)	0.2619 (3)	0.4540 (3)	−0.5972 (4)	2.5 (1)
Zn(2)	0.00150 (5)	0.24999 (4)	−0.49864 (5)	1.35 (2)	O(11)	0.4939 (5)	0.2581 (4)	−0.0135 (5)	4.2 (2)
Zn(3)	$^1/_2$	$^1/_2$	$-^1/_2$	1.51 (3)	H(1)	0.168 (4)	0.474 (4)	−0.886 (4)	1.4
P(1)	0.2216 (1)	0.00917 (8)	−0.3687 (1)	1.20 (4)	H(2)	0.379 (4)	0.003 (4)	−0.290 (4)	1.4
P(2)	0.1137 (1)	0.48565 (9)	−0.7267 (1)	1.17 (3)	H(3)	0.244 (6)	0.091 (5)	0.234 (7)	3.6
O(1)	0.2383 (4)	0.0772 (4)	0.1282 (4)	3.2 (1)	H(4)	0.312 (6)	0.122 (5)	0.064 (6)	3.6
O(2)	0.0860 (3)	0.0387 (3)	−0.2369 (3)	2.4 (1)	H(5)	−0.082 (5)	0.241 (5)	−0.081 (6)	2.5
O(3)	−0.1210 (4)	0.2054 (3)	−0.0028 (4)	2.1 (1)	H(6)	−0.077 (5)	0.258 (4)	0.092 (6)	2.5
O(4)	−0.0269 (3)	0.3730 (2)	−0.7118 (3)	1.4 (1)	H(7)	0.566 (5)	0.390 (4)	−0.823 (6)	3.1
O(5)	0.2175 (3)	0.1317 (2)	−0.5024 (3)	1.4 (1)	H(8)	0.709 (6)	0.450 (5)	−0.732 (6)	3.1
O(6)	−0.0362 (3)	0.3652 (2)	−0.2871 (3)	1.7 (1)	H(9)	0.434 (6)	0.246 (4)	−0.466 (5)	2.5
O(7)	0.2059 (3)	−0.1350 (2)	−0.4605 (3)	1.8 (1)	H(10)	0.602 (5)	0.238 (5)	−0.460 (6)	2.5
O(8)	0.6138 (4)	0.4598 (3)	−0.7529 (4)	2.6 (1)	H(11)	0.477 (7)	0.323 (6)	−0.082 (7)	5.0
O(9)	0.5196 (4)	0.2867 (3)	−0.4167 (4)	2.0 (1)	H(12)	0.562 (7)	0.204 (6)	−0.031 (8)	5.0
$Zn_3Na_2(HPO_3)_4$									
Zn(1)	0.9227 (2)	$^1/_4$	0.5665 (1)	1.19 (7)	O(2)	1.083 (1)	$^1/_4$	0.4550 (8)	2.9 (5)
Zn(2)	0.5867 (1)	0.4303 (1)	0.33775 (9)	1.48 (5)	O(3)	0.709 (2)	$^1/_4$	0.522 (1)	5.0 (8)
P(1)	0.5327 (4)	$^1/_4$	0.5062 (3)	1.3 (2)	O(4)	0.4093 (8)	0.5282 (6)	0.2987 (5)	1.7 (3)
P(2)	1.0605 (5)	$^1/_4$	0.3363 (3)	1.3 (2)	O(5)	0.4778 (9)	0.3539 (6)	0.4508 (6)	2.2 (3)
P(3)	1.1201 (3)	0.0773 (2)	0.6914 (2)	1.4 (1)	O(6)	0.7806 (8)	0.5047 (6)	0.3819 (5)	2.1 (3)
Na(1)	0.7715 (5)	−0.0357 (4)	0.5679 (3)	2.5 (2)	O(7)	1.133 (1)	0.3524 (6)	0.2907 (6)	2.3 (3)
O(1)	0.9661 (9)	0.1121 (6)	0.6379 (6)	2.2 (3)					
$Zn_3K_2(HPO_3)_4$									
Zn(1)	0.75089 (8)	0.43576 (8)	0.5592 (1)	1.27 (4)	O(5)	0.6431 (5)	0.5563 (5)	0.9502 (8)	2.5 (3)
Zn(2)	0.57359 (9)	0.67656 (8)	0.8827 (1)	1.68 (5)	O(6)	0.5304 (5)	0.2026 (5)	0.4533 (7)	1.9 (3)
Zn(3)	1.07447 (9)	0.18308 (8)	0.5869 (1)	1.63 (5)	O(7)	0.5038 (6)	0.3617 (5)	0.3036 (7)	2.5 (3)
K(1)	1.0198 (2)	0.4469 (2)	0.7385 (3)	2.2 (1)	O(8)	0.6511 (5)	0.7052 (5)	0.3517 (8)	2.3 (3)
K(2)	0.4734 (2)	0.4456 (2)	0.7547 (2)	2.2 (1)	O(9)	0.8520 (5)	0.6932 (5)	0.3817 (9)	2.6 (3)
P(1)	0.5795 (2)	0.2991 (2)	0.4040 (3)	1.6 (1)	O(10)	0.8453 (5)	0.5719 (5)	0.9919 (7)	2.4 (3)
P(2)	0.7535 (2)	0.5096 (2)	0.9315 (3)	1.3 (1)	O(11)	0.9998 (6)	0.3596 (5)	0.2725 (8)	2.5 (3)
P(3)	0.9214 (2)	0.3030 (2)	0.3722 (3)	1.5 (1)	O(12)	0.9649 (5)	0.2051 (5)	0.4288 (7)	2.1 (3)
P(4)	0.7454 (2)	0.6565 (2)	0.4369 (3)	1.5 (1)	H(1)	0.654 (7)	0.271 (7)	0.31 (1)	1 (2)
O(1)	0.7397 (5)	0.5456 (4)	0.4155 (8)	2.3 (3)	H(2)	0.767 (7)	0.429 (7)	1.03 (1)	3 (2)
O(2)	0.8826 (5)	0.3680 (5)	0.5052 (8)	2.5 (3)	H(3)	0.815 (7)	0.280 (7)	0.27 (1)	2 (2)
O(3)	0.6204 (5)	0.3581 (5)	0.5422 (7)	1.9 (3)	H(4)	0.729 (8)	0.680 (7)	0.56 (1)	4 (3)
O(4)	0.7766 (6)	0.4763 (6)	0.7676 (8)	3.2 (4)					
$Zn_3Ba(HPO_3)_4(H_2O)_6$									
Ba	$^1/_2$	0.0122 (1)	$^3/_4$	1.25 (2)	O(7)	0.6935 (2)	−0.551 (1)	0.4154 (3)	2.1 (2)
Zn(1)	$^1/_2$	0	$^1/_2$	1.19 (4)	O(8)	0.7476 (2)	−0.3251 (9)	0.6219 (3)	2.1 (2)
Zn(2)	0.69196 (3)	−0.5542 (1)	0.54345 (5)	1.33 (3)	O(9)	0.6976 (2)	−0.897 (1)	0.5923 (4)	2.3 (2)
P(1)	0.57134 (7)	−0.4984 (3)	0.6038 (1)	0.85 (5)	H(1)	0.615 (3)	−0.48 (1)	0.679 (4)	1.0
P(2)	0.74318 (7)	−0.4581 (3)	0.3719 (1)	1.18 (6)	H(2)	0.726 (3)	−0.52 (1)	0.287 (4)	1.4
O(1)	0.4203 (2)	0.0240 (9)	0.5528 (3)	1.7 (2)	H(3)	0.398 (4)	0.13 (2)	0.532 (5)	2.7
O(2)	0.5304 (2)	−0.2726 (8)	0.5998 (3)	1.3 (2)	H(5)	0.594 (4)	−0.46 (1)	0.841 (5)	2.3
O(3)	0.5385 (2)	0.2548 (8)	0.6036 (3)	1.7 (2)	H(6)	0.545 (3)	−0.48 (1)	0.867 (5)	2.3
O(4)	0.5609 (2)	−0.484 (1)	0.8172 (3)	2.0 (2)	H(7)	0.656 (4)	0.01 (2)	0.802 (6)	3.2
O(5)	0.6299 (3)	−0.006 (1)	0.7634 (4)	2.8 (2)	H(8)	0.637 (4)	0.07 (2)	0.722 (6)	3.2
O(6)	0.6054 (2)	−0.4855 (9)	0.5272 (3)	1.6 (2)					

tetrahedral geometries, as the metrical data in Table III indicate. The H atoms bound directly to the P atoms were located on a difference electron density map; however, their positions were not refined. The remaining two protons could not be located, but are presumed to reside on the terminal oxygen atoms O(5) and O(6). Thus the compound contains, formally, Zn^{2+} ions and the conjugate anion of phosphorous acid, $H_2PO_3^-$. The structure is built of ZnO_6 octahedra linked to $HPO_2(OH)$ tetrahedra via shared corners. The octahedra share edges to form infinite helical chains along the *c* axis. These chains are connected in the *a*–*b* plane by bridging phosphite groups to form the unusual repeat pattern shown in Figure 2. The remarkable aspect of the structure is that the connectivity is such as to create large circular cavities running parallel to *c*. These voids are essentially infinite tunnels of constant diameter (ca. 6 Å) running throughout the structure. The cavities are lined by the terminal –OH and –H groups of the phosphite anions. As mentioned earlier, TGA data on a bulk sample indicates that the compound contains approximately 3 mol of H_2O/mol of Zn. Though we could not locate any water molecules in the X-ray structure, it is highly likely that such molecules are present in the channels, hydrogen-bonded to the terminal P–OH groups. We believe that given the size of the channels and the large number of hydrogen bonding sites in them, the water molecules are disordered to the point that their individual contributions to the diffraction intensities are minimal.

As the cavities are lined with acidic protons (P–O*H*), the compound appeared to have potential as an ion-exchange material. This potential is diminished somewhat by the fact that the compound is highly soluble in water and is unstable with respect to thermal dehydration. (Efforts to remove the water by heating a bulk sample at 100 °C gave a product whose X-ray powder pattern was radically different from that of the hydrated starting

Table III. Selected Bond Distances (Å) and Angles (deg)

$Zn(H_2PO_3)_2{\cdot}3H_2O$							
Zn–O(3)	2.03 (1)	Zn–O(2)	2.16 (1)	P(1)–O(1)	1.52 (1)	P(2)–O(2)	1.47 (1)
Zn–O(1)	2.07 (1)	Zn–O(2)	2.16 (1)	P(1)–O(3)	1.52 (1)	P(2)–O(4)	1.51 (1)
Zn–O(4)	2.11 (1)	Zn–O(1)	2.16 (1)	P(1)–O(5)	1.54 (1)	P(2)–O(6)	1.56 (2)
O(1)–Zn–O(1)	89.0 (2)	O(2)–Zn–O(1)	94.6 (5)	O(3)–Zn–O(1)	92.3 (5)	O(1)–P(1)–O(5)	109.5 (8)
O(4)–Zn–O(2)	94.4 (6)	O(3)–Zn–O(1)	173.0 (5)	O(1)–Zn–O(4)	88.9 (6)	O(3)–P(1)–O(5)	107.8 (8)
O(4)–Zn–O(2)	93.3 (6)	O(3)–Zn–O(4)	90.8 (6)	O(1)–Zn–O(2)	99.5 (5)	O(2)–P(2)–O(4)	115.3 (8)
O(4)–Zn–O(1)	171.3 (5)	O(3)–Zn–O(2)	87.4 (5)	O(1)–Zn–O(2)	79.6 (5)	O(2)–P(2)–O(6)	108 (1)
O(2)–Zn–O(2)	172.2 (4)	O(3)–Zn–O(2)	93.5 (5)	O(1)–P(1)–O(3)	114.0 (8)	O(4)–P(2)–O(6)	110.5 (9)
O(2)–Zn–O(1)	77.6 (5)						
$Zn_2(HPO_3)_2(H_2O)_4{\cdot}H_2O$							
Zn(1)–O(1)	2.164 (3)	Zn(2)–O(5)	1.976 (2)	P(1)–H(2)	1.32 (3)	P(2)–H(1)	1.30 (3)
Zn(1)–O(2)	1.980 (3)	Zn(2)–O(4)	2.000 (2)	P(1)–O(2)	1.495 (3)	P(2)–O(10)	1.489 (3)
Zn(1)–O(3)	2.131 (3)	Zn(3)–O(8)	2.165 (3)	P(1)–O(7)	1.525 (2)	P(2)–O(6)	1.520 (2)
Zn(2)–O(6)	1.950 (2)	Zn(3)–O(9)	2.121 (3)	P(1)–O(5)	1.546 (2)	P(2)–O(4)	1.544 (2)
Zn(2)–O(7)	1.959 (2)	Zn(3)–O(10)	1.990 (3)				
O(1)–Zn(1)–O(1)	180.00	O(6)–Zn(2)–O(4)	108.9 (1)	O(9)–Zn(3)–O(8)	95.2 (1)	O(7)–P(1)–O(5)	112.2 (1)
O(2)–Zn(1)–O(1)	91.1 (1)	O(7)–Zn(2)–O(5)	111.1 (1)	O(10)–Zn(3)–O(9)	86.2 (1)	H(1)–P(2)–O(10)	109 (1)
O(3)–Zn(1)–O(3)	180.00	O(7)–Zn(2)–O(4)	99.0 (1)	H(2)–P(1)–O(2)	111 (1)	H(1)–P(2)–O(6)	105 (1)
O(3)–Zn(1)–O(1)	92.6 (1)	O(5)–Zn(2)–O(4)	111.6 (1)	H(2)–P(1)–O(7)	103 (1)	H(1)–P(2)–O(4)	106 (1)
O(2)–Zn(1)–O(2)	180.00	O(8)–Zn(3)–O(8)	180.00	H(2)–P(1)–O(5)	108 (1)	O(10)–P(2)–O(6)	114.7 (2)
O(2)–Zn(1)–O(3)	88.3 (1)	O(10)–Zn(3)–O(8)	92.4 (1)	O(2)–P(1)–O(7)	113.8 (2)	O(10)–P(2)–O(4)	109.2 (1)
O(6)–Zn(2)–O(7)	106.7 (1)	O(10)–Zn(3)–O(10)	180.00	O(2)–P(1)–O(5)	108.8 (1)	O(6)–P(2)–O(4)	111.6 (1)
O(6)–Zn(2)–O(5)	117.8 (1)	O(9)–Zn(3)–O(9)	180.00				
$Zn_3Na_2(HPO_3)_4$							
Zn(1)–O(3)	1.86 (1)	Zn(2)–O(6)	1.937 (7)	P(2)–O(2)	1.52 (1)	Na(1)–O(7)	2.391 (8)
Zn(1)–O(2)	1.95 (1)	Zn(2)–O(4)	1.966 (7)	P(3)–O(4)	1.507 (7)	Na(1)–O(4)	2.395 (8)
Zn(1)–O(1)	1.949 (7)	P(1)–O(3)	1.49 (1)	P(3)–O(1)	1.512 (7)	Na(1)–O(5)	2.489 (8)
Zn(2)–O(7)	1.926 (7)	P(1)–O(5)	1.523 (7)	P(3)–O(6)	1.529 (7)	Na(1)–O(1)	2.587 (9)
Zn(2)–O(5)	1.936 (7)	P(2)–O(7)	1.507 (7)	Na(1)–O(6)	2.389 (8)	Na(1)–O(2)	2.904 (7)
O(3)–Zn(1)–O(2)	116.0 (6)	O(7)–Zn(2)–O(6)	108.0 (3)	O(6)–Zn(2)–O(4)	114.4 (3)	O(7)–P(2)–O(2)	109.3 (4)
O(3)–Zn(1)–O(1)	108.4 (3)	O(7)–Zn(2)–O(4)	103.9 (3)	O(3)–P(1)–O(5)	111.2 (4)	O(4)–P(3)–O(1)	112.3 (4)
O(2)–Zn(1)–O(1)	102.1 (3)	O(5)–Zn(2)–O(6)	113.9 (3)	O(5)–P(1)–O(5)	113.3 (6)	O(4)–P(3)–O(6)	113.8 (4)
O(1)–Zn(1)–O(1)	120.0 (4)	O(5)–Zn(2)–O(4)	97.4 (3)	O(7)–P(2)–O(7)	112.5 (7)	O(1)–P(3)–O(6)	110.5 (4)
O(7)–Zn(2)–O(5)	118.7 (3)						
$Zn_3K_2(HPO_3)_4$							
Zn(1)–O(4)	1.896 (7)	Zn(3)–O(10)	1.935 (6)	P(3)–O(2)	1.522 (7)	K(1)–O(4)	3.047 (7)
Zn(1)–O(2)	1.932 (6)	Zn(3)–O(12)	1.936 (6)	P(4)–O(9)	1.490 (7)	K(1)–O(1)	3.262 (7)
Zn(1)–O(3)	1.935 (6)	P(1)–O(6)	1.510 (7)	P(4)–O(1)	1.524 (6)	K(2)–O(7)	2.690 (7)
Zn(1)–O(1)	1.944 (6)	P(1)–O(3)	1.518 (6)	P(4)–O(8)	1.526 (7)	K(2)–O(8)	2.724 (7)
Zn(2)–O(8)	1.896 (6)	P(1)–O(7)	1.529 (7)	K(1)–O(11)	2.652 (8)	K(2)–O(6)	2.733 (7)
Zn(2)–O(7)	1.931 (6)	P(2)–O(4)	1.504 (7)	K(1)–O(9)	2.691 (7)	K(2)–O(3)	2.841 (7)
Zn(2)–O(5)	1.939 (7)	P(2)–O(10)	1.508 (7)	K(1)–O(12)	2.725 (7)	K(2)–O(5)	2.918 (7)
Zn(2)–O(6)	1.942 (6)	P(2)–O(5)	1.516 (7)	K(1)–O(2)	2.830 (7)	K(2)–O(1)	3.011 (7)
Zn(3)–O(11)	1.932 (7)	P(3)–O(11)	1.508 (7)	K(1)–O(10)	2.857 (7)	K(2)–O(5)	3.077 (7)
Zn(3)–O(9)	1.934 (7)	P(3)–O(12)	1.519 (7)				
O(4)–Zn(1)–O(2)	103.1 (3)	O(8)–Zn(2)–O(6)	106.4 (3)	O(9)–Zn(3)–O(12)	106.8 (3)	O(10)–P(2)–O(5)	113.9 (4)
O(4)–Zn(1)–O(3)	111.5 (3)	O(7)–Zn(2)–O(5)	103.7 (3)	O(10)–Zn(3)–O(12)	103.6 (3)	O(11)–P(3)–O(12)	113.7 (4)
O(4)–Zn(1)–O(1)	112.6 (3)	O(7)–Zn(2)–O(6)	108.7 (3)	O(6)–P(1)–O(3)	112.1 (4)	O(11)–P(3)–O(2)	109.4 (4)
O(2)–Zn(1)–O(3)	115.1 (3)	O(5)–Zn(2)–O(6)	103.5 (3)	O(6)–P(1)–O(7)	113.5 (4)	O(12)–P(3)–O(2)	112.6 (4)
O(2)–Zn(1)–O(1)	105.9 (3)	O(11)–Zn(3)–O(9)	112.0 (3)	O(3)–P(1)–O(7)	110.2 (4)	O(9)–P(4)–O(1)	109.7 (4)
O(3)–Zn(1)–O(1)	108.4 (3)	O(11)–Zn(3)–O(10)	107.4 (3)	O(4)–P(2)–O(10)	110.2 (4)	O(9)–P(4)–O(8)	112.2 (4)
O(8)–Zn(2)–O(7)	111.3 (3)	O(11)–Zn(3)–O(12)	106.7 (3)	O(4)–P(2)–O(5)	113.6 (4)	O(1)–P(4)–O(8)	109.8 (4)
O(8)–Zn(2)–O(5)	122.5 (3)	O(9)–Zn(3)–O(10)	119.3 (3)				
$Zn_3Ba(HPO_3)_4(H_2O)_6$							
Zn(1)–O(2)	2.067 (4)	Zn(2)–O(6)	1.950 (4)	P(2)–O(8)	1.516 (5)	Ba–O(2)	2.945 (4)
Zn(1)–O(3)	2.073 (4)	Zn(2)–O(9)	1.953 (5)	P(2)–O(9)	1.519 (5)	Ba–O(4)	3.021 (5)
Zn(1)–O(1)	2.163 (5)	P(1)–O(3)	1.506 (5)	P(2)–O(7)	1.526 (5)	Ba–O(1)	3.039 (5)
Zn(2)–O(8)	1.918 (5)	P(1)–O(2)	1.507 (4)	Ba–O(3)	2.876 (4)	Ba–O(4)	3.053 (6)
Zn(2)–O(7)	1.935 (5)	P(1)–O(6)	1.548 (4)	Ba–O(5)	2.905 (6)		
O(2)–Zn(1)–O(2)	180.00	O(1)–Zn(1)–O(1)	180.00	O(7)–Zn(2)–O(9)	111.5 (2)	O(2)–P(1)–O(6)	111.0 (2)
O(2)–Zn(1)–O(3)	85.2 (2)	O(8)–Zn(2)–O(7)	115.0 (2)	O(6)–Zn(2)–O(9)	100.6 (2)	O(8)–P(2)–O(9)	112.6 (3)
O(2)–Zn(1)–O(1)	85.8 (2)	O(8)–Zn(2)–O(6)	116.0 (2)	O(3)–P(1)–O(2)	113.0 (3)	O(8)–P(2)–O(7)	113.4 (3)
O(3)–Zn(1)–O(3)	180.00	O(8)–Zn(2)–O(9)	113.1 (2)	O(3)–P(1)–O(6)	112.4 (3)	O(9)–P(2)–O(7)	111.8 (3)
O(3)–Zn(1)–O(1)	85.1 (2)	O(7)–Zn(2)–O(6)	99.0 (2)				

material, indicating significant changes in the framework structure on heating. The identity of the dehydrated phase(s) is as yet unknown. To try to get around the solubility problem, we attempted an ion-exchange reaction in the absence of water. This experiment, described in the Experimental Section under the synthesis of $Zn_3Na_2(HPO_3)_4$, involved reacting an ethanolic solution of NaOH with $Zn(H_2PO_3)_2{\cdot}3H_2O$ suspended in absolute ethanol. Although the solid appeared not to dissolve, clearly dissociation did occur, as the product of the reaction, $Zn_3Na_2(HPO_3)_4$, bears no structural resemblance to $Zn(H_2PO_3)_2{\cdot}3H_2O$ (cf Figures 2 and 4). Therefore, it cannot be considered to have resulted from a simple ion-exchange reaction.

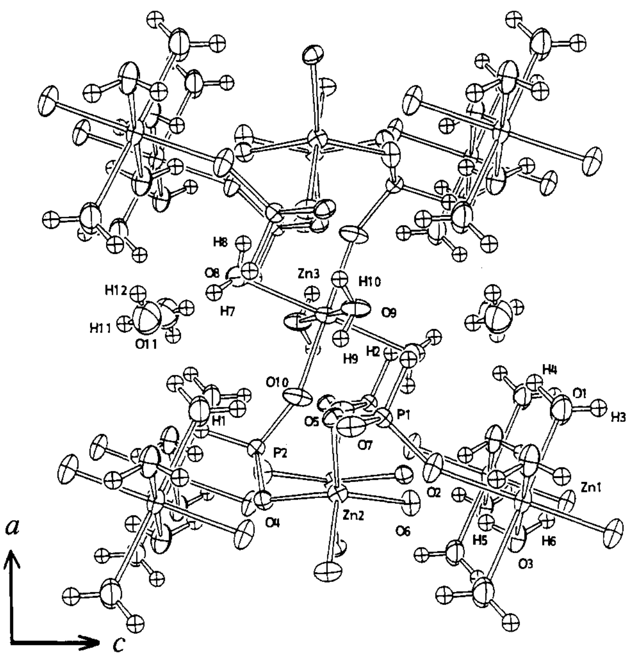

Figure 3. Perspective view of the $Zn_2(HPO_3)_2(H_2O)_4{\cdot}H_2O$ structure along the *b* axis.

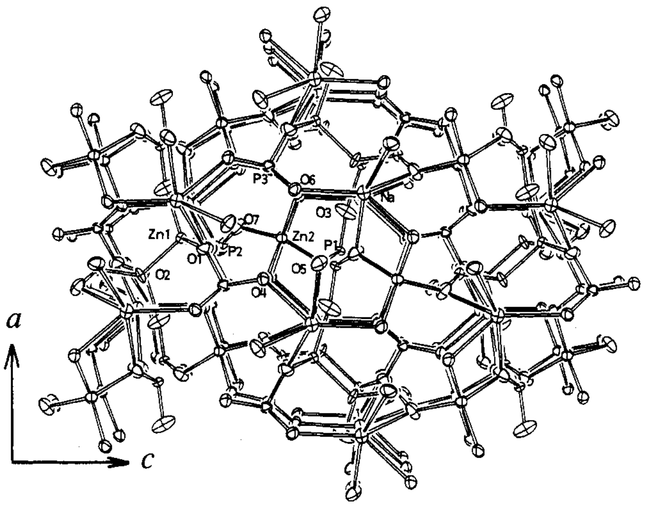

Figure 4. Perspective view of the $Zn_3Na_2(HPO_3)_4$ structure along the *b* axis.

We are currently seeking to exploit the acid–base chemistry of the channels via intercalation reactions of organic bases in nonaqueous solvents. The results of this work will be described in a subsequent report.

$Zn_2(HPO_3)_2(H_2O)_4{\cdot}H_2O$. This compound resulted from an attempt to prepare $Zn(H_2PO_3)_2{\cdot}3H_2O$ directly from ZnO and H_3PO_3. The structure is shown in Figure 3. There are three crystallographically independent Zn atoms. Zn(1) and Zn(3) are octahedrally coordinated to two phosphite oxygen atoms and four water molecules, while the Zn(2) atom is tetrahedrally bonded to four phosphite oxygen atoms. The positions of all the hydrogen atoms were determined from difference electron density maps and included in the refinement. The metrical data in Table III show the Zn coordination polyhedra to be quite regular. Simultaneous occurrence of octahedral and tetrahedral Zn has precedence in phosphate chemistry. Two examples are hopeite, $Zn_3(PO_4)_2{\cdot}4H_2O$,[21] and $NaZn_2P_3O_{10}{\cdot}9H_2O$.[22] Octahedra of the type $ZnO_2(H_2O)_4$ occur in hopeite and in the phase $K_4Zn(P_3O_9)_2{\cdot}4H_2O$.[23] The structural details of the octahedral Zn coordination in the present compound parallel those in the phosphates. Namely, Zn–O(water) bonds are significantly longer than Zn–O(phosphate or phosphite) bonds (2.12–2.17 vs 1.98–2.05 Å). Our reported tetrahedral Zn–O bond distances are similar to previously reported values.[21,22,24] The tetrahedral geometries of the phosphite groups are also generally regular. In each case, the P–O bond involving the oxygen bonded to the octahedral Zn atom is distinctly shorter than those of the oxygens bridging the tetrahedral Zn atom.

The Zn polyhedra are linked by bridging phosphite groups so as to produce channels running parallel to the chains of polyhedra along the *b* axis. These channels contain water molecules of crystallization (atom O(11)) that are probably weakly hydrogen bonded to the coordinated water molecules that line the channel. Two H atoms (H(7) and H(4)) occupy the third and fourth tetrahedral bonding sites of atom O(11), though the distances (O···H) are rather long (1.96 (5) and 2.04 (5) Å). The thermal weight loss curve (TGA) fails to distinguish between coordinated and uncoordinated water, showing a continuous loss of 5 mol of H_2O between 60 and 200 °C. However, we have done so in the chemical formula, $Zn_2(HPO_3)_2(H_2O)_4{\cdot}H_2O$, based upon the X-ray results. An interesting aspect of the structure is that while the symmetry is low (triclinic, $P\bar{1}$) for an inorganic material, the unit cell is very close to tetragonal and the Zn atoms are all either on or close to special positions, giving the appearance of higher symmetry. This compound is insoluble in water and appears to be a dominant phase in the Zn–phosphite system as it is the one usually isolated from mixtures of $ZnCl_2$ and H_3PO_3 under a variety of conditions.

$Zn_3Na_2(HPO_3)_4$. This compound was first prepared as the result of an attempt to substitute Na^+ for H^+ in $Zn(H_2PO_3)_2{\cdot}3H_2O$. The structure, shown in Figure 4 along the *b* axis, is completely unrelated to that of the initial zinc hydrogen phosphite (Figure 2). The Zn atoms are in tetrahedral environments of phosphite oxygens. Each phosphite group bridges three Zn atoms. The framework is completed by the sodium ions, which sit in an irregular coordination site, interacting with six different oxygen atoms at distances ranging from 2.389 (8) to 2.904 (7) Å. Thus, the Na^+ ions serve to bridge all the ZnO_4 and HPO_3 tetrahedra in the structure. The resulting framework can be viewed as consisting, in part, of a series of three fused eight-membered rings, one containing atoms O(4)–Zn(2)–O(6)–Na–O(4)–Zn(2)–O(6)–Na, the second, O(4)–Zn(2)–O(6)–P(3)–O(4)–Na–O(1)–P(3), and the third, Na–O(6)–P(3)–O(1)–Na–O(6)–P(3)–O(1). This rather compact framework is propagated mainly in the *a–c* plane and is repeated in infinite columns of atoms along *b*. Six of the seven independent oxygen atoms interact with the Na^+ ion and so are triply bridging. The remaining oxygen, O(3), is ca. 3.58 Å from the sodium and bridges only Zn(1) and P(1). Though O(3) is far from Na in the structure, it is not really out of harm's way, as it sits almost directly below the sodium along *b*. For a Na^+ ion to move in a direct line along *b*, it would have to pass within 0.80 Å of O(3). Since this close an encounter is unreasonable, O(3) represents a barrier to motion of the Na^+ ions either for exchange or conduction. At best, it would require a major detour, and since O(1) is only ca. 2.50 Å away from the site of the bottleneck, no such pathway may exist for the sodium ion. The sodium ion is an integral part of the framework, and hence, the framework does not allow the sodium ion to move. Thus, this material is not like the NASICONs, in which Na^+ ions move freely through channels in a transition-metal silicophosphate lattice.[25,26]

$Zn_3K_2(HPO_3)_4$. Since the structure of the sodium phase was completely different from that of the parent zinc phosphite, it was of interest to determine whether other alkali metals would yield isostructural phases. The potassium compound was found to have the same formula but a different structure (Figures 5 and 6). As in $Zn_3Na_2(HPO_3)_4$, the structure is built of corner-sharing ZnO_4 and HPO_3 tetrahedra bridged by K^+ ions. However, the nature of the framework is altered by the coordination of the potassium ion. The two independent K^+ ions are in 7-fold coordination sites

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(24) Averbuch-Pouchot, M. T.; Durif, A. *Acta Crystallogr., Sect. B* **1978**, *35*, 151–152.

(25) Goodenough, J. B.; Hong, H. Y.-P.; Kafalas, J. A. *Mater. Res. Bull.* **1976**, *11*, 203–220.

(26) Hong, H. Y.-P. *Mater. Res. Bull.* **1976**, *11*, 173–182.

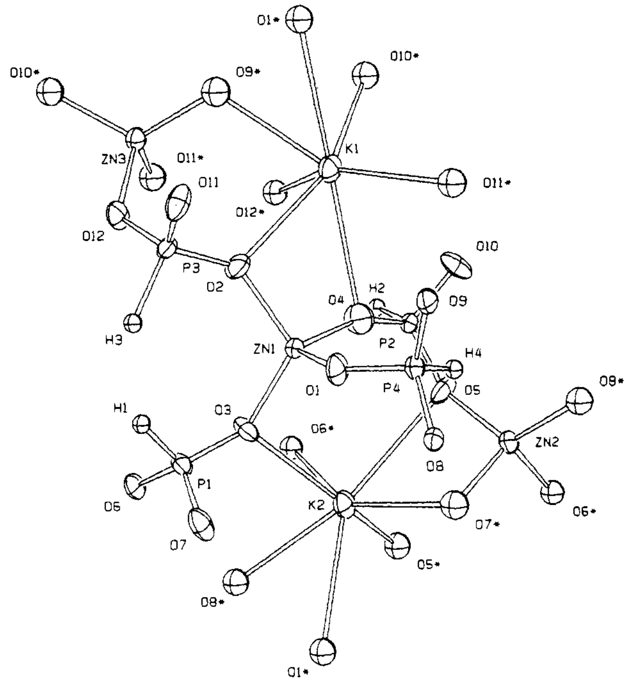

Figure 5. Coordination environments about zinc and potassium and the connectivities to the HPO_3 tetrahedra in $Zn_3K_2(HPO_3)_4$.

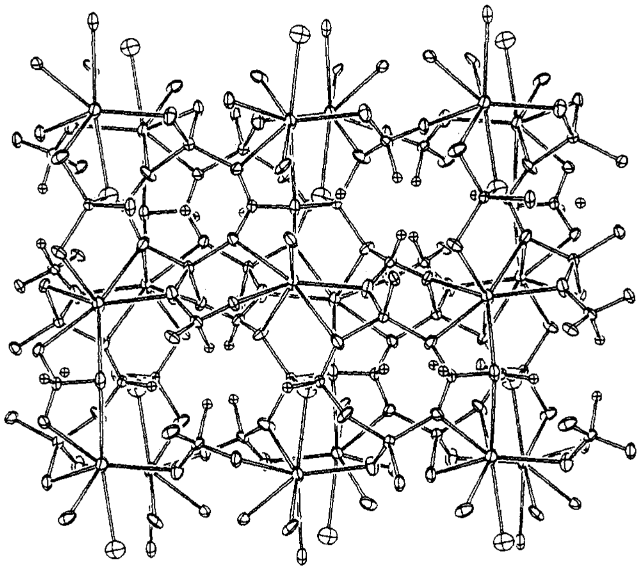

Figure 6. Extended view of the $Zn_3K_2(HPO_3)_4$ structure. Note the cavities lined by the phosphite hydrogen atoms.

with K–O distances in the range 2.652 (8)–3.262 (7) Å for K(1) and 2.690 (7)–3.077 (7) Å for K(2). These distances are significantly longer than the Na–O distances (2.389 (8)–2.904 (7) Å) in $Zn_3Na_2(HPO_3)_4$, as we would expect from the differences in ionic radii of K^+ (1.33 Å) and Na^+ (0.97 Å).[27] The K^+ ion is too large to fit in the site occupied by Na^+ in $Zn_3Na_2(HPO_3)_4$, and as a result, the K^+ bridges the ZnO_4 and HPO_3 tetrahedra in a different manner than does Na^+. The resulting framework (Figure 6) is more open than that in the sodium compound. In particular, there are tunnels bounded by 8-membered rings containing two Zn, two P, and four O atoms that run approximately parallel to the *c* axis. These channels are lined by the phosphite hydrogen atoms.

This result further supports the notion that the alkali metal is the critical element about which the Zn^{2+} and $HPO_3{}^{2-}$ ions coalesce to form the observed structure.

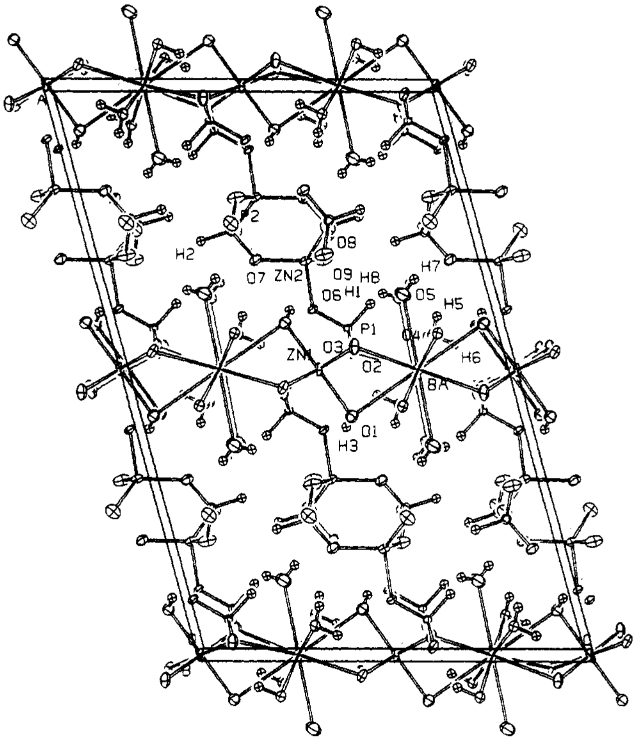

Figure 7. Extended view of the $Zn_3Ba(HPO_3)_4(H_2O)_6$ structure in the *a–c* plane.

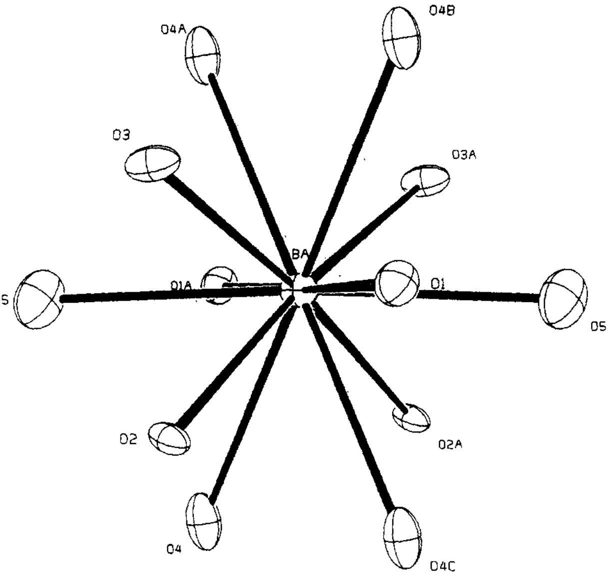

Figure 8. The 12-fold coordination about barium in $Zn_3Ba(HPO_3)_4(H_2O)_6$. The "A" and "B" designations denote symmetry-equivalent atoms. The coordination sphere comprises four phosphite oxygen atoms (O(2) and O(3)) and eight water molecules (O(1), O(4), and O(5)).

$Zn_3Ba(HPO_3)_4(H_2O)_6$. Prompted by the results for sodium and potassium, we turned to the divalent alkaline-earth metals and prepared the barium zinc phosphite shown in Figure 7. In this structure, the Zn occurs in both octahedral and tetrahedral coordination. The octahedral Zn is of the type $ZnO_4(H_2O)_2$, which is also seen in the phosphate $Zn_2NaP_3O_{10}\cdot 9H_2O$.[22] The metrical data for the Zn coordination geometries are similar to reported values for Zn phosphates.[21-24] The Ba^{2+} ions are in 12-fold coordination with interactions to four phosphite oxygens and eight water molecules at distances ranging from 2.876 (4) to 3.053 (6) Å (Figure 8). The Ba^{2+} ions bridge the Zn(1) octahedron and P(1) tetrahedron, not interacting directly at all with the Zn(2) and P(2) tetrahedra. As a result, this structure is more open than the Na^+ and K^+ structures. In fact, it has strong aspects of a two-dimensional layer-type structure. Specifically, one can view

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[27] Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925–946.

the structure as consisting of layers parallel to the *b–c* plane that contain the Zn(1), P(1), and Ba polyhedra and are linked by the P(2) and Zn(2) polyhedra. Alternatively, there are 2-dimensional slabs running parallel to [101] that contain the Ba, Zn(2), P(1), and P(2) polyhedra, with the Zn(1) atoms in between. Finally, the Zn and P polyhedra join to form a layer of sorts parallel to the *a–b* plane with only the Ba^{2+} ions in between.

Conclusion

Some very simple aqueous reactions of zinc ions and phosphorous acid, together with an alkali or alkaline-earth metal in some cases, have yielded five new compounds with novel structures. This diversity is due, in part, to the Zn^{2+} ion's lack of a strong preference for octahedral versus tetrahedral coordination. The ability of the zinc ion to exist in a variety of coordination environments ($ZnO_4(H_2O)_2$, $ZnO_2(H_2O)_4$, etc.) allows structures to form with different packing arrangements of the tetrahedral HPO_3^{2-} ions, particularly in the presence of a second metal atom. In addition, the regularity of the Zn coordination polyhedra permits symmetrical connectivities with the phosphite groups that are conducive to the formation of infinite chains and sheets. Thus, while copper hydrogen phosphite, $Cu(H_2PO_3)_2$, contains dimers of edge-sharing Jahn–Teller distorted CuO_6 octahedra with four short (1.92–1.98 Å) and two long (2.33, 3.15 Å) Cu–O distances,[28] the analogous Zn compound, $Zn(H_2PO_3)_2{\cdot}3H_2O$, has a unique open framework containing infinite chains of edge-sharing ZnO_6 octahedra bridged by the phosphite groups (Figure 2).

Though the phosphate and phosphite ions both possess tetrahedral geometry, it is perhaps more apt to consider the phosphite as a pyramidal group in its structural chemistry since the H atom that occupies the fourth vertex of the HPO_3 tetrahedron does not bridge to other atoms. The results presented here suggest that, unlike the phosphates, the phosphite structures will tend to have open cavities lined by the phosphite hydrogen atoms, since these behave as "dead ends" in propagating the frameworks. In mixed-metal phosphites, the second metal atom (e.g., Na^+, K^+, etc.) plays a significant role in the framework due to the reduced bridging ability of the phosphite group compared to phosphate. The dependence of the observed framework on the identity of the second metal atom leads to a diversity of structures in the zinc–phosphite system. We are continuing to explore the preparation of new structure types in these phosphite systems.

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Supplementary Material Available: Table SI, listing anisotropic thermal parameters and experimental crystallographic details (6 pages); Table SII, listing calculated and observed structure amplitudes (58 pages). Ordering information is given on any current masthead page.

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(28) *Structure Reports*; Calvert, L. D., Trotter, J., Eds.; Oosthoek, Scheltema, Holkema: Utrecht, The Netherlands, 1975; Vol. 39A, p 282.

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Mercury Complexes with One-Dimensional Chain Structures. Syntheses and Crystal Structures of $[Hg(C_5H_4NS)(CH_3CO_2)]_n$, $Hg(C_5H_4NS)_2$, and $Hg(CH_2P(S)Ph)_2$

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Reaction of $Hg(OAc)_2$, $OAc^- = CH_3CO_2^-$, with 1 equiv of mercaptopyridine, C_5H_5NS, in CH_2Cl_2 at 22 °C gives the compound $Hg(OAc)(C_5H_4NS)$ (**1**) in 82% yield. Hg atoms in **1** are bridged by the C_5H_4NS ligand to form a one-dimensional chain complex. Reaction of $Hg(OAc)_2$ with 2 equiv of C_5H_5NS in CH_2Cl_2 at 22 °C produces the complex $Hg(C_5H_4NS)_2$ (**2**) in 92% yield. **1** can be converted to **2** by the addition of 1 equiv of C_5H_5NS. Reaction of $HgCl_2$ with 2 equiv of Li(MTP), MTP = CH_2PPh_2S, in THF at −78 °C gives $Hg(MTP)_2$ (**3**) in 65% yield. The structures of **1**–**3** were determined by single-crystal X-ray diffraction. **2** and **3** form one-dimensional chain structures in the solid with weak Hg–S interactions. **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.693$ (5) Å, $b = 12.991$ (5) Å, $c = 8.110$ (4) Å, $\beta = 103.45$ (4)°, and $Z = 4$. **2** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.078$ (2) Å, $b = 4.0873$ (6) Å, $c = 12.533$ (2) Å, $\beta = 101.253$ (7)°, and $Z = 2$. **3** crystallizes in the monoclinic space group $C2/c$ with $a = 25.090$ (8) Å, $b = 10.886$ (5) Å, $c = 9.189$ (4) Å, $\beta = 91.83$ (3)°, and $Z = 4$.

Introduction

Syntheses and characterization of one-dimensional chain transition-metal compounds are of great current interest due to their unique and fascinating physical and chemical properties and their important application in catalysis, biological systems, and solid-state chemistry.[1] Extended one-dimensional chain complexes are especially interesting not only because of their possible anisotropic properties but also because of their value as a model for the study of bonding in the solid state.[1,2] Among the known one-dimensional inorganic compounds, square-planar one-dimensional platinum complexes are probably the best studied. Recently a new class of one-dimensional Au^I chain complexes with short metal–metal separations has also been reported.[3,4] Our interest in one-dimensional inorganic polymers and attempts to obtain a better understanding of the metal–metal interactions in such complexes have lead us to synthesize one-dimensional chain mercury compounds. A few one-dimensional chain Hg^{II} compounds are known. However, most of them contain conventional inorganic ligands such as halide, hydroxide, and pseudohalide.[5] Goodgame and co-workers recently reported a very interesting mercury complex, $Hg(C_4H_6NO)_2$, which readily binds to metal

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(1) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York and London, 1981–1983; Vol. 1–3.

(2) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 846.

(3) (a) Mazany, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801. (b) Mazany, A. A. Ph.D. Thesis, Case Western Reserve University, 1984. (c) Jones, P. G. *Gold Bull.* **1981**, *14*, 102.

(4) (a) Murray, H. H.; Briggs, D. A.; Garzon, G.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. *Organometallics* **1987**, *6*, 1992. (b) Wang, S.; Fackler, J. P., Jr.; King, C.; Wang, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3308.

(5) Wilkinson, G., Abel, E. W., Gillard, R. D., McCleverty, J. A., Eds.; *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, England, 1987; Vol. 5, Chapter 56.2, p 1047.

0020-1669/89/1328-2615$01.50/0