

Structure of a Novel Layered Zirconium Diphosphonate Compound:



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We report the structure of a crystalline zirconium bisphosphonate compound, solved *ab initio* from X-ray powder diffraction data and refined by the Rietveld method. The structure of this material is unlike any other reported tetravalent metal phosphonate. The formula of this crystalline compound is $\text{Zr}_2(\text{O}_3\text{PCH}_2\text{CH}_2\text{-viologen-CH}_2\text{CH}_2\text{PO}_3)\text{F}_{6-n}\text{Cl}_n\cdot 2\text{H}_2\text{O}$ ($n \leq 2.5$), which was confirmed by electron probe microanalysis of single (5–30 μm) crystals. This compound crystallizes in the space group $P2_1/c$, $a = 6.6679(2)$ Å, $b = 12.5871(3)$ Å, $c = 13.5837(3)$ Å, $\beta = 101.739(3)^\circ$, $Z = 2$. The structure is composed of layers stacked perpendicular to the b direction. The individual lamellae consist of double chains of ZrF_3O_3 octahedra, bridged by phosphono-viologen groups. In this structure the zirconium centers are formally negatively charged and stack above and below the viologen groups of an adjacent layer. Elemental analyses of the title compound prepared under different conditions as well as a mixed phosphate/phosphonate $[\text{Zr}(\text{O}_3\text{POH})(\text{O}_3\text{PCH}_2\text{CH}_2(\text{bipyridinium})\text{CH}_2\text{CH}_2\text{PO}_3)_{0.5}\text{-Cl}]$ suggest that minimization of the electrostatic repulsion of adjacent viologen groups is important in determining the structures of these materials.

Introduction

Tetravalent metal phosphonates [i.e., $\text{M}(\text{O}_3\text{PR})_2$] are often poorly crystalline due to their high insolubility. The submicron to micron crystal size of zirconium phosphonates make single-crystal X-ray diffraction studies nearly impossible. The structures of these materials consist of alternating organic and inorganic layers. The inorganic layers of these materials are thought to have the same bonding as is observed in $\alpha\text{-Zr}(\text{O}_3\text{POH})_2\cdot\text{H}_2\text{O}$, $\alpha\text{-ZrP}$, based on spectroscopic and X-ray powder diffraction data.¹ Recently Poojary et al. have shown that the structure of tetravalent metal phosphonates can be deduced from powder X-ray data if the material is crystalline enough; the structure of $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$ has been solved using X-ray powder diffraction data.² The structure of $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$ is very similar to that of $\alpha\text{-ZrP}$. The principal difference between the two structures is that the metal atoms lie strictly in a plane, which forces the tetrahedra of the phenyl phosphonate compound to tilt away from the layer normal slightly (i.e., P–C is not parallel to the layer normal). This

tilting decreases the steric repulsions of the adjacent phenyl groups.

We recently reported the intriguing photochemical properties of zirconium viologen-bisphosphonate compounds, prepared by reacting ZrOCl_2 with $\text{H}_2\text{O}_3\text{PCH}_2\text{-CH}_2(\text{bipyridinium})\text{CH}_2\text{CH}_2\text{PO}_3\text{H}_2\text{X}_2$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in the presence of HF (used to retard precipitation), these materials will be abbreviated as $\text{ZrPV}(\text{X})$.³ The solids undergo photoreduction of the viologen group, resulting in the production of an unusually long-lived viologen radical cation. The photochemistry is attributed to thermal reduction of the photochemically excited viologen by the halide. The photochemistry has a strong halide dependence with Cl^- being most efficient and I^- the least efficient in the Cl^- , Br^- , and I^- series. The halide dependence has been attributed to the ability of the halide to undergo a series of reactions that trap the halide radical and prevent charge recombination with the viologen. It is this trapping mechanism and the close-packed nature of the solid that allows the viologen radical to live for many months in the presence of air.

$\text{ZrPV}(\text{X})$ compounds are highly crystalline, leading to well resolved powder X-ray diffraction patterns, with 2θ values that are unaltered by changing the halide. The structure of the title compound was determined by conventional methods using powder diffraction data. The structure of this material is unlike any other reported zirconium phosphates or phosphonates. Rather than having the expected formula for a tetravalent bisphosphonate compound [i.e., $\text{Zr}(\text{O}_3\text{P-R-PO}_3)$], $\text{Zr:P} =$

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1:2], these metal phosphonates have equal numbers of Zr and P atoms. The material giving rise to the observed diffraction pattern is predominantly the fluoride compound, i.e., $Zr_2(O_3P-R^{2+}-PO_3)F_{6-n}X_n$; $n \leq 2.5$; X = Cl, Br, I. The structure is composed of layers made up of double chains of ZrF_3O_3 octahedra bridged by the organic viologen groups. In this paper we discuss the structure of this novel metal phosphonate, as well as elemental analyses and photochemical properties of these and related materials.

Experimental Section

Synthesis. The synthesis of the sample used in the X-ray analysis is a variation of one reported by Alberti et al., for the growth of large single crystals of α -ZrP.⁴ The viologen bisphosphonate (0.25 g, $H_2O_3PCH_2CH_2$ (bipyridinium) $CH_2CH_2PO_3H_2Cl_2$) and 50% aqueous HF (0.32 g) were dissolved in 10 mL of H_2O . An aqueous solution containing $ZrOCl_2$ (0.181 g) was added to the viologen-bisphosphonate solution, and the total volume adjusted to 25 mL. The reaction mixture was sealed in a plastic tube and heated in an oil bath to 55 °C. The temperature was raised 1 °C/day for 30 days. The resulting solid was washed with H_2O and methanol and air-dried.

Chloride and bromide salts were prepared in the absence of HF by hydrolyzing the viologen bisphosphonate tetraethyl ester with either HCl or HBr, in the presence of $Zr(SO_4)_2$. The viologen bisphosphonate tetraethyl ester dibromide (0.25 g) was dissolved in 10 mL of water. $Zr(SO_4)_2 \cdot nH_2O$ (Aldrich Chemical Co., 0.243 g) was dissolved in 10 mL of water and added to the viologen solution. Concentrated HBr (1 mL) was added and the reaction was heated to reflux for 7 days. The resulting solid was filtered and washed with water, methanol, and acetone and air-dried.

The chloride salt was prepared in a similar fashion. The viologen bisphosphonate tetraethyl ester dibromide (0.25 g) and NaCl (0.23 g) were dissolved in 10 mL of water. $ZrOCl_2$ (0.25 g) was dissolved in 10 mL of water and added to the viologen-phosphonate solution. Two drops of concentrated HCl was added and the reaction heated to reflux for 7 days. The resulting solid was isolated as described above.

$(Zr(O_3POH)(O_3PCH_2CH_2$ (bipyridinium) $CH_2CH_2PO_3)_{0.5})$ was prepared by refluxing the viologen bisphosphonate, phosphoric acid, zirconyl chloride, and HF in 1 M HCl as reported elsewhere.⁵

Samples prepared in the presence of HF under conventional reflux conditions were prepared as reported elsewhere.³

Data Collection, Structure Solution, and Refinement. Step scanned X-ray power diffraction data for the sample (packed into a flat aluminum sample holder) were collected by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data were collected between 2 and 80° in 2θ with a step size of 0.02° and a count time of 15 s/step. Data were mathematically stripped of the $K\alpha_2$ contribution, and peak picking was conducted by a modification of the double-derivative method.⁶ The powder pattern was indexed by Ito methods^{7a} on the basis of the first 20 observed lines. The best solution which indexed all the lines, indicated a monoclinic unit cell with lattice parameters $a = 6.672$ Å, $b = 12.6$ Å, $c = 13.589$ Å, and $\beta = 101.77^\circ$. The same solution was also obtained by the program TREOR.^{7b} The indexed reflections showed systematic absences of the type $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicating the space group $P2_1/c$.

Table 1. Crystallographic Data for $Zr_2(O_3PCH_2CH_2NC_5H_4C_5H_4NCH_2CH_2PO_3)F_6 \cdot 2H_2O$

pattern range (2θ), deg	8–80
step scan increment (2θ), deg	0.02
step scan time, s	15
radiation source	rotating anode
wavelength, Å ($K\alpha_1$, $K\alpha_2$)	1.5406, 1.5444
empirical formula	$Zr_2P_2C_{14}H_{20}N_2F_6O_8$
space group	$P2_1/c$
a , Å	6.6679(2)
b , Å	12.5871(3)
c , Å	13.5837(4)
β , deg	101.739(3)
Z	2
no. of contributing reflections	1366
no. of geometric observations	52
P–O distances and tolerance (Å)	1.53(1)
P–C distance and tolerance (Å)	1.81(2)
ZrO ₆ distances and tolerance (Å)	2.05(2)
O–O distances for PO ₄ (Å)	2.55(1)
O–O distances for ZrO ₆ (Å)	2.66(1)
no. of structural parameters	57
no. of profile parameters	11
R_{wp}	0.160
R_p	0.118
R_F	0.053
$R_{wp} = (\sum w(I_o - I_c)^2 / \sum [wI_o^2])^{1/2}$	$R_p = (\sum I_o - I_c) / \sum I_c$
$R_F = \langle F_o - F_c \rangle / \langle F_o \rangle$	

Integrated intensities were extracted from the profile over the range $8^\circ < 2\theta < 60^\circ$ by decomposition (MLE) methods as described earlier.⁸ This procedure produced 74 reflections of which 69 were nonoverlapping. The intensities of the overlapping peaks were divided by the number of contributors (in most cases two) and included in the data set for structure analysis in the TEXSAN⁹ series of single-crystal programs. The two strong peaks in the electron density map (MITHRIL)¹⁰ were identified as the Zr and P atom positions. A Patterson map computed using the same data set confirmed the position of these atoms. A difference Fourier map computed using the Zr and P positions yielded the positions of the three phosphonate oxygens and positions of three atoms coordinated to Zr atom which were later identified as F atoms. The positions of these atoms were used for Rietveld refinement in GSAS.¹¹

The raw data were transferred to the GSAS program package for full-profile refinement. In the early stages of refinement, the atomic positions were refined with soft constraints consisting of both Zr–O and P–O bond distances and O–O nonbonded distances, these constraints are listed in Table 1. The carbon and nitrogen atoms of the viologen phosphonate group and the lattice water molecules were located in the subsequent difference Fourier maps. The aliphatic chains and viologen group was refined with the C–C and C–N distances constrained to normal values. All the atoms were refined isotropically. In the final cycles of refinement the shifts in all the parameters were less than their estimated standard deviations. Neutral atomic scattering factors were used for all atoms. No corrections were made for anomalous dispersion, absorption, or preferred orientation.

Crystallographic and experimental parameters are given in Table 1, final positional and thermal parameters in Table 2, and bond lengths and angles in Table 3, and the final Rietveld refinement difference plot is shown in Figure 1.

Microprobe Analysis. Electron probe microanalysis (EPMA) was performed with a CAMECA SX-50 in the Electron Microbeam Facility of the Princeton Materials Institute. Analyses were performed using an accelerating voltage of 15 kV and a regulated beam current of 20 nA. Both secondary

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Table 2. Positional and Thermal Parameters for $Zr_2(O_3PCH_2CH_2NC_5H_4C_5H_4NCH_2CH_2PO_3)F_6 \cdot 2H_2O$

	x	y	z	$U_{iso}, \text{\AA}^2$
Zr1	0.8002(7)	0.0921(3)	0.1325(3)	0.017(2)
P1	0.290(2)	0.0308(7)	0.1134(7)	0.021(2)
F1	0.762(3)	0.231(1)	0.054(1)	0.040(1)
F2	0.825(3)	0.954(1)	0.213(1)	0.040 ^b
F3	0.860(3)	0.184(1)	0.259(1)	0.040 ^b
O1	0.495(2)	0.092(1)	0.147(1)	0.026(2)
O2	0.727(3)	0.003(1)	-0.001(1)	0.026 ^c
O3	0.102(2)	0.093(1)	0.126(1)	0.026 ^c
O(W)	0.250(4)	0.258(2)	0.353(2)	0.026 ^c
N1	0.512(3)	0.949(2)	0.362(2)	0.025(2)
C1	0.303(3)	0.911(2)	0.189(1)	0.030(2)
C2	0.294(3)	0.931(2)	0.302(2)	0.030 ^d
C3	0.659(4)	0.871(2)	0.372(3)	0.030 ^d
C4	0.852(4)	0.890(2)	0.435(2)	0.030 ^d
C5	0.888(2)	0.986(2)	0.485(3)	0.030 ^d
C6	0.774(4)	0.072(2)	0.442(2)	0.030 ^d
C7	0.567(4)	0.049(2)	0.396(2)	0.030 ^d

^a $U_{iso} = B_{iso}/8\pi^2$. ^b Constrained to be equal to U_{iso} of F1.

^c Constrained to be equal to U_{iso} of O1. ^d Constrained to be equal to U_{iso} of C1.

Table 3. Bond Lengths (Å) and Bond Angles (deg) for $Zr_2(O_3PCH_2CH_2NC_5H_4C_5H_4NCH_2CH_2PO_3)F_6 \cdot 2H_2O$ ^a

Zr1-O1	2.08(1)	P1-O1	1.55(1)
Zr1-O2	2.09(1)	P1-O2	1.58(1)
Zr1-O3	2.03(1)	P1-O3	1.52(1)
Zr1-F1	2.04(1)	P1-C1	1.81(1)
Zr1-F2	2.04(1)	C1-C1	1.58(2)
Zr1-F3	2.04(1)	C2-N1	1.53(2)
		N1-C3	1.37(2)
		N1-C7	1.32(1)
		C3-C4	1.41(2)
		C4-C5	1.38(2)
		C5-C5'	1.51(2)
		C5-C6	1.38(2)
		C6-C7	1.42(2)
O(W)---F2	2.63	F2---O(W)---F3	94
O(W)---F3	2.81		
O1-Zr1-O2	91(1)	O1-P1-O2	108(1)
O1-Zr1-O3	177(1)	O1-P1-O3	114(1)
O1-Zr1-F1	92(1)	O1-P1-C1	108(1)
O1-Zr1-F2	86(1)	O2-P1-O3	110(1)
O1-Zr1-F3	87(1)	O2-P1-C1	108(1)
O2-Zr1-O3	92(1)	O3-P1-C1	108(1)
O2-Zr1-F1	92(1)	P1-C1-C2	114(1)
O2-Zr1-F2	89(1)	C1-C2-N1	109(2)
O2-Zr1-F3	177(1)	C2-N1-C3	123(2)
O3-Zr1-F1	89(1)	C2-N1-C7	118(2)
O3-Zr1-F2	93(1)	N1-C3-C4	119(1)
O3-Zr1-F3	90(1)	C3-C4-C5	120(1)
F1-Zr1-F2	177(1)	C4-C5-C6	117(2)
F1-Zr1-F3	86(1)	C4-C5-C5'	114(3)
F2-Zr1-F3	93(1)	C5'-C5-C6	111(2)
		C5-C6-C7	116(2)
		C6-C7-N1	120(1)
		C7-N1-C3	119(1)

^a Prime indicates the C5 atom related by a center of symmetry.

and backscattered electron images were used to locate sample areas that were suitable for analysis. The excitation volume for a point analysis of zirconium viologen phosphonate is approximately $1 \mu\text{m}^3$ for the above instrumental conditions. Standard materials used to calibrate X-ray lines of interest are as follows: P K α [$\text{Ca}_5(\text{PO}_4)_3\text{F}$], Zr L α (ZrO_2), F K α (BaF_2), and O K α (Al_2O_3). Matrix corrections were performed using the $\Phi(\rho Z)$ method.¹²

The individual analyses were performed on single crystals or clusters of three or more crystals and are given in Figure 4. All of the mole ratios have been normalized to Zr = 1.00.

Photochemical Studies. The chloride and bromide salts prepared by decomposition of the esters were each placed in a

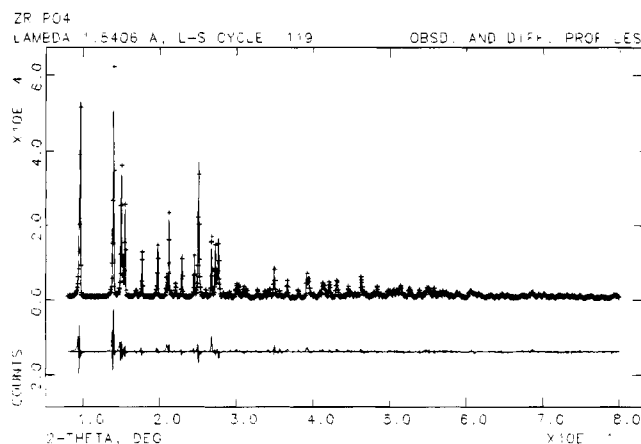


Figure 1. Observed (+) and calculated (-) profiles (X-ray intensity versus 2θ) for the Rietveld refinement. The bottom curve is the difference plot on the same scale. The larger residuals for the first two peaks are due to the peak asymmetry. The intensity of the second reflection is also effected by preferred orientation.

quartz vessel and evacuated. They were photolyzed side by side with a 550 W medium pressure Hg arc lamp. The samples were kept close to room temperature during the photolysis.

Results and Discussion

The slow thermal precipitation technique used for preparing the microcrystalline samples for powder X-ray diffraction was developed for growing very large single crystals of α -ZrP.⁴ It was hoped that this would lead to crystals of the zirconium viologen-bisphosphonate compound large enough for single-crystal X-ray diffraction studies. A highly crystalline sample was obtained, but the particle size ($1-30 \mu\text{m}$) was too small for single-crystal studies. Preparation of these zirconium phosphonate compounds by reflux methods yields materials that give powder X-ray diffraction patterns identical to those for materials prepared by the slow thermal precipitation, but the particle sizes for the former materials are much smaller ($0.5-5 \mu\text{m}$). If HF is left out of the synthesis, powdered solids are obtained. However, these materials have very low crystallinity, often giving only a single peak in their powder X-ray diffraction pattern, centered at 17.5\AA .

Powder structure analysis of zirconium viologen-bisphosphonate, prepared by slow thermal precipitation, shows that it has a new and very interesting structure. In this structure the Zr atoms are octahedrally coordinated by three fluoride ions and three phosphonate oxygens, in a meridional configuration (Figure 2). Two of the zirconium-bound phosphonate oxygens (O1 and O3) link the octahedra into a chain, running parallel to the a axis. Centers of symmetry produce another chain adjacent to the first. These two symmetry related chains are linked by P-O2-Zr bonds (Figure 2). These isolated double chains are held together by the viologen phosphonate groups and thus form a layer in the ac plane. The c glide produces another layer which is shifted both along the b and c directions (Figure 3). In this structure the Zr centers bear a formal negative charge. Adjacent layers pack with the zirconium octahedra above and below the cationic viologen groups, minimizing electrostatic interactions. The distance from F1 to the nearest carbon atom (C6 of the viologen group) is 2.94\AA . All other contacts are above 3.2\AA .

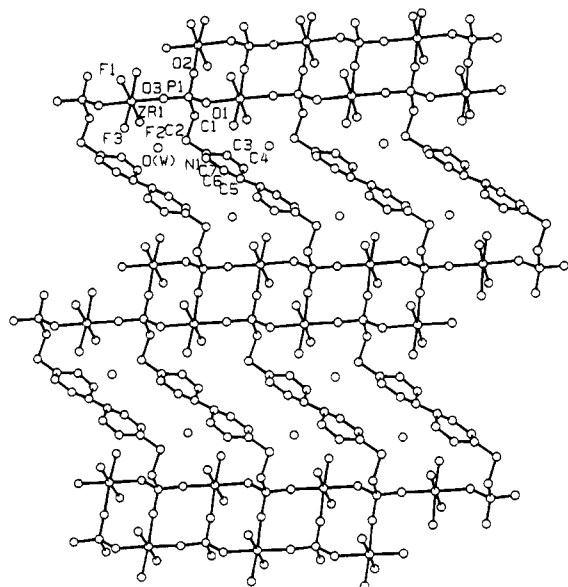


Figure 2. Portion of the structure in the unit cell as viewed along the b axis. The a axis is horizontal, and the c axis is vertical.

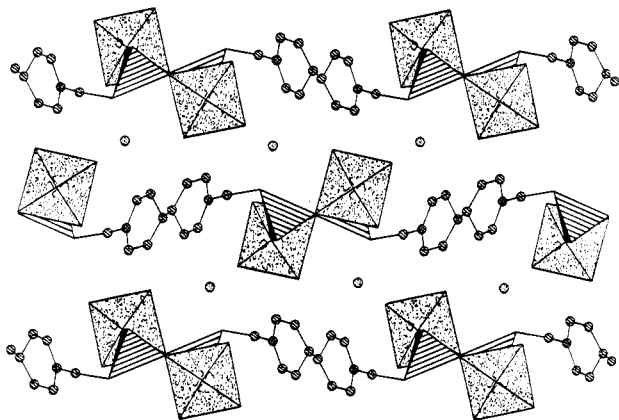


Figure 3. Projection of the structure down the a axis. The b axis is horizontal and the c axis is vertical.

The only interaction between the glide-related layers is hydrogen bonds involving the water molecules and two of the coordinated F atoms (F2 and F3). A center of symmetry resides between the pyridinium groups of the bipyridine which makes all the atoms in this group coplanar.

Quantitative elemental analyses by electron microprobe for Zr, P, and F are shown in Figure 4. For the sample used in the X-ray diffraction study, some of the crystals had an identical Zr:P:F stoichiometry (1:1:3) of the proposed structure. All of the crystals probed show the Zr:P ratio to be 1:1. The F:Zr ratio varies over a wide range (from 1.5 to 3), with an average value of 2.2:1. Microprobe analyses were also performed on crystals prepared by reflux methods. For these the Zr:P ratio is consistently 1:1. Fluoride ions are present to some degree in all of these solids, with the F:Zr ratio varying from 1.3 to 2.7. Of 11 data points, we were not able to observe any crystals that had a F:Zr ratio of 3:1. However, the crystal sizes in these batches were much smaller, and it was impossible to examine single crystals. The average ratio of F:Zr was 2:1, which is similar to that found for the material prepared by slow thermal precipitation. The average values for the F:Zr ratios

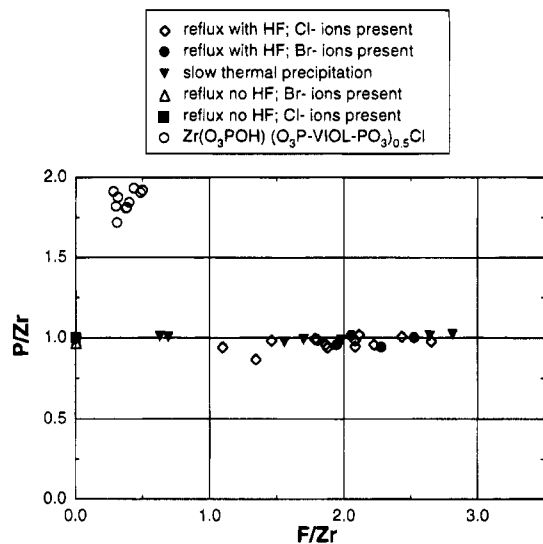


Figure 4. Electron probe microanalyses (EPMA) for F, Zr, and P. All of the mole ratios have been normalized to $Zr = 1.00$. Individual analyses were performed on single crystals or clusters of ≤ 3 crystals.

are based on a relatively small number of data points (8–10 data points per sample) and thus may not represent the bulk composition. Microprobe analysis of the samples prepared without fluoride show a Zr:P ratio of 1:1 and no detectable fluoride.

A ratio of 1:2 for Zr:P would be expected based on the formulas of the previously reported zirconium phosphonates [i.e., $Zr(O_3PR)_2$].¹ The fact that all of the zirconium phosphonates prepared from the viologen-bisphosphonate give ratios of 1:1 suggests that they all have similar structures, unlike those of the other reported zirconium phosphonates. Substitution of other halide ions into the fluoride sites on Zr may not significantly decrease the crystallinity of the metal phosphonate. The materials prepared without HF give Zr:P ratios very close to the 1:1 ratio of the materials prepared with HF. Unfortunately, these materials are not crystalline enough to get any information from their powder X-ray diffraction patterns.

The deficiency of fluoride (from the expected 1:3 ratio for Zr:F) in these materials is compensated for with chloride ions. When examined by EPMA all of the samples showed very low levels of chloride. One explanation for the measured low levels of chloride is that chloride is migrating away from the site of EPMA analysis, *via* volatilization or interdiffusion or some combination of the two mechanisms. Either mechanism would result in artificially low chloride concentrations. To test this hypothesis, samples were dissolved with base, and the dissolved chloride ion titrated with silver ion.¹³ The sample used for powder X-ray study (prepared by slow thermal precipitation) is highly crystalline and does not dissolve readily in basic solution. Treatment of this compound with base, followed by titration of the resulting suspension gave a ratio of Zr:Cl of 1.02 ± 0.05 . Treatment of this suspension with fluoride ion leads to additional dissolution of the title compound. Further titration of the solution shows significantly more free chloride ion. The combined chloride analyses

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lead to a total Zr:Cl ratio of $1:1.3 \pm 0.2$. The material prepared with no HF present is poorly crystalline and readily dissolves in base. The ratio of Zr:Cl for this fluoride free material would be 1:3 if all of the fluoride ions in the structure were replaced with chloride; the observed Zr:Cl ratio for this compound is $1:2.7 \pm 0.1$.

The photochromic behavior of the materials prepared under reflux in the presence of HF have been reported previously.³ Upon exposure to ultraviolet light, the crystalline solids immediately turn blue, indicating the formation of viologen radical cation. The blue color gradually fades over several hours to a pale blue color that persists indefinitely. The chloride and bromide salts prepared in the absence of HF do not behave in exactly the same manner as the more crystalline solids on photolysis. They do not change color upon exposure to ultraviolet light in the presence of air. Under an inert atmosphere, both turned blue when exposed to ultraviolet light. The rate of photoreduction for the chloride salt was decidedly faster than that of the bromide salt. Both were immediately bleached when O₂ was introduced into the sample. These observations are consistent with the poorly crystalline nature of these materials. The longevity of the colored state of the crystalline materials is due to the ability of the lattice itself to prevent diffusion of oxygen to the reduced viologen. The poorly crystalline materials contain sufficient defects such that this diffusion is not significantly restricted.

The samples prepared by slow thermal precipitation give the same photochromic behavior as those reported previously.³ It was found that the sample also turned blue in the X-ray beam. Both the X-ray diffraction and EPMA studies show that the zirconium viologen-bisphosphonate materials prepared in the presence of HF all have substantial amounts of fluoride incorporation. The fluoride in these materials is not expected to be involved in the photoreduction of viologen, since the photoexcited viologen will oxidize chloride and bromide but not fluoride. This hypothesis was tested by examining the pure fluoride material (i.e., a sample with no halide other than fluoride). Treating a solution of ZrOCl₂ with the viologen bisphosphonate tetraphenyl borate salt in the presence of HF yields a microcrystalline solid, whose X-ray powder diffraction pattern is identical to those of ZrPV(X).¹⁴ In this case, there are no chloride or bromide ions present in the solution the crystals are grown from and the tetraphenyl borate ion is too large to be taken up into the lattice. The pure fluoride material shows no photoreduction of viologen either in the presence of oxygen or under anaerobic conditions. Charge transfer from a free halide ion to a photoexcited viologen molecule has been proposed as part of the photochemical process. The structural and photochemical data together suggest that the photochemical charge transfer observed for ZrPV(X) comes either from "ZrO₃F₂X⁻" (X = chloride, bromide, or

iodide) or from a free halide ion substituted into the lattice water site (the displaced water would be bound to Zr). Unfortunately, these two possibilities are not readily distinguishable for ZrPV(X). The latter of the two possibilities would give rise to a mechanism for charge transfer identical to the one proposed previously.³ Charge transfer from a free halide ion is certainly viable in this class of materials, since related materials¹⁵ which definitely contain free chloride or bromide ions are more readily photoreduced than ZrPV(X) materials.

An interesting question that this structure raises is why do these materials crystallize in this unconventional manner? Steric interactions between adjacent organic groups is most likely not responsible, since phenyl- and (alkylphenyl)phosphonic acids lead to the common layered structure type.¹ The structure could be the result of electrostatic repulsion of adjacent viologen groups. In this novel structure the viologen molecules are much further apart than they would be in the conventional zirconium phosphonate structure. All of the nonbonded contacts between the adjacent viologen groups are above 3.5 Å, while in the case of Zr(O₃PC₆H₅)₂ some contacts as short as 3.0 Å are observed between the carbon atoms of the neighboring phenyl groups.² If electrostatic repulsion of the viologen groups leads to this novel structure, then insulating adjacent viologens from each other may lead to a more conventional structure and stoichiometry (i.e., Zr(O₃PR)₂ type of material with Zr:P = 1:2). This insulation may be provided by phosphate groups in the mixed phosphate/phosphonate compound, whose proposed formulation is Zr(O₃POH)(O₃PCH₂CH₂(bipyridinium)CH₂CH₂PO₃)_{0.5}Cl.⁵ This material has the phosphate groups intimately mixed with the phosphonates leading to a porous structure. Electron microprobe analysis of this material leads to a F:Zr:P ratio of 0.4:1.0:1.85 (Figure 4).¹⁶ The Zr:P ratio is very similar to that expected for a normal Zr phosphonate or phosphate compound, giving support to the proposal that electrostatic repulsions lead to the novel structure type. The level of fluoride in these materials is much lower than that found in the pure phosphonate compound, and a significant amount of chloride is observed by titration.

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(15) E.g., Zr(O₃PR)(O₃PCH₂CH₂(bipyridinium)CH₂CH₂PO₃)_{0.5}Cl, R = H, OH; Vermeulen, L. A.; Thompson, M. E. *Chem. Mater.* **1994**, *6*, 77–81.

(16) Chloride ion titration by the procedure described above give a Zr:Cl ratio for this compound of $1:0.7 \pm 0.1$.

(14) A related procedure was used to prepare ZrPV(I) (see ref 3b).