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A Novel Staged Form of Layered Zirconium Phosphonates with Methyl and *p*-Aminobenzyl Pendant Groups

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Zirconium phosphonates, $Zr(O_3PR)_2$, are layered compounds whose structure follows the basic structural motif[1] of zirconium phosphate, $Zr(O_3POH)_2$. In these compounds, the zirconium atoms form stacked planes held together by the attractive interactions of the R groups that project into the interlayer region from both sides of any given zirconium plane.[2,3] Mixed zirconium phosphonates, $Zr(O_3PR)_x(O_3PR')_{2-x}$, can be formed by coprecipitation of the zirconium in the presence of two different phosphonic acids,[4−7] leading to the formation of a porous material if the two organic groups on the phosphonic acids are sufficiently different in size. These mixed compounds usually contain a random distribution of the organic groups such that all layers have identical stoichiometry. In such systems, the interlayer spacing (*d*-space) is a function of pendant group stoichiometry, and has a generally linear dependence on component mole fraction.

With this communication, we report that in the course of an extensive investigation into the physical/chemical attributes that underlie the one-dimensional interlayer spatial variation,[8,9] an unusual material was found to exist at $x = 0.25$ that can only be interpreted as a staged, alternating mixed/pure layered zirconium phosphonate.

The systems selected for these studies incorporated *p*-aminobenzyl as the large group and methyl as the small group, $Zr(O_3PCH_2C_6H_4NH_2)_x(O_3PCH_3)_{2-x}$. In this $Zr(pab)_x(me)_{2-x}$ family of compounds, x was varied from 0.0 to 2.0 in regular increments. All preparations followed the general procedure[9] of adding zirconyl chloride to stoichiometric amounts of the appropriate phosphonic acids as an aqueous solution, refluxing for several days, and isolating the product at room temperature.

A representation of the unit cell for the compound $x = 1.0$ is depicted as Figure 1. In addition, the amino moiety allows for assimilation of HCl, conveniently providing an additional system to investigate, $Zr(pabHCl)_x(me)_{2-x}$. The two series will also be referred to as the deprotonated and protonated systems, respectively.

X-ray diffraction was employed to measure *d*-space values for the systems. Typical results are displayed in Figure 2, where the first-order 001 diffraction peaks occur at angles whose 2θ values are easily converted to interlayer spacing values via the Bragg equation. A plot of such values as a function of stoichiometry is shown as Figure 3. For example, in panels (a) and (c) of Figure 2, respectively, the $Zr(pabHCl)_2$ and $Zr(me)_2$ compounds exhibit the lowest-angle (first order) diffractions that transform to *d*-space endpoints of Figure 3. The generally linear behavior of the interlayer spacing dependence on composition was as expected, and resembles Vegard's law for lattice parameters in metal alloys.[10]

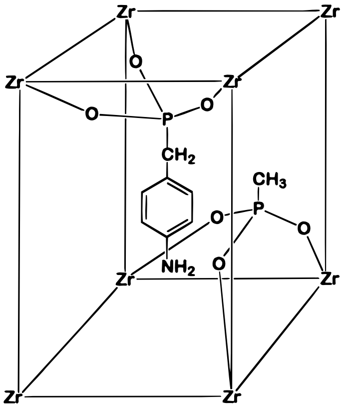

Figure 1. Unit cell representation of zirconium phosphonates. For the compound shown, the stoichiometry is $x = 1.0$. An extended lattice would reveal that each zirconium atom is bonded to six oxygen atoms, forming an octahedral coordination environment.

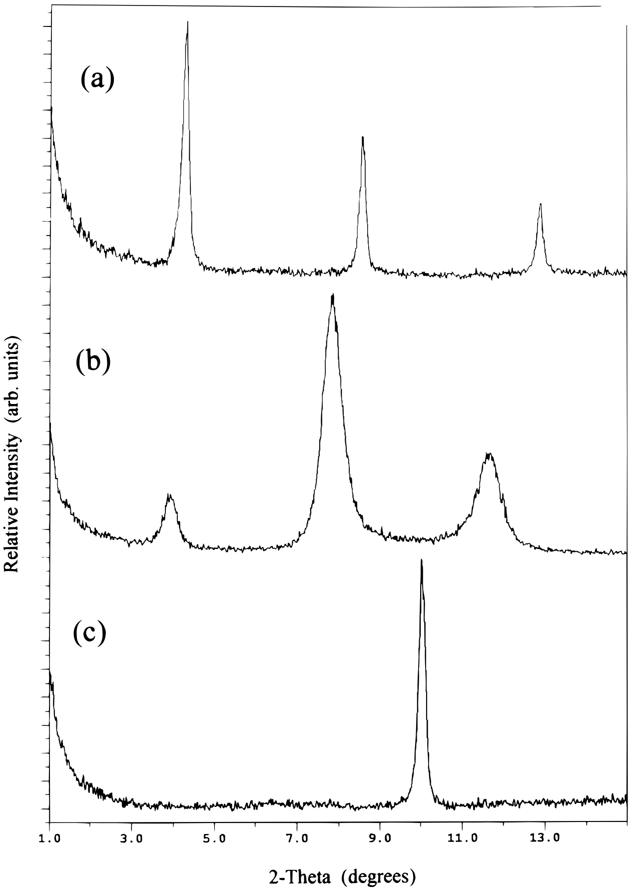

Figure 2. X-ray diffraction patterns of (a) $Zr(pabHCl)_2$, (b) $Zr(pabHCl)_{0.25}(me)_{1.75}$, and (c) $Zr(me)_2$.

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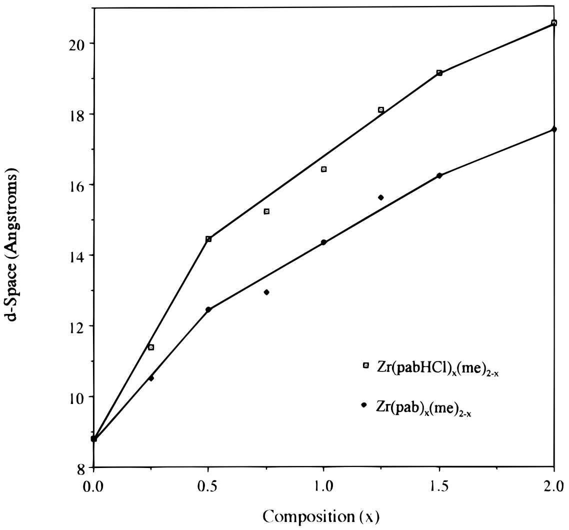

Figure 3. Variation in *d*-space measured by XRD as a function of pendant group composition, for Zr(pabHCl)$_x$(me)$_{2-x}$ and Zr(pab)$_x$(me)$_{2-x}$.

For one of the stoichiometries, $x = 0.25$ in both the protonated and the deprotonated series, we observed that an interesting anomaly obtains. Panel (b) of Figure 2 shows the XRD trace for this material, whose lowest-angle scattering peak (which is atypically less intense than the second peak) occurs at an angle that is smaller than even the bis(*p*-aminobenzyl) compound, displayed in panel (a). Clearly, this simple model contradicts Vegard's law; in fact, the expected *d*-space value should be fairly close to the all-methyl value. On the other hand, employing the interpretation that, instead, it is the second XRD peak that corresponds to the first-order scattering of the randomly mixed, $x = 0.25$ compound, one obtains an interlayer *d*-space value that does indeed follow the Vegard's law behavior. These calculated vaues are included as the $x = 0.25$ data points of Figure 3.

This fitting assignment of the second peak (at $2\theta = 7.78°$) and the unusual XRD intensity pattern suggest that this material is comprised of two distinct, coprecipitated crystallites: the randomly mixed $x = 0.25$ compound rationalized above, and a "staged" compound possessing a much larger *d*-space. Segregation of zirconium phosphonates into staged materials in which alternating layers possess different compositions has previously been observed.[11-16] In these systems, each of the two types of layers contained only one kind of pendant group. For our $x = 0.25$ case, a large discrepancy between predicted and observed *d*-space values would exist under an analogous interpretation.

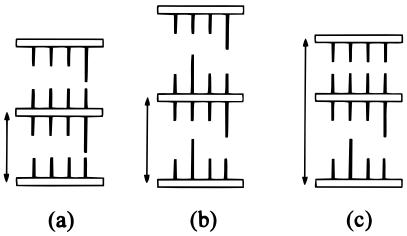

Figure 4. Schematic representations of structural possibilities for zirconium phosphonates Zr(R)$_x$(R′)$_{2-x}$, where R and R′ are large and small pendant groups, respectively. Layers are organized as (a) randomly mixed $x = 0.25$, (b) randomly mixed $x = 0.5$, and (c) segregated, staged arrangement of layers with $x = 0.5$ followed by $x = 0.0$, for an overall stoichiometry of $x = 0.25$. Arrows indicate repeating *d*-space dimension.

Table 1. Comparisons of *d*-Space Values for Zr(pabHCl)$_x$(me)$_{2-x}$ and Zr(pab)$_x$(me)$_{2-x}$

	d-space (Å)	
system	protonated series	deprotonated series
Zr(me)$_2$	8.8	8.8
Zr(pab)$_2$	20.5	17.5
Zr(pab)$_{0.5}$(me)$_{1.5}$	14.5	12.4
predicted: Zr(me)$_2$ + Zr(pab)$_{0.5}$(me)$_{1.5}$	23.3	21.2
observed: Zr(pab)$_{0.25}$(me)$_{1.75}$	23.0	21.6

However, a layer containing only methyl groups, followed by a layer of the $x = 0.50$ mixed stoichiometry, translates to a predicted *d* spacing that essentially coincides with one obtained from the observed, low-angle scattering at $2\theta = 3.83°$. (Clearly, a configuration of layers in this manner produces a compound whose overall stoichiometry of $x = 0.25$ is identical to its "randomized" cocrystallite.) This novel situation is schematically depicted in Figure 4. As Table 1 shows, predicted and observed *d*-space values of the new, staged material are within a few percent of each other. That is, adding the dimensions of an all-methyl layer (8.8 Å) to that of the $x = 0.5$ compound (14.5 and 12.4 Å for the protonated and deprotonated cases, respectively) yields predicted *d*-space values of 23.3 and 21.2 Å. This compares very favorably to the experimentally observed values of 23.0 and 21.6 Å for the respective compounds.

While segregated zirconium phosphonates have been reported before, our results represent the first instance where these materials contain, in alternating fashion, an interlayer region of one moiety and an interlayer region of two, randomly mixed groups. A potential exists for forming new materials in which two adjacent layers may be individually adjusted to possess specific, differentiated properties.

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