

Figure 1. Stern-Volmer plots of the quenching by ferrocene of the luminescence intensity (C) of $[\text{Ru}(\text{bpy})_3]^{2+}$ in DMF at 22 °C and of the photoanation reaction, in terms of the disappearance of $[\text{Ru}(\text{bpy})_3]^{2+}$ (☆, line A) and the production of $[\text{Ru}(\text{bpy})_2(\text{DMF})\text{Br}]^+$ (○, line B). Slopes (M^{-1}): 2530 ± 620 (A); 2825 ± 580 (B); 826 ± 6 (C). 0.10 M Bu_4NBr was present in all samples.

which the states would be in thermal equilibrium.⁶ Furthermore, the larger K_{SV} for the photosubstitution reaction implies either a longer lifetime for the ligand field state or a larger bimolecular quenching constant. A longer lifetime could result if the ligand field state were lower in energy than the luminescing charge-transfer state, whereas deactivation by more than one ferrocene electronic state could account for differences in the bimolecular quenching constant. Some evidence that the ligand field and charge-transfer states may not be in equilibrium has been presented recently.⁷

There remains the possibility that a chemical rather than a photophysical process is responsible for the observed differences in K_{SV} . Ion pairs and triplets are known to play a significant role in the photoanation reaction,³ although we have at this time no suggestion for a way in which ferrocene might interfere with the process. Ferrocene was chosen as the quencher, in fact, precisely because it was neutral (thus unlikely to affect ion-pairing equilibria) and relatively robust in comparison with other neutral complexes that were tried. However, suggestive in this respect is the previously reported Stern-Volmer constant for quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ emission (chloride salt) by ferrocene in ethanol⁸ of 5300 M^{-1} (6 times greater than our value in DMF), which is more remarkable in that the viscosity of ethanol is greater than that of DMF.

Under the conditions of these experiments, ferrocene itself undergoes photolysis. Two photoproducts could be isolated after irradiation of solutions containing only ferrocene. Bromide had no effect on the photolysis. The quantum yields were very low (ca. 10^{-3}), and even at ferrocene concentrations

in the range of those used in the quenching studies, analysis of the Ru photolysate absorption spectrum after 50% of the $[\text{Ru}(\text{bpy})_3]^{2+}$ had reacted led to an estimate that less than 10% of the ferrocene had reacted. Nevertheless, oxidation of ferrocene by excited $[\text{Ru}(\text{bpy})_3]^{2+}$ cannot be ruled out as an explanation of the present experiment.

Experimental Section

Solutions $4.85 \times 10^{-5} \text{ M}$ in $[\text{Ru}(\text{bpy})_3]\text{Br}_2$ and 0.10 M in tetrabutylammonium bromide in DMF, with ferrocene concentrations between 0 and $1.61 \times 10^{-3} \text{ M}$, were deoxygenated by bubbling N_2 through for 20 min and irradiated at 436 nm with use of an Oriel 500-W Hg lamp and a liquid filter train.⁹ Photolysis was interrupted periodically and absorption spectra were recorded. The spectrum corresponding to the ferrocene present was subtracted. The resulting spectra were resolved³ into the separate contributions from $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(\text{DMF})\text{Br}]^+$, and $[\text{Ru}(\text{bpy})_2\text{Br}_2]$. Plots of concentration vs. time were linear at least until 40% of the reactant had been consumed. Ferrioxalate actinometry⁹ was used to determine the incident light intensity.

Registry No. $[\text{Ru}(\text{bpy})_3]\text{Br}_2$, 15388-41-7; Br^- , 24959-67-9; $[\text{Ru}(\text{bpy})_2(\text{DMF})\text{Br}]^+$, 73663-67-9; DMF, 68-12-2; ferrocene, 102-54-5.

(9) Calvert, J. G.; Pitts, J. N. Jr. "Photochemistry"; Wiley: New York, 1966.

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The Mixed-Component Layered Tetravalent Metal Phosphonate System $\text{Th}(\text{O}_3\text{P}-\text{C}_6\text{H}_5)_x(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5)_{2-x}$

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Layered tetravalent metal phosphonates constitute a unique class of materials in which various organic groups are covalently appended in nearly close-packed arrays onto the basal surfaces of an inorganic sheet (Figure 1).¹ One feature of these solids that has particularly attracted our interest is the possibility of manipulation of their surface textural properties by variation of the organic groups. More specifically, we were concerned with the preparation and characterization of products having two different groups present within the microenvironment. Single-phase solid solutions, ordered single phases, or multiphase products could conceivably occur when precipitating mixtures of phosphonates with M^{4+} , and we have seen examples of all of these outcomes in our work.²

Conceptually, one simple means of introducing microporosity into mixed-component layered phosphonates is to have present both small and large groups, the latter serving to prop the layers apart, as is depicted in Figure 2. We chose to test this premise using for the two groups phenyl and biphenyl, since chemical similarity maximizes the likelihood of solid-solution formation. Thorium was used as the metal ion because it tends to yield more crystalline products (as gauged by the width of X-ray diffraction reflections). Therefore, we undertook the preparation of the series of products $\text{Th}(\text{O}_3\text{P}-\text{C}_6\text{H}_5)_x(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5)_{2-x}$ for $x = 0, 0.2, 0.4, 0.6, \dots, 2.0$, that is, for the series in which the mole fraction ratios of phenyl and biphenyl varied from 0 to 1 at one-tenth increments.

Experimental Section

With use of methodology previously developed in our work, the preparation of the series was accomplished by adding together solutions

(7) Rillema, D. P.; Allen, G.; Meyer, T. J. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; American Chemical Society: Washington, DC, 1982; INOR 270.

(8) Wrighton, M. S.; Pdungsap, L.; Morse, D. L. *J. Phys. Chem.* **1975**, *79*, 66.

† Deceased Aug 16, 1982.

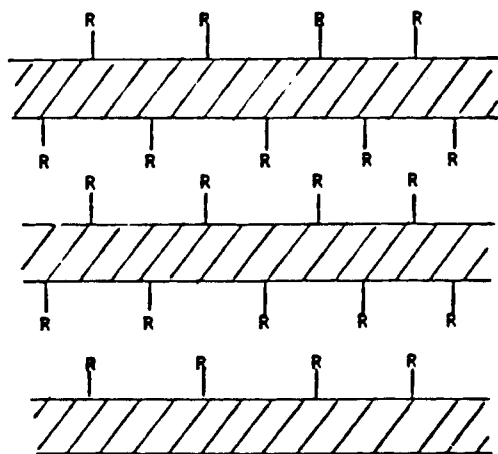
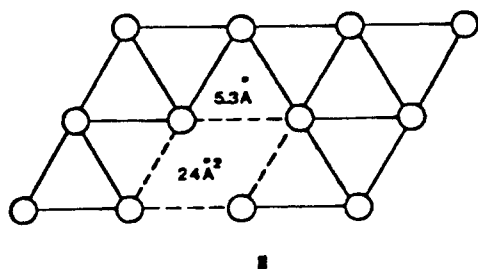
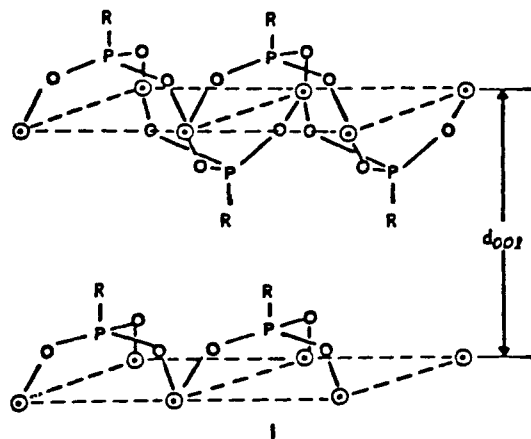


Figure 1. Structure of the tetraivalent metal phosphonates: (I) skeletal view of the framework (● denotes the metal ions); (II) basal projection of the sites; (III) end-on model of the lamella.

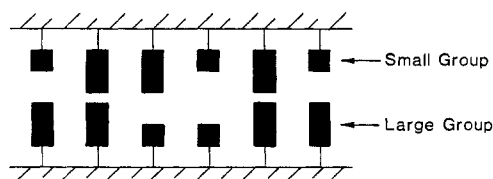


Figure 2. Model of how pores might be formed by the action of abutting large groups in the presence of smaller ones.

of thorium nitrate and the two phosphonic acids $\text{H}_2\text{O}_3\text{P}-\text{C}_6\text{H}_5$ and $p\text{-H}_2\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$ in the appropriate molar ratio, and in excess

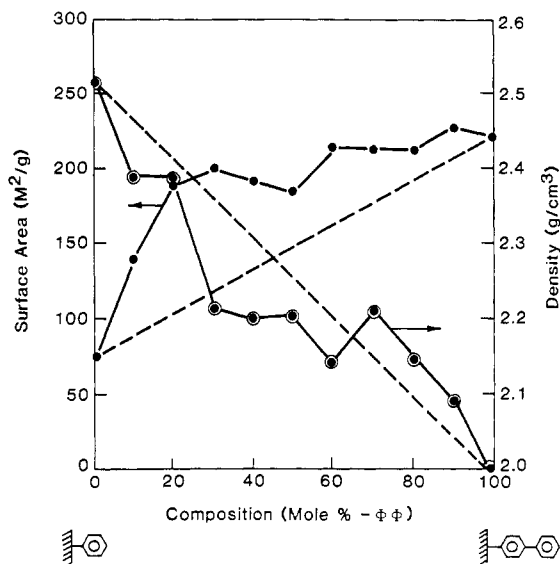


Figure 3. Variation of surface area and density of the products with composition.

over the thorium ion. Acetic acid- H_2O was used as the solvent to ensure solubility of starting materials. After 1 h of reflux, the resulting precipitates were filtered, washed well with methanol, and dried at 105°C to constant weight. Carbon analyses were systematically low for the products, but we have previously encountered this problem, presumably due to the formation of refractories in combustion. The phosphorus analyses were satisfactory, and in addition in several cases we hydrolyzed the products in alkaline aqueous solution and verified the phosphonate ratio by ^{31}P NMR. As a result, the presumed compositions are felt to be reliable at least to within 10% of the stated values.

Surface areas of the products were measured with use of a conventional one-point BET method on a Quantasorb instrument, and true powder densities were determined with a helium null pycnometer. Consequently, the surface area found was only nitrogen available, while density was refined by displaced helium. So only voids inaccessible to helium will lower the measured density relative to that of a well-packed standard (a single-component product). The densities found for the end members of the series are within about 2% of the calculated values. Errors may be somewhat higher for the intermediate products, since smaller samples were available.

Results and Discussion

Plotted in Figure 3 are the experimentally found surface areas and densities for the series, compared with straight-line trends expected for linear behavior. (The changing molecular weight of the intermediate products would rigorously require that the units on the ordinates be in molar rather than weight designation; however, the effect is inconsequential for our purposes.) These results are seen to be in qualitative agreement with a picture involving introduction of increasing numbers of void spaces as the phenyl/diphenyl ratio increases—voids that may or may not be accessible to nitrogen and helium, depending on their contiguity and the permeability of the gases. Therefore, some lowering of density and increase in surface area is expected and observed.

In order to ensure that the surface area effects are not arising from significant changes in particle size in going across the series, we examined the scanning electron micrographs of all of the products. Though the composite particles were not

- (1) Alberti, G.; Costantino, U.; Alluli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113. Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.
- (2) Dines, M. B.; DiGiacomo, P. M.; Callahan, K. P.; Griffith, P. C.; Lane, R. H.; Cooksey, R. E. *Abstr. Rep.—Am. Chem. Soc.* **1981**, 182nd, INOR 44; *ACS Symp. Ser.* **1982**, No. 192, 223.
- (3) Details of the preparation of this and other previously unreported phosphonic acid derivatives will appear in a forthcoming publication.

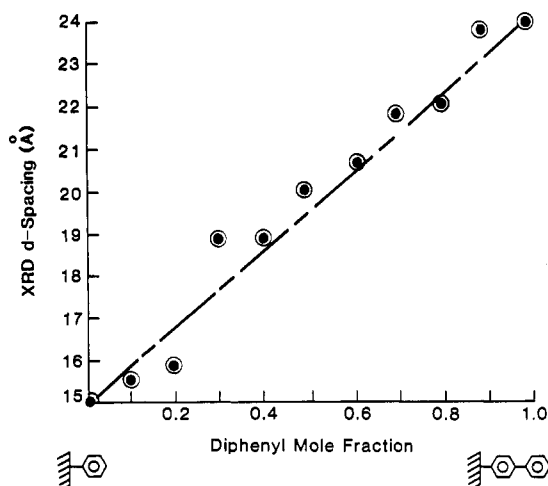


Figure 4. Dependence of the layer-layer spacing on compositional variation.

of a particularly homogeneous size distribution, there were not apparent any trends paralleling the surface area variation.

Figure 4 presents the X-ray-diffraction-determined interlayer distances for the series. Clearly, for the 0.3–0.8 biphenyl mole fraction compositions there is apparent a linear dependence with molar ratio of the groups. This observation is not consistent with the picture given in Figure 2. According to that view, one would expect to see an extended region of structure having the biphenyl–biphenyl distance (24 Å), which might drop to the biphenyl–phenyl distance (ca. 19.5 Å) and there be maintained until collapse to the phenyl–phenyl distance as some low biphenyl mole fraction is reached. A more fitting explanation of the XRD data, as well as the modest density diminution in the intermediate compositional region, is that strain imposed by the incipient voids forces the biphenyl groups to bend away from their normal orientation in an effort to better accommodate the space allowed, thus resulting in a continuously decreasing interlayer distance. Density should be somewhat lower than expected for close-packed phases, due to ineffective space filling (see Figure 5), and one might even expect some increase in surface area resulting from such porosity. At the extreme compositions 0.1, 0.2, and 0.9 there is some evidence of discontinuous interlayer dilation presumably arising from abutment or “roof collapse” effects.

In the tetravalent phosphonates there is permitted approximately 24 Å² of cross-sectional area per site on the basal surface. Since the area required for a phenyl ring is about 18 Å², there does appear to be room for the suggested bending away from a strictly perpendicular orientation.⁴ In addition, there is likely some flexibility in the inorganic framework that could assist in the redirection of the organic groups yet maintain the lamellar structure.

There is a phenomenon well-known to clay mineralogists called “interstratification” in which mixed phases occur as randomly staged substances.⁵ Whereas each individual layer is of a pure phase, they stack upon one another willy-nilly, yielding broad averaged *d* spacings. While such a corresponding situation could be occurring in the present case, it is considered less likely than the explanation offered above since no variations in density would be expected. On the other

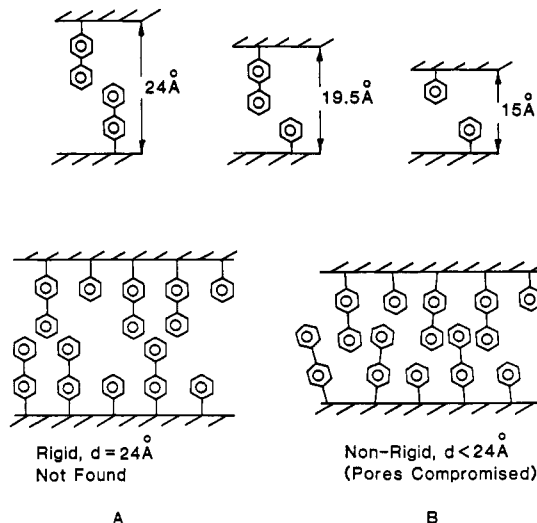


Figure 5. Alternative structures of an intermediate and end members of the series: (top) pure-phase biphenyl, ordered phenyl-biphenyl, and phenyl-phenyl compounds; (bottom) situation for the propped structure (A) and situation for the bending of biphenyl groups, which compromises pores (B).

hand, the remarkable linearity seen in Figure 4 seems less consistent with the rationale presented.

Regardless of which of the two situations is in actuality operating—partial interdigitation or interstratification of pure-phase layers—the data do show that it is possible to prepare mixed-component compounds of differing groups within the interlayer region but that such an approach is not satisfactory for inclusion of significant microporosity.

Registry No. Th(O₃P-C₆H₅)₂, 75406-79-0; Th(O₃P-C₆H₄-C₆H₅)₂, 83947-44-8; Th(O₃P-C₆H₅)(O₃P-C₆H₄-C₆H₅), 83947-45-9.

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Iron Benzoquinone Dioxime Complexes. Electronic Effects on Axial Ligation to Ferrous Dioximes

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The ability of a macrocyclic ligand to “tune” the chemistry of the metal is a recurring theme in metalloporphyrins and related complexes. When substituents do not conjugate directly with the macrocycle π system, the substituent effects are typically small. For example, replacing methyl¹ by phenyl² in bis(glyoxime) (Fe(DMGH)₂ vs. Fe(DPGH)₂) or in tetraimine systems³ (Fe(Me₄[14]tetraeneN₄) (FeTIM) vs. Fe(Ph₄[14]tetraeneN₄) results in minor spectral shifts (less than 50 nm) and changes in axial ligation (spanning about one order of magnitude). The spectra and axial ligation to iron porphyrins vary only slightly for proto-, meso-, deuterio-, diacetyl-,⁴ and tetraphenylporphyrin⁵ and somewhat more for octa-

(4) In the single-component compounds there is not enough room for any significant “interdigitation”. This is borne out by the fact that the interlayer distances are just what would be expected for the bilayered, noninterpenetrating structure.
(5) Reynolds, R. C. In “Crystal Structures of Clay Minerals and their X-Ray Identification”; Brindley, G. W., Brown, G., Eds.; Mineralogical Society: London, 1980; Chapter 4.

(1) Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 590.
(2) Vaska, L.; Yamaji, T. *J. Am. Chem. Soc.* **1971**, *93*, 6673.
(3) Hamilton, D. E.; Lewis, T. J.; Kildahl, N. K. *Inorg. Chem.* **1979**, *18*, 3364.
(4) Traylor, T. G.; White, D. K.; Campbell, D. H.; Berzins, A. P. *J. Am. Chem. Soc.* **1981**, *103*, 4932.
(5) Stanford, M. A.; Swartz, J. C.; Phillips, T. E.; Hoffman, B. M. *J. Am. Chem. Soc.* **1980**, *102*, 4492.