Figure 2. Temperature dependence of the luminescence lifetime of (A) $Ru(bpy)_2(py)_2^{2+}$ and (B) $Ru(bpy)_2(CH_3CN)_2^{2+}$ in dichloromethane.

yield for photoanation is strongly temperature dependent[5] but the reaction is complicated by additional temperature-dependent reactions involving competitive ring closure and chelate loss. There are currently no measurements of the efficiency of the initial ring-opening reaction. In addition to the fact that the overall photosubstitution process of Ru$(bpy)_3^{2+}$ is more complex, the effective symmetry of the disubstituted complexes may be such that the photoactive state in these complexes is inherently lower in energy than in the triply chelated complex. Interestingly, the assignment of the state that is responsible for the temperature dependence of the emission lifetime in $Ru(bpy)_3^{2+}$ as d–d was based primarily on the suppostion that photosubstitution is a consequence of populating that state.[2]

At present, there is little direct evidence to support alternative reaction paths for photoanation. We are, however, currently exploring the possibility of direct population of a d–d state from the initially populated charge-transfer state. Direct population of the d–d state would, in this case, be competitive with population of the emitting CT state. This idea is consistent with the small value and the relative ordering of the emission efficiencies of $Ru(bpy)_2(py)_2^{2+}$ and $Ru(bpy)_2$-$(CH_3CN)_2^{2+}$. In the latter case, 30% of the absorbed photons results in photochemical reactions and is thus not available for emission. In keeping with this trend, the complex Ru-$(bpy)_2(imidazole)_2^{2+}$ exhibits luminescence at room temperature comparable in intensity to that of $Ru(bpy)_3^{2+}$ and has a very low quantum yield for photoanation.

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Layered Compounds with Alternating Organic and Inorganic Layers: Vanadyl Organophosphonates

Sir:

Layered solids consisting of alternating inorganic and organic layers[1-8] are interesting because of their sorptive and catalytic properties. Compounds of this type fall into three main classes. Members of the most common class contain macroanionic inorganic layers of metal oxide or sulfide alternating with layers of charge-balancing organic cations. Examples include clays exchanged with organoammonium cations[2] and amine intercalation compounds of the layered transition-metal oxides and dichalcogenides.[3,4] In the second class, organic ligands are coordinated to transition-metal ions located within the inorganic layers, for example, $NiL_2Ni(C-N)_4$[5] $MoO_3(C_5H_5N)$,[6] and $VOPO_4(C_5H_5N)$.[7] In the third class of compound, organic groups are attached to inorganic layers by covalent bonds. Primary examples are zirconium organophosphonates and organophosphates, $Zr(RPO_3)_2$ and $Zr(ROPO_3)_2$, in which a variety of organic groups (R) are attached to the zirconium phosphate layers by covalent P–C or P–O–C bonds.[8] Compounds of the first two classes are commonly formed by intercalation of the organic groups between the preformed layers of the inorganic host, while compounds of the third class are usually crystallized directly from solutions of ionic precursors.

In recent work, the structure and topochemistry of vanadium hydrogen phosphate, $VO(HPO_4) \cdot 0.5H_2O$, have been elucidated.[9] The structure is composed of layers with hydrogen phosphate OH groups directed into the interlayer space, reminiscent of the structure of zirconium hydrogen phosphate.[10] This structural similarity has led us to attempt the synthesis of vanadium organophosphonates, which would be

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Table I. Lattice Parameters for Vanadium Organophosphonates

compd	a, Å	b, Å	c, Å
$VO(C_6H_5PO_3) \cdot H_2O \cdot C_2H_5OH$	9.96	12.06	9.69
$VO(C_6H_5PO_3) \cdot 2H_2O$	10.03	9.69	9.77
$VO(p\text{-}CH_3OC_6H_4PO_3) \cdot H_2O \cdot C_2H_5OH$	10.05	13.04	9.88
$VO(p\text{-}CH_3OC_6H_4PO_3) \cdot 2H_2O$	10.08	11.27	9.78
$VO(p\text{-}C_6H_5C_6H_4PO_3) \cdot 2H_2O$	9.96	13.94	9.77

analogous to the zirconium compounds in having an organic group replacing the hydroxyl of the hydrogen phosphate. In this paper we report the first members of a new family of vanadium organophosphonates, $VO(RPO_3) \cdot 2H_2O$, which have layered inorganic/organic structures and show unusual intercalation reactions with alcohols.

Phenylphosphonic acid reacts with V_2O_5 in refluxing 95% ethanol to form light blue $VO(C_6H_5PO_3) \cdot H_2O \cdot C_2H_5OH$. The ethanol can be removed by washing the solid with water at 60 °C followed by vacuum drying at 100 °C. Subsequent exposure to ambient moisture gives blue-green $VO(C_6H_5PO_3) \cdot 2H_2O$.[11] Similar reactions of V_2O_5 with (p-methoxyphenyl)phosphonic acid give $VO(p\text{-}CH_3OC_6H_4PO_3) \cdot H_2O \cdot C_2H_5OH$ and $VO(p\text{-}CH_3OC_6H_4PO_3) \cdot 2H_2O$.[12] p-Biphenylylphosphonic acid[13] reacts with V_2O_5 to give a material that appears from initial examination by powder X-ray diffraction to consists of two phases. A single phase, $VO(p\text{-}C_6H_5C_6H_4PO_3) \cdot 2H_2O$, is obtained by washing with water.[14] The X-ray powder diffraction patterns of the new compounds are sharp, indicating their microcrystallinity. The patterns were indexed by using the orthorhombic unit cells listed in Table I. The b lattice parameter corresponds to the interlayer separation and increases as the size of the para substituent on the phenyl group increases. In the hydrates, the b axis expands by 1.58 and 4.25 Å when methoxy and phenyl groups are substituted in the para position of the phenyl group in the phenylphosphonate. The comparable changes in the van der Waals dimensions of the phenylphosphonic acids measured from CPK models are 2.2 and 4.4 Å. These data are consistent with a structure in which the organic groups are nearly perpendicular to the layers and the phenyl groups from opposing layers interpenetrate. The layered structure is further supported by the platelike crystallite morphology observed in scanning electron micrographs, by the enhanced intensities of the $0k0$ diffraction peaks resulting from preferred orientation, and by the alcohol intercalation experiments (below). The a and c lattice parameters are similar for the three compounds, suggesting the same intralayer arrangement of vanadium and phosphorus atoms. The measured densities and the observed cell volumes indicate 4 formula units per unit cell ($Z = 4$).

The new compounds are layered, but their structures are not analogous to that of $VO(HPO_4) \cdot 0.5H_2O$. In the orthorhombic structure of the hydrogen phosphate, which also has $Z = 4$, the intralayer dimensions are 7.42 and 9.61 Å. There
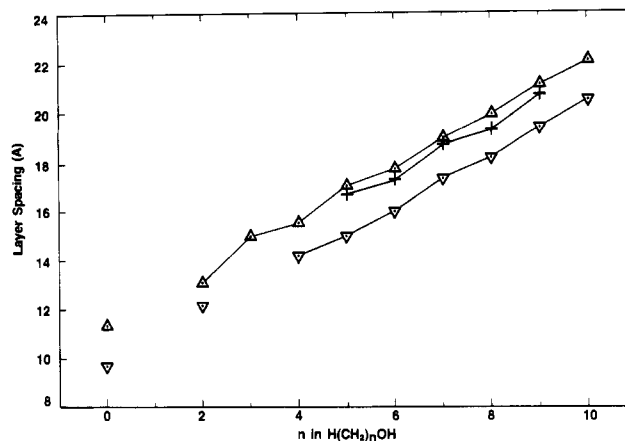

Figure 1. Layer spacings of n-alkanol intercalation compounds of $VO(C_6H_5PO_3) \cdot 2H_2O$ (▽) and n-alkanol (△) and phenylalkanol (+) intercalation compounds of $VO(CH_3OC_6H_4PO_3) \cdot 2H_2O$.

is no distortion of this layer which can enlarge the 7.42-Å axis to the ~10-Å parameter observed in the organophosphonates while maintaining the connectivity of the structure with reasonable V–O and P–O bond lengths. Further, the magnetic susceptibility measured from 4 to 300 K obeys the Curie–Weiss law with $\mu = 1.71$ μ_B and $\Theta = 4.3$ K with little indication of $V^{4+}-V^{4+}$ magnetic interaction.[15] In contrast, the corresponding data for the hydrogen phosphate show pairwise antiferromagnetic exchange interactions below 100 K[9] arising from the presence of the triply bridged vanadium(IV) *pairs* in the structure. The difference between the two structure types probably results from packing constraints imposed by the phenyl groups. Four interpenetrating phenyl groups, each with a van der Waals area of $3.6 \times 6.3 = 23$ Å^2 nearly close-pack on the observed layer are of 98 Å^2 but cannot be accommodated by the smaller layer area of the hydrogen phosphate structure (71 Å^2). We note that in the bilayer structure of $MoO_3(C_5H_5N)$ the pyridine molecules are similarly packed, each occupying a layer surface area of 28 Å^2.[6]

Understanding the details of the connectivity of the $V=O^{2+}$, RPO_3^{2-}, and H_2O groups within the layers requires a complete structure determination and must await large enough single crystals. However, the data above suggest a structure in which VO_6 octahedra are isolated from each other and have connectivity $VO_{1/1}O_{3/2}(H_2O)_{2/1}RPO_{3/2}$. The TGA data show that the water molecules are in different environments. One molecule of water is lost below 100 °C and the second at about 230 °C. This difference suggests the presence of water molecules coordinated both cis and trans with respect to the vanadyl oxygen atom. We propose that the cis-coordinated water molecule occupies a position within the layer and with three oxygen atoms from separate phosphonate groups completes the equatorial coordination of the vanadium octahedron. The introduction of one water molecule per vanadium into the layer of the hydrogen phosphate structure is sufficient to account for the increase in layer area required to accommodate the phenyl groups.

Further supporting this structural model, vanadyl phenylphosphonate and vanadyl (p-methoxyphenyl)phosphonate intercalate alcohols. When reacted with excess alcohol at 95–100 °C, they take up one alcohol molecule per formula unit. The b axis expands while the a and c parameters remain almost unchanged. Phenyl alcohols, $C_6H_5(CH_2)_mOH$, are also intercalated for $m > 0$. In Figure 1, the b axis spacings of n-alkanol intercalated $VO(C_6H_5PO_3) \cdot 2H_2O$ and $VO(p\text{-}CH_3OC_6H_4PO_3) \cdot 2H_2O$ are plotted against the carbon number

(11) V_2O_5 (6 g, 33 mmol) and $C_6H_5PO_3H_2$ (16.4 g, 66 mmol) are refluxed in 95% EtOH for 6 d. The product (92%) is isolated by filtration. The organic oxidation product $CH_3CH(OEt)_2$ is observed by GLC in the supernatant. Anal. Calcd for $VO(C_6H_5PO_3) \cdot H_2O \cdot C_2H_5OH$: C, 33.47; H, 4.56; P, 10.79; V, 17.74. Found: C, 32.39; H, 4.22; P, 11.2; V, 18.5. The P/V ratio is 1, but the absolute values of P and V are high and C is low, suggesting that the ethanol content is less than one molecule per vanadium. The same compound could be prepared from excess $C_6H_5PO_3H_2$ or from $VOSO_4 \cdot 3H_2O$ or $VO(acac)_2$ as the vanadium source. Anal. Calcd for $VO(C_6H_5PO_3) \cdot 2H_2O$: C, 27.82; H, 3.50; P, 11.96; V, 19.66. Found: C, 27.81; H, 3.45; P, 11.6; V, 19.9.

(12) Yield: 97%. Anal. Calcd for $VO(CH_3OC_6H_4PO_3) \cdot H_2O \cdot C_2H_5OH$: C, 34.09; H, 4.77; P, 9.77; V, 16.06. Found: C, 33.97; H, 4.51; P, 9.96; V, 16.14. Calcd for $VO(CH_3OC_6H_4PO_3) \cdot 2H_2O$: C, 29.08; H, 3.84; P, 10.71; V, 17.62. Found: C, 29.65; H, 4.07; P, 10.92; V, 17.69.

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(14) Yield: 94%. Anal. Calcd for $VO(C_{12}H_9PO_3) \cdot 2H_2O$: C, 43.01; H, 3.91; P, 9.24; V, 15.20. Found: C, 43.03; H, 3.91; P, 9.32; V, 15.11.

(15) Magnetic susecptibility was measured by Dr. D. C. Johnston using the Faraday method.

of the *n*-alkanol. Phenylalkanol intercalation compounds of VO(*p*-CH$_3$OC$_6$H$_4$PO$_3$)·2H$_2$O are included by assuming the effective chain length of the phenyl group is equivalent to four methylene groups ($n = m + 4$). The data for methanol are omitted because single phases could not be produced, possibly due to some replacement of both water molecules in the dihydrate structure. The slopes of the lines in Figure 1 given the average layer spacing increase for each additional methylene group in the alkanol chain. The data for $n > 3$ give values of 1.03–1.09 Å/CH$_2$ unit. Since the maximum increase is 1.27 Å/CH$_2$ unit for an all trans alkyl chain, the data indicate a single layer of alkanol molecules between the vanadium phosphorus layers, with the alkanol chains inclined at an angle of 54–59°. The mean angle is close to that predicted (55°) for an all trans chain oriented so that the first bond is perpendicular to the layers. The alternation in spacing between odd and even values of *n*, which is most pronounced for phenyl alcohols, is also expected from this orientation. Monolayer formation and the stoichiometry of one alkanol molecule per formula unit suggest that in the organophosphonates the intercalant molecules are associated with specific sites on the interlayer surface. This behavior is in contrast to that observed in alcohol intercalation compounds of other layered solids, for example, *α*-VOSO$_4$,[16] Zr(HPO$_4$)$_2$,[17] and clays,[18] which intercalate alkanols in bilayer arrangements.

The synthetic and intercalation chemistry of vanadyl organophosphonates is currently being extended to alkyl systems and also to organic substituents that introduce functional groups into the interlayer space, thereby enabling further chemical modification.

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Models of Oxidized Heme Proteins. Preparation and Characterization of a *trans*-Dioxoruthenium(VI) Porphyrin Complex

Sir:

High-valent iron porphyrin complexes have been suggested for the oxidized states of the peroxidases,[1] and similar intermediates have been implicated in the oxygen-transfer reactions of cytochrome P-450[2] and the dioxygen reduction of cytochrome oxidase.[3] An understanding of the redox chemistry mediated by these enzymes has been hampered by the insta-
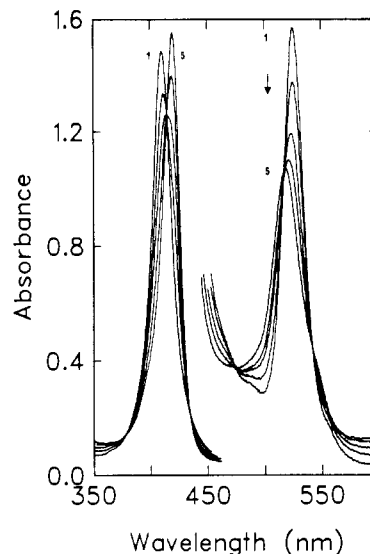

Figure 1. Visible spectral changes resulting from the titration of 6.7 × 10⁻⁶ M RuTMP(CO) in CH$_2$Cl$_2$ with increments of mCPBA. Equivalents of mCPBA present in solutions: (1) 0; (2) 0.5; (3) 1.0; (4) 1.5; (5) 1.9.

bility of these oxidized iron–heme intermediates and by the lack of simple chemical models for these reactive states. Synthetic examples of an oxoiron(IV) prophryin[4] and an oxoiron(IV) porphyrin cation radical[5] are now known; however, the thermal instability of each has prevented their isolation as pure solids. The periodic relationship of iron and ruthenium suggests that the latter could provide stable examples of oxidized metalloporphyrins. The oxidation of ruthenium(II) porphyrin complexes to *μ*-oxoruthenium(IV) dimers has recently been described,[6] and the reactivity of ruthenium(III) porphyrins for the catalytic oxygenation of hydrocarbons has been noted.[7] An oxoruthenium(IV) porphyrin cation radical was suggested as the reactive intermediate in this system. We describe here the isolation and characterization of the first *trans*-dioxoruthenium(VI) porphyrin complex.

The addition of mCPBA to a methylene chloride solution of (5,10,15,20-tetramesitylporphyrinato)ruthenium(II) carbonyl[8] [RuTMP(CO) (**1**)] led to the appearance of a new species, **2**. The spectrophotometric titration of a 6.7 × 10⁻⁶ M solution of RuTMP(CO) with increments of mCPBA showed a smooth conversion of **1** to **2**, which was complete upon the addition of 2.0–2.5 equiv of mCPBA (Figure 1). The isosbestic points in the visible spectra at 380, 416, 478, 518, and 543 nm indicate that only **1** and **2** were present in appreciable quantities during this transformation. The identical reaction was observed when iodosylbenzene was used as the oxidant.

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