Acknowledgment. We acknowledge the support of the Welch Foundation and the National Science Foundation (Grant NSF 8708625).

Supplementary Material Available: Listings of crystallographic parameters, atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and hydrogen coordinates and isotropic thermal parameters for **1** (6 pages); a listing of observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

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Intercalation in the Linear-Chain Compound $MoO_2HPO_4{\cdot}H_2O$

The structure of hydrated molybdenyl hydrogen phosphate, $MoO_2HPO_4{\cdot}H_2O$ consists of bent MoO_2 groups coordinated by water molecules and linked into double chains by tetrahedral PO_3OH units. This one-dimensional material has been shown to undergo reversible intercalation reactions with a variety of small organic molecules, particularly alcohols, and water to form new crystalline phases in which the molybdenyl phosphate chains remain essentially unaltered. The molybdenum coordination in the host is approximately octahedral with three bonds to hydrogen phosphate groups, a trans pair delineating the chain, and the other in the $MoO_2(OH_2)$ plane connecting to the other half of the double chain.[1] Powder X-ray diffraction and infrared data demonstrate that the intercalated species are hydrogen-bonded between the inorganic chains.

$MoO_2HPO_4{\cdot}H_2O$[1] shows structural similarities to $UO_2HPO_4{\cdot}H_2O$,[2] β-$VOHPO_4{\cdot}2H_2O$,[3] $Zr(HPO_4)_2{\cdot}nH_2O$,[4] and particularly $VOHPO_4{\cdot}4H_2O$,[5] where tetrahedral (hydrogen) phosphate groups link together the approximately octahedrally coordinated transition metals. As the metal oxidation state rises in this family of compounds, the coordination environment of the metal ion becomes increasingly distorted, with one short vanadium–oxygen bond in β-$VOHPO_4{\cdot}2H_2O$ and two molybdenum–oxygen double bonds in $MoO_2HPO_4{\cdot}H_2O$. The uranium and zirconium materials together with β-$VOHPO_4{\cdot}2H_2O$ have two-dimensional layer structures, but $VOHPO_4{\cdot}4H_2O$ has a double-chain structure similar to that of molybdenyl hydrogen phosphate. Intercalation reactions with a range of small organic molecules[6–9] are well-known in this type of compound. For example, materials of composition $VOPO_4{\cdot}(1–2)ROH$ may be synthesized from anhydrous $VOPO_4$ via a vapor-phase reaction with ROH; the alcohol molecules in these intercalates may be displaced by water. Other vanadium compounds that undergo intercalation reactions with alcohols are vanadium organophosphonates[10,11] and layered vanadium sulfates.[12]

Table I

intercalated species	reacn time at 298 K in vapor	stoichiom of product
H_2O	3 days	$MoO_2HPO_4{\cdot}3.9(\pm0.1)H_2O$
CH_3OH	3 days	$MoO_2HPO_4{\cdot}H_2O{\cdot}2.0(\pm0.2)CH_3OH$
CH_3OH	3 days and 1 h (air)	$MoO_2HPO_4{\cdot}H_2O{\cdot}1.0(\pm0.05)CH_3OH$
CH_3CH_2OH	1 month	$MoO_2HPO_4{\cdot}H_2O{\cdot}0.6(\pm0.1)CH_3CH_2OH$
$(CH_3)_2CHOH$	3 months	$MoO_2HPO_4{\cdot}H_2O{\cdot}1.0(\pm0.1)$-$(CH_3)_2CHOH$

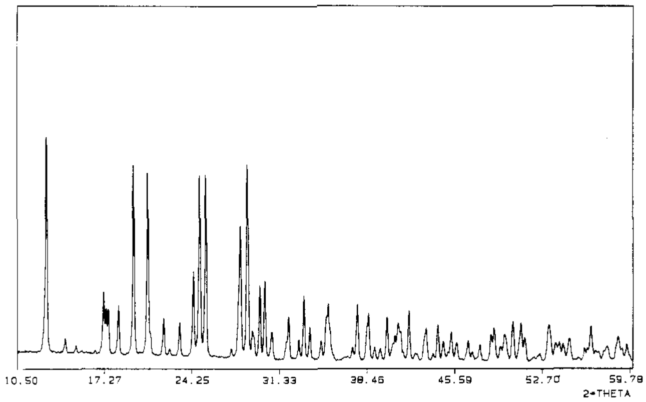

Figure 1. Powder X-ray diffraction data collected from $MoO_2HPO_4{\cdot}4H_2O$ in the 2θ range 10–60° with Cu $K\alpha_1$ radiation.

$MoO_2HPO_4{\cdot}H_2O$ was prepared by following the method described by Kierkegaard.[13] The intercalation of alcohols and additional water was achieved by equilibration of the crystalline solid with the vapor above the liquid in a closed apparatus. Reactions with water and methanol vapor were generally complete within 3 days; however, reactions with the larger species (ethanol, 2-propanol) took several weeks. Heating $MoO_2HPO_4{\cdot}H_2O$ with DMSO resulted in a different type of reaction, in which water was displaced from the solid. The progress of the reaction was most easily followed by using Raman spectroscopy. Although minor shifts (10–15 cm^{-1}) were observed in most cases, the bands are strong and sharp; particularly diagnostic in determing the extent of reaction is the disappearance of the substrate band at 885 cm^{-1} (presently unassigned), which is not observed in any of the intercalates.

Successful reactions have been achieved with a large range of alcohols and amines, but we report here our results for the better characterized water, methanol, ethanol, and 2-propanol intercalates. Table I summarizes the stoichiometry of the intercalation products as determined from weight changes during the uptake reaction, with thermogravimetric and C, H, N analyses. For methanol an initial product of approximate formula $[MoO_2HPO_4{\cdot}H_2O].2CH_3OH$ was converted to a more stable 1:1 intercalate at 30 °C after 1 h in air. In general for the alcohol intercalates the initial product seemed to undergo further slow transformations when removed from the saturated vapor.

Powder X-ray diffraction data were collected for each of the materials with use of an INEL position sensitive detector based system. The data obtained for the higher hydrate $[MoO_2HPO_4{\cdot}H_2O]{\cdot}3H_2O$ is shown in Figure 1. A feature of all the diffraction patterns, including the parent material, is a strong reflection at approximately 28.1° (*d* spacing 3.152 Å), which

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Table II. Cell Dimensions and Densities

compd	refined cell params[a]	density, g cm^{-3}	
		calcd	measd
$MoO_2HPO_4 \cdot H_2O$ (**1**)	6.986, 6.344, 6.710 90.0, 109.9, 90.0	2.90	2.89
$MoO_2HPO_4 \cdot 3.94(\pm 0.1)H_2O$	9.436 (1), 6.312 (2), 7.716 (1) 108.15 (2), 75.32 (1), 97.70 (2)	2.31	2.32
$MoO_2HPO_4 \cdot H_2O \cdot (CH_3)_2COH$	13.07 (2), 6.349 (4), 8.29 (3) 90.0, 106.5 (2), 90.0	3.04	2.7[b]
$MoO_2HPO_4 \cdot H_2O \cdot CH_3OH$	6.983 (4), 6.342 (2), 16.96 (2) 90.0, 90.0, 90.0	2.42	2.39

[a] The first row for each compound entry gives the *a*, *b*, and *c* values (in Å) and the second row the α, β, and γ values (in deg). [b] This sample was unstable and decomposed slowly in the haloalkane flotation mixture.

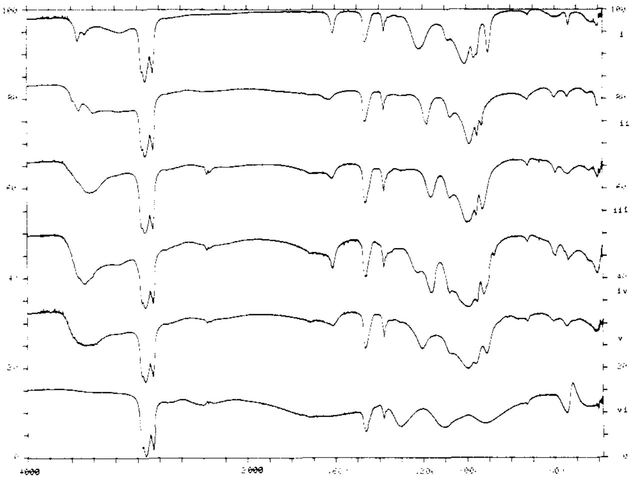

Figure 2. Infrared spectra of (i) $MoO_2HPO_4 \cdot H_2O$, (ii) $MoO_2HPO_4 \cdot 4H_2O$, (iii) $MoO_2HPO_4 \cdot H_2O \cdot CH_3OH$, (iv) $MoO_2HPO_4 \cdot H_2O \cdot C_2H_5OH$, (v) $MoO_2HPO_4 \cdot H_2O \cdot (CH_3)_2CHOH$, and (vi) KH_2PO_4.

corresponds to half the repeat distance along the molybdenyl phosphate chains. The indexing of the data was attempted by using the VISSER program[14] following careful calibration of the apparatus. High figures of merit were found for the materials $[MoO_2HPO_4 \cdot H_2O] \cdot CH_3OH$ and $[MoO_2HPO_4 \cdot H_2O] \cdot 3H_2O$; fewer good-quality peaks were obtained for $[MoO_2HPO_4 \cdot H_2O] \cdot (CH_3)_2CHOH$, but the data could be successfully indexed manually. For these phases the data were fully indexed and the cell parameters refined; results are summarized in Table II. Densities calculated from these unit cells and the determined compositions are also compared with those measured by flotation in Table II. Indexation of the 1:2 methanol and 1:1 ethanol intercalates was of poorer quality, and we are unsure of the true unit cells in these materials.

Infrared data, collected on a Perkin-Elmer 1700 FT instrument for each of the materials, are shown in Figure 2 together with those of the parent compound and KH_2PO_4. The absorption at 3150 cm^{-1} in $MoO_2HPO_4 \cdot H_2O$ has been assigned to the OH stretch of the strongly hydrogen bonded hydrogen phosphate group (OH- - -O = 1.75 Å) which links the double chains together. Following intercalation this band weakens considerably, indicating that this hydrogen bond is broken, consistent with the intercalation of the organic molecules between the chains. The ethanol and methanol intercalates show some absorption at around this wavenumber, probably indicating a strongly hydrogen bonded OH is present after the reaction. A broad absorption is apparent around 3400 cm^{-1}, which would indicate the formation of several weaker hydrogen bonds in the intercalates probably between the OH groups on the guest species and molybdenyl phosphate chains. The strong absorption at 1620 cm^{-1} remains in all the spectra, indicating that the molybdenyl remains coordinated to water. In addition, very broad, weak bands at around 2300 and 1700 cm^{-1} are strongly reminiscent of the "type I"[15] spectrum of KH_2PO_4 and may indicate that very strong hydrogen bonds (OH- - -O = 1.5 Å) are formed between the hydrogen phosphate and the intercalate OH groups.

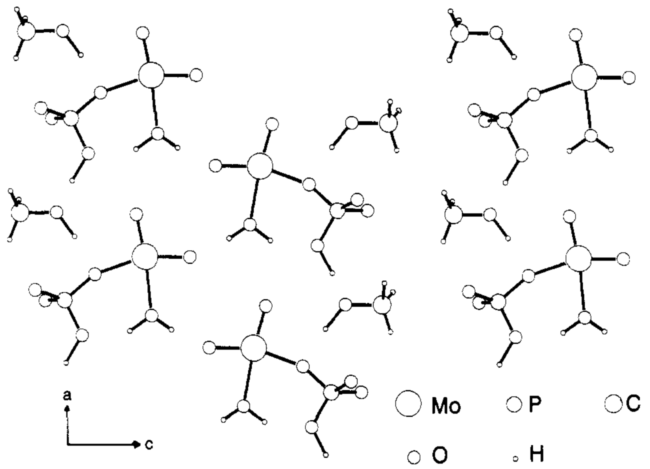

Figure 3. Section of the proposed structure of $MoO_2HPO_4 \cdot H_2O \cdot CH_3OH$ viewed down the molybdenyl hydrogen phosphate double chains (larger units). Interleaving sections are related by a center of inversion, generating the double chains along *b* with alternating approximately octahedral molybdenum and tetrahedral phosphorus as in the parent material (**1**). The smaller methanol molecules form a double row in the *a* direction strongly hydrogen bonded to the hydrogen phosphate group.

In all cases the reactions were found to be reversible; intercalated products heated in air to 70 °C reverted to the parent structure as shown by powder X-ray diffraction.

Discussion. The intercalates of methanol and the higher hydrate are the most highly crystalline products and have thus been easiest to characterize. The unit cell of $MoO_2HPO_4 \cdot 4H_2O$ can be derived from that of the parent material by tilting of the molybdenyl chains and some expansion of the *a* and *c* directions to accommodate the additional water molecules. We intend to investigate this material further as a potential fast proton conductor by analogy with α-zirconium phosphate and hydrogen uranyl phosphate which have well-characterized high proton mobility.[16] The parent compound $MoO_2HPO_4 \cdot H_2O$ is a relatively poor proton conductor, as it has no interchain water molecules that can help in proton transfer through a Grotthus type mechanism.[17] The unit cell of $[MoO_2HPO_4 \cdot H_2O] \cdot CH_3OH$ can be obtained from that of the parent compound by an expansion of 0.25 Å along the *a* direction and doubling of *c′* (the parent compound cell diagonal) to give a new orthorhombic cell. Systematic absences in the X-ray powder pattern indicate that the configuration of some of the molybdenyl phosphate chains has become inverted, probably by proton migration. A proposed structure in the space group *Pnma* is shown in Figure 3, where methanol has become incorporated in channels between alternate layers of the molybdenyl hydrogen phosphate chains. An X-ray pattern calculated on this basis is shown in Figure 4 in comparison with the experimental data and is in good

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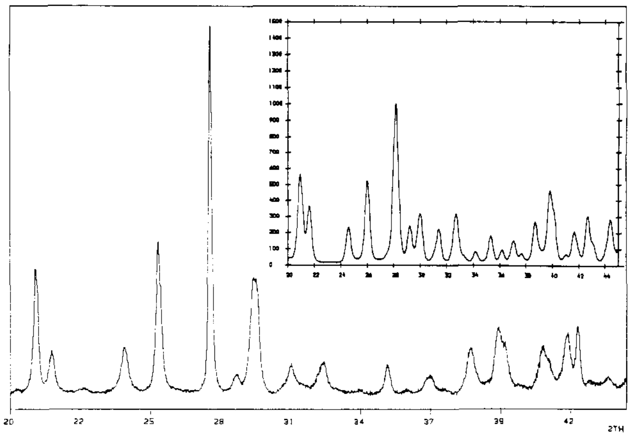

Figure 4. Powder X-ray diffraction data obtained from $MoO_2HPO_4 \cdot H_2O \cdot CH_3OH$. The inset gives the calculated pattern over the same angular range for the structure shown in Figure 3.

agreement, supporting this model. Structure determination with high-resolution powder X-ray and neutron diffraction methods is in progress.

$MoO_2HPO_4 \cdot H_2O$ has been shown to undergo reversible intercalation reactions; as such this system may provide a vehicle for the preparation of mixed inorganic–organic polymers with alternating molybdenyl phosphate and carbon-based chains.

Acknowledgment. We thank the SERC for grants in association with this work and D. B. Currie for assistance with the powder X-ray work.

Supplementary Material Available: Table SI, listing the atomic coordinates used for the calculated powder X-ray diffraction pattern in Figure 4 (1 page). Ordering information is given on any current masthead page.

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Stereoselective Electron-Transfer Reaction between Ferrocytochrome *c* and Tris(acetylacetonato)cobalt(III)

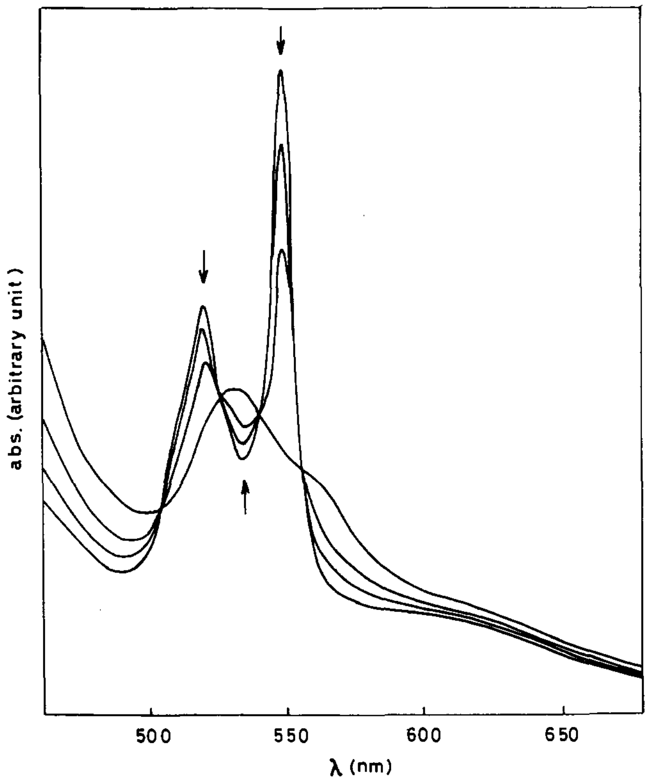

Figure 1. Absorption spectral changes in the $Co(acac)_3$ reduction by cyt *c*(II). Reaction conditions: pH 4.0,[4] $\mu = 0.1$ M, [cyt *c*(II)] = 2.0×10^{-5} M, [$Co(acac)_3$] = 2.5×10^{-3} M. Spectra were taken at the following times (h): 0, 0.5, 2, 38.

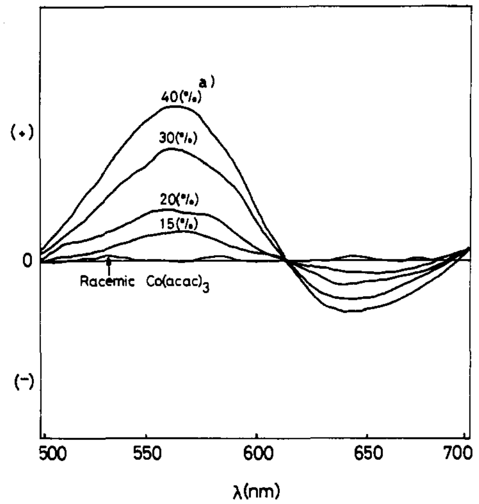

Figure 2. CD spectra of remaining $Co(acac)_3$ ((a) ethanol volume percent). Reaction conditions: pH 4.0,[4] $\mu = 0.1$ M.

In the last decade, there has been considerable interest in electron-transfer reactions between biological molecules and transition-metal complexes,[1] because many biological molecules participating in electron-transfer reactions include transition-metal ions in their important sites. However, stereoselectivity has not been investigated yet in such electron-transfer reactions,[2] whereas high stereoselectivity is one of the important characteristic features of biological reactions. In the present work, a stereoselective electron-transfer reaction between ferrocytochrome *c* (cyt *c*(II)) and the hydrophobic tris(acetylacetonato)cobalt(III), $Co(acac)_3$, is investigated. $Co(acac)_3$ is selected here as a substrate, because

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