Chemistry of Materials **1990**, *2*, 91-93

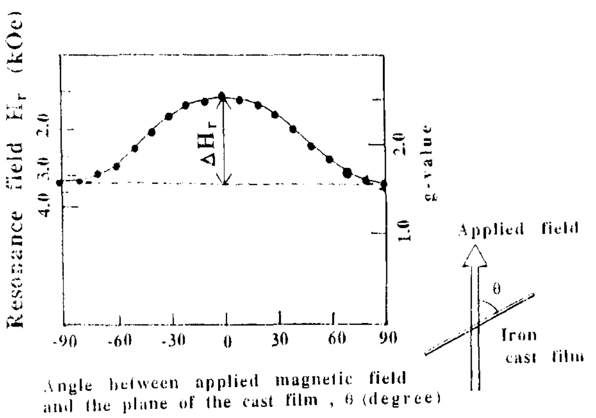

Figure 4. Angular dependence of the resonance magnetic field of a composite cast film of $FeCl_2$.

magnetic anisotropy. The composite cast films were maintained at given temperatures (20–80 °C) for an hour and their ESR spectra were measured at room temperature. The ΔH_r remained unchanged up to 60 °C but drastically decreased from 1.3 to 0.3 kOe at the temperature region between 60 and 80 °C. The gel-to-liquid crystal phase transition of the matrix bilayer was shown to occur at 68 °C by differential scanning calorimetry.[9] X-ray diffraction of this composite film gave peaks only up to the second order after heat treatment at 80 °C for an hour, indicating that the multilayered structure of the cast film became disordered by heat treatment at temperatures above the phase transition. Therefore, the observed magnetic anisotropy is produced by anisotropic crystal growth during the hydrolysis of $FeCl_2$. The magnetite particles formed remain anisotropic due to the regular, multilayer structure of the matrix film. However, once the multilayer structure is disordered by its phase transition to the liquid-crystalline state, the original orientation of magnetite particles is lost.

In this paper, the in situ formation of iron compounds in cast multibilayer films and their magnetic properties are described. Magnetite was produced as confirmed by electron diffraction. The magnetic anisotropy of iron oxide composite film is achieved by ordered orientation of magnetite particles in a ordered multibilayer film.

Acknowledgment. We thank Dr. T. Katuki of Riken Denshi Co. for the VSM measurement.

Registry No. Fe_3O_4, 1317-61-9.

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Hydrothermal Synthesis and Single-Crystal Structural Characterization of the Layered Vanadium(IV) Phosphate $VOC_6H_5PO_3 \bullet H_2O$

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Metal organophosphonates form a group of layered solid compounds with alternating organic and inorganic layers. Such compounds exhibit interesting sorption and catalytic properties and serve as models for organic/inorganic interfaces.[1,2] Vanadyl organophosphonates have been shown to intercalate alcohols by coordination of the intercalating molecule to the vanadium atom in the inorganic vanadium phosphate layer.[3] Previous interpretation of the mechanisms of these intercalation reactions has relied on assessment of the variation in unit cell dimensions determined by powder X-ray diffraction data as both the size of the organic group attached to phosphorus and the intercalating alcohol molecule were varied. Detailed structural information has been unavailable due to the lack of suitable single crystals for X-ray analysis, despite numerous and varied attempts at crystal growth. We have now found that crystals of vanadium organophosphonates and the corresponding arsenates can be grown under hydrothermal conditions. In this report, we describe the hydrothermal synthesis and single-crystal structure of $VO(C_6H_5PO_3)\cdot H_2O$ and compare its structure and properties with a phase of similar composition previously described.[3a]

An excess (0.952 g) of $C_6H_5PO(OH)_2$ was added to 0.30 g of V_2O_3 (both reagents obtained from Alfa, V:P = $^2/_3$), and the mixture[4] was placed in a 23-mL Teflon-lined autoclave (Parr Instruments). The reaction vessel was filled to 80% capacity with distilled water, sealed, and maintained at 200 °C and autogenous pressure for 4 days. At the end of this period the resulting platy, light green solid (0.660 g, 68.5% yield based on V) was removed, washed several times with distilled water (a blue filtrate indicated the presence of unreacted VO^{2+}), and dried in air at ambient temperature.

Powder X-ray diffraction analysis indicated a single-phase, layered material had been produced with multiple orders of a 14.2-Å layer spacing readily apparent. Chemical analysis[5] suggested the formula $VOC_6H_5PO_3\cdot H_2O$. Thermogravimetric analysis (2 °C/min) in air showed a multistep weight loss starting at 200 °C corresponding to loss of a water molecule followed by loss and/or reaction of the organic component. The total weight loss observed (31.8%) corresponded to complete conversion of the material to $VOPO_4$. A crystal of $VOC_6H_5PO_3\cdot H_2O$ of reasonable quality was selected for structural characterization[6] by X-ray crystallography after survey of a large number of inferior crystals that were twinned along the layer stacking axis. Despite the modest quality of the data obtained, a consistent structural solution was found.

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(4) Similar experiments substituting V_2O_4 and $VOSO_4$ as vanadium sources resulted in polycrystalline materials (87.1% and 41.5% yields, respectively); V_2O_5 as starting reagent produced low yields (24.9%) of single-crystal material. Powder X-ray diffractograms were identical in all cases with those obtained from V_2O_3 generated samples.

(5) Bulk elemental analysis: 20.38% V, 12.74% P, 29.87% C, 2.90% H. Calcd for $VPO_5C_6H_7$: 21.13% V, 12.85% P, 29.90% C, 2.92% H.

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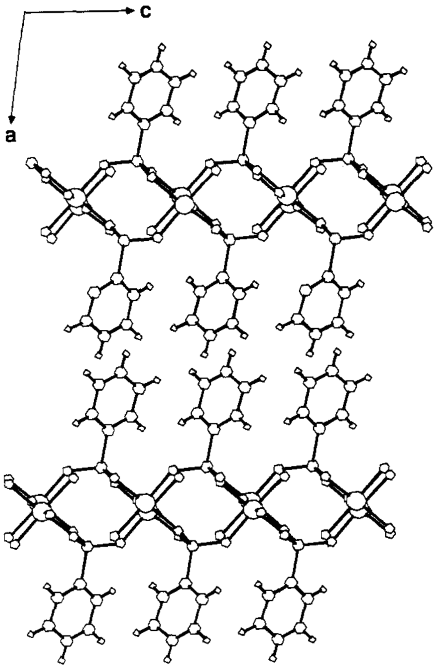

Figure 1. View of the *ac* plane of $VOC_6H_5PO_3{\cdot}H_2O$ showing the vanadium/phosphorus oxide layer separated by a bilayer of phenyl groups.

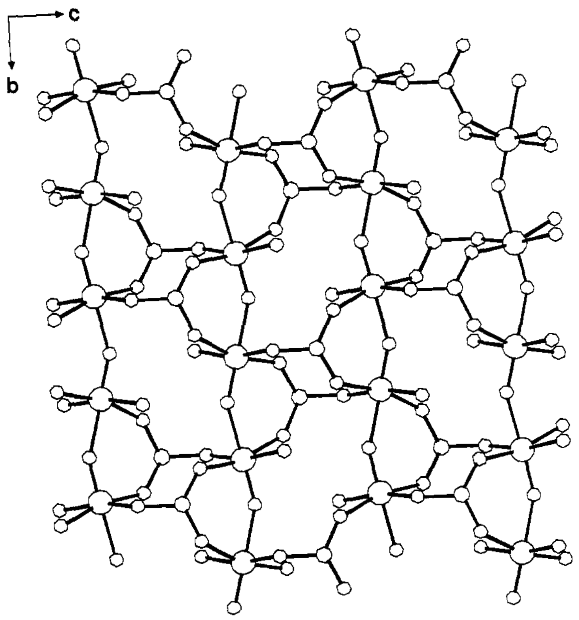

Figure 2. View of the *bc* plane of $VOC_6H_5PO_3{\cdot}H_2O$ illustrating the -V-O-V- chains of the corner-sharing VO_6 octahedra. The phenyl groups, which occupy the fourth coordination site of each phosphorus tetrahedron, have been omitted for clarity. The unshared oxygen atom in each vanadium octahedron is a water molecule.

The structure of $VOC_6H_5PO_3{\cdot}H_2O$ consists of layers of corner-sharing VO_6 octahedra and PO_3C tetrahedra. Phenyl groups (Figure 1) extend out from both sides of the oxide layer, resulting in a layer repeat distance of 14.14 (2) Å. Each of these groups is anchored to the layer by a P–C covalent bond, with the phenyl carbon atom occupying the fourth coordination site of each phosphate tetrahedron. The oxide layer (Figure 2) is comprised of corner-sharing VO_6 octahedra and phosphate tetrahedra. The octahedra share an axial oxygen, forming —V=O—V— chains that run parallel to the *b* axis within the layer. These chains have alternating short (1.610 (9) Å) and long (2.14 (1) Å) V–O bonds. Each chain is separated from the next by phosphate tetrahedra, which bond to two adjacent vanadium oxide octahedra in one chain and a single VO_6 in a neighboring chain. Each octahedron in a chain shares a phosphate tetrahedron with the VO_6 group on either side of it, introducing "kinks" into the —V=O—V— chains (∠V-O-V = 148.4 (5)°). The chains are similar to those found in β-$VOPO_4$.[7] The fourth bond in the phosphate tetrahedron extends into the interlayer space to the carbon atom of a phenyl group. A molecule of water completes the coordination sphere of the vanadium octahedron, occupying a position trans to the phosphate tetrahedron which links the vanadium atom to two VO_6 groups in the adjacent —V=O—V— chain.

We previously reported[3a] the synthesis of the dihydrate of vanadyl phenylphosphonate, $VO(C_6H_5PO_3){\cdot}2H_2O$, by the reaction of V_2O_5 with phenylphosphonic acid in refluxing 95% ethanol/water, which yielded single crystals of inadequate size for structure determination. However, powder X-ray diffraction data from the microcrystalline material established that the phase was a layered compound with orthorhombic cell constants a = 10.03 Å, b = 9.69 Å, and c = 9.77 Å, where the *b* lattice constant corresponds to the interlayer separation. Indirect evidence from magnetic and thermogravimetric data, from the intercalation behavior with alcohols, and from structural considerations suggested the structure, which can be described as $VO_{1/1}O_{3/2}(H_2O)_{2/1}C_6H_5PO_{3/2}$, is closely related to that of the mineral newberyite, $MgHPO_4{\cdot}3H_2O$,[8] shown in Figure 3. In $VO(C_6H_5PO_3){\cdot}2H_2O$ the phenyl groups from adjacent layers interpenetrate, and two water molecules are coordinated in positions trans and cis to the vanadyl oxygen atom. These water molecules can be removed thermally, at 100 and 230 °C, respectively. Removal of both water molecules results in a loss of crystallinity that is not recovered by annealing below the temperature at which the compound decomposes (350 °C). In contrast the trans water molecule can be reversibly intercalated below 230 °C.

The inorganic layer portion of the crystal structure of $VOC_6H_5PO_3{\cdot}H_2O$ is closely related to that proposed for the dihydrate. However, the difference of one water molecule in the vanadium coordination sphere drastically alters the way in which the phenyl groups pack in the interlayer. Within the inorganic layer, the vanadium atoms which are coordinated $VO_{1/1}O_{3/2}(H_2O)_{2/1}$ in the dihydrate become $VO_{5/2}(H_2O)_{1/1}$ in the monohydrate through the formation of —V=O—V— chains. Several other vanadium phosphates,[9] e.g., $VOPO_4{\cdot}2H_2O$ and $VO(HPO_4){\cdot}{}^1/_2H_2O$, show this general type of dehydration behavior, though in these

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(6) Due to the layered nature of $VOC_6H_5PO_3{\cdot}H_2O$, crystals of the material were prone to flaking, which complicated solution of the structure. The structure was solved by Molecular Structure Corp., Woodlands, TX. Crystal data: monoclinic, $C2/c$ (No. 15), a = 28.50 (3) Å, b = 7.18 (2) Å, c = 9.42 (2) Å, β = 97.1 (2)°, V = 1912 (8) Å^3, Z = 8, D(calcd) = 1.661 g/cm^3, (Mo Kα)λ = 0.71069 Å, T = 23 °C. A Rigaku AFC6R diffractometer, with graphite monochrometer and 12-kW rotating anode generator, was used to collect 1868 reflections ($2\theta < 50°$) on a lime-green, plate-shaped crystal (0.45 × 0.45 × 0.05 mm). Of these, 1828 were unique, R_{int} = 0.078, and 1092 observed ($I > 3\sigma(I)$) with 118 variable parameters. An empirical absorption coefficient, using the program DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158) was applied to the data which resulted in transmission factors between 0.60 and 1.42. The structure was solved by direct methods and refined by full-matrix least-squares refinement; all non-hydrogen atoms were refined anisotropically. R = 0.091, R_w = 0.109, GOF = 3.03. Highest peak on the final difference Fourier map: 0.96 e$^-$/Å^3. All computations were performed using TEXSAN (TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985).

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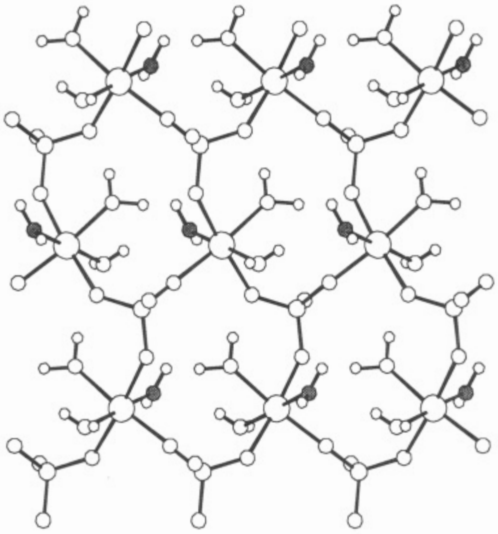

Figure 3. View of the structure of newberyite, $MgHPO_4{\cdot}3H_2O$.[8] In the structure proposed for $VO(C_6H_5PO_3){\cdot}2H_2O$, V replaces Mg in newberyite, a phenyl group replaces the hydroxyl group on phosphorus, and the stippled water molecule is replaced by a vanadyl oxygen atom.

examples condensation occurs between layers rather than within a single layer. The formation of chains within a layer results in an available area of 68 Å^2 to accommodate two pendant phenyl groups on each side of the layer. Each phenyl group has van der Waals dimensions of approximately $3.6 \times 6.3 = 23$ Å^2, consequently phenyl groups from adjacent layers cannot interpenetrate completely but instead form a bilayer arrangement as shown in Figure 1. In contrast, the presence of an extra water molecule coordinated to vanadium in the dihydrate structure increases the layer area to 98 Å^2, sufficient to allow a structure with interpenetrating phenyl groups.

The magnetic susceptibilities of both compounds were measured over the temperature range 4–300 K. The reciprocal susceptibility data for the dihydrate were linear over the whole temperature range, while corresponding data for the monohydrate exhibit an increase in inverse susceptibility below ~15 K, reflecting antiferromagnetic coupling along the —V═O—V— chains. At higher temperatures both compounds have susceptibilities close to the value calculated for V^{4+} ions with $S = {}^1/_2$ and $g = 2$. The detailed form of $\chi(T)$ for the monohydrate has not yet been fully analyzed but will be described in detail in a future publication.[10]

The similarity between the two structures suggests that they might be interconvertible. Dehydration of the dihydrate below 210 °C does not lead to structural rearrangement, and intercalation of alcohols or water into the resulting monohydrate remains a reversible process. Attempts to break the —V═O—V— chains in the hydrothermally synthesized monohydrate have been partially successful. For example, a very slow reaction with hexanol is observed at 150 °C which may indicate reformation of the dihydrate type layers.[11] In principle, the two structures can be interconverted topotactically without breaking any bonds other than those between the trans water molecule and the vanadium atom. In practice, the two phases are difficult to interconvert below the temperature at which the cis water molecule is lost because of the extensive reorganization of the structure required by the repacking of the organic groups. The formation of the two phases under the different synthetic conditions can be understood. The dihydrate structure is obtained in the presence of ethanol which is incorporated during the reaction coordinated trans to the vanadyl oxygen. The presence of this coordinating molecule stabilizes formation of the more open dihydrate layer structure. In a subsequent step this ethanol molecule is replaced by water to form the dihydrate. The monohydrate is formed at temperatures above the decomposition temperature of the dihydrate.

The layered compound $VOC_6H_5PO_3{\cdot}H_2O$ has been prepared and characterized by single-crystal X-ray diffraction. The structure is consistent with and supports the previously proposed structural model for the dihydrate. The two structures are similar in the V–P–O connectivity but are substantially different in the organization of the organic interlayers. Comparison of the two compounds illustrates the complex interplay that occurs between the inorganic layer connectivity and the interlayer organic packing in determining the overall structure of systems with alternating inorganic and organic layers.

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Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, least-squares planes, and bond distances and angles and a diagram showing thermal ellipsoids and atom labels (6 pages); observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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[11] Treatment of powdered $VOC_6H_5PO_3{\cdot}H_2O$ with hexanol under refluxing conditions results in partial (17%) intercalation of the alcohol as indicated by powder X-ray diffraction (a second 00*l* line, observed at 15.2 Å) and thermogravimetric analysis. Attempts to remove the intercalate with water at 70 °C for 3 days were unsuccessful, suggesting a strong interaction between the alcohol and the layered material.

Morphological and Compositional Characterization of Copper–Cobalt Spinel Made by Mechanochemical Reactions

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Copper–cobalt spinels with general formula $Cu_xCo_{3-x}O_4$ ($x < 1.0$) are well-known for their high catalytic activity toward the oxidation of CO to CO_2. Furthermore when $x > 0.6$, they remain active even in the presence of a catalytic poison such as SO_2.[1–4]

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