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Note Added in Proof. The evolution of carbon dioxide in the transformation of $Ru_6(CO)_{18}^{2-}$ to $Ru_6C(CO)_{16}^{2-}$ (eq 5) has been confirmed by trapping as barium carbonate (82% yield).

Registry No. $[(Ph_3P)_2N]_2[Ru_6(CO)_{18}]$, 62501-17-1; $[Et_4N]_2[Ru_6C(CO)_{16}]$, 73413-28-2; $[(Ph_3P)_2N]_2[Ru_6C(CO)_{16}]$, 73413-27-1; $[Et_4N]_2[Ru_6(CO)_{18}]$, 82639-14-3; $Ru_6C(CO)_{17}$, 27475-39-4; $[Et_4N]_2[Os_6(CO)_{18}]$, 82639-15-4; $Os_6(CO)_{18}$, 59069-01-1; $Os_6C(CO)_{17}$, 82706-16-9; $[Et_4N]_2[Os_{10}C(CO)_{24}]$, 82639-16-5; Na, 7440-23-5; $Ru_3(CO)_{12}$, 15243-33-1; $FeCl_3$, 7705-08-0; $Os_3(CO)_{12}$, 15696-40-9.

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Coordination Intercalation Reactions of the Layered Compounds $VOPO_4$ and $VOAsO_4$ with Pyridine

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Coordination intercalation compounds of the layered mixed oxides $VOPO_4$ and $VOAsO_4$ with pyridine and 4-substituted pyridines have been obtained. With pyridine, the tetragonal phases $VOPO_4(py)$ (a = 6.207 (1), c = 9.589 (2) Å) and $VOAsO_4(py)$ (a = 6.403 (1), c = 9.661 (1) Å) are formed. The lattice constants and infrared spectra show that pyridine is coordinated to vanadium and is perpendicular to the oxide layers. Little or no reduction of V^{5+} occurs, and the host layers are preserved on reaction. $VOPO_4$ also reacts with 4-phenylpyridine and 4,4′-bipyridine, although the reactions are slower and the products less crystalline than in the pyridine case.

Introduction

Intercalation reactions of neutral host lattices usually occur via electron transfer between the guest species and the host lattice. The reaction mechanism is well established for the intercalation chemistry of the transition-metal dichalcogenides with alkali metals[1] and organometallic compounds.[2] Formation of the "neutral" organic intercalation compounds such as $TaS_2(py)_{1/2}$ has also been shown to involve reduction of the host lattice and cointercalation of both neutral and protonated pyridine.[3] In contrast, we have shown recently[4] that molybdenum trioxide reacts with pyridine and 4,4′-bipyridine under anhydrous conditions to form layered compounds without reduction of Mo(VI). In these compounds the pyridine molecules are coordinated directly to molybdenum atoms, and the structure is built of layers of composition $MoO_3(py)$ or $MoO_3(4,4'\text{-bpy})_{1/2}$. These new compounds can be envisioned as resulting from intercalation of the layered hydrate $MoO_3{\cdot}H_2O$, which has a similar structure.[5] The coordinated water molecule in $MoO_3{\cdot}H_2O$ is replaced by the stronger donor ligand pyridine without major disruption of the host structure. In fact, $WO_3(py)$ was prepared by reaction of $WO_3{\cdot}H_2O$ with pyridine. These results for MoO_3 and WO_3 suggest the possibility of a broader class of coordination intercalation reactions for layered compounds that contain metal centers either with vacant coordination sites or with easily replaceable ligands. The layered compounds vanadyl phosphate and vanadyl arsenate satisfy these criteria and form coordination intercalation compounds. In this paper, we report the reactions of these host lattices with pyridine.

Table I. Lattice Constants of Tetragonal $MOXO_4$ Compounds

compd	a, Å	c, Å	ref
$VOPO_4$	6.014 (7)	4.434 (2)[a]	6
$VOAsO_4$	6.33	4.18	12
$NbOPO_4$	6.387 (1)	4.104 (1)	7
$NbOAsO_4$	6.57	4.08	13
$TaOPO_4$	6.425 (3)	4.001 (3)	8
$VOSO_4$	6.261 (3)	4.101 (3)	11
$VOMoO_4$	6.6078 (2)	4.264 (3)	9
$MoOPO_4$	6.1768 (3)	4.2932 (3)	10

[a] Samples of $VOPO_4$ prepared by other workers using slightly different methods were reported to have lattice parameters a = 6.20 and c = 4.11 Å.[14] Our values agree with the latter.

Vanadyl phosphate, $VOPO_4$, has two well-characterized polymorphs,[6] one of which (α-$VOPO_4$) is layered and is isostructural with a number of other compounds including $NbOPO_4$,[7] $TaOPO_4$,[8] $VOMoO_4$,[9] $MoOPO_4$,[10] and α-$VOSO_4$.[11] X-ray powder diffraction data and chemical behavior suggest that $VOAsO_4$[12] and $NbOAsO_4$[13] also have similar structures. The structure of α-$VOPO_4$ is tetragonal with space group $P4/n$. The ab plane is made up of octahedra and tetrahedra that are linked through corner sharing, as shown in Figure 1. Each octahedron is joined to four different tetrahedra. The tetragonal layers are joined along the c axis by corner sharing of the remaining two trans vertices of the octahedron, as shown in Figure 2. The six oxygen atoms around the vanadium form

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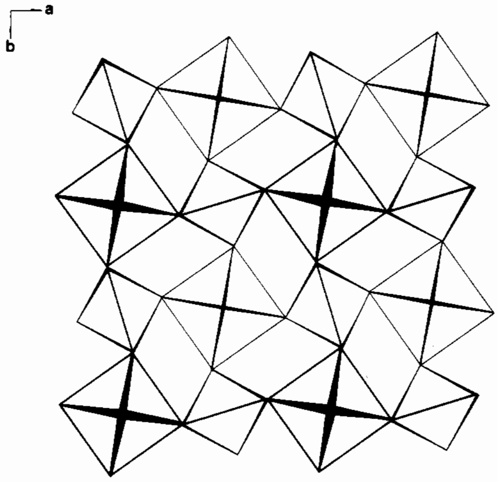

Figure 1. Structure of $VOPO_4$ viewed down the *c* axis (from crystallographic coordinates of ref 6).

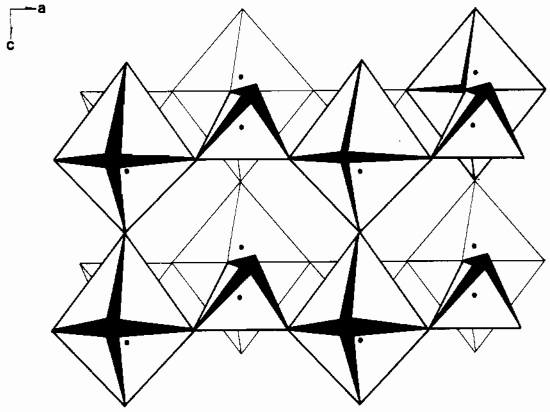

Figure 2. Structure of $VOPO_4$ viewed down the *b* axis (from crystallographic coordinates of ref 6).

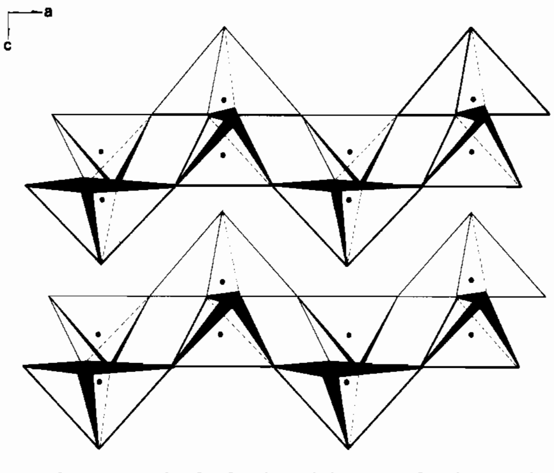

Figure 3. Structure of $VOPO_4$ viewed down the *b* axis, showing the vanadium coordination as square pyramidal (from crystallographic coordinates of ref 6).

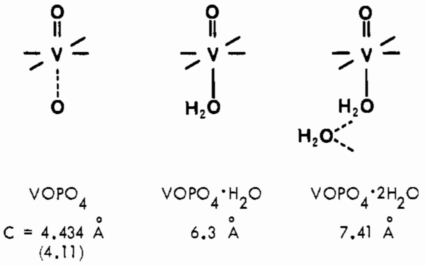

Figure 4. Schematic representation of the layer separation of $VOPO_4$ hydrates.

Table II. Lattice Constants of Tetragonal $MOXO_4$ Hydrates

compd	*a*, Å	*c*, Å	ref
$VOPO_4 \cdot 2H_2O$	6.21	7.41	14, 15
$VOPO_4 \cdot H_2O$	*a*	6.3	15
$VOAsO_4 \cdot 3H_2O$	6.39	8.08	12
$VOAsO_4 \cdot 2H_2O$	6.37	7.39	12
$NbOPO_4 \cdot 3H_2O$	6.39	8.04	16
$NbOPO_4 \cdot H_2O$	6.41	7.14	16
$NbOAsO_4 \cdot 4H_2O$	6.65	7.93	13
$VOSO_4 \cdot H_2O$	6.3	6.1	17

[a] Not determined.

an almost regular octahedron, but the vanadium atom is displaced from the center of the octahedron along the *c* axis, resulting in alternating long and short V—O bonds of lengths 2.85 and 1.58 Å. The short bond is typical of a V═O vanadyl group, involving filled oxygen p orbitals in both σ and π bonding. The long bond distance is considerably greater than the sum of the ionic radii, 1.94 Å, and is expected to be weak. Alternatively, the structure could be described as being composed of VO_5 square pyramids, with the layers being held together only by weak coordination of the apical vanadyl oxygen of one square pyramid to the open square face of a vanadium pyramid in the adjacent layer, as represented in Figure 3. This weak interlayer binding makes $VOPO_4$ and its analogues attractive as potential hosts for coordination intercalation reactions. The vanadyl oxygen, because of its strong bonding to the interlayer vanadium, is a relatively poor ligand for the vanadium in the adjacent layer and should be replaceable by other molecules that are stronger ligands.

The lattice parameters of several isostructural $MOXO_4$ compounds are given in Table I. Several of the members of this series of compounds are known to form hydrates. These include $VOPO_4$,[14,15] $VOAsO_4$,[12] $NbOPO_4$,[16] $NbOAsO_4$,[13] and $VOSO_4$.[17-22] The number of water molecules per formula unit varies from 1 to 6. Some of these hydrates are of particular interest because they exhibit tetragonal layer structures similar to those of the corresponding anhydrous compounds. No single-crystal X-ray studies on $MOXO_4$ hydrates with layer structures have been reported, so the details of the structures are not known, but the X-ray powder data indicate structural similarity to the anhydrous compounds. The lattice parameters tabulated in Table II show that the structures of the hydrates remain tetragonal with little change in the *a* axis while the *c* axis expands to incorporate the water molecules. A probable structural model for the hydrates has a $MOXO_4$ layer essentially identical with that of the anhydrous compounds, with the layers separated by breaking the long axial bond of the MO_6 octahedron and replacing the oxygen from the adjacent layer in the coordination sphere with a water molecule. The water molecules in excess of one per formula unit are then held

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between the layers by hydrogen bonding to the coordinated water molecule as well as to each other and the $MOXO_4$ layer oxygens. The variation of the linkage of the octahedra along the layer axis is represented schematically in Figure 4. The compounds listed in Table II can be thermally dehydrated to the corresponding anhydrous $MOXO_4$ compounds of Table I.

Molecules other than water can be incorporated between the layers. The compound $NbOPO_4 \cdot 2H_3PO_4 \cdot 5H_2O$ has excess H_3PO_4 between the $NbOPO_4$ layers, as shown by infrared spectroscopy and X-ray powder data ($a = 6.47$, $c = 11.20$ Å).[23] $NbOAsO_4 \cdot 2H_3AsO_4 \cdot 5H_2O$ is analogous.[24] Ladwig reported the swelling of $VOPO_4$ in excess water, as well as in ethanol, butylamine, ammonia, and phosphoric acid.[15] $VOSO_4$ makes a series of adducts of the formula $VOSO_4 \cdot 2ROH$ with straight-chain alcohols from C_2 to C_{10} that exhibit layer spacings varying from 12.9 to 37.5 Å.[25]

Experimental Section

Powder X-ray diffraction patterns were obtained with a Philips wide-angle goniometer and Cu Kα radiation. Samples were prepared in a glovebox and were protected from atmosphere by Kapton film. Infrared spectra were measured in KBr disks with a Digilab Fourier transform instrument. Thermogravimetric analyses were carried out on Du Pont Thermal Analyzer Models 951 and 990 in an oxygen atmosphere with a heating rate of 10 °C/min from room temperature to 600 °C. Elemental analyses for V, P, C, H, and N were performed by Galbraith Laboratories, Knoxville, TN. Pyridine was dried by prolonged refluxing over BaO, followed by distillation. 4-Phenylpyridine and 4,4′-bipyridine were purified by sublimation.

Synthesis of Vanadium Phosphate and Vanadium Arsenate Host Lattices. $VOPO_4 \cdot 2H_2O$. V_2O_5 (24 g) was refluxed in a solution of distilled water (580 mL) and concentrated H_3PO_4 (136 mL) for 16 h in air. A yellow, crystalline solid was isolated by vacuum filtration. The product was washed sparingly with distilled water and then ethanol and dried by suction in air. $VOPO_4 \cdot 2H_2O$ (46 g) was recovered and identified by X-ray powder diffraction and thermogravimetric analysis.[15]

$VOPO_4 \cdot H_2O$. A sample of $VOPO_4 \cdot 2H_2O$ was heated at 50–55 °C under a constant flow of helium for 14–16 h to ensure the removal of only one water molecule per molecule of $VOPO_4$. The resulting $VOPO_4 \cdot H_2O$ was transferred into a He drybox without exposure to air.

α-$VOPO_4$. A sample of $VOPO_4 \cdot 2H_2O$ was heated at 250–275 °C under a constant flow of helium for 4 h to remove both water molecules. The anhydrous $VOPO_4$ was transferred into a He drybox without exposure to air.

$VOAsO_4 \cdot 2H_2O$. V_2O_5 (8.5 g) was refluxed in a solution of $H_3AsO_4 \cdot {}^1/_2H_2O$ (99 g, Cerac) in 200 mL of distilled water for 3 days. A very dark yellow homogeneous solution resulted. This solution was evaporated to less than 50 mL, resulting in the crystallization of a yellow solid, which was isolated by vacuum filtration, washed sparingly with distilled water and ethanol, and then dried by suction. $VOAsO_4 \cdot 2H_2O$ (18.2 g) was recovered and identified by X-ray powder diffraction and thermal analysis.[12] $VOAsO_4 \cdot 2H_2O$ was ground, sieved to 80–100 mesh, and dehydrated at 200 °C in helium to give anhydrous $VOAsO_4$.

Synthesis of Pyridine Intercalation Compounds. $VOPO_4(py)$. Method A. $VOPO_4 \cdot 2H_2O$ (0.8 g) was refluxed in 10 mL of reagent grade pyridine for 4 days. The resulting yellow-green solid was separated by vacuum filtration, washed with toluene, and dried by suction in air. This product was refluxed in 10 mL of fresh pyridine for 6 more days. This final product was isolated by vacuum filtration, washed with toluene, and dried by suction in air. The product was identified by X-ray powder diffraction, TGA, elemental analysis, and IR spectroscopy as described below.

Method B. In an inert-atmosphere glovebox, pyridine (1 mL) was added to anhydrous $VOPO_4$ (0.25 g) in a small Pyrex tube. The tube was evacuated to 0.1 torr, sealed, and heated at either 100, 125, 150, or 170 °C for 4 days. The product was separated by vacuum filtration in the drybox, washed with toluene, and dried by suction. In each case, a yellow powder was obtained as the product and was characterized as above. The results are summarized in Table IV. $VOAsO_4(py)$ was prepared in a similar way by heating anhydrous $VOAsO_4$ with pyridine at 150 °C for 10 days.

Table III. X-ray Powder Data for $VOPO_4(C_5H_5N)$ ($a = 6.207$ (1), $c = 9.589$ (2) Å; $\lambda = 1.5405$ Å)

hkl	$2\theta_{obsd}$, deg	d_{obsd}, Å	d_{calcd}, Å	*I*
001	9.27	9.53	9.59	100
101	17.01[a]	5.208	5.211	5
002	18.49[a]	4.794	4.794	66
110	20.22[a]	4.388	4.389	3
	20.88	4.251		<1
102	23.43[a]	3.794	3.794	5
	24.32	3.657		<1
112	27.5	3.24	3.238	shoulder
003	27.90[a]	3.195	3.196	5
200	28.73[a]	3.105	3.104	5
201	30.25[a]	2.952	2.953	6
103	31.44[a]	2.843	2.842	5
202	34.39[a]	2.605	2.605	2
004	37.5	2.396	2.397	2
212	37.5	2.396	2.402	
104	40.25	2.239	2.236	8
203	40.25	2.239	2.227	
114	43.0	2.102	2.104	<1
213	43.0	2.102	2.096	
311	47.2	1.924	1.923	2
005	47.2	1.924	1.918	
302	47.8	1.901	1.900	2
204	47.8	1.901	1.897	

[a] Used in lattice parameter refinement.

$VOPO_4(4,4'\text{-bpy})_{1/2}$. A 0.500-g sample of $VOPO_4 \cdot 2H_2O$ was heated with 0.395 g of anhydrous 4,4′-bipyridine in toluene for 3 days at 110 °C in a sealed tube containing activated molecular sieves to remove the evolved water. The product was isolated by filtration and physical removal of the molecular sieves.

$VOPO_4(4\text{-Phpy})$. Anhydrous $VOPO_4$ was heated with 4-phenylpyridine in xylene at 200 °C. After 8 days, the reaction was interrupted and the solid was ground in a micronizing mill. The reaction was then continued for 40 days. Analysis showed only partial conversion of $VOPO_4$ to $VOPO_4(4\text{-Phpy})$.

Results

$VOPO_4(py)$. $VOPO_4$, $VOPO_4 \cdot H_2O$, and $VOPO_4 \cdot 2H_2O$ all react with pyridine to form coordination intercalates. The simplest procedure is to reflux $VOPO_4 \cdot 2H_2O$ with pyridine for 10 days to ensure complex reaction. The product is yellow with a slight green tint, indicating that the vanadium(V) has not been significantly reduced. The powder X-ray diffraction pattern of the product (Table III) can be indexed on a tetragonal unit cell with $a = 6.207$ (1) and $c = 9.589$ (2) Å. The systematic absences for $hk0$ lines when $h + k \neq 2n$ demonstrate the retention of the n glide plane of $VOPO_4$. These data clearly indicate that the tetragonal $MOXO_4$ layer structure has been preserved, while the c axis has expanded by ~5.5 Å over that of anhydrous $VOPO_4$. Elemental analysis indicates a stoichiometry of $VOPO_4(C_5H_5N)$. Thermogravimetric analysis in oxygen to anhydrous $VOPO_4$ as the final product gave a total weight loss of 32.2%, in good agreement with that calculated from the 1:1 stoichiometry, 32.8%. $VOPO_4(C_5H_5N)$ was also prepared by direct reaction of dry pyridine with anhydrous $VOPO_4$ at temperatures ranging from 100 to 170 °C. The results of varying the temperature and time of reaction are given in Table IV. The extent of reaction is determined by TGA analysis where the total weight loss in O_2 corresponds to the pyridine content and x is the stoichiometry in the formula $VOPO_4(C_5H_5N)_x$. Thus $x = 1.0$ would represent complete reaction of the $VOPO_4$. As can be seen, the reaction of anhydrous $VOPO_4$ with pyridine is slower than that

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Table IV. Reactions of Pyridine with Anhydrous $VOPO_4$

synthesis conditions	x(TGA)	lattice const	$V^{4+}:x$
$VOPO_4 \cdot 2H_2O$ + py, 10 days, reflux	0.97	$a = 6.207^a$ $c = 9.589^a$	0.027
$VOPO_4$ + dry py, 14 days, 100 °C	0.36	$a = 6.21$ $c = 9.1-9.6$	0.023
$VOPO_4$ + dry py, 14 days, 125 °C	0.82	$a = 6.216^a$ $c = 9.566^a$	0.016
$VOPO_4$ + dry py, 4 days, 150 °C	0.75	$a = 6.21$ $c = 9.51-9.58$	0.013
$VOPO_4$ + dry py, 4 days, 170 °C	0.85	$a = 6.20$ $c = 9.51$	0.015
$VOPO_4 \cdot H_2O$ + dry py, 6 days, 150 °C	0.87	$a = 6.21$ $c = 9.47-9.56$	
$VOPO_4$ + dry py-d_5, 10 days, 150 °C	0.93	$a = 6.24$ $c = 9.57$	0.029

[a] These lattice constants were determined by least-squares refinement of powder data. All other lattice constants were determined by the position of the 001 lines (c) and the 200 line (a). x(TGA) was determined from the weight loss observed by heating the sample to 600 °C in oxygen to form $VOPO_4$. $V^{4+}:x$ was estimated from double integration of the V^{4+} ESR signal.

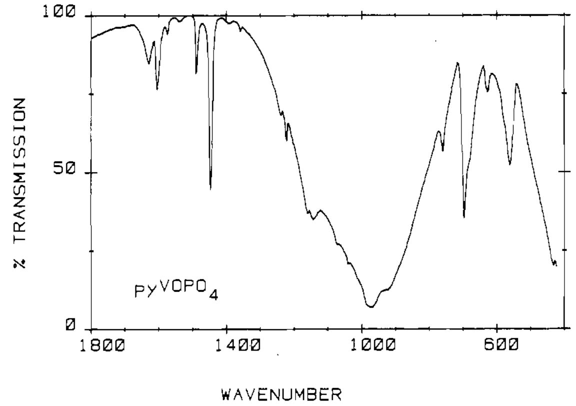

Figure 5. Infrared spectrum of $VOPO_4(C_5H_5N)$.

of $VOPO_4 \cdot 2H_2O$, but the products are very similar, as shown by the X-ray, IR, and ESR data.

The ESR spectra of the samples were measured in order to determine the amount of V^{4+} formation. All samples, including the starting $VOPO_4$ and $VOPO_4 \cdot 2H_2O$, show an ESR signal that exhibits hyperfine coupling typical of V^{4+}. Double integration of the signals allows one to estimate the amount of V^{4+} per mole in the sample. These results are tabulated in Table IV as $V^{4+}:x$; the amount of V^{4+} is about 1–2% of the total vanadium.

Infrared spectroscopy can be used to distinguish various modes of pyridine binding in solids. Studies on alumina surfaces have distinguished among physisorbed pyridine, Brønsted-coordinated pyridine, and Lewis-coordinated pyridine.[26] The infrared spectrum of a typical $VOPO_4(C_5H_5N)$ sample is shown in Figure 5. Similar spectra are observed for all samples, the only important difference being a small variation in the relative intensity of the 1538-cm^{-1} band. The region of interest in determining the mode of pyridine binding is from 1650 to 1400 cm^{-1}, the pyridine ring stretching vibrations. The strong band at 1446 cm^{-1} is characteristic of Lewis-bound pyridine, i.e., a pyridine coordinated to a transition-metal ion. Brønsted-bound pyridine, i.e., pyridinium ion, has its strongest IR band at ~1540 cm^{-1}. A band at 1538 cm^{-1} is observed, but it is weak and variable, being strongest in the sample which was prepared from $VOPO_4 \cdot H_2O$. In all samples, the 1450-cm^{-1} band of coordinated pyridine is much more intense than the 1540-cm^{-1} band of pyridinium ion, $C_5H_5NH^+$.

Table V. Infrared Absorptions of C_5H_5N (and C_5D_5N in Parentheses) Complexes of $VOPO_4$ and $ZnCl_2$

	$VOPO_4$(py)	$\nu(D)/\nu(H)$	$Zn(py)_2Cl_2{}^a$	$\nu(D)/\nu(H)$
ν_{C-H}	3090 (2295)	0.75	3109 (2293)	0.74
	3075 (2280)	0.74	3066 (2273)	0.74
ν_{ring}	1628 (1589)	0.98		
	1605 (1560)	0.97	1607 (1566)	0.97
	1573 (1539)	0.98	1573 (1539)	0.98
	1538 (1462?)	0.95		
	1489 (1347)	0.90	1486 (1320)	0.89
	1447 (1316)	0.91	1449 (1311)	0.90
δ_{C-H}	1239 (. . .)		1245 (992)	0.79
	1222 (. . .)		1216 (890)	0.73
	. . . (831)		1069 (832)	0.78
	760 (. . .)		756 (561)	0.74
	695 (534)	0.77	699 (533)	0.76
δ_{ring}	626 (602)	0.96	648 (630)	0.96
	431 (. . .)		423 (384)	0.91

[a] Reference 27.

A deuterium-labeling study has allowed us to assign the pyridine bands in the spectrum of $VOPO_4(C_5H_5N)$. A sample of $VOPO_4(C_5D_5N)$ was prepared from anhydrous $VOPO_4$ and pyridine-d_5. The infrared spectra and the isotope shifts were compared to the analogous data of Foulds et al.[27] for $Zn(C_5H_5N)_2Cl_2$, a well-characterized molecular coordination compound of pyridine. The data are presented in Table V. The agreement between the frequencies and isotope shifts between the two compounds convincingly demonstrates that the mode of pyridine binding is the same in each.

When pure, completely characterized samples of $VOPO_4$, $VOPO_4 \cdot H_2O$, or $VOPO_4 \cdot 2H_2O$ are reacted with pyridine, intercalation compounds are formed with little or no vanadium reduction. However, when $VOPO_4$ that has been briefly exposed to atmospheric moisture is reacted with pyridine or when molecular sieves are included in the reaction of $VOPO_4 \cdot H_2O$ with pyridine to remove water, different products with the same apparent composition $VOPO_4(C_5H_5N)$ are observed. These compounds contain large amounts of V(IV) (ca. 20% of the total vanadium) and are dark green. The X-ray patterns are not well-defined and show only the first three $00l$ reflections giving c axis values 0.1–0.2 Å smaller than those of the unreduced products. The infrared spectra are also markedly different and do not show the bands characteristic of coordinated pyridine. The dominant feature is an intense absorption at 1580 cm^{-1}. It is clear that in these reactions a redox process occurred and both protonated and neutral bases were introduced into the host lattice. The reaction is not presently well understood, but it is likely that vanadium reduction occurs by oxidation of pyridine as has previously been observed in pyridine intercalation of tantalum disulfide.[3]

$VOPO_4$(4,4′-bpy) and $VOPO_4$(4-Phpy). Anhydrous $VOPO_4$ did not react appreciably with 4,4′-bipyridine in toluene or xylene at temperatures varying from 120 to 200 °C. However, when $VOPO_4 \cdot 2H_2O$ was used as the starting material, 4,4′-bipyridine was incorporated into the $VOPO_4$ lattice. When $VOPO_4 \cdot 2H_2O$ was heated with excess 4,4′-bipyridine in toluene in the presence of molecular sieves at 120 °C for 3 days, a new phase was formed. X-ray examination revealed the presence of some anhydrous $VOPO_4$ along with a distinct $00l$ series for l = 1–4 corresponding to a layer spacing of 13.0 Å. Thermal analysis showed a weight loss corresponding to the composition $VOPO_4(bpy)_{0.4}$. It is not readily apparent whether this corresponds to a mixture of $VOPO_4$ and $VOPO_4(bpy)_{0.5}$ with both

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Table VI. X-ray Powder Data for $VOAsO_4(C_5H_5N)$ ($a = 6.403$ (1), $c = 9.661$ (1) Å; $\lambda = 1.5405$ Å)

hkl	$2\theta_{obsd}$, deg	d_{obsd}, Å	d_{calcd},[a] Å	*I*
001	9.16	9.646	9.661	>100
101	16.58	5.342	5.337	30
002	18.33	4.836	4.831	100
001 ($VOAsO_4$)	21.32	4.164	4.18[b]	45
111	21.8 (sh)	4.07	4.100	
102	23.04	3.857	3.856	12
112	26.9 (br)	3.31	3.304	5
200	27.84	3.202	3.202	60
200 ($VOAsO_4$)	28.2 (sh)	3.16	3.17[b]	
201	29.36	3.039	3.039	70
103	31.06	2.877	2.877	10
202	33.55	2.669	2.669	25
113	34.12	2.625	2.624	4
104	39.74	2.266	2.260	13
220	39.74	2.266	2.264	13
203	39.74	2.266	2.270	13
220 ($VOAsO_4$)	40.46	2.228	2.25[b]	6
unindexed	41.34	2.182		4
114	42.39	2.130	2.131	7
301	43.58	2.075	2.084	5
002 ($VOAsO_4$)	43.76	2.067	2.09[b]	2
222	44.54	2.032	2.050	3
310	44.54	2.032	2.025	3
302	46.46	1.953	1.9524	4
312	48.8 (br)	1.86	1.8675	3
303	51.37	1.777	1.7791	8
115	51.37	1.777	1.7772	8
320	51.37	1.777	1.7760	8
400	57.53	1.601	1.6008	11
401	58.38	1.579	1.5793	12

[a] Lattice constants determined by least-squares refinement of 13 sharp, well-resolved maxima. [b] From ref 16.

nitrogen donors coordinated or to a mixture of $VOPO_4$ and a complex with a monodentate bipyridine ligand, $VOPO_4(bpy)_{1.0}$. Reactions conducted at higher temperatures for longer times did not result in pure phases of $VOPO_4(bpy)_x$. When the reaction was carried out at 150 °C for 58 days, the same 13-Å phase was seen in the X-ray pattern, together with anhydrous $VOPO_4$ and a third phase with a spacing of 10.1 Å. Thermal analysis showed the ligand to $VOPO_4$ stoichiometry to be $x = 0.56$. By going to a lower reaction temperature (110 °C), we avoided the formation of anhydrous $VOPO_4$ and obtained single-phase $VOPO_4(bpy)_{0.5}$. The product was not very crystalline but did show the first three 00*l* layer lines corresponding to a 13.2 ± 0.1 Å *c* axis. Thermogravimetric analysis showed loss of bipyridine centered at 250 °C corresponding to a stoichiometry of $VOPO_4(bpy)_{0.49}$. If the molecular sieves were not included in the synthesis, a different phase containing over 1 equiv of bpy and diffraction peaks at 11.3, 9.5, and 8.1 Å was obtained.

The reaction of 4-phenylpyridine with $VOPO_4$ is very slow. After the anhydrous $VOPO_4$ was heated with excess 4-phenylpyridine in xylene solution for ~50 days at 200 °C with an intermediate grinding in a micronizing mill, the reaction was still incomplete. The X-ray diffraction pattern of the pale green product showed a significant amount of unreacted $VOPO_4$. However, a well-developed series of four sharp 00*l* reflections appear corresponding to a layer spacing of 14.2 Å. TGA analysis indicates a ligand to $VOPO_4$ ratio of about 0.6, which corresponds to a mixture of $VOPO_4$ and $VOPO_4(C_6H_5C_5H_4N)_{1.0}$.

$VOAsO_4$(py). This compound was obtained as a greenish yellow solid by direct reaction of $VOAsO_4$ with pyridine. The reaction is slower than for $VOPO_4$, and after 10 days at 150 °C a small amount of unreacted $VOAsO_4$ can be seen in the X-ray powder pattern. No significant reduction of vanadium occurs. Thermal analysis in oxygen to $VOAsO_4$ indicates an overall stoichiometry of $VOAsO_4(C_5H_5N)_{0.9}$, somewhat low in pyridine due to the presence of unreacted $VOAsO_4$.

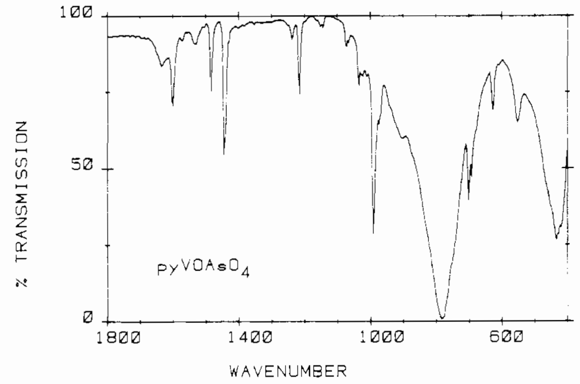

Figure 6. Infrared spectrum of $VOAsO_4(C_5H_5N)$.

Table VII. Layer Spacing in $VOXO_4$-Ligand Compounds

compd	*c*, Å	Δ*c*,[a] Å
$VOPO_4$(py)	9.59	5.48
$VOAsO_4$(py)	9.66	5.48
$VOPO_4$(4-Phpy)	14.2	10.1
$VOPO_4(4,4'\text{-bpy})_{0.5}$	13.0	8.9

[a] Difference in *c* of intercalation compound and that of the corresponding anhydrous $MOXO_4$.

The X-ray powder pattern of $VOAsO_4(C_5H_5N)$ was indexed with a tetragonal unit cell with lattice constants $a = 6.403$ and $c = 9.661$ Å and is given in Table VI. The powder pattern is similar to that of $VOPO_4(C_5H_5N)$ with the slightly larger lattice parameters reflecting the larger AsO_4 tetrahedron. The infrared spectrum, shown in Figure 6, corresponds exactly to that of the phosphate analogue in the region 1650–1100 cm^{-1}, where the bands for coordinated pyridine appear (cf. Figure 5). The AsO_4 stretching vibrations are at significantly lower energy than the PO_4 vibrations, so the V=O stretch can clearly be distinguished at 992 cm^{-1}. The vanadyl stretching mode is seen at 1030 cm^{-1} in anhydrous $VOAsO_4$ and at 1010 cm^{-1} in $VOAsO_4 \cdot 2H_2O$. As the donor ability of the ligand trans to V=O increases in the series $VOAsO_4$, $VOAsO_4 \cdot 2H_2O$, and $VOAsO_4(C_5H_5N)$, where the ligands are vanadyl groups from adjacent layers, water, and pyridine, respectively, the multiple-bond character of the V=O group decreases, resulting in a lower V=O stretching frequency.

As in the case of $VOPO_4$, the reaction conditions during preparation of $VOAsO_4(C_5H_5N)$ are important. If anhydrous $VOAsO_4$ made by dehydrating unground $VOAsO_4 \cdot 2H_2O$ crystals is used, no reaction with pyridine is observed at 150 °C, because of the larger crystallite size. When $VOAsO_4 \cdot 2H_2O$ was refluxed in pyridine for 6 days, an orange solid resulted, which gave a broad X-ray pattern. Thermal analysis indicated a 2.5:1 stoichiometry of pyridine:$VOAsO_4$, and the infrared spectrum shows bands characteristic of both protonated and coordinated pyridine. This reaction is not yet understood and is not observed in the corresponding reaction of $VOPO_4 \cdot 2H_2O$.

Discussion

The coordination intercalation compounds $VOPO_4$(py) and $VOAsO_4$(py) have been synthesized. In these compounds, it has been established through X-ray and spectral data that the intercalating ligand, pyridine, is directly coordinated to the metal sites in the metal oxide layer and that essentially all available sites are occupied.

The layer spacings of the various compounds reported in this paper are listed in Table VII. Also tabulated are the layer expansions relative to the corresponding unsubstituted $VOXO_4$. Intercalation of pyridine expands the layer separation of $VOPO_4$ and $VOAsO_4$ by 5.5 Å. This is consistent with a

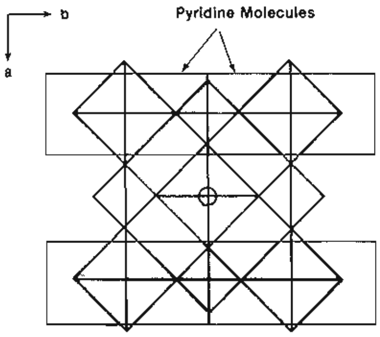

Figure 7. van der Waals area occupied by pyridine molecules coordinated to the surface of a single $\mathrm{VOPO_4}$ layer, demonstrating the possibility of ligand interpenetration.

bonding model that has pyridine coordinated to vanadium with the ligand plane perpendicular to the layers. While it is difficult to predict exactly the *c* axes of these coordination intercalates without knowledge of the metal–ligand bond distance and the structural details of the oxide layer itself, it can be assumed that these factors remain constant as the ligand size increases. Thus, from CPK molecular models, the difference in van der Waals length along the coordination axis between pyridine and 4-phenylpyridine can be easily measured and compared directly to the observed *c*-axis differences. The 4.6-Å expansion observed on going from $\mathrm{VOPO_4(py)}$ to $\mathrm{VOPO_4(4\text{-}Phpy)}$ corresponds closely to the differences in length of the ligands (4.4 Å). This indicates that, in the $\mathrm{VOPO_4}$ compounds, pyridine molecules from adjacent layers interpenetrate, since the total expansion is that caused by a single ligand. On the $\mathrm{VOPO_4}$ layer surface, the coordination sites are 6.2 Å apart. This is only a little less than the van der Waals width of pyridine, 6.4 Å, allowing the ligands to line up along the *a* axis as shown in Figure 7 and stack in an interlocking fashion along the *c* axis.

The ligand-packing arrangement in $\mathrm{VOPO_4(py)}$ is different from that of the analogous $\mathrm{MoO_3}$ compound,[4] which has coordination sites 5.3 Å apart. On the $\mathrm{MoO_3}$ surface the pyridine molecules are more densely packed so no interpenetration of ligands from adjacent layers is possible. As a result the *c*-axis difference in $\mathrm{MoO_3(py)}$ and $\mathrm{MoO_3(4\text{-}Phpy)}$ is 8.8 Å, twice the difference in length of the ligands.

In summary, vanadyl phosphate and arsenate react with pyridine and 4-substituted pyridines to form coordination intercalation compounds. The pyridine molecules replace either a coordinated water molecule in $\mathrm{VOPO_4{\cdot}2H_2O}$ or a vanadyl oxygen from an adjacent layer in the anhydrous hosts. In the compounds the pyridine molecules are perpendicular to the oxide layers and little or no reduction of the $\mathrm{V^{5+}}$ centers occurs. Reactions with 4-substituted pyridines are much slower than with pyridine itself, and the products are less crystalline than those formed with pyridine. These coordination intercalation compounds are analogous to those previously reported for $\mathrm{MoO_3}$ and $\mathrm{WO_3}$. We are currently extending this general type of reaction to other $\mathrm{MOXO_4}$ host lattices.

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Registry No. $\mathrm{VOPO_4{\cdot}2H_2O}$, 12293-87-7; $\mathrm{VOPO_4{\cdot}H_2O}$, 61156-00-1; α-$\mathrm{VOPO_4}$, 12395-27-2; $\mathrm{VOAsO_4{\cdot}2H_2O}$, 12291-57-5; $\mathrm{VOPO_4(py)}$, 82648-60-0; $\mathrm{VOPO_4(4,4'\text{-}bpy)}$, 82648-61-1; $\mathrm{VOPO_4(4\text{-}Phpy)}$, 82648-62-2; $\mathrm{VOAsO_4(py)}$, 82648-63-3.

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Eight-Coordinate Complexes of Molybdenum with 1,1-Dithio Ligands. Synthesis, Electrochemistry, and Spectroscopic Properties

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Syntheses, characterization, and electrochemical and spectroscopic properties are reported for a series of eight-coordinate molybdenum(V) complexes with 1,1-disubstituted ethylenedithiolate ($\mathrm{Mo(S_2C_2R_2)_4{}^{3-}}$; R = CN, COOEt), dithiocarbamate ($\mathrm{Mo(S_2CNEt_2)_4{}^{+}}$), and thioxanthate ($\mathrm{Mo(S_2CS\text{-}}t\mathrm{\text{-}Bu)_4{}^{+}}$) ligands. The compounds each exhibit a reversible Mo(V) → Mo(VI) oxidation and a reversible Mo(V) → Mo(IV) reduction with the exception of $\mathrm{Mo(S_2CS\text{-}}t\mathrm{\text{-}Bu)_4{}^{+}}$, for which no oxidation is observed. The half-wave potentials of these reversible processes span a range of +1.2 to −1.7 V vs. SCE in $\mathrm{CH_3CN}$ and $\mathrm{CH_2Cl_2}$. Irreversible oxidation of some of the Mo(VI) species and irreversible reduction of some of the Mo(IV) species also are observed. Thin-layer spectroelectrochemistry is used to obtain visible spectra of the oxidized and reduced complexes, establish the Nernstian character of the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox couples, and investigate the catalytic behavior of the electrogenerated Mo(VI) species, $\mathrm{Mo(S_2CNEt_2)_4{}^{2+}}$.

Introduction

The occurrence of Mo–S bonding in molybdenum-containing enzymes[2] has generated current interest in complexes of this metal with sulfur-containing ligands.[3] 1,1-Dithio ligands[4] form sulfur-rich complexes with most transition metals. Dithiocarbamates,[5-7] thioxanthates,[7] and dithiobenzoates[7-9] form tetrakis complexes with the higher oxidation states of molybdenum and thereby provide an eight-sulfur ($\mathrm{MoS_8}$) coordination environment for this element.

In this paper we report the preparation and characterization of a new series of eight-coordinate molybdenum complexes with the dinegative ethylenedithiolate (ed) ligands 1,1-di-

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