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A New Route to Organic Intercalates Consisting of Vanadium Pentoxide and Pyridines: $(4\text{-}H_2N\text{-}C_5H_5NH)V_2O_5$**

Yongkui Shan, Rui H. Huang, and Songping D. Huang*

Layered intercalation compounds have attracted increased research attention due to their applications in such diverse areas as rechargeable batteries, heterogeneous catalysis, and ion exchange.[1] Interest is particularly high in the insertion of organic molecules into layered hosts for the purpose of synthesizing organic–inorganic composite materials with well-defined stoichiometries and organized structures.[2–7] Such materials may possess hybrid properties that have a synergism of the properties shown by the host and the guest.[3, 8] Pyridine and its derivatives are the class of organic Lewis bases that has been most investigated for intercalation in a variety of layered hosts including transition metal dichalcogenides,[4] metal phosphorus trisulfides,[9] metal oxides,[10, 11] and metal phosphates.[12, 13]

The conventional synthetic scheme for intercalating such molecules into layered hosts entails a direct reaction of the guest with the host lattice.[1e] Such heterogeneous reactions usually afford products with insufficient crystallinity. As a result, definitive structural information with regard to the arrangement of the organic molecules in the interlamellar space is difficult to obtain. Contradicting structural models have sometimes been proposed for the same host–guest system based on X-ray powder diffraction results.[14] Recently, hydrothermal techniques have been demonstrated to facilitate the synthesis and single-crystal growth of organic-based intercalation compounds.[15] For example, α- and β-$(enH_2)_{0.5}$-V_2O_5 (en = ethylenediamine)[16] as well as $(DABCOH_2)V_6O_{14}$ (DABCO = 1,4-diazabicyclo[2.2.2]octane)[17] have been synthesized by the hydrothermal technique and structurally characterized by X-ray single-crystal analysis.

We have been interested in synthesizing novel microporous–mesoporous composite materials using layered compounds containing intercalated small molecules (e.g. pyridines, alkylamines, and alkalimetal ions) as starting materials in liquid crystal templating reactions. Here we describe the hydrothermal synthesis and X-ray structure of $(4\text{-}H_2N\text{-}C_5H_5NH)V_2O_5$ (**1**), the first pyridine intercalation compound to be characterized by single-crystal X-ray analysis. This study has not only provided insight into the molecular orientation of the pyridine ring with respect to the host layer, but has also shed light on the formation mechanisms of the pyridine intercalate under hydrothermal conditions.

The structure of **1** was determined by X-ray single-crystal analysis.[18] Compound **1** crystallizes in the monoclinic system with an asymmetric unit containing two V, five O, five C, two N, and seven H atoms in general positions. Both V atoms have square-pyramidal coordination with double-bonded O atoms occupying the axial positions. The structure can best be described as a two-dimensional intercalation compound of the organic $(4\text{-}H_2N\text{-}C_5H_5NH)^+$ cations into the anionic $[V_2O_5]^-$ layers (Figure 1). Each $[V_2O_5]^-$ layer is formed parallel to the [001] plane consisting of distorted VO_5 square pyramids linked by edge- and corner-sharing O atoms. Figure 2 gives a projection of a $[V_2O_5]^-$ layer in **1**, and the bonding modes of the V and O atoms in the layer. The square pyramids share two edges of their base with neighboring square pyramids to form double ribbons along the [100] direction in such a way that the axial vertices alternatively point up and down. The ribbons are then connected with one another along the same direction through corner sharing. Because all the ribbons within a layer adopt the same orientation, the vertices of neighboring ribbons point in opposite directions across the corner-shared O atoms. Overall, the orientation of the square pyramids alternates up and down along the [001] direction. The O atoms are engaged in terminal (O2 and O4), doubly

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[*] Prof. S. D. Huang,[+] Dr. Y. Shan
Department of Chemistry and
Center for Materials Research and Characterization
University of Puerto Rico
P.O. Box 23346, San Juan, PR 00931 (USA)

Dr. R. H. Huang
Department of Chemistry and
Center for Fundamental Materials Research
Michigan State University
East Lansing, MI 48824 (USA)

[+] Permanent address:
Department of Chemistry
Kent State University
Kent, OH 44242 (USA)
Fax: (+1) 330-672-3816
E-mail: shuang1@kent.edu

[**] This work was supported by the U.S. National Science Foundation and the Department of Energy (OSR-9452893 and DE-FC02-91ER-75674). S.D.H. is a recipient of the NSF CAREER award from 1998–2002 (DMR-9733275).

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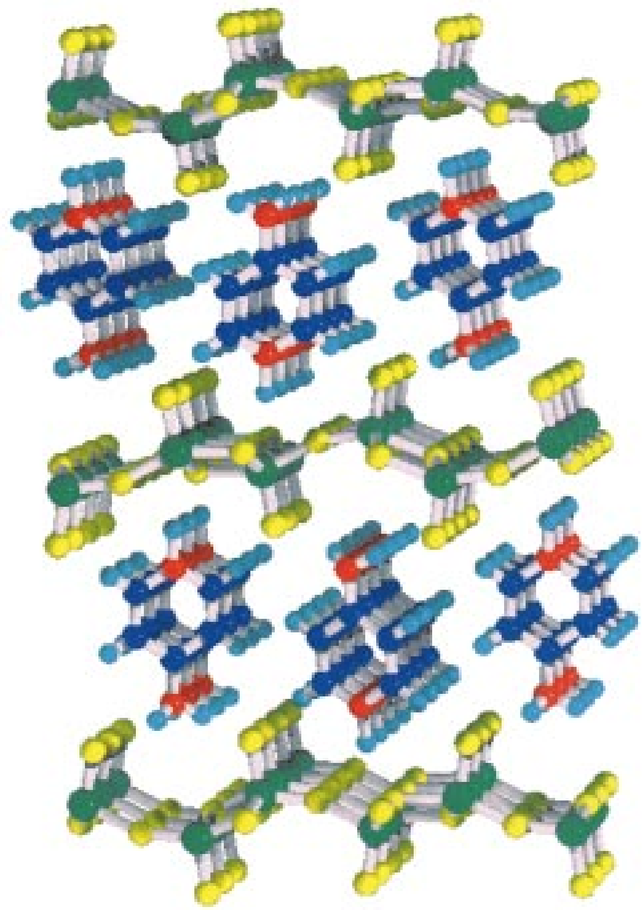


Figure 1. The structure of **1**, as viewed down the *a* axis. V: green, O: yellow, C: blue, N: red, H: turquoise.

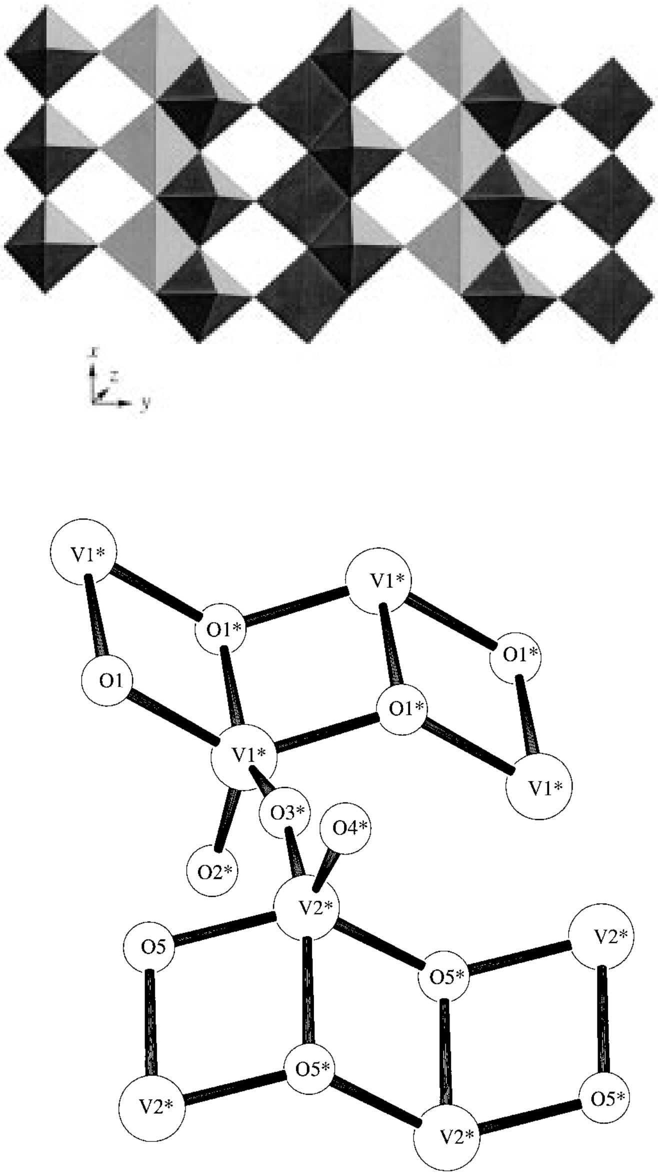


Figure 2. The projection of a $[V_2O_5]^-$ layer in **1** along the *c* axis and the bonding modes of the V and O atoms in **1**. Selected bond lengths [Å]: V1–O1 1.935(7), V1–O1 1.948(7), V1–O1 2.000(6), V1–O2 1.605(7), V1–O3 1.902(7), V2–O3 1.720(7), V2–O4 1.615(7), V2–O5 1.919(7), V2–O5 1.899(7), V2–O5 2.003(7).

bridging (O3), and triply bridging coordination (O1 and O5). The layers are stacked along the [001] direction with the 4-aminopyridine molecules occupying the interlamella space with their C_2 axis perpendicular to the layers (Figure 1). There are significant $\pi-\pi$ stacking interactions between the aromatic organic molecules in each column along the *a* axis; the rings are parallel to each other and are separated by about 3.57 Å.

The FT-IR spectrum of **1** clearly shows that the pyridine N atom is protonated (characteristic ν(N–H) bands at 3322 (s) and 3172 cm^{-1} (s) and stretching vibrations of the pyridinium ring at 1667 (s and br), 1600 (s), and 1543 cm^{-1} (s)), while the NH_2 group remains unprotonated (characteristic ν(N–H) band at 3497 cm^{-1}). The latter is a strong and extremely broad band, indicating that this amino substituent is involved in significant hydrogen bonding. These findings are consistent with the corresponding pK_a values of 9.11 and 1.18. In fact, the two N atoms in the $4\text{-}H_2N\text{-}C_5H_5NH^+$ ion form hydrogen bonds with the triply-bridging and terminal O atoms in the vanadium oxide layers above and below, respectively (N1–O1 2.97(1), N2–O2 2.90(1), N2–O4 2.89(1) Å). On the other hand, electron spectroscopy chemical analysis (ESCA) gave two overlapping peaks for $V2p_{2/3}$ at 517.5 and 516.0 eV with approximately equal intensities, suggesting a mixed valence state of V^{5+}/V^{4+} in a 1:1 ratio in **1**. Although V1 and V2 are both in a square-pyramidal environment, the V–O bond lengths around V2 are shorter than their counterparts around V1, and the differences are statistically significant (see the legend to Figure 2). We therefore assign the oxidation state of V1 as +4, and of V2 as +5. This assignment of oxidation states was supported by the valence sum calculations,[19] which gave a value of 4.21 for V1 and 4.99 for V2.

The magnetic susceptibility measurements performed with a SQUID showed that **1** is paramagnetic in the entire temperature region between 300 to 2 K (Figure 3a). The molar susceptibility rises sharply when the temperature is decreased from 3 to 2 K (Figure 3b). The field dependency measurements confirmed the ferromagnetic behavior at 1.8 K (Figure 3c). The fitting of the high-temperature (above 130 K) data with the Curie–Weiss law yielded $\theta = 197$ and

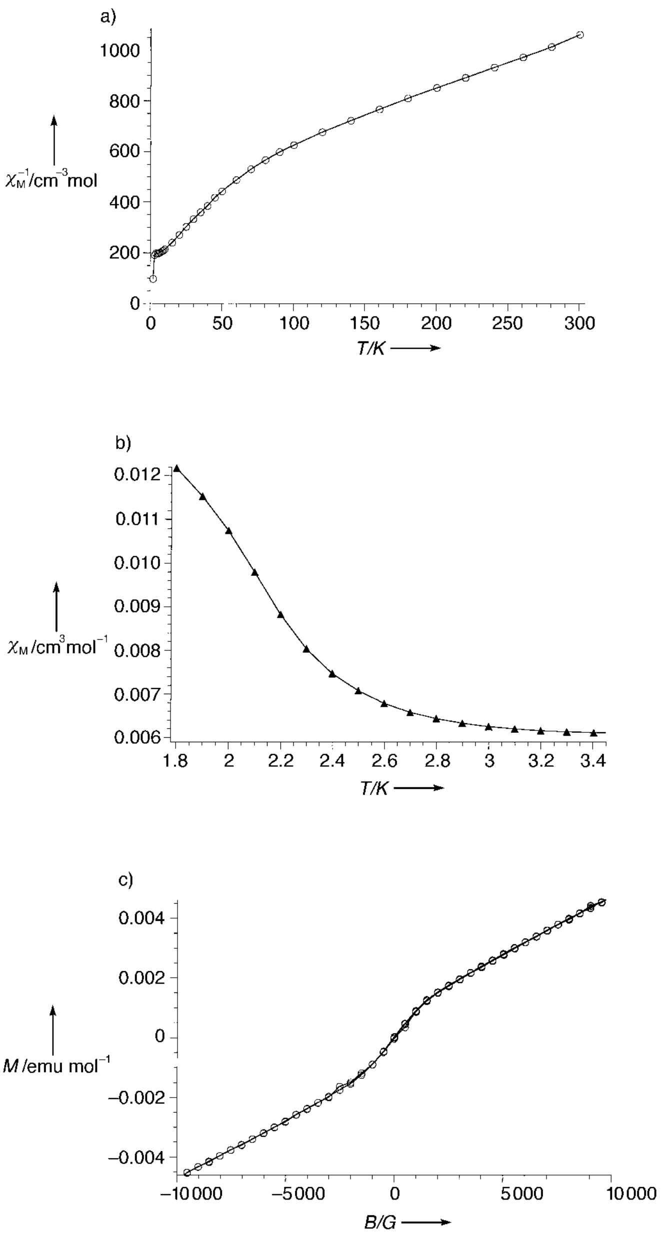


Figure 3. a) Inverse molar magnetic susceptibility of **1** as a function of temperature at 200 G. b) The temperature dependency of the molar magnetic susceptibility near 2 K at 500 G. c) The field dependency of the magnetization at 1.8 K.

$C = 0.51$. The latter is close to 0.374, suggesting an $S = 1/2$ spin system. The magnetic behavior of **1** is distinct from those of the other layered mixed-valence V^{4+}/V^{5+} oxide materials reported thus far in the literature. For example, at low x values the xerogel bronzes $A_xV_2O_5 \cdot nH_2O$ ($A = K$, Cs; $0.05 \leq x \leq 0.6$) are Curie–Weiss-type paramagnets showing temperature-independent paramagnetism (TIP) because the V^{4+} centers are isolated.[20] As the concentration of the V^{4+} spins increases, the materials show strong antiferromagentic coupling between the neighboring d^1 centers. Recently, Zubieta et al. described the synthesis and magnetic properties of the new layered vanadium oxide compounds $(en)_2M[V_6O_{14}]$ ($M =$ Zn, Cu; **2**) and $[(en)_2Cu]_2[V_{10}O_{25}]$ (**3**), which feature interlamellar coordination with metal–amine complexes.[21] The layers in **2** and **3** are built up from $V^{4+}O_5$ square pyramids and $V^{5+}O_4$ tetrahedra and show paramagnetism with anomolously low magnetic moments, probably due to the spin paring within the states that are delocalized in the entire layers.

Careful comparison of the structural details of the $[V_2O_5]^-$ layers in **1** with those of the starting material V_2O_5 reveals a substantial reorganization of the VO_5 pyramids in the formation of **1**.[22] A naturally occurring mineral form of vanadium pentoxide, known as shcherbinaite, has an orthorhombic layered structure that also consists of edge-shared VO_5 double ribbons connected by corner sharing.[23] However, because the neighboring ribbons adopt opposite orientations, the vertices of neighboring ribbons point in the same direction across corner-shared O atoms. Figure 4 gives a schematic representation of the layer reorganization from V_2O_5 to **1**. Thus, the formation of **1** cannot be considered a topotactic reaction. This term is usually reserved for reactions in which the structural integrity of the host lattice is retained upon insertion of a guest species.

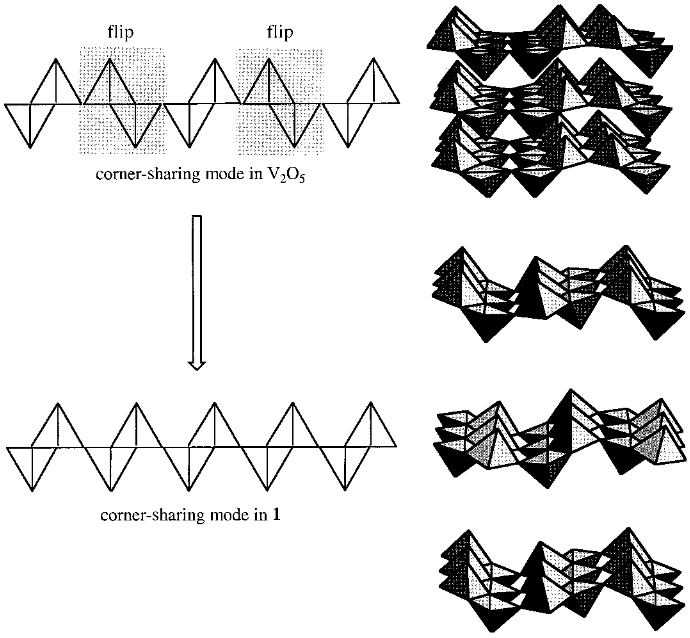
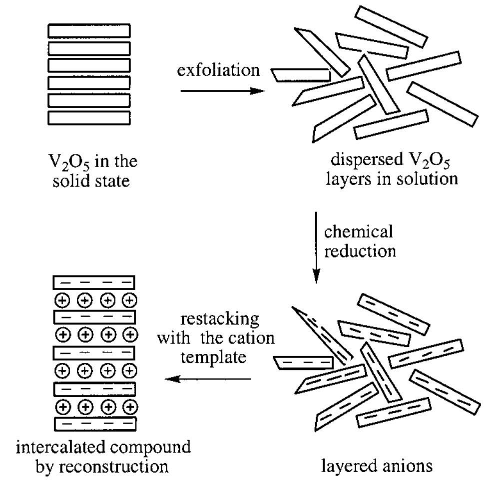


Figure 4. Schematic representation of the layer reorganization upon formation of **1** from V_2O_5.

Instead, **1** is likely to be formed through the layer exfoliation–reduction–restacking process illustrated in Scheme 1. Vanadium pentoxide dissolves slightly in water to form a pale yellow solution containing dispersed V_2O_5 layers.[24] Because of methanol present in the hydrothermal synthesis, the exfoliated layers are readily reduced to give lamella anions,[25] which are restacked with the organic cations to form the new intercalation compound.[7b, 8c] We suggest that the structural reorganization in the $[V_2O_5]^-$ layers is caused by the cation templating effect; that is, in addition to the above-mentioned hydrogen bonds, the narrower grooves in **1** also allow for C–H$\cdots$O hydrogen bonding between the aromatic ring and the terminal O atoms (C4–O2 3.02(2), C2–O4 3.07(1) Å; see also Figure 1).



Scheme 1. Possible layer exfoliation – reduction – restacking process in the formation of **1**.

Experimental Section

A sample of V_2O_5 (100 mg, 0.55 mmol), 4-aminopyridine (104 mg, 1.10 mmol), and H_2O/MeOH (50/50 v/v, 0.5 mL) was sealed in a thick-walled Pyrex tube. The tube was heated at 110 °C for eight days, and pure black, thin needles of **1** were obtained in about 92 % yield based on V_2O_5. The product was purified by washing with water and acetone.

The phase identity and homogeneity of **1** was confirmed by comparing the experimental X-ray powder diffraction patterns of the bulk material with those calculated from the single-crystal X-ray data.

Received: June 25, 1998
Revised version: February 25, 1999 [Z12053IE]
German version: *Angew. Chem.* **1999**, *111*, 1864 – 1868

Keywords: hydrothermal synthesis • intercalations • magnetic properties • mixed valence compounds • vanadium oxide

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