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Strong Electron-Acceptor Methylviologen Dications Confined in a 2D Inorganic Host: Synthesis, Structural Characterization, Charge Transport and Electrochemical Properties of $(MV)_{0.25}V_2O_5$

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The *N*,*N*′-dimethyl-4,4′-bipyridinium dication, also known as methylviologen or paraquat (abbreviated as MV^{2+} hereafter) is widely used as an electron-transfer indicator in the studies of biological, chemical, and photochemical redox reactions.[1] In the past two decades, the potential applications of methylviologen in solar energy conversion and storage have garnered great attention.[2−4] Interest is particularly high in the incorporation of such photoactive organic molecules into polymeric organic or solid-state inorganic matrixes. Such a host−guest approach may increase the thermal/photochemical stability and the efficiencies of photoinduced charge separation.[5−9] Furthermore, the composite materials can sometimes possess useful properties that are not found in either the host or the guest alone.[10] Among many inorganic compounds that are suitable as host structures, layered metal oxides and phosphates occupy a prominent position for exploring artificial photochemical and photophysical processes in the restricted media.[11−13]

We have been interested in synthesizing layered organic−inorganic compounds with viologens confined in an electrically conductive 2D system to explore novel electrochemical or photochemical energy storage processes in such materials. In this communication, we describe the synthesis, characterization, charge transport, and electrochemical properties of $(MV)_{0.25}V_2O_5$ (**1**), the first viologen-containing layered oxide compound to be characterized by single-crystal X-ray analysis.[14]

The conventional synthetic scheme for preparing intercalation compounds of V_2O_5 entails a direct reaction of the guest with either solid V_2O_5 or its xerogels.[15−18] However, such heterogeneous reactions usually afford insoluble powdery products, rendering their purification, crystallization, and structural characterization difficult. Recently, dissolution-restacking of V_2O_5 layers has become a powerful method for synthesizing organic intercalates of V_2O_5 in a single-crystal form.[19−22] This synthesis is typically carried out under hydrothermal conditions in the presence of a strong organic Lewis base such as an organic amine or pyridine as the molecular template. However, we have found the method to be ineffective in introducing the methylviologen dication, a molecule with negligible Lewis basicity, into the V_2O_5 system. Instead, the use of the iodide salt of methylviologen can cause V_2O_5 to undergo reductive layer reconstruction in aqueous solution, forming a novel multilayered compound with the MV^{2+} cations as the template. Thus, when MVI_2 and V_2O_5 in the molar ratio of 1 to 3.8 were refluxed in a flask equipped with a condenser, iodine crystals were sublimed onto the condenser, and dark green $(MV)_{0.25}V_2O_5$ (**1**), as determined by elemental analysis,[23] was formed in solution as micrometer-sized crystallites in essentially quantitative yield based on V_2O_5. The FT-IR spectrum of **1** clearly confirms the presence of methylviologen cations inside a partially reduced V_2O_5 host.[24] The X-ray powder diffraction (XRD) patterns of **1** are predominated by reflections in the family of (*hk*0), indicating a layered structure.

Single-crystal X-ray analysis shows that **1** belongs to the triclinic system.[25] The asymmetric unit contains one and half methylviologen molecules, 12 V and 30 O atoms in general positions. All the 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 multilayered compound of the methylviologen $(C_{12}H_{14}N_2)^{2+}$ cations inside the anionic $\{V_2O_5\}^{0.5-}$ layers as shown in Figure 1. Each $\{V_2O_5\}^{0.5-}$ layer is formed parallel to the [110] plane and consists of distorted VO_5 square pyramids linked by edge- and corner-sharing O atoms. There are strong interactions between the aromatic organic molecules and the inorganic layers as seen in the space-filling model (see Figure 1 of the Supporting Information). The valence sum calculations[26] showed that three of the total 12 V atoms can be assigned the oxidation state as +4, and nine V atoms as +5. Finally, there is a substantial reorganization of the VO_5 pyramids in **1** as compared with the pristine V_2O_5 (see Scheme 1 of the Supporting Information). Therefore, the formation of **1** is not attainable via 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. Rather, a reductive layer reconstruction process must be involved in the synthesis of **1**. This method represents a new convenient approach to introducing a variety of other non-Lewis base organic as well as organometallic compounds into the V_2O_5 layers.[27]

The potential utilization of hybrid organic−inorganic semiconductors such as **1** in electronic devices requires an understanding of electron transport in these quasi-two-dimensional systems. While much work has been done on the doped, layered inorganic transition metal "bronzes" (e.g., $Li_xV_2O_5$),[28] hybrid organic−inorganic layered systems offer far greater opportunities for "crystal engineering" of interesting and useful materials.[29] We present in Figure 2 the resistivity of a powder compact of **1** as a function of temperature. Note that the geometric factor is not precisely defined for the sample, and therefore, there is substantial uncertainty in the absolute value of $\rho(T)$. The data were taken using a standard dc four-probe technique. The steep increase with decreasing *T*, characteristic of a semiconductor, is similar to that observed in other layered oxide systems. Perhaps the most obvious model of transport is small polaron hopping. The inset shows the data as $\log[\rho(T)/T]$ versus $1/T$, which should be approximately linear within the polaronic theory with the slope a measure of the hopping activation energy. The fact that the data are manifestly not linear indicates either a distribution of hopping energies, the physical inapplicability of the

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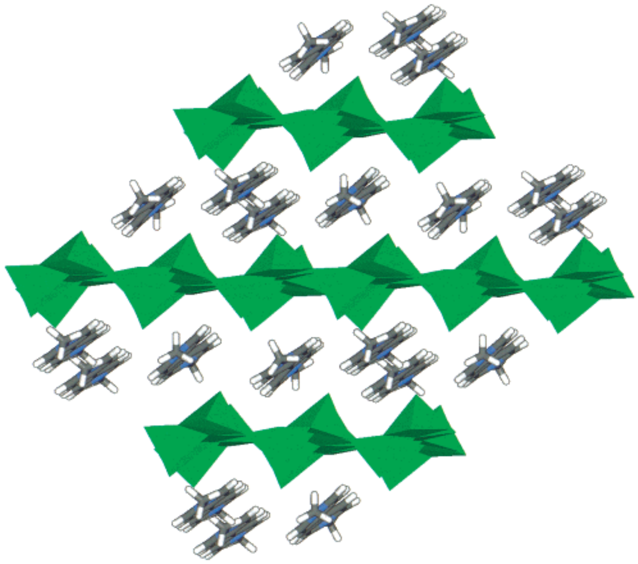

Figure 1. Structure of **1** as viewed down the *c* axis. V−O polyhedron: green, C: gray, N: blue, H: white.

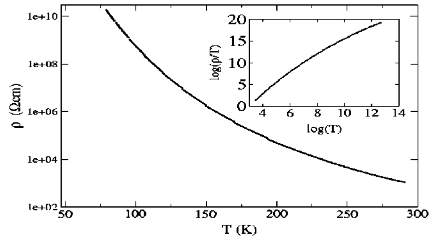

Figure 2. Resistivity of a polycrystalline compact of **1** as a function of temperature. The small jumps in $\rho(T)$ are due to changes in the measuring current. Inset: small polaron-hopping transport plot.

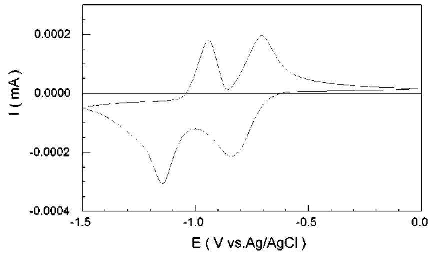

Figure 3. Cyclic voltammogram of **1** drop-cast on a glassy carbon electrode; scan rate = 10 mV/s

small polaron model, or effects due to the polycrystalline nature of the sample. Transport studies on single crystals of this and other related compounds are in progress.

The cyclic voltammetric studies of **1** carried out using a glassy-carbon working electrode showed two couples of cathodic/anodic peaks centered at ca. −0.77 V and −1.04 V respectively as shown in Figure 3. The redox potentials of these peaks are slightly shifted from the solution redox potentials of $MV^{\bullet+}/MV^{2+}$ at ca. −0.74 V and $MV^0/MV^{\bullet+}$ at −1.01 V under the same experimental conditions. The high and steady peak currents found in the repetitive CV cycles with **1** in a graphite matrix indicate that the insertion and deinsertion of the Li^+ ions in **1** is facile and reversible.[30]

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Supporting Information Available: Space-filling model, Scheme 1 (PDF). Crystallographic information file (CIF) for **1**. This material is available free of charge via the Internet at http://pubs.acs.

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(23) Elemental analysis of $(MV)_{0.25}V_2O_5$: Calcd for $C_3H_{3.5}N_{0.5}O_5V_2$: C, 15.77; H, 1.54; N, 3.07; Found: C, 15.55; H, 1.65; N, 3.03.
(24) In addition to the characteristic vibrations of methylviologen, two medium bands at 1007 and 824 cm^{-1}, attributed to the V═O stretching and O−V−O bending vibrations, were found in the IR spectrum of **1**.
(25) Recrystallization of the dark green crystallites from water in a sealed tube at 110 °C afforded X-ray diffraction quality single crystals of **1**. X-ray crystallographic data: asymmetric unit = $C_{18}H_{21}N_3O_{30}V_{12}$, tricliclinic $P(-1)$ (No. 2), $a = 11.568(1)$ Å, $b = 13.424(2)$ Å, $c = 14.266(2)$ Å, $\alpha = 67.015(2)°$, $\beta = 72.957(2)°$, $\gamma = 84.403(2)°$, $V = 1949.6(4)$ Å^3, $Z = 2$, $T = 295$ K, semiempirical adsorption correction on the raw data using SADABS, structure solution and refinement based on 3463 reflections with $I_o = 2.0\sigma(I_o)$ converged at $R = 0.088$, $R_w = 0.180$ and goodness-of-fit = 1.01.
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