# $[V^{iv}V^{v}O_4(OH)\bullet 0.5H_2O]_n$: The First Two-dimensional V-O Layered Cations with Interlamellar Water Molecules and $OH^-$ Anion

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The new mixed valence layered cluster compound, $[V^{v}V^{iv}O_4(OH)\cdot 0.5H_2O]_n$, contains the first two-dimensional V-O cation $[V^{v}V^{iv}O_4]_n^{n+}$ with water molecules and $OH^-$ anions interlayer region, and it's structure was determinated by crystal X-ray diffraction, EPR and TG analysis.

Recent developments in the chemistry of polyoxovanadium cluster reflect their relevance to bioinorganic chemistry,[1] sol-gel chemistry,[2] geochemistry,[3] catalysis and materials science.[4] While the vanadium oxides, $V_xO_y{\cdot}H_2O$, have historically constituted the major focus of attention. These compounds are capable of intercalating a variety of neutral and charged guest species such as water moleculles,[5] alkali-metal ions,[6] organic amines,[7] alcohols,[8] pyridine,[9] benzidine[10] etc. The resulting intercalation compounds usually retain the lamellar structure with the guest species occupying the interlayer regions. Partial reduction of $V^{5+}$ to $V^{4+}$ has been observed upon intercalation with alkylamines, ammonia, pyridine and benzidine. In the case of aniline,[11] the reduction of the vanadium oxide host and the simultaneous oxidative polymerization of guest molecules in the interlayer regions have been observed. However, the structural information about these intercalating compounds is very limited due to the lack of good quality single crystals. Since the hydrothermal techniques are used to prepare these compounds, the novel two and three-dimensional reduced vanadium phosphates containing various organic or inorganic cations were obtained and reported.[12] To our knowledge, only two-dimensional V-O neutral molecules[5] and V-O anions[7] were discovered in layered V-O cluster compounds, and no example which contain two-dimensional V-O cationis was determinated. In this communication, we report the hydrothermal synthesis and structure of intercalated vanadium oxide $[V^{v}V^{iv}O_4(OH)\cdot 0.5H_2O]_n$ 1,[13] in which the first two dimensional V-O layered cation $[V^{v}V^{iv}O_4]_n^{n+}$ were observed.

Compound 1 was prepared by a hydrothermal reaction. A mixture of $NH_4VO_3$ (0.4 g), $CH_3NH_2$ (0.5 ml), and $H_2O$ (10 ml) was neutralized to pH=8.0 with 50% phosphorous acid. It was sealed in a 15 $cm^{-3}$ Teflonlined reactor, which was kept at 160 °C for seven days. After being cooled to room temperature, a thin black plates crystals were isolated (0.11 g, yield 31% based on V). Anal. Calcd. for $H_2\,O_{5.5}\,V_2$, H: 1.04; V: 53.12%. Found: H, 1.12; V, 52.96%. The IR spectrum of 1 exhibited intence bands at 940 $cm^{-1}$, attributed to $\nu(V{=}O)$, and feature at 3650-3000 $cm^{-1}$ characteristic of $OH^-$ and $H_2O$.

The single crystal X-ray analysis[13] of the thin black plates revealed 1 as a layered structure containing vanadium oxide layers with the water molecules in the interlayer region, as shown in Figure 1(a). The $OH^-$ anion and water molecule are disordered, and their occupancy factors are 0.5 and 0.25, respectively. The $OH^-(H_2O)$ in the different interlayers are separated from each other by a distance of 7.65 Å along the c axis. They form strong hydrogen bonds with the adjacent vanadium oxide layers above and below. The O atoms of $OH^-$ anion and water molecules in short contact with the terminal oxygen atom O(2) at an $OH^-(Ow)$---O(t) distance of 2.46(1) Å. In the same interlayer, the $OH^-$ anions are involved in strong hydrogen bonding interactions with the water molecules. The shortest OH---O(w)distance is 2.63(1)Å along a and b axis. The two-dimensional V-O layered cations [Figure1(b)] contain infinite of edge-sharing distorted $VO_5$ square pyramids running parallel to the a and b axis. The vanadium oxide layers are connected together by four-bridging oxygen atoms(O(1)). To compare another vanadium oxide, the first two-dimensional layered V-O cluster cations was discovered in compound 1. There are two kinds of oxygen atoms in the V-O layered cation: terminal oxygen and four-bridging oxygen atoms. It is essential condition of the vanadium oxide layer that there is only one kind of bridging oxygen atoms(four-bridging O atom). The metal to oxygen distances vary as follows: to one terminal oxygen atom 1.558(3) Å, to four $\mu_4$-O atoms 1.9720(12) Å, the shortest V---V distances are 2.9361(12) Å. The assignment of the oxidation state for the vanadium atoms is consistent with the coordination geometry and is confirmed by bond valence sums calculation. By using an empirical bond valence calculation[14], $S=(R/1.79)^{-5.1}$ (S=bond valance and R=bond lengths), it is established that the V atoms possess 4.5 of formal oxidation state in 1. In the UV spectra, absorption of 900-2000 $nm^{-1}$ can be ascribed to electron transition between $V^{4+}$ and $V^{5+}$. The EPR spectrum of the title compound 1 clearly indicates that there exist vanadium atoms

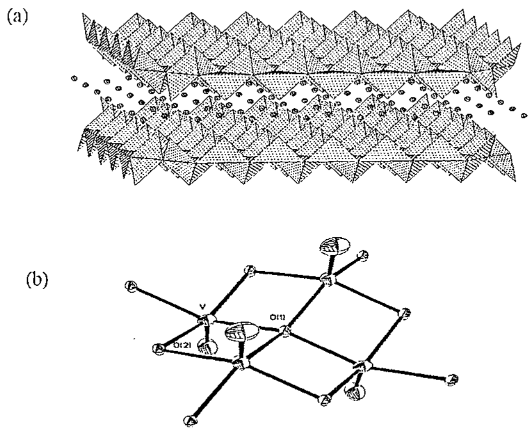

**Figure 1.** (a) A view of the structure of $[V^{v}V^{iv}\,O_4(OH)\cdot 0.5H_2O]_n$ 1 down the b axis showing the layered nature. (b) The structure of the V-O layer $[V^{v}V^{iv}\,O_4]^{n+}_{n}$.

with +4 oxidation state (g=1.966). The conductivity measurements of compound **1** in the temperature range 25-60 °C show that the conductivity of oxide 1 is $1.05\times10^{-5}$($s.cm^{-1}$) at 60 °C. The general trend for **1** is that the conductivity increases with temperature. The measurements indicate that the compound **1** is semiconductor.

Thermogravimetric analysis(TG) of **1**, carried out under air atmosphere with a heating rate of 10 °C $min^{-1}$ shows two step for weight in which lost weights are 4.950 %(60-201 °C) and 4.725(201-447°C), the lost weights correspond to the release of the $H_2O$ and $OH^-$, respectively. Also from TG curve, we found 3.636% of increasing weight between 447 and 513 °C ($2\ V^{4+} + 0.5\ O_2 \rightarrow 2V^{5+} + O^{2-}$ ). The calculating result obtained from the amount of the increasing weight that $V^{4+} : V^{5+}$ is 1: 1 in compound **1**.

In summary, a novel layered $OH^-$ anions and water molecule intercalated novel mixed valence two-dimensional V-O layered cluster compound, $[V_2O_4{\cdot}(OH){\cdot}0.5H_2O]_n$ **1**, has been hydrothemally synthesized and its single-crystal structure determined. In which the first layered V-O cation $[V^{v}V^{iv}O_4]_n^{n+}$ were observed, and it has good conductivity.

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13 X-Ray structure data for 1. Tetragonal, space group I-42m, a=b=3.7240(10) c=15.401(3)Å, U=213.58(9) $Å^3$, Z=4. A black plate crystal with dimensions of 0.20×0.20×0.14 mm was mounted on a glass fiber. Data were collected on a Siemens P4 four circle diffcractometer at 20 °C in the rang $5.3° < 2\theta < 49.8°$ using the $\omega$-$2\theta$ scan technique. No decay of the crystal was observed through the data collection. A total of 242 reflections were collected of which 97 reflections with $I_0 > 2\sigma(I_0)$ were used. An empirical absorption correction based on $\psi$ scans was applied. The structure was solved by direct methods and refined using SHELXL93 software. All the non-hydrogen atoms were refined anisotropically. The OH- anion and water molecule are disordered, their occupancy factors are 0.5 and 0.25, and were refined with the same coordinates and anisotropic thermal parameters. Structure solution and refinement based on 100 reflections and 14 parameters gave $R(R_w)=0.443(0.1287)$. An attempt to refine the structure in space group I4/mmm and I-4 were unsuccessful (oxygen atoms were non-positive, R1 are 0.092 and 0.075). Atomic coordinates, bond lengths and angles, and terminal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC) .

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