Influence of $[\text{VO}_4]^{3-}$ Bridges on Magnetic Coupling in Ba$_2$V$_3$O$_9$ Studied by Molecular Orbital Calculations

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A molecular orbital study is presented of the magnetic coupling in the one-dimensional vanadium oxide Ba$_2$V$_3$O$_9$ with a bridge formed by two different types of VO$_4$ tetrahedra. The concept of complementary versus counter-complementary effect has been used to explain the structural origin of the magnetic behavior of the compound. Namely, the observed antiferromagnetic coupling is dominated by the orbital complementarity of the V(1) tetrahedra sharing only one oxygen corner with two adjacent VO$_6$ octahedra. The second type of V(2) tetrahedra does not provide a noticeable contribution to the magnetic coupling due to the orbital counter-complementarity of the bridging ligand.

Key Words: Vanadyl vanadate, Magnetic coupling, Extended Hückel calculations

Introduction

Mixed valence vanadium oxides have attracted the interest of researchers due to a wide variety of their structural and physical properties. Most of the structures have magnetic V$^{4+}$ (d$^1$) ions and form low-dimensional spin systems. The structure of Ba$_2$V$_3$O$_9$ consists of infinite chains of V$^{4+}$O$_4$ octahedra. These distorted octahedra are connected with each other through the two V$^{5+}$O$_4$ tetrahedra. The magnetic properties of these chains were studied in detail by Kaul and co-workers. The temperature dependence of the susceptibility for the solid revealed an antiferromagnetic coupling with a sizeable strength of the magnetic intrachain susceptibility for the solid revealed an antiferromagnetic coupling with a sizeable strength of the magnetic intrachain susceptibility.

We analyze herein the different magnetic contribution of the two VO$_4$ bridges for the magnetic exchange interaction between the V$^{4+}$ ions. The atomic parameters used in the calculations are given in Table 1.

Crystal Structure and Molecular Models

Ba$_2$V$_3$O$_9$ consists of infinite [V$^4_2$O$_9$]$_n^-$ chains. This stoichiometry supposes a presence of one V$^{4+}$ ion (six coordinated) and two V$^{5+}$ ions having a tetrahedral coordination, leading to the structural formula of [VO(VO$_3$)$_2$]$^2-$. The chains are not connected to each other. Each chain is formed by VO$_6$ octahedra linked via two VO$_4$ tetrahedra and an oxygen atom unshared with the tetrahedra (Figure 1(a)). The paramagnetic vanadium(IV) centers are all in an octahedral geometry, in which the six coordination sites are occupied with oxygen atoms from vanadyl V=O groups and the [VO$_3$]$^2-$ bridges. All VO$_6$ octahedra are significantly distorted with the vanadium atom displaced towards one of the oxygen atoms. This leads to the formation of a short V-O bond (1.69 Å indicating the typical distance for vanadyl bond in the V$^{4+}$ polyhedra), an opposite long V-O bond (2.24 Å), and four equatorial V-O$_{eq}$ bonds (average length of 2.00 Å).

This feature leads to the splitting of the $t_{2g}$ levels of the V$^{4+}$ ion (six coordinated) and two V$^{5+}$ ions having a tetrahedral coordination, leading to the structural formula of [VO(VO$_3$)$_2$]$^2-$. The chains are not connected to each other. Each chain is formed by VO$_6$ octahedra linked via two VO$_4$ tetrahedra and an oxygen atom unshared with the tetrahedra (Figure 1(a)). The paramagnetic vanadium(IV) centers are all in an octahedral geometry, in which the six coordination sites are occupied with oxygen atoms from vanadyl V=O groups and the [VO$_3$]$^2-$ bridges. All VO$_6$ octahedra are significantly distorted with the vanadium atom displaced towards one of the oxygen atoms. This leads to the formation of a short V-O bond (1.69 Å indicating the typical distance for vanadyl bond in the V$^{4+}$ polyhedra), an opposite long V-O bond (2.24 Å), and four equatorial V-O$_{eq}$ bonds (average length of 2.00 Å).

Table 1. Atomic parameters used in EH calculations

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<th>Atom</th>
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Figure 1. (a) Segment of the octahedral chain structure of Ba$_2$V$_3$O$_9$ and (b) its binuclear vanadium(IV) model. The light gray and small red circles represent the V and O atoms, respectively.
vanadium atom destabilizing the \( d_e \) and \( d_g \) orbitals above the \( d_{xy} \) orbital (we assume a local coordinate system such that the \( z \)-axis is taken parallel to the vanadyl bond with the \( x \)- and \( y \)-axis approximately along the V-O\(_{eq} \) directions). This implies that the unpaired electrons of the V\(^{4+} \) ions occupy the \( d_{xy} \) orbitals. Consequently, the vanadium 3\( d \_\alpha \) orbitals of two adjacent octahedra make \( \pi \)-antibonding interactions with the oxygen 2\( p \) orbitals of the shared edge of the bridging tetrahedra which provide a good superexchange interaction along the chain.

There are two different types of VO\(_4 \) tetrahedra in the structure. One type of the VO\(_4 \) tetrahedra [V(1)] links octahedra by sharing only one oxygen corner whereas another type [V(2)] connects two adjacent octahedra via the two oxygen atoms. Within tetrahedra the V-O distances to oxygen atoms shared with VO\(_4 \) octahedra are longer than the V-O distances to unshared oxygen atoms. The average V-O bond lengths for V(1) and V(2) atoms are 1.72 and 1.71 Å, respectively. The adjacent V\(^{4+}\) ions have a separation of 3.01 Å. The significant antiferromagnetic coupling may be explained by a superexchange interaction through each of the two bridging tetrahedra which connect the two V\(^{4+} \) octahedra. The contribution of the oxygen atom from vanadyl V=O group is almost nil, since the \( p \) orbitals of the axially bridged oxygen are not of the correct symmetry to overlap with the \( d_{xy} \) orbital of V(IV). Thus, we conclude that a sizeable magnetic exchange between the V\(^{4+} \) ions along the chain is mostly mediated by the bridging VO\(_4 \) tetrahedra.

We have adopted appropriate molecular models to analyze the different magnetic contribution of the two VO\(_4 \) bridges to the magnetic coupling for this compound. The dimer model used is shown in Figure 1(b). The model was taken from the crystal structure (model 1). In order to analyze independently the role of each VO\(_4 \) bridge, we also built single VO\(_4 \)-bridged models 2 and 3 by removing one of the two VO\(_4 \) tetrahedra. In the dimer unit, the V\(^{4+} \) ions are linked by V-O-V and V-[V(2)O\(_4\)]-V bridges in model 2 and by V-O-V and V-[V(1)O\(_4\)]-V bridges in model 3. In the two situations, the magnetic exchange is propagated principally via the \( d_{xy} \) orbitals of the V\(^{4+} \) ions which interact with the appropriate 2\( p \) orbitals of the oxygen atoms of the VO\(_4 \) bridge.

### Results and Discussion

The strength of the exchange coupling is mainly associated with the overlap interactions between the magnetic orbitals of the metal centers and the highest occupied molecular orbitals (HOMOs) of the bridging ligands. By symmetry, the HOMO and HOMO-1 of a given bridging ligand mix with the symmetric (\( d_s \)) and antisymmetric (\( d_a \)) combinations of magnetic orbitals (\( d_{xy} \), \( d_{yz} \), and \( d_{xz} \)) to give the corresponding SOMOs (singly occupied molecular orbitals) \( \phi_s \) and \( \phi_a \). The interactions of these filled ligand orbitals with the metal \( d \_\alpha \) orbitals are, of course, antibonding. Hoffmann and coworkers\(^7\) have analyzed exchange interactions in bimetallic complexes in terms of pairwise interactions of these molecular orbitals. According to Hoffmann’s approach, the magnetic coupling constant \( J \) is built by a ferromagnetic and an antiferromagnetic contribution. The former one is considered to be proportional to the square of the energy gap (\( \Delta e \)) between the two SOMOs. When the energy gap is very small, the ferromagnetic coupling interaction is dominant.

To quantify the relative effectiveness of the two VO\(_4 \) bridges to magnetically couple the V\(^{4+} \) ions, we have performed a computational experiment in which we calculate \( \Delta e \) with one of the bridges completely deactivated. First, the whole molecule is divided in two fragments, the VO\(_4 \) bridge (fragment A) and the rest of the model (fragment B). Subsequently, the molecular orbitals of the isolated fragments are calculated and superimposed to form the AB molecule. All the covalent interactions between the V\(^{4+} \) centers and the V(1) bridge are completely eliminated by freezing the V(1) bridge and the calculated energy difference between the two SOMOs is solely due to the coupling over the V(2) bridge. The same procedure is applied taking the V(2) bridge as a frozen fragment and activating only the coupling through the V(1) bridge. Results calculated for the three models are listed in Table 2.

The first obvious conclusion that can be extracted from Table 2 is that the V(1) bridge is by far more effective in the coupling of the magnetic moments of the V\(^{4+} \) ions than the V(2) bridge. This is reflected in the calculated \( \Delta e \) values. Furthermore, an antisynergistic effect of the two bridges can be readily explained with the theory of orbital complementarity and counter-complementarity of Nishida et al.\(^8\) and McKee et al.\(^9\). The explanation is based on the Hoffmann’s model, which relates the energy gap (\( \Delta e \)) of the magnetic orbitals to the coupling parameter: the larger the energy separation, the stronger the antiferromagnetic interaction between the two V\(^{4+} \) centers. The exchange interactions in magnetic solids of transition metal ions are well described by the \( \Delta e \) values obtained from EHMO calculations.\(^10\)

As mentioned, model 1 represents the real situation in the solid. The overall exchange interaction for the solid is found to be antiferromagnetic with a coupling constant of \(-94 \) K.\(^3\) We make a comparison of the magnetic contribution of the two VO\(_4 \) bridging ligands in this model. First, comparison of the results obtained for models 1 and 2 allows evaluating the role of the V(1)-centered tetrahedra. Since its removal from model 1 results in a large reduction in the antiferromagnetic contribution \( \Delta e \) we conclude that the V(1) tetrahedra provide a substantial antiferromagnetic coupling. As can be seen in

![Table 2](image-url)

\( \Delta e \) values [in meV units] are given in parentheses.
The role of the V(2) centered tetrahedra. Since its removal results in the magnetic coupling. Because of symmetry, the magnetic orbitals \( d_s \) and \( d_\lambda \) of V(2) centers interact with the HOMO and HOMO-1 of the V(2)O\(_4\) bridge through the \( \pi \) pathway, respectively. The energies of the symmetric (\( \phi_S \)) and antisymmetric (\( \phi_\lambda \)) orbitals are both raised, as shown in Figure 3. Consequently, a change in the energy gap that separates the \( \phi_S \) and \( \phi_\lambda \) orbitals becomes very small, which leads to the weak antiferromagnetic contribution. This is due to an orbital counter-complementarity phenomenon of the V(2)O\(_4\) bridge.

Obviously, there is a significant difference of the magnetic contributions between the two VO\(_4\) bridging ligands; i.e., one is a very weak antiferromagnetic and the other is rather strong antiferromagnetic contribution to the coupling. This indicates that the antiferromagnetic coupling interaction in the two VO\(_4\)-bridged divanadium(IV) model is mainly determined by the V(1)O\(_4\) bridging ligand. In addition, the magnetic exchange parameter is predicted to be more than 5 times larger for V(1)O\(_4\) than for V(2)O\(_4\) bridge (i.e., 9450/1750 = 5.4), which is consistent with the tendency in the calculated \( J \) values (see Table 2).

**Conclusion**

In order to explore the essential reason for the difference between the magnetic contributions of the two VO\(_4\) ligands bridging V\(^{4+}\) ions in Ba\(_2\)V\(_2\)O\(_9\), the molecular orbital analysis was made. The magnetic properties can be understood in an EHMO picture by considering the interaction of the symmetric and antisymmetric magnetic orbitals with the HOMO and HOMO-1 (mainly O 2p orbitals) of the VO\(_4\) bridges. The isolated exchange interaction of the V(1)O\(_4\) bridge is more than 5 times larger than that of the V(2)O\(_4\) bridge, illustrated by the square of SOMO gap (97.2 meV and 41.8 meV) in the models 2 and 3 freezing one of the two bridges. The global magnetic coupling in Ba\(_2\)V\(_2\)O\(_9\) is dominated by the orbital complementary interaction between the V\(^{4+}\) octahedra through the V(1)O\(_4\) tetrahedra sharing one oxygen atom with the octahedra. The V(2)O\(_4\) tetrahedra bridging two adjacent V\(^{4+}\) octahedra and the oxygen atoms unshared with tetrahedra have a very small influence on the magnetic coupling. It can be concluded that the antiferromagnetic coupling in Ba\(_2\)V\(_2\)O\(_9\) is almost exclusively due to the V(1)O\(_4\) bridge and the V(2)O\(_4\) bridge is only of secondary importance.

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**References**