Magnetic Couplings in Vanadium Aromatic Sandwich Complexes and Their Crystals by Using DFT Methods

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Received: May 11, 2005; In Final Form: August 15, 2005

Using density functional theory, we have theoretically studied the origin of ferromagnetic coupling of spins in the long multiple deckers of vanadium sandwich complexes with benzene (Bz). This is done by calculating the band structure of their infinite one-dimensional (1D) crystals along the periodic (=Z) direction. We find that the magnetic coupling can be ascribed to spin polarization in the band (=those derived from d_{z^2}) whose k states are not involved in the formation of partial covalent bonds between vanadium atoms and benzene rings. We have also studied magnetic and electronic properties of multiple deckers of a naphthalene (Np)−vanadium complex. We find that there is a stronger covalent interaction as well as a stronger electrostatic interaction between V and Np rings than between V and Bz rings. This suggests that there is a possibility of longer multiple deckers of a Np−V complex. In addition, ferrimagnetic coupling of spins is expected, resulting in a magnetic moment 45% larger than that of the Bz−V complex at the same length. For their 1D crystals, band structure analysis also shows that the origin of magnetic coupling in long multiple deckers should be similar to that of Bz−V multiple deckers.

Introduction

Stimulated by the development of gas-phase synthesis of organometallic compounds using the laser vaporization technique, transition metal−benzene complexes Bz_nM_m have been widely investigated both experimentally[1−4] and theoretically.[5−8] For 3d transition metal complexes, two kinds of structures were proposed, linear multiple decker sandwich structures for the earlier transition metals (M = Sc, Ti, and V) and rice-ball structures for the late transition metals (M = Fe, Co, and Ni). Particular attention has been paid to a vanadium complex, since mass spectra showed that it had the biggest tendency to form multiple deckers among all the 3d transition metals investigated. In addition, it exhibits ferromagnetic coupling of spins and displays a chiral conformation at terminal units,[9] which can make it one of the most promising candidates for molecular devices. However, there has been no complete explanation for the origin of ferromagnetic coupling in terms of its electronic structure. For example, Yasuike and Yabushita have merely showed that the formation of the multiple-decker sandwich complexes is mainly due to the delocalization of metal dδ electrons via the LUMOs of benzene molecules.[6] Therefore, it would be valuable to make a detailed investigation of the electronic structure of vanadium multiple deckers, which can be conveniently done by considering an infinite one-dimensional (1D) crystal. In addition, it would be also interesting to investigate if aromatic compounds larger than benzene can make similar multiple deckers, since they can hold more than one transition metal atom in the sandwiched region. According to the author's knowledge, there is no experimental report for that. This work is aimed at answering these questions by using theoretical methods.

Theoretical Methods

Our total energy calculations are performed with the Vienna ab initio simulation program (VASP).[10,11] Electron−ion interaction is described by the projector augmented wave (PAW) method,[12] which is basically a frozen-core all-electron calculation. The exchange-correlation effect is treated within the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE).[13] Solution of the Kohn−Sham (KS) equation is obtained by using the Davison blocked iteration scheme followed by the residual vector minimization method.[11] All the valence electrons of chemical elements are explicitly considered in the KS equation. For vanadium, all the 3d electrons as well as 3p electrons are explicitly treated as valence electrons. We adopt a supercell geometry in which k-space sampling is done with a Γ-point for molecular systems. For this, we use large supercells that guarantee interatomic distances between neighboring cells greater than 8.20 Å. Cutoff energy is set sufficiently high (=400 eV) to guarantee accurate results, and the conjugate gradient method is employed to optimize the geometry until the Hellmann−Feynman force exerted on an atom is less than 0.03 eV/Å. All the results rely on the spin-polarized calculation. In addition, our calculation does not restrict a system to a specified symmetry. Rather, we allow the full relaxation of geometry so that molecular symmetry can change. Related to this, we note that our recent work on a benzene−Li−benzene sandwich complex showed that our PBE calculation with PAW was accurate within 0.l eV when it was compared with a more sophisticated calculation G3(MP2).[14] We have also considered one-dimensional (1D) crystals in which sandwich complexes are infinitely stacked along one (Z) direction, for its k-point sampling 15 points are used along the periodic direction. When necessary, single-point GAUSSIAN calculations were made using the optimized

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10.1021/jp0524577 CCC: $30.25

TABLE 1: Binding Energies (D_e) and Spin Multiplicities of Benzene−Vanadium Complexes (L = Bz, m = 1) and Naphthalene−Vanadium Complexes (L = Np, m = 2) for the Processes $L_{n+1}V_{mn} \rightarrow L_nV_{m(n-1)} + LV_m$ and Vertical Ionization Energies (IE) of $Bz_{n+1}V_n$

	D_e (eV)			multiplicity		IE		
L	expt^a	this work	other work	this work	other work	expt^e	this work	other work
				LV_m				
Bz	0.79	1.64	2.09^b 0.67^c 0.81^d	2	2^b 4^c 6^d	5.11 ± 0.04	5.63	5.71^f 5.53^g
Np		4.64		5				
				L_2V_m				
Bz	3.19	3.46	3.64^b 3.13^c 3.57^d	2	2^{b-d}	5.75 ± 0.03	5.81	5.96^f 5.87^g
Np		4.59		3				
				L_3V_{2m}				
Bz		2.51	2.76^b 2.32^c	3	$3^{b,c}$ 1^d	4.70 ± 0.04	4.75	4.82^f 4.73^g
Np		3.57		5				

[a] Values quoted in ref 7. [b] Data obtained from BPW91 calculations with 6-311G** basis set quoted in ref 8. [c] Data obtained from BPW91 calculations with Lanl2dz basis set quoted in ref 8. [d] Data obtained from BPW91 calculations with double numerical basis with polarization (DNP) quoted in ref 7. [d]Data obtained from R/ROMP2 calculations quoted in ref 6. [e] Values quoted in ref 8. [f] Data obtained from BPW91 calculations with 6-311G** basis set quoted in ref 8. [g] Data obtained from BPW91 calculations with Lanl2dz basis set quoted in ref 8.

TABLE 2: NBO Charges of Specified Atoms or Group of Atoms, Wiberg Bond Indices, and Bond Lengths between Various Bonds (Å)

param	Bz_2V	Bz_3V_2	NpV_2	Np_2V_2	Np_3V_4
$q(V)^a$	0.62	0.72	0.60	0.81	0.81
$q(R)^b$	−0.31	−0.41 −0.61	−0.30	−0.40	−0.84 −1.54
$O(V-C)^c$	0.24	0.24 0.37	0.20−0.46	0.14−0.36	0.18−0.41 0.14−0.24
$O(V-R)^d$	1.44	1.44 2.22	1.94	3.15	3.59 2.40
$O(V_1-V_2)^e$			1.29	0.62	1.05
$l(V_1-V_2)^f$			2.38	2.66	2.71
$l(V-R)^g$	1.67	1.63 1.73	1.60	1.72	1.69 1.77

[a] NBO charges of metal atoms. [b] NBO charges of benzene rings. For triple deckers, the numbers correspond to terminal rings and the central ring in sequence. [c] WBI for metal−carbon bonds, where carbon atoms belong to benzene rings. See footnote b *f*or the meaning of two numbers. [d] WBI for metal−carbon bonds summed up for all carbon atoms of each ring. See footnote *b* for the meaning of two numbers. [e] WBI for V−V bonds. See footnote *b* for the meaning of two numbers. [f] V−V distance. [g]Interatomic distances between metal and aromatic rings. See footnote *b* for the meaning of two numbers.

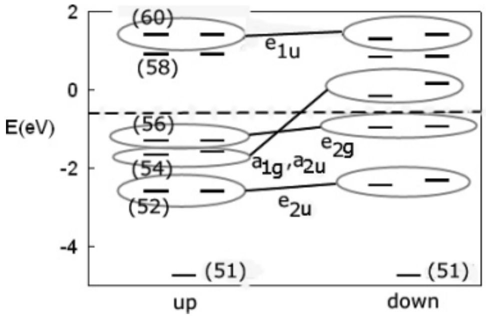
geometries obtained from our PAW calculations. Explicitly, natural bond orbital (NBO) analysis[15] was performed with the 6-311G** basis set implemented in the GAUSSIAN03 program.[16]

Results

We first consider the thermochemical data in Table 1. We define the dissociation energy (D_e) of a complex with the relation $D_e[Bz_{(n+1)}V_n] = E[Bz_nV_{(n-1)}] + E[BzV] - E[Bz_{(n+1)}V_n]$. Zero point energy is not included. For comparison, we show the results of another DFT calculation based on the exchange functional of Becke combined with the correlational functional of Perdew−Wang[17] (BPW91) implemented in GAUSSIAN program reported elsewhere, since it has been reported to be generally more reliable for 3d transition metals than any other forms of exchange-correlation functional. For BzV($\mu = \mu_B$), we find that our datum disagrees with experimental data but qualitatively agrees more with recent BPW91 results calculated with 6-311G** basis set.[8] [Henceforth, magnetic moment of a complex to a specific direction will be shown in parentheses.] It is strange that BPW91 calculation is in better agreement with experimental datum when the Lanl2dz basis set is adopted in combination with an appropriate pseudopotential.[8] We note that there is inconsistency in the BPW91-predicted spin multiplicity of ground-state configuration depending upon the used basis set. Our PBE calculation with PAW shows that its spin multiplicity is a doublet, which is in an agreement with the BPW91/6-311G** calculation. For double and triple deckers, we have optimized structures starting from the configurations in which metal atoms are sandwiched between two benzene rings with D_{6h} symmetry, since that configuration was reported to be the most stable one among three possible ones for the double decker.[8] For the double decker, Table 2 shows that the V−R distance is 1.67 Å, where R denotes a benzene ring. For the triple decker, the table also shows that vanadium atoms are closer to terminal rings (=1.63 Å) than to the central benzene ring (=1.73 Å), which is in an agreement with BPW91 calculation.[8] Our PBE-predicted dissociation energy as well as spin multiplicity is in a good agreement with BPW91/6-311G** data. We also find the ferromagnetic coupling of spins for Bz_3V_2 in consistency with the recent BPW91/6-311G** calculation. We recall that the earlier BPW91/DNP calculation exhibited antiferromagnetic coupling,[7] showing sensitivity of results to the used basis set. This kind of problem would rarely happen in our calculation, since VASP does not rely on localized orbital basis sets but on the projected augmented plane wave, for which it is well-known that there is a systematic convergence of results as the cutoff energy is increased. Table 1 also shows that our PBE calculations are in a good agreement with experimental results for the vertical ionization energies of vanadium−benzene complexes. In short, our PBE calculation with PAW is at least as much reliable as the BPW91/6-311G** calculation.

Table 2 lists partial charges on the metal atoms and benzene rings of double and triple deckers obtained from the NBO analysis in the GAUSSIAN03 program. Also shown are Wiberg bond indices (WBI)[18] for the bonds between metal atoms and carbon atoms of appropriate benzene rings [=C(R)] and their sum over all carbon atoms of each benzene ring. For the entire sandwich complexes investigated, we first find that vanadium atoms are in the low oxidation state of +1 at most, as evidenced by NBO charges on them. To understand this, we consider a simple process 2Bz + V → Bz_2V. The sum of the binding energies in Table 1 shows that there is still a strong binding (E_b = 3.98 eV) in the process. Therefore, a weak electrostatic interaction between the vanadium atom and two negatively charged benzene rings ($q = -0.31$) alone cannot account for the observed binding energy. For comparison, we note that the binding energy (=−1.11 eV) of lithium sandwich complex Bz_2Li is much smaller in the corresponding process involving a Li atom instead of a vanadium, even though the NBO charge (=+0.92) at lithium atom is larger.[14] This strongly suggests that there should be a significant amount of covalent interaction between the vanadium atom and carbon atoms in the benzene rings, which plays a dominant role in stabilizing the vanadium multiple deckers. In fact, Table 2 shows that the bond order is 0.24/vanadium−carbon bond in Bz_2V. [The corresponding order is practically zero (=0.01) in $LiBz_2$, indicating the dominant

SCHEME 1: Energy Level Diagram of Bz_3V_2 for Spin-Up (Left) and -Down States (Right)



role played by the electrostatic stabilization in the lithium complex.] Therefore, total vanadium−ring covalent bonds amount to 1.44 (=0.24 × 6) bonds/V−Bz in Bz_2V.

Electronic structure analysis will give us a clear idea on the mechanism of different magnetic couplings as well as the bonding nature in the triple decker Bz_3V_2. Scheme 1 shows its relative energy levels and orbital nature in a simplified picture. First, spin-up and -down valence states are occupied up to $n = 57$ and 55, respectively. For both spins, our analysis of l,m-projected local electronic density of states (LDOS) shows that all the states $n = (1-51, 58, 59)$ basically correspond to benzene-derived states or 3p(V) states with no appreciable contribution from 4s(V) or 3d(V) states. Specifically, $n = 51$ corresponds to a combination of HOMO2's of the rings R_1 and R_3, where HOMO2 represents one of the two degenerate HOMOs of a benzene ring. Similarly, $n = 58$ and 59 correspond to combinations of LUMO1s and LUMO2s (=two degenerate LUMOs) of the rings, respectively. On one hand, $n = 52-57$, 60, and 61 are essentially 3d(Zn)-derived states. 4s(V)-derived states lie more than 5 eV above the HOMO level, implying that two 4s(V) electrons are transferred to 3d(V)-derived states. Therefore, there are 10 valence electrons coming from two vanadium atoms that occupy six and four spin-up and spin-down 3d-derived states of the complex, respectively. To understand this, we first note that D_{6h} symmetry of the triple-decker complex Bz_3V_2 splits 10 3d(V)-derived levels into six sets, each set corresponding to a different irreducible representation. We recall that five 3d(V) levels of the complex Bz_2V split into three irreducible representations, where $d_{x^2-y^2}$ and d_{xy} belong to e_{2g}, d_{z^2} belongs to a_{1g}, and d_{xz} and d_{yz} belong to e_{1g}. (The Z axis is parallel to the direction of stacking of benzene rings.) KS molecular orbitals of Bz_3V_2 are obtained from bonding and antibonding interactions of each of $3d(V_1)$ orbitals of one vanadium atom V_1 with that of the other vanadium atom V_2 in an imaginary process $2Bz_2V \rightarrow Bz_3V_2 + Bz$. For example, $d_{xz}(V_1) + d_{xz}(V_2)$ and $d_{yz}(V_1) + d_{yz}(V_2)$ jointly form the basis of the irreducible representation E_{1u}. Similarly, $d_{xz}(V_1) - d_{xz}(V_2)$ and $d_{yz}(V_1) - d_{yz}(V_2)$ also form the basis of E_{1g}. (Here, plus and minus signs represent bonding and antibonding interactions, respectively, i.e., interactions between two orbitals with the same and different phases at interaction sites.) In short, four e_{1g}(V)-derived orbitals from two Bz_2V units split into two e_{1u} and two e_{1g} orbitals when the triple decker is formed. Similarly, two a_{1g}-derived orbitals split into an a_{1g} and an a_{2u} orbital, and four e_{2g}-derived orbitals, into two e_{2g} and two e_{2u} orbitals from bonding and antibonding interactions, respectively. Four e_{2g}-derived orbitals are stabilized by symmetry-allowed interactions with ring π states, making two of them ($=e_{2u}$) the lowest in energy among all the 10 d(V)-derived orbitals. Figure 1a shows that $n = 52$ (spin-up and -down) indeed represents an e_{2u} orbital ($=e_{2u}{}^1$) in interaction with a LUMO state of R_2 through four δ bonds. Similarly, $n = 53$ (spin-up and -down) represents the other e_{2u} orbital ($=e_{2u}{}^2$) in interaction with the other LUMO of R_2. The interactions can be represented by $(+)d_{x^2-y^2}(V_1)-LUMO1(R_2)(-)d_{x^2-y^2}(V_2)$ and $(+)d_{xy}(V_1)-LUMO2(R_2)(-)$-$d_{xy}(V_2)$, respectively, where R_2 is the benzene ring at the center of the complex. Figure 1b shows that states $n = 56\uparrow$ (spin-up) and $n = 54\downarrow$ (spin-down) represent an e_{2g} orbital ($=e_{2g}{}^1$) which is derived from a combination of $d_{x^2-y^2}$ orbitals and is in a symmetry-allowed interaction with LUMO1 of R_1 and R_3. Consequently, there is a formation of eight partial δ bonds between carbon atoms of those rings and vanadium atoms. It is very easy to verify that there cannot be an interaction of this orbital with any $\pi(R_2)$ orbital. Similarly, in $n = 57\uparrow$ and $n = 55\downarrow$, the other e_{2g} state ($=e_{2g}{}^2$) derived from a combination of d_{xy} orbitals also interacts with LUMO2 of R_1 and R_3, also forming eight partial δ-bonds. On the other hand, there is little bonding interaction of two a_{1g}- and four e_{1g}-derived orbitals with ring π states, leaving them generally energetically higher than e_{2g}-derived orbitals. In addition, e_{1g}-derived orbitals lie even

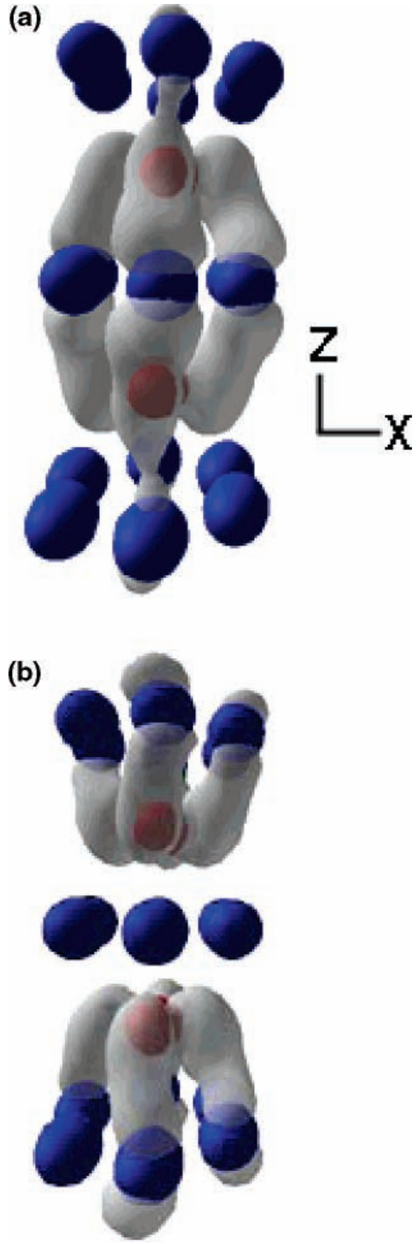


Figure 1. Electron density distributions in the states $52\uparrow$ (a) and $56\uparrow$ (b).

higher than a_{1g}-derived orbitals. This is quite similar to the case of the splitting of energy levels in tetrahedral field. In fact, the lobes of the electron density of e_{1g}-derived orbitals point to C═C bonds and carbon atoms of three benzene rings which are negatively charged, while those of a_{1g}-derived orbitals direct to the centers of the rings corresponding to a charge hole. Related to this, it is worth noting that our separate NBO analysis with 6-311G** basis set shows that the charges on the benzene rings are −0.41, −0.61, and −0.41 for R_1, R_2, and R_3, respectively (see Table 2), which can be clearly ascribed to the orbital nature of four e_{2g}-derived orbitals occupied for both spins. In other words, four 3d electrons, which exclusively belonged to vanadium atoms before complex formation, transfer part of their electron density to two LUMO orbitals of the benzene rings upon the formation of the triple-decker complex by occupying four e_{2g}-derived orbitals. This results in negative charge in the benzene rings. However, metal−ligand interaction is not purely electrostatic, and the concept of ligand field theory is applicable. In fact, there are overlaps between the d orbitals of the metals and empty orbitals of ligand groups. This is also consistent with our analysis showing a strong covalence of V−C(Bz) bonds in the double decker V_2Bz. Indeed, our similar analysis for the triple decker shows that the NBO charge (=+0.72) on the vanadium atoms of the triple decker is comparable to that (=+0.62) of the double decker (see Table 2). In addition, WBI for each of six pairs of V_1−C(R_1) is 0.24, and that for each of V_1−C(R_2) is 0.37. Therefore, total bond orders amount to 1.44 (=0.24 × 6) and 2.22 (=0.37 × 6) for V_1−R_1 and V_1−R_2 bonds, respectively. In short, vanadium atoms form one and half bonds with pheriperal benzene rings, which was also the case of the double decker. They also form more than double bonds with the central ring. So we can envision that this system is a dimer of Bz−V, where Bz−V bonds inside the chain are stronger than the terminal ones. In turn, this observation also suggests that the terminal benzene rings could be more reactive toward polymerization.

Compared to the case of spin-up states, Scheme 1 shows that a_{1g}-derived orbitals (=a_{1g} and a_{2u}) are energetically higher than e_{2g} orbitals (=$e_{2g}{}^1$ and $e_{2g}{}^2$) in spin-down states. Consequently, both spin states of the e_{2g} orbitals are fully filled, while only spin-up states of a_{1g}-derived orbitals are filled. This seems to correlate with the fact that e_{2g} orbitals are involved in the formation of partial covalent bonds as explained above, while a_{1g}-derived orbitals are not. To describe it in more detail, the spin pairing of electrons in e_{2g} orbitals results in more stable partial bonds between vanadium atoms and carbon atoms of the benzene rings even with the sacrifice of spin-pairing energy. Meanwhile, a spin pairing in a_{1g}-derived orbitals would only bring about energy loss, since no covalent bond formation is involved. This is the origin of magnetic coupling in the benzene−vanadium triple decker.

Here, we delve into the one-dimensional crystal of the vanadium complex. We find a stable energy minimum at the lattice constant L_z = 3.40 Å, which is nearly the same as the Bz−Bz distance (=3.37 Å) in the triple decker. In this process, the optimal lattice constant (L_z) was found by considering total energy as a function of the lattice parameter along the z axis, where the total energy for each L_z is obtained after geometry optimization. A primitive cell contains one chemical unit of BzV. Lattice energy defined by the process BzV(μ=μ_B) → BzV(1D)(μ=μ_B) is 2.59 eV, which amounts to the energy gain from embedding one unit of BzV in the infinite 1D crystal. It is almost the same as the value (=2.51 eV) of $D_e[Bz_3V_2]$ shown in Table 1. Therefore, adding one BzV to the infinite crystal is energetically at least as favorable as adding it to the triple decker. Importantly, there is a ferromagnetic coupling of spins when the crystal is formed. This is in an agreement with a recent calculation on a large cluster Bz_7V_6 which also showed a similar coupling.[9] Figure 2 shows its band structure along the periodic (=Z) direction obtained from our spin-polarized calculation. We first find that most of the bands around Fermi level are nearly flat, almost representing strongly localized molecular states. This has already been expected from the large metal−metal distance in the triple decker Bz_3V_2 which does not allow effective overlap between d-states of vanadium atoms. In fact, we find bands 17−21 represent those derived from atomic d-states of vanadium. Namely, n = 19 is derived from a_{1g} states and n = 20 and 21 represent e_{2g}(V)-derived bands which are still doubly degenerate after crystal formation. n = 20 and 21 exhibit exceptionally large dispersions when compared to other bands shown in the figure. This is simply due to large overlaps between e_{2g}(V) states (=$d_{x^2-y^2}$ and d_{xy}) and LUMOs(R) along the lattice direction. Consequently, the overlap results in a nearly complete delocalization of electron density within the whole crystal through the formation of δ-bonds at the zone boundary ($k = \pi/L_z$), which can be easily understood by simply applying the Bloch theorem to this state.[19] (Note that we do not need a subscript for R, since there is only one benzene ring in the primitive cell.) According to the theorem, for these bands (n = 20 and 21), Γ-point represents bonding interactions of e_{2g}(V) orbitals in two adjacent cells similarly to the case of $e_{2g}(Bz_3V_2)$. However, this does not mean that there really is a bonding between them. Rather, the absence of a symmetry-allowed interaction with π orbitals of the benzene ring located between them makes the bands energetically the highest at Γ-point. We may note that, for Bz_3V_2, there is also a relatively large splitting (~1.29 eV) between e_{2g}(V)-derived orbitals of different symmetries, i.e., between e_{2g} (Bz_3V_2) and $e_{2u}(Bz_3V_2)$ states. (See also Scheme 1.) For both spins, bands are completely filled up to n = 18. For spin-up bands, n = 19−21 are also completely filled. On one hand, they are partially filled for spin-down bands, showing characteristics of a metallic system. This also implies that electric conduction should be dominated by highly dispersive bands n = 20 and 21 through δ-bonds between vanadium and benzene rings. On the other hand, the complete filling of the

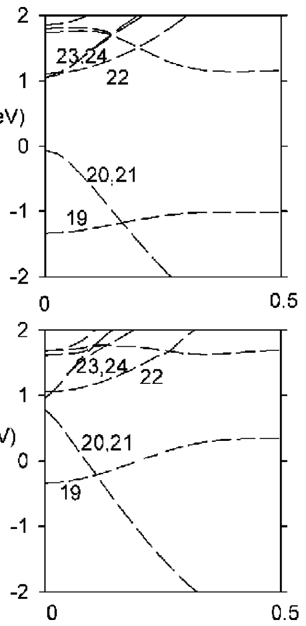


Figure 2. Band structure of the BzV(1D) crystal for spin-up (a) and −down (b) states.

a_{1g}(V)-derived band for spin-up states and half-filling of the band for spin-down states contribute only half (=0.5 μ_B) to the net magnetic moment. Another contribution of 0.5 μ_B to the net magnetic moment comes from spin polarization in e_{2g}-derived bands, i.e., complete filling of spin-up states and three-fourths filling of spin-down states. This is different from the case of the triple decker Bz_3V_2 in which magnetization is entirely originated from the spin polarization in a_{1g}(V)-derived states. As explained above, a simple consideration of the Bloch theorem indicates that the spin polarization in e_{2g}-derived bands of the crystal can be ascribed to a large destabilization of k states around Γ-point of the bands due to a strong localization of electron density around vanadium atoms. This destabilization reflects bulk environment different from that of surface. [To understand this, we note that only one of three peripheral Bz rings of the triple decker is in a chemical environment which is similar to that in the 1D crystal, while the other two are strongly subject to surface effect. Importantly, for the $e_{2g}(Bz_3V_2)$ states, we have already noted that the surface effect introduced δ-bonds between vanadium atoms and benzene rings on the surface. Meanwhile, e_{2g}-derived bands of the 1D crystal are not subject to such bonds at Γ-point because of the absence of the surface effect.] This is in agreement with our observation that the states which reinforce covalent bonds between vanadium atoms and benzene rings are spin-paired despite unfavorable spin-pairing energy. Namely, k states of e_{2g}-derived bands are not spin-paired around Γ-point, since they are not involved in the formation of covalent bonds between vanadium atoms and the Bz rings, while k states around the band edge are spin-paired because they are indeed involved in the formation of the bonds. Noting that the difference in the electronic structures of the triple decker and the 1D crystal is largely originated from the presence or absence of the surface effect, we can easily expect that the magnetic coupling in multiple deckers of reasonable size can be explained on the basis of a 1D crystal. As the number of stacking units increases, electronic properties should be less dominated by the surface effect.

Our finding is further supported by the calculation of binding energy and magnetic moment of benzene−chromium sandwich complexes. First of all, we find that the dissociation energies of double (=3.20 eV) and triple deckers (=2.25 eV) show no additional stabilization with respect to those (=3.46 and 2.51 eV) of benzene−vanadium complexes shown in Table 1. This can be easily expected from our analysis of electronic structure. For example, the electronic structure of $Bz_3Cr_2(\mu=0)$ is similar to that shown in Scheme 1 other than the filling of two more states $n = 56\downarrow$ (=a_{1g} state) and $57\downarrow$ (=a_{2u} state), which can be understood from the prediction of zero magnetic moment. Spin pairings in these states do not enforce any kind of covalent bond between chromium and Bz rings, not leading to additional stabilization of the complex.

Next, we consider the complex Np_nV_m. Table 1 shows that the dissociation energy $D_e[NpV_2]$ (=4.64 eV) of NpV_2 defined for the process $NpV_2(\mu = 4\mu_B) \rightarrow Np + 2V(\mu = 5\mu_B)$ is much larger than the corresponding datum (=1.64 eV) for BzV. NpV_2 adopts the syn conformation of two vanadium atoms with respect to the Np ring, which is more stable than the anti conformation by 1.16 eV. This is mainly because there is a covalent bond between two vanadium atoms in the syn conformation, while the bond is not possible in the anti conformation. Indeed, our analysis shows that the bond order between the two vanadium atoms is 1.29 in the syn conformation (see Table 2). Dissociation energy (=4.59 eV in Table 1) of Np_2V_2 defined for the process $Np_2V_2(\mu = 2\mu_B) \rightarrow Np + NpV_2(\mu = 4\mu_B)$ is also larger than that for its benzene analogue (=3.46 eV) by an appreciable amount (=1.13 eV). When the double decker is formed, bonding between two vanadium atoms is weakened as seen from decreased bond order (=0.62 in Table 2) between them. However, the sum of the bond orders (=3.15 in Table 2) of all the V−C(R) bonds over C(R) belonging to the same Np ring is much larger, indicating a much stronger binding between the vanadium atoms and the Np rings. Consequently, the binding energy (=−9.23 eV) of the overall process $2Np + 2V \rightarrow Np_2V_2$ is much larger than that (=−5.12 eV) of the process $2Bz + V \rightarrow Bz_2V$. Dissociation energy (=3.57 eV in Table 1) of Np_3V_4 ($\mu = 4\mu_B$) is also larger than that of Bz_3V_2. For the triple decker, Table 2 shows that we can expect a charge transfer from vanadium atoms to Np rings which is much larger than the transfer in the double decker, as manifested in larger partial charges (=−0.84 and −1.54) on the peripheral and central Np rings, respectively. In fact, this observation suggests that the central Np ring is in the oxidation state of −2. All these observations shows that the sandwich-forming tendency of $Np_{n+1}V_{2n}$ is much more pronounced than that of $Bz_{n+1}V_n$. Noting that Bz sandwich complexes were experimentally identified at least up to Bz_7V_6 from the mass spectroscopy, we can expect that the Np sandwich complex would be identified in much longer sizes. In addition, it is worth noting that there is a ferromagnetic coupling of spins in the process of forming the triple decker from the double decker as shown by the doubling of magnetic moment. Moreover, the magnetic moment of $Np_{n+1}V_{2n}$ is twice as large as that of $Bz_{n+1}V_n$ at the same stacking size. Therefore, multiple deckers $Np_{n+1}V_{2n}$ are expected to be much more useful for molecular magnets than their Bz analogues.

To study magnetic coupling in the long multiple deckers, we simply consider the 1D crystal NpV_2(1D). Our calculation shows that the lattice constant (=3.50 Å) is almost the same as that for its benzene analogue. Meanwhile, the lattice energy (=−3.40 eV) is found to be larger than that (=−2.59 eV) for the BzV(1D) crystal by an appreciable amount, also suggesting the possibility of existence of very long multiple deckers. Although the calculated magnetic moment (=1.45μ_B) indicates that there is an incomplete ferromagnetic (ferrimagnetic) coupling of spins for this 1D crystal, the moment is still 45% larger than that in its Bz analogue.

Again, electronic structure analysis will gives us a better understanding on the binding of the sandwich complexes. Here, we focus on the triple decker. Since its detailed electronic structure is much more complicated than that of Bz_3V_2, we only describe some important features. Our analysis of l,m-projected electronic DOS shows that three of four states derived from four linear combinations of $d_{z^2}(V_1)-d_{z^2}(V_4)$ of four vanadium atoms are occupied for spin-up states, while only one of the corresponding spin-down states is occupied. This contributes three-fourths (=3μ_B) to the net magnetic moment. The remaining one-fourth comes from the spin polarization in the states derived from linear combinations of d_{xy}(V) as well as those of $d_{x^2-y^2}$(V). In consistency with this, states derived from d_{yz} and d_{xz} states are almost completely unoccupied, not making any appreciable contribution to the magnetic moment.

It is relatively easier to consider the electronic structure of NpV_2(1D). As shown in Figure 3, however, it is still much more complicated than that of the BzV(1D). We first note that there are two d-derived bands per each of five d orbitals since there are two vanadium atoms in a primitive cell. As in the case of BzV(1D), bands derived from linear combinations of d_{z^2} orbitals are almost flat and are represented by flat portions of bands 32

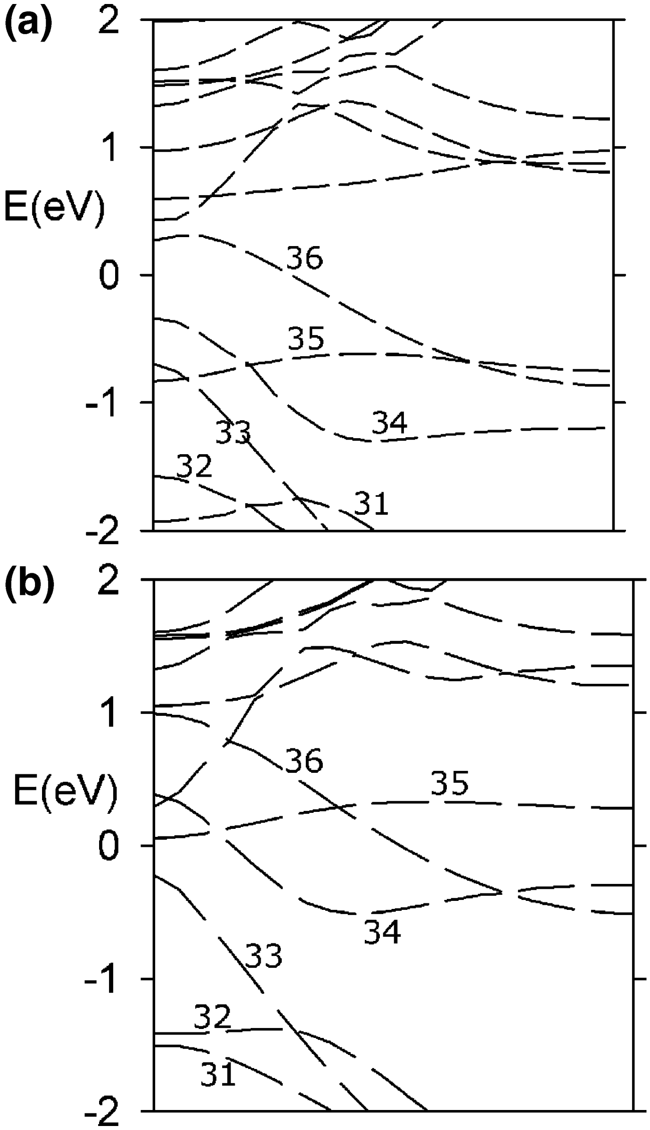


Figure 3. Band structure of NpV$_2$(1D) crystal for spin-up (a) and −down (b) states.

and 34 and the entire states of band 35. Since the flat portions of bands 32 and 34 are completely filled for both spins, their contribution to the spin-polarization is insignificant. However, d_{z^2}-derived states are expected to contribute 1 μ_B to the net magnetic moment, since the band 35 is completely filled for spin-up and completely unfilled for spin-down. Band 36, which is derived from the antibonding combination of d_{xy}(V) states from two vanadium atoms, is about half and one-fourth filled for spin-up and -down, respectively. Similar to the case of BzV(1D), therefore, it should contribute much of the remaining 0.45μ_B to the net magnetic moment. The relatively larger dispersion of the band also implies that there is a large delocalization of electron density along the crystal direction through a symmetry-allowed interaction with a π(Np) state (=LUMO+4) at the zone boundary (see Figure 4a). Meanwhile, simple symmetry consideration in conjunction with the Bloch theorem also implies that Γ-point of the band should represent a $d_{xy}(V_1)-d_{xy}(V_2)$ orbital (=antibonding interaction of two d_{xy} orbitals) without interacting with a π(Np) state. Namely, there cannot be a symmetry-allowed interaction with any ring π state at this state (See Figure 4b). In other words, as in the case of BzV(1D), states around the Γ-point of the band are not spin-paired since they are not involved in the formation of any kind of covalent bond between vanadium and Np rings. Their electron densities are mainly concentrated on vanadium atoms. This is the reason the band 36 is only partially filled. Another band (n = 33) which is derived from the bonding interaction of d_{xy}(V) states is completely filled for both spins, making no contribution to the net magnetic moment. States derived from $d_{x^2-y^2}$(V) generally lie higher than the d_{xy}(V)-derived states. To be more concrete, they appear as dispersive portions of the bands 32 and 34 as well as a whole band at 1.3 eV above Fermi level, making a small contribution to the magnetic moment. All the bands derived from d_{xz}(V) and d_{yz}(V) lie highest (=0.5 eV above Fermi level) among all the d(V)-derived bands, being completely empty for both spins. In short, the magnetization is originated from spin-unpairing in one of the d_{z^2}-derived bands as well as from incomplete spin-pairing in d_{xy}(V)- and $d_{x^2-y^2}$(V)-derived bands.

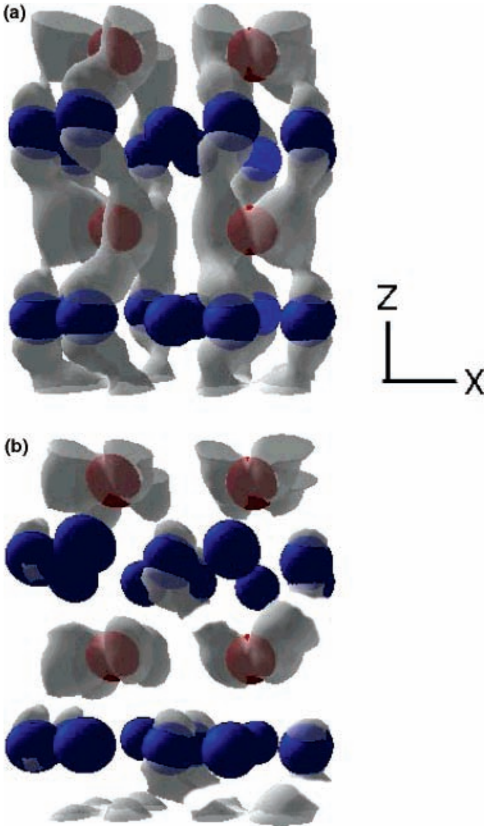


Figure 4. Electron density distributions in the state n = 36 of the NpV$_2$(1D) crystal at the zone boundary (a) and Γ-point (b). For better understanding, two unit cells are considered. Hydrogen atoms are not shown.

Conclusion

Our band structure analysis of the 1D crystal of the complex as well as the electronic structure analysis of the triple decker shows that the ferromagnetic coupling of spins in the benzene−vanadium multiple deckers is originated from the spin-polarization in the (n,k) states which have nothing to do with the formation of benzene−vanadium covalent bonds. This is also the case of the naphthalene−vanadium sandwich complexes, although there are some differences between the two in detail. [As a matter of fact, the symmetry of a Np molecule which is lower than that of a Bz molecule and the bigger complexity of its electronic structure bring about an incomplete ferromagnetic coupling of spins in the 1D crystal of the naphthalene−vanadium complex.] This was also supported by additional calculation of dissociation energies and magnetic moments of benzene–chromium sandwich complexes. Finally, we have also shown that the naphthalene–vanadium sandwich complex can exist in longer stacking sizes on the basis of the lattice energy of its 1D crystal. This is particularly important, since the benzene–vanadium complex was experimentally identified up to Bz_7V_6. In addition, the complex is expected to exhibit a magnetic moment which is 45% larger than that of the benzene–vanadium complex of the same size, making it potentially much more useful for molecular magnets.

Acknowledgment. We appreciate Jeonju University for financial support.

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