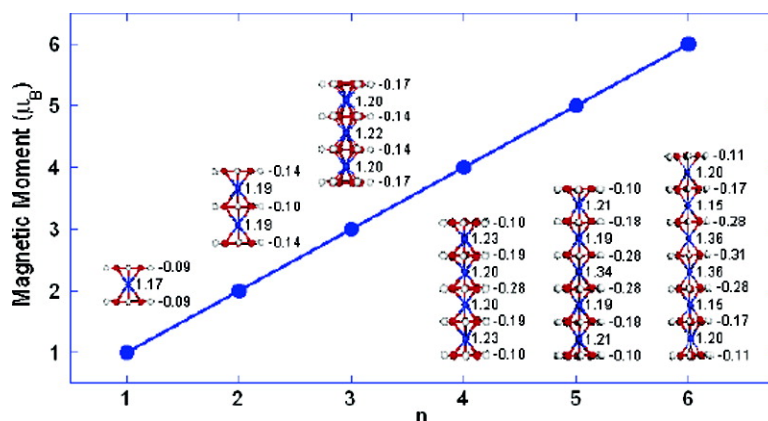


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*J. Am. Chem. Soc.*, **2005**, 127 (9), 2812-2813 • DOI: 10.1021/ja043807q • Publication Date (Web): 10 February 2005

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## Structure and Magnetism of $V_nBz_{n+1}$ Sandwich Clusters

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Since the discovery of ferrocene ( $C_5H_5$ )<sub>2</sub>Fe and determination of its structure, explorations of sandwich and other complexes of metal atoms with organic molecules evolved into a sovereign area (see, for example, ref 1 and citations therein). The ever-growing interest in these complexes stems from their wide-reaching relevance to catalysis, novel magnetic and optical materials, polymers, molecular recognition, and medical and other applications.<sup>1</sup> Among the systems under active current investigation are  $V_nBz_m$  ( $Bz = C_6H_6$ ) complexes. Mass spectrometric<sup>2,3</sup> and ion mobility<sup>3</sup> measurements suggested that they are particularly stable at  $m = n-1$ ,  $n$ , and  $n+1$ , and that their energetically preferred structures are linear sandwiches of alternating V and Bz units. Computations<sup>3-5</sup> on  $V_nBz_{n+1}$ ,  $n \leq 3$ , provided additional support for these structures. Experimental investigations of  $V_nBz_m$  complexes also include photo-<sup>6</sup> and collision-induced<sup>3,6b</sup> dissociation; dipole moment measurements;<sup>7</sup> and EPR,<sup>8-10</sup> PES,<sup>11</sup> and IR<sup>9,12,13</sup> spectroscopy. Data obtained in EPR measurements<sup>8-10</sup> on VBz and VBz<sub>2</sub> were used to estimate their magnetic moments as  $1\mu_B$ . Recent Stern-Gerlach deflection experiments<sup>14</sup> extend the evidence for the magnetic nature of  $V_nBz_{n+1}$  to  $n \leq 4$ .

In addition to the geometric structure, theoretical explorations of these systems examined their electronic,<sup>3-5,15</sup> bonding,<sup>3-5,15</sup> vibrational,<sup>9,12,13,15b</sup> and magnetic<sup>3-5,9,10,15</sup> characteristics. The most recent computational study<sup>5b</sup> of  $V_nBz_{n+1}$ ,  $n \leq 3$ , corroborates the linear sandwich arrangement of these complexes as the energetically most preferred one, but revises in part earlier predictions<sup>5a</sup> on their magnetic moments.

The goal of this communication is to revisit the geometric, electronic, and magnetic properties of  $V_nBz_{n+1}$  and to extend the analyses to  $n \leq 6$ . We report here results of high-accuracy density functional theory (DFT) computations performed within gradient-corrected version of DFT with the BLYP<sup>16,17</sup> exchange-correlation functional. DFT-optimized all-electron DZVP basis sets<sup>18a</sup> were used for all atoms (see ref 18a for V and ref 18b for C and H). The choice of the functional and the basis sets was guided by extensive tests performed on neutrals and cations of  $V_n$ ,  $n = 1-4$ , Bz, and VBz<sub>m</sub>,  $m = 1-2$ , using a variety of alternatives (the details will be given elsewhere).

In this study, we explored only linear sandwich arrangements of  $V_nBz_{n+1}$ ,  $n \leq 6$ , clusters and the VBz complex, and we performed full optimization of their structures considering different spin-multiplicity states. Breaking the symmetry of the wavefunction<sup>19</sup> was used to compute low-spin states not compatible with a single determinant of symmetry-adapted orbitals. Normal mode analysis was used to verify that the optimized configurations indeed represent stable equilibria. The geometric, energetic, and electronic characteristics of the most stable form for each cluster size are summarized in Table 1.

**Table 1.** Point Group Symmetry (PGS), Electronic State (ES), Binding Energy ( $BE_{VBz}$ ), HOMO-LUMO Gap ( $\Delta$ ), and Adiabatic (AIP) and Vertical (VIP) Ionization Potentials (IP) of the Most Stable Structure of  $V_nBz_{n+1}$ ,  $n = 1-6$ . The Measured (exp) IPs Are Also Shown

system	PGS	ES	$BE_{VBz}$ (eV)	$\Delta$ (eV)	IP (eV)		
					AIP	VIP	exp <sup>d</sup>
VBz <sub>2</sub>	$D_{6h}$	$^2A_{1g}$	2.98	1.74	5.54	5.75	$5.75 \pm 0.03$
V <sub>2</sub> Bz <sub>3</sub>	$D_{6h}$	$^3A_{2u}$	2.20	1.22	4.51	4.70	$4.70 \pm 0.04$
V <sub>3</sub> Bz <sub>4</sub>	$D_{6h}$	$^4A_{2u}$	2.12	0.19	3.89	4.06	$4.14 \pm 0.05$
V <sub>4</sub> Bz <sub>5</sub>	$D_2$	$^5A$	2.33	0.41	3.64	3.83	$3.83 \pm 0.05$
V <sub>5</sub> Bz <sub>6</sub>	$D_2$	$^6A$	2.34	0.46	3.40	3.64	$3.66 \pm 0.05$
V <sub>6</sub> Bz <sub>7</sub>	$D_2$	$^7B_1$	2.32	0.41	3.27	3.47	

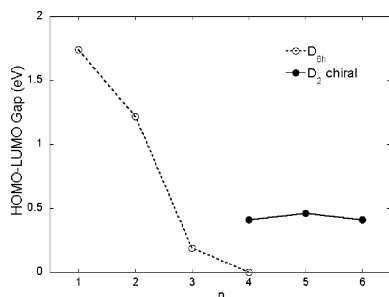
Examination of the binding energy  $BE_{VBz}(n)$  of a terminal VBz unit in  $V_nBz_{n+1}$ ,

$$BE_{VBz}(n) = E(VBz) + E(V_{n-1}Bz_n) - E(V_nBz_{n+1})$$

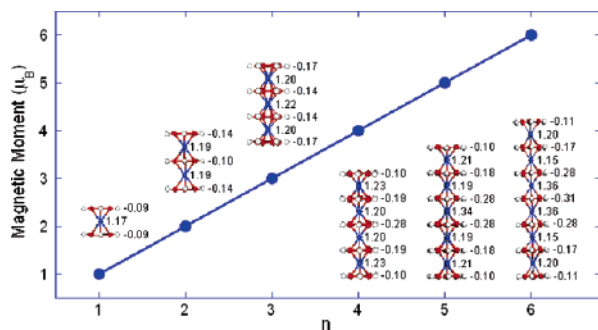
where  $E(A)$  is the total energy of the fully relaxed unit A, shows that the effective range of interaction of a terminal VBz with the rest of the cluster does not extend beyond the length of the  $n = 4$  complex. The value of  $BE_{VBz}(1) = 2.98$  eV (to be compared with earlier computational estimates of 3.57<sup>5a</sup> and 3.64 eV<sup>5b</sup>) is in very good agreement with the experimental estimates of 3.03<sup>2</sup> and 3.19 eV.<sup>5a</sup> An interesting finding regarding the configurations of the complexes is that the  $D_{6h}$  symmetry of the energetically most preferred structure in the size range  $n = 1-3$  (a result that agrees with what has been obtained in ref 5b) changes to the lower  $D_2$  symmetry in the size range  $n = 4-6$ . A closer examination of the structures in this latter size range shows that they are, in fact, chiral.

The reason underlying the lowering of the symmetry of the cluster at  $n = 4$  can be inferred from Figure 1, which depicts the HOMO-LUMO gap as a function of cluster size. As is clear from the figure, imposition of the  $D_{6h}$  symmetry on the sandwich structure of V<sub>4</sub>Bz<sub>5</sub> results in exact ( $e_{2g}$ ) degeneracy of the HOMO and the LUMO. The energetically preferred departure from this symmetry in the most stable equilibrium configuration of this complex is thus a consequence of the Jahn-Teller effect. To quantify the transition from the  $D_{6h}$  to  $D_2$  symmetry in the structure of V<sub>4</sub>Bz<sub>5</sub>, we note that the accompanying lowering in the total energy is  $\sim 0.19$  eV (about 1.4% of the binding energy referred to  $n$  V atoms and  $n+1$  Bz molecules) and the rotations of the successive Bz molecules with respect to a terminal Bz are  $\sim 0.4^\circ$ ,  $\sim 1.8^\circ$ ,  $\sim 3.1^\circ$ , and  $\sim 3.5^\circ$ , respectively. The fact that the chiral  $D_2$  structure persists as the preferred configuration for  $n = 5$  and 6 is consistent with and can be understood in terms of the finite ( $n = 4$ ) effective range of interaction discussed above. The V<sub>5</sub>Bz<sub>6</sub> and V<sub>6</sub>Bz<sub>7</sub> clusters can be obtained by adding, respectively, VBz and V<sub>2</sub>Bz<sub>2</sub> (or, alternatively, two separate VBz units) to either end of the energetically favored chiral V<sub>4</sub>Bz<sub>5</sub>. Preserving the overall chiral structure facilitates the indistinguishability between the two terminal V<sub>4</sub>Bz<sub>5</sub>

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**Figure 1.** HOMO–LUMO gap of the most stable structure of  $V_nBz_{n+1}$ . See the text for details.



**Figure 2.** Total (graph) and partial (numbers) magnetic moments of the most stable structure of  $V_nBz_{n+1}$  as a function of  $n$ .

units in these clusters as the “original”  $V_4Bz_5$ . On the basis of these considerations, one may expect  $V_7Bz_8$  to be also chiral.

Examination of the ionization potentials shows an excellent agreement between the computed VIP and the measured IP. The total and partial (per each V atom and Bz molecule) magnetic moments of the most stable configurations of the complexes are shown in Figure 2. The magnetic moments of the V atoms are slightly larger than  $1\mu_B$ , and they vary only a little with the size of the complex and/or the position of the atom in the complex. The Bz molecules possess small negative magnetic moments, which vary to a larger degree with the complex size and/or the position in the complex. The total magnetic moment of the complexes increases linearly with their size, which is consistent with what has been found earlier for the cases  $n \leq 3$ .<sup>5b</sup> In agreement with the EPR measurements,<sup>8–10</sup> our computations specify the total magnetic moment of  $1\mu_B$  for the most stable state of not only  $VBz_2$  but also  $VBz$ . Therefore, a phenomenological picture of the total magnetism in the most stable configurations of  $V_nBz_{n+1}$  complexes is a ferromagnetically ordered set of one  $VBz_2$  unit and  $n - 1$   $VBz$  units each possessing a magnetic moment of  $1\mu_B$ .

We identified a number of alternative equilibrium configurations and spins of the sandwich  $V_nBz_{n+1}$  complexes with energies close to those of the corresponding most stable structures (cf. Table 1). The characteristics of these alternative configurations for  $n = 2–5$  are listed in Table 2. The energy of the antiferromagnetic singlet  $V_2Bz_3$  is only 0.003 eV higher than that of the ferromagnetic triplet state. An alternative configuration of  $V_3Bz_4$  is a ferrimagnetic doublet, with energy 0.007 eV higher than that of the ferromagnetic quartet state. We have found two energetically close configurations for  $V_4Bz_5$ . One is a ferrimagnetic triplet; the other is an antiferromagnetic singlet. Their energies are, respectively, 0.062 and 0.143 eV higher than that of the ferromagnetic quintet. Two alternative configurations are also found for  $V_5Bz_6$ . The first is a ferrimagnetic doublet; the second is a ferrimagnetic quartet. Their energies are, respectively, 0.156 and 0.210 eV higher than that of the ferromagnetic sextet. In Table 2 we also present the “effective” magnetic moment for each  $V_nBz_{n+1}$  obtained as a multiplicity-weighted

**Table 2.** PGS, Spin-Multiplicity (M), and Energy ( $\Delta E$ ) of  $V_nBz_{n+1}$  Complexes of Higher Energy<sup>a</sup>

system	PGS	M	$\Delta E$ (eV)	$\bar{S}$ ( $\mu_B$ )	$\exp^{14}(\mu_B)$
$V_2Bz_3$	$D_{6h}^*$	1	0.003	1.5	$1.3 \pm 0.2$
$V_3Bz_4$	$D_{6h}$	2	0.007	2.3	$1.7^{+0.3}_{-0.5}$
$V_4Bz_5$	$D_2^*$	3	0.062	2.9	$2.0^{+1.1}_{-1.2}$
	$D_2^*$	1	0.143		
$V_5Bz_6$	$D_2^*$	2	0.156	3.7	
	$D_2$	4	0.210		

<sup>a</sup>  $\bar{S}$  and  $\exp$  are the computed average and measured total magnetic moments, respectively. Asterisks indicate states obtained using broken symmetry wavefunctions. See the text for details.

average of the magnetic moments of its most stable and alternative configurations presented in Tables 1 and 2. Comparison of these effective magnetic moments with the recently measured ones,<sup>14</sup> which are also listed in Table 2, shows a good overall agreement between the two. For the case of  $VBz_2$ , the computed value of  $1\mu_B$  is to be compared with the measured estimate of 0.7–1.0  $\mu_B$ .

In summary, we presented results on and analyses of the structural, energetic, electronic, and magnetic properties of sandwich  $V_nBz_{n+1}$ ,  $n = 1–6$ , complexes obtained within a DFT framework and compared them with the available experimental data. Of particular interest is the prediction of the chiral nature of the complexes with  $n \geq 4$ . The chirality and the magnetism of these systems make them attractive candidates as building units in design and assembly of nanosystems with coupled optical and magnetic functionalities.

**Acknowledgment.** This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U.S. Department of Energy under Contract No. W-31-109-Eng-38.

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JA043807Q