

Ferromagnetism in One-Dimensional Vanadium–Benzene Sandwich Clusters

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Molecular magnets display novel properties that make them promising candidates for future applications in high-density information storage and quantum computing.¹ Because of their finite size, these systems display behavior not observed in macroscopic magnetic systems, for example resonant magnetization tunneling phenomena. In recent years, low-dimensional magnetic materials have attracted much attention from both fundamental and applied points of view. Motivated by theoretical predictions,² much interest has been focused on the area of one-dimensional (1D) magnetic nanomaterials, for example single-chain magnets synthesized using intricately tailored organometallic materials.^{3,4} Here we present molecular beam deflection results for a novel class of high-spin molecular magnets: 1D, multidecker organometallic sandwich clusters formed from vanadium and benzene. The magnetic moments were found to increase with the number of vanadium atoms in the cluster, showing that the unpaired electrons on the metal atoms couple ferromagnetically.

The regulation of electronic and magnetic interactions between metal atoms in organometallic complexes has been investigated, for example, through studies of charge transfer in linear chains of alternating metallocenium donors and polycyano hydrocarbon acceptors.⁵ Paramagnetic complexes are particularly attractive candidates for use as building blocks in low-dimensional magnetic materials because the coordinatively unsaturated metal atom(s) that carry spin can also serve as junction points in the fabrication of 1D, 2D, and 3D networks. A related class of molecular magnets consists of bare metal clusters such as Ni_n and Fe_n ($n = 10^1$ – 10^3) that display per-atom magnetic moments that are typically larger than those of the corresponding bulk solids.^{6–11} One of the strategies in producing “designer” molecular magnets and clusters having particular magnetic properties involves tuning the spin alignment of the constituent paramagnetic metal atoms via choice of the counterions and ligands.

Examples of simple organometallic sandwich complexes have been known for decades and include bis(η^5 -cyclopentadienyl)iron and bis(η^6 -benzene)chromium. These compounds are typical of the sandwich species that can be generated by conventional organometallic synthesis methods.¹² Very recently, it has been shown that organometallic complexes can be formed as clusters efficiently via the gas-phase reaction of laser-vaporized metal atoms with benzene.¹³ Subsequent spectroscopic studies and other characterization methods have confirmed that these species indeed possess multidecker sandwich structures.^{13c,14,15}

Here we present the results of magnetic deflection measurements of the isolated V_n(C₆H₆)_{n+1} complexes. The smallest member of this series, V(C₆H₆)₂, was originally synthesized in the 1950s.^{16a} It

is a 17-electron system, in which one unpaired d-electron from the vanadium metal atom occupies the nonbonding d_σ orbital localized on the metal atom. Magnetic susceptibility measurements and electron paramagnetic resonance (EPR) studies have confirmed that bis(η^6 -benzene)vanadium is paramagnetic, with $S = 1/2$ and $g \approx 2$, where S is the spin quantum number of the complex.^{12,16b} Quantum chemical calculations predict that as n (i.e., the number of layers) in V_n(C₆H₆)_{n+1} increases, the electron density in the d_δ bonding orbitals will delocalize along the molecular axis, and that the d_δ bonding orbitals coexist with the d_σ nonbonding orbitals in the valence region.¹⁷ The magnetic properties of these multidecker complexes depend on whether the spins of the nonbonding d_σ electrons display parallel (ferromagnetic) or antiparallel (antiferromagnetic) coupling.

The magnetic moments of the V_n(C₆H₆)_m complexes were determined by molecular beam magnetic deflection with a Stern–Gerlach magnet.¹⁸ Vanadium vapor produced via laser vaporization was carried by helium into a flow tube reactor, where benzene vapor was injected. The subsequent reaction of the metal atoms and benzene forms a variety of V_n(C₆H₆)_m product species. The 4 ms residence time of the complexes within the flow reactor was sufficient to ensure that the complexes were thermally equilibrated to the flow tube temperature (variable between 60 and 300 K) prior to expansion.¹⁸ The collimated molecular beam passed through the gap of a dipole gradient electromagnet with gradients $\partial B/\partial z$ up to 210 Tm⁻¹. The complexes were detected 0.9 m downstream of the deflection magnet using laser photoionization time-of-flight (TOF) mass spectrometry implemented in the position-sensitive mode,¹⁹ a technique which maps the spatial distribution of the molecular beam along the z axis onto the time domain. The deflection was determined by quantitatively comparing the temporal profiles of the mass peaks in the field-on with those of the field-off.

In the photoionization mass spectra of vanadium–benzene clusters, the peaks corresponding to the “complete” sandwich V_n(C₆H₆)_{n+1} complexes appear prominently. The effect of the inhomogeneous magnetic field is to symmetrically broaden the spatial distribution of the V_n(C₆H₆)_{n+1} complexes in the $\pm z$ direction, and is qualitatively the same behavior as would be observed for a beam of paramagnetic atoms such as silver or sodium. Unlike the original Stern–Gerlach experiment, however, the individual Zeeman components are not fully resolved due to the combined effects of finite beam width, instrumental resolution limitations, and spin–rotation interactions (*vide infra*).

Figure 1 shows a detailed view of the position-sensitive time-of-flight (PSTOF) mass peak corresponding to V(C₆H₆)₂ and V₂(C₆H₆)₃ recorded with and without the magnetic field. This spatial broadening is caused by the Zeeman splitting of the beam into $2S + 1$ equally spaced beamlets.²⁰ In the case of V(C₆H₆)₂, the ground electronic state is ²A_{1g}, so the number of beamlets is taken to be

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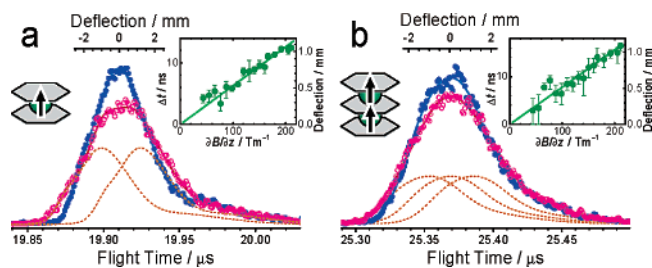


Figure 1. Broadening of TOF peaks of $V(C_6H_6)_2$ and $V_2(C_6H_6)_3$ by the magnetic field gradient at $T = 154$ K. (●, $\partial B/\partial z = 0$; ○, $\partial B/\partial z = 205$ Tm^{-1}) Solid lines indicate modeled TOF profiles for zero-field profile and simulated broadened profile. Beamlets are shown by dashed lines. Insets show the deflection magnitude of the outmost beamlet obtained by the “beamlet” model.

Table 1. Magnetic Moments μ_z/μ_B for $V_n(C_6H_6)_{n+1}$ Clusters^a

	μ_z 154 K/ μ_B	μ_z 296 K/ μ_B
$V(C_6H_6)_2$	0.8 ± 0.1	$0.8^{+0.2}_{-0.1}$
$V_2(C_6H_6)_3$	1.3 ± 0.2	1.3 ± 0.3
$V_3(C_6H_6)_4$	$1.7^{+0.3}_{-0.5}$	$2.1^{+0.6}_{-1.3}$
$V_4(C_6H_6)_5$	$2.0^{+1.1}_{-1.2}$	

^a μ_z values correspond to the outmost beamlets with the maximum M_S .

$2S + 1 = 2$.^{16,21} In the beamlet model, the broadened peak profile is expressed by the superposition of zero-field profiles. As shown in Figure 1a, the simulated beam profile assuming two beamlets reproduces the observed data well, and the plot of the broadening against magnetic gradient clearly shows linear dependence. From the slope, the z -component of the magnetic moment, μ_z , for $V(C_6H_6)_2$ is found to be $0.8 \pm 0.1 \mu_B$ and $0.8^{+0.2}_{-0.1} \mu_B$ at 154 and 296 K, respectively.

Figure 1b shows the PSTOF profiles of $V_2(C_6H_6)_3$ recorded with the field gradient on and off. The plausible spin states for $V_2(C_6H_6)_3$ are singlet or triplet, corresponding to antiparallel or parallel electron spin in d_σ orbitals, respectively. The curve-fitting analysis clearly reveals broadening of the beam, indicating that $V_2(C_6H_6)_3$ is not a singlet molecule. The observed broadening is well represented by the sum of three zero-field beamlets, equally spaced. From the slope, the magnetic moment of $V_2(C_6H_6)_3$ was determined as $1.3 \pm 0.2 \mu_B$ at 154 K and as $1.3 \pm 0.3 \mu_B$ at 296 K. This is the first experimental evidence for the existence of triplet $V_2(C_6H_6)_3$. The observation that the measured moment is smaller than the expected spin-only value of $2 \mu_B$ can be traced to the effects of spin-rotation interactions (*vide infra*).

Larger $V_n(C_6H_6)_{n+1}$ complexes also displayed beam broadening induced by the Stern–Gerlach magnet, and the obtained values are summarized in Table 1. First, the linear increase of the magnetic moment is apparent for complexes generated at both $T = 154$ and 296 K. Both plots exhibit the same trend within the experimental uncertainties, indicating that the spin alignment is invariant with temperature in this range of T . The monotonic increase of $V_n(C_6H_6)_{n+1}$ magnetic moments indicates that the spins of the nonbonding d_σ electrons on the V metal centers align ferromagnetically, giving rise to magnetic moments which scale linearly with the number of layers. It should be noted that the magnetic moments obtained in this work are smaller than the predicted value of the spin-only ($g = 2$) and EPR experiments ($g = 1.987$) for $V(C_6H_6)_2$.^{16b,21b} Because the measurements were carried out in the gas phase, the rotational degrees of freedom can couple to the spin degree of freedom, leading to reduced moments^{22,23} as a result of avoided crossings among the Zeeman sublevels.²⁴

The origin of the observed ferromagnetic spin alignment is due to the spin polarization involving the sandwiched benzene ligand. The plausible mechanism of ferromagnetic interaction in these sandwich complexes has been theoretically investigated, and is believed to be due to an intra-atomic exchange interaction within the metal d orbitals along with a partial charge transfer between the d_σ and benzene LUMO.¹⁷ Although the d_σ orbital is characterized as a nonbonding orbital, the intra-atomic exchange interaction between d_σ and d_δ leads to ferromagnetic ordering through the intervening benzene ligands in this one-dimensional system. In fact, very recent theoretical calculations consistently show that electron-spin multiplicities in the ground state are 2, 3, and 4 for $V_n(C_6H_6)_{n+1}$ ($n = 1-3$).²⁵ Soft-landing of size-selected ferromagnetic vanadium–benzene clusters onto nanoscale designed surfaces is an emerging approach that is expected to open new possibilities for exploiting these complexes as nanomagnetic building blocks in applications such as recording media or spintronic devices.

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