Multiple-decker and ring sandwich formation of manganese–benzene organometallic cluster anions: Mn$_n$Bz$_n^-$ ($n=1$–5 and 18)

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Organometallic multiple-decker sandwich clusters are topics of great interest due to their unique electronic and magnetic properties originating from anisotropic structures. We report a joint anion photoelectron spectroscopic and computational study on a new family of manganese (Mn)–benzene (Bz) anionic clusters Mn$_n$Bz$_n^-$.

1. Introduction

Molecular magnetism has received considerable attention due to potential technological applications for high-density information storage, quantum computing, and molecular spintronics. A variety of single-molecule magnets (SMMs), whose individual molecules act as a magnet, have been developed since the discovery of the first SMM, a manganese (Mn)–oxo cluster [Mn$_n$O$_m$]$_2^+$. Mn-based SMMs have been most investigated due to the significant contribution of Mn electrons to their spin states and magnetic anisotropy. More recently, one-dimensional (1D) polymer chains called single-chain magnets (SCMs) have been demonstrated to show magnetic properties analogous to those of SMMs. They can be viewed as 1D systems composed of high-spin magnetic units when compared with 0D SMMs.

A popular approach towards making better performing SMMs/SCMs is to realize a high-spin ground state with a large magnetic anisotropy. Major progress in this direction has been often made through appropriate modulation of existing systems. For example, a strategic choice of bridging ligands has been demonstrated to induce effective exchange interactions with a large anisotropy in the metal–ligand system. On the other hand, their local electronic structures have to be characterized not only to understand their molecular magnetism but also to gain a concept for future SMM/SCM developments. At this point, there are several fruitful contributions from the field of cluster research. They have shown that clusters are appropriate models for nanoscale magnetism, which can be described as a function of cluster size.

Clusters are also expected as a potential building block for designer SMMs/SCMs. Organometallic sandwich clusters are topics of great interest due to their unique electronic and magnetic properties originating from anisotropic structures. For example, vanadium (V) atoms and benzene (Bz) molecules are piled up alternately to form multiple-decker sandwich structures (V$_m$Bz$_n$, m = n - 1, n, and n + 1), exhibiting a monotonous increase in their magnetic moments with increasing number of sandwich layers. While this observation has stimulated numerous theoretical attempts to explore metal–ligand sandwich based SMM/SCMs, experimental approaches remain challenging.

Here we report the size-dependent geometric and electronic structures on a new class of Mn–Bz cluster anions, Mn$_n$Bz$_n^-$ ($n=1$–5 and 18), by means of anion photoelectron spectroscopy in combined with theoretical calculations. We first show experimental and theoretical evidences of multiple-decker formation for Mn$_n$Bz$_n^-$ ($n=1$–5) through quite different stacking forms that...
contrast with the linear V-Bz clusters. Then we computationally investigate extremely high-spin ring Mn$_{18}$Bz$_{18}$ clusters, whose motifs can intriguingly be recognized as a “cluster of Mn$_{18}$Bz$_{4}$ clusters”.

2. Experimental and computational methods

2.1 Experimental methods

Mn$_n$Bz$_m^-$ clusters were generated in the gas phase using a laser vaporization and supersonic expansion method. Briefly, a Mn metal rod sample was ablated with the second harmonic (532 nm) light pulses of a Nd$^{3+}$:YAG laser at a 10 Hz repetition rate. The Mn vapor was reacted with helium-diluted Bz gas (at 3 atm) that was introduced using a pulsed valve (General Valve Series 9), and then very intense supersonic pulses of helium carrier gas at 40 atm, obtained by using a high-pressure Even–Lavie pulsed valve, were used to cool the hot species mixture of atoms and clusters. The resulting cluster anions were then extracted to a linear time-of-flight mass spectrometer. The anions were mass-selected and photodetached using the second (532 nm, 2.33 eV), third (355 nm, 3.49 eV), and fourth (266 nm, 4.66 eV) harmonic outputs of another Nd$^{3+}$:YAG laser. The kinetic energies of the detached photoelectrons were measured using a magnetic bottle-type photoelectron spectrometer. The electron binding energies were then obtained using the energy-conservation relationship $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$, EBE, and EKE are the photon energy, electron binding energy, and electron kinetic energy, respectively.

2.2 Computational methods

In order to explore the structures of Mn–Bz clusters, density functional theory (DFT) calculations were performed at the unrestricted BP86$^{30,31}$ level, implemented in the Gaussian 09 program package$^{32}$ using the def2-TZVP$^{33}$ basis sets. The Molekel program$^{34}$ was used for molecular visualization. The vertical detachment energies (VDEs) of each of the optimized anions were calculated to compare with the experimental values. Details of the computational method are provided in the ESI.$^\dagger$

It is important to correctly evaluate the energy orderings of different spin states of Mn$_n$Bz$_m^-$ clusters, as it has been pointed out that the current DFT methods for transition metal-based organometallic systems have a specific problem that the spin multiplicity of a global-minimum structure depends on the functional employed. In this study, Mn$_{18}$Bz$_{18}^-$ were optimized using various functionals to calculate the ADE/VDE values of Mn$_{18}$Bz$_{4}^-$, and the BP86 was adopted on the basis of the reasonable agreements with the experimental values (see Tables S2 and S3 in the ESI$^\dagger$).

3. Results and discussion

3.1 Mass distribution of Mn$_n$Bz$_m^-$

Fig. 1 shows a typical mass spectrum of gas-phase produced Mn$_n$Bz$_m^-$ cluster anions. It was taken by using a pulse duration of 280 μs for the Bz pulsed valve. Changes of the duration were found to significantly affect both the mass intensity and distribution (vide infra). The mass assignments were reconfirmed by the experiment using $d_6$-benzene (C$_6$D$_6$; see Fig. S1 in the ESI$^\dagger$). The spectrum indicates that various compositions of Mn$_n$Bz$_m^-$ are generated; in particular, Mn$_n$Bz$_{n-1}$ and Mn$_n$Bz$_{n+1}^-$ are more intense than Mn$_n$Bz$_{n}$ with $m \leq n - 2$. Other mass species are mostly classified into either pure Mn$_n^-$ (marked by ■) or incomplete Mn–Bz cluster anions (marked by ●) which have a single Bz molecule and which cannot be assigned to Mn$_n$Bz$_m^-.$

We assessed how the mass distribution is affected by kinetic conditions (i.e., Bz introduction time) in the cluster source, which were qualitatively controlled by changing the duration of the Bz pulsed valve. Relative abundances of Mn$_n$Bz$_m^-$ with different valve durations employed are depicted in Fig. 2, showing that the production of Mn$_n$Bz$_{m}$ with large $m$ (e.g., $m = n$) is much more diminished by limiting the Bz introduction time than that of other Bz-poor Mn$_n$Bz$_{m}$ (Mn$_n$Bz$_{1}$, Mn$_n$Bz$_{3}^-$, and $m \leq n - 2$ for $n \geq 3$). In contrast, the mass distribution of the Bz-poor Mn$_n$Bz$_{m}$ (for each $n$) is not shifted irrespective of the experimental conditions. Taken into account that the mass distribution of kinetically generated species must be controlled by the concentration of reactants, these characteristics suggest that the production of most Mn$_n$Bz$_{m}$ ($m = n - 1, n$, and $n + 1$) can be ruled by a kinetic process while the others (i.e., Mn$_n$Bz$_{2}^-$, Mn$_n$Bz$_{4}^-$, and $m \leq n - 2$ for $n \geq 3$) would experience a thermodynamic cluster growth. The difference in cluster growth mechanisms could also cause coexistence of energetically higher structural isomers for some sizes of Mn$_n$Bz$_m^-$, which is discussed in the following subsection.

The present study hereafter concentrates on the structural and electronic properties of Mn$_n$Bz$_m^-$ (i.e., $m = n$) according to their high abundances in the mass spectra.
3.2 Photoelectron spectra and structural assignments of Mn$_n$Bz$_m$$^-$ (n = 1–3)

Fig. 3a shows the photoelectron spectra of Mn$_n$Bz$_m$$^-$ (n = 1–3) taken with 355 nm radiation. The additional spectra measured with different wavelengths (532 nm and 266 nm; Fig. S2 in the ESI†) exhibit a photon energy-independent feature. Each peak maximum in the spectra provides VDE and the first VDEs of ESI† with different wavelengths (532 nm and 266 nm; Fig. S2 in the ESI†) taken with 355 nm radiation. The additional spectra measured with 355 nm radiation. The calculated VDEs of the plausible structures are indicated below the spectra with vertical bars. Bold-faced labels right to the VDE bars are denoted to identify the structures. For Mn$_n$Bz$_m$$^-$, a vibrational progression is also shown. (b) Front and side views of the most plausible structures for each Mn$_n$Bz$_m$$^-$ (n = 1–3) with their symmetries and electronic states. Typical bond lengths are indicated in Å. Bonds are visible for C–C, C–H, and Mn–C with distances of 1.4 Å (inset of Fig. 3a), which is assignable to a stretching mode between Mn and Bz in the excited state of neutral Mn$_1$Bz$_1$. The first sharp peak of Mn$_1$Bz$_1$$^-$ also determines an adiabatic detachment energy (ADE) of 0.58 ± 0.07 eV, which reflects the electron affinity of Mn$_1$Bz$_1$.

Our DFT calculations found the most plausible structures for Mn$_n$Bz$_m$$^-$ (n = 1–3) as depicted in Fig. 3b. The calculated VDEs of these structures are in good agreement with the experimental data (Fig. 3a and Table 1). Mn$_1$Bz$_1$$^-$ was identified as the quintet spin state having a C$_{2v}$ (pseudo-C$_{6v}$) half-sandwich structure 1 (Fig. 3b). The other spin states are higher in energy and are ruled out due to inconsistency of VDEs (Table S3 in the ESI†). This observation of the lowest-lying 1 is in line with the thermodynamic behavior of Mn$_1$Bz$_1$$^-$ (Fig. 2). For neutral Mn$_1$Bz$_1$, the quartet state with perfect C$_{6v}$ symmetry (Fig. S3 in the ESI†) was obtained and the calculated ADE of Mn$_1$Bz$_1$$^-$ (0.59 eV) agrees well with the experimental value. Both the higher VDEs of 1.22 and 2.98 eV are ascribed to electronic excited states of the neutral Mn$_1$Bz$_1$.

Both Mn$_2$Bz$_2$$^-$ and Mn$_1$Bz$_1$$^-$ were identified as 2a and 3a (Fig. 3b), respectively. Both exhibit alternating sandwich structures with C$_1$ (pseudo-C$_3$) symmetry, where Mn atoms and Bz molecules are alternately stacked. They adopt relatively high spin states of 2$S + 1 = 6$ (2a) and 11 (3a). Energetically closer 2b and 3b (Fig. 3c) might be minor products which contribute to the photoelectron spectra. Our extensive searches further found structural isomers (Fig. S4 and S5 as well as Tables S4 and S5, ESI†), some of which are even lower in energy than 2a or 3a.
3.3 Photoelectron spectra and structural assignments

The photoelectron spectra of Mn$_4$B$_4^-$ and Mn$_5$B$_5^-$ are shown in Fig. 4a. The VDEs of Mn$_4$B$_4^-$ and Mn$_5$B$_5^-$ are determined to be 2.16 ± 0.08 and 2.16 ± 0.07 eV, respectively, according to the peak maxima of the broad features in the 532 nm spectra (Fig. S2 in the ESI). As the kinetic generation is also the case for Mn$_4$B$_4^-$ and Mn$_5$B$_5^-$ (Fig. 2), we focus on the possibilities of multiple-decker sandwich structures. Assuming a monotonic increase of the Mn$_n$B$_n^-$ spin multiplicities, the calculations found Mn$_4$B$_4^-$ (4) and Mn$_5$B$_5^-$ (5) with 2S + 1 = 14 and 17, respectively, as depicted in Fig. 4b. It is noted that both 4 and 5, in addition to 3a, have an unprecedented “tilted” form, representing continuous η$^5$ binding of Mn$_n$(η$^5$-B$_z$)$_1$ units. Both the calculated VDEs (Table 1 and Table S6 in the ESI) are in line with the experimental values, showing the high spin-state multiple-decker formation of Mn$_4$B$_4^-$ and Mn$_5$B$_5^-$.

### Table 1

| Cluster | VDE (eV)  |
|---------|-----------|
| Mn$_3$B$_3^-$ | 2.06 ± 0.06$^d$ |
| Mn$_4$B$_4^-$ | 2.16 ± 0.07 |
| Mn$_5$B$_5^-$ | 2.16 ± 0.08 |

$^a$ Obtained from the 532 nm spectra (Fig. S2 in the ESI) unless otherwise noted because photoelectron resolution is better at smaller photon energies. $^b$ Labels of anions (Fig. 3b, c and 4b) and final electronic states are denoted in parentheses. For Mn$_5$B$_5^-$ and Mn$_3$B$_3^-$ the peak maxima of the broad features in the 532 nm spectra (Fig. 4b) are not shown because several TD-DFT calculations met fatal problems such as “Fatal Problem: The smallest beta delta epsilon is not capable of taking alternating sandwich structures due to binding energies (eV) indicate coexistence of structural isomers (Fig. 3c), respectively. In particular, 3c is a so-called rice-ball cluster with a metal core surrounded by Bz molecules. It is generally concluded that such rice-ball clusters would become dominant under the thermodynamic conditions regarding Bz-poor (e.g., n = 1) Mn$_n$B$_m^-$, which are not capable of taking alternating sandwich structures due to smaller m (< n − 1).

3.4 Computational anticipation of ring-structured Mn$_{18}$B$_{18}^-$

According to the bottom-up approach presented, the size evolution of the Mn$_n$B$_m^-$ clusters was assumed to be terminated at a finite number n, in stark contrast to the linear V–Bz system.$^{19}$ Here we computationally anticipate a couple of
ring-structured $\text{Mn}_{18}\text{Bz}_{18}^{-/0}$, as it was estimated from the extrapolation of the structures 3a, 4, and 5 that the cyclization of $\text{Mn}_{n}\text{Bz}_{n}^{-}$ occurs at $n = 18$. Starting from a $C_{18h}$ geometry, $\text{Mn}_{18}\text{Bz}_{18}^{-/0}$ were optimized as given in Fig. 5a (details are summarized in Table S7 in the ESI†). Surprisingly, the neutral $\text{Mn}_{18}\text{Bz}_{18}$ retains $C_{18h}$ symmetry. The $\text{Mn}_{18}\text{Bz}_{18}^{-/0}$ adopt extremely high spin states: the anion and neutral take $2S + 1 = 54$ and 55, respectively. In both cases, the calculations on the neighboring spin states found higher energies or even met convergence problems within $C_{18h}$ or $C_2$ symmetry. In fact, both the spin state and the cohesive energies per $\text{Mn}_n(\eta^4\text{Bz})_1$ unit of $\text{Mn}_{18}\text{Bz}_{18}^{-}$ are very consistent with the extrapolation from those of $\text{Mn}_n\text{Bz}_n^{-}$ ($n = 1–5$), as shown in Fig. 5b and Fig. S7, respectively. These findings could suggest synthetic feasibility of the large $\text{Mn}_{18}\text{Bz}_{18}^{-/0}$ rings via possible exothermic aggregations of small $\text{Mn}_n\text{Bz}_n^{-}$.

Fig. 6a shows the frontier Kohn–Sham (KS) orbitals in the $\alpha$ spin part of the neutral $\text{Mn}_{18}\text{Bz}_{18}$. The $\alpha$-HOMO has an extensively delocalized bonding character, and can be divided into contributions from the $\alpha$-HOMOs of each quartet-state $\text{Mn}_1\text{Bz}_1$ unit (inset of Fig. 6a), as if the $\text{Mn}_{18}\text{Bz}_{18}$ exists as a cluster of the $\text{Mn}_1\text{Bz}_1$ clusters. The degenerate $\alpha$-HOMO –1 and $\alpha$-HOMO –2, and several other $\alpha$-valence orbitals (6 sets of degenerate and 1 nondegenerate; see Fig. S8 in the ESI†) are isomorphous to the $\alpha$-HOMO. Interestingly, each delocalized $\text{Mn}_{18}\text{Bz}_{18}$ orbital allows us to define the number of its orbital nodes $k$, analogously to $\pi$ conjugated hydrocarbon systems. Particularly unusual for $\text{Mn}_{18}\text{Bz}_{18}$ is that the smaller number of nodes is rather associated with the energetically higher orbital. These characteristics are further highlighted by comparing with the frontier orbitals of [18]annulene ($C_{18}H_{18}$), which has a 18-membered ring structure with 18 $\pi$ electrons (Fig. 6b and Fig. S9 in the ESI†). An intelligible explanation of such delocalized electron systems can be provided by a simple Hückel model: for cyclic conjugated systems, each molecular orbital energy $\varepsilon_k$ is given as

$$
\varepsilon_k = \alpha + 2\beta \cos \left( \frac{2\pi k}{N} \right) \quad \left(0 \leq k \leq \frac{N}{2}\right) \tag{1}
$$

where the Hückel parameters $\alpha$ and $\beta$ are employed. The number of basis functions $N$ is set to 18 in both cases of $\text{Mn}_{18}\text{Bz}_{18}$ and $C_{18}H_{18}$, in which fragment (or atomic) orbitals of each $\text{Mn}_1\text{Bz}_1$ and $C$ are treated, respectively. To apply this model, KS orbital energies were plotted against $k$ and fit by eqn (1); namely, the plots for the $\text{Mn}_{18}\text{Bz}_{18} \alpha$-HOMO and lower-lying isomorphous orbitals are shown in Fig. 6c. The same analysis was done for the $C_{18}H_{18}$ frontier orbitals as plotted in Fig. 4d. From the figure the simple Hückel model can describe the $\text{Mn}_{18}\text{Bz}_{18}$ plot but claims a positive $\beta$ which contrasts the conventional cases as demonstrated for $C_{18}H_{18}$.

In the following, we indicate that the positive $\beta$ of $\text{Mn}_{18}\text{Bz}_{18}$ originates from its strong intra-atomic exchange interactions within the Mn 3d electrons. Let us recall the definition of the Hückel parameter $\beta = \langle \phi_i | H | \phi_j \rangle$, where two fragments (or atoms) having basis functions $\phi_i$ and $\phi_j$ are next to each other. The Hückel Hamiltonian $H$ is composed of the kinetic term and the electrostatic potentials by nuclei and other electrons; as its resonance integral name implies, $\beta$ is in general not significantly affected by two-electron repulsive interactions (the last term in $H$; i.e., $\sum_{i<j} r_{ij}^{-1}$, where $r_{ij}$ is the distance between two electrons), thus resulting in $\beta < 0$. Therefore the positive $\beta$ implies significant contributions from the two-electron interactions in the $\text{Mn}_{18}\text{Bz}_{18}$ frontier orbitals. According to previous studies the intra-atomic exchange interactions within the metal 3d orbitals induce localized positive and negative spin densities on each metal atom and benzene molecule, respectively, thus stabilizing the ferromagnetic spin ordering in multiple-decker $\text{Mn}_n\text{Bz}_{n+1}$. Indeed, this should be also the case for $\text{Mn}_{18}\text{Bz}_{18}$ due to a pretty large negative spin density ($\rho_s = -0.52$) for each Bz and the positive spin density of $\rho_s = 3.52$ per a Mn atom.
3.5 Magnetism of Mn$_{18}$Bz$_{18}$ in solid-state physics

The periodic nature of Mn$_{18}$Bz$_{18}$ could allow further discussion on its magnetism from a solid-state point of view. When the aforementioned intra-atomic exchange interactions are restated as the on-site Coulomb repulsion $U$ in the Hubbard model,\(^4\) the Mn$_{18}$Bz$_{18}$ could be then treated as a $U \gg t$ case (where $t$ is a transfer integral). Despite the high spin state of the Mn$_{18}$Bz$_{18}$, such $U \gg t$ systems (often referred to as Mott insulators) are believed to usually exhibit an antiferromagnetic ordering of spins.\(^4\) In this sense, the magnetism within the Mn$_{18}$Bz$_{18}$ cluster might be uncommonly understood from Heisenberg’s original picture of ferromagnetism,\(^4\) which is based on Coulomb interactions combined with the Pauli exclusion principle. Interestingly,
several attempts have employed the Hubbard model to prove that, in certain lattices, the spin-independent Coulomb interactions can cause a ferromagnetic alignment. Taken together, the low-dimensional and periodic nature of the Mn_{18}Bz_{18} cluster could be therefore exploited as a substantial model for investigating nanoscale magnetism, which allows not only the bottom-up (molecular) but also top-down (solid-state) approaches.

4. Conclusions

We have investigated a series of Mn–Bz cluster anions, Mn_{n}Bz_{n}^{-} (n = 1–5), through a joint photoelectron spectroscopic and DFT study. We have shown that Mn_{n}Bz_{n}^{-} clusters form multiple-decker sandwich structures with the characteristic tilted Mn–Bz stacking and the high-spin states. Furthermore, a couple of ring-structured Mn_{18}Bz_{18}^{-/0} have been found with the aid of a linear extrapolation from the Mn_{6}Bz_{n}^{-} clusters. Importantly, the neutral Mn_{18}Bz_{18} cluster exhibits several striking features, namely, the high symmetry [C_{18h}] structure, the high spin state (2S + 1 = 55), and the extensively delocalized electrons.

Lastly, the completely planar (2D) structure of Mn_{18}Bz_{18} at a finite size, when compared to infinite sandwich chain cases, might be advantageous for controlling the cluster’s surface morphology (e.g., adsorption states), whose importance in keeping the cluster’s functionality has been demonstrated through soft and reactive-landing techniques. We hope that the current work will stimulate synthetic and functionalization efforts on Mn_{18}Bz_{18}^{-/0} as a building block of future SMMs/SCMs.

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