Harnessing Colossal Magnetic Anisotropy in Sandwiched $3d^2$ -Metallocenes

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Abstract: Single-molecule magnet based quantum technology is gaining attentions in recent years with growing focus on achieving higher barrier of magnetization reversal. Metallocenes owing unique sandwiched-structure, assure themselves as plausible molecular systems for development of novel SMMs. Here in this work, we have explicitly investigated metallocenes of first row transition metal elements, along with their one electron oxidized (cationic) and reduced (anionic) analogues, for their magnetic anisotropies (D) adopting multi-reference *ab initio* calculations. Herein, we report the unprecedented high D values for $3d^2$ systems among all the $3d$ -metallocenes.

Single molecule magnets (SMMs) manifest slow relaxation of magnetization and are characterized by large energy barrier (U_{eff}) to the magnetic moment reversal.¹ Their possible applications as ultra-high-density magnetic storage devices², magnetic qubits and molecular spintronics^{3,4} mark their significance in the field of nanomagnetic research. Despite discovery of several molecular magnets, rapid growth of SMM-based technology is rather impeded by their critical device fabrications. The fundamental challenge is the loss of magnetic anisotropy (D) in the fabrication process due to loss of axial-symmetry of the molecule as a result of molecule-substrate interactions.⁵ The double-decker **TbPc₂** possess a large magnetic anisotropy along the principle molecular axis with large effective energy barrier of 514.3 cm^{-1} .^{6,7} The engineered grafting of such double-decker SMM becomes facile due to π -conjugated macro-cyclic ring retaining the uni-axial molecular symmetry intact.⁸⁻¹¹ Apart from unique structural feature and large U_{eff} barrier, the exotic electronic structure makes **TbPc₂** as one of the most promising SMMs' contender for technological applications.¹²⁻¹⁴ The sandwiched metallocenes, with similar structure as of **TbPc₂**, could also be the suitable alternatives. In this context, a series of sandwiched dysprosium metallocene complexes were synthesized by McClain et al. and magnetic relaxation barrier upto 1468 cm^{-1} was achieved by modification in the molecular structure.¹⁵ Singh et al. have also examined the electronic structures and magnetic anisotropies of sandwiched actinide complexes attaining highest barrier height upto 1832 cm^{-1} .¹⁶

Among $3d$ -transition metal's metallocenes, ferrocene has gained wide attention due to its ample applications in catalysis, functional materials and nanotechnology.¹⁷ Nawa et al. have attempted theoretically to quantify magnetic anisotropy energy (E_{MA}) of $3d$ -series metallocenes for $M=\text{Cr, Mn, Fe, Co, Ni}$; based on constraint DFT method.¹⁸ The exceptional redox chemistry of ferrocene, along with its reversibly oxidized and reduced derivatives, has been highlighted by Walawalkar et al.¹⁹ However, owing to low-spin ground state, the potential of ferrocene as SMM has not been successfully explored until 2021, when Goodwin et al.

Figure 1. Orbitals used in active space for CASSCF(6,7) calculations for $[\text{VCp}_2]^{+1}$ complex, including two ligand-mixed orbitals ($d_{xz}-p_z$, $d_{yz}-p_z$) and five metal d -orbitals.

reported notable D value of -4.42 cm^{-1} employing electron paramagnetic resonance spectroscopy (EPR), but computed -36.4 cm^{-1} using SA-CASSCF method for derivatized ferrocene anion with high-spin ($S = \frac{3}{2}$) ground state.²⁰ Apart from this, vanadocene complex, $[\text{VCp}_2]^0$, has been perceived with positive D value of $2.86\text{--}2.90\text{ cm}^{-1}$.²¹

Prompted by the robust magnetic anisotropy possessed by the double-decker systems, in this work, we strive to find out as well as engineer the highest magnetic anisotropy among first-row transition metal based metallocenes in three different oxidation states i.e., neutral (0), cationic (+1) and anionic (-1). On account of this, electronic structures of all the complexes have been probed employing state-of-the-art *ab initio* calculations. Among all the studied systems, $[\text{VCp}_2]^{+1}$ is found to possess bent geometry therefore, we have examined magneto-structural correlations by subtle variation of ligands on the Cp rings for this complex to engender different Cp-M-Cp angles.

The molecular geometries of all the complexes, in addition to their cationic and anionic counterparts, have been optimized in all their possible spin-states at UB3LYP/def2-TZVP level along with def2/J auxiliary basis set.^{22,23} The magnetic anisotropy (D) value has been extracted from multireference wavefunction based calculations i.e., complete active space self-consistent field (CASSCF) approach²⁴ including the dynamical correlations using second order N-electron valence state perturbation theory (NEVPT2) method.²⁵ The extended active space consisting of 4 electrons from the ligands along with the n electrons of metal in two ligand-mixed orbitals and five d -orbitals i.e., CAS($n+4,7$) is considered. The converged active orbitals for the vanadocene cation (d^2) obtained from CAS(6,7) active space are shown in Figure 1. The detailed criteria used for the selection of active space and number of roots remains the same as discussed in our previous work and is explained in section 1.1 of supporting information.²⁶ All the calculations have been performed using ORCA.^{27,28}

The adiabatic ground states for neutral, cationic and

Figure 2. Spin density of all d^2 configured systems obtained at UB3LYP/def2-TZVP level with isovalue of $0.005 \mu_B/\text{\AA}^3$. Their ground state electron occupations (with dominant contribution) and orbital ordering at the bottom part.

anionic 3d-metallocenes have been investigated employing UB3LYP/def2-TZVP methodology. Further, their ground spin-states are confirmed by multireference calculations i.e., (CASSCF-NEVPT2) where a good match is observed for all the complexes, except for $[\text{MnCp}_2]^+$ which is observed to be in intermediate-spin state from DFT in contrast to the high-spin state from CASSCF-NEVPT2 (Table S2 and S5 in S.I.) The energies of these complexes in the possible spin-states are tabulated in Table S1-S3. Since zero field splitting is observed for systems with $S > \frac{1}{2}$, therefore, in view of no or only one unpaired electron exhibited by the complexes stabilized in low-spin state, we have examined complexes with intermediate and high-spin ground state i.e. Ti, V, Cr, Mn and Ni metallocenes to further inspect their magnetic anisotropies. Among them, $[\text{VCp}_2]^0$ complex with d^3 electronic configuration shows positive sign of magnetic anisotropy with $D = 2.54 \text{ cm}^{-1}$ which agrees well with the experimentally reported value of $2.86\text{-}2.90 \text{ cm}^{-1}$ obtained from HF-EPR by Timothy et al.²¹ Interestingly, the magnetic anisotropy of $[\text{NiCp}_2]^0$ complex with d^8 configuration i.e., a configuration that differs from d^3 by five d electrons ($d^8 = d^{3+5}$), also marks positive value, with $D = 56.72 \text{ cm}^{-1}$. This trend is recently observed by Briganti et al. where they observed similar orientation of magnetic anisotropy tensors of lanthanoid complexes, differing by seven f electrons designated as f^{n+7} effect.²⁹ To rationalize the large difference between D values of the two complexes, an analysis of energy ordering of molecular d -orbitals of the respective complexes has been performed as shown in Figure S2-S4. For $[\text{VCp}_2]^0$ complex, the observed energy gap between ground and first excited state is fairly large, i.e. 13878.0 cm^{-1} (Figure S2), therefore, the energy required for the first electronic transition between the two states is quite large leading to smaller spin-orbit coupling and consequently, small D value is observed. Contrary to this, for $[\text{NiCp}_2]^0$ complex, the first electronic transition occurs with small energy gap of 7236.7 cm^{-1} (Figure S2) between the two states, so comparably large positive D value is attained. Moving further to $[\text{MnCp}_2]^0$ complex with d^5 electronic configuration, a minuscule D value of -0.98 cm^{-1} is obtained which is the result of quenching of orbital angular momentum for the d^5 high spin-state, leading to absence of first order spin-orbit coupling. So, the small value emerges as the result of second order spin-orbit coupling between the high-spin ground state and low-spin excited state. In case of $[\text{CrCp}_2]^0$ complex, moderate D value of -20.63 cm^{-1} is observed. Surprisingly, giant magnetic anisotropy is witnessed for d^2 configured $[\text{TiCp}_2]^0$ complex with $D = -67.39 \text{ cm}^{-1}$.

Such stupendous anisotropy value for the d^2 system en-

couraged us to explore its isoelectronic species. Thus, beyond curiosity, we proceeded to the cationic and anionic congeners of $[\text{TiCp}_2]^0$ complexes to scrutinize their magnetic behaviour. Therefore, an in-depth investigation of $[\text{VCp}_2]^+$ cation and $[\text{ScCp}_2]^-$ anion is done. However, to our surprise, the DFT optimized geometry of $[\text{VCp}_2]^+$ cation was observed to be slightly bent with Cp-M-Cp angle of 151.85° and a smaller D value of -10.76 cm^{-1} is computed for this. The distortion in its geometry from linear to the bent one is imputed to pseudo Jahn-Teller or second-order Jahn-Teller effect.^{30,31} Apart from the geometry, vanadocene cation also possesses spin-density which is distinct to rest of the linear d^2 systems (Figure 2). To understand this dissimilarity, we looked into the wavefunction of the ground state obtained from CASSCF calculations. It is observed that the dominant contribution of ground state wavefunction comes from 42% of $d_{xy}^1 d_{yz}^1 d_{x^2-y^2}^0 d_{xz}^0 d_{yz}^0$ configuration and 35% from $d_{xy}^1 d_{x^2-y^2}^1 d_{yz}^0 d_{xz}^0 d_{yz}^0$ configuration (Figure 2). Thus, its ground state is a mixture of two configurations with almost equal contribution which explicitly explains the perceptible orientation of spin-density. Also, this intriguing ground spin-state induces spontaneous symmetry breaking in the linear geometry. In contrast to this, rest of the linear cases have wavefunction of the ground state with dominant contribution from only one configuration i.e., $d_{xy}^1 d_{yz}^1 d_{x^2-y^2}^0 d_{xz}^0 d_{yz}^0$ leading to symmetrical spin-density for these cases.

The structurally linear $[\text{TiCp}_2]^0$ complex with significant D value incited us to investigate if we can play with the structure of bent $[\text{VCp}_2]^+$ cation in an effort to enhance its D value. With this aim, we studied the magneto-structural correlations and varied the Cp-M-Cp angle from 150° to 180° increasing in steps of 5° (Figure 3), where **a-g** refer to $[\text{VCp}_2]^+$ geometries with Cp-M-Cp angle of $150^\circ\text{-}180^\circ$. Accordingly, D value is observed to escalate with the increase in Cp-M-Cp angle and an incredibly large value of -147.01 cm^{-1} is realized for the conformation with almost linear structure i.e., having Cp-M-Cp angle of 179.23° (quasi-optimized linear geometry with two imaginary frequencies, **d'** in Figure 3). Moreover, the energy of this linear geometry is close to the bent geometry, with energy difference of only 19.69 kJ/mol . A prudent comparison of Cp-M-Cp angle with D value highlights the pivotal role of symmetry of metallocene for the intriguing property of magnetic anisotropy (Figure 3). It is deduced that the bent geometry brings about quenching of orbital angular momentum and hence produces low magnetic anisotropy value for the complex. Following this, we attempted to tune the coordination environment around the metal centre in order to achieve linear geometry with larger angle of Cp-M-Cp. To accomplish this objective, we engineered different complexes, differing by the substituents on the Cp rings of $[\text{VCp}_2]^+$ cation. The different complexes with different substitutions on Cp rings are shown in Figure 3, where **a'**, **b'**, **c'**, **d'** refer to $[\text{VCp}_2(\text{Et})_6]^+$, $[\text{VCp}_2(\text{Me})_{10}]^+$, $[\text{VCp}_2(t\text{-Bu})_6]^+$, $[\text{VCp}_2]^+$ (linear) respectively. To this end, it is elucidated that subtle variation of the substituents on Cp rings may engender improvement in the Cp-M-Cp angle and thereupon the respective magnetic anisotropy values.

Figure 3. The variation of D value obtained for **a-g** by varying Cp-M-Cp angle from 150°-180° (solid red line) and with disparate ligand substitutions on the cyclopentadienyl rings of $[\text{VCp}_2]^+1$ complex (**b'-c'**). **d'** is the linear quasi-optimized geometry.

The ethyl group substituted at three alternate positions (**a'** in Figure 3) of each cyclopentadienyl ring yields an angle of 153.61°. However, methyl group substituted at all the carbon atoms of Cp rings (**b'** in Figure 3) results in somewhat larger angle of 159.81°. The highest angle of 163.19° is achieved by substituting the bulky *tert*-butyl group on the three alternate positions of Cp rings (**c'** in Figure 3). Subsequent hike in this angle by tailoring the substituents on both Cp rings marks noticeable enhancement in the magnetic anisotropy values from -10.76 cm⁻¹ for the bent $[\text{VCp}_2]^+1$ (**a** in Figure 3) to -41.54 cm⁻¹ for the *t*-butyl substituted vanadocene cation $[\text{VCp}_2(\text{t-Bu})_6]^+1$ (**c'** in Figure 3). The enhancement in D value by modifying the Cp-M-Cp angle towards 180° has also been observed in the dysprosium metallocene complexes.¹⁵ In contrast to this, $[\text{ScCp}_2]^{-1}$ anion with d^2 configuration results in a smaller D value which is ascribed to spin delocalization from ligand-mixed orbitals of Sc metal center to the p_z orbitals of carbon atoms of cyclopentadiene rings as observed from the spin-density plot shown in Figure 2. This is also confirmed by the computed spin moment value of 1.41 μ_B on Sc atom which is very low as compared to other transition elements of d^2 configuration, like it is 2.07 μ_B on V atom for $[\text{VCp}_2]^+1$. (Table 1).

Prompted by the superior single molecule magnetic behaviour of isoelectronic counterpart of d^2 configured metallocene, we pursued the cationic and anionic contenders of all other metallocenes in an attempt to investigate their magnetic behaviour. Among the cationic species, d^3 configured $[\text{CrCp}_2]^+1$ complex (isoelectronic with neutral $[\text{VCp}_2]^0$) and d^8 (d^{3+5}) configured $[\text{CuCp}_2]^+1$ complex (isoelectronic with $[\text{NiCp}_2]^0$) yield positive D values of 4.55 and 44.79 cm⁻¹ respectively, complementing with $[\text{VCp}_2]^0$ and $[\text{NiCp}_2]^0$. The cationic complex of $[\text{MnCp}_2]^+1$ (isoelectronic with $[\text{CrCp}_2]^0$) also produces consistent results with negative D value of -14.16 cm⁻¹. Moving towards anionic counterparts, small D values with positive or negative signs, consistent with isoelectronic neutral metallocene complexes are obtained and are tabulated in Table 1.

By monitoring sequential values of all the neutral metallocenes along with their cationic and anionic counterparts, we propose that d^2 configured species advances as the supe-

Table 1. Computed D values of 3d-series metallocene systems together with their cationic and anionic analogues (cm⁻¹) obtained from SA-CASSCF/NEVPT2 calculations. The complexes are arranged in descending order of D values.

Complex	d^n	S^a	μ_B (B.M.) ^b	D value (cm ⁻¹)
$[\text{VCp}_2]^+1$	d^2	1	2.07	-147.01 ^c
$[\text{TiCp}_2]^0$	d^2	1	1.78	-67.39
$[\text{NiCp}_2]^0$	d^{3+5}	1	1.29	56.72 ^d
$[\text{CoCp}_2]^{-1}$	d^{3+5}	1	1.79	23.57 ^e
$[\text{FeCp}_2]^{-1}$	d^{2+5}	3/2	2.85	-22.10 ^e
$[\text{CrCp}_2]^0$	d^4	1	2.02	-20.63
$[\text{MnCp}_2]^+1$	d^4	1	2.24	-8.34
$[\text{ScCp}_2]^{-1}$	d^2	1	1.41	-5.21
$[\text{CrCp}_2]^+1$	d^3	3/2	3.18	4.55
$[\text{VCp}_2]^0$	d^3	3/2	2.85	2.54 ^f
$[\text{VCp}_2]^{-1}$	d^4	1	1.90	-1.36
$[\text{MnCp}_2]^{-1}$	d^6	2	3.98	1.30
$[\text{TiCp}_2]^{-1}$	d^3	3/2	2.51	1.20
$[\text{CuCp}_2]^+1$	d^{3+5}	1	0.48	0.84
$[\text{MnCp}_2]^0$	d^5	5/2	4.59	-0.98
$[\text{CrCp}_2]^{-1}$	d^5	5/2	4.73	-0.38

^a Ground-state spin of the respective complex.

^b μ_B is the spin magnetic moment at the metal center obtained from Löwdin population analysis at UB3LYP/def2-TZVP level.

^c This is obtained for the linear quasi-optimized geometry, whereas the bent structure possesses much lower value of -10.76 cm⁻¹.

^d Magnetic anisotropy energy (E_{MA}) of 3.71 and -10.88 cm⁻¹ was reported for neutral metallocenes of Co and Ni respectively by Nawa et al. using GGA with FLAPW method.¹⁸

^e Goodwin et al. has computed D value of -36.4, 25.6 cm⁻¹ for six *tert*-butyl substituted anionic metallocenes of Fe and Co respectively using SA-CASSCF.²⁰

^f Positive D value of 2.86-2.90 cm⁻¹ was obtained for $[\text{VCp}_2]^0$ complex employing HFEPR and *ab initio* methods by Timothy et al.²¹

rior materials for single molecule magnets exhibiting colossal magnetic anisotropy, provided spin density is localized on the metal centre and no spin-polarization is ensued, which is actually explicated by $[\text{ScCp}_2]^{-1}$ complex possessing lower D value.

Amidst all the examined metallocenes of first row transition metal series, the systems with d^2 configurations ($[\text{VCp}_2]^+1$, $[\text{TiCp}_2]^0$) are established with unprecedented high magnetic anisotropy values. For $[\text{VCp}_2]^+1$ system, we have perceived direct relation of Cp-M-Cp angle with the magnetic anisotropy, i.e. D value. The stable geometry of the complex may be tuned by fine modification of ligands to achieve the higher value of magnetic anisotropy. As the structure of the complex approaches to the linear sandwich, by sterically encumbering the cyclopentadiene rings with distinct ligands, the magnetic anisotropy proclaims concurrent enhancement (Figure 3). The depicted outcome of the whole series imparts new insights to sandwiched structures of transition metals together with their reduced and oxidized analogs.

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Supporting Information Available: Computational methodology including selection of active space used for multireference calculations, computed adiabatic spin-state energies, splitting of *d*-orbital energy levels, vertical excitation energies of all modelled complexes.

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