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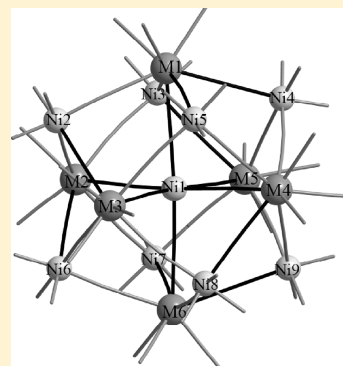
# Exploring the Sources of the Magnetic Anisotropy in a Family of Cyanide-Bridged Ni<sub>9</sub>Mo<sub>6</sub> and Ni<sub>9</sub>W<sub>6</sub> Systems: A Density Functional Theory Study

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Supporting Information

**ABSTRACT:** A density functional theory (DFT) study of the magnetic coupling interactions and magnetic anisotropy in a family of experimentally synthesized Ni<sub>9</sub>Mo<sup>V</sup> and Ni<sub>9</sub>W<sup>V</sup> systems is presented. Our calculations show that for all of our selected Ni<sub>9</sub>M<sub>6</sub> systems, the intramolecular magnetic coupling interactions are ferromagnetic, and the ground-state spins are 12. All of the  $D$  values of Ni<sub>9</sub>W<sub>6</sub> systems come mainly from the contribution of the  $D_i$  of W<sub>6</sub>(CN)<sub>48</sub>Ni extracted from Ni<sub>9</sub>W<sub>6</sub>, and the influence of the eight surrounding Ni including the ligands on their magnetic anisotropy is very small. Although the surrounding Ni bounded by different ligands have a small influence on all  $D$  values for our selected complexes, they decide on the core structures of W<sub>6</sub>(CN)<sub>48</sub>Ni, which dominate their magnetic anisotropy. Thus, to obtain a Ni<sub>9</sub>W<sub>6</sub> system having a large negative  $D$ , we can use different ligands bound to Ni to obtain a good core structure of W<sub>6</sub>(CN)<sub>48</sub>Ni with a large negative  $D$  value. All  $D$  values of Ni<sub>9</sub>Mo<sub>6</sub> systems also come mainly from the contribution of  $D_i$  of the Mo<sub>6</sub>(CN)<sub>48</sub>Ni, which is positive or negative but very small; most of these systems do not behave as single-molecule magnets.



## INTRODUCTION

During the past 20 years, single-molecule magnets (SMMs) having an energy barrier that could eventually lead to applications for information storage and quantum computing at the molecular level have been studied extensively experimentally and theoretically.<sup>1–6</sup> The energy barrier that controls the reversal of the magnetic moment for integer spin systems is  $|D|S^2$  ( $|D|(S^2 - 1/4)$  for half-integer systems), where  $D$  is the zero-field splitting parameter and  $S$  is the total ground-state spin of the molecule. Therefore, the requirements for SMMs to have high barriers are a large negative  $D$  parameter. Recently, a new series of M<sub>9</sub>M<sub>6</sub> (M' = Mn<sup>II</sup>, Ni<sup>II</sup> or Co<sup>II</sup>; M = Mo<sup>V</sup> or W<sup>V</sup>)<sup>3–5</sup> systems have received much attention for having high-spin ground states. However, the  $D$  values of most of them are almost close to 0. Recently, Song and co-workers synthesized {Co<sup>II</sup><sub>9</sub>[M(CN)<sub>8</sub>]<sub>6</sub>·(CH<sub>3</sub>OH)<sub>24</sub>} (M = Mo<sup>V</sup> or W<sup>V</sup>)<sup>3</sup> systems using Co<sup>II</sup> to substitute Mn<sup>II</sup> or Ni<sup>II</sup>, which both have a negative  $D$ . Furthermore, the synthesized [Ni<sup>II</sup>{Ni<sup>II</sup>(bpy)}<sub>8</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub> (M = Mo<sup>V</sup> or W<sup>V</sup>; bpy = 2,2'-bipyridine)<sup>6,7</sup> substituting three CH<sub>3</sub>OH molecules bound to each peripheral Ni<sup>II</sup> coordination sphere with (bpy)(H<sub>2</sub>O) in [Ni<sup>II</sup>{Ni<sup>II</sup>(CH<sub>3</sub>OH)<sub>3</sub>}]<sub>6</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub> (M = Mo<sup>V</sup> or W<sup>V</sup>)<sup>4</sup> by Hong and co-workers also has a negative  $D$  value. Our previous calculations<sup>8</sup> have shown that the substitution of metal ions is not the main reason that Co<sup>II</sup><sub>9</sub>M<sub>6</sub> (M = Mo<sup>V</sup> or W<sup>V</sup>)<sup>3</sup> exhibit SMM behaviors, whereas the unsymmetrical distribution of three CH<sub>3</sub>OH ligands surrounding each Co<sup>II</sup> is the main one. We wonder whether the substitution of CH<sub>3</sub>OH using (bpy)(H<sub>2</sub>O) bound to each Ni<sup>II</sup> is the

cause of the magnetic anisotropy in [Ni<sup>II</sup>{Ni<sup>II</sup>(bpy)}<sub>8</sub>(μ-CN)<sub>30</sub>·{M(CN)<sub>3</sub>}]<sub>6</sub> (M = Mo<sup>V</sup> or W<sup>V</sup>).<sup>6</sup>

To investigate the origin of the magnetic anisotropy in [Ni<sup>II</sup>{Ni<sup>II</sup>(bpy)}<sub>8</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub> (M = Mo<sup>V</sup> or W<sup>V</sup>),<sup>6,7</sup> we selected complexes [Ni<sup>II</sup>{Ni<sup>II</sup>(CH<sub>3</sub>OH)<sub>3</sub>}]<sub>6</sub>(μ-CN)<sub>30</sub>·{M(CN)<sub>3</sub>}]<sub>6</sub>,<sup>4</sup> [Ni<sup>II</sup>{Ni<sup>II</sup>(bpy)}<sub>8</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub>,<sup>6,7</sup> and the newly synthesized [Ni<sup>II</sup>{Ni<sup>II</sup>(tmphen)(CH<sub>3</sub>OH)}<sub>6</sub>·{Ni<sup>II</sup>(H<sub>2</sub>O)<sub>3</sub>}]<sub>2</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub> (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline),<sup>9</sup> where M is Mo<sup>V</sup> or W<sup>V</sup>. The detailed description of the structures can be found in refs 4, 6, 7, and 9. Here, we mainly show their structural differences.

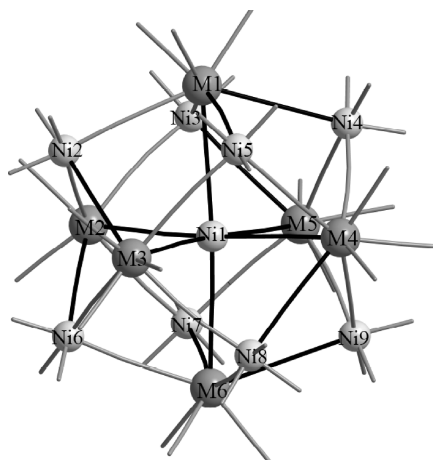
## DESCRIPTION OF THE COMPLEXES

The six selected complexes have a similar core structure to that sketched in Figure 1. The main structural difference in them is that they have different terminal ligands bound to each Ni<sup>II</sup> except for the central Ni<sup>II</sup>. For complex [Ni<sup>II</sup>{Ni<sup>II</sup>(CH<sub>3</sub>OH)<sub>3</sub>}]<sub>6</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub>,<sup>4</sup> there are three CH<sub>3</sub>OH ligands bound to each Ni<sup>II</sup>, while there is only one (bpy)(H<sub>2</sub>O) surrounding each Ni<sup>II</sup> for [Ni<sup>II</sup>{Ni<sup>II</sup>(bpy)}<sub>8</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub>.<sup>6,7</sup> However, the terminal ligands surrounding each Ni<sup>II</sup> are not the same for [Ni<sup>II</sup>{Ni<sup>II</sup>(tmphen)(CH<sub>3</sub>OH)}<sub>6</sub>·{Ni<sup>II</sup>(H<sub>2</sub>O)<sub>3</sub>}]<sub>2</sub>(μ-CN)<sub>30</sub>{M(CN)<sub>3</sub>}]<sub>6</sub>.<sup>9</sup> One tmphen and one CH<sub>3</sub>OH are bound to each one of six Ni<sup>II</sup>, while three H<sub>2</sub>O are bound

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**Figure 1.** General core structure of complexes  $\text{Ni}_9\text{M}_6$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ). The equatorial and apical cyanides are represented as gray and dark bonds, respectively.

to every one of the other two  $\text{Ni}^{\text{II}}$ . For simplicity, we denote complexes  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{CH}_3\text{OH})_3\}_8(\mu\text{-CN})_{30}\{\text{Mo}^{\text{V}}(\text{CN})_3\}_6]$  and  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{CH}_3\text{OH})_3\}_8(\mu\text{-CN})_{30}\{\text{W}^{\text{V}}(\text{CN})_3\}_6]$  as  $\text{Ni}_9\text{Mo}_6\text{-}(\text{CH}_3\text{OH})_{24}$  and  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$ , respectively. Similarly, complexes  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{bpy})_3\}_8(\mu\text{-CN})_{30}\{\text{Mo}^{\text{V}}(\text{CN})_3\}_6]$ ,  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{bpy})_3\}_8(\mu\text{-CN})_{30}\{\text{W}^{\text{V}}(\text{CN})_3\}_6]$ ,  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{tmphen})(\text{CH}_3\text{OH})_3\}_6\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_2(\mu\text{-CN})_{30}\{\text{Mo}^{\text{V}}(\text{CN})_3\}_6]$ , and  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{tmphen})(\text{CH}_3\text{OH})_3\}_6\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_2(\mu\text{-CN})_{30}\{\text{W}^{\text{V}}(\text{CN})_3\}_6]$  are denoted as  $\text{Ni}_9\text{Mo}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ ,  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ ,  $\text{Ni}_9\text{Mo}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , respectively, according to their structural differences.

For all of the selected complexes, there are 30 cyano-bridged  $\text{M}-\text{Ni}$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ) interactions in which 6 are associated with radial (rad) moieties and 24 with tangential (tang)  $\text{M}-\text{CN}-\text{Ni}$  moieties. Two types of exchange pathways, radial and tangential, exist for the approximate octahedral symmetry of the  $\text{Ni}_9\text{M}_6$  core. References 10 and 11 show that the  $[\text{Mo}(\text{CN})_8]^{3-}$  units in  $\text{Ni}_9\text{Mo}_6$  have a shape close to dodecahedron ( $\text{DD}$ ,  $\text{D}_{2d}$ ) geometry, and therefore, they have the apical (ap) and equatorial (eq) nature of the bridging cyanide. Each  $\text{M}$  ion is connected to the central  $\text{Ni}^{\text{II}}$  ion through an apical cyanide (radial pair). Each ion of  $\text{M}2-\text{M}5$  is connected to three peripheral  $\text{Ni}$  atoms through equatorial cyanides (tangential pairs) and to a fourth  $\text{Ni}$  atom by means of an apical cyanide (tangential pair). For  $\text{M}1$  and  $\text{M}6$ , two peripheral  $\text{Ni}$  atoms through equatorial cyanides and two  $\text{Ni}$  by means of apical cyanides connect them, respectively. Therefore, for the radial  $\text{M}-\text{CN}-\text{Ni}$  moieties, there are only the apical bridging cyanides, but there are two types of the cyanides, apical and equatorial for those tangential  $\text{M}-\text{CN}-\text{Ni}$  moieties.<sup>11</sup>

## COMPUTATIONAL DETAILS

In the calculations of  $J$ , the isotropic exchange interactions of the local spin moments are considered. The spin Hamiltonian for a general polynuclear complex can be expressed as

$$\hat{H} = \sum_{i>j} -2J_{ij}\hat{S}_i\hat{S}_j \quad (1)$$

where  $J_{ij}$  are the pairwise coupling constants between the paramagnetic centers of centers  $i$  and  $j$  and  $\hat{S}_i$  and  $\hat{S}_j$  are the spin

operators of the different paramagnetic centers  $i$  and  $j$ . The anisotropy Hamiltonian splits the  $(2S + 1)$  spin states, and ignoring the isotropic  $S(S + 1)$  terms, it can be expressed as

$$\hat{H} = D\left(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2\right) + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (2)$$

where  $\hat{S}$  and  $\hat{S}_z$  are the total spin operator of the molecule and its axial component, respectively.  $D$  and  $E$  are the axial and rhombic components of the anisotropy, respectively.

In calculations of  $J$ , the spin-orbit coupling is not considered by us. Basically, we need to calculate the energy of  $n + 1$  spin distributions for a system with  $n$  different exchange coupling constants. We can use these energy values to build up a system of  $n$  equations and then to obtain different  $J$  values. In the present work, we only consider the exchange interactions between nearest neighbors.

If all interactions through apical cyanides are assumed to be approximately equal, and likewise for all interactions through equatorial cyanides for six  $\text{Ni}_9\text{M}_6$  systems, three different spin state energies must be calculated to obtain the two types of  $J_{\text{ap}}$  and  $J_{\text{eq}}$ . The spin Hamiltonian, considering only the exchange coupling terms, can be expressed as (see Figure 1)

$$\begin{aligned} \hat{H} = & -2J_{\text{ap}}(\hat{S}_{\text{Ni}1}\hat{S}_{\text{M}1} + \hat{S}_{\text{Ni}1}\hat{S}_{\text{M}2} + \hat{S}_{\text{Ni}1}\hat{S}_{\text{M}3} + \hat{S}_{\text{Ni}1}\hat{S}_{\text{M}4} + \hat{S}_{\text{Ni}1}\hat{S}_{\text{M}5} \\ & + \hat{S}_{\text{Ni}1}\hat{S}_{\text{M}6} + \hat{S}_{\text{Ni}2}\hat{S}_{\text{M}3} + \hat{S}_{\text{Ni}3}\hat{S}_{\text{M}5} + \hat{S}_{\text{Ni}4}\hat{S}_{\text{M}1} + \hat{S}_{\text{Ni}5}\hat{S}_{\text{M}1} \\ & + \hat{S}_{\text{Ni}6}\hat{S}_{\text{M}2} + \hat{S}_{\text{Ni}7}\hat{S}_{\text{M}6} + \hat{S}_{\text{Ni}8}\hat{S}_{\text{M}4} + \hat{S}_{\text{Ni}9}\hat{S}_{\text{M}6}) \\ & - 2J_{\text{eq}}(\hat{S}_{\text{Ni}2}\hat{S}_{\text{M}1} + \hat{S}_{\text{Ni}2}\hat{S}_{\text{M}2} + \hat{S}_{\text{Ni}3}\hat{S}_{\text{M}1} + \hat{S}_{\text{Ni}3}\hat{S}_{\text{M}2} \\ & + \hat{S}_{\text{Ni}4}\hat{S}_{\text{M}4} + \hat{S}_{\text{Ni}4}\hat{S}_{\text{M}5} + \hat{S}_{\text{Ni}5}\hat{S}_{\text{M}3} + \hat{S}_{\text{Ni}5}\hat{S}_{\text{M}4} \\ & + \hat{S}_{\text{Ni}6}\hat{S}_{\text{M}3} + \hat{S}_{\text{Ni}6}\hat{S}_{\text{M}6} + \hat{S}_{\text{Ni}7}\hat{S}_{\text{M}2} + \hat{S}_{\text{Ni}7}\hat{S}_{\text{M}5} + \hat{S}_{\text{Ni}8}\hat{S}_{\text{M}3} \\ & + \hat{S}_{\text{Ni}8}\hat{S}_{\text{M}6} + \hat{S}_{\text{Ni}9}\hat{S}_{\text{M}4} + \hat{S}_{\text{Ni}9}\hat{S}_{\text{M}5}) \end{aligned} \quad (3)$$

where  $\hat{S}_{\text{Ni}1-9}$  and  $\hat{S}_{\text{M}1-6}$  are the spin operators of each  $\text{Ni}$  and  $\text{M}$  center (see Figure 1). Three spin states for each complex are as follows: 1 with  $S = 12$  (all spins up), 2 with  $S = 10$  (the central  $\text{Ni}$  with spin down), and 3 with  $S = 6$  (all  $\text{Mo}$  or  $\text{W}$  atoms with spins down). The equations to extract  $J_{\text{ap}}$  and  $J_{\text{eq}}$  values for six  $\text{Ni}_9\text{M}_6$  systems are as follows

$$J_{\text{ap}} = (E_2 - E_1)/18 \quad (4)$$

$$J_{\text{eq}} = (E_3 + E_1 - 2E_2)/54 \quad (5)$$

To obtain  $J$ , Gaussian 03 calculations<sup>12</sup> were performed with the popular hybrid functional B3LYP proposed by Becke<sup>13,14</sup> and Lee et al.,<sup>15</sup> which can provide  $J$  values in excellent agreement with the experimental data for transition-metal complexes<sup>16</sup> and a guess function generated with the Jaguar 7.0 code.<sup>17</sup> Stoll-Preuss quasi-relativistic pseudopotentials have been employed for  $\text{Mo}$  and  $\text{W}$  atoms<sup>18,19</sup> with a basis set with a contraction scheme (311111/22111/411) combined with the triple- $\zeta$  all-electron basis set proposed by Ahlrichs et al. for the other elements.<sup>20</sup> The convergence standard of the system energy was set to be smaller than  $10^{-7}$  hartree, reaching the precision required for the evaluation of  $J$ .

To obtain  $D$ , Orca 2.8.0 calculations<sup>21</sup> were performed with the generalized gradient approximation (GGA) PBE<sup>22</sup> functional, which is a good choice confirmed by Neese and other authors.<sup>23</sup> As expected, other functionals that are based on GGA yield very similar results and are therefore not reported. The spin-orbit coupling (SOC) operator used was the efficient

**Table 1.** Calculated and Experimental Ground-State Spin  $S$ , Exchange Coupling Constant  $J$  ( $J_{\text{ap}}$  and  $J_{\text{eq}}$ ) ( $\text{cm}^{-1}$ ), Zero-Field Splitting Parameter  $D$  ( $\text{cm}^{-1}$ ), Transverse Anisotropy Parameter  $E$  ( $\text{cm}^{-1}$ ), and Magnetic Anisotropy Barrier (MAB)  $|D|S^2$  ( $\text{cm}^{-1}$ )

		$S$		$J_{\text{ap}}$		$J_{\text{eq}}$		$D$		$E$	$ D S^2$	
		cal.	exp.	cal.	cal.	cal.	cal.	exp.	cal.	cal.	cal.	exp.
$\text{Ni}_9\text{M}_6(\text{CH}_3\text{OH})_{24}$	$\text{Ni}_9\text{Mo}_6(\text{CH}_3\text{OH})_{24}^4$	12	12	10.1	11.5	0.02	pos.		0.002			
	$\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}^4$	12	12	9.4	13.5	0.04	pos.		0.001			
$\text{Ni}_9\text{M}_6(\text{bpy})_8(\text{H}_2\text{O})_8$	$\text{Ni}_9\text{Mo}_6(\text{bpy})_8(\text{H}_2\text{O})_8^7$	12	12	9.7	12.1	−0.03	−0.08		−0.003	4.3	11.5	
	$\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8^6$	12	12	9.0	14.3	−0.14	−0.23		−0.002	20.2	33.0	
$\text{Ni}_9\text{M}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$	$\text{Ni}_9\text{Mo}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6^9$	12	12	7.2	18.1	0.02	0.05		−0.003	2.9		
	$\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6^9$	12	12	6.8	24.1	−0.09	0.04		−0.001	13.0	4.3	

**Table 2.** Calculated Spin–Spin and Spin–Orbit Coupling Contributions to  $D$  ( $\text{cm}^{-1}$ )

		$D_{\text{soc}}$				
	$D_{\text{tot}}$	$m = 12$	$m = -12$	$m = 11$ ( $\alpha$ )	$m = 11$ ( $\beta$ )	$D_{\text{ss}}$
$\text{Ni}_9\text{Mo}_6(\text{CH}_3\text{OH})_{24}$	0.02	−0.002	0.007	0.003	0.004	0.004
$\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$	0.04	−0.04	0.08	0.11	−0.12	0.006
$\text{Ni}_9\text{Mo}_6(\text{bpy})_8(\text{H}_2\text{O})_8$	−0.03	0.02	−0.013	−0.021	0.004	0.001
$\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$	−0.14	0.031	−0.211	−0.092	0.135	−0.004
$\text{Ni}_9\text{Mo}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$	−0.02	0.007	0.025	−0.121	0.078	−0.009
$\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$	−0.09	0.619	−0.095	−0.867	0.258	−0.008

implementation of the multicenter spin–orbit mean-field (SOMF) concept developed by Hess et al.<sup>24</sup> The spin–spin contributions to the  $D$  values were also included, although they are very small for our selected complexes.<sup>23</sup> The coupled-perturbed (CP) method proposed by Neese,<sup>23</sup> which uses revised prefactors for the spin–flip terms and solves a set of coupled perturbed equations for the SOC perturbation, was used. All calculations were performed with triple- $\zeta$  with one polarization function def2-TZVP<sup>25</sup> basis set for all atoms. The scalar relativistic treatment (ZORA) was used in all calculations. The large integration grid (grid = 5)<sup>26</sup> was applied to elements W, Mo, and Ni for ZORA calculations. Tight convergence criteria were used in order to ensure that the results are well converged with respect to technical parameters.

## RESULTS AND DISCUSSION

**Evaluation of  $J$  and  $D$ .** At first, we undertook a theoretical computational study based on hybrid density functional theory (DFT) B3LYP<sup>27</sup> to estimate the exchange coupling constants and to verify the intramolecular ferromagnetic interactions in the complexes  $\text{Ni}_9\text{M}_6(\text{CH}_3\text{OH})_{24}$ ,<sup>4</sup>  $\text{Ni}_9\text{M}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ ,<sup>6,7</sup> and  $\text{Ni}_9\text{M}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ). According to eqs 3–5, we calculated the two types of  $J_{\text{ap}}$  and  $J_{\text{eq}}$ , which are shown in Table 1. Their values are positive, suggesting that (i) the intramolecular interactions are all ferromagnetic for the orthogonal  $t_{2g}$  orbitals in M and  $e_g$  in  $\text{Ni}^{\text{II}}$  and (ii) that the ground-state spin  $S$  should be 12 for all of them.

We then used the PBE<sup>22</sup> method to calculate the zero-field splitting parameter  $D$  and the transverse anisotropy parameter  $E$  of six systems (see Table 1). To thoroughly analyze the contributions to  $D$ , we gave the calculated spin–spin<sup>23</sup> coupling and SOC<sup>24</sup> contributions, separately, for six selected complexes, shown in Table 2. As expected, the spin–spin contributions to

$D$  are all very small for all complexes (see Table 2), and the negative  $D$  values of  $\text{Ni}_9\text{M}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ) and  $\text{Ni}_9\text{M}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  come mainly from the  $m = -12$  and 11 ( $\alpha$ ) spin–flip contributions.<sup>23a,28</sup>

The calculated  $E$  values for all complexes are very small (see Table 1), showing that the quantum mechanical magnetization tunneling in our studied systems can be omitted. As indicated in Table 1, the calculated and experimental  $D$  values of  $\text{Ni}_9\text{M}_6(\text{CH}_3\text{OH})_{24}$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ) are all positive, and those of  $\text{Ni}_9\text{M}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ) and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  are negative, which suggests that complexes  $\text{Ni}_9\text{M}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  behave as SMMs, whereas  $\text{Ni}_9\text{M}_6(\text{CH}_3\text{OH})_{24}$  does not. Although our calculated  $D$  values have small differences from the experimental results for the intrinsic inaccuracy of the GGA functional,<sup>28,29</sup> they have the same signs, except for  $\text{Ni}_9\text{Mo}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , they are qualitatively correct, and they scale with respect to them for all complexes. Moreover, our calculated results show that the magnetic anisotropy energy barrier of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  is larger than that of  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , in agreement with experiments (see Table 1). However, why does  $\text{Ni}_9\text{M}_6(\text{CH}_3\text{OH})_{24}$ , which has  $\text{CH}_3\text{OH}$  ligands bound to each Ni, not behave as a SMM? Is it the use of (bpy)( $\text{H}_2\text{O}$ ) or tmphen to substitute  $\text{CH}_3\text{OH}$  that causes the magnetic anisotropy of the  $\text{Ni}_9\text{M}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ) and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ ? In the next sections, we will give the answer from thoroughly investigation of the origin of the magnetic anisotropy in the  $\text{Ni}_9\text{M}_6$  systems.

**Comparison and Quantitative Analysis of the Magnetic Anisotropy.** First, we will investigate whether the difference of the surrounding ligands bound to each  $\text{Ni}^{\text{II}}$  will influence the magnetic anisotropy of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ . From examining the structures of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$



**Table 3.** Calculated Ground-State Spin  $S$ , Zero-Field Splitting Parameter  $D$  ( $\text{cm}^{-1}$ ), and MAB  $|D|S^2$  ( $\text{cm}^{-1}$ ) for Five Modeled Structures

	$S$	$D$	$ D S^2$
$\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6\{(\text{bpy})(\text{H}_2\text{O})\}_2^a$	12	−0.10	14.4
$\text{Ni}_9\text{W}_6\{(\text{bpy})(\text{H}_2\text{O})\}_6(\text{H}_2\text{O})_6^b$	12	−0.13	18.7
$\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}^c$	12	−0.14	20.2
$\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{18}(\text{H}_2\text{O})_6^d$	12	−0.11	15.8
$\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8^e$	12	0.05	

<sup>a</sup>The obtained model using two  $(\text{bpy})(\text{H}_2\text{O})$  to substitute two  $(\text{H}_2\text{O})_3$  of  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ .<sup>9</sup> <sup>b</sup>The obtained model using two  $(\text{H}_2\text{O})_3$  to substitute two  $(\text{bpy})(\text{H}_2\text{O})$  of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ .<sup>6</sup> <sup>c</sup>The obtained model using eight  $(\text{CH}_3\text{OH})_3$  to substitute eight  $(\text{bpy})(\text{H}_2\text{O})$  of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ .<sup>6</sup> <sup>d</sup>The obtained model using six  $(\text{CH}_3\text{OH})_3$  to substitute six  $(\text{tmphen})(\text{CH}_3\text{OH})$  of  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ .<sup>9</sup> <sup>e</sup>The obtained model using eight  $(\text{bpy})(\text{H}_2\text{O})$  to substitute eight  $(\text{H}_2\text{O})_3$  of  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$ .<sup>4</sup>

there is only one  $(\text{bpy})(\text{H}_2\text{O})$  surrounding each  $\text{Ni}^{\text{II}}$  for  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{bpy})\}_8(\mu\text{-CN})_{30}\{\text{W}(\text{CN})_3\}_6]$ ; however, the terminal ligands surrounding each  $\text{Ni}^{\text{II}}$  are not the same for  $[\text{Ni}^{\text{II}}\{\text{Ni}^{\text{II}}(\text{tmphen})(\text{CH}_3\text{OH})\}_6\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_2(\mu\text{-CN})_{30}\{\text{W}(\text{CN})_3\}_6]$ .<sup>9</sup> One  $\text{tmphen}$  and one  $\text{CH}_3\text{OH}$  are bound to each one of six  $\text{Ni}^{\text{II}}$ , while three  $\text{H}_2\text{O}$  are bound to every one of the other two  $\text{Ni}^{\text{II}}$ . To investigate whether three  $\text{H}_2\text{O}$  bound to every one of the other two  $\text{Ni}^{\text{II}}$  will influence the  $D$  value of  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , except for the different  $(\text{tmphen})(\text{CH}_3\text{OH})$  ligands, we used  $(\text{bpy})(\text{H}_2\text{O})$  to substitute two  $(\text{H}_2\text{O})_3$  for  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  and obtained the model  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6\{(\text{bpy})(\text{H}_2\text{O})\}_2$ . Similarly, two corresponding  $(\text{bpy})(\text{H}_2\text{O})$  were replaced by two  $(\text{H}_2\text{O})_3$  for  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  to obtain the model  $\text{Ni}_9\text{W}_6\{(\text{bpy})(\text{H}_2\text{O})\}_6(\text{H}_2\text{O})_6$ . The detailed structures of the above models are shown in Figure S1 (see Supporting Information). The same methods were used to calculate the  $D$  values of the above two models (they are not optimized). The calculated  $D$  values are shown in Table 3, where the  $D$  values of the two models are almost the same as those of their original ones. The above results show that using two  $(\text{H}_2\text{O})_3$  bound to  $\text{Ni}^{\text{II}}$  to substitute two  $(\text{bpy})(\text{H}_2\text{O})$  has a small influence on the magnetic anisotropy. In the next section, we will give the reason using qualitative theory.

Second, to investigate whether the  $(\text{bpy})(\text{H}_2\text{O})$  or  $(\text{tmphen})(\text{CH}_3\text{OH})$  ligands bound to  $\text{Ni}^{\text{II}}$  in complexes  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  compared with the  $\text{CH}_3\text{OH}$  in  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  are the origin of the magnetic anisotropy of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , we used  $(\text{CH}_3\text{OH})_3$  to substitute  $(\text{bpy})(\text{H}_2\text{O})$  for  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $(\text{tmphen})(\text{CH}_3\text{OH})$  for  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  and then obtained models  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  and  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{18}(\text{H}_2\text{O})_6$ , respectively.  $(\text{CH}_3\text{OH})_3$  of complex  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  were also replaced by  $(\text{bpy})(\text{H}_2\text{O})$  to obtain the model  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ . The detailed structures of the above models are shown in Figure S1 (see Supporting Information). In all of the calculations, the replaced structures are not optimized for the reason that we only investigate the influence of the external ligands on the magnetic anisotropy, that is, we are not looking for new complexes. The calculated  $D$  values of the above two models are shown in Table 3, where two of them are similar to the original ones, which shows that the surrounding ligands bound to  $\text{Ni}^{\text{II}}$  have a small influence on their magnetic anisotropy of our

investigated complexes. In the next section, we will give the reason using qualitative theory.

**Qualitative Analysis of the Magnetic Anisotropy.** As we know, the main component of the magnetic anisotropy of the ground state ( $D$ ) usually comes from the projection of the single-site anisotropies ( $D_i$ ) onto the spin ground state  $S$  (eq 6), while dipolar and anisotropic interactions yield only minor contributions especially for cyanide-bridged complexes because the metal–metal distances within them are long.<sup>30</sup>

$$D = \sum_{i=1}^N d_i D_i \quad (6)$$

where  $i$  numbers the  $N$  metal centers and the  $d_i$  values are projection coefficients. Equation 6 is derived in the strong-exchange limit for a spin cluster. From examining the structures of our selected six complexes, we find that the structures of the isolated parts including Ni are almost similar for the same molecule but are different between six complexes. However, the core isolated parts of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  for six complexes have similar structures, but are not the same completely. Thus, to examine and differentiate the sources of the magnetic anisotropy of six complexes, we decomposed each complex into nine isolated parts, eight isolated pieces that each consists of one  $\text{Ni}^{\text{II}}$  ion and its surrounding ligands and one isolated part  $\text{W}_6(\text{CN})_{48}\text{Ni}$ . All of the isolated pieces were taken from the original structures and not optimized. The four different isolated parts including Ni extracted from  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$ ,  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ , and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  are  $[\text{Ni}(\text{CH}_3\text{OH})_3(\text{CN})_3]^-$ ,  $[\text{Ni}(\text{H}_2\text{O})_3(\text{CN})_3]^-$ ,  $[\text{Ni}(\text{bpy})(\text{H}_2\text{O})(\text{CN})_3]^-$ , and  $[\text{Ni}(\text{tmphen})(\text{CH}_3\text{OH})(\text{CN})_3]^-$ . Except for the above isolated parts, each of the three complexes leaves the isolated part  $\text{W}_6(\text{CN})_{48}\text{Ni}$ . The structures of the fragments are shown in Figure S3 in Supporting Information. Our calculations show that the first two isolated parts are close to easy-plane systems, while the next two of  $[\text{Ni}(\text{bpy})(\text{H}_2\text{O})(\text{CN})_3]^-$  and  $[\text{Ni}(\text{tmphen})(\text{CH}_3\text{OH})(\text{CN})_3]^-$  both have an easy axis (see Table 4).

The calculated  $D$  values show that the isolated part  $\text{W}_6(\text{CN})_{48}\text{Ni}$  extracted from  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  is an easy-plane system and the other two isolated parts extracted from  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  both have an easy axis.

The spin population (SP) on  $\text{Ni}^{\text{II}}$  for each of the five fragments was calculated using hybrid functional B3LYP for comparison with the value of the corresponding whole structure, which was calculated using B3LYP. The calculated SP on  $\text{Ni}^{\text{II}}$  is about 1.7 e, which is similar to those of the whole molecules (about 1.7 e; see Table S1 in Supporting Information). As we can see, the carbon atoms of the CN groups are not saturated in the fragment calculations. To investigate the influence of the saturated carbon atoms on the magnetic anisotropy, we used a neutral NCH group instead of a bare CN group carrying a negative charge to obtain the saturated fragments of  $[\text{Ni}(\text{CH}_3\text{OH})_3(\text{NCH})_3]^{2+}$ ,  $[\text{Ni}(\text{H}_2\text{O})_3(\text{NCH})_3]^{2+}$ ,  $[\text{Ni}(\text{bpy})(\text{H}_2\text{O})(\text{NCH})_3]^{2+}$ , and  $[\text{Ni}(\text{tmphen})(\text{CH}_3\text{OH})(\text{NCH})_3]^{2+}$ . For  $\text{W}_6(\text{CN})_{48}\text{Ni}$ , we also used the neutral NCH groups to substitute the bare CN groups bound to W to obtain the new fragment of  $\text{W}_6(\text{NCH})_{42}(\text{CN})_6\text{Ni}$ . The calculated easy-type, ground-state spin  $S$ , zero-field splitting parameter  $D$ , transverse anisotropy parameter  $E$ , magnetic anisotropy barrier (MAB) and SP on  $\text{Ni}^{\text{II}}$  for each of the saturated fragments are shown in Table 5.

**Table 4.** Easy-Type, Ground-State Spin  $S$ , Zero-Field Splitting Parameter  $D$  ( $\text{cm}^{-1}$ ), Transverse Anisotropy Parameter  $E$  ( $\text{cm}^{-1}$ ), MAB ( $\text{cm}^{-1}$ ), and Spin Population (SP) ( $e$ ) on  $\text{Ni}^{\text{II}}$  for Each of the Five Isolated Parts Extracted from Three Complexes

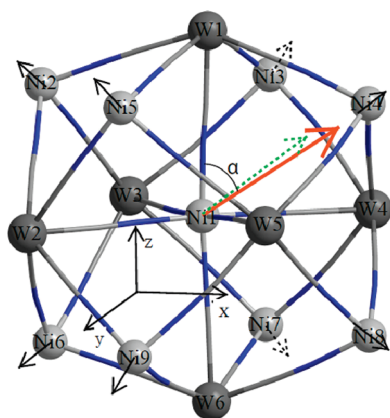
	$[\text{Ni}(\text{CH}_3\text{OH})_3(\text{CN})_3]^-$	$[\text{Ni}(\text{H}_2\text{O})_3(\text{CN})_3]^-$	$[\text{Ni}(\text{bpy})(\text{H}_2\text{O})(\text{CN})_3]^-$	$[\text{Ni}(\text{tmphen})(\text{CH}_3\text{OH})(\text{CN})_3]^-$	$\text{W}_6(\text{CN})_{48}\text{Ni}$
type	easy plane	easy plane	easy axis	easy axis	
$S$	1	1	1	1	4
$D$	0.85	1.0	−2.28	−2.41	$0.25,^a -1.56,^b -1.06^c$
$E$	0.15	0.09	0.25	−0.56	$0.053,^a -0.007,^b -0.005^c$
MAB			2.28	2.41	$25.0,^b 17.0^c$
SP <sup>d</sup>	1.6813	1.7086	1.6853	1.6824	$1.6891,^a 1.6923,^b 1.6870,^c$

<sup>a</sup> Calculated value of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  extracted from  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$ . <sup>b</sup> Value from  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ . <sup>c</sup> Value from  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ . <sup>d</sup> Calculated value using the B3LYP functional.

**Table 5.** Easy-Type, Ground-State  $S$ , Zero-Field Splitting Parameter  $D$  ( $\text{cm}^{-1}$ ), Transverse Anisotropy Parameter  $E$  ( $\text{cm}^{-1}$ ), MAB ( $\text{cm}^{-1}$ ), and SP ( $e$ ) on  $\text{Ni}^{\text{II}}$  for Each of the Five Saturated Fragments

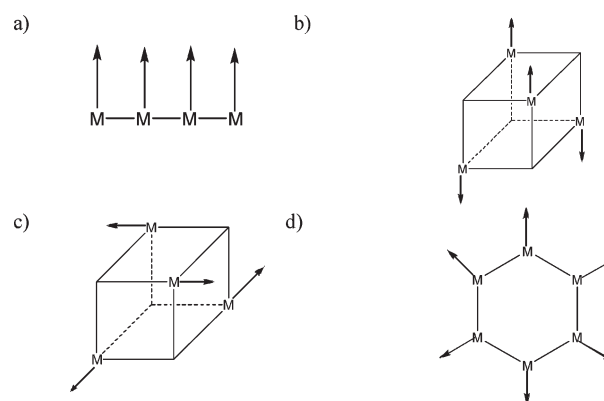
	$[\text{Ni}(\text{CH}_3\text{OH})_3(\text{NCH})_3]^{2+}$	$[\text{Ni}(\text{H}_2\text{O})_3(\text{NCH})_3]^{2+}$	$[\text{Ni}(\text{bpy})(\text{H}_2\text{O})(\text{NCH})_3]^{2+}$	$[\text{Ni}(\text{tmphen})(\text{CH}_3\text{OH})(\text{NCH})_3]^{2+}$	$\text{W}_6(\text{NCH})_{42}(\text{CN})_6\text{Ni}$
type	easy plane	easy plane	easy axis	easy axis	
$S$	1	1	1	1	4
$D$	0.45	0.59	−1.70	−2.01	$0.22,^a -1.53,^b -0.98^c$
$E$	0.04	0.03	−0.16	−0.41	$0.047,^a -0.01,^b -0.014^c$
MAB			1.70	2.01	$24.5,^b 15.7^c$
SP <sup>d</sup>	1.6726	1.6910	1.6658	1.6689	$1.6885,^a 1.6933,^b 1.6881,^c$

<sup>a</sup> Calculated value of  $\text{W}_6(\text{NCH})_{42}(\text{CN})_6\text{Ni}$  extracted from  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$ . <sup>b</sup> Value from  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ . <sup>c</sup> Value from  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ . <sup>d</sup> Calculated value using the B3LYP functional.

**Figure 2.** Directions of the hard axes on eight surrounding Ni (black arrows), the hard axis on  $\text{W}_6(\text{CN})_{48}\text{Ni}$  (green arrow), and the whole hard axis on  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  (red arrow).

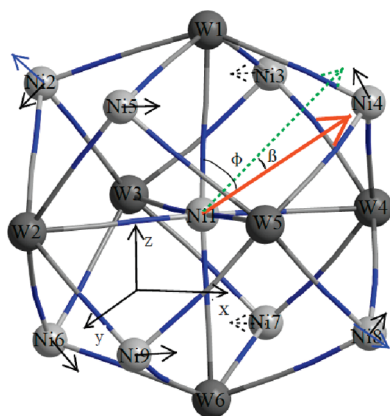
From Table 5, we find that the SPs on  $\text{Ni}^{\text{II}}$  are similar to those of the unsaturated fragments in Table 4. The calculated  $D$  values are a little smaller than those of the unsaturated ones. However, their directions of the easy axes and the easy types are the same. Thus, we consider that the saturated carbon atoms of CN groups using a neutral NCH group instead of a bare CN group have a small influence on the magnetic anisotropy in the fragment calculations.

First, to investigate why complex  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  does not behave as a SMM, we give the hard axes on each  $[\text{Ni}_6(\text{CH}_3\text{OH})_3(\text{CN})_3]^-$  and  $\text{W}_6(\text{CN})_{48}\text{Ni}$  and the whole hard axis of  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$ , which are shown in Figure 2.

**Figure 3.** (a,b) Collinear easy-axis ( $D_i < 0$ ) and (c,d) orthogonal (or radial) hard-axis ( $D_i > 0$ ) alignments required for the negative  $D$  value for molecules. Arrows in (a,b) and (c,d) represent easy and hard axes, respectively.<sup>31</sup> Copyright 2005, Wiley.

Oshio and co-workers<sup>31</sup> show that collinear local easy-axis and orthogonal local hard-axis alignments give negative  $D$  value, whereas  $D$  will be close to zero when the local easy-axis alignments are orthogonal or the local hard axis is collinear (see Figure 3<sup>31</sup>).

From Figure 2, the radial hard axes on Ni2, Ni4, Ni6, and Ni8 induce a negative  $D_i$  sum value, as Figure 3d indicated, and their total easy axis is along the  $y$  axis. Similarly, the radial hard axes on Ni3, Ni5, Ni7, and Ni9 also induce a negative  $D_i$  sum value, and their total easy axis is along the  $x$  axis. The above two easy axes (one is along the  $y$  axis, and the other is along the  $x$  axis) form an easy plane, and thus the total hard axis contributed to by eight



**Figure 4.** General directions of the easy axes on eight surrounding Ni (black arrows), the hard axes on Ni2 and Ni8 for complex  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  (blue arrows), the easy axis on  $\text{W}_6(\text{CN})_{48}\text{Ni}$  (green arrow), and the whole easy axis (red arrow).

surrounding  $[\text{Ni}(\text{CH}_3\text{OH})_3(\text{CN})_3]^-$  is along to the  $z$  axis. Therefore, the  $D_i$  sum value contributed to by eight  $[\text{Ni}(\text{CH}_3\text{OH})_3(\text{CN})_3]^-$  should be positive, and its projection onto the whole easy axis (red arrow in Figure 2) is relatively smaller for the larger  $\alpha$  angle, which is about  $53^\circ$ . On the other hand, the local hard axis on  $\text{W}_6(\text{CN})_{48}\text{Ni}$  and the whole hard axis on complex  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  have the similar orientations, and thus, the contribution of the positive  $D_i$  value of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  (see Table 4) to all  $D$  should be positive. It is concluded that complex  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  does not behave as a SMM.

Second, we will investigate why  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  behave as SMMs, why the influence of the difference of the surrounding ligands bound to each  $\text{Ni}^{\text{II}}$  on their magnetic anisotropy is small, and why the surrounding ligands bound to  $\text{Ni}^{\text{II}}$  have a small influence on their magnetic anisotropy. Considering the similar orientations on each Ni,  $\text{W}_6(\text{CN})_{48}\text{Ni}$ , and all structures for  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , we give the general easy axes on eight surrounding Ni (two of them are hard axes for  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ ,  $\text{W}_6(\text{CN})_{48}\text{Ni}$ , and the whole complex, which are shown in Figure 4).

For  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ , the easy axes on the above four Ni (Ni2, Ni3, Ni4, and Ni5) are almost orthogonal (see Figure 4), and thus, the contribution of the four  $D_i$  of Ni to the total  $D$  is positive, and the hard axis formed by the four Ni atoms is closely along the  $z$  axis. Similarly, four easy axes on Ni6, Ni7, Ni8, and Ni9 form an easy plane, and the hard axis is also closely along the  $z$  axis. Therefore, the local  $D_i$  sum contributed to by eight surrounding Ni is positive, and its hard axis is along the  $z$  axis. For the larger  $\Phi$  angle (about  $53.6^\circ$ ; see Figure 4) compared with the angle  $\beta$  (about  $38.6^\circ$ ), the projection of the positive sum of the  $D_i$  contributed to by eight surrounding Ni onto the whole easy axis (red arrow) is relatively small.<sup>32</sup> Thus, the whole negative  $D$  of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  comes mainly from the projection of the negative  $D_i$  of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  (see Table 4) onto the whole easy axis (the angle  $\beta$  between the easy axes of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  and the whole structure is about  $38.6^\circ$ ; see Figure 4).

For  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$ , only the hard axes on Ni2 and Ni8 are different from those of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  (see the blue arrows on Ni2 and Ni8 in Figure 4). The summarized  $D_i$  will be positive for the parallel alignment of the

two hard axes on Ni2 and Ni8. However, the contributions of the two  $D_i$  of Ni2 and Ni8 are very small for the angle between their hard axes and the whole easy axis being close to  $90^\circ$ . Thus, the whole negative  $D$  of  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  also mainly comes from the projection of the negative  $D_i$  of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  (see Table 4) onto the whole easy axis. In conclusion, using  $(\text{bpy})(\text{H}_2\text{O})$  to substitute two  $(\text{H}_2\text{O})_3$  for  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  or two  $(\text{H}_2\text{O})_3$  to replace two  $(\text{bpy})(\text{H}_2\text{O})$  for  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  has a small influence on their magnetic anisotropy (see Table 3) because the whole negative  $D$  mainly comes from the contribution of the negative  $D_i$  of  $\text{W}_6(\text{CN})_{48}\text{Ni}$ .

Finally, for the same reason that the whole  $D$  comes mainly from the contribution of the  $D_i$  of  $\text{W}_6(\text{CN})_{48}\text{Ni}$ , the influence on their magnetic anisotropy of using  $(\text{CH}_3\text{OH})_3$  to substitute  $(\text{bpy})(\text{H}_2\text{O})$  in  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $(\text{tmphen})(\text{CH}_3\text{OH})$  in  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  or using  $(\text{bpy})(\text{H}_2\text{O})$  to replace  $(\text{CH}_3\text{OH})_3$  in  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  is very small (see Table 3).

Here, we do not discuss the sources of the magnetic anisotropy of  $\text{Ni}_9\text{Mo}_6$  because most of them do not behave as SMMs (see Table 1), although they have similar structures to those of  $\text{Ni}_9\text{W}_6$ . According to the above analysis, all  $D$  values of  $\text{Ni}_9\text{Mo}_6$  systems also come mainly from the  $D_i$  of  $\text{Mo}_6(\text{CN})_{48}\text{Ni}$  contribution. Our calculations show that most of the  $D_i$  of  $\text{Mo}_6(\text{CN})_{48}\text{Ni}$  are positive and very small. Hence, all  $D$  values of most of  $\text{Ni}_9\text{Mo}_6$  are positive and very small.

As we know, it is only possible in the strong exchange limit when the spin mixing effects on the isotropic exchange interaction are negligible. For our studied molecules, the  $J$  between M and Ni (on the order of  $10\text{ cm}^{-1}$ ; see Table 1) are larger than those of the local anisotropy parameter  $D$  (on the order of  $2\text{--}3\text{ cm}^{-1}$ ; see Table 4). Thus, it is valid to treat separately the isotropic interaction and the magnetic anisotropy in our studied complexes. This validity can also be confirmed from the data in Table S1 (see Supporting Information), which show that the splitting of the different spin states due to the isotropic coupling is much larger than that of the width of the ground-state manifold caused by the spin–orbit interaction (see Table 1) for each of them. For example, the splitting of the different spin states of  $E_1$  with  $S = 12$  and  $E_3$  with  $S = 6$  due to the isotropic coupling is about  $1095\text{ cm}^{-1}$  for  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$ , which is much larger than the width of the ground-state manifold caused by the spin–orbit interaction of  $20.2\text{ cm}^{-1}$ .

## CONCLUSIONS

DFT calculations on six  $\text{Ni}_9\text{M}_6$  ( $\text{M} = \text{Mo}^{\text{V}}$  or  $\text{W}^{\text{V}}$ ) systems to explore the origin of their magnetic anisotropy show that (1) complex  $\text{Ni}_9\text{W}_6(\text{CH}_3\text{OH})_{24}$  does not behave as a SMM because the contributions of the  $D_i$  of eight surrounding  $[\text{Ni}(\text{CH}_3\text{OH})_3(\text{CN})_3]^-$  and the left  $\text{W}_6(\text{CN})_{48}\text{Ni}$  to the whole  $D$  are both positive; (2) for the large  $\Phi$  angle (about  $53.6^\circ$ ; see Figure 4), the projection of the positive  $D_i$  summation contributed to by eight surrounding Ni onto the whole easy axis is very small. Therefore, the whole negative  $D$  values of  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and  $\text{Ni}_9\text{W}_6(\text{tmphen})_6(\text{CH}_3\text{OH})_6(\text{H}_2\text{O})_6$  come mainly from the projection of the negative  $D_i$  of  $\text{W}_6(\text{CN})_{48}\text{Ni}$  onto the whole easy axis; (3) for the same reason that the whole  $D$  comes mainly from the contribution of the  $D_i$  of  $\text{W}_6(\text{CN})_{48}\text{Ni}$ , the influence on their magnetic anisotropy of using  $(\text{CH}_3\text{OH})_3$  to substitute  $(\text{bpy})(\text{H}_2\text{O})$  for  $\text{Ni}_9\text{W}_6(\text{bpy})_8(\text{H}_2\text{O})_8$  and



(tmphen)(CH<sub>3</sub>OH) for Ni<sub>9</sub>W<sub>6</sub>(tmphen)<sub>6</sub>(CH<sub>3</sub>OH)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub> or using (bpy)(H<sub>2</sub>O) to replace (CH<sub>3</sub>OH)<sub>3</sub> for Ni<sub>9</sub>W<sub>6</sub>-(CH<sub>3</sub>OH)<sub>24</sub> is very small. However, although the contributions of the surrounding Ni bounded by different ligands to the whole *D* are very small in our selected complexes, the different ligands bound to Ni have an influence on the core structure of W<sub>6</sub>-(CN)<sub>48</sub>Ni, which is the main resource of their magnetic anisotropy. Hence, it is a good way for experimental chemists to synthesize Ni<sub>9</sub>W<sub>6</sub> systems with large negative *D* values using different ligands bound to Ni to obtain the good core structures of W<sub>6</sub>(CN)<sub>48</sub>Ni that have larger negative *D* values. In our selected Ni<sub>9</sub>M<sub>6</sub> systems, the contributions of the local *D<sub>i</sub>* of the surrounding Ni to the whole *D* are very small because the distributions of the ligands bound to each Ni are closely symmetric. Therefore, a good way to increase the negative *D* of Ni<sub>9</sub>M<sub>6</sub> systems is also to distribute the terminal ligands unsymmetrically around the Ni magnetic ions, as already indicated in one of our previous papers.<sup>8</sup>

## ■ ASSOCIATED CONTENT

**Supporting Information.** Table S1 shows three spin state energies of Ni<sub>9</sub>W<sub>6</sub>(CH<sub>3</sub>OH)<sub>24</sub>, Ni<sub>9</sub>W<sub>6</sub>(bpy)<sub>8</sub>, and Ni<sub>9</sub>W<sub>6</sub>-(tmphen)<sub>6</sub>(CH<sub>3</sub>OH)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>. Table S2 shows the SPs on each metal ion of Ni<sub>9</sub>W<sub>6</sub>(CH<sub>3</sub>OH)<sub>24</sub>, Ni<sub>9</sub>Mo<sub>6</sub>(bpy)<sub>8</sub>(H<sub>2</sub>O)<sub>8</sub>, and Ni<sub>9</sub>W<sub>6</sub>(tmphen)<sub>6</sub>(CH<sub>3</sub>OH)<sub>6</sub>(H<sub>2</sub>O)<sub>6</sub>. Figure S1 shows the different models to be calculated. Figure S2 shows three types of cyanides. Figure S3 shows the structures of five isolated parts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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