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On the Origin of Magnetic Anisotropy in Cyanide-Bridged Co_9M_6 (M = Mo^V or W^V) Systems: A DFT Study

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Our calculations show that the substitution of metal ions using Co^{II} is not the main reason that $Co^{II}{}_9M_6$ (M = Mo^V or W^V) exhibits single-molecule-magnet behavior, whereas the unsymmetrical distribution of three CH_3OH ligands surrounding each Co^{II} is the main one.

The magnetic properties of high-spin molecules having an energy barrier that prevents easy reversal of the magnetic moment have been extensively studied experimentally and theoretically over the past years.[1−6] Some of those high-spin molecules present slow relaxation of their magnetization, which could eventually lead to applications for information storage and quantum computing at the molecular level.[2] 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 single-molecule magnets (SMMs) to have high barriers are a large ground-state spin and a large negative D parameter.

In these high-spin SMMs, a new series of $[M'\{M'(MeOH)_3\}_8(\mu\text{-CN})_{30}\{M(CN)_3\}_6]$ (M' = Mn^{II}, Ni^{II}, or Co^{II}; M = Mo^V or W^V)[3−5] systems have received much attention for having high-spin ground states. The D values of most of them are almost close to zero, but $\{Co^{II}{}_9[M(CN)_8]_6(CH_3OH)_{24}\}$ (M = Mo^V or W^V)[3] synthesized by Song and co-workers has a negative D value. Although they have similar structures, why is the obtained $Co^{II}{}_9M_6$ (M = Mo^V or W^V)[3] system using Co^{II} to substitute Mn^{II} or Ni^{II} SMMs and the other M'_9M_6 (M' = Mn^{II} or Ni^{II}; M = Mo^V or W^V)[4,5] is not? Is substitution of the metal ions the main reason that $Co^{II}{}_9M_6$ (M = Mo^V or W^V)[3] exhibits SMM behavior? In this paper, we will give the answer.

To investigate why the $Co^{II}{}_9M_6$ (M = Mo^V or W^V)$_7$ system using Co^{II} to substitute other metal ions behaves as a SMM, we selected complexes $[M'\{M'(MeOH)_3\}_8(\mu\text{-CN})_{30}\{M(CN)_3\}_6]$ (M' = Ni^{II}; M = Mo^V or W^V)[4] except $Co^{II}{}_9M_6$ (M = Mo^V or W^V).[3] The detailed descriptions of the structures are shown in below.

$\{Co^{II}{}_9[Mo^V(CN)_8]_6(CH_3OH)_{24}\}$[3] ($Co_9Mo_6$), which is comprised of 15 cyanide-bridged metal ions, namely, 9 Co^{II} ions (S = ${}^3/_2$) and 6 Mo^V ions (S = ${}^1/_2$), giving a total of 33 unpaired electrons, is sketched in Figure 1.

There are 30 cyano-bridged Mo−Co interactions, of which 6 are associated with radial (rad) moieties and 24 with tangential (tang) Mo−CN−Co moieties. Two types of exchange pathways, radial and tangential, exist for the approximate octahedral symmetry of the Co_9Mo_6 core. References 3 and 6 show that the $[Mo(CN)_8]^{3-}$ units in Co_9Mo_6 have a shape close to dodecahedron (D_{2d}) geometry, and so they have the apical (ap) and equatorial (eq) nature of the bridging cyanide. Each Mo^V ion is connected to the central Co^{II} ion through an apical cyanide (radial pair), to three peripheral Co atoms through equatorial cyanides (tangential pairs), and to a fourth Co atom by means of an apical cyanide (tangential pair). Therefore, for the radial Mo−CN−Co moieties, there are only apical bridging cyanides, but there are two types of cyanides: apical and equatorial for those tangential Mo−CN−Co moieties. The detailed description of complex Co_9Mo_6 can be found in ref 3. Complexes Co_9W_6,[3] Ni_9Mo_6,[4] and Ni_9W_6[4] are isostructural to Co_9Mo_6. You can consult the above description about Co_9Mo_6 or refs 3 and 4.

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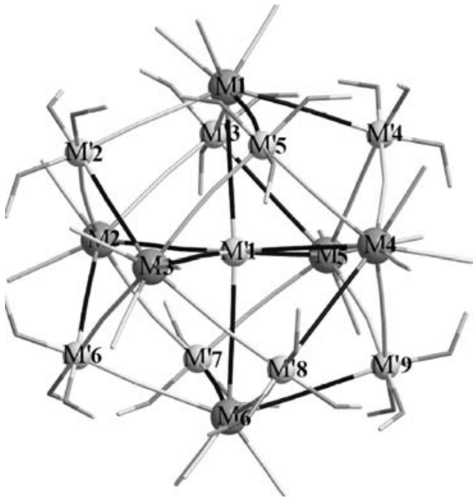

Figure 1. General molecular structure of the Co_9Mo_6, Co_9W_6, Ni_9Mo_6, and Ni_9W_6 complexes ($M' = Co^{II}$ and $M = Mo^{V}$ for Co_9Mo_6; $M' = Co^{II}$ and $M = W^{V}$ for Co_9W_6; $M' = Ni^{II}$ and $M = Mo^{V}$ for Ni_9Mo_6; $M' = Ni^{II}$ and $M = W^{V}$ for Ni_9W_6). The equatorial and apical cyanides are represented as gray and black bonds, respectively.

At first, to verify the intramolecular antiferromagnetic interactions in Co_9Mo_6 and Co_9W_6 systems[3] and ferromagnetic interactions in Ni_9Mo_6 and Ni_9W_6,[4] we undertook a theoretical computational study based on hybrid density functional theory (DFT) B3LYP[7] (see the Supporting Information for details) to estimate their exchange coupling constants. If all interactions through apical cyanides are assumed to be approximately equal and likewise for all interactions through equatorial cyanides for complexes Co_9Mo_6, Co_9W_6, Ni_9Mo_6, and Ni_9W_6, we can obtain two types of J_{ap} and J_{eq} through the calculation of three different spin-state energies for each of them, respectively. The two calculated types of J_{ap} and J_{eq} are shown in Table 1, where the calculated J_{ap} values of Co_9Mo_6 and Co_9W_6 are all negative, but their J_{eq} values are positive.

However, according to eqs 3 and 4 in the Supporting Information, the spin state ($S = {}^{21}/_2$) energy E_3 of Co_9Mo_6 or Co_9W_6 is the smallest, which suggests that all Co$\cdots$Mo or Co$\cdots$W interactions should be antiferromagnetic, in agreement with the experimental results and the fact that the whole molecule should be arranged with a ground-state spin of ${}^{21}/_2$, whereas the calculated J_{ap} and J_{eq} of Ni_9Mo_6 and Ni_9W_6 are all positive, consistent with the experiments, which suggests that their intramolecular interactions are ferromagnetic and that the ground-state spin S should be 12.

Then, we used the Perdew−Burke−Ernzerhof[8] method (see the Supporting Information for details) to calculate the zero-field-splitting parameter D and the transverse anisotropy parameter E of the Co_9Mo_6 and Co_9W_6 systems, respectively. The D and E values were all obtained in their spin ground states. For the presence of the unquenched orbital contribution and strong spin−orbital interaction that stabilizes a Kramers doublet as a ground state of Co^{II}, the effects of the unquenched orbital angular momentum should be included in the calculations of D.[9] However, considering the limitations of DFT methods (the unquenched orbital angular momentum of Co^{II} arising from its orbital degeneracy cannot be considered within DFT, which is for single-determinant methods),[10] we do not take into account the effects of the unquenched orbital angular momentum in the calculations of D. Moreover, Park and Holmes' work[11] shows that the DFT-calculated D of Fe_2Co_2[12] is qualitatively correct compared to the experiment without considering the unquenched orbital angular momentum contributions of Co^{II}. The magnetic anisotropy of Co^{II} and also other ions such as Mn^{III}- or Mn^{II}-based systems with the unquenched angular orbital contribution has been intensively discussed theoretically and experimentally.[9,10,13]

As Table 1 indicated, the calculated and experimental D values of Co_9Mo_6 and Co_9W_6 are all negative, which shows that complexes Co_9Mo_6 and Co_9W_6 behave as SMMs, whereas Ni_9Mo_6 and Ni_9W_6 do not because of their positive D values. Although the calculated D values have some differences from the experimental values, they give the correct sign of D. So, they can be used to qualitatively investigate the origin of magnetic anisotropy in our selected systems. The calculated E values of all complexes are all very small, showing that the quantum-mechanical magnetization tunneling in our studied systems can be omitted.

As is known, the main component of 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 1), while dipolar and anisotropic interactions yield only minor contributions, especially for cyanide-bridged complexes, in which the metal−metal distances are long.[14]

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

where i is the number of N metal centers and the d_i values are projection coefficients. Equation 1 is derived in the strong-exchange limit for a spin cluster. Because zero-field splittings are tensor quantities, the projection of the single-site zero-field splittings onto the spin ground state may vanish when the metal-ion arrangement approaches a cubic symmetry. The cluster core in each of Co_9Mo_6 and Co_9W_6 is almost in an idealized O_h symmetry, and so their D values should be close to zero. From thorough observation of the structures of Co_9Mo_6 and Co_9W_6, however, the distributions of the three CH_3OH ligands connected to each Co^{II} are not completely symmetrical, which will change the directions of the Jahn−Teller axes on Co^{II}. Therefore, three unsymmetrical CH_3OH ligands surrounding Co^{II} in Co_9Mo_6 and Co_9W_6 may be responsible for their negative D values. To verify our conclusion, we distributed three CH_3OH ligands symmetrically around Co^{II} through adjustment of the positions of the CH_3OH ligands (the adjusted structure data of the Co_9Mo_6

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Table 1. Calculated and Experimental Ground-State Spins S, Exchange Coupling Constant J (J_{ap} and J_{eq}, cm^{-1}), Zero-Field-Splitting Parameter D (cm^{-1}), Transverse Anisotropy Parameter E (cm^{-1}), and Magnetic Anisotropy Barrier $|D|S^2$ [$|D|(S^2 - {}^1/_4)$ for Half-Integer Systems] (cm^{-1})

	S		J_{ap}	J_{eq}	D			E	$\|D\|S^2$ ($S = {}^{21}/_2$)	
					calcd					
	calcd	expt	calcd	calcd	$S = {}^{21}/_2$	$S = {}^{33}/_2$	expt	calcd	calcd	expt
Co_9Mo_6[3]	${}^{21}/_2$	${}^{21}/_2$	−20.3	9.6	−0.32, 0.05[a]	−0.11, 0.03[a]	negative	0.02, 0.01[a]	35.2	
Co_9W_6[3]	${}^{21}/_2$	${}^{21}/_2$	−24.1	11.2	−0.36, 0.08[a]	−0.13, 0.05[a]	negative	0.01, 0.02[a]	40.0	19.3
Ni_9Mo_6[4]	12	12	10.1	11.5	0.014, 0.008[a]		positive	0.002	12	0.0
Ni_9W_6[4]	12	12	9.4	13.5	0.019, 0.010[a]		positive	0.000	12	0.0

[a] The value for the corresponding adjusted structure.

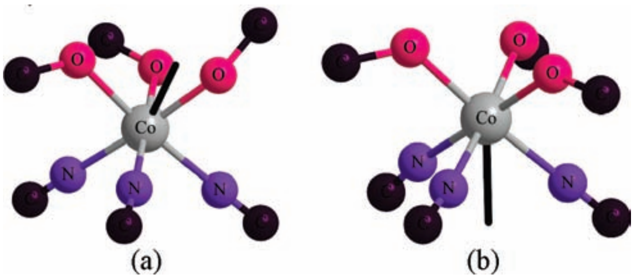

Figure 2. (a) Scheme of the original unsymmetrical piece of $[(CH_3OH)_3Co(CN)_3]$ ($D = -4.00$ cm^{-1}) and the corresponding local easy axis (black sticks). (b) Adjusted symmetrical piece of $[(CH_3OH)_3Co(CN)_3]$ ($D = -2.64$ cm^{-1}) and the corresponding local easy axis (black sticks). H atoms were omitted for clarity.

and Co_9W_6 can be found in the Supporting Information). The adjusted piece is shown in Figure 2b, where three CH_3OH ligands symmetrically distribute around Co^{II}. Three O−Co−O or O−Co−N angles for each of the two pieces are almost the same (their average O−Co−O and O−Co−N angles are 87.90° and 174.96°, respectively), but three C−O−Co−N angles are different for the original piece (Figure 2a; the average C−O−Co−N angle for the original piece is 104.30° but is 162.00° for the adjusted one).

As expected, the calculated D values of the adjusted Co_9Mo_6 and Co_9W_6 are positive and close to zero (see Table 1), which shows that three unsymmetrical CH_3OH ligands surrounding Co^{II} are the main reason that Co_9Mo_6 and Co_9W_6 exhibit SMM behavior. However, three CH_3OH ligands surrounding each Ni^{II} in Ni_9Mo_6 and Ni_9W_6 almost symmetrically distribute around Ni^{II}, which results in their D values being close zero. If we distribute three CH_3OH ligands symmetrically around Ni^{II}, the obtained D values of Ni_9Mo_6 and Ni_9W_6 are also close to zero (see Table 1). Hong and coworkers used $[(bpy)(H_2O)]$ (bpy = 2,2′-bipyridine) to replace $[CH_3OH]_3$ around Ni^{II} and then obtained complexes $[Ni\{Ni(bpy)(H_2O)\}_8\{W(CN)_8\}_6]$[15] and $[Ni\{Ni(bpy)(H_2O)\}_8\{Mo(CN)_8\}_6]$,[16] which both behave as SMMs. Moreover, Dunbar and co-workers substituted CH_3OH using tmphen (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) to synthesize $[Ni\{Ni(tm\text{-}phen)(CH_3OH)\}_6\{Ni(H_2O)_3\}_2(\mu\text{-}CN)_{30}\{W(CN)_3\}_6]$,[17] which also behaves as a SMM. Their experimental results confirm that the unsymmetrical distributions of the terminal ligands around Ni^{II} are the origin of their negative D values.

To further confirm our conclusion, we calculated the D values of the unsymmetrical (the original one) and symmetrical (the adjusted one) pieces of $[(CH_3OH)_3Co(CN)_3]$, respectively, and show their easy axes in Figure 2. From Figure 2, the directions of the easy axes on the symmetrical and unsymmetrical pieces of $[(CH_3OH)_3Co(CN)_3]$ are not the same (their D values are both negative and possess easy axes). Oshio and Nakano[18] show that collinear local easy-axis and orthogonal local hard-axis alignments give negative D values, whereas D will be close to zero when local easy-axis alignments are orthogonal or local hard-axis alignments are collinear. The easy axes on the symmetrical pieces of $[(CH_3OH)_3Co(CN)_3]$ in the adjusted complexes Co_9Mo_6 or Co_9W_6 are almost orthogonal, which results in the D value being close to zero, whereas the negative D value of Co_9Mo_6 or Co_9W_6 comes from the unorthogonal easy axes on the unsymmetrical pieces of $[(CH_3OH)_3Co(CN)_3]$ in them.

DFT calculations on four M'_9M_6 systems to explore the origin of magnetic anisotropy in cyanide-bridged Co_9M_6 (M = Mo^V or W^V) systems show that the substitution of metal ions is not the main reason that $Co^{II}_9M_6$ (M = Mo^V or W^V) exhibits SMM behavior, whereas the unsymmetrical distribution of three CH_3OH ligands surrounding each Co^{II} is the main one. Therefore, distributing the terminal ligands unsymmetrically around magnetic ions such as Co^{II}, Ni^{II}, Mn^{II}, etc., is a good way to obtain a negative D value for M'_9M_6 systems.

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Supporting Information Available: Computational details and coordinates of the adjusted structures of Co_9Mo_6 and Co_9W_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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