

Symmetry and Topology Determine the Mo^V–CN–Mn^{II} Exchange Interactions in High-Spin Molecules

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The two conditions that the ground state of a compound must meet in order to behave as a single-molecule magnet^[1] are a high spin and a significant anisotropy (i.e. a large uniaxial zero-field-splitting parameter). It is not surprising, therefore, that an increasing number of polynuclear transition-metal compounds are currently being reported in which the individual spins of the metal atoms are coupled through exchange interactions in such a way so as to produce a high total molecular spin. In this context, the highest spin proposed to date corresponds to [Mn{Mn(MeOH)₃}(μ-NC)₃₀–{Mo(CN)₃}₆]·5 MeOH·2 H₂O,^[2] a compound that comprises Mo^V and Mn^{II} centers, abbreviated from here on as Mn₉Mo₆ (see Figure 1). In such a compound, a total spin of 51/2 would result from ferromagnetic interactions between the Mo and Mn ions through cyanide bridging ligands. However, for the analogous Mn₉W₆ compound,^[3] a total spin of 39/2 has been postulated and is consistent with antiferromagnetic coupling between neighboring W and Mn atoms (i.e. an overall ferrimagnetic arrangement). In other compounds of varying

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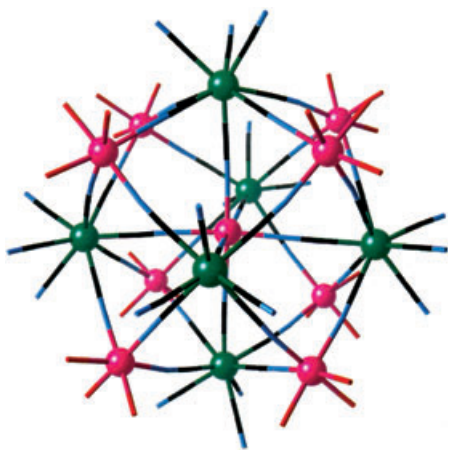


Figure 1. Molecular structure of the Mn_9Mo_6 complex (Mn magenta, Mo green; light blue, black, and red cylinders represent bonds to N, C, and O atoms, respectively). The carbon atoms of the methanol groups are omitted for clarity.

dimensionality based on Group 6 octacyanomethylate(v) anions,^[4–7] whose magnetic behavior is determined by the same type of $\text{M}^{\text{V}}\cdots\text{Mn}^{\text{II}}$ ($\text{M} = \text{Mo}, \text{W}$) exchange interactions, antiferromagnetism rather than ferromagnetism is observed in all cases (see Supporting Information for more details). All these compounds have in common the b_2^1 electron configuration for M in the $[\text{M}(\text{CN})_8]^{3-}$ anion and $t_{2g}^3 e_g^2$ for Mn^{II} , so it is not easy to explain why the cyanide-mediated exchange coupling is antiferromagnetic in all cases except Mn_9Mo_6 , for which ferromagnetic coupling was assigned according to the available experimental data.

From a qualitative theoretical point of view,^[8] the metal d orbitals that carry the unpaired electrons at each metal atom can interact through the π orbitals of the bridging cyanide groups to lead to an orbital gap, which should result in a significant antiferromagnetic contribution that tends to pair up the spins of the two types of metal ions. Although the proposed ferromagnetic behavior has been justified by using kinetic-exchange theory,^[9] a qualitative molecular-orbital analysis supports the existence of only antiferromagnetic interactions.^[7] Even if Mn_9Mo_6 is no longer the only known compound with a spin of 51/2 (a Mn_{25} complex with the same total spin has been reported recently^[10]), clarification of the nature of the $\text{M}^{\text{V}}\cdots\text{Mn}^{\text{II}}$ exchange interaction is of importance, given the robustness and versatility of $[\text{M}(\text{CN})_8]^{3-}$ anions^[11] as building blocks for complex systems with high spin as well as the doubts that the attribution of an $S = 51/2$ spin state to the Mn_9Mo_6 complex have generated.^[10] We therefore undertook a theoretical computational study based on density functional theory (DFT, B3LYP method; see Supporting Information for details) for dinuclear models as well as for the whole Mn_9Mo_6 complex to estimate the exchange-coupling constants in the cyano-bridged $\text{Mo}^{\text{V}}\text{--Mn}^{\text{II}}$ compounds in an attempt to shed some light on their controversial magnetic behavior. Additionally, a polarized neutron diffraction experiment was performed on a single crystal of $[\text{Mn}\{\text{Mn}(\text{MeOH})_3\}_8(\mu\text{-NC})_{30}[\text{Mo}(\text{CN})_3]_6\cdot 5\text{MeOH}\cdot 2\text{H}_2\text{O}$ to offer unambiguous experimental evidence of the exact nature of the magnetic ground state of the Mn_9Mo_6 cluster.

The structure of Mn_9Mo_6 can be described as a centered cube of Mn^{II} cations, with the Mo^{V} ions capping its six faces (Figure 1) to thus form its dual octahedron. Such a geometrical compound, comprised of a cube and an octahedron as observed for the Mn_9Mo_6 core, appears as a member of the constellation of polyhedra in M. C. Escher's wood engraving "Stars" and can be seen at the upper left corner of Figure 2.

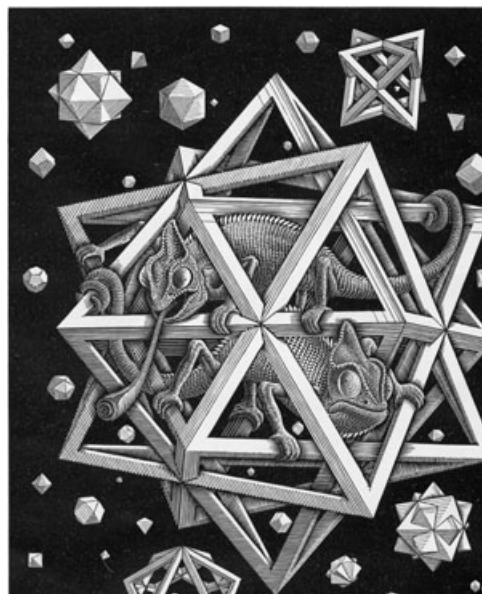


Figure 2. M. C. Escher's wood engraving "Stars" (1948), which shows the compound of a cube and an octahedron in the upper left corner. (Copyright 2005, The M. C. Escher Company, Holland. All rights reserved. www.mcescher.com).

The central Mn is radially bridged to the six Mo atoms by cyanide ligands, and the peripheral Mn atoms are bridged by tangential cyanides to three neighboring Mo atoms that form a triangular face of the Mo_6 octahedron. Furthermore, each Mo atom has three terminal cyano ligands that lead to octacoordinate Mo atoms, best described as triangular dodecahedra, as ascertained from continuous shape measures (CSHMs)^[12] of the three independent $[\text{Mo}(\text{CN})_8]^{3-}$ anions in the asymmetric unit of Mn_9Mo_6 (see Supporting Information). The central Mn atom is clearly octahedral, and the coordination spheres of peripheral Mn atoms, completed by methanol molecules, are also identified as octahedra from their CSHMs. Remarkably, the Mn_9 and Mo_6 cores are very well described (see Supporting Information) as a centered cube and an octahedron, respectively, despite the low molecular symmetry (C_2) and even if the approximate D_{2d} symmetry of the MoC_8 dodecahedra and the octahedral pseudosymmetry of the metal cores are not in accord.

From the above description of the molecular structure, the following observations can be made with regards to the exchange-interaction pathways. Of the thirty cyano-bridged $\text{Mo}\cdots\text{Mn}$ interactions, six are associated with radial moieties and twenty-four with tangential $\text{Mo}\text{--}\text{CN}\text{--}\text{Mn}$ moieties. The molecular symmetry (C_2 point group) reduces them to three radial and twelve tangential nonequivalent $\text{Mo}\cdots\text{Mn}$ interactions, whereas the approximate octahedral symmetry of the

Mn₉Mo₆ core leaves only two types of exchange pathways, radial and tangential.

In an independent dodecahedral [Mo(CN)₈]^{3−} anion, the unpaired electron resides in a d_{xy} orbital (Figure 3), as imposed by the local D_{2d} symmetry because all the ligands

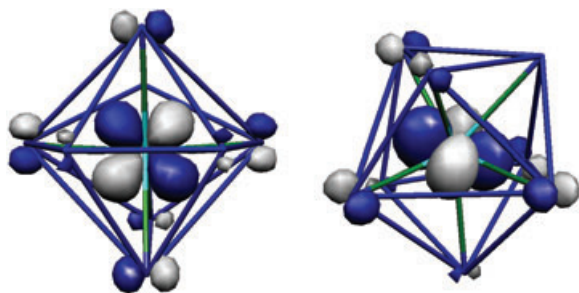


Figure 3. Representation of two different orientations of the molecular orbital that bears the unpaired electron for the mononuclear model [Mo(CN)₈]^{3−}, which corresponds to atom Mo3 in the Mn₉Mo₆ complex. Left: down the C₂ axis of the approximate D_{2d} symmetry; right: with the same orientation that the uppermost Mo atom has in Figure 1.

lie in its nodal planes, whereas the remaining d orbitals are all metal–ligand σ antibonding. From Figure 3 it is clear that the d_{xy} orbital is able to interact with the π-type orbitals of the cyano bridges of all eight ligands. However, in a dodecahedron there are four *equatorial* ligands that form angles of about 19° with the mean equatorial plane (perpendicular to the unique C₂ symmetry axis) and four *apical* ligands at approximately 39°. The former equatorial ligands are much better oriented to π-interact with the Mo d_{xy} orbital, and we should expect the exchange interaction to be more strongly antiferromagnetic when mediated by equatorial than by apical cyanide ligands. A careful analysis of the molecular structure tells us that each Mo^V ion is connected to the central Mn^{II} ion through an apical cyanide, to three peripheral Mn atoms through equatorial cyanides, and to a fourth Mn atom by means of an apical cyanide.

We calculated the exchange-coupling constants (*J*) of several representative dinuclear models extracted from the Mn₉Mo₆ molecule that present different types of exchange interactions from the point of view of the molecular (i.e. radial or tangential) and local (i.e. equatorial or apical) symmetries (Table 1). The calculated *J* values are all negative which suggests that all Mo⋯Mn exchange interactions in Mn₉Mo₆ are antiferromagnetic and that the whole molecule should be ferrimagnetically arranged with a net spin of 39/2. Furthermore, we see that all interactions through equatorial bridges are roughly twice as strong (*J* ≈ −20 cm^{−1} in d–g) as those through apical cyanides (*J* ≈ −12 cm^{−1} in a–c), as expected from overlap arguments. In contrast, neither the radial or tangential character of the interaction, nor the variations in the Mo–C–N and C–N–Mn bond angles (160–180° and 156–178°, respectively) seem to have a significant influence on the calculated values of *J*.

To verify our above conclusions, we performed calculations on dinuclear models of the chain compound Mn₃Mo₂,^[5] which has three different Mo⋯Mn interactions per Mo atom. The three nonequivalent interactions present in this com-

Table 1: Calculated exchange-coupling constants ($H = -J\mathbf{S}_1\mathbf{S}_2$) for dinuclear models of the Mn₉Mo₆ compound (a–g) and the interactions in a Mn₃Mo₂ chain compound (x–z).^[a]

Interaction	Metal atoms	Type	Bridge	<i>J</i> [cm ^{−1}]
a	Mo1–Mn1	rad	ap	−12.4
b	Mo3–Mn1	rad	ap	−11.4
c	Mo1–Mn4	tang	ap	−12.2
d	Mo1–Mn5	tang	eq	−18.2
e	Mo1–Mn3	tang	eq	−21.6
f	Mo1–Mn2	tang	eq	−18.9
g	Mo2–Mn4	tang	eq	−22.8
x	Mo1–Mn2	–	ap	−9.9
y	Mo1–Mn1	–	ap	−10.7
z	Mo1–Mn1′	–	ap	−7.9

[a] [Mo(CN)₇(μ-CN)Mn(NC)₃]^{6−} is representative of the radial (rad) Mo–Mn pairs, and [Mo(CN)₇(μ-CN)Mn(NC)₂(MeOH)₃]^{3−} is representative of the tangential (tang) pairs. The apical (ap) or equatorial (eq) nature of the bridging cyanide relative to the dodecahedral coordination sphere of the Mo atom is also indicated.

pound correspond to apical bridging cyanides, and the calculated *J* values for the corresponding dinuclear models (x–z, Table 1) are predicted to be about −11 cm^{−1}, which consistently describe antiferromagnetic Mo^V⋯Mn^{II} interactions of the order of magnitude found for all apically bridged Mo–Mn pairs. In yet another compound, Mn₃W₂ with bipyridine,^[4] the two different Mn–CN–W interactions correspond to apical positions of the W dodecahedra and the experimentally derived value of *J* is −12.0 cm^{−1}, which remarkably coincides with our calculated values for Mn–CN–Mo apical interactions.

The final theoretical evidence for antiferromagnetic exchange in Mn₉Mo₆ comes from calculations on the whole complex (2790 basis functions required) in three different spin configurations, with *S* = 51/2 (all spins up), *S* = 41/2 (the central Mn with spin down), and *S* = 39/2 (all Mo atoms with spins down). The *S* = 39/2 function appears to be lowest in energy which thus confirms the qualitative conclusion of our calculations on dinuclear models that antiferromagnetic Mo⋯Mn interactions are favored. If all interactions through apical cyanides are assumed to be approximately equal and likewise for all interactions through equatorial cyanides, we can obtain from the calculated energies average values for the corresponding coupling constants, *J*_{ap} = −9.0 cm^{−1} and *J*_{eq} = −23.8 cm^{−1}, in excellent agreement with the results for dinuclear models.

The antiferromagnetic nature of Mn–Mo interactions in Mn₉Mo₆ is confirmed by the experimental results obtained from polarized neutron diffraction (PND) studies (see Supporting Information). Note that the single crystals of the cluster are extremely unstable in the absence of mother liquor and their exposure in air or argon atmospheres for a few minutes leads to a structural transformation. For this reason, a determination of the spin of the ground state for this compound is not easily obtained from the magnetic measurements. PND experiments performed on a single crystal of the Mn₉Mo₆ cluster within the mother liquor gives access to the experimental magnetic structure factors that are the Fourier components of the magnetization density. Owing to the small

size of the crystal, a limited set of reflections was obtained. However, comparison of the experimental data and the three different models ($S = 51/2$, $S = 41/2$, and $S = 39/2$) unambiguously supports (Table 2) the ferrimagnetic model ($S = 39/2$).

Table 2: Experimental and calculated magnetic structure factors of the Mn_9Mo_6 compound for $S = 51/2$ (ferromagnetic), $S = 41/2$, and $S = 39/2$ (ferrimagnetic) models.

h, k, l	Magnetic structure factor, $F_M(h, k, l)$ [μ_B]			
	neutrons	$S = 51/2$	$S = 41/2$	$S = 39/2$
−2 2 1	15(8)	−1.4	8.9	18.2
2 0 2	−24(1)	−5.4	−7.2	−22.2
4 0 2	20(3)	38.7	−19.3	8.3
−2 0 4	27(2)	4.6	7.5	23.5
−12 0 6	67(8)	53.7	−21.5	47.6
0 6 8	−33(3)	−27.7	12.1	−26.6
1 5 9	36(8)	25.9	−13.6	25.6
Reliability factors ^[a]				
$R(F_M)$ ^[b]		0.47	1.19	0.26
$R_w(F_M)$ ^[c]		0.84	0.89	0.22
GOF ^[d]		11.1	12.0	3.0

[a] The agreement factors, R and weighted R_w (with $w = 1/\sigma^2$), and the goodness of fit (GOF) are indicated. [b] $R(F_M) = (\sum_{hkl} ||F_M^o| - |F_M^c||) / (\sum_{hkl} |F_M^o|)$. [c] $R_w(F_M) = [(\sum_{hkl} w(|F_M^o| - |F_M^c|)^2) / (\sum_{hkl} w|F_M^o|^2)]^{1/2}$. [d] $\text{GOF} = [(\sum_{hkl} w(|F_M^o| - |F_M^c|)^2) / (N_o - N_v)]^{1/2}$. N_o = number of reflections, N_v = number of parameters, w = weighting scheme.

In Table 2 are reported the results of the least-squares refinements performed on the basis of the experimental magnetic structure factor (F_M) values for the three different models. The absolute magnitudes of the manganese magnetic moments were fixed to $5\mu_B$ with sign arrangements that correspond to the three different models and the scale factor was refined. The best reliability factors were obtained for the $S = 39/2$ ferrimagnetic model ($R_w(F_M) = 22\%$), while the two other models led to weighted agreement factors greater than 80%.

The calculated spin density for the single determinant ferrimagnetic state with $S = 39/2$ of Mn_9Mo_6 (Figure 4) offers us a wealth of information on the electronic structure and the mechanism of the exchange interaction. Characteristic features of this map can be interpreted as resulting from the interplay between spin delocalization and spin polarization,^[13] notably the numerical values of atomic spin densities. Additionally, the following observations can be made about the three-dimensional shape of the spin density: 1) At each Mo atom, the spin density has the shape of the d_{xy} orbital, with the same orientation relative to the $\text{Mo}(\text{CN})_8$ dodecahedron as with the independent monomer (Figure 3); 2) Although the spin densities at the C and N atoms of the bridging cyanides are opposite to those of the neighboring metal atom, which suggests a predominance of spin polarization over spin delocalization, this effect could also be attributed to a delocalization of the metal unpaired electrons through the π system of the cyanide mostly to the N atoms.^[13] This effect is also seen in the significant spin population at the N atom but not at the C atom of the terminal cyanides; 3) The spin density on the cyanide ligands shows the form of p orbitals centered

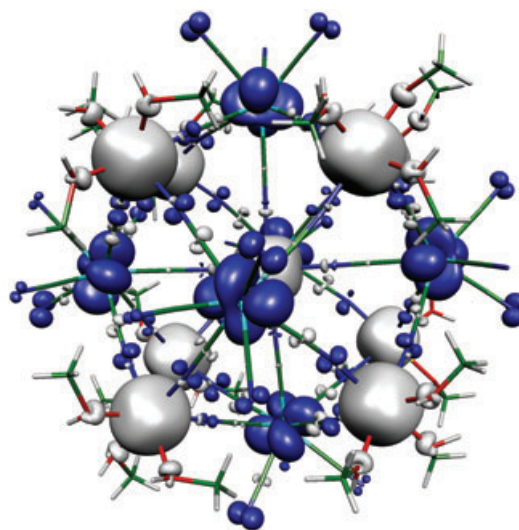


Figure 4. Representation of the spin density that corresponds to the $S = 39/2$ ground state of the Mn_9Mo_6 complex (clear and dark regions indicate positive and negative spin populations, respectively).

at the C and N atoms. Note that this p-orbital shape indicates that it is mostly the Mo^V cation that transfers spin density to the bridge, as its perpendicular π system, which interacts equally with Mn^{II} but not with Mo^V , shows no significant unpaired-spin population; 4) The shape of the spin density at the Mn atoms is nearly spherical, as expected for a set of five d orbitals with one unpaired electron each, even if slightly distorted toward cubes with the Mn–N bonds at the face centers. We recall that the t_{2g}^3 manifold is cubic whereas the e_g^2 manifold is octahedral,^[14] and the combination of a cube and an octahedron should give a spherical spin density for a $t_{2g}^3 e_g^2$ configuration. Slight deviation from sphericity at the Mn atoms results from the lesser spin density at the e_g orbitals relative to the t_{2g} orbitals owing to a significant delocalization of the former through σ bonding; 5) The σ delocalization of the $\text{Mn}^{II} e_g$ electrons can be clearly seen at the O atoms of the terminal MeOH ligands by the approximate shape of an sp^3 hybrid orbital. Also the N atoms of the cyanide bridges present a small amount of positive σ -type spin density in the region of the Mn–N bonds which is consistent with the shape of an sp hybrid. The coexistence of positive σ and negative π spin density at the same metal atom is a remarkable feature of the complex electronic structure of Mn_9Mo_6 .

Both the exchange-coupling constants and the spin-density map calculated for Mn_9Mo_6 show a fascinating interplay between the local symmetries of the building blocks and the topological symmetry of the molecular assembly. Hence, antiferromagnetic interactions between Mo^V and Mn^{II} are imposed by the d orbital pattern of the dodecahedral coordination sphere of the former rather than by the molecular symmetry, with apical and equatorial cyanides mediating exchange interactions of varying strengths that differ by a factor of approximately two. On the other hand, while the spin populations at the metal atoms conform to their approximate local symmetry, D_{2d} for Mo and O_h for Mn, they are repeated throughout the molecule with a topology that results from applying the symmetry operations

of the approximately O_h -symmetric Mn_9Mo_6 core. On their side, the spin populations of bridging cyanides show the signature of their local $C_{\infty v}$ symmetry, disseminated throughout the molecule with the approximate O_h symmetry of the metallic framework. In summary, what is initially perceived from the molecular structure as one of the stars in the Escher galaxy, with the shape of a cube–octahedron compound, is revealed by an analysis of its magnetic structure to be a planetary system that orbits around the central Mn atom in which each Mo and Mn planet is surrounded by satellite ligands with dodecahedral and octahedral shapes, respectively.

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