Combined Ligand Field and Density Functional Theory Analysis of the Magnetic Anisotropy in Oligonuclear Complexes Based on Fe$^{III}$–CN–M$^{II}$ Exchange-Coupled Pairs

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Magnetic anisotropy in cyanide-bridged single-molecule magnets (SMMs) with Fe$^{III}$–CN–M$^{II}$ (M = Cu, Ni) exchange-coupled pairs was analyzed using a density functional theory (DFT)-based ligand field model. A pronounced magnetic anisotropy due to exchange was found for linear Fe$^{III}$–CN–M$^{II}$ units with fourfold symmetry. This results from spin–orbit coupling of the [Fe$^{III}$(CN)$_6$]$^{3-}$ unit and was found to be enhanced by a tetragonal field, leading to a $^2E_g$ ground state for Fe$^{III}$. In contrast, a trigonal field (e.g., due to $\tau_2$ Jahn–Teller angular distortions) led to a reduction of the magnetic anisotropy. A large enhancement of the anisotropy was found for the Fe$^{III}$–CN–Ni$^{II}$ exchange pair if anisotropic exchange combined with a negative zero-field splitting energy of the $S$ ground state of Ni$^{II}$ in tetragonally compressed octahedra, while cancellation of the two anisotropic contributions was predicted for tetragonal elongations. A recently developed DFT approach to Jahn–Teller activity in low-spin hexacyanometalates was used to address the influence of dynamic Jahn–Teller coupling on the magnetic anisotropy. Spin Hamiltonian parameters derived for linear Fe–M subunits were combined using a vector-coupling scheme to yield the spin Hamiltonian for the entire spin cluster. The magnetic properties of published oligonuclear transition-metal complexes with ferromagnetic ground states are discussed qualitatively, and predictive concepts for a systematic search of cyanide-based SMM materials are presented.

1. Introduction

The search for single-molecule magnets (SMMs), which are spin clusters with low-temperature blocking of the magnetization, has led to the synthesis and characterization of a large number of oligonuclear, cyanide-bridged com-

[References and footnotes are omitted for brevity.]

Published in "Inorganic Chemistry 47(7): 2449–2463, 2008" which should be cited to refer to this work.
In this work, we studied the magnetic anisotropy in magnetic clusters of singly bridged FeIII-CN-MII (M = Cu, Ni) pairs having a low-spin ground state for the [Fe(CN)6]3− site. Previous density functional theory (DFT) calculations showed that a strictly linear FeIII-CN-CuII bridge with an octahedral [Fe(CN)6]3− site induces strong anisotropy in the S = 1 ground state of the Cu-Fe pair.22 This anisotropy emerges from unquenched orbital momenta in the 2T2g ground state of FeIII and their mixing with the spin via first-order spin–orbit coupling. Therefore, the total spin of the cluster is an ill-defined quantity, and the isotropic exchange −JS†·S breaks down. Jahn–Teller coupling within the 2T2g ground state of [Fe(CN)6]3− is significant and governed by the activity of the τ2g vibrational modes, which distort the octahedral geometry toward a trigonally compressed D3d structure.23,24 This distortion is large enough to induce anisotropy in the magnetic susceptibility and the g tensor, which leads to a consistent description of the experimental magnetic and spectroscopic data of [Fe(CN)6]3− and [Mn(CN)6]3−.24 We have now extended these studies to FeIII-CN-CuII and FeIII-CN-NIi exchange-coupled pairs and larger spin clusters built from these pairs.

Theoretical models for anisotropic exchange coupling have been an area of focus since the early days of magnetocchemistry. The seminal work by Dirac25 considered exchange contributions from different orbital pairs. Their importance for magnetic anisotropy was recognized by Van Vleck and Huang,26–28 and the theory was further developed by

Levy,29,30 Lines,31 Kahn,32 and Drillon and Georges,33 group-theoretical arguments for anisotropic exchange coupling were pioneered by Tsukerblat and co-workers.34–39 Applications to various systems, such as Ti3Cl93−40–48 oxo-bridged triangular FeIII-CuII-CO3 40 cyano-bridged CrIIIFeII49 carboxylyato-bridged dinuclear CO350,51 trigonal bipyramidal cyano-bridged MnII-MnIII52–57 dinuclear Yb35−58 YbBr35−,58 and YbCrBr35−,59,60 a CuII–FeIII pair with a low-spin porphyrin FeIII center,61–64 and spin–spin coupling in

molecular magnets based on the [Mo(CN)₆]³⁻ complex have been reported. Orbital degeneracy and strong spin–orbit coupling of MoIII in the last of these led to an extremely anisotropic ground-state Kramers doublet of the Ising type. Ideas concerning ways to control the magnetic anisotropy in oligonuclear complexes, based on simple angular overlap model and extended Hückel calculations, have been published. Anisotropic exchange has usually been described using perturbation theory with a modified version of the kinetic exchange model, which involves metal-to-metal electron transfer processes mediated by the bridging ligands. However, ferromagnetic coupling described by potential terms has usually been ignored by the kinetic model. Ab initio studies of magnetic anisotropy have been confined to single paramagnetic centers or organic radicals and, due to size constraints, only scarcely applied to oligonuclear transition-metal complexes. Current DFT methods and perturbation theory for the computation of zero-field splitting in oligonuclear paramagnetic molecules have restricted applicability in the case of orbital degeneracy or near-degeneracy, such as that encountered in the FeIII–CuII and FeIII–NiII exchange pairs discussed here.

We have developed a DFT-based ligand field theory (LFDFT) that allows one to deduce in a parametric form all of the terms (i.e., the ligand field matrix, Coulomb repulsion, and spin–orbit coupling terms) in the model Hamiltonian. LFDFT has been used to calculate optical spectra, EPR g and hyperfine-coupling parameters, both static and dynamic Jahn–Teller coupling of mononuclear complexes, and isotropic magnetic exchange coupling in dinuclear transition-metal complexes. We now describe an extension of this model to the anisotropic g and D tensors in dinuclear transition-metal complexes and show how coupling of the local g and single- (D) and two-center (D₂) anisotropy tensors in oligonuclear cyanometalates can be used to discuss their anisotropic magnetic properties from first principles. The effect of spin–orbit coupling and static as well as dynamic Jahn–Teller coupling on the magnetic anisotropy of FeIII–CuII and FeIII–NiII exchange-coupled pairs is studied in detail. The new approach described in this work was used to qualitatively analyze published magnetic properties of spin clusters based on FeIII–CuII and FeIII–NiII exchange-coupled pairs with ferromagnetic ground states. On the basis of these results, predictive concepts for a systematic search of cyanide-based SMM materials are presented.

2. Theory

Here, we consider FeIII–CN–MII exchange pairs having the geometry shown in Figure 1. The octahedral low-spin [Fe(CN)₆]³⁻ site has a triply degenerate ground state (T₂g) in Griffith’s notation, with t₂g-axial orbitals, g, η, and ζ. When combined with the spins (α and β), this gives rise to six degenerate microstates, which are split by spin–orbit and Jahn–Teller coupling. In square planar complexes and tetragonally elongated or compressed octahedral complexes, there is a weak exchange coupling of these microstates, involving the 2B₁g(dₓ²−₃z²) or A₁g(dₓ²) ground state of CuII in an FeIII–CuII pair or the A₃g(dₓ²−₃z², d₃z²) ground state of NiII in an FeIII–NiII pair. We consider the ground states of CuII and NiII to be well-defined and include all of the orbital effects on their spin ground states in the effective g-tensor values, with positive deviations from the spin-only values (g₀ = 2), and in the zero-field splitting tensor D₂ for NiII.

Figure 1. Model dinuclear complex of C₆ symmetry used for the calculation of the anisotropic exchange coupling. Atom labels used in the notation for the selected bond distances given in Table 2 are shown.
In eq 1 are then transformed using the eigenvectors of the orbital degrees of freedom due to the degeneracy of the 2T2g spin angular momentum operator for M II. and ligand field operators, respectively, for [Fe(CN)6]3-

The exchange coupling term  \( J \) of Two Exchange-Coupled Ions in Oh and Its Subgroups, Consistent with a Linear Fe-CN-M Bridge with Fourfold Symmetry

\[ H_{\text{exc}} = \sum_{\mu \neq \nu, \xi \neq \eta} J_{\mu \nu} \mathbf{s}_1 \mu \cdot \mathbf{s}_2 \nu \]  

where  \( J_{\mu \nu} (\mu = \xi, \eta, \zeta) \) are the orbital exchange coupling constants between the spins  \( s_{\mu} \) of the singly occupied magnetic orbitals  \( d_\xi \) (\( \xi \)),  \( d_\eta \) (\( \eta \)), and  \( d_\zeta \) (\( \zeta \)) of FeIII and the unpaired spins  \( (\xi, \eta, \zeta) \) of MII. In eq 2, we assume a  \( C_{av} \) pseudosymmetry for each FeIII-MII pair with the local z axis along the FeIII-CN-MII bridge (see Figure 1). This defines two exchange coupling parameters,  \( J_{\xi \zeta} = J_{\eta \zeta} \equiv J(E) \) and  \( J_{\zeta \zeta} \equiv J(B_{2g}) \), for each FeIII-MII pair, when the off-diagonal terms  \( J_{\mu \nu} (\mu \neq \nu) \) are neglected. The well-aligned magnetic orbitals  \( (\xi, \eta, \zeta) \) and the matrices that represent all of the operators in eq 1 are then transformed using the eigenvectors of the ligand field operator  \( H_{\text{LF}} \) on each center, in order to ensure invariance of the results with respect to the orbital rotations.

The matrix that represents  \( H_{\text{LF}} \) is given in a general form without any assumptions. It describes angular and radial distortions of each [Fe(CN)6^3-] unit of the oligonuclear cluster, which may arise from Jahn–Teller distortions, low-symmetry crystal packing effects, or asymmetry of the ligands. For the sake of the qualitative analysis presented here, we start with octahedral \((O_6)\) [Fe(CN)6]^3- and restrict the treatment to a particular form of \( H_{\text{LF, J-T}} \) for the Jahn–Teller effect that operates within the 2T2g ground state of [Fe(CN)6]^3-. It has been shown that for the five Jahn–Teller-active  \( e_g \) and  \( t_2g \) vibrations, coupling of the 2T2g ground state of [Fe(CN)6]^3- to the trigonal modes  \( t_2g \) is dominant. This leads to the stabilization of a  \( D_{4h} \)-distorted 2\( \text{A}1g \) ground state derived from a trigonally compressed octahedron. Within the \((\xi, \eta, \zeta)\) orbital basis, the  \( H_{\text{IF}} \) term in eq 1 is described by the matrix  \( H_{\text{IF}} \) given in eq 3:

\[ H_{\text{IF}} = \begin{bmatrix} K_1(Q_x^2 + Q_y^2 + Q_z^2) & -V_xQ_z & -V_yQ_y \\ -V_xQ_z & \frac{1}{2}K_1(Q_x^2 + Q_y^2 + Q_z^2) & -V_yQ_y \\ -V_yQ_y & -V_yQ_y & \frac{1}{2}K_1(Q_x^2 + Q_y^2 + Q_z^2) \end{bmatrix} \]

where  \( Q_x, Q_y, Q_z \) are the components of the  \( t_2g \) octahedral mode;  \( V_x \) is the linear vibronic coupling constant; and  \( K_1 \) is the harmonic force constant. Terms which depend on  \( V \) describe the forces which distort the regular octahedral geometry, while the elastic force reflected by the harmonic term (i.e., the diagonal matrix elements of eq 3) tends to preserve it. An energy level diagram as a function of geometric distortion along the  \( D_{4h} \) distortion pathway is presented in Figure 2. The ratio between the Jahn–Teller stabilization energy  \( E_{\text{JT}} \) and the energy of the  \( t_2g \) vibration is of importance for the treatment described below. Calculation of energy levels using eq 1 requires knowledge of all of the parameters of the model. An LF-DFT-based procedure has been used to calculate the spin–orbit coupling constant, of the  \( g \) tensors of Cu and Ni, the orbital reduction factor of Fe,87 the orbital constants. The manifold of ground-state spin levels and excited states computed on the basis of eq 1 makes possible the interpretation of magnetic, EPR, and optical spectroscopic data.
Figure 2. Cross section of the ground-state potential energy surface of \([\text{Fe(CN)}_6]^{\text{3-}}\) along the trigonal \((1,1,1)\) and \((-1,-1,-1)\) directions in the subspace of the \(t_{2g}\) modes, which stabilize the \(^3A_{1g}\) ground state (trigonal compression, absolute minimum) and \(^3E_g\) excited state (trigonal elongation, saddle point), respectively. The \(Q_t\) distortion (inset), the Jahn–Teller stabilization energy \(E_T\), and the zero-point vibrational energy \(\Delta \hbar \omega_{0/2}\) are shown. The following values of the vibronic coupling parameters were used: \(V_t = 1052\ \text{cm}^{-1}/\AA\), \(K_t = 6069\ \text{cm}^{-1}/\AA^2\) (eq 3) and \(\Delta \hbar \omega_{0/2} = 140\ \text{cm}^{-1}\); also taken into account, but for the sake of simplicity not included in eq 3, were the second-order vibronic coupling terms \(K_s = 449\ \text{cm}^{-1}/\AA^2\) and \(L_s = 1584\ \text{cm}^{-1}/\AA^2\).

\((s_1' = 1/2)\) with the real spin of \(\text{Cu}^{\text{II}}\) \((s_2 = 1/2)\) or \(\text{Ni}^{\text{II}}\) \((s_2' = 1)\). This is described by the spin Hamiltonian given in eq 4:

\[
\hat{H}_{\text{spin}} = -J_s \hat{s}_1' \cdot \hat{s}_2 + \sum_{ij} \left( D_{ij} D \hat{S}_i \cdot \hat{S}_j + \mu_B \hat{s}_i \cdot \hat{g}_i \cdot \mathbf{B} \right) + \mu_B \hat{S}_j \cdot \left( \mathbf{T}_g \mathbf{T}_j \right) \cdot \mathbf{B}
\]

where \(J\) is the isotropic coupling constant, \(D_{ij}\) and \(A_{ij}\) are the traceless tensors for symmetric and antisymmetric exchange, respectively, \(D_2\) is the zero-field splitting tensor for \(\text{Ni}^{\text{II}}\), and \(g_1\) and \(g_2\) are the effective \(g\) tensors for the \([\text{Fe(CN)}_6]^{\text{3-}}\) and \(\text{Cu}^{\text{II}}\) or \(\text{Ni}^{\text{II}}\) sites, respectively. The traceless symmetric exchange tensor \(D_{12}\) is

\[
D_{12} = \begin{bmatrix}
D_{xx} & D_{xy} & D_{xz} \\
D_{xy} & D_{yy} & D_{yz} \\
D_{xz} & D_{yz} & D_{zz}
\end{bmatrix}
\]

where \(D\) and \(E\) are the axial and orthorhombic splitting parameters, respectively. The traceless antisymmetric exchange tensor \(A_{12}\) is

\[
A_{12} = \begin{bmatrix}
0 & A_z & -A_y \\
-A_z & 0 & A_x \\
A_y & -A_x & 0
\end{bmatrix}
\]

There is a symmetry restriction for the number of independent nonzero components of \(D_{12}\) and \(A_{12}\): the spin operators \(\hat{s}_1'\) and \(\hat{s}_2\) transform according to the \(T_{1g}\) irreducible representation of the \(O_h\) point group, and the direct product \(T_{1g} \otimes T_{1g}\) spans the symmetric irreducible representations \(A_{1g}\) \((\hat{s}_1' \cdot \hat{s}_2)\), \(E_g\) \((D_{12}\) diagonal terms\), and \(T_{2g}\) \((D_{12}\) off-diagonal terms) as well as the antisymmetric \(T_{1g}\) \((A_{12}\) irreducible representation. Upon reduction to the main axes of the \(D_{12}\) tensor, only those components of \(D_{12}\) and \(A_{12}\) that are totally symmetric in \(O_h\) and its subgroups are nonzero. Thus, only \(J\) in \(O_h\) and only one parameter, \(D\) (which emerges from the diagonal elements of the \(D_{12}\) tensor in \(C_{2v}\)), the symmetry of a linear \(\text{Fe–CN–M}\) bridge), are nonzero (Figure 1 and Table 1). In this particular case, \(D_{12}\) assumes the simple form given by eq 7:

\[
D_{12} = \begin{bmatrix}
-\frac{2}{3}D & 0 & 0 \\
0 & -\frac{2}{3}D & 0 \\
0 & 0 & \frac{4}{3}D
\end{bmatrix}
\]

It follows from the matrices of eqs 1 and 4 that all of the parameters can be determined. A similar approach to the exchange problem for a dinuclear \(\text{Fe}^{\text{III}}–\text{CN–Cu}^{\text{II}}\) complex has been described previously and applied to the important problem of the spin levels of a cyanide-bridged derivative of the enzyme cytochrome oxidase. However, the large number of model parameters did not allow the method to be applied quantitatively at that time.

We now consider an oligonuclear cluster derived from \(\text{Fe}^{\text{III}}–\text{Cu}^{\text{II}}\) and \(\text{Fe}^{\text{III}}–\text{Ni}^{\text{II}}\) dinuclear building blocks. As long as there is a 1:1 mapping of the ground spin eigenstates of the Hamiltonians of eqs 1 and 4 (i.e., as long as the energy separation between the ground and excited electronic states is much larger than the exchange coupling energy, which is strictly valid for all of the cases considered here, as shown in the Supporting Information), the parameters of eq 4 can be determined, and the total Hamiltonian of the spin cluster is given by eq 8:

\[
\hat{H}_{\text{total}} = \sum_{ie} \left[ -J_{ie} \hat{S}_i \cdot \hat{S}_j + \sum_{j} \left[ \hat{S}_j \cdot \left( \mathbf{T}_g \mathbf{T}_j \right) \cdot \mathbf{B} + \mu_B \hat{S}_j \cdot \left( \mathbf{T}_g \mathbf{T}_j \right) \cdot \mathbf{B} \right] \right] + \sum_{ie} \left[ \hat{S}_j \cdot \left( \mathbf{T}_g \mathbf{T}_j \right) \cdot \mathbf{B} \right]
\]

where the single summations run over all of the \(\text{Fe}^{\text{III}}, \text{Cu}^{\text{II}},\) and \(\text{Ni}^{\text{II}}\) ions (contained in the sets labeled \{Fe\}, \{Cu\}, and \{Ni\}, respectively); the double summation runs over all of the \(\text{Fe}^{\text{III}}–\text{M}^{\text{II}}\) pairs; \(T_{1g}, T_{2g},\) and \(T_{3g}\) are the matrices which transform the local Cartesian axes \((x, y, z)\) of each \(\text{Fe}^{\text{III}}\) and \(\text{M}^{\text{II}}\) magnetic center and each \(\text{Fe}^{\text{III}}–\text{M}^{\text{II}}\) exchange pair, respectively, into the global axes \((x, y, z)\); and \(\hat{S}_i'\) and \(\hat{S}_j\) are the spin operators in the global frame. Application of this spin Hamiltonian operator to the basis composed of all possible products of single-ion spin functions produces Hermitian matrices having dimensions of \(8 \times 8\) or \(18 \times 18\), \(16 \times 16\) or \(36 \times 36\), \(32 \times 32\) or \(108 \times 108\), and \(256 \times 256\) or \(1296 \times 1296\) for \(\text{Cu or Ni}_{2}\)Fe, \(\text{Cu or Ni}_{2}\)Fe, \(\text{Cu or Ni}_{2}\)Fe, and \(\text{Cu or Ni}_{2}\)Fe, respectively. These matrices were diagonalized numerically using standard routines.
The ground-state potential energy surface of [Fe(CN)₆]³⁻ is very flat. There are four minima having $D_{4h}$ symmetry, which are only 135 cm⁻¹ more stable than the minimum having regular octahedral symmetry (Figure 2). Therefore, the geometry of the Fe₃⁻–CN–M⁻ pair may still have $C_{4v}$ symmetry upon time averaging, but the dynamics of the system may populate all of the minima (this is the dynamic Jahn–Teller effect; see Figure S.3b in the Supporting Information). A limited number of studies have addressed the effect of dynamic Jahn–Teller coupling on the magnetic exchange coupling. Dynamic Jahn–Teller coupling has been applied in order to analyze the temperature dependence of the magnetic anisotropy of [Fe(CN)₆]³⁻, and the same approach is applied here for the Fe₃⁻–CN–M⁻ exchange-coupled pairs. Details are given in the Supporting Information.

3. Computational Details

DFT computations were performed using the Amsterdam Density Functional program (ADF). The LDA-VWN functional, which is known to perform better than GGA for geometries, in particular for metal–ligand bond distances, was employed in all of the calculations. Large Slater-type orbital triple–ζ basis sets including one polarization function (p-type for H and d-type for C and N) and the frozen-core approximation (up to 3p for the metal ions and 1s for carbon and nitrogen) were used. The Fe₃⁻–CN–M⁻ model system is shown in Figure 1; Fe–C and M–N bond distances from DFT geometry optimizations compared reasonably well with those reported for analogous compounds (Table 2). The ground state of Cu⁰ was chosen to have a single electron in the dₓ² orbital, implying a tetragonally compressed geometry with maximum unpaired spin density directed toward Fe. For Ni⁰, we chose a $A₂g$ ground state having two unpaired electrons in the $e_g$ orbitals ($d_{x²−y²}$). Exchange coupling energies $J(E)$ and $J(B₂)$ were obtained from spin-polarized broken-symmetry DFT calculations, using both the spin-projected $^{98,99}$ and spin-unprojected $^{100−102}$ methods. Different functionals were tested, including the pure DFT functionals VWN, $^{97}$ PW91, $^{103,104}$ PBE, $^{105}$ and OPBE $^{[106]}$ which is a combination of Perdew, J. P.; Burke, K.; Ernzerhof, M. (105) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, N. J.; Singh, D. J.; Fiolhais, C. Phys. Rev. B 1992, 46, 6671.

Handy’s optimized exchange (OPT$^{[106]}$) and the PBE correlation PBE$^{[106]}$ as well as hybrid functionals with various degrees of exact Hartree–Fock exchange, namely, the popular B3LYP $^{[107]}$ (20% HF) and its modifications with more (B1LYP, $^{[108]}$ 25% HF) or less (B3LYP $^{[109]}$, 15% HF) exchange (see discussions of the performance of these functionals, $^{[111−115]}$ the role of the self-interaction error, $^{[116−118]}$ and a new development $^{[119]}$). Computed values of $J(E)$ and $J(B₂)$ (see Table S.1 in the Supporting Information) showed a strong dependence on the functional. Because of the orthogonality of the magnetic orbitals, i.e., $σ$ for Cu⁰ and Ni⁰ and π for [Fe(CN)₆]³⁻ (see Figure S.1 in the Supporting Information), a ferromagnetic exchange coupling was calculated in all cases [$J(π) > 0$]. We chose to use a B1LYP functional, which reproduced the correct order of magnitude of the exchange coupling energies (see Table S.1 in the Supporting Information). Alternative choices did not change the results qualitatively (see Figure S.4 in the Supporting Information). Values of $J(π)$ and $J(π)$ for the Fe–Cu and Fe–Ni pairs are listed in Table 3.

4. Results and Discussion

4.1. Linear ($C_{6v}$) Dinuclear Fe–CN–M Building Blocks with Octahedral [Fe(CN)₆]³⁻ Sites. 4.1.1. The Fe₃⁻–CN–Cu²⁺ Pair. The $^{3}T_{2g}$ ground state of [Fe(CN)₆]³⁻ splits by spin–orbit coupling into a ground-state doublet $^{3}A_{2g}$.
the spin eigenfunctions. The spin ground state (B1) is weakly with the magnetic b2 orbital (d
3
)
spin–orbit coupling constant of [Fe(CN)
6
]3
−
is small, and the singly occupied a1 orbital (d
α
) of Cu
1
II
are provided in the Supporting Information) are given in eq 9:

\[
\begin{align*}
E(B_1) &= \frac{1}{6} J(\xi) - \frac{1}{12} J(\xi_2) \\
E(B_2) &= -\frac{1}{6} J(\xi) + \frac{1}{4} J(\xi_2) \\
E(E) &= \frac{1}{6} J(\xi) - \frac{1}{12} J(\xi_2)
\end{align*}
\]

Figure 3 visualizes these energy expressions and also lists the spin eigenfunctions. The spin ground state (B1) is nonmagnetic. However, the B2–B1 energy separation [J(B2)/3] is small, and the singly occupied a1 orbital (d\_z) of Cu interacts weakly with the magnetic b2 orbital (d\_\_z) of \( \delta \)-type Fe, resulting in a very small exchange energy of \( J(B_2) = 1.6 \text{ cm}^{-1} \). This can be compared with the much larger energy, \( J(B_2) = 19.4 \text{ cm}^{-1} \), arising from the \( \sigma/\pi \) interaction of the Cu a1 (d\_z) and Fe e (d\_\_z, d\_\_\_z) orbitals. The latter places the state above the ground state by 6.47 \text{ cm}^{-1}. Calculations showed that configuration mixing of the ground-state spin levels (B1, B2, and E) with the excited-state levels [which result from the Cu\_II a1 (d\_z)–Fe\_III U(\( \kappa \), \( \lambda \), \( \mu \), \( \nu \)) exchange coupling] is vanishingly small (see the Supporting Information); nevertheless, we accounted for such mixing in all of the calculations. From a comparison of the numerical results with the eigenstates of the spin Hamiltonian \( H_{\text{rhop}} \) (eq 4), the values of the parameters \( J, D \) (eq 7), \( g_{\gamma} \) (for Fe), and \( g_{\gamma} \) (for Cu) were deduced (eq 10).

\[
J = -\frac{2}{9} J(\xi) - \frac{1}{9} J(\xi_2) = -4.49 \text{ cm}^{-1}
\]

\[
D = \frac{1}{3} J(\xi) - \frac{1}{3} J(\xi_2) = 5.94 \text{ cm}^{-1}
\]

\[
g_{1+} = g_{1y} = g_{1z} = -\frac{2}{3} - \frac{4}{3} \kappa = -1.72
\]

\[
g_{2x} = g_{2z} = 2.18; \quad g_{2z} = 2.00
\]

It is remarkable that in the dinuclear model, the local tensors \( g_{\gamma} \) and \( g_{\gamma} \) couple with different signs, leading to the interesting and unexpected result that the E term, which usually is ascribed to the magnetic \( M_s = \pm 1 \) pair in a ferromagnetically coupled pair with \( s = \frac{1}{2} \) ions and has a negative value of \( D \), is in this case highest in energy with small [for \( g_{\gamma}(E) \) or vanishing [for \( g_{\gamma}(E) \)] g-tensor components (eq 11).

\[
g_{1}(E) = g_{1+} + g_{2z} = 0.28; \quad g_{\gamma}(E) = 0
\]

In contrast, the B1 and B2 states are composed of an equal admixture of \( M_s = +1 \) and \( M_s = -1 \) spin functions and are nonmagnetic. However, an external magnetic field \( B \) (with magnitude \( B \)) parallel to \( z \) leads to mixing of these states and thus tends to induce \( M_s = +1 \) (or \( M_s = -1 \)) magnetic moments. Because the B2–B1 energy separation is small and the local tensors \( g_{\gamma} \) (Fe) and \( g_{\gamma} \) (Cu) couple with the same sign in the off-diagonal Zeeman term (eq 12), even weak magnetic fields can induce magnetic behavior.

\[
H(B_1, B_2) = \begin{bmatrix}
0 & \mu_B(-g_{1+} + g_{2z})B \\
\mu_B(-g_{1+} + g_{2z})B & \frac{1}{3} J(B_2)
\end{bmatrix}
\]

This is shown by the dependence of the energy terms on the magnetic field parallel and perpendicular to the \( z \) axis of the dinuclear model (Figure 4). A strong anisotropy with an easy axis oriented in the \( z \) direction is predicted. Therefore, if the rate of magnetic relaxation is small [i.e., if
of these states in terms of the exchange coupling energies and the kinetic exchange model, which takes into account the exchange terms as well as the single-ion zero-field isotropic energy gaps, respectively (Figure 5). Both of these states on the magnetic field parallel and perpendicular to the z axis of the pair (Figure 6), a strong anisotropy in the z direction is predicted. From the computed DFT values of $J(E)$ and $J(B)$ (12.9 and 0 cm$^{-1}$, respectively), eq 10 gave the values $J = -2.87$ cm$^{-1}$ and $D = 4.30$ cm$^{-1}$ for the parameters of the spin Hamiltonian (eq 4). As in the case of the Fe$^{III}$--Cu$^{II}$ pair, the quantities $-E_D$ and $E_J$ can be defined and used in analogy to $U$ and $J$ to quantify the anisotropic and isotropic energy gaps, respectively (Figure 5). Both of the exchange terms as well as the single-ion zero-field splitting ($D_Ni$) affect the value of $-E_D$ (eq 14).

$$-E_D = \frac{1}{3} J(E) - \frac{2}{6} J(B) - D_Ni$$  \hspace{1cm} (14)

The parameter $D_Ni$ is known to vary over a wide range, from positive values (e.g., 9.47 cm$^{-1}$) in tetragonally elongated octahedra of Ni$^{II}$ to negative values (e.g., $-6.1$ cm$^{-1}$) in compressed octahedral structures. Therefore, the anisotropy gap $-E_D$ (calculated using DFT to be 4.3 cm$^{-1}$ due to exchange-only contributions) can largely be tuned by ligand-enforced distortions within the Ni$^{III}$N$_6$ building block. A reduction or enhancement of this energy is predicted for positive or negative values of $D_Ni$, respectively.

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4.1.2. The Fe$^{III}$--CN--Ni$^{II}$ Pair. The $E''(\alpha'', \beta'')$ ground state of Fe$^{III}$ couples with the $S = 1$ spin of Ni$^{II}$, giving rise to three Kramers doublets: the ground state, $E''(1)$, and two excited spin states, $E''(2)$, and $E'$. Expressions for the energies of these states in terms of the exchange coupling energies $J(E)$ and $J(B)$ and the Ni$^{II}$ zero-field splitting energy $D_Ni$ are given in eq 13 (complete matrices are given in the Supporting Information).

$$E(E''(1)) = -\frac{1}{3} J(E) + \frac{2}{6} J(B) + \frac{1}{3} D_Ni$$

$$E(E''(2)) = -\frac{2}{3} D_Ni$$

$$E(E') = \frac{1}{3} J(E) - \frac{2}{6} J(B) + \frac{1}{3} D_Ni$$  \hspace{1cm} (13)

An energy diagram for these states is shown in Figure 5, which also lists the spin eigenfunctions. In contrast to the Fe$^{III}$--Cu$^{II}$ pair, all of the spin states of the Fe$^{III}$--Ni$^{II}$ pair are doubly degenerate because of the odd number of spins (Kramers degeneracy). As for Cu$^{II}$, there is an in-phase coupling of the local tensors $g_i$(Fe) and $g_2$(Ni) in the $E''(1)$ spectrum of phonons (a “phonon bottleneck”), single-molecule magnetic behavior in a given time frame and in an applied external magnetic field may result. We refer to such a situation as a single-molecule metamagnet (SMMM).

It is worth noting that because of the unusual coupling of the $g_1$ and $g_2$ tensors, the calculated values of $J$ and $D$ have signs opposite to those conventionally assumed ($J > 0$, $D < 0$). It is interesting to note that a positive value of $D$ (10.16 cm$^{-1}$) was observed in inelastic neutron scattering experiments on the dinuclear complex Br$_3$Yb$^{III}$Br$_3$Cr$^{II}$Br$_3$ with ferromagnetic Yb$^{III}$--Cr$^{II}$ coupling. Because of the unusual signs of $D$ and $J$, the energies $E_D$ and $E_J$ have been introduced in Figure 3. We use them in analogy to the well-known quantities $U$ and $J$.

The large magnetic anisotropy in linear Fe$^{III}$--CN--Cu$^{II}$ pairs is consistent with qualitative results obtained for Mn$^{III}$--CN--Mn$^{II}$ pairs having the same bridging geometry using the kinetic exchange model, which takes into account both Ising-like ($S_{Mo-S_{Mo}}$) and isotropic ($S_{Mo-S_{Mo}}$) exchange terms. Similar results obtained for Cr$^{III}$--CN--Fe$^{II}$ pairs using the same model have been reported.

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**Figure 5.** Spin energy levels and spin functions for the Fe$^{III}$--CN--Ni$^{II}$ exchange pair of $C_{6v}$ symmetry. The values ±1 and 0 are the spins of Ni$^{II}$, and $\alpha'$ and $\beta'$ are the effective spins of Fe$^{III}$. The following parameters were used for the $C_{6v}$ energy levels: $J(E)$ = 12.9 cm$^{-1}$, $J(B)$ = 0 cm$^{-1}$, and $\zeta(Fe) = 345$ cm$^{-1}$. The energy levels of the pair in $D_oh$ symmetry (obtained by collapsing the Ni$^{II}$ and Fe$^{III}$ nuclei) and the effect of the zero-field splitting of Ni$^{II}$ ($D_Ni = -2.63$ cm$^{-1}$) on the spin energy gap parameter $-E_D$ are also shown.

**Figure 6.** Zeeman splitting of the spin levels of the Fe$^{III}$--CN--Ni$^{II}$ pair in a magnetic field (a) parallel and (b) perpendicular to the bridging z axis. The following parameters were used: $k(Fe) = 0.79$, $g_{x,y,z}(Ni) = 2.30$, and $D_Ni = 0$ (values of the other parameters were the same as in Figure 5).
4.1.3. Origin of the Magnetic Anisotropy in Fe–CN–M Pairs. The large magnetic anisotropy of the Fe–CN–M pairs is intrinsically related to the unquenched orbital moments of the \( ^2T_{2g}(\xi, \eta, \zeta) \) ground state of Fe\( ^{III} \), whose \( \xi \) and \( \zeta \) components have the proper symmetry for an Fe–M exchange pathway to emerge via the \( \pi \) orbitals of CN\(^{-} \). The \( M_L = \pm 1 \) orbital moments play a particularly important role for the spin levels. As seen in eqs 10 and 14, the magnetic anisotropy is dominated by \( J(E) \). As \( J(E) \) is obtained from DFT, it is a complex, many-electronic quantity, which includes various charge transfer excitations starting from the nominal purely ionic ground-state configuration (Figure 7). These include electronic transitions from (to) the fully occupied (empty) \( \pi \) bonding (antibonding) orbitals \( 2e \) (\( 3e \)) of CN\(^{-} \), which create \( \alpha \) (\( \beta \)) spin densities on CN\(^{-} \), and from the \( \sigma \) orbital \( 5a_1 \) of CN\(^{-} \), which lead to a \( \beta \) spin density on that orbital. An energy decomposition analysis of \( J(E) \) described elsewhere\(^{22} \) shows that the \( 2e(CN) \rightarrow e(Fe) \) and \( 5a_1(CN) \rightarrow a_1(Fe) \) donations dominate the sign of the \( J(E) \) ferromagnetic coupling energy, while the \( e(Fe) \rightarrow 3e(CN) \) back-donation yields a large but negative contribution which reduces \( J(E) \).

4.2. Effect of Jahn–Teller Distortions of the [Fe(CN)]\(_6^{3-}\) Site. 4.2.1. Static Jahn–Teller Distortions. The spin levels of Fe\( ^{III} \)–CN–Cu\(^{II} \) and Fe\( ^{III} \)–CN–Ni\(^{II} \) pairs change significantly when Jahn–Teller distortions along the trigonal axes of the octahedral [Fe(CN)]\(_6^{3-}\) site are superimposed on the \( C_4 \) symmetry (Figure 8). There are four possible pathways for these distortions, which correlate with the body diagonals of the cube inscribed in the [Fe(CN)]\(_6^{3-}\) octahedron (see Figure S3.b in the Supporting Information).

The trigonal distortion along the \( x = y = z \) direction (defined by \( Q_x = Q_y = Q_z = Q; \) and visualized in the inset of Figure 2) reduces the \( C_4 \) symmetry toward \( C_3 \), with a symmetry plane that bisects the coordinate axes in the \( x = y = -x = -y = -z \) direction and parallel to \( z \). In agreement with the decrease in symmetry, the excited E spin state of the Fe–Cu pair splits, and its \( A'' \) component approaches the lower-lying \( A' \) and \( A'' \) spin states. With greater distortion (increasing \( Q_z \)), and concomitant quenching of the orbital angular momentum due to the \( C_4 \rightarrow C_3 \) symmetry reduction, the pattern of a ground-state spin triplet (split in zero field) and an excited-state singlet of the ferromagnetic Fe\( ^{III} \)–Cu\(^{II} \) pair gradually starts to emerge (Figure 8a). This effect is much stronger for trigonal compression (leading to the energy minimum of the ground-state potential energy surface) than for trigonal elongation. Likewise, upon \( Q_z \) distortion, the excited \( E''(2) \) spin state of the Fe\( ^{III} \)–Ni\(^{II} \) pair drops in energy and approaches the \( E''(1) \) ground state, i.e., the zero-field-split \( S = 3/2 \) ground-state quartet and the \( S = 1/2 \) excited-state doublet are formed. Therefore, Jahn–Teller distortions tend to restore the usual spin coupling scheme in \( s_1 = s_2 = 1/2 \) and \( s_1 = 1/2, s_2 = 1 \) ferromagnetically coupled pairs. The anisotropic and isotropic gap energies \(-E_D \) and \( E_J \), respectively, which are indicated in Figure 8, manifest these changes in an impressive way. Upon distortion, \(-E_D \) decreases and \( E_J \) increases for both Fe\( ^{III} \)–Cu\(^{II} \) (Figure 9) and Fe\( ^{III} \)–Ni\(^{II} \) (Figure 10). Figure 10 compares the cases of tetragonal compression (negative values of the zero-field splitting energy \( D_{H0} \)) and tetragonal elongation (positive values of \( D_{H0} \)) of the \( S = 1 \) ground state of the octahedral Ni\(^{II} \) complex with the case of no distortions around Ni\(^{II} \). In these calculations, we have assumed that the tetragonal axes of Ni\(^{II} \) and the Fe–CN–Ni bridge of the Fe\( ^{III} \)–Ni\(^{II} \) pair are parallel. Negative values of \( D_{H0} \) lead to a drastic increase of the anisotropy, while positive values lead to a partial or
complete cancellation of the contributions to \(-E_D\). The energy \(E_J\) is also affected by \(D_{90}\) in a significant way (Figure 10b).

It should be noted that the auxiliary quantities \(-E_D\) and \(E_J\) have only been introduced for the purpose of interpretation, i.e., to quantify the information described by as many as nine parameters \(J\) and the parameters in eqs 5 and 6 that define the tensors \(D_{12}\) and \(A_{12}\) in the exchange coupling operator (eq 4)). In Table 4 we list these parameters for the \(\text{Fe}^{3+}-\text{Cu}^{II}\) and \(\text{Fe}^{3+}-\text{Ni}^{II}\) pairs, both without Jahn–Teller distortions \((Q_4 = 0)\) and with the distortion that corresponds to the trigonal minimum of \([\text{Fe}(\text{CN})_6]^{3-}\) \((Q_4 = 0.128 \text{ Å})\). As the symmetry decreases from \(C_{4v}\) to \(C_{3v}\), as many as nine different parameters result, in agreement with the general orientation of the \(D_{12}\) and \(A_{12}\) tensors within the adopted global Cartesian frame. These can be reduced to the five independent parameters \(J, D, E, A_s,\) and \(A_t\) in the coordinate frame in which \(D_{12}\) is diagonal [see Table 1, \(C_{4v} \rightarrow C_{3v}(C_2,\sigma_d) \rightarrow C_3\); values of these five parameters are given in Table 4 for the \(\text{Fe}^{3+}-\text{Ni}^{II}\) pair. As expected, \(D\) is negative \((D = -6.09 \text{ cm}^{-1})\), with main axes of \(D_{12}\) which undergo a specific rotation as a result of the \(Q_4\) activity (see Table 4).

A very pronounced orthorhombic component \((E = 0.77 \text{ cm}^{-1})\) emerges along with significant antisymmetric exchange \((A_t = -0.29 \text{ cm}^{-1}, A_s = -1.12 \text{ cm}^{-1})\) due to Dzialoshinski–Moriya exchange coupling. This needs to be taken into account when modeling the magnetic properties.

### 4.2.2. Dynamic Jahn–Teller Distortions

Dynamic distortions related to the very flat ground-state potential energy surface of \([\text{Fe}(\text{CN})_6]^{3-}\) with trigonal \((D_{90})\) minima, which are only 135 cm\(^{-1}\) more stable than the nondistorted \(O_h\) geometry, induce specific changes in the spin coupling parameters of the \(\text{Fe}^{3+}-\text{Ni}^{II}\) pair, which we consider here as an example. Similar behavior has been calculated for the \(\text{Fe}^{3+}-\text{Cu}^{II}\) pair. As shown by the dependence of the energy \(-E_D\), the anisotropy decreases as the vibronic coupling strength \(\lambda = E_{VT}(3\hbar \omega_0/2)\) increases (Figure 11). Calculations have shown that the dynamic Jahn–Teller coupling \((\lambda)\) is small for \([\text{Fe}(\text{CN})_6]^3-\), and its effect on \(-E_D\) is very small. Also, there is no strong interplay between the anisotropy of \(\text{Ni}^{II}\) \((D_{90})\) and the dynamic Jahn–Teller coupling. However, the effect of \(\lambda\) on the magnetic anisotropy is significant for the isoelectronic \([\text{Mn}(\text{CN})_6]^4-\) ion, for which a much stronger vibronic coupling has been predicted. Dynamic Jahn–Teller coupling also tends to decrease the anisotropy of the \(g\) tensor of the \(\text{Fe}^{3+}-\text{Ni}^{III}\) pair. As \(\lambda\) increases, the large \(g_z\) component decreases while \(g_t\) and \(g_s\) [which are zero in \(C_{4v}\) and in the static Jahn–Teller coupling limit (see Table 4)] start to increase. The effect of dynamic Jahn–Teller coupling is found to be particularly pronounced when the exchange anisotropy \((D)\) and the \(\text{Ni}^{II}\) single-ion anisotropy \((D_{90})\) counteract each other, i.e., when \(D\) and \(D_{90}\) have different signs.

### 4.3. Influence of Strain on the Magnetic Anisotropy

Strain effects due to an asymmetric ligand sphere or crystal packing forces can split the \(\text{Fe}^{3+}\) \(T_{2g}\) ground state and modify the magnetic anisotropy. Strains having the symmetries of the components of the \(r_{2g}\) normal mode are formally described by a matrix of the form of eq 3, with a single energy parameter \(S\) (the radial strain, which replaces \(V_t\)) and angular distortions \(Q_4, Q_6\), and \(Q_7\) (angular strains, which replace \(Q_4, Q_6,\) and \(Q_7\), respectively); these are usually known from crystal structure data. Here we restrict our attention to strain having trigonal symmetry \((C_3, Q_s = Q_5 = Q_6 = Q_7)\). Its effect on the magnetic anisotropy for \(\text{Fe}^{3+}-\text{Cu}^{II}\) and \(\text{Fe}^{3+}-\text{Ni}^{II}\) pairs is qualitatively reflected by Figures 9 and 10a, respectively. These changes may be very large \((S_I \gg V_t)\) and therefore induce partial or complete quenching of the magnetic anisotropy. With angular strain alone \((S_s = V_t)\), quenching of orbital momenta due to trigonal compressions is predicted to be stronger than that due to trigonal elongation. The reduction of the magnetic anisotropy is due to the symmetry reduction \((C_i = C_{4v} + D_{90})\), which leads to a complete loss of orbital degeneracy. This is not necessarily the case for tetragonal \((D_{4h})\) strain having a \(C_4\) axis that
coincides with the Fe–CN–M linear bridge. The latter is described by eq 15 in terms of $\Delta_{D_{4h}}$, the energy for tetragonal splitting of the $^2T_{2g}$ ground term. This splitting yields either a $^2E_g$ or a $^2B_{2g}$ ground term, depending on the sign of $\Delta_{D_{4h}}$ ($\Delta_{D_{4h}} > 0$ or $\Delta_{D_{4h}} < 0$, respectively). As shown in Figure 12, both the magnetic anisotropy ($-E_D$) and the isotropic exchange energy ($E_J$) are greatly enhanced for tetragonal strain that leads to a $^2E_g$ ground state on Fe$^{III}$. In contrast, both parameters are strongly quenched if a nondegenerate $^2B_{2g}$ ground state becomes separated from a $^2E_g$ excited state with an energy gap $\Delta_{D_{4h}}$ comparable to or larger than the spin–orbit coupling energy $3\zeta/2$.

$$H_{D_{4h}} = \begin{bmatrix} \frac{-\Delta_{D_{4h}}}{2} & 0 & 0 \\ 0 & \frac{-\Delta_{D_{4h}}}{2} & 0 \\ 0 & 0 & \Delta_{D_{4h}} \end{bmatrix}$$ (15)

5. Comparison with Experimental Data

A large number of oligonuclear cyanometalates containing Cu$^{II}$ or Ni$^{II}$ combined with low-spin Fe$^{III}$ and having ferromagnetic ground states have been synthesized and

- Table 4. Values (in cm$^{-1}$) of the Parameters in the Exchange Hamiltonians for Fe$^{III}$–CN–Cu$^{II}$ and Fe$^{III}$–CN–Ni$^{II}$ Exchange Pairs Having Jahn–Teller-Distorted [Fe(CN)$_6$]$^{4-}$ Octahedra Corresponding to the Minima of $D_{12}$ Symmetry$^a$ on the Ground-State Potential Energy Surface$^{b,c}$

<table>
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<tr>
<th>$J$</th>
<th>$D$</th>
<th>$E$</th>
<th>$D_{x^2}$</th>
<th>$D_{y^2}$</th>
<th>$D_{z^2}$</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
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<tr>
<td>$Q_e = 0^d$</td>
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<td>0</td>
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<td>-5.87</td>
<td>0.83</td>
<td>-0.40</td>
</tr>
<tr>
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<td>-0.14</td>
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<td>0</td>
<td>0</td>
<td>-1.89</td>
<td>-3.78</td>
<td>0.86</td>
<td>-0.14</td>
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$^a$ Calculated with $Q_e = Q_d = Q_b = Q_e = 0.128$ Å; values of the vibronic coupling parameters used in the calculations are specified in Figure 2, and those of the other parameters are specified in Figures 3 (Fe–Cu) and 5 (Fe–Ni). $^b$ Parameter values for the Fe$^{III}$–CN–M$^{II}$ complexes without Jahn–Teller distortions on [Fe(CN)$_6$]$^{4-}$ ($Q_e = 0$) are included for the sake of comparison. Ground-state $g$ tensors (normalized to a ground-state spin of $\pm 3/2$) are $g_{xx} = 0$ and $g_e = 6.35$; to get the $g$ values for the ground-state effective spin, the reported ones should be divided by 3. The angles between the direction of the large components of the $g$ tensors and the $x$, $y$, and $z$ axes of the global coordinate frame are 90° ($x$, $y$) and 0° ($z$). $^c$ For the calculation of the exchange Hamiltonian parameters, full configuration mixing between the ground-state spin multiplet and the electronically excited states was taken into account (in contrast to eq 10). $^d$ Parameter values of the exchange Hamiltonian which diagonalize the $D_{12}$ tensor of the Fe$^{III}$–Ni$^{II}$ pair. The angles between the direction of the unique $D_{12}$ component (~ 6.09 cm$^{-1}$) and the $x$, $y$, and $z$ axes of the ground state frame are 23, 68, and 87°, respectively. Ground-state $g$ tensors (normalized to a ground-state spin of $\pm 3/2$) are $g_{x,y} = 0$ and $g_z = 8.66$; to get the $g$ values for the ground-state effective spin, the reported ones should be divided by 3. The angles between the direction of the large components of the $g$ tensors and the $x$, $y$, and $z$ axes of the global coordinate frame are 73° ($x$, $y$) and 25° ($z$).
Ni₄Fe₄ cubane complexes. Effective thermal barriers for reorientation of the magnetization, and Zero-Field Splitting Parameters (D and E) in Trinuclear FeIII-NiII-FeIII, Rectangular (FeIII)₂(MIV)₃, Trigonal Bipyramidal (M1)₂(M2)₃ (M1 = FeIII, NiII, M2 = CuII, NiII, FeIII), and Heterocubane NiIIIFeIII Exchange Complexes

Table 5. Spin Ground States (S), Exchange Coupling Constants (J in \( H_{exc} = -JS\cdotS \)), Calculated (U) and Experimental (\( U_{eff} \)) Effective Energy Barriers for Reorientation of the Magnetization, and Zero-Field Splitting Parameters (D and E) in Trinuclear FeIII-NiII-FeIII, Rectangular (FeIII)₂(MIV)₃, Trigonal Bipyramidal (M1)₂(M2)₃ (M1 = FeIII, NiII, M2 = CuII, NiII, FeIII), and Heterocubane NiIIIFeIII Exchange Complexes

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<th>( U_{eff} )</th>
<th>U</th>
<th>D</th>
<th>E</th>
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* All energies in cm⁻¹. Calculated from U using the equation \( U = S²|D| \) for integer spins. From a fit to field-dependent magnetization. Inaccurate because of the proximity of the excited S = 1 spin state, which is only 2.76 cm⁻¹ above the ground state. Calculated from D using the equation \( U = (S² − 1/4)|D| \) for half-integer spins S. Positive zero-field splitting parameter of 2.4 for NiII.³ Positive zero-field splitting parameter of 5.8 for NiII.¹² Positive zero-field splitting parameter of 8.8 for NiII.¹² Positive zero-field splitting parameter of 11.³ Positive zero-field splitting parameter of 8.8 for NiII.¹² Positive zero-field splitting parameter of 9.7 for NiII.¹² Positive zero-field splitting parameter of 8.8 for NiII.¹²

Characterized (Table 5). These include trinuclear FeIII-NiII complexes containing trans- and cis-(Fe-CN)₂NiII₂ units,¹ heterometallic square-shaped MIIFe₂ complexes,⁵⁻⁸ trigonal bipyramidal MIIFe₂ structures,²⁻³⁻¹² and heterometallic NiIIFe₂ cubane complexes,⁴⁻¹² Effective thermal barriers \( U_{eff} \) for the reversal of magnetization, obtained by temperature-dependent ac susceptibility measurements, indicate that only three of the systems, cis-FeII-NiII,¹ FeII-NiIII,² and FeII-CuI,⁹ display SMM behavior. In nine other systems, a negative D value was deduced from a fit to field-dependent magnetizations (Table 5). Despite having similar cluster topologies and the same type of ferromagnetic ground state, seven other systems with integer-spin ground states (trans-Fe₂Ni, three Fe₂Cu₂ compounds, and three Fe₂Ni₃ compounds) demonstrated no SMM behavior. What is the reason for these striking differences?

We have performed calculations of the spin levels of clusters containing FeIII and CuII or NiII, based on the vector coupling scheme used in the Theory section; the topologies and coordinate systems used in these calculations are specified in Figure 13. The exchange coupling tensors of FeIII-CuI and FeIII-NiII pairs having linear Fe-CN-M bridges and no angular distortion of [Fe(CN)₆]³⁻ assume a simple form in which only two exchange coupling tensors (D and J) are needed in order to describe each pair. The local g and D tensors of the dinuclear units can be coupled to yield the spin levels and magnetic properties of entire magnetic clusters. Ground-state spin multiplicities, spin gap energies (relative to the ground state) and multiplicities of the lowest excited spin states, and magnetizations as a function of direction and the magnitude of the applied magnetic field [in the low-field (B = 0.2 T) and high-field (B = 7 T) limits] are provided in Table 6. Values of the g tensor for spin clusters having a doubly degenerate (bistable) ground state are listed in Table 7. The calculations yielded a sizable spin gap energy, comparable in magnitude to that reported for CuII-Fe₂ (−D = 5.7 cm⁻¹, Table 5) for only three of the systems, namely, linear Fe-II, trans-Cu-Fe, and Ni-Fe-Ni. In these examples, a large, field-independent magnetization along the easy axis (oriented in the z direction) and almost zero perpendicular magnetization were obtained, and the calculated g-tensor components (Table 7) reflect this anisotropy. A very small spin energy gap was calculated for

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all of the other systems. As the field-dependent ground-state magnetization values (Table 6) indicate, there is a strong effect of the magnetic field on the ground state via mixing of the closely spaced ground and excited spin states. There is a cancellation of the large anisotropies of the individual $\text{Fe}^{III}\text{--Cu}^{II}$ and $\text{Fe}^{III}\text{--Ni}^{II}$ pairs when their local $\mathbf{D}_{12}$ and $\mathbf{g}$ tensors are coupled in magnetic clusters of high symmetry, such as the $\text{M}_{5}\text{Fe}_{2}$ and $\text{M}_{2}\text{Fe}_{4}$ complexes. Magnetic anisotropies for $\text{Cu}_{2}\text{Fe}_{2}$, in both the magnetization and the effects of the magnetic field on the ground state via mixing, are found to be small. This contrasts with the high values of $\mathbf{g}$-tensor components for $\text{Cu}_{3}\text{Fe}_{2}$, in both the magnetization and the effects of the magnetic field on the ground state via mixing.

### Table 6. Energies (in cm$^{-1}$) and Multiplicities of the Ground$^a$ and Lowest-Excited Spin States and Field-Dependent Ground-State Magnetizations$^b$ (in Bohr Magnets) of Highly Symmetric Oligonuclear Model Spin Clusters Built Up from $\text{Fe}^{III}\text{-M}^{II}$ Cyanide-Bridged Pairs$^c,d$

<table>
<thead>
<tr>
<th>complex</th>
<th>ground-state multiplicity</th>
<th>lowest-excited spin state</th>
<th>$B = 0.2$ T</th>
<th>$B = 7$ T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M$, multiplicity</td>
<td>$M_1$, 0.11</td>
<td>$M_1$, 1.74</td>
</tr>
<tr>
<td>CuFe</td>
<td>1</td>
<td>53</td>
<td>1.02</td>
<td>2.95</td>
</tr>
<tr>
<td>NiFe</td>
<td>2</td>
<td>4.30</td>
<td>2</td>
<td>2.61</td>
</tr>
<tr>
<td>trans-CuFe</td>
<td>2</td>
<td>6.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-NiFe</td>
<td>2</td>
<td>4.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis-CuFe</td>
<td>2</td>
<td>0.64</td>
<td>2</td>
<td>2.68</td>
</tr>
<tr>
<td>cis-NiFe</td>
<td>4</td>
<td>1.78</td>
<td>4</td>
<td>5.10</td>
</tr>
<tr>
<td>CuFe$_2$</td>
<td>1</td>
<td>1.29</td>
<td>1</td>
<td>3.70</td>
</tr>
<tr>
<td>NiFe$_2$</td>
<td>1</td>
<td>1.94</td>
<td>4</td>
<td>6.21</td>
</tr>
<tr>
<td>CuFe$_2$</td>
<td>2</td>
<td>1.11</td>
<td>2</td>
<td>6.47</td>
</tr>
<tr>
<td>NiFe$_2$</td>
<td>1</td>
<td>0.35</td>
<td>3</td>
<td>8.31</td>
</tr>
<tr>
<td>CuFe$_4$</td>
<td>1</td>
<td>2.37</td>
<td>2</td>
<td>7.23</td>
</tr>
<tr>
<td>NiFe$_4$</td>
<td>1</td>
<td>0.12</td>
<td>2</td>
<td>12.20</td>
</tr>
</tbody>
</table>

$^a$ Energies of the spin ground states are set at zero. $^b$ Magnetizations $M_x$, $M_y$, and $M_z$ are defined with respect to the global Cartesian axes established for each model complex as shown in Figure 13. $^c$ Data for the constituent dinuclear $\text{Fe}^{III}\text{-M}^{II}$ units are given for the sake of comparison. Calculations have been done using the pair model, adopting a regular (non-distorted) octahedral $[\text{Fe(CN)}_6]^{3-}$ unit, assuming fourfold (pseudo)symmetry of each $\text{M}^2\text{-NC}\text{--Fe}$ bridge, and coupling the local $\mathbf{g}$ and $\mathbf{D}$ tensors of each pair to the tensors of the total cluster. Values of the isotropic spin coupling energy $J$ and the parameter $D$ that defines the local anisotropy $\mathbf{D}$ tensor for each $\text{M}^2\text{--Fe}$ pair were $-4.49$ and $5.93$ cm$^{-1}$, respectively, for $\text{Fe}^{III}\text{--Cu}^{II}$ and $-2.87$ and $4.30$ cm$^{-1}$, respectively, for $\text{Fe}^{III}\text{--Ni}^{II}$. Other parameter values for $\text{Fe}^{III}$ were $k = 0.79$ and $\delta = 4.15$ cm$^{-1}$. Values of the $\mathbf{g}$-tensor components were $g_x = g_y = g_z = 2.30$ for $\text{Ni}^{II}$, $g_x = 2.18$ and $g_y = g_z = 2.00$ for $\text{Cu}^{II}$ and $\text{CuFe}$, $g_x = g_y = 2.05$ and $g_z = 2.25$ for $\text{CuFe}_2$ with the directions of $g_{x,y,z}$ taken to be within and perpendicular to, respectively, the $\text{Fe}^2\text{--Cu}^2\text{--Fe}^2$ ($i = 1, 2, 3$) plane, and $g_x = g_y = g_z = 2.116$ for $\text{CuFe}_2$ and $\text{CuFe}_4$. $^d$ Bold print indicates a system having a field-independent magnetic moment and strong anisotropy.

### Table 7. Values of $g$-Tensor Components$^a$ for Oligonuclear Model Spin Clusters Containing $\text{Fe}^{III}$ and $\text{Cu}^{II}$ or $\text{Ni}^{II}$ and Having Doubly Degenerate (Bistable) Spin Ground States$^b$

<table>
<thead>
<tr>
<th>spin cluster</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe</td>
<td>0</td>
<td>0</td>
<td>6.351</td>
</tr>
<tr>
<td>trans-CuFe</td>
<td>0.379</td>
<td>0.379</td>
<td>5.693</td>
</tr>
<tr>
<td>trans-NiFe</td>
<td>0</td>
<td>0</td>
<td>10.920</td>
</tr>
<tr>
<td>cis-CuFe</td>
<td>2.294</td>
<td>3.860</td>
<td>3.860</td>
</tr>
<tr>
<td>CuFe</td>
<td>4.862</td>
<td>4.862</td>
<td>4.160</td>
</tr>
</tbody>
</table>

$^a$ See Figure 13 for the definition of the global Cartesian axes $x$, $y$, and $z$ for each spin cluster. $^b$ See Table 4 for definitions and numerical values of the local $\text{Ni}^{II}$ and $\text{Cu}^{II}$ $\mathbf{g}$ tensors. $^c$ Values of the $\mathbf{g}$-tensor components are given with respect to an $s' = 1/2$ effective spin; to get the $\mathbf{g}$-tensor components of the actual spin, the values from the table must be divided by the total number of $s = 1/2$ spins (i.e., by 3 for NiFe and trans- and cis-CuFe or 5 for trans-NiFe and CuFe).

### Table 8. Deviations ($\delta$) (in deg) of the C--$\text{Fe}^{III}$--C Angles $\alpha$ from 90° (the Value Corresponding to a $[\text{Fe(CN)}_6]^{3-}$ Complex Without Angular Distortions) and Deviations ($\delta \beta$ and $\delta \gamma$) (in deg) of the C--$\text{Fe}^{III}$--N and C--$\text{N}^{III}$--M Angles $\beta$ and $\gamma$, Respectively, from 180° (the Value Corresponding to Ideally Linear Fe--C--N--M Units), As Derived From Structural Data on CuFe$_2$ and NiFe$_2$ Spin Clusters

<table>
<thead>
<tr>
<th>Fe--M pair</th>
<th>$\delta \alpha$(C--$\text{Fe}^{III}$--C)</th>
<th>$\delta \beta$(C--$\text{Fe}^{III}$--N)</th>
<th>$\delta \gamma$(C--$\text{N}^{III}$--M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_4$--Cu$_1$</td>
<td>-3.1</td>
<td>-2.4</td>
<td>-10.4</td>
</tr>
<tr>
<td>Fe$_4$--Cu$_2$</td>
<td>-0.8</td>
<td>-3.1</td>
<td>-7.3</td>
</tr>
<tr>
<td>Fe$_4$--Cu$_3$</td>
<td>-1.8</td>
<td>-3.6</td>
<td>-8.8</td>
</tr>
<tr>
<td>Fe$_3$--Cu$_1$</td>
<td>-3.6</td>
<td>-3.2</td>
<td>-6.0</td>
</tr>
<tr>
<td>Fe$_3$--Cu$_2$</td>
<td>-3.4</td>
<td>-1.9</td>
<td>-8.3</td>
</tr>
<tr>
<td>Fe$_3$--Cu$_3$</td>
<td>0.9</td>
<td>-2.8</td>
<td>-8.5</td>
</tr>
<tr>
<td>Ni$_4$--Ni$_1$</td>
<td>-1.9</td>
<td>-0.8</td>
<td>-4.2</td>
</tr>
<tr>
<td>Ni$_4$--Ni$_2$</td>
<td>0.5</td>
<td>-0.9</td>
<td>-10.8</td>
</tr>
</tbody>
</table>

$^a$ See Figure 13 for definitions of atom labels.

Based on the Jahn–Teller description. Therefore, a full calculation using the exact angular geometry in each magnetic cluster is mandatory when modeling the magnetic data.

In addition to $\delta \alpha$, the geometry of the Fe--CN--M bridge is expected to affect the anisotropy. Because the Fe$^{III}$--CN bond is stronger than the CN--M$^{II}$ bond, deviations ($\delta \gamma$) of the C--N--M angle due to angular strain and packing forces are expected to be larger than those ($\delta \beta$) of the Fe--C--N angle. This expectation is supported by the data in Table 8. It has been shown experimentally\(^1\) and by DFT calculations\(^125\) (see also ref 126) that nonzero values of $\delta \gamma$ decrease the overlap of the magnetic orbitals and reduce the exchange coupling energy $J^2(E)$. In contrast, $J^2(B_2)$ is expected to increase in magnitude. This must be taken into account in quantitative studies.

From the comparison between the computational results for model clusters of high symmetry and the reported magnetic data, we conclude that symmetry reduction (as revealed by the reported angular distortions) plays a different role.
role in trans-M₃Fe than in M₂Fe₂ and M₄Fe₄ complexes. Angular distortions reduce the magnetic anisotropy of the linear Cu–Fe–Cu and Ni–Fe–Ni structures but induce anisotropy in the higher-symmetry M₂Fe₂ (Dₘ) and M₄Fe₄ (Tₘ) clusters. This conclusion is supported by experimental data on highly symmetric Cu₄[FeIII]₂ cyanide-bridged face-centered cubic clusters that demonstrate SMM behavior.¹³,¹⁸

A large and accidental ground-state degeneracy of 4 is predicted for the regular cis-Ni₃Fe, Ni₃Fe₂, and Ni₃Fe₄ spin clusters having C₄v, D₂h, and Tₘ symmetries, respectively, and an even larger degeneracy (12) is found in the lowest excited state of Fe₂Ni₆, which lies only 0.21 eV above the ground state. When coupled to angular distortions, these degenerate ground states can be modified by antisymmetric exchange, which can be very large even for small values of δα (see Table 4). This might help to explain the atypical relaxation behavior reported for the Fe₄Ni₄ SMM.⁴

The effect of tetragonal strain (Figure 12) is manifested by bulk magnetic susceptibility, ESR, and Mössbauer data on the cyanide-bridged Fe₃CuCl₃ heteronuclear complex in [Fe(P)CN(Cu(N₄))ClO₄]·3H₂O [P = α,α,α,α-tetrakis(o-nicotinamido)phenyl] porphyrin].⁶ Stabilization of the non-degenerate 2B₂g ground state of Fe₃III (negative Δα₃) and the small positive value of J(B₂) lead to an S' = 1 ground state and an S' = 0 excited state that are estimated by EPR to be separated by only 0.25 cm⁻¹. Using the DFT values for J(E) and J(B₂), we have been able to reproduce this energy gap with a strain energy of Δα₃ = −1000 cm⁻¹. Reported small values of the anisotropic and antisymmetric exchange parameters extracted from a simulation of the ESR spectrum nicely manifest the quenching of orbital momenta due to lifting of the orbital degeneracy of the 2T₂g ground state of Fe₃III. However, subtle effects arising from the coordination geometry of the Fe₃III site may tune the anisotropic splitting of the S' = 1 sublevels over a wide range, leading to a spin-singlet ground state (Mₛ = 0) and the absence of an EPR signal, as reported for the CN⁻ derivative of the oxidized form of the enzyme cytochrome oxidase, which has a pair of ferromagnetically coupled CuII and low-spin Fe₃III sites and a similar S' = 1 ground state.⁶¹,⁶²

6. Conclusions

1. A large magnetic anisotropy having an easy axis of magnetization along the cyanide bridge is predicted for Fe₃III–MII (M = Cu, Ni) pairs with linear Fe₃III–CN–MII bridging geometry and regular [Fe(CN)₃]⁻ octahedra. It arises from the orbital angular momentum in the 2T₂g ground state of [Fe(CN)₃]⁻ which is transmitted to the spin ground state of the cluster by an orbital-dependent exchange mechanism. Enhancement of the exchange anisotropy is predicted to occur when it is combined with the single-ion anisotropy of NiII with a negative sign of D (leading to an Mₛ = ±1 < Mₛ = 0 splitting of the S = 1 ground state of NiII). This implies that the NiII₄ octahedra are tetragonally compressed with a tetragonal axis aligned along the bridge.

2. In contrast to the MnIII-based SMM,¹²⁷–¹²⁹ Jahn–Teller coupling is not always favored for SMMs in spin clusters composed of Fe₃III–CuII and Fe₃III–NiII cyanide-bridged exchange-coupled pairs. Both CuII and FeIII are Jahn–Teller active (for FeIII, the Jahn–Teller coupling is relatively small but on the same order of magnitude as the spin–orbit coupling interaction). A trigonal distortion of as little as 2–3° in the [Fe(CN)₆]³⁻ site is able to destroy the magnetic anisotropy, i.e., to reduce the spin anisotropy gap energy (−E₀ or U) in both the Fe₃III–CuII and Fe₃III–NiII pairs (Figures 9 and 10a, respectively). This is also the case in trans-Cu–Fe–Cu and -Ni–Fe–Ni complexes. Therefore, in the synthesis of new SMM materials, it is necessary to pay attention to the angular geometry and electronic structure of the Fe₃III site, as revealed by absorption spectra due to d–d transitions. The Fe–CN bond is strong, and it is expected that Fe–CN distortions are less important. However, this may change for cyanide complexes having different ligands in the coordination sphere of Fe₃III (e.g., in magnetic clusters composed of the Fe(CN)₆ units in [Fe(Tp)(CN)₃] [Tp = hydrotris(pyrazolyl)borate], which impose a trigonal geometry,²⁻⁹ and in the [Fe(P)CN-Cu(N₄)]²⁺ [P = α,α,α,α-tetrakis(o-nicotinamidophenyl) porphyrin] complex,⁶³ which has tetragonal symmetry). On the basis of t₂g orbital splittings (reported from EPR measurements¹³⁰ to be as large as 2900 cm⁻¹), it is expected that ancillary ligands can significantly modify the magnetic anisotropy. In particular, for cyanide complexes of FeIII with ligands inducing a 1Eg ground state, an increase of the magnetic anisotropy of the FeIII–CN–MII pairs is predicted (as discussed in the section on strain).

3. Symmetry reduction is found to increase the magnetic anisotropy in spin clusters with high symmetry and partial or complete cancellation of the Fe₃III–CuII and Fe₃III–NiII local anisotropy tensors, as in M₂Fe₂ and M₄Fe₄.

4. The use of NiII instead of CuII complex precursors seems to be preferable; it yields more-regular MIII polyhedra and can add a negative single-ion anisotropy contribution to the SMM in certain cases. The latter effect can be under chemical control (i.e., enforcement of tetragonal compression rather than elongation in the NiL₆ precursor).

5. Dynamic Jahn–Teller coupling in hexacyanometalate 2T₂g ground states is found to reduce the magnetic anisotropy to an extent that depends on the vibronic coupling strength. The effect is found to be weak with [Fe(CN)₆]⁻⁻ but may become important with other hexacyanometalates, such as [Mn(CN)₆]⁻⁻.

6. A procedure for computing the anisotropic exchange in oligonuclear clusters derived from Fe₃III–MII pairs, which involves two parameters J(E) and J(B₂) that define a CuII pseudosymmetry around each pair, has been proposed. Mixing of the magnetic orbitals due to deviations from this

ideal geometry is taken into account by explicit consideration of the ligand field distortions around each FeIII center. From such calculations, the isotropic constant $J$ and the magnetic anisotropy described by the symmetric (D) and antisymmetric (A) tensors of each FeIII–MII pair can be deduced and then added using a vector coupling scheme to yield exchange coupling tensors for the whole cluster. Qualitative discussions based on a high-symmetry concept related in this work to the Jahn–Teller effect can be extended to quantitative studies that focus on systems with strongly irregular Fe(CN)$_6^{3-}$ geometries or on low-spin FeIII–cyanide complexes containing other ligands in the coordination sphere of FeIII.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft (SPP 1137 “Molecular Magnetism”) and the University of Heidelberg is gratefully acknowledged. We thank J. R. Long and B. M. Bartlett (Berkeley, CA) for a preprint of their work (ref 2) prior to publication, S. Piligkos (University of Copenhagen, Denmark) for computational help, and G. Rajaraman for stimulating discussions.

A combined ligand field and density functional theory analysis of the magnetic anisotropy in oligonuclear complexes based on Fe$^{III}$-CN-M$^{II}$ exchange-coupled pairs

Mihail Atanasov, Peter Comba and Claude A. Daul

Supplementary Material
Figure S.1 The magnetic orbitals in the $^2B_1 (e^4b_2^1)$ and $^2E (e^3b_2^2)$ states of [Fe(CN)$_6$]$^{3-}$ (top), and of the $^2A_1 (d_{z^2})$ ground state of [Cu(NH$_3$)$_4$NC]$^{1+}$ (bottom) from broken symmetry DFT calculations using a B1LYP functional.

**Full Derivation of the Hamiltonian of the Fe$^{III}$-CN-Cu$^{II}$ Pair**

The matrix of exchange Hamiltonian $-J_{ij} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j$, with $i$ and $j$ denoting the magnetic orbitals on center 1 and 2, within the spin only basis $\alpha_i \alpha_j$, $\beta_i \alpha_j$, $\alpha_i \beta_j$ and $\beta_i \beta_j$ is given by:

$$H_{ex}(i,j) = \begin{pmatrix}
  \alpha_i \alpha_j & \beta_i \alpha_j & \alpha_i \beta_j & \beta_i \beta_j \\
  -\frac{1}{4}J_{ij} & 0 & 0 & 0 \\
  0 & \frac{1}{4}J_{ij} & -\frac{1}{2}J_{ij} & 0 \\
  0 & -\frac{1}{2}J_{ij} & \frac{1}{4}J_{ij} & 0 \\
  0 & 0 & 0 & -\frac{1}{4}J_{ij}
\end{pmatrix} \quad (S.1)$$

The operator $\hat{H}_{so} = \zeta \hat{\mathbf{L}} \cdot \hat{\mathbf{s}}$ of the spin-orbit coupling interaction of [Fe(CN)$_6$]$^{3-}$ is represented within the $t_{2g}$ $(\xi, \eta, \zeta)\alpha$ and $(\xi, \eta, \zeta)\beta$ spin-orbital basis as follows (the spin-orbit coupling constant $\zeta$ is defined as positive for Fe$^{III}$):
Combining eqs S1, S2 with the Jahn-Teller Hamiltonian (eq.3), we arrive at the total Hamiltonian (S.3), represented by the product of the spin-orbit basis of Fe$^{III}$ and the spin-only basis of Cu$^{II}$ $\alpha',\beta'$:

$$H_{so} = \begin{pmatrix}
\xi\alpha_1 & \eta\alpha_1 & \zeta\alpha_1 & \xi\beta_1 & \eta\beta_1 & \zeta\beta_1 \\
0 & -\frac{i}{2}\zeta & 0 & 0 & 0 & \frac{1}{2}\zeta \\
\frac{i}{2}\zeta & 0 & 0 & 0 & 0 & -\frac{i}{2}\zeta \\
0 & 0 & 0 & -\frac{1}{2}\zeta & \frac{i}{2}\zeta & 0 \\
0 & 0 & -\frac{i}{2}\zeta & 0 & \frac{i}{2}\zeta & 0 \\
\frac{1}{2}\zeta & \frac{i}{2}\zeta & 0 & 0 & 0 & 0
\end{pmatrix}$$

\[ (S.2) \]

\[ ([\xi,\eta,\zeta]\alpha_1 ; (\xi,\eta,\zeta)\beta_1] \alpha' \text{ and } [(\xi,\eta,\zeta)\alpha_1 ; (\xi,\eta,\zeta)\beta_1] \beta' \]
\[
\begin{pmatrix}
(\xi, \alpha_1) \alpha' & (\eta, \alpha_1) \alpha' & (\zeta, \alpha_1) \alpha' & (\xi, \beta_1) \alpha' & (\eta, \beta_1) \alpha' & (\zeta, \beta_1) \alpha' & (\xi, \alpha_1) \beta' & (\eta, \alpha_1) \beta' & (\zeta, \alpha_1) \beta' & (\xi, \beta_1) \beta' & (\eta, \beta_1) \beta' & (\zeta, \beta_1) \beta'
\end{pmatrix}
\]

\[
H = \begin{pmatrix}
-\frac{J^{(2)}(E)}{4} & -\frac{i}{2} \xi - V, \xi & -V, \xi & 0 & 0 & \frac{i}{2} \xi & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{i}{2} \xi - V, \xi & -\frac{J^{(2)}(E)}{4} & -V, \xi & 0 & 0 & -i \frac{i}{2} \xi & 0 & 0 & 0 & 0 & 0 & 0 \\
-V, \xi & -\frac{J^{(2)}(E)}{4} & -\frac{i}{2} \xi & -\frac{i}{2} \xi - V, \xi & -V, \xi & \frac{i}{2} \xi & 0 & 0 & -\frac{J^{(2)}(E)}{2} & 0 & 0 & 0 \\
0 & 0 & -\frac{i}{2} \xi & -\frac{J^{(2)}(E)}{4} & -V, \xi & -\frac{i}{2} \xi & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{1}{2} \xi & \frac{i}{2} \xi & 0 & -V, \xi & -\frac{J^{(2)}(E)}{4} & \frac{J^{(2)}(E)}{2} & 0 & 0 & 0 & -\frac{J^{(2)}(E)}{2} & 0 & 0 \\
0 & 0 & 0 & -\frac{i}{2} \xi & -\frac{i}{2} \xi - V, \xi & -\frac{i}{2} \xi & 0 & 0 & 0 & 0 & 0 & \frac{i}{2} \xi \\
0 & 0 & 0 & 0 & -\frac{J^{(2)}(E)}{2} & \frac{J^{(2)}(E)}{4} & -V, \xi & 0 & 0 & 0 & 0 & i \frac{i}{2} \xi \\
0 & 0 & 0 & 0 & 0 & -\frac{J^{(2)}(E)}{2} & -V, \xi & -\frac{J^{(2)}(E)}{4} & 0 & \frac{i}{2} \xi & \frac{i}{2} \xi & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{2} \xi & -\frac{i}{2} \xi - V, \xi & -\frac{i}{2} \xi & -\frac{J^{(2)}(E)}{4} & -V, \xi & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{2} \xi & -\frac{i}{2} \xi - V, \xi & -\frac{J^{(2)}(E)}{4} & -V, \xi & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{2} \xi & -\frac{i}{2} \xi - V, \xi & -\frac{i}{2} \xi & -\frac{J^{(2)}(E)}{4}
\end{pmatrix}
\]

(S.3)
We now focus on the particular case of a Fe\textsuperscript{III}-CN-Cu\textsuperscript{II} pair of C\textsubscript{4v} symmetry with no Jahn-Teller distortions on [Fe(CN)\textsubscript{6}]\textsuperscript{3-}. We make use of the eigenfunctions of $H_{SO}$ in the form given in reference \textsuperscript{90} of the manuscript. $E''(\alpha'',\beta'')$ and $U'(\mu,\nu,\kappa,\lambda)$, defined by the column vectors $\mathbf{e}(i)$ ($i=\alpha'', \beta'', \mu, \nu, \kappa, \lambda$), lead to the following matrix, which transforms $H_{SO}$ (eq.S.2) into this basis:

$$\begin{bmatrix}
\mathbf{e}(\alpha'') & \mathbf{e}(\beta'') & \mathbf{e}(\mu) & \mathbf{e}(\nu) & \mathbf{e}(\kappa) & \mathbf{e}(\lambda)
\end{bmatrix} = 
$$

$$T = 
\begin{bmatrix}
0 & \frac{i}{\sqrt{3}} & -
\frac{i}{\sqrt{2}} & 0 & -
\frac{i}{\sqrt{6}} & 0 \\
0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & 0 & -
\frac{1}{\sqrt{6}} & 0 \\
\frac{i}{\sqrt{3}} & 0 & 0 & -
\frac{i}{\sqrt{2}} & 0 & 0 \\
\frac{i}{\sqrt{3}} & 0 & 0 & \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\
-\frac{1}{\sqrt{3}} & 0 & 0 & -
\frac{1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{2}} \\
0 & -
\frac{i}{\sqrt{3}} & 0 & 0 & -
\frac{i}{\sqrt{2}} & 0 
\end{bmatrix}$$

(S.4)

The transformed matrix $T'HT_{SO}T$ is diagonal with eigenvalues $-\zeta[E''(\alpha'',\beta'')]$ and $\zeta/2[U'(\mu,\nu,\kappa,\lambda)]$ and with a Zeeman Hamiltonian in the $z$ direction [i.e. $\hat{H}_{z\hat{z}} = \mu_B(s_z + k\hat{z})B_z$], given by (S.5) and with an effective $M_s'$ value of each of the components of $E''(\alpha'',\beta'')$ and $U'(\mu,\nu,\kappa,\lambda)$ as indicated.

$$M_{s}' = \begin{bmatrix}
\alpha'' & \beta'' & \mu & \nu & \kappa & \lambda \\
1/2 & -1/2 & 3/2 & 1/2 & -1/2 & -3/2
\end{bmatrix}$$

$$H'_{z\hat{z}} = \mu_B B_z
\begin{bmatrix}
-\frac{1}{3} & -\frac{2}{3}k & 0 & 0 & 0 & \frac{\sqrt{2}}{3}(2+k) & 0 & 0 \\
0 & \frac{1}{3} + \frac{2}{3}k & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 - k & 0 & 0 & 0 & 0 & 0 \\
-\frac{\sqrt{2}}{3}(2+k) & 0 & 0 & \frac{1}{3} - \frac{1}{3}k & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{3} + \frac{1}{3}k & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 + k & 0 & 0 
\end{bmatrix}$$

(S.5)
The Fe$^{III}$ [E"(\alpha'',\beta'')] , $M_s' = \pm 1/2$, U'(\mu,\nu,\kappa,\lambda); M_{s,}=\pm 3/2, \pm 1/2, ]$ - Cu$^{II}$ [\alpha',\beta'(m_{s,}=\pm 1/2)] pair states, can then easily be classified according to the total $M_s = M_s'\pm m_s$ value. Using eq.S.4, $H$ can be reduced to a block diagonal form, and utilizing the $C_4v$ symmetry, we arrive at the symmetry-adapted functions of the Fe-Cu pair states and the corresponding energy expressions:

$M_s=\pm 2$:  
\[ H(E) = \frac{1}{2} \zeta - \frac{1}{4} J(\hat{E}) \quad (S.6) \]

$M_s=\pm 1$:  
\[ H(E) = \begin{bmatrix} -\zeta - \frac{1}{6} J(\hat{E}) - \frac{1}{12} J(\hat{B}_2) & \frac{1}{6 \sqrt{2}} [J(\hat{E}) + J(\hat{B}_2)] & \frac{1}{\sqrt{6}} J(\hat{E}) \\ \frac{1}{6 \sqrt{2}} [J(\hat{E}) + J(\hat{B}_2)] & \frac{1}{2} \zeta + \frac{1}{12} J(\hat{E}) - \frac{1}{6} J(\hat{B}_2) & \frac{1}{6 \sqrt{2}} J(\hat{B}_2) \\ \frac{1}{\sqrt{6}} J(\hat{E}) & \frac{1}{2 \sqrt{3}} J(\hat{E}) & \frac{1}{2} \zeta + \frac{1}{4} J(\hat{E}) \end{bmatrix} \quad (S.7) \]

$M_s=0$:  
\[ B_1(E") = \frac{1}{\sqrt{2}} (-\beta'' \alpha'' + \alpha'' \beta'') \quad B_1(U') = \frac{1}{\sqrt{2}} (\kappa \alpha'' + \nu \beta') \]
\[ \begin{bmatrix} -\zeta - \frac{1}{8} J(\hat{E}) - \frac{1}{12} J(\hat{B}_2) & \frac{1}{6 \sqrt{2}} [-J(\hat{E}) + J(\hat{B}_2)] \\ \frac{1}{6 \sqrt{2}} [-J(\hat{E}) + J(\hat{B}_2)] & \frac{1}{2} \zeta - \frac{1}{12} J(\hat{E}) - \frac{1}{6} J(\hat{B}_2) \end{bmatrix} \quad (S.8) \]

$B_2(E") = \frac{1}{\sqrt{2}} (\beta'' \alpha'' + \alpha'' \beta'') \quad B_2(U') = \frac{1}{\sqrt{2}} (\kappa \alpha'' - \nu \beta'')$
\[ \begin{bmatrix} -\zeta - \frac{1}{8} J(\hat{E}) + \frac{1}{4} J(\hat{B}_2) & \frac{1}{2 \sqrt{2}} [J(\hat{E}) + J(\hat{B}_2)] \\ \frac{1}{2 \sqrt{2}} [J(\hat{E}) + J(\hat{B}_2)] & \frac{1}{2} \zeta - \frac{1}{12} J(\hat{E}) + \frac{1}{2} J(\hat{B}_2) \end{bmatrix} \quad (S.9) \]

As follows from (S.8) and (S.9), there is configuration mixing between the pair of states of lowest energy $B_1(E")$, $B_2(E")$ and $B_1(U')$, $B_2(U')$. Using perturbation theory we obtain
for the second order energy change, where exchange terms in the denominator have been neglected. With the values of $J(2E) = 19, J(2B_L) = 1.6$

$$\Delta E[B_1(\Gamma_7)] = -\frac{1}{108} \left[ \frac{J(2B_L) - J(2E)}{\zeta} \right]^2$$  \hspace{1cm} (S.10)

$$\Delta E[B_2(\Gamma_7)] = -\frac{1}{12} \left[ \frac{J(2B_L) + J(2E)}{\zeta} \right]^2$$  \hspace{1cm} (S.11)

and $\zeta = 345$ (all in cm$^{-1}$) we obtain $\Delta E[B_1(E'')] = -0.008$ cm$^{-1}$ and $\Delta E[B_2(E'')] = -0.106$ cm$^{-1}$, that is negligible influence on the ground state spin levels from the Fe$^{III}(U')$ - Cu$^{II}$ excited spin states.

The energies of the lowest four spin states, which arise from Fe$^{III}(E'')$ - Cu$^{II}$ exchange coupling, are given by (as derived in reference 19 in the manuscript and the Supporting Information 1):

$$H_{Fe(\Gamma_7)Cu} = \begin{bmatrix}
\frac{1}{6} J(2E) & 0 & 0 & -\frac{1}{3} \delta J(2E) \\
0 & -\frac{1}{6} J(2E) + \frac{1}{12} J(2B_L) & \frac{1}{6} J(2B_L) & 0 \\
0 & \frac{1}{6} J(2B_L) & -\frac{1}{6} J(2E) + \frac{1}{12} J(2B_L) & 0 \\
-\frac{1}{3} \delta J(2E) & 0 & 0 & \frac{1}{6} J(2E) - \frac{1}{12} J(2B_L)
\end{bmatrix}$$  \hspace{1cm} (S.12)

with $\delta J(2E)$ to account for the possible decrease of symmetry $C_{4v} \rightarrow C_{2v}$:

$$\delta J(2E) = \frac{J_{zz} - J_{yy}}{2}$$  \hspace{1cm} (S.13)

$$J(2E) = \frac{J_{zz} + J_{yy}}{2}$$  \hspace{1cm} (S.14)

The parameters J, D and E in the spin Hamiltonian $\hat{H}_{sph}$ (S.15, i.e. a simplified form of eq.4) are derived by comparing S.12 with the representation of $\hat{H}_{sph}$ using the basis $\alpha''\alpha'$, $\beta''\alpha'$, $\alpha''\beta'$, $\beta''\beta'$;

$$\hat{H}_{sph} = -J s_1^z s_2^z + \frac{2D}{3} (2s_1^z s_2^z - s_1^x s_2^x - s_1^y s_2^y) + 2E (s_1^z s_2^z - s_1^y s_2^y)$$  \hspace{1cm} (S.15)
In going from (S.15) to (S.16) we make use of the following substitutions:

\[
-H_{\text{sph}} = \begin{bmatrix}
-\frac{1}{4}J + \frac{1}{3}D & 0 & 0 & E \\
0 & -\frac{1}{4}J - \frac{1}{3}D & -\frac{1}{2}J - \frac{1}{3}D & 0 \\
0 & -\frac{1}{2}J - \frac{1}{3}D & \frac{1}{4}J - \frac{1}{3}D & 0 \\
E & 0 & 0 & -\frac{1}{4}J + \frac{1}{3}D
\end{bmatrix}
\] (S.16)

\[
-s_{i}^{\dagger}s_{2} \Rightarrow \begin{bmatrix}
-\frac{1}{4} & 0 & 0 & 0 \\
0 & \frac{1}{4} & -\frac{1}{2} & 0 \\
0 & -\frac{1}{2} & \frac{1}{4} & 0 \\
0 & 0 & 0 & -\frac{1}{4}
\end{bmatrix}
\] (S.17)

\[
2s_{1x}^{\dagger}s_{2x} - s_{1x}^{\dagger}s_{2x} - s_{1y}^{\dagger}s_{2y} \Rightarrow \begin{bmatrix}
\frac{1}{2} & 0 & 0 & 0 \\
0 & -\frac{1}{2} & \frac{1}{2} & 0 \\
0 & -\frac{1}{2} & \frac{1}{2} & 0 \\
0 & 0 & 0 & \frac{1}{2}
\end{bmatrix}
\] (S.18)

\[
s_{1x}^{\dagger}s_{2x} - s_{1y}^{\dagger}s_{2y} = \begin{bmatrix}
0 & 0 & \frac{1}{2} \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\frac{1}{2} & 0 & 0
\end{bmatrix}
\] (S.19)

These can be derived, using the direct products $s_{i} \otimes s_{j}$ (i,j=x,y,z) of the spinmatrices for $s=1/2$. 
\[
\begin{align*}
\alpha & \beta & \alpha & \beta & \alpha & \beta \\
\mathbf{s}_x &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \\
\mathbf{s}_y &= \frac{i}{2} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}; \\
\mathbf{s}_z &= \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}; \\
\end{align*}
\] (S.20)

\[
\begin{align*}
-\frac{1}{4}J + \frac{1}{3}D &= \frac{1}{6}J(\hat{\zeta}E) - \frac{1}{12}J(\hat{\zeta}B_2) \\
-\frac{1}{2}J - \frac{1}{3}D &= \frac{1}{6}J(\hat{\zeta}B_2) \\
E &= -\frac{1}{3}J(\hat{\zeta}E)
\end{align*}
\] (S.21, S.22, S.23)

From (S.21) and (S.22) result the expressions of J and D (eq.14).

Is it always possible to derive the parameters of the spin Hamiltonian from first principle calculations? There is a configuration mixing between the spin multiplets due to the E’-Cu\textsuperscript{II} and the multiplets due to the U’-Cu\textsuperscript{II} interaction via exchange coupling terms. In the discussed example, \(\zeta \gg J(\hat{\zeta}E), J(\hat{\zeta}B_2)\) and the parameters J,D and E (S.21-S.23) can be uniquely determined. However, starting from Fe\textsuperscript{III}-CN-Cu\textsuperscript{II} with a C\textsubscript{4v} geometry and octahedral [Fe(CN)\textsubscript{6}]\textsuperscript{3-}, and introducing a D\textsubscript{3d} Jahn-Teller distortion U’ splits and starts to mix with E’. In Figure S.2, we plot the electronic energy levels of [Fe(CN)\textsubscript{6}]\textsuperscript{3-} in dependence of the ratio \(V_rQ_3/\zeta\) [obtained by diagonalization of the Hamiltonian S.3 with \(J(\hat{\zeta}E)=J(\hat{\zeta}B_2)=0\)]. It follows, that the electronic ground state is well separated from the excited states both in \(O_h\) and in the distorted D\textsubscript{3d} geometries. One can understand this result if one transforms the spin-orbit coupling matrix into the trigonal basis of eq.S.24.
Figure S.2. Electronic levels of $[\text{Fe(CN)}_6]^{3-}$ in dependence of the vibronic coupling energy in units of $\zeta$.

In this basis, $H_{\text{JT}}$ is diagonal with the energies of $^2A_1$ and $^2E$, given by $-2V_1Q_1$ and $V_1Q_1$, respectively.

$$\varphi(A_1) = \frac{1}{\sqrt{3}} (\zeta + \eta + \zeta)$$

$$\varphi(E_y) = \frac{1}{\sqrt{2}} (\zeta - \eta)$$

$$\varphi(E_x) = \frac{1}{\sqrt{6}} (-\zeta - \eta + 2\zeta)$$

(S.24)

While $^2A_1$ is the ground state for trigonally compressed geometries, it is of $^2E$ symmetry in elongated geometries. However the $^2E$ term splits to first order by spin-orbit coupling with an energy difference between the ground state $E'(1)$ and the $E''$ lowest excited state given by $\zeta$. It is again much larger than $J(^2E)$ and $J(^2B_2)$. Therefore, one can safely apply the spin-Hamitonian (eq.4) and deduce its parameters by comparison with the eigenvalues of eq.(1) in the whole range of Jahn-Teller-distorted geometries between $Q_z = -0.256$ and $-0.256\text{Å}$. In the given example (Table 5, $Q_z = 0.128$ Å for Fe-Cu) one first diagonalizes $H_{\text{SO}} + H_{\text{JT}}$, including the Zeeman matrix with a small magnetic field ($B_z = 0.0001$ T), providing the proper components $\alpha''$ and $\beta''$ of the
ground state Kramers doublet E'(1) (Figure S.2). With the resulting eigenvectors, one transforms the Hamiltonian (eq.S.3), yielding the following traceless matrix (with energies in cm\(^{-1}\)) of the ground state spin levels:

\[
\begin{bmatrix}
3.038 & 0.615 & 0.200(-1+i) & -2.933(1-i) \\
0.615 & -3.038 & 0.020(-1+i) & 0.200(1-i) \\
0.200(-1-i) & 0.020(-1-i) & -3.038 & -0.615 \\
-2.933(1+i) & 0.200(1+i) & -0.615 & 3.038 \\
\end{bmatrix}
\]

(S.25)

One can show, using simple manipulations (as described e.g. by eq.S.15-S.20), that within the \(\alpha''\alpha'\), \(\beta''\alpha'\), \(\alpha''\beta'\) and \(\beta''\beta'\) basis, the spin-Hamiltonian of eq.4 leads to the matrix representation given by eq. S.26. From the comparison of S.25 and S.26 the spin-Hamiltonian parameters of Fe-Cu from Table 5 has been obtained (entry for \(Q_{x} = 0.128 \, \text{Å}\)).

Finally, within the spin-only basis and without distortions on \([\text{Fe(CN)}_6]^3-\), the Zeeman operator \(\hat{H}_{z_1}\) is represented by the matrices given in eq.S.27-S.29, showing directly the coupling of the local g-tensors of Fe\(^{III}\) and Cu\(^{II}\).

\[
\begin{bmatrix}
\frac{1}{3}D - \frac{1}{4}J & \frac{1}{4}(D_{xx} - iD_{yx} + iA_x - A_y) & \frac{1}{4}(D_{xx} - iD_{yx} - iA_x + A_y) & E - \frac{1}{2}iD_{yy} \\
\frac{1}{4}(D_{yy} + iD_{yx} + iA_x + A_y) & \frac{1}{4}(D_{xx} - iD_{yx} - iA_x + A_y) & \frac{1}{4}(D_{xx} - iD_{yx} + iA_x - A_y) & E + \frac{1}{2}iD_{yy} \\
\frac{1}{4}(D_{yx} + iD_{yy} - iA_y + A_x) & \frac{1}{4}(D_{yy} - iD_{yx} + iA_x - A_y) & \frac{1}{4}(D_{yy} - iD_{yx} + iA_x - A_y) & E - \frac{1}{2}iD_{yy} \\
\frac{1}{4}(D_{yx} - iD_{yy} + iA_y + A_x) & \frac{1}{4}(D_{yy} - iD_{yx} - iA_x + A_y) & \frac{1}{4}(D_{yy} - iD_{yx} + iA_x - A_y) & E + \frac{1}{2}iD_{yy} \\
\end{bmatrix}
\]

(S.26)

\[
\begin{bmatrix}
0 & -\frac{1}{3} - \frac{2}{3}k & \frac{1}{2}g_{2x} & 0 \\
-\frac{1}{3} - \frac{2}{3}k & 0 & 0 & \frac{1}{2}g_{2x} \\
\frac{1}{2}g_{2x} & 0 & 0 & -\frac{1}{3} - \frac{2}{3}k \\
0 & \frac{1}{2}g_{2x} & -\frac{1}{3} - \frac{2}{3}k & 0 \\
\end{bmatrix}
\]

(S.27)
The Hamiltonian and the z component of the Zeeman matrix for the Fe$^{III}$-CN-Ni$^{II}$ Pair

Applying consistently the same procedure as for the Fe$^{III}$-Cu$^{II}$ pair, we have derived the matrix of the Hamiltonian (eq.1) which results from the spin coupling between [Fe(CN)$_6$]$^{3-}$ and the S=1 (M$_s$=±1,0) ground state of Ni$^{II}$ for a binuclear unit with C$_{4v}$ symmetry. Restricting to the manifold of the six spin states pertaining to the coupling of the [Fe(CN)$_6$]$^{3-}$ in its ground state E" and the S=1 state of Ni$^{II}$, we list the energy matrix in eq. S.30 and the z component of the Zeeman matrix in eq.31. Exchange coupling parameters have already been specified for the Fe$^{III}$-Cu$^{II}$ pair, D$_{Ni}$ is the zero-field splitting parameter of Ni$^{II}$. We notice, that in the ground (excited) E"(1) [E"(2)] spin states D$_{Ni}$ is added (subtracted) from the diagonal energy term, thus leading to an increase (decrease) of the spin energy gap for negative (positive) values of D$_{Ni}$. Taking the difference between the diagonal matrix elements, i.e. E(α,"0; β",0)-E(α","1; β","1) eq.18 is derived.

As in the case of the Fe$^{III}$-Cu$^{II}$ pair, spin Hamiltonian theory is applicable for the Fe$^{III}$-Ni$^{II}$ spin-cluster of a general C$_s$ symmetry, and the parameters of eq.4 can be derived from a comparison between the (traceless) 6x6 energy matrix (eq.S.32, Q$_z$= 0.128 Å) and the spin Hamiltonian, written in the parametric form of eq.S.33. Numerical values are listed in Table 5.
Finally g-tensor values of the Fe$^{III}$-Cu$^{II}$ and Fe$^{III}$-Ni$^{II}$ with bistable ground states listed in Table 9 have been calculated using a well documented procedure (reference 87 of the manuscript).
\[
H = \begin{bmatrix}
\frac{1}{3}J(\hat{\chi}E) - \frac{1}{6}J(\hat{\chi}B_z) + \frac{1}{3}\mathcal{D}_N & 0 & 0 & -\frac{\sqrt{2}}{3}\delta J(\hat{\chi}E) & 0 & 0 \\
0 & -\frac{1}{3}J(\hat{\chi}E) + \frac{1}{6}J(\hat{\chi}B_z) + \frac{1}{3}\mathcal{D}_N & \frac{1}{3}\sqrt{2}J(\hat{\chi}B_z) & 0 & 0 & 0 \\
0 & 0 & -\frac{2}{3}\mathcal{D}_N & \frac{1}{3}\sqrt{2}J(\hat{\chi}B_z) & 0 & 0 \\
-\frac{\sqrt{2}}{3}\delta J(\hat{\chi}E) & 0 & 0 & -\frac{2}{3}\mathcal{D}_N & \frac{1}{3}\sqrt{2}J(\hat{\chi}B_z) & 0 \\
0 & 0 & 0 & -\frac{1}{3}\sqrt{2}J(\hat{\chi}B_z) & -\frac{1}{3}J(\hat{\chi}E) + \frac{1}{6}J(\hat{\chi}B_z) + \frac{1}{3}\mathcal{D}_N & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{3}\sqrt{2}J(\hat{\chi}B_z) & -\frac{1}{3}J(\hat{\chi}E) + \frac{1}{6}J(\hat{\chi}B_z) + \frac{1}{3}\mathcal{D}_N
\end{bmatrix}
\]

(S.30)

\[
\begin{bmatrix}
\alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \\
-\frac{1}{3} - \frac{2}{3}k + g_{z2} & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{3} + \frac{2}{3}k + g_{z2} & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{3} - \frac{2}{3}k & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{3} + \frac{2}{3}k & 0 & 0 \\
0 & 0 & 0 & 0 & -\frac{1}{3} - \frac{2}{3}k - g_{z2} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{3} + \frac{2}{3}k - g_{z2}
\end{bmatrix}
\]

(S.31)
$H_{\text{sph}} = \begin{bmatrix}
\alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \\
4.039 & 0.995 & 0.0995(-1+i) & -2.669(1-i) & 0 & 0 \\
0.995 & -4.039 & -0.107(1-i) & 0.0995(1-i) & 0 & 0 \\
0.0995(-1-i) & -0.107(1+i) & 0 & 0 & -0.0995(1-i) & -2.669(1-i) \\
-2.669(1+i) & 0.0995(1+i) & 0 & 0 & -0.107(1-i) & 0.0995(1-i) \\
0 & 0 & -0.0995(1+i) & -0.107(1+i) & -4.039 & -0.995 \\
0 & 0 & -2.669(1+i) & 0.0995(1+i) & -0.995 & 4.039
\end{bmatrix}$

(S.32)

$H_{\text{qph}} = \begin{bmatrix}
\alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \\
\frac{2}{3}D - \frac{1}{2}J & \frac{1}{2}(D_{\omega} - iD_{\omega} - iA_{\omega} - A_{\omega}) & \frac{1}{2\sqrt{2}}(D_{\omega} - iD_{\omega} + iA_{\omega} + A_{\omega}) & \frac{\sqrt{2}E - \frac{i}{\sqrt{2}}D_{\omega}}{\sqrt{2}E + \frac{i}{\sqrt{2}}D_{\omega}} & 0 & 0 \\
\frac{1}{2}(D_{\omega} + iD_{\omega} + iA_{\omega} - A_{\omega}) & \frac{2}{3}D + \frac{1}{2}J & -\frac{\sqrt{2}}{3}D - \frac{1}{\sqrt{2}}J - \frac{i}{\sqrt{2}}A_{\omega} & \frac{1}{2\sqrt{2}}(-D_{\omega} + iD_{\omega} - iA_{\omega} - A_{\omega}) & 0 & 0 \\
\frac{1}{2\sqrt{2}}(D_{\omega} + iD_{\omega} - iA_{\omega} + A_{\omega}) & 0 & \frac{1}{2\sqrt{2}}(D_{\omega} - iD_{\omega} + iA_{\omega} + A_{\omega}) & \frac{\sqrt{2}E - \frac{i}{\sqrt{2}}D_{\omega}}{\sqrt{2}E + \frac{i}{\sqrt{2}}D_{\omega}} & 0 & 0 \\
\sqrt{2}E + \frac{i}{\sqrt{2}}D_{\omega} & 0 & \frac{1}{2\sqrt{2}}(-D_{\omega} - iD_{\omega} + iA_{\omega} - A_{\omega}) & 0 & 0 & 0 \\
0 & 0 & \frac{1}{2\sqrt{2}}(D_{\omega} + iD_{\omega} - iA_{\omega} + A_{\omega}) & -\frac{\sqrt{2}}{3}D - \frac{1}{\sqrt{2}}J + \frac{i}{\sqrt{2}}A_{\omega} & \frac{1}{2\sqrt{2}}(-D_{\omega} + iD_{\omega} - iA_{\omega} - A_{\omega}) & 0 & 0 \\
0 & 0 & 0 & \frac{\sqrt{2}E + \frac{i}{\sqrt{2}}D_{\omega}}{\sqrt{2}E - \frac{i}{\sqrt{2}}D_{\omega}} & \frac{1}{2\sqrt{2}}(-D_{\omega} - iD_{\omega} + iA_{\omega} - A_{\omega}) & \frac{1}{2\sqrt{2}}(-D_{\omega} + iD_{\omega} - iA_{\omega} - A_{\omega}) & \frac{1}{2\sqrt{2}}(-D_{\omega} + iD_{\omega} + iA_{\omega} + A_{\omega}) & \frac{2}{3}D - \frac{1}{2}J
\end{bmatrix}$

(S.33)
Dynamic Jahn-Teller Coupling

Since the Fe$^{\text{III}}$-CN bond is stronger than the Cu$^{\text{II}}$-NC and Ni$^{\text{II}}$-NC bonds, we can restrict vibronic coupling to the [Fe(CN)$_6$]$^{3-}$ unit and consider only the $\tau_{2g}$ mode for its vibronic levels. One can readily extend eq.1 with the nuclear kinetic and potential energy operators (eq.S.34); $\hbar \omega_\tau$ is the energy of the three-dimensional harmonic oscillator

$$\hat{H}_{\text{vib}} = \frac{1}{2} \hbar \omega_\tau (\hat{P}_z^2 + \hat{P}_\eta^2 + \hat{P}_\zeta^2 + \hat{Q}_z^2 + \hat{Q}_\eta^2 + \hat{Q}_\zeta^2) \quad (\text{S.34})$$

(93 cm$^{-1}$ for [Fe(CN)$_6$]$^{3-21}$); $\hat{P}_i$ and $\hat{Q}_i$ are dimensionless operators related to the observables for momentum and position and given by eq.S.35. The vibronic eigenfunctions $\Psi$ of the total Hamiltonian $\hat{H} + \hat{H}_{\text{vib}}$ are expressed as a linear combination of products of the spin-orbital basis functions $\varphi_i$ of $\hat{H}$ and the eigenstates of the states of $\hat{H}_{\text{vib}}$ (the three-dimensional harmonic oscillator functions $\chi_j(\hat{Q}_z^i)\chi_k(\hat{Q}_\eta^i)\chi_l(\hat{Q}_\zeta^i)$) up to the level $n_v$:

$$\Psi = \sum_{i=1}^{6} \sum_{j} \sum_{k} \sum_{l} \sum_{j+k+l=0}^{n_v} c_{ijkl} \varphi_i(\chi_j(\hat{Q}_z^i)\chi_k(\hat{Q}_\eta^i)\chi_l(\hat{Q}_\zeta^i)) \quad (\text{S.36})$$

The total basis size $N_v$ without exploitation of the vibronic symmetries is given by eq.S.37,

$$N_v = n_{\text{sp}} 6[\frac{n_v(n_v^2 + 6n_v + 11)}{6} + 1] \quad (\text{S.37})$$
where $n_M$ is the spin-degeneracy of Cu$^{II}$ ($n_M=2$) or Ni$^{II}$ ($n_M=3$). For the moderate vibronic coupling strength obtained in [Fe(CN)$_6$]$^{3-}$ good accuracy (equal or better than 2%) for the calculated lowest 4 or 6 spin states for Fe$^{III}$-Cu$^{II}$ and Fe$^{III}$-Ni$^{II}$, respectively, and for the g-tensor has been achieved with $n_v=6$, leading to a total dimension of the vibronic matrix of 1008x1008 and 1512x1512, respectively.

Fig.S.3. (a) The Fe$^{III}$-M$^{II}$ (M$^{II}$=Cu$^{II}$,Ni$^{II}$: white, Fe$^{III}$: black) pair with a linear Fe$^{III}$-CN-M$^{II}$ ($C_4v$) bridge and a regular [Fe(CN)$_6$]$^{3-}$ center; the arrows indicate the directions for optimal $\pi$-overlap between the singly occupied $t_{2g}$ ($d_{xz,yz}$) orbitals of Fe$^{III}$ ($t_{2g}^5$) and the fully occupied $d_{xz}, d_{yz}$ orbitals of Cu$^{II}$ (Ni$^{II}$). (b) The Fe$^{III}$-M$^{II}$ (M$^{II}$=Cu$^{II}$,Ni$^{II}$) pair with a trigonally distorted [Fe(CN)$_6$]$^{3-}$ center and a $^{2}A_{1g}$ ($d_{z^2}$, $D_{3d}$) ground state with $d_{z^2}$ lobes pointing towards the body diagonals of a cube with four different (but equivalent) geometries (minima of the ground state potential energy surface, misalignment of the singly occupied $d_{z^2}$ orbital of [Fe(CN)$_6$]$^{3-}$ and the $\pi$ ($d_{xz},d_{yz}$) orbitals of Cu$^{II}$ (Ni$^{II}$)).
Effect of the DFT functional on the exchange parameters \( J(B_2)[\text{Fe}^{III}(e_g^4b_{2g}^{-1})-\text{Cu}^{II}] \) and \( J(E) \) \( [\text{Fe}^{III}(e_g^3b_{2g}^{-2})-\text{Cu}^{II}] \) and further on the spin-levels and the magnetic anisotropy on \( \text{Fe}^{III}-\text{CN}-\text{Cu}^{II} \) exchange pairs without \( (C_4v) \) and with \( (C_s) \) Jahn-Teller distortions of \( \tau_{2g} \) type.

Table S.1. The exchange coupling energy (\( J \), in cm\(^{-1}\), \( \Delta H_{ex}=-J_S S_2 \)) for the exchange pair \( \text{Fe}^{III}-\text{CN}-\text{Cu}^{II}(d_{z^2}) \) from DFT broken spin DFT calculations with (SP) and without (SUP) spin-projection, in dependence of the adopted functional and the electronic configuration of \( \text{Fe}^{III} \), in comparison with the value deduced from magnetic data.

<table>
<thead>
<tr>
<th>electronic configuration of ( [\text{Fe}(\text{CN})_6]^{3-} )</th>
<th>( J )</th>
<th>VWN</th>
<th>PW91</th>
<th>PBE</th>
<th>OPBE</th>
<th>B3LYP 20%HF</th>
<th>B1LYP 25%HF</th>
<th>B3LYP* 15%HF</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_2^{e^4} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( J_{\text{SP}} )</td>
<td>-45.2</td>
<td>-67.7</td>
<td>-69.2</td>
<td>-112.9</td>
<td>-6.4</td>
<td>1.6</td>
<td>-16.2</td>
<td>17.0(^c)</td>
<td></td>
</tr>
<tr>
<td>( J_{\text{SUP}} )</td>
<td>-22.6</td>
<td>-33.9</td>
<td>-34.7</td>
<td>-56.5</td>
<td>-3.2</td>
<td>0.8</td>
<td>-8.1</td>
<td>13.8; 3.9 (^d)</td>
<td></td>
</tr>
<tr>
<td>( b_2^{e^3} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( J_{\text{SP}} )</td>
<td>114.6</td>
<td>95.2</td>
<td>95.2</td>
<td>103.2</td>
<td>27.4</td>
<td>19.4</td>
<td>35.5</td>
<td>20.9 (^e)</td>
<td></td>
</tr>
<tr>
<td>( J_{\text{SUP}} )</td>
<td>57.3</td>
<td>47.6</td>
<td>47.6</td>
<td>51.6</td>
<td>13.7</td>
<td>9.7</td>
<td>17.7</td>
<td>5.0 (^f)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculated with the spin-projected formula: \( J_{\text{SP}}=(E_{\text{BS}}-E_{\text{HS}})/(2S_1S_2) \); \( E_{\text{BS}} \) and \( E_{\text{HS}} \) are the energies of the \( (\uparrow\downarrow) \) broken-spin and the \( (\uparrow\uparrow) \) high-spin Slater determinants.

\(^b\) Calculated with the spin-unprojected formula: \( J_{\text{SUP}}=(E_{\text{BS}}-E_{\text{HS}})/(2S_1S_2+S_2) \), \( S_2 \leq S_1 \);

\(^c\) Reported from a fit to magnetic susceptibility data of the \( \text{Cu}_3\text{Fe}_2 \) SMM with a \( d_{x^2-y^2} \) ground state of \( \text{Cu}^{II} \); to compare with the calculated numbers \( (d_{z^2} \) ground state of \( \text{Cu}^{II} \)), the experimental energy has to be multiplied by \( 2/\sqrt{3} \).

\(^d\) Reported for the two distinct \( \text{Fe}^{III}-\text{CN}-\text{Cu}^{II} \) exchange coupled pairs in the \( \text{Fe}^{III}_2\text{Cu}^{II}_3 \) complex

\([\{\text{Cu(rac-CTH)}\}_3\{\text{Fe(CN)}_6\}_2] \cdot 2\text{H}_2\text{O}, \text{rac-CTH}=\text{rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane from simulations using a Heisenberg Hamiltonian.}\(^{19}\)

\(^e\) Reported from Monte Carlo simulations of the magnetic properties of heterobimetallic chain

\([\{\text{Fe}^{III}(\text{bpym})(\text{CN})_4\}_2\text{M}^{II}(\text{H}_2\text{O})_2\}_2 \cdot 6\text{H}_2\text{O}, \text{bpym}=2,2’\text{-bipyrimidine using an isotropic Heisenberg model.}\(^{20}\)

\(^f\) Reported from a fit of the isotropic \( J \) to magnetic susceptibility data on the bimetallic complex

\([\{\text{Fe}^{III}(\text{phen})(\text{CN})_4\}_2\text{Cu}^{II}(\text{H}_2\text{O})_2\}_2 \cdot 4\text{H}_2\text{O} \).\(^{21}\)
Footnote

1 Matrix S.12 differs in sign compared to the one given in manuscript reference 22 (and derived in detail the Supporting information there). This is because real spins rather than effective spins of Fe$^{III}$ have been employed in the cited work (implying $g$ tensors of Fe$^{III}$ and Cu$^{II}$ which are of the same sign). This has lead to the conventional negative $D$ and a positive $J$ values. Here we should stress, this is only possible if $J(2B_2)=0$, in which case $B_1$ and $B_2$ (Figure 3) become accidentally degenerate. In a consistent description however, one should keep to the definitions and sign conventions of manuscript reference reference 93 which allows also to provide a correct symmetry description.