Covalently Linked Dimer of Mn$_3$ Single-Molecule Magnets and Retention of Its Structure and Quantum Properties in Solution

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Supporting Information

ABSTRACT: [Mn$_3$O(O$_2$CMe)$_3$(dpd)$_3$](I$_3$)$_2$ has been obtained from the reaction of 1,3-di(pyridin-2-yl)propane-1,3-dione dioxime (dpdH$_2$) with triangular [Mn$_{3	ext{III}}$O(O$_2$CMe)(py)$_3$](ClO$_4$). It comprises two [Mn$_{3	ext{III}}$O]$_7^+$ triangular units linked covalently by three dioximate ligands into a [Mn$_3$]$^2_2$ dimer. Solid-state dc and ac magnetic susceptibility measurements reveal that each Mn$_3$ subunit of the dimer is a separate single-molecule magnet (SMM) with an $S = 6$ ground state and that the two SMM units are very weakly ferromagnetically exchange coupled. High-frequency EPR spectroscopy on a single crystal displays signal splittings indicative of quantum superposition/entanglement of the two SMMs, and parallel studies on MeCN/toluene (1:1) frozen solutions reveal the same spectral features. The dimer thus retains its structure and inter-Mn$_3$ coupling upon dissolution. This work establishes that covalently linked molecular oligomers of exchange-coupled SMMs can be prepared that retain their oligomeric nature and attendant SMM quantum mechanical coupling in solution, providing a second phase for their study and demonstrating the feasibility of using solution methods for their deposition on surfaces and related substrates for study.

INTRODUCTION

Single-molecule magnets (SMMs) are molecules that function as nanoscale magnetic particles below their blocking temperature, $T_B$, as a result of their significant magnetic moment and easy-axis magnetooisotropy that lead to a large (vs $kT$) barrier to magnetization relaxation. They bring to nanomagnetism the advantages of molecular chemistry (ambient-temperature synthesis, solubility, crystallinity, monodispersity, organic ligands, etc.), and these have been crucial in demonstrating that SMMs also display fascinating quantum phenomena such as quantum tunneling of magnetization (QTM), quantum phase interference, spin–spin cross relaxation, and quantum entanglement. SMMs have consequently been proposed as qubits for quantum information processing and as components in molecular spintronics devices. These potential applications of SMMs require the quantum mechanical coupling of two or more SMMs to each other or to other components of a device while maintaining the intrinsic single-molecule properties of each SMM. Such couplings were successfully identified for hydrogen-bonded supramolecular pairs of $S = 9/2$ [Mn$_4$O$_3$Cl$_4$(O$_2$CET)$_3$(py)$_3$] SMMs and manifested as exchange-biased QTM, quantum superposition states, and quantum entanglement of SMMs. However, reliance on hydrogen bonding to provide the inter-SMM interactions was a weakness of the previous work, since it is not so easy to control the oligomerization or guarantee retention of the oligomeric structure in solution. We therefore recently extended this work to aggregates of Mn SMMs linked by covalent organic linkages to provide greater control of various aspects of the oligomerization while still targeting molecular oligomers rather than polymers. We recently reported a [Mn$_4$]$^4_4$ tetramer of SMMs, covalently linked with dioximate linker groups, as the first result of this new direction. It provided proof-of-feasibility for our chosen approach and for developing molecular multiqubit systems based on SMMs in which the quantum-mechanically coupled aggregates might be stable to dissociation in solution and thus provide a route for deposition of aggregates on surfaces without complications from fragmentation or other loss of structural integrity on dissolution, the problems almost always associated with hydrogen-bonded supramolecules or hydrogen-bonded or covalently linked 0-, 1-, 2-, or 3-D aggregates. The methodology also provides a convenient means via ligand design to tune the strengths (and ferro- or antiferromagnetic nature) of the inter-SMM coupling, as has been reported, for example, in the coupling strength in a series of Cr$_7$Ni dimers by modifying the...
aromatic linker. Ferromagnetic coupling within dimeric or trimeric molecular aggregates is relatively rare but has sometimes been achieved in non-SMMs through a spin polarization mechanism even when the metal ions are well separated. An additional challenge with SMM oligomers that we had to now also address was the desire to achieve parallel alignment of the easy axes of the constituent SMM units to allow application of an external field parallel to these axes and thus minimize the number of parameters that must be included in order to model the nebulous and fragile quantum properties that are a major driving force of the program.

We report here a covalently linked dimer of Mn₃ SMMs obtained using a specially designed dioximate linker that also ensures parallel easy axes and show that the dimer exhibits weak ferromagnetic inter-Mn₃ exchange coupling. High-frequency electron paramagnetic resonance (HF-EPR) studies on a single crystal establish that the dimer exhibits quantum mechanical coupling leading to quantum superposition states (entanglement) of the two SMMs. Further, we demonstrate for the first time that this situation persists upon dissolution, the superposition states being detected by HF-EPR spectroscopy on a frozen solution.

**RESULTS AND DISCUSSION**

**Synthesis and X-ray Structure.** The synthesis of a dioximate-linked dimer of Mn₃ SMMs is based on the previous observation that the mono-oxime mpkoH will react with non-SMM [Mn₃O(O₂CMe)₆(py)₃][ClO₄] (1) to give [Mn₃O(O₂CMe)₆(mpko)₃][ClO₄] (2), which has an S = 6 ground state and is an SMM. The cation of 2 (Figure 1) has C₃ symmetry with the acetate and mpko⁻ ligands on opposite sides of the Mn₃ plane. The tripodal arrangement of oximates suggested that their replacement with dioximates should give molecular oligomers rather than polymers. This was confirmed with dioxime dpdH₂ (Figure 1), which gave a rectangular [Mn₃]₄ tetramer, but the conformationally flexible dpd⁻ linkers were not “preprogrammed” to produce a particular structural topology, and neither were the Mn₃ planes parallel.

With proof-of-feasibility of the oligomerization strategy established, the first targeted oligomer was now a [Mn₃]₂ dimer with the two Mn₃ planes parallel to facilitate subsequent study of the quantum properties. Consideration of basic principles from the supramolecular chemistry field led to selection of dioxime dpdH₂ (Figure 1), a fusion of two mpkoH units at the Me group. The single sp³ carbon atom at the center reduces the conformational flexibility, and according to the directional bonding approach for constructing supramolecules, the combination of a ~109° ditopic dioximate with a tritopic Mn₃ unit should yield a [Mn₃]₂ dimer with three linker groups and parallel Mn₃ planes. Moreover, the firm binding by tridentate pyridyloximate groups of three dpd⁻ linkers was considered favorable for imparting rigidity and robustness to the resulting dimer, hopefully leading to retention of the structure in solution. Also important in the selection of dpdH₂ was that a single sp³ carbon atom was expected to ensure that the superexchange interaction between two Mn₃ SMMs would be very weak (but nonzero) and thus merely a small perturbation on a two-SMM system. We found no previous use of dpdH₂ in inorganic chemistry.

The dpdH₂ was synthesized using reported procedures for the dione and conversion to the dioxime. Reaction of 1 with dpdH₂ and I₂ in a 2:3:6 molar ratio in CH₂Cl₂/EtOH (25:1 v/v) gave a dark brown solution, which was filtered, and the filtrate was allowed to slowly concentrate by evaporation to give black crystals of [Mn₆O₂(O₂CMe)₆(dpd)₃][ClO₄] (1) (eq 1). I₂ was added to prevent reduction of some of the MnIII to MnII, as sometimes seen during preliminary studies of oligomerization of triangular Mn¹¹ complexes.

\[
2[Mn₃O(O₂CMe)₆(py)₃]⁺ + 3dpdH₂ → [Mn₆O₂(O₂CMe)₆(dpd)₃]^{12⁺} + 6MeCO₂H + 6py
\]

Complex 3 crystallizes in trigonal space group P31c with the cation on a crystallographic C₃ axis. As targeted by the choice of dpdH₂, the structure of the Mn²⁺ cation consists of two [Mn₃(μ₃-O)]⁷⁻ units linked by three dpd⁻ groups to give a [Mn₃]₂ dimer of crystallographic D₃h symmetry (Figure 2). The two Mn₃ planes are thus parallel. Each Mn₃ unit is an equilateral triangle (Table 1) and structurally very similar to that of monomer 2, comprising a [Mn₃(μ₃-O)]⁷⁻ triangular unit whose edges are each bridged by one acetate and one pyridyloximate group and with the μ₃-O⁻ ions lying slightly (~0.29 Å) above their Mn₃ plane. The Mn¹¹ oxidation states were confirmed by bond valence sum (BVS) calculations (Table S1, Supporting Information), and their Jahn–Teller elongation axes (green bonds in Figure 2, right) are clearly along the O(carb)–Mn–O(ax) bonds (Table 1) and aligned in a propeller fashion, again as in 2. Inspection of the crystal packing shows that not only are the two Mn₃ planes of each dimer parallel but also all dimer molecules are oriented identically (Figure S1, Supporting Information). There are no close interdimer contacts between carboxylate groups, with the
shortest separation being ∼3.7 Å (Figure S2, Supporting Information, top). Also, the shortest distance between Mn ions of adjacent dimers is ∼8.16 Å, suggesting that dipolar interactions between different [Mn₃]₂ dimers can be neglected. This is consistent with the absence of an exchange bias in the magnetization hysteresis loops for monomer 2, where the separations between adjacent Mn₃ molecules are comparable to those between adjacent dimers in 3. This will be important to the magnetic and EPR discussions below.

**Magnetic Studies.** Two important questions needing to be addressed by the magnetic studies on 3 were (i) is each Mn₃ subunit still an SMM with S = 6 and (ii) is there any evidence for a weak inter-Mn₃ interaction within the [Mn₃]₂ dimer? Variable-temperature, direct current (dc) magnetic susceptibility (χM) measurements were performed on dried samples of 3, restrained in eicosane to prevent torquing, in an applied field of 1.0 kG (0.10 T) and in the 5.0–300 K range. χM per dimer increases steadily from 25.93 cm³ K mol⁻¹ at 300 K to a quasi-plateau value of 40.04 cm³ K mol⁻¹ at 20 K and then increases steeply to 45.70 cm³ K mol⁻¹ at 5.0 K (Figure 3). The profile above 20 K is the same as that for monomer 2 and is as expected for ferromagnetic coupling within each Mn₃ unit giving an S = 6 ground state. The quasi-plateau value at low T is as expected for two ostensibly noninteracting S = 6 units with g slightly <2.0, which is typical for MnIII; the spin-only (g = 2.0) value for S = 6 is 21 cm³ K mol⁻¹ and thus 42 cm³ K mol⁻¹ for a dimer of noninteracting S = 6 units. The increase in χM per dimer at T < 20 K is assigned to very weak ferromagnetic coupling between the two S = 6 Mn₃ units, and thus, at extremely low T it would be expected to approach the value for an S = 12 ground state (χM = 78 cm³ K mol⁻¹ for g = 2.0). The data thus indicate that each Mn₃ unit does indeed still possess an S = 6 ground state (as does monomer 2) and that there is a weak ferromagnetic inter-Mn₃ interaction.

Attempts to fit the 20–300 K data to an equilateral triangle model were unsatisfactory (Figure S3, Supporting Information), assignable to the crystallographic symmetry masking small local distortions from equilateral symmetry; the latter were seen for 2 and related monomers that had no crystallographic symmetry. The 20–300 K data were thus fit to the theoretical χM vs T expression for a dimer of Mn₃ planar isosceles triangles, assuming the two Mn₃ units are non-interacting.

A similar treatment of magnetic data was performed for a [Cu₃]₂ dimeric molecule reported previously. The Heisenberg–Dirac–Van Vleck (HDVV) spin Hamiltonian is given in eq 2, which can be converted into the equivalent form in eq 3

\[
\hat{H} = -2J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3) - 2J'(\hat{S}_2\cdot\hat{S}_3) \tag{2}
\]

\[
\hat{H} = -J(\vec{\hat{s}}_\alpha^2 - \vec{\hat{s}}_\beta^2 - \vec{\hat{s}}_\gamma^2) - J'(\vec{\hat{s}}_\beta^2 - \vec{\hat{s}}_\gamma^2 - \vec{\hat{s}}_\alpha^2) \tag{3}
\]

using the substitutions \(\vec{\hat{s}}_\alpha = \hat{S}_1 + \hat{S}_2\) and \(\hat{S}_\gamma = \hat{S}_3\); \(\vec{\hat{s}}_\beta\) is the total spin of the unit, taking values of \(S = 0–6\) since \(S_1 = S_2 = S_3 = 2\). The eigenvalues of eq 3 are given by eq 4.
\[ E(S_T, S_h) = -J[S_T(S_T + 1) - S_h(S_h + 1)] - J'[S_h(S_h + 1)] \]  

(4)

The fit (solid line in Figure 3) gave \( J = +6.8(1) \text{ cm}^{-1} \), \( J' = +26.3(4) \text{ cm}^{-1} \), and \( g = 1.95(1) \), with temperature-independent paramagnetism (TIP) held constant at \( 600 \times 10^{-6} \text{ cm} \text{ mol}^{-1} \). These values, including the TIP, are comparable to those for 2 and other MnIII triangular units.45,50 The root-mean-square \( J \) vs \( J' \) error surface for the fit (Figure S4, Supporting Information) shows (i) a second local minimum of slightly lower quality with \( J = +20.4(1) \text{ cm}^{-1} \), \( J' = -0.8(4) \text{ cm}^{-1} \), and \( g = 1.95(1) \), corresponding to the second means of distorting an equilateral triangle to isosceles (as expected, the two minima = 1.95(1), corresponding to the second means of distorting an equilateral Mn3 units.45 The root-mean-square \( J \) vs \( J' \) region between the two minima are related, both with an average \( f_{av} \) of 13.3 cm\(^{-1}\)) and (ii) the \( J = J' \) region between the two fit minima is a saddle point, supporting the poor fit of the data to an equilateral triangle model.

To confirm the ground state of each Mn3 and to estimate the axial zero-field splitting parameter, \( D \), magnetization (\( M \)) data were collected in the 1.8–10 K range in dc fields (\( H \)) up to 7 T and are plotted as \( M/N\mu_B \) vs \( H/T \) in Figure 4 (\( N \) is Avogadro’s constant, and \( \mu_B \) is the Bohr magneton). Data in the 1–7 T range (lower fields were avoided to minimize interference from the very weak inter-Mn3 interactions, see below) were fit by diagonalization of the spin Hamiltonian matrix assuming only the ground state is populated, incorporating uniaxial anisotropy (\( DS_z^2 \)) and Zeeman terms and employing a full powder average. The spin Hamiltonian is given by eq 5 (\( S_z \) is the easy-axis (\( z \)) spin projection, and \( \mu_B \) is the vacuum permeability).

\[ \hat{H} = DS_z^2 + g\mu_B\mu_0S_z\mathbf{H} \]  

(5)

The best fit (solid lines in Figure 4) gave \( S = 6, D = -0.24(1) \text{ cm}^{-1} \), and \( g = 1.89(1) \). The overall fit is good, but some discrepancies between the experimental data and the fit lines point to the influence of some effects not incorporated in eq 5, such as inter-Mn3 interactions and the presence of rhombic anisotropy, \( E_r \), the latter consistent with isosceles rather than equilateral Mn3 units.

Alternating current (ac) susceptibility data on 3 in the 1.8–15 K range were collected using a 3.5 G ac field at frequencies up to 1500 Hz. The in-phase \( \chi''_M \) (Figure S) is very similar to the dc \( \chi_M \) in the 5.0 \( \leq T \leq 15 \) K range: \( \chi''_M \) is 45.89 and 40.18 cm\(^3\) K mol\(^{-1}\) at 5.0 and 15 K, respectively, essentially identical within experimental error to the \( \chi_M \) of 45.70 and 40.53 cm\(^3\) K mol\(^{-1}\) at these temperatures. This indicates that the dc data is negligibly affected by Zeeman population problems from the 0.1 T field. Below 5.0 K, \( \chi_M \) can be seen to continue increasing until \( \sim 2 \) K, where frequency-dependent decreases appear due to slow magnetization relaxation of the Mn3 SMM units. Concomitant with the latter are out-of-phase \( \chi''_M \) signals (Figure S). Since each Mn3 unit is in its ground state by \( \sim 20 \) K, the 1.8–15 K data were simulated using the program MAGPACK,51 to a model comprising two \( S = 6 \) units with exchange interaction \( J_{12} \) of the indicated magnitudes. \( g \) was held constant at 1.91.

![Figure 4](image-url)  

Figure 4. Magnetization (\( M \)) data per Mn3 unit of 3 plotted as \( M/N\mu_B \) vs \( H/T \). Solid lines are the fit of the data; see text for fit procedure and obtained fit parameters.

![Figure 5](image-url)  

Figure 5. Alternating current susceptibility data for 3: (top) in-phase \( \chi'_M \) vs \( T \) plot at the indicated frequencies; (middle) out-of-phase \( \chi''_M \) vs \( T \) plot; and (bottom) MAGPACK simulation of the \( \chi'_M \) vs \( T \) data at 5 Hz ac frequency (excluding two lowest T points) as two \( S = 6 \) units with exchange interaction \( J_{12} \) of the indicated magnitudes. \( g \) was held constant at 1.91.
to be a dimer of $S = 6$ Mn$_3$ SMMs with a very weak inter-Mn$_3$ ferromagnetic interaction ($J_{12}$).

If there are weak interdimer antiferromagnetic interactions present, these would serve to decrease $\chi_M T$ below 15 K. Thus, the observed increasing $\chi_M T$ below 15 K would then be the net sum of an increase from intradimer ferromagnetic interactions and a decrease from antiferromagnetic ones between adjacent dimers. If this were the case, the obtained $J_{12}$ from the simulation, indicating insigniﬁcant contributions to the $\chi_M T$ below 15 K from effects other than the intradimer $J_{12}$.

We assign the ferromagnetic nature of the $J_{12}$ coupling as arising from a spin polarization mechanism through the central sp$^3$ C atom, caused by spin density delocalized into the d$p_d^2-\pi$ systems from the Mn $d_x$ magnetic orbitals (Figure 6). This will dominate the direct $\sigma$-spin delocalization from the Mn $d_x$ ($d_z$) orbitals through the $\sigma$ backbone, which would favor antiferromagnetic coupling but is expected to attenuate rapidly with the number of bonds.

The combined structural and magnetic data for 3 emphasize that this dimeric [Mn$_3$]$_2$ molecule is distinctly different from all other Mn$_6$ molecules reported in the literature that can be described as containing two Mn$_3$ triangular units.[$2$-$5$,$7$-$9$] $3$ is a [Mn$_3$]$_2$ dimer of two very weakly coupled Mn$_3$ SMMs connected by a long dioximate linker, whereas the other Mn$_6$ molecules contain monatomic oxo bridges and thus much stronger couplings between their two halves, and they are therefore best described as Mn$_6$ monomers.

**High-Frequency EPR (HF-EPR) Spectroscopy.** HF-EPR studies were carried out on a single crystal of 3 to accurately determine the axial spin Hamiltonian parameters for each Mn$_3$ unit and the inter-Mn$_3$ exchange coupling strength, $J_{12}'$. Measurements were then performed on a MeCN/toluene (1:1 v/v) solution of 3 to determine if the dimers remain intact in solution and, if so, to what extent any quantum mechanical coupling seen in the solid state between the two Mn$_3$ units is affected.

Assuming an S = 6 ground state and neglecting off-diagonal transverse anisotropy terms, the effective spin Hamiltonian (to fourth order) for an isolated/uncoupled Mn$_3$ SMM is given by eq 6 for a field applied parallel to its easy axis ($\langle H||z \rangle$).$^{57,58}$ For two coupled Mn$_3$ SMMs, the effective dimer Hamiltonian ($\hat{H}_D$) is given by eq 7, where the last term describes the exchange coupling within the dimer.

$$\hat{H}_D = \hat{H}_4 + \hat{H}_2 - 2J_{12}\hat{S}_1\hat{S}_2$$

(7)

As reported elsewhere,$^{60}$ the dimer Hamiltonian matrix can be separated into the diagonal and off-diagonal terms given in eq 8, where $\hat{S}_i^\pm$ denote raising/lowering operators and

$$\hat{H}_D = \hat{H}_0 + \hat{H}'$$

(8)

$J_1$ and $J_0$ characterize the longitudinal and transverse exchange interaction strengths, respectively. The eigenvectors of $\hat{H}_0$ may be expressed as products of the uncoupled eigenvectors, $|m_i\rangle$ and $|m_j\rangle$, associated with the individual halves of the dimer (the solutions to eq 6); these are abbreviated $|m_i m_j\rangle$.

The EPR transitions associated with $\hat{H}_0$ are primarily those of the individual Mn$_3$ units, with small corrections that take into account the longitudinal exchange bias $[-2J_{m_i m_j}]$ between the two dimer halves. Previous simulations for a dimer of $S = 9/2$ Mn$_3$ SMMs in which only the easy-axis component $[-2J_{m_i m_j}]$ of the exchange interaction is operative show that the low-temperature HF-EPR spectrum is barely discernible from that of an isolated Mn$_3$ monomer, with more-or-less evenly spaced resonances and a fairly smooth peak-to-peak variation in intensity.$^{11}$ The spectrum is simple because any EPR transition involving one Mn$_3$ unit (subject only to a longitudinal bias from the other Mn$_3$) is degenerate with the same transition involving the other Mn$_3$ unit (subject to the same longitudinal bias), i.e., the eigenvalues of $\hat{H}_0$ are invariant with respect to any permutation of the spin labels. However, the situation is different when the off-diagonal term in eq 8, $\hat{H}'$, is included. This interaction gives rise to a true quantum mechanical coupling of the two Mn$_3$ units so that EPR transitions can no longer be described as excitations of individual Mn$_3$ SMMs. $\hat{H}'$ mixes (entangles) the uncoupled product states, $|m_i m_j\rangle$, in a manner that conserves the total angular momentum, $M = m_i + m_j$, giving rise to eigenvectors that are either symmetric (S) or antisymmetric (A) superpositions of the original product states. The eigenvalues remain invariant to permutations of spin labels. However, the entanglement lifts all degeneracies that existed among uncoupled product states, e.g., the $M = -11$ states $|11, -5\rangle$ and $|11, -6\rangle$ (see inset to Figure 7). The outcome is a far more complex EPR spectrum, provided coherence is maintained among superposition states on EPR time scales ($\sim$ns).$^{60}$

For the single-crystal HF-EPR measurements, the sample was first aligned in situ to have its easy axis parallel to the applied magnetic field ($\langle H||z \rangle$). The spectra in Figure 7 were recorded at 148.7 GHz for several temperatures, and the best simulations are included below each experimental trace. As noted above, the spectra are more complex than those for an isolated SMM, with uneven peak spacings and intensities indicating coherent coupling between the two Mn$_3$ units of the dimer. Indeed, the spectra bear no resemblance to either those obtained for isolated Mn$_3$ SMMs (equivalent to $J_{12} = 0$ in the present case)$^{55,61,62}$ or the well-known Mn$_6$ SMMs (equivalent to...
Figure 7. Temperature-dependent single-crystal HF-EPR absorption spectra for 3 at 148.7 GHz, with $H || z$ and at the indicated temperatures. Simulations are included below each experimental trace (see text for further explanation). Some of the HF-EPR peaks are labeled according to assignments given in the inset and Figure S6, Supporting Information.\(^{48}\) The inset represents the lowest 10 (out of 169 total) high-field eigenstates of the dimer, labeled according to their spin projection $M = m_1 + m_2$ and parity (symmetric ($S$) or even = blue; antisymmetric ($A$) or odd = red); vertical displacement represents energy ($M = -12$ is the ground state), while the horizontal axis has no significance. Several of the HF-EPR transitions labeled in the main figure are represented by vertical arrows in the inset.

Figure 8. Compilation of peak positions and frequencies extracted from multifrequency (from ~70 to 200 GHz) single-crystal and solution HF-EPR spectra such as those displayed in Figures 7 and 9. Each series of resonances ($a, b, c, d, e, f, g, h$, etc., see legend) lies on a straight line corresponding to the energy difference between pairs of eigenstates in Figure S6, Supporting Information. As can be seen, good agreement with theoretical expectations is achieved at all frequencies.

Figure 9. Solution HF-EPR spectra for 3 (10 mM in MeCN/toluene, 1:1 v/v) at 148.8 GHz and at the approximate temperatures indicated. Absorption ($I$) extends from the parallel ($H || z$) to the perpendicular ($H || xy$) components of the single-crystal spectrum (see lower inset and main text for further explanation). In the experimental derivative mode ($dI/dH$) spectra, the parallel and perpendicular components are separated by strong $g = 2.00$ signals close to 5.3 T (most likely due to isotropic impurity spins in the frozen glass and sample holder). Simulations are included below each experimental trace (see text for further explanation), and the 4 K single-crystal spectrum ($H || z$) from Figure 7 is also included for further comparison; simulations do not reproduce the impurity signals. Some of the HF-EPR peaks have been labeled according to assignments given in Figures 7 and S6, Supporting Information.\(^{48}\) (Inset) Simulated 4 K absorption spectrum along with the corresponding derivative ($dI/dH$).

strongly coupled Mn\(_3\) triangles, i.e., $J_{12} > |D|$\(^{62,63}\). The strongest resonances have been labeled, with peak assignments given in the inset and in Figure S6, Supporting Information.\(^{48}\) All transitions conserve parity, i.e., excitations only take place from $S$ ($A$) states to $S$ ($A$) states (see inset to Figure 7). The simulation parameters are $D = -0.22$ cm\(^{-1}\), $B^A_0 = -7 \times 10^{-5}$ cm\(^{-1}\), $g = 2.00$, and isotropic exchange $J_z = J_{xy} = J_{12} = +0.025$ cm\(^{-1}\); an asymmetric distribution in $D$ ($\sigma' = 0.004$ cm\(^{-1}\), $\sigma'' = 0.02$ cm\(^{-1}\)) was included to reproduce the line shapes. The values of $D$ and $J_{12}$ are in excellent agreement with those deduced from the fits to low-temperature ac susceptibility and $M$ vs $H$ data, confirming the ferromagnetic coupling within the dimer. Overall, excellent agreement is achieved between the simulations and single-crystal HF-EPR measurements, not only in Figure 7 but also at many other frequencies in the 70–200 GHz range, as seen in Figure 8.

Temperature-dependent HF-EPR spectra recorded at 148.8 GHz in derivative mode ($dI/dH$; $I$ is the absorption intensity) for a 10 mM solution of 3 are displayed in Figure 9; the data are noisier than those in Figure 7 due to the low spin concentration. Because the measurement is performed on molecules frozen into a glass, EPR absorption occurs for all possible molecular orientations. Hence, the spectrum spans from the lowest field transitions for a crystal (for which $H || z$) to those at the highest field (for which $H || \perp z$). $dI/dH$ then gives a peak (or dip) at each point in the absorption spectrum corresponding to the onset of a new EPR transition (see lower inset to Figure 9);\(^{64}\) thus, peaks occur for molecules with $H || z$, while dips occur for molecules with $H || xy$. In this way, one may
directly compare solution $dl/dH$ spectra to those obtained in absorption mode for a single crystal (see 4 K data in Figure 7). Rigorous $dl/dH$ simulations generated from orientation-averaged spectra are included below each experimental trace; exactly the same Hamiltonian parameters were employed as those given above, with $g_\sigma = 1.94$. As can be seen in Figure 9, excellent agreement is obtained both between experiment and simulation and between the solution and the single-crystal spectra. The clear observation of peaks $b$ and $c$ at 4 K (as well as others such as $a$) provides strong confirmation that the dimers remain intact in solution and that they retain the entanglement observed in the solid state.

Although no clear rhombic $E$ term could be detected from the HF-EPR measurements, it proved essential to include a significant strain in $E$ (Hahn—Teller axes can potentially project significant anisotropy into the $xy$ plane, but exact $C_3$ symmetry of the $Mn^3$ units would lead to a cancellation of the second-order transverse anisotropy ($E$). Nevertheless, disorder (especially in a frozen solution) could account for an emergence of a significant distribution in $E$ due to local deviations from $C_3$ symmetry. The latter was also suggested to be occurring in the solid state to explain the fits of the variable-temperature susceptibility and magnetization data and the asymmetric distribution in $D$.

## CONCLUSIONS

A [$Mn_3$]$_2$ SMM dimer has been targeted and achieved employing covalent dpd$^{2-}$ dioximate linkers. The triangular Mn$_3$ units are parallel, each has an $S = 6$ ground state from intra-Mn$_3$ ferromagnetic couplings, and the inter-Mn$_3$ interaction ($J_{12}$) is also ferromagnetic for the first time in SMM oligomers, but very weakly so. There is no evidence from any of the data for noticeable interactions (dipolar or superexchange) between adjacent dimers in the solid state, which is consistent with the absence of any significant interdimer contacts in the crystal structure and the large separations between Mn ions in adjacent dimers.

The $J_{12}$ interaction quantum mechanically couples the two Mn$_3$ SMMs in each dimer, generating superposition states and entanglement that are manifested as splittings in the HF-EPR spectra. The same features at the same spectral positions are observed in a frozen solution, the first time that this quantum coupling of two separate SMMs has been detected in this phase. This spectral similarity suggests that the structure is quite robust and resists any significant deformation/distortion that might affect such a weak inter-Mn$_3$ coupling. In addition, the range of solvent environments that the dimer molecules experience due to the many C—H—N hydrogen bonds, $\pi-\pi$ stacking, and other interactions possible with polar MeCN and aromatic toluene solvent molecules similarly have no discernible effect on the strength of the inter-Mn$_3$ coupling. Thus, their study in solution opens up a new direction in coupled-SMM oligomers, and their robustness also offers a feasible means for their deposition on surfaces for device studies. Finally, studies in progress are targeting higher SMM oligomers with parallel easy axes, inter-SMM coupling, and robustness in solution.

## EXPERIMENTAL SECTION

All manipulations were performed under aerobic conditions using chemicals and solvents as received unless otherwise stated. The dioxime dpdH$_2$ was synthesized following a reported procedure.$^{47}$

**Synthesis of [$Mn_3O_5(O_2CMe)_6(dpdl)]_2$ (3).** Reaction of $1.044$ g (0.050 mmol) with dpdH$_2$ (0.019 g, 0.075 mmol) and I$_2$ (0.038 g, 0.15 mmol) in CH$_3$Cl$_2$/EtOH (25 mL/1 mL) gave a dark brown solution. The latter was also suggested to be occurring in the solid state to explain the fits of the variable-temperature susceptibility and magnetization data and the asymmetric distribution in $D$.$^{66}$

The asymmetric unit consists of a $1/6$ Mn$_{12}^{4+}$ cluster and two $1/6$ $I_1^-$ counterions located on 3 symmetry elements. The $I_1^-$ ions were heavily disordered and could not be modeled properly; thus, the program SQUEEZE$^{68}$ a part of the PLATON package of crystallographic software,$^{69}$ was used to calculate the disorder area and remove its contribution to the overall intensity data.

### Table 2. Crystal Data and Structure Refinement Parameters for Complex 3

<table>
<thead>
<tr>
<th>formula</th>
<th>$C_{61}H_{44}I_6Mn_{12}O_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$fw$, g mol$^{-1}$</td>
<td>2240.05</td>
</tr>
<tr>
<td>space group</td>
<td>P5 1c</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>16.5692(10)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>16.5692(10)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>18.2847(11)</td>
</tr>
<tr>
<td>$\alpha$, deg</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>90</td>
</tr>
<tr>
<td>$\gamma$, deg</td>
<td>120</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>4347.3(6)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$T$, K</td>
<td>100(2)</td>
</tr>
<tr>
<td>radiation, Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>$\mu$, mm$^{-1}$</td>
<td>3.036</td>
</tr>
<tr>
<td>$R$, $[I &gt; 2\sigma(I)]$</td>
<td>0.0496</td>
</tr>
<tr>
<td>$wR_F$ ($F^2$, all data)</td>
<td>0.1383</td>
</tr>
</tbody>
</table>

The asymmetric unit consists of a $1/6$ Mn$_{12}^{4+}$ cluster and two $1/6$ $I_1^-$ counterions located on 3 symmetry elements. The $I_1^-$ ions were heavily disordered and could not be modeled properly; thus, the program SQUEEZE$^{68}$ a part of the PLATON package of crystallographic software,$^{69}$ was used to calculate the disorder area and remove its contribution to the overall intensity data.
High-Frequency EPR (HF-EPR) Spectroscopy. HF-EPR spectra were collected at the Electron Magnetic Resonance facility of the U.S. National High Magnetic Field Laboratory. Oriented single-crystal measurements were performed using a high-sensitivity cavity perturbation technique that additionally permits two-sample rotation relative to the applied magnetic field direction. 

A vector network analyzer was employed as a tunable microwave source and phase-sensitive detector, enabling measurements over a wide frequency range spanning from the fundamental TE_{011} mode (51 GHz with a quality factor Q = 20 000) of the cylindrical cavity to frequencies in excess of 200 GHz, corresponding to higher-order modes of the cavity. In order to avoid sample degradation due to solvent loss, wet single crystals were coated with paratone-N oil immediately after removal from their mother liquor and then cooled initially under 1 atm of He gas. Single-crystal spectra were recorded in absorption mode. Angle-dependent measurements (not shown) were initially carried out in order to align (to within 5°) the magnetic field with the magnetic easy (z) axis of the crystal. For solution samples, spectra were collected using a broad band (10–700 GHz) transmission probe in which microwaves are propagated in to and out of a 17 T superconducting magnet through cylindrical light pipes.

Tunable microwave radiation was generated using a phase-locked Virginia Diodes solid-state source operating at \(13 \pm 1\) GHz, followed by a chain of solid-state multipliers and amplifiers. Field modulation was employed in conjunction with a phase-sensitive homodyne detection scheme using a cold bolometer, yielding derivative mode detection.

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**REFERENCES**


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