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A New Family of Trinuclear Nickel(II) Complexes as **Single-Molecule Magnets**

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Abstract: Three new trinuclear nickel (II) complexes with the general compo- $[Ni_3L_3(OH)(X)](ClO_4)$ sition have been prepared in which $X = Cl^{-1}$ (1), OCN^{-} (2), or N_3^{-} (3) and HL is the tridentate N,N,O donor Schiff base ligand 2-[(3-dimethylaminopropylimino)methyl]phenol. Single-crystal structural analyses revealed that all three complexes have a similar Ni3 core motif with three different types of bridging, namely phenoxido (μ_2 and μ_3), hydroxido (μ_3), and μ_2 -Cl (**1**), $\mu_{1,1}$ -NCO (**2**), or μ_{11} -N₃ (3). The nickel(II) ions adopt a compressed octahedron geometry. Single-crystal magnetization measurements on complex 1 revealed that the pseudo-three-fold axis of Ni₃ corresponds to a magnetic easy axis, being

consistent with the magnetic anisotropy expected from the coordination structure of each nickel ion. Temperaturedependent magnetic measurements indicated ferromagnetic coupling leading to an S=3 ground state with 2J/k=17, 17, and 28 K for 1, 2, and 3, respectively, with the nickel atoms in an approximate equilateral triangle. The high-frequency EPR spectra in combination with spin Hamiltonian simulations that include zero-field splitting parameters $D_{\rm Ni}/k = -5, -4, \text{ and } -4 \text{ K}$ for 1, 2, and 3, respectively, reproduced the EPR

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Introduction

Single-molecule magnets (SMMs) have attracted considerable interest in recent years owing to their potential applications in information storage and quantum computing at the molecular level.^[1-3] These systems exhibit slow relaxation of their magnetization and function as a magnet below their blocking temperature $(T_{\rm B})$. The origin of the anisotropic

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202795. ORTEP-3 view of the [Ni₃L₃(OH)X]⁺ cations of 2 and 3, IR and electronic absorption spectra of 1-3, magnetism data for 2 and 3, and CIF files.

spectra well after a anisotropic exchange term was introduced. Anisotropic exchange was identified as $D_{i,i}$ k = -0.9, -0.8, and -0.8 K for 1, 2, and 1, 2, 1,3, respectively, whereas no evidence of single-ion rhombic anisotropy was observed spectroscopically. Slow relaxation of the magnetization at low temperatures is evident from the frequency-dependence of the out-of-phase ac susceptibilities. Pulsed-field magnetization recorded at 0.5 K shows clear steps in the hysteresis loop at 0.5-1 T, which has been assigned to quantum tunneling, and is characteristic of single-molecule magnets.

barrier (Δ) in the majority of SMMs results mainly from the spin ground state (S) and the uniaxial anisotropy of the molecule.^[4] The magnetic anisotropy has to be of the Ising-type, that is, the zero-field splitting parameter (D) must be negative to ensure that the $m = \pm S$ states are the lowest in energy and the m=0 state the highest (for integer spin; for noninteger spin $m = \pm \frac{1}{2}$ would be the highest).^[5] A significant barrier to the reversal of the magnetic moment results in a hysteresis of the magnetization that is of purely molecular origin.^[2a, b, 6, 7] An interesting feature of these molecules is that they show quantum tunneling of magnetization (QTM).^[7b,8] High-frequency electron paramagnetic resonance (HF-EPR) is a useful tool for determining the sign and magnitude of the D value of such magnetic clusters.^[9]

Since the discovery of the first SMM behavior of the dodecanuclear mixed-valent manganese complex [Mn₁₂O₁₂- $(O_2CMe)_{16}(OH_2)_4$ with an S=10 ground state, ^[3c,10] various derivatives of such Mn₁₂ species have been synthesized and investigated.^[11] Continuing effort is being devoted to the synthesis and characterization of new polynuclear clusters that display slow magnetic relaxation below a certain $T_{\rm B}$ and have potential practical applications. Although most of the homometallic SMMs contain Mn^{III},^[12] other metal ions such as V^{III} ,^[13] Fe^{III} ,^[14] Co^{II} ,^[15] or $Ni^{II[5a,16]}$ have also been found to be very promising. In general, SMM behavior is

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well characterized in high-nuclearity molecules, which should, in the ideal case, be well isolated in the crystal lattice.^[6,17] However, the lowering of the nuclearity of SMMs is also an important issue for obtaining simple model systems with a small number of quantum energy levels. In this regard, a unique example of a Mn^{III} dimer possessing an S = 4 spin ground state and exhibiting slow magnetization relaxation at low temperatures with the clear signature of SMM behavior has been reported by Miyasaka et al.^[18]

It is often claimed that SMM behavior is a rare phenomenon for Ni^{II} clusters.^[16a,c] The combined effect of a lowsymmetry ligand field and spin–orbit coupling can lead to appreciable zero-field splitting for Ni^{II}. The potential of the nickel(II) ion for SMMs was underlined when a Ni₁₂ complex, the first Ni^{II} SMM, was reported in 2001.^[19] Since then, only a few more SMMs of nickel(II), Ni₂₁,^[16a] Ni₈,^[16b] Ni₁₀,^[16c] and Ni₄^[16d,e] complexes, have been reported. A few ferromagnetically coupled oxido-bridged complexes containing the trinuclear Ni₃ core have been reported, but they possessed positive *D* values and consequently did not behave as SMMs.^[20,21]

Herein we report the synthesis, crystal structures, and magnetic behavior of a new family of heterobridged (phenoxido, hydroxido, and halo or pseudohalo) Ni3 trinuclear complexes with the formulae $[Ni_3L_3(OH)(Cl)](ClO_4)$ (1), $[Ni_{3}L_{3}(OH)(OCN)](ClO_{4})$ (2), and $[Ni_{3}L_{3}(OH)(N_{3})](ClO_{4})$ (3) bearing the tridentate N.N.O donor Schiff base ligand 2-[(3-dimethylaminopropylimino)methyl]phenol (HL). These ferromagnetically coupled trinuclear complexes have been shown to be novel SMMs by single-crystal magnetization data, ac susceptibility measurements, and pulsed-field magnetization experiments. HF-EPR measurements on polycrystalline specimens of the complexes 1-3 have also been performed and analyzed to characterize these Ni₃ SMMs. To our knowledge, these three trinuclear complexes are so far the smallest Ni^{II} clusters that exhibit unambiguous SMM behavior.

Results and Discussion

Synthesis of the complexes: The complexes were synthesized by allowing the Schiff base to react with $Ni(ClO_4)_2 \cdot 6H_2O$ in a solution of methanol followed by the addition of an aqueous solution of NaCl (for 1), NaOCN (for 2), or NaN₃ (for 3) in molar ratios of 2:2:1. Triethylamine was added to deprotonate the Schiff base ligand and also to make the solution slightly alkaline (pH \approx 8). The crystal field stabilization energies of the Schiff base ligands, derived from the 1,3-propanediamine derivatives and salicylaldehyde, are usually lower than their ethylenediamine analogues^[22] due to the longer M-N distances and consequently the hexacoordinated Ni^{II} is stabilized.^[23,24] The chelating tridentate ligand coordinates to the $\mathrm{Ni}^{\mathrm{II}}$ centers as usual to occupy three coordination sites (Scheme 1). In a slightly alkaline medium, the hydroxido ion bridges three metal centers. However, this coordination mode of the hydroxido ion is not very common



Scheme 1. Synthesis of the complexes 1-3.

as steric hindrance may destabilize the resulting tetrahedral arrangement of $Ni_3(OH)$ until and unless it gains some additional stability by other means.^[25] In the present system, the three mononuclear units are assembled around the hydroxido ion in such a way that two of the three phenoxido groups and one halogen or pseudo-halogen form a cyclic peripheral bridge, whereas the other phenoxido atom bridges the three Ni^{II} ions on the side opposite the hydroxido group. Such a bridging pattern seems helpful in holding the trinuclear core together.

IR and UV/Vis spectra of complexes 1–3: For each of the three complexes, the presence of a broad band at 3431 (1), 3451 (2), and 3449 cm⁻¹ (3) can be assigned to the v(OH) of the triply bridging hydroxido group. Another characteristic sharp band is located at 1629, 1628, and 1628 cm⁻¹ for compounds **1**, **2**, and **3**, respectively, due to the azomethine v(C=N). Complexes **2** and **3** each show a single absorption band at 2179 and 2056 cm⁻¹ due to the cyanate and azide group, respectively, consistent with the presence of only one type of these ions in their structures. In all three complexes, a characteristic strong peak for the stretching vibration of uncoordinated perchlorate is observed at 1094 cm⁻¹. The FTIR spectra of compounds **1–3** are shown in Figures S1–S3 in the Supporting Information.

The absorption bands in the electronic spectra, recorded in methanol solution, are very similar for all three complexes (see Figures S4-S6 in the Supporting Information). All three complexes exhibit a distinct band (ε) at 626 (200), 624 (110) and 629 nm $(145 \text{ M}^{-1} \text{ cm}^{-1})$ for **1**, **2**, and **3**, respectively, which can be assigned to the spin-allowed d-d transition ${}^{3}T_{1g}(F) \leftarrow {}^{3}A_{2g}$. Another weaker broad band centered at 990 (130), 995 (45), and 997 nm $(12.5 \text{ m}^{-1} \text{ cm}^{-1})$ for **1**, **2**, and 3, respectively, and well separated from the first band can be assigned to the transition ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$. A third band at 369 (48000), 366 (45000), and 371 nm (47000 M^{-1} cm⁻¹) for 1, 2, and 3, respectively, is much higher in intensity than the two lower-energy transitions; this intensity is typical of bands that are a result of mixing of LMCT with the ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ transition.^[26-29] These values are in agreement with values reported in the literature for octahedral Ni^{II} compounds.

Structures of complexes 1–3: The structures of the three compounds **1–3** are isomorphous, crystallize in the *Pbcm* space group, and are constructed of discrete trinuclear cat-



ions $[Ni_3L_3(\mu_3\text{-OH})X]^+$ (X = Cl⁻, OCN⁻, or N₃⁻) and a noncoordinated perchlorate anion required to balance the charge. The perspective view of the trinuclear structure of **1** is shown in Figure 1a; complexes **2** and **3** have similar molecular structures (shown in Figure S7 in the Supporting Information). Selected bond lengths and bond angles are summarized in Tables 2 and 3, respectively. The nickel(II) ions



Figure 1. a) ORTEP-3 view of the $[Ni_3L_3(OH)Cl]^+$ cation of complex 1 (thermal ellipsoids at the 30% level) including the atomic numbering scheme. Methyl groups of amine nitrogen atoms have been omitted for clarity. b) Double face-sharing tri-octahedron presentation of compound 1. c) Molecular arrangement of 1 viewed along the crystallographic *c* axis. Only the nickel and coordinated atoms in four molecules are shown.

FULL PAPER

of the trinuclear complexes 1-3 are arranged as isosceles triangles with two equivalent Ni(1)...Ni(2) distances of 2.908(5) (for 1), 2.901(7) (for 2), and 2.904(7) Å (for 3) and one slightly elongated basal edge Ni1...Ni1' of 3.026(4) (for 1), 2.939(6) (for 2), and 2.964(6) Å (for 3). A mirror plane passing through Ni(2) bisects the triangle. The trinuclear isosceles Ni3 core is bridged by one µ3-hydroxido oxygen atom O(3) and another μ_3 -bridging phenoxido oxygen atom O(2) of the Schiff base ligand L on the opposite side of the Ni_3 plane. The distances of O(2) and O(3) from the Ni_3 plane are 1.338(2) and 1.122(3) Å, 1.320(3) and 1.147(4) Å, and 1.323(3) and 1.141(4) Å for 1, 2, and 3, respectively. Along the equal sides of the isosceles triangle the nickel ions are also linked by μ_2 -bridging phenoxido oxygen atoms, O(1) of L. A μ_2 -bridging chloride (for 1), $\mu_{1,1}$ -NCO (for 2), or $\mu_{1,1}$ -N₃ (for 3) acts as an additional bridge along the elongated edge. Thus, for all three complexes, two of the nickel atoms, Ni(1) and Ni(1)', are linked by two oxygen atoms and one chloride (for 1) or a nitrogen atom (for 2 and 3) sharing a face; again, they both share the adjacent face with Ni(2) by linking through a triple oxygen bridge (Figure 1b; for compounds 2 and 3, see Figure S8 in the Supporting Information).

All three nickel atoms in the molecule exhibit distorted octahedron geometries, but the environments are not equivalent. In addition to the bridging atoms, as mentioned above, two symmetry related nickel atoms, Ni(1) and Ni(1)', are bonded to the facially coordinated monoanionic tridentate L through the amine nitrogen atom N(1), the imine nitrogen atom N(2), and the phenoxido oxygen atom O(1), whereas Ni(2) is coordinated to three donor atoms of L in a meridional configuration. For all three nickel atoms, the distortion from the ideal octahedral geometry is evident from the observed cis angles, which are in the range 77.55(7)-101.54(8), 77.92(10)-103.12(14), and 77.93(10)-103.76(14)°, and the trans angles at the nickel(II) centers of 151.22(7)-171.60(9), 150.09(9)-172.55(11), and 150.34(9)-172.13(11)° for 1-3, respectively. The geometry around Ni(2) can be described as a compressed octahedron with two short axial bonds from the μ_3 -hydroxido O(3) and the imine nitrogen N(2). The four donor atoms O(1), O(2), O(1)', and N(3) form the basal plane of Ni(2) in all three complexes 1-3. The r.m.s. deviation of the four basal donor atoms from their mean plane around Ni(2) is 0.062 (for 1), 0.076 (for 2), and 0.073 Å (for 3). The deviation of the Ni(2) atom from the same plane is 0.263(1), 0.268(1), and 0.267(1) Å for 1-3, respectively. Similarly, the coordination environment of Ni(1) may also be considered as a tetragonally compressed octahedron with short bonds from the imine nitrogen N(2)and hydroxido oxygen O(3) in the two axial positions. The r.m.s. deviations of the four coordinating atoms O(1), O(2), N(1), and Cl(1) (for 1) or N(5) (for 2 and 3) that constitute the basal planes of the three complexes are 0.0224 (for 1), 0.046 (for 2), and 0.049 Å (for 3) from their respective leastsquare mean plane and the displacement of the Ni(1) atom is 0.181(1), 0.185(4), and 0.195(1) Å from the same plane for 1, 2, and 3 respectively.

Trinuclear nickel(II) complexes with a Ni₃ core motif similar to that of the present complexes have been reported with bridging oxygen atoms of phenoxido,^[30] amino alcohol,^[31] and carbohydrate systems.^[21,32] A similar oxido-bridged core has also been found in the two heterometallic clusters Ni₃M'O₄ (M'=K and Na).^[20] However, to our knowledge, complexes **1–3** are the first examples of such motifs in which a chlorine or nitrogen atom acts as a bridging atom along with the oxido bridges, making the bridging system heteroatomic. These differences seem to have a marked effect on their magnetic properties as no previously reported Ni₃ clusters have shown SMM behavior.

Magnetic properties: The magnetic properties of 1-3 show the same general trends, and for brevity the data presented will focus on 1, the data and simulations for 2 and 3 can be found in the Supporting Information. Detailed bulk magnetization and high-field EPR analyses resolve subtle yet distinct differences in the size of the exchange coupling and anisotropy in 1-3. Hence it is of interest to examine the differences in magnetic properties due to substitution at the Ni₃ core motif.

Direct current magnetization: Figure 2a shows the magnetic susceptibility of **1** at an applied field of 500 Oe. The ferromagnetic coupling between nickel ions is clearly indicated by the increase in $\chi_m T$ on lowering the temperature. The $\chi_m T$ maximum in the $\chi_m T$ versus T plot for **1** is 7.59 cm³K mol⁻¹ at T=10 K. The $\chi_m T$ value at 300 K is 4.34 cm³K mol⁻¹, greater than the value of 3.97 cm³K mol⁻¹ calculated for three uncoupled S=1 centers, which demonstrates remaining ferromagnetic correlation between ions at high temperature. The S=3 high-spin ground state is also evident by inspection of the magnetization with an applied field at 1.8 K (Figure 2b). The slow saturating contribution above 1 T is attributed to the rotation of magnetization on each nickel ion canted from each other as a result of magnetic anisotropy and magnetic exchange coupling.^[33]

There are two types of nickel(II) ions and also two types of Ni···Ni geometries (Figure 1a) in the molecule. Attempts to fit multiple exchange constants to the susceptibility curve resulted in non-univocal parametrization. Hence, to simplify the model, a pseudo-three-fold axis is assumed at the center of the Ni₃ core and the magnetic parameters were determined by considering it an equilateral triangle. The strength of the isotropic exchange interaction between nickel ion sites can be calculated by using the spin Hamiltonian in Equation (1).^[34]

$$\hat{H} = -2J(\hat{s}_1\hat{s}_2 + \hat{s}_1\hat{s}_3 + \hat{s}_2\hat{s}_3) + \sum_{i=1,2,3} \mu_{\rm B}B\tilde{g}\hat{s}_i \tag{1}$$

The exchange constant J is extracted by simulating $\chi_m T$ against the measured data between 25 and 300 K. The J values obtained from simulations of $\chi_m T$ versus T indicate variation in exchange constants for compounds **1** through to **3**, with J/k = 8.5, 8.5, and 14 K, respectively (± 0.25 K). The



Figure 2. a) $\chi_m T$ vs. *T* for polycrystalline **1** measured at 500 Oe. The solid line represents a calculation based on Equation (1) with J/k=8.5 K, $g_{xx}=g_{yy}=2.3$, and $g_{zz}=2.4$. b) *M* vs. *H* plot for polycrystalline **1**. Solid and broken lines represent calculations carried out with the Brillouin functions with S=3 and three times S=1, respectively, and g=2.30.

calculated curve is superposed in Figure 2a (Figure S9 in the Supporting Information for the other compounds). At lower temperatures, zero-field splitting (ZFS) is appreciable, intermolecular exchange may be significant, and there may be contributions from paramagnetic impurities.

Because compound 1 exists as an orthorhombic crystal system with Z=4, the molecules are arranged in a zigzag manner. Thus, there are two distinct axial anisotropy orientations in the unit cell (Figure 1c). A canted spin structure is also assumed for the single-ion magnetic moments belonging to each molecule. Both an appreciable cant angle of the spin structure and slow relaxation of spin dynamics originate the strong magnetic anisotropy, and several weak ferromagnets showing SMM-like behavior have been reported recently.^[35] Thus, we have a great motivation to characterize the anisotropy and investigate the SMM behavior of the molecular architectures of complexes 1–3.

The single-crystal magnetization of 1 was successfully studied. The uniaxial magnetic moment with respect to the Ni₃ triangle was confirmed by the single-crystal experiment (Figure 3). The crystallographic *b* and *a* directions correspond to the first and second magnetic easy axes, respective-



Figure 3. Single-crystal magnetization data for 1 measured at 1.8 K.

ly, and the c direction to the hard axis. The mapping of the magnetic moments onto the molecule shown in Figure 4 is plausible because the magnetic moment along the normal axis is located parallel to the ab plane. The c direction has no component of the magnetic moment at zero field. Thus, the uniaxial anisotropy has been characterized with respect to the molecular structure and is compatible with the negative D value found in the EPR study. The calculations of the single-crystal magnetization performed with the parameters determined by EPR spectroscopy are presented in Figure S11 in the Supporting Information.

The negative *D* value may be related to the compressed octahedron geometry around the nickel ions through the known magnetostructure relationship.^[36] As shown in Figure 4, the compression occurs along the Ni–O(hydroxido) bond for each nickel ion. Assuming that the uniaxial magnetic anisotropy coincides with the compressed axis, the moments are not collinear, but the ferromagnetic coupling of the three nickel spins causes the total magnetic moment to grow in the normal direction with respect to the Ni₃ plane. The angles between this normal and the crystallographic *b* axis are 36.5, 36.0, and 35.9° for complexes **1**, **2**,



Figure 4. Directions of compressed distortion for each nickel ion in 1. Only the nickel ions, coordinated atoms, and phenoxido group are shown for clarity.

and **3**, respectively. On the other hand, the component parallel to the Ni_3 plane is cancelled out in the molecule. In short, the Ni_3 triangular molecule has a pseudo-three-fold axis, which corresponds to the magnetic easy axis of the whole molecule.

High-frequency EPR spectroscopy: HF-EPR spectroscopy is a useful tool for investigating spin anisotropy in magnetic clusters behaving as SMMs. The spectra of a polycrystalline specimen of **1** are displayed in Figure 5 and show fine structure due to ZFS (for direct comparison of the EPR spectra of **1–3**, see Figures S12 and S13 in the Supporting Information). The spectra show several absorptions with the resonant magnetic field increasing with increasing microwave frequency (95–405 GHz). The g value was initially estimated to be approximately 2 from the slope in the frequency versus field diagram, which is consistent with the allowed absorption of the nickel spins.



Figure 5. a) Selected HF-EPR spectra of a polycrystalline specimen of **1**. The spectra are offset in proportion to the frequency. The g=2 dotted line is shown for a guide to the eye. b) Variable-temperature HF-EPR spectra of polycrystalline **1** recorded at 405 GHz.

Two dominant features are apparent in Figure 5(b) at 4.2 K; the strongest absorption found in the low-field region (6.8 T) and the second strongest absorption at the high-field region (16.0 T). Both absorptions have been assigned to absorptions from the ground state. This assignment is supported by variable-temperature experiments. At high temperatures, the absorptions from the ground state are weakened in accord with the Curie law. As Figure 5b shows, the absorptions at 6.8 and 16 T clearly exhibit such a temperature dependence. On the other hand, the temperature dependence of several absorptions between these absorptions do not obey the Curie law, which indicates that they are related to transitions in the excited states. These features are comparable to the HF-EPR spectra of $[Mn_{12}]$ -, $[^{37}]$, $[Mn_{3}]$ -, $[^{12c}]$ [Fe₄]-, $[^{14b}]$ and [Fe₇]-based^[38] SMMs.

Strong exchange limit interpretation of the HF-EPR spectra: Within the strong exchange limit approximation (i.e., $|J| \ge |D|$), and ignoring the possible transverse anisotropy contribution, the Hamiltonian of the ground-state spin multiplet can be written as Equation (2). For the simplest case

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 5

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 77

with ZFS smaller than the Zeeman energy, the resonance fields for the various $m \rightarrow m+1$ transitions are given by Equation (3)^[39,40] in which B_0 is the resonant field of the free electron, $D' = D_{S=3}/g\mu_{\rm B}$, and θ is the angle between the unique axis z and the external magnetic field.

$$\hat{H} = -|D_{S=3}|\hat{S}_Z^2 + g\mu_{\rm B}B_Z\hat{S}_Z \tag{2}$$

$$B(m \to m+1) = \frac{g_{\rm e}}{g} \left[B_0 - D' \frac{2m+1}{2} \left(3\cos^2 \theta - 1 \right) \right]$$
(3)

When the external field is applied parallel to z, the signals are equally spaced by 2|D'|. In the case of D' < 0, the transition involving the lowest-energy m level occurs at a low field (less than B_0 ; for the Zeeman diagram with more accurate treatment, see Figure 8a). The observed low-field lines correspond to the resonances of crystallites with their unique axis parallel to the external magnetic field. The lowest-field absorption, assignable to $m = -3 \rightarrow -2$ (red data points in Figure 6), is the strongest, and accordingly it is concluded that the D' value is negative. Extrapolation of the frequency versus field diagram gives the zero field energy gap between $m = \pm -3$ to $m = \pm -2$ (5 | DS = 3 |) at 200 GHz.



Figure 6. Frequency versus field diagram for 1. Red solid lines and blue broken lines represent the easy-axis and hard-plane calculations, respectively.

Given that the spectra were recorded on polycrystalline specimens, both axial (easy axis) and in-plane (hard plane) absorptions are observed. When the D value is negative, the latter appear as appreciable peaks at a field higher than B_0 .^[37–39] The highest-field absorption data points are the strongest of the hard-plane data owing to a negative D (for the Zeeman diagram, see Figure 8b). Extrapolation of the highest-field absorption data points gives a ZFS energy of 100 GHz, just half the value derived from the z axial data, which indicates that the present analysis based on the $(3\cos^2\theta - 1)$ dependence [Eq. (3)] is plausible. The optimized D and g parameters are $D_{S=3}/k = -1.90(3)$ K and g=2.24(1)

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for **1**, $D_{S=3}/k = -1.78(1)$ K and g = 2.282(8) for **2**, and $D_{S=3}/k$ k = -1.67(3) K and g = 2.21(2) for **3** (see Figure S14 in the Supporting Information). Given the scale of the ZFS relative to the size of the exchange coupling J, the system cannot be described accurately within the strong exchange and hence attempts to simulate the spectra of complex 1 with an S=3 effective Hamiltonian [as expressed in Eq. (2)] were unsatisfactory.

Spin-Hamiltonian simulations of the HF-EPR spectra: Quantitative analysis of the EPR spectra requires simulation of the recorded spectra based on an exchange-coupled spin Hamiltonian. Simulations based on Equation (1) with the addition of axial anisotropy results in the approximate reproduction of the main EPR features observed for compound 1. The parameters obtained in this simulation are $D_{\rm Ni}/k = -9$ K and $g_{xx} = g_{yy} = 2.2$ and $g_{zz} = 2.4$. The relationship between the single ion D_{Ni} and the effective molecular $D_{S=3}$ can be estimated by using the pairwise vector coupling approach,^[40] which leads to the relationship $D_{S=3} = D_{Ni}/5$ when intermediate exchange coupling contributions are considered to be negligible. In this context, the single ion D_{Ni} of -9 K is consistent with the estimation made by extrapolation of the frequency versus field diagram: $|D_{S=3}| = 1.9 \text{ K}$ (Figure 6).

The inclusion of dipolar spin-spin interaction anisotropy within the model,^[41] as expressed in the Hamiltonian Equation (4), is found to reproduce the measured spectra accurately. Exchange anisotropy is frequently important for the interpretation of the EPR spectra of exchange-coupled transition-metal clusters. Despite the presence of exchange anisotropy (typically, anisotropy in the order of 1 cm⁻¹ is reasonably accepted^[41b]), it is often only possible to resolve exchange anisotropy from single-ion anisotropy effects by the analysis of high-resolution spectroscopic techniques such as multi-frequency EPR spectroscopy. For compound 1, discrimination of exchange anisotropy from single-ion anisotropy leads to single ion $D_{\rm Ni}/k = -5.0$ K and $D_{i,i}/k = -0.9$ K. The effect of canting local anisotropy tensors in line with the compressed distortion of each nickel ion (see Figure 4) was also investigated, however, for simplicity, the principal axes for the single-ion and dipolar anisotropies were aligned perpendicular to the plane made by the Ni₃ triangle.

$$\begin{aligned} \hat{H} &= -2J(\hat{s}_{1}\hat{s}_{2} + \hat{s}_{1}\hat{s}_{3} + \hat{s}_{2}\hat{s}_{3}) + \sum_{i=1,2,3} \mu_{\mathbf{B}}B\tilde{g}\tilde{s}_{i} \\ &+ \sum_{i=1,2,3} D_{Ni} \left(s_{z,i}^{2} - \frac{1}{3}s_{i}(s_{i}+1) \right) \\ &+ \sum_{i,j=1,2,3}^{i < j} \hat{s}_{i} \begin{pmatrix} -D_{i,j} & 0 & 0 \\ 0 & -D_{i,j} & 0 \\ 0 & 0 & 2D_{i,j} \end{pmatrix} \hat{s}_{j} \end{aligned}$$
(4)

Figure 7 shows the results of simulations at 4.2 K for all measured frequencies 95-405 GHz. All major features are reproduced at the correct resonance fields and mismatches



Figure 7. Top: Selected HF-EPR spectra of polycrystalline 1. Bottom: Spin-Hamiltonian simulations based on Equation (4).



Figure 8. Zeeman diagrams for a) parallel and b) perpendicular sample orientations calculated for compound **1** at 405 GHz. The strongest transition probabilities are denoted in dark gray, and the light-gray lines mark the present 405 GHz energy quanta.

in the absorption intensities may arise from nonequilibrium thermal population in the measured spectra due to the high sweep rate of the pulsed magnetic field.

The EPR spectra of 2 and 3 are almost the same. This indicates that despite the differences in isotropic exchange, evidence of such effects on anisotropies and g values is not observed for the substitution of NCO by N₃. Figure S13 in the Supporting Information shows the EPR spectra of 1–3 recorded at 4.2 K. The total anisotropy is slightly reduced in 2 and 3 relative to 1. Simulations of the EPR spectra of 2 based on Equation (4) result in the parameters $D_{Ni}/k = -4 \text{ K}$, $D_{i,j}/k = -0.8 \text{ K}$, and $g_{xx} = g_{yy} = g_{zz} = 2.3$, with J/k a fixed

FULL PAPER

constant determined from susceptibility simulations (see Figure S15 in the Supporting Information).

Calculated Zeeman diagrams for 1 are shown in Figure 8 (for similar diagrams for 2 and 3, see Figure S16 in the Supporting Information). The strongest EPR transition probabilities are shown in dark gray. At 4.2 K, the strongest excitations emanate from within the ground-state S=3 multiplet. The irregular signal intensity, most evident in the region of 12–14.5 T of the 405 GHz spectra, originates from the hard-plane oriented crystallites of the polycrystalline samples; the excited-state resonances are shown in Figure 8b in the same field region. Owing to the rapid field sweep of pulsed-field EPR spectroscopy, it is possible that some none-quilibrium electron population exists resulting in the observation of stronger absorption intensities for the excited-state resonances.

Single-molecule magnetic behavior: In general, the negative D values and high-spin ground states are responsible for the activation energy $E_{\rm a}$ of the magnetization reorientation, which give rise to the slow dynamics of magnetization reversal typical of SMMs. To confirm the possible slow magnetization reversal, we measured the ac magnetic susceptibility of 1 (Figure 9; for the results for 2 and 3, see Figure S17 in the Supporting Information). A clear frequency dependence was observed after a dc bias field of 1000 Oe was applied to reduce possible quantum tunneling of the magnetization.^[42] Unfortunately, a peak for $\chi^{"}$ cannot be seen above 1.8 K, and no meaningful Cole-Cole plot was drawn. The value of $E_{\rm a}$ was estimated according to Equation (5), based on the Arrhenius equation,^[43] to be $E_a/k=9.6(6)$ K with $\tau_0=3\times$ 10^{-8} s for 1 (Figure 9b; for the results for 2 and 3, see Figure S18 in the Supporting Information). Under these conditions, the magnetization relaxation time was estimated to be in the order of a minute at 0.5 K and 10^{-4} s at 1.5 K.

$$\ln\left(\chi''/\chi'\right) = \ln\left(2\pi\nu\tau_0\right) + E_{\rm a}/kT \tag{5}$$

From Equation (5), the energy barrier for the magnetization reversal of an S=3 species is given by $9|D_{S=3}|$, and it is estimated to be 17 K for **1**. The results of the full spin-Hamiltonian simulation [Eq. (4)] give a barrier within the S=3 manifold of 18.6 K. These values are comparable to the value determined from the ac susceptibility measurements ($E_a/k=9.6$ K). A similar effective energy barrier is often found for various SMMs due to thermally activated quantum tunneling through one of the higher *m* levels.^[39,44]

To observe the SMM behavior, we performed pulsed-field magnetization experiments with a liquid ³He cryostat below 2 K. Magnetic hysteresis was recorded at 0.5 K with a field scan rate of 3.2 Tms^{-1} (Figure 10). A jump in the magnetization can be observed in the range 0.5–1.0 T for **1**. Furthermore, the derivative of the magnetization clearly shows a structure resulting from the contributions of a few small jumps (for the results for **2** and **3**, see Figure S19 in the Supporting Information). The origin of the hysteresis in magnetization is not singularly attributable to the quantum tunnel-

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Figure 9. a) ac susceptibilities for **1** measured at the dc bias field of 1000 Oe. χ' and χ'' represent the in-phase and out-of-phase components, respectively. b) Natural logarithm of the ratio of χ''/χ' vs. 1/T for **1**. E_a and τ_0 were estimated by fitting the experimental χ''/χ' data to Equation (5).



Figure 10. Top: Pulsed-field magnetization curve for **1** measured at 0.5 K. Bottom: Derivative of the magnetization curves measured at 0.5 K with field scanning rates of 3.2, 10.6, and 21.2 Tms^{-1} . The dashed lines denote the positions of magnetization jumps.

ing of magnetization to avoid crossings. Indeed, nonequilibrium thermal population is responsible for the broad nature of the dominant jump in the dM/dB curve. In addition to this, the first jump (shoulder in the dM/dB plot) at around 0.4 T cannot be attributed to the quantum tunneling of magnetization either, because this shoulder moves depending on the field sweep rate. Shifts with increasing field rate confirm the origin of these features to be the competition between thermal relaxation and a change in the Zeeman energy from the ramped magnetic field. Despite this, two smaller, sharper, features at 0.6 and 1 T are independent of the field scanning rate. Calculated level crossings within the lowest-energy spin multiplet correspond to these observed level crossing features. At 1 T, the jump in magnetization is ascribed to the level crossing between the lowestenergy Zeeman split pair of doublets when the field direction is close to the easy axis (1.2 T in the calculation). The feature at 0.6 T corresponds to the avoided crossing between the highest-energy Zeeman split doublet and singlet when the field direction has a component in the hard plane. These features are regarded as a characteristic of the SMMs, as is typically found in, for example, $[Mn_{12}]$.^[37,38]

Conclusion

The N,N,O donor tridentate Schiff base ligand HL has allowed the synthesis of a new family of complexes with a very rare type of triangular Ni^{II} core that is capped by μ_3 -hydroxido

and μ_3 -phenoxido bridges at the opposite side of the Ni₃ plane. The core structure is supported by two μ_2 -phenoxido bridges and an exchangeable μ_2 -non-oxido X group (X=Cl (1), NCO (2), and N_3 (3)) at the periphery. The tripodal hydroxido and phenoxido oxygen atoms seem to play an important role as ferromagnetic couplers as well as a regulator for uniaxial magnetic anisotropy. The short axial bonds to the imine nitrogen of the Schiff base and the hydroxido group lead to the compressed octahedral geometry around Ni^{II} that is likely to be responsible for its negative D parameter. In general, a negative D favors SMM behavior, although some exceptional cases have been reported with a positive D.^[46] The small bridging angles between the Ni^{II} ions make the intramolecular coupling ferromagnetic with S=3. As a result, the present Ni₃ systems form a novel family of single-molecule magnets.

Although tetranuclear nickel systems with a cubane-type core and other nuclearities have been well investigated in relation to ground-state high-spin multiplicity and SMM behavior,^[47] the present complexes are the first Ni₃ systems to show magnetic properties typical of SMM. The interesting feature of this trinuclear family is that 1) the X bridge is exchangeable and 2) the trinuclear core is stable. The effective D value of the molecule and the intramolecular exchange coupling J can in principle be tuned by changing the X atom. Of the present complexes, although a change in X from Cl to N did not result in any significant variation of their magnetic properties, a larger X (e.g., Br or I) is expected to have an appreciable effect. Moreover, the stability of the trinuclear core would allow the synthesis of similar compounds with counter ions other than perchlorate that should have different intermolecular interactions between the SMM units, which has been found to be important in the variation of QTM properties of SMMs.^[6] Such studies are in progress in our laboratories.

Experimental Section

Materials: The diamine and salicylaldehyde were purchased from Aldrich and Spectrochem Chemical Co, respectively. All the chemicals were of reagent grade and used without further purification.

Synthesis of the Schiff base ligand: The Schiff base 2-[(3-dimethylaminopropylimino)methyl]phenol (HL) was prepared by the condensation of salicylaldehyde (1.05 mL, 10 mmol) and N,N-dimethyl-1,3-propanediamine (1.26 mL, 10 mmol) in methanol (10 mL) as reported earlier.^[23] Synthesis of [Ni₃L₃(OH)(Cl)](ClO₄) (1): Ni(ClO₄)₂·6H₂O (1.828 g, 5 mmol), dissolved in methanol (10 mL), was added to a methanolic solution (10 mL) of the Schiff base HL (5 mmol) with constant stirring. After around 15 min, an aqueous solution (2 mL) of NaCl (0.146 g, 2.5 mmol) was added with slow stirring followed by the addition of triethylamine (1.05 mL, 7.5 mmol). Slow evaporation of the resulting green solution gave a dark-green microcrystalline compound. The green solid was then filtered, washed with diethyl ether, and dissolved in CH₃CN. X-ray-quality deep-green single crystals of compound 1 were obtained by slow evaporation of the acetonitrile solution. Yield: 1.18 g (75%); IR (KBr pellet): $\tilde{v} = 3431$ (br, O–H), 1629 cm⁻¹ (C=N); UV/Vis (CH₃OH): λ_{max} (ϵ) = 369 (48000), 626 (200) and 990 nm (130 $dm^3 mol^{-1}cm^{-1}$); elemental analysis calcd (%) for $C_{36}H_{52}Cl_2N_6O_8Ni_3$ (943.81): C 45.81, H 5.55, N 8.90; found: C 45.70, H 5.45, N 8.85.

Synthesis of $[Ni_3L_3(OH)(OCN)](ClO_4)$ (2) and $[Ni_3L_3(OH)(N_3)](ClO_4)$ (3): The procedures used for the synthesis of 2 and 3 were the same as that used for complex 1, except that an aqueous solution (2 mL) of NaOCN (0.162 g, 2.5 mmol; for 2) or NaN₃ (0.162 g, 2.5 mmol; for 3) was added instead of NaCl. Block-shaped deep-green X-ray-quality single crystals of compounds 2 and 3 were obtained by slow evaporation of the acetonitrile solutions.

2: Yield: 1.11 g (70%); IR (KBr pellet): $\tilde{\nu}$ =3451 (br, O–H), 1628 (C=N), 2179 cm⁻¹ (OCN⁻); UV/Vis (CH₃OH): λ_{max} (ε)=366 (45000), 624 (110), 995 nm (45 dm³mol⁻¹cm⁻¹); elemental analysis calcd (%) for C₃₇H₅₂N₇O₉ClNi₃ (950.38): C 46.76, H 5.51, N 10.32; found: C 46.71, H 5.49, N 10.23.

3: Yield: 1.19 g (75%); IR (KBr pellet): $\tilde{\nu}$ =3449 (br, O–H), 1628 (C=N), 2057 cm⁻¹ (N₃⁻); UV/Vis (CH₃OH): λ_{max} (ε)=371 (47000), 629 (145), 997 nm (12.5 dm³mol⁻¹cm⁻¹); elemental analysis calcd (%) for C₃₆H₅₂N₉O₈ClNi₃ (950.39): C 45.50, H 5.51, N 13.26; found: C 45.46, H 5.45, N 13.20.

Physical measurements: Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin–Elmer 240C elemental analyzer. IR spectra ($4500-500 \text{ cm}^{-1}$) in KBr pellets were recorded with a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra (1400-350 nm) in CH₃OH (for **1-3**) were recorded with a Hitachi U-3501 spectrophotometer. Magnetic susceptibilities of a polycrystalline specimen of **1-3** were measured with a Quantum Design MPMS SQUID magnetometer equipped with a 7 T coil in the range 1.8–100 K. The magnetic responses were corrected for the diamagnetic data of the sample holder measured separately. The diamagnetic contribution of the sample itself was estimated by using Pascal's constant. The ac magnetic susceptibilities of polycrystalline samples were recorded with a Quantum Design PPMS ac/dc magnetometer down to 1.8 K.

Low-temperature magnetization was measured with a conventional inductive probe in pulsed-magnetic fields and a temperature as low as 0.5 K was reached by using a ³He cryostat.^[48] Polycrystalline specimens (typically 20 mg) were mounted in a capillary made of polyimide Kapton. The sample was not fixed within the sample tube and then it was aligned along the magnetic field direction. After applying the magnetic field several times, the orientation effect was saturated and the magnetization curves obtained in further shots were found to be identical. HF-EPR spectra of polycrystalline samples were obtained with a pulsed-field spectrometer (of our own design).^[49] The sample was packed in a polyethylene case. The radiation was produced by Gunn oscillators and backward traveling wave oscillators. The temperature was controlled by using a ⁴He cryostat. **Crystallographic data collection and refinement**: Suitable single crystals of each complex were mounted on a Bruker SMART diffractometer equipped with a graphite monochromator and $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. The structures were solved by the Patterson method by using SHELXS-97. All non-hydrogen positions were found and refined with anisotropic temperature factors. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. All calculations were carried out by using SHELXS-97,^[50] SHELXL-97,^[51] PLATON-99,^[52] ORTEP-32,^[53] and WinGX system Ver-1.64.^[54] Data collection, structure refinement parameters, and crystallographic data for the three complexes are given in Table 1. Selected bond lengths and bond angles are summarized in Tables 2 and 3.

Table 1	Crystellogra	mbia data	for com	mlavag 1
Table 1.	Crystanogra	ipine uata	TOT COIL	ipiexes 1

	1	2	3
formula	C36H52Cl2N6O8Ni3	C37H52N7Ni3O9Cl	C36H52N9O8ClNi3
$M_{\rm r}$	943.81	950.38	950.39
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	Pbcm (No. 57)	Pbcm (No. 57)	Pbcm (No. 57)
a [Å]	10.6866(4)	10.8901(3)	10.8770(3)
b [Å]	25.8091(9)	25.8920(8)	25.9404(8)
c [Å]	14.9408(5)	14.7248(4)	14.7270(4)
$V[Å^{-3}]$	4120.8(3)	4151.9(2)	4155.3(2)
Z	4	4	4
$D_{\rm c} [{\rm g}{\rm cm}^{-3}]$	1.521	1.520	1.519
$\mu [\mathrm{mm}^{-1}]$	1.542	1.472	1.470
F(000)	1968	1984	1984
R(int)	0.072	0.059	0.079
total reflections	50444	50037	51 623
unique reflec-	4401	4515	4704
tions			
$I > 2\sigma(I)$	3491	3251	3063
<i>R</i> 1, <i>wR</i> 2	0.0387, 0.1172	0.0441, 0.1117	0.0436, 0.1228
T [K]	296	293	293

Table 2. Selected bond lengths [Å] for complexes 1–3.

Bond	1	2	3	
Ni(1)-O(1)	2.042(2)	2.049(2)	2.046(2)	
Ni(1)-O(2)	2.219(2)	2.183(2)	2.192(2)	
Ni(1)-O(3)	2.047(2)	2.046(3)	2.050(3)	
Ni(1)-N(1)	2.127(2)	2.128(3)	2.124(3)	
Ni(1)-N(2)	1.999(2)	2.003(3)	1.997(3)	
$Ni(1)-X^{[a]}$	2.473(2)	2.167(3)	2.155(4)	
Ni(2)-O(1)	2.196(2)	2.203(2)	2.206(2)	
Ni(2)-O(2)	2.058(3)	2.052(3)	2.054(3)	
Ni(2)-O(3)	2.022(2)	2.015(3)	2.014(3)	
Ni(2)-O(1)'	2.196(2)	2.203(2)	2.206(2)	
Ni(2)-N(3)	2.126(4)	2.127(4)	2.124(5)	
Ni(2)-N(4)	2.009(3)	2.012(4)	2.005(4)	

[a] X = Cl(1) (for 1) or N(5) (for 2 and 3). Symmetry code: '=x, y, 1/2-z (for 1); x, y, 3/2-z (for 2); x, y, 1/2-z (for 3).

CCDC-843832 (1), -843833 (2), and -843834 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Spin Hamiltonian Simulations: EPR simulations were performed by using the EasySpin package.^[55] Magnetization and magnetic susceptibility simulations were performed by using MAGPROP.^[56]

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FULL PAPER

Table 3. Bond angles [°] in the metal coordination spheres of complexes 1–3.

Bond angle	1	2	3
O(1)-Ni(1)-O(2)	77.55(7)	77.92(10)	77.93(10)
O(1)-Ni(1)-O(3)	82.70(8)	82.05(11)	82.20(11)
O(1)-Ni(1)-N(1)	101.54(8)	101.89(11)	102.30(11)
O(1)-Ni(1)-N(2)	92.37(8)	91.90(11)	92.04(11)
O(2)-Ni(1)-O(3)	70.38(8)	71.31(11)	71.01(11)
O(2)-Ni(1)-N(1)	171.60(9)	172.55(11)	172.13(11)
O(2)-Ni(1)-N(2)	101.11(8)	100.24(12)	100.28(12)
O(3)-Ni(1)-N(1)	101.22(9)	101.25(12)	101.17(12)
O(3)-Ni(1)-N(2)	170.88(9)	170.43(13)	170.35(13)
N(1)-Ni(1)-N(2)	87.25(9)	87.21(12)	87.58(12)
O(1)-Ni(2)-O(2)	77.74(5)	77.39(6)	77.45(6)
O(1)-Ni(2)-O(3)	79.53(5)	79.03(6)	79.16(6)
O(1)-Ni(2)-N(3)	100.59(5)	100.92(7)	100.85(7)
O(1)-Ni(2)-N(4)	98.05(5)	98.35(7)	98.26(7)
O(1)-Ni(2)-O(1)'	151.22(7)	150.09(9)	150.34(9)
O(2)-Ni(2)-O(3)	74.24(10)	74.72(14)	74.63(14)
O(2)-Ni(2)-N(3)	168.94(11)	169.44(15)	169.28(15)
O(2)-Ni(2)-N(4)	93.02(13)	92.02(17)	92.22(18)
O(1)'-Ni(2)-O(2)	77.74(5)	77.39(6)	77.45(6)
O(3)-Ni(2)-N(3)	94.69(12)	94.72(16)	94.65(16)
O(3)-Ni(2)-N(4)	167.27(14)	166.74(18)	166.84(19)
O(1)'-Ni(2)-O(3)	79.53(5)	79.03(6)	79.16(6)
N(3)-Ni(2)-N(4)	98.04(15)	98.54(19)	98.51(19)
O(1)'-Ni(2)-N(3)	100.59(5)	100.92(7)	100.85(7)
O(1)'-Ni(2)-N(4)	98.05(5)	98.35(7)	98.26(7)
Ni(1)-O(1)-Ni(2)	86.59(7)	85.96(9)	86.07(9)
Ni(1)-O(2)-Ni(1)'	85.97(8)	84.60(12)	85.08(12)
Ni(1)-O(2)-Ni(2)	85.58(8)	86.41(11)	86.23(11)
Ni(1)'-O(2)-Ni(2)	85.58(8)	86.41(11)	86.23(11)
Ni(1)-O(3)-Ni(2)	91.24(8)	91.17(12)	91.22(12)
Ni(1)'-O(3)-Ni(2)	91.24(8)	91.17(12)	91.22(12)
Ni(1)-O(3)-Ni(1)'	95.31(12)	91.78(15)	92.61(15)
X ^a -Ni(1)-O(1)	159.47(6)	155.77(11)	154.78(12)
X ^a -Ni(1)-O(2)	84.13(5)	80.74(12)	79.96(14)
X ^a -Ni(1)-O(3)	82.48(6)	80.35(13)	79.26(13)
$X^{a}-Ni(1)-N(1)$	95.22(7)	97.78(13)	97.96(15)
$X^{a}-Ni(1)-N(2)$	100.27(7)	103.12(14)	103.76(14)
Ni(1)-X ^a -Ni(1)'	75.43(4)	85.39(16)	86.93(19)

[a] X = Cl(1) (for 1) or N(5) (for 2 and 3). Symmetry code: '=x, y, 1/2-z (for 1); x, y, 3/2-z (for 2); x, y, 1/2-z (for 3).

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11

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Single-Molecule Magnets

R. Biswas, Y. Ida, M. L. Baker, S. Biswas, P. Kar, H. Nojiri, T. Ishida,* A. Ghosh*.....

A New Family of Trinuclear Nickel(II) Complexes as Single-Molecule Magnets



Nickel(II) magnets. A new family of trinuclear Ni^{II} complexes with phenoxido (μ_2 and μ_3), hydroxido (μ_3), and μ_2 -Cl, $\mu_{1,1}$ -NCO, or $\mu_{1,1}$ -N₃ bridges have been prepared that form face-sharing coordination polyhedra (see figure). The three complexes exhibit a dominant ferromagnetic exchange coupling with sizable uniaxial anisotropy. The slow magnetization relaxation, the hysteresis of the pulsed-field magnetization, a magnetic easy axis, and the high-frequency EPR spectra show that these complexes constitute a new class of single-molecule magnets.