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Article

Combining Azide, Carboxylate, and 2-Pyridyloximate Ligands in Transition-Metal Chemistry: Ferromagnetic Ni^{II}_5 Clusters with a Bowtie Skeleton

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The combined use of the anion of phenyl(2-pyridyl)ketone oxime ($ppko^-$) and azides (N_3^-) in nickel(II) carboxylate chemistry has afforded two new Ni^{II}_5 clusters, $[Ni_5(O_2CR')_2(N_3)_4(ppko)_4(MeOH)_4]$ [R′ = H (**1**), Me (**2**)]. The structurally unprecedented $\{Ni_5(\mu\text{-}N_3)_2(\mu_3\text{-}N_3)_2\}^{6+}$ cores of the two clusters are almost identical and contain the five Ni^{II} atoms in a bowtie topology. Two N_3^- ions are end-on doubly bridging and the other two ions end-on triply bridging. The end-on μ_3-N_3^- groups link the central Ni^{II} atoms with the two peripheral metal ions on either side of the molecule, while the Ni···Ni bases of the triangles are each bridged by one end-on μ-N_3^- group. Variable-temperature, solid-state direct-(dc) and alternating-current (ac) magnetic susceptibility, and magnetization studies at 2.0 K were carried out on both complexes. The data indicate an overall ferromagnetic behavior and an $S = 5$ ground state for both compounds. The ac susceptibility studies on **1** reveal nonzero, frequency-dependent out-of-phase (χ_M'') signals at temperatures below ~3.5 K; complex **2** reveals no χ_M'' signals. However, single-crystal magnetization versus dc field scans at variable temperatures and variable sweep rates down to 0.04 K on **1** reveal no noticeable hysteresis loops, except very minor ones at 0.04 K assignable to weak intermolecular interactions propagated by nonclassical hydrogen bonds.

Introduction

Polynuclear complexes (clusters[1] or coordination clusters[2]) of 3d metals at intermediate oxidation states have become of particular interest in recent times.[3] This interest is a result of their relevance to bioinorganic chemistry[4,5] and to the special class of molecule-based magnetic materials known as single-molecule magnets (SMMs).[6] SMMs are discrete molecules that exhibit slow relaxation of the magnetization at low temperatures and display magnetic hysteresis analogous to that observed in bulk magnets, thus representing a molecular, or "bottom-up", approach to nanoscale magnetism with several potential applications.[7] Even more fascinating is the fact that they show strong evidence of quantum effects.[8] Most SMMs are clusters of exchange-coupled 3d metal ions protected by a shell of ligands. Their magnetic behavior results from the combination of a large ground-state spin (S) with a

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large Ising (or easy-axis) type of magnetoanisotropy, as gauged by a negative, axial zero-field-splitting parameter (*D*).

From the above brief discussion, it is becoming clear that there continues to be a need for new synthetic methodologies to new polynuclear metal complexes and new SMMs, with efforts directed toward defining and enhancing the parameters that govern high-spin and/or SMM behavior.[2,9] In the development of new synthetic routes to metal clusters, the choice of ligands is always a key issue.[10,11] Examples of simple and flexible ligands include the anions of aliphatic or aromatic alcohols (i.e., alkoxides),[12] alcohol amines,[12b,13] *gem*-diol and hemiketal forms of pyridyl ketones,[12b,14,15] pyridyl alcohols[16] and dialcohols,[12b,17] salicylaldo(keto)ximes,[9b,18] pyridyloximes[19] and dioximes,[19,20] and others.[21] Most 3d metal clusters reported to date have been obtained by utilizing this so-called serendipitous assembly,[11] where simple metal salts or preformed small clusters (mainly containing simple carboxylate ligands) react with multitopic ligands under a variety of conditions.

A modern trend is the employment of three ligands in the reaction systems (a combination of ligands or "ligand blends").[22] The loss of a degree of synthetic control is more than compensated for by the vast diversity of structural types using a combination of ligands. As part of such efforts, we have recently initiated a project in which the general carboxylate/azide/2-pyridyloxime ($R'CO_2^-/N_3^-$/LNOH) ligand combination is used in nickel(II) chemistry; our goal is to obtain clusters with interesting structures and magnetic properties. Ni^{II} has shown promise in the synthesis of both SMMs[6c] and spin-phonon traps,[23] with the former taking advantage of its significant single-ion anisotropy and the latter of its paramagnetic nature when confined with a highly symmetric cluster. However, homometallic SMMs containing Ni^{II} ions are surprisingly uncommon[24] despite the fact that mononuclear nickel(II) complexes have been shown to possess appreciable $|D|$,[25] e.g., $> 10\ cm^{-1}$. Carboxylate ions are famous for exhibiting a huge variety of coordination modes. The azide anion, N_3^-, is one of the most commonly employed inorganic bridging ligands in the design of polynuclear 3d metal complexes[26] with characteristic

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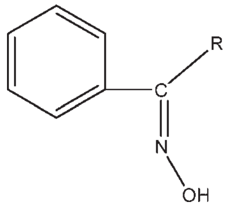
Scheme 1



R = H, Me, Ph, 2-pyridyl, NH$_2$

and tunable physical properties. This ligand is very popular in the field of molecular magnetism[27] because of its ability to mediate ferromagnetic coupling under certain conditions. 2-Pyridyloximes (Scheme 1; R = H, Me, Ph, py, NH$_2$, etc.) are a subclass of oximes that are currently popular ligands in coordination chemistry.[19] The anions of these molecules (2-pyridyloximate ligands) are particularly versatile in that they possess chelating and bridging (μ_2-μ_4) capabilities; the activation of 2-pyridyloximes by 3d metal centers toward further reactions is also becoming a fruitful area of research.[28] Such ligands have been key "players" in several areas of single-molecule[29] and single-chain[30] magnetism.

In the present work, we have used phenyl(2-pyridyl)ketone oxime (ppkoH; R = Ph in Scheme 1) in combination with carboxylate (HCO_2^- and $MeCO_2^-$) and azide ligands in nickel(II) chemistry. The reactions of Ni^{II} sources and ppkoH had previously given $[Ni_3(ppko)_6]$,[31] $[Ni_3(HCO_2)_2(ppko)_3(ppkoH)_2]^+$,[31] $[Ni_6(SO_4)_2(ppko)_8]$,[32] $[Ni_6(SO_4)_4(OH)(ppko)_3(ppkoH)_3(solvent)_3]$ (solvent = H$_2$O, MeOH),[35] and $[Ni_2(ppko)_3(L)](ClO_4)$,[36] where L is the tridentate capping ligand 1,4,7-trimethyl-1,4,7-triazacyclononane. Only two of these complexes are based on ppko$^-$/R′CO$_2^-$ ligation. Note that there are no nickel(II) complexes containing both ppko$^-$ and N_3^- ligands. We targeted different Ni$_x$ products by use of the *ternary* R′CO$_2^-$/N$_3^-$/ppkoH ligand system and have successfully isolated two new Ni$^{II}_5$ comlexes with an $S = 5$ ground state and a bowtie metal topology. This work can be considered as a continuation of our interest in homo- and heterometallic clusters based on 2-pyridyloximate[28a−c,29a,29b,31−35,37] and pyridyldioximate[20a−c] ligands.

Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using reagents and solvents as received. ***Warning!*** *Azide and perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities and treated with utmost care at all times using plastic spatulas.*

$[Ni_5(O_2CH)_2(N_3)_4(ppko)_4(MeOH)_4]$ (1). Method A. A pale-green solution of Ni(ClO$_4$)$_2$·6H$_2$O (0.366 g, 1.00 mmol) in MeOH (10 mL) was added dropwise over 10 min to a stirred solution of ppkoH (0.159 g, 0.80 mmol), NaN$_3$ (0.065 g, 1.00 mmol), and NaO$_2$CH (0.082 g, 1.21 mmol) in MeOH (20 mL). The resulting reddish-brown solution was stirred for an additional 10 min and filtered and the filtrate left undisturbed to concentrate slowly by evaporation at room temperature. X-ray-quality orange-brown crystals of the product slowly grew over 1 week. The crystals were washed with cold MeOH (0.5 mL) and Et$_2$O (3 × 2 mL) and dried under vacuum. The yield was ~45%. The dried solid was determined by analysis to be solvent-free. Anal. Calcd (found) for $C_{54}H_{54}N_{20}Ni_5O_{12}$: C, 44.16 (44.26); H, 3.71 (3.80); N, 19.08 (18.96). IR (KBr, cm^{-1}): 3366(mb), 3050(m), 2944(w), 2092(s), 2061(s), 1590(s), 1524(m), 1460(s), 1438(m), 1390(w), 1346(m), 1262(w), 1210(m), 1122(s), 1026(w), 974(m), 786(m), 748(m), 706(s), 644(m), 606(w), 452(w).

Method B. Solid NiSO$_4$·6H$_2$O (0.158 g, 0.60 mmol) was added to a solution of ppkoH (0.119 g, 0.60 mmol) and NaOMe (0.033 g, 0.60 mmol) in MeOH (20 mL). The solid soon dissolved, and the resulting red solution was stirred for 5 min, during which time a solution of NaN$_3$ (0.039 g, 0.60 mmol) in MeOH (5 mL) was added in small portions. A noticeable color change from red to brown occurred, and the mixture was filtered to remove Na$_2$SO$_4$. The homogeneous filtrate was stirred for a further 1 h and layered with Et$_2$O (30 mL). Slow mixing gave X-ray-quality crystals of the product. The crystals were collected by filtration, washed with cold MeOH (1 mL) and Et$_2$O (2 × 2 mL), and dried in air. The yield was 68%. The identity of the product was confirmed by elemental analyses, IR spectroscopic comparison with an authentic material from method A, and unit cell determination. Anal. Calcd (found) for $C_{54}H_{54}N_{20}Ni_5O_{12}$: C, 44.16 (44.32); H, 3.71 (3.61); N, 19.08 (18.83).

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$[Ni_5(O_2CMe)_2(N_3)_4(ppko)_4(MeOH)_4]\cdot 0.25H_2O$ (2·0.25H$_2$O). To a colorless solution of ppkoH (0.198 g, 1.00 mmol) in MeOH (20 mL) was added solid $Ni(O_2CMe)_2\cdot 4H_2O$ (0.249 g, 1.00 mmol). The resulting green solution was stirred for 15 min, during which time solid NaN_3 (0.063 g, 1.00 mmol) was added in small portions to give a red homogeneous solution. The stirring was maintained for an additional 10 min. Layering of the solution with a solvent mixture comprising Et_2O/*n*-hexane [25 mL, 1:1 (v/v)] gave X-ray-quality orange crystals of the product. The crystals were collected by filtration, washed with Et_2O (2 × 5 mL), and dried under vacuum. The yield was 72%. The dried solid was determined by analysis to be solvent-free **2**. Anal. Calcd (found) for $C_{56}H_{58}N_{20}Ni_5O_{12}$: C, 44.93 (44.97); H, 3.91 (4.06); N, 18.72 (18.95). IR (KBr, cm^{-1}): 3422(mb), 2091(s), 2059(s), 1595(s), 1565(m), 1521(sh), 1462(s), 1442(m), 1416(m), 1384(m), 1342(w), 1292(w), 1267(w), 1240(w), 1215(m), 1206(sh), 1123(s), 1104(m), 1031(w), 977(m), 783(w), 748(m), 709(s), 661(m), 643(m), 501(wb), 450(m).

X-ray Crystallography. Data for complex **1** were collected on an Oxford Diffraction Xcalibur-3 diffractometer (equipped with a Sapphire CCD area detector) at 100 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A suitable crystal was attached to glass fibers using silicone grease. The structure was solved by direct methods using *SIR92*[38] and refined by full-matrix least-squares techniques on F^2 with *SHELXL-97*.[39] Some residual electron density in the accessible voids of the structure was too disordered to refine as solvent molecules; therefore, the *SQUEEZE* procedure[40] of *PLATON* was employed to remove the contribution of the electron density in the solvent region from the intensity data. The solvent-free model and intensity data were used for the final results reported here. The non-H atoms were treated anisotropically. All H atoms were placed in calculated ideal positions and refined as riding on their respective C atoms, except those of the HCO_2^- and MeOH ligands, which were located from a difference Fourier map and refined isotropically. The programs used were *CRYSALIS CCD*[41] for data collection, *CRYSALIS RED*[41] for cell and data refinement, *WINGX*[42] for crystallographic calculations, and *MERCURY*[43] and *DIAMOND*[44] for molecular graphics.

Data for a selected crystal of **2**·0.25H$_2$O were collected at Station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, using a Bruker Platinum 200 CCD diffractometer (ω_0 rotation with narrow frames, synchrotron radiation at 0.7749 Å, and a silicon 111 monochromator). The structure was solved by direct methods and refined using the *SHELX-TL* suite of programs.[45] All non-H atoms were refined anisotropically, except those at less than half-occupancy. H atoms were placed in geometrically suitable positions where possible, whereas the methyl H atoms were found in the difference map and constrained using a riding model. Hydroxyl H atoms were found in the difference map and allowed to refine freely. Displacement parameter restraints were used in the modeling of the one of the ppko$^-$ ligands. Ratios of the displacement parameters up to around 5:1 (max:min) were left; even if this is not ideal, this reflects a slight disorder in the system and a split-site model would not yield any new chemical information.

Table 1. Crystallographic Data for Complexes **1** and **2**·0.25H$_2$O

	1	**2**·0.25H$_2$O
formula[a]	$C_{54}H_{54}N_{20}Ni_5O_{12}$	$C_{56}H_{58.50}N_{20}Ni_5O_{12.25}$
fw/g mol^{-1}[a]	1468.72	1501.28
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
a, Å	11.736(1)	14.4167(13)
b, Å	12.029(1)	24.334(2)
c, Å	13.870(1)	19.8508(17)
α, deg	111.05(1)	90
β, deg	100.12(1)	95.628(2)
γ, deg	109.84(1)	90
V, Å^3	1617.18(16)	6930.4(10)
Z	2	4
T, K	100(2)	193(2)
radiation, Å	0.710 73[b]	0.774 90[c]
ρ_{calcd}, g cm^{-3}	1.508	1.439
μ, mm^{-1}	1.502	1.770
measd/unique reflns	19 536/5230	38 752/10 649
R_{int}	0.0256	0.0584
obsd reflns	4498	8557
R1[d,e]	0.0313	0.0418
wR2[e,f]	0.0744	0.1254
GOF on F^2	1.071	1.039
$\Delta\rho_{max,min}$, e Å^{-3}	0.703, −0.333	0.879, −0.686

[a] Including solvate molecules. [b] Mo Kα radiation. [c] Synchrotron radiation. [d] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [e] For observed [$I > 2\sigma(I)$] reflections. [f] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Unit cell parameters and structure solution and refinement data for the two complexes are listed in Table 1.

Physical Studies. Microanalyses (C, H, and N) were performed by the in-house facilities of the University of Patras (Greece). IR spectra (4000−450 cm^{-1}) were recorded using Perkin-Elmer 16 PC and Bruker IFS-125 Fourier transform spectrometers with samples prepared as KBr pellets. Variable-temperature magnetic studies for **1** and **2** were performed at the University of Barcelona using a DSM5 Quantum Design SQUID magnetometer operating at 0.3 T in the 30−300 K range and at 0.03 T in the 30−2 K range to avoid saturation effects. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. Low-temperature (< 1.8 K) magnetic studies were performed at Grenoble using an array of micro-SQUIDs.[46] The high sensitivity of this magnetometer allows the study of single crystals on the order of 10−500 μm. The field can be applied in any direction by separately driving three orthogonal coils. Crystals were maintained in mother liquor to avoid degradation and covered with grease for protection during transfer to the micro-SQUID and subsequent cooling.

Results and Discussion

Syntheses and IR Spectra. The two previously studied clusters in Ni^{II}/R′CO$_2^-$/ppkoH chemistry are characterized by antiferromagnetic exchange interactions. Thus, the ground-state spin of $[Ni_3(HCO_2)_2(ppko)_3(ppkoH)_2]^+$[31] is intermediate between $S = 0$ and 1, while $[Ni_4(O_2CMe)_4(ppko)_4(MeOH)_2]$[35] has a diamagnetic spin ground state. Our approach was to employ a third bridging ligand in the Ni^{II}/R′CO$_2^-$/ppkoH reaction system that typically gives ferromagnetic interactions and that can thus increase the chances of a larger ground-state S value. The N_3^- ion bridging in the end-on (EO) fashion is a strong ferromagnetic

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mediator for a wide range of M−N−M angles, and it thus represents a well-recognized route to high-spin species and SMMs,[26] although its use in combination with pyridyloximes is still in its infancy.[26,28d,37h,47]

A variety of reactions were explored with different solvents and under different reagent ratios, and other conditions before the following successful procedures were identified. The reaction of $Ni(ClO_4)_2 \cdot 6H_2O$, ppkoH, NaN_3, and NaO_2CH in a 1.2:1:1.2:1.5 ratio in MeOH afforded a reddish-brown solution, from which was subsequently isolated **1** in 45% yield. Its formation is summarized in eq 1. The MeOH solvent was necessary to ensure solubility of the $NaClO_4$ produced. Small variations in the Ni^{II}/ppkoH/N_3^-/HCO_2^- ratio also gave complex **1**.

$$\begin{aligned} &5Ni(ClO_4)_2 \cdot 6H_2O + 6NaO_2CH + 4ppkoH + 4NaN_3 \\ &+ 4MeOH \xrightarrow{MeOH} [Ni_5(O_2CH)_2(N_3)_4(ppko)_4(MeOH)_4] \\ &\qquad + 4HCO_2H + 10NaClO_4 + 30H_2O \qquad (1) \end{aligned}$$

Complex **1** could also be prepared from a HCO_2^--free reaction system. The 1:1:1 reaction between $NiSO_4 \cdot 6H_2O$, ppkoH, and NaOMe (to help deprotonation of the ligand) in MeOH gave a red solution. When the solution was treated with 1 equiv of NaN_3 in MeOH, white Na_2SO_4 was precipitated. The addition of Et_2O into the brown homogeneous filtrate produced **1** in ~70% yield The formation of the complex using this method can be summarized in eq 2. The methoxide ions play a double role in the reaction. They act as proton acceptors to facilitate the formation of $ppko^-$ ligands, while a percentage of them are oxidized to HCO_2^- during the aerial aggregation process.[31,48] It is well-known that small alkoxides are susceptible to oxidation by air.[49] The nature of the base in MeOH is crucial for identity of the product; reaction schemes involving other bases, such as LiOH or Et_3N, gave noncrystalline, formate-free materials that we were not able to further characterize. It should be mentioned at this point that the chemical and structural identity of the products from the general $NiSO_4 \cdot 6H_2O$/ppkoH/MeO^-/N_3^- reaction system depends on the solvent used. In *N*,*N*-dimethylformamide, the azide-free cluster $[Ni_6(SO_4)_2(ppko)_8]$[32] forms, whereas this reaction scheme in MeCN gives the dinuclear complex $[Ni_2(N_3)_2(ppko)_2(ppkoH)_2]$.[50]

$$\begin{aligned} &5NiSO_4 \cdot 6H_2O + 4ppkoH + 6NaOCH_3 + 4NaN_3 + 2O_2 \\ &\xrightarrow{MeOH} [Ni_5(O_2CH)_2(N_3)_4(ppko)_4(CH_3OH)_4] \\ &\qquad + 5Na_2SO_4 + 32H_2O \qquad (2) \end{aligned}$$

Both preparative routes to complex **1** give *only* crystals of the product. No powder material that could be due to NiO was detected.

In a next step, we wondered if the $MeCO_2^-$ analogue of **1** could be prepared and thus pursued its synthesis. There are two reasons to prepare such a complex: (i) to determine if it would be isostructural with **1**, and (ii) if it is isostructural, to assess any influence of the H versus Me difference on magnetochemical properties. The 1:1:1 reaction between $Ni(O_2CMe)_2 \cdot 4H_2O$, ppkoH, and NaN_3 in MeOH gave a red solution from which was subsequently isolated **2** in very good yield (~70%). The employment of extra base, i.e., OH^- or MeO^-, is not necessary because the $MeCO_2^-$ ions can act as proton acceptors, facilitating the formation of the $ppko^-$ ligands; however, the addition of an external base does not affect the product identity. Using $Ni(ClO_4)_2 \cdot 6H_2O$ and $NaO_2CMe \cdot 3H_2O$ in place of $Ni(O_2CMe)_2 \cdot 4H_2O$ led again to complex **2** but in appreciably lower yields (20−30%).

The presence of coordinated MeOH molecules in dried samples of **1** and **2** is manifested by broad bands of medium intensity at ~3370 and ~3420 cm^{-1}, respectively, assigned to ν(OH); their broadness and relatively low frequency are both indicative of hydrogen bonding. The spectra of **1** and **2** exhibit intense bands at ~2090 and ~2060 cm^{-1}, which are assigned to the asymmetric stretching mode, ν_{as}(NNN), of the EO azide groups.[27b] The appearance of two bands in each spectrum possibly reflects the presence of two different types of EO azido ligands in the complexes (vide infra). The in-plane deformation mode of the 2-pyridyl ring of free ppkoH at 622 cm^{-1}[32] shifts upward in the spectra of **1** (644 cm^{-1}) and **2** (643 cm^{-1}), confirming the involvement of the ring N atom in coordination.[51] Several bands appear in the 1600−1400 cm^{-1} region for the two complexes; contributions from the $\nu(C{=}N)_{oximate}$, $\delta(CH_3)$, δ(OH) (>1580 cm^{-1}), $\nu_{as}(CO_2)$, and $\nu_s(CO_2)$ are expected in this region, but overlap with the stretching vibrations of the aromatic $ppko^-$ rings renders assignments and a discussion of the coordination shifts difficult. The medium-intensity band at 1094 cm^{-1} for free ppkoH has been assigned to the $\nu(NO)_{oxime}$ mode.[34] The wavenumber of this vibration increases to ~1120 cm^{-1} in **1** and **2**. This shift to higher frequencies has been discussed and is in accordance with the fact that, upon deprotonation and oximate-*O* coordination, there is a higher contribution of N=O to the electronic structure of the oximate group; consequently, the ν(NO) vibration shifts to a higher wavenumber relative to that for the free oxime ligand.[37b,h,52]

Description of Structures. Partially labeled structures of complexes **1** and **2** are shown in Figures S1 in the Supporting Information and 1, respectively. The metallic skeleton and two views of the core of complex **2** are illustrated in Figures 2 and 3, respectively. Selected interatomic distances and angles for **1** and **2** are listed in Tables 2 and 3, respectively. Because the molecular structures of the two complexes are very similar, only the structure of the representative compound **2** will be described in detail.

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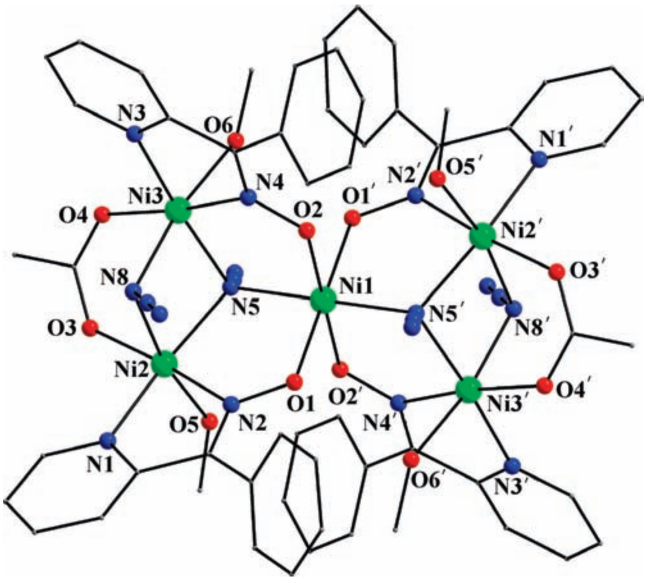


Figure 1. Partially labeled plot of the Ni_5 molecule of **2**. Primed and unprimed atoms are related by the crystallographic inversion center. Color scheme: Ni, green; O, red; N, blue; C, gray.

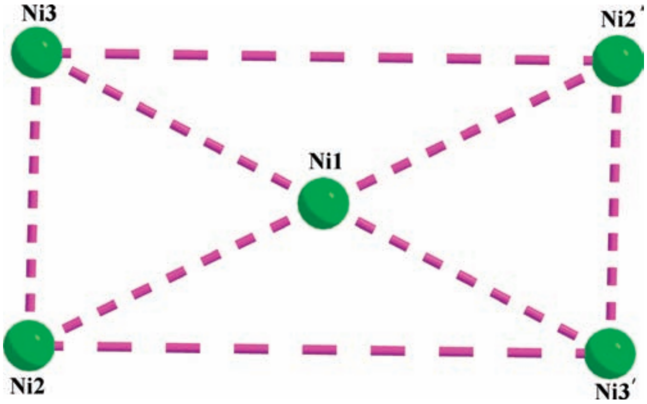


Figure 2. Ni_5 skeleton of **2** showing its centered rectangular metal topology.

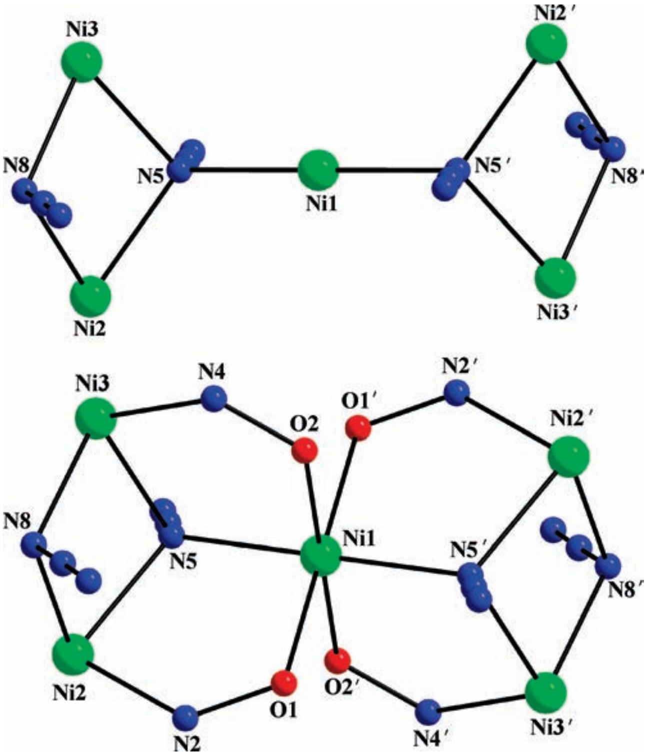


Figure 3. $\{Ni_5(\mu\text{-}N_3)_2(\mu_3\text{-}N_3)_2\}^{6+}$ core of **2** (top) and a more detailed representation emphasizing its $\{Ni_5(\mu\text{-}N_3)_2(\mu_3\text{-}N_3)_2(\mu\text{-}ONR'')_4\}^{2+}$ ($R''NO^-$ = ppko$^-$) description (bottom). The color scheme is as in Figure 1. Atoms N2, O1, N4, and O2 and their symmetry equivalents belong to the oximate groups of the ppko$^-$ ligands.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Complex **1**[a,b]

Ni1···Ni2	3.391(1)	Ni2−N2	2.021(2)
Ni1···Ni3	3.384 (1)	Ni2−N5	2.085(2)
Ni2···Ni3	3.026(1)	Ni2−N8	2.098(2)
Ni2···Ni2′	6.782(1)	Ni3−O4	2.042 (2)
Ni2···Ni3′	6.062(1)	Ni3−O6	2.125(2)
Ni3···Ni3′	6.768(1)	Ni3−N3	2.031(2)
Ni1−O1	2.057 (2)	Ni3−N4	2.022(2)
Ni1−O2	2.078 (2)	Ni3−N5	2.100(2)
Ni1−N5	2.072(2)	Ni3−N8	2.098(2)
Ni2−O3	2.062 (2)	N2−O1	1.342(3)
Ni2−O5	2.125 (2)	N4−O2	1.338(3)
Ni2−N1	2.031(2)		
O1−Ni1−O2	92.2(1)	O6−Ni3−N8	171.3(1)
O1−Ni1−N5	95.9 (1)	N3−Ni3−N5	174.0 (1)
O2−Ni1−N5′	83.5(1)	Ni1−N5−Ni2	109.3(1)
O3−Ni2−N2	176.3 (1)	Ni1−N5−Ni3	108.4(1)
O5−Ni2−N8	172.9 (1)	Ni2−N5−Ni3	92.6(1)
N1−Ni2−N5	173.1(1)	Ni2−N8−Ni3	92.3(1)
O4−Ni3−N4	175.6 (1)		

[a] Symmetry code: ′ = $-x, 1-y, -z$. [b] The numbering scheme of this complex (Figure S1 in the Supporting Information) is identical with that used for complex **2** (Figure 1).

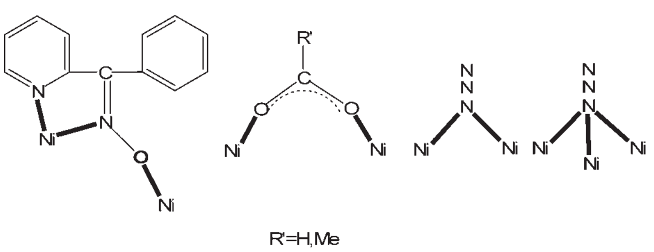
The molecule of **2** consists of 5 Ni^{II} atoms held together by two EO triply bridging N_3^- ions (N5 and its symmetry equivalent), two EO doubly bridging N_3^- ions (N8 and its symmetry equivalent), two *syn,syn*-η^1:η^1:μ-$MeCO_2^-$ groups (O3/O4 and its symmetry equivalent), and four η^1:η^1:η^1:μ-ppko$^-$ ligands (O1/N2 and O2/N4 and their symmetry equivalents). Peripheral ligation is provided by four terminal MeOH ligands on Ni2, Ni3, Ni2′, and Ni3′. The coordination modes of the bridging ligands that are present in **1** and **2** are shown in Scheme 2. The five Ni^{II} atoms are disposed in a centered parallelogram, which is planar by virtue of a crystallographic inversion center in the middle (at Ni1). An alternative description of the metal topology is as two Ni^{II} triangles (Ni1−Ni2−Ni3 and Ni1−Ni2′−Ni3′) with a common vertex (a bowtie). Each triangle is nearly isosceles, with the Ni1···Ni2, Ni1···Ni3, and Ni2···Ni3 distances being 3.401(1), 3.372(1), and 3.054(1) Å, respectively. Each diatomic oximate group bridges between the central Ni^{II} atom and one peripheral metal ion. A bridging $MeCO_2^-$ ligand spans the base (Ni2···Ni3 and Ni2′···Ni3′) of each isosceles triangle. The Ni2···Ni3 and Ni2′···Ni3′ bases of the triangles are each bridged by one EO μ-N_3^- group. The EO μ_3-N_3^- group links the central Ni^{II} atom, with the two peripheral metal ions on either side of the molecule. The donor atom (N5) of this group lies 0.871 Å out of the plane of the three associated Ni^{II} atoms; two of the angles subtended at N5 by the three Ni^{II} atoms are significantly larger (109.2 and 108.0 ° for the angles derived from the central Ni^{II} atom) than the third angle (93.7° for the angle to the peripheral Ni^{II} atoms). The core is $\{Ni_5(\mu\text{-}N_3)_2(\mu_3\text{-}N_3)_2\}^{6+}$ (Figure 3, top). This core has not been observed either in discrete Ni_5 clusters or as a recognizable subfragment of higher-nuclearity Ni^{II} clusters. If we consider all of the

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Complex **2**$\cdot$0.25H_2O[a]

Ni1$\cdots$Ni2	3.401(1)	Ni2−N2	2.036(3)
Ni1$\cdots$Ni3	3.372(1)	Ni2−N5	2.096(3)
Ni2$\cdots$Ni3	3.054 (1)	Ni2−N8	2.112(3)
Ni2$\cdots$Ni2′	6.803(1)	Ni3−O4	2.031(3)
Ni2$\cdots$Ni3′	6.045 (1)	Ni3−O6	2.129(3)
Ni3$\cdots$Ni3′	6.743(1)	Ni3−N3	2.029(3)
Ni1−O1	2.067(3)	Ni3−N4	2.024(3)
Ni1−O2	2.080(2)	Ni3−N5	2.090(3)
Ni1−N5	2.078(3)	Ni3−N8	2.122(3)
Ni2−O3	2.046(3)	N2−O1	1.334(4)
Ni2−O5	2.116(3)	N4−O2	1.331(4)
Ni2−N1	2.043(3)		
O1−Ni1−O2	93.1 (1)	O6−Ni3−N8	170.6(1)
O1−Ni1−N5	96.1(1)	N3−Ni3−N5	175.0(1)
O2−Ni1−N5′	83.3(1)	Ni1−N5−Ni2	109.2(1)
O3−Ni2−N2	174.7(1)	Ni1−N5−Ni3	108.1(1)
O5−Ni2−N8	168.8(1)	Ni2−N5−Ni3	93.7(1)
N1−Ni2−N5	173.2(1)	Ni2−N8−Ni3	92.3(1)
O4−Ni3−N4	173.6(1)		

[a] Symmetry code: ′ = $^1/_2 - x$, $^1/_2 - y$, $-z$.

Scheme 2



bridging oximate groups as part of the core, then it becomes $\{Ni_5(\mu\text{-}N_3)_2(\mu_3\text{-}N_3)_2(\mu\text{-}ONR'')_4\}^{2+}$ ($R''NO^- $ = ppko$^-$); see Figure 3, bottom.

Ni2 and Ni3 are bound to an O_2N_4 set of donor atoms, while Ni1 forms a NiO_4N_2 chromophore. Thus, all of the Ni^{II} atoms are six-coordinate with distorted octahedral geometry, with the main distortion arising from the relatively small bite angle of the chelating parts of the ppko$^-$ groups. The Ni$\cdots$Ni separations in the pentanuclear molecule reflect the nature of the bridging groups connecting each pair of Ni^{II} atoms. The distance between the central nickel and each outer nickel remains roughly constant at ~3.4 Å, with these being in each case enclosed in a five-membered ring. Such Ni^{II} atoms are separated by one monatomic bridge (μ_3-N_3^-) and one diatomic bridge (an oximate group). Ni2 and Ni3 (and their symmetry equivalents), separated by one triatomic (OCO) and two monatomic azide bridges, have the shortest separation [3.054(1) Å]. The μ-N_3^- atom N8 bridges Ni2 and Ni3 in a perfectly symmetric manner; thus, the Ni2−N8 and Ni3−N8 bond distances are equal [2.112(3) and 2.122(3) Å]. The μ_3-N_3^- atom N5 bridges the three Ni^{II} atoms almost symmetrically; thus, the Ni(1,2,3)−N5 bond distances are in the narrow 2.078(3)−2.096(3) Å range. The larger Ni−μ_3-N_3^-−Ni angles [109.2(1) and 108.0(1)°] correspond to the pairs Ni1/Ni2 and Ni1/Ni3 in which the Ni^{II} atoms are separated by one monatomic bridge and one diatomic bridge, whereas the smaller one [93.7(1)°] corresponds to the triply bridged metal ions (Ni2/Ni3).

The crystal structure of **2**$\cdot$0.25H_2O is stabilized by O(MeOH)$\cdots$O(lattice H_2O) [O$\cdots$O = ~2.9 and 3.0 Å] hydrogen bonds and C−H$\cdots$N(azide) [C$\cdots$N = 3.51 Å] and C−H$\cdots$O(acetate) [C$\cdots$O = ~3.2 Å] supramolecular interactions,[52] i.e., nonclassical hydrogen bonds. These classical and nonclassical hydrogen bonds create a three-dimensional (3D) network.

Table 4. Intramolecular Hydrogen Bonds for Complex **1**[a]

D−H$\cdots$A	D$\cdots$A [Å]	H$\cdots$A [Å]	D−H$\cdots$A [deg]	symmetry operator of A
O5−H5$\cdots$O2	2.785(3)	2.04(3)	161(3)	$-x, -y + 1, -z$
O6−H6$\cdots$O1	2.740(3)	1.94(4)	162(4)	$-x, -y + 1, -z$

[a] A = acceptor atom; D = donor atom.

The structure of the pentanuclear molecule of **1** is very similar to that of **2**, with the essential difference being the replacement of the acetate ligands in the latter by formate groups in the former. Each coordinated MeOH hydroxyl group is intramolecularly hydrogen-bonded to a coordinated oximate O atom. The dimensions of the two crystallographically unique hydrogen bonds are listed in Table 4. The pentanuclear molecules of **1** form chains through C14 (a 2-pyridyl C atom)−H14$\cdots$N8 (the donor atom of μ-N_3^-) weak supramolecular interactions, with the C14$\cdots$N8 and N8$\cdots$H14 distances being 3.553 and 2.658 Å, respectively; see Figure S2 in the Supporting Information. The chains form 3D networks through weak C−H$\cdots$O(formate) interactions (C−H$\cdots$O = ~3.5 Å).

The bond distances around the Ni^{II} atoms in **1** and **2** are typical of those found in octahedrally coordinated nickel(II) complexes with O and N ligation.[20a,31−36,37b,37h,37i]

Complexes **1** and **2** join a rather large family of Ni$^{II}_5$ clusters with N and/or O donors possessing the metal ions in various topologies, such as linear,[54] helical,[55] tetrahedral-centered on a fifth Ni^{II} atom,[56] tetrahedral with the fifth Ni^{II} atom lying at the midpoint of one Ni$\cdots$Ni edge,[37h] defective corner-shared dicubane,[57] capped triple helical,[58] closed cagelike,[37j] triple-stranded helical,[59] pentagonal,[60] 12-metallacrown-4 with an encapsulated Ni^{II} ion,[61] capsule-shaped with five coplanar Ni^{II} atoms,[62] well-separated Ni_2 and Ni_3

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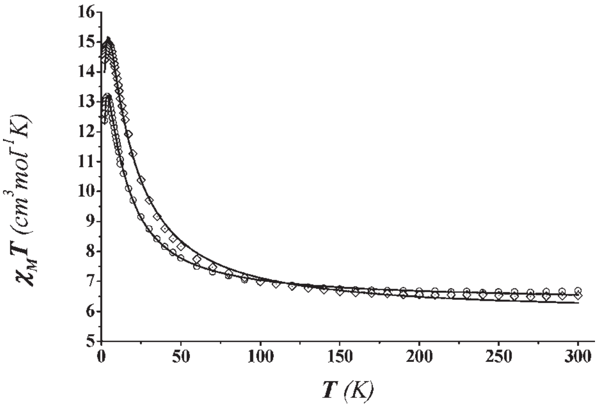


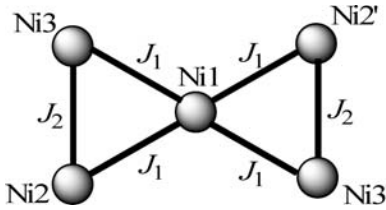
Figure 4. Plots of $\chi_M T$ vs T for complexes **1** (dotted circles) and **2** (dotted squares). The solid line is the fit of the data; see the text for the fit parameters.

subunits,[63] trigonal-bipyramidal,[64] and rectangular-centered on a fifth Ni^{II}atom.[65] Compounds **1** and **2** belong to the last subfamily of Ni^{II}_5 clusters. They are only the second and third structurally characterized Ni^{II}_5 complexes with bridging azido ligands; the first one is complex $[Ni_5\{pyCOpyC(O)(OMe)py\}_2(O_2CMe)_4(N_3)_4(MeOH)_2]$,[55] in which the ligand is the monoanion of the keto-hemiketal form of di-2,6-(2-pyridylcarbonyl)pyridine. Complexes **1** and **2** are also members of a small group of nonorganometallic polynuclear metal complexes of ppko$^-$, which currently comprises Ni^{II},[31−36] $Mn^{II/IV}$,[47c] Mn^{III},[66a] $Mn^{II/III}$,[66b] Cu^{II},[67] $Co^{II/III}$,[68] and Zn^{II}.[69]

Magnetochemistry. Variable-temperature direct-current (dc) magnetic susceptibility studies were performed on powdered samples of compounds **1** and **2** in applied fields of 0.3 T (300−30 K) and 0.03 T (30−2.0 K). The data for **1** and **2** are plotted as $\chi_M T$ versus T in Figure 4.

The two complexes exhibit a similar behavior. The room temperature $\chi_M T$ values are 6.69 (for **1**) and 6.53 (for **2**) cm^3 K mol^{-1}, slightly higher than the spin-only value of 6.05 cm^3 K mol^{-1} with $g = 2.2$ expected for a cluster of five noninteracting $S = 1$ Ni^{II} atoms. The $\chi_M T$ product increases slightly with decreasing temperature in the range 300−100 K, before increasing more rapidly below this temperature to maximum values of 13.18 cm^3 K mol^{-1} at 3.7 K for **1** and 14.96 cm^3 K mol^{-1} at 4.5 K for **2**. The product sharply decreases at lower temperatures, reaching the values of 12.38 (for **1**) and 14.41 (for **2**) cm^3 mol^{-1} K at 2.0 K. This behavior indicates an overall ferromagnetic behavior, and the $\chi_M T$ values at the maxima suggest a ground-state $S = 5$ value. The decrease in $\chi_M T$ below ~4 K is assigned to either zero-field splitting within the ground state, Zeeman effects, and/or weak antiferromagnetic intermolecular interactions. Magnetization data collected at 2.0 K show a continuous increase of M as the field increases, reaching a nonsaturated value close to 8 in $M/N\beta$ units under an external field of 5 T.

Scheme 3



To fit and interpret the magnetic susceptibility data of **1** and **2**, first it is necessary to find all possible magnetic pathways in the bowtie structural type. Close inspection of the very similar and symmetric molecular structures (Figures 1 and S1 in the Supporting Information) reveals that there are only two different exchange pathways and thus two different J coupling constants (from now onward, the numbering scheme that will be used is the same as that used in the real structures). J_1 is associated with the four interactions between the central Ni1 ion and the four peripheral Ni^{II} centers through one EO triply bridging N_3^- ion and one bridging diatomic oximate group from a ppko$^-$ ligand; J_2 is associated with the two equal Ni2···Ni3 and Ni2′···Ni3′ interactions, each through a triply $(\mu_3\text{-}N_3^-)/(\mu\text{-}N_3^-)/(\eta^1{:}\eta^1{:}\mu\text{-}O_2CR)$ bridging scheme. The spin Hamiltonian for such a system, illustrated in Scheme 3, is given by eq 3.

$$H = -J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3 + \hat{S}_1\cdot\hat{S}_{2'} + \hat{S}_1\cdot\hat{S}_{3'}) - J_2(\hat{S}_2\cdot\hat{S}_3 + \hat{S}_{2'}\cdot\hat{S}_{3'}) \quad (3)$$

The fitting of the experimental data was performed by means of the analytical expression derived from the spin Hamiltonian of eq 3, with the addition of an overall Weiss parameter $(T - \theta)$ in order to cover the whole temperature range studied (including the low-temperature decrease of $\chi_M T$). The best-fit parameters are $J_1 = 2.58(2)$ cm^{-1}, $J_2 = 11.7(3)$ cm^{-1}, $g = 2.247$ (3), and $\theta = 0.93(1)$ K for **1** and $J_1 = 4.93(7)$ cm^{-1}, $J_2 = 14.6(5)$ cm^{-1}, $g = 2.188(5)$, and $\theta = 0.52(1)$ K for **2**; the agreement factor, defined as $R = \sum[(\chi_M)^{calc} - (\chi_M)^{obs}]^2/\sum[(\chi_M)^{obs}]^2$, is 1.1×10^{-4} and 8.1×10^{-5} for **1** and **2**, respectively. A fragment containing one EO azido group and one diatomic oximate group (J_1 in our case) has been reported in Na_2Ni_{12},[37h] Ni_{14},[37h] and Ni_7[37j] clusters, but a reliable fit was performed only in the case of the Ni_7 compound. In spite of the fact that the structural parameters are not

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fully comparable (the azido bridge in the fragment of the Ni_7 compound is μ instead of μ_3, and the Ni−N−Ni angle is larger than those in **1** and **2**), the interaction was reported also to be ferromagnetic, as occurs for J_1 in the present complexes. In contrast, there is more information in the literature concerning bis(azido)(carboxylato) bridges between two Ni^{II} centers;[24e,70] the exchange interaction was found to be ferromagnetic in all cases. Perhaps the best comparison can be made with complex $[Ni_3(O_2CMe)_3(N_3)_3(py)_5]$ (py = pyridine),[70e] which presents the same $(\mu\text{-}N_3)(\mu_3\text{-}N_3)(\eta^1{:}\eta^1{:}\mu\text{-}O_2CR')$ bridging unit (with very similar structural parameters) as those found in **1** and **2**; a J value of $+15.7\ cm^{-1}$ was reported to be comparable to the J_2 value in the present Ni_5 complexes.

For a system of five $S = 1$ centers that are in a bowtie topology and interact according to the $2J$ model of eq 3, the ground-state S values 1, 3, and 5 are possible depending on the J_2/J_1 ratio. For positive J_1 and J_2 values, i.e. for a fully ferromagnetic system, the ground state is $S = 5$ and this is clearly isolated from other spin levels.

Alternating current (ac) studies were performed in the 1.8−5 K range using a 4 G ac field oscillating at frequencies (ν) in the 5−1440 Hz range. If the magnetization vector can relax fast enough to keep up with the oscillating field, then there is no imaginary (out-of-phase) susceptibility signal (χ_M''). However, if the barrier to magnetization relaxation is significant compared to the thermal energy (kT), then there is a nonzero χ_M''; in addition, χ_M'' will be frequency-dependent. Such frequency-dependent χ_M'' signals are a characteristic signature of the superparamagnetic-like properties of a SMM but, by themselves, do not prove the SMM behavior.[71]

The ac magnetic susceptibility behaviors of **1** and **2** are different. For complex **1**, there is an appearance of frequency-dependent χ_M'' signals below ~3.5 K (Figure 5); only the tails of the peak are visible above 1.8 K (the operating limit of our SQUID magnetometer), with the peak maxima lying at lower temperatures. The χ_M'' signals indicate a possible SMM behavior for **1**. Complex **2** does not exhibit an out-of-phase ac magnetic susceptibility signal down to 1.8 K.

Hysteresis Studies below 1.8 K for Complex 1. In order to confirm whether complex **1** is a new SMM, we performed magnetization versus applied dc-field studies on single crystals of **1** at temperatures down to 0.04 K using a micro-SQUID apparatus.[46] The observation of hysteresis loops in such studies represents the diagnostic property of a magnet, including SMMs and superparamagnets below their blocking temperature (T_B). The observed magnetization responses for **1** are shown in Figure 6 (top) at a fixed dc-field sweep rate of $0.004\ T\ s^{-1}$ and at temperatures in the range of 0.04−1.0 K and in Figure 6 (bottom) at 0.04 K and in the sweep-rate range of $0.002-0.140\ T\ s^{-1}$. Some minor hysteresis was observed but with a very narrow coercivity that did not change noticeably with either decreasing temperature or increasing scan rate in the 0.04−1.0 K and $0.002-0.140\ T\ s^{-1}$ ranges. This is clearly not the superparamagnet-like behavior expected of an SMM.[71b] However, the tiny two-step

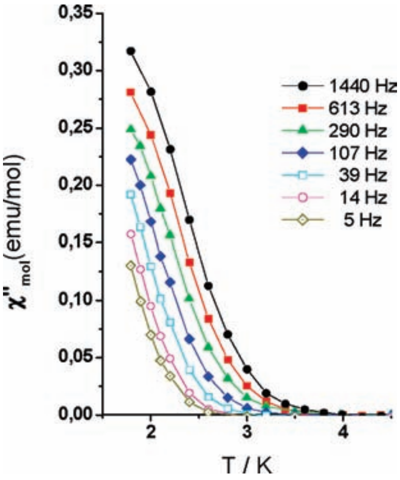

Figure 5. Out-of-phase (χ_M'') vs T ac susceptibility signals for **1** in a 4 G field oscillating at the indicated frequencies.

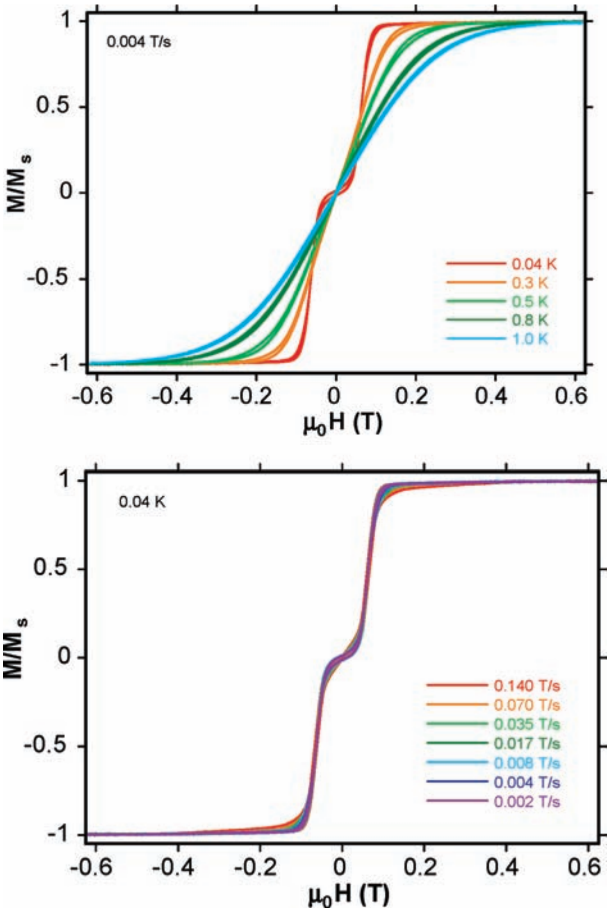

Figure 6. Magnetization (M) vs dc applied magnetic field (H) hysteresis loops for a single crystal of **1** at the indicated temperatures and a fixed-field sweep rate of $0.004\ T\ s^{-1}$ (top) and at the indicated field sweep rates and a fixed temperature of 0.04 K (bottom). The magnetization is normalized to its saturation value, M_S.

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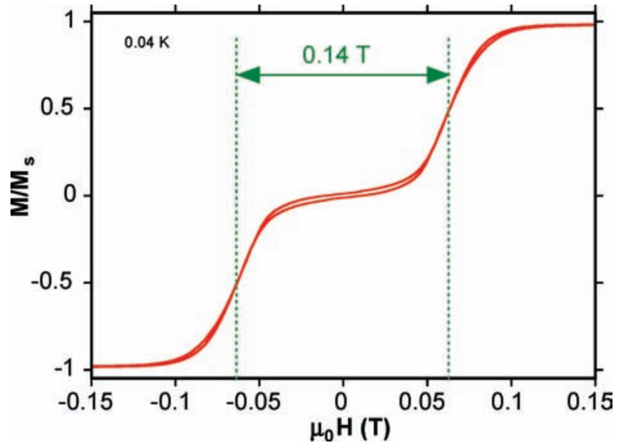

Figure 7. Expansion of the +0.15 to −0.15 T field range in the magnetization (*M*) vs dc applied magnetic field (*H*) hysteresis loop for a single crystal of **1** at 0.04 K and 0.004 T s^{-1} showing the exchange-biased measurement position. *M* is normalized to its saturation value, M_S.

hysteresis at 0.04 K appears to be real. An interesting feature in the loops is the fact that, upon sweeping of the field back from either extreme toward zero field, the magnetization begins to decrease before reaching zero field. This shift from zero field is indicative of an exchange bias[8c,d] from neighboring molecules, i.e., the influence of intermolecular antiferromagnetic exchange interactions on the magnetization relaxation dynamics of a molecule. For a single crystal of a SMM that has negligible intermolecular exchange interactions, the first step in the hysteresis loop due to quantum tunneling of magnetization occurs at zero field when the external field is oriented parallel to the easy axis of the crystal. The observed behavior of **1** is consistent with the observation in its crystal structure of one-dimensional (1D) chains of Ni_5 molecules linked by nonclassical C−H···N hydrogen bonds,[53b] with the chains further interacting through nonclassical C−H···O hydrogen bonds,[53a] and there are likely also some contributions from intermolecular dipolar interactions between the relatively large ground state $S = 5$ spins. Similar behavior has been seen in Fe_{19},[72] Fe_9,[73] Mn_8Ce,[74] and Ni_4 SMMs,[24g] which also exhibit intermolecular interactions.

As reported earlier, for both isolated dimers of interacting molecules[7e,d] and also 3D networks of interacting molecules,[75] the strength of the intermolecular exchange coupling constant *J* can be calculated from the field shift that it causes in the hysteresis loops. Closer inspection of the hysteresis loop at 0.04 K (Figure 7) indicates an exchange bias of 0.07 T (70 mT) on either side of the zero field. From this can be calculated *J*, by using the expression in eq 4, appropriate for the $H = -2J\hat{S}_i\cdot\hat{S}_j$ convention

$$J = -g\mu_B\mu_0 H_{ex}/k_B S \tag{4}$$

where H_{ex} is the exchange-biased field (i.e., the shift from zero field), k_B is the Boltzmann constant, *g* is the electronic *g* factor, μ_B is the Bohr magneton, and μ_0 is the vacuum permeability.[75] The calculation gives $J = -0.021$ K, and from this can be calculated the exchange interaction energy $-2JS^2$ of 1.05 K. The interaction is thus antiferromagnetic, as expected, and stronger compared to previous examples, for example, in complex $[Mn^{III}_8Ce^{IV}O_8(O_2CMe)_{12}(H_2O)_4]$.[74] If the antiferromagnetic intermolecular interactions are weak, as in the $Mn^{III}_8Ce^{IV}$ cluster, then they are merely a perturbation of the SMM properties, and such compounds can be described as exchanged-biased SMMs.[74] If they are not as weak as they seem to be for **1**, then the crystal may be better described as containing antiferromagnetically ordered 1D, two-dimensional (2D), or 3D extended networks.[74] We, therefore, conclude that any real hysteresis is only evident at 0.04 K and that this is most probably not due to single-molecule properties but to intermolecular interactions.

Conclusions and Perspectives

The initial use of the $R'CO_2^-/N_3^-/ppko^-$ ligand combination in Ni^{II} cluster chemistry has provided access to two new Ni^{II}_5 complexes, **1** and **2**, with unusual structures containing the metal ions in a bowtie topology and not seen before in the coordination chemistry of 2-pyridyloximes. Both complexes have a ground-state spin of $S = 5$. Ac susceptibility studies on the formate complex **1** display the appearance of frequency-dependent out-of-phase signals. However, magnetization vs dc field sweeps down to 0.04 K revealed true (but very slight) hysteresis only at 0.04 K, which we assign to the intermolecular nonclassical hydrogen bonding seen in the crystal structure. We believe that there is an absence of significant single-molecule barrier (vs kT) to magnetization relaxation, and most probably **1** is not an SMM. The clear observation of χ_M'' signals below 3.5 K is thus unusual. The tiny barrier responsible for the almost insignificant hysteresis at 0.04 K is not expected to give χ_M'' signals at higher temperatures up to 3.5 K. Typically, complexes that exhibit significant tails of ac χ_M'' signals at >1.8 K then reveal clear hysteresis in dc magnetization sweeps assignable to an SMM with T_B of at least ~0.6 K or more.[71b] Thus, we cannot offer an unequivocal explanation of the origin of the χ_M'' signals, except to state that it should be due to a combination of factors such as intermolecular interactions, phonon bottlenecks, and perhaps other contributions.[71b]

As far as future perspectives are concerned, analogues of **1** and **2** with 2-pyridinealdoxime (R = H in Scheme 1) are not known to date, and it is currently not evident whether the synthesis and stability of such Ni^{II}_5 clusters are dependent on the particular nature of the R substituent on the oxime C atom. $Ni^{II}/ppko^-/N_3^-$ chemistry, i.e., omission of carboxylates from the reaction system studied in this work, is also completely unexplored, and work in progress has just unearthed the interesting new bowtie cluster $[Ni_5(N_3)_4(ppko)_4(ppkoH)_4](ClO_4)_2$, in which four EO doubly bridging N_3^- ions and two μ_3 oximate groups provide the bridges between the central and external Ni^{II} atoms.[76] We are also pursuing substitution of the bridging carboxylate and terminal MeOH ligands of **1** and **2** by bulkier ligands of similar chemical nature in an effort to magnetically insulate the Ni^{II}_5 molecules; such

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studies give valuable information[24g] on the dynamic magnetic properties of structurally similar complexes.

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Supporting Information Available: Crystallographic data for complexes **1** and **2**·0.5H_2O in CIF format, partially labeled plot of the Ni_5 molecule of **1** (Figure S1), a portion of the chain formed by the pentanuclear molecules of **1** (Figure S2), and the analytical expression used for the fits of the magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.