

Magnetic Properties



New Classes of Ferromagnetic Materials with Exclusively End-on Azido Bridges: From Single-Molecule Magnets to 2D Molecule-Based Magnets

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Abstract: A new, flexible synthetic route, which does not require the co-presence of any organic chelating/bridging ligand but only the “key” precursor Me_3SiN_3 , has been discovered and led to a new class of inorganic materials containing exclusively end-on azido bridges; the reported 3d-metal clusters and coordination polymers exhibit ferromagnetic, single-molecule magnet, and long-range magnetic ordering properties.

Polynuclear metal complexes (also named “metal clusters”) and coordination polymers are two families of inorganic materials, which have served to convey the classical, “Werner-type” coordination chemistry into a new, modern era of molecular nanoscience. Classical coordination chemistry makes use of relatively simple ligands, for example, NH_3 , Cl^- , and H_2O , with the resulting, in vast majority mononuclear, complexes showing applications in the fields of catalysis and biology.^[1] On the other hand, the synthesis of metal cluster compounds and coordination polymers has always demanded the employment of polydentate bridging organic ligands, which serve to link the metal centers into a large polymetallic structure.^[2] Indeed, several organic ligands have been used to date, from simple and flexible carboxylates^[3] to more bulky and robust polyalcohols, oximes, and Schiff bases,^[4] all leading to structural motifs with interesting physical properties.

Molecular magnetism is the area of research, which deals with the study of the magnetic-exchange interactions and magnetostructural correlations in polymetallic molecular compounds.^[5] Ferromagnetism, single-molecule magnetism, and long-range magnetic ordering are undoubtedly some of the

most attractive subfields of molecule-based magnetism. For instance, single-molecule magnets (SMMs) exhibit slow relaxation because of an energy barrier to magnetization reversal created by action of a negative axial zero-field splitting, D , on the spin ground state, S .^[6] SMMs can find use in potential applications, such as high-density information storage, quantum computing, and spin-based molecular electronics.^[7]

Azido (N_3^-) ligand has been known for years as one of the most flexible, multitopic, and versatile groups in coordination chemistry, capable of bridging many metal centers and leading to beautiful structures with interesting magnetic properties.^[8,9] In the magnetism arena, it is now established that end-on (EO) bridging azides can promote strong ferromagnetic exchange interactions between the metal-spin carriers, thus leading to high-spin molecules, SMMs, and molecule-based magnets with long-range ferromagnetic ordering or spin-canting behaviors.^[9] In addition to the magnetic properties, inorganic metal-azide compounds with a large $\text{N}_3^-/\text{M}^{n+}$ ratio could be potentially considered as high-energy materials due to their ability to form polymeric networks of single-bonded nitrogen with energy densities nearly three times greater than those of conventional highly explosive materials.^[10]

However, in all previously reported metal cluster compounds and coordination networks, azides have been always employed in conjunction with organic bridging/chelating ligands. Although necessary for the thermodynamic stability and crystallinity of the resulting molecular species, the presence of organic ligands often affects the magnetic properties and dynamics of the compounds, leading to competing antiferromagnetic interactions, moderate-to-weak magnetic couplings, and low-lying excited states, among others.^[8,9] A potential solution to overcome these problems and construct strongly ferromagnetic systems is the discovery of new synthetic strategies for the assembly of polymetallic-azido structures without the co-presence of organic chelating/bridging ligands. Herein, we demonstrate a new route to purely inorganic-bridged, transition-metal-azido clusters, and coordination polymers, which exhibit strong ferromagnetic, SMM, and long-range magnetic ordering behavior. We also show that access to such a unique class of ferromagnetic inorganic, N-rich and O-free materials becomes feasible through the use of Me_3SiN_3 as the azido-ligand precursor without requiring the addition of any organic chelate.

The reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, NEt_3 , and Me_3SiN_3 in a 1:1:4 molar ratio in MeCN led to a pink solution, which was layered with Et_2O to give next day pink plate-like crystals of $[\text{Co}^{\text{II}}(\text{N}_3)_{12}]^{2-}$

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(MeCN)₁₂(ClO₄)₂ (**1**) in 75% yield. A similar reaction with Ni(ClO₄)₂·6H₂O in place of Co(ClO₄)₂·6H₂O gave the isomorphous [Ni^{II}₇(N₃)₁₂(MeCN)₁₂(ClO₄)₂ (**2**) as green plates in 78% yield.

Given the structural similarity of clusters **1** and **2** (Figure 1), only the structure of the former will be discussed in detail. The centrosymmetric heptanuclear dication of **1** (Figure 1, left) contains an almost ideal planar hexagon of alternating Co^{II} atoms surrounding a central, seventh Co^{II} atom. The Co₇ disk-like unit is held together by 12 N atoms of six 3.30 (or μ₃-1,1,1) and six 2.20 (or μ-1,1) end-on bridging azido ligands. The former type of N₃⁻ groups bridge the Co₆ hexagon with the central Co atom, and the latter bridge the Co₂ pairs of the hexagon. Peripheral ligation is completed by 12 terminal MeCN solvate molecules, two on each of the external Co^{II} atoms. All Co atoms are six-coordinate with near-octahedral geometries. The [Co₇(μ₃-N₃)₆(μ-N₃)₆]²⁺ inorganic core of **1** (Figure 1, right) can alternatively be described as consisting of six {Co₃(N₃)₄} partial-cubane units, each double face sharing, and all six vertex shar-

ing at the central Co^{II} atom. Complex **1** has a layered structure, with layers of N atoms from azides above and below the Co₇ plane. The Co₇ dication has virtual or imposed C₃ symmetry. The Co...Co separations and Co-(μ-N₃)-Co angles span the range 3.228–3.279 Å and 95.0–103.0°, respectively (Figure S1 in the Supporting Information).^[11] The packing of the Co₇ clusters shows large intermetallic separations between Co^{II} atoms of neighboring molecules, with the closest intermolecular Co...Co distance being 8.13 Å. Complex **1** belongs to a family of structurally known disk-like Co₇ clusters albeit being the first solely bridged by μ- and μ₃-EO azido groups.^[12] Of significant importance is the fact that **1** (and **2**) consist of 1.7:1 N₃⁻/metal ratio, the highest reported to date for any polynuclear metal system with a nuclearity larger than four, which renders these species potentially attractive for high energy density materials study.^[13] Furthermore, **1** and **2** are the first metal clusters in moderate oxidation states, which are exclusively bridged by azido groups and stabilized without the co-presence of any additional organic N,O-bridging/chelating ligand.

To elucidate the static and dynamic magnetic properties of the heptanuclear compounds, solid-state direct current (dc) and alternating current (ac) magnetic-susceptibility studies were performed on fresh crystalline samples of **1** and **2** in the 1.8–300 K range. Extensive discussion of the magnetostructural properties of the entirely ferromagnetic **2** is provided in the Supporting Information (Figures S7–S9). Under a dc field of 1 kG (0.1 T), the value of χ_MT for **1** at 300 K is 25.10 cm³ mol⁻¹ K, which is much higher than the spin-only value of seven high-spin, S = 3/2, Co^{II} ions (13.13 cm³ mol⁻¹ K), indicating significant orbital contributions of the distorted octahedral Co^{II} ions. Upon cooling, the χ_MT product rapidly increases to a maximum of 74.53 cm³ mol⁻¹ K at 14 K and then decreases sharply to a value of 46.79 cm³ mol⁻¹ K at 2 K (Figure 2). The data above 150 K obey the Curie–Weiss law with C = 21.06 cm³ mol⁻¹ K and θ = +48.7 K, clearly suggesting an overall ferromagnetic coupling between the Co^{II} centers (Figure S2 in the Supporting Information).

Considering the bridging ligation in the Co₇ core of **1**, we attempted to simulate the magnetic data by using the fitting models previously employed by Gao for the structurally similar [Co^{II}₇(N₃)₉(OMe)₃(bzip)₆]²⁺ (bzip = 2-benzoyl pyridine) with an approximate S₆ symmetry.^[12a] The program used for fitting all the magnetic data was PHI,^[14] and all J values are referred to the –J Hamiltonian. The fitting of the high-T (> 150 K) regime gave an

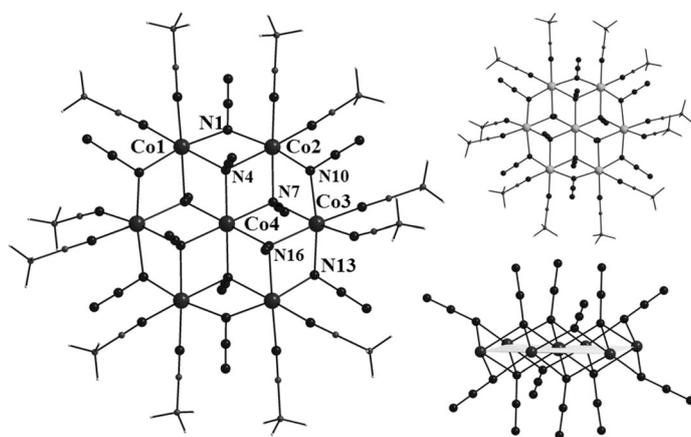


Figure 1. Partially labeled representations of the dications of complexes **1** (left) and **2** (top, right), and a side view of the [Co₇(μ₃-N₃)₆(μ-N₃)₆]²⁺ core (bottom, right).

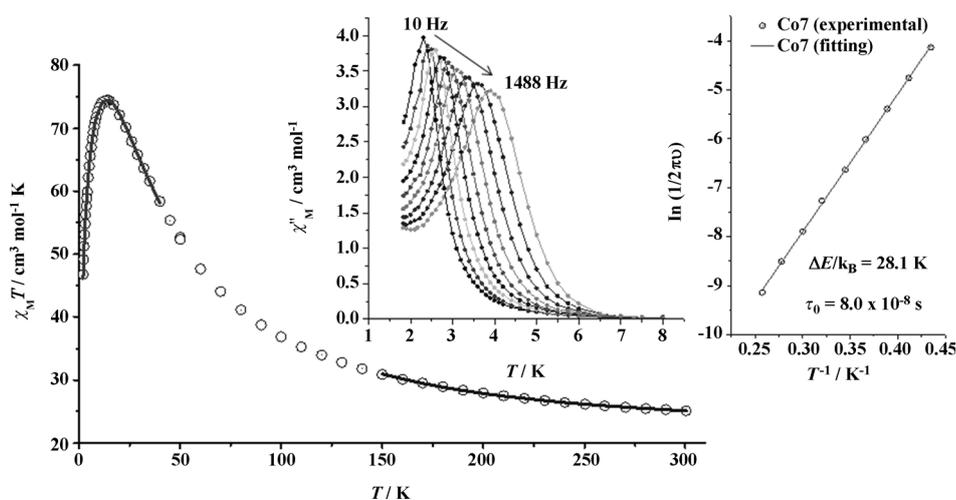


Figure 2. χ_MT versus T plot for **1** in a 1 kG field. The solid lines are the fits of the data; see the text for the fit parameters. Inset: out-of-phase (χ''_M) versus T ac susceptibility signals for **1** under a 0.1 T static dc field, with a 4.0 G ac field oscillating at various frequencies, and the Arrhenius plot from the peak maxima.

average $J_{av} = +9.34 \text{ cm}^{-1}$ with each $S_{Co} = 3/2$ and $g = 2.50$; fit with $2J$ values tended to give very similar J parameters. For the low- T region (2–40 K) we considered an effective spin $S'_{Co} = 1/2$ system; an excellent fit was obtained with $J_{av} = +29.4 \text{ cm}^{-1}$, $zJ' = -0.11 \text{ cm}^{-1}$, and $g = 6.63$. This further confirms the strong intracluster ferromagnetic interactions in **1**, which lead to an effective spin ground state of $S = 7/2$. The field-dependent magnetization studies were also performed at the temperature range 1.8–6.8 K with the isofield lines being far from superposition, indicating significant magnetoanisotropy. An excellent fit of the reduced magnetization data was obtained assuming a well-isolated, $S = 7/2$ ground state with $D = -5.55 \text{ cm}^{-1}$ and $g = 6.56$ (Figure S3 in the Supporting Information).

Another evidence for the possible SMM behavior of **1** is the observation of strong and frequency-dependent out-of-phase (χ_M'') ac signals below 6 K in zero-applied dc field, although no peak maxima were observed for the majority of frequencies down to 1.8 K (Figure S4 in the Supporting Information). It is now well-established that the effective energy barrier, U_{eff} for the magnetization reversal of an SMM can be tuned by the application of a small external dc field, which suppresses the fast tunneling usually seen for almost all Co^{II} SMMs.^[15] That was also the case for **1**; application of a 0.1 T dc field resulted in an appreciable shift of the in-phase (χ_M' , Figure S5 in the Supporting Information) and out-of-phase (χ_M'') ac signals at higher T , and thus the peak maxima were clearly detected for all high- and low-ac frequencies. An Arrhenius plot constructed from the ac χ_M'' versus T data of Figure 2 (inset) gave $\Delta E/k_B = 28.1 \text{ K}$ (19.6 cm^{-1}) and $\tau_0 = 8.0 \times 10^{-8} \text{ s}$, in which τ_0 is the pre-exponential factor. Compared with all the previously reported Co^{II}_7 disks, **1** is a stronger ferromagnetic system due to the presence of 2.20 and 3.30 EO azides; **2** has a very well isolated ground-state spin value as was evidenced by the similar EPR spectra at 4 and 23 K (Figure S6 in the Supported Information); and **3** is a better field-induced SMM with an energy barrier amongst the highest reported to date for any polynuclear Co^{II} SMM.^[15,16]

In light of the magnetostructural findings resulted from the employment of Me_3SiN_3 in divalent 3d-metal chemistry, we attempted to develop this synthetic strategy further, now to more redox-active 3d-metals. Thus, the aerobic reaction of $Fe(ClO_4)_2 \cdot xH_2O$, NEt_3 , and Me_3SiN_3 in a 1:1:4 molar ratio in MeCN led to dark orange crystals of the mixed-valence compound $[Fe^{II}Fe^{III}(N_3)_5(MeCN)_2]_n$ (**3**) in 52% yield. Complex **3** is a neutral 2D coordination polymer (Figure 3) with the asymmetric unit consisting of two iron centers bridged by five 2.20 (or $\mu-1,1$) end-on azido ligands; peripheral ligation is provided by two terminal MeCN molecules. Due to the crystallographic C_2/c point group symmetry, Fe1 and Fe3 are half-occupied, whereas Fe2 is fully occupied in the asymmetric unit. The metal ions oxidation states were assigned based on metric parameters and bond-valence sum (BVS) calculations.^[17] As a result, Fe1 and Fe3 atoms are +2 and Fe2 is +3, confirming the mixed-valence description for **3**; all metal atoms are high-spin and six-coordinate with distorted FeN_6 octahedral geometries.^[11]

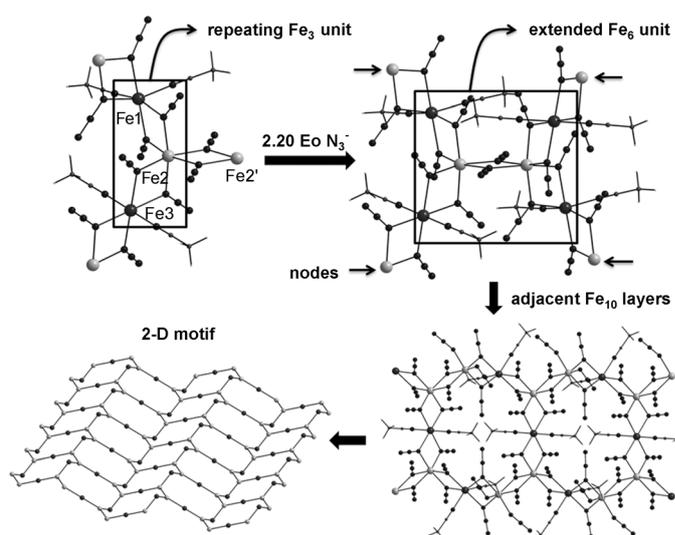


Figure 3. “Building up” the 2D polymer **3** from simpler fragments. Color scheme: Fe^{II} dark green, Fe^{III} yellow, N blue, C dark gray, H light gray.

The repeating $\{Fe^{II}_2Fe^{III}(N_3)_7(MeCN)_2\}$ unit is not linear but bent, with an $Fe1 \cdots Fe2 \cdots Fe3$ angle of 119.1° . Two N_3^- groups, bound to the central Fe2 atom, become 2.20 EO, serving to bridge the $\{Fe^{II}_2Fe^{III}(N_3)_7(MeCN)_2\}$ unit with an adjacent one. The $Fe2-(\mu_{1,1}-N_3)_2-Fe2'$ subunit is strictly planar. The resulting $\{Fe^{II}_4Fe^{III}_2(N_3)_{14}(MeCN)_4\}$ moieties are further linked by 2.20 EO N_3^- groups (bound to the “nodal” Fe1 and Fe3 atoms) to finally form aesthetically pleasing $[Fe^{II}_4Fe^{III}_6(N_3)_{26}(MeCN)_8]_\infty$ cyclic units, which create an extended 2D network of ladder-like hexagonal layers. The $Fe \cdots Fe$ intralayer separations and $Fe-(\mu_{1,1}-N_3)-Fe$ angles span the range 3.331–3.393 Å and 102.5 – 106.7° , respectively.^[11] The shortest interlayer distance is 9.47 Å. To our knowledge, **3** is the first 2D coordination polymer containing solely EO N_3^- groups. It is by far the compound with the highest $N_3^-/metal$ ratio (2.5:1) and a unique member of a new, emerging class of azido-rich/ligand-free multidimensional coordination polymers.

Dc magnetic susceptibility studies on a polycrystalline sample of **3** were performed (Figure 4, top) and the data at the high- T region (300–80 K) were consistent with ferromagnetic interactions between the $Fe^{II/III}$ centers through the EO N_3^- bridges, as reflected in a continuous increase of $\chi_M T$ product from a value of $9.0 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $21.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 80 K. The data above 120 K follow the Curie–Weiss law with $C = 7.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\theta = +61.0 \text{ K}$, confirming the strong ferromagnetic coupling between the Fe centers (Figure S10 in the Supporting Information). Below 80 K, the $\chi_M T$ product steeply rises, reaching a maximum value at $T \approx 34 \text{ K}$; such behavior is attributed to a long-range ferromagnetic ordering of the spins.^[18] To characterize the low- T behavior of **3**, field-cooled magnetization measurements were performed under different fields (0.1–0.3 T). The χ_M and $\chi_M T$ products are strongly field dependent showing an increase of their values as the field decreases, reaching a $\chi_M T$ value of $335.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 35 K (under a field of 0.1 T) and thus confirming the ordered phase (Figure S11 in the Supporting Information). All curves

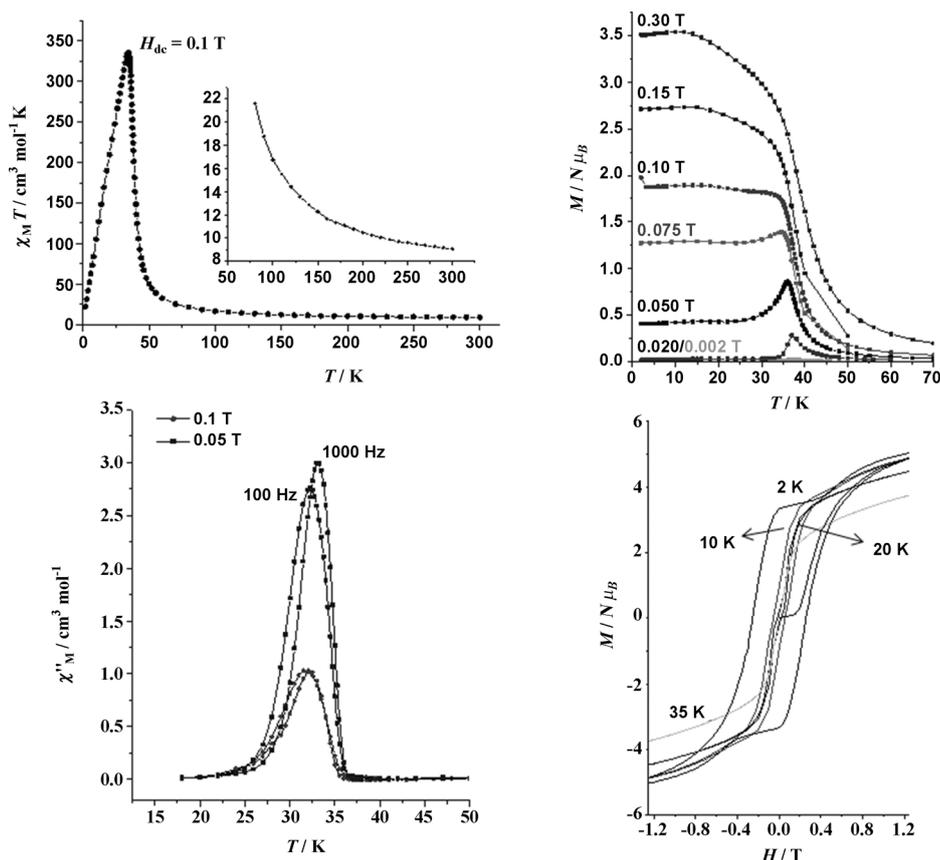


Figure 4. Top (left): $\chi_M T$ versus T plot in a 1 kG field and (top, right) field-cooled magnetization plots for **3**. Bottom (left): thermal dependence of the χ_M'' component of the ac susceptibility of **3** at different frequencies and static fields and (bottom, right) isothermal magnetization plots at different temperatures.

join at $T \approx 45$ K. In the 50–300 K region, all plots follow exactly the same trend, which corresponds to the simple paramagnetic phase of the system. To assess the effect of any possible interlayer interactions on the magnetic properties of **3**, weaker fields (0.002–0.075 T) have been employed. The system retains the same ordering peak albeit the susceptibility seems to be vanished on cooling when the field is < 0.002 T.^[11] Such behavior is indicative of interlayer interactions and the field to overcome such effects has been estimated to approximately 0.1 T. Toward that end, magnetization versus field studies have been also carried out, and it is clear that under a low field of 0.02 T the system practically does not get magnetized, indicating that the magnetization is not spontaneous (Figure 4, top). For intermediate fields, the system is partially magnetized and keeps the same magnetization value down to 2 K, suggesting that interlayer interactions are not effective. The thermal dependence of the ac susceptibility of **3** was also recorded at various frequencies. Under an ac field of 4 G, the system does not show any out-of-phase peak, consistent with the lack of remnant magnetization. However, under static fields of 0.05 and 0.1 T, the χ_M'' component (Figure 4, bottom) exhibits nice peaks that correspond to an ordered system. Under larger fields (i.e., 0.3 T), the system remains blocked and the ac signals are diminished. It is noted that the χ_M' (Figure S12 in the Supporting Information) and χ_M'' peaks are slightly unsymmetrical in

shape with the low- T side showing some frequency dependence. This is indicative of some complicated dynamic relaxation process, tentatively attributed to the restricted movement of domain walls upon approaching T_c .^[19] Finally, the ferromagnetically ordered 2D system showed magnetization hysteresis loops, still observable at approximately 20 K, with a remnant magnetization corresponding to 3.3 electrons and a coercive field of approximately 0.25 T at 2 K (Figure 4, bottom).

In conclusion, we have reported a new, flexible synthetic route for the isolation of ferromagnetic polynuclear 3d-metal complexes and coordination polymers without requiring the simultaneous presence of any organic chelating/bridging ligand. The pioneer employment of Me_3SiN_3 precursor under the reported aerobic and basic conditions seems to be the key for unveiling a new class of exclusively end-on azido-bridged inorganic materials with beautiful structural motifs and fascinating

magnetic properties. In addition to the interesting magnetic properties, the described compounds could potentially show a variety of other applications, for example, in the fields of high-energy materials and catalysis. Such studies, together with the further development of this chemistry in other 3d-, 4f-, and 3d/4f-metals, are currently in progress.

Experimental Section

CAUTION!!! Perchlorate and azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.

Synthesis of **1**

To a stirred, pink solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.07 g, 0.2 mmol) and NEt_3 (0.03 mL, 0.2 mmol) in MeCN (10 mL) was added Me_3SiN_3 (0.11 mL, 0.8 mmol). The resulting deep-pink solution was stirred for 10 min, filtered, and carefully layered with Et_2O (20 mL). Next day, large in size, X-ray quality pink plate-like crystals of **1** were collected by filtration, washed with cold MeCN (2×2 mL) and dried in air. The yield was 75%. Selected IR data (ATR): $\tilde{\nu} = 3356$ (w), 3002 (w), 2089 (vs), 2063 (vs), 1635 (w), 1412 (w), 1365 (w), 1284 (m), 1229 (w), 1095 (sb), 1031 (m), 933 (w), 673 (w), 623 cm^{-1} (m); elemental analysis (%) calcd for **1** ($M_w = 1608.31$ g mol^{-1}): C 17.92, H 2.26, N 41.80; found: C 17.69, H 2.16, N 42.02.

Synthesis of 2

This complex was prepared in the same manner as complex **1** but using Ni(ClO₄)₂·6H₂O (0.07 g, 0.2 mmol) instead of Co(ClO₄)₂·6H₂O. Next day, large in size, X-ray quality green plate-like crystals of **2** were collected by filtration, washed with cold MeCN (2×2 mL) and dried in air. Yield: 78%. IR data are almost superimposable with these reported for **1**; elemental analysis (%) calcd for **2** (M_w=1606.63 g mol⁻¹): C 17.94, H 2.26, N 41.85; found: C 18.05, H 2.32, N 41.68.

Synthesis of 3

To a stirred orange solution of Fe(ClO₄)₂·xH₂O (0.05 g, 0.2 mmol) and NEt₃ (0.03 mL, 0.2 mmol) in MeCN (10 mL) was added Me₃SiN₃ (0.11 mL, 0.8 mmol). The resulting dark orange red solution was stirred for 10 min, filtered, and carefully layered with Et₂O (20 mL). After one day, slow mixing gave dark orange-red prismatic crystals of **3**, suitable for X-ray diffraction studies, which were collected by filtration, washed with cold MeCN (2×2 mL), and dried in air. Yield: 52%. Selected IR data (ATR): $\tilde{\nu}$ =3220 (mb), 2062 (vs), 1618 (w), 1341 (w), 921 (w), 645 cm⁻¹ (wb); elemental analysis (%) calcd for **3** (M_w=403.90 g mol⁻¹): C 11.90, H 1.50, N 58.95; found: C 11.74, H 1.38, N 59.09.

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