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Photoswitchable Heterotrimetallic Chain Based on Octacyanomolybdate, Copper, and Nickel: Synthesis, Characterization, and Photomagnetic Properties

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Taking into account the general interest in photoswitchable nanomagnets, we present an original synthetic route to well-defined photoswitchable heterotrimetallic complexes. Our strategy demonstrates the feasibility of using a "molybdenum−copper" switchable complex with terminal cyanide ligands as relevant synthons for the rational design and synthesis of heterotrimetallic photoswitchable molecular architectures. Starting from a pentanuclear compound based on an octacyanometalated precursor, $[Mo^{IV}(CN)_4(CNCu^{II}(Me2en)_2)_4]^{4+}$, and a $[Ni^{II}(cyclam)]^{2+}$ assembling building block, we succeeded in synthesizing a photoswitchable heterotrimetallic chain, denoted as $\{NiMo_2Cu_7\}_n$. The compound has been characterized by single-crystal X-ray diffraction, UV−vis and IR spectroscopies, and powder magnetic and photomagnetic susceptibility measurements. Before irradiation, the compound behaves as a paramagnet with eight independent spin carriers (Cu^{II} d^9, $S = \frac{1}{2}$, and Ni^{II} d^8, $S = 1$). After irradiation, a long-lived metastable state persists until relatively high temperature (120 K) and is thermally reversible.

Much effort is currently devoted to the implementation of molecular-scale memory devices[1] or switches.[2] In this regard, valence tautomers,[3] spin-crossover compounds,[4] and molecular magnets[5] are species of interest because their magnetic properties can be controlled by external stimuli.[6] Light is one such stimuli. As a benchmark illustration, there is the photoswitchable high-spin molecule $MoCu_6$, based on copper and octacyanomolybdate inorganic precursors.[7]

This compound and its analogues[8] are viewed as prototypes of those specialized photochemical molecular devices[9] intended for molecular spintronics[10] and are referred to as photomagnetic molecular devices (PMMDs).[10] Another valuable advance in the field comes from recent works devoted to photomagnetic particles,[11] especially $Mo(CN)_8CuNi$ coordination nanoparticles,[11a] which have revealed the possibility of triggering superparamagnetism by light. Out of these issues, it appears that integration of the above-mentioned light-switchable behaviors within a single smart molecule is naturally the next step toward photoswitchable molecular nanomagnets.[12] One such promising heterotrime-

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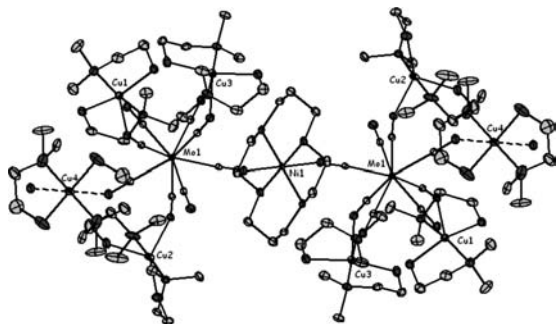† Université Pierre et Marie Curie.
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Figure 1. ORTEP drawing of the molecular structure of {[(Ni-(cyclam))(Mo(CN)$_8$)$_2$(Cu(Me2en)$_2$)$_7$]$^{8+}$}.

tallic entity, [(Ni^{II}(cyclam))(Mo^{IV}(CN)$_8$)$_2$(Cu^{II}(Me2en)$_2$)$_7$]-(ClO$_4$)$_8$ 4H$_2$O, namely, the {NiMo$_2$Cu$_7$} chain, is herein described (Figure 1).

The present approach is adapted from the modular synthetic strategy.[14] Keeping the working principle of the switching effect, that is, the photoinduced electron transfer between the Mo^{IV} core and one of the cyano-bridged Cu^{II} atoms (Mo^{IV}–Cu^{II} → Mo^{V}–Cu^{I}), a Ni^{II}-based building block was incorporated into the inorganic assembly. In doing so, spin and anisotropy are at one and the same time enhanced (i) at the local level, thanks to the well-known intrinsic features of Ni^{II},[15] and (ii) at the level of the whole supramolecular architecture, by virtue of its heterotrimetallic composition and asymmetric shape.

The synthesis of such heteropolymetallic assemblies, moreover, of high nuclearity is actually a real challenge in coordination chemistry because of intervening equilibria in solution (especially an exchange ligand between metallic centers) and also characterization difficulties. Simply considering heterotrimetallic complexes, reported examples are rare in the literature,[16] and only a few of them can be considered as functional species.

The stepwise synthetic strategy has been devised as follows: various well-defined and fully characterized MoCu$_n$ oligonuclear compounds are at our disposal (n = 1, 2, 4, 6) to be used as new building blocks (via their free cyanide ligands) for complexing the anisotropic assembler (e.g., M = Ni^{II} or Mn^{III} ions) and designing Ni–Mo–Cu or Mn–Mo–Cu heterotrimetallic assemblies. To limit adverse ligand redistribution in solution, the choice of the precursors is of determining importance. For mononuclear complexes forming either the dangling spin carriers (Cu^{II}-based) or the assembling element (Ni^{II}-based), the selection of blocking polydentate ligands is imposed by taking into consideration

(i) stability and selectivity factors, (ii) the intramolecular steric hindrance, and (iii) redox compatibility. From our experience of Cu^{II} chemistry, a N,N-dimethylethylenediamine (Me2en) bidentate ligand has been selected because it gives a stable and suitable [Mo^{IV}(CN)$_4$(CNCu^{II}(Me2en)$_2$)$_4$]$^{4+}$ pentanuclear complex, denoted as MoCu$_4$(Me2en). For what concerns the Ni^{II} complex, the macrocyclic tetraamine (1,4,8,11-tetrazatetradecane, denoted as cyclam) ligand ensuring a square-planar coordination has been chosen for the stability of the complex with Ni^{II} and to avoid ligand exchange with the copper species. Reacting the heterobimetallic MoCu$_4$(Me2en) building block with the [Ni^{II}(cyclam)]$^{2+}$ assembling unit gave the targeted heterotrimetallic compound, obtained as dark-blue diamond-shaped crystals.

Elemental analysis, IR spectroscopy, electronic absorption, and crystallography confirm the identity of the species. The IR spectrum shows the intense distinctive bands of perchlorate anions (around 1090 cm^{-1}), indicating the presence of charged cationic complexes. In the frequency range of 2000–2200 cm^{-1}, the large asymmetric stretching band of cyanide CN^{-} is observed at 2106 cm^{-1}, with shoulders at 2117, 2122, and 2145 cm^{-1} attributed to terminal and bridging cyanide ligands. The UV–vis spectrum recorded in a water–acetonitrile mixture is similar to the one obtained from the solid state, showing several bands at 280, 430, and 574 nm, characteristic of individual chromophores. The spectrum looks very similar to that of bare MoCu$_4$(Me2en), without a distinguishable band related to a metal-to-metal charge transfer (MMCT) such as a Mo^{IV}–Cu^{II} intervalence transition. Single-crystal X-ray diffraction reveals that the system crystallizes in a triclinic system, space group P$\bar{1}$, with the following cell parameters: a = 12.709(2) Å, b = 15.259(3) Å, c = 21.177(4) Å, α = 69.932(14)°, β = 77.268(11)°, γ = 71.426(10)°, and V = 3628.1(11) Å^3. The asymmetric unit is comprised of half of a Ni^{II}, one Mo^{IV}, and three and a half Cu^{II} metal ions, together with their respective ligands (cyclam, cyanide, and Me2en) as well as ClO$_4$$^{-}$ anions. The structure can be described as a chain formed by a nonanuclear NiMo$_2$Cu$_6$ compound, whose exact formula is [(Ni^{II}(cyclam))(Mo^{IV}(CN)$_8$)$_2$(Cu^{II}(Me2en)$_2$)$_6$]$^{6+}$, made up of two MoCu$_3$ units linked to a single nickel ion (as a bridge) located on an inversion center. The Ni^{II}Mo^{IV}$_2$Cu^{II}$_6$ entity cocrystallizes with an additional mononuclear Cu^{II} complex, forming a chain denoted as {Ni^{II}Mo^{IV}$_2$Cu^{II}$_7$}$_n$. The distance between the subunits (2.67 Å) is considered as a semicoordination bond,[17] and there exists de facto a nonnegligible interaction between the octacyanometalate moiety and the [Cu(Me2en)$_2$]$^{2+}$ complex. No ligand redistribution between nickel and copper metal cations is apparently observed. The analysis of the bond lengths (2.67 Å for Cu–N and 2.17 Å for Ni–N in apical positions) is consistent with crystallographic data in the literature. In addition to the elemental analysis, this confirms the presence of the three metallic ions in the molecular structure.

The magnetic and photomagnetic properties of the product have been studied and are in conformity with the expected properties. Before irradiation, the χT product, where χ is the

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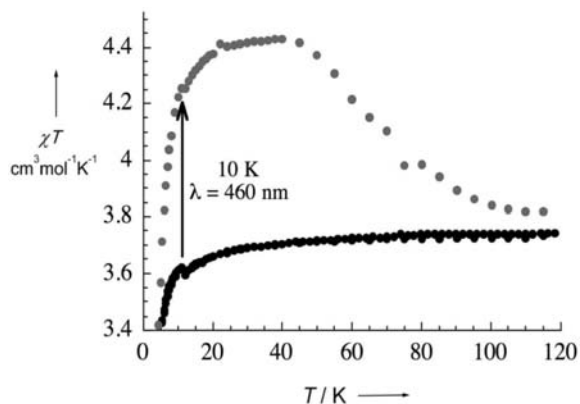
Figure 2. Thermal dependence of the $\chi_M T$ product for $\{[Ni^{II}Mo^{IV}_2Cu^{II}_7]\}_n$: black circles, before irradiation; gray circles, after irradiation; dashed line, after irradiation and $T > 300$ K.

magnetic susceptibility and T the temperature, remains constant at 3.7 cm^3 mol^{-1} K down to 50 K. This is in good agreement with the expected value of 3.63 cm^3 mol^{-1} K calculated for isolated spins: seven Cu^{II} ions (d^9, $S = {}^1/_2$) and one Ni^{II} ion (d^8, $S = 1$), separated by the diamagnetic Mo^{IV} ion. Below 50 K, the decrease of the χT product is indicative of either intra- and/or intermolecular antiferromagnetic interactions between the spin carriers. After 12 h of blue light irradiation (460 nm) at 10 K (Supporting Information), χT increases up to 4.2 cm^3 mol^{-1} K. When the temperature is varied, the $\chi_M T$ product reaches a plateau at 4.4 cm^3 mol^{-1} K until 50 K and then decreases continuously to 120 K but remains higher than the χT product of the nonirradiated compound. After annealing of the sample at room temperature, the thermal dependence of the $\chi_M T$ recovers exactly the values measured before irradiation, indicating unambiguously the reversibility of the process (Figure 2).

As suggested[7] and demonstrated elsewhere for other MoCu systems,[11b] we propose a mechanism to explain the observed photomagnetic effect, based on an electron transfer from Mo^{IV} (d^2, $S = 0$) to Cu^{II} (d^9, $S = {}^1/_2$), leading to a paramagnetic Mo^V (d^1, $S = {}^1/_2$) center and a diamagnetic Cu^I (d^{10}, $S = 0$). The metastable state might be described, in the first approximation, as [Ni^{II}Mo$^V_2$Cu$^I_2$Cu$^{II}_5$] with a $S = {}^5/_2$ spin (χT theoretical value: 4.375 cm^3 mol^{-1} K with g

= 2), assuming ferro- and antiferromagnetic interaction between Mo^V/Cu^{II} and Mo^V/Ni^{II}, respectively, as observed in the literature.[7,18,19]

The evidence of photomagnetic properties, with high-spin values and anisotropy, might suggest promising properties such as a slow relaxation of the magnetization of the metastable state. Unfortunately, preliminary results performed using a microsquid after irradiation below 2 K indicate that the compound does not behave as a switchable single-chain magnet. Nevertheless, the present strategy might be applied for other molecular structures with more efficient properties.

[(Ni^{II}(cyclam))(Mo^{IV}(CN)$_8$)$_2$(Cu^{II}(Me2en)$_2$)$_7$](ClO$_4$)$_8$ is the first photoswitchable heterotrimetallic chain. Using a MoCu switchable complex with terminal cyanide ligands as relevant synthons for the rational design and synthesis of heterotrimetallic (photoswitchable) molecular architectures is demonstrated. The present study opens the field of new photomagnetic chains, photoactive heterotrimetallic complexes, and dendritic architectures toward switchable nanomagnets.

Supporting Information Available: Experimental section for MoCu$_4$(Me2en) and NiMo$_2$Cu$_7$, UV−vis and photomagnetic studies, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-665290 contains the supplementary crystallographic data for the heterotrimetallic chain. These data may be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html.

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