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Tuning the Spin Ground State in Heterononanuclear Nickel(II)−Copper(II) Cylinders with a Triangular Metallacyclophane Core

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Two new heterometallic $Ni^{II}{}_{n}Cu^{II}{}_{(9-n)}$ complexes [n = 1 (**2**) and 2 (**3**)] have been synthesized following a multicomponent self-assembly process from a n:(3 − n):2:6 stoichiometric mixture of Ni^{2+}, Cu^{2+}, L^{6-}, and $[CuL']^{2+}$, where L and L′ are the bridging and blocking ligands 1,3,5-benzenetris(oxamate) and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, respectively. Complexes **2** and **3** possess a unique cyclindrical architecture formed by three oxamato-bridged trinuclear linear units connected through two 1,3,5-substituted benzenetris(amidate) bridges, giving a triangular metallacyclophane core. They behave as a ferromagnetically coupled trimer of two (**2**)/one (**3**) $S = {}^1/_2$ $Cu^{II}{}_3$ plus one (**2**)/two (**3**) $S = 0$ $Ni^{II}Cu^{II}{}_2$ linear units with overall $S = 1$ $Ni^{II}Cu^{II}{}_8$ (**2**) and $S = {}^1/_2$ $Ni^{II}{}_2Cu^{II}{}_7$ (**3**) ground states.

The molecularly programmed self-assembly of polynuclear coordination compounds of well-defined shape and nanometric size from metal ions of preferred coordination geometries and suitably designed polytopic organic ligands is a major topic in metallosupramolecular chemistry.[1] Both homo- and heterometallic cages,[2] rings,[3] and grids[4] of varying nuclearity are included in this family. Besides their fascinating structures and relevant insights into ligand-directed, metal-assisted self-assembly processes, they can display unique magnetic properties, which result from the particular assembling topology of the paramagnetic metal ions by the bridging ligands. Thus, nanosized polymetallic species with either low- ($S = {}^1/_2$) or high-spin ($S \gg {}^1/_2$) ground states are extensively studied in recent years as examples of molecular nanomagnets for future applications in quantum information processing.[5,6] In the former case, the spin-up ($m_S = +{}^1/_2$) and spin-down ($m_S = -{}^1/_2$) configurations of the $S = {}^1/_2$ ground state can be considered as a two-level system that can play the role of a quantum bit (Qubit) in modern quantum computers because of the superposition of the spin-up/spin-down levels.[6]

In the search for polynuclear coordination compounds with predetermined structures and spin topologies,[7] we have prepared the homometallic nonacopper(II) complex of formula $\{[Cu_3L_2(H_2O)_2][CuL']_6\}(ClO_4)_6 \cdot 12H_2O$ (**1**), with L and L′ being C_3-symmetric tris(bidentate) bridging and tridentate blocking ligands, respectively [L = 1,3,5-benzenetris-(oxamate) and L′ = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine; Chart 1].[8] Complex **1** exhibits a cylindrical architecture with an overall "trimer-of-trimers" topology. Each $Cu^{II}{}_9$ cylinder consists of three moderately strong antiferromagnetically coupled, oxamato-bridged $S = {}^1/_2$ $Cu^{II}{}_3$ linear units ($J = -106$ cm^{-1}), which are weakly ferromagnetically coupled through the two 1,3,5-benzene spacers ($j = +7.8$ cm^{-1}) to give an overall $S = {}^3/_2$ ground state.[8] Importantly, the three central Cu^{II} ions at the triangular metallacyclophane core of **1** are not square-planar, one or two axial positions being occupied by weakly bound water molecules and/or perchlorate counteranions. That being so, the stepwise substitution of the central square-pyramidal or octahedral Cu^{II}

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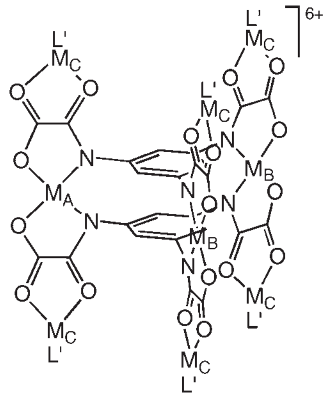
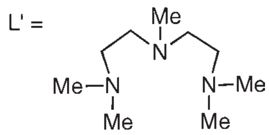
Chart 1





	M_A	M_B	M_C
1	Cu^{II}	Cu^{II}	Cu^{II}
2	Ni^{II}	Cu^{II}	Cu^{II}
3	Cu^{II}	Ni^{II}	Cu^{II}

ions ($S_{Cu} = {}^1/_2$) in **1** by octahedral high-spin Ni^{II} ($S_{Ni} = 1$) instead of square-planar low-spin Ni^{II} ($S_{Ni} = 0$) ions, would afford heterobimetallic analogues possessing different spin ground states. Here we report the syntheses, crystal structures, and magnetic properties of two such heterononanuclear nickel(II)−copper(II) derivatives of the general formula $\{[Ni_nCu_{(3-n)}L_2(H_2O)_4][CuL'_6]\}(ClO_4)_6\cdot 9H_2O$ with $n = 1$ (**2**) and 2 (**3**) (Chart 1).

Complexes **2** and **3** were synthesized in a one-pot reaction from the 1:6 stoichiometric mixture of $[Ni_nCu_{(3-n)}L_2]^{6-}$ and $[CuL']^{2+}$ (see the Supporting Information). This was a strict ligand-directed, metal-assisted multicomponent self-assembly process because the putative trinuclear nickel(II)−copper(II) complexes, $[Ni_nCu_{(3-n)}L_2]^{6-}$, were not isolated, but they were prepared in situ from a mixture of Ni^{2+}, Cu^{2+}, and L^{6-} in the appropriate n:(3 − n):2 molar ratio [n = 1 (**2**) and 2 (**3**)]. This situation contrasts with that of **1**, which was synthesized in a step-by-step reaction from the previously isolated trinuclear copper(II) complex of formula $Na_6[Cu_3L_2]\cdot 11.5H_2O$.[9] The chemical identity of **2** and **3** was established by elemental analyses (C, H, N, Cl, Ni, and Cu). The structure of **2** was determined by single-crystal X-ray diffraction using synchrotron radiation (see the Supporting Information).

The structure of **2** consists of heterononanuclear nickel(II)−copper(II) cations, $\{[NiCu_2L_2(H_2O)_4][CuL'_6]\}^{6+}$ (Figure 1), weakly coordinated and uncoordinated perchlorate anions, and crystallization water molecules. Each $Ni^{II}Cu^{II}_8$ cation has a crystallographically imposed C_2 molecular symmetry, whereby the Ni(1) and Cu(2) central atoms are disordered among two symmetrically equivalent positions with a half-occupancy factor each. They exhibit an elongated octahedral geometry formed by two amidate nitrogen atoms [Ni−N = 2.033(9) and 2.066(9) Å; Cu−N = 1.983(9) and 2.013(9) Å] and two carboxylate oxygen atoms [Ni−O = 2.007(11) and 2.020(9) Å; Cu−O = 2.046(11) and 2.057(9) Å] from the oxamato groups of each L ligand in the basal plane, with the apical positions being occupied by two water molecules [Ni−Ow = 2.067(12) and 2.39(2) Å; Cu−Ow = 2.00(2) and 2.47(12) Å]. The remaining Cu(3) central atom also exhibits an elongated octahedral geometry formed by two amidate nitrogen atoms [Cu−N = 1.988(7) Å] and two carboxylate oxygen atoms [Cu−O = 2.037(7) Å] from the

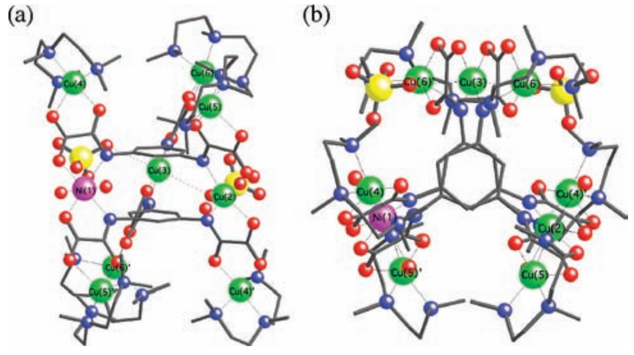


Figure 1. (a) Front and (b) top views of the heterononanuclear cationic unit of **2** with the numbering scheme for the metal atoms (weak coordinative bonds with the perchlorate anions are represented by dashed lines). Selected intermetallic distances (Å) with standard deviations in parentheses: Ni(1)−Cu(2) 7.007(10), Ni(1)−Cu(3) 6.838(7), Ni(1)−Cu(4) 5.359(7), Ni(1)−Cu(5)^I 5.353(7), Cu(2)−Cu(3) 6.961(8), Cu(2)−Cu(4)^I 5.346(7), Cu(2)−Cu(5) 5.310(7), Cu(3)−Cu(6) 5.447(2), and Cu(3)−Cu(6)^I 5.447(2) [symmetry code: I, x, $-y+1$, $-z+{}^1/_2$].

oxamato groups of each L ligand in the basal plane, while two weakly bound perchlorate anions occupy the apical positions [$Cu-OClO_3$ = 2.90(3) Å].

As in **1**, the $Ni^{II}Cu^{II}_8$ cations of **2** possess a "trimer-of-trimers" structure with a rare cylindrical architecture.[10] They are made up of two Cu^{II}_3 and one $Ni^{II}Cu^{II}_2$ oxamato-bridged linear units forming the walls of the cylinder, which are connected through two 1,3,5-substituted benzene spacers between the central metal atoms. This leads to a triangular metallacyclic core of the [3.3.3](1,3,5)cyclophane-type with a π-stacked arrangement of the two almost coplanar benzene rings [interplanar C−C distances in the range of 3.257(9)−3.326(8) Å; Figure 1a]. Moreover, they are not eclipsed but slightly tilted by 17.2(3)° around the cylindrical molecular axis passing through the centroid of each benzene ring, causing thus an overall torsion of the whole cylinder molecule about the triangular $Cu^{II}_2Ni^{II}(m\text{-}N_3C_6H_3)_2$ metallacyclophane core [M−N−C−C torsion angles (M = Ni or Cu) in the range of 109.8(7)−115.7(7)°; Figure 1b]. Hence, each $Ni^{II}Cu^{II}_8$ cation of **2** is chiral with a propeller-like triple helical arrangement of the three oxamato-bridged trinuclear units about the double 1,3,5-benzenetris(amidate) bridge, with both enantiomers (Δ and Λ) being present in the solid state (Figure S1, Supporting Information). This nanosized heterononanuclear cylinder molecule has approximate dimensions of 10.725(2) Å length and 3.963(2) Å radii (defined as the average separation between the peripheral metal atoms of each trinuclear unit and that between the central metal atoms and the center of the triangular metallacyclophane core, respectively).

The magnetic properties of **2** and **3** in the form of $\chi_M T$ versus T plots, with χ_M being the molar magnetic susceptibility per nonanuclear unit and T the temperature, are consistent with pure $Ni^{II}Cu^{II}_8$ (**2**) and $Ni^{II}_2Cu^{II}_7$ (**3**) complexes, allowing one thus to discard the occurrence of a statistical mixture of $Ni^{II}_nCu^{II}_{(9-n)}$ complexes (n = 0−3; Figure 2). Least-squares fittings of the experimental data of **2** and **3** were performed according to an effective spin Hamiltonian for a "trimer-of-trimers" model that takes into account the magnetic coupling between the $S_1 = S_2 = {}^1/_2$ ground states of

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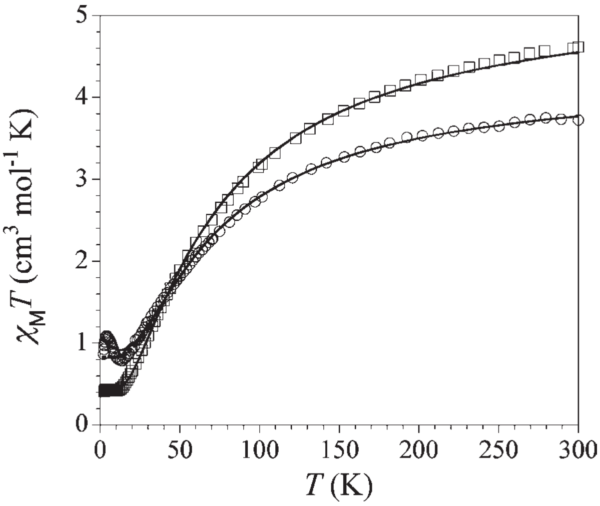

Figure 2. Temperature dependence of $\chi_M T$ for **2** (○) and **3** (□). The solid and dotted lines are the best-fit curves (see the text).

each Cu^{II}_3 linear unit in **2** (eq 1 for **2** with $S_{1B} = S_{2B} = S_{iC} = S_{iC'} = S_{Cu} = {}^1/_2$ for $i = 1-3$ and $S_{3A} = S_{Ni} = 1$; eq 2 for **3** with $S_{1A} = S_{iC} = S_{iC'} = S_{Cu} = {}^1/_2$ for $i = 1-3$ and $S_{2B} = S_{3B} = S_{Ni} = 1$),[11] where J and J' are the intratrimer magnetic coupling parameters within the Cu^{II}_3 and $Ni^{II}Cu^{II}_2$ units respectively, j_{eff} is the effective intertrimer magnetic coupling parameter between the Cu^{II}_3 units, and g_{Ni} and g_{Cu} are the Landé factors of the high-spin Ni^{II} and Cu^{II} ions, respectively, which were assumed to be identical in order to preclude overparametrization ($g = g_{Ni} = g_{Cu}$). In this perturbational model, the value of j_{eff} is related to that of j between the two central Cu^{II} ions within the triangular $Cu^{II}_2Ni^{II}$ metallacyclophane core by $j_{eff} = (1/9)j$.[11] At room temperature, $\chi_M T$ is equal to 3.72 (**2**) and 4.61 (**3**) $cm^3\ mol^{-1}$ K, values that are smaller than those expected for the sum of one (**2**)/two (**3**) high-spin Ni^{II} ions plus eight (**2**)/seven (**3**) Cu^{II} ions [$\chi_M T = 4.41$ (**2**) and 5.10 (**3**) $cm^3\ mol^{-1}$ K with $g_{Ni} = g_{Cu} = 2.10$] magnetically isolated.

$$\mathbf{H} = -J(\mathbf{S}_{1B}\cdot\mathbf{S}_{1C} + \mathbf{S}_{1B}\cdot\mathbf{S}_{1C'}) - J(\mathbf{S}_{2B}\cdot\mathbf{S}_{2C} + \mathbf{S}_{2B}\cdot\mathbf{S}_{2C'}) - J'(\mathbf{S}_{3A}\cdot\mathbf{S}_{3C} + \mathbf{S}_{3A}\cdot\mathbf{S}_{3C'}) - j_{eff}\mathbf{S}_1\cdot\mathbf{S}_2 + g_{Ni}\mathbf{S}_{3A}\beta H + g_{Cu}(\mathbf{S}_{1B} + \mathbf{S}_{2B} + \mathbf{S}_{1C} + \mathbf{S}_{1C'} + \mathbf{S}_{2C} + \mathbf{S}_{2C'} + \mathbf{S}_{3C} + \mathbf{S}_{3C'})\beta H \quad (1)$$

$$\mathbf{H} = -J(\mathbf{S}_{1A}\cdot\mathbf{S}_{1C} + \mathbf{S}_{1A}\cdot\mathbf{S}_{1C'}) - J'(\mathbf{S}_{2B}\cdot\mathbf{S}_{2C} + \mathbf{S}_{2B}\cdot\mathbf{S}_{2C'}) - J'(\mathbf{S}_{3B}\cdot\mathbf{S}_{3C} + \mathbf{S}_{3B}\cdot\mathbf{S}_{3C'}) + g_{Ni}(\mathbf{S}_{2B} + \mathbf{S}_{3B})\beta H + g_{Cu}(\mathbf{S}_{1A} + \mathbf{S}_{1C} + \mathbf{S}_{1C'} + \mathbf{S}_{2C} + \mathbf{S}_{2C'} + \mathbf{S}_{3C} + \mathbf{S}_{3C'})\beta H \quad (2)$$

Upon cooling, $\chi_M T$ for **2** first decreases to reach a minimum of 0.78 cm^3 K mol^{-1} at 14.0 K. This value is close to that expected for two doublet ($S_1 = S_2 = 2S_{Cu} - S_{Cu} = {}^1/_2$) and one singlet ($S_3 = 2S_{Cu} - S_{Ni} = 0$) states arising from the two Cu^{II}_3 and one $Ni^{II}Cu^{II}_2$ linear units, respectively ($\chi_M T = 0.83$ $cm^3\ mol^{-1}$ K with $g = 2.10$). This high-temperature magnetic behavior results from the moderately strong antiferromagnetic intratrimer coupling between the peripheral Cu^{II} ions and the central Cu^{II} ($J = -57.0\ cm^{-1}$) or high-spin Ni^{II} ions ($J' = -49.0\ cm^{-1}$) through the oxamato bridges (dotted line in Figure 2). Then, $\chi_M T$ for **2** increases to reach a maximum value of 1.09 cm^3 K mol^{-1} at 4.0 K, which corresponds to that of a triplet ground state ($S = S_1 + S_2 + S_3 = 1$) for the $Ni^{II}Cu^{II}_8$ molecule ($\chi_M T = 1.10$ $cm^3\ mol^{-1}$ K with $g = 2.10$). This low-temperature magnetic behavior results from the effective ferromagnetic intertrimer coupling ($j_{eff} = +3.6\ cm^{-1}$) between the $S_1 = S_2 = {}^1/_2$ Cu^{II}_3 linear units (solid line in Figure 2). As in **1**, this effective ferromagnetic intertrimer coupling is mediated by the double 1,3,5-benzenetris(amidate) bridge between the two central Cu^{II} ions within the triangular $Cu^{II}_2Ni^{II}$ metallacyclophane core ($j = 9j_{eff} = +32.4\ cm^{-1}$). Finally, $\chi_M T$ for **2** decreases abruptly upon further cooling, more likely because of the zero-field splitting effects of the $S = 1$ $Ni^{II}Cu^{II}_8$ ground state and/or antiferromagnetic intermolecular interactions.

On the other hand, $\chi_M T$ for **3** decreases continuously upon cooling to reach a plateau between 2.0 and 10.0 K with a $\chi_M T$ value of 0.41 cm^3 K mol^{-1}, which corresponds to that of a doublet ground state ($S = S_1 + S_2 + S_3 = {}^1/_2$) for the $Ni^{II}_2Cu^{II}_7$ molecule ($\chi_M T = 0.41$ $cm^3\ mol^{-1}$ K with $g = 2.10$). This magnetic behavior is consistent with one $S_1 = {}^1/_2$ Cu^{II}_3 and two $S_2 = S_3 = 0$ $Ni^{II}Cu^{II}_2$ linear units resulting from the moderately strong antiferromagnetic intratrimer coupling between the peripheral Cu^{II} ions and the central Cu^{II} ($J = -52.8\ cm^{-1}$) or high-spin Ni^{II} ions ($J' = -47.9\ cm^{-1}$) through the oxamato bridges (solid line in Figure 2).

In summary, we have developed a general synthetic procedure for the multicomponent self-assembly of heterometallic $Ni^{II}_nCu^{II}_{(9-n)}$ cylinders with predetermined metal stoichiometry [$n = 1$ (**2**) and 2 (**3**)] as well as predictable ground spin states [$S = (3-n) \times {}^1/_2 = 1$ (**2**) and ${}^1/_2$ (**3**)]. Current efforts are devoted to investigating the potentiality of the $S = {}^1/_2$ $Ni_2^{II}Cu^{II}_7$ cylinder as a Qubit in quantum information processing.

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Supporting Information Available: X-ray crystallographic data in CIF format, preparation and characterization of **2** and **3**, and crystal packing views of **2** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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