# Inorganic Chemistry

**Communication**

# Using Ln$^{III}$[15-MC$_{Cu^{II}(N)(S)-pheHA}$-5]$^{3+}$ Complexes To Construct Chiral Single-Molecule Magnets and Chains of Single-Molecule Magnets

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The {Dy$^{III}$[15-MC-$_{Cu^{II}(N)(S)-pheHA}$-5]}$^{3+}$ complex displays slow magnetic relaxation behavior in a frozen solution at low temperature, whereas the analogous Ho$^{III}$ structure does not exhibit similar behavior.

Metallacrowns (MCs) provide a convenient geometry that allows for a high density of metal atoms to be placed in a small volume. In addition, the molecular topology of these clusters allows the single-ion-anisotropy axes to be aligned, leading to large, axial molecular anisotropies. The large number of magnetic nuclei found in these clusters results in interesting magnetic properties[1] with potential single-molecule magnetism. For example, in the ferromagnetically coupled Gd$^{III}$(NO$_3$)$_3$[15-MC$_{Cu^{II}(N)picHA}$-5],[1] five Cu$^{II}$ ions and one Gd$^{III}$ ion are placed within an area of ∼35 Å$^2$,[1] with the Jahn−Teller axes of all five Cu$^{II}$ ions oriented perpendicular to the MC ring. These structural constraints could lead to interesting magnetic properties for other members of the 15-MC-5 system, where the Ln ion possesses an orbitally degenerate ground state.

We have previously reported the X-ray crystal structures and syntheses for a series of {Ln$^{III}$[15-MC$_{Cu^{II}(N)(S)-pheHA}$-5]}$^{3+}$ complexes.[2,3] Each individual MC has the same basic structural feature regardless of the nature of the Ln$^{III}$ ion. The MC face is nearly planar with five Cu$^{II}$ ions incorporated into the MC ring, and an Ln$^{III}$ ion is bound within the central cavity. The use of (S)-phenylalaninehydroxamic acid [(S)-pheHA] provides a planar MC structure with pseudo-five-fold symmetry, placing the Cu$^{II}$ ions 108° relative to each other within this plane (Figures S1 and S2 in the Supporting Information). In addition, (S)-pheHA introduces chirality into the MC structure. When enantiopure chiral ligands are chosen, enantiopure chiral MCs can be synthesized.[4]

{Ln$^{III}$[15-MC$_{Cu^{II}(N)(S)-pheHA}$-5]}$^{3+}$ complexes made with (S)-pheHA have been crystallized into two distinct polymorphs, with the choice of solvent being the determining factor.[2,3] With water as the solvent, a {Ln$^{III}$[15-MC$_{Cu^{II}(N)pheHA}$-5]}$^{3+}$ dimer is observed in the solid state (Figure 1).[2] In the dimer model, the phenyl rings of each MC are oriented toward each other to form a hydrophobic pocket. In contrast, a 5:1 solvent mixture of methanol/water results in a helical structure (Figure 2).[3] In the helix, a carbonyl O of one MC binds axially to a Cu$^{II}$ ion of an adjacent MC. The O$_{carbonyl}$−Cu$^{II}$ bond is perpetuated down an $S_4$ screw axis, which is parallel to the face of the MC. Viewed down the screw axis, the MCs form the sides of a "square", with the phenyl rings directed to the outside (Figure S3 in the Supporting Information). The phenyl rings serve to isolate adjacent helices from each other. The shortest Gd$^{III}$−Gd$^{III}$ and Cu$^{II}$−Cu$^{II}$ distances in a Gd$^{III}$[15-MC$_{Cu^{II}(N)(S)-pheHA}$-5] helix are 12.2 and 8.64 Å, respectively. The solid is homochiral, with the choice of ligand determining the pitch of the helix. The use of (S)-pheHA results in the plus (P) helix ($P4_1$), while the use of (R)-pheHA yields the minus (M) helix ($P4_3$).

Because specific Ln$^{III}$ ions possess a large magnetic moment and a large magnetoanisotropy due to an orbitally degenerate ground state, we questioned whether {Ln$^{III}$[15-MC$_{Cu^{II}(N)(S)-pheHA}$-5]}$^{3+}$ complexes could behave as single-molecule magnets (SMMs). Precedent exists in the literature as a monolanthanide,[5] and several Ln$^{III}$−transition metal (TM) systems[6] behave as SMMs. Moreover, the first mixed Ln−TM SMMs described were isostructural Tb$^{III}_2$Cu$^{II}_2$ and Dy$^{III}_2$Cu$^{II}_2$ complexes.[6a]

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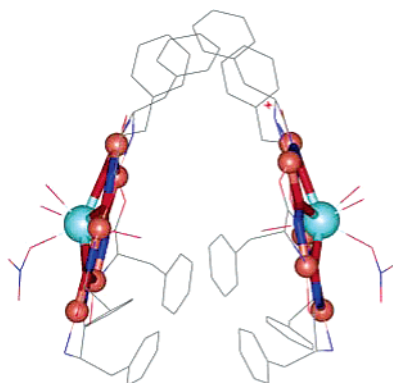
**Figure 1.** Two 15-MC-5 complexes that form a dimer in the solid state when crystallized from water.[2] Color scheme: aqua spheres, $Ln^{III}$; gold spheres, $Cu^{II}$; gray lines, C; red tubes, O; blue tubes, N.
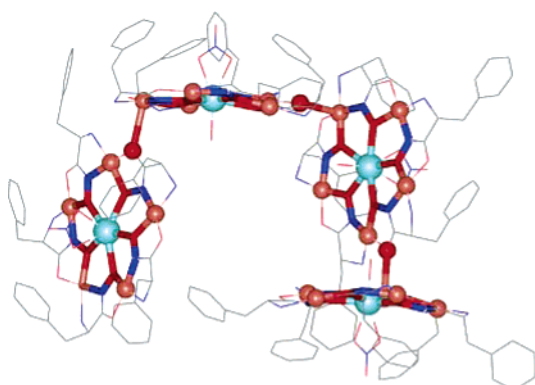


**Figure 2.** 15-MC-5 complexes form a helix with a carbonyl O binding axially to a $Cu^{II}$ ion of an adjacent MC when crystallized from a 5:1 mixture of methanol/water.[3] See Figure 1 for color scheme.

Given that $\{Ln^{III}[15\text{-}MC_{Cu^{II}(N)(S)-pheHA}\text{-}5]\}^{3+}$ complexes form one-dimensional chains in the solid state, this assembly opens an avenue to an another class of molecules known as single-chain magnets (SCMs), which are closely related to SMMs.[7] Several SCMs have been identified, with a $[Cu^{II}_2\text{-}Tb^{III}]_n$ chain[7b] being the only Ln–TM SCM.

In addition to their potential SMM and SCM behavior, the $Ln^{III}[15\text{-}MC_{Cu^{II}(N)(S)-pheHA}\text{-}5]$ system provides an opportunity to combine the properties of chirality and magnetism in one molecule. Rikken and Raupach were the first to show an observable magnetochiral effect in magnetochiral dichroism (MCD) experiments in 1997;[8] however, few chiral molecular magnets have been synthesized,[9] with only two reports of chiral SMMs.[10] In both reports, simple chiral carboxylate ligands were substituted for the acetate ligand in the original SMM, $Mn_{12}$–acetate.[11] The magnetic behaviors of these complexes were very similar to that of $Mn_{12}$–

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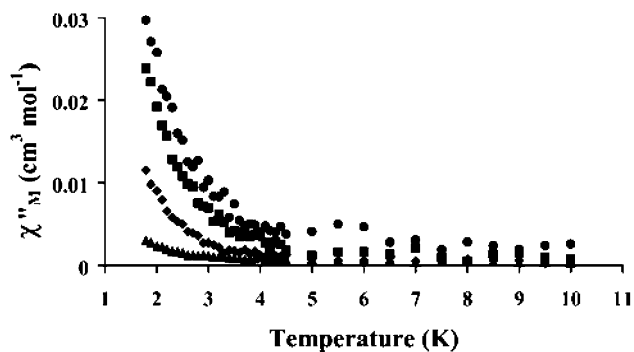
acetate, and no magnetochiral effects were observed. Because the $\{Ln^{III}[15\text{-}MC_{Cu^{II}(N)(S)-pheHA}\text{-}5]\}^{3+}$ complexes are chiral, $Ln^{III}$–$Cu^{II}$ clusters have been identified as SMMs, and $\{Ln^{III}\text{-}[15\text{-}MC_{Cu^{II}(N)(S)-pheHA}\text{-}5]\}^{3+}$ clusters can be crystallized as isolated single chains, we explored whether the dimer (**1**) and/or helical (**2**) polymorphs of $\{Ln^{III}[15\text{-}MC_{Cu^{II}(N)(S)-pheHA}\text{-}5]\}^{3+}$ ($Ln^{III} = Dy^{III}$ and $Ho^{III}$) could behave as chiral SMMs or SCMs.

Variable-field dc magnetization measurements were performed on eicosane mulls of $\mathbf{Dy^{III}\text{-}1}$, $\mathbf{Ho^{III}\text{-}1}$, $\mathbf{Dy^{III}\text{-}2}$, and $\mathbf{Ho^{III}\text{-}2}$. The magnetization does not saturate at 5 K in magnetic fields up to 5.5 T (Figures S4−S7 in the Supporting Information). In an effort to saturate the magnetization of $\mathbf{Ho^{III}\text{-}1}$ and $\mathbf{Ho^{III}\text{-}2}$, high-field magnetization measurements were conducted at lower temperatures and higher applied fields using a vibrating sample magnetometer. At temperatures of 0.65 K and applied magnetic fields up to 30 T, the magnetization did not saturate for either complex (Figures S8 and S9 in the Supporting Information). The magnetization increases linearly with the applied field strength above 5 T. This could be due to a large temperature-independent paramagnetism or, more likely, field-induced level crossing and/or the population of low-lying exciting states. Reduced magnetization plots reveal nesting behavior, indicating that the ground state(s) are highly magnetoanisotropic (Figures S10 and S11 in the Supporting Information).

Variable-temperature dc magnetic susceptibility measurements were conducted at 0.2 T between 5 and 300 K on a Quantum Design MPMS magnetometer. The $\chi T$ behaviors for $\mathbf{Dy^{III}\text{-}1}$, $\mathbf{Ho^{III}\text{-}1}$, $\mathbf{Dy^{III}\text{-}2}$, and $\mathbf{Ho^{III}\text{-}2}$ are similar and exhibit a decrease in $\chi T$ at low temperatures (Figures S12−S15 in the Supporting Information). For $\mathbf{Dy^{III}\text{-}1}$, the $\chi T$ value decreases from 300 K ($\chi T = 14.6$ cm$^3$ K mol$^{-1}$) to a minimum at 5 K ($\chi T = 13.8$ cm$^3$ K mol$^{-1}$), while for $\mathbf{Ho^{III}\text{-}1}$, $\chi T$ decreases from 300 K ($\chi T = 13.5$ cm$^3$ K mol$^{-1}$) to a minimum at 2 K ($\chi T = 7.7$ cm$^3$ K mol$^{-1}$). Similarly, the $\chi T$ value for $\mathbf{Dy^{III}\text{-}2}$ decreases from 14.1 cm$^3$ K mol$^{-1}$ at 300 K to 12.0 cm$^3$ K mol$^{-1}$ at 5 K, and $\chi T$ for $\mathbf{Ho^{III}\text{-}2}$ decreases from 300 K (13.9 cm$^3$ K mol$^{-1}$) to a minimum at 4.5 K ($\chi T = 8.8$ cm$^3$ K mol$^{-1}$). The strong spin−orbit coupling of the $Ln^{III}$ ions, coupled with the ligand-field splitting of the ground state terms, likely results in the observed decrease in $\chi T$ at low temperatures. Exchange coupling parameters could not be determined from these measurements because of the complexity of the MC ring $Cu^{II}$−$Cu^{II}$ interactions, the $Ln^{III}$−$Cu^{II}_5$ interaction, and the presence of orbital angular momentum arising from the f electrons of the $Ln^{III}$ ions.

Variable-temperature ac magnetic susceptibility measurements with zero applied dc magnetic field and a 3.5-G ac alternating drive field operating at frequencies between 10 and 1000 Hz reveal that $\mathbf{Dy^{III}\text{-}1}$, $\mathbf{Ho^{III}\text{-}1}$, $\mathbf{Dy^{III}\text{-}2}$, and $\mathbf{Ho^{III}\text{-}2}$ all possess a frequency-dependent response in the solid state. This is indicative of either SMM behavior, glassy behavior, magnetic ordering, or a combination of these phenomena (Figures S16−S23 in the Supporting Information). The in-phase and out-of-phase measurements for $\mathbf{Dy^{III}\text{-}1}$ and $\mathbf{Dy^{III}\text{-}2}$ are frequency-dependent below 4.5 K. Using the in-phase magnetic susceptibility before the onset

**Figure 3.** Out-of-phase ac magnetic susceptibility of a frozen solution of **Dy$^{III}$** in methanol: ●, 1000 Hz; ■, 500 Hz; ◆, 100 Hz; ▲, 10 Hz.
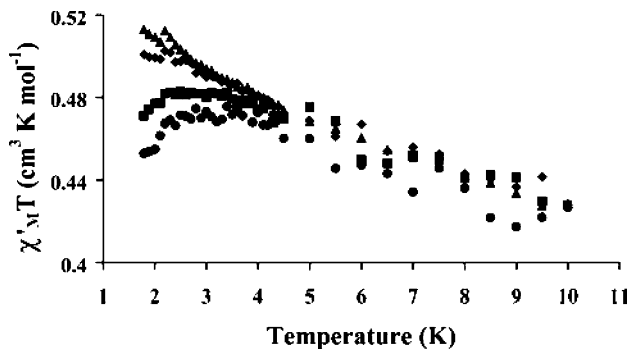


**Figure 4.** In-phase ac magnetic susceptibility of a frozen solution of **Dy$^{III}$** in methanol: ●, 1000 Hz; ■, 500 Hz; ◆, 100 Hz; ▲, 10 Hz.

of frequency-dependent behavior,[11] $\chi'T$ values of 13.6 and 11.6 cm$^3$ K mol$^{-1}$ can be extrapolated for **Dy$^{III}$-1** and **Dy$^{III}$-2**, respectively. The out-of-phase magnetic susceptibility data for **Ho$^{III}$-1** and **Ho$^{III}$-2** are frequency-dependent below 6.0 K. Using the in-phase magnetic susceptibility data before the onset of frequency-dependent behavior,[11] $\chi'T$ values of 9.4 and 9.6 cm$^3$ K mol$^{-1}$ are extrapolated for **Ho$^{III}$-1** and **Ho$^{III}$-2**, respectively.

To determine whether the solid-state ac magnetic behavior of the complexes is due to SMM behavior, ac susceptibility measurements were performed on frozen solutions of **Dy$^{III}$** and **Ho$^{III}$** in methanol. In solution, the helical structures are not observed because the molecules are fully dissociated and solvated. This has been confirmed by mass spectrometry experiments.[2,3] The **Ho$^{III}$** complex in a frozen solution does not display a frequency-dependent ac magnetic susceptibility signal above 2 K (Figures S24 and S25 in the Supporting Information). However, the **Dy$^{III}$** complex in frozen methanol does display a frequency-dependent ac magnetic susceptibility response, strongly supporting our assertion that **Dy$^{III}$** is a SMM (Figures 3 and 4). In the solid state, the ac behavior of the **Ho$^{III}$** complex is likely due to glassy behavior and/or the onset of magnetic ordering, with further complications arising from the SMM behavior as in the **Dy$^{III}$** complex.

The question arises as to whether the **Dy$^{III}$-2** complex should be considered a SCM or a one-dimensional chain of SMMs. One might anticipate that **Dy$^{III}$-2** would behave as a SCM because each chain is well separated from adjacent chains by the outside phenyl rings, which results in long metal−metal distances. Thus, these chains should meet the SCM criterion that the chains be well isolated from their nearest neighbors.[7a] However, the ac magnetic susceptibility results indicate that the helical polymorph is *not* a SCM. Hendrickson and co-workers have recently reported a similar system in which tetranuclear Mn clusters are bridged by Cl anions to form a one-dimensional chain that displays a frequency-dependent ac magnetic susceptibility signal.[12] They consider this system to be a chain of SMMs. Miyasaka, Clérac, and co-workers have shown that SCMs may be generated by ferromagnetically coupling SMMs.[13] The SCM of SMMs has a higher blocking temperature than the isolated SMM. The **Dy$^{III}$** helical polymorph does not exhibit an enhanced ac magnetic susceptibility signal because of the different arrangement within the solid state. Furthermore, the nature of the polymorph does not seem to have a large effect on the magnetic behavior because the dimer and helical counterparts show roughly the same magnitude of $\chi''$ values at 2 K. Therefore, it is likely that the nature of the polymorph is not significant to the onset of a frequency-dependent ac magnetic susceptibility signal, but the nature of the central cation is of paramount importance.

In addition, these magnetic complexes are chiral and may potentially display magnetochiral properties. However, MCD experiments conducted on frozen solutions of **Dy$^{III}$** and **Ho$^{III}$** in methanol show no observable magnetochiral effects down to 2 K. The fact that the complexes do not display magnetochiral effects is not surprising given that ac magnetic susceptibility experiments indicated that the blocking temperature of these complexes is below 2 K.

In conclusion, we have identified a new member of the small family of Ln$^{III}$−TM SMMs and the first chiral SMM not based on the Mn$_{12}$−acetate framework. Future work on these complexes will concentrate on understanding the Ln$^{III}$−Cu$^{II}_5$ ring interactions.

**Supporting Information Available:** Elemental analyses of **Dy$^{III}$-1**, **Dy$^{III}$-2**, **Ho$^{III}$-1**, and **Ho$^{III}$-2** and additional figures including magnetization plots and variable-temperature ac and dc magnetic susceptibility plots of all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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