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Communications to the Editor

Spin Robustness of a New Hybrid Inorganic−Organic High-Spin Molecule

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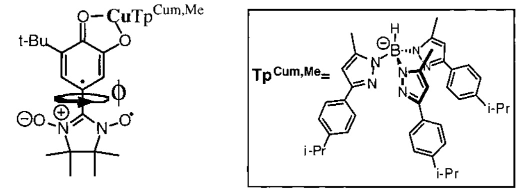
An attractive feature of molecule-based magnetic materials is that they can be built from multiple, entirely different spin carriers. This "spin diversity" allows the coexistence of properties associated with each constituent functionality and opens the door for new properties resulting from the synergistic relationships between organic and inorganic components. Therefore, understanding the relationship between magnetic exchange interactions and electronic structure in discrete, spin-diverse molecular systems is of paramount importance in the development of multiproperty, high-spin, molecule-based magnetic materials.[1−7] However, certain applications for these high-spin, multiproperty materials require their use in noncondensed phases including polymer-dispersed magnetooptical switching/storage devices[8] and in vivo biological probes[9,10] Although strong ferromagnetic coupling is assured when nondisjoint, $S = 1$ organic species assume planar geometries, this coupling can be dramatically reduced, or even reversed in solution where bond torsions (ϕ) attenuate delocalization (see Scheme 1).[11−21] Herein we present the results of variable-temperature, variable-field magnetic circular dichroism (VTVH MCD) studies that directly probe the "spin robustness" of the ligand **NN-SQ**, which is sensitive to the torsion angle ϕ, within spin diverse **NN-SQCuTp**$^{\mathbf{Cum,Me}}$ in a solid solution.[22]

Scheme 1



NN-SQCuTp$^{\mathbf{Cum,Me}}$

The complete Heisenberg exchange Hamiltonian for this three-spin system is given below:

$$H = -2J_{\mathrm{Cu-SQ}}(S_{\mathrm{Cu}}\cdot S_{\mathrm{SQ}}) - 2J_{\mathrm{SQ-NN}}(S_{\mathrm{SQ}}\cdot S_{\mathrm{NN}}) \qquad (1)$$

Solid-state magnetic susceptibility studies have confirmed that strong ferromagnetic exchange is present in **NN-SQCuTp**$^{\mathbf{Cum,Me}}$, and the intraligand coupling between the paramagnetic *ortho*-SQ and NN groups is substantial.[22] Therefore, the variable-temperature magnetic susceptibility of **NN-SQCuTp**$^{\mathbf{Cum,Me}}$ was fit to a two-spin model yielding $\boldsymbol{J}_{\mathrm{Cu-SQNN}} = +75.6$ cm^{-1} according to the simplified exchange Hamiltonian:

$$H = -2J_{\mathrm{Cu-SQNN}}(S_{\mathrm{Cu}}\cdot S_{\mathrm{SQNN}}) \qquad (2)$$

with S_{SQNN} representing the spin operator of the strongly ferromagnetically coupled $S = 1$ ligand (**NN-SQ**) and S_{Cu} representing the spin operator of the $S = {}^{1}/_{2}$ cupric ion. The solid solution VTVH MCD data for **NN-SQCuTp**$^{\mathbf{Cum,Me}}$ was acquired as a polystyrene thin film, and is presented in Figure 1. The data can be fit to a modified Brillouin function[23] for the MCD intensity of an isolated $S_{\mathrm{T}} = {}^{3}/_{2}$ spin system with $g = 1.97$.[24] The magnetization data clearly indicate that the two ferromagnetic pairwise exchange interactions, $J_{\mathrm{Cu-SQ}}$ and $J_{\mathrm{SQ-NN}}$, predominate within the solvated **NN-SQCu** unit at low temperatures. Interestingly, the magnitude of these exchange interactions is a direct probe of the torsional flexibility within the **NN-SQ** linkage as well as changes in Cu−SQ bonding which can occur in a solution environment, and these may be assessed using VT MCD

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(24) The MCD intensity as a function of temperature and magnetic field was monitored using the negative 17500 cm^{-1} *C*-term band of **NN-SQCuTp**$^{\mathbf{Cum,M}}$. This feature is not observed in the electronic absorption spectrum of this complex. Since the electronic absorption spectra of **NN-SQCuTp**$^{\mathbf{Cum,M}}$ and the Zn complex **NN-SQZnTp**$^{\mathbf{Cum,M}}$ are virtually identical, we have tentatively assigned the 17500 cm^{-1} MCD feature as a Cu ligand field transition possessing weak absorption intensity.

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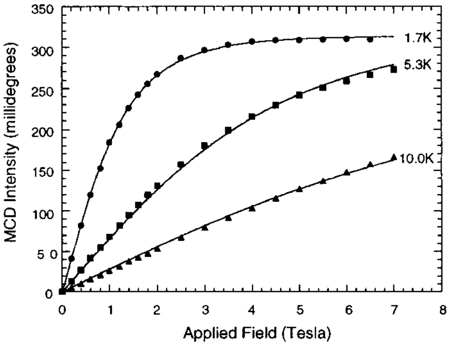

Figure 1. VTVH MCD magnetization of **NN-SQCuTp$^{\mathbf{Cum,M}}$** obtained as a polystyrene thin film. The solid lines represents the best fit to the modified Brillouin function given in ref 23.

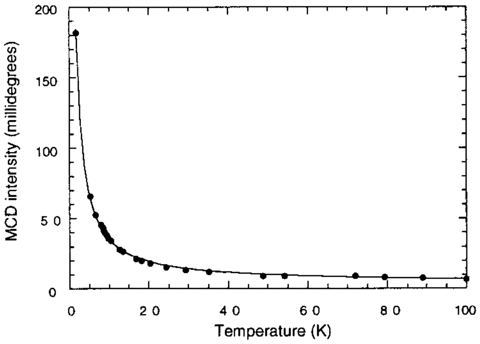

Figure 2. VT MCD data collected by monitoring the intensity of the 17500 cm^{-1} MCD band as a function of temperature. The solid line through the data is the best fit to a Curie law expression.

spectroscopy in the linear or low-field limit. The 1T MCD intensity of **NN-SQCuTp$^{\mathbf{Cum,Me}}$** is plotted as a function of temperature in Figure 2, where the solid line through data represents the best fit to the Curie law. The Curie law behavior provides evidence that population of higher energy S_T states may not occur at temperatures less than 100 K, and we assign a conservative lower limit of ~20 cm^{-1} for the quartet-doublet splitting.[25]

Detailed magnetic studies on solvated high-spin molecules are extremely important for investigating the impact of intercluster (zJ') interactions on the ground-state magnetic behavior as well as evaluating the effects of static or dynamic intramolecular distortions, such as the effect of a torsional rotation about the SQ-NN bond on J_{SQ-NN}. The former allows for a considerably more accurate determination of the intrinsic single-ion anisotropy,[23] while **NN-SQ** torsional distortions can have deleterious effects on the magnitude of the ferromagnetic intraligand exchange interaction. The VTVH MCD studies presented here clearly show that the two independent exchange interactions present in **NN-SQCuTp$^{\mathbf{Cum,Me}}$** are ferromagnetic in nature when the complex is solvated in a polymer matrix. Therefore, any distortions about the torsion angle, ϕ, which occur in solvated **NN-SQCuTp$^{\mathbf{Cum,Me}}$** do not affect the sign of the two pairwise exchange interactions, and the ferromagnetic coupling present in the **NN-SQ** unit is a particularly important design element in the construction of high-spin, spin-diverse building blocks for the construction of inorganic–organic hybrid molecular magnetic materials.

Variable-temperature, variable-field MCD spectroscopy has conclusively shown that the quartet ($S_T = {}^3/_2$) ground state of **NN-SQCuTp$^{\mathbf{Cum,Me}}$** is maintained when solvated, and the **NN-SQCu** unit may be a choice candidate for the construction of higher spin cluster materials finding applications in noncondensed phases. In addition to probing the nature of the ground state, MCD spectroscopy provides detailed information on electronic excited states, allowing the inherent electronic structure to be evaluated in terms of the ground-state magnetic properties.[26] Thus, the application of MCD spectroscopy to problems in molecular magnetism will allow for detailed magnetic/electronic structure correlations to be formulated in multiproperty magnetic materials. These studies are currently underway on a series of **NN-SQMTp$^{\mathbf{Cum,Me}}$** complexes, where we expect to develop a more complete understanding of their potential as building blocks for the formation of spin-diverse molecule-based magnetic materials.

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Supporting Information Available: MCD spectrum of **NN-SQCu-Tp$^{\mathbf{Cum,M}}$** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] We do not see evidence for population of the $S_T = {}^1/_2$ state. The fact that we *do not* see evidence for population of this $S_T = {}^1/_2$ state at ~100 K has allowed us to set a conservative lower limit on the magnitude of the quartet–doublet splitting.

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