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Importance of the Anisotropic Exchange Interaction for the Magnetic Anisotropy of Polymetallic Systems

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A prerequisite to understand and subsequently to allow applications of the magnetic properties of polymetallic exchange coupled systems is a detailed insight into the magnetic properties of their elementary building blocks and the interaction between them. Such an understanding passes through the quantification of the relative contributions of single-ion and exchange terms to the overall magnetic properties of the system. In the general case, the quantification of these two kinds of contribution is possible when numerous spin-states are experimentally observed since single-ion and exchange terms project differently on the ground and various excited spin-states of an exchange coupled system.

The spectroscopic techniques commonly used to probe the magnetic properties of paramagnetic systems, namely electron paramagnetic resonance (EPR) and inelastic neutron scattering (INS), rarely provide well-resolved data giving detailed information on excited states of exchange coupled systems owing to line broadening because of factors such as fast spin relaxation. We present here highly resolved multifrequency (X-, K-, and Q-band) CW-EPR spectra (shown in Figure 1 and in the Supporting Information section) obtained on a heterooctametallic ring $[Me_2NH_2][Cr(III)_7Cd(II)F_8((CH_3)_3CCOO)_{16}]$ (**1**). The spectra of **1** provide a rare example of a polymetallic system where detailed information on the spin-Hamiltonian parameters of excited spin-states is experimentally observed.

1 crystallizes in the *P*4 space group with the molecules located on fourfold symmetry sites.[1] Thus, there is only one molecular magnetic site per unit cell. Within the molecule, the metal ions are located on the edges of an octagon with site occupancy $^7/_8$ and $^1/_8$ for Cr(III) and Cd(II), respectively. Previous magnetic susceptibility studies on **1** showed, by use of an isotropic spin-Hamiltonian within the irreducible tensor operator[2] (ITO) formalism, that the isotropic exchange parameter J_{Cr-Cr} (see eq 1) is antiferromagnetic and of the order of $-5.8\ cm^{-1}$. Under these conditions **1** is characterized by a paramagnetic $S = {}^3/_2$ ground spin-state and two low-lying $S = {}^1/_2$ and $S = {}^5/_2$ excited spin-states with energy 6.78 and 15.25 cm^{-1} above the ground state, respectively. All of these three spin-states are thermally accessible at the temperature of measurement (5 K).

An interpretation approach of the EPR spectra of **1** within the "strong exchange limit" or "giant spin approximation" (GSA) is intrinsically problematic since it would assume that the total spin *S* is a good quantum number. This assumption holds so long as inter-spin-state mixing effects are negligible. Such inter-spin-state mixing effects strongly depend on the presence of single-ion and exchange anisotropy terms in the spin-Hamiltonian of the system and are inversely proportional to the energy gap between admixed spin-states. The relatively small magnitude of the isotropic exchange in **1** makes that inter-spin-state mixing effects are expected to be non-negligible. In this case to use the GSA we would require a model that would incorporate not only a set of spin-Hamiltonian parameters for each experimentally observed spin-state but also parameters corresponding to off-diagonal matrix elements between spin-states to take into account the inter-spin-state mixing effects. One can easily see that such a model could require a very large number of parameters. In very recent work, Hill and Hendrickson outlined the limitations of the GSA in interpreting the EPR data of a $\{Ni_4\}$ cubane,[3] in particular in relation to the necessity of accounting for exchange controlled inter-spin-state mixing effects by introducing higher order terms to the usual form of the GSA spin-Hamiltonian.

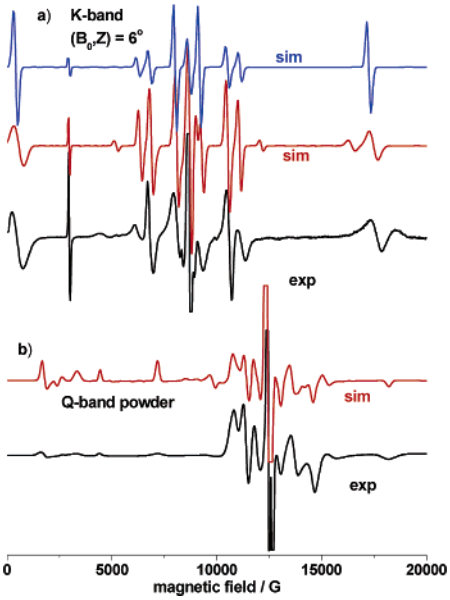

Figure 1. Experimental (black), simulated within an effective subspace of dimension 30 by 30 (red) and simulated with the 12 lowest eigenvectors of full length (blue), CW-EPR spectra of **1** at 5 K. (a) Single-crystal spectra at 23.9144 GHz. A slight misalignment of the order of 5° between the external magnetic field and the molecular *Z* axis, due to manual positioning of the crystal on a silica surface, was included to obtain the best agreement between the experimental and simulated spectra. (b) Polycrystalline powder spectra at 34.0458 GHz. All simulations were made with: $J_{Cr-Cr} = -5.800\ cm^{-1}$, $g_{Cr} = 1.960$, $D_{Cr} = -0.145\ cm^{-1}$, $D_{Cr-Cr} = -0.098\ cm^{-1}$, and isotropic Gaussian linewidths of 100 G. In the case of the effective subspace simulations (red), a Gaussian distribution of D_{Cr} with $\sigma = 0.007\ cm^{-1}$ was used.

To go beyond the GSA model and compute exactly spin expectation values of, or transition moments between, thermally

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populated eigenstates, it is necessary numerically to diagonalize spin-Hamiltonian matrices of dimension $N = \Pi(2S_i + 1)$, with S_i the spin quantum number of the *i*th center. Numerical diagonalization of large matrices by full-matrix algorithms is currently prohibited by unrealistic computation time and memory storage requirements. However, only a few thermally populated eigenstates have to be taken into account for the description of the low-temperature magnetic properties of a polymetallic system.

To circumvent the above technical limitations we adapted to the spin-Hamiltonian formalism an iterative approach that exploits the sparsity of the Hamiltonian matrix, known as the Davidson algorithm.[4] The approach allows the exact computation of the low lying eigenvalues and eigenvectors of interest within realistic computation times and memory storage requirements. It also allows the simultaneous inclusion of single-ion and exchange anisotropy terms in the spin-Hamiltonian without requiring that the total spin S is a good quantum number. The converged low-lying eigenvectors, each of them of dimension N, can directly be used for the computation of quantities such as spin expectation values or transition moments. Alternatively, they may be used in a unitary transformation of the full Hamiltonian to generate an effective operator accurate in the subspace defined by the converged eigenvectors.

For the simulation of the EPR spectra of **1** we use the following spin-Hamiltonian:

$$\begin{aligned}\hat{H} = \sum_i \mu_\mathrm{B}\vec{B}R_i \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} \mathrm{R}_i^* \hat{S}_i + \\ \sum_i \hat{S}_i R_i \begin{pmatrix} -D_i/3 + E_i & 0 & 0 \\ 0 & -D_i/3 - E_i & 0 \\ 0 & 0 & 2D_i/3 \end{pmatrix} R_i^* \hat{S}_i + \\ \sum_{i<j} \left\{ \hat{S}_i R_{ij} \begin{pmatrix} -2J_{ij} - D_{ij} & 0 & 0 \\ 0 & -2J_{ij} - D_{ij} & 0 \\ 0 & 0 & -2J_{ij} + 2D_{ij} \end{pmatrix} R_{ij}^* \hat{S}_j \right\} \quad (1)\end{aligned}$$

where the summation runs over all single ions of the system, R_i and R_{ij} are the relevant Euler rotation matrices and the other symbols have their usual meaning. Application of this spin-Hamiltonian operator to the direct product single-ion basis-set functions produces a hermitian matrix of dimension $N = 16384$ that we numerically diagonalize by the Davidson algorithm.

For the simulation of the EPR spectra of **1** we use only four parameters of which $J_{\mathrm{Cr-Cr}}$ and g_{Cr}, can be independently determined by magnetic susceptibility and INS measurements.[1,5] We use a first-neighbor isotropic exchange parameter, $J_{\mathrm{Cr-Cr}}$, of -5.800 cm^{-1}, and an isotropic *g*-value ($g_{\mathrm{Cr}} = 1.960$) for all Cr(III) centers. Our spin-Hamiltonian model assumes that the single ion anisotropy tensors, $\mathbf{D}_i$, have their largest principal component along the molecular Z axis (perpendicular to the plane of the wheel) and one of the two axial components along the radius of the wheel. Furthermore it assumes that the anisotropic exchange tensors, $\mathbf{D}_{ij}$, have their largest principal component along the intermetallic vector and one of the two axial components along the molecular Z axis. To further reduce the number of varied parameters we neglect single-ion rhombic terms. The only remaining free parameters in the spin-Hamiltonian are the single-ion anisotropy and the anisotropic exchange parameters, D_{Cr} and $D_{\mathrm{Cr-Cr}}$, respectively. The EPR spectra of **1** can then be simulated with $D_{\mathrm{Cr}} = -0.145$ cm^{-1} and $D_{\mathrm{Cr-Cr}} = -0.098$ cm^{-1}. The anisotropic exchange parameter is included in our model because the splittings, at zero field, within the $S = {}^5/_2$ second excited spin-state (three Kramers doublets split by 0.174 and 0.218 cm^{-1}) mainly depend on this parameter. The interpretation of INS spectra obtained on **1**,[5] did not require introduction of this term because of the lower resolution of INS compared to EPR. Consequently, the single-ion anisotropy term of **1** determined by INS should be understood as including both single-ion and anisotropic exchange effects. In the upper panel of Figure 1, the blue simulation was obtained by taking into account the twelve lowest eigenvectors of length N and treating all the terms in (1) simultaneously. The red simulation in the same panel was obtained from a subspace diagonal with respect to all zero-field terms, thus accounting for all field-independent state mixing.[6] The matrix representation of the Zeeman terms was then generated in this basis. Comparison of the computed resonance fields in the above two simulated spectra reveals maximum deviations of the order of 30 G, much smaller than the line width of the observed transitions. Thus, this effective subspace is describing the behavior of **1** over the full range of the applied external magnetic field with deviations much less than the experimental line width. Consequently, we can use this computationally more efficient effective subspace to compute the powder spectra of **1** at Q- and X-band (bottom panel of Figure 1 and Supporting Information) with satisfactory accuracy.

In conclusion, by using a spin-Hamiltonian that directly relates to the structure of a large exchange coupled system, we can analyze the obtained highly resolved EPR spectra to give direct quantification of the contributions of single-ion and exchange anisotropy terms to the magnetic properties of the system. Our approach allows an exact treatment of the anisotropic Hamiltonian and the generation of highly accurate effective subspaces. The obtained energy level pattern of **1** not only reproduces previous results obtained by INS studies[5] but also allows a detailed insight into the nature of the low-lying multiplets. The interpretation of these spectra show that the anisotropic exchange parameter, as it has recently been shown by theory,[7] makes a significant contribution to the zero-field splitting of the various spin multiplets of a system. Previously this term has often been neglected in discussing molecular magnets. In future we will apply our new approach to the analysis of magnetic circular dichroism and magnetic susceptibility data.

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Supporting Information Available: Picture of **1**, experimental and simulated single crystal and polycrystalline powder CW-EPR spectra of “Cr$_7$Cd” at K- and X-band. This material is available free of charge via the Internet at http://pubs.acs.org.

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