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Magnetic Excitations in Tetrameric Clusters of Polyoxometalates Observed by Inelastic Neutron Scattering. Evidence for Anisotropic Exchange Interactions in Cobalt(II) Clusters

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Polyoxometalate complexes are proving especially valuable for the study of magnetic interactions in clusters.[1] Many of these molecular metal oxides have structures that permit the inclusion of well-isolated clusters of paramagnetic ions with various nuclearities and definite topologies and geometries. A good example of this ability is provided by the complexes obtained from the lacunary trivacant Keggin ligands $[PW_9O_{34}]^{9-}$ and paramagnetic transition metal ions. In these a rich diversity of magnetic clusters with nuclearities 3, 4, and 9 can be created with ferromagnetic interactions resulting in high spin multiplicities, as well as antiferromagnetic clusters with spin frustration and clusters with competing ferro- and antiferromagnetic interactions.[2]

In this communication inelastic neutron scattering (INS) is used to determine the energies of the different spin states of the tetrameric clusters M_4O_{16} encapsulated in between two $[PW_9O_{34}]^{9-}$ anions, where M^{2+} = Mn, Co, and Ni (Figure 1). This spectroscopic technique has proved to be very powerful for the direct determination of the exchange interactions in magnetic clusters.[3−5] They serve as molecular models for the more complicated magnetic systems with extended interactions. Molecular concepts can be used for the representation of the various interactions in the data analysis. In contrast to extended systems, exact solutions of the respective effective Hamiltonians are obtained either analytically or numerically.

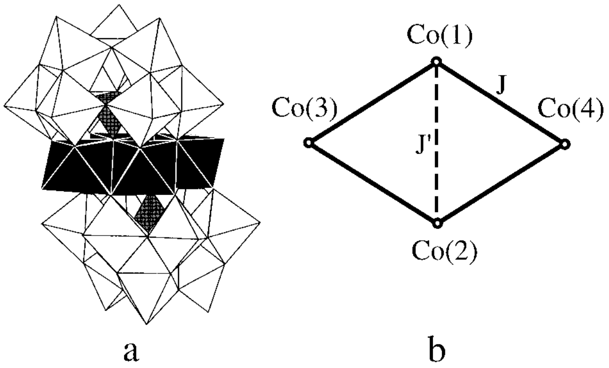

Figure 1. (a) Structure of the $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ complex. (b) Tetramer symmetry and principal exchange interactions.

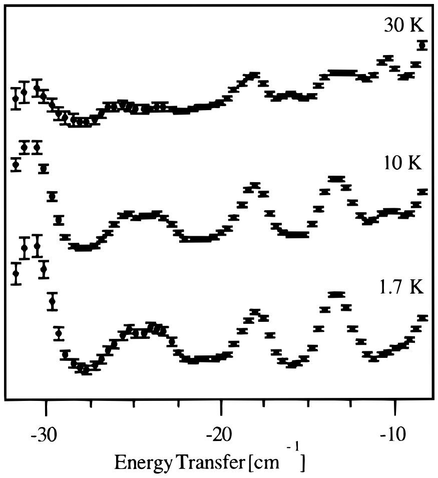

Figure 2. Inelastic neutron-energy loss spectra at 1.7, 10, and 30 K of $K_{10}[Co_4(D_2O)_2(PW_9O_{34})_2]\cdot 20D_2O$ obtained on IN6 at ILL, Grenoble, France, using a neutron wavelength $\lambda = 4.1$ Å.

High-resolution INS spectra of fully deuterated polycrystalline samples of the three potassium salts of these polyoxoanions $K_{10}[M_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ were obtained on the instrument IN6 at ILL, Grenoble, France. They reveal a rich fine structure in the energy range up to 32 cm^{-1}; see the spectra of Co_4O_{16} (Figure 2) as an example. The structure of the tetramers created in these polyoxotungstates consists of four coplanar $M^{II}O_6$ distorted octahedra sharing edges with a rhomblike shape[6] as shown in Figure 1b. There are two principal exchange pathways indicated by the two parameters J and J'. The combined action of spin−orbit coupling and low-symmetry crystal field splits the $^4T_1$ single-ion ground state of Co^{2+} into six anisotropic Kramers doublets.[7] Assuming that only the lowest single-ion level is relevant for the excitations reported here and allowing for an axial spin-anisotropy, we can write the following effective spin Hamiltonian for the exchange coupling:[5]

$$\hat{H} = -2J_z(S_{1z}S_{3z} + S_{1z}S_{4z} + S_{2z}S_{3z} + S_{2z}S_{4z}) - 2J_{xy}(S_{1x}S_{3x} + S_{1x}S_{4x} + S_{2x}S_{3x} + S_{2x}S_{4x} + S_{1y}S_{3y} + S_{1y}S_{4y} + S_{2y}S_{3y} + S_{2y}S_{4y}) - 2J'_z(S_{1z}S_{2z}) - 2J'_{xy}(S_{1x}S_{2x} + S_{1y}S_{2y}) \quad (1)$$

Magnetic susceptibility data down to liquid-He temperature are often used to determine exchange parameters and thus the strength and nature of the most important pathways. For the present tetranuclear magnetic clusters, however, and in particular

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for Co_4O_{16}, the information content of magnetic susceptibility data is insufficient for a determination of all the relevant parameters (including those derived from the Zeeman Hamiltonian).[2b,c] The additional information provided by INS becomes invaluable. In Figure 2 six cold peaks are identified by simple inspection, the peaks at 10.2, 12.5, and 15.7 cm^{-1} obviously being hot. The magnetic nature of these excitations was confirmed by their dependence on the scattering angle. This dependence is significantly different from the one expected for vibrational excitations; it is therefore an important means of distinction. The transitions shown in Figure 2 correspond to magnetic excitations of the tetramer by neutron-energy loss. We also measured the corresponding energy-gain spectra in which the energy transfer is from the cluster to the neutrons. The two modes correspond to the Stokes and Antistokes modes in Raman spectroscopy. From a complete analysis of all the data the energy splitting pattern in Figure 3 was obtained. This energy splitting results from exchange interactions, and we can try to fit the eigenvalues of eq 1 to reproduce it. A good reproduction of the energy pattern is obtained with the following parameters:

$$J_z = 10.2\ \mathrm{cm}^{-1} \quad J_{xy} = 4.21\ \mathrm{cm}^{-1} \quad J'_z = 4.04\ \mathrm{cm}^{-1} \quad J'_{xy} = 0.87\ \mathrm{cm}^{-1} \qquad (2)$$

Both interactions are ferromagnetic and anisotropic, thus leading to the $M = \pm 2$ ground level, which is in good agreement with the results of EPR and magnetic measurements.[2b] Evidence for an exchange anisotropy is thus clearly demonstrated by INS.

On the basis of the wave functions obtained by diagonalizing the Hamiltonian (1) with the parameters (2) and using a formula derived for the differential scattering-cross section, the relative intensities of the various transitions in Figure 3 and their dependence on the scattering angle can be calculated. A comparison with the experimental data clearly shows that the model needs to be refined, despite the good reproduction of the energy splitting. We are presently exploring the effect of antisymmetric exchange on the energies and intensities of the magnetic excitations.

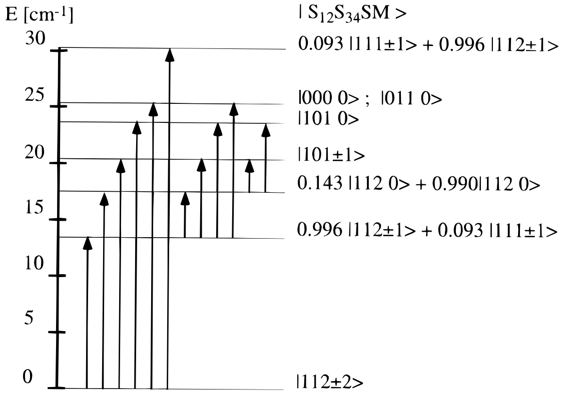

Figure 3. Exchange-splitting diagram derived from the high-resolution INS experiments. Arrows correspond to observed transitions. The magnetic quantum numbers correspond to the fit derived from eq 1 and the parameters listed in the text.

In summary, we conclude that for the tetrameric complexes Mn_4O_{16}, Co_4O_{16}, and Ni_4O_{16} INS provides a much deeper and more detailed insight into the nature of the magnetic coupling than bulk techniques.

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