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Magnetic and Resonance Properties of Molecule-based Magnets

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We report on a comparative investigation of the structural and magnetic properties of copper-containing siloxanolate complexes $Cu_N[(R SiO_2)_N]_2(Ligand)$ (N=6,8,10; R=Me,Et,Ph; $Ligand$=DMF,EtOH) having a sandwich-like molecular structure. All molecule-based complexes exhibit a similar structure consisting of planar rings of N=6,8 or 10 Cu(II) atoms sandwiched by two N-membered cyclosiloxanolate fragments. Within the rings, adjacent Cu^{2+} ions are linked by pairs of siloxanolate oxygen atoms, which provide the main exchange path for the $S = \frac{1}{2}$ spins. The analysis of the magnetic data, with particular emphasis placed on the high-temperature behaviour, together with the structural information enables us to correlate the evolution of the average exchange coupling J between the magnetic $S = \frac{1}{2}$ centres of the quantum ring as a function of the number N of magnetic sites to the structural changes of the molecular crystals. Our analysis reveals indications that structural-related inhomogeneities of the exchange couplings may have a significant influence on the low-temperature magnetic behaviour of quantum ring systems.

The molecular complex of $\{Cu_6[(PhSiO_2)_5]_2(OH)_2(bipy)_2\}4(DMF)3(H_2O)$ differs from the known hexacopper (II) cluster compounds in its unique $S = \frac{1}{2}$ arrangement: each molecule contains two linear oxygen-bridged three-site Cu(II) strings which are parallel to each other. Magnetic measurements reveal an antiferromagnetic intra-trimer exchange interaction J/k_B=85K as the dominant magnetic coupling of the complex. By introducing a weak antiferromagnetic inter-trimer coupling J'/k_B=3.5K, a satisfactory description of the magnetic behaviour over a wide range of temperature and magnetic field is obtained. The low temperature single crystal ESR study clearly demonstrates that the molecular ground state of the complex is a singlet-triplet state, which is typical for an effective S=1 spin. From the temperature dependence of the ESR spectra it was found that the progressive formation of the S=1 ground state of the molecule occurs only below 40K when the excited doublet and the quartet states of individual trimers with J/k_B=85K become completely thermally depopulated. The ESR measurements indicate that the weak intermolecular and intertrimer exchange interactions lead to significant exchange averaging effects of magnetic resonance of the complex, forming the broad quasi-isotropic spectrum at high temperatures.