LOW-SYMMETRY EFFECTS IN METALLACRYPTATE SINGLE-MOLECULE MAGNETS

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Introduction

In a previous report, we presented a preliminary characterization of a Mn26 metallacryptate (a three-dimensional metallacrown) that exhibits single-molecule magnet (SMM) behavior. [1] The magnetic characterization of [MnII4MnIII22(pdol)12(OCH3)12(O)16(N3)6]1 and [MnII4MnIII22(pdol)12(OCH3)12(O)16(OH)2(H2O)(OCH3)3]ClO4.5CH3OH 2, where the azide anions of 1 are replaced by water, hydroxide, and methoxide, are presented in this report.

Experimental

VTVH DC magnetization measurements were performed on a VSM coupled to a 3He refrigeration system capable of temperatures as low as 0.55 K. A water-cooled resistive Bitter magnet was used to provide continuous magnetic field sweeps between 0 and 30 T. Isothermal magnetization measurements were performed between 0.6 K and 4.5 K. The VSM measurements were conducted at the NHMFL-FSU. Isofield VT DC magnetic susceptibility measurements were performed at 0.25 T on a Quantum Design MPMS SQUID magnetometer from 2 K to 300 K. All DC magnetic susceptibility data were collected on powdered samples suspended in eicosane to prevent torqueing of the sample at high applied DC fields. AC magnetic susceptibility measurements were made on powdered samples in an AC drive field operating at 100-5000 Hz with no applied DC field. A Quantum Design MPMS SQUID magnetometer was used in the 2–10 K range with a 3.5 G AC drive field, and a custom AC susceptometer at the NHMFL-FSU was used in the 0.3–6 K range with a 50 G AC drive field.

Results and Discussion

The structural characterization of complexes 1 and 2 reveal that each has a metallacryptand shell that encapsulates a manganese oxide core. Variable-temperature DC magnetic susceptibility measurements on 2 indicate a paramagnetic ground state that results from overall antiferromagnetic interaction in the cluster, with χT values decreasing from 300 K (51.5 cm3 K mol−1) to 2 K (19.9 cm3 K mol−1). Variable-temperature AC magnetic susceptibility measurements imply that both 1 and 2 behave as single-molecule magnets (SMM’s). Fitting the frequency dependent out-of-phase magnetic susceptibility to the Arrhenius equation yields an effective energy barrier to magnetization relaxation of 11.5 cm−1 for 1 and 25.1 cm−1 for 2. The larger value for 2 is in agreement with its lower molecular symmetry, larger magnetoanisotropy, and higher ground spin state compared to that of 1.

Conclusions

Complexes 1 and 2 expand the known SMM family to include metallacrowns, a type of metallamacrocycle. In addition, it is one of the largest manganese clusters to display SMM behavior and the largest with non-carboxylate ligands. As a result of the lower molecular symmetry and larger ground spin state, 2 was shown to have a higher energy barrier to magnetization relaxation than 1.

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References