Unmasking magnetic anisotropy: single molecular magnet behavior from NMR analysis of spin density distribution

Valentin Novikov, Alexander Pavlov, Yan Voloshin

Nesmeyanov Institute of Organoelement Compounds, RAS, Moscow, Russia

Single-molecule magnets (SMMs), the term referring to chemical compounds exhibiting slow magnetic relaxation and magnetic hysteresis of purely molecular origin, have been discovered in the early 1990. Since then, they emerged as perspective components for information storage, quantum computing, spintronics, and magnetic refrigeration. A necessary condition for a compound to be an SMM is a large axial magnetic anisotropy D that splits the energy levels of a metal ion under zero magnetic field and gives rise to an energy barrier between the states with opposite directions of the magnetic moment $U = |D|S^2$ (or, for non-integer S, $U = |D|(S^2 - 1/4)$).

The method of choice for detecting a large magnetic anisotropy is magnetometry, which often allows determining both the *D* value and the effective barrier height *U*. This technique, however, is quite demanding and requires accumulation of large array of data at different values of magnetic field at very low temperatures. If the purity of the compound is not ideal, which is often the case for complexes with metal atoms in unusual oxidation states, the obtained results should also be interpreted with extreme care.

For the same purpose, we suggest to use NMR spectroscopy coupled with DFT calculations for evaluating the magnetic anisotropy of transition metal complexes in solutions based on a linear dependence of pseudocontact paramagnetic shifts on the anisotropy of the magnetic susceptibility. Paramagnetic shifts extracted from experimental NMR spectra have two components: the dipolar component , which depends on polar coordinates of the corresponding nuclei in the coordinate frame of the unpaired electron and the value of the magnetic anisotropy, and the contact Fermi component, which is governed by the distribution of the density of the unpaired electron. As modern DFT calculations allow obtaining a reliable picture of spin density distribution, they have been used to estimate Fermi shifts with the remaining part of the paramagnetic shifts considered dipolar in origin and thus to extract the value of magnetic anisotropy at different temperatures. The temperature dependence of the magnetic anisotropy was fitted using van Vleck formula to get the *D* value.

The measurements only require a high resolution NMR spectrometer and a reasonable number of ^{1}H NMR spectra to be collected at different temperatures. The proposed approach is also immune to the presence of any impurities, as long as they allow detecting the signals of the compound under study.

In particular, this method allowed us to analyze a large library of cobalt(II) cage complexes to identify those with the largest magnetic anisotropy (25.1×10^{-32} m^3 at room temperature), which corresponds to a very large negative *D* value of -90 cm^{-1}. The magnetochemical measurements confirmed the large magnetic anisotropy and a resulting SMM behavior (with an effective barrier U = 156 cm^{-1}) of a chosen cobalt(II) compound. Therefore, this NMR-based approach paves the way towards fast and inexpensive prescreening of possible SMM candidates.