Strong Magnetic Coupling in Molecular Magnets through Direct Metal-Metal Bonds

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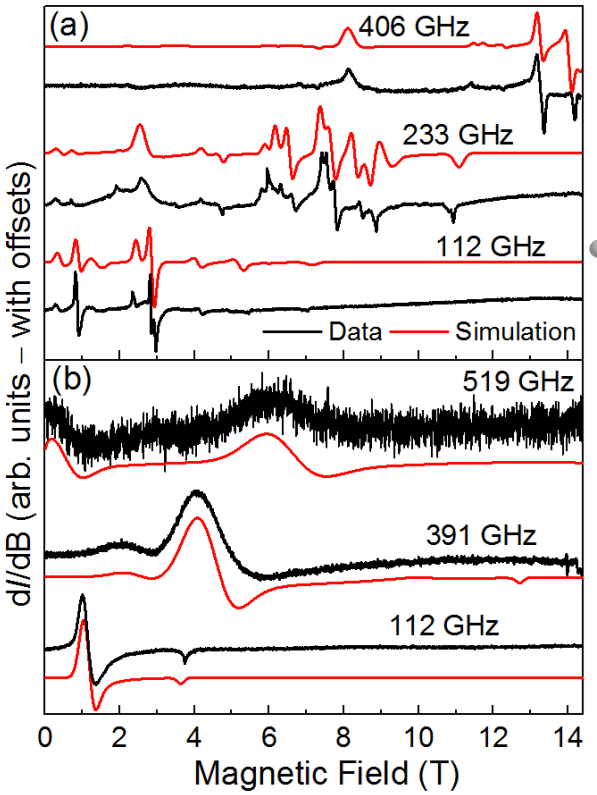
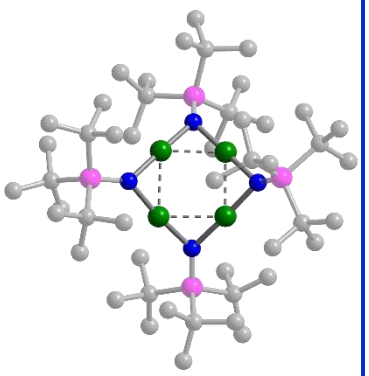
Magnetic molecules that retain their magnetization below a characteristic blocking temperature (T_B) – so-called single-molecule magnets (SMMs) – are of great interest for future information storage technologies. Up to now, attempts at coupling multiple anisotropic magnetic ions have involved weak superexchange interactions mediated via non-magnetic bridging atoms. *This study demonstrates direct metal-metal orbital overlap in a series of M_4 (M = Ni, Cu) clusters, resulting in itinerant electron magnetism similar to metallic ferromagnets.*

High-field, high-frequency (from 112GHz to 519GHz) electron paramagnetic resonance (HFEPR) measurements were performed on neutral and cationic forms of $[Ni_4(NP^tBu_3)_4]^{0/+}$ (^{t}Bu = *tert*-butyl, see Figure) in order to accurately ascertain the spin ground states and interaction parameters associated with these new SMMs. *High-fields and frequencies were essential due to very large spectral splittings resulting from strong magnetic anisotropy*.

The combination of HFEPR and magnetic data with correlated electronic structure calculations provides fundamental insights into the electronic itinerancy and strong ferromagnetic coupling in molecules featuring direct metal-metal orbital overlap. As such, *these investigations suggest new strategies for designing SMMs with strongly coupled giant spin ground states and enhanced blocking temperatures.*





(a) Spin, $S = 2$
$D = -1.93$ cm^{-1}
(b) Spin $S = {}^5/_2$
$D = +7.95$ cm^{-1}

Figure: (Left) Multi-frequency, derivative-mode (d*I*/dB, where *I* is transmitted intensity) HFEPR spectra for powder samples of (a) neutral and (b) cationic $[Ni_4(NP^tBu_3)_4]^{0/+}$. Spectral simulations are included with the experimental data. (Right) Molecular structure along with the deduced spin states and axial zero-field splitting parameters, *D*, a measure of the associated magnetic anisotropy.

Facilities and instrumentation used: EMR program, 15/17 Tesla Transmission Spectrometer.

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