

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

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Funding Grants: G. S. Boebinger (NSF DMR-1644779); S. Hill (NSF DMR-1610226); J. R. Long (NSF CHE-1800252).



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 (HFEP) measurements were performed on neutral and cationic forms of $[Ni_4(NP^tBu_3)_4]^{0/+}$ ($tBu = tert$ -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 HFEP 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.*

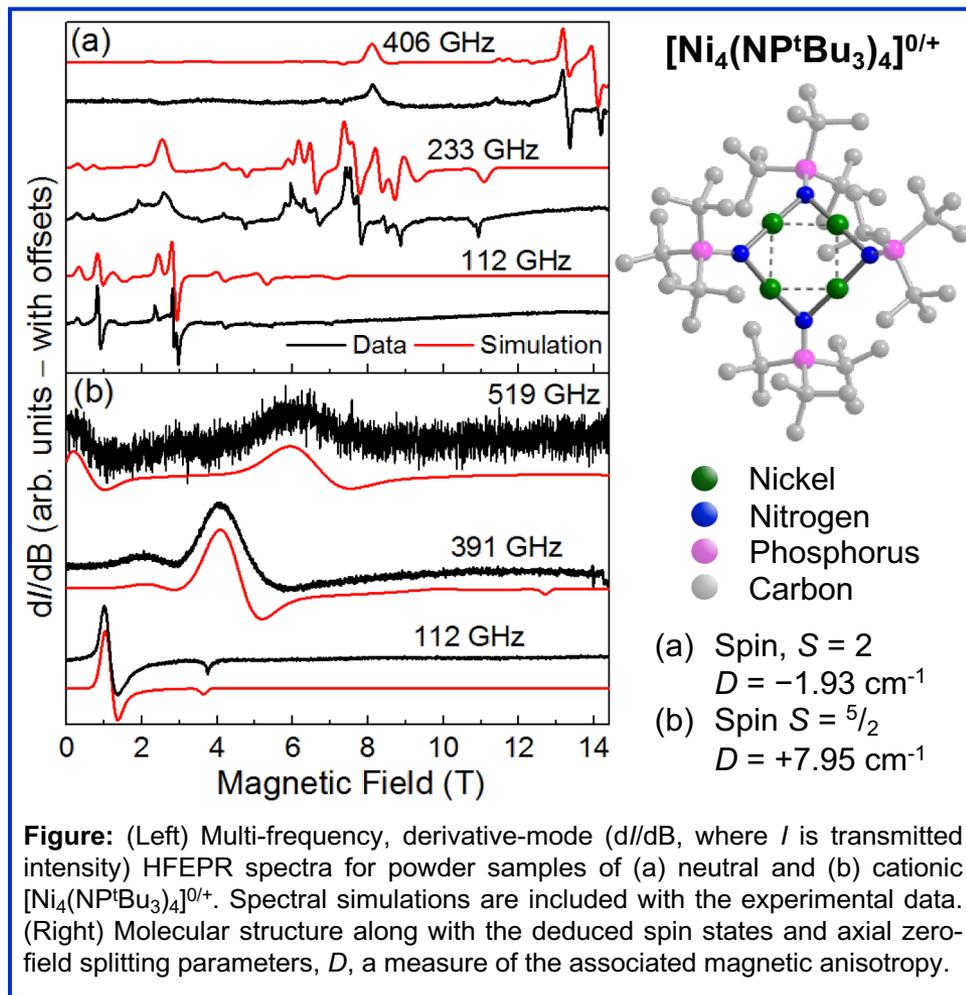


Figure: (Left) Multi-frequency, derivative-mode (dI/dB , where I is transmitted intensity) HFEP spectra for powder samples of (a) neutral and (b) cationic $[Ni_4(NP^tBu_3)_4]^{0/+}$. Spectral simulations are included with the experimental data. (Right) Molecular structure along with the deduced spin 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.

Citation: Chakarawet, K.; Atanasov, M. E.; Marbey, J.; Bunting, P. C.; Neese, F.; Hill, S.; Long, J. R., *Strong Electronic and Magnetic Coupling in M_4 ($M = Ni, Cu$) Clusters via Direct Orbital Interactions Between Low-Coordinate Metal Centers*, Journal of the American Chemical Society, **142**, 19161-19169 (2020) doi.org/10.1021/jacs.0c08460