Magneto-Structural Correlations in a Transition Metal Complex

E. A. Suturina[1,2], J. Nehrkorn[3], J. M. Zadrozny[4,5], J. Liu[5,6], M. Atanasov[1,6], T. Weyhermüller[1], D. Maganas[1], S. Hill[5], A. Schnegg[3], E. Bill[1], J. R. Long[4], F. Neese[1]

1. Max Planck Institute for Chemical Energy Conversion; 2. Novosibirsk State University; 3. Helmholtz-Zentrum Berlin; 4. UC Berkeley; 5. Northwestern; 5. NHMFL; 6. University of Oxford; 6. Bulgarian Academy of Sciences

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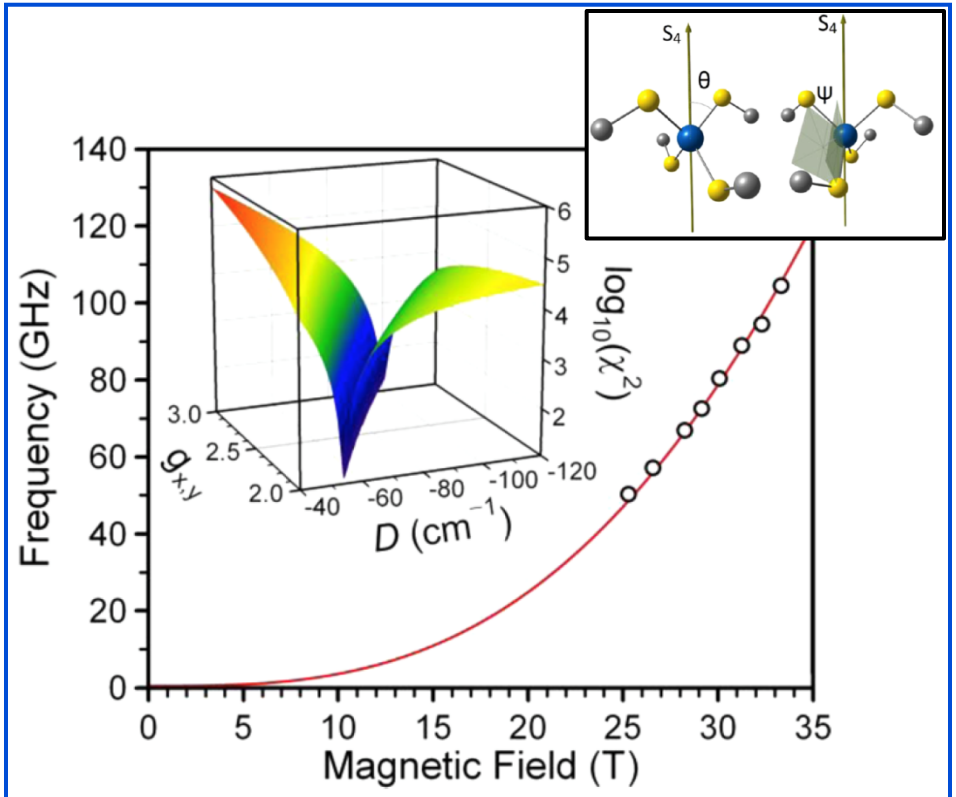
In the field of modern inorganic materials science, magneto-structural correlations in transition-metal complexes have been used to rationally design molecules with desirable magnetic properties. *These magnetic properties, in turn, can be related to the electronic and geometric structures to provide powerful insights into important catalytic processes and active sites in metallo-proteins*. To this end, two pseudo-tetrahedral cobalt-II complexes, denoted as $[Co^{II}(SPh)_4]^{2-}$ complexes, were synthesized to mimic the $[Fe^{II}(S\text{-cysteine})_4]^{2-}$ sites in the Fe−S protein rubredoxin. In this case, cobalt-II provides a powerful electron paramagnetic resonance (EPR) probe, although its extreme magnetic anisotropy necessitates the use of very high magnetic fields (see figure).

The present study combines theory, magnetometry, high-field EPR, and magneto-optical techniques to precisely determine the magnetic anisotropy parameters of $(PPh_4)_2[Co^{II}(SPh)_4]$ and $(NEt_4)_2[Co^{II}(SPh)_4]$. The results reveal a surprisingly strong dependence of these parameters on the S−Co−S angle, θ, and the C−S−Co−S torsion angle, ψ, around the CoS_4 core (see upper inset), with the axial anisotropy ($2D$) changing both sign (easy-axis/easy-plane) and magnitude. *These findings are important both in the area of bio-inorganic chemistry, and in the development of improved molecular nanomagnets with enhanced magnetic anisotropy.*



EPR peak positions (main panel) with the field applied in the hard plane of $(PPh_4)_2[Co(SPh)_4]$. The fit error surface (inset) reveals an inter-dependence between the zero-field splitting parameter, D, and the electronic g-matrix elements, $g_{x,y}$, a situation which is resolved through the combination of magnetic and magneto-optical data.

Facilities: EMR & DC Field (35 T, 32 mm bore resistive magnet)

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