Synthesis and Magnetic Properties of Two-Coordinate Transition Metal Complexes

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Electronic Structure

• Molecular magnets exhibit properties of both classical & quantum systems such as magnetic hysteresis & quantum tunneling of magnetization, respectively
• Larger magnetic anisotropy yields larger spin-reversal barriers ($U_{\text{eff}}$) and greater thermal stability of magnetization

Magnetism

• dc magnetic susceptibility confirms well isolated $M_J = \pm 9/2$ ground state (solid lines are simulations from $ab$ initio calculations)

Synthesis

• Design requirements: Co(II) in linear coordination environment with three-fold symmetry
• $[\text{C(SiMe}_3\text{)}]^{-}$ and $[\text{C(SiMe}_2\text{Ph}_3\text{)}]$ reduces Co(II) in situ
• Addition of aryl-oxide or alkoxide to ligand arms reduces electron density at central carbanion

Electronic Structure

• Lanthanide-like non-Aufbau electron filling arises from extremely weak ligand field
• Ab initio calculations indicate interelectron repulsion favors
  
  
  $d_{x^2-y^2}, d_{xy}$

  rather than the more electronically crowded
  
  $d_{xz}, d_{yz}$

• High resolution x-ray crystallography and QTAIM analysis confirms non-Aufbau d-orbital filling (orbital occupations as a percentage of total d-electron density in red)

Electron Configuration

$S = \frac{3}{2}, L = 3, J = \frac{9}{2}$