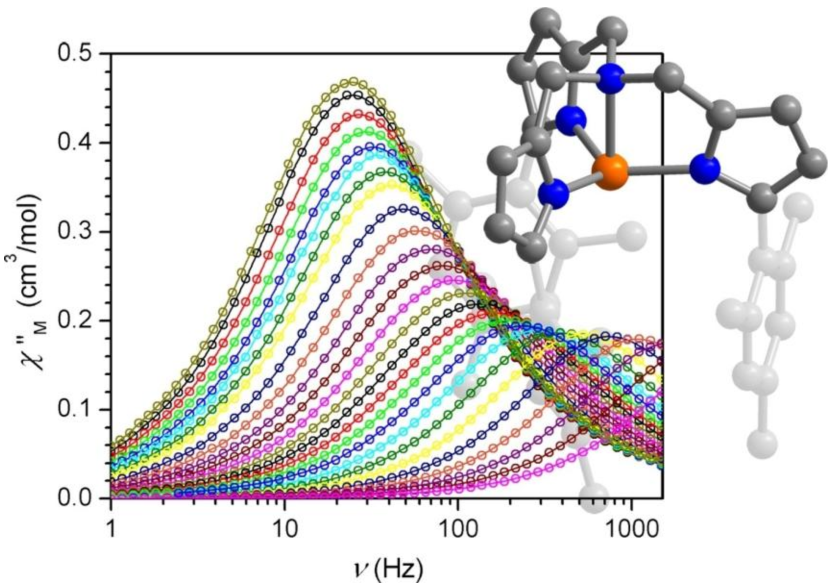
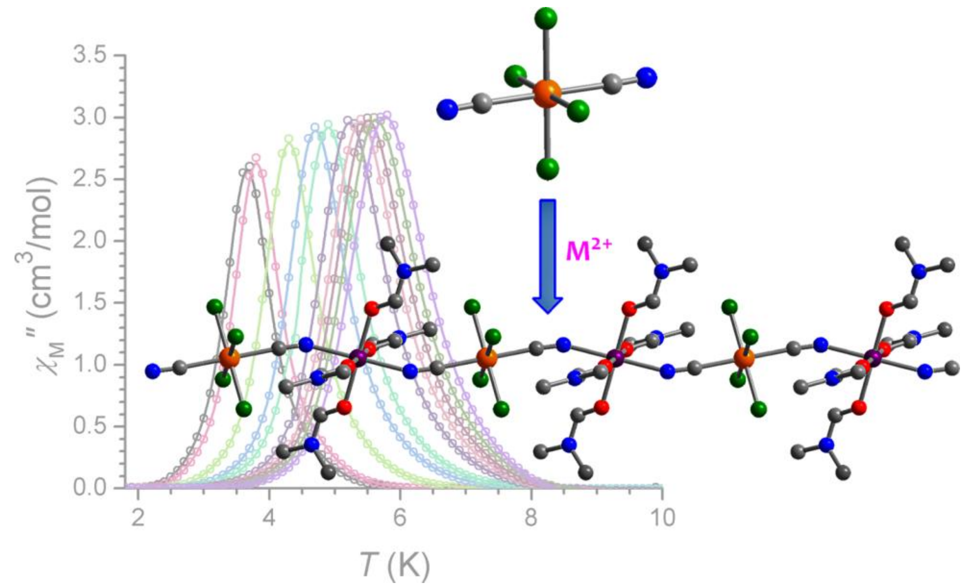
Slow Magnetic Relaxation in a High-Spin Iron(II) Complex and a Series of 1D Coordination Solids

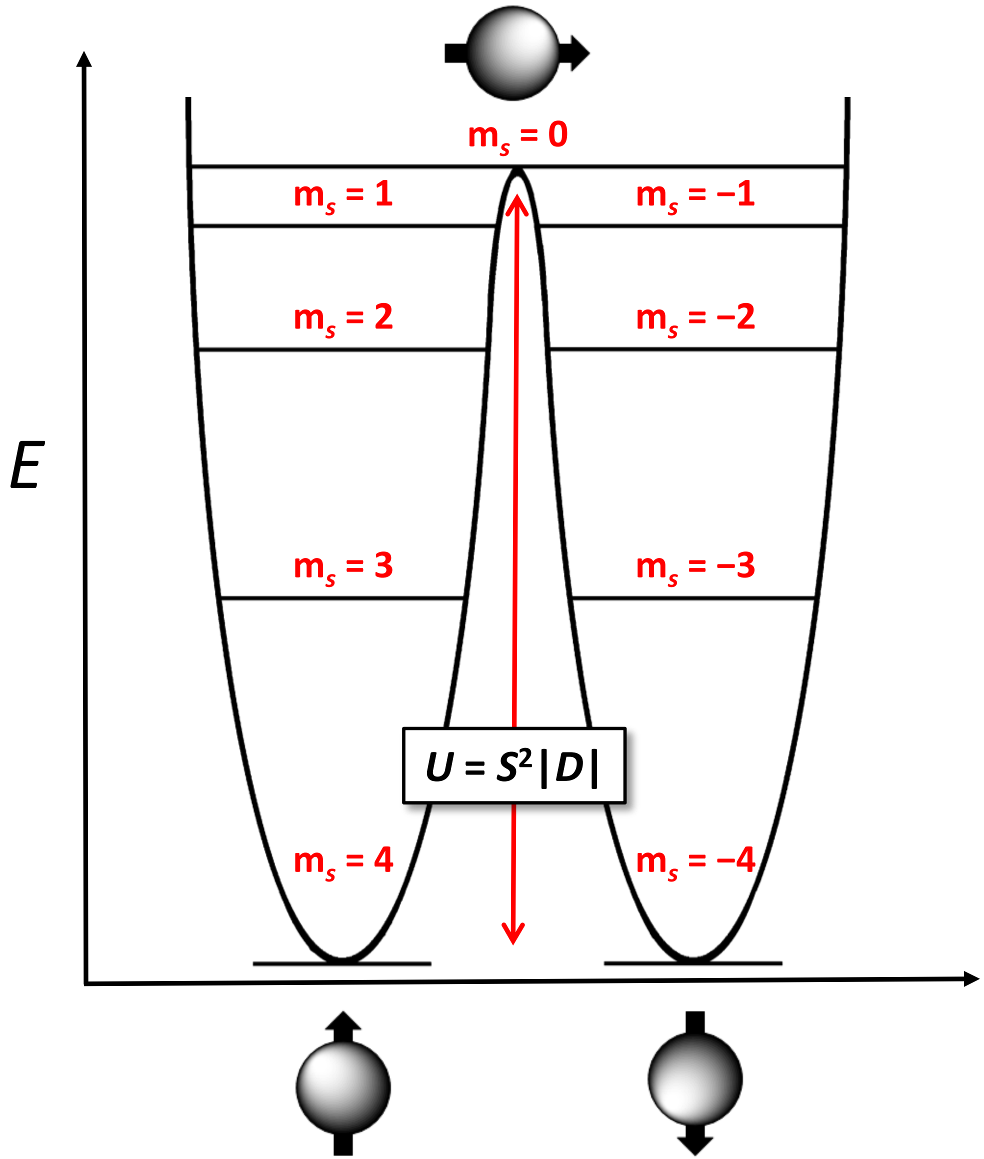




David Harris

Dept. of Chemistry, UC Berkeley

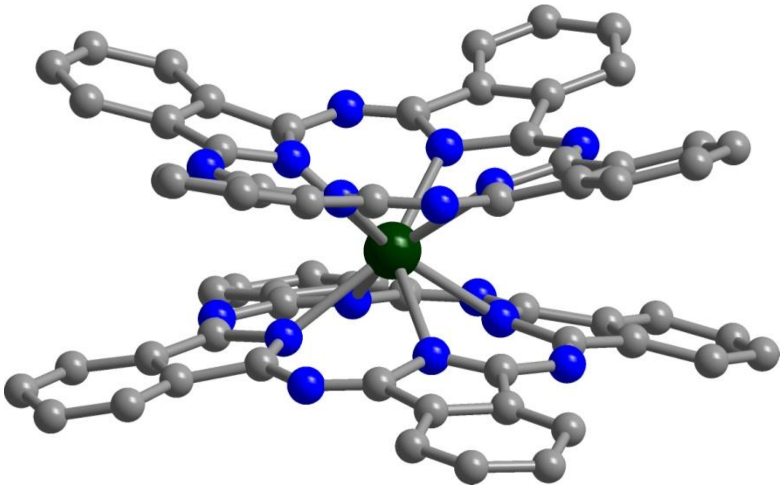
Single-Molecule Magnets



- High-Spin Ground State (***S***)
- Molecular "Easy Axis" Stemming from Uniaxial Anisotropy (***D***)
- Spin-Reversal Barrier:

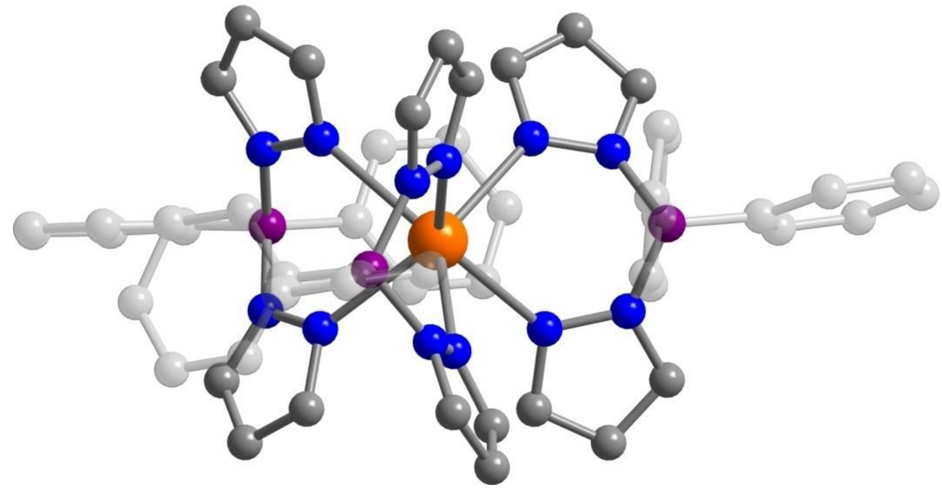
$$U = S^2|D|$$

Slow Magnetic Relaxation in Mononuclear f-Element Complexes



$[Pc_2Ln]^-$
Ln = Tb, Dy, Ho

Ishikawa, et al *JACS* **2003**, *125*, 8694
Ishikawa, Sugita, Wernsdorfer *JACS* **2005**, *127*, 3650

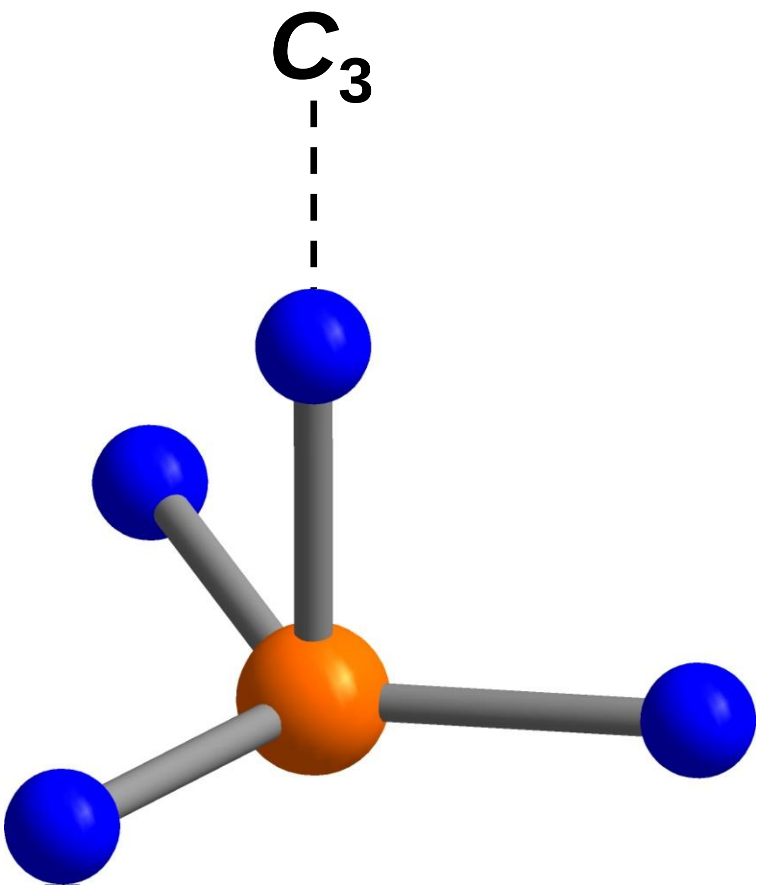


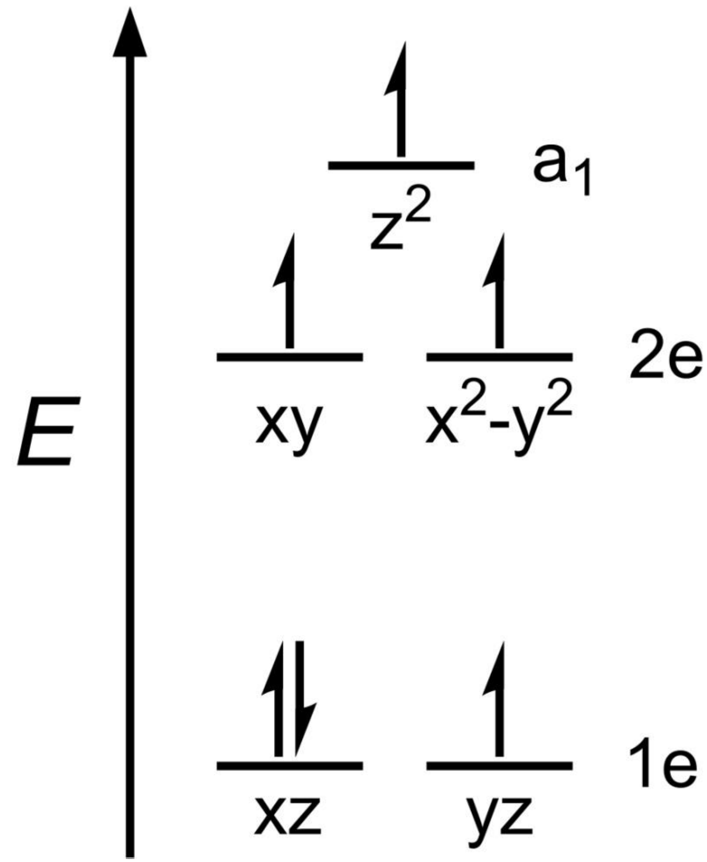
$[(Ph_2BPz_2)_3U]$

Rinehart, Long *JACS* **2009**, *131*, 12558

- slow relaxation stems from highly-anisotropic ground-states

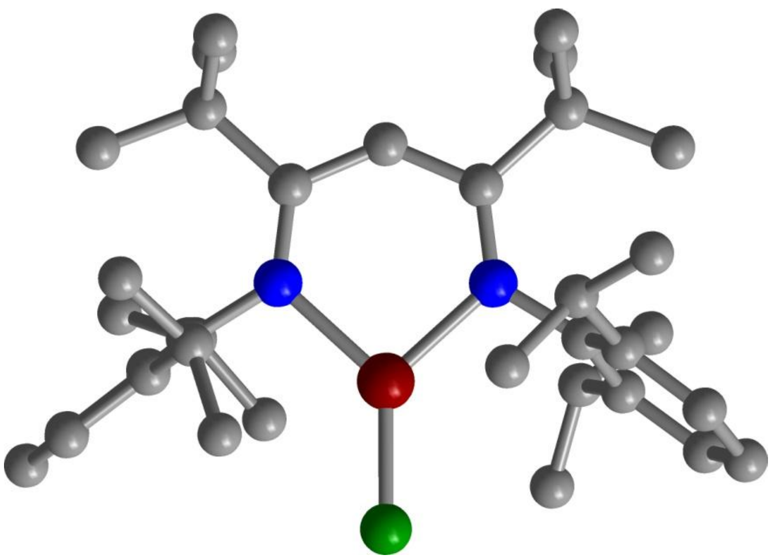
C_3-Symmetric High-Spin Iron(II) as a Source of Anisotropy





***S* = 2, *D* ≠ 0**

Zero-Field Splitting in Trigonal High-Spin Iron(II) Complexes

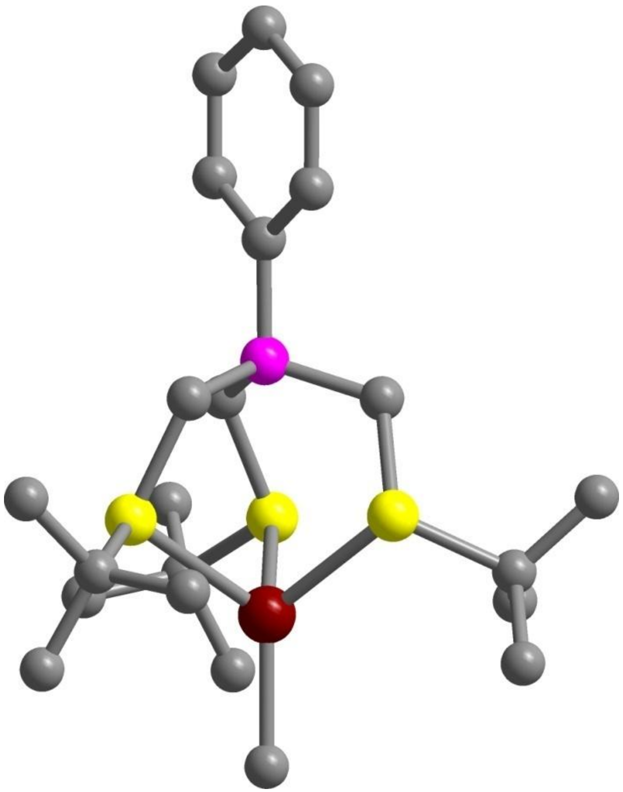


[LFeX]

X = CH_3, Cl, NHTol, NH^{t}Bu

***D* ≥ 50 cm^{-1}**

Andres, Bominaar, Smith, Eckert, Holland, Münck
JACS **2001**, *124*, 3012

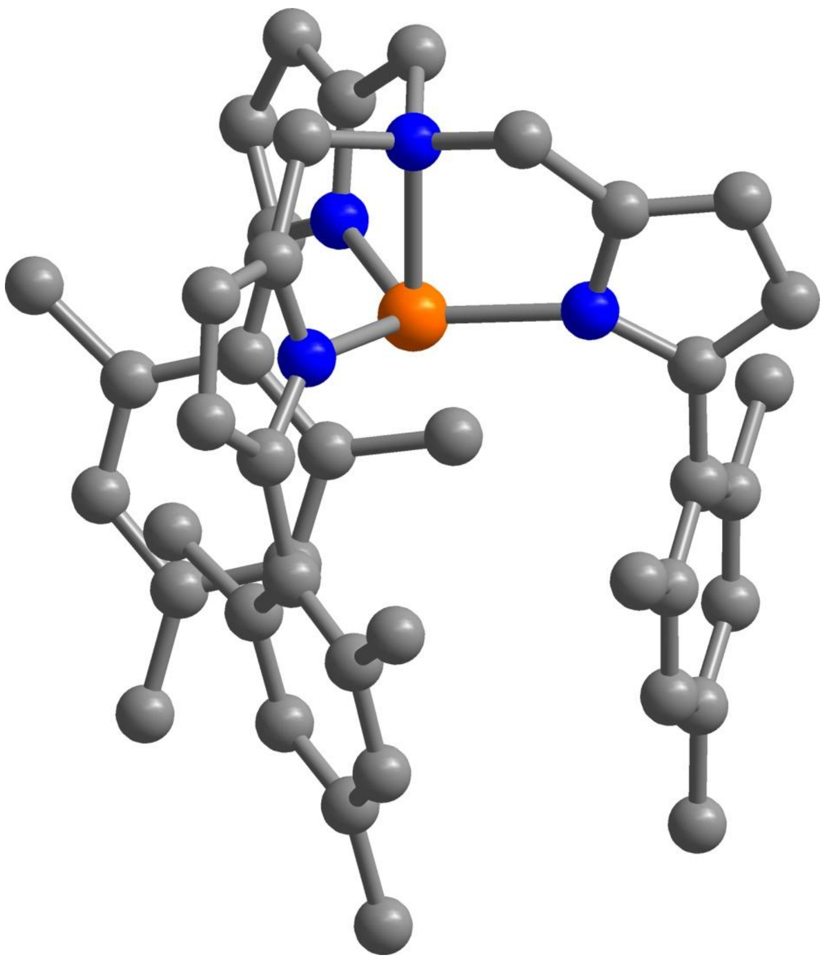


[(PhTt^{tBu})FeMe]

***D* = -37 cm^{-1}**

Popescu, Mock, Stoian, Dougherty, Yap, Riordan
Inorg. Chem. **2009**, *48*, 8317

A High-Spin Iron(II) Complex Approximating C_3 Symmetry

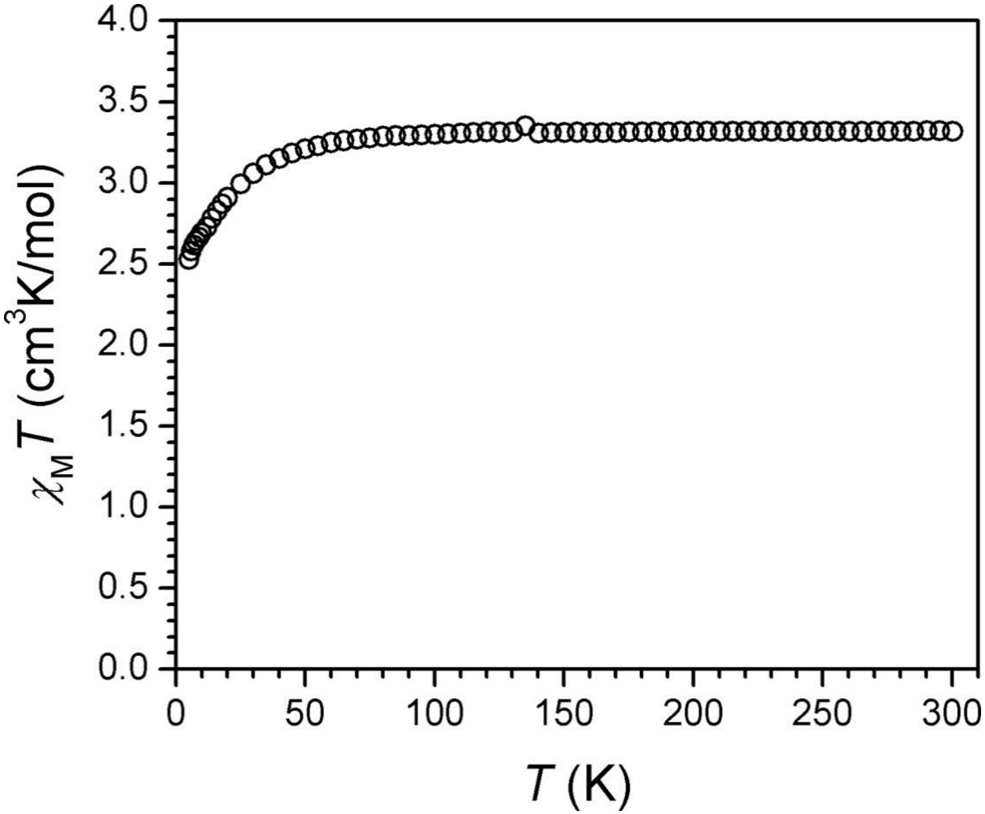


$[(tpa^{Mes})Fe]^-$

Selected Interatomic Distances (Å) and Angles (°)	
Fe-N_{apical}	2.172(1)
Fe-N_{basal}	2.024(3)
	2.008(3)
	2.041(2)
N_{basal}-Fe-N_{basal}	122.4(1)
	115.3(1)
	117.4(1)

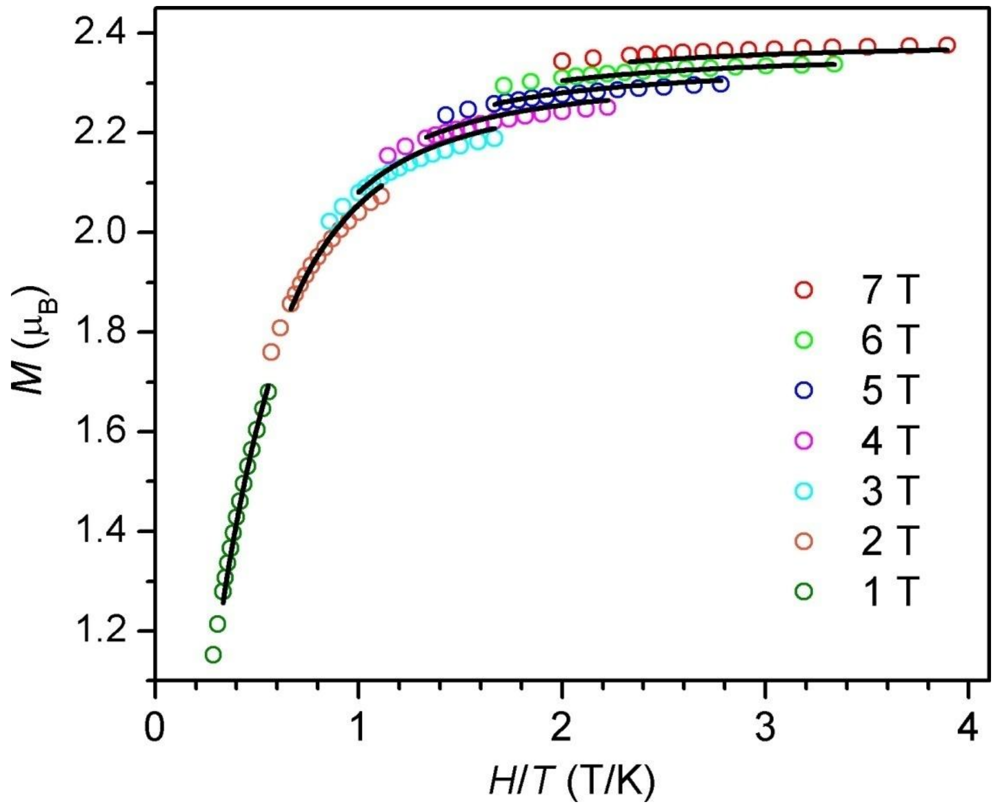
Harman, Chang *JACS* **2007**, *129*, 15128

Confirmation of S = 2 Ground-State in $[(tpa^{Mes})Fe]^{-}$



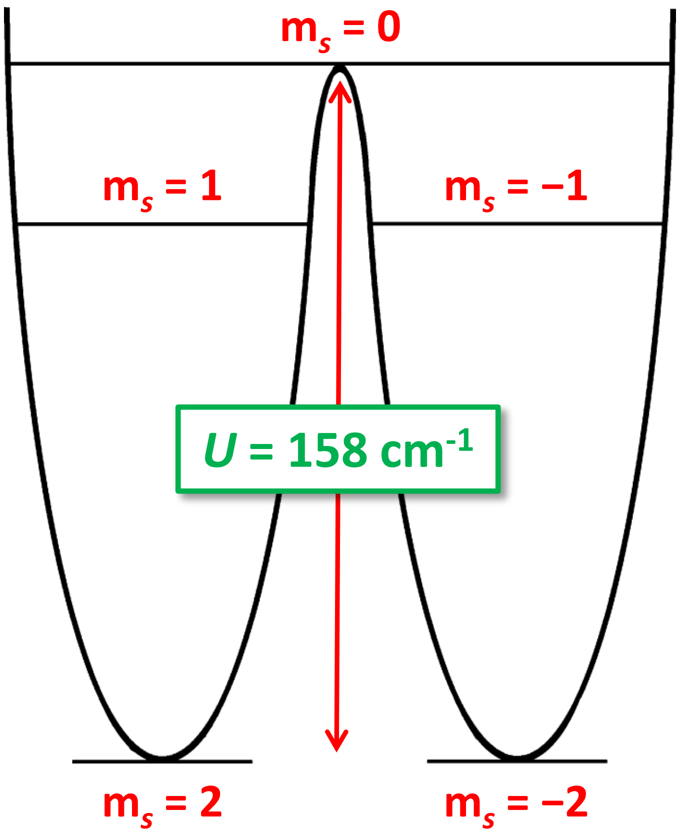
- high-temperature value of $\chi_M T$ = 3.32 cm^{3}mol/K confirms S = 2 ground-state
- downturn in $\chi_M T$ at low temperature indicative of magnetic anisotropy

Immense Magnetic Anisotropy in $[(\mathrm{tpa}^{\mathrm{Mes}})\mathrm{Fe}]^{-}$



- data fit using $\hat{H} = D\hat{S}_z^{\,2} + E(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}) + g_{iso}\mu_B \boldsymbol{S}\cdot\boldsymbol{B}$
- fit gives D = -39.6 cm^{-1} and E = -0.4 cm^{-1}
- EPR silent to 14.5 T and ν = 400 GHz

Theoretical Spin-Reversal Barrier for $[(\mathrm{tpa}^{\mathrm{Mes}})\mathrm{Fe}]^{-}$



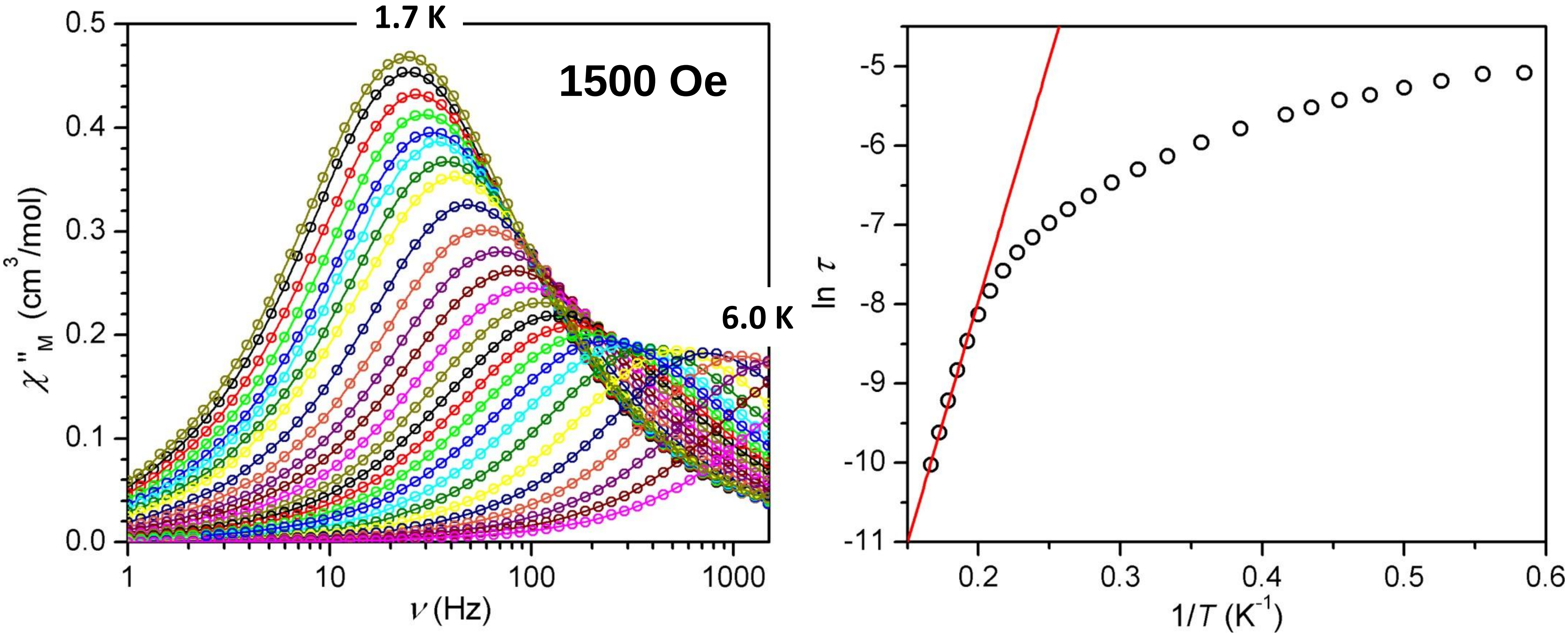
high-spin ground-state:
$S = 2$

uniaxial anisotropy:
$D = -39.6\ \mathrm{cm}^{-1}$

spin-reversal barrier:
$U = S^2|D| = 158\ \mathrm{cm}^{-1}$

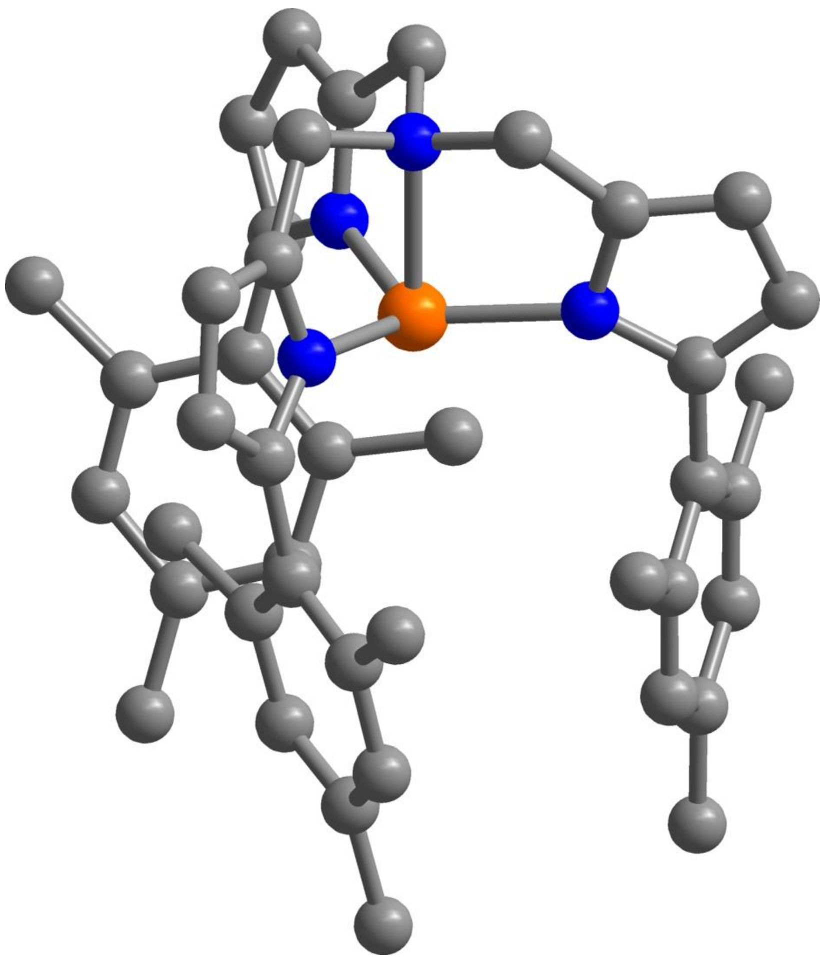
- ac susceptibility measurement shows no χ_M'' signal at $\nu < 1500$ Hz and $T > 1.8$ K
- lack of slow relaxation likely due to quantum tunneling of magnetization

Slow Magnetic Relaxation in $[(tpa^{Mes})Fe]^{-}$



- fit to high-temperature data gives U_{eff} = 42 cm^{-1} and τ_0 = 2 x 10^{-9} s
- τ approaches pure tunneling regime at low temperature

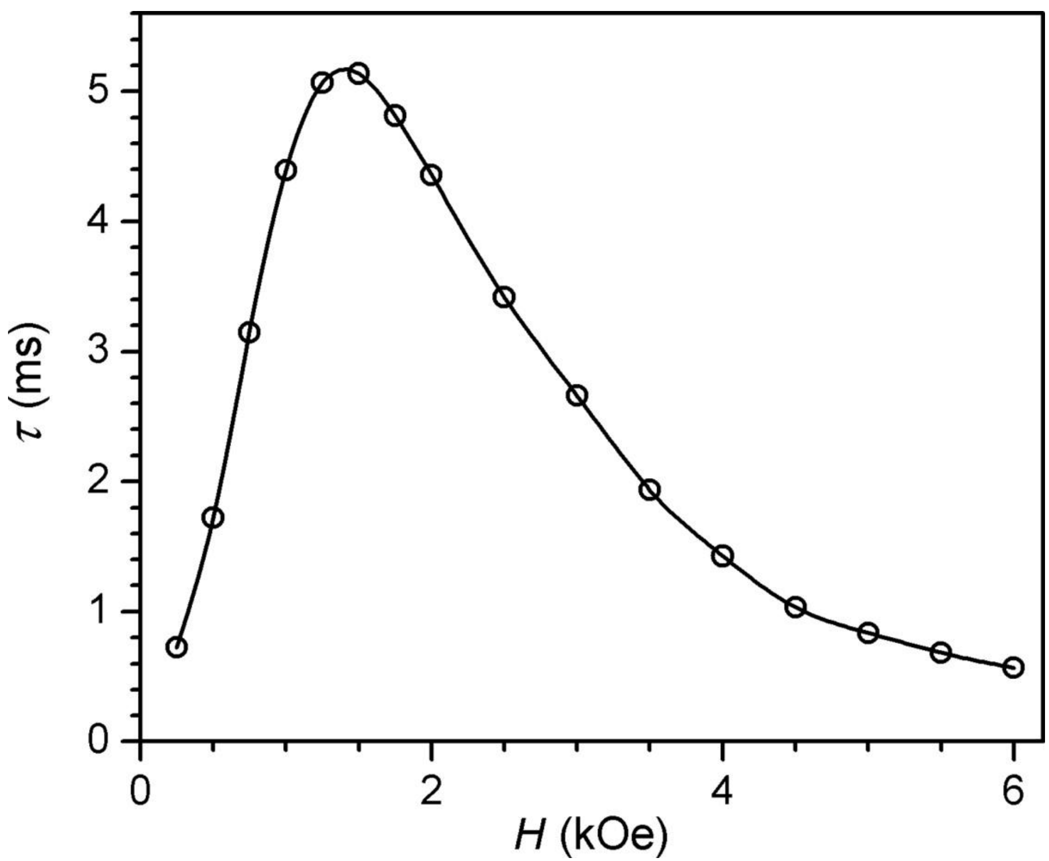
A High-Spin Iron(II) Complex Approximating C_3 Symmetry



$[(tpa^{Mes})Fe]^-$

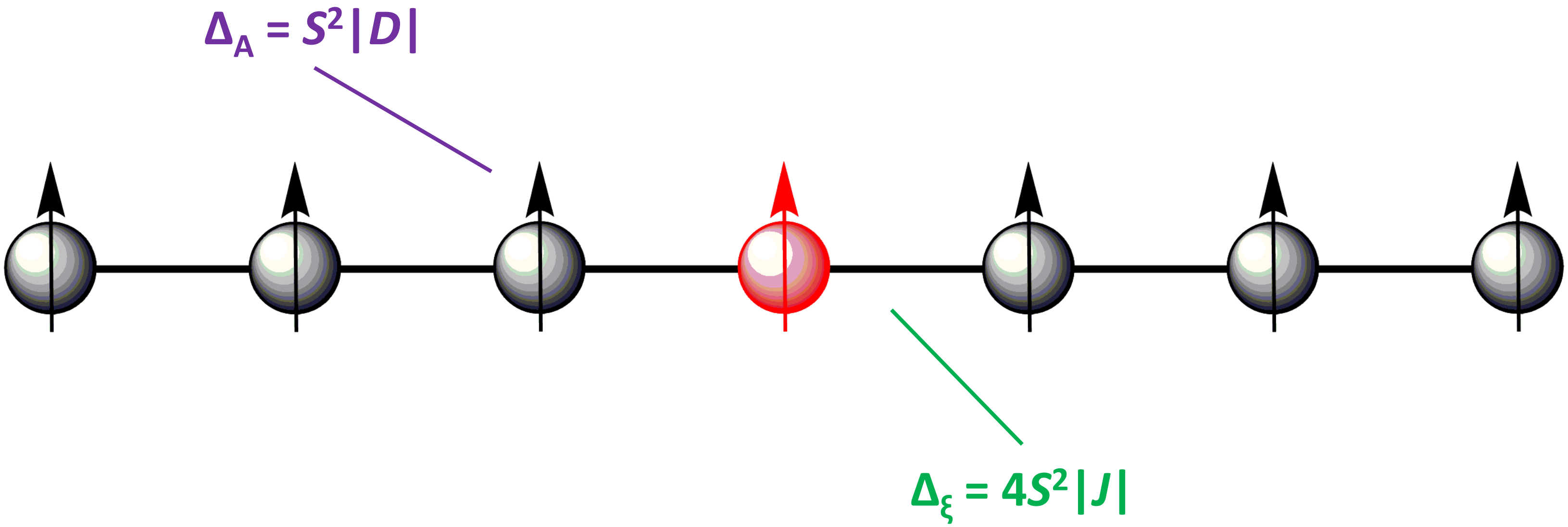
Selected Interatomic Distances (Å) and Angles (°)	
$Fe\text{-}N_{apical}$	2.172(1)
$Fe\text{-}N_{basal}$	2.024(3)
	2.008(3)
	2.041(2)
$N_{basal}\text{-}Fe\text{-}N_{basal}$	122.4(1)
	115.3(1)
	117.4(1)

Field Dependence of Relaxation Time in $[(tpa^{Mes})Fe]^{-}$



- maximum in relaxation time occurs at ca. 1500 Oe

Spin-Reversal Barrier in Single-Chain Magnets



$$\Delta_\tau = 2\Delta_\xi + \Delta_A = S^2(8J + D)$$

- relationships with *S*, *D*, and *J* only apply to Ising systems ($D/J > {}^4/_3$ with narrow domain walls)

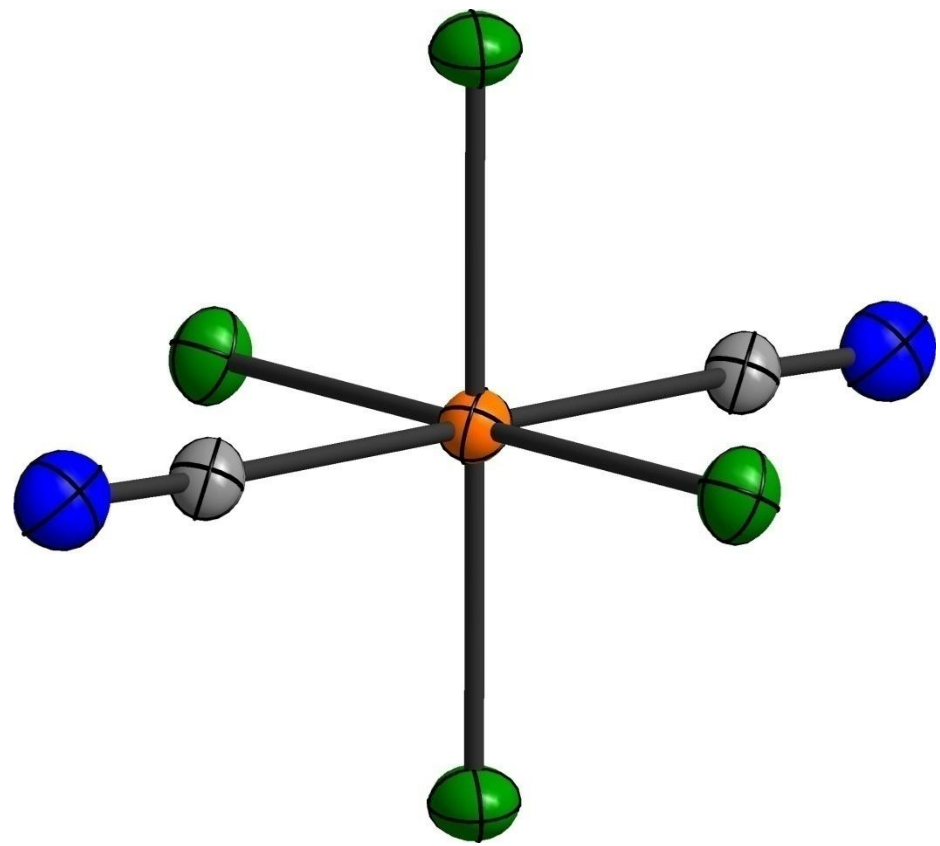
Formation of a New Cyanometalate Building Unit

cis-$ReCl_4(thf)_2$

+

2 CN^-

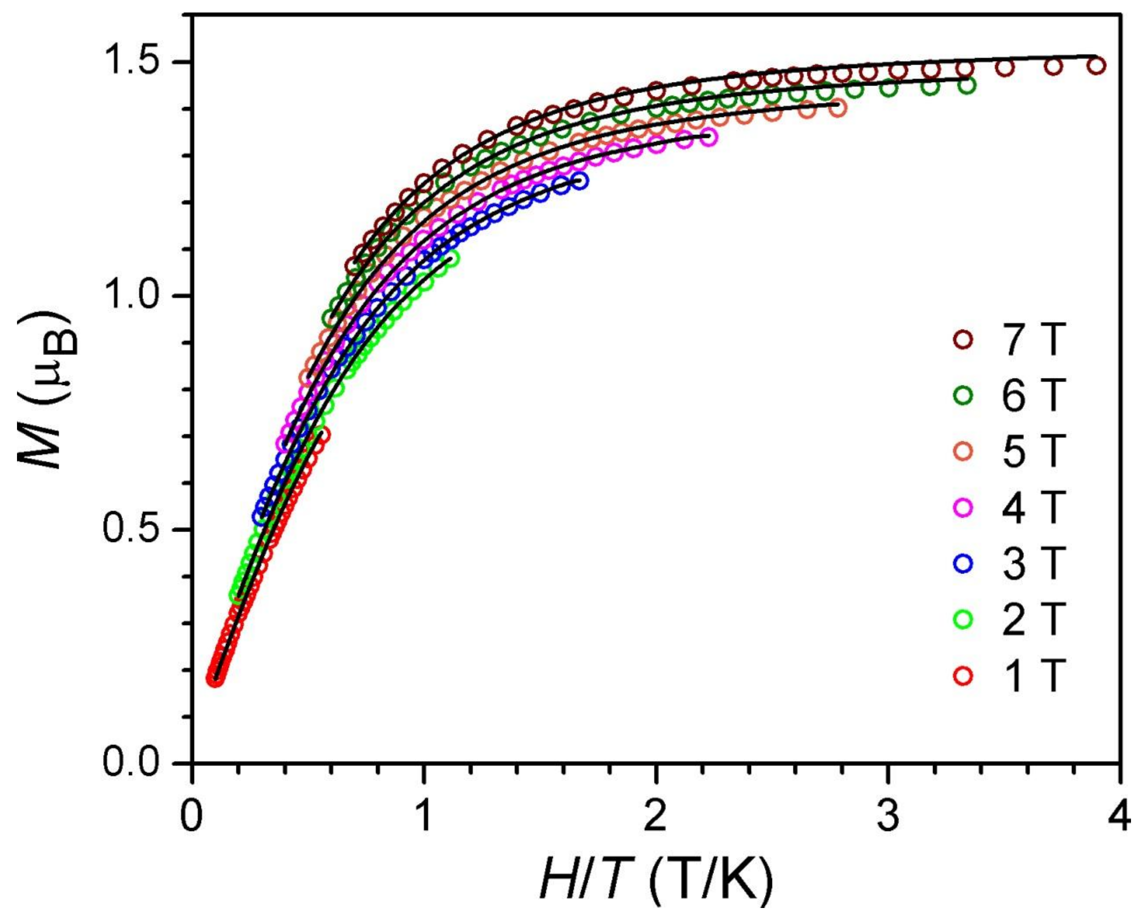
$\xrightarrow[\text{DMF}]{}$



$[ReCl_4(CN)_2]^{2-}$

- magnetic measurements confirm $S = {}^3/_2$

Strong Magnetic Anisotropy in $[(tpa^{Mes})Fe]^{-}$

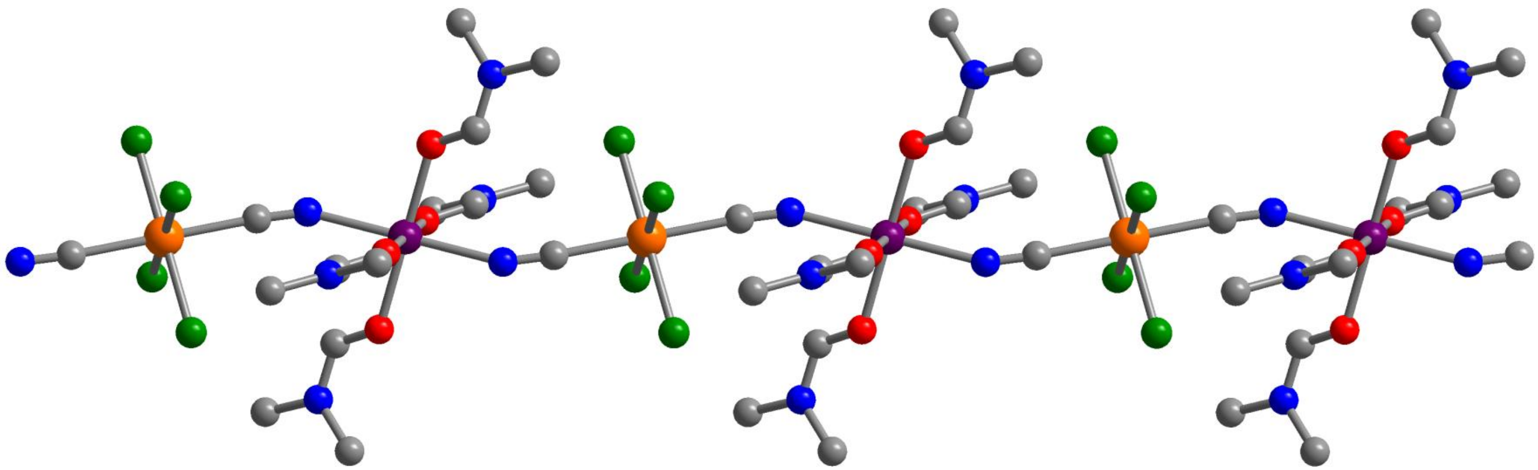


- fits give D = -14.4 cm^{-1} and E = -1 x 10^{-3} cm^{-1}

Formation of a Series of 1D Coordination Solids

$$[ReCl_4(CN)_2]^{2-} + [M(H_2O)_6]^{2+} \text{ (M = Mn, Fe, Co, Ni, Cu)}$$

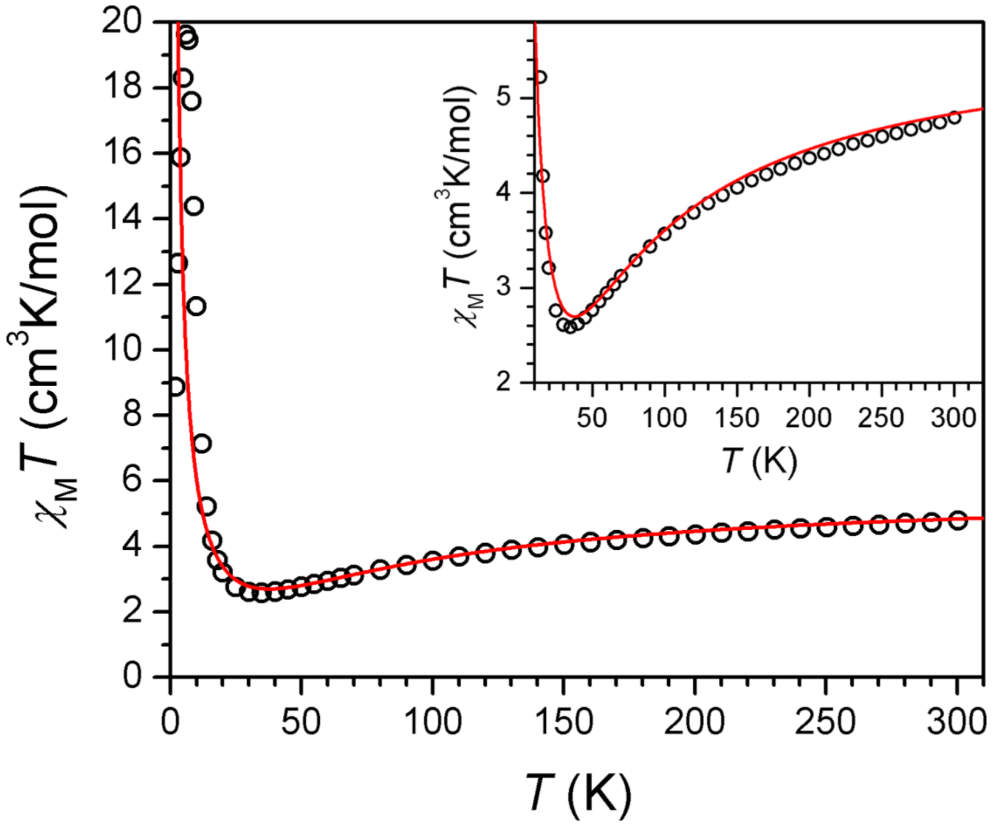
$$\downarrow \text{DMF}$$



$(DMF)_4MReCl_4(CN)_2$

(M = Mn, Fe, Co, Ni, Cu)

Variable-Temperature dc Susceptibility Data for $MnRe(CN)_2$ Solid



- minimum in $\chi_M T$ indicative of intrachain AF coupling
- fit to the data gives $J = -5.5$ cm^{-1}

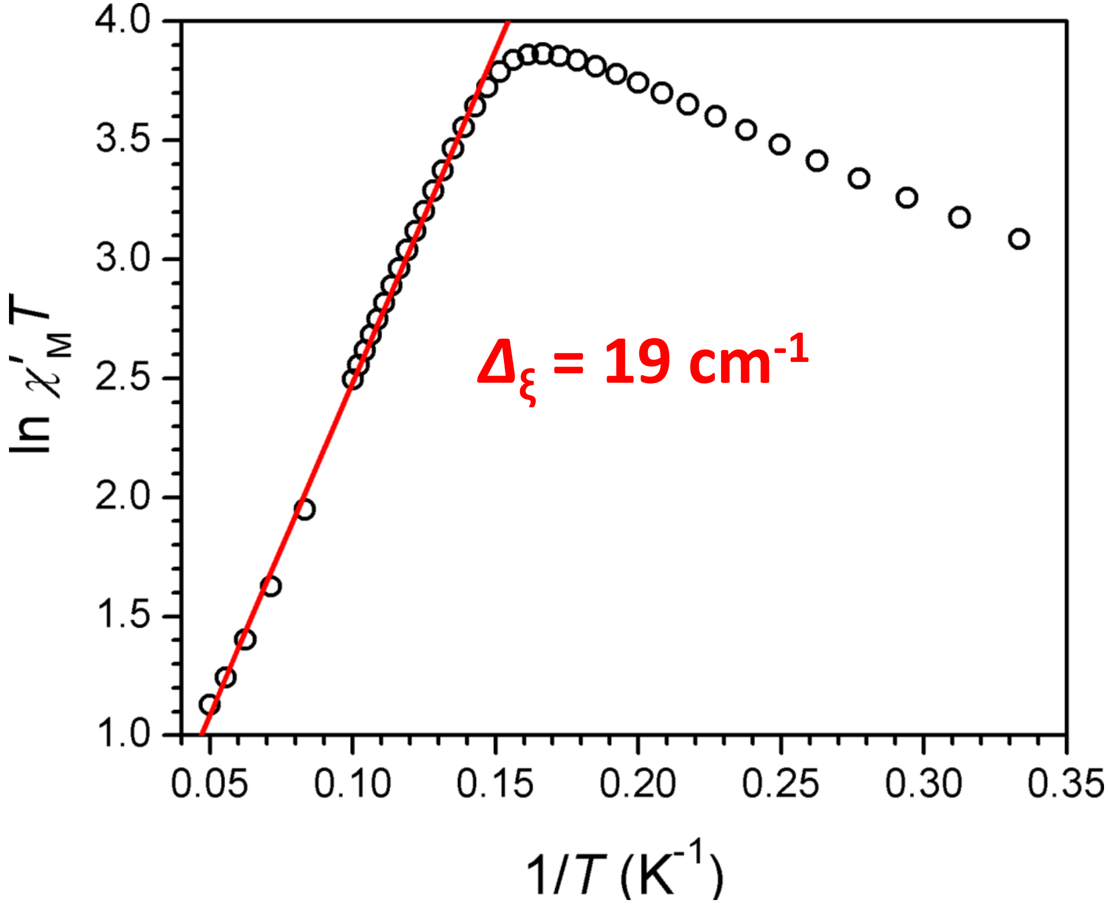
Summary of Coupling Strength in 1D Solids

M	J	$4\|JS_1S_2\|$	Δ_ξ	Δ_τ	Δ_A
Mn	-5.5	68	19	31	7.6
Fe	4.8	64	28	56	30
Co	2.4	22	11	14	–
Ni	3.7	23	9.0	22	19

All energies are expressed in cm^{-1}.

Evaluating the 1D Nature of $MnRe(CN)_2$ Solid

$$\chi T \propto exp(\Delta_\xi / k_B T)$$



Summary of Correlation Energies of 1D Solids

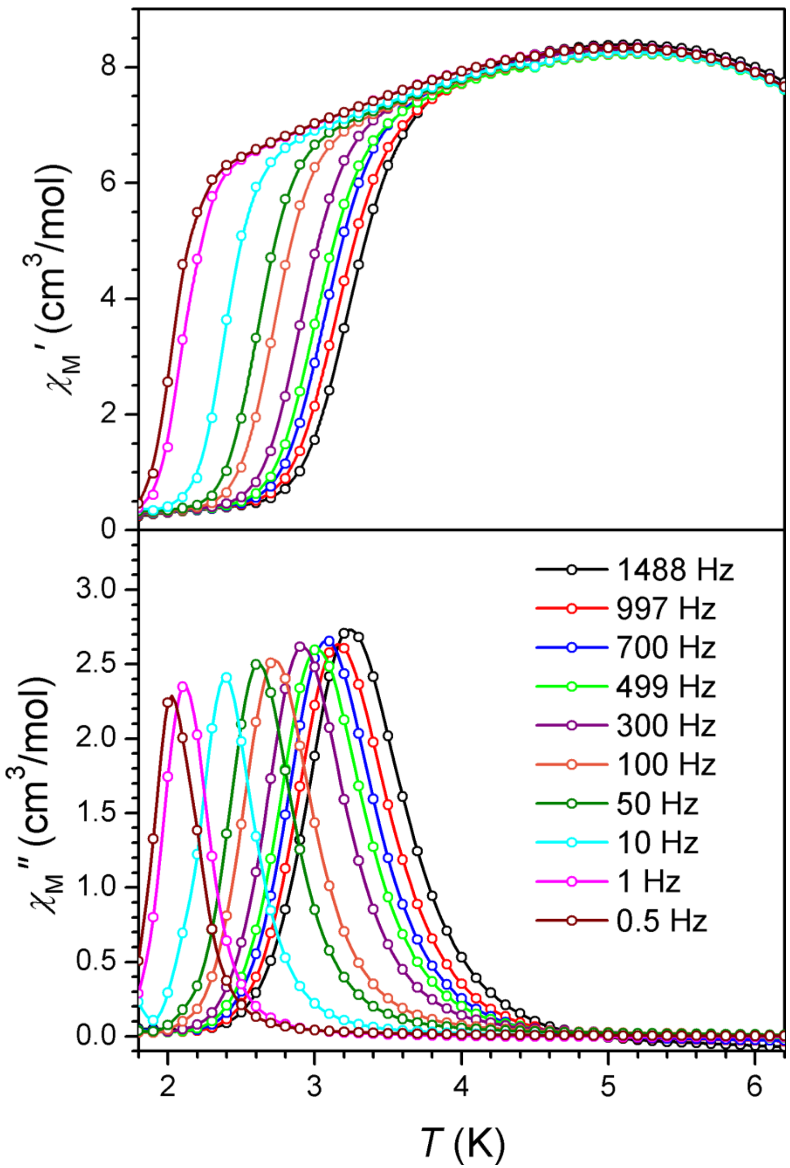
Does $\Delta_\xi = 4|JS_1S_2|$?

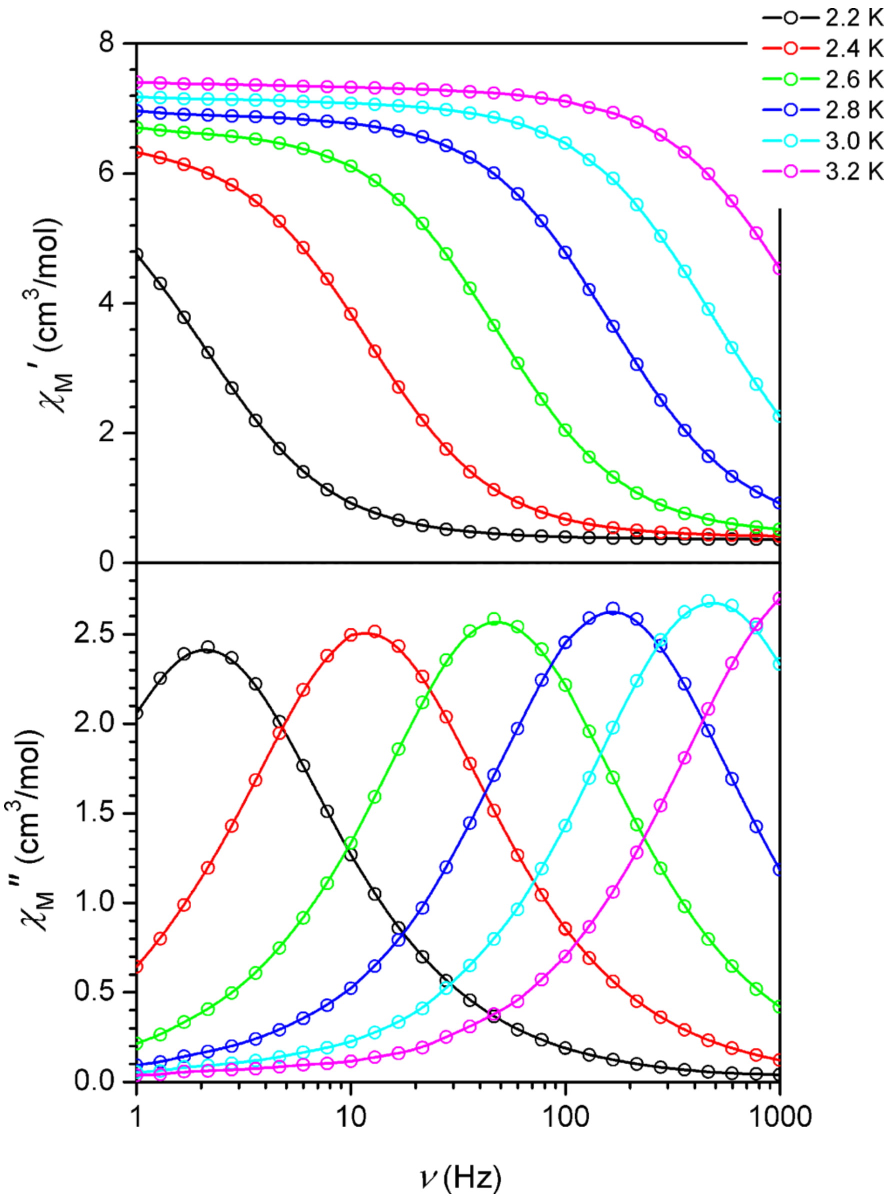
M	J	$4\|JS_1S_2\|$	Δ_ξ	Δ_τ	Δ_A
Mn	-5.5	68	19	31	7.6
Fe	4.8	64	28	56	30
Co	2.4	22	11	14	–
Ni	3.7	23	9.0	22	19

All energies are expressed in cm^{-1}.

- ***Not in Ising limit!***

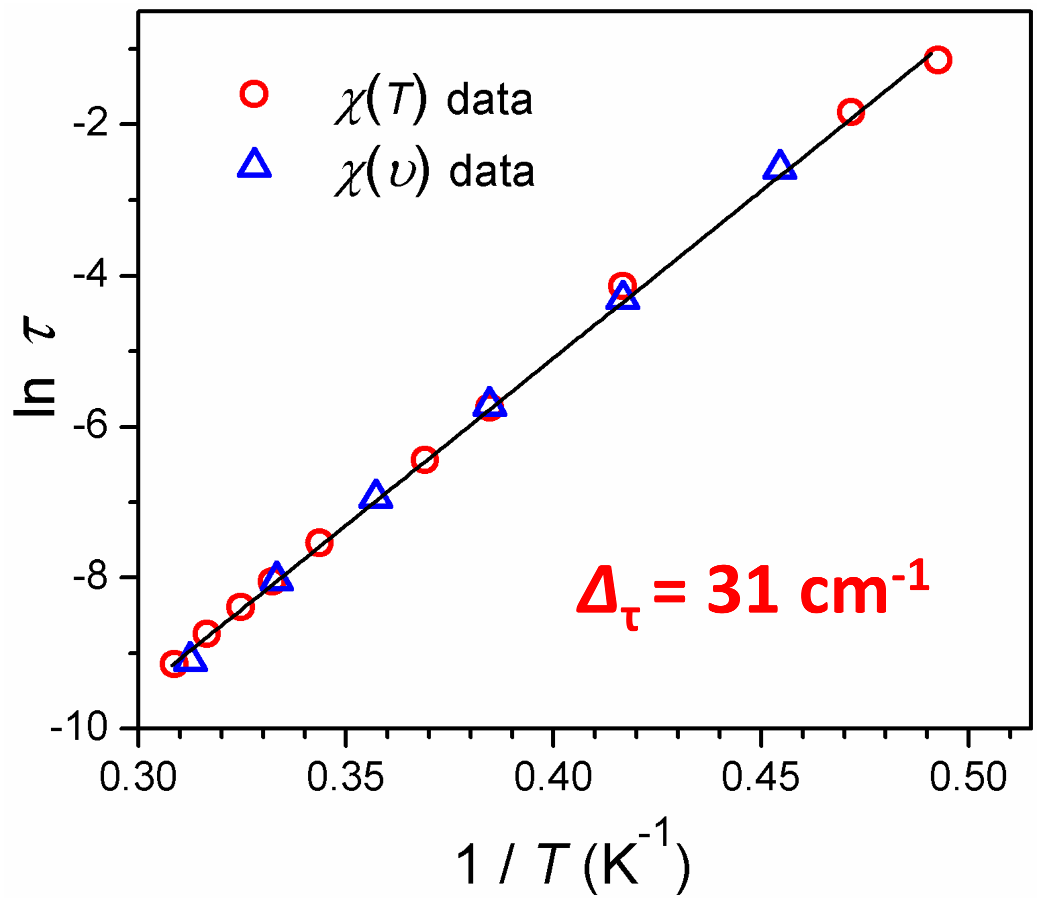
Magnetization Dynamics of $MnRe(CN)_2$ Solid





Arrhenius Dependence of Relaxation Time

$$\tau = \tau_0 exp(\Delta_\tau / k_B T)$$

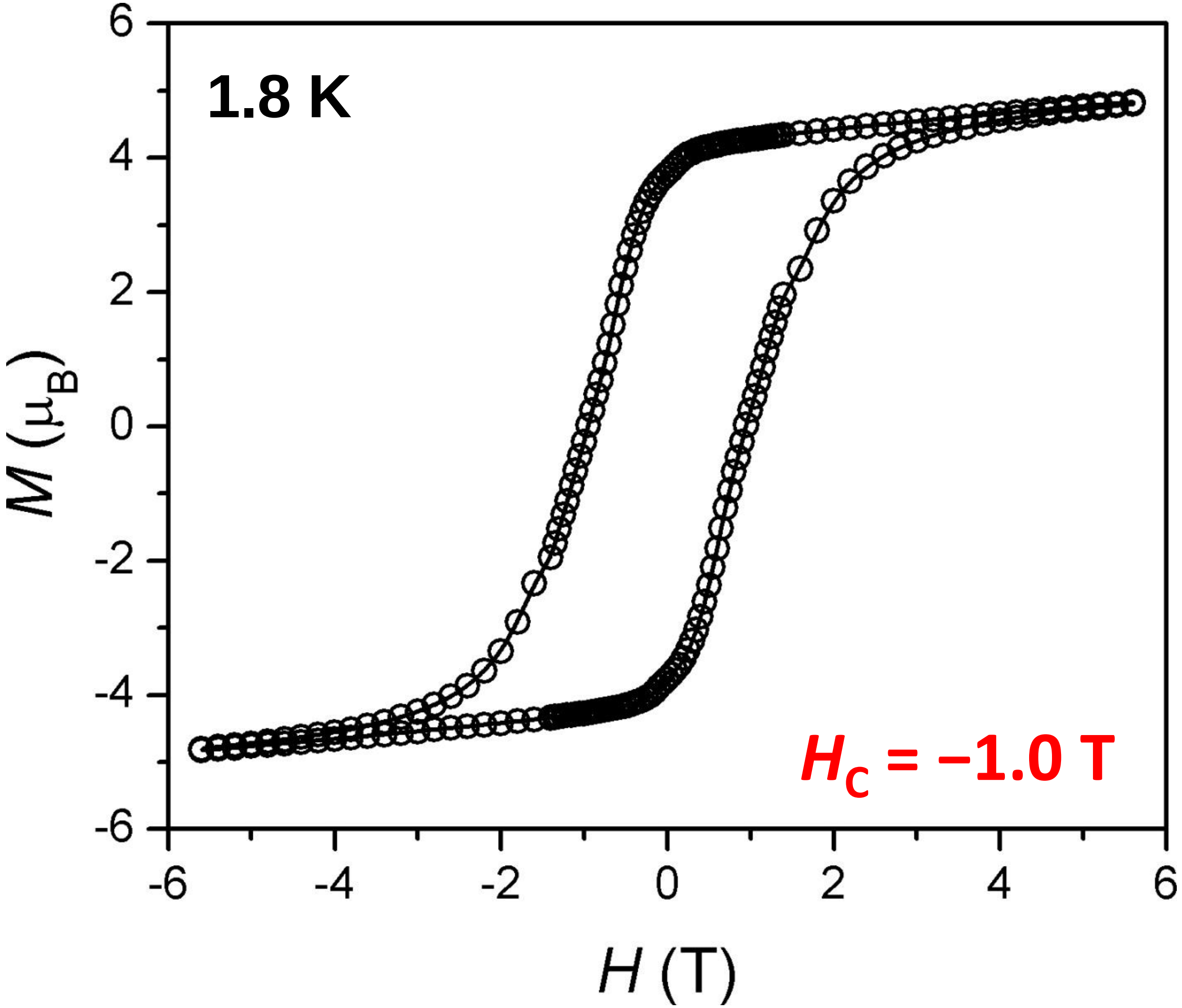


Summary of Slow Relaxation in 1D Solids

M	J	$4\|JS_1S_2\|$	Δ_ξ	Δ_τ	Δ_A
Mn	-5.5	68	19	31	7.6
Fe	4.8	64	28	56	30
Co	2.4	22	11	14	–
Ni	3.7	23	9.0	22	19

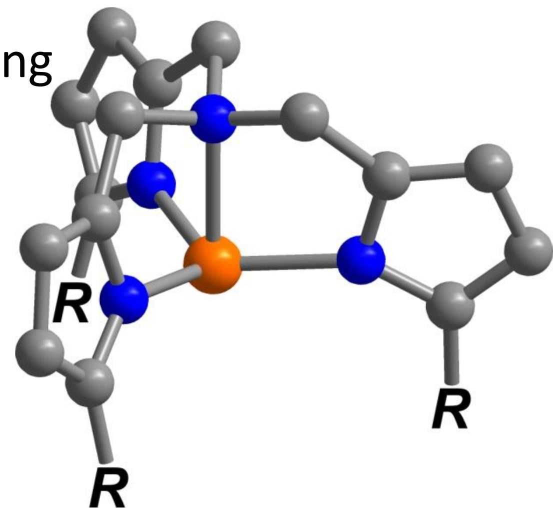
All energies are expressed in cm^{-1}.

Classical Magnet Behavior in $FeRe(CN)_2$ Solid



Future Directions

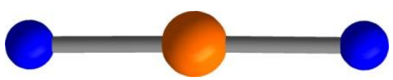
- Rationalize trends in slow relaxation, anisotropy, and tunneling across series of $[(tpa^{R})Fe]^{-}$ complexes

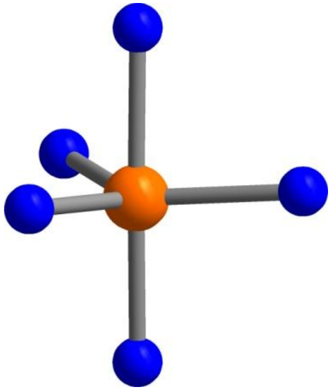


R = ^{t}Bu, Ph, F_2Ph, *o*-Tol, Mes, $^{i}Pr_3$Ph

- Prepare high-spin iron(II) complexes featuring rigorous three-fold symmetry

- Investigate other high-spin metal ions in coordination environments giving rise to unquenched orbital angular momentum





Acknowledgments

People

Prof. Jeffrey Long

Dr. Rodolphe Clérac

Danna Freedman

Hill Harman

Miriam Bennett

Prof. Stephen Hill

Dr. Andrew Ozarowski

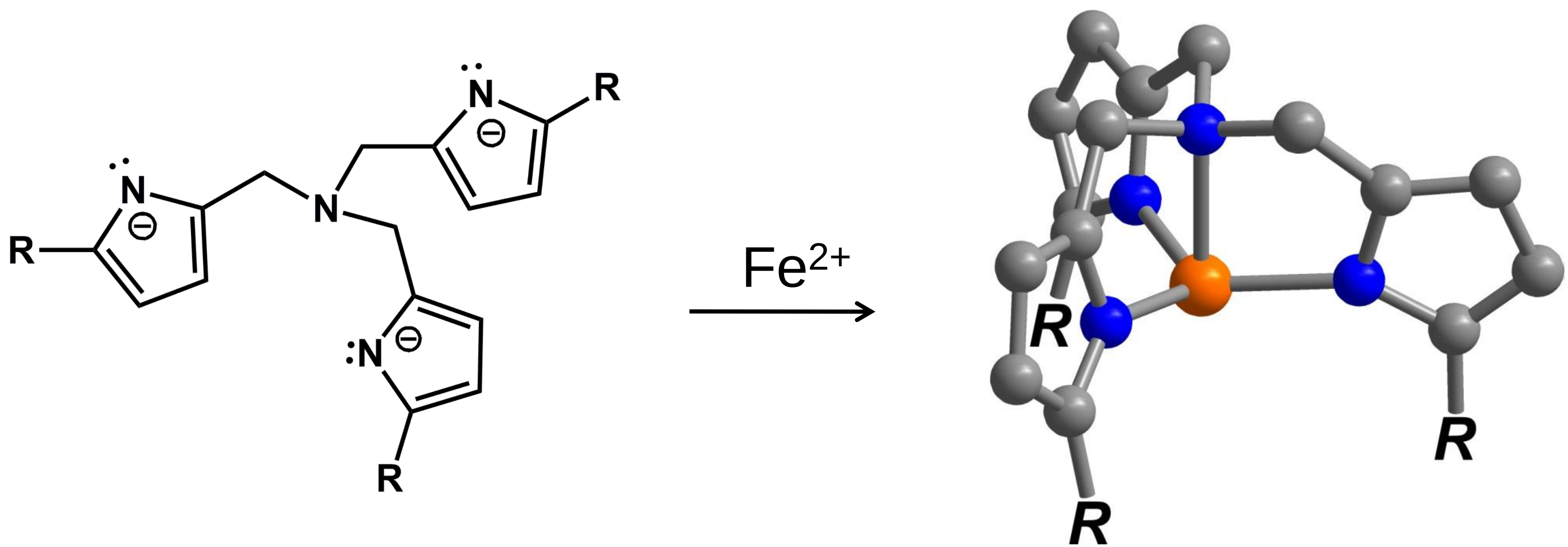
Jeff Rinehart

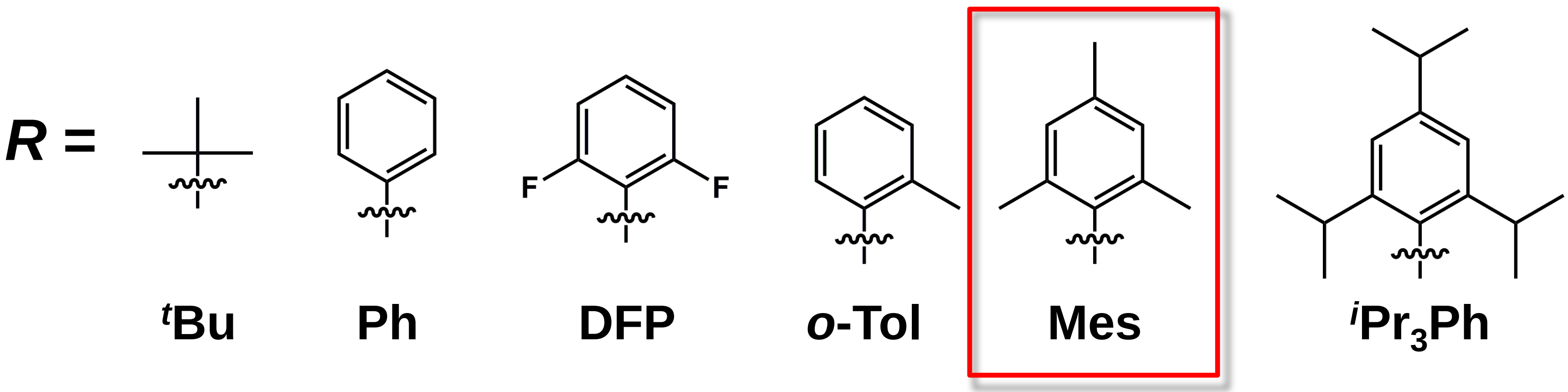
Funding

NSF

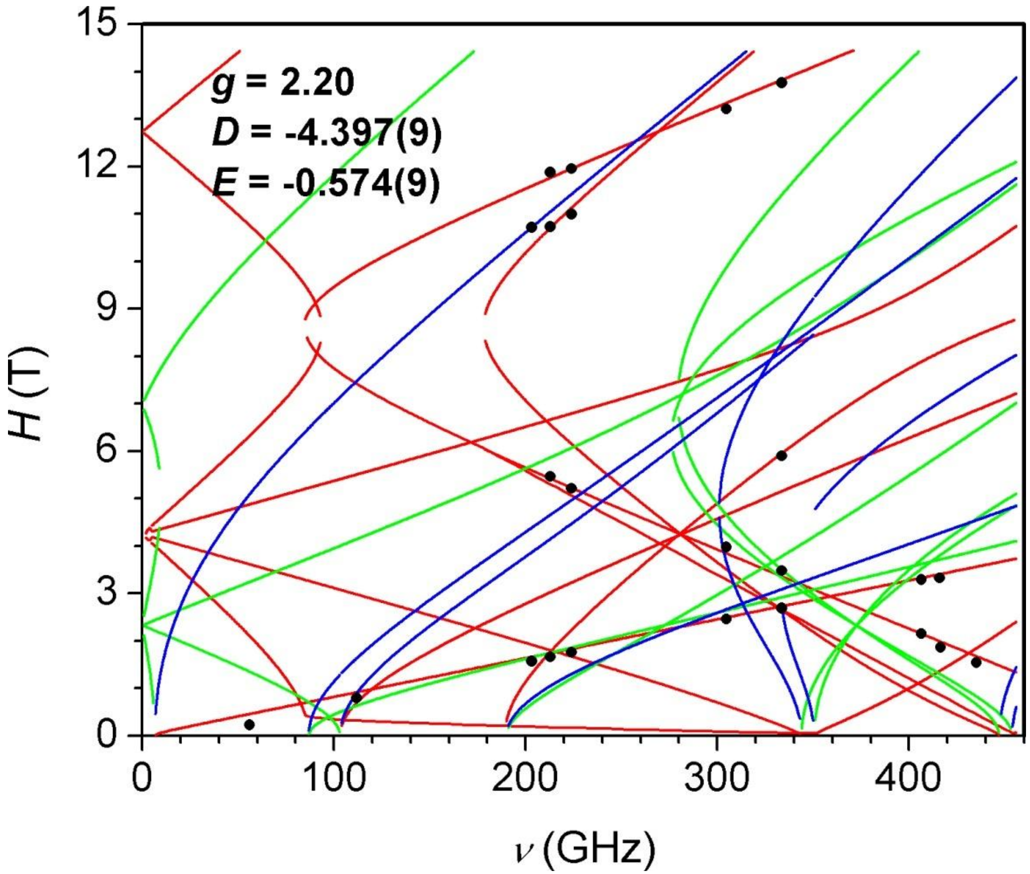
Tyco Electronics

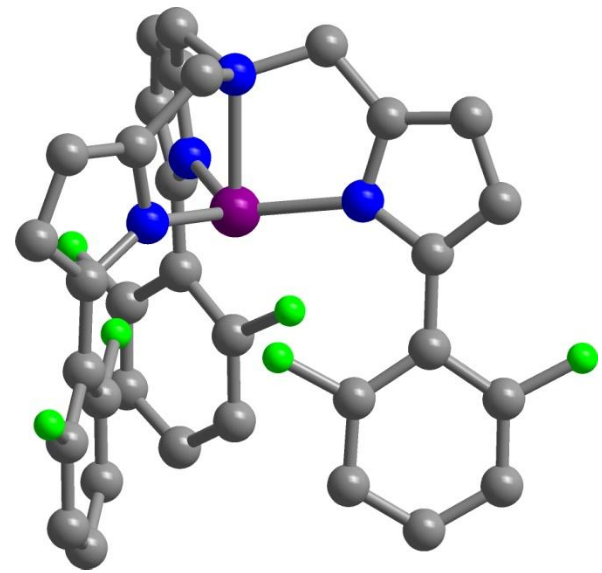
A Series of Trigonal Pyramidal High-Spin Iron(II) Complexes





High-Field EPR Spectra for [(tpa^{DFP})Fe]$^{-}$

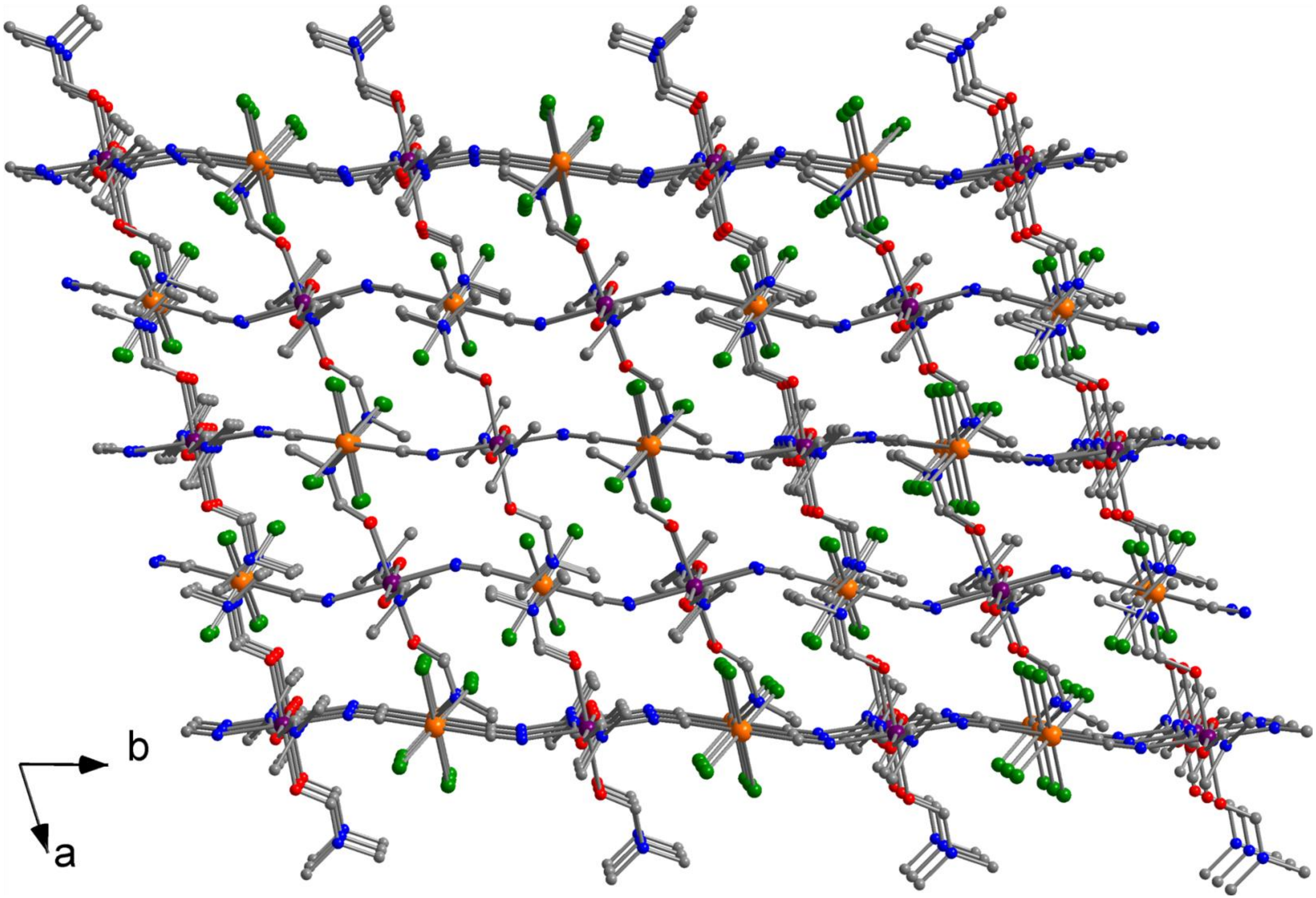




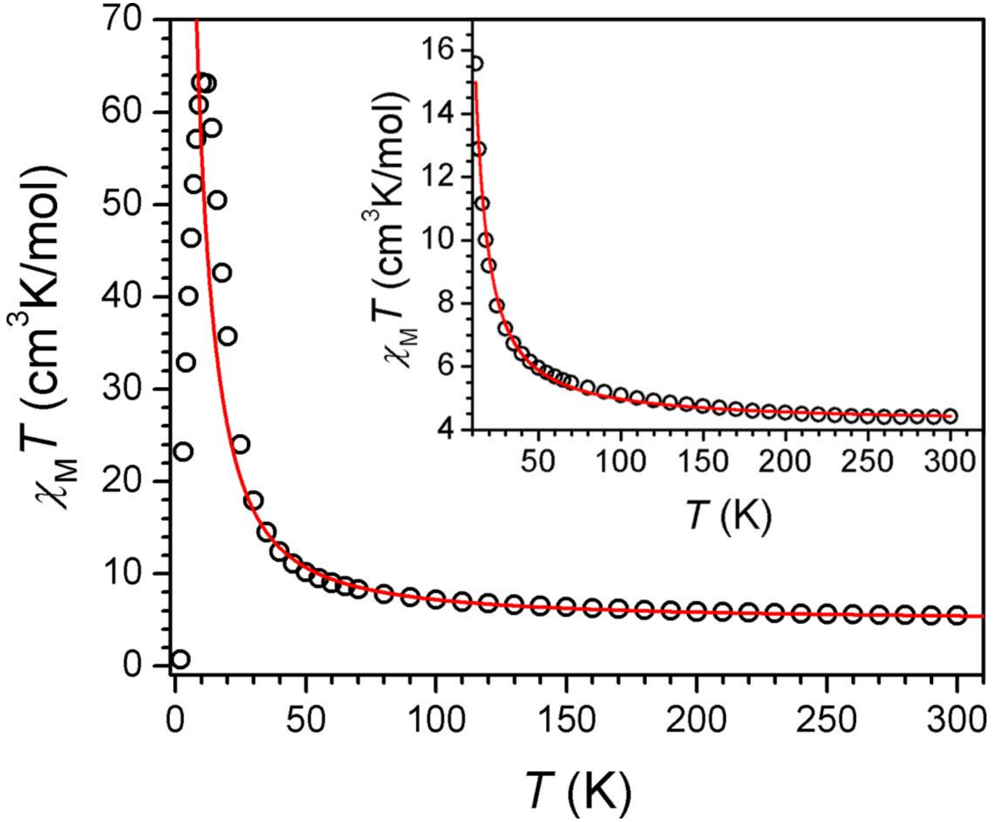
[(tpa^{DFP})Fe]$^{-}$

- negative sign of D obtained by temperature-dependence of spectra
- values comparable to those obtained from magnetization data (D = -6.22, E = -0.1 cm^{-1})
- no observable slow magnetic relaxation in [(tpa^{DFP})Fe]$^{-}$

Packing Diagram of $(DMF)_4MReCl_4(CN)_2$



Variable-Temperature dc Susceptibility Data for $FeRe(CN)_2$ Solid



- rise in $\chi_M T$ indicative of intrachain ferromagnetic coupling
- fit to the data gives J = 4.8 cm^{-1}