Spin Crossover in Transition Metal Complexes

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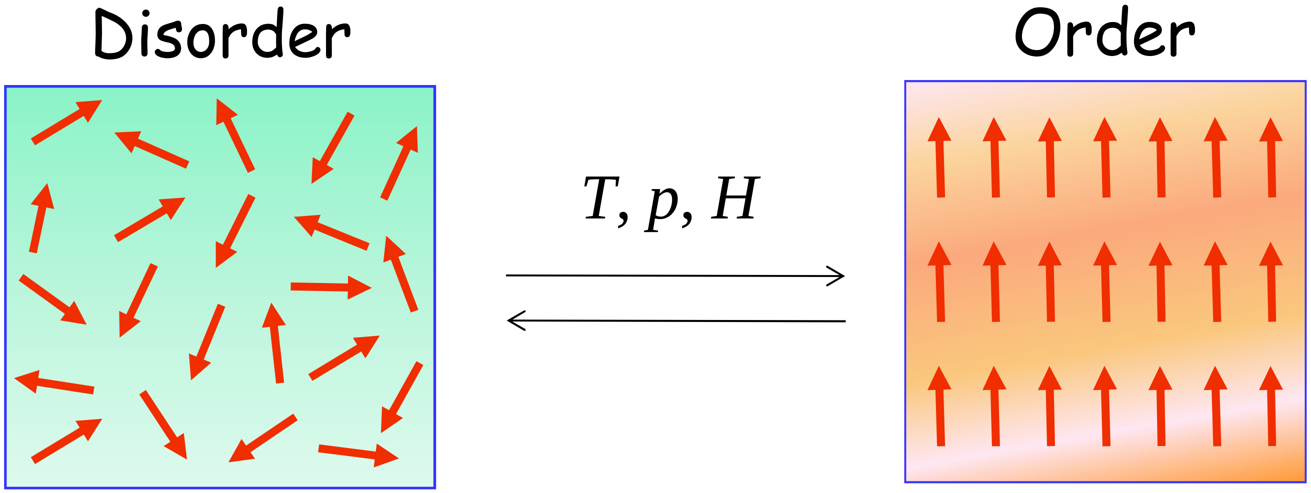
Outline

1. The origins of spin crossover (SCO)
2. Characterization methods
3. Examples of SCO in transition metal complexes
4. The role of cooperativity in SCO
5. Pressure- and light-driven SCO
6. Charge-transfer induced spin transitions

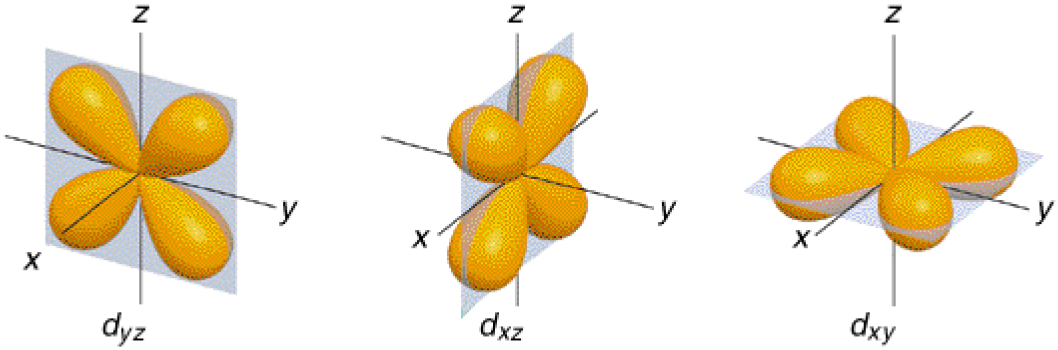
Magnets



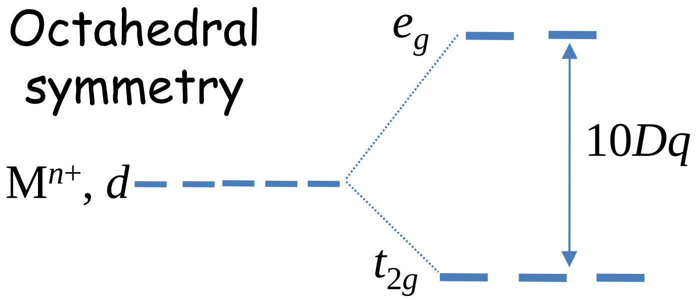
Magnetic bistability is the fundamental cause for the development of technologies utilizing magnetic materials

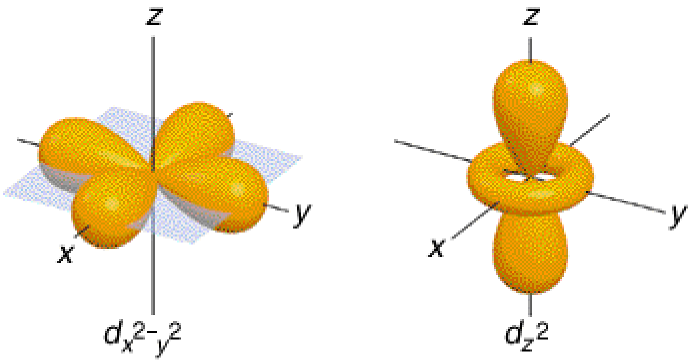
The simplest example:
two states of the electron spin

Splitting of d-Orbitals by the Ligand Field



Octahedral symmetry



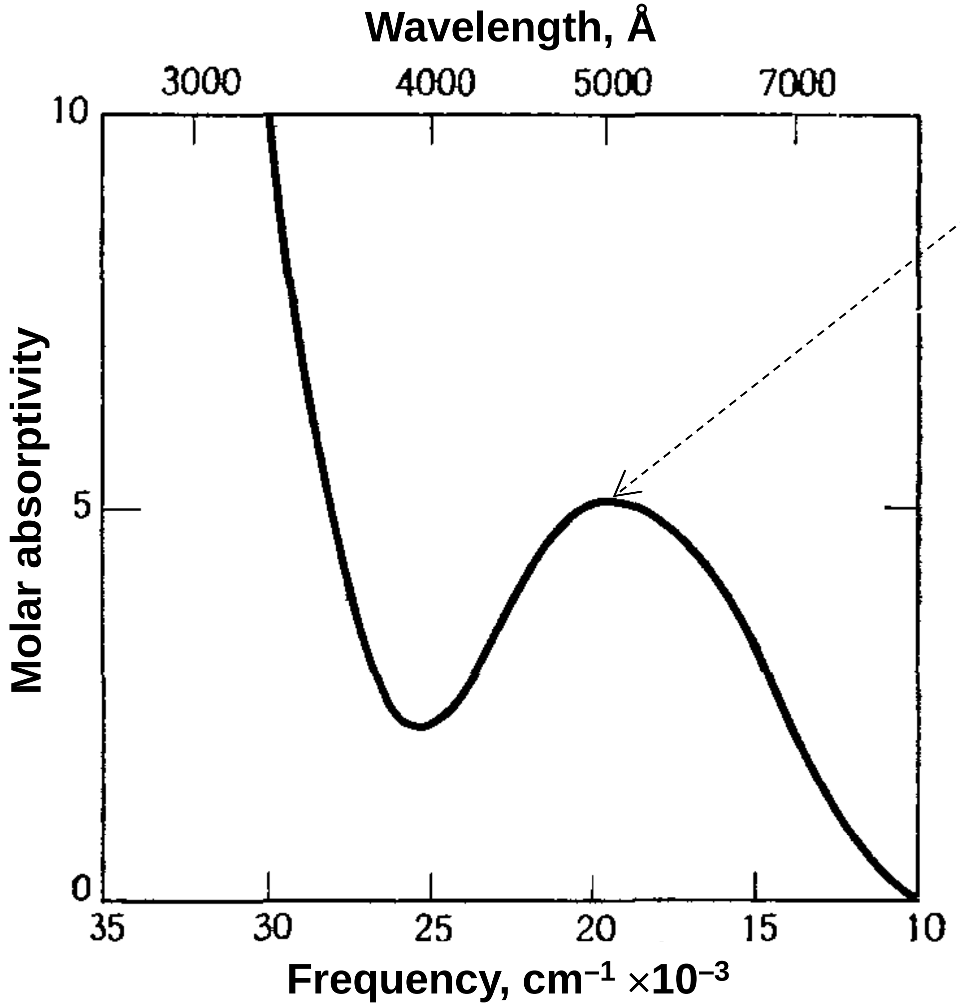


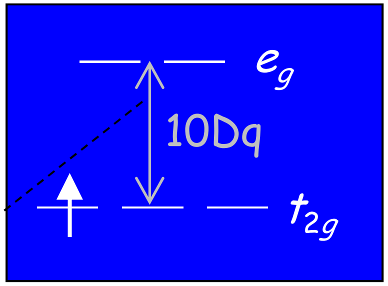
Spectrochemical series of ligand-field strength:

$I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^- < OH^- < H_2O <$
$NCS^- <$ py $< NH_3 <$ en $< NO_2^- < PPh_3 < CN^- < CO$

Absorption Spectroscopy

Optical absorption spectrum of [Ti(H$_2$O)$_6$]$^{3+}$



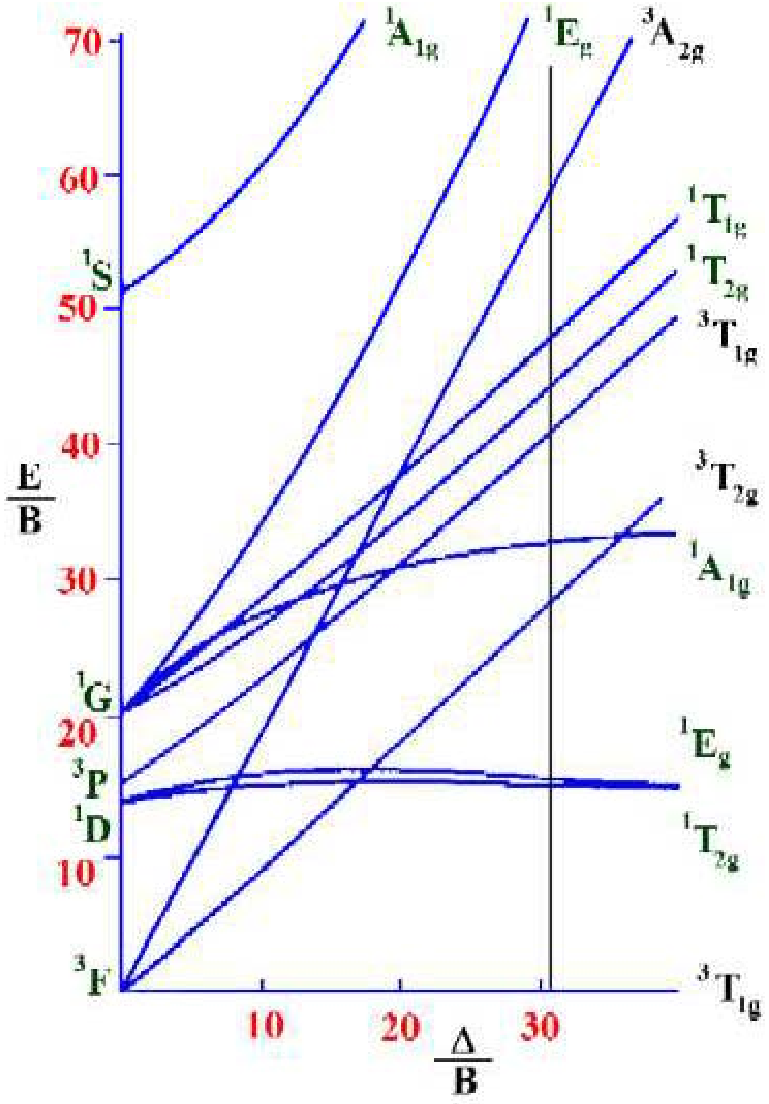


Ti^{3+}, 3d^1

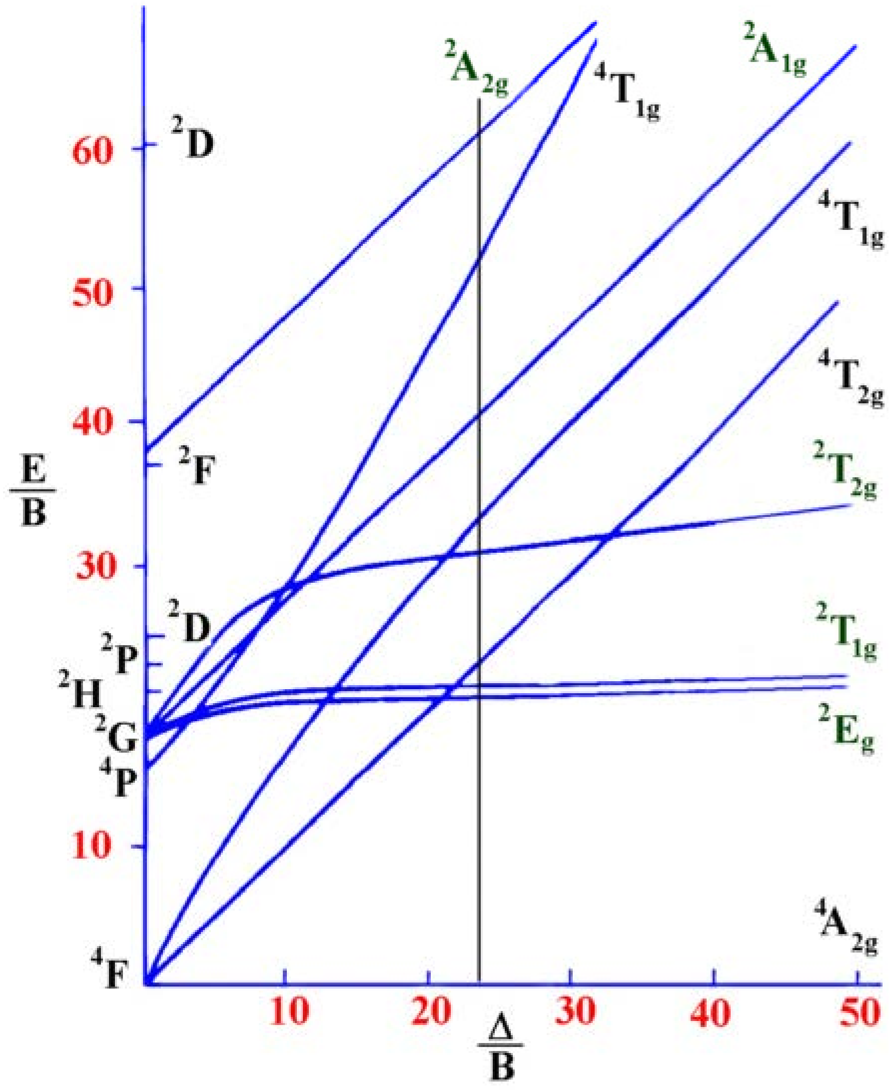
10Dq = $\Delta_o \approx$ 20,000 cm^{-1}

Tanabe-Sugano Diagrams

d^2 Ion

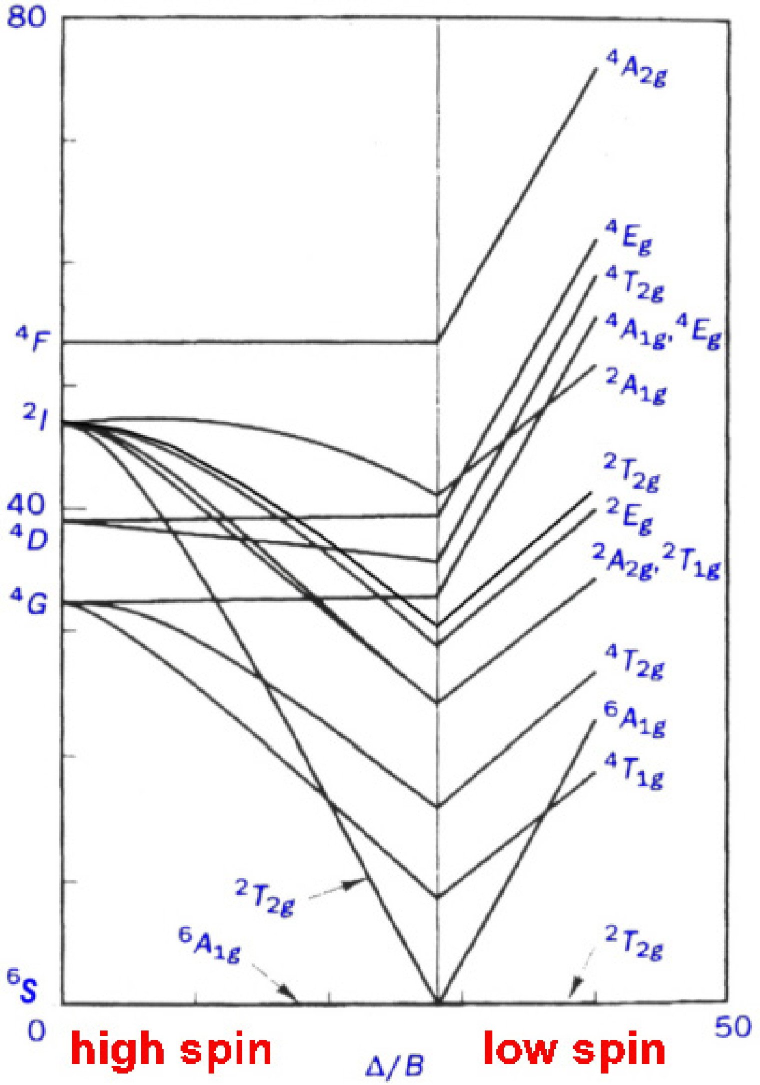


d^3 Ion

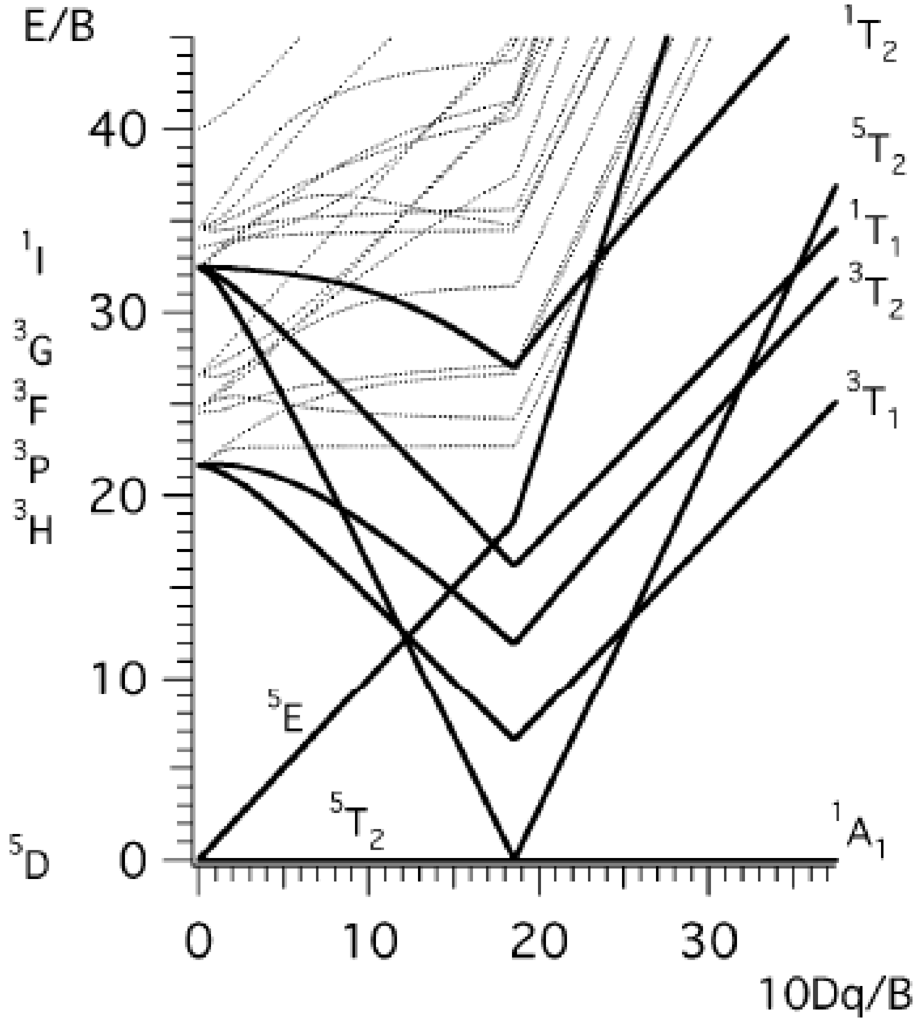


Tanabe-Sugano Diagrams

d^5 Ion



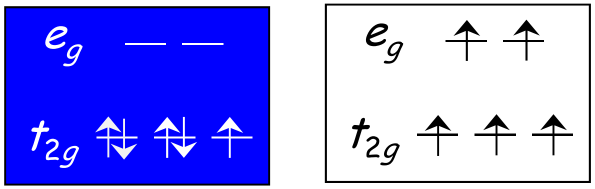
d^6 Ion



The History of SCO Phenomenon

- Observed for d^4, d^5, d^6, d^7 metal ions
- These ions exhibit two possible electron configurations in the octahedral ligand field
- Switching between the states is achieved by changing temperature, pressure, or by photoexcitation

Example – d^5 ion



LS, S = 1/2 HS, S = 5/2

- 1931 – Cambi and Szego observed SCO in Fe(III) dithiocarbomates
- Pauling initially explained their results by the change in the bond type from covalent to ionic
- Orgel was the first to suggest the correct explanation based on the change in the spin state of the ion

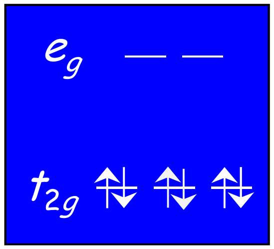
- Interesting sequence in 1950s:
  - Ligand field theory established
  - Mössbauer effect discovered
  - Spin crossover explained

Cambi, L.; Szegö, L. *Ber. Deutsch. Chem. Gesell.* **1931**, *64*, 167.
Pauling, L. *J. Am. Chem. Soc.* **1937**, *59*, 633.
Orgel, L. E. 10th Chemical Conference, Brussels, **1956**, 289.

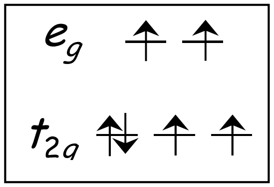
Spin Crossover (SCO) in Fe(II) complexes

About 90% of reported cases of SCO have been observed in Fe(II) complexes

LS, S = 0



HS, S = 2

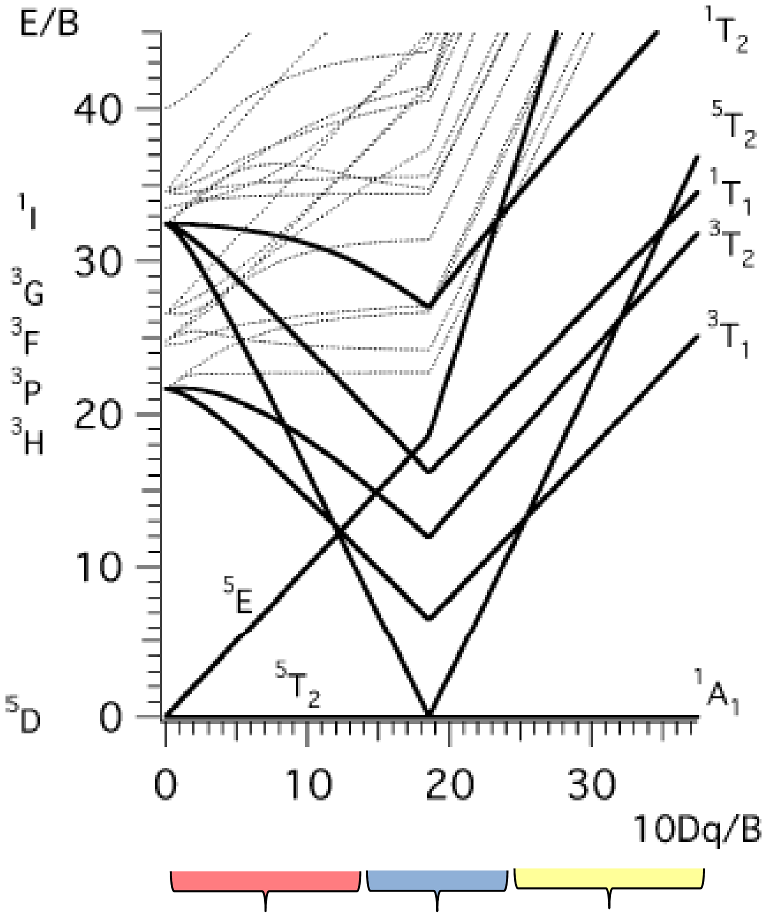


$10Dq > \Pi$

$10Dq < \Pi$

$10Dq$ – ligand-field splitting

Π – electron pairing energy

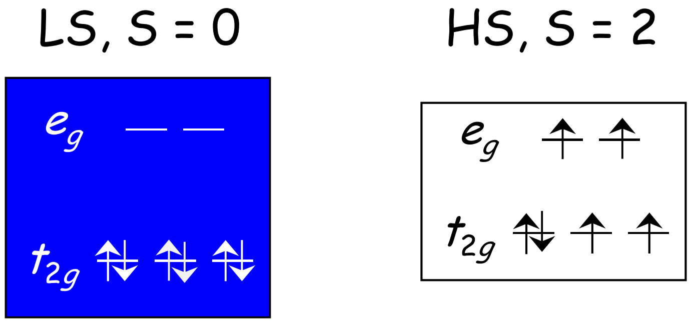


Complexes: HS SCO LS

Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

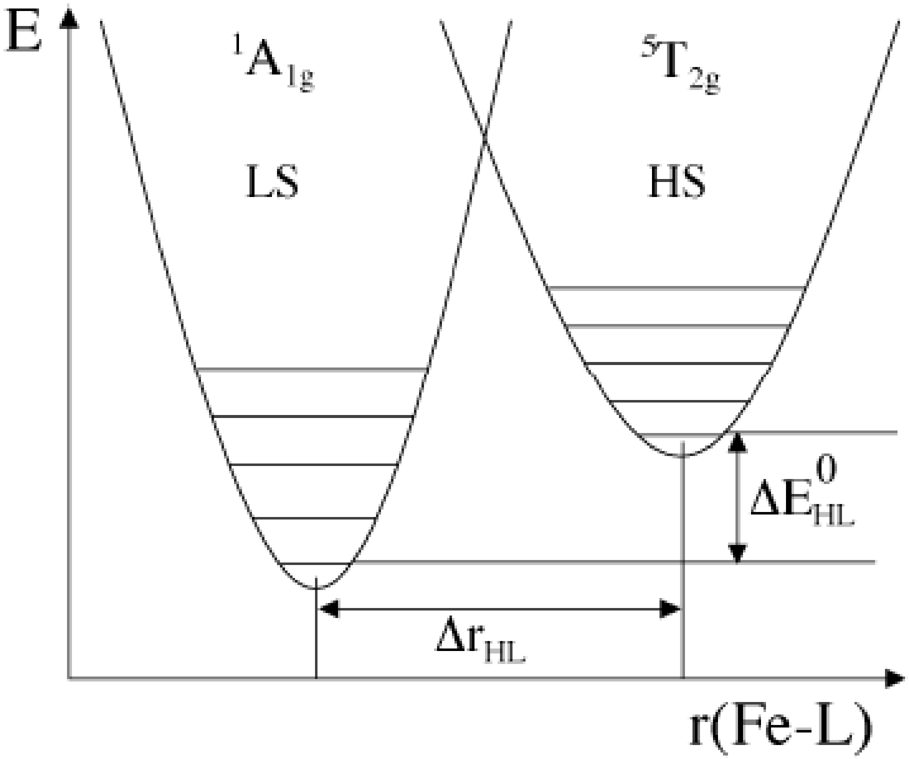
Metal-Ligand Distances

The antibonding orbitals (e_g*) are populated only in the HS state



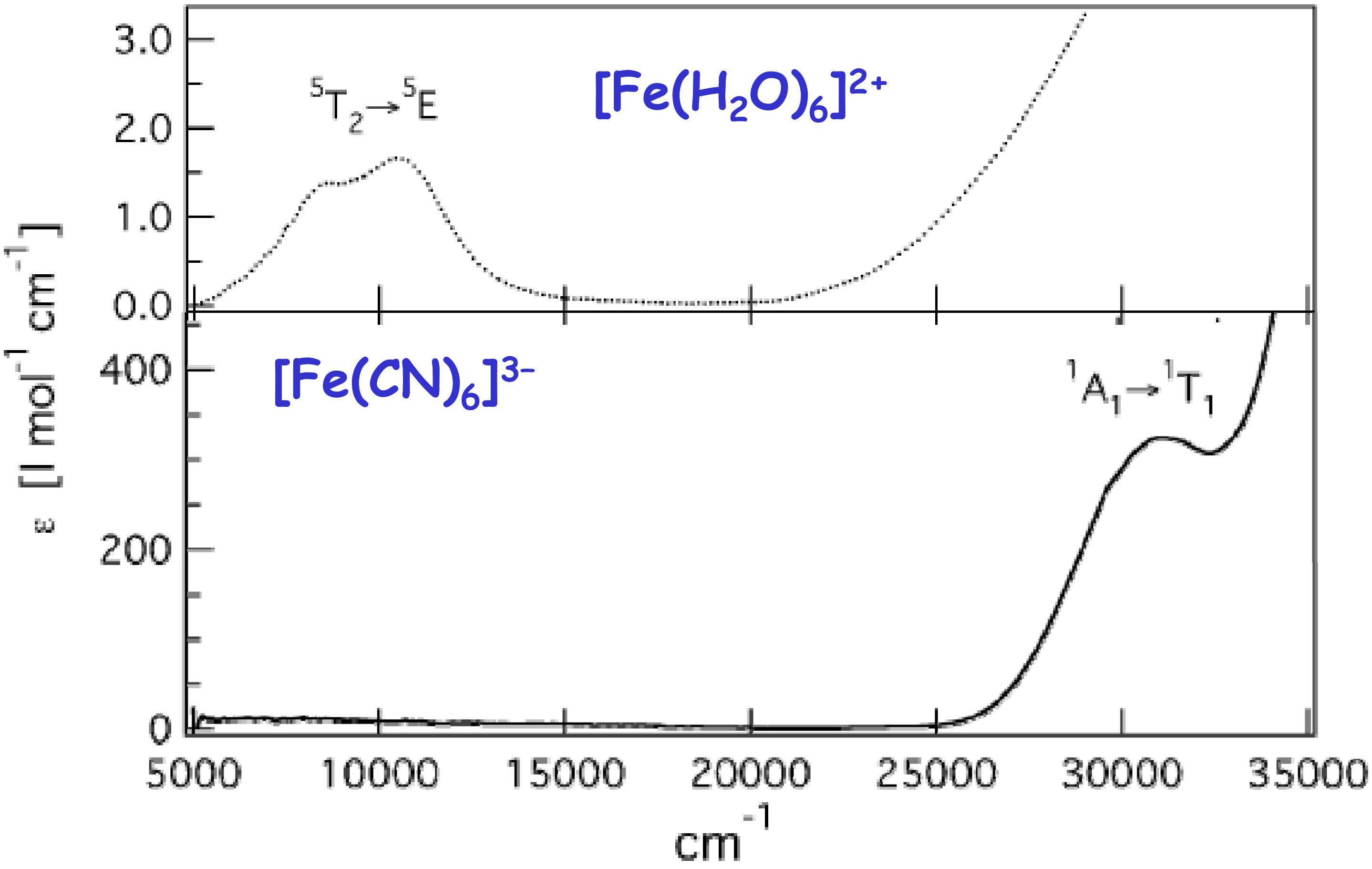
r(Fe–L): 1.95-2.00 Å 2.15-2.20 Å

- Useful relationship:
  10Dq ~ $1/r^n$ (n = 5 – 9)
- Using the average r(Fe-L) for SCO complexes, one can estimate that $10Dq_{LS}/10Dq_{HS}$ ~ 1.75
- <u>Important</u>: the Fe-N bond lengths and orbital overlap change upon SCO, and therefore 10Dq is different for the LS and HS states of the same complex



Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

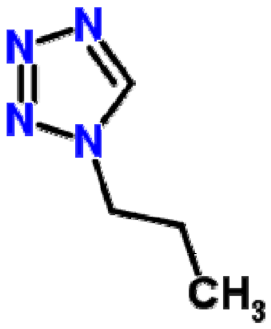
Absorptions Spectra of HS and LS Complexes

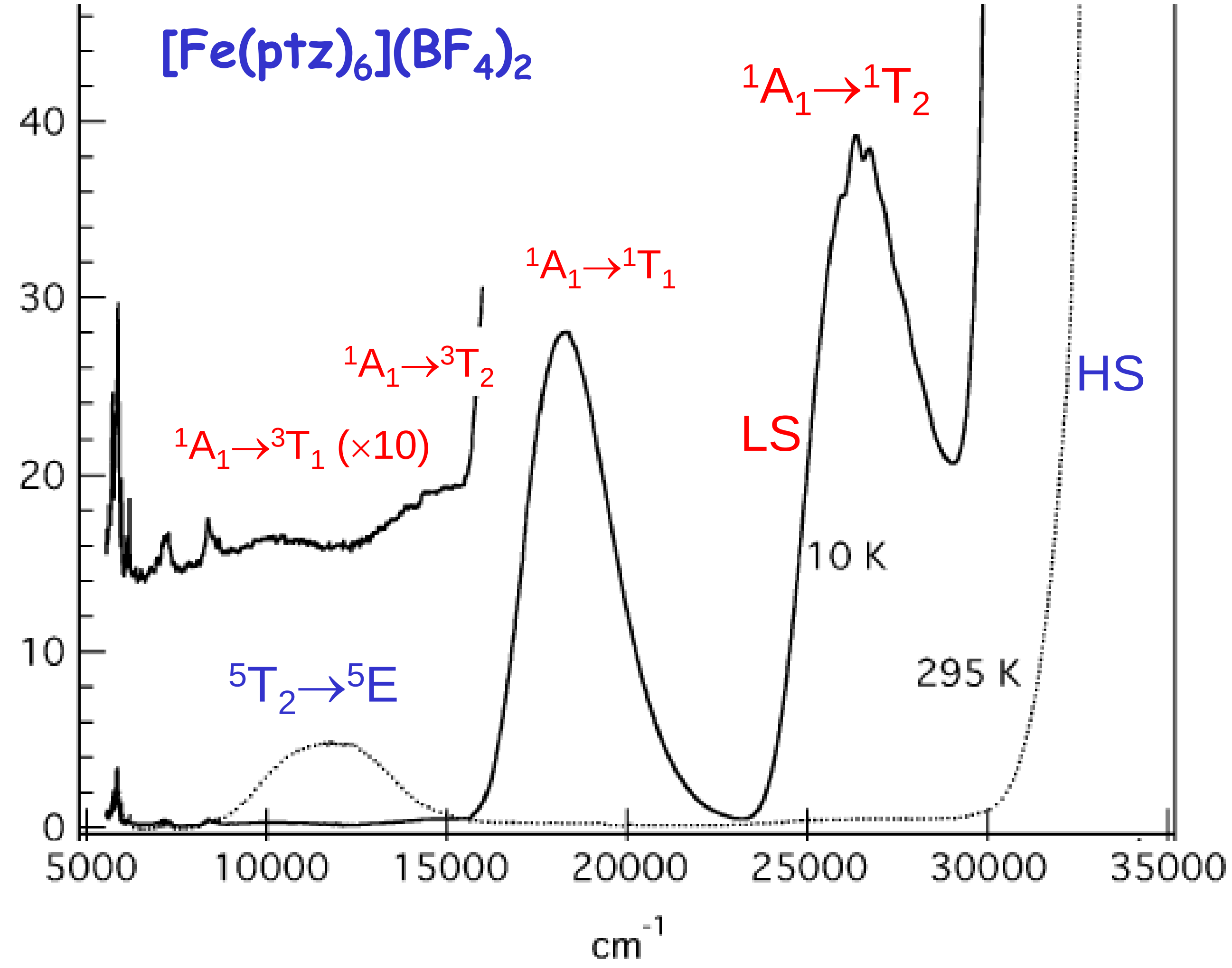


$10Dq, cm^{-1}$
10,000
33,000

Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

Absorption Spectra of SCO Complexes





$10Dq^{HS} = 11\,800$ cm^{-1} **$10Dq^{LS} = 19\,410$ cm^{-1}**

Hauser, A. *J. Chem. Phys.* **1991**, *94*, 2741.

Pairing Energy and Ligand-Field Strength

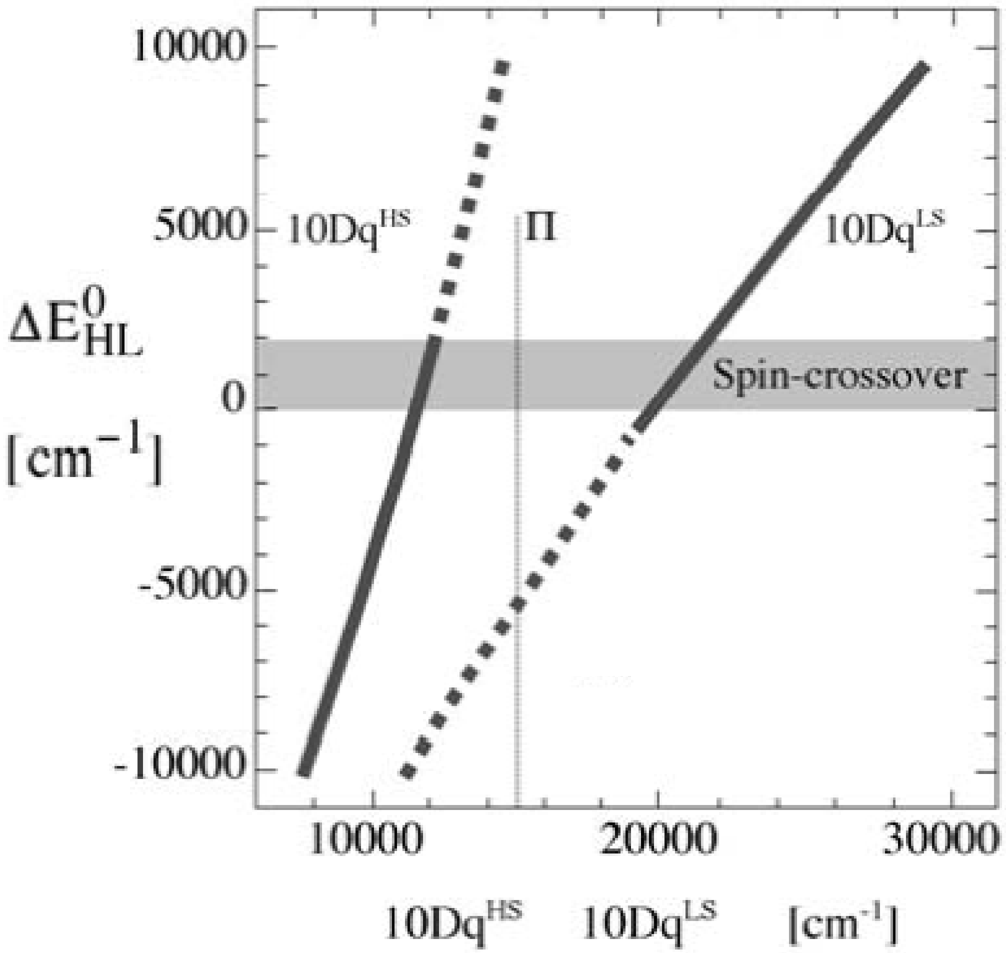
- The pairing energy is about the same in the LS and HS states: $\Pi \approx$ **15,000 cm^{-1}** for Fe(II) complexes
- 10Dq is changing during the spin transition:

  $\mathbf{10Dq_{HS} < 10Dq_{LS}}$

- If $10Dq_{HS} < 10{,}000$ cm^{-1} or $10Dq_{LS} > 23{,}000$ cm^{-1}, the SCO is impossible
- Conditions for observation of SCO in Fe(II) complexes:

$10Dq_{HS} \approx 11{,}000 – 12{,}500$ cm^{-1}

$10Dq_{LS} \approx 19{,}000 – 22{,}000$ cm^{-1}



$\Delta E^0_{HL} = E^0_{HS} – E^0_{LS}$

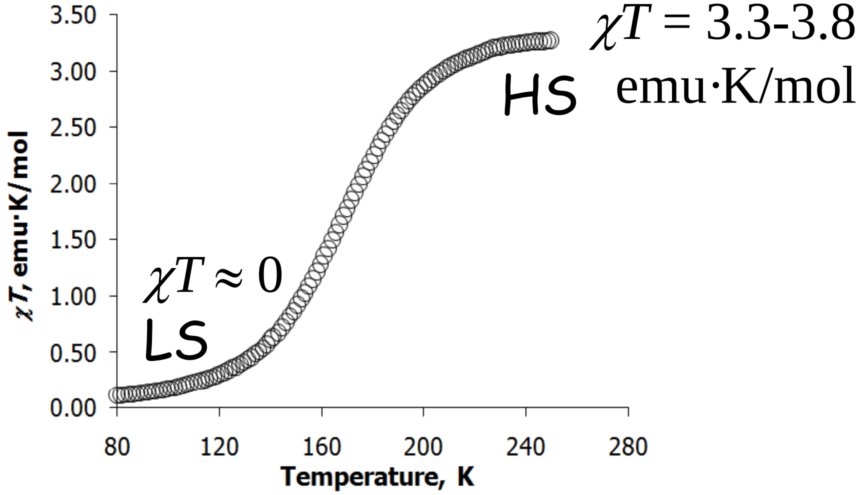
Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.

Characterization Methods

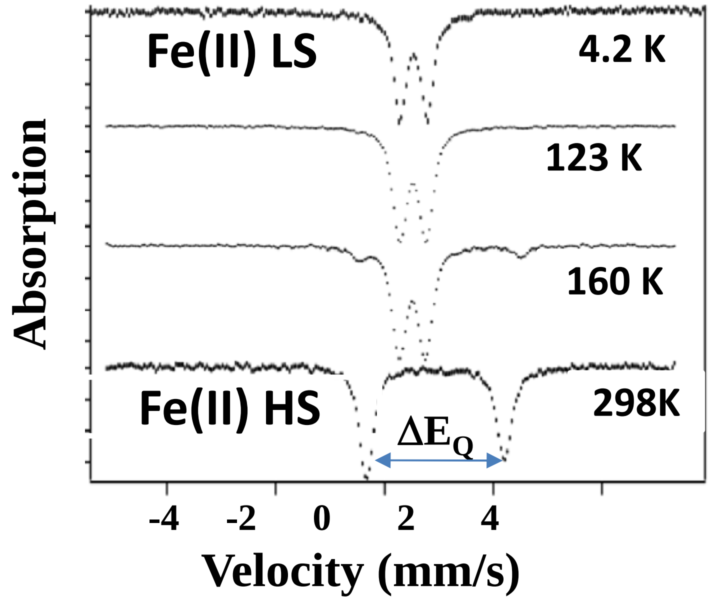
Crystallography

	LS	HS
d(Fe^{II}-N) (Å)	1.95-2.00	2.15-2.20

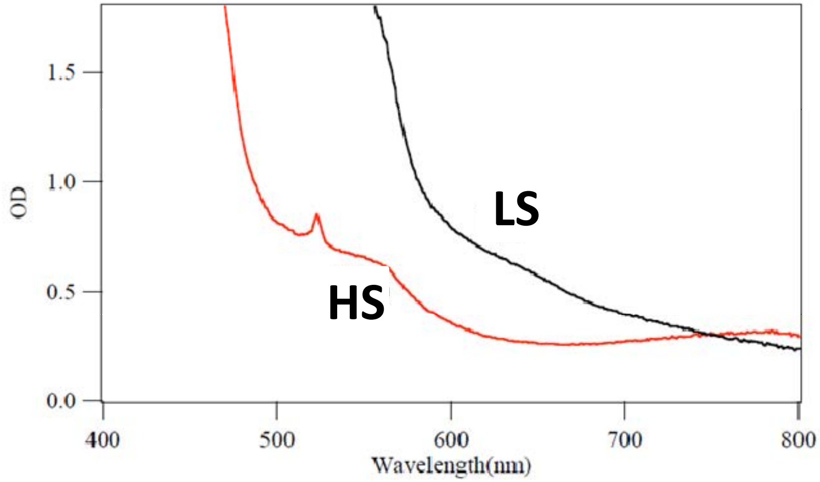
Mangetometry



^{57}Fe Mössbauer Spectroscopy

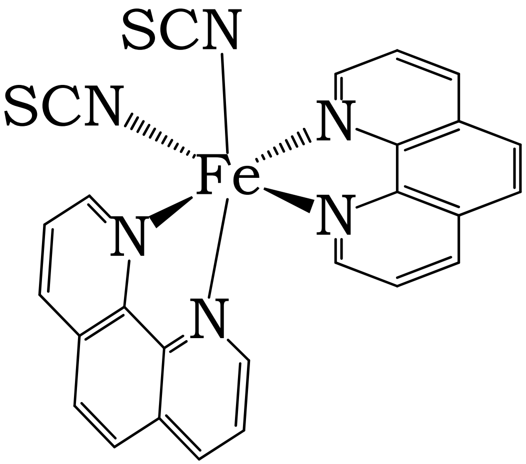


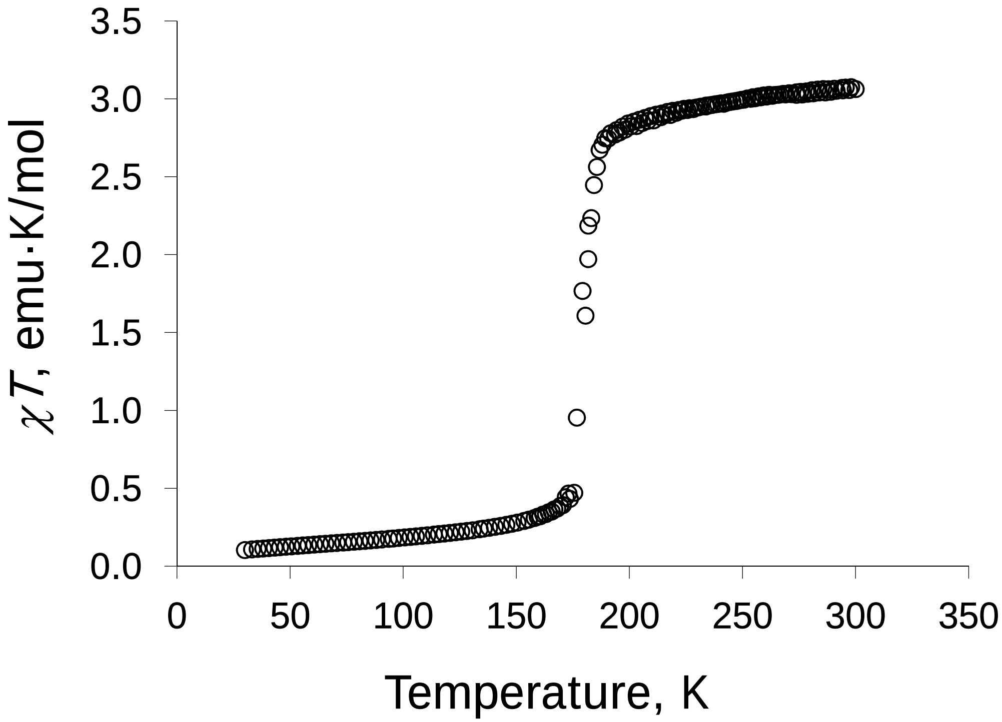
Other spectroscopic techniques



Magnetometry

The first reported
SCO complex of Fe(II)



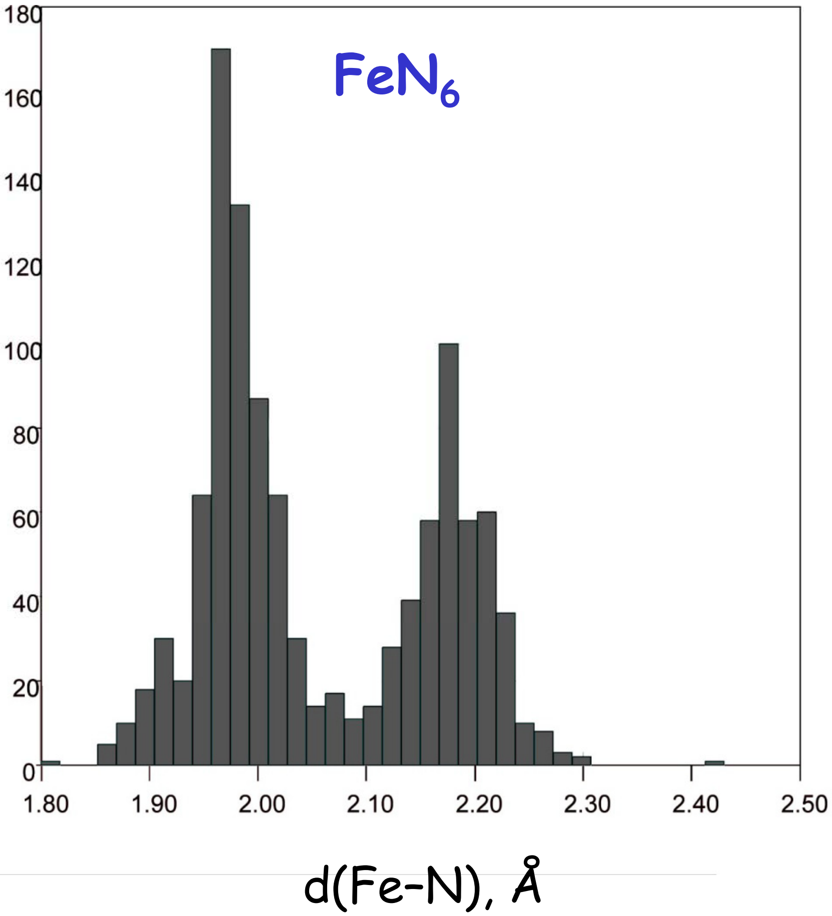


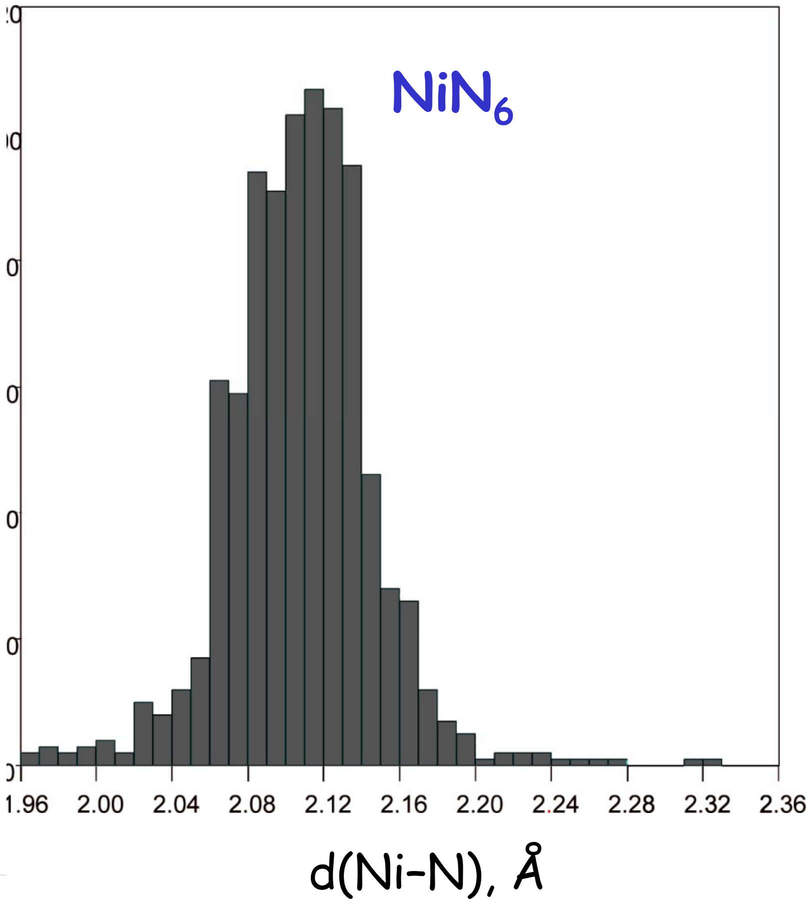
At $T_{1/2}$ = 180 K,

$$\gamma_{\mathrm{HS}} = \frac{[\mathrm{Fe}]_{\mathrm{HS}}}{[\mathrm{Fe}]_{\mathrm{total}}} = \frac{[\mathrm{Fe}]_{\mathrm{HS}}}{[\mathrm{Fe}]_{\mathrm{HS}} + [\mathrm{Fe}]_{\mathrm{LS}}}$$

König, Madeja *Chem. Commun.* **1966**, 61-62.

Crystallography





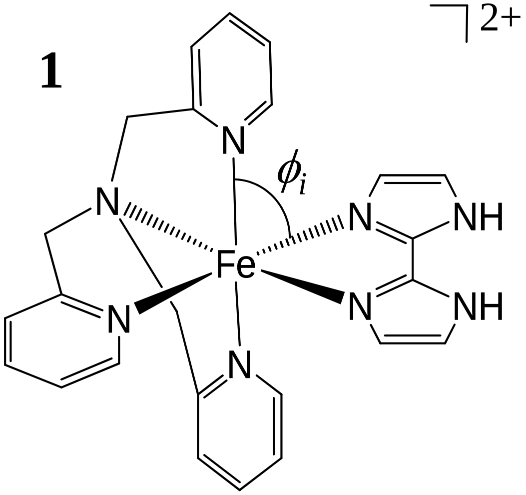
Guionneau, P.; Marchivie, M.; Bravic, G.; Létard, J.-F.; Chasseau, D. *Top. Curr. Chem.* **2004**, 234, 97-128.

Crystallography

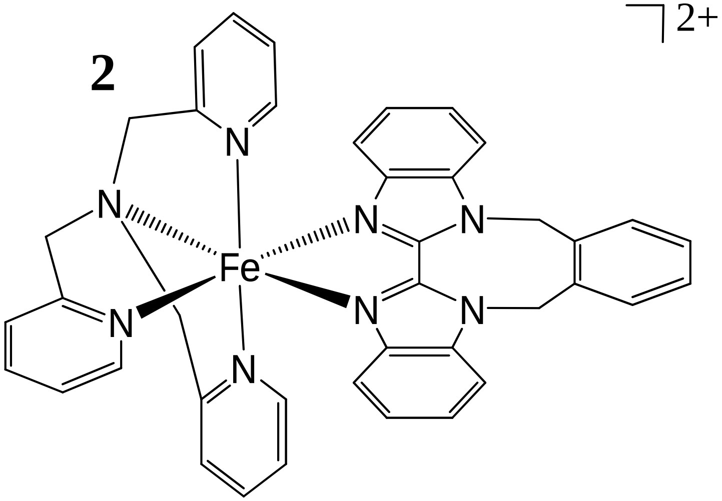
Formula	$FeCl_2O_8N_8C_{32}H_{30}$ (**1**)		$FeCl_2O_{9.2}N_8C_{41.2}H_{38.8}$ (**2**$\cdot 1.5CH_3OH$)	
Temperature	123 K	210 K	123 K	210 K
Space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/n$ (11)	$P2_1/n$ (11)
V, Å^3	3231.06	3372.03	4716.8	4768.89
d(Fe–N)$_{av}$, Å	2.002(4)	2.184(4)	2.188(4)	2.188(3)
Σ(N-Fe-N), deg	71.9(2)	118.1(2)	166.9(2)	165.5(1)

$$\Sigma = \sum_{i=1}^{12} \left|\phi_i - 90\right|$$

1

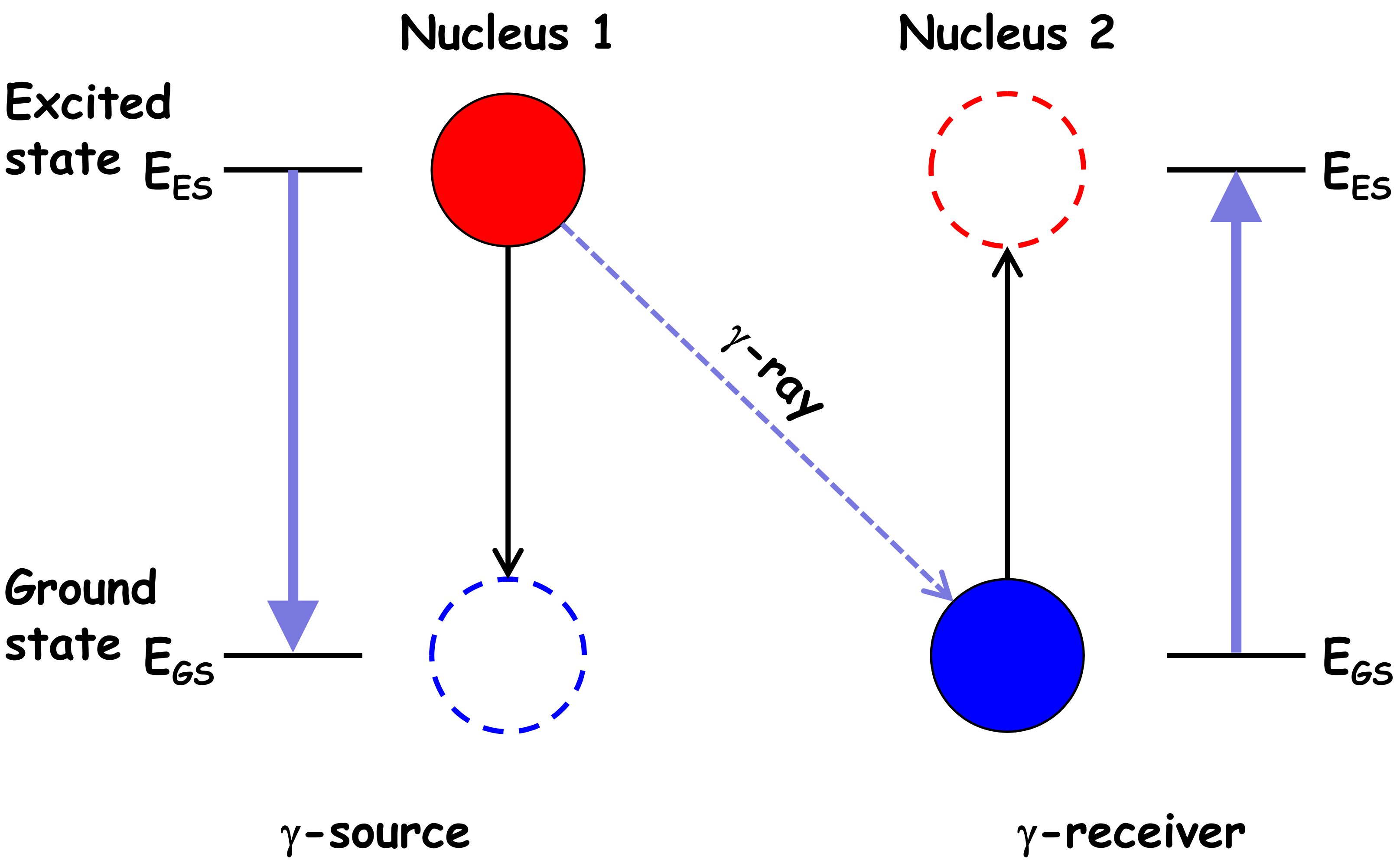


2



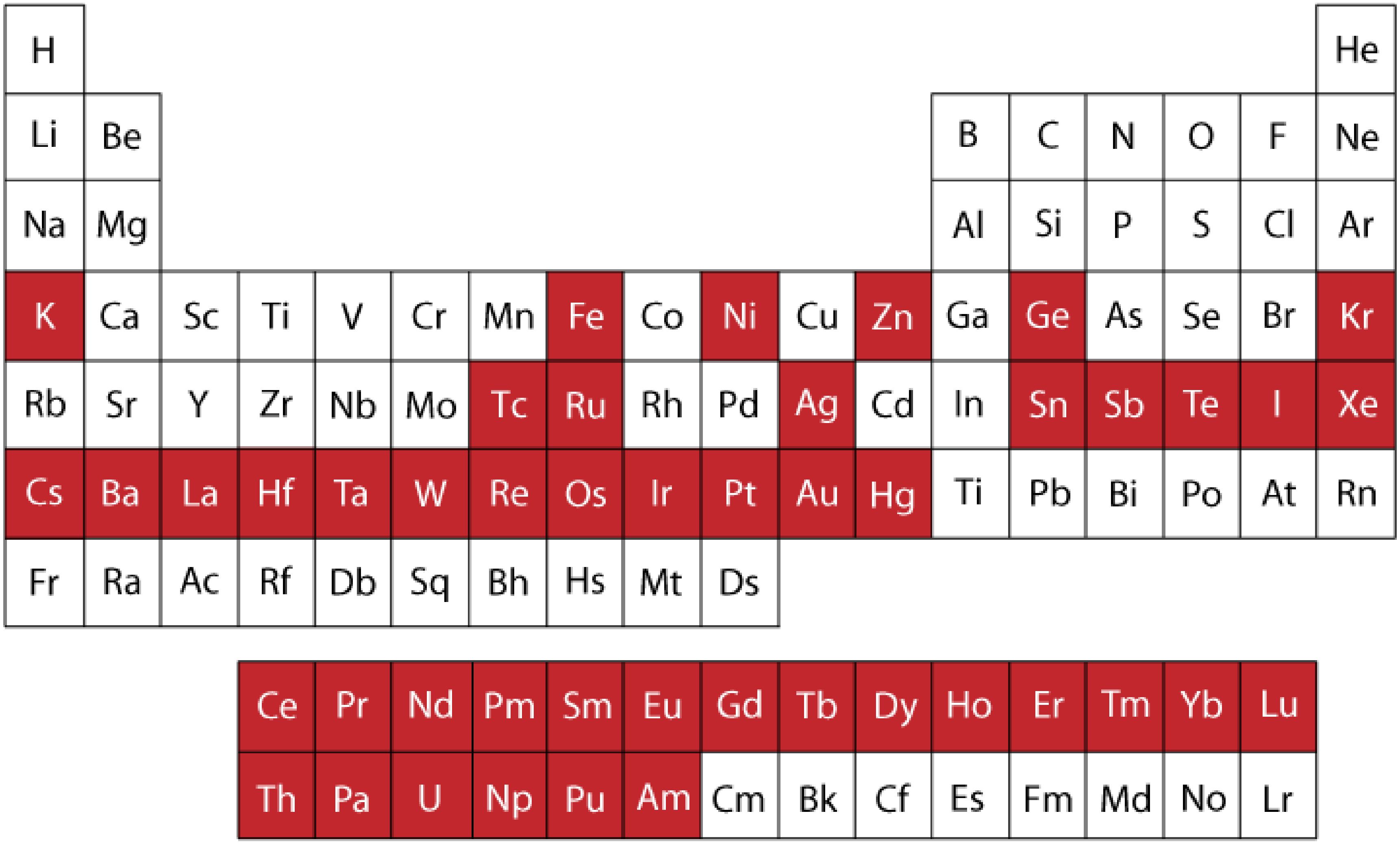
Phan, H.; Chakraborty, P.; Chen, M.; Calm, Y. M.; Kovnir, K.; Keniley, L. K.; Hoyt, J. M.; Knowles, E. S.; Besnard, C.; Meisel, M. W.; Hauser, A.; Achim, C.; Shatruk, M. *Chem. Eur. J.* **2012**, *18*, 15805-15815.

Mössbauer Spectroscopy



Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

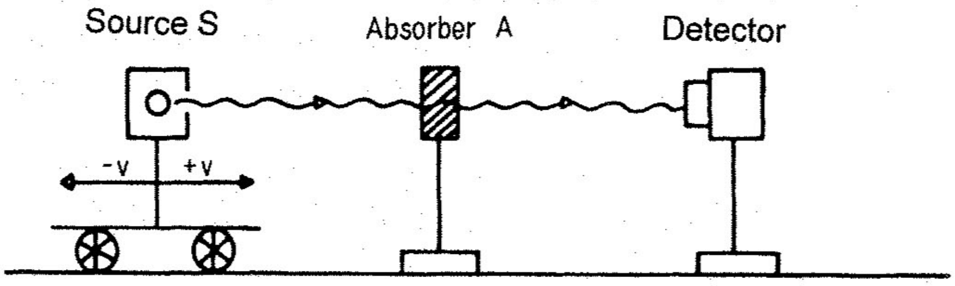
Mössbauer Periodic Table

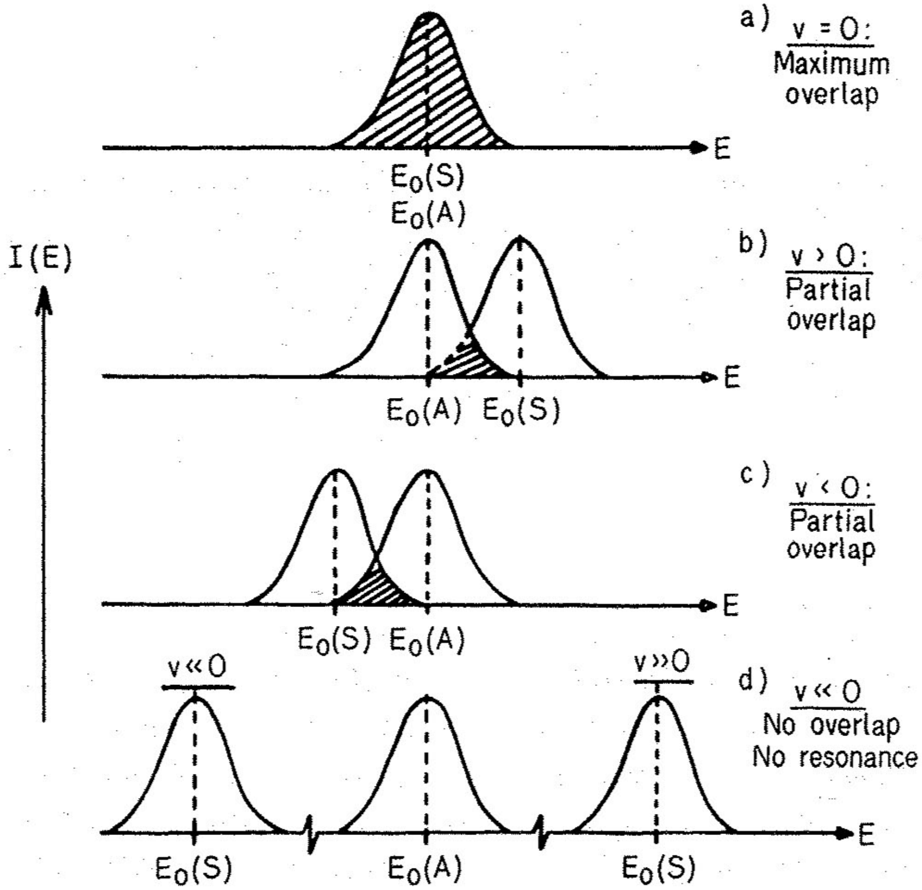


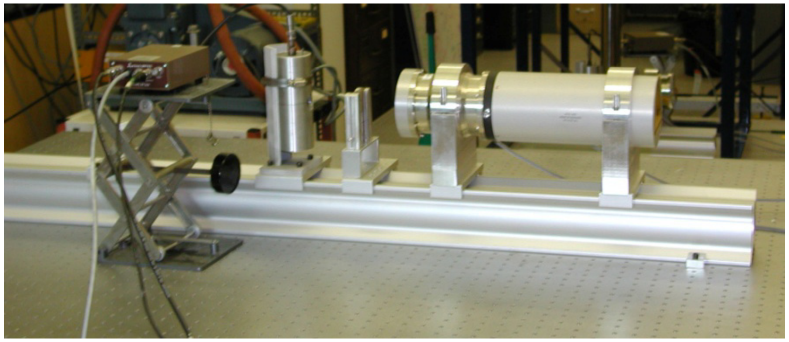
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
🟥 K	Ca	Sc	Ti	V	Cr	Mn	🟥 Fe	Co	🟥 Ni	Cu	🟥 Zn	Ga	🟥 Ge	As	Se	Br	🟥 Kr
Rb	Sr	Y	Zr	Nb	Mo	🟥 Tc	🟥 Ru	Rh	Pd	🟥 Ag	Cd	In	🟥 Sn	🟥 Sb	🟥 Te	🟥 I	🟥 Xe
🟥 Cs	🟥 Ba	🟥 La	🟥 Hf	🟥 Ta	🟥 W	🟥 Re	🟥 Os	🟥 Ir	🟥 Pt	🟥 Au	🟥 Hg	Ti	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sq	Bh	Hs	Mt	Ds								
			🟥 Ce	🟥 Pr	🟥 Nd	🟥 Pm	🟥 Sm	🟥 Eu	🟥 Gd	🟥 Tb	🟥 Dy	🟥 Ho	🟥 Er	🟥 Tm	🟥 Yb	🟥 Lu	
			🟥 Th	🟥 Pa	🟥 U	🟥 Np	🟥 Pu	🟥 Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

Experimental Implementation

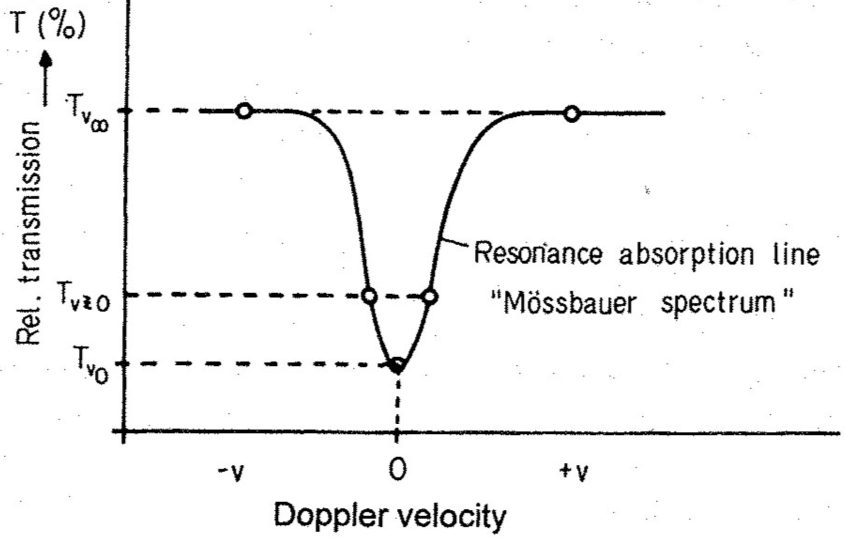






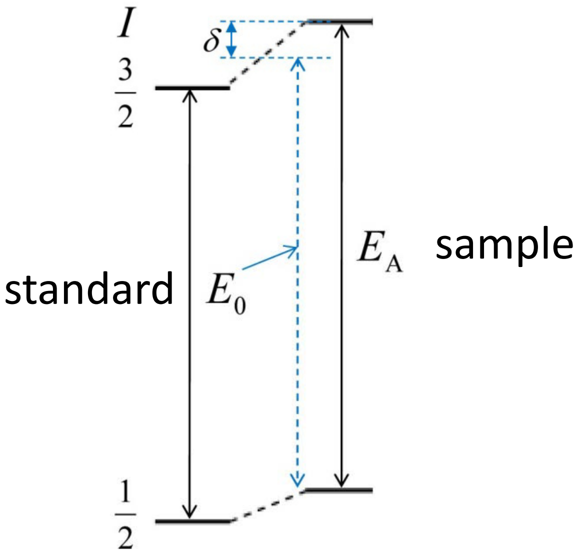
Variation of the source speed causes the change in energy due to the Doppler effect

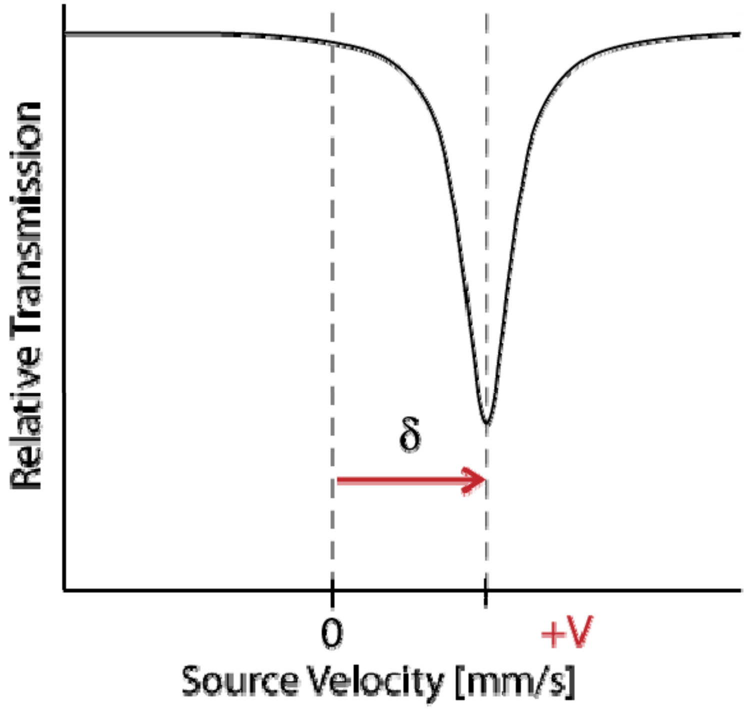
Mössbauer spectrum:

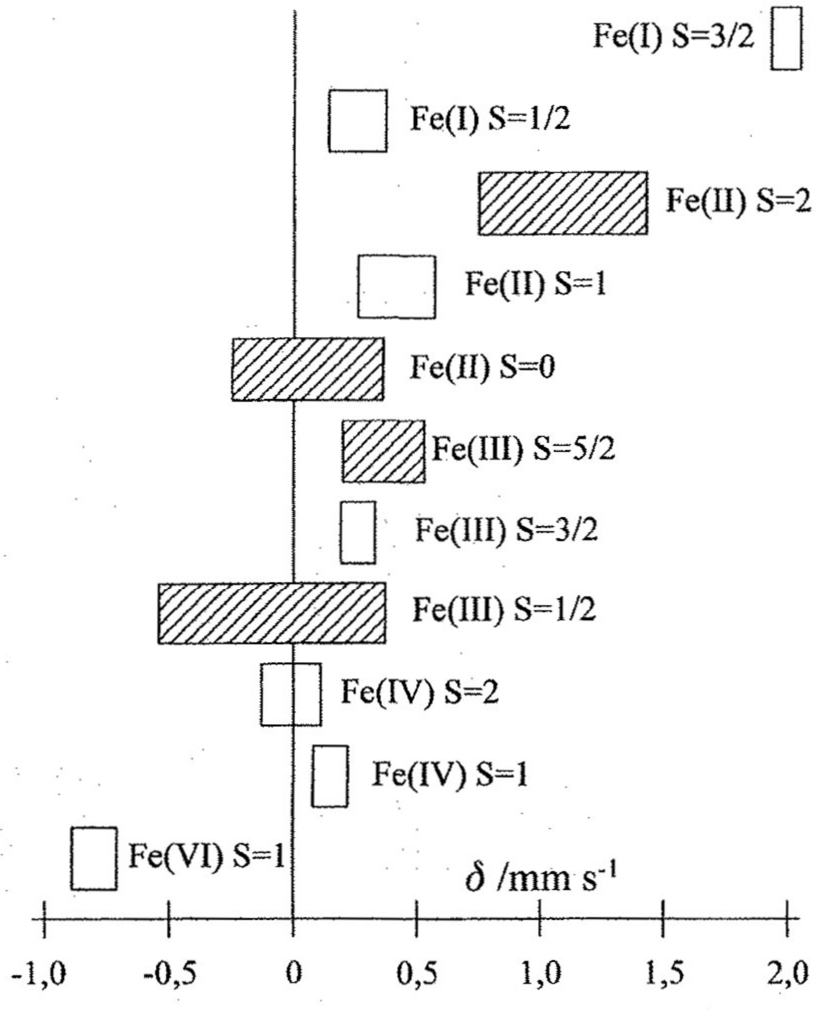


Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

Isomer Shift

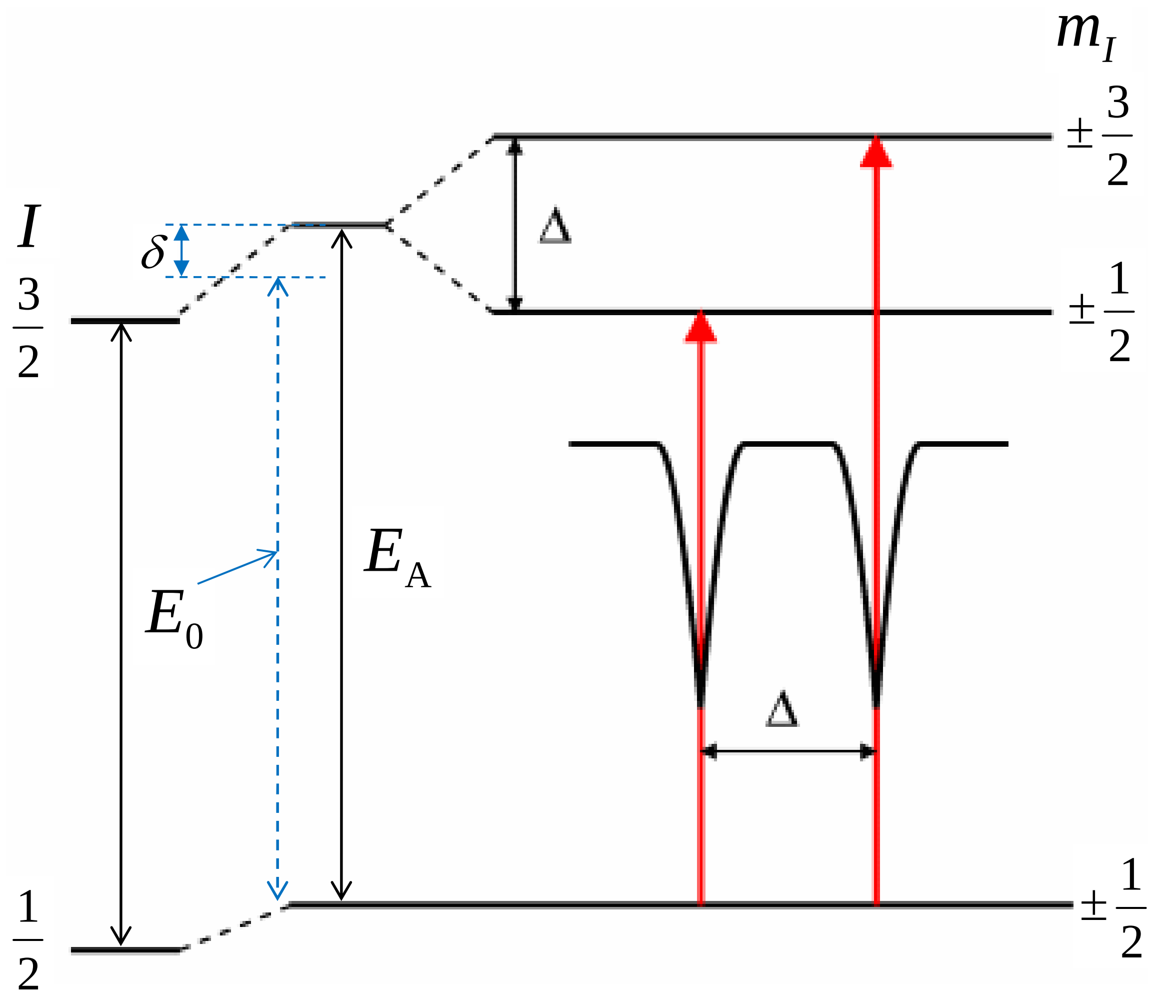






Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

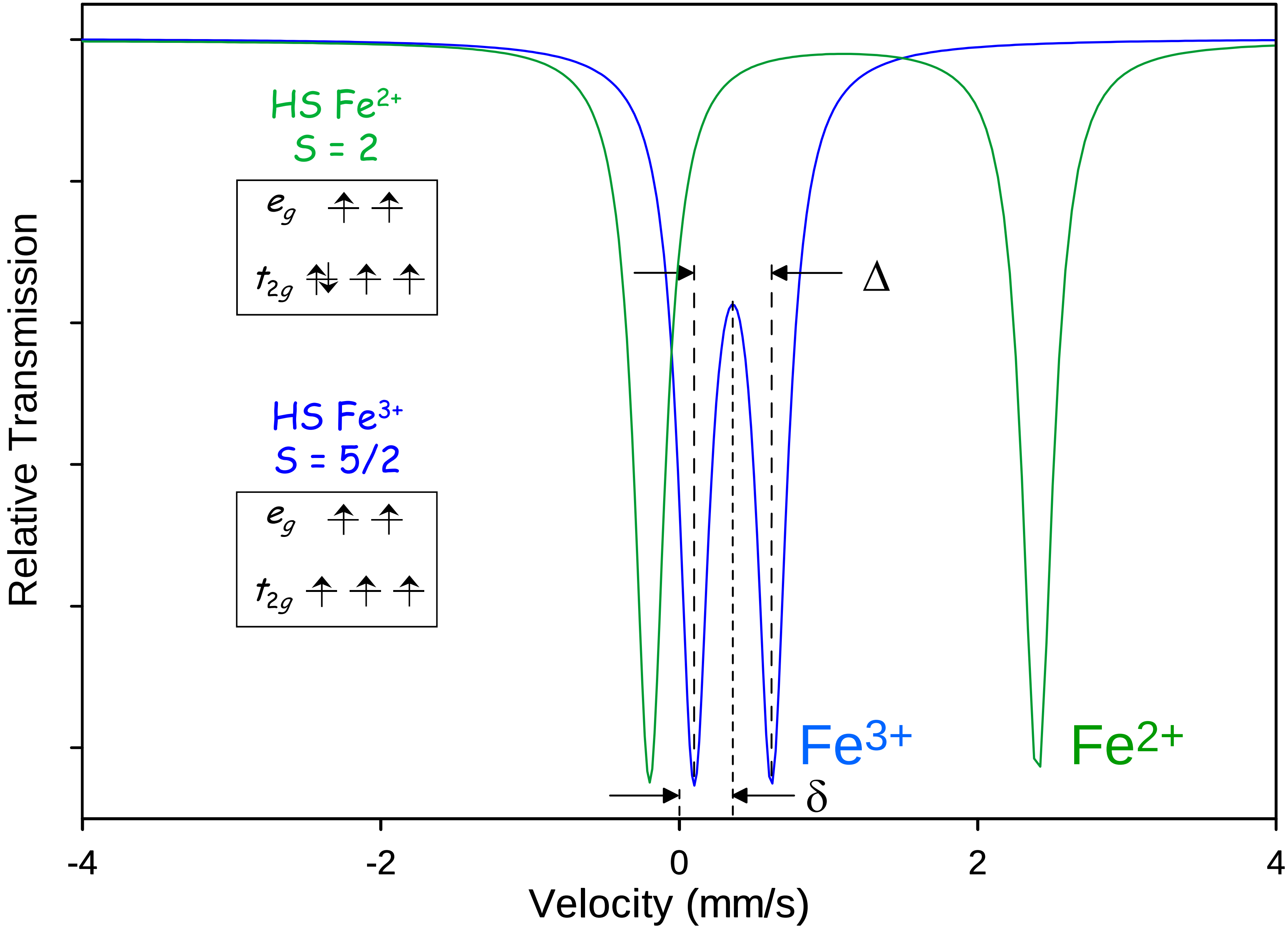
Quadrupole Splitting (I=3/2, ^{57}Fe)



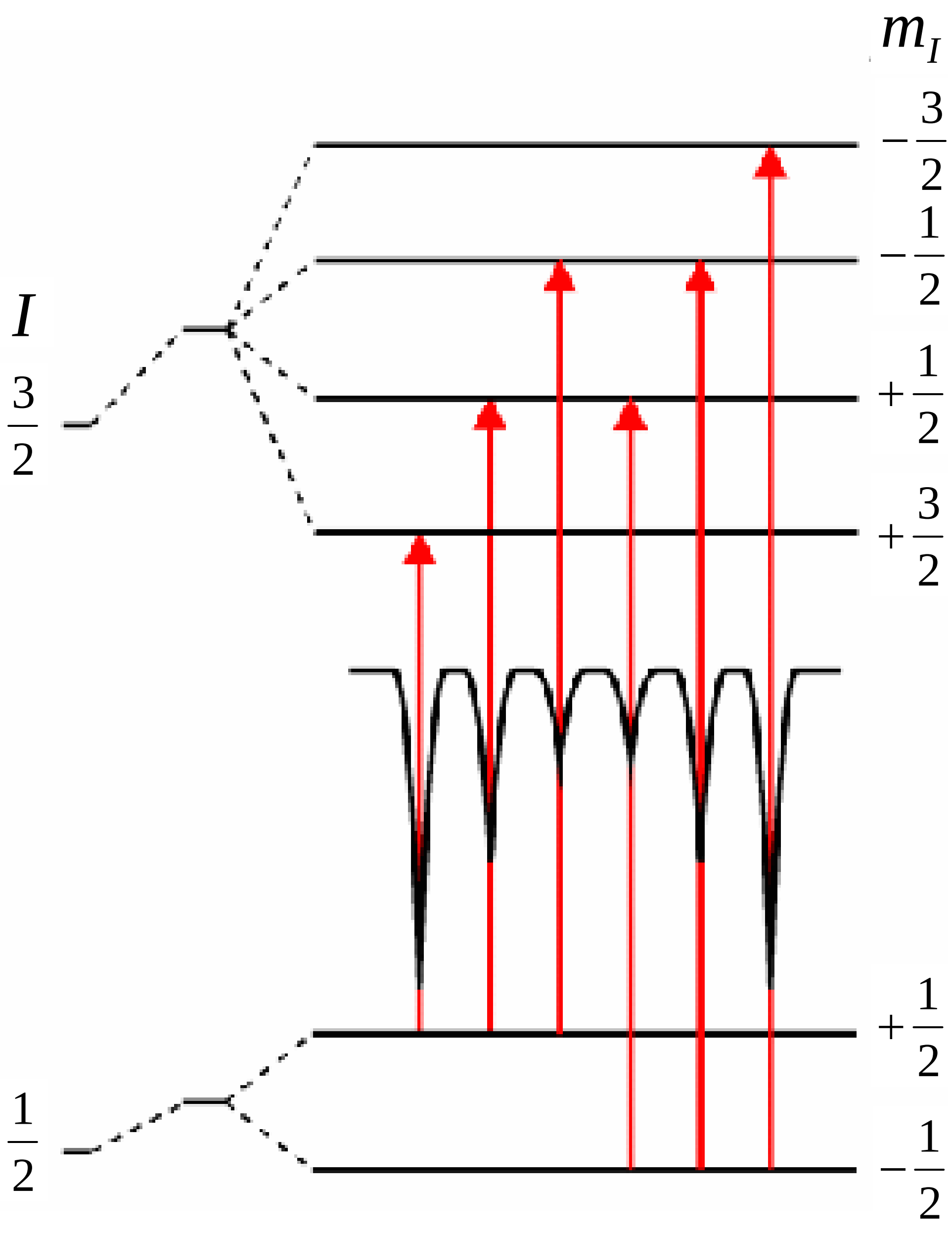
- The quadrupole splitting arises from asymmetric distribution (gradient) of electron density around the absorbing nucleus

Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

Example: High-Spin Fe^{2+} and Fe^{3+} Ions



Magnetic Hyperfine Splitting (I=3/2,^{57}Fe)



- Selection rule: $\Delta m_I = 0, \pm 1$
  $\Delta I = \pm 1$

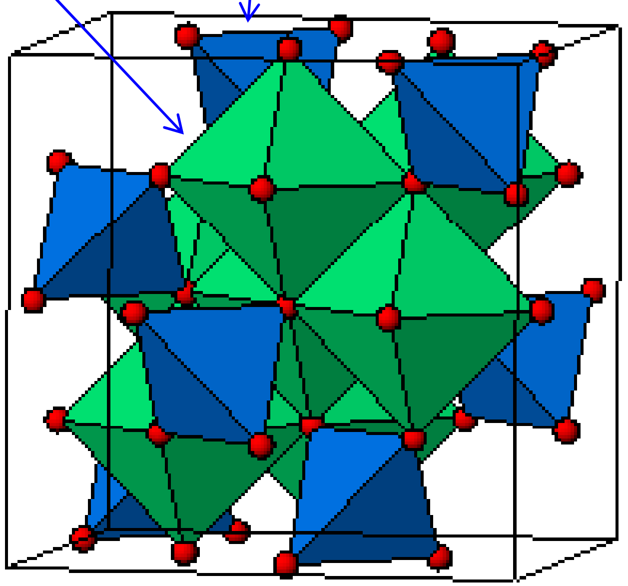
- The magnetic hyperfine splitting in a Mössbauer spectrum is an indication of magnetic ordering or an applied magnetic field.

Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

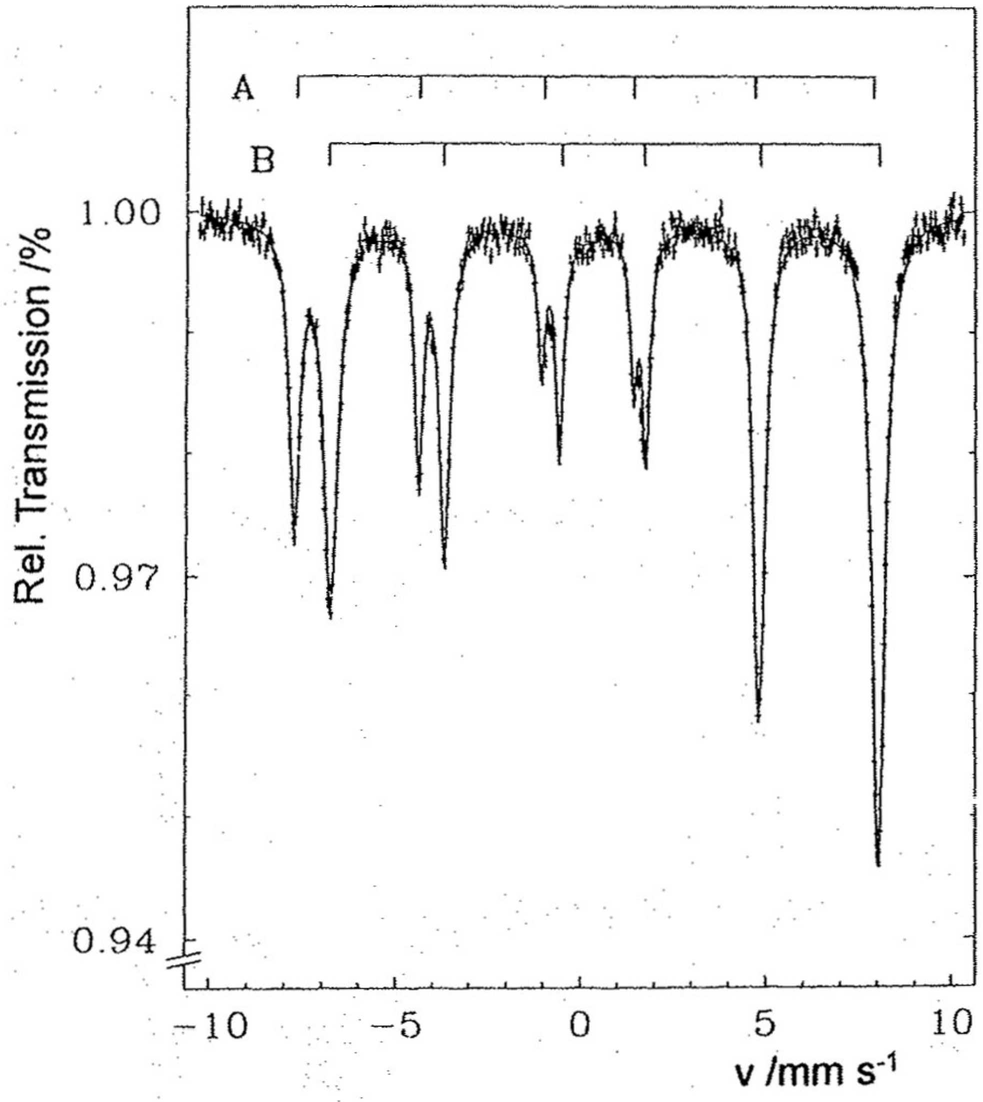
Example: Magnetite, Fe_3O_4

Site B: Fe^{2+}/Fe^{3+}

Site A: Fe^{3+}



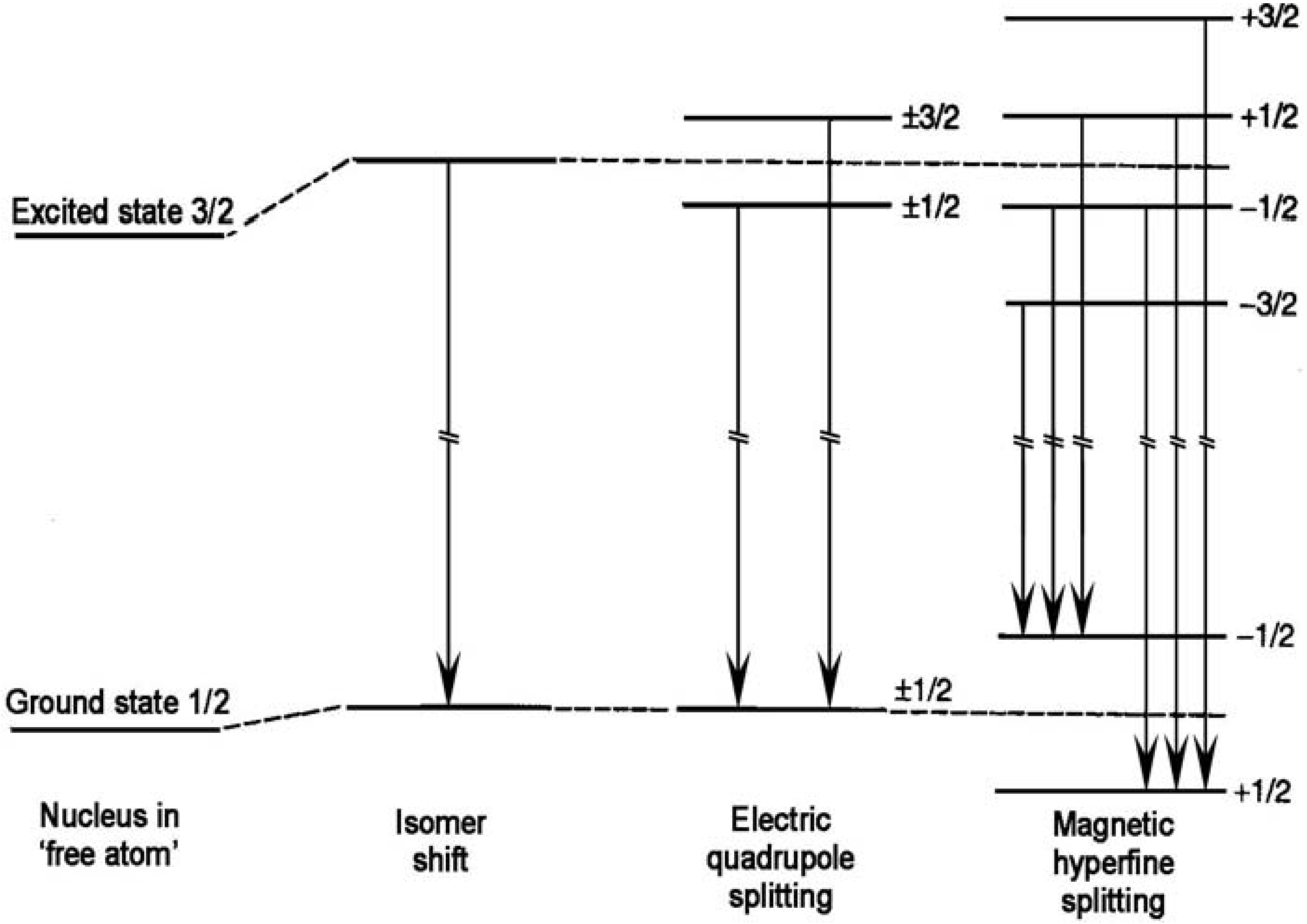
Site B: Class III mixed-valent system



Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

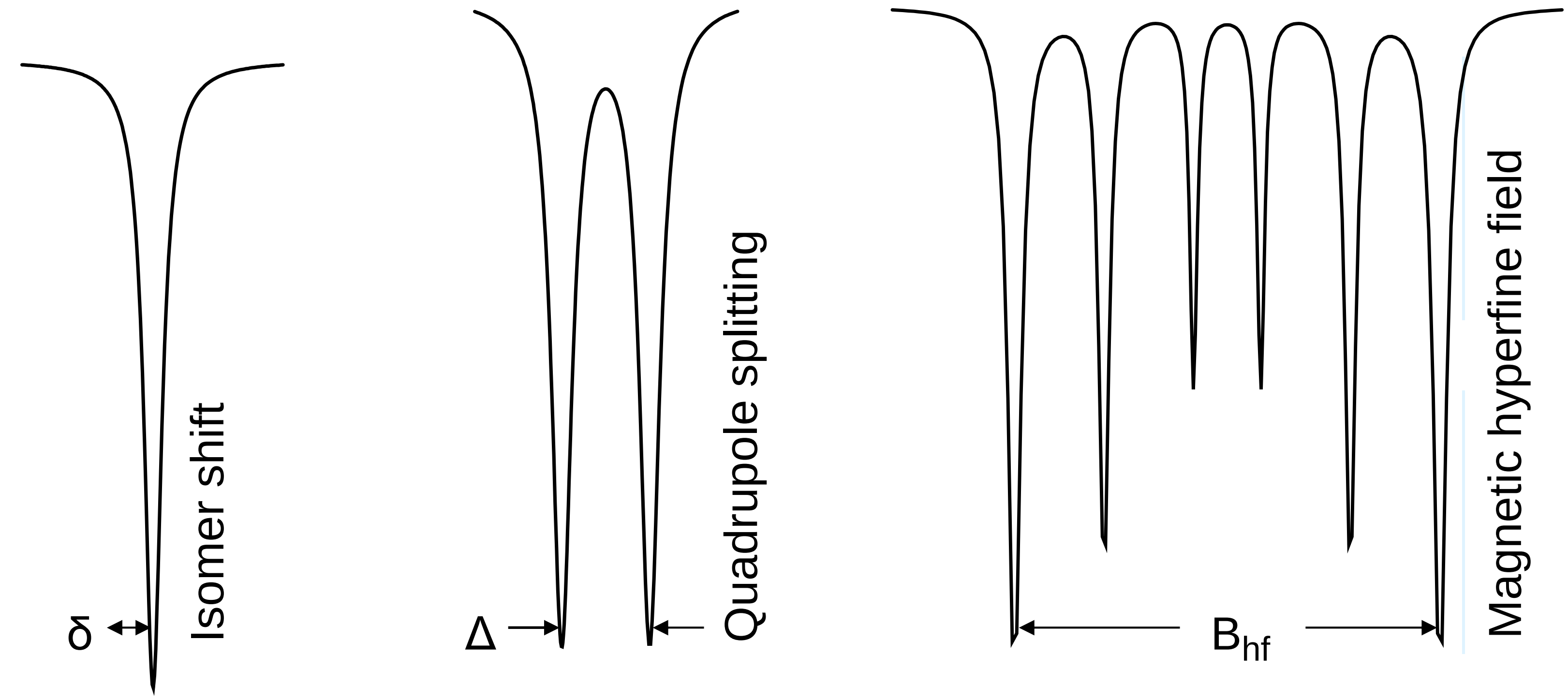
Splitting of Nuclear Energy Levels (I=3/2,^{57}Fe)

Depending on the local environments of Fe atoms and magnetic properties, Mössbauer spectra can consist of a singlet, a doublet, or a sextet.



Appearance of Mössbauer Spectra

Depending on the local environments of Fe atoms and magnetic properties, Mössbauer spectra can consist of a <u>singlet</u>, a <u>doublet</u>, or a <u>sextet</u>.



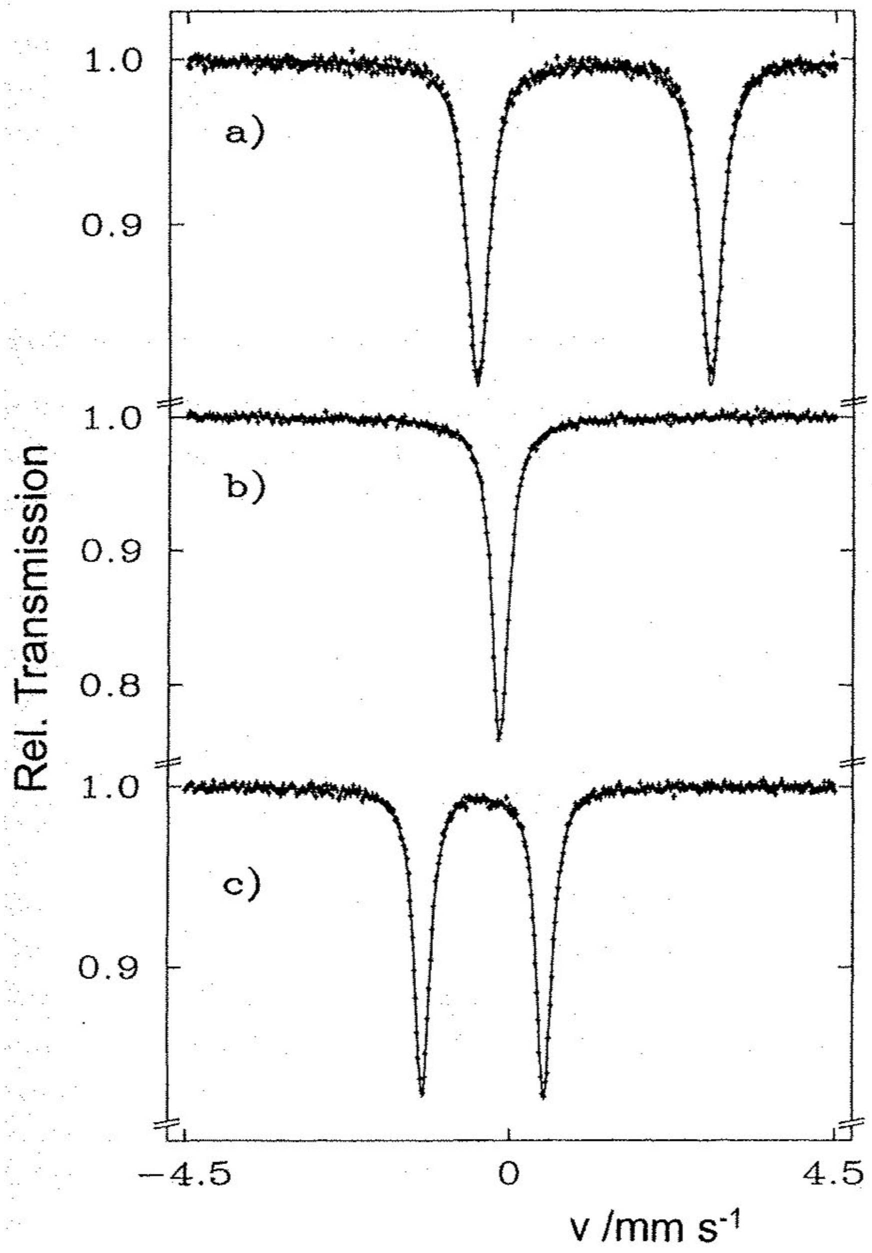
Symmetric charge
No magnetic field

Asymmetric charge
No magnetic field

Symmetric or asymmetric charge
Magnetic field (internal or external)

Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

Example: Various Fe(II) Complexes



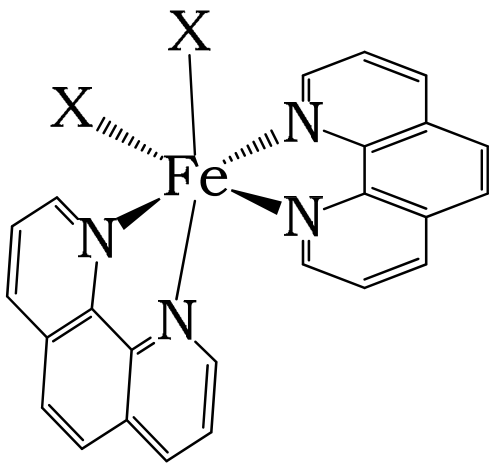
$FeSO_4 \cdot 7H_2O$
high-spin

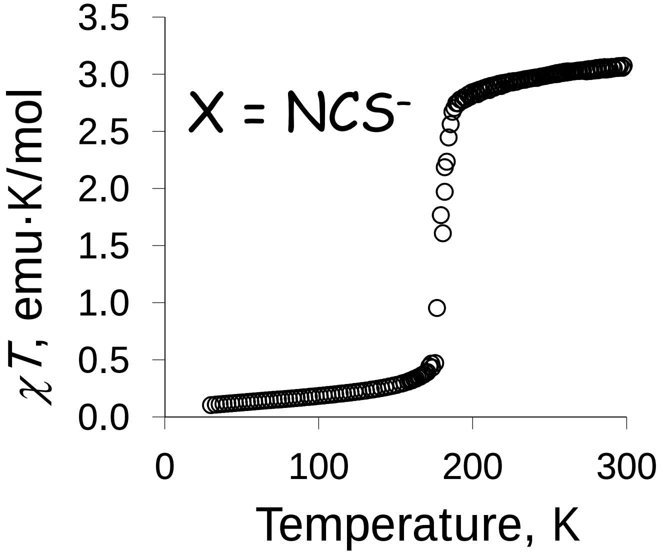
$K_4[Fe(CN)_6] \cdot 3H_2O$
low-spin

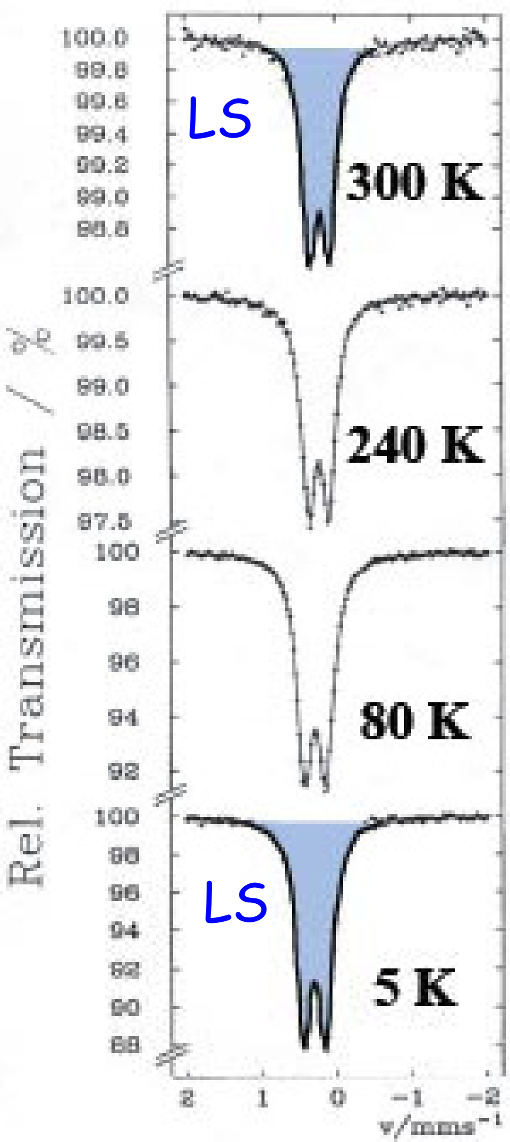
$Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$
low-spin

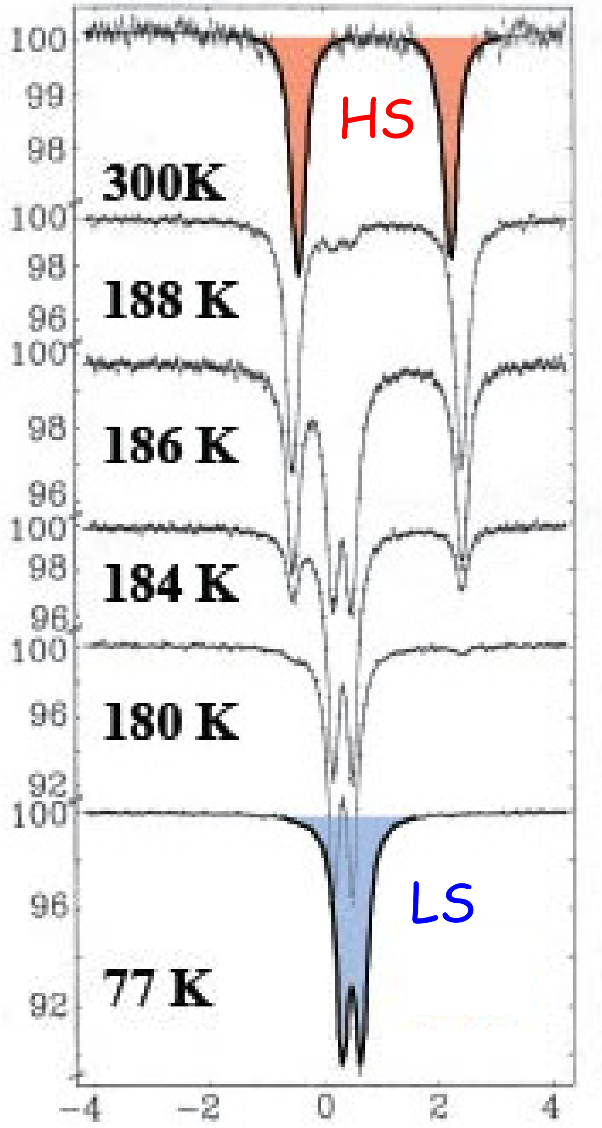
Gütlich, P. *Lectures Notes on Mössbauer Spectroscopy*. University of Mainz.

Example: $[Fe(phen)_3]Cl_2$ vs. $Fe(phen)_2(NCS)_2$



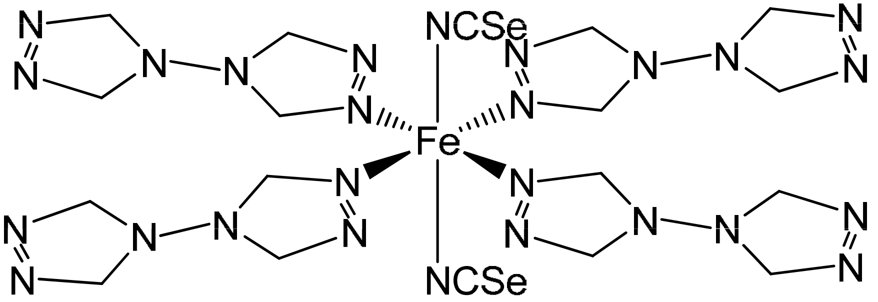






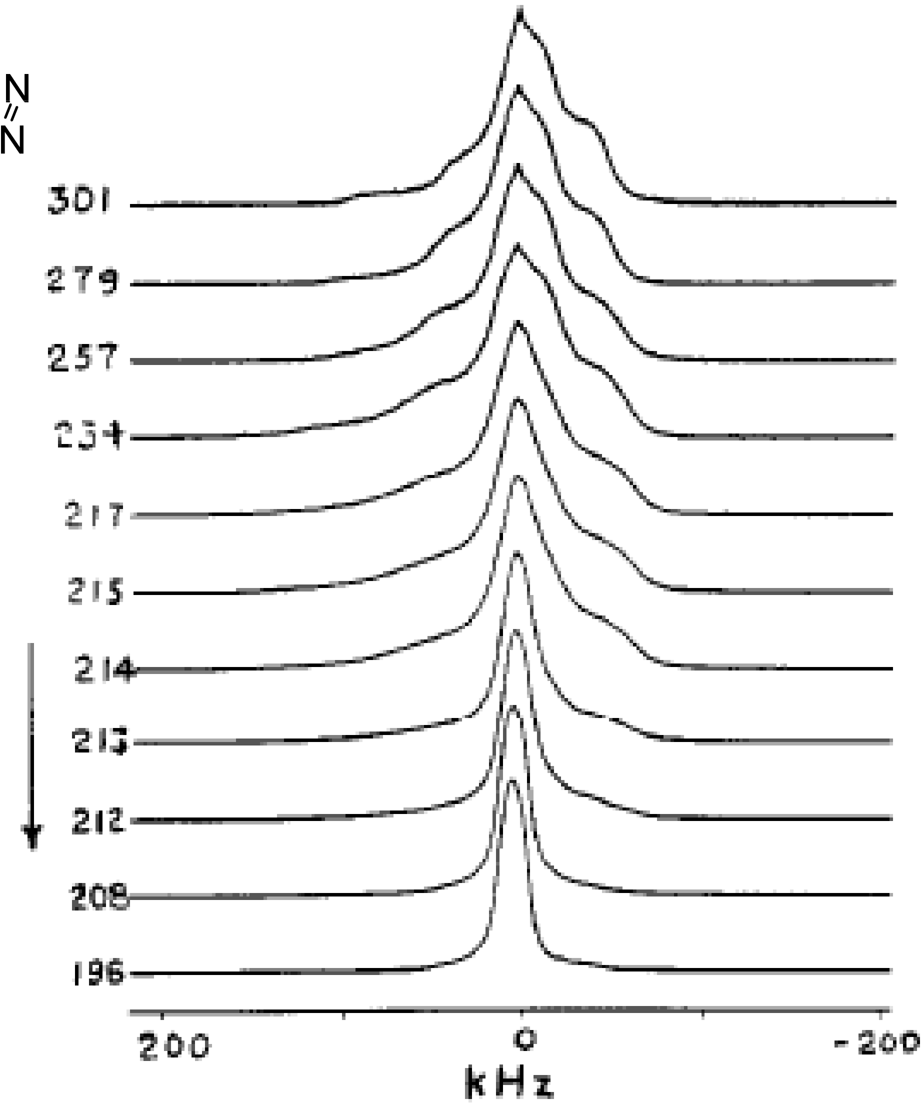
Gütlich, P. *Lectures Notes on Mössbauer Spectroscopy*. University of Mainz.

NMR Spectroscopy



$Fe(\mu_2\text{-}btr)_2(NCSe)_2$

[Coordination polymer]

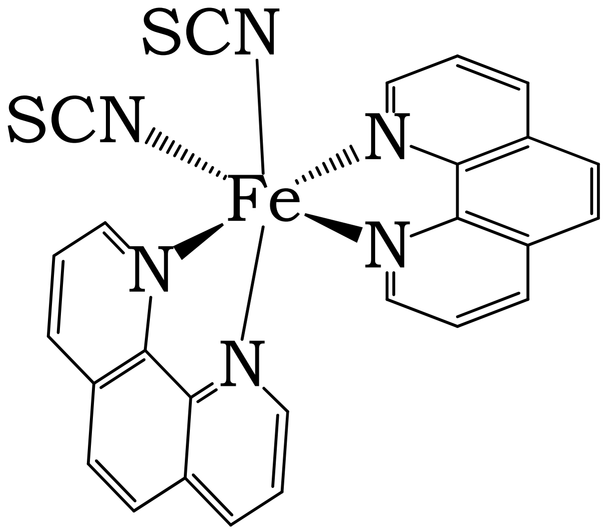


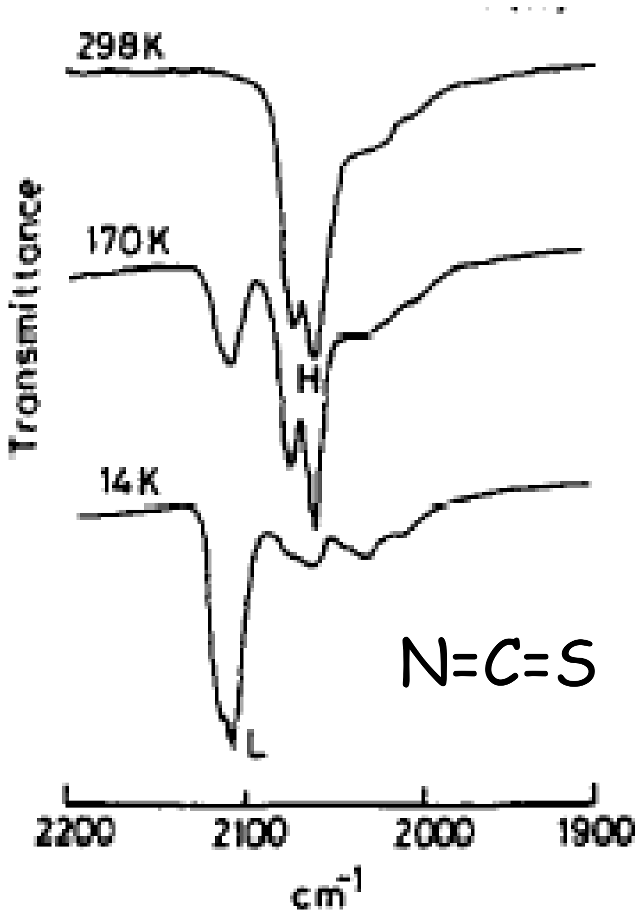
The linewidth is much narrower in the LS state due to the absence of spin-spin relaxation:

the S = 0 spin state does not interact with the nuclear spin; as a result, the excited-state lifetime is higher in the LS state.

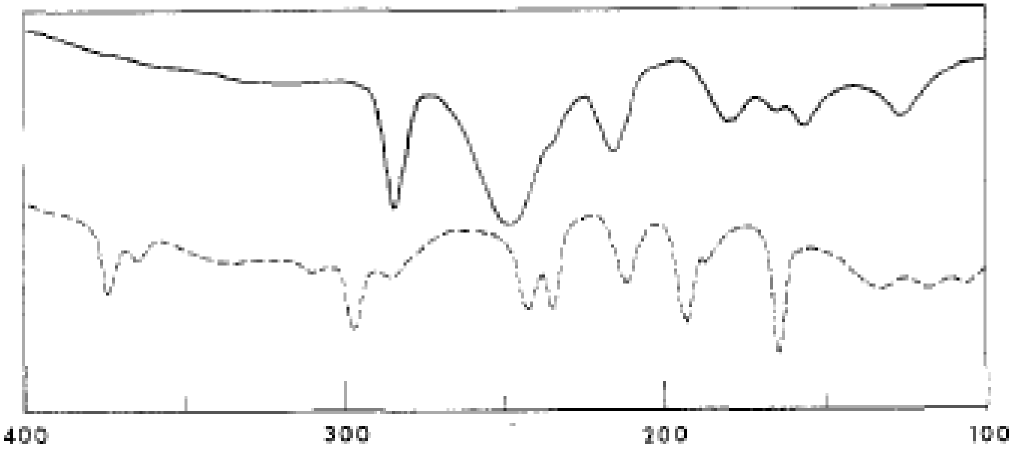
Ozarowski, A.; Shunzhong, Y.; McGarvey, B. R.; Mislankar, A.; Drake, J. E. *Inorg. Chem.* **1991**, *30*, 3167-3174.

IR Spectroscopy





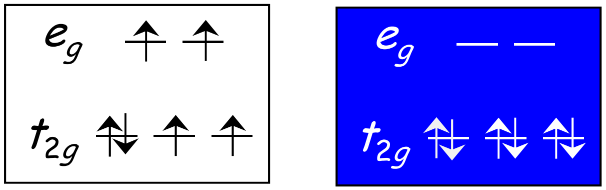
M-N



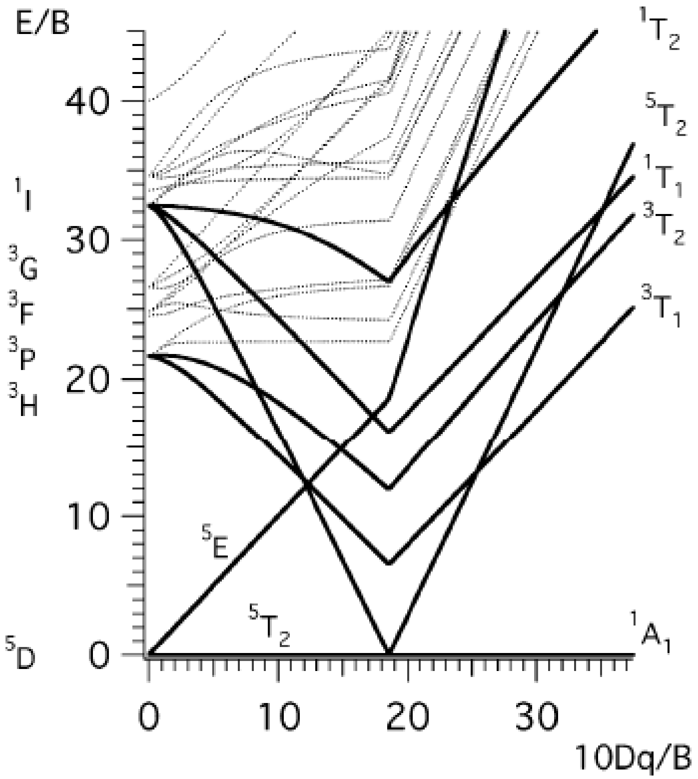
Sankar, G.; Thomas, J. M.; Varma, V.; Kulkarni, G. U.; Rao, C. N. R. *Chem. Phys. Lett.* **1996**, *251*, 79-83.

The Physics of Spin Crossover

Fe(II), d^6



LS, S = 2 HS, S = 0



- Two contributions to the total electron energy are important:
  - d-orbital splitting, $10Dq$
  - d-electron pairing energy, $\Pi \approx 15{,}000\ \mathrm{cm}^{-1}$ for Fe^{2+}
- SCO is possible when

$$10Dq_{\mathrm{HS}} < \Pi < 10Dq_{\mathrm{LS}}$$

- SCO is not possible when

$$10Dq_{\mathrm{HS}} < 10{,}000\ \mathrm{cm}^{-1} \text{ or}$$
$$10Dq_{\mathrm{LS}} > 23{,}000\ \mathrm{cm}^{-1}$$

- Conclusion:

  The SCO depends on the ligand field and the charge on the metal ion

- Spectrochemical series:

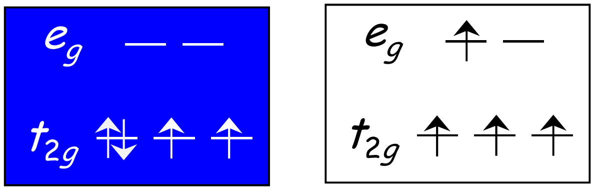
  $I^- < Br^- < Cl^- < SCN^- < NO_3^- < F^-$
  $< OH^- < H_2O < NCS^- < py < NH_3$
  $< en < NO_2^- < PPh_3 < CN^- < CO$

Ground States of d^4-d^7 Metal Ions

Configuration	**Ion**	**HS**	**LS**
d^4	Cr(II) Mn(III)	^5E_g, S = 2	$^3T_{1g}$, S = 1
d^5	Mn(II) Fe(III)	$^6A_{1g}$, S = 5/2	$^2T_{2g}$, S = 1/2
d^6	Fe(II) Co(III)	$^5T_{2g}$, S = 2	$^1A_{1g}$, S = 0
d^7	Co(II) Ni(III)	$^4T_{1g}$, S = 3/2	^2E_g, S = 1/2

Garcia, Y.; Gütlich, P. *Top. Curr. Chem.* **2004**, *234*, 49-62.

Spin Crossover in Complexes of d^4 Metal Ions

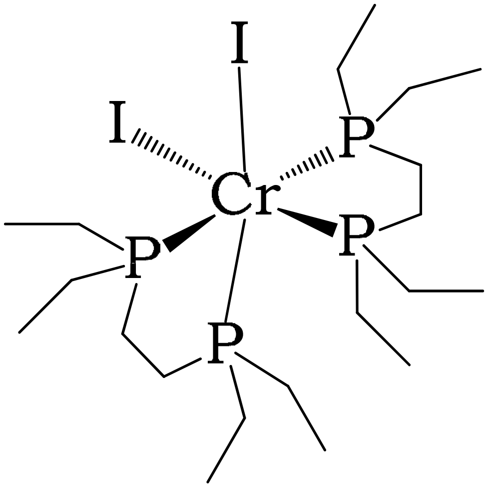


LS, S = 1   HS, S = 2

Cr(II), Mn(III)

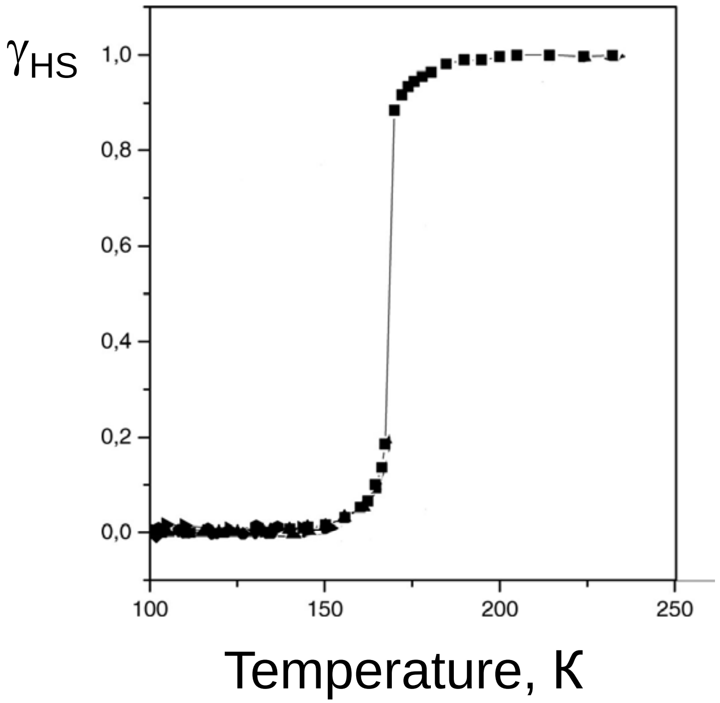
$Cr(depe)_2I_2$

the first example of
SCO in Cr(II) complexes



The ligand-field effect:

- $Cr(depe)_2I_2$ – SCO at $T_{1/2}$ = 170 K
- $Cr(depe)_2Br_2$ – LS, but contains a small admixture of the HS state at R.T.
- $Cr(depe)_2Cl_2$ – LS at all temperatures



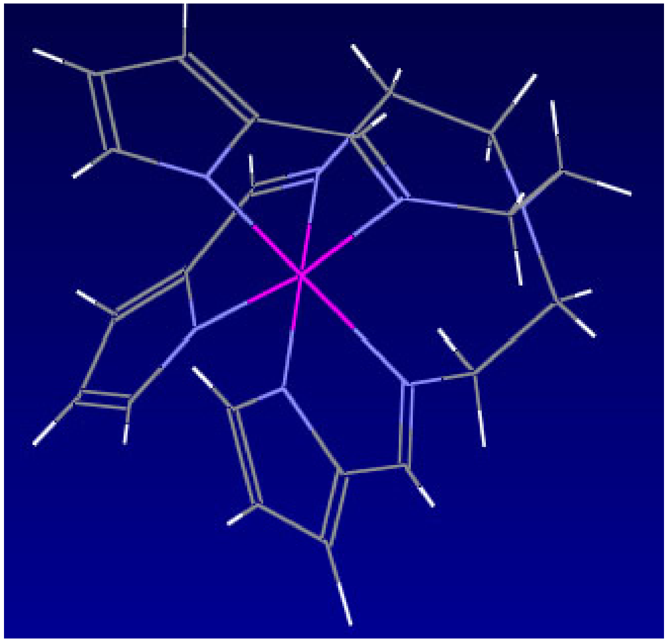
Halepoto, D. M.; Holt, D. G. L.; Larkworthy, L. F.; Leigh, G. L.; Povey, D. C.; Smith, G. W. *Chem. Commun.* **1989**, 1322.

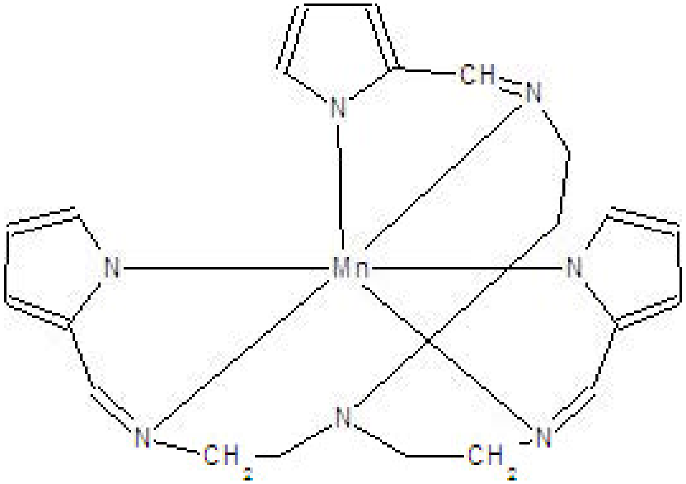
Girolami, G. S.; Wilkinson, G.; Galas, A. M.; Thornton-Pett, M.; Hursthouse, M. B. *Dalton* **1985**, 1339.

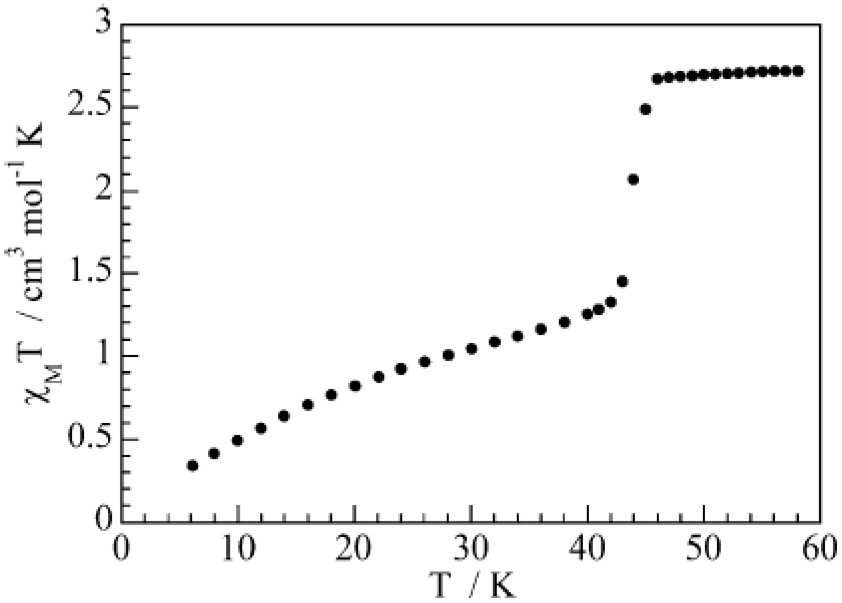
Spin Crossover in Complexes of d^4 Metal Ions

Mn(trp)

the first example of
SCO in d^4 complexes

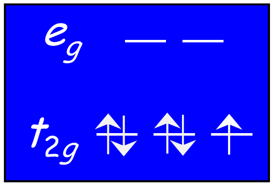




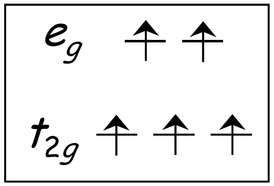


Sim, P. G.; Sinn, E. *J. Am. Chem. Soc.* **1981**, *103*, 241.

Spin Crossover in Complexes of d^5 Metal Ions



LS, S = 1/2

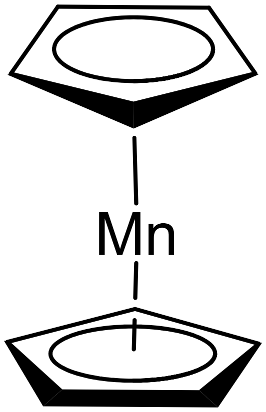


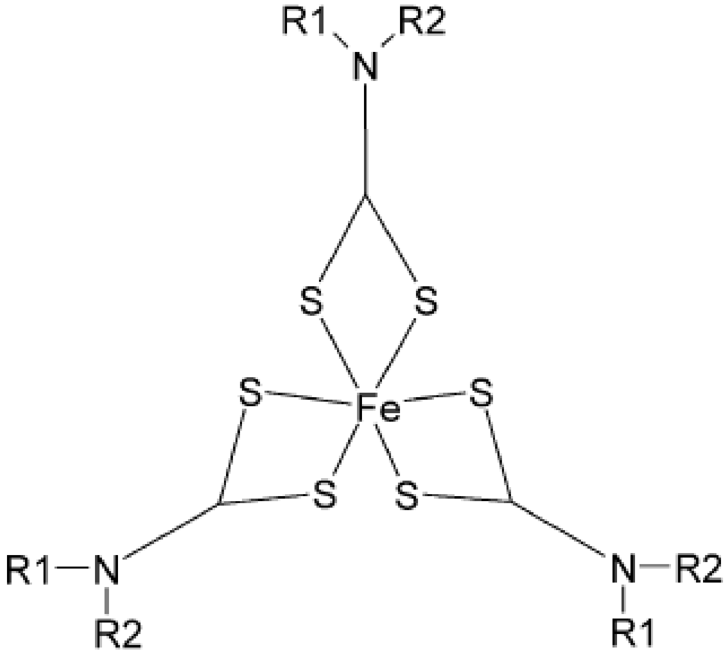
HS, S = 5/2

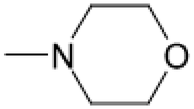
Mn(II), Fe(III)

$MnCp_2$

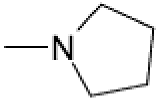
manganocene



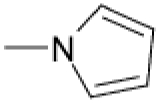




4-morpholine



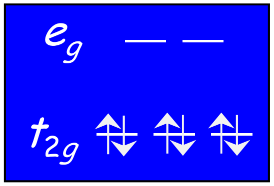
1-pyrrolidone



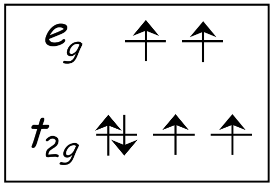
1-pyrrole

Ammeter, J. H.; Bucher, R.; Oswald, N. *J. Am. Chem. Soc.* **1974**, *96*, 7883.
Garcia, Y.; Gütlich, P. *Top. Curr. Chem.* **2004**, *234*, 49-62.

Spin Crossover in Complexes of d^6 Metal Ions



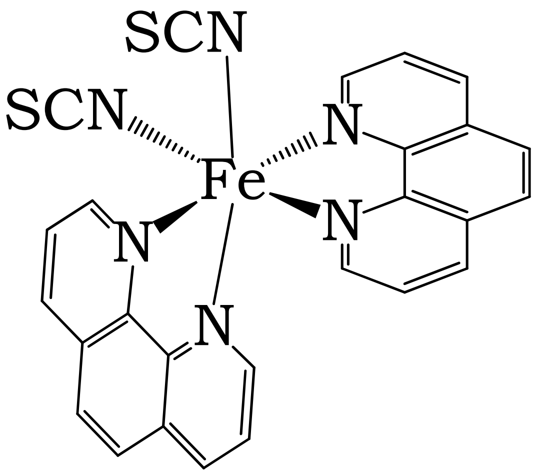
LS, S = 0

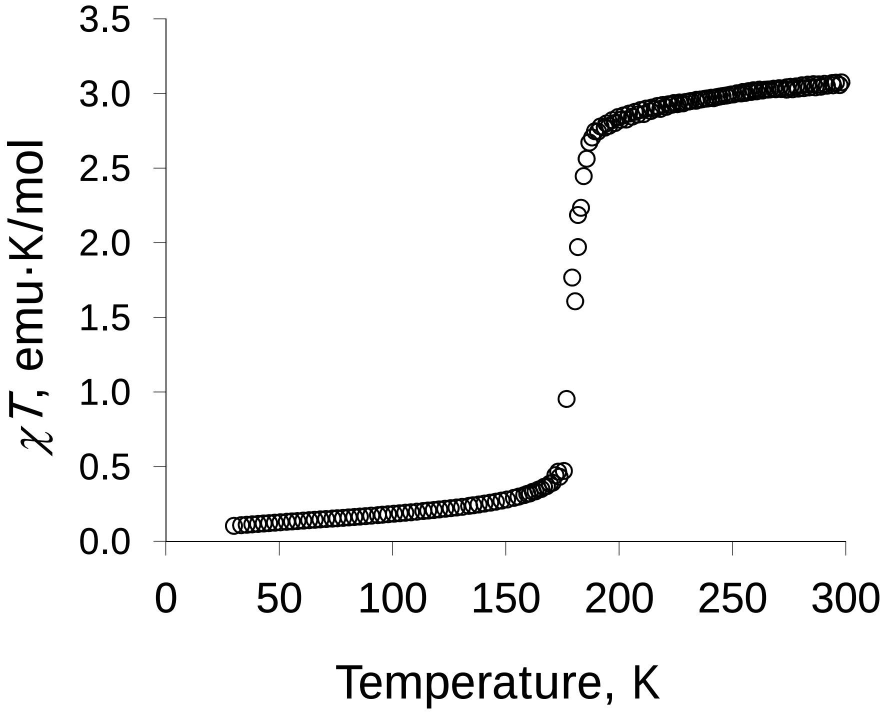


HS, S = 2

Fe(II), Co(III)

$Fe(phen)_2(NCS)_2$

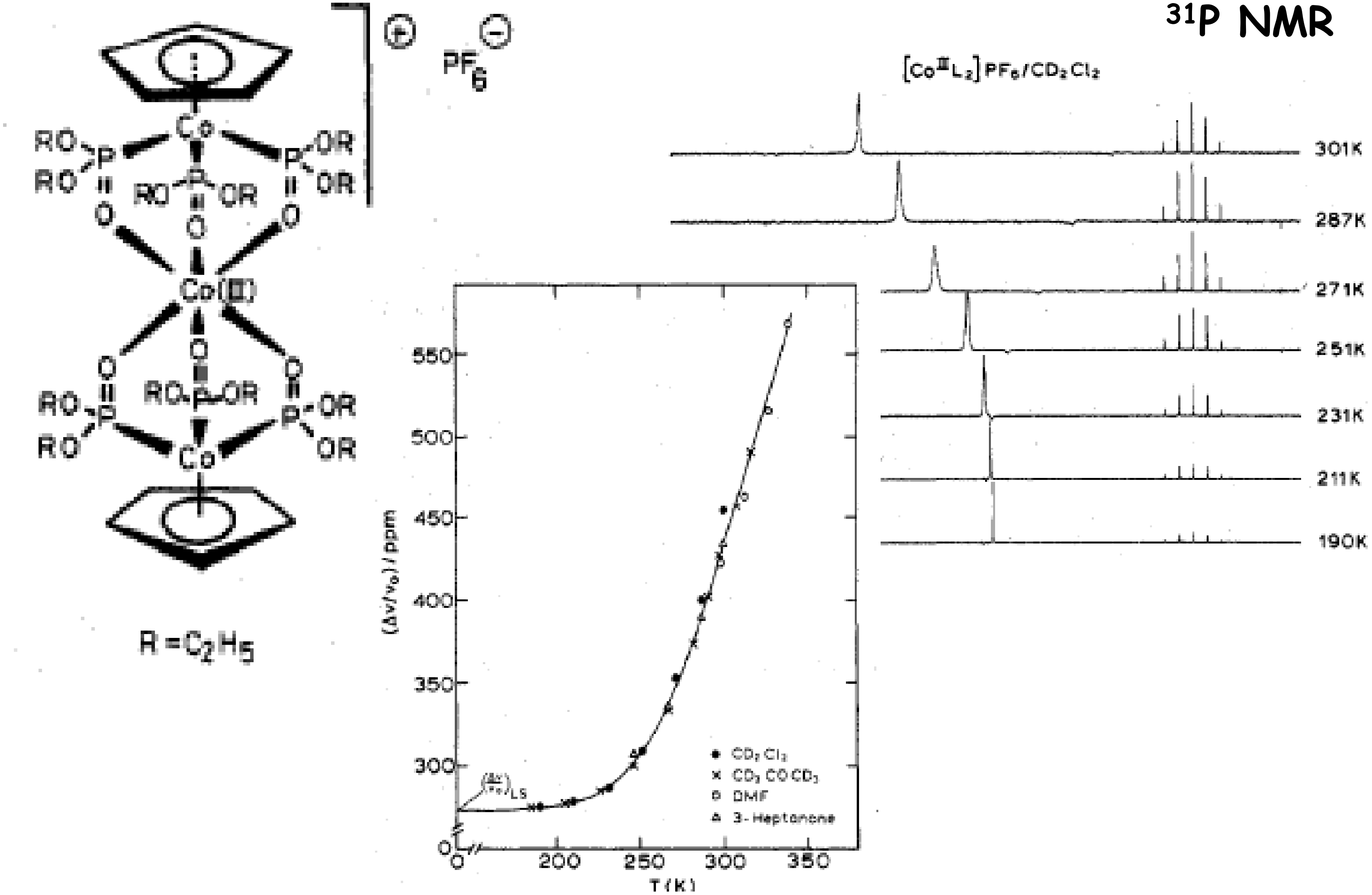




König, Madeja *Chem. Commun.* **1966**, 61-62.

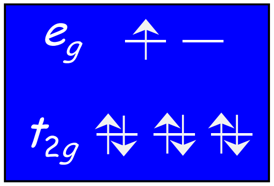
Spin Crossover in Complexes of d^6 Metal Ions

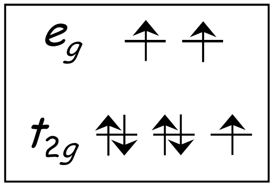
^{31}P NMR



Gütlich, P.; McGarvey, B. R.; Kläui, W. *Inorg. Chem.* **1980**, *19*, 3704-3706.

Spin Crossover in Complexes of d^7 Metal Ions



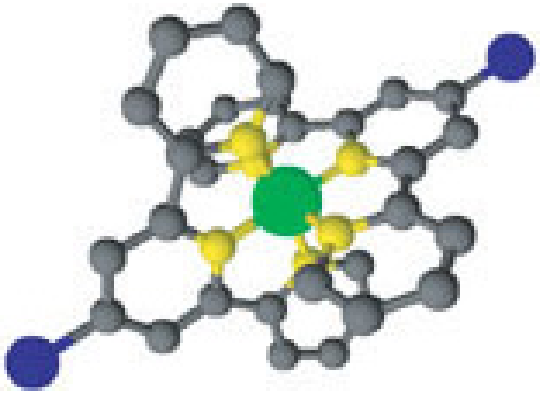


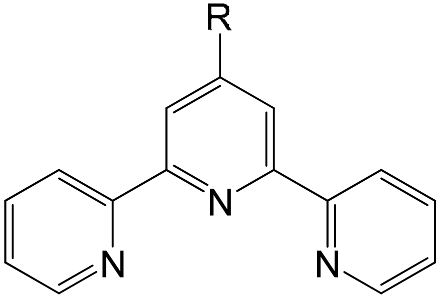
LS, S = 1/2 HS, S = 3/2

Co(II), Ni(III)

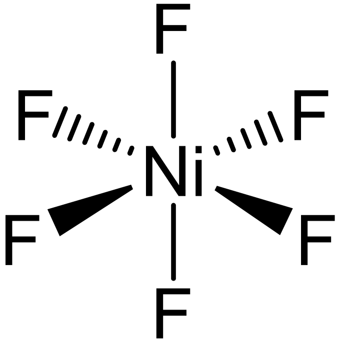
$[Co(terpy)_2]X_2$

X = Cl^-, Br^-, etc.





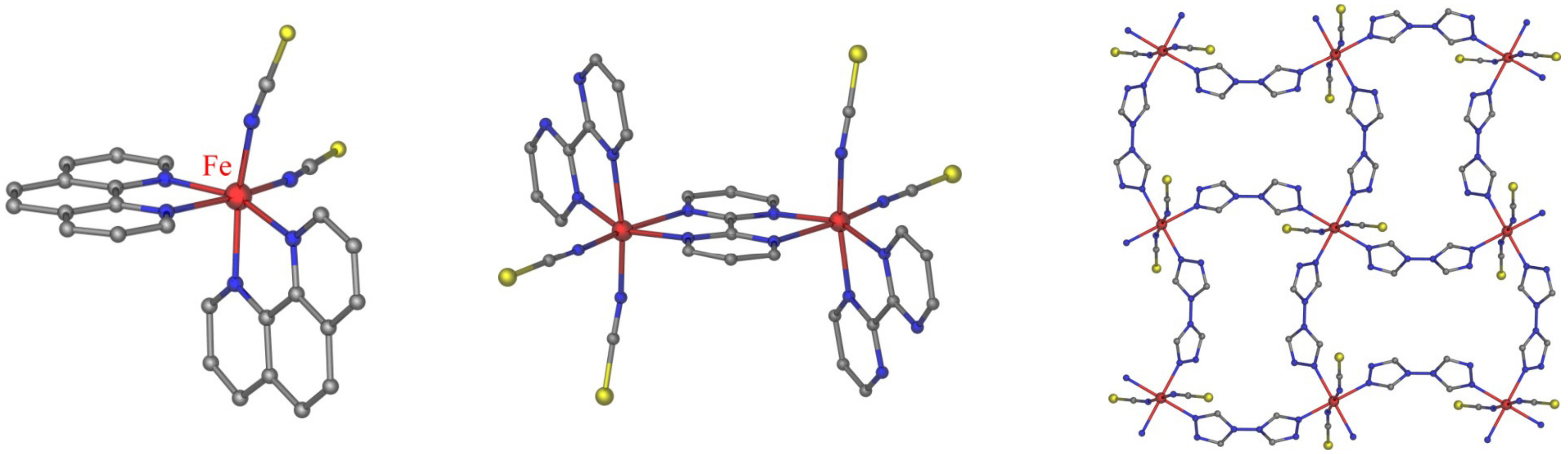
$[NiF_6]^{3-}$



Goodwin, H. A. *Top. Curr. Chem.* **2004**, *234*, 23-47.

Reinen, D.; Friebel, C.; Propach, V. *Z. Anorg. Allg. Chem.* **1974**, *408*, 187.

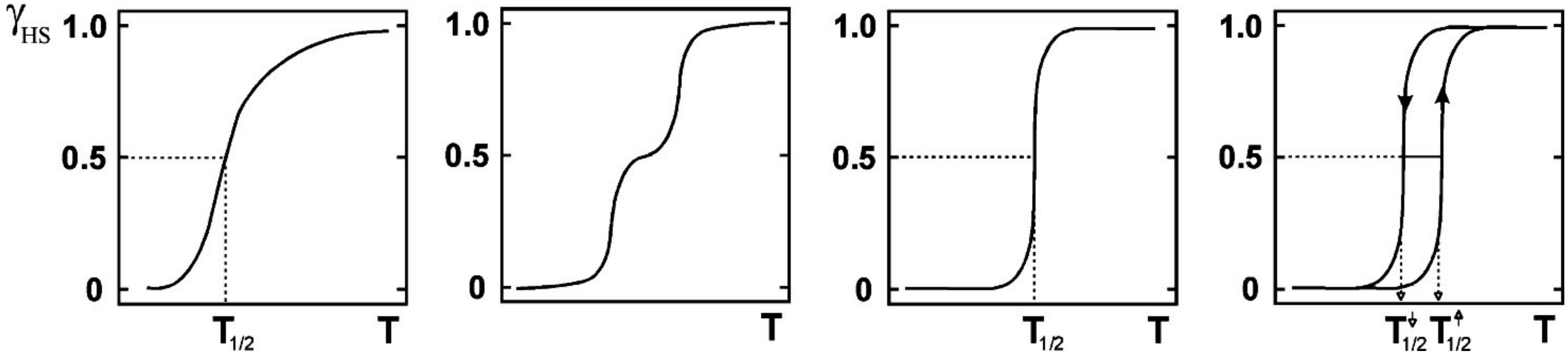
Classification of SCO Compounds by Nuclearity



Mono- and Binuclear Complexes

Extended 1D, 2D, and 3D structures

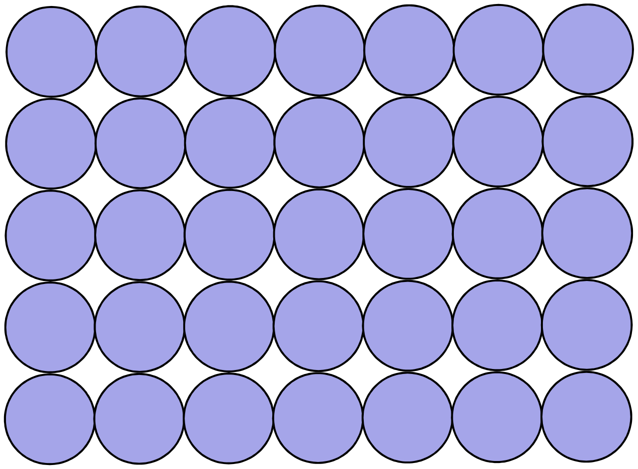
(Usually) higher cooperativity of the spin transition



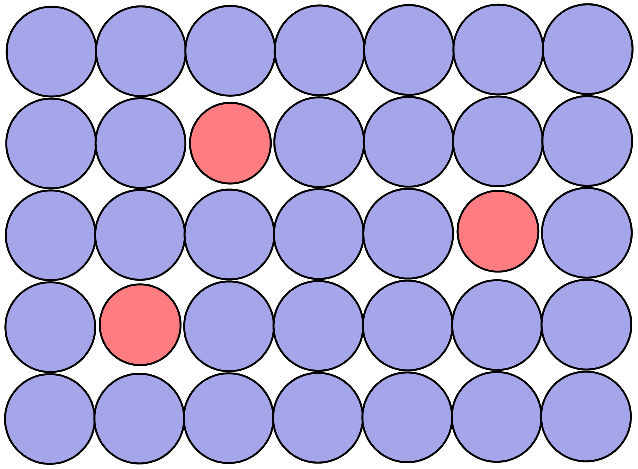
Gütlich, P.; Goodwin, H. A. *Top. Curr. Chem.* **2004**, *234*, 1-47.

Cooperativity of the Spin Transition

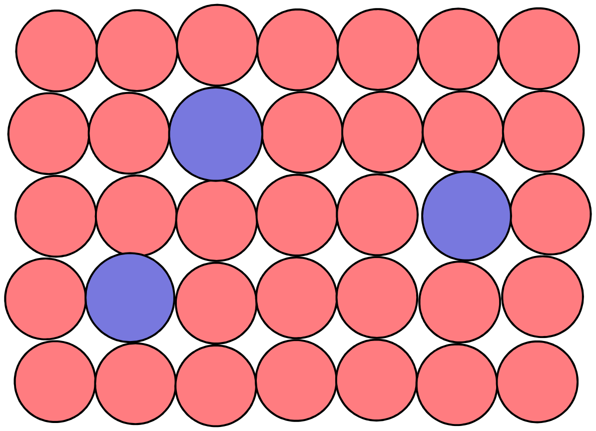
HS Latice



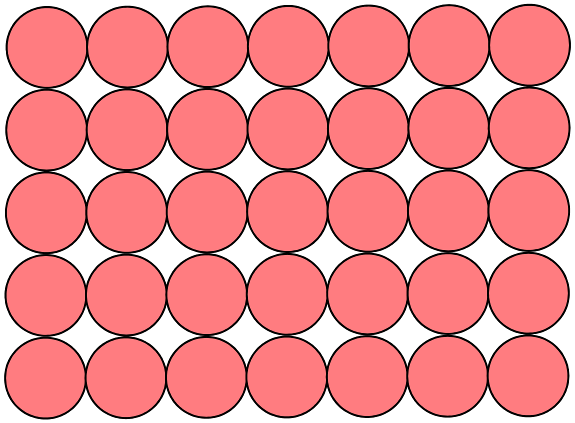
LS in the HS Latice



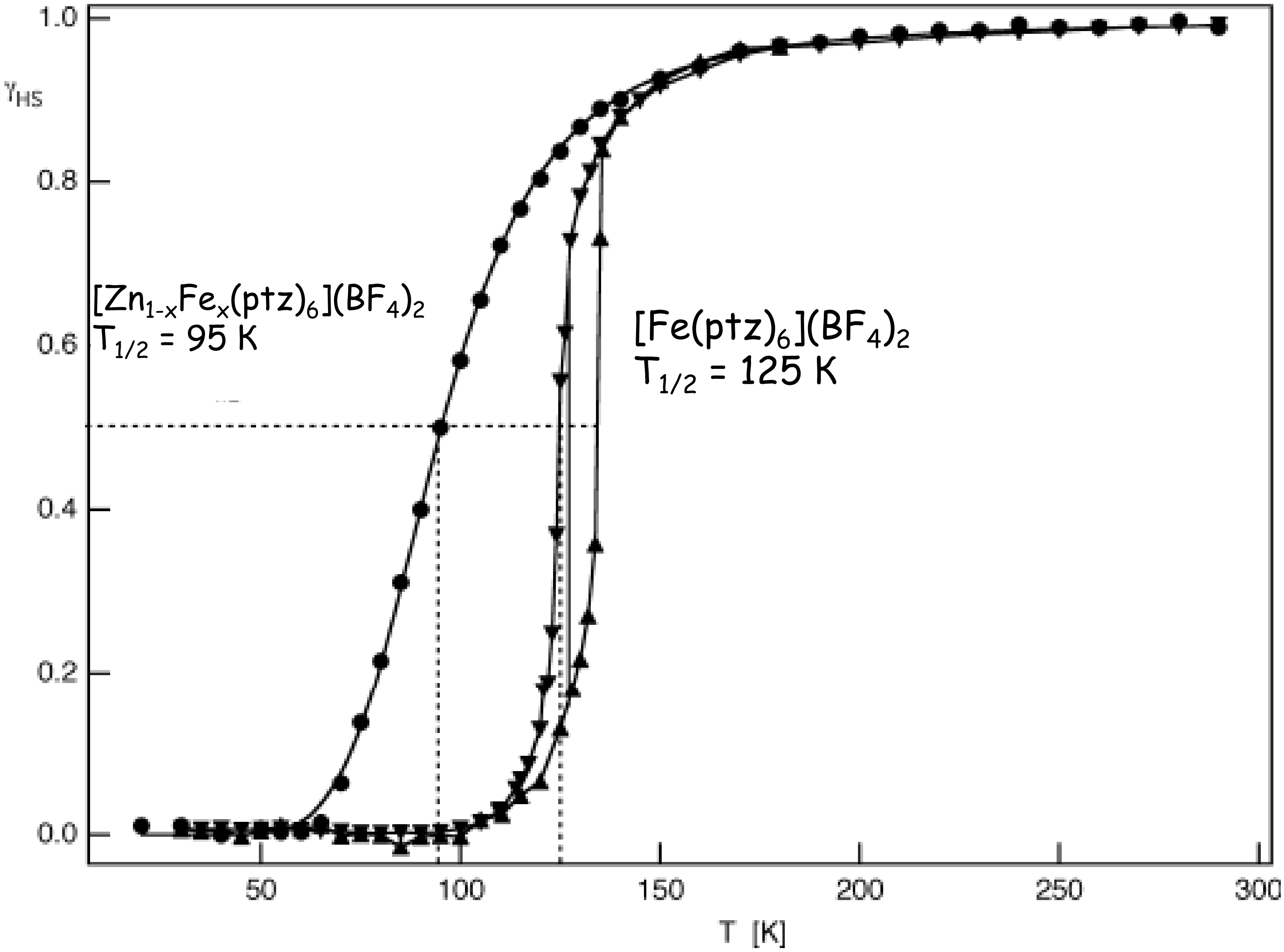
HS in the LS Latice



LS Latice



Cooperativity of the Spin Transition



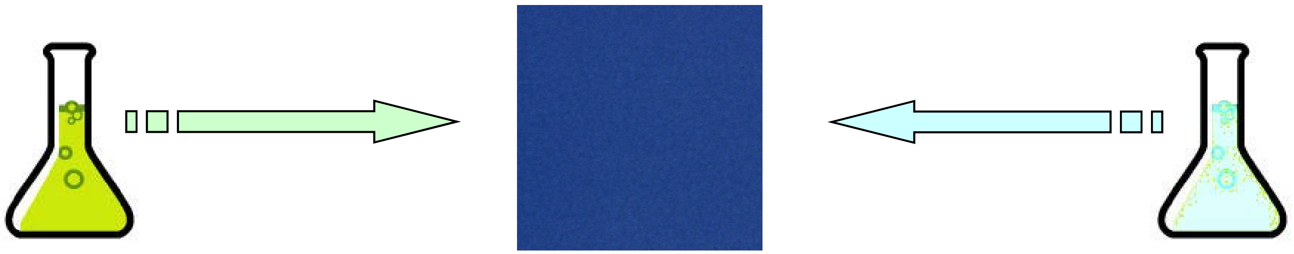
$[Zn_{1-x}Fe_x(ptz)_6](BF_4)_2$
$T_{1/2}$ = 95 K

$[Fe(ptz)_6](BF_4)_2$
$T_{1/2}$ = 125 K

Hauser, A.; Gütlich, P.; Spiering, H. *Inorg. Chem.* **1986**, *25*, 4245.

Prussian Blue – The First Synthetic Coordination Compound

Diesbach and Dippel (Berlin, 1703)



Green vitriol
($FeSO_4$)

Prussian Blue

Potash
(K_2CO_3)

[+ox blood]

$Fe_4[Fe(CN)_6]_3 \cdot n\,H_2O$

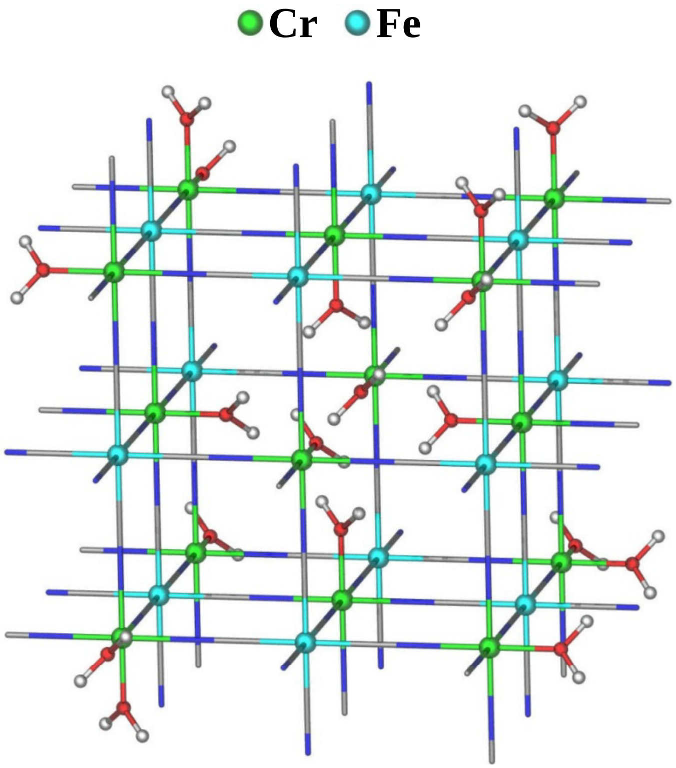
- Blue industrial pigment
- Blue paint (Picasso's blue period)

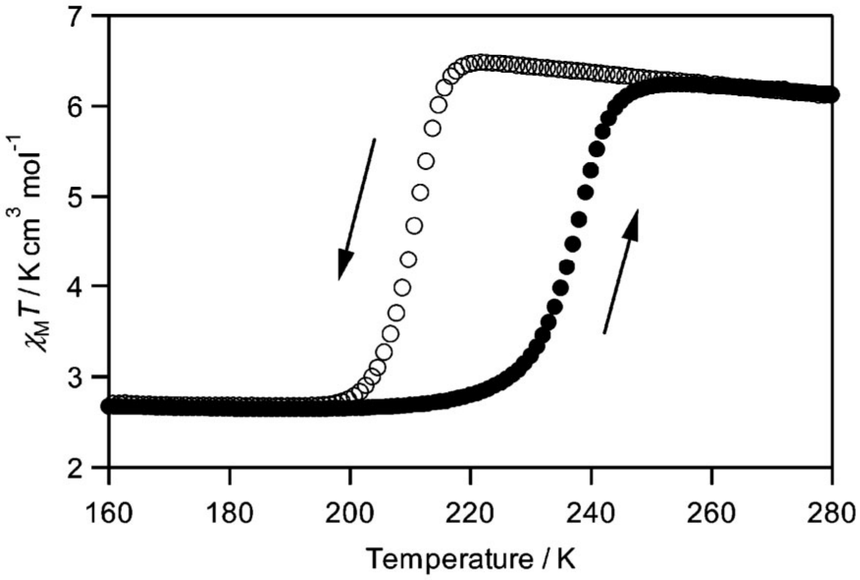
Woodward, M. D. *Philos. Trans.* **1724**, *33*, 15-17.
Brown, J. *Philos. Trans.* **1724**, *33*, 17-24.
http://www.artchive.com/artchive/P/picasso_blue.html

SCO in Prussian Blue Analogues

$Cs\{Fe^{II}[Cr^{III}(CN)_6]\} \cdot x\,H_2O$ – Fe^{II}–N≡C–Cr^{III} (isomer):

- abrupt SCO due to increased cooperativity
- thermal hysteresis (ΔT = 27 K)

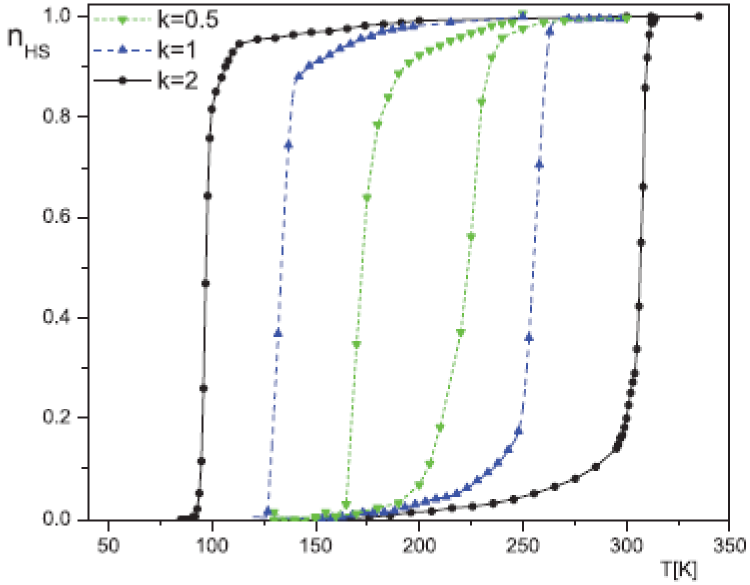




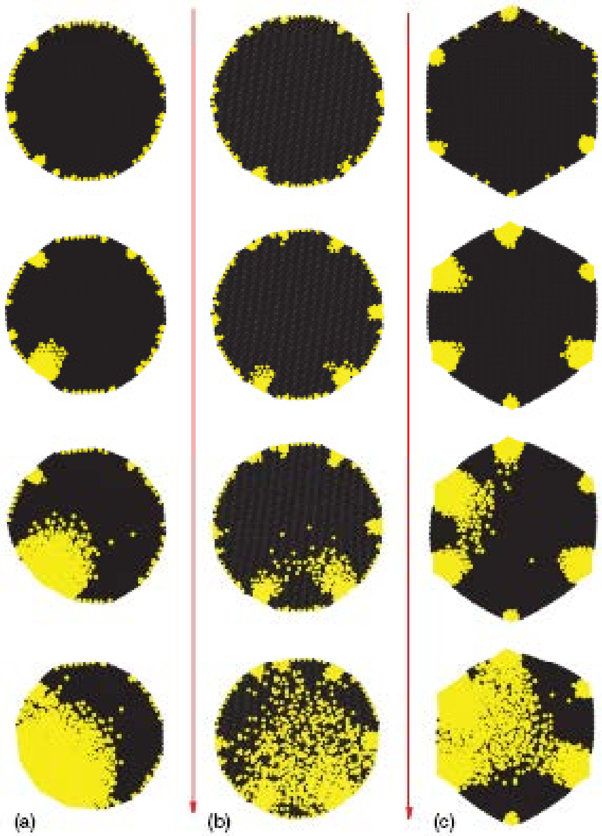
Kosaka, W.; Nomura, K.; Hashimoto, K.; Shin-ichi, O.
J. Am. Chem. Soc. **2005**, *127*, 8590

Cooperativity of the Spin Transition

Fixed ligand field,
variable cooperativity

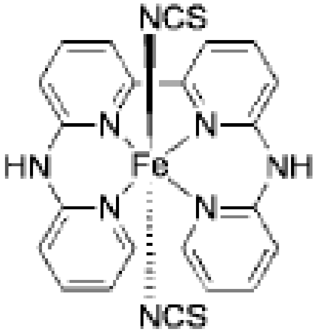


Propagation of SCO
(Monte Carlo simulation)



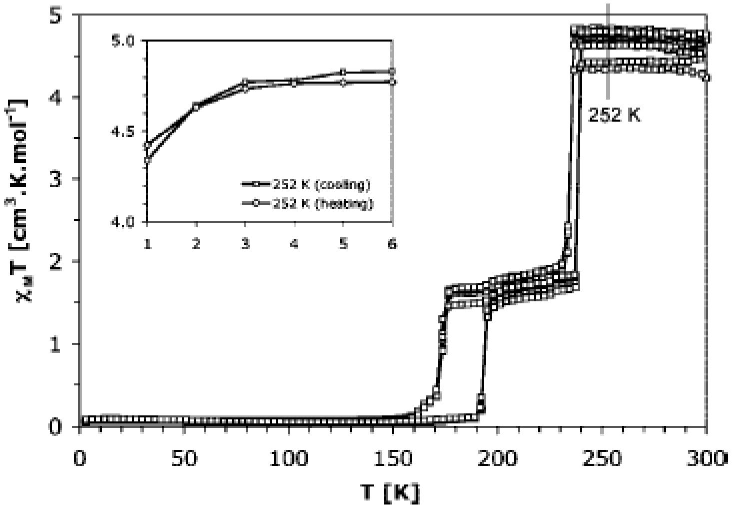
Enachescu, C.; Nishino, M.; Miyashita, S.; Stoleriu, L.; Stancu, A. *Phys. Rev. B* **2012**, *86*, 054114

Cooperativity of the Spin Transition



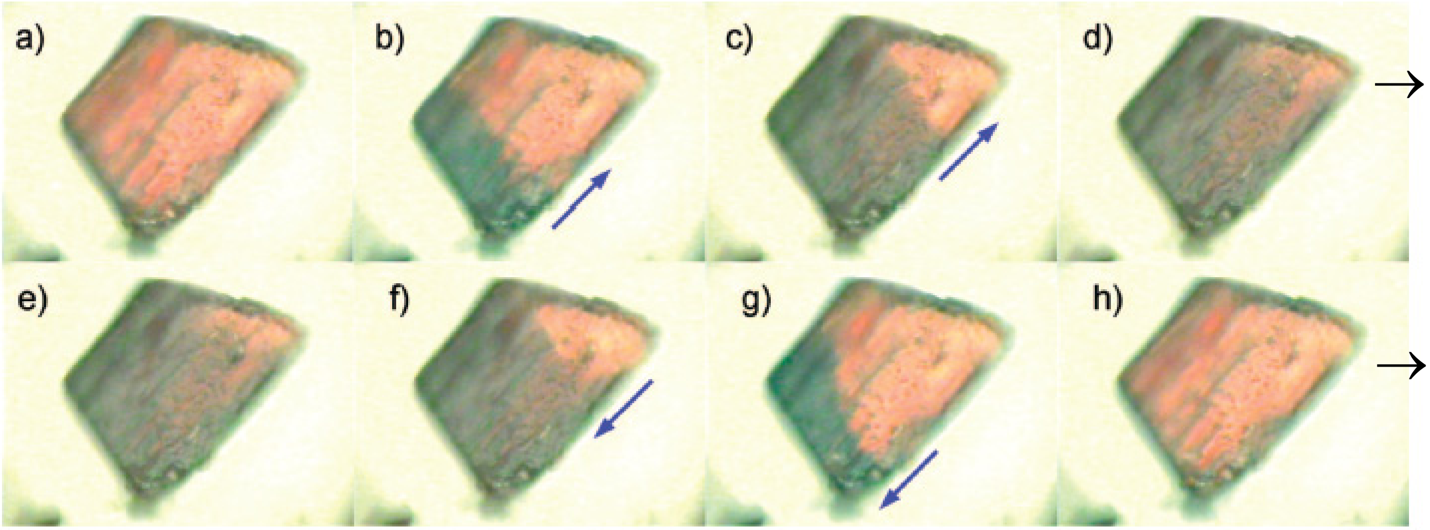
1
trans-[Fe(bapbpy)(NCS)$_2$]

Two-step SCO



253 K → → 243 K

243 K → → 253 K



Reedijk, J. et al. *Chem. Mater.* **2009**, *21*, 1123.

Spin Crossover Under Pressure

- Under applied external pressure, the LS state is stabilized with respect to the HS state
- $\Delta d(\text{Fe-L})_{LS \rightarrow HS} \sim 0.1$ Å for Fe(III)
  0.2 Å for Fe(II)

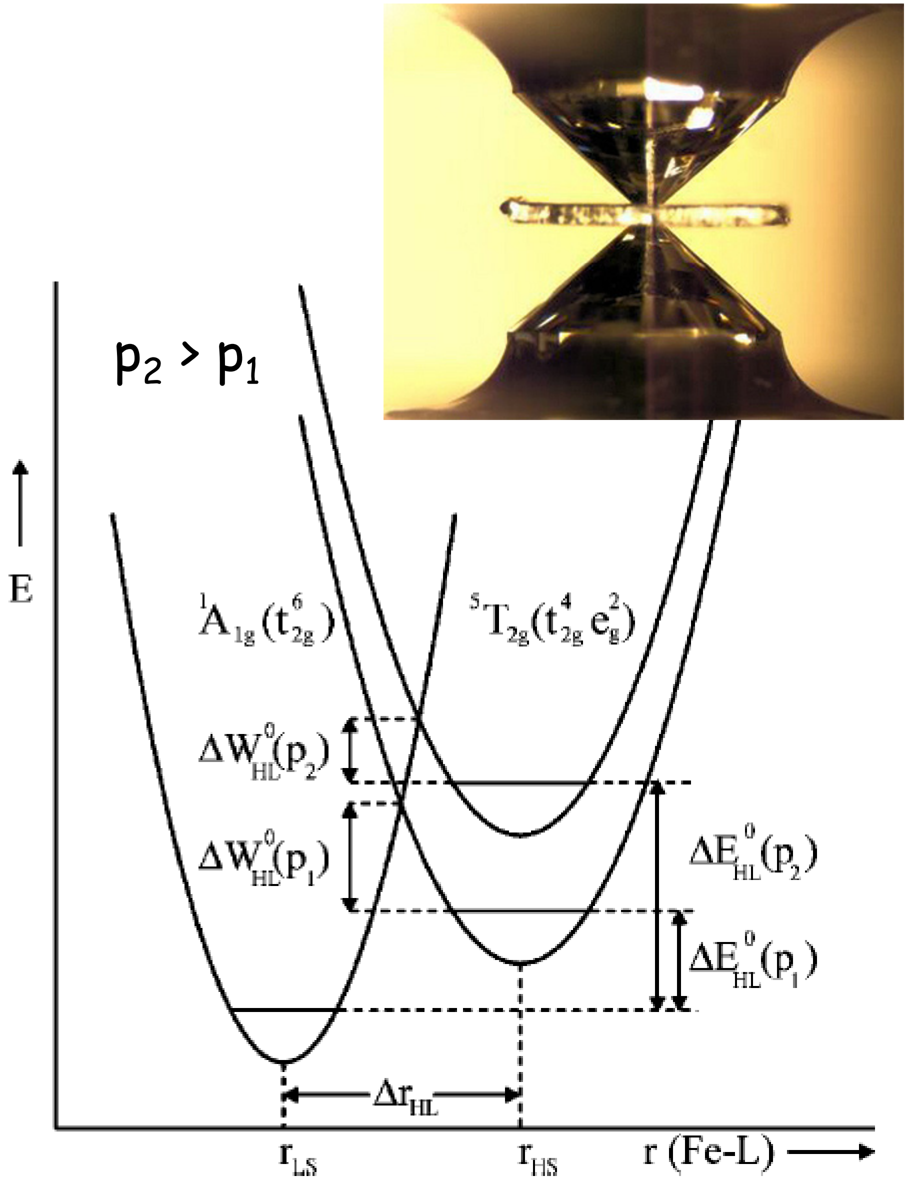
- Experimental conditions:

✓ Hydrostatic presure is preferred, in order to avoid defect formation and shear dislocations

✓ Pressure-transmitting fluid:
He, Ar, or mineral oil

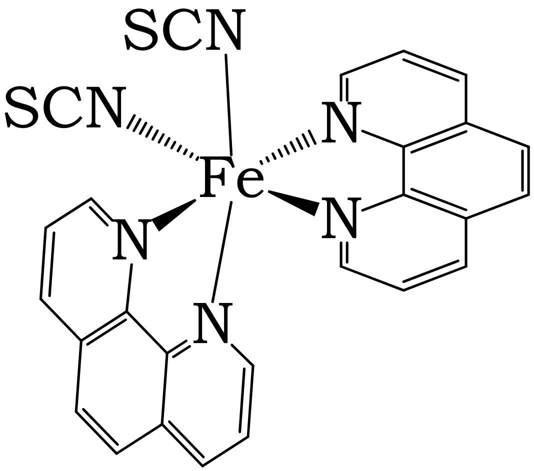
✓ Below 1 GPa: clamp cells
Above 1 GPa: diamond anvil cells

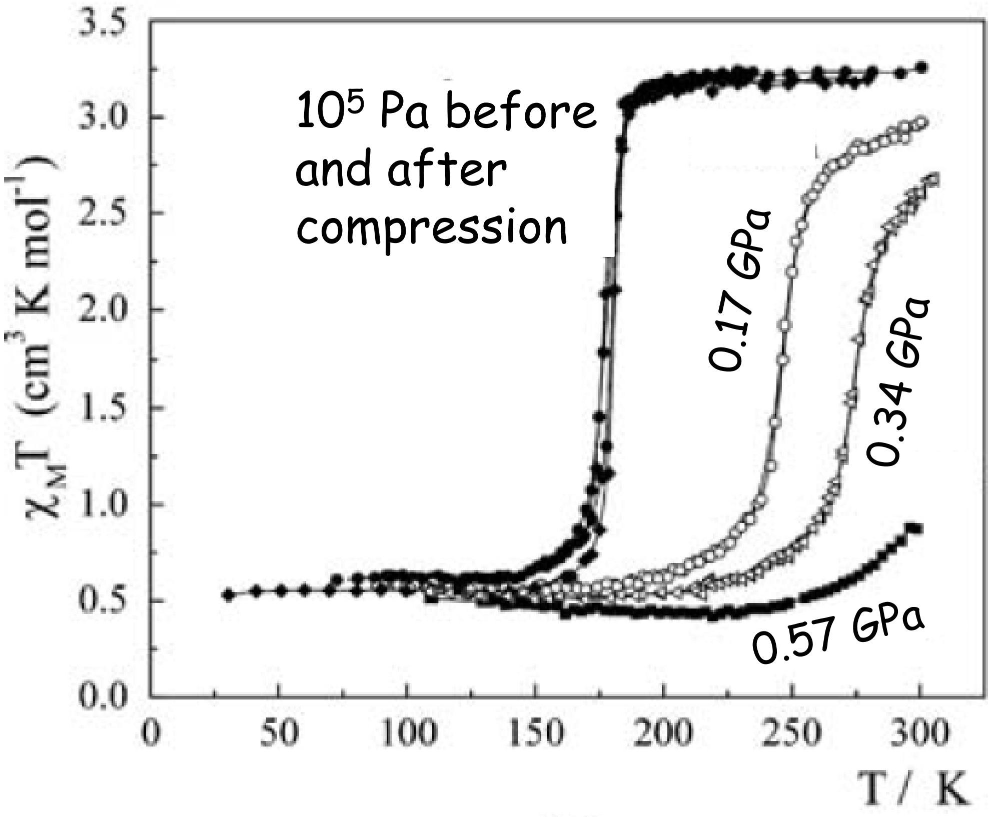
✓ 1 GPa = 10 kbar ~ 10,000 atm



Gütlich, P.; Ksenofontov V.; Gaspar, A. B. *Coord. Chem. Rev.* **2005**, *249*, 1811.

SCO Under Pressure: $Fe(phen)_2(NCS)_2$

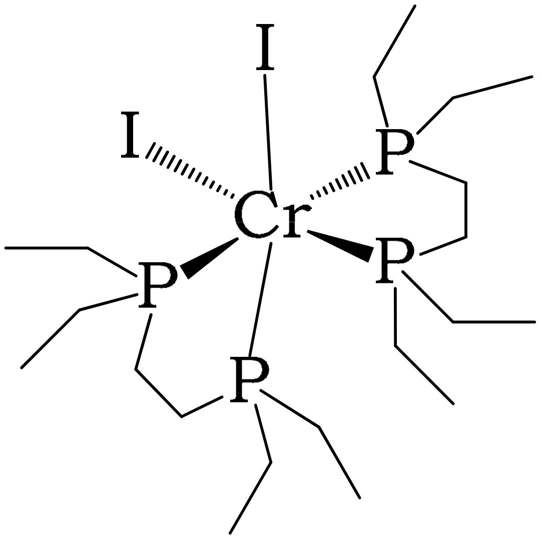


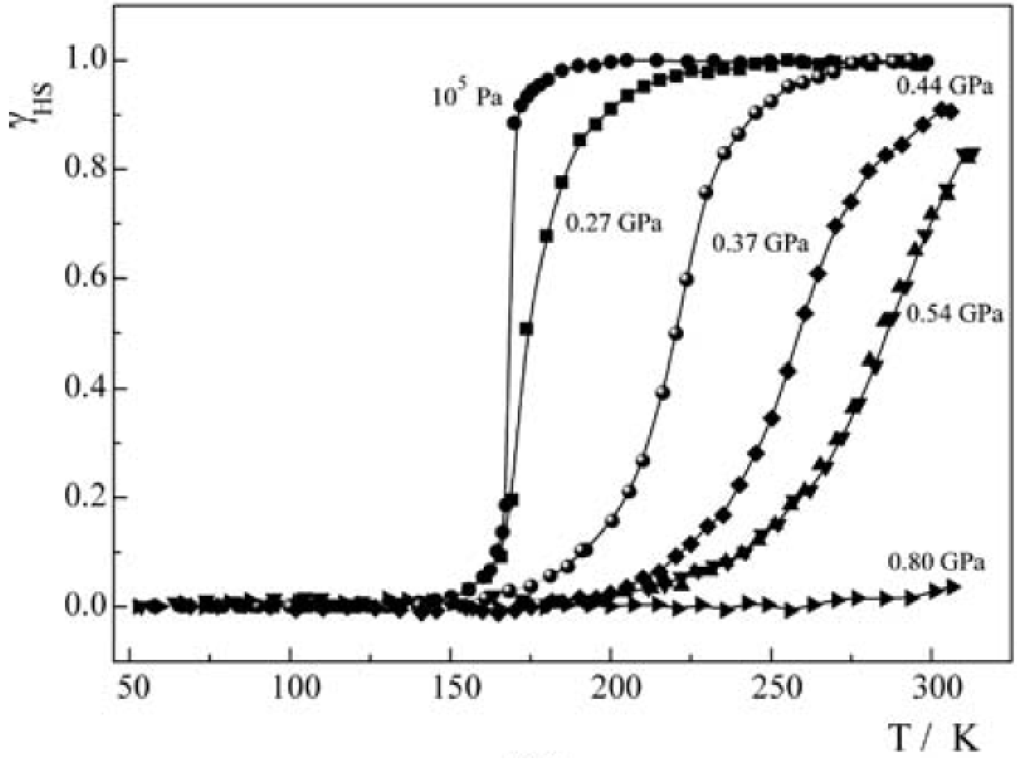


- Under increasing pressure, the spin transition is shifted to higher temperatures
- The transition broadens because of increasing defect concentration under pressure

Gütlich, P.; Gaspar, A. B.; Ksenofontov V.; Garcia, Y. *J. Phys. Cond. Matter* **2004**, *16*, 1.

SCO Under Pressure: $\mathrm{Cr(depe)_2I_2}$

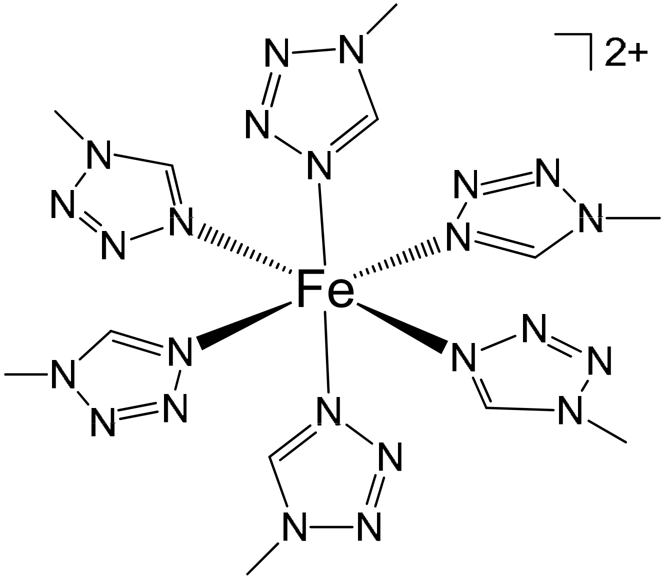


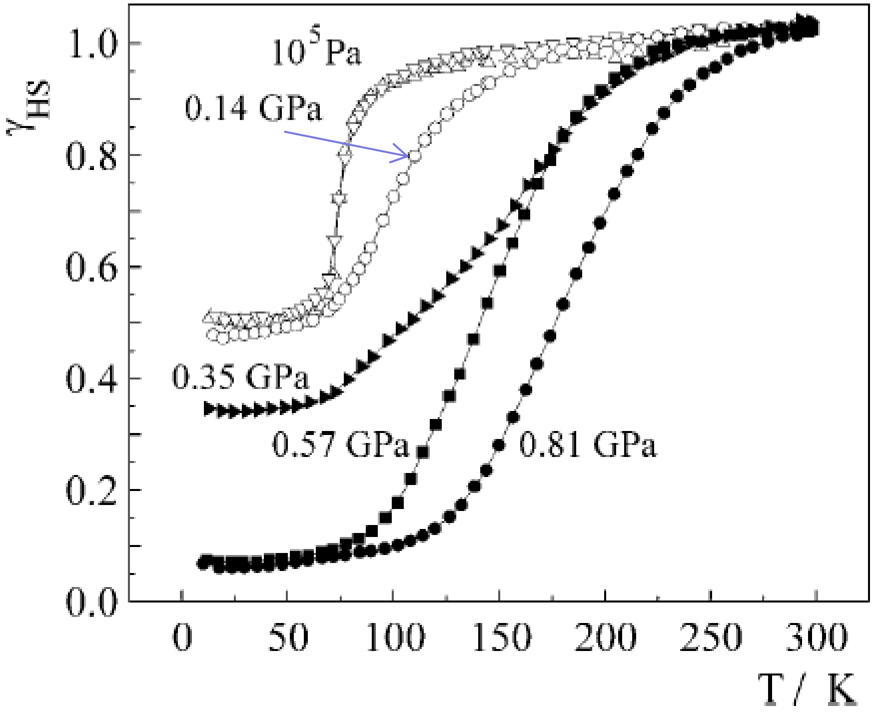


- At low pressures, the effect is small, but the changes become much more pronounced at p > 0.3 GPa
- The initial "delay" is caused by high compressibility of I^-
- At 0.80 GPa and above, the complex exists only in the LS state

Gütlich, P.; Gaspar, A. B.; Ksenofontov V.; Garcia, Y. *J. Phys. Cond. Matter* **2004**, *16*, 1.

SCO Under Pressure: $[Fe(mtz)_6](BF_4)_2$



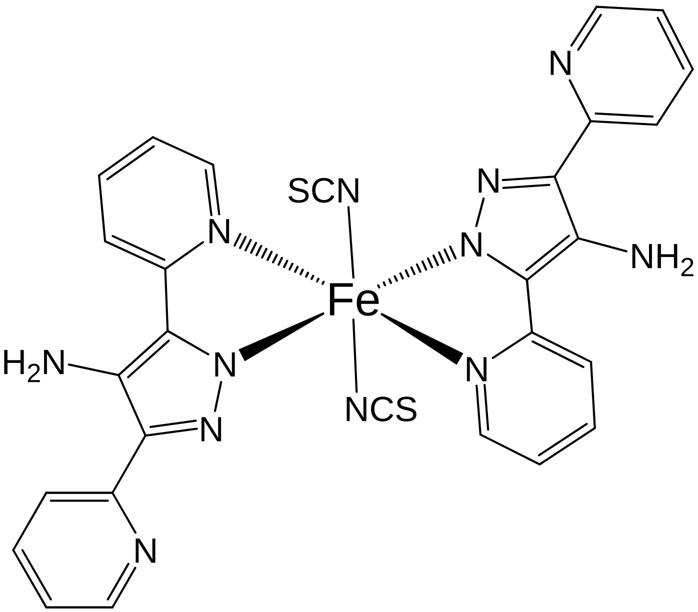


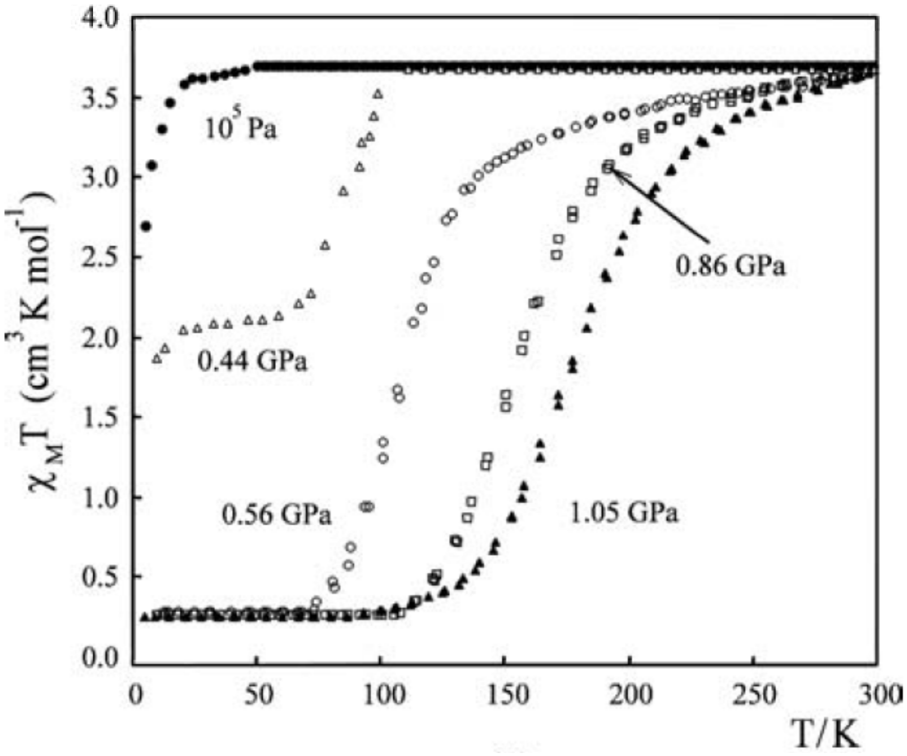
- Under ambient pressure:

  The extent of the HS→LS transition is only 50%, because there are two inequivalent Fe(II) sites in the crystal structure
- Above 0.57 GPa, the complete SCO is observed

Hinek, R.; Gütlich, P.; Hauser, A. *Inorg. Chem.* **1994**, *33*, 567-572.

SCO Under Pressure: $Fe(abpt)_2(NCS)_2$





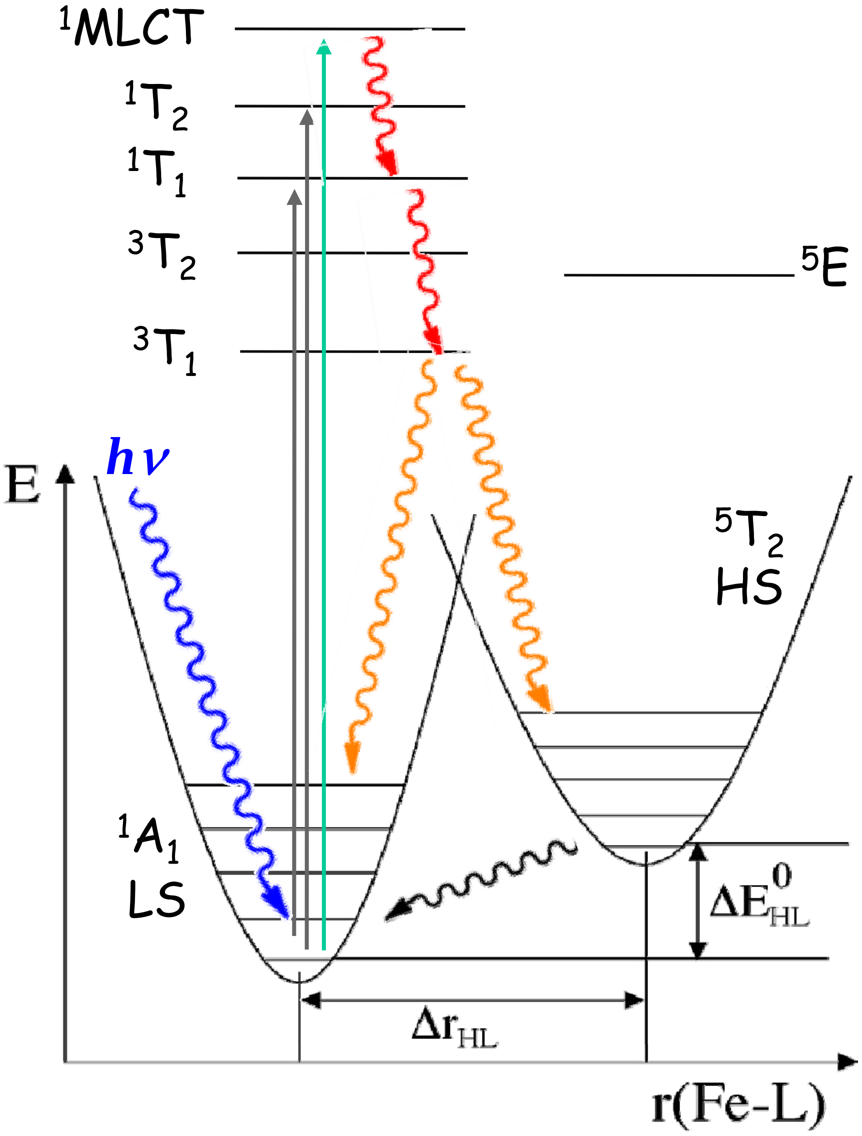
- Under ambient pressure, this complex exists only in the HS state
- Applied pressure causes SCO

- The incomplete SCO at low pressures is explained by the slow kinetics that result in the “frozen” HS→LS equilibrium.

Gaspar, A. B.; Muñoz, M. C.; Moliner, N.; Ksenofontov, V.; Levchenko, G.; Gütlich, P.; Real, J. A. *Monats. Chem.* **2003**, *134*, 285.

Photoinduced SCO (LIESST)

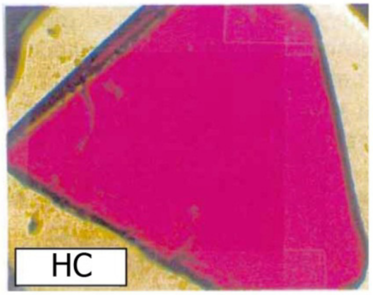
- Irradiation into characteristic absorption bands of the LS state results in photoinduced population of the metastable HS state.
- This phenomenon is known as Light-Induced Excited Spin State Trapping, or **LIESST**

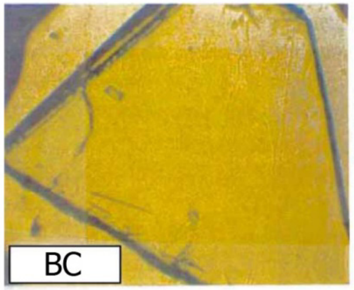


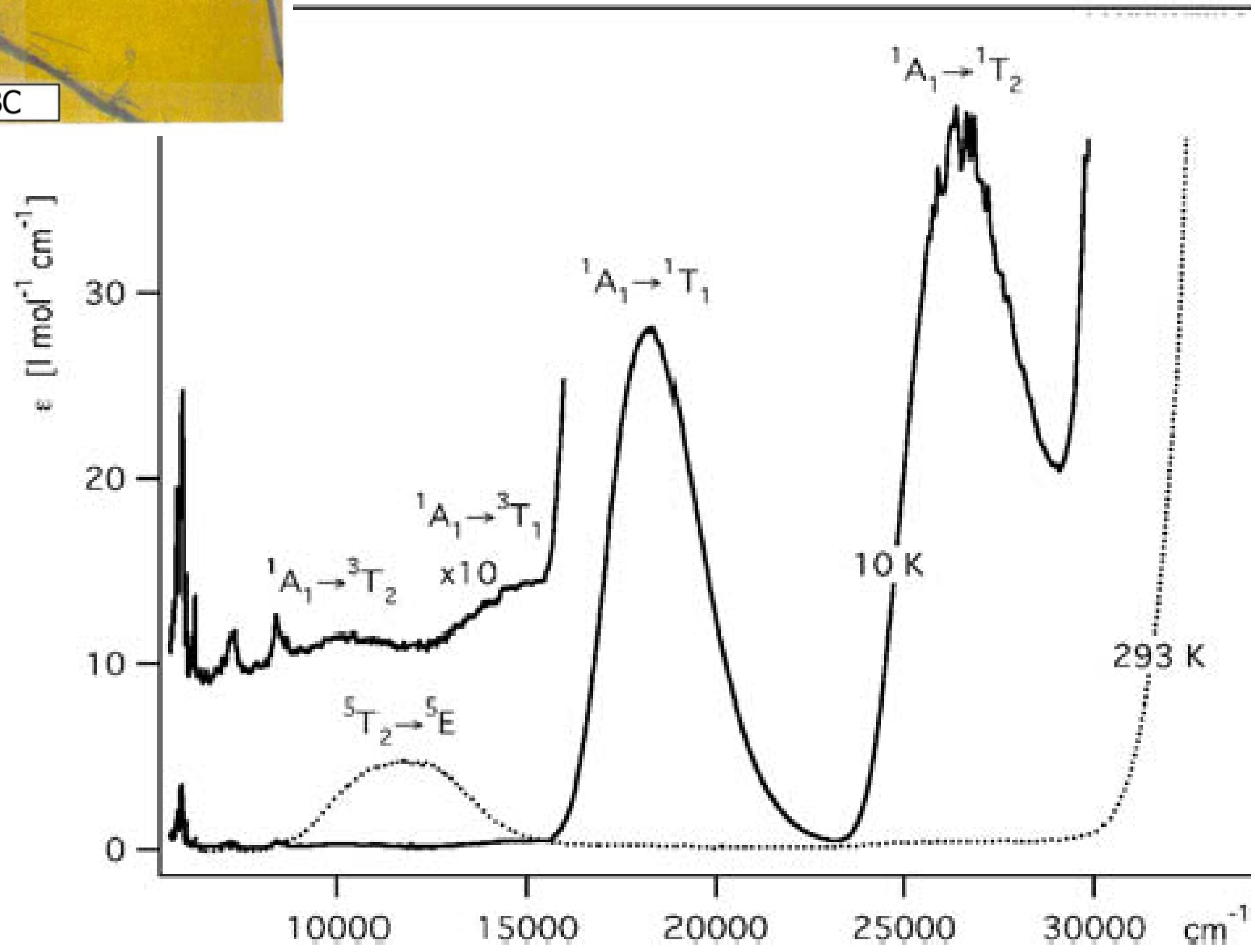
Hauser, A. *Top. Curr. Chem.* **2004**, *234*, 155-198.

LIESST: The First Observation

$[Fe(ptz)_6](BF_4)_2$







Ground States:

- LS = $^1A_1$
- HS = $^5T_2$

Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543.

LIESST: The First Observation

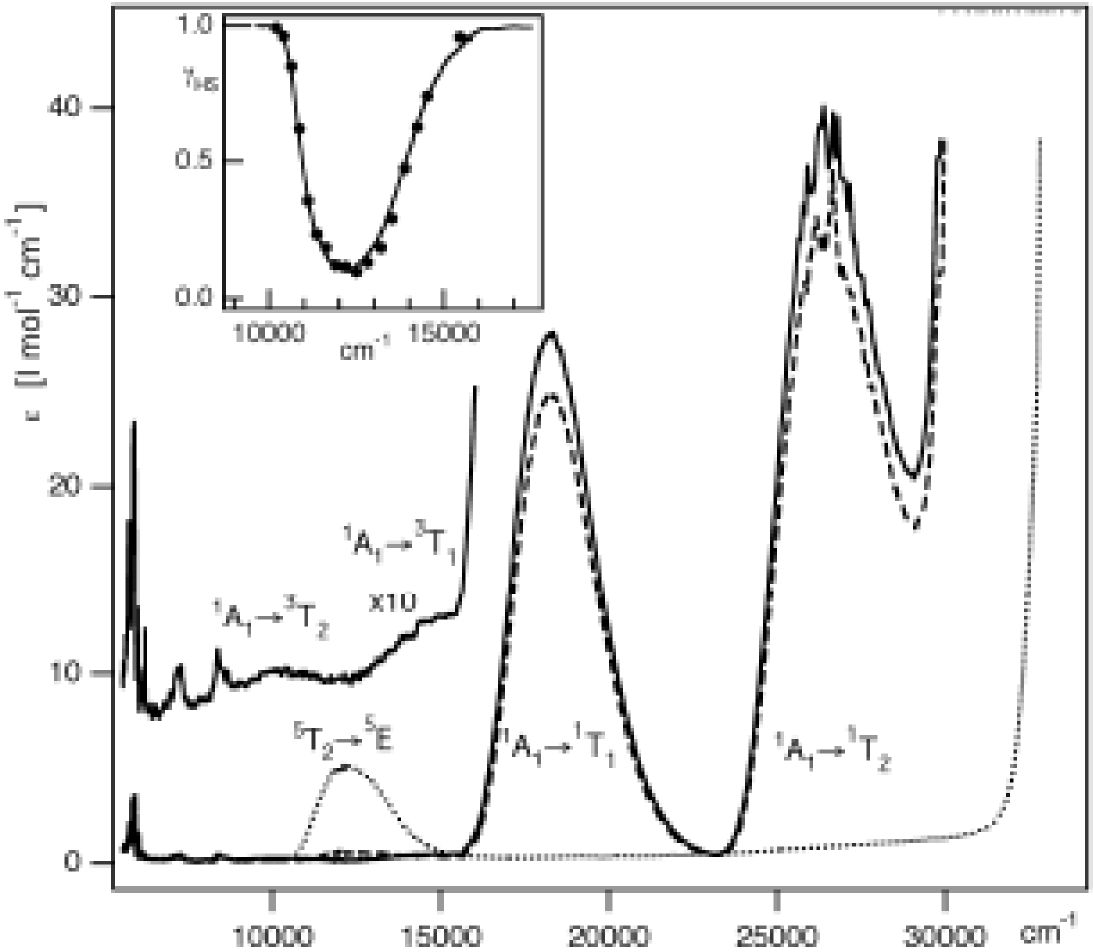
$[Fe(ptz)_6](BF_4)_2$

Three spectra at 10 K:

— after slow cooling from 300 K to 10 K, the complex is in the LS state

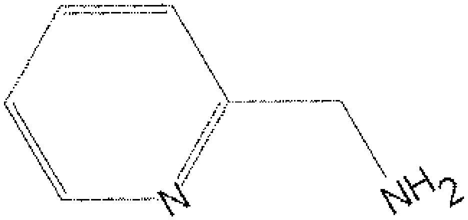
···· irradiation with λ = 515 nm at 10 K causes spin transition (LIESST) into the metastable HS state

--- irradiation with λ =830 nm at 10 K causes a reverse spin transition (RLIESST) into the ground LS state



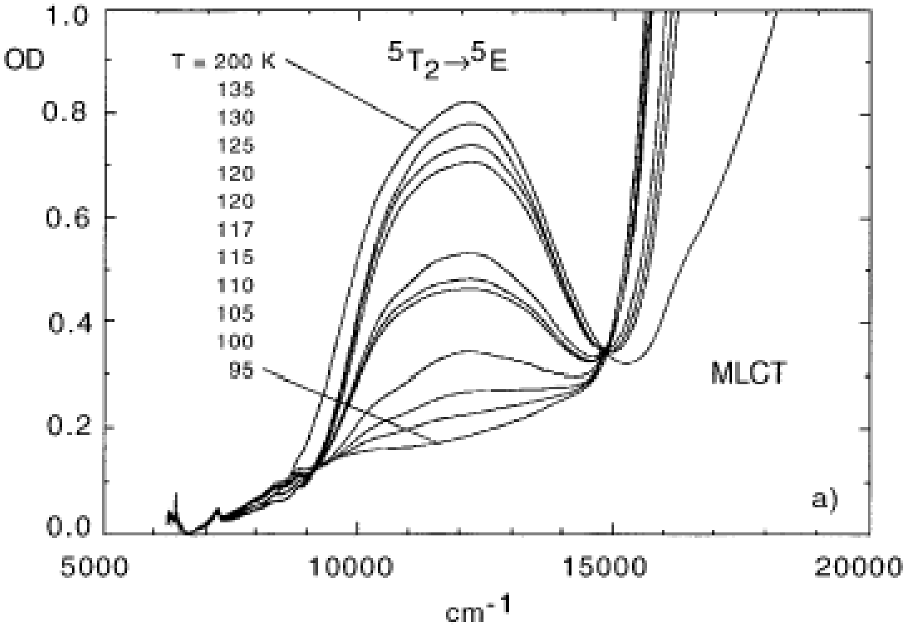
Hauser, A. *Chem. Phys. Lett.* **1986**, *124*, 543.

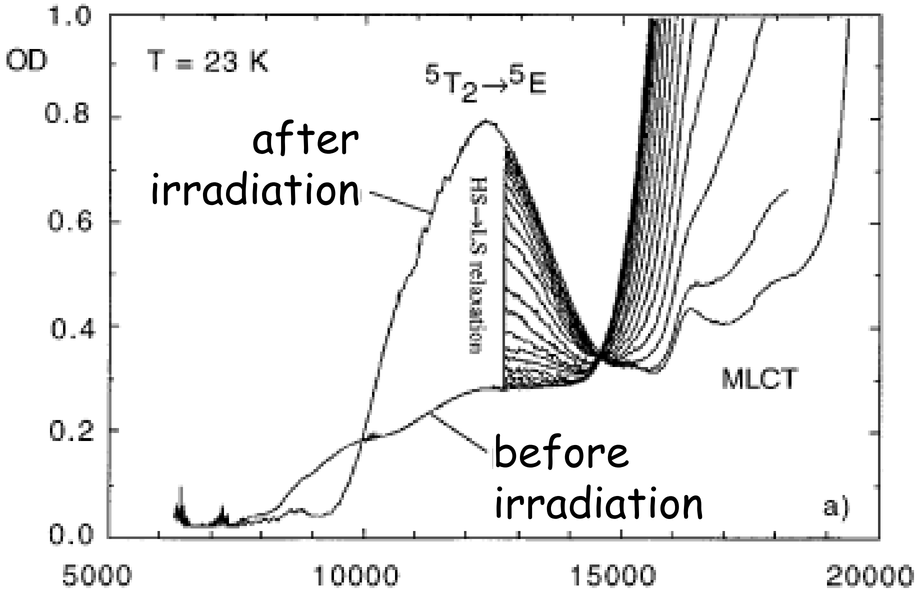
LIESST: Stability of Crystals



$[Fe(pic)_3]Cl_2$

- Crystals of this compound are converted into fine powder under irradiation at 23 K
  (λ = 515 nm)

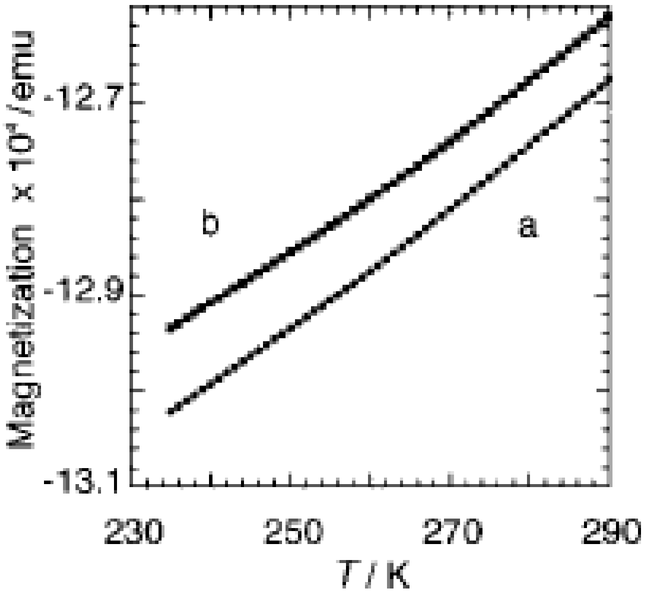

Temperature-dependent spectra

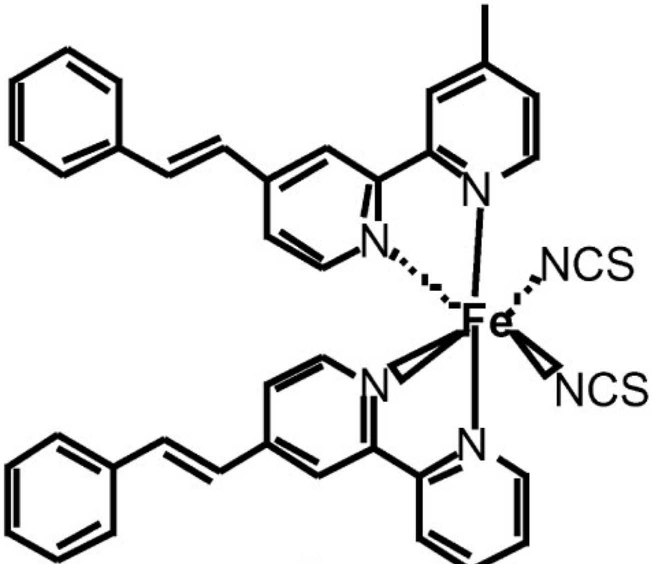

Before and after irradiation at 23 K

Romstedt, H.; Hauser, A.; Spiering, H. *J. Phys. Chem. Solids* **1998**, *59*, 265.
Vef, A.; Manthe, U.; Gütlich, P.; Hauser, A. *J. Chem. Phys.* **1994**, *101*, 9326.

Ligand-Induced SCO

- The LS → HS transition takes place due to the change in the d-orbital splitting when the ligand is photoisomerized
- The advantage of this approach is the possibility to realize the photoinduced transition even at room temperature

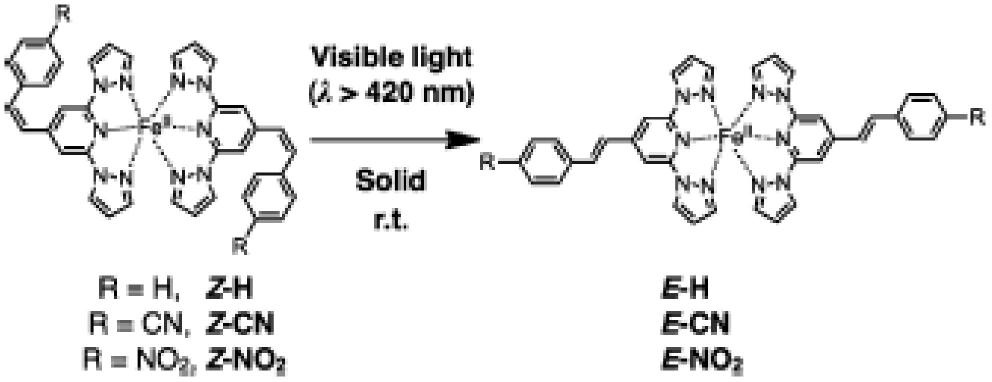


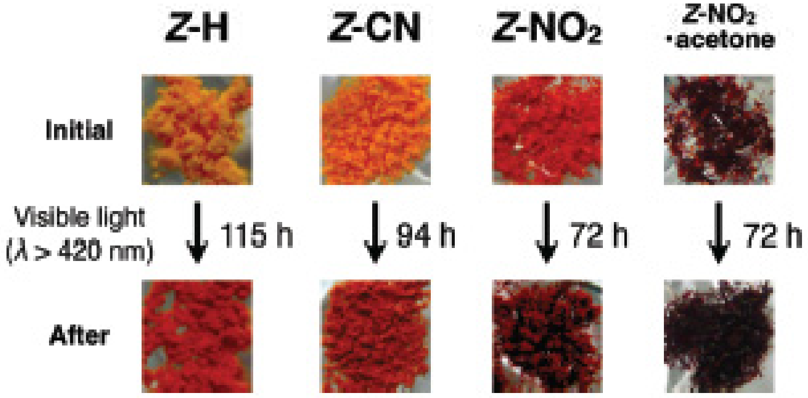


C_t

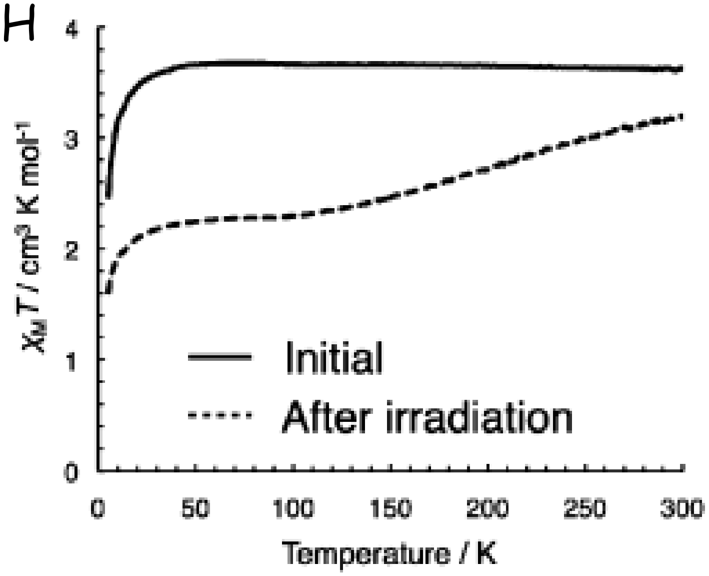
Boillot et al. *New J. Chem.* **1999**, 179-183.

Ligand-Induced SCO

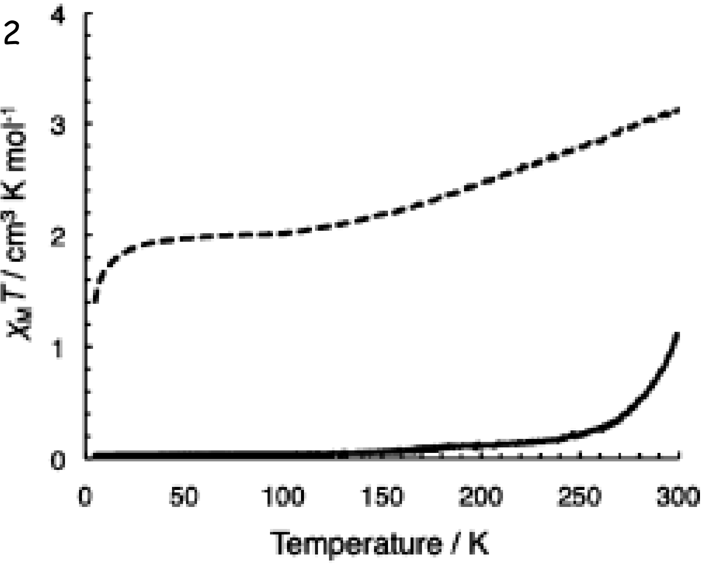




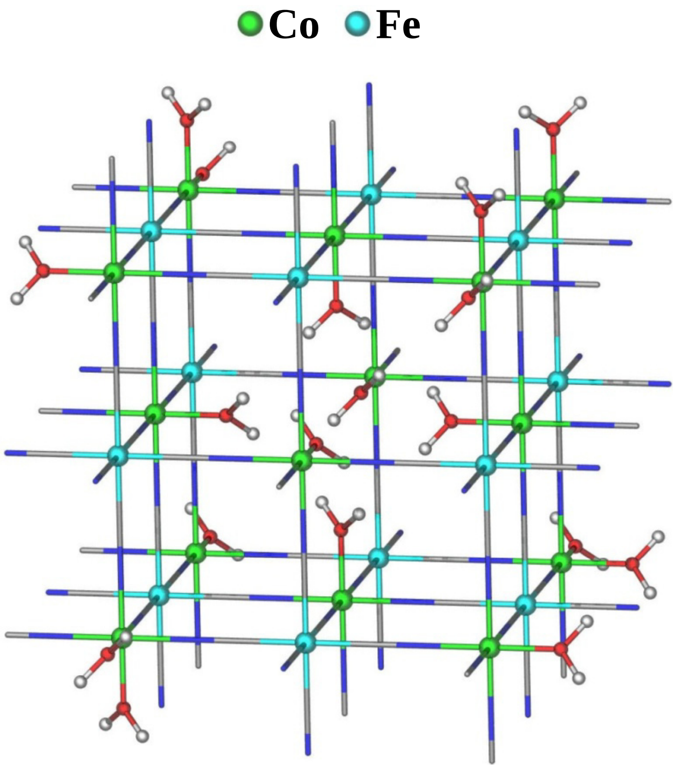
R = H



R = NO_2

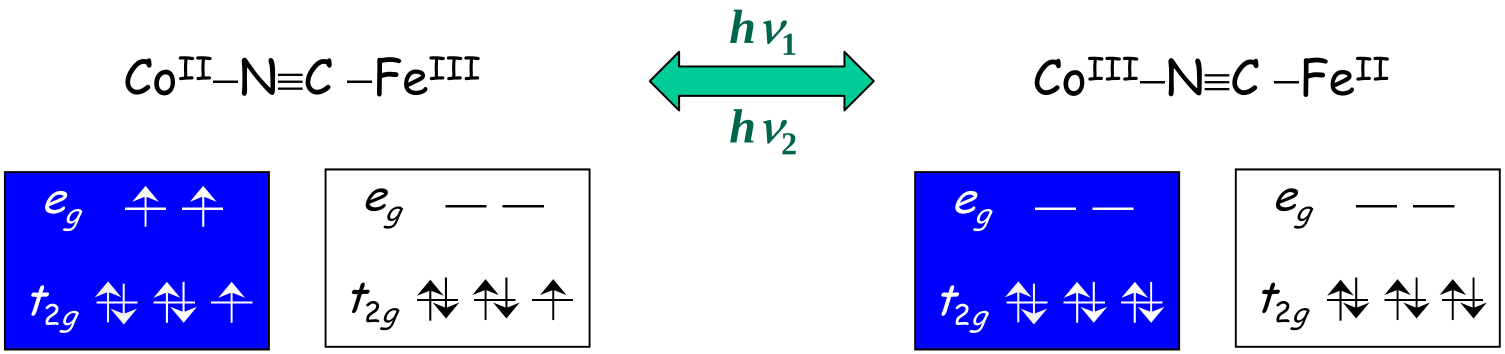


Nishihara, H. et al. *Inorg. Chem.* **2012**, *51*, 5188.



Charge-Transfer Induced Spin Transition (CTIST)

- $A_xCo_{3-x}[Fe(CN)_6]_2 \cdot H_2O$; A = K, Rb
- This is the first famous example of photomagnetic switching in a molecule-based material
- A reversible electron transfer between the Co and Fe centers results in photoswitchable magnetic behavior



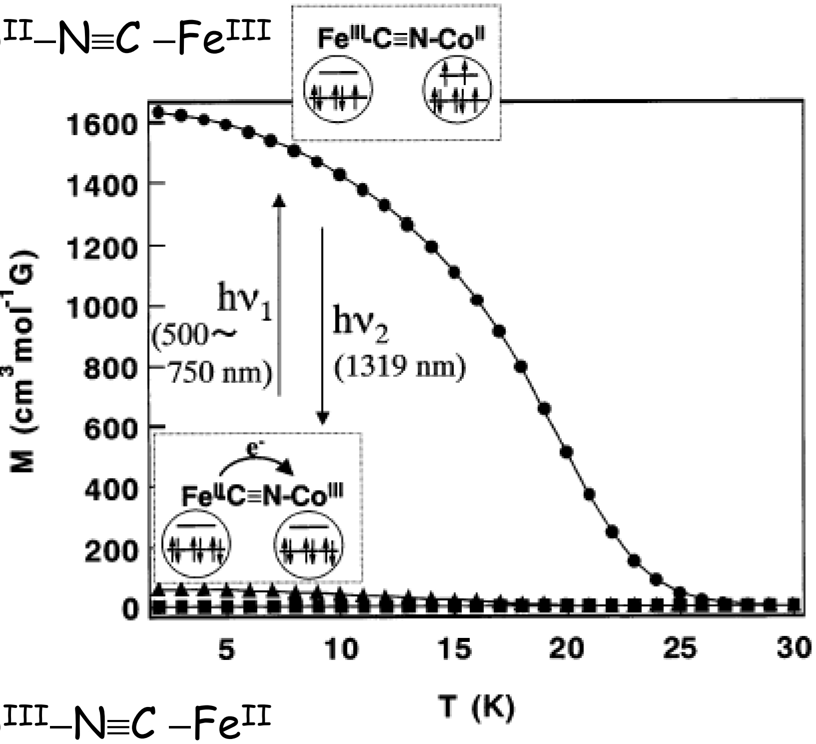
$$Co^{II}–N{\equiv}C–Fe^{III} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} Co^{III}–N{\equiv}C–Fe^{II}$$

HS, $S = 3/2$ LS, $S = 1/2$ LS, $S = 0$ LS, $S = 0$

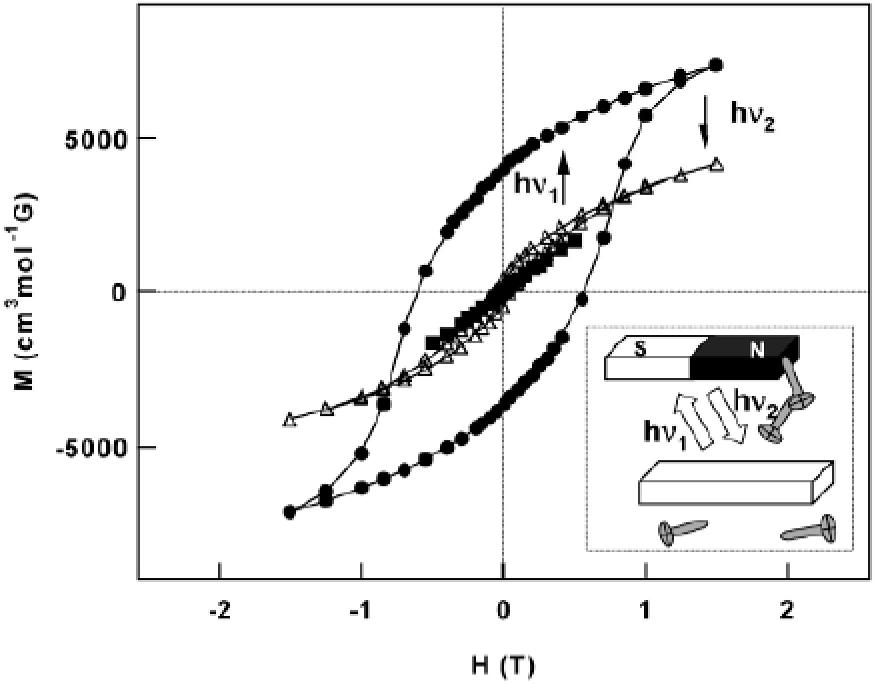
Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704-705.

Photomagnetism in $A_xCo_{3-x}[Fe(CN)_6]_2 \cdot nH_2O$

Co^{II}–N≡C –Fe^{III}

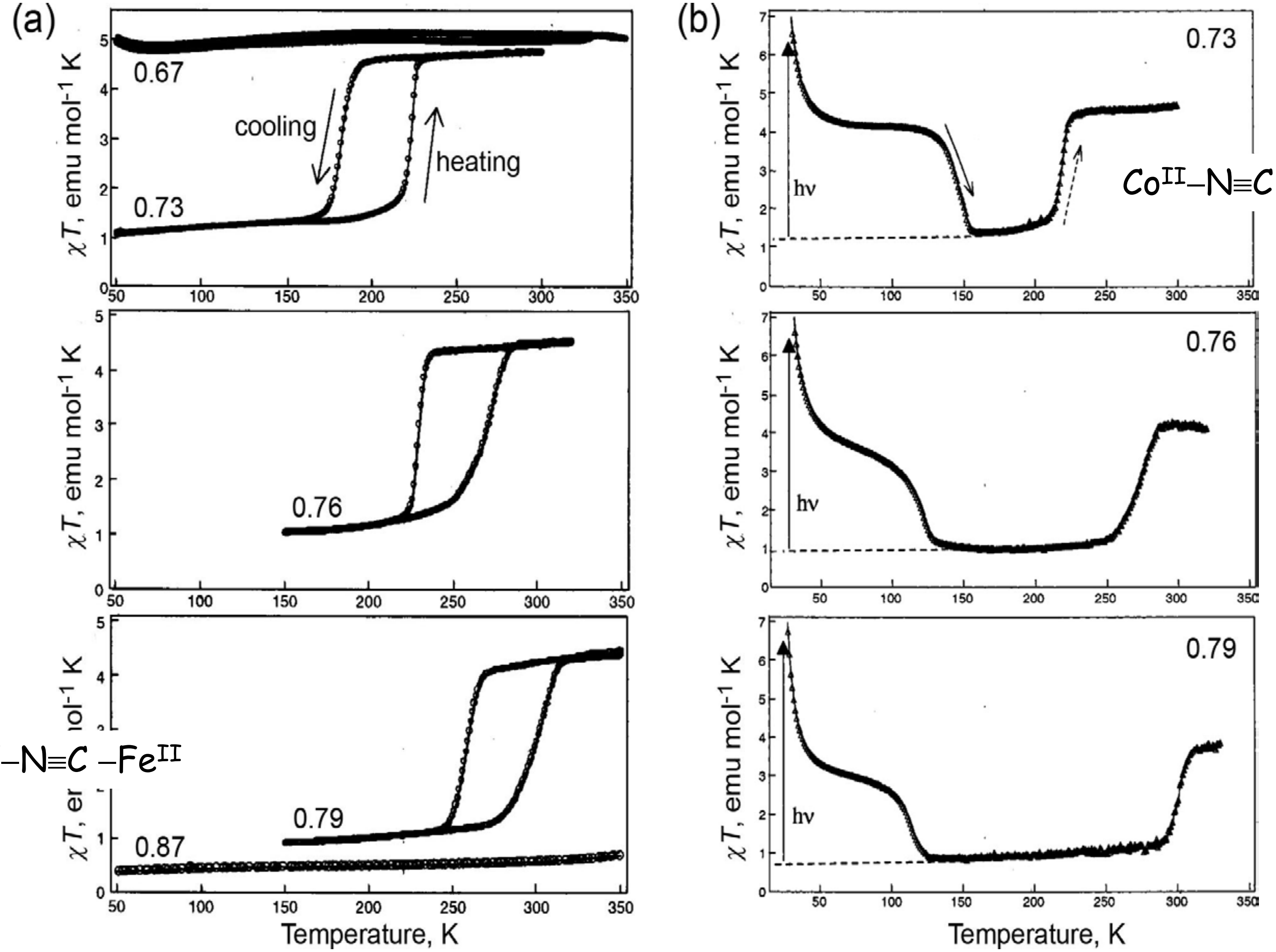


Co^{III}–N≡C –Fe^{II}



Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704-705.

Photomagnetism in $A_xCo_{3-x}[Fe(CN)_6]_2 \cdot nH_2O$



$Co^{II}–N{\equiv}C–Fe^{III}$

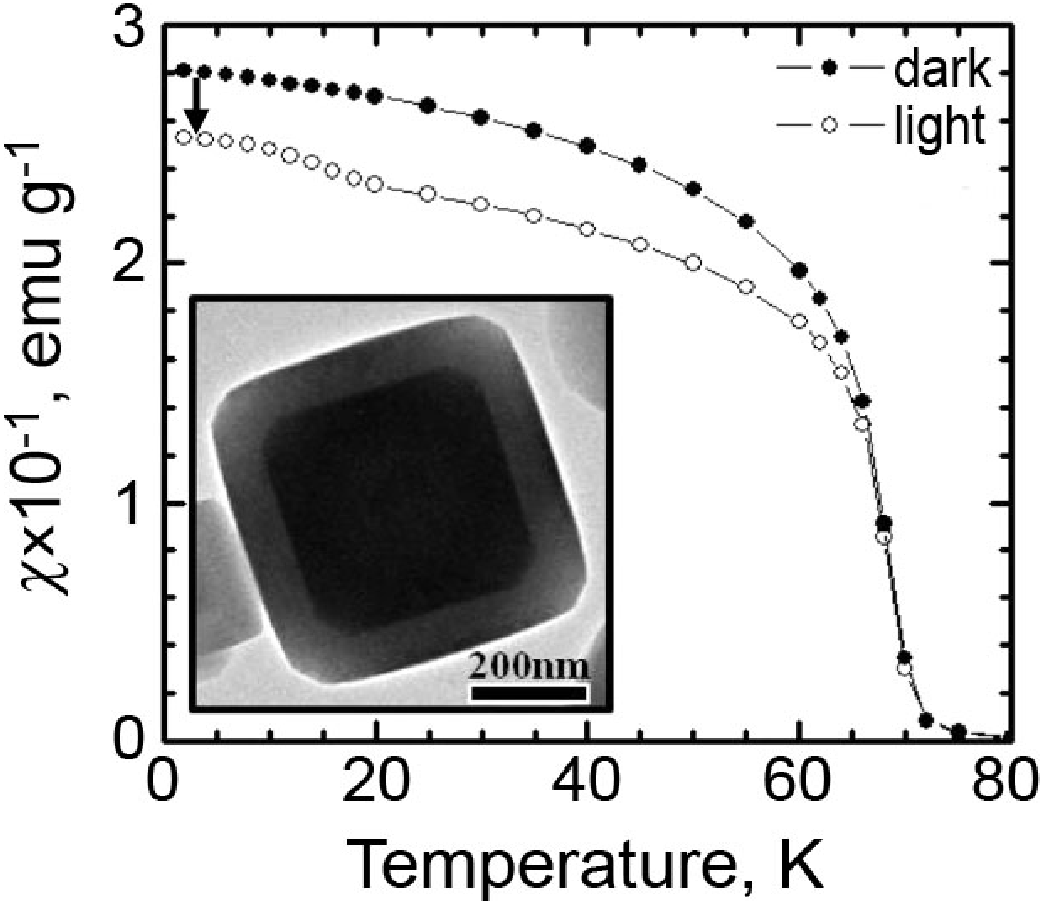
$Co^{III}–N{\equiv}C–Fe^{II}$

Shimamoto, N.; Ohkoshi, S.; Sato, O.; Hashimoto, K. *Inorg. Chem.* **2002**, *41*, 678-684.

SCO in Nanoparticles

$Ni_3[Cr(CN)_6]_2$ - shell

$RbCo[Fe(CN)_6]$ - core



Dumont, M. F.; Knowles, E. S.; Guiet, A.; Pajerowski, D. M.; Gomez, A.; Kycia, S. W.; Meisel, M. W.; Talham, D. R. *Inorg. Chem.* **2011**, *50*, 4295-4300.

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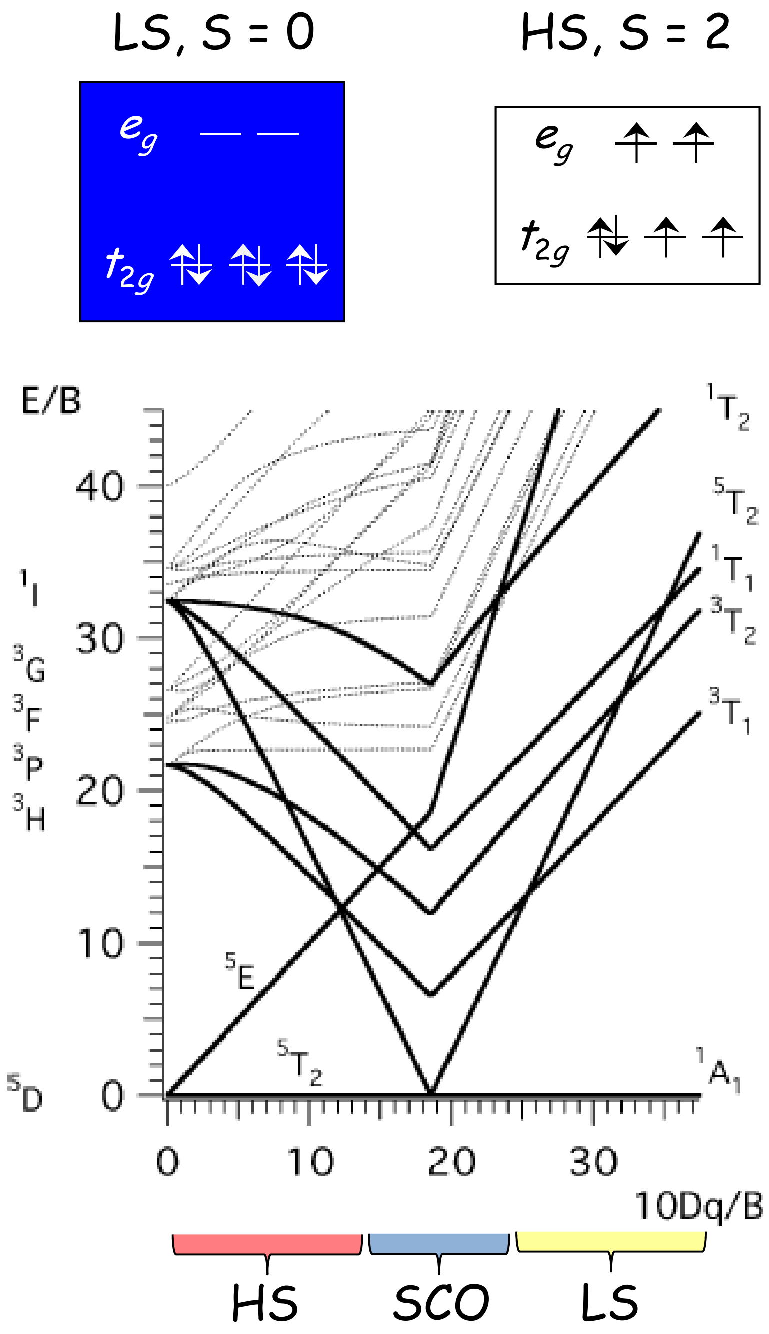

Gütlich, P.; Goodwin, H. A. *Top. Curr. Chem.* **2004**, *233*, 1-47.
Hauser, A. *Top. Curr. Chem.* **2004**, *233*, 49-58.
Hashimoto, K., et al. *Science* **1996**, *272*, 704-705.