

Magnetic interactions in doped "ferric stars"

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Motivation

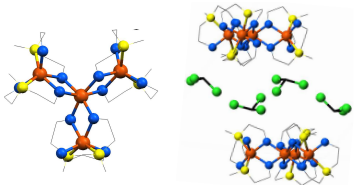
- "Ferric stars" emerged as molecular magnets chemically related to "ferric wheels", but with non-zero ground-state spin.
- It has been demonstrated that Fe can be substituted by other transition metal ions. However, no details about structure or substitution sites are so far known.
- "Ferric stars" are appealing as simple yet non-trivial model systems to study substitution geometry, magnetic ground state, and magnetic interactions from first principles, with the aim to choose ways to tune desirable magnetic characteristics.

Interaction within the SPP137

- Institut für Organische Chemie, Universität Erlangen-Nürnberg (R. Saalfrank, A. Scheurer): synthesis and crystal structure determination;
- Physikalisches Institut III, Universität Erlangen-Nürnberg (P. Müller, S. Alam): STM imaging of deposited "ferric stars";
- Universität Osnabrück – Fachbereich Physik (M. Neumann, A. Takacs): X-ray spectroscopy of pure and doped "ferric stars".

Substance

[MFe₃(NCH₂(CH₂CH₂O)₂)₄]4CHCl₃, Saalfrank et al., Chem. Eur. J. 7, 2765 (2001).
M: Fe or Cr. Solvent here: chloroform; also known to crystallize with dichloromethane, diethylether and tetramethylheptane.



Single "ferric star" molecule in the top view (left) and side view of the molecules packed in the crystal structure with chloroform (right). Hydrogen atoms are omitted, and carbon chains are shown as wireframe.

Calculation method:

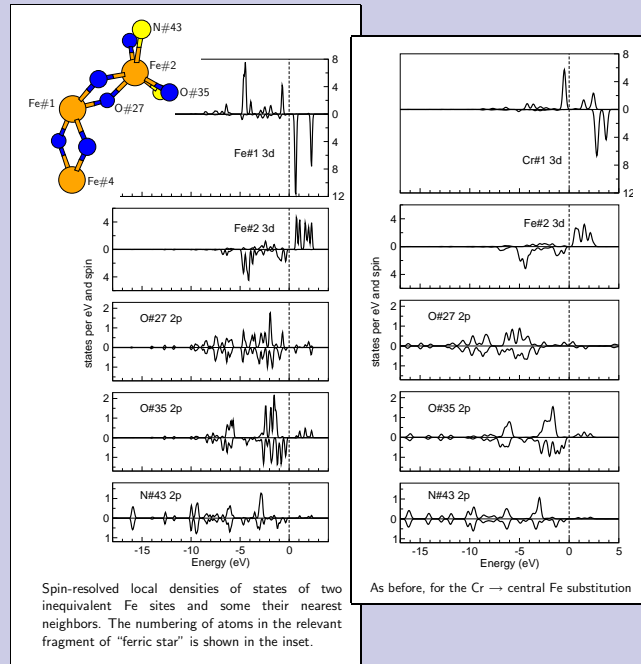
SIESTA, see *J.Phys.Chem.Mat.* 14, 2745 (2002), <http://www.uam.es/siesta>
– norm-conserving pseudopotentials
– localized basis of numerical orbitals (exact confinement, multiple- ζ , polarization orbitals)
– no symmetry constraints; LDA or GGA
– accurate forces and stress tensor available
– non-collinear magnetic density possible
Here: GGA, free isolated molecule (118 atoms) in a 22×22×18 Å simulation box.
Basis functions: double- ζ (H, C, N);
double- ζ with polarization orbitals (O);
triple- ζ with s -polarization orbitals (V–Cu).

What is done:

- systematic substitution of Fe by V ... Cu in two non-equivalent positions;
- trial of all magnetic configurations;
- extraction of ground-state properties (density of states, charge and spin density, one-electron wavefunctions) and comparison of (well converged) energies of metastable magnetic configurations.

The calculations below are done for a single molecule of a fixed geometry, corresponding to the structure crystallized with chloroform. Substitutions of Fe in the central and peripheral site assumed the same unchanged structure. Additional calculations have been also performed or are in progress:

- real (periodic) crystal structure with solvent molecules (CHCl₃ and CH₂Cl₂);
- relaxed structure of a single molecule;
- relaxed structure of a single molecule with central Cr substitution.



Spin-resolved local densities of states of two inequivalent Fe sites and some their nearest neighbors. The numbering of atoms in the relevant fragment of "ferric star" is shown in the inset.

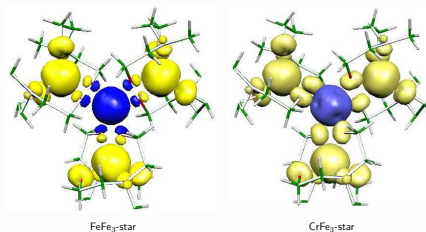
As before, for the Cr → central Fe substitution

Results of calculations with substituted central atom

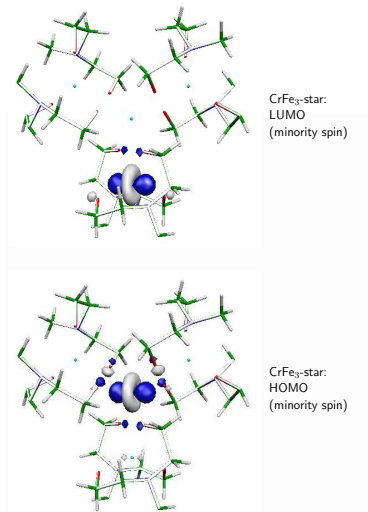
$N_{\uparrow} - N_{\downarrow}$ → 2.97, 3.96×2, -3.95
HOMO-LUMO gap (eV) → 0.67
local magnetic moments of M and three Fe atoms (μ_B)
 E_{tot} relative to the FM configuration (meV)

	$\uparrow\downarrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\downarrow\uparrow$
V	1.79, 3.93×2, 3.93 16.39 0	-1.67, 3.93×2, 3.93 13 = -2+5+5+5	1.76, 3.94×2, -3.93 7 = 2+5+5-5	-1.70, 3.93×2, -3.94 3 = -2+5+5-5
Cr	3.04, 3.96×2, 3.96 18 = 3+5+5+5 0.52	-2.85, 3.96×2, 3.95 12 = -3+5+5+5	2.97, 3.96×2, -3.95 8 = 3+5+5-5	-2.92, 3.96×2, -3.96 2 = -3+5+5-5
Mn	3.70, 3.91×2, 3.89 18.31 0	-3.00, 3.94×2, 3.95 11 = -4+5+5+5	3.72, 3.92×2, -3.94 9 = 4+5+5-5	-3.64, 3.94×2, -3.91 1 = -4+5+5-5
Fe	4.07, 3.97×2, 3.97 20 = 5+5+5+5 0.54	-3.95, 3.93×2, 3.93 10 = -5+5+5+5	4.03, 3.97×2, -3.93 10 = 5+5+5-5	-3.98, 3.93×2, -3.97 0 = -5+5+5-5
Co	0.29, 3.93×2, 3.93 15 = 0+5+5+5 0.94	-2.85, 3.91×2, 3.92 11 = -4+5+5+5	0.08, 3.93×2, -3.93 5 = 0+5+5+5	-2.88, 3.91×2, -3.97 1 = -4+5+5-5
Ni	1.16, 3.89×2, 3.88 16 = 1+5+5+5 0.01	-0.59, 3.92×2, 3.90 14 = -1+5+5+5	1.01, 3.87×2, -3.92 6 = 1+5+5-5	-0.81, 3.92×2, -3.85 4 = -1+5+5-5
Cu	falls down to ⇒	-0.79, 3.87×2, 3.87 13 = -2+5+5+5	0.07, 3.87×2, -3.84 5 = 0+5+5+5	-0.83, 3.84×2, -3.97 3 = -2+5+5-5

Spin density isosurfaces (at ±0.06 e/Å³) in the magnetic ground state



Induced magnetization is found on the ligands, notably O and N atoms, neighboring to Fe and M. This is similar to the situation in "ferric wheels". The effective (delocalized) spin of the Heisenberg model for Fe is enhanced from the value corresponding to the local magnetic moment (nearly 4 μ_B) to $S=5/2$, as if for the Fe³⁺ configuration (see the tables). The effective spin associated with the doping Cr is essentially confined to the impurity site only (see the tables and the above figure of spin density distribution); similarly for Mn and V. For Co and Ni one finds the enhancement of effective spin due to magnetization of neighbors, like in the case of Fe. The situation with Co, Ni and Cu is however complicated by the presence of different magnetic solutions (high-spin and low-spin).



CrFe₃-star in its ground-state magnetic configuration has a gap of 0.96 eV in the minority-spin channel (= spin-up in the DOS figure above). This is different from undoped FeFe₃-star with a gap in the majority-spin channel. The figure shows Kohn-Sham wavefunctions of the lowest unoccupied molecular orbital (top) and the highest occupied molecular orbital (bottom).

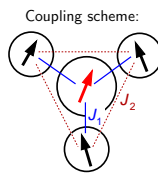
Results of calculations with substituted peripheral atom

$N_{\uparrow} - N_{\downarrow}$ → 3.98, 3.97×2, -1.73
HOMO-LUMO gap (eV) → 0.21
local magnetic moments of three Fe atoms and M (μ_B)
 E_{tot} relative to the FM configuration with central substitution (meV)

	$\uparrow\downarrow$	$\uparrow\uparrow$	$\downarrow\downarrow$	$\downarrow\uparrow$
V	3.98, 3.96×2, 1.76 16.33 0	3.98, 3.97×2, -1.73 13 = 5+5+5-2	-3.09, 3.94×2, 1.77 7 = -5+5+5+2	-3.89, 3.94×2, -1.80 0
Cr	3.91, 3.96×2, 2.73 17.20 0	3.96, 3.97×2, -1.65 12 = 5+5+5-3	-3.87, 3.94×2, 2.68 8 = -5+5+5+3	-3.84, 3.46×2, -2.76 2.63
Mn	4.01, 3.97×2, 3.74 19 = 5+5+5+4 0.03	4.02, 3.97×2, -3.73 11 = 5+5+5+4	-3.94, 3.94×2, 3.74 9 = -5+5+5+4	-3.97, 3.93×2, -3.79 1 = -5+5+5-4
Fe	4.07, 3.97×2, 3.97 20 = 5+5+5+5 0.54	4.03, 3.97×2, -3.93 10 = 5+5+5+5	-3.95, 3.93×2, 3.93 5 = 0+5+5+5	-3.98, 3.93×2, -3.97 0 = -5+5+5-5
Co	4.06, 3.97×2, 2.86 19 = 5+5+5+4 0.28	4.01, 3.97×2, -2.81 11 = 5+5+5+4	-3.93, 3.93×2, 2.82 9 = -5+5+5+4	-3.98, 3.93×2, -2.86 1 = -5+5+5-4
Ni	4.06, 3.97×2, 1.81 18 = 5+5+5+3 0.25	3.98, 3.97×2, -1.75 12 = 5+5+5-3	-3.90, 3.91×2, 1.76 8 = -5+5+5+3	-3.98, 3.93×2, -1.81 2 = -5+5+5-3
Cu	falls down to ⇒	3.85, 3.96×2, -0.77 13 = 5+5+5-2	-3.77, 3.93×2, 0.79 7 = -5+5+5+2	⇐ falls down to

Estimate of coupling constants

Heisenberg model: $\mathcal{H} = - \sum_{i \neq j} J_{ij} S_i S_j$



Estimations for FeFe₃:
– $J_1 \approx 10.82$ meV = 126 K,
– $J_2 \approx 10.82$ meV = 3.5 K.
(Compare "ferric wheels":
– $J \approx 80$ K from calc.,
– ~ 20 K from exp.)

For doped MFe₃ systems

- (M–Fe nearest-neighbour coupling only):
– J_{V-Fe} : 220 K – J_{Cr-Fe} : 50 K
– J_{Co-Fe} : 150 K – J_{Ni-Fe} : 280 K

Magnetic configurations

- The most stable solutions are of either $\uparrow\downarrow$ or $\downarrow\uparrow$ type. Both cases favour antiparallel coupling of the central spin to its neighbours.
- V, Cr, Mn and Fe possess "rigid" magnetic moments, corresponding to
S=1 (V 3d² → V³⁺),
S=3/2 (Cr 3d³ → Cr³⁺),
S=2 (Mn 3d⁴ → Mn³⁺),
S=5/2 (Fe 3d⁵ → Fe³⁺).
- Co, Ni and Cu appear in different metastable magnetic states either in the high-spin or in the low-spin configuration:
low-spin Co S=0 (Co 3d⁶d³ → Co³⁺),
Ni S=1/2 (Ni 3d⁷d³ → Ni³⁺),
Cu S=0 (Cu 3d⁸d³ → Cu³⁺);
high-spin Co S=2 (Co 3d⁶d³ → Co³⁺),
Ni S=3/2 (Ni 3d⁷d³ → Ni³⁺),
Cu S=1 (Cu 3d⁸d³ → Cu³⁺).
- On doping, Cr, Mn and Cu would definitely tend to substitute the central Fe atom; V, Co and Ni – one of peripheral atoms.