Supporting Information

Bis(α-Diimine)iron Complexes: Electronic Structure Determination by Spectroscopy and Broken Symmetry Density Functional Theoretical Calculations.

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Magnetic Measurements

Diagonalization of the Hamiltonian was performed with the routine ZHEEV from the LAPACK Library[a] and the magnetic moments were obtained from first order numerical derivative dE/dB of the eigen values. The powder summations were done by using a 16-point Lebedev grid.[b,c] Pascal Constants for diamagnetic corrections were taken from ref. d+e

a) The LAPACK Linear Algebra Package is written in Fortran77 and provides routines for solving systems of simultaneous linear equations, least-squares solutions of linear systems of equations, eigenvalue problems, and singular value problems. The routines are available at http://www.netlib.org/lapack/
b) Lebedev, V. I.; Laikov, D. N., Doklady Math. **1999**, *59*, 477.
c) A Fortran code to generate Lebedev grids up to order L=131 is available at http://server.ccl.net/cca/software/SOURCES/
d) O'Connor, C. J., *Prog. Inorg. Chem.* **1982**, *29*, 203 - 283.
e) Weast, R. C.; Astle, M. J., CRC Handbook of Chemistry and Physics. CRC Press Inc.: Boca Raton, Florida, **1979**.

Figure S1 Magnetic Susceptibility and magnetic saturation measurements for **2**

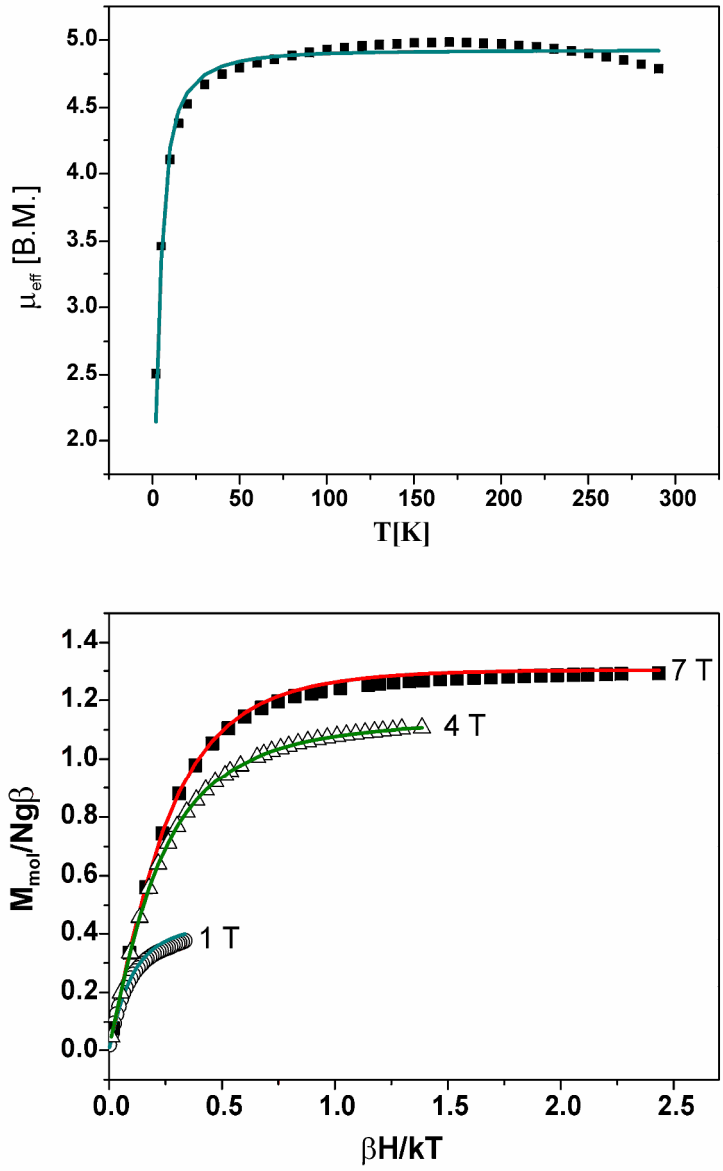


Figure S2 Magnetic Susceptibility and magnetic saturation measurements for **6**

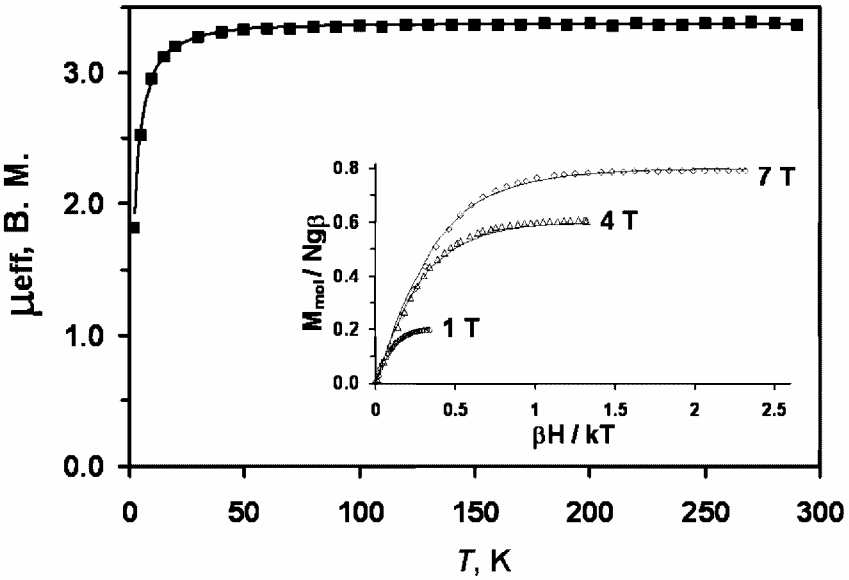
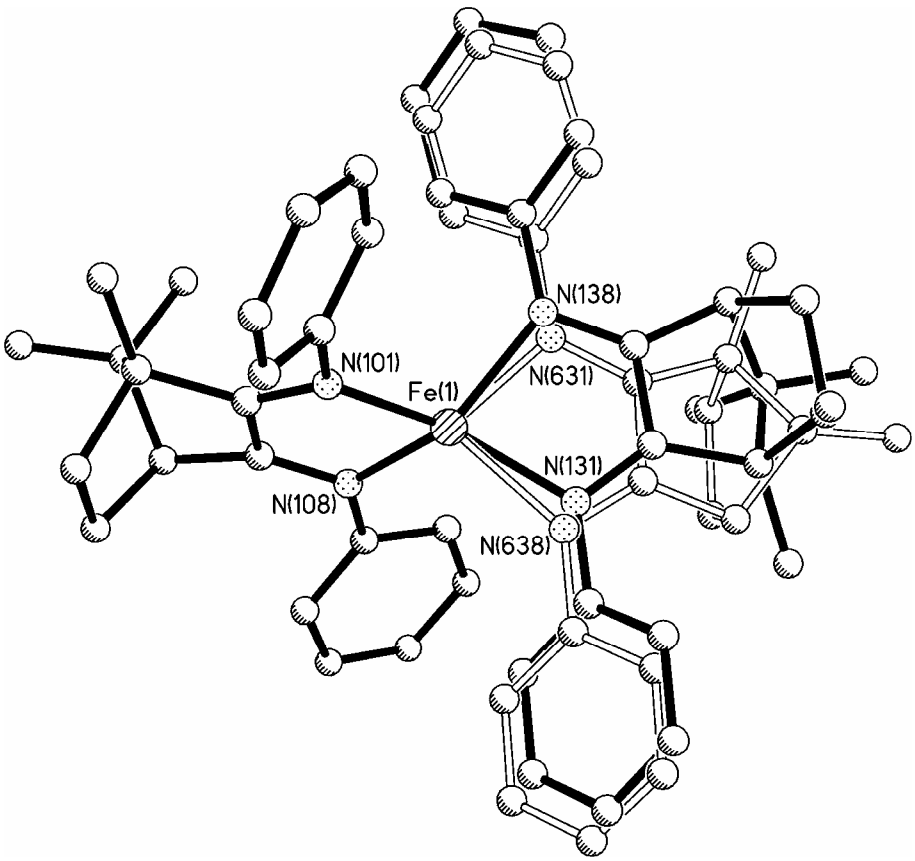
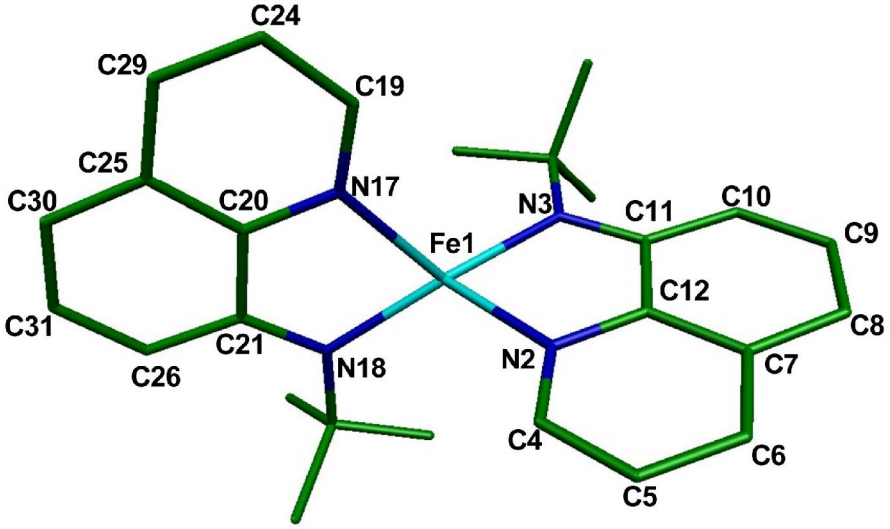


Figure S3 Disorder of one of the two crystallographically independent molecules in crystals of **6**. The solid part represents the main component owing an occupation factor of about 0.56 (transoid). The second part is cisoid and is about 0.44 occupied



DFT Calculations

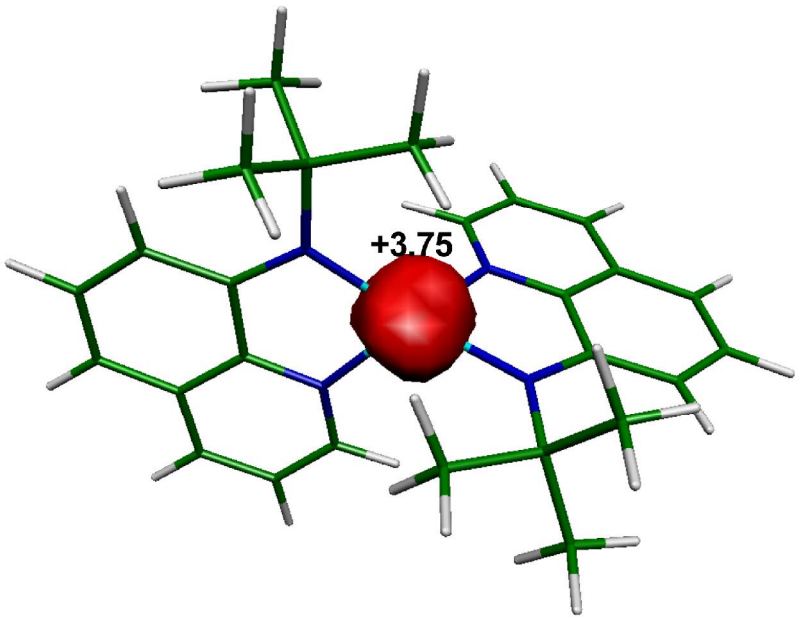
DFT Calculation of **1**. S = 2, B3LYP, Spin-unrestricted Kohn-Sham Functional



Calculated bond lengths and calculated dihedral angel between coordination planes of **1**.

[$Fe^{II}(^{3}L)_2$]	**calcd. bond length**
Fe1-N3	2.014
Fe1-N2	2.126
Fe1-N17	2.127
Fe1-N18	2.013
N2-C4	1.326
N2-C12	1.364
C4-C5	1.409
C5-C6	1.381
C7-C12	1.433
C6-C7	1.421
C7-C8	1.418
C8-C9	1.383
C9-C10	1.410
C10-C11	1.413
C11-C12	1.463
N3-C11	1.365
N17-C20	1.364
N17-C19	1.326
C19-C24	1.409
C24-C29	1.381
C29-C25	1.421
C25-C20	1.433
C20-C21	1.463
C21-N18	1.365
C25-C30	1.418
C30-C31	1.383
C31-C26	1.410
C26-C21	1.413
Dihedral angle between planes defined by N2-Fe1-N3 and N17-Fe1-N18	**Calculated dihedral angel** **88.8°**

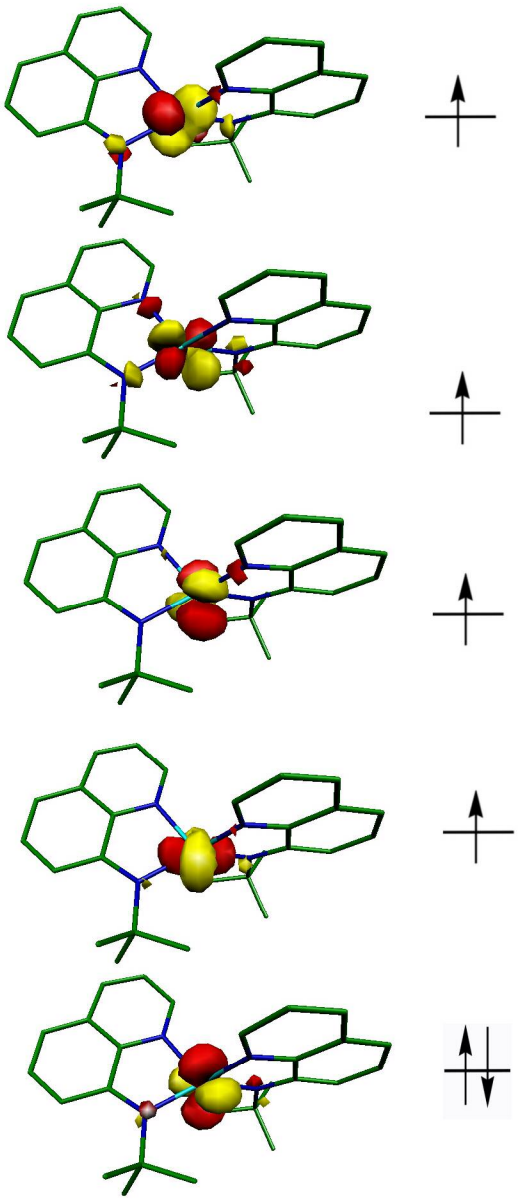
Spin Density Map of **1**



Mulliken Population Analysis of **1**

Fe	3.754692
N2	0.020739
N3	0.031445
C4	0.012018
C5	-0.004132
C6	0.007530
C7	-0.005917
C8	0.032891
C9	-0.015081
C10	0.037469
C11	-0.003494
C12	-0.003614
C13	0.004407
C14	-0.001131
C15	0.002148
C16	0.001952
N17	0.020773
N18	0.031649
C19	0.011880
C20	-0.003497
C21	-0.003575
C22	0.004517
C23	-0.001425
C24	-0.004101
C25	-0.005932
C26	0.037574
C27	0.002097
C28	0.001995
C29	0.007463
C30	0.032968
C31	-0.015120

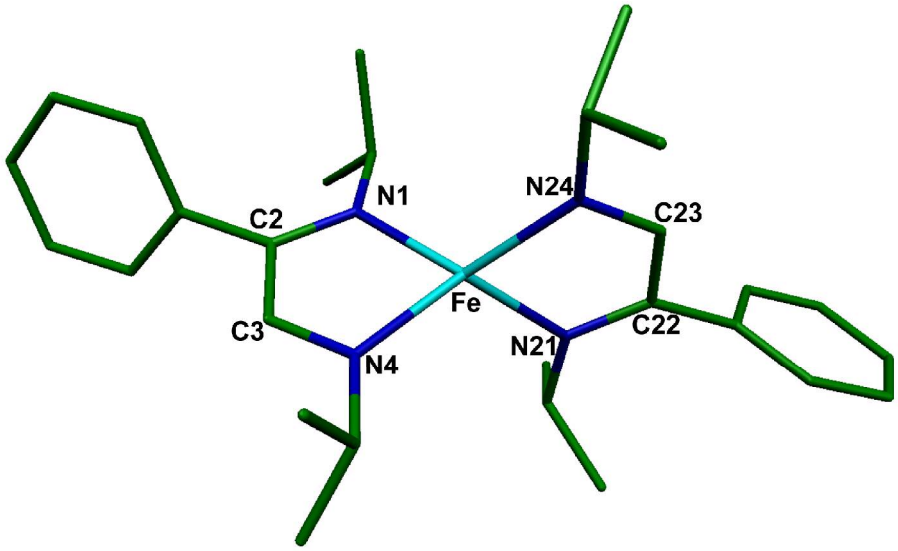
Qualitative MO scheme of **1**



Experimental and calculated isomer shift and quadrupole splitting in the zero-filed Mössbauer spectrum of **1**

	Expt.	**Calcd.**
IS (mms^{-1})	0.77	0.70
QS (mms^{-1})	2.13	2.15
η		0.2

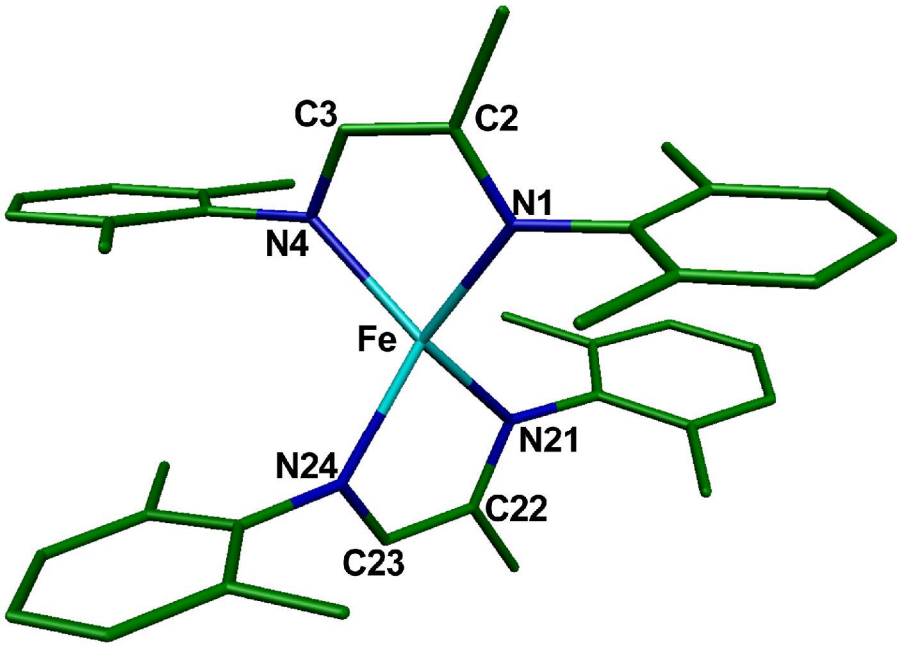
DFT Calculation of **3** .BS(4,2), Ms = 1, B3LYP, Spin-unrestricted Kohn-Sham Functional



Calculated bond lengths and calculated dihedral angel between coordination planes of **3**

$[Fe^{II}(^{1}L^{\bullet})_2]$	**calcd. bond length [Å]**
Fe1-N1	2.038
Fe1-N4	2.006
Fe1-N21	2.028
Fe1-N24	2.014
N1-C2	1.348
C2-C3	1.420
C3-N4	1.336
N21-C22	1.350
C22-C23	1.420
C23-N24	1.335
Dihedral angle between planes defined by N1-Fe1-N4 and N21-Fe1-N24	**Calculated dihedral angel 88°**

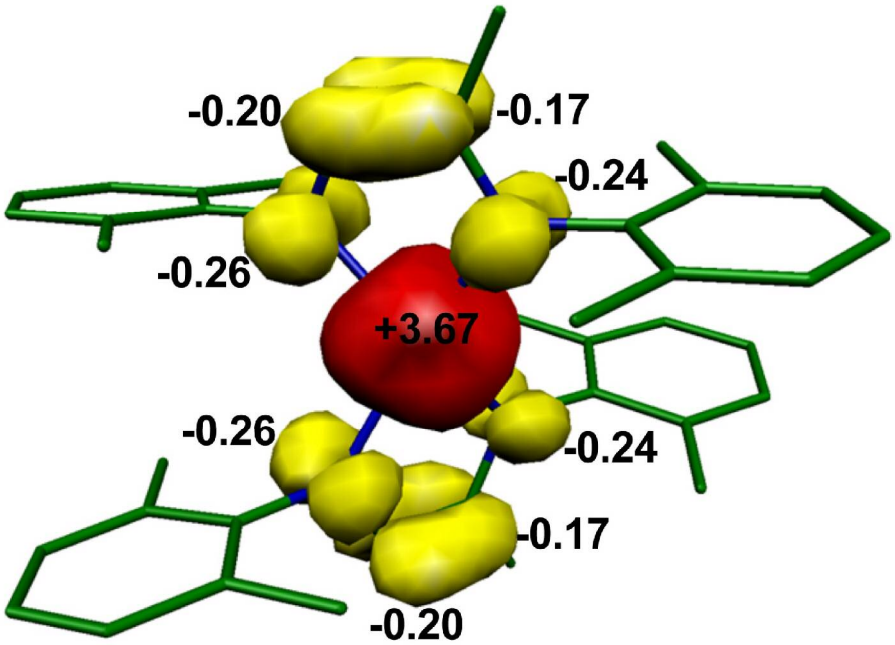
DFT of **5**. BS(4,2), Ms = 1, B3LYP, Spin-unrestricted Kohn-Sham Functional



Calculated bond lengths and calculated dihedral angel between coordination planes of **5**

$[Fe^{II}(^2L^{\bullet})_2]$	**calcd. bond length [Å]**
Fe1-N1	2.108
Fe1-N4	2.088
Fe1-N21	2.103
Fe1-N24	2.090
N1-C2	1.345
C2-C3	1.412
C3-N4	1.338
N21-C22	1.346
C22-C23	1.413
C23-N24	1.337
Dihedral angle between planes defined by N1-Fe1-N4 and N21-Fe1-N24	**Calculated dihedral angel 56°**

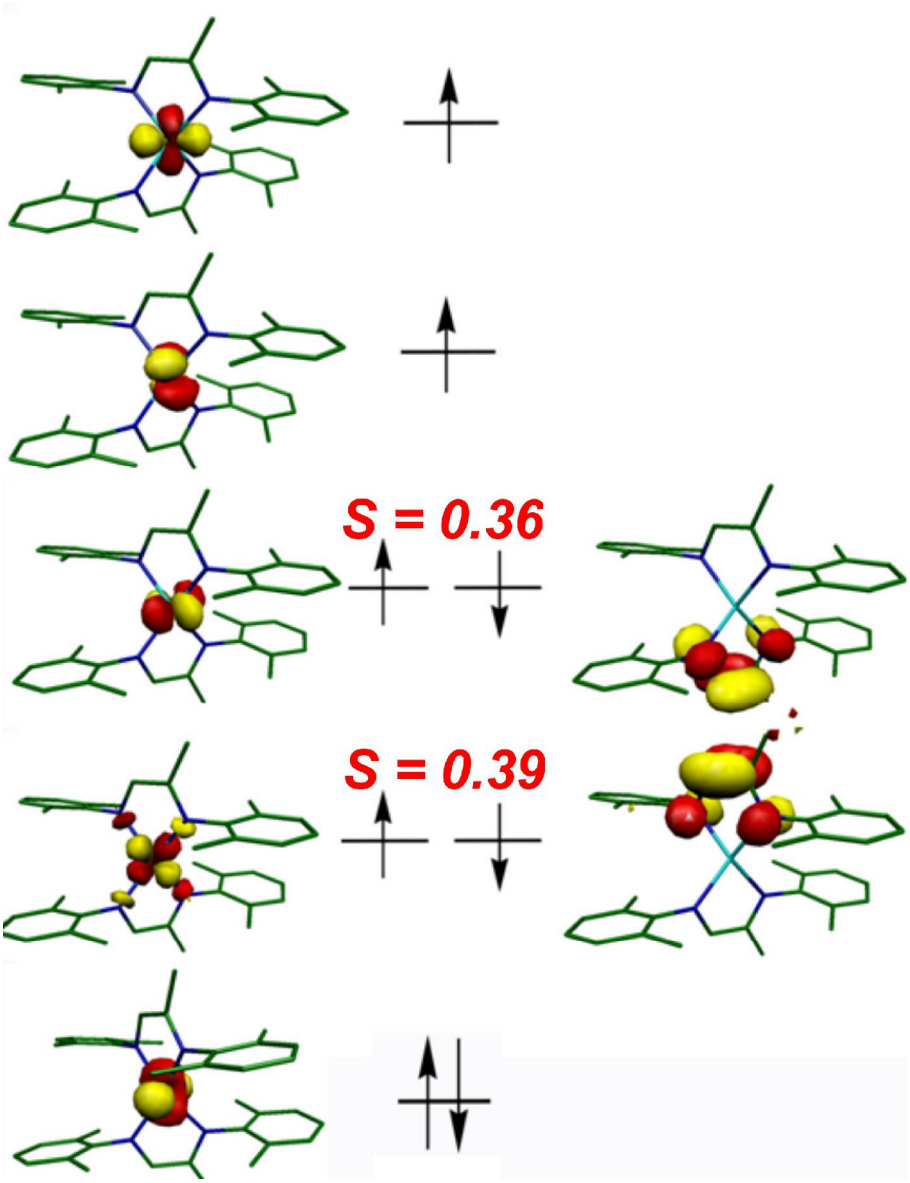
Spin Density Map of **5**



Mulliken Population Analysis of **5**

Fe	3.675694
N4	-0.262514
N24	-0.260663
N1	-0.238531
N21	-0.237646
C2	-0.170807
C3	-0.201835
C22	-0.169332
C23	-0.203834

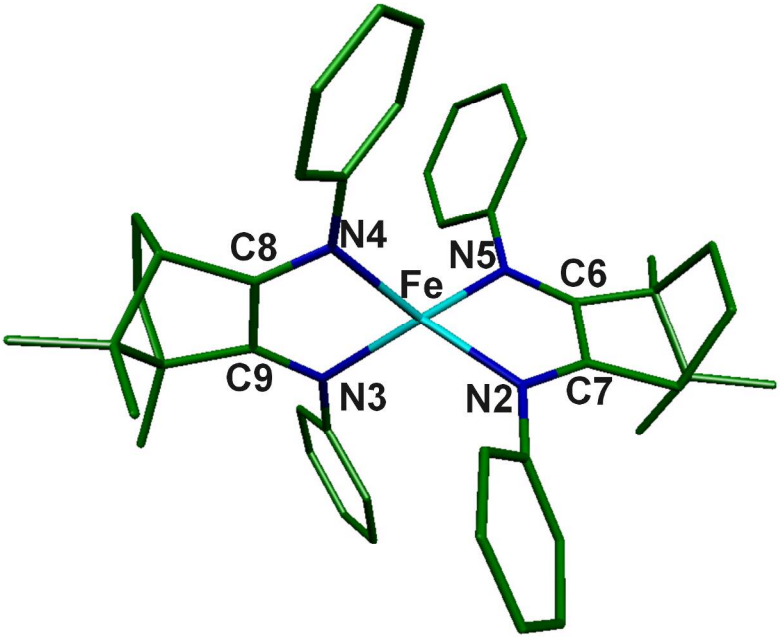
Qualitative MO scheme of **5**



Experimental and calculated isomer shift and quadrupole splitting in the zero-filed Mössbauer spectrum of **5**

	Expt.	**Calcd.**
IS (mms^{-1})	0.59	0.68
QS (mms^{-1})	2.82	2.95
η		0.08

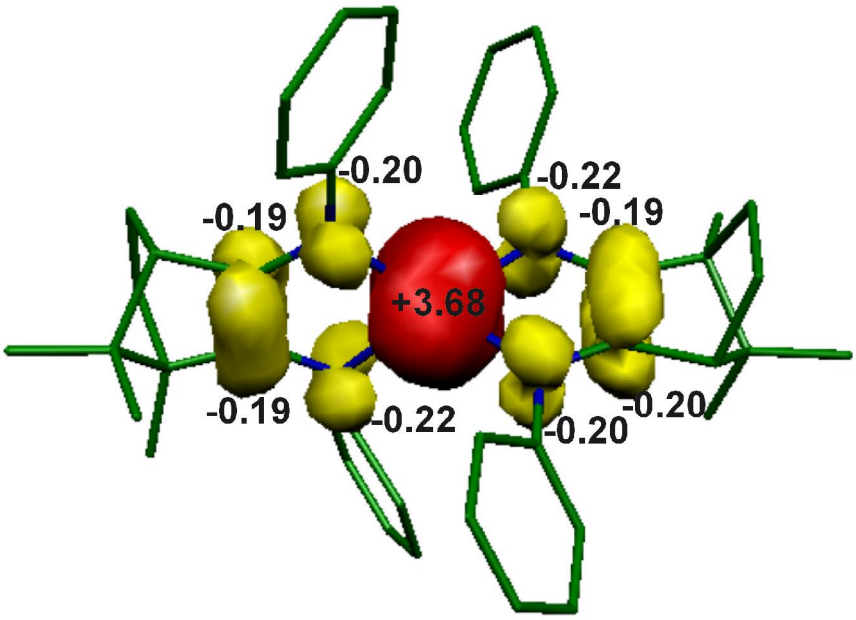
DFT Calculations of **6**. BS(4,2), Ms = 1, B3LYP, Spin-unrestricted Kohn-Sham Functional



Calculated bond lengths and calculated dihedral angel between coordination planes of **6**

$[Fe^{II}(^3L^{\bullet})_2]$	**calcd. bond length [Å]**
Fe1-N2	2.056
Fe1-N3	2.055
Fe1-N4	2.051
Fe1-N5	2.049
N3-C9	1.341
C8-C9	1.419
C8-N4	1.341
N2-C7	1.341
C6-C7	1.420
C6-N5	1.340
Dihedral angle between planes defined by N2-Fe1-N3 and N4-Fe1-N5	**Calculated dihedral angel 76.4°**

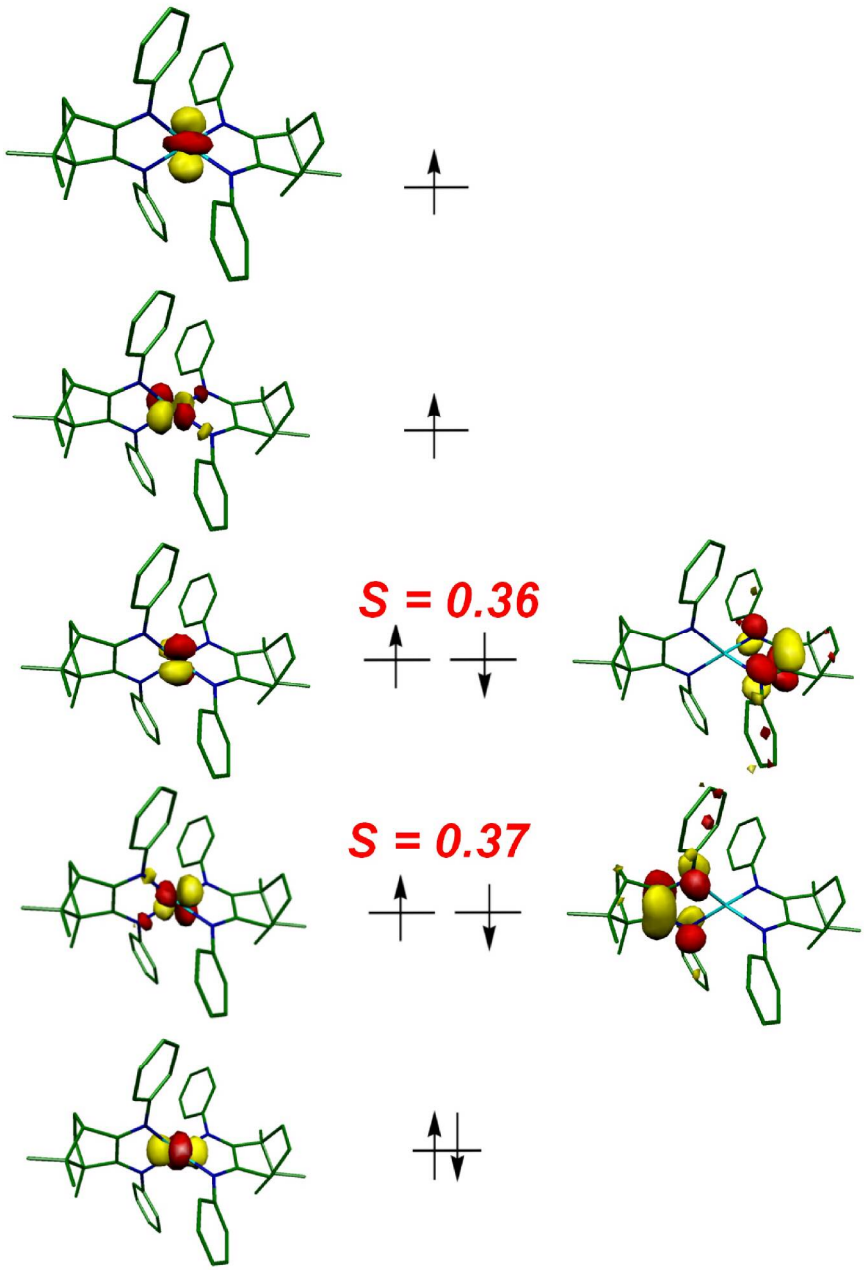
Spin Density Map of **6**



Mulliken population analysis of **6**

Fe	3.685384
N2	-0.203188
N3	-0.216402
N4	-0.205024
N5	-0.222119
C6	-0.186688
C7	-0.197780
C8	-0.191322
C9	-0.185046

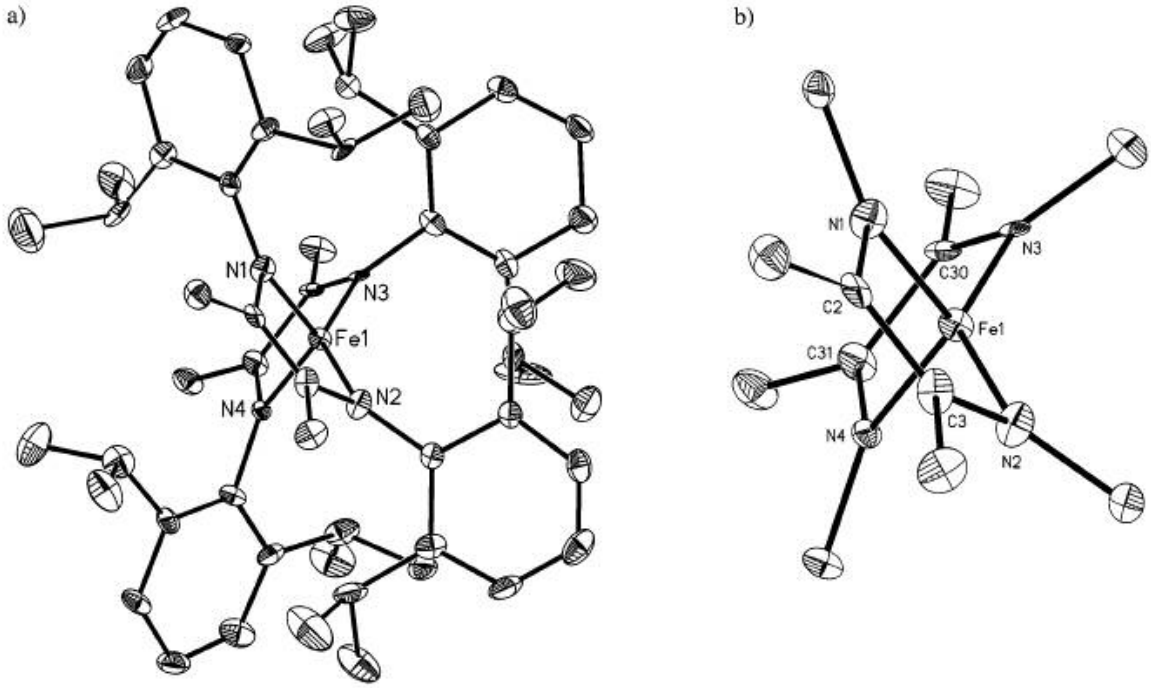
Qualitative MO scheme of **6**



Experimental and calculated isomer shift and quadrupole splitting in the zero-filed Mössbauer spectrum of **6**

	Expt.	**Calcd.**
IS (mms^{-1})	0.65	0.51
QS (mms^{-1})	3.63, 4.19	-4.43
η		0.73

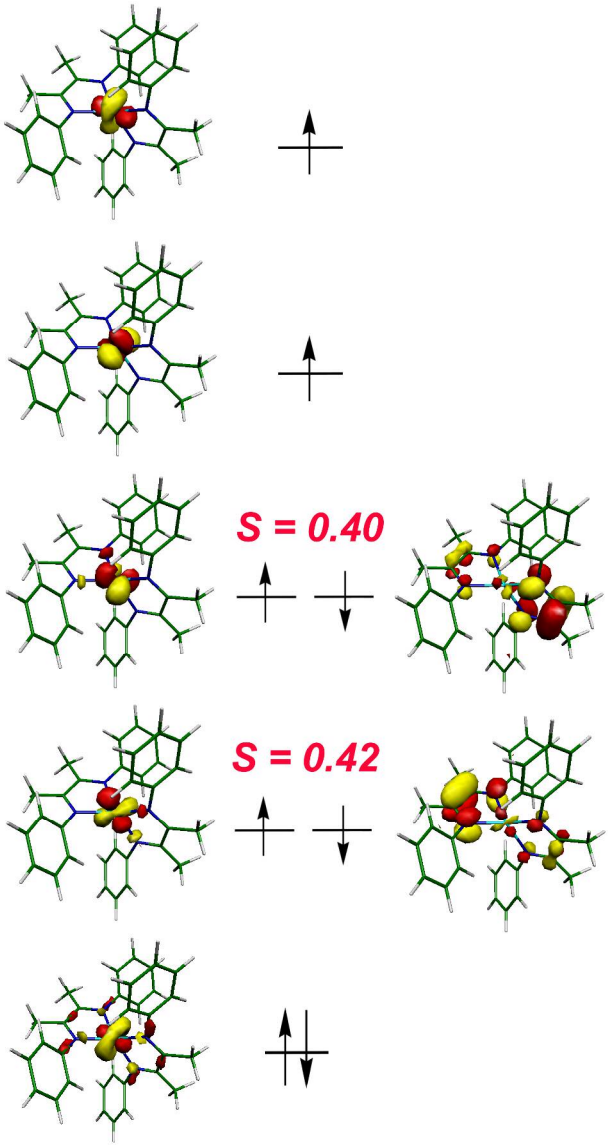
DFT Calculations of **8**



Calculated bond distances of **8** (labeling as in the crystal structure; ref. 4)

	Calc. bond dist. [Å]
Fe1-N1	2.058
Fe1-N2	2.049
Fe1-N3	2.059
Fe1-N4	2.049
N1-C2	1.347
C2-C3	1.431
C3-N2	1.347
N3-C30	1.344
C30-C31	1.431
C31-N4	1.349

Qualitative MO scheme of **8**



Spin density plot of the tetrahedral **8**.