Ligand Field Influence on the Electronic and Magnetic Properties of Quasi-Linear Two-Coordinate Iron(II) Complexes

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Discussion of the magnetic fits obtained in the absence of any independent knowledge of the ligand field.

The results for the best fits of $\chi_M T$ for **1 – 3**, obtained in the absence of any independent prior knowledge of their ligand-field parameters are given in the Tables S1A and S1B. Based on our fitting attempts we conclude that the temperature dependence of $\chi_M T$ obtained between 2 and 300 K does not contain enough information to permit a reliable determination of the ligand field parameters for our systems. This is based on several observations: First, in addition to B_2^0, B_4^0 has at most a minor influence, and B_2^2 and B_4^4 have virtually no influence on the quality of the fit. Second, one obtains rather different B_2^0 values depending on the initial starting value used for B_2^0, Table S1B, i.e., multiple minima can be found depending on the initial values. Third, if the *ab initio* derived B_2^0, B_4^0, B_2^2, and B_4^4 parameters are used as starting values in a fit for **3**, the results depart significantly from the starting *ab initio* values, Table S1C. Sequential refinement of one parameter at a time followed by its constraint, in the order B_2^0, B_4^0, B_2^2 and B_4^4, yields very little if any change in the $\chi_M T$ f(T) after the use of B_2^0, except for a small influence of B_4^0 in compound **3**. Finally, any attempt to include $N\alpha$ in the fits either fails or yields totally unreasonable fits with huge B_2^0 and B_4^0 values.

These findings are consistent with the large orbital splitting expected from the ligand field. The complex multidimensional landscape of the residual error function is dominated by strongly negative values of B_2^0. Under this condition, an infinite number of parameterisations are possible as the thermodynamic magnetic susceptibility data are unable to provide precise information on the electronic structure and the subtlety of the magnetic states are concealed. The fitting algorithm, however, is

unaware of this and therefore will merrily try and find the rock-bottom numerical match to the data, even if the results have no physical meaning. Thus we conclude that, at least for two-coordinate iron(II) complexes, it is not possible to obtain nor to confirm *ab initio* calculations of the ligand field parameters by fitting $\chi_M T\,f(T)$, but acceptable *simulations* of the magnetic properties with the *ab initio* parameters are possible and provides some experimental support for the validity of these calculations.

Table S1A. Initial Best Fit Iron(II) Magnetic Properties[a] of the **1 – 3**

Complex	B_2^0, cm^{-1}	B_4^0, cm^{-1}	$N\alpha$, emu/mol	κ	*Residual*
Fe{N(SiMe$_2$Ph)$_2$}$_2$, **1**	–94(3)	1.6(1)	0.00065[b]	0.22(1)	0.141
Fe{N(SiMePh$_2$)$_2$}$_2$, **2**	–148(10)	1.3(1)	0.00050[b]	0.23(2)	0.029
Fe(Ar^{Pri4})$_2$, **3**	–57(2)	7.3(5)	0[b]	0.74(2)	0.129

[a]$g = 2$, $S = 2$, $L = 2$, and $\lambda = -103$ cm^{-1} fixed for all fits and with the estimated errors given in parentheses. [b]Parameter constrained to the value given.

Table S1B. Initial and Refined Parameters for Fe(Ar^{Pri4})$_2$, **3**

B_2^0, cm^{-1}, initial value	B_2^0, cm^{-1} refined value	κ	*Residual*
–15 to –71	–28.2	0.73	0.1533
–72 to –90	–127	0.80	0.230

[a]$g = 2$, $S = 2$, $L = 2$, $\lambda = -103$ cm^{-1} and $N\alpha = 0$ fixed for all fits.

Table S1C. Ab-initio and Refined Parameters for Fe(Ar^{Pri4})$_2$, **3**

Type	B_2^0, cm^{-1}	B_4^0, cm^{-1}	B_2^2, cm^{-1}	B_4^4, cm^{-1}	κ	*Residual*
Ab-initio	–384	6.41	115	–4.70	0.835	0.311
Refined	–151	2.58	-35.5	1.31	0.80	0.25

[a]Obtained with $g = 2$, $S = 2$, $L = 2$, $\lambda = -103$ cm^{-1} and $N\alpha = 0$ fixed for all fits.

Table S2. CASPT2 Ligand Field and Spin-Orbit Parameterisation with Descent in Symmetry for **3**.

Complex	Iron(II) site symmetry	B_2^0, cm^{-1}	B_4^0, cm^{-1}	B_4^4, cm^{-1}	B_2^2, cm^{-1}	κ
Fe(Ar^{Pri4})$_2$, **3**	$D_{\infty h}$	–374	2.34	-	-	-
	D_{2d}	–374	2.34	–11.2	-	-
	C_1[a]	–367	1.89	–8.05	171	-
	C_1[b]	–366	1.71	–8.35	178	0.857

[a]$\hat{H}_{LF}$ only. [b]$\hat{H}_{LF} + \hat{H}_{SOC}$ with an optimal $\lambda = -101$ cm^{-1}.

Figure S1. The temperature dependence of $\chi_M T$ obtained at 0.01 T between 2 and 300 K for Fe{N(SiMe$_2$Ph)$_2$}$_2$, **1** (red points), with the CASSCF calculated results (red line), the ligand field simulation (blue line), and the ligand field simulation with a fitted orbital reduction factor, κ, (black line). Inset: The equivalent results in terms of μ_{eff}. The parameters associated with these simulations are given in Table 2.

Fe-*L* bond length evaluation

The Fe-*L* bond lengths for most of the model complexes were also evaluated by CASSCF optimisation, see Table S3 and Figure S2. This employed the same CASSCF methodology as for the main complexes, i.e. a minimal active space of the five 3d orbitals, with the ANO-RCC-VDZ basis set. The optimisation only concerned the Fe-*L* bond lengths with all other parameters fixed. The state average CASSCF energy of the five Configuration State Functions was used to find the minimum energy. Once the optimal bond length was determined, the ligand field strength was extracted as explained in the main text. All attempts to find the optimise the bond length for [Fe(CO)$_2$]$^{2+}$ failed, so the value from X-Ray crystallography was employed.
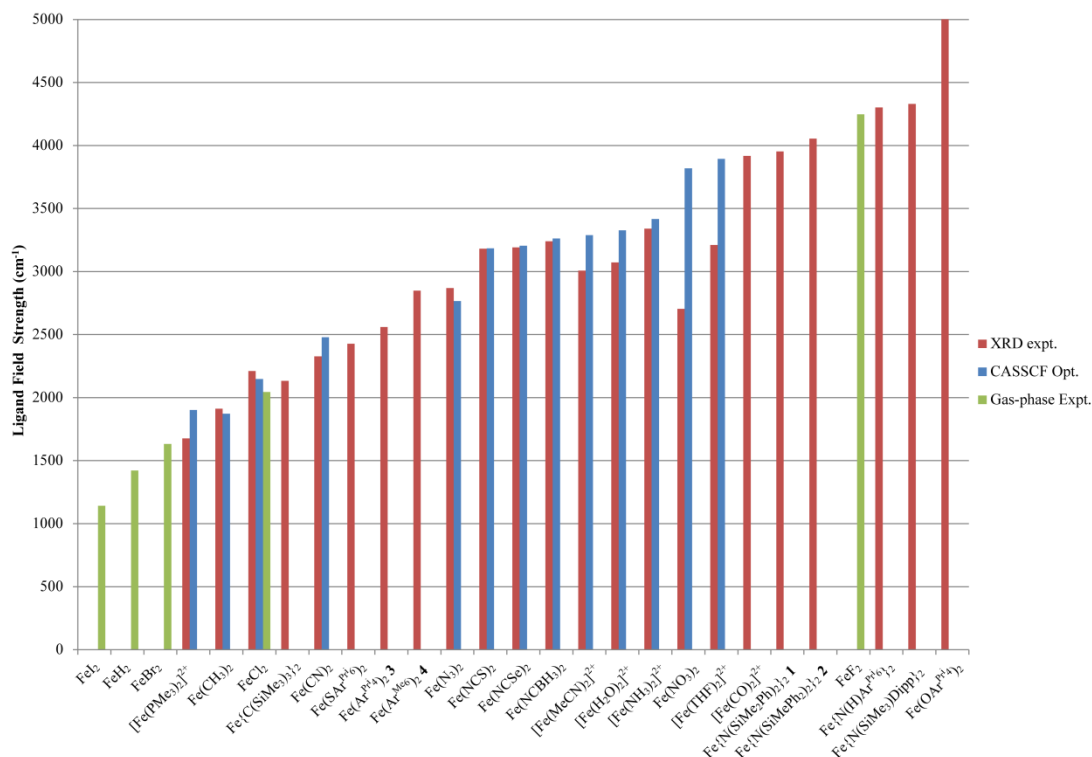
Figure S2. Ligand field strength per ligand for each model complex, with different Fe-*L* bond lengths.

Table S3. Bond length (BL) and ligand field strengths (LFS) for model complexes.

Complex	X-Ray Expt.		CASSCF Opt.		Gas-phase Expt.	
	BL, Å	LFS, cm^{-1}	BL, Å	LFS, cm^{-1}	BL, Å	LFS, cm^{-1}
FeI$_2$	-	-	-	-	2.46	1141
FeH$_2$	-	-	-	-	1.65	1421
FeBr$_2$	-	-	-	-	2.28	1631
[Fe(PMe$_3$)$_2$]$^{2+}$	2.24(2)	1676	2.57	1901	-	-
Fe(CH$_3$)$_2$	2.12(1)	1912	2.09	1872	-	-
FeCl$_2$	2.36(1)[1,2]	2210	2.22	2148	2.13	2044
Fe(CN)$_2$	1.94(3)	2326	2.04	2478	-	-
Fe(N$_3$)$_2$	2.04(3)	2868	1.93	2765	-	-
Fe(NCS)$_2$	2.01(9)	3180	1.98	3184	-	-
Fe(NCSe)$_2$	2.01(9)	3191	1.98	3204	-	-
Fe(NCBH$_3$)$_2$	2.01(9)	3239	1.93	3262	-	-
[Fe(MeCN)$_2$]$^{2+}$	2.13(11)[3,4]	3007	2.00	3288	-	-
[Fe(H$_2$O)$_2$]$^{2+}$	2.12[5]	3071	2.06	3327	-	-
[Fe(NH$_3$)$_2$]$^{2+}$	2.00(2)	3339	2.10	3416	-	-
Fe(NO$_3$)$_2$	2.22(7)[6–8]	2704	1.93	3819	-	-
[Fe(THF)$_2$]$^{2+}$	2.14(2)[9]	3210	1.95	3893	-	-
[Fe(CO)$_2$]$^{2+}$	1.81(4)	3917	-	-	-	-
FeF$_2$	-	-	-	-	1.75	4247

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