Supporting Information

A Detailed *Ab Initio* First-Principles Study of the Magnetic Anisotropy in a Family of Trigonal Pyramidal Iron(II) Pyrrolide Complexes

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Table S1. Mn-N Bond distances (in Å), N-Mn-N bond angles (in ^{o}) and parameters of geometrical distortions as quantified by $\rho(\varepsilon_s)$, $\rho(\varepsilon_s)$ and $\rho(\varepsilon_s)$ of the $[Mn(tpaR)]^-$ model complexes from DFT geometry optimizations.

	$[Mntpa^{Tbu}]^-$	$[Mntpa^{Mes}]^-$	$[Mntpa^{Ph}]^-$	$[Mntpa^{Dfp}]^-$	$[MnN_4C_{15}N_{15}]^-$
r_1	2.222	2.246	2.266	2.292_5	2.230
r_2	2.055	2.064	2.050	2.085	2.049
r_3	2.058	2.061	2.053	2.088	2.051
r_4	2.057	2.064	2.053	2.086	2.050
α_{23}	117.76	117.61	117.98	116.99	118.08
α_{24}	117.62	117.14	118.03	116.20	118.17
α_{34}	117.56	117.14	117.13_5	117.15	117.54
β_{12}	81.18	80.86	81.24	79.47	81.68
β_{13}	81.07	81.02	81.23_5	79.60	81.65
β_{14}	81.09	80.82	81.20	79.56	81.62
$\rho(\varepsilon_s)$	0.002	0.002	0.002	0.002	0.001
$\rho(\varepsilon_d)$	0.005	0.014	0.026	0.026	0.017
$\rho(\varepsilon_o)$	0.003	0.005_5	0.001	0.003_5	0.002

Derivation of eqs.11 and Zeeman matrices for ^{5}E (in-state vibronic coupling and spin-orbit coupling effects)

Applying consistently eq.8 we get the following non-zero matrix elements of the $\hat{H}_{SOC}$ operator within the $\left|M_s, M_l\right\rangle$ basis classified according to the total $M_j=M_s+M/2$ value:

	M_J:	
$\left\langle -2,-1\right|\hat{H}_{SOC}\left|-2,-1\right\rangle = -\varsigma/2$	-5/2	
$\left\langle 2,1\right|\hat{H}_{SOC}\left|2,1\right\rangle = -\varsigma/2$	5/2	
$\left\langle -1,-1\right|\hat{H}_{SOC}\left|-1,-1\right\rangle = -\varsigma/4$	-3/2	
$\left\langle 1,1\right|\hat{H}_{SOC}\left|1,1\right\rangle = -\varsigma/4$	3/2	
$\left\langle 0,-1\right|\hat{H}_{SOC}\left|0,-1\right\rangle = 0$	-1/2	(S1)
$\left\langle 0,1\right|\hat{H}_{SOC}\left|0,1\right\rangle = 0$	1/2	
$\left\langle -1,1\right|\hat{H}_{SOC}\left|-1,1\right\rangle = \varsigma/4$	-1/2	
$\left\langle 1,-1\right|\hat{H}_{SOC}\left|1,-1\right\rangle = \varsigma/4$	1/2	
$\left\langle -2,1\right|\hat{H}_{SOC}\left|-2,1\right\rangle = \varsigma/2$	-3/2	
$\left\langle 2,-1\right|\hat{H}_{SOC}\left|2,-1\right\rangle = \varsigma/2$	3/2	

Within the same basis the $\hat{H}_{LF}$ operator (eq.10) can only mix basis vectors with the same M_s but different M_l values. Expression for the non-zero matrix elements in terms of the complex parameter δ (eq.10) are:

$$\left\langle -2,-1\right|\hat{H}_{LF}\left|-2,1\right\rangle = \delta$$
$$\left\langle -2,1\right|\hat{H}_{LF}\left|-2,-1\right\rangle = \delta^*$$
$$\left\langle 2,1\right|\hat{H}_{LF}\left|2,-1\right\rangle = \delta^*$$
$$\left\langle 2,-1\right|\hat{H}_{LF}\left|2,1\right\rangle = \delta \qquad \text{(S2)}$$
$$\left\langle -1,-1\right|\hat{H}_{LF}\left|-1,1\right\rangle = \delta$$
$$\left\langle -1,1\right|\hat{H}_{LF}\left|-1,-1\right\rangle = \delta^*$$
$$\left\langle 1,1\right|\hat{H}_{LF}\left|1,-1\right\rangle = \delta^*$$
$$\left\langle 1,-1\right|\hat{H}_{LF}\left|1,1\right\rangle = \delta$$
$$\left\langle 0,-1\right|\hat{H}_{LF}\left|0,1\right\rangle = \delta$$
$$\left\langle 0,1\right|\hat{H}_{LF}\left|0,-1\right\rangle = \delta^*$$

Combining eqs.(S1) and (S2) we get the following 2x2 matrices pertaining to the pairs of states as follows

M_J=-5/2 M_J=-3/2
|-2,-1> |-2,1>

$$\begin{bmatrix} -\zeta/2 & \delta \\ \delta^* & \zeta/2 \end{bmatrix} \tag{S3}$$

M_J=5/2 M_J=3/2
|2,1> |2,-1>

$$\begin{bmatrix} -\zeta/2 & \delta^* \\ \delta & \zeta/2 \end{bmatrix} \tag{S4}$$

M_J=-3/2 M_J=-1/2
|-1,-1> |-1,1>

$$\begin{bmatrix} -\zeta/4 & \delta \\ \delta^* & \zeta/4 \end{bmatrix} \tag{S5}$$

M_J=3/2 M_J=1/2
|1,1> |1,-1>

$$\begin{bmatrix} -\zeta/4 & \delta^* \\ \delta & \zeta/4 \end{bmatrix} \tag{S6}$$

M_J=-1/2 M_J=1/2
|0,-1> |0,1>

$$\begin{bmatrix} 0 & \delta \\ \delta^* & 0 \end{bmatrix} \tag{S7}$$

Diagonalization of the matrices eqs.(S3)-(S7) yields eq.11. The representation of $\hat{H}_{SOC}$ and $\hat{H}_{LF}$ within the basis of the product of the eigenfunctions of $\hat{S}^2$, $\hat{S}_z$ and $\hat{L}_z$ (eq.7) is particularly useful when $\zeta >> |\delta|$. This is the case for the considered complexes. In the other extreme $\zeta << |\delta|$ a representation with the real basis $\left|{}^5E, d_{xz}\right\rangle$ and $\left|{}^5E, d_{yz}\right\rangle$ would be more appropriate. Within this representation $\hat{H}({}^5E) = \hat{H}_{SOC} + \hat{H}_{LF}$ takes the form:

$$\left|xz,-2\right\rangle \quad \left|xz,-1\right\rangle \quad \left|xz,0\right\rangle \quad \left|xz,1\right\rangle \quad \left|xz,2\right\rangle \quad \left|yz,-2\right\rangle \quad \left|yz,-1\right\rangle \quad \left|yz,0\right\rangle \quad \left|yz,1\right\rangle \quad \left|yz,2\right\rangle$$

$$\hat{H}({}^5E) = \begin{bmatrix} -\delta_1 & 0 & 0 & 0 & 0 & i(\zeta/2)+\delta_2 & 0 & 0 & 0 & 0 \\ 0 & -\delta_1 & 0 & 0 & 0 & 0 & -i\zeta/4+\delta_2 & 0 & 0 & 0 \\ 0 & 0 & -\delta_1 & 0 & 0 & 0 & 0 & \delta_2 & 0 & 0 \\ 0 & 0 & 0 & -\delta_1 & 0 & 0 & 0 & 0 & i\zeta/4+\delta_2 & 0 \\ 0 & 0 & 0 & 0 & -\delta_1 & 0 & 0 & 0 & 0 & -i\zeta/2+\delta_2 \\ -i\zeta/2+\delta_2 & 0 & 0 & 0 & 0 & \delta_1 & 0 & 0 & 0 & 0 \\ 0 & i\zeta/4+\delta_2 & 0 & 0 & 0 & 0 & \delta_1 & 0 & 0 & 0 \\ 0 & 0 & \delta_2 & 0 & 0 & 0 & 0 & \delta_1 & 0 & 0 \\ 0 & 0 & 0 & -i\zeta/4+\delta_2 & 0 & 0 & 0 & 0 & \delta_1 & 0 \\ 0 & 0 & 0 & 0 & i\zeta/2+\delta_2 & 0 & 0 & 0 & 0 & \delta_1 \end{bmatrix}$$

(S8)

Within the same representation the operators $\hat{S}_z$ and $\hat{L}_z$ are represented by:

$$\hat{L}_z(\hat{S}_z) = \begin{bmatrix} (-2) & 0 & 0 & 0 & 0 & i & 0 & 0 & 0 & 0 \\ 0 & (-1) & 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 \\ 0 & 0 & (0) & 0 & 0 & 0 & 0 & -i & 0 & 0 \\ 0 & 0 & 0 & (1) & 0 & 0 & 0 & 0 & -i & 0 \\ 0 & 0 & 0 & 0 & (2) & 0 & 0 & 0 & 0 & i \\ -i & 0 & 0 & 0 & 0 & (-2) & 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 & 0 & 0 & (-1) & 0 & 0 & 0 \\ 0 & 0 & i & 0 & 0 & 0 & 0 & (0) & 0 & 0 \\ 0 & 0 & 0 & i & 0 & 0 & 0 & 0 & (1) & 0 \\ 0 & 0 & 0 & 0 & -i & 0 & 0 & 0 & 0 & (2) \end{bmatrix} \quad \text{(S9)}$$

The different representations of $\hat{H}(^5E) = \hat{H}_{SOC} + \hat{H}_{LF}$ (eqs.S3-S7) and eq.S8 illustrates the reciprocation of electrostatic and electromagnetic forces in ligand field theory, a phenomenon which becomes especially interesting in situations where $\delta(LF)$ and $\zeta(SOC)$ become comparable (not encountered in the studied complexes but possible in complexes with 4d and 5d metals, see discussion by A.D.Liehr, J.Phys.Chem. 1960, 64, p.43-51).

The (A_1,A_2) spin-orbit ground state of ^5E in a trigonal ligand field.

In D_3 symmetry and restricting to spin-orbit coupling within the manifold of the ^5E (d^6) term the ground state of Fe^{II} consists of a pair of two accidentally degenerate A_1 and A_2 electronic levels with wave functions given in eq.S10 and S11, respectively.

$$\Psi_1(A_1) = \frac{1}{2}(|d^+_{z2}d^+_{x2-y2}d^+_{yz}d^+_{xy}| - i|d^+_{z2}d^+_{x2-y2}d^+_{xz}d^+_{xy}| - |d^-_{z2}d^-_{x2-y2}d^-_{yz}d^-_{xy}| - i|d^-_{z2}d^-_{x2-y2}d^-_{xz}d^-_{xy}|) \quad \text{(S10)}$$

$$\Psi_2(A_2) = \frac{1}{2}(-|d^+_{z2}d^+_{x2-y2}d^+_{yz}d^+_{xy}| + i|d^+_{z2}d^+_{x2-y2}d^+_{xz}d^+_{xy}| - |d^-_{z2}d^-_{x2-y2}d^-_{yz}d^-_{xy}| - i|d^-_{z2}d^-_{x2-y2}d^-_{xz}d^-_{xy}|) \quad \text{(S11)}$$

In writing down eqs.S10 and S11 we utilise the electron-hole formalism (Sugano, S.; Tanabe, Y., Kamimura, "Multiplets of Transition-Metal Ions in Crystals", Academic Press, New York, 1970, p.86) allowing us to analyse wave functions due to the d^6 configuration in terms of the more simple complementary states for a d^4 configuration. Applying the $(1/2)\hat{L}_z$ and the $\hat{S}_z$ operators to the functions Φ_1 and Φ_2 defined in eqs.S12 and S13 we can easily prove that they behave as eigenfunctions of these operators as indicated. In terms of these functions we can rewrite $\Psi_1(A_1)$ and $\Psi_2(A_2)$ in the form of S14 and S15.

$$\Phi_1 = \left|2,\frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}(|\, d^+_{z2}d^+_{x2-y2}d^+_{yz}d^+_{xy}\,| - i\,|\, d^+_{z2}d^+_{x2-y2}d^+_{xz}d^+_{xy}\,|) \quad \text{(S12)}$$

$$\Phi_2 = \left|-2,-\frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}(|\, d^-_{z2}d^-_{x2-y2}d^-_{yz}d^-_{xy}\,| + i\,|\, d^-_{z2}d^-_{x2-y2}d^-_{xz}d^-_{xy}\,|) \quad \text{(S13)}$$

$$\Psi_1 = \frac{1}{\sqrt{2}}[\left|2,\frac{1}{2}\right\rangle - \left|-2,-\frac{1}{2}\right\rangle] \quad \text{(S14)}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[-\left|2,\frac{1}{2}\right\rangle - \left|-2,-\frac{1}{2}\right\rangle] \quad \text{(S15)}$$

For the sake of convenience we now convert Ψ_1 and Ψ_2 pertaining for d^4 into their equivalent representations - $\Psi_1^{'}$ and $\Psi_2^{'}$ for d^6. To this end we apply the time reversal operator K on Ψ_1 and Ψ_2 leading to equations S16 and S17.

$$\Psi_1^{'} = \hat{K}\Psi_1 = \frac{1}{\sqrt{2}}[\hat{K}\left|2,\frac{1}{2}\right\rangle - \hat{K}\left|-2,-\frac{1}{2}\right\rangle] = \frac{1}{\sqrt{2}}[\left|-2,-\frac{1}{2}\right\rangle + \left|2,\frac{1}{2}\right\rangle] \quad \text{(S16)}$$

$$\Psi_2^{'} = \hat{K}\Psi_2 = \frac{1}{\sqrt{2}}[-\hat{K}\left|2,\frac{1}{2}\right\rangle - \hat{K}\left|-2,-\frac{1}{2}\right\rangle] = \frac{1}{\sqrt{2}}[-\left|-2,-\frac{1}{2}\right\rangle + \left|2,\frac{1}{2}\right\rangle] \quad \text{(S17)}$$

The Zeeman operator $\hat{H}_Z$ represented in the $\Psi_1^{'}$ and $\Psi_2^{'}$ basis is given by eq.(S18):

$$\begin{matrix} & \left|\Psi_1^{'}\right\rangle & \left|\Psi_2^{'}\right\rangle \end{matrix}$$

$$\hat{H}_Z = \begin{bmatrix} -\Delta & 5\beta H \\ 5\beta H & \Delta \end{bmatrix} \quad \text{(S18)}$$

In a first approximation the $\Psi_1^{'}$ and $\Psi_2^{'}$ states are degenerate (*Δ=0*). However, configuration interaction with the excited states leads to a small splitting with Δ>0. With the parameter set of trigonal [Fe(tpa^{Tbu})]$^-$ (Table 6b) we calculate Δ=0.054 cm^{-1}. It follows from eq.(S18) that already magnetic fields that are larger than 200-300 Gauss are enough to overcome the splitting *2Δ* and to magnetically polarize and split the pair.

We should note that the wavefunctions S14-S15 with $M_l^{'} = \pm\frac{1}{2}$ refer to a symmetry, which is well defined (*D_3*) in the absence of an applied magnetic field in which symmetry $\Psi_1^{'}$ and $\Psi_2^{'}$ belong to the *A_1* and *A_2* irreducible representations of the *D_3* point group . Applying a field parallel to the C_3 axis, the symmetry is lowered from a *D_3* to a *C_3*. In this symmetry the eigenfunctions of the orbital angular momentum operator $\hat{L}_z$ with $M_l = \pm 1$ behave as pseudo Kramers states with $M_l^{'} = \pm 1/2$.

Applying the symmetry operations of the *D_3* group – *C_3* and $C_2(\perp C_3)$ to $\left|-2,-1\right\rangle$ and $\left|2,1\right\rangle$ we obtain (Zare, R.N. Angular Momentum, John Wiley &Sons New York, eq.3.52 and Table 3.1)

$$\hat{C}_3 |-2,-1\rangle = |-2,-1\rangle$$
$$\hat{C}_3 |2,1\rangle = |2,1\rangle$$
$$\hat{C}_2 |-2,-1\rangle = |2,1\rangle \qquad \text{(S19)}$$
$$\hat{C}_2 |2,1\rangle = |-2,-1\rangle$$

and further:

$$C_3\Psi'_1 = +1\Psi'_1$$
$$C_3\Psi'_2 = +1\Psi'_2$$
$$C_2\Psi'_1 = +1\Psi'_1 \qquad \text{(S20)}$$
$$C_2\Psi'_2 = -1\Psi'_2$$

Thus we verify that Ψ'_1 and Ψ'_2 transform as the A_1 and A_2 irreducible representations of the D_3 group. An applied magnetic field parallel to C_3 removes the C_2 axis. Thus Ψ'_1 and Ψ'_2 become of the same symmetry (A, C_3 point group) and start mix.

It is shown in Figure S1 that the A_1-A_2 ground state energy separation strongly depends on the the N_{axial}-Fe-$N_{equatorial}$ angle. Within the range of variations of this angle in the considered systems, this separation is negligibly small and is dominated by the small off-axial distortions. However it strongly increases for $\beta<80^o$ and can become responsible for a fast lost of the magnetizations already in complexes with strictly trigonal symmetry.

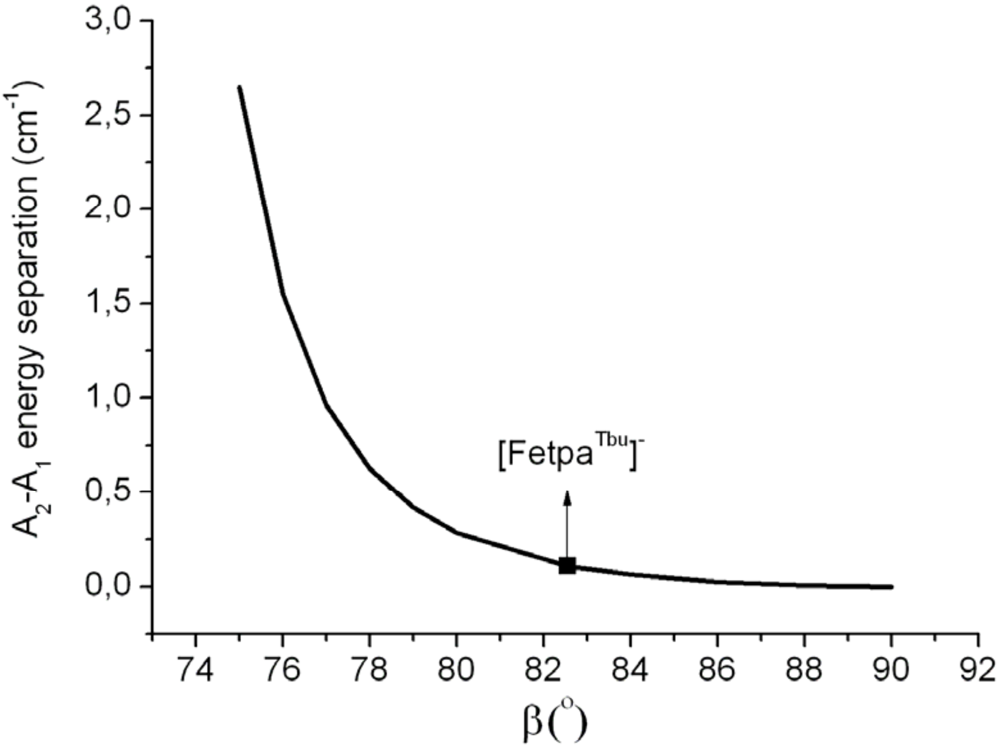

Figure S1. Dependence of the A_2-A_1 energy separation 2Δ on the N $_{axial}$ – Fe – N$_{equatorial}$ angle β. The plot has been prepared using the parameters of Table 6b (CASSCF set).The point corresponding to the $[Fetpa^{Tbu}]^-$ is indicated.

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Orthorhombic splitting of the ground state magnetic pair.

The parameters D, B_{40} and E have been obtained from the energy separation between the ground state magnetic pair A_1,A_2 and the third, fourth and fifth spin-orbit excited states employing the SH of eq.14. Neglecting the A_1 and A_2 splitting in trigonal symmetry we can apply eq.30 along with values of D, B_{40} and E (Table 5a, experimental geometries, CASSCF results) given by perturbation theory and calculate values of ΔE:

	$[Fetpa^{Mes}]$-	$[Fetpa^{Ph}]$-	$[Fetpa^{Dfp}]$-
$\Delta E(cm^{-1})$:	0.046	0.052	0.720

These are in excellent agreement with the CASSCF values (0.054, 0.056 and 0.623 cm^{-1}). There is no need of introducing quartic orthorhombic term $E_4(S_+^4 + S_-^4)$ to reproduce the CASSCF values of ΔE.

Effects of covalent reduction of the spin-orbit coupling constant (relativistic nephelauxetic effect) on the parameters *D* and B_{40}

Correlated electronic structure methods tend to overestimate atomic-like parameters –the parameters of interelectronic repulsion *B* and *C* and the spin-orbit coupling constant ζ (however DFT yield heavily underestimate values, Atanasov, M., Daul, C.A., Rauzy, C., *Structure and Bonding*, **2004**, *106*, 97-125). Since the energies of the spin-allowed d-d transition do not explicitly depend on *B* and *C*, the parameters *D* and B_{40} are not significantly affected by the latter parameters. In Figures S2 and S3 we plot the dependence of *D* and B_{40} on the reduction of ζ over its CASSCF value (ζ_o):

$$\beta = 1 - \frac{\varsigma}{\zeta_o} \qquad \text{(S21)}$$

The notation β has been used here by convention (to be distinguished from the angle β defined in Figure 2 and used in Table 2 and Figure S1) . In agreement with the simplified equations of Table 1 both *D* and B_{40} decrease nearly linearly with increasing β values. This is different to the case of orbitally non-degenerate ground states, where the values of $D \sim \zeta^2$ and thus decreases much steeper with increasing covalence (increasing β).

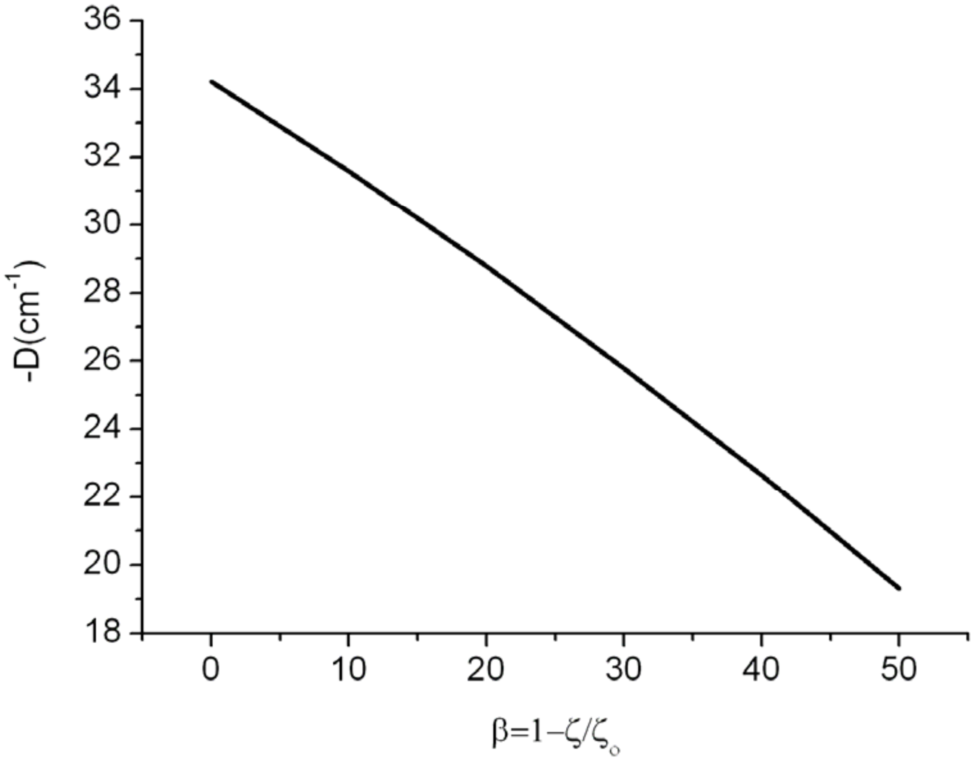


Figure S2 Dependence of *D* on the relativistic nephelauxetic effect as quantified by the parameter β.

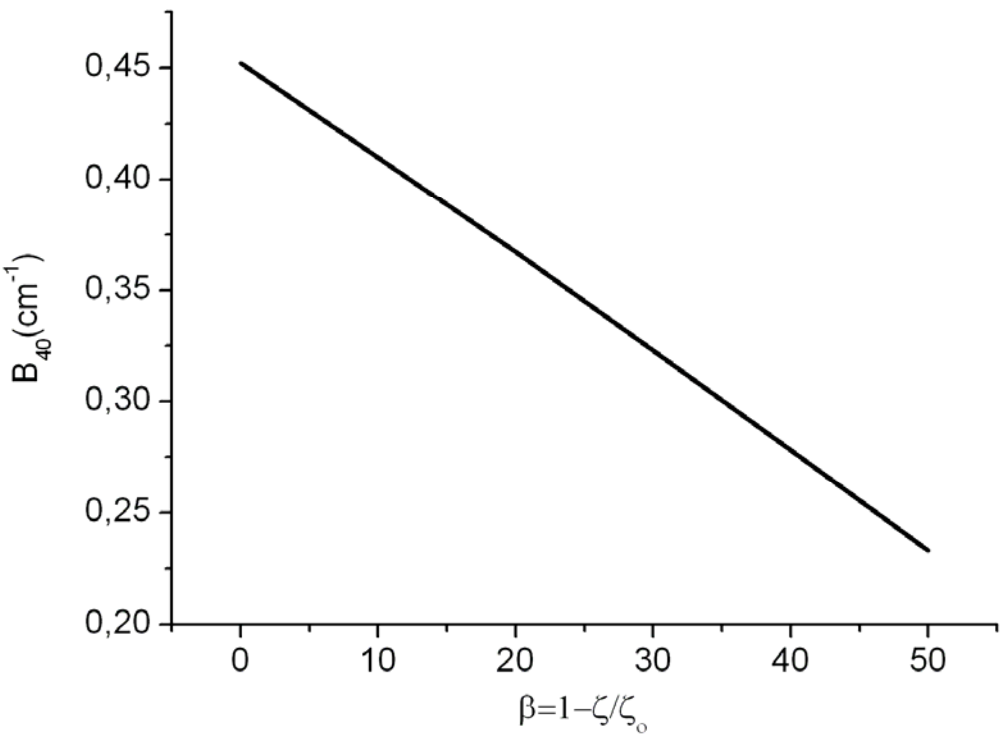


Figure S3. Dependence of B_{40} on the relativistic nephelauxetic effect as quantified by the parameter β.

Determination of the sign of the Parameter *E*

The sign of the orthorhombic splitting parameter *E* can be determined experimentally, by measuring magnetizations on single crystals or theoretically, by calculations of the magnetization tensor along the x and y directions (see Figure 2 for the orientation of these axes with respect to the molecular frame). Here we derive equations for M_x, M_y and M_z.

For the sake of simplicity we focus on the form of the SH of eq.13. With a magnetic field oriented parallel to the x, y and z axes we have the following matrix representations of $\hat{H}_{ZFS} + \hat{H}_Z$:

B||*x:*

$$\begin{matrix} & |2+\rangle & |2-\rangle & |1+\rangle & |1-\rangle & |0\rangle \end{matrix}$$

$$\hat{H}_{ZFS} + \hat{H}_Z = \begin{bmatrix} 2D & 0 & g_o\beta B_x & 0 & 2\sqrt{3}E \\ 0 & 2D & 0 & g_o\beta B_x & 0 \\ g_o\beta B_x & 0 & -D+3E & 0 & g_o\beta B_x\sqrt{3} \\ 0 & g_o\beta B_x & 0 & -D-3E & 0 \\ 2\sqrt{3}E & 0 & g_o\beta B_x\sqrt{3} & 0 & -2D \end{bmatrix} \tag{S22}$$

B||*y:*

$$\begin{matrix} & |2+\rangle & |2-\rangle & |1+\rangle & |1-\rangle & |0\rangle \end{matrix}$$

$$\hat{H}_{ZFS} + \hat{H}_Z = \begin{bmatrix} 2D & 0 & 0 & g_o\beta B_y i & 2\sqrt{3}E \\ 0 & 2D & g_o\beta B_y i & 0 & 0 \\ 0 & -g_o\beta B_y i & -D+3E & 0 & 0 \\ -g_o\beta B_y i & 0 & 0 & -D-3E & g_o\beta B_y i\sqrt{3} \\ 2\sqrt{3}E & 0 & 0 & -g_o\beta B_y i\sqrt{3} & -2D \end{bmatrix} \tag{S23}$$

B||*z*

$$\begin{matrix} & |2+\rangle & |2-\rangle & |1+\rangle & |1-\rangle & |0\rangle \end{matrix}$$

$$\hat{H}_{ZFS} + \hat{H}_Z = \begin{bmatrix} 2D & -2g_o\beta B_z & 0 & 0 & 2\sqrt{3}E \\ -2g_o\beta B_z & 2D & 0 & 0 & 0 \\ 0 & 0 & -D+3E & -g_o\beta B_z & 0 \\ 0 & 0 & -g_o\beta B_z & -D-3E & 0 \\ 2\sqrt{3}E & 0 & 0 & 0 & -2D \end{bmatrix} \tag{S24}$$

Eqs.22-24 have been derived by transforming $\hat{H}_{ZFS}$ (eq. 15 with B_{40}=0) and the corresponding matrix representations of the Zeeman operator $\hat{H}_Z$ from the $|\pm2\rangle$, $|\pm1\rangle$ and $|0\rangle$ spin eigenfunctions for S=2 into the basis of eqs.S25-26 and $|0\rangle$:

$$|2\pm\rangle = \frac{1}{\sqrt{2}}[|2\rangle \pm |-2\rangle] \qquad \text{(S25)}$$

$$|1\pm\rangle = \frac{1}{\sqrt{2}}[|1\rangle \pm |-1\rangle] \qquad \text{(S26)}$$

Focussing on negative values of D=-|D| and E=-|E| and utilizing qs.22-24 along with second order perturbation theory yields the following expressions for the ground state level pair $|2\pm\rangle$:

B||x:

$$|2+\rangle: \; -2|D| - \frac{3E^2}{|D|} - \frac{(g_o\beta)^2}{3(|D|-|E|)}B_x^2 \qquad \text{(S27)}$$

$$|2-\rangle: \; -2|D| - \frac{(g_o\beta)^2}{3(D|+|E|)}B_x^2 \qquad \text{(S28)}$$

B||y:

$$|2+\rangle: \; -2|D| - \frac{3E^2}{|D|} - \frac{(g_o\beta)^2}{3(|D|+|E|)}B_y^2 \qquad \text{(S29)}$$

$$|2-\rangle: \; -2|D| - \frac{(g_o\beta)^2}{3(|D|-|E|)}B_y^2 \qquad \text{(S30)}$$

and

B||z:

$$2g_o\beta B >> \frac{3E^2}{|D|} \qquad \text{(S31)}$$

$$|\pm2\rangle: \; -2|D| - \frac{3E^2}{2|D|} \pm 2g_o\beta B_z \qquad \text{(S32)}$$

$$2g_o\beta B << \frac{3E^2}{|D|} \qquad \text{(S33)}$$

$$|2+\rangle: \; -2|D| - \frac{3E^2}{|D|} - \frac{4(g_o\beta B)^2|D|}{3E^2} \qquad \text{(S34)}$$

$$\left|2-\right\rangle : \; -2|D| + \frac{4(g_o\beta B)^2 |D|}{3E^2} \qquad \text{(S35)}$$

To this end we apply the Van Vleck formula:

$$M = NB\frac{\sum_n (E_n^{(1)})^2 / kT - 2E_n^{(2)} \exp(E_n^{(o)} / kT)}{\sum_n \exp(E_n^{(o)} / kT)} \qquad \text{(S36)}$$

with

$$E_n = E_n^{(o)} + E_n^{(1)}B + E_n^{(2)}B^2 \qquad \text{(S37)}$$

and obtain

$$M_x = \frac{1}{3}(NB)(g_o\beta)^2[2|D| + \frac{3E^3}{|D|kT}]/(D^2 - E^2) \qquad \text{(S38)}$$

$$M_y = \frac{1}{3}(NB)(g_o\beta)^2[2|D| - \frac{3E^3}{|D|kT}]/(D^2 - E^2) \qquad \text{(S39)}$$

and

$$M_x - M_y = (g_o\beta)^2 BN\frac{2|E|^3}{|D|(D^2 - E^2)kT} \qquad \text{(S40)}$$

It follows from eq S40, that for negative D and E, $M_x > M_y$. For $D<0$ and $E>0$ we have to change the sign of E in eqs.S27-S30 and S38-40; this leads to $M_y > M_x$.

For M_z at low temperatures and high magnetic fields eqs.S31-S32 cannot be applied. In this case the general equation for the magnetization is valid (Kahn, O,, Molecular Magnetism, Wiley-VCH, New York, eq.1.3.6) and has been used along with the energy levels given by eq.S33. This leads to:

$$M_z = N(2g_o\beta)\tanh(2g_o\beta B / kT) \qquad \text{(S39)}$$

For small magnetic fields (eqs.S33-S35) the magnetization drops to zero.

Eq.S40 helps to rationalize the dependence of M_x and M_y with B/T and the conclusions about the sign of E drawn in Section III.3.

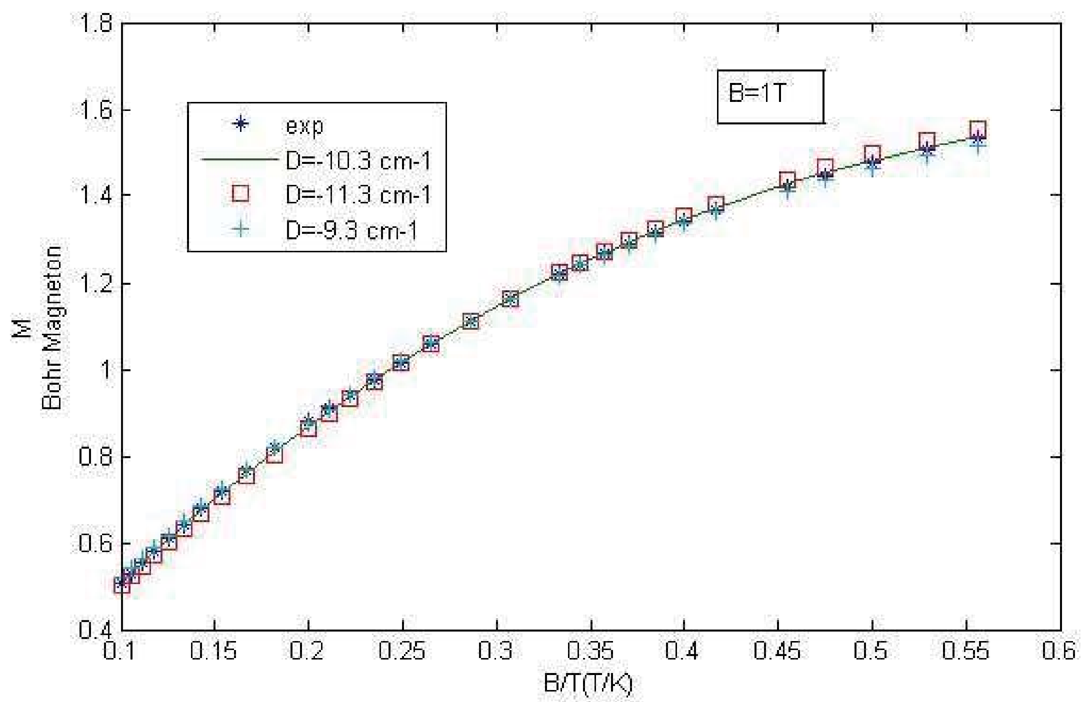
Fitting parameters of the SH for complexes 1-4 using the spin-Hamiltonian of eq.14 (*D*, B_{40}, *E* and *g*).

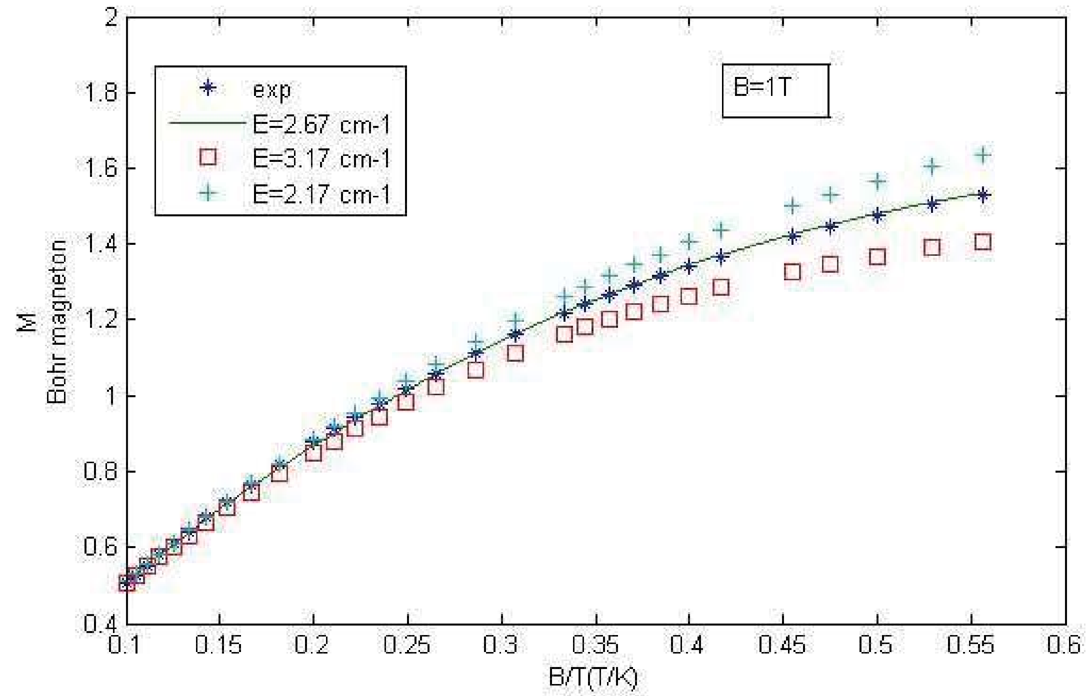
Parameters of the SH of eq. 14 have been obtained by a fit to experimental magnetizations (*M*) minimizing the standard deviation σ between experimental and calculated M; parameter values and standard deviations – minimum values of σ are listed in Table 5a. It should be noted, that only parameter ranges for each parameter rather than unique values can be given. The error bar for each parameter ΔP_i has been calculated as the numerical solution of eq.S40 which defines the increase of σ from its value corresponding to the minimum of the fit (Table 5a) to an arbitrary but rather conservatively chosen increment of 0.01:

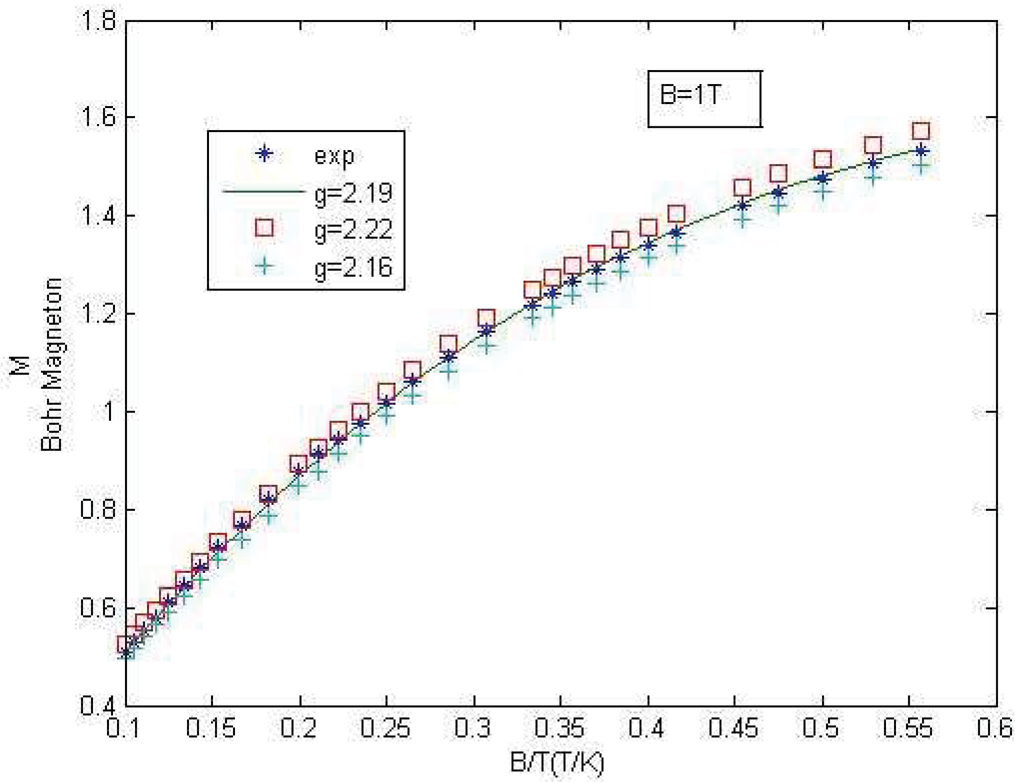
$$\sigma(...P_i^o + \Delta P_i...) - \sigma(...P_i^o...) = 0.01 \qquad \text{(S40)}$$

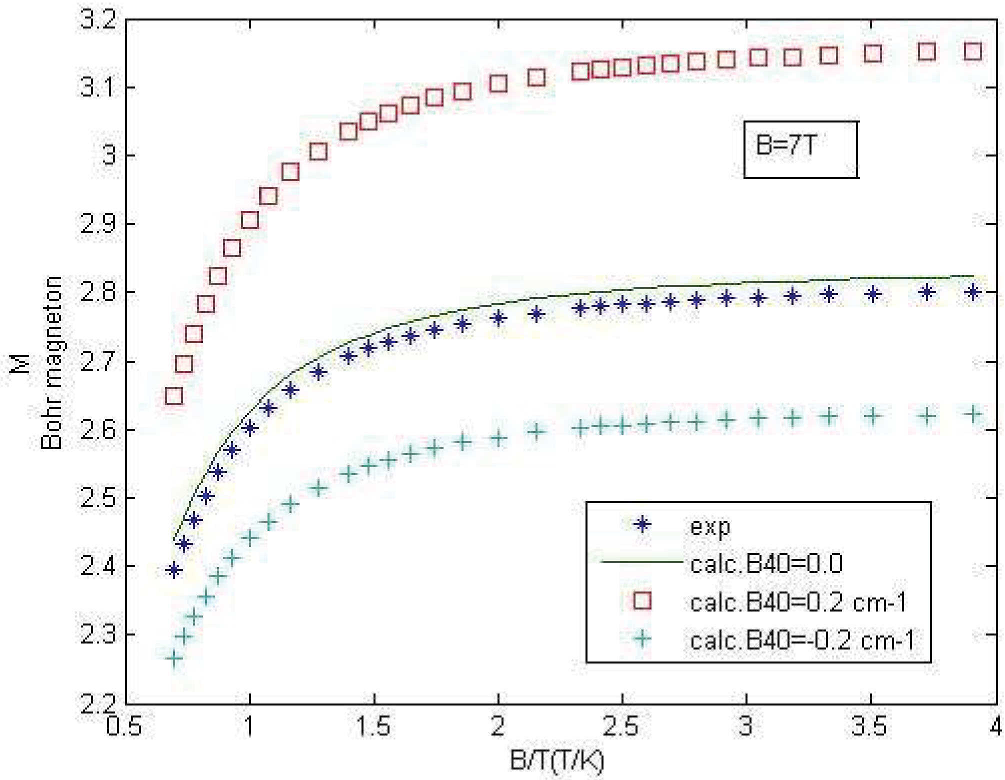
i=1 to 4 (i.e. *D*, B_{40}, *E* and *g* for the SH of eq.14).

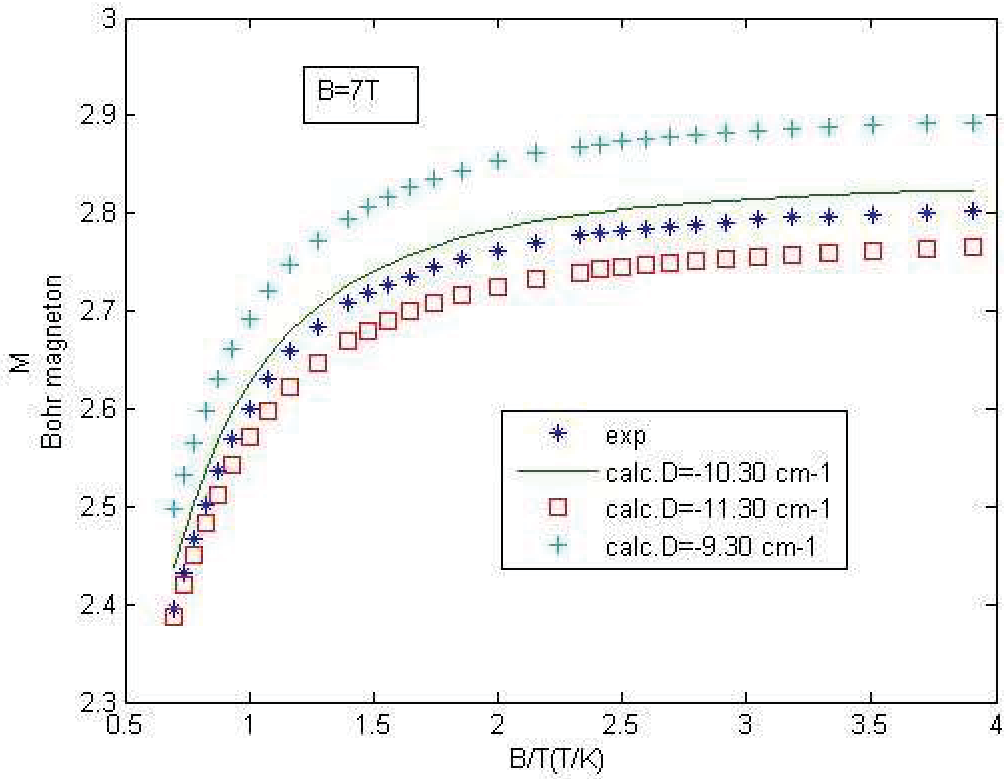
Below we plot for complex **4** the experimental *M* (stars) and calculated *M* (using fit parameters from Table 5a, solid lines) along with *M* calculated using variations of *D*, B_{40}, *E* and *g*, illustrating their effect on the low-field (*B*=1 T) and high-field (*B*=7 T) *M* values (Figure S4). We further show a complete set of experimental versus reproduced (using fitted parameters from Tables 5a) magnetisation for complexes **1-4**.

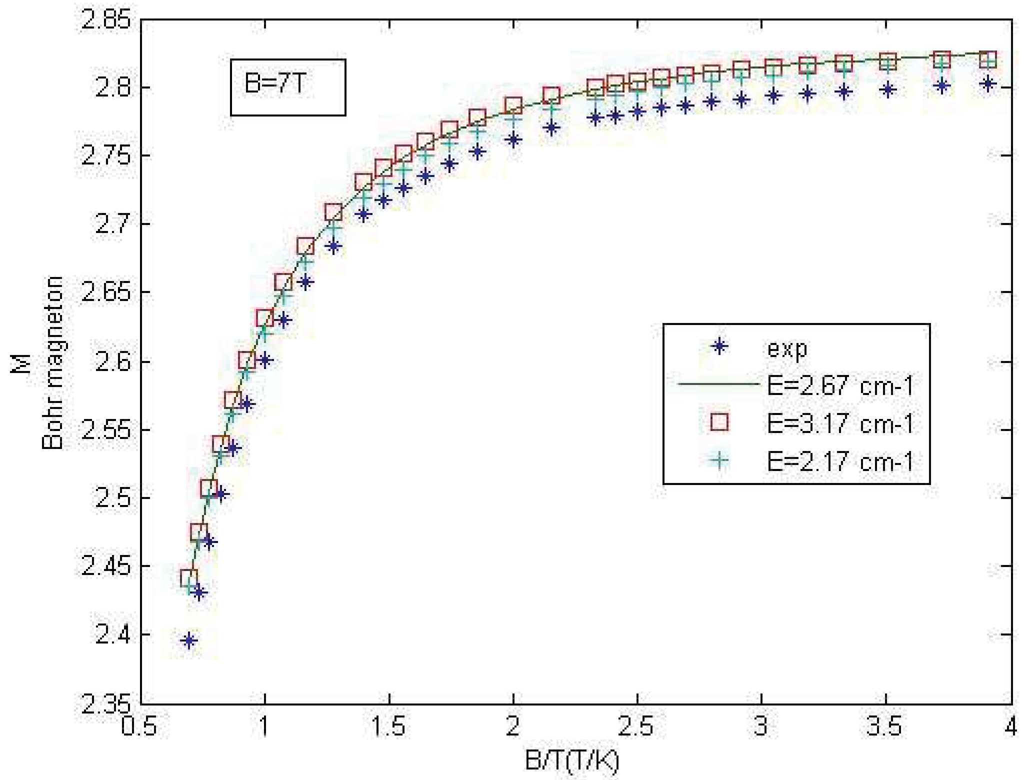


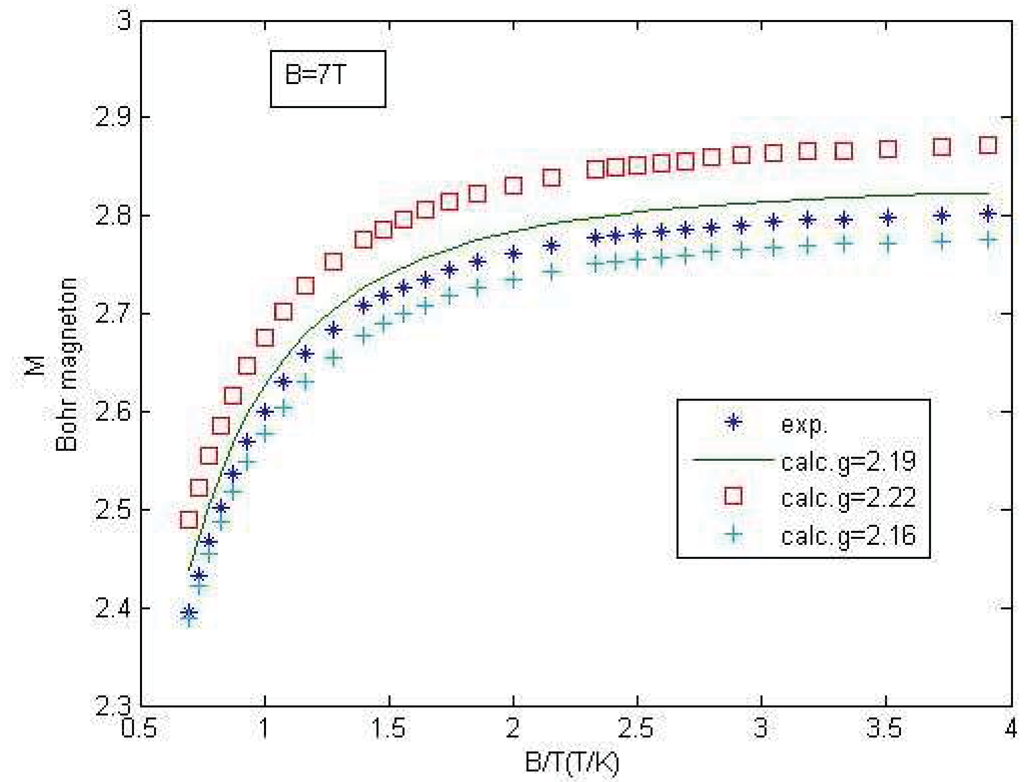

exp
E=2.67 cm-1
E=3.17 cm-1
E=2.17 cm-1
B=1T
M
Bohr magneton
B/T(T/K)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6


B=1T
exp
g=2.19
g=2.22
g=2.16
M
Bohr Magneton
B/T(T/K)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0.6


B=7T
M
Bohr magneton
B/T(T/K)
exp
calc.B40=0.0
calc.B40=0.2 cm-1
calc.B40=-0.2 cm-1


B=7T
M
Bohr magneton
B/T(T/K)
exp
calc.D=-10.30 cm-1
calc.D=-11.30 cm-1
calc.D=-9.30 cm-1





Figures S4 Experimental (exp. plotted with stars, adopted from Ref.2) and simulated (solid lines) $M(B{=}1\text{T})$ and $M(B{=}7\text{T})$ data sets for **4**. Parameter values of D, B_{40}, E and g for the simulation are those given for $[Fe(tpa^{Dfp})]^-$ in Table 5a. The changes of M with variations of D, B_{40}, E and g are shown.

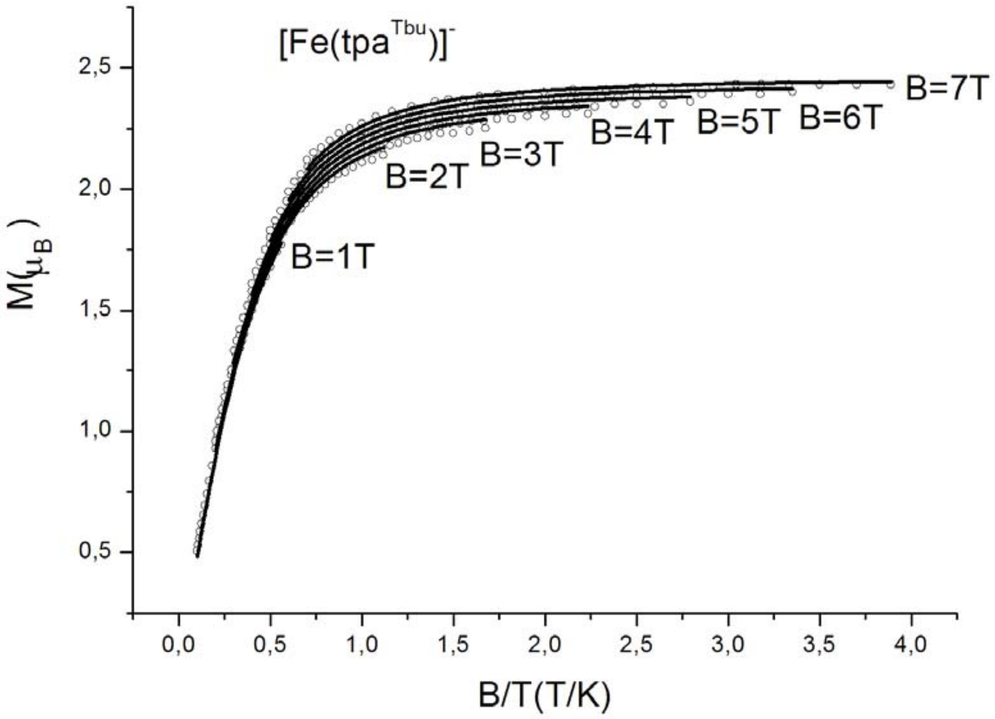


Figure S5: Magnetisations of $[Fe(tpa^{Tbu})]^-$ (from Ref.2, open circles); black lines represent fits to the data (From Ref.2) using parameter values from Table 5a.

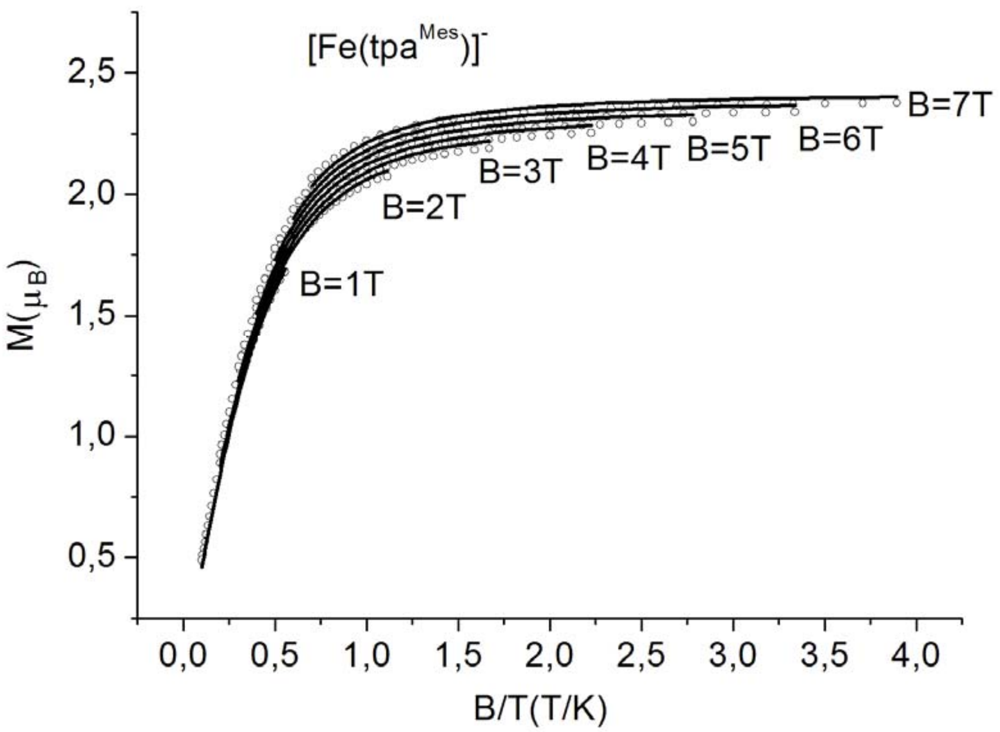


Figure S6: Magnetisation data for $[Fe(tpa^{Mes})]^-$ (from Ref.1, open circles); black lines represent fits to the data using parameter values from Table 5a.

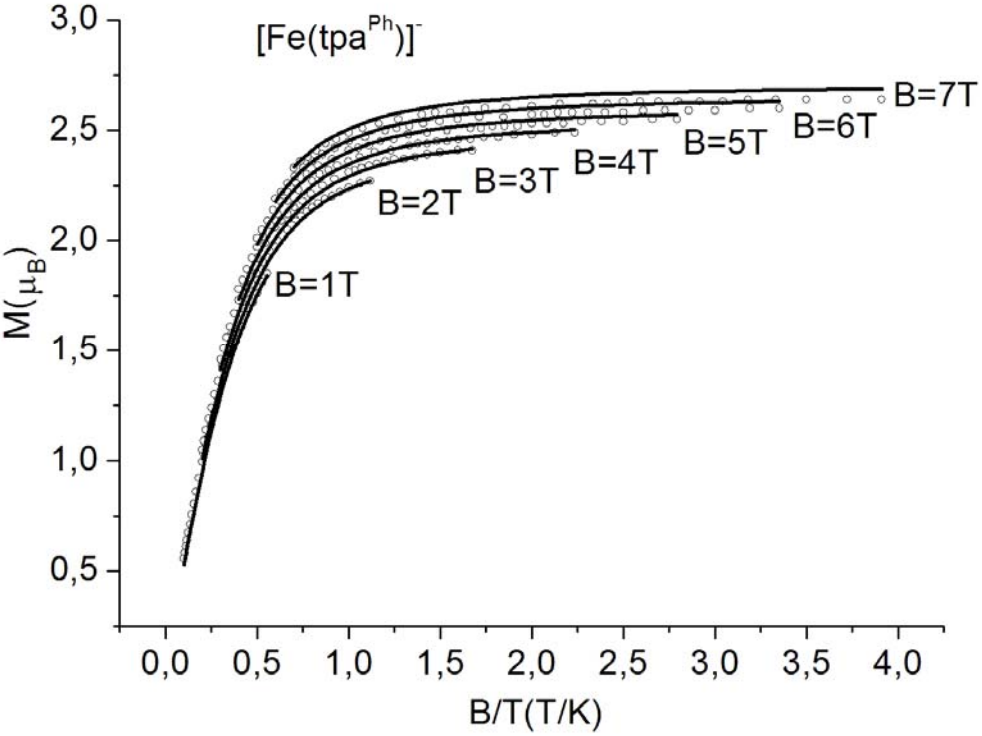


Figure S7: Magnetisation data for $[Fe(tpa^{Ph})]^-$ (from Ref.2, open circles); black lines represent fits to the data using parameter values from Table 5a.

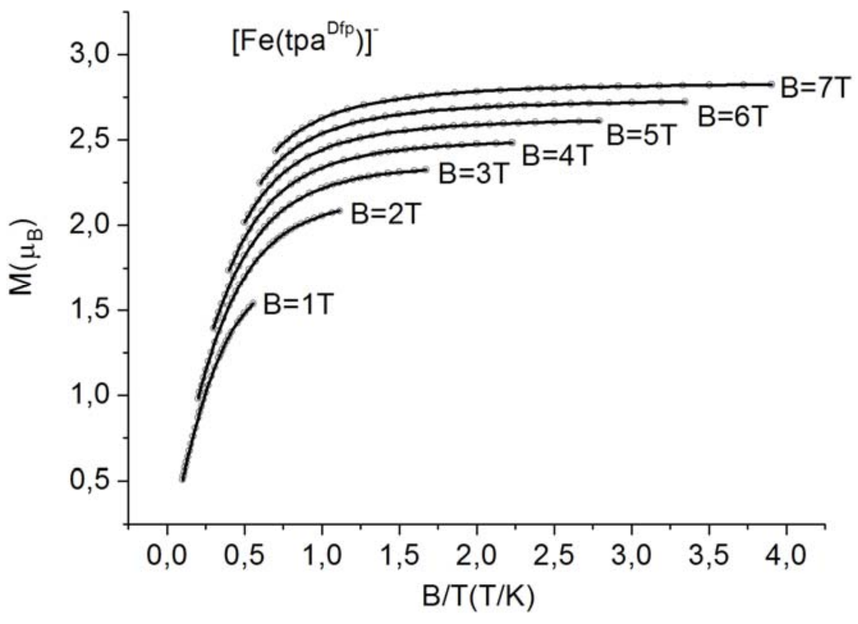


Figure S8: Magnetisation data for $[Fe(tpa^{Dfp})]^-$ (from Ref.2, open circles); black lines represent fits to the data using parameter values from Table 5a.

Computational Details

Geometry optimizations of complexes **1-4** have been done using ORCA Program version 2.7 (Revision 0); SVN: $Rev:2022$ starting with Cartesian coordinates as given by the X-Ray structures following a reorientation (see Figure 2).

Sample input file for [Fe(tpa^{Mes})]$^{-}$ (complex **2**) including starting coordinates from X-ray data:

```
!UKS PBE VDW ZORA def2-TZVP def2-TZVP/J Opt  PAL8

* xyz -1 5
Fe          0.00000000000000    0.00000000000000    0.00000000000000
N           0.00000000000000    0.00000000000000    2.17167114453363
N           1.99099897510995    0.00000000000000    0.26379490349725
N          -0.98395490984738   -1.76587999277164    0.28386885443118
N          -0.90357561917498    1.79501236940530    0.23928180899212
C          -0.14187914406252    1.42074186063419    2.56382193685946
C          -0.99369782480254    2.15993429031768    1.56880749121509
C          -1.76307385855470    3.27914414372072    1.70926799361105
C          -2.17804469237225    3.64387371495520    0.41265221129622
C          -1.65230629335355    2.72915546847988   -0.46468867191985
C          -1.71059027870829    2.72177348403337   -1.94978432653500
C          -2.86092007720031    2.31292448452040   -2.63722554605749
C          -2.85683876892262    2.30224398492551   -4.02325945251546
C          -1.75306266813002    2.68705814277966   -4.76320788533635
C          -0.63384939088317    3.11107004903557   -4.07671974750176
C          -0.58909007428828    3.14054496065854   -2.69129693725112
C          -4.08605523607590    1.85586289950995   -1.90136835882983
C          -1.78211544480456    2.64185658202563   -6.26336860175073
C           0.63992398951979    3.63647651800355   -1.97935195244449
C           1.29714784936030   -0.58409964091614    2.56233335972929
C           2.36355517405425   -0.18838622607481    1.57386554985700
C           3.71807600696502   -0.04635097367243    1.70509355862681
C           4.21435412269732    0.25313730254351    0.42619402220715
C           3.14137464610067    0.28717399845063   -0.43839721423588
C           3.07434322302432    0.59626271654062   -1.88178019968010
C           3.53706937373736    1.81799483538771   -2.38551237973581
C           3.40013044246743    2.10307384332197   -3.74179740816378
C           2.80891060456836    1.22128309604984   -4.63452909310604
C           2.40113843182834   -0.00044880746512   -4.13077945184305
C           2.53102786324511   -0.33320186222803   -2.79520745821928
C           4.15908187412616    2.85968772086655   -1.49356690959605
C           2.65699829652313    1.57035575413529   -6.09144647581569
C           2.19061919811124   -1.72437410934340   -2.33763029581083
C          -1.15603770476297   -0.81888239933278    2.57180929721264
C          -1.35860115593307   -1.94308072201779    1.59132209713186
C          -1.97158374418927   -3.16480606481194    1.75767540569303
C          -1.97671272569102   -3.77567632717455    0.49255534968657
C          -1.35452254889384   -2.91784294713421   -0.39054451781747
C          -1.03901015125567   -3.12017749886475   -1.82502613711854
C          -0.53379198429647   -4.36004632175264   -2.29584324152850
C          -0.17531023721966   -4.49266035705132   -3.62905440809386
C          -0.27754555292143   -3.46894976248027   -4.54726987778839
C          -0.78610181237172   -2.27349835238612   -4.08555719973218
C          -1.17891618205909   -2.08116424261538   -2.76315129714939
C          -0.36846712819665   -5.56696204122312   -1.41438143971823
C           0.15649408147975   -3.62531115937006   -5.97619963440051
C          -1.73826428451335   -0.73450807768019   -2.40846086349931
H          -0.54698699851031    1.47025082888944    3.42215028214872
```

```
H             0.72060145592606    1.82252206132041    2.59781671557438
H            -1.97725854920506    3.72403546754497    2.51992057534808
H            -2.72153790381957    4.38761298478565    0.18379171312594
H            -3.63982255287708    2.01898849992468   -4.48058117109145
H             0.12960585890778    3.38843314978547   -4.56653156025136
H            -0.94788434532075    2.94338098689547   -6.60769721793289
H            -1.93742480877432    1.74834586769125   -6.55030362023569
H            -2.47675847543780    3.20264300666653   -6.58310312589716
H             1.53715958254411   -0.26803108702285    3.42667460436240
H             1.22218932333788   -1.53162632725506    2.58256225124934
H             4.22329204715485   -0.13494466633006    2.50675249505564
H             5.12559018508259    0.40654344502325    0.19542339136764
H             3.73197467197103    2.93173362797128   -4.06760052148550
H             2.01187865024449   -0.63406348386168   -4.72180957315345
H             3.14307287553394    0.94910889357806   -6.62107387492496
H             1.73580396292622    1.53263663237978   -6.33076329010785
H             2.98710138779813    2.44630249676720   -6.24702714043448
H            -1.00091757173412   -1.17898960002992    3.43596311936190
H            -1.93327645569985   -0.27246895871050    2.58862018503601
H            -2.31796020187492   -3.52241190759402    2.56639554935786
H            -2.34276136155312   -4.62819183459247    0.28479458391147
H             0.15479005592587   -5.33464219255943   -3.92645266824282
H            -0.87576414909589   -1.55183882487631   -4.69624344628394
H             0.84716334673777   -3.00058098306457   -6.16794548922211
H             0.48307364944891   -4.50634469991602   -6.11173836029872
H            -0.58071949116833   -3.46711302412388   -6.55208377926655
H             0.16082283337446   -6.21586621742383   -1.86161051601954
H             0.06055678543038   -5.31403176102485   -0.60316395661337
H            -1.22205819607706   -5.93637970589681   -1.21712762388231
H             4.99424395829049    2.54313489252481   -1.17289109191852
H             4.29280165731348    3.66291319824090   -1.98534161622611
H             3.58215203339597    3.03373678627125   -0.75694653130966
H            -2.44585831691566   -0.83916124748000   -1.78539938229582
H            -2.06726780913748   -0.31507498417986   -3.19408077851015
H             1.99223178644043   -2.26499356711484   -3.09279779164833
H             2.92994740912745   -2.08996287619936   -1.86844738910568
H             1.43506698677186   -1.69039194428909   -1.76251187461534
H            -1.05363259783966   -0.20013256344588   -2.02588120723260
H             1.26366593096976    3.96456225890250   -2.61628149100823
H             0.39894396301216    4.33852157458354   -1.38489730711317
H             1.03066353845943    2.92584133983453   -1.48852352168367
H            -4.44257019756341    2.58148967909823   -1.40260044789338
H            -4.73239692216034    1.55176505693257   -2.52777051157940
H            -3.85462057749737    1.14842505587282   -1.31222213233025
*
```

Coordinates obtained from a geometry optimization of $[Fe(tpa^{Mes})]^-$

```
92
Coordinates from ORCA-job geometry optimization
  Fe      0.050751      0.084495     -0.006222
  N       0.003052      0.032834      2.210527
  N       2.017648     -0.009507      0.295347
  N      -0.960766     -1.643466      0.216161
  N      -0.896064      1.835168      0.308136
  C      -0.135201      1.445174      2.616533
  C      -1.031021      2.147309      1.645171
  C      -1.979125      3.149832      1.819321
  C      -2.452577      3.474922      0.520876
  C      -1.761569      2.662076     -0.383110
  C      -1.795103      2.670468     -1.852798
  C      -3.001733      2.504784     -2.569674
```

C	-2.970218	2.445124	-3.968841
C	-1.774057	2.536683	-4.686714
C	-0.593460	2.753309	-3.967907
C	-0.585000	2.840213	-2.572786
C	-4.316197	2.341610	-1.852103
C	-1.746907	2.372266	-6.183937
C	0.701327	3.155615	-1.858931
C	1.295448	-0.582308	2.577297
C	2.357885	-0.121296	1.625477
C	3.706358	0.175816	1.797091
C	4.214201	0.486768	0.506859
C	3.154074	0.358647	-0.396452
C	3.113010	0.519506	-1.859090
C	3.577332	1.699050	-2.484836
C	3.412766	1.859803	-3.866052
C	2.798688	0.884592	-4.656344
C	2.403049	-0.304923	-4.036548
C	2.563490	-0.513126	-2.663657
C	4.184068	2.818122	-1.680662
C	2.530211	1.118718	-6.119556
C	2.209341	-1.853200	-2.078382
C	-1.182503	-0.789414	2.525742
C	-1.332960	-1.886683	1.517769
C	-1.891740	-3.155879	1.638063
C	-1.847667	-3.727704	0.345305
C	-1.268717	-2.782016	-0.515361
C	-0.952474	-2.927789	-1.943078
C	-0.416870	-4.144183	-2.449990
C	-0.075656	-4.245643	-3.804732
C	-0.234317	-3.185315	-4.699529
C	-0.775064	-1.999585	-4.198288
C	-1.132111	-1.851470	-2.854845
C	-0.132729	-5.333776	-1.568584
C	0.200907	-3.294125	-6.137348
C	-1.692924	-0.526856	-2.434905
H	-0.510153	1.538506	3.656065
H	0.885071	1.868174	2.585254
H	-2.279454	3.600826	2.763612
H	-3.188231	4.233815	0.259680
H	-3.908125	2.282632	-4.510466
H	0.354527	2.861899	-4.503973
H	-0.981269	3.016453	-6.643603
H	-1.504962	1.332148	-6.464522
H	-2.722352	2.615831	-6.632037
H	1.568438	-0.359523	3.628153
H	1.143485	-1.673131	2.489581
H	4.259375	0.154311	2.734943
H	5.238727	0.750390	0.252618
H	3.742697	2.795642	-4.329331
H	1.949395	-1.102378	-4.633586
H	2.637240	0.189533	-6.700628
H	1.497928	1.479852	-6.275957
H	3.212722	1.874457	-6.537404
H	-1.132898	-1.197028	3.555827
H	-2.043079	-0.096977	2.481101
H	-2.288765	-3.605664	2.546613
H	-2.202419	-4.714317	0.060162
H	0.359513	-5.183814	-4.164656
H	-0.920711	-1.145663	-4.868330
H	1.148059	-2.752321	-6.308311
H	0.360884	-4.343537	-6.427324
H	-0.546064	-2.855742	-6.818363
H	0.613950	-5.988873	-2.044453

H	0.230566	-5.014304	-0.581158
H	-1.037565	-5.937660	-1.385498
H	5.213377	2.582225	-1.365487
H	4.212753	3.747553	-2.269606
H	3.609577	2.986543	-0.757327
H	-2.405954	-0.614878	-1.605652
H	-2.164223	-0.008553	-3.281224
H	2.018091	-2.587513	-2.872855
H	3.022338	-2.207769	-1.424197
H	1.310952	-1.811374	-1.448014
H	-0.891765	0.167539	-2.100001
H	1.439000	3.569855	-2.560391
H	0.518307	3.864430	-1.037298
H	1.148209	2.260845	-1.401709
H	-4.718467	3.312312	-1.519136
H	-5.062766	1.873662	-2.512041
H	-4.190593	1.732966	-0.944458

Input coordinates for a geometry optimization of [Fe(tpa)^{Tbu}]$^{-}$ (complex **1**) adopted from X-ray data:

Fe	0.000000000	0.000000000	0.000000000
N	-0.000006372	0.000105626	2.144438000
N	2.013475577	0.000000000	0.263165078
N	-1.006727753	1.743740363	0.263069266
N	-1.006749354	-1.743702780	0.263241656
C	1.250660069	-0.674726743	2.527858846
H	1.517360360	-0.432140717	3.562111566
H	1.054361134	-1.749524884	2.478479815
C	4.227600259	0.311480342	0.539013875
H	5.261866887	0.535012479	0.334453597
C	3.685241389	-0.074867623	1.785371127
H	4.215820976	-0.211990521	2.715505710
C	3.187709289	0.361916235	-0.367778097
C	3.193943303	0.860333938	-1.797479004
C	4.638623444	0.935262042	-2.315848139
H	5.123434297	-0.043277728	-2.294345544
H	4.648969239	1.294901781	-3.347847429
H	5.238415370	1.625753676	-1.720716215
C	2.333934581	-0.265998041	1.578590362
C	2.389331111	-0.065715731	-2.716670541
H	1.341000886	-0.134804187	-2.414485873
H	2.394636407	0.310660735	-3.742859069
H	2.795047653	-1.078356586	-2.717870560
C	2.597591155	2.265509342	-1.844876397
H	3.201299429	2.960670883	-1.257211773
H	2.554516962	2.639896036	-2.872250758
H	1.585922470	2.295145165	-1.437946031
C	-0.040903053	1.420660549	2.527750932
H	-0.385069130	1.530674097	3.562228953
H	0.988141564	1.788037491	2.479804948
C	-2.383530087	3.505509978	0.538835200
H	-3.094226717	4.289577587	0.334274788
C	-1.777715126	3.229083086	1.785190308
H	-1.924966357	3.756759723	2.715470306
C	-1.907297736	2.579650395	-0.367904273
C	-2.342110924	2.335730816	-1.797569616
C	-3.129361254	3.549356121	-2.316002435
H	-2.524345328	4.458223608	-2.292898714
H	-3.445482905	3.378795123	-3.348064967
H	-4.028270706	3.723220099	-1.721593937
C	-0.936545914	2.154366273	1.578460972

C	-1.137857608	2.101869671	-2.716788807
H	-0.555935072	1.227363134	-2.415415298
H	-1.466295635	1.919397325	-3.743332476
H	-0.462965075	2.959240360	-2.717066728
C	-3.260854832	1.116683561	-1.844838154
H	-4.160447387	1.287546373	-1.249400545
H	-3.571485653	0.898264269	-2.871447617
H	-2.776946899	0.224066854	-1.445962870
C	-1.209779917	-0.745559484	2.527854223
H	-1.133252733	-1.097667480	3.562457514
H	-2.042603950	-0.038233300	2.479150243
C	-1.844075570	-3.816911111	0.539198926
H	-2.167462365	-4.824499577	0.334857606
C	-1.907542413	-3.153952035	1.785505566
H	-2.291202672	-3.545273575	2.715699024
C	-1.280407724	-2.941621792	-0.367629630
C	-0.851814812	-3.196331173	-1.797291380
C	-1.509240520	-4.484962098	-2.315600427
H	-2.599035731	-4.414111988	-2.293747777
H	-1.202897549	-4.675166312	-3.347240603
H	-1.211762973	-5.349503367	-1.719921769
C	-1.397402903	-1.888134764	1.578658667
C	-1.251447340	-2.036557751	-2.716584653
H	-0.786928836	-1.094031562	-2.415484717
H	-0.930001987	-2.230818533	-3.742996377
H	-2.331430589	-1.880922451	-2.716723750
C	0.663281045	-3.382467204	-1.844603449
H	0.964078875	-4.252755749	-1.256921779
H	1.007872418	-3.534713442	-2.872143333
H	1.194117997	-2.520388305	-1.438172208

Optimized geometry for complex (**1**)

71

FeC27N4H39

Fe	0.000000000	0.000000000	0.000000000
N	0.000000000	0.000000000	2.187146183
N	1.968606993	0.000000000	0.281752249
N	-0.984521500	1.711694474	0.283514844
N	-1.010142417	-1.696725501	0.288645108
C	1.235499103	-0.736375298	2.524446727
H	1.537666092	-0.572269167	3.579007086
H	0.983506222	-1.805321472	2.405685569
C	4.200620286	0.283113607	0.496437898
H	5.236106752	0.518773274	0.259822798
C	3.689862046	-0.153670494	1.753475560
H	4.251936850	-0.330658939	2.669209358
C	3.116554870	0.380033961	-0.374613641
C	3.054847670	0.952587352	-1.771557259
C	4.469127123	1.151409443	-2.328691669
H	5.008499898	0.192628802	-2.377424425
H	4.417032873	1.579322201	-3.343024924
H	5.044593702	1.839602512	-1.690663310
C	2.322952956	-0.315700383	1.582636013
C	2.279820573	0.019562375	-2.714936242
H	1.261357488	-0.166237334	-2.338940393
H	2.192452791	0.469524514	-3.718079469
H	2.781330963	-0.956257518	-2.799568609
C	2.340737698	2.318581469	-1.714397064
H	2.922050063	3.021841859	-1.098356431
H	2.224790983	2.742541024	-2.726963279
H	1.342420831	2.218177055	-1.262419670

C	0.014182805	1.437051833	2.532779425
H	-0.291246257	1.609739183	3.585119549
H	1.067051249	1.755547050	2.430571596
C	-2.290514605	3.549002695	0.495013177
H	-2.992173083	4.346288104	0.258138415
C	-1.671493003	3.304385408	1.754814258
H	-1.783438854	3.884993682	2.669460966
C	-1.855026051	2.550277530	-0.375817337
C	-2.332181223	2.234922208	-1.775195925
C	-3.193399809	3.381615978	-2.317510898
H	-2.616708768	4.318904677	-2.356140297
H	-3.542994641	3.140098537	-3.334599464
H	-4.073747959	3.543891598	-1.676779158
C	-0.884026593	2.174664224	1.585259342
C	-1.145802231	2.019006908	-2.727263452
H	-0.487747930	1.220227116	-2.352521758
H	-1.501303158	1.728057083	-3.730188922
H	-0.540612802	2.934240073	-2.811025595
C	-3.183915779	0.949910151	-1.729853780
H	-4.078819763	1.113550700	-1.109710321
H	-3.502435245	0.654337852	-2.744828713
H	-2.613154020	0.120741369	-1.286787529
C	-1.253008495	-0.704051351	2.536311306
H	-1.246638480	-1.050456753	3.589720961
H	-2.053425088	0.050258696	2.432701438
C	-1.923637207	-3.755043787	0.492145112
H	-2.253032729	-4.763664627	0.251249636
C	-2.017267109	-3.106009376	1.757170603
H	-2.449307461	-3.504891099	2.673848381
C	-1.293594106	-2.865751844	-0.378709006
C	-0.788577689	-3.098589071	-1.784144287
C	-1.350946320	-4.410847087	-2.342601324
H	-2.451283664	-4.382783126	-2.374796231
H	-0.971770431	-4.577621616	-3.364024080
H	-1.045427255	-5.262411769	-1.715450794
C	-1.448206453	-1.851228810	1.591597921
C	-1.202488577	-1.948996649	-2.715367696
H	-0.826800590	-0.984478944	-2.339592084
H	-0.787967436	-2.101380529	-3.726123906
H	-2.298084616	-1.873546601	-2.782748773
C	0.750967682	-3.187572751	-1.749464795
H	1.065426208	-4.050410007	-1.142179983
H	1.160365494	-3.300249322	-2.768619638
H	1.178708645	-2.280081143	-1.297797576

Input coordinates for a geometry optimization of $[Fe(tpa)^{Ph}]^-$ (complex **3**) adopted from X-ray data:

Fe	0.000000000	0.000000000	0.000000000
N	0.000000000	0.000000000	2.160635020
N	2.005192654	0.000000000	0.233124417
N	-1.052357680	1.701803934	0.249896461
N	-1.044770801	-1.706530459	0.215959333
C	-1.435165197	-2.823355929	-0.506109090
C	-1.896668616	-3.792712539	0.368841582
H	-2.285305383	-4.762153819	0.097422599
C	1.343979132	-0.459705225	2.558266233
H	1.594826629	-0.140765326	3.576902678
H	1.329110773	-1.552580948	2.553340976
C	2.356983178	0.036716764	1.560115180

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C       -2.678631678      3.247963081      0.460136221
H       -3.449868758      3.961787135      0.216050424
C        4.148077552      0.682208886      0.423318408
H        5.149098154      0.994748960      0.169431014
C       -2.178483210      2.970526453      1.734486922
H       -2.491662592      3.422721653      2.663727955
C        3.148495320      0.445202945     -1.929197762
C       -0.253464038      1.403504276      2.551192801
H       -0.620163087      1.483405345      3.581498189
H        0.717426697      1.912086085      2.504564345
C       -1.196613692      2.026004490      1.577748069
C        3.659063753      0.449516317      1.708535119
H        4.200195153      0.550385885      2.637526339
C        3.128606414      0.399227231     -0.468175988
C       -1.978079868      2.455504300     -0.439501590
C       -2.128142722      2.357342157     -1.881992770
C       -1.272360007     -2.004085406      1.539497061
C       -1.788002957     -3.275042299      1.661640250
H       -2.075464266     -3.765793738      2.579885196
C       -1.079014493     -0.922566692      2.564980798
H       -0.901897076     -1.343691106      3.562308713
H       -1.995906968     -0.323880653      2.627391743
C       -1.113159996      1.873930365     -2.696795093
H       -0.147175360      1.637435384     -2.264808899
C       -1.361601528     -2.882294498     -1.970250406
C       -1.259349725     -4.104796346     -2.633946294
H       -1.150846383     -5.013310641     -2.053371844
C        2.176719817     -0.192978066     -2.698356023
H        1.397214155     -0.767515941     -2.211399895
C       -3.316016649      2.747431651     -2.512817089
H       -4.133201070      3.124378537     -1.909427344
C        4.170747568      1.107117993     -2.616800022
H        4.937967784      1.628012416     -2.057271799
C        2.218165034     -0.175039092     -4.081839363
H        1.456479601     -0.698009064     -4.647205604
C        3.257809301      0.480440634     -4.727657688
H        3.305643619      0.488513279     -5.810549110
C       -1.480816111     -1.742380831     -2.750025327
H       -1.630990408     -0.780405650     -2.278233378
C       -1.280033004     -4.179587493     -4.007472893
H       -1.198232285     -5.147227422     -4.489490702
C       -1.276840468      1.753409377     -4.059955787
H       -0.455267816      1.391578020     -4.665656647
C       -3.483741976      2.620984664     -3.865645837
H       -4.425580063      2.917212563     -4.313964730
C        4.216912765      1.109003899     -3.987432586
H        5.028960725      1.626796232     -4.486633233
C       -1.493048530     -1.819595735     -4.138079047
H       -1.613013645     -0.912420931     -4.716046754
C       -2.482880062      2.109678763     -4.648703955
H       -2.616864709      2.011961500     -5.719817994
C       -1.399840425     -3.038983008     -4.763481871
H       -1.425157941     -3.101589060     -5.845683763
```

Optimized geometry for complex (**3**)

```
65
FeC33N4H27
Fe       0.000000000      0.000000000      0.000000000
N        0.000000000      0.000000000      2.228862944
N        1.971016571      0.000000000      0.267437249
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N	-1.000279557	1.703750539	0.265054454
N	-1.024248170	-1.688063853	0.284478668
C	-1.248090485	-2.834009405	-0.448427726
C	-1.589967299	-3.880091779	0.420982619
H	-1.845808300	-4.896600336	0.128373303
C	1.336497833	-0.520669838	2.585165762
H	1.622134180	-0.242312603	3.619226858
H	1.251375409	-1.621219850	2.540490454
C	2.344285735	-0.032161237	1.590623170
C	-2.678539774	3.223638880	0.439430699
H	-3.462149889	3.926439291	0.162644819
C	4.121176883	0.700917844	0.421551406
H	5.118554609	1.030256137	0.136992920
C	-2.179448243	2.972017982	1.740606524
H	-2.508780521	3.426995738	2.673523585
C	3.007420830	0.565607554	-1.903914546
C	-0.218213419	1.418874851	2.582914247
H	-0.596011030	1.530532857	3.618954188
H	0.776205697	1.897599492	2.530952285
C	-1.153716072	2.039761012	1.591256304
C	3.664631377	0.394007597	1.726911233
H	4.229499073	0.456426630	2.655586681
C	3.056304642	0.450082202	-0.454997044
C	-1.932126915	2.432611781	-0.445632132
C	-2.014772865	2.367513526	-1.896542795
C	-1.231744511	-2.002769480	1.605915501
C	-1.581114252	-3.346893200	1.733276120
H	-1.817020864	-3.868814583	2.659361493
C	-1.116021906	-0.894949228	2.607118405
H	-0.993021811	-1.287322185	3.636082094
H	-2.023785657	-0.265220491	2.591580402
C	-0.913890292	1.952322232	-2.676374539
H	0.021403427	1.680874418	-2.180959784
C	-1.154170846	-2.839549753	-1.899453355
C	-0.957774556	-4.040100493	-2.615064898
H	-0.840518403	-4.970860094	-2.055821757
C	2.047515821	-0.138512458	-2.662651505
H	1.342189468	-0.805369414	-2.157466870
C	-3.191064171	2.747176230	-2.578197523
H	-4.061628673	3.050541488	-1.992586653
C	3.929405420	1.372258596	-2.604890376
H	4.666746399	1.942769652	-2.036008991
C	2.008328905	-0.037436060	-4.052061880
H	1.253329984	-0.605975092	-4.599216230
C	2.929880606	0.766790301	-4.731087806
H	2.899789801	0.846131338	-5.819891214
C	-1.275586250	-1.647487821	-2.645785668
H	-1.474950457	-0.704091738	-2.130021489
C	-0.884790392	-4.047144407	-4.006770617
H	-0.723785940	-4.991592777	-4.533054190
C	-0.986404003	1.918680383	-4.067914764
H	-0.107357688	1.600834018	-4.632932005
C	-3.261452686	2.715581160	-3.969603027
H	-4.188658497	3.008369618	-4.469064276
C	3.891945362	1.469257210	-3.994379045
H	4.613733290	2.108536867	-4.509282454
C	-1.199016055	-1.654986956	-4.037516766
H	-1.310390490	-0.710838726	-4.575051720
C	-2.159897865	2.299782612	-4.727905832
H	-2.216533780	2.273204406	-5.818275152
C	-1.001607705	-2.854101628	-4.730952413
H	-0.941930814	-2.860256869	-5.821451616

Input coordinates for a geometry optimization of [Fe(tpa)^{Dfp}]$^{-}$ (complex **4**) adopted from X-ray data:

Fe	0.000000000	0.000000000	0.000000000
N	0.000000000	0.000000000	2.196045012
N	2.017699366	0.000000000	0.312882261
N	-0.940462669	1.786754744	0.273004811
N	-1.123371008	-1.676003333	0.283122646
F	1.010625133	1.344540838	-1.875844575
F	-1.793659814	0.329023110	-1.998122022
F	0.478269379	-1.609903828	-2.034893903
F	-1.702134842	5.025590322	-2.071476398
C	2.374523024	-0.147665182	1.617525362
C	-1.672281620	2.713649161	-0.433229894
F	5.414116436	-0.309342133	-2.049350258
C	-2.235920913	3.628291821	0.445833589
H	-2.849799478	4.469173498	0.167936202
C	3.731669217	0.017297731	1.778068076
H	4.280368828	-0.048175233	2.705265805
F	-3.561892663	-4.038054287	-2.020955887
C	-1.849998849	3.253480633	1.734244102
H	-2.096553002	3.752382528	2.659029328
C	-1.725420204	2.682570944	-1.896160361
C	-1.547829017	-2.793658040	-1.885377739
C	-1.716275752	3.818388599	-2.698304616
C	2.119898716	0.950705442	-2.565122668
C	3.187717355	0.263745342	-0.379214806
C	-1.996929345	-3.155588161	1.735955829
H	-2.320235729	-3.609431823	2.660528802
C	-1.046961958	2.142827724	1.591732175
C	-1.755897335	1.507659451	-2.666954552
C	-1.385007162	-1.939083820	1.597144602
C	-1.743828747	1.447818731	-4.029081941
H	-1.778508546	0.480690455	-4.511942159
C	4.287239802	0.158202955	-2.649944714
C	4.253829383	0.263507840	0.506796820
H	5.285726611	0.433038212	0.251092338
C	-1.135796091	-0.853560140	2.599098074
H	-0.968038288	-1.261426866	3.601955030
H	-2.010024907	-0.198232042	2.657195761
C	-0.572827347	-2.213502772	-2.676564282
C	-1.597576315	-2.758856557	-0.426785157
C	-1.687916147	3.828849453	-4.078946042
H	-1.662989799	4.779775917	-4.593772890
C	-0.173707430	1.423784169	2.588220142
H	-0.577468498	1.491302952	3.603788576
H	0.826498020	1.866014834	2.598014385
C	-2.142619590	-3.678762898	0.448772484
H	-2.597223830	-4.616728331	0.177754920
C	1.307356879	-0.555295632	2.589149627
H	1.559065927	-0.254364704	3.612147884
H	1.194775939	-1.643975581	2.589559209
C	3.187367538	0.458011234	-1.830057859
C	-1.705256267	2.627196884	-4.748560579
H	-1.697133368	2.604202355	-5.830950994
C	-2.538130167	-3.424194862	-2.658250970
C	-2.546611581	-3.433541441	-4.038405707
H	-3.363168671	-3.932363888	-4.544328697
C	2.066147944	1.111848602	-3.917242986

H	1.173041326	1.519098864	-4.370192513
C	-0.534606869	-2.189507971	-4.046774419
H	0.294197123	-1.702967732	-4.542787004
C	3.177287126	0.756364680	-4.650254547
H	3.176950949	0.867015378	-5.727278254
C	-1.550477646	-2.800906253	-4.725672978
H	-1.554279820	-2.807451988	-5.808829207
C	4.292056852	0.281065193	-4.008862768
H	5.186461138	0.003763269	-4.551918730

Optimized geometry for complex (**4**)

65
FeC33N4H21F6

Fe	0.000000000	0.000000000	0.000000000
N	0.000000000	0.000000000	2.228905099
N	1.981463290	0.000000000	0.304172821
N	-0.972284292	1.728394784	0.323697155
N	-1.058373236	-1.687549079	0.287526976
F	0.991873501	1.463647876	-1.884487257
F	-2.214692298	0.205280750	-1.787268104
F	0.566749384	-1.523878450	-1.999651154
F	-1.607402229	4.904414013	-2.186391831
C	2.345613962	-0.225207356	1.604559697
C	-1.656514610	2.678631630	-0.409063554
F	5.354703196	-0.438924749	-2.109953826
C	-2.071907183	3.715831864	0.442249699
H	-2.639618601	4.593558110	0.144416513
C	3.731938698	-0.134017887	1.751064296
H	4.296691635	-0.260625709	2.673138534
F	-3.336515630	-4.252772986	-2.078017106
C	-1.632148361	3.380050021	1.741123795
H	-1.775658995	3.955725336	2.654018345
C	-1.838182635	2.557156027	-1.849833115
C	-1.406682142	-2.858702183	-1.883370808
C	-1.774936864	3.664324474	-2.722224113
C	2.086831074	1.028608477	-2.569645628
C	3.148688140	0.218888495	-0.408476449
C	-2.039582055	-3.135211709	1.738648555
H	-2.412300708	-3.565964818	2.666227959
C	-0.948709904	2.166898733	1.620569611
C	-2.040510587	1.333771114	-2.524769185
C	-1.395777108	-1.903275845	1.595644774
C	-2.098242123	1.190058446	-3.905233067
H	-2.232936981	0.190647554	-4.320623439
C	4.248224647	0.118644302	-2.677467341
C	4.247877188	0.133533315	0.466358063
H	5.291052151	0.266084905	0.195410197
C	-1.188760278	-0.793399209	2.583910952
H	-1.126493440	-1.186431340	3.619568855
H	-2.041986271	-0.092940198	2.542777457
C	-0.417503668	-2.207581274	-2.652468908
C	-1.516254000	-2.776006253	-0.434801775
C	-1.837197678	3.580039712	-4.107859036
H	-1.751857101	4.496188358	-4.693091103
C	-0.093053834	1.423528470	2.605624736
H	-0.466108760	1.548584735	3.642939660
H	0.941407233	1.810873776	2.576337984
C	-2.131972687	-3.686214030	0.445363065

```
H       -2.581808623    -4.634747240     0.168778522
C        1.282877175    -0.634641682     2.582298516
H        1.585977608    -0.401797314     3.623983581
H        1.107585926    -1.723965760     2.521794249
C        3.157436503     0.459966846    -1.844039896
C       -1.988572158     2.327168816    -4.708361901
H       -2.030349598     2.239461076    -5.794853794
C       -2.324835652    -3.574251317    -2.687058982
C       -2.296574697    -3.617032957    -4.075110540
H       -3.067904065    -4.187009911    -4.593970538
C        2.053854455     1.209741784    -3.945072793
H        1.161116907     1.654451449    -4.387498026
C       -0.343698149    -2.209132547    -4.037653375
H        0.465460616    -1.655390844    -4.515248225
C        3.163235717     0.831424977    -4.703087643
H        3.165552201     0.966356837    -5.785285901
C       -1.298726654    -2.922880952    -4.763910746
H       -1.264131853    -2.941872187    -5.853702749
C        4.274635255     0.284607499    -4.056103187
H        5.165357328    -0.028944945    -4.601464002
```

Geometries of the truncated clusters have been obtained by freezing the [Fe(tpa)]- core, replacing the substituents by H-atoms and adjusting their positions from a constraint geometry optimization; here an input file for complex (**2**)

```
#
# Fe(tpa)-Mes with hydrogens as substituents
#
! UKS PBE VDW ZORA def2-TZVP def2-TZVP/J Grid4 NoFinalGrid TightSCF Opt
! Pal8

%scf maxiter 150 shift shift 0.25 erroff 0.1 end end

%geom
   Constraints
      {C 10 C} {C 16 C} {C 22 C}
   end
   InvertConstraints true
end

*xyz -1 5
Fe       0.000000000     0.000000000     0.000000000
N        0.000000000     0.000000000     2.217863878
N        1.974888222     0.000000000     0.261305485
N       -0.928830710    -1.764916753     0.284275262
N       -1.017182199     1.714399825     0.293784213
C       -0.192655062     1.414305203     2.593741332
C       -1.138524557     2.052592520     1.625778852
C       -2.126556939     3.016334283     1.796880025
C       -2.640471068     3.288721713     0.501697768
C       -1.932598006     2.485422091    -0.397761407
H       -1.979556482     2.464344836    -1.476383989
C        1.325730183    -0.548592550     2.570982883
C        2.346899963    -0.064452159     1.586053384
C        3.684037561     0.295798368     1.721659203
C        4.151037485     0.597459054     0.413910689
C        3.079410420     0.400954877    -0.463162029
H        3.022118443     0.491500321    -1.537773379
C       -1.141080214    -0.865759764     2.577570570
```

```
C       -1.263127164     -1.992681456      1.598898930
C       -1.762275337     -3.281956971      1.760713544
C       -1.719241937     -3.882433711      0.480977119
C       -1.200690254     -2.933303497     -0.413735599
H       -0.985353644     -3.055425556     -1.464456783
H       -0.550048802      1.516194900      3.638640776
H        0.806921497      1.880923460      2.530682345
H       -2.427287277      3.476412031      2.736650379
H       -3.414367646      4.007947552      0.238777583
H        1.609969222     -0.288618059      3.610250154
H        1.220715259     -1.646851684      2.511987889
H        4.256530907      0.321380313      2.647647094
H        5.157397386      0.899687136      0.131622704
H       -1.052319553     -1.245724158      3.615565532
H       -2.032360919     -0.213159269      2.535331158
H       -2.120216971     -3.726642671      2.687822445
H       -2.035479657     -4.890322974      0.226588319
*
```

Geometries of truncated clusters (used in calculating the data in Tables 3c and 5b):

Coordinates of truncated complex (**1**):

```
35
FeC15N4H15
Fe       0.000000000      0.000000000      0.000000000
N       -0.000002927      0.000004501      2.187146000
N        1.968606653      0.000000000      0.281754434
N       -0.984520789      1.711695763      0.283510195
N       -1.010143809     -1.696724094      0.288647386
C        1.235496175     -0.736370670      2.524449323
H        1.537661441     -0.572262045      3.579010135
H        0.983502558     -1.805316764      2.405690085
C        4.200619566      0.283112484      0.496441416
H        5.236106195      0.518770606      0.259827314
C        3.689860299     -0.153668227      1.753479899
H        4.251933538     -0.330655313      2.669214121
C        3.116555030      0.380031312     -0.374611358
H        3.075717780      0.758956768     -1.299137390
C        2.322951093     -0.315697904      1.582638551
C        0.014181055      1.437057458      2.532775695
H       -0.291249641      1.609747112      3.585115890
H        1.067049410      1.755551893      2.430568307
C       -2.290513117      3.549004918      0.495002763
H       -2.992171682      4.346289720      0.258126020
C       -1.671493417      3.304389569      1.754805054
H       -1.783440395      3.884999847      2.669450588
C       -1.855024127      2.550277153     -0.375825278
H       -2.170654317      2.341672978     -1.301492926
C       -0.884027456      2.174668130      1.585253586
C       -1.253011636     -0.704045199      2.536310999
H       -1.246642924     -1.050448100      3.589722014
H       -2.053428107      0.050264493      2.432698613
C       -1.923639623     -3.755041924      0.492150623
H       -2.253035222     -4.763662994      0.251257386
C       -2.017270446     -3.106004696      1.757174911
H       -2.449312313     -3.504883812      2.673853099
C       -1.293595199     -2.865751661     -0.378704481
H       -0.959469126     -3.019802095     -1.308557798
C       -1.448209560     -1.851225032      1.591599862
```

Coordinates of truncated complex (**2**) - output from the given sample input file:

```
35
Coordinates from ORCA-job fen4pbeopt-H
  Fe      0.000025     -0.000013     -0.000020
  N       0.000025     -0.000020      2.217844
  N       1.974913     -0.000027      0.261286
  N      -0.928818     -1.764925      0.284250
  N      -1.017146      1.714393      0.293770
  C      -0.192621      1.414286      2.593726
  C      -1.138486      2.052582      1.625765
  C      -2.126512      3.016330      1.796869
  C      -2.640424      3.288725      0.501688
  C      -1.932556      2.485423     -0.397774
  H      -1.979515      2.464349     -1.476396
  C       1.325751     -0.548622      2.570962
  C       2.346925     -0.064486      1.586034
  C       3.684065      0.295755      1.721641
  C       4.151067      0.597416      0.413893
  C       3.079438      0.400922     -0.463180
  H       3.022147      0.491471     -1.537791
  C      -1.141061     -0.865773      2.577548
  C      -1.263116     -1.992691      1.598873
  C      -1.762273     -3.281964      1.760684
  C      -1.719243     -3.882437      0.480946
  C      -1.200685     -2.933307     -0.413764
  H      -0.985349     -3.055428     -1.464485
  H      -0.550014      1.516175      3.638626
  H       0.806959      1.880897      2.530668
  H      -2.427239      3.476407      2.736641
  H      -3.414315      4.007957      0.238770
  H       1.609992     -0.288653      3.610230
  H       1.220729     -1.646881      2.511963
  H       4.256558      0.321330      2.647629
  H       5.157429      0.899639      0.131606
  H      -1.052303     -1.245741      3.615542
  H      -2.032337     -0.213166      2.535311
  H      -2.120217     -3.726650      2.687792
  H      -2.035488     -4.890323      0.226554
```

Coordinates of truncated complex (**3**):

```
35
FeC15N4H15
Fe       0.000000000      0.000000000      0.000000000
N       -0.000023935     -0.000006059      2.228863000
N        1.971013808      0.000000000      0.267458786
N       -1.000282481      1.703749354      0.265048994
N       -1.024250146     -1.688065014      0.284463059
C       -1.248084898     -2.834007913     -0.448448624
C       -1.589970924     -3.880093100      0.420954661
H       -1.845808105     -4.896600546      0.128339478
C        1.336470375     -0.520677687      2.585179374
H        1.622095612     -0.242322582      3.619244028
H        1.251349040     -1.621227430      2.540499534
C        2.344269274     -0.032165337      1.590648290
C       -2.678544475      3.223637478      0.439412055
H       -3.462152202      3.926437975      0.162620049
C        4.121172181      0.700917592      0.421597848
H        5.118553719      1.030256301      0.137050928
C       -2.179467425      2.972012676      1.740593031
H       -2.508809737      3.426987317      2.673507820
H        3.022707471      0.529522441     -1.451235899
C       -0.218240586      1.418867713      2.582917067
```

```
H       -0.596049469      1.530522293      3.618952937
H        0.776178223      1.897592235      2.530966875
C       -1.153733199      2.039756036      1.591250978
C        3.664612839      0.394002943      1.726952290
H        4.229470993      0.456419734      2.655634117
C        3.056309930      0.450083878     -0.454962143
C       -1.932122569      2.432613325     -0.445645543
H       -1.988923617      2.387866630     -1.443027018
C       -1.231761472     -2.002773921      1.605896573
C       -1.581131814     -3.346898510      1.733249346
H       -1.817048030     -3.868822777      2.659330705
C       -1.116049484     -0.894957577      2.607104585
H       -0.993059626     -1.287333289      3.636068186
H       -2.023812548     -0.265228783      2.591558663
H       -1.183483407     -2.837815230     -1.446353355
```

Coordinates of truncated complex (**4**)

```
35
FeC15N4H15
Fe       0.000000000      0.000000000      0.000000000
N       -0.000021884      0.000008952      2.228905000
N        1.981460924      0.000000000      0.304192009
N       -0.972285956      1.728397592      0.323680293
N       -1.058377296     -1.687546792      0.287523305
C        2.345597821     -0.225203224      1.604583504
C       -1.656507459      2.678632154     -0.409091222
C       -2.071907757      3.715835803      0.442213747
H       -2.639615639      4.593561954      0.144371032
C        3.731921102     -0.134014382      1.751101919
H        4.296665119     -0.260619192      2.673182596
C       -1.632162611      3.380058737      1.741093103
H       -1.775682110      3.955738316      2.653984508
H       -1.781162778      2.595268578     -1.397783216
H       -1.440937694     -2.832843847     -1.430344907
C        3.148692962      0.218883752     -0.408446036
C       -2.039602237     -3.135202174      1.738640597
H       -2.412330568     -3.565952022      2.666217588
C       -0.948723510      2.166906598      1.620551025
C       -1.395794448     -1.903267522      1.595638268
C        4.247873056      0.133531867      0.466400310
H        5.291050722      0.266080714      0.195462289
C       -1.188786390     -0.793387766      2.583902049
H       -1.126531187     -1.186415075      3.619562377
H       -2.042011789     -0.092927868      2.542757275
C       -1.516252341     -2.776006675     -0.434806478
C       -0.093078355      1.423539766      2.605618038
H       -0.466143300      1.548600506      3.642928047
H        0.941382894      1.810883890      2.576339620
C       -2.131980448     -3.686210313      0.445356225
H       -2.581814378     -4.634743788      0.168770720
C        1.282851265     -0.634632325      2.582313941
H        1.585941067     -0.401784071      3.624000764
H        1.107558881     -1.723956036      2.521812162
H        3.154712085      0.384491478     -1.394618903
```

Sample input files for restricted open shell Hartree-Fock calculations
(preparing input orbitals for correlated CASSCF and NEVPT2 calculations:

Complex (**2**) experimental geometry:

```
#
# Complex 2 Fe(tpa)-Mes, geometry taken from X-ray data
#
! TZVP TightSCF Pal8

%basis
 newgto  fe "def2-TZVPP" end
# newauxgto  fe "TZVPP_C" end
 newgto  n "def2-TZVP" end
# newauxgto  n "TZV_C" end
 newgto  h "def2-SVP" end
# newauxgto  h "SV_C" end
 newgto  c "def2-TZVP(-df)" end
# newauxgto  c "TZV_C" end
end



%scf maxiter 75 shift shift 0.25 erroff 0.1 end
     hftyp rohf
     rohf_case sahf
     rohf_numop 2
     rohf_norb[1] 5
     rohf_nel[1] 6
end

*xyz -1 5
Fe              0.00000000000000    0.00000000000000    0.00000000000000
N               0.00000000000000    0.00000000000000    2.17167114453363
N               1.99099897510995    0.00000000000000    0.26379490349725
N              -0.98395490984738   -1.76587999277164    0.28386885443118
N              -0.90357561917498    1.79501236940530    0.23928180899212
C              -0.14187914406252    1.42074186063419    2.56382193685946
C              -0.99369782480254    2.15993429031768    1.56880749121509
C              -1.76307385855470    3.27914414372072    1.70926799361105
C              -2.17804469237225    3.64387371495520    0.41265221129622
C              -1.65230629335355    2.72915546847988   -0.46468867191985
C              -1.71059027870829    2.72177348403337   -1.94978432653500
C              -2.86092007720031    2.31292448452040   -2.63722554605749
C              -2.85683876892262    2.30224398492551   -4.02325945251546
C              -1.75306266813002    2.68705814277966   -4.76320788533635
C              -0.63384939088317    3.11107004903557   -4.07671974750176
C              -0.58909007428828    3.14054496065854   -2.69129693725112
C              -4.08605523607590    1.85586289950995   -1.90136835882983
C              -1.78211544480456    2.64185658202563   -6.26336860175073
C               0.63992398951979    3.63647651800355   -1.97935195244449
C               1.29714784936030   -0.58409964091614    2.56233335972929
C               2.36355517405425   -0.18838622607481    1.57386554985700
C               3.71807600696502   -0.04635097367243    1.70509355862681
C               4.21435412269732    0.25313730254351    0.42619402220715
C               3.14137464610067    0.28717399845063   -0.43839721423588
C               3.07434322302432    0.59626271654062   -1.88178019968010
C               3.53706937373736    1.81799483538771   -2.38551237973581
C               3.40013044246743    2.10307384332197   -3.74179740816378
C               2.80891060456836    1.22128309604984   -4.63452909310604
C               2.40113843182834   -0.00044880746512   -4.13077945184305
C               2.53102786324511   -0.33320186222803   -2.79520745821928
C               4.15908187412616    2.85968772086655   -1.49356690959605
C               2.65699829652313    1.57035575413529   -6.09144647581569
C               2.19061919811124   -1.72437410934340   -2.33763029581083
C              -1.15603770476297   -0.81888239933278    2.57180929721264
```

C	−1.35860115593307	−1.94308072201779	1.59132209713186
C	−1.97158374418927	−3.16480606481194	1.75767540569303
C	−1.97671272569102	−3.77567632717455	0.49255534968657
C	−1.35452254889384	−2.91784294713421	−0.39054451781747
C	−1.03901015125567	−3.12017749886475	−1.82502613711854
C	−0.53379198429647	−4.36004632175264	−2.29584324152850
C	−0.17531023721966	−4.49266035705132	−3.62905440809386
C	−0.27754555292143	−3.46894976248027	−4.54726987778839
C	−0.78610181237172	−2.27349835238612	−4.08555719973218
C	−1.17891618205909	−2.08116424261538	−2.76315129714939
C	−0.36846712819665	−5.56696204122312	−1.41438143971823
C	0.15649408147975	−3.62531115937006	−5.97619963440051
C	−1.73826428451335	−0.73450807768019	−2.40846086349931
H	−0.54698699851031	1.47025082888944	3.42215028214872
H	0.72060145592606	1.82252206132041	2.59781671557438
H	−1.97725854920506	3.72403546754497	2.51992057534808
H	−2.72153790381957	4.38761298478565	0.18379171312594
H	−3.63982255287708	2.01898849992468	−4.48058117109145
H	0.12960585890778	3.38843314978547	−4.56653156025136
H	−0.94788434532075	2.94338098689547	−6.60769721793289
H	−1.93742480877432	1.74834586769125	−6.55030362023569
H	−2.47675847543780	3.20264300666653	−6.58310312589716
H	1.53715958254411	−0.26803108702285	3.42667460436240
H	1.22218932333788	−1.53162632725506	2.58256225124934
H	4.22329204715485	−0.13494466633006	2.50675249505564
H	5.12559018508259	0.40654344502325	0.19542339136764
H	3.73197467197103	2.93173362797128	−4.06760052148550
H	2.01187865024449	−0.63406348386168	−4.72180957315345
H	3.14307287553394	0.94910889357806	−6.62107387492496
H	1.73580396292622	1.53263663237978	−6.33076329010785
H	2.98710138779813	2.44630249676720	−6.24702714043448
H	−1.00091757173412	−1.17898960002992	3.43596311936190
H	−1.93327645569985	−0.27246895871050	2.58862018503601
H	−2.31796020187492	−3.52241190759402	2.56639554935786
H	−2.34276136155312	−4.62819183459247	0.28479458391147
H	0.15479005592587	−5.33464219255943	−3.92645266824282
H	−0.87576414909589	−1.55183882487631	−4.69624344628394
H	0.84716334673777	−3.00058098306457	−6.16794548922211
H	0.48307364944891	−4.50634469991602	−6.11173836029872
H	−0.58071949116833	−3.46711302412388	−6.55208377926655
H	0.16082283337446	−6.21586621742383	−1.86161051601954
H	0.06055678543038	−5.31403176102485	−0.60316395661337
H	−1.22205819607706	−5.93637970589681	−1.21712762388231
H	4.99424395829049	2.54313489252481	−1.17289109191852
H	4.29280165731348	3.66291319824090	−1.98534161622611
H	3.58215203339597	3.03373678627125	−0.75694653130966
H	−2.44585831691566	−0.83916124748000	−1.78539938229582
H	−2.06726780913748	−0.31507498417986	−3.19408077851015
H	1.99223178644043	−2.26499356711484	−3.09279779164833
H	2.92994740912745	−2.08996287619936	−1.86844738910568
H	1.43506698677186	−1.69039194428909	−1.76251187461534
H	−1.05363259783966	−0.20013256344588	−2.02588120723260
H	1.26366593096976	3.96456225890250	−2.61628149100823
H	0.39894396301216	4.33852157458354	−1.38489730711317
H	1.03066353845943	2.92584133983453	−1.48852352168367
H	−4.44257019756341	2.58148967909823	−1.40260044789338
H	−4.73239692216034	1.55176505693257	−2.52777051157940
H	−3.85462057749737	1.14842505587282	−1.31222213233025

*

Sample input files for a CASSCF and NEVPT2 calculations (complex 2, experimental geometry), reading the geometries, basis function and wavefunctions:

```
#
# Complex 2, Fe(tpa)-Mes, experimental geometry
#
! def2-TZVP  def2-TZV/C  moread Pal8

%moinp "longexp_rohf_full.gbw"

%basis
newgto    fe  "def2-TZVPP" end
newauxgto fe "def2-TZVPP/C"  end
newgto n "def2-TZVP" end
newauxgto n "def2-TZV/C" end
newgto h "def2-SVP" end
newauxgto h "def2-SV/C" end
newgto c "def2-TZVP(-f)" end
newauxgto c "def2-TZV/C" end
end

%scf
MaxDisk 40000
end



#%scf rotate {79, 81, 90, 0, 0} end end

%casscf
  nel 6
  norb 5
  mult 5,3
  nroots 5,45
  shiftup 0.5
  shiftdn 0.5
  trafostep RI
  nevpt2 true
  nev_tpre 1e-10
  rel
  PrintLevel 3
  dosoc true
  nreducedstates 10
  gtensor true
  end
  maxiter 150
end

*xyz -1 5
Fe              0.00000000000000    0.00000000000000    0.00000000000000
N               0.00000000000000    0.00000000000000    2.17167114453363
N               1.99099897510995    0.00000000000000    0.26379490349725
N              -0.98395490984738   -1.76587999277164    0.28386885443118
N              -0.90357561917498    1.79501236940530    0.23928180899212
C              -0.14187914406252    1.42074186063419    2.56382193685946
C              -0.99369782480254    2.15993429031768    1.56880749121509
C              -1.76307385855470    3.27914414372072    1.70926799361105
C              -2.17804469237225    3.64387371495520    0.41265221129622
C              -1.65230629335355    2.72915546847988   -0.46468867191985
C              -1.71059027870829    2.72177348403337   -1.94978432653500
C              -2.86092007720031    2.31292448452040   -2.63722554605749
C              -2.85683876892262    2.30224398492551   -4.02325945251546
```

C	-1.75306266813002	2.68705814277966	-4.76320788533635
C	-0.63384939088317	3.11107004903557	-4.07671974750176
C	-0.58909007428828	3.14054496065854	-2.69129693725112
C	-4.08605523607590	1.85586289950995	-1.90136835882983
C	-1.78211544480456	2.64185658202563	-6.26336860175073
C	0.63992398951979	3.63647651800355	-1.97935195244449
C	1.29714784936030	-0.58409964091614	2.56233335972929
C	2.36355517405425	-0.18838622607481	1.57386554985700
C	3.71807600696502	-0.04635097367243	1.70509355862681
C	4.21435412269732	0.25313730254351	0.42619402220715
C	3.14137464610067	0.28717399845063	-0.43839721423588
C	3.07434322302432	0.59626271654062	-1.88178019968010
C	3.53706937373736	1.81799483538771	-2.38551237973581
C	3.40013044246743	2.10307384332197	-3.74179740816378
C	2.80891060456836	1.22128309604984	-4.63452909310604
C	2.40113843182834	-0.00044880746512	-4.13077945184305
C	2.53102786324511	-0.33320186222803	-2.79520745821928
C	4.15908187412616	2.85968772086655	-1.49356690959605
C	2.65699829652313	1.57035575413529	-6.09144647581569
C	2.19061919811124	-1.72437410934340	-2.33763029581083
C	-1.15603770476297	-0.81888239933278	2.57180929721264
C	-1.35860115593307	-1.94308072201779	1.59132209713186
C	-1.97158374418927	-3.16480606481194	1.75767540569303
C	-1.97671272569102	-3.77567632717455	0.49255534968657
C	-1.35452254889384	-2.91784294713421	-0.39054451781747
C	-1.03901015125567	-3.12017749886475	-1.82502613711854
C	-0.53379198429647	-4.36004632175264	-2.29584324152850
C	-0.17531023721966	-4.49266035705132	-3.62905440809386
C	-0.27754555292143	-3.46894976248027	-4.54726987778839
C	-0.78610181237172	-2.27349835238612	-4.08555719973218
C	-1.17891618205909	-2.08116424261538	-2.76315129714939
C	-0.36846712819665	-5.56696204122312	-1.41438143971823
C	0.15649408147975	-3.62531115937006	-5.97619963440051
C	-1.73826428451335	-0.73450807768019	-2.40846086349931
H	-0.54698699851031	1.47025082888944	3.42215028214872
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H	-1.97725854920506	3.72403546754497	2.51992057534808
H	-2.72153790381957	4.38761298478565	0.18379171312594
H	-3.63982255287708	2.01898849992468	-4.48058117109145
H	0.12960585890778	3.38843314978547	-4.56653156025136
H	-0.94788434532075	2.94338098689547	-6.60769721793289
H	-1.93742480877432	1.74834586769125	-6.55030362023569
H	-2.47675847543780	3.20264300666653	-6.58310312589716
H	1.53715958254411	-0.26803108702285	3.42667460436240
H	1.22218932333788	-1.53162632725506	2.58256225124934
H	4.22329204715485	-0.13494466633006	2.50675249505564
H	5.12559018508259	0.40654344502325	0.19542339136764
H	3.73197467197103	2.93173362797128	-4.06760052148550
H	2.01187865024449	-0.63406348386168	-4.72180957315345
H	3.14307287553394	0.94910889357806	-6.62107387492496
H	1.73580396292622	1.53263663237978	-6.33076329010785
H	2.98710138779813	2.44630249676720	-6.24702714043448
H	-1.00091757173412	-1.17898960002992	3.43596311936190
H	-1.93327645569985	-0.27246895871050	2.58862018503601
H	-2.31796020187492	-3.52241190759402	2.56639554935786
H	-2.34276136155312	-4.62819183459247	0.28479458391147
H	0.15479005592587	-5.33464219255943	-3.92645266824282
H	-0.87576414909589	-1.55183882487631	-4.69624344628394
H	0.84716334673777	-3.00058098306457	-6.16794548922211
H	0.48307364944891	-4.50634469991602	-6.11173836029872
H	-0.58071949116833	-3.46711302412388	-6.55208377926655
H	0.16082283337446	-6.21586621742383	-1.86161051601954
H	0.06055678543038	-5.31403176102485	-0.60316395661337

H	-1.22205819607706	-5.93637970589681	-1.21712762388231
H	4.99424395829049	2.54313489252481	-1.17289109191852
H	4.29280165731348	3.66291319824090	-1.98534161622611
H	3.58215203339597	3.03373678627125	-0.75694653130966
H	-2.44585831691566	-0.83916124748000	-1.78539938229582
H	-2.06726780913748	-0.31507498417986	-3.19408077851015
H	1.99223178644043	-2.26499356711484	-3.09279779164833
H	2.92994740912745	-2.08996287619936	-1.86844738910568
H	1.43506698677186	-1.69039194428909	-1.76251187461534
H	-1.05363259783966	-0.20013256344588	-2.02588120723260
H	1.26366593096976	3.96456225890250	-2.61628149100823
H	0.39894396301216	4.33852157458354	-1.38489730711317
H	1.03066353845943	2.92584133983453	-1.48852352168367
H	-4.44257019756341	2.58148967909823	-1.40260044789338
H	-4.73239692216034	1.55176505693257	-2.52777051157940
H	-3.85462057749737	1.14842505587282	-1.31222213233025
*			