Electronic Supplementary Information (ESI): Benchmarks for transition metal spin-state energetics: Why and how to employ experimental reference data?

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1 Details of WFT calculations in Table 1 (main article)

1.1 Total energies

New results provided in Table 1 (main article) were computed using the protocol described in ref 23, which is summarized in section 1.2 below. Table S1 contains the total energies used to calculate the energy differences reported in the main article.

Table S1: Total energies (a.u.) for selected calculations reported in Table 1 (main article)

complex	geometry	theory level/basis set	LS	HS
$^{1,5}[Fe(NCH)_6]^{2+}$	g1	CCSD(T*)-F12a/T(D)	−1822.620687	−1822.631267
		CCSD(T)/T(D)	−1822.190756	−1822.210493
		CCSD(T)/T(D)-DK	−1831.339861	−1831.353321
	g2	CCSD(T*)-F12a/T(D)	−1822.610506	−1822.630382
		CCSD(T)/T(D)	−1822.178562	−1822.207896
		CCSD(T)/T(D)-DK	−1831.329325	−1831.351509
	g3	CCSD(T*)-F12a/T(D)	−1822.619769	−1822.630637
	g4	CCSD(T*)-F12a/T(D)	−1822.620318	−1822.630743
		CCSD(T)/T(D)	−1822.187972	−1822.206915
		CCSD(T)/T(D)-DK	−1831.336545	−1831.350052
$^{1,3}[Co(NH_3)_5(NO)]^{2+}$	ref. 87	CASPT2/T(D)-DK	−1804.245394	−1804.362687
		FC-CASPT2/T(D)-DK	−1803.915114	−1803.923354
		CCSD(T)/T(D)-DK	−1804.475611	−1804.457834
		FC-CCSD(T)/T(D)-DK	−1804.047128	−1804.033611
		CCSD(T)/T(D)	−1793.806368	−1793.789715
		CCSD(T*)-F12a/T(D)	−1794.114254	−1794.093728

1.2 Computational protocol from ref 23

Estimates of the CCSD(T)/CBS relative energies are obtained using the explicitly-correlated CCSD(T*)-F12a approach of Werner with co-workers[S1,S2] as implemented in Molpro.[S3,S4] Here, (T*) denotes the standard (T) triples contribution to the correlation energy scaled by the $E_{\rm corr}^{\rm MP2\text{-}F12}/E_{\rm corr}^{\rm MP2}$ correlation energy ratio in order to approximately correct the (T) for the basis set incompleteness error.[S2,S5] The reference energy includes the standard CABS singles correction. Because the implementation of F12 methods in Molpro can only be used with

Table S2: Definitions of basis sets T(D)-DK and T(D), and auxiliary basis sets used in F12 calculations (see ref 23, main article).

basis set	Fe,Co	N,O	C,H
T(D)-DK	cc-pwCVTZ-DK[S6]	cc-pVTZ-DK[S7]	cc-pVDZ-DK[S7]
T(D)	cc-pwCVTZ[S6]	cc-pVTZ[S8]	cc-pVDZ[S8]
T(D),df_basis[a]	aug-cc-pVTZ/mp2fit[S9]	aug-cc-pVTZ/mp2fit[S10]	aug-cc-pVDZ/mp2fit[S10]
T(D),df_basis_exch[b]	def2-TZVPP/jkfit[S11]	aug-cc-pVTZ/jkfit[S12]	aug-cc-pVDZ/jkfit[S12]
T(D),ri_basis[c]	def2-TZVPP/jkfit[S11]	aug-cc-pVTZ/optri[S13]	aug-cc-pVDZ/optri[S13]

[a]Basis set for density fitting. [b]Density fitting basis for computing the exchange and Fock operators. [c]Basis for the resolution of the identity.

the non-relativistic Hamiltonian, scalar-relativistic effects are estimated separately using conventional CCSD(T) calculations and additively corrected in order to obtain the final estimate of energy with the scalar-relativistic effects included:

$$\Delta E^{\text{CCSD(T), rel}}_{\text{final}} = \Delta E^{\text{CCSD(T), nrel}}_{\text{final}} + \Delta E^{\text{CCSD(T), rel}}_{\text{T(D)-DK}} - \Delta E^{\text{CCSD(T), nrel}}_{\text{T(D)}}, \quad (1)$$

$$\Delta E^{\text{CCSD(T), nrel}}_{\text{final}} = \Delta E^{\text{CCSD(T*)-F12a}}_{\text{T(D)}} \quad (2)$$

where "rel" denotes scalar-relativistic calculations (second-order Douglas–Kroll–Hess level), "nrel" denotes non-relativistic calculations. The basis sets used, T(D) and T(D)-DK, as well as corresponding auxiliary basis sets for F12 calculations, are defined in Table S2. The CBS limits for CASPT2 and CASPT2/CC energies are estimated assuming transferability of the basis set incompleteness error from the results of CCSD(T) calculations using the identical basis set, T(D)-DK:

$$\Delta E^{\text{CASPT2, rel}}_{\text{final}} = \Delta E^{\text{CASPT2, rel}}_{\text{T(D)-DK}} + \Delta E^{\text{CCSD(T), rel}}_{\text{final}} - \Delta E^{\text{CCSD(T), rel}}_{\text{T(D)-DK}} \quad (3)$$

$$\Delta E^{\text{CASPT2/CC, rel}}_{\text{final}} = \Delta E^{\text{CASPT2, rel}}_{\text{final}} + \left(\Delta E^{\text{CCSD(T), rel}}_{\text{T(D)-DK}} - \Delta E^{\text{FC-CCSD(T), rel}}_{\text{T(D)-DK}}\right) - \left(\Delta E^{\text{CASPT2, rel}}_{\text{T(D)-DK}} - \Delta E^{\text{FC-CASPT2, rel}}_{\text{T(D)-DK}}\right). \quad (4)$$

The prefix "FC" denotes that the outer-core 3s3p electrons of the transition metal are frozen; otherwise these are correlated. All other core electrons (1s of C, N, O) are always frozen.

The CCSD(T) calculations for open-shell states (HS) are based on the ROHF reference wave function. For compatibility with the results published in the literature, the calculations for $[Co(NH_3)_5(NO)]^{2+}$ employ the partially spin-adapted formulation, ROHF/RCCSD(T),[S14] whereas those for $[Fe(NCH)_6]^{2+}$ employ the ROHF/UCCSD(T) formulation.

1.3 Additional CC results

To complete the discussion of CC calculations for $[Fe(NCH)_6]^{2+}$ and $[Co(NH_3)_5(NO)]^{2+}$ presented in the main article, one can look into the leading singles and doubles amplitudes as well as the convergence pattern of the CC energy by splitting the CCSD(T) energy into components: the reference (HF) energy, the CCSD correlation energy and the (T) correction. CCSDT calculations have not been reported for these systems as too expensive.

For $[Fe(NCH)_6]^{2+}$ the leading amplitudes were thorougly analyzed already in ref 77 (in their supporting information) where the interested reader is referred for details. It was found that the leading singles amplitudes are about 0.06–0.07 (larger in the singlet state), the leading doubles amplitudes are about 0.025 (comparable in both spin states). The orbitals involved in the leading excitations are mainly combinations of the Fe 3d with ligand orbitals of the σ and π ligand orbitals of the appropriate symmetry; these are known to be important in describing correlation effects related to metal–ligand donation and backdonation as well as "double-shell"/"orbital breathing" effects.[S15,S16] The T_1 and D_1 diagnostics are larger in the LS state (showing larger orbital relaxation effects), but they are still within safe thresholds ($T_1 < 0.05$, $D_1 < 0.15$) suggested for TM complexes in ref 90, main article. Overall, $[Fe(NCH)_6]^{2+}$ appears to be a well behaving system for single-reference CC calculations. However, note that the correlation energy contributes significantly to the relative energy in order to overcome very strong bias towards the HS state at the HF level (Table S3). The differential correlation effect at the CCSD(T) level is about 80 kcal/mol favoring the LS state, of which about 16% is from the triples. Large contributions from the triples rather typically occur in TM complexes (see for example, ref. 23).

Table S3: Additional CC results for $[Fe(NCH)_6]^{2+}$. [a,b]

	LS	HS	ΔE
HF	−1828.533035	−1828.674593	−88.8
$CCSD_{corr}$	−2.672707	−2.565487	67.3
(T)	−0.134119	−0.113241	13.1
CCSD(T)	−1831.339861	−1831.353321	−8.4
T_1 diagnostic	0.025	0.015	
D_1 diagnostic	0.093	0.046	

[a] All results from scalar-relativistic calculations with the T(D)-DK basis set; g1 geometries; ROHF/UCCSD(T) for HS state. [b] Total energies in a.u., energy differences $E(HS) - E(LS)$ in kcal/mol.

For the second complex, $[Co(NH_3)_5(NO)]^{2+}$, the leading CC amplitudes are given in Table S4, the splitting of the CCSD(T) energy and diagnostics in Table S5, whereas the orbitals participating in the leading excitations are shown in Figures S1 and S2. In this complex, the leading singles amplitudes are greater than 0.2, with the maximum value of 0.34 in the singlet state, resulting in the T_1 and D_1 diagnostics beyond the literature criteria (see above). The doubles amplitudes of almost 0.2 are also found in both spin states. The orbitals involved in the leading excitations are combinations of the Co 3d with the NO π^*, π and NH_3 lone pairs, which are known to be important in describing significant correlation effects in metal–nitrosyl complexes.[S17] Total correlation effects are thus very significant in both spin states (in fact, greater in magnitude than for the first complex despite a smaller number of correlated electrons). Somewhat surprisingly, however, the correlation energies in both spin states are quite comparable leading to differential effects within a few kcal/mol only (cf Table S5). Thus, based on large T-amplitudes $[Co(NH_3)_5(NO)]^{2+}$ appears to have pronounced non-dynamic correlation effects, making it potentially challenging to reliably compute the correlation energies in single-reference CCSD(T) calculations. However, strong correlation effects in both spin states tend to nicely balance, resulting in the energy difference which may be still reliable at the CCSD(T) due to the cancellation of errors.

Table S4: Leading singles and doubles amplitudes for $[Co(NH_3)_5(NO)]^{2+}$. [a]

	state	$\lvert t_i^a\rvert$ or $\lvert t_{ij}^{ab}\rvert$	orbitals involved[b] i	j	a	b	spin case
singles with $\lvert t_i^a\rvert \geq 0.06$	LS	0.340	45		49		
		0.097	41		52		
	HS	0.277	44		47		$\alpha\alpha$
		0.199	44		47		$\alpha\beta$
		0.168	44		45		$\alpha\beta$
		0.137	26		48		$\alpha\beta$
		0.132	38		48		$\alpha\beta$
		0.117	26		48		$\alpha\alpha$
		0.108	38		48		$\alpha\alpha$
		0.101	45		47		$\alpha\alpha$
		0.070	43		46		$\alpha\beta$
		0.070	35		48		$\alpha\beta$
doubles with $\lvert t_{ij}^{ab}\rvert \geq 0.05$	LS	0.173	45	45	49	49	
	HS	0.198	44	44	47	47	$\alpha\beta$
		0.094	44	44	47	45	$\alpha\beta$
		0.078	38	38	48	48	$\alpha\beta$
		0.058	46	44	47	46	$\alpha\beta$

[a]From scalar-relativistic calculations with the T(D)-DK basis set; ROHF/RCCSD for HS state. [b]Orbitals numbered in the order of increasing energy (including core) in one irrep of the computational C_1 symmetry; for contour plots, see Figures S1 and S2.

Table S5: Additional CC results for $[Co(NH_3)_5(NO)]^{2+}$. [a,b]

	LS	HS	ΔE
HF	−1801.913909	−1801.906480	4.7
$CCSD_{corr}$	−2.438821	−2.432378	4.0
(T)	−0.122881	−0.118976	2.5
CCSD(T)	−1804.475611	−1804.457834	11.2
T_1 diagnostic	0.054	0.047	
D_1 diagnostic	0.371	0.252	

[a]All results from scalar-relativistic calculations with the T(D)-DK basis set; ROHF/RCCSD(T) for HS state. [b]Total energies in a.u., energy differences $E(\mathrm{HS}) - E(\mathrm{LS})$ in kcal/mol.

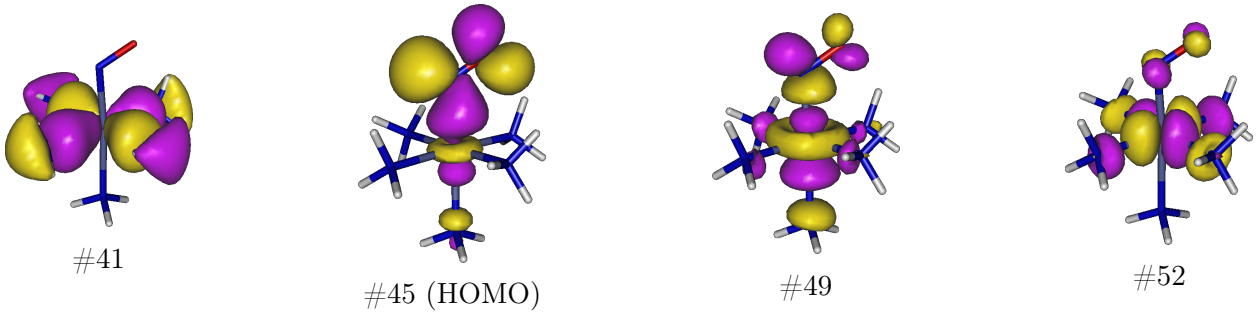

Figure S1: Orbitals involved in the single and double excitations of largest amplitudes for $[Co(NH_3)_5(NO)]^{2+}$ in the LS state; contour plots are drawn for the value of ± 0.04 bohr$^{-3/2}$.

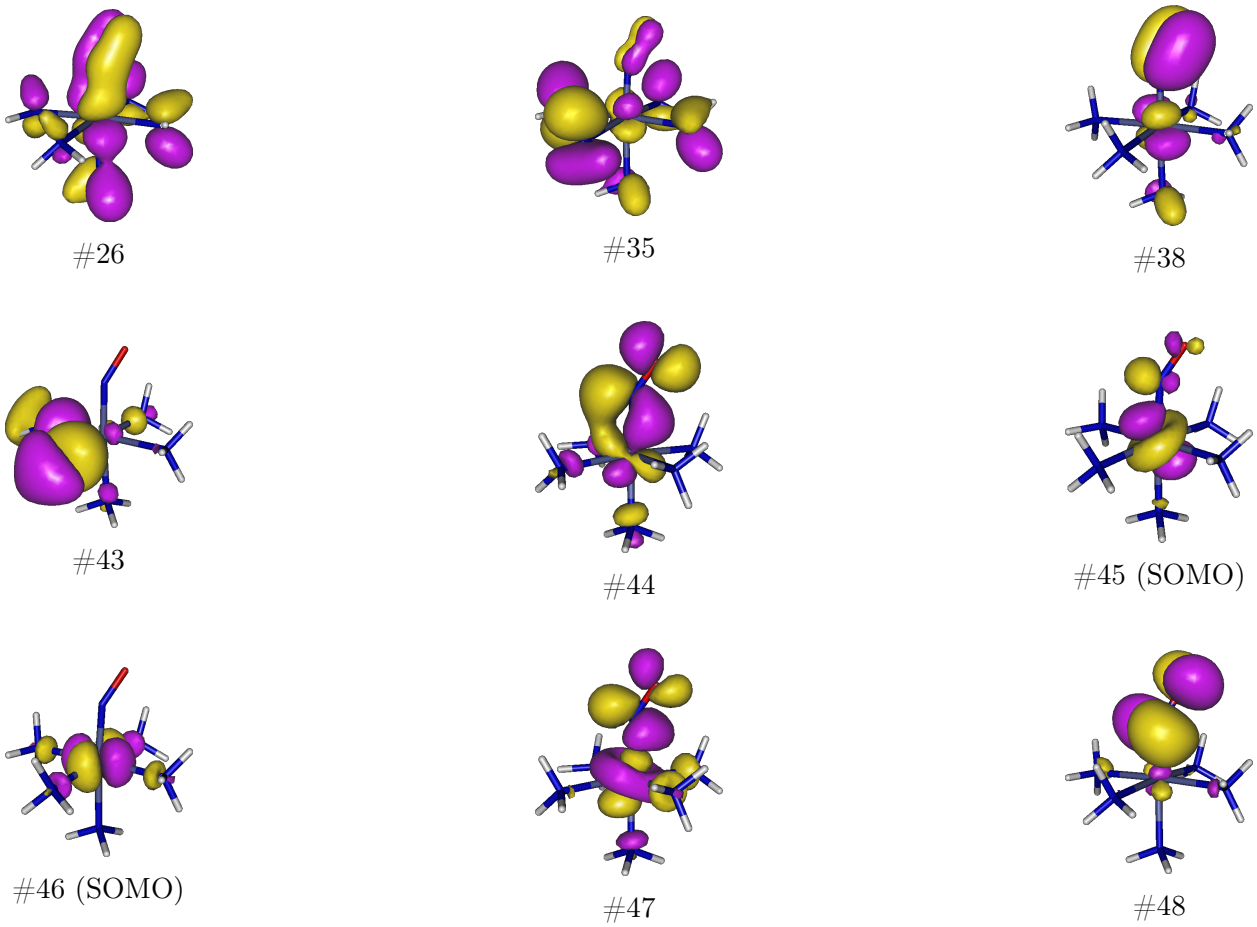

Figure S2: Orbitals involved in the single and double excitations of largest amplitudes for $[Co(NH_3)_5(NO)]^{2+}$ in the HS state; contour plots are drawn at the value of ± 0.04 bohr$^{-3/2}$.

2 Vibrational enthalpy and entropy corrections

Table S6: Vibrational enthalpy and zero-point corrections for some SCO complexes[a,b]

complex[c,d]	temp[e]	theory level	Δ ZPE	ΔH_{vib}
$^{1,5}[Fe^{II}(phen)_2(NCS)_2]$	176	PBE-D3	−2.3	−1.6
		PBE0-D3	−2.6	−1.7
		PBE0-D3, COSMO	−2.7	−1.6
$^{1,5}[Fe^{II}(tacn)_2]^{2+}$	349	PBE-D3	−2.5	−1.1
		PBE0-D3	−2.8	−1.5
		PBE0-D3, COSMO	−2.9	−1.5
$^{1,5}[Fe(1\text{-bpp})_2]^{2+}$	259	PBE-D3	−2.2	−1.0
		PBE0-D3	−2.2	−1.1
		PBE0-D3, COSMO	−2.2	−1.1
$^{2,6}[Fe^{III}(acac_2trien)]^{+}$	250	PBE-D3	−2.5	−1.6
		PBE0-D3	−1.8	−1.2
		PBE0-D3, COSMO	−1.7	−1.0
$^{2,6}[Mn^{II}Cp_2]$	180	PBE-D3	−1.7	−0.9
		PBE0-D3	−1.9	−1.3
		PBE0-D3, COSMO	−2.4	−1.6

[a] Values in kcal mol^{-1}; energy/enthalpy differences defined with respect to the state of lower multiplicity. [b] Computed under harmonic approximation from frequencies obtained at the DFT level with indicated functional, the def2-TZVP basis set, within the RI-J approximation, the D3 correction is that with Becke-Johnson damping; for COSMO model $\varepsilon = \infty$; calculations performed with Turbomole 7.5. [c] Superscripts gives multiplicities of the spin states for calculation of the energy/enthalpy difference (for instance, "1, 5" denotes the singlet and quintet states). [d] Ligand abbreviations: phen = 1,10-phenantroline; tacn = 1,4,7-triazacyclononane; 1-bpp = 2,6-di(pyrazol-1-yl)pyridine; H_2acac_2trien = Schiff base obtained from the 1:2 condensation of triethylenetetramine with acetylacetone; Cp = cyclopentadienyl. [e] Experimental $T_{1/2}$ in K, as reported for each complex (refs S18–S21 and ref 146, main article), which was used to calculate the enthalpy correction.

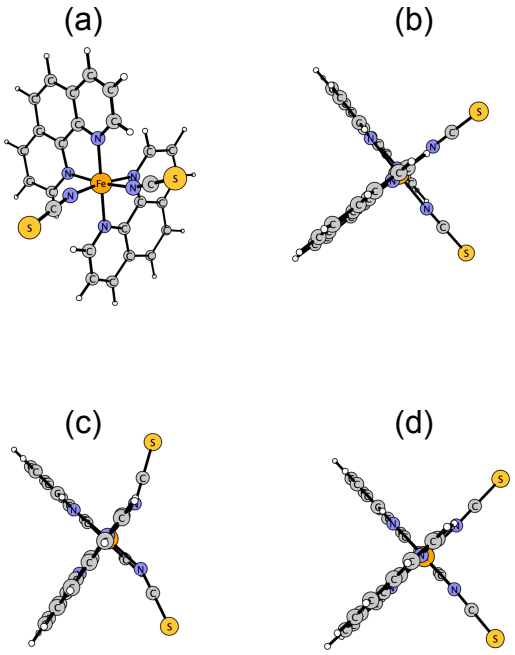

Figure S3: Crystal structure of $[Fe(phen)_2(NCS)_2]$ (KEKVIF01) in two views (a, b) and geometry of the singlet state optimized at the PBE0-D3(BJ)/def2-TZVP level in gas phase (c) and in COSMO model (d). Different arrangement of the NCS ligands is seen for case (c) as compared with cases (b) or (d).

2.1 Expressions for thermochemical corrections, $H_{\mathbf{vib}}$ and $S_{\mathbf{vib}}$

Both corrections are expressed as a sum of contributions from all normal modes

$$H_{\mathrm{vib}} = N_A \sum_i H_i, \tag{5}$$

$$S_{\mathrm{vib}} = R \sum_i S_i, \tag{6}$$

where the contributions from the i-th normal mode under the harmonic oscillator approximation read:

$$H_i^{\mathrm{harm}} = \frac{1}{2} h\nu_i + \frac{h\nu_i}{e^{\frac{h\nu_i}{kT}} - 1}, \tag{7}$$

$$S_i^{\mathrm{harm}} = \frac{h\nu_i}{kT} \frac{1}{e^{\frac{h\nu_i}{kT}} - 1} - \ln\left(1 - e^{-\frac{h\nu_i}{kT}}\right) \tag{8}$$

(where N_A is the Avogadro number, h is the Plack constant, k is the Boltzmann constant, $R = N_A k$ is the gas constant, T is absolute temperature, ν_i are vibrational frequencies).

For the quasi-harmonic model of Cramer and Truhlar (QH-CT), the same expressions are used; only the frequencies below the cutoff value are raised to the cutoff value. For the quasi-harmonic model of Grimme and Head-Gordon (QH-GHG) with the cutoff frequency ν_0, the expressions are as follows:

$$H_i^{\text{QH-GHG}} = \tfrac{1}{2} h\nu_i + f_i \left(H_i^{\mathrm{harm}} - \tfrac{1}{2} h\nu_i\right) + (1 - f_i) \times \tfrac{1}{2} kT, \tag{9}$$

$$S_i^{\text{QH-GHG}} = f_i S_i^{\mathrm{harm}} + (1 - f_i)\, S_i^R(\nu_i), \tag{10}$$

where f_i is the damping factor for i-th mode

$$f_i = \frac{1}{1 + (\nu_0/\nu_i)^4} \tag{11}$$

and S_i^R is the entropy of 1-dimensional rigid rotor

$$S_i^R = \tfrac{1}{2}\left(1 + \ln \frac{\pi kT}{h\,(\nu_i + \kappa)}\right) \tag{12}$$

rotating with frequency $\nu_i + \kappa$, where

$$\kappa = \frac{h}{8\pi^2 B_{\mathrm{av}}} = 0.028\,\mathrm{cm}^{-1} \text{ for } B_{\mathrm{av}} = 10^{-44}\,\mathrm{kg\,m}^2. \tag{13}$$

This is equivalent to Grimme's original formulation (ref 140, main article), but for convenience and simplicity expressed in terms of frequency, rather than "the moment of interia μ for a free-rotor with the same frequency." The constant B_{av} introduced by Grimme is the limiting value of inertia for such a rotor in the case of very low frequency (large μ) and corresponds to the constant κ in eq. (13). Note that the enthalpy of the 1-dimensional rotor in eq. (9) is $\frac{1}{2}kT$ from the equipartition theorem.

In the low-T limit ($kT \ll h\nu_i$) the enthalpy goes to the ZPE

$$H_i \approx \tfrac{1}{2}h\nu_i, \tag{14}$$

which holds true for both harmonic and QH-GHG model (note that eq. (9) is chosen to preserve the ZPE; the raising of low frequencies in the QH-CT model affects the ZPE).

In the high-T limit ($kT \gg h\nu_i$) the harmonic approximation predicts that each vibrational mode contributes an enthalpy of kT. This result is from the classical equipartition theorem, but also can also be obtained from eq. (7) by using the series expansion

$$\frac{x}{e^x - 1} = \frac{1}{1 + \frac{1}{2}x + \mathcal{O}(x^2)} = 1 - \tfrac{1}{2}x + \mathcal{O}(x^2) \tag{15}$$

valid for $x \ll 1$ (where $x = h\nu_i/kT$). Thus, under the harmonic approximation the vibrational contribution to the SCO enthalpy change vanishes in the high-T limit because the

number of modes is identical for both spin states and all modes contribute equally. Interestingly, this is not the case for QH-GHG model because the high-T limit of eq. (9) is

$$H_i^{\text{QH-GHG}} \approx \tfrac{1}{2}(1 - f_i)h\nu_i + \tfrac{1}{2}(1 + f_i)kT \tag{16}$$

and thus for high temperatures the leading term in the SCO enthalpy change (difference of corrections for the HS and LS states) reads

$$\Delta H^{\text{QH-GHG}} \approx \tfrac{1}{2}kT \times \sum_i \left(f_i^{\text{HS}} - f_i^{\text{LS}}\right). \tag{17}$$

The above expression goes to $-\infty$ for very large T because the factor multiplying the $\frac{1}{2}kT$ term is negative (as long as there are more low-frequency modes in the HS than in the LS state, which is typically the case).

3 Characterization of environmental effects

3.1 Definitions of structural and direct solvation effects

To define solvation effects and their partitioning into the direct and structural components, four separate calculations have be performed for each interesting energy difference (ΔE):

(g/g) energy calculation in the gas phase for the gaseous geometry,

(s/g) energy calculation in the solution for the gaseous geometry,

(g/s) energy calculation in the gas phase for the geometry optimized in solution,

(s/s) energy calculation in the solution for the geometry optimized in solution.

The total solvation effect δ_{total} is defined by comparing the energies for gaseous (g/g) and fully solvated (s/s) models:

$$\delta_{\text{total}} = \Delta E_{(\text{s/s})} - \Delta E_{(\text{g/g})}. \tag{18}$$

The two intermediate models (g/s) and (s/g) are used to define the direct component δ_{direct}

$$\delta_{\text{direct}} = \frac{\delta^{(1)}_{\text{direct}} + \delta^{(2)}_{\text{direct}}}{2}, \tag{19}$$

$$\delta^{(1)}_{\text{direct}} = \Delta E_{(\text{s/g})} - \Delta E_{(\text{g/g})}, \tag{20}$$

$$\delta^{(2)}_{\text{direct}} = \Delta E_{(\text{s/s})} - \Delta E_{(\text{g/s})} \tag{21}$$

and the structural component δ_{struct} of the solvation effect

$$\delta_{\text{struct}} = \frac{\delta^{(1)}_{\text{struct}} + \delta^{(2)}_{\text{struct}}}{2}, \tag{22}$$

$$\delta^{(1)}_{\text{struct}} = \Delta E_{(\text{g/s})} - \Delta E_{(\text{g/g})}, \tag{23}$$

$$\delta^{(2)}_{\text{struct}} = \Delta E_{(\text{s/s})} - \Delta E_{(\text{s/g})}. \tag{24}$$

These two components of the total solvation effect are by definition additive, i.e.

$$\delta_{\text{tot}} = \delta_{\text{struct}} + \delta_{\text{direct}}. \tag{25}$$

See also scheme in Figure S4.

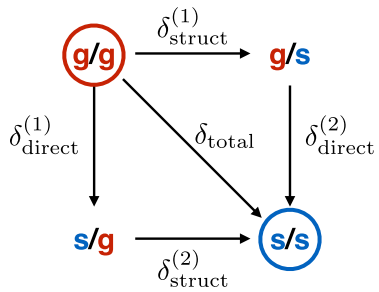

Figure S4: Scheme to illustrate definition of the total solvation effect (δ_{tot}) and its partitioning into the direct and structural components (δ_{direct}, δ_{struct})

3.2 Details of calculations in Table 3 (main article)

CASSCF/CASPT2 energy calculations in solution employed the PCM solvation model as implemented in OpenMolcas.[S22] For vertical excitation energies, non-equilibrium solvation was used for the excited state and equilibrium solvation for the ground state. The calculations were performed for geometries optimized at the DFT:BP86-D3/def2-TZVP level either in gas phase or in solution (using the COSMO model of respective solvent: water $\varepsilon = 80$ or acetonitrile $\varepsilon = 37.5$). Core electrons, but not outer-core electrons of the TM, were frozen in the CASPT2 calculations. The IPEA shift parameter was set to the recommended value of 0.25 a.u. and the imaginary shift of 0.1 a.u. was used.

$\mathbf{[Fe(H_2O)_6]^{3+}}$. The details of the calculations are similar as in ref 116. The basis set used was cc-pwCVTZ-DK (Fe), cc-pVTZ-DK (O) and cc-pVDZ-DK (H). The relativistic effects were modeled at the second-order Douglas-Kroll level. The active space (9,12) was used for the sextet ground state ($^6A_{1g}$) and the lowest quartet ($^4T_{1g}$) ligand field state. Three spatial components of the $^4T_{1g}$ state were computed together in state-averaged CASSCF

calculations. (They are degenerate to within the numerical accuracy for the symmetric geometry of the $^6A_{1g}$ state, used in the calculation of the vertical energy difference, but not for the optimized geometry of the quartet state, used in the calculation of the adiabatic energy difference; in this case, the lowest of the three energies was taken to obtain the adiabatic energy.) All calculations were performed under the C_i symmetry, where the d orbitals belong to a_g irrep. To calculate the LMCT excitation energy, the active space was extended (15,15) by including three additional a_u orbitals being combinations of the O lone pairs. State-averaged calculations were performed to compute the lowest 9 sextet roots of the A_u symmetry, of which the lowest energy one (component of the triply degenerate state) was taken to obtain the LMCT excitation energy being reported here. The total and relative energies are given in Table S7.

Table S7: CASPT2 energies for $[Fe(H_2O)_6]^{3+}$

state	g/g	s/g	g/s	s/s
	CASPT2 total energies (a.u). +1729			
$^6A_{1g}$	−0.166542	−0.901108	−0.168025	−0.903064
$^4T_{1g}$ vertical	−0.078481	−0.813106	−0.087449	−0.822344
	−0.078480	−0.813145	−0.087449	−0.822300
	−0.078480	−0.813181	−0.087449	−0.822362
$^4T_{1g}$ adiabatic	−0.092310	−0.838379	−0.090716	−0.846474
^{6}LMCT vertical	0.007790	−0.718653	0.022866	−0.704639
	excitation energies (kcal/mol)			
$^4T_{1g}$ vertical	55.3	55.2	50.6	50.7
$^4T_{1g}$ adiabatic	46.6	39.4	48.5	35.5
^{6}LMCT vertical	109.4	114.5	119.8	124.5

$[Ru(bpy)Cl_2(CO)_2]$. The ground state and two lowest singlet excited states of A_1 symmetry (point group C_{2v}) were obtained from state-averaged CASSCF/CASPT2 calculations. The active space of 14 electrons in 14 active orbitals was composed of combinations of the five Ru 4d orbitals, the combinations of CO π^* orbitals in a_1 and b_1 irreps strongly overlapping with the Ru 4d orbitals in the same irreps, the a_1 combination of the Cl lone pairs, as well as two π and two π^* orbitals of the bpy ligand (in b_1 and a_2 irreps). The basis sets used

was cc-pwCVTZ-PP (for Ru) and cc-pVDZ (for other atoms). The pseudopotential for Ru atom accounts for relativistic effects. Total and relative energies are reported in Table S8.

Table S8: CASPT2 vertical energies for $[Ru(bpy)Cl_2(CO)_2]$

state	g/g	s/g	g/s	s/s
CASPT2 total energies (a.u.) +1733				
^{1}GS (1^1A_1)	−1.050984	−1.068425	−1.050642	−1.068235
^{1}LMCT (2^1A_1)	−0.908854	−0.915373	−0.909904	−0.916504
^{1}MC(3^1A_1)	−0.845370	−0.874155	−0.846402	−0.875530
excitation energies (kcal/mol)				
^{1}LMCT (2^1A_1)	89.2	96.0	88.3	95.2
^{1}MC(3^1A_1)	129.0	121.9	128.2	120.9

Table S9: DFT adiabatic energies for other complexes from Table 3 (main article)

complex	state	g/g	s/g	g/s	s/s
BP86-D3/def2-TZVP total energies (a.u.) + const[a]					
$[Fe(tacn)_2]^{3+}$ [b]	^2A	−0.308065	−0.846537	−0.306126	−0.847735
	^6A	−0.266214	−0.796295	−0.264972	−0.797260
$[Fe(1\text{-bpp})_2]^{2+}$ [c]	$^1A_1$	−0.915461	−1.116100	−0.915304	−1.116147
	^5A	−0.873697	−1.070779	−0.873294	−1.070644
$[Fe(3\text{-bpp})_2]^{2+}$ [c]	$^1A_1$	−0.959710	−1.167920	−0.959502	−1.168121
	^5A	−0.918486	−1.123328	−0.917970	−1.123243
relative energies (kcal/mol)					
$[Fe(tacn)_2]^{3+}$ [b]	$^6A - {}^2A$	26.3	31.5	25.8	31.7
$[Fe(1\text{-bpp})_2]^{2+}$ [c]	$^5A - {}^1A_1$	26.2	28.4	26.4	28.6
$[Fe(3\text{-bpp})_2]^{2+}$ [c]	$^5A - {}^1A_1$	25.9	28.0	26.1	28.2

[a] const = 2067 for $[Fe(tacn)_2]^{3+}$, 2660 for $[Fe(1\text{-bpp})_2]^{2+}$ and $[Fe(3\text{-bpp})_2]^{2+}$. [b]Optimized under C_2 symmetry; solvent is methanol ($\varepsilon = 32.613$). [c]Optimized under D_{2d} symmetry for singlet, C_2 (vacuum) or C_1 (solvent) for quintet state; solvent is acetone ($\varepsilon = 20.493$).

3.3 Electrostatic potential and ESP charges

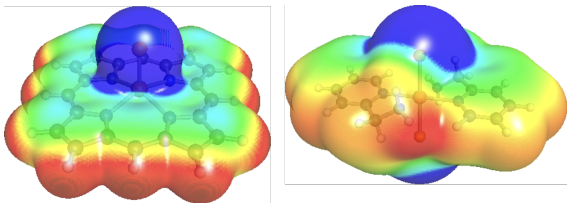

Figure S5: Molecular electrostatic potentials of [FeP(Cl)] (*left*) and [Fe(amp)$_2$Cl$_2$] (*right*) in the HS state mapped on the molecular Van der Waals surface (Red – positive, blue – negative values). Calculations at the BP86-D3/def2-TZVP level in vacuum.

Table S10: Metal–ligand bond distances and ESP charges for [FeP(Cl)] and [Fe(amp)$_2$Cl$_2$] [a]

		[FeP(Cl)]		[Fe(amp)$_2$Cl$_2$]	
		vacuum	COSMO[b]	vacuum	COSMO[b]
distance (Å)	Fe–N	2.096	2.089	2.188	2.159
				2.247	2.217
	Fe–Cl	2.198	2.239	2.380	2.455
ESP charge[c]	Fe	0.223	0.219	0.180	0.277
	N	−0.221	−0.229	−0.038	−0.060
				0.029	−0.005
	Cl	−0.412	−0.512	−0.626	−0.753

[a]Calculations at the BP86-D3/def2-TZVP level, Turbomole v7.0; assuming HS state for both complexes. [b]Methanol ($\varepsilon = 33$). [c]Fitted to the electrostatic potential at spherical shells of grid points around the atoms using Bragg–Slater radii.

Table S11: Metal–ligand bond distances and ESP charges for $[CuCl_4]^{2-}$ and FeF_6^{3-} [a]

	$[CuCl_4]^{2-}$		$[FeF_6]^{3-}$	
	vacuum	COSMO[b]	vacuum	COSMO[b]
M–X distance (Å)	2.367	2.320	2.050	1.978
ESP charge[c] M	0.793	0.718	1.702	1.634
ESP charge[c] X	−0.698	−0.679	−0.784	−0.772

[a]Calculations at the BP86-D3/def2-TZVP level, Turbomole v7.0, spin states: doublet for $[CuCl_4]^{2-}$ and sextet for $[FeF_6]^{3-}$. [b]Water ($\varepsilon = 80$). [c]Fitted to the electrostatic potential calculated at spherical shells of grid points around the atoms using Bragg–Slater radii.

3.4 Periodic DFT calculations, Table 4 (main article)

Periodic DFT calculations were performed with Quantum Espresso (QE) v6.7[S23] using a very similar methodology as described by Vela *et al.* (ref. 108, main article). Variable cell geometry optimizations were performed using the PBE functional with Grimme's disperstion correction D3(BJ) and Hubbard-type correction (DFT+U in the simplified version of Cococcioni and de Gironcoli,[S24] with $U = 2.65$ eV as recommended by Vela *et al.* for Fe^{II} complexes), with the convergence thresholds 2.0×10^{-4} Ry/bohr on forces, 2.0×10^{-6} Ry on total energy changes between two consecutive points, and 0.5 kbar for the variable-cell pressure. Vanderbilt's ultrasoft pseudopotentials from the GBRV collection[S25] were used and the cutoffs for expansion of wave function and density in the plane wave basis set were set to 70 Ry (ecutwfc) and 560 Ry (ecutrho), respectively. Sampling of the reciprocal space was limited to the Γ point. Optimizations were performed assuming either singlet (LS) or quintet (HS) state for all Fe^{II} complexes (the total magnetization per unit cell was set either to 0 or $4Z$, where $Z = 2$ is the number of Fe atoms per unit cell).

Initial coordinates were taken from published crystal structures of $[Fe(1\text{-bpp})_2][BF_4]_2$ and $[Fe(1\text{-bpp})_2][PF_6]_2$ (ref 146 and 147, main article), deposited in the Cambridge Crystallographic Data Center (CCDC) under IDs XENBEX03 and ADIYUH. In the latter crystal structure the PF_6^- anions are disordered over two equally occupied orientations. As QE cannot explicitly handle disordered crystals, only one of these orientations was kept during the DFT optimization and it was checked that both possible choices lead to the singlet–quintet splittings being almost identical (to within 0.02 kcal/mol per Fe).

To quantify crystal packing effect (CPE) on the singlet–quintet energy difference, subsequent single-point calculations were performed with ecutwfc= 35 Ry and ecutrho = 280 Ry for the crystal structure (optimized as described above) and isolated $[Fe(1\text{-bpp})_2]^{2+}$ ion (optimized at the BP-D3/def2-TZVP level). The isolated ion was placed in the cubic lattice with a large cell dimension (60 bohr) to reduce unphysical interaction with its periodic images; the Makov-Payne correction[S26] was additionally used to correct the energy for long-

range electrostatics. As suggested by Vela et al., several U values were tested in single-point calculations to find the value ($U = 2.13$ eV) which best reproduces the experimental energy difference for crystalline $[Fe(1\text{-bpp})_2][BF_4]_2$, i.e.

$$\Delta E_{\mathrm{ad}} = \Delta H - \Delta H_{\mathrm{vibr}} = 5.2 \text{ kcal/mol},$$

where $\Delta H = 4.1$ kcal/mol (ref 146) and $\Delta H_{\mathrm{vibr}} = -1.1$ kcal/mol (Table S6). The same U value was used to determine the singlet–quintet splitting for isolated $[Fe(1\text{-bpp})_2]^{2+}$. The CPE was calculated as the difference in the singlet–quintet splitting between the crystal and the isolated ion. As can be seen from the results (Table S12 and S13), the spin–state splitting is very sensitive to the U, but in the same way for the crystals as for isolated ion, making the CPEs almost independent on U.

Table S12: Total and relative energies for $[Fe(1\text{-bpp})_2][BF_4]_2$ and $[Fe(1\text{-bpp})_2][PF_6]_2$ crystals.

U [a]	$[Fe(1\text{-bpp})_2][BF_4]_2$ [b]			$[Fe(1\text{-bpp})_2][PF_6]_2$ [b]		
	E_{HS} [c]	E_{LS} [c]	$\Delta E_{\mathrm{HS–LS}}$ [d]	E_{HS} [c]	E_{LS} [c]	$\Delta E_{\mathrm{HS–LS}}$ [d]
2.00	−564.139863	−564.129549	6.5	−670.471431	−670.493796	−14.0
2.13	−564.136564	−564.128300	5.2	−670.468652	−670.492619	−15.0
2.65	−564.123562	−564.123473	0.1	−670.457765	−670.488067	−19.0

[a]Value in eV. [b]Crystal energy per single Fe (there are two in unit cell). [c]Value in hartree. [d]Value in kcal/mol.

Table S13: Total and relative energies for isolated $[Fe(1\text{-bpp})_2]^{2+}$ and estimated CPEs on the singlet–quintet splitting for $[Fe(1\text{-bpp})_2][BF_4]_2$ and $[Fe(1\text{-bpp})_2][PF_6]_2$ crystals.

U [a]	isolated $[Fe(1\text{-bpp})_2]^{2+}$			CPE [b,d]	
	E_{HS} [c]	E_{LS} [c]	$\Delta E_{\mathrm{HS–LS}}$ [d]	$[Fe(1\text{-bpp})_2][BF_4]_2$	$[Fe(1\text{-bpp})_2][PF_6]_2$
2.00	−362.319914	−362.308530	7.1	−0.7	−21.2
2.13	−362.316510	−362.307167	5.9	−0.7	−20.9
2.65	−362.303082	−362.301898	0.7	−0.7	−19.8

[a]Value in eV. [b]Difference in $\Delta E_{\mathrm{HS-LS}}$ between the crystal and isolated ion. [c]Value in hartree. [d]Value in kcal/mol.

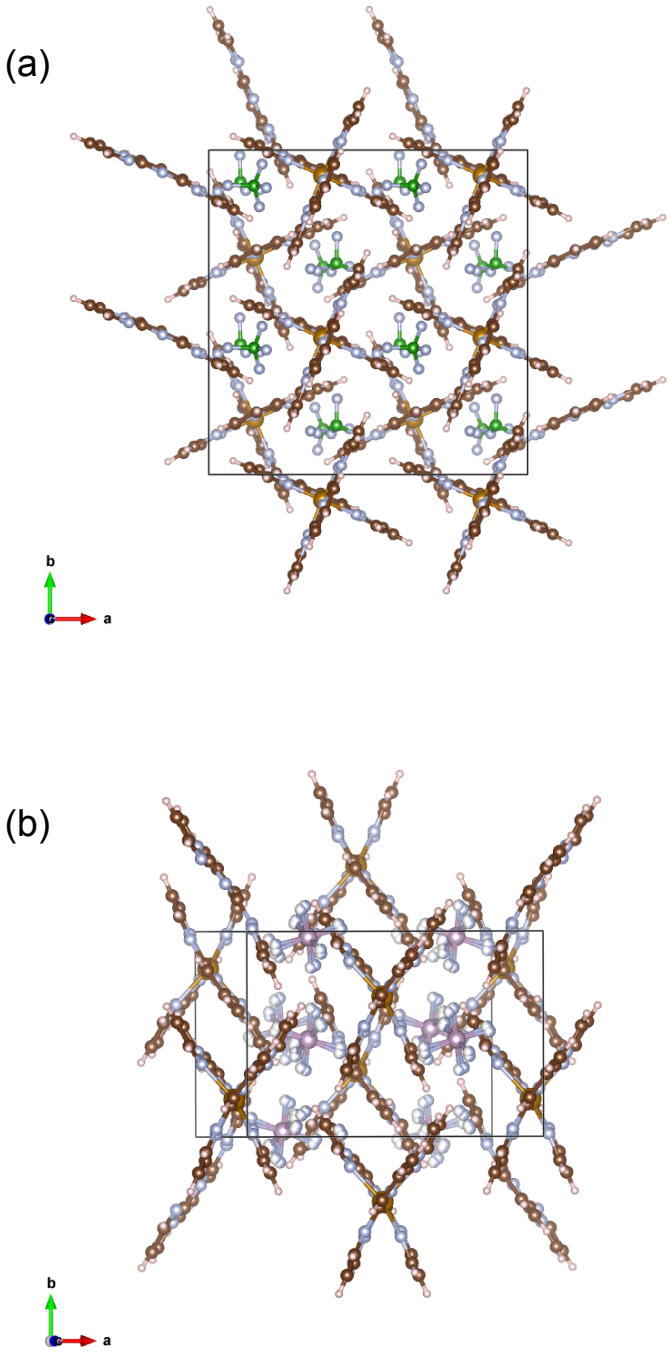

Figure S6: A view of crystal packing in the experimental crystal structures of (a) $[Fe(1\text{-bpp})_2][BF_4]_2$ (XENBEX03, $2 \times 2 \times 1$ supercell) and (b) $[Fe(1\text{-bpp})_2][PF_6]_2$ (ADIYUH), showing a distortion from the ideal D_{2d} geometry in the case of (b). Both structures are viewed approximately along the main C_2 axes of the $[Fe(1\text{-bpp})_2]^{2+}$ ions.

3.5 Details of calculations in Table 5 (main article)

CASSCF/CASPT2 calculations were performed using OpenMolcas.[S22] The basis set used was cc-pwCVTZ-DK (Co), cc-pVTZ-DK (N), cc-pVDZ-DK (Cl, and cc-pVDZ-DK (H). The relativistic effects were modelled at the second-order Douglas–Kroll level. The active space $(10, 10)$ was composed of five with predominant Co 3d character, two describing Co–N covalent bonds of approximate e_g symmetry, and three Co double-shell orbitals corresponding of approximate t_{2g} symmetry. The three lowest triplet states (components of the octahedral $^1T_{1g}$ term) were computed together in SA-CASSCF. Coordinates used are either from the PBE0/def2-TZVP optimization (in gas phase or within the COSMO solvation model) or taken from crystal structure of $[Co(en)_3]Cl_3$ at $T = 90$ K (IRIRAC01) or at $T = 193$ K (IRIRAC). For the crystal structure, all X−H bond lenghts (X=C, N) were increased by 10% compared with the crystallographic ones. This is necessary to obtain realistic distances to hydrogen atoms and leads to much lower total energies, but does not influence the excitation energy significantly (the difference is within 0.1 kcal/mol). The Ewald potential of the infinite ionic lattice was optionally included in the calculations for the cluster model. The Ewald potential was generated by including a suitable finite array of point charges generated by the program of Derenzo and co-workers[S27] (the procedure was similar as described for another example in ref 23, main article). Ideal ionic lattice was assumed, with charges -1 centered on Cl atoms and $+3$ centered on Co atoms.

The average excitation energy reported in Table 5 (main article) is defined as

$$\Delta E_{ve} = \frac{E_1 + E_2 + E_3}{3} - E_0 \tag{26}$$

and the spread as

$$\max(E_1,\, E_2,\, E_3) - \min(E_1,\, E_2,\, E_3), \tag{27}$$

where E_0 to E_3 are energies reported in Table S14.

Table S14: Total CASPT2 energies[a] for $[Co(en)_3]^{3+}$ and cluster model $\{[Co(en)_3]Cl_9\}^{6-}$

geometry	singlet	triplet		
	E_0	E_1	E_2	E_3
model: $[Co(en)_3]^{3+}$				
gaseous	−1.151949	−1.107324	−1.107399	−1.107523
COSMO	−1.148648	−1.096411	−1.096265	−1.096338
crystal 90 K	−1.141026	−1.088092	−1.087896	−1.087939
crystal 90 K [b]	−0.900111	−0.847252	−0.847217	−0.847313
crystal 193 K	−1.141561	−1.088573	−1.088825	−1.088751
model: $\{[Co(en)_3]Cl_9\}^{6-}$				
crystal 90 K	−0.924603	−0.873693	−0.873551	−0.873093
crystal 193 K	−0.927931	−0.877130	−0.877167	−0.876656
model: $\{[Co(en)_3]Cl_9\}^{6-}$ + Ewald				
crystal 90 K	−4.340860	−4.289762	−4.289551	−4.289389
crystal 193 K	−4.334898	−4.283957	−4.283770	−4.283641

[a]All values in atomic units (a.u.), shifted by 1961 for $[Co(en)_3]^{3+}$ or 6111 for $\{[Co(en)_3]Cl_9\}^{6-}$. [b]The crystallographic X−H distances not increased by 10%.

4 Optimized Cartesian coordinates

4.1 $Ru(bpy)_2Cl_2(CO)_2$

```
27
Ru(bpy)Cl2(CO)2, BP-D3/def2TZVP, vacuum, singlet GS
Ru     0.0000000     0.0000000     1.9753912
N      0.0000000    -1.3261229     0.3065271
N      0.0000000     1.3261229     0.3065271
C      0.0000000    -1.2965065     3.3069903
C      0.0000000     1.2965065     3.3069903
O      0.0000000     2.1232781     4.1160353
O      0.0000000    -2.1232781     4.1160353
Cl    -2.4020410     0.0000000     1.7737598
Cl     2.4020410     0.0000000     1.7737598
C      0.0000000     0.7363858    -0.9172618
C      0.0000000    -0.7363858    -0.9172618
C      0.0000000     2.6666115     0.3928977
C      0.0000000    -2.6666115     0.3928977
C      0.0000000     3.4887880    -0.7291819
C      0.0000000     2.8979101    -1.9919213
C      0.0000000     1.5098124    -2.0838005
C      0.0000000    -3.4887880    -0.7291819
C      0.0000000    -2.8979101    -1.9919213
C      0.0000000    -1.5098124    -2.0838005
H      0.0000000    -3.0851118     1.3971522
H      0.0000000     3.0851118     1.3971522
H      0.0000000     4.5704738    -0.6038231
H      0.0000000    -4.5704738    -0.6038231
H      0.0000000     3.5086893    -2.8947260
H      0.0000000    -3.5086893    -2.8947260
H      0.0000000    -1.0302326    -3.0603433
H      0.0000000     1.0302326    -3.0603433
```

```
27
Ru(bpy)Cl2(CO)2, BP-D3/def2TZVP, COSMO acetonitrile, singl GS
Ru     0.0000000     0.0000000     1.9685871
N      0.0000000    -1.3278039     0.3048190
N      0.0000000     1.3278039     0.3048190
C      0.0000000    -1.2980161     3.3034855
C      0.0000000     1.2980161     3.3034855
O      0.0000000     2.1147888     4.1236090
O      0.0000000    -2.1147888     4.1236090
Cl    -2.4134113     0.0000000     1.7934703
Cl     2.4134113     0.0000000     1.7934703
C      0.0000000     0.7362678    -0.9210895
C      0.0000000    -0.7362678    -0.9210895
C      0.0000000     2.6707117     0.3925922
C      0.0000000    -2.6707117     0.3925922
C      0.0000000     3.4913633    -0.7304879
C      0.0000000     2.8990719    -1.9929266
C      0.0000000     1.5100993    -2.0867249
C      0.0000000    -3.4913633    -0.7304879
C      0.0000000    -2.8990719    -1.9929266
C      0.0000000    -1.5100993    -2.0867249
H      0.0000000    -3.0964075     1.3936774
H      0.0000000     3.0964075     1.3936774
H      0.0000000     4.5728333    -0.6049941
H      0.0000000    -4.5728333    -0.6049941
H      0.0000000     3.5087169    -2.8961024
H      0.0000000    -3.5087169    -2.8961024
H      0.0000000    -1.0313592    -3.0636216
H      0.0000000     1.0313592    -3.0636216
```

4.2 $[Fe(1\text{-}bpp)_2]^{2+}$

```
51
[Fe(1bpp)2]2+ BP-D3/def2TZVP, vacuum, singlet
Fe     0.0000000     0.0000000     0.0000000
N      0.0000000     0.0000000     1.8855833
C      0.8275106    -0.8275106     2.5566804
C      0.8628158    -0.8628158     3.9472517
H      1.5329850    -1.5329850     4.4813799
C      0.0000000     0.0000000     4.6336586
H      0.0000000     0.0000000     5.7230545
C     -0.8628158     0.8628158     3.9472517
H     -1.5329850     1.5329850     4.4813799
C     -0.8275106     0.8275106     2.5566804
N      1.5888517    -1.5888517     1.6656946
N      1.3602222    -1.3602222     0.3208799
C      2.1835038    -2.1835038    -0.3320778
H      2.1914355    -2.1914355    -1.4169757
C      2.9487735    -2.9487735     0.5770205
H      3.6965315    -3.6965315     0.3395139
C      2.5504460    -2.5504460     1.8357023
H      2.8686507    -2.8686507     2.8220073
N     -1.5888517     1.5888517     1.6656946
N     -1.3602222     1.3602222     0.3208799
C     -2.1835038     2.1835038    -0.3320778
H     -2.1914355     2.1914355    -1.4169757
C     -2.9487735     2.9487735     0.5770205
H     -3.6965315     3.6965315     0.3395139
C     -2.5504460     2.5504460     1.8357023
H     -2.8686507     2.8686507     2.8220073
N      0.0000000     0.0000000    -1.8855833
C      0.8275106     0.8275106    -2.5566804
C      0.8628158     0.8628158    -3.9472517
H      1.5329850     1.5329850    -4.4813799
C      0.0000000     0.0000000    -4.6336586
H      0.0000000     0.0000000    -5.7230545
C     -0.8628158    -0.8628158    -3.9472517
H     -1.5329850    -1.5329850    -4.4813799
C     -0.8275106    -0.8275106    -2.5566804
N      1.5888517     1.5888517    -1.6656946
N      1.3602222     1.3602222    -0.3208799
C      2.1835038     2.1835038     0.3320778
H      2.1914355     2.1914355     1.4169757
C      2.9487735     2.9487735    -0.5770205
H      3.6965315     3.6965315    -0.3395139
C      2.5504460     2.5504460    -1.8357023
H      2.8686507     2.8686507    -2.8220073
N     -1.5888517    -1.5888517    -1.6656946
N     -1.3602222    -1.3602222    -0.3208799
C     -2.1835038    -2.1835038     0.3320778
H     -2.1914355    -2.1914355     1.4169757
C     -2.9487735    -2.9487735    -0.5770205
H     -3.6965315    -3.6965315    -0.3395139
C     -2.5504460    -2.5504460    -1.8357023
H     -2.8686507    -2.8686507    -2.8220073
```

```
51
[Fe(1bpp)2]2+ BP-D3/def2TZVP, vacuum, quintet
Fe     0.0000000     0.0000000     0.2507890
N      0.0880334     2.1060607    -0.0267423
C     -0.6829310     2.9143768     0.7165734
C     -0.6935742     4.2987220     0.5552800
H     -1.3175614     4.9439942     1.1694525
C      0.1431341     4.8331361    -0.4283052
H      0.1648241     5.9109363    -0.5872322
C      0.9596199     4.0059636    -1.2043497
H      1.6165637     4.4232316    -1.9640630
C      0.8972012     2.6359514    -0.9564432
N     -1.4559932     2.2135293     1.6600933
N     -1.2813363     0.8541819     1.7571958
C     -2.1224617     0.4541644     2.7172063
H     -2.1649874    -0.5955835     2.9900600
C     -2.8464617     1.5431671     3.2452612
H     -3.5934357     1.5256476     4.0305688
C     -2.3965616     2.6502165     2.5542089
H     -2.6714950     3.6959159     2.6326741
N      1.6637886     1.6664521    -1.6296667
N      1.5046896     0.3529576    -1.2662180
C      2.3604119    -0.3348427    -2.0288806
H      2.4180179    -1.4142561    -1.9294058
C      3.0808657     0.5229004    -2.8858173
H      3.8403980     0.2542269    -3.6109840
C      2.6126898     1.7918847    -2.6085378
H      2.8821734     2.7547507    -3.0273228
N     -0.0880334    -2.1060607    -0.0267423
C      0.6829310    -2.9143768     0.7165734
C      0.6935742    -4.2987220     0.5552800
H      1.3175614    -4.9439942     1.1694525
C     -0.1431341    -4.8331361    -0.4283052
H     -0.1648241    -5.9109363    -0.5872322
C     -0.9596199    -4.0059636    -1.2043497
H     -1.6165637    -4.4232316    -1.9640630
C     -0.8972012    -2.6359514    -0.9564432
N      1.4559932    -2.2135293     1.6600933
N      1.2813363    -0.8541819     1.7571958
C      2.1224617    -0.4541644     2.7172063
H      2.1649874     0.5955835     2.9900600
C      2.8464617    -1.5431671     3.2452612
H      3.5934357    -1.5256476     4.0305688
C      2.3965616    -2.6502165     2.5542089
H      2.6714950    -3.6959159     2.6326741
N     -1.6637886    -1.6664521    -1.6296667
N     -1.5046896    -0.3529576    -1.2662180
C     -2.3604119     0.3348427    -2.0288806
H     -2.4180179     1.4142561    -1.9294058
C     -3.0808657    -0.5229004    -2.8858173
H     -3.8403980    -0.2542269    -3.6109840
C     -2.6126898    -1.7918847    -2.6085378
H     -2.8821734    -2.7547507    -3.0273228
```

51

[Fe(1bpp)2]2+ BP-D3/def2TZVP, COSMO acetone, singlet

Fe	0.0000000	0.0000000	0.0000000
N	0.0000000	0.0000000	1.8845107
C	0.8258395	-0.8258395	2.5561940
C	0.8629711	-0.8629711	3.9452849
H	1.5346994	-1.5346994	4.4746897
C	0.0000000	0.0000000	4.6315008
H	0.0000000	0.0000000	5.7204054
C	-0.8629711	0.8629711	3.9452849
H	-1.5346994	1.5346994	4.4746897
C	-0.8258395	0.8258395	2.5561940
N	1.5868524	-1.5868524	1.6668782
N	1.3607362	-1.3607362	0.3221607
C	2.1852502	-2.1852502	-0.3277767
H	2.1992561	-2.1992561	-1.4120983
C	2.9471824	-2.9471824	0.5871846
H	3.6952073	-3.6952073	0.3523915
C	2.5454716	-2.5454716	1.8452829
H	2.8561618	-2.8561618	2.8362852
N	-1.5868524	1.5868524	1.6668782
N	-1.3607362	1.3607362	0.3221607
C	-2.1852502	2.1852502	-0.3277767
H	-2.1992561	2.1992561	-1.4120983
C	-2.9471824	2.9471824	0.5871846
H	-3.6952073	3.6952073	0.3523915
C	-2.5454716	2.5454716	1.8452829
H	-2.8561618	2.8561618	2.8362852
N	0.0000000	0.0000000	-1.8845107
C	0.8258395	0.8258395	-2.5561940
C	0.8629711	0.8629711	-3.9452849
H	1.5346994	1.5346994	-4.4746897
C	0.0000000	0.0000000	-4.6315008
H	0.0000000	0.0000000	-5.7204054
C	-0.8629711	-0.8629711	-3.9452849
H	-1.5346994	-1.5346994	-4.4746897
C	-0.8258395	-0.8258395	-2.5561940
N	1.5868524	1.5868524	-1.6668782
N	1.3607362	1.3607362	-0.3221607
C	2.1852502	2.1852502	0.3277767
H	2.1992561	2.1992561	1.4120983
C	2.9471824	2.9471824	-0.5871846
H	3.6952073	3.6952073	-0.3523915
C	2.5454716	2.5454716	-1.8452829
H	2.8561618	2.8561618	-2.8362852
N	-1.5868524	-1.5868524	-1.6668782
N	-1.3607362	-1.3607362	-0.3221607
C	-2.1852502	-2.1852502	0.3277767
H	-2.1992561	-2.1992561	1.4120983
C	-2.9471824	-2.9471824	-0.5871846
H	-3.6952073	-3.6952073	-0.3523915
C	-2.5454716	-2.5454716	-1.8452829
H	-2.8561618	-2.8561618	-2.8362852

51

[Fe(1bpp)2](2+), BP-D3/def2TZVP, COSMO acetone, quintet

Fe	-0.0010955	0.0001832	-0.0015772
N	0.1760775	2.1043513	0.0001098
C	-0.5941632	2.8463604	0.8085593
C	-0.5209416	4.2360429	0.8491786
H	-1.1559726	4.8241220	1.5073983
C	0.4085760	4.8482890	0.0039701
H	0.5005696	5.9335526	0.0054963
C	1.2220571	4.0907386	-0.8431373
H	1.9472395	4.5654100	-1.4997552
C	1.0603874	2.7084421	-0.8064310
N	-1.4644394	2.0701684	1.5955367
N	-1.4464704	0.7089312	1.4284944
C	-2.3369183	0.2273245	2.3008322
H	-2.5099395	-0.8430043	2.3552972
C	-2.9345053	1.2712942	3.0383488
H	-3.6889615	1.1887549	3.8120680
C	-2.3584030	2.4341793	2.5628341
H	-2.5139483	3.4719878	2.8345345
N	1.7880032	1.7990903	-1.5956038
N	1.5420750	0.4597826	-1.4313928
C	2.3389700	-0.1624138	-2.3052441
H	2.3300776	-1.2465059	-2.3620438
C	3.1029886	0.7681783	-3.0409279
H	3.8327115	0.5619772	-3.8152988
C	2.7301511	2.0101648	-2.5626413
H	3.0574065	3.0077894	-2.8322756
N	-0.1760286	-2.1045770	-0.0005128
C	0.5948505	-2.8462023	0.8076579
C	0.5231136	-4.2359790	0.8477393
H	1.1587029	-4.8236027	1.5058351
C	-0.4056444	-4.8489326	0.0022039
H	-0.4964952	-5.9342889	0.0032813
C	-1.2198356	-4.0918240	-0.8446385
H	-1.9444819	-4.5669351	-1.5015371
C	-1.0596066	-2.7093871	-0.8072915
N	1.4641605	-2.0693056	1.5949988
N	1.4443791	-0.7081162	1.4283068
C	2.3342126	-0.2254829	2.3007236
H	2.5058669	0.8450435	2.3555252
C	2.9332198	-1.2688278	3.0379397
H	3.6875593	-1.1854575	3.8116841
C	2.3586483	-2.4323745	2.5621460
H	2.5155831	-3.4700549	2.8335336
N	-1.7881216	-1.8003475	-1.5960200
N	-1.5432375	-0.4609898	-1.4310636
C	-2.3407225	0.1611526	-2.3044707
H	-2.3327793	1.2452755	-2.3606895
C	-3.1040526	-0.7695899	-3.0405992
H	-3.8339927	-0.5634930	-3.8147885
C	-2.7301743	-2.0115792	-2.5630667
H	-3.0566558	-3.0093151	-2.8332268

4.3 $[Fe(3\text{-}bpp)_2]^{2+}$

```
51
[Fe(3bpp)2]2+ BP-D3/def2TZVP, vacuum, singlet
Fe   -0.0000000    0.0000000    0.0000000
N     0.0000000   -0.0000000   -1.9184480
C    -0.8392730   -0.8392730   -2.5883434
C    -0.8582778   -0.8582778   -3.9849127
H    -1.5312588   -1.5312588   -4.5142529
C     0.0000000   -0.0000000   -4.6805298
H    -0.0000000    0.0000000   -5.7702047
C    -1.6260989   -1.6260989   -1.6542424
N    -1.3516416   -1.3516416   -0.3508855
N    -2.1518562   -2.1518562    0.3741571
H    -2.1163451   -2.1163451    1.3879205
C    -2.9334454   -2.9334454   -0.4221456
H    -3.6404115   -3.6404115   -0.0013056
C    -2.6217079   -2.6217079   -1.7357655
H    -3.0594802   -3.0594802   -2.6250311
N     0.0000000    0.0000000    1.9184480
C    -0.8392730    0.8392730    2.5883434
C    -0.8582778    0.8582778    3.9849127
H    -1.5312588    1.5312588    4.5142529
C     0.0000000    0.0000000    4.6805298
H    -0.0000000   -0.0000000    5.7702047
C    -1.6260989    1.6260989    1.6542424
N    -1.3516416    1.3516416    0.3508855
N    -2.1518562    2.1518562   -0.3741571
H    -2.1163451    2.1163451   -1.3879205
C    -2.9334454    2.9334454    0.4221456
H    -3.6404115    3.6404115    0.0013056
C    -2.6217079    2.6217079    1.7357655
H    -3.0594802    3.0594802    2.6250311
C     0.8392730    0.8392730   -2.5883434
C     0.8582778    0.8582778   -3.9849127
H     1.5312588    1.5312588   -4.5142529
C     1.6260989    1.6260989   -1.6542424
N     1.3516416    1.3516416   -0.3508855
N     2.1518562    2.1518562    0.3741571
H     2.1163451    2.1163451    1.3879205
C     2.9334454    2.9334454   -0.4221456
H     3.6404115    3.6404115   -0.0013056
C     2.6217079    2.6217079   -1.7357655
H     3.0594802    3.0594802   -2.6250311
C     0.8392730   -0.8392730    2.5883434
C     0.8582778   -0.8582778    3.9849127
H     1.5312588   -1.5312588    4.5142529
C     1.6260989   -1.6260989    1.6542424
N     1.3516416   -1.3516416    0.3508855
N     2.1518562   -2.1518562   -0.3741571
H     2.1163451   -2.1163451   -1.3879205
C     2.9334454   -2.9334454    0.4221456
H     3.6404115   -3.6404115    0.0013056
C     2.6217079   -2.6217079    1.7357655
H     3.0594802   -3.0594802    2.6250311
```

```
51
[Fe(3bpp)2]2+ BP-D3/def2TZVP vacuum, quintet
Fe   -0.0000000    0.0000000   -0.1580344
N     0.3664567   -2.0874561    0.0152616
C    -0.3008084   -2.9501312   -0.7857140
C    -0.0868627   -4.3292198   -0.7009046
H    -0.6246254   -5.0142357   -1.3548544
C     0.8307890   -4.8055648    0.2396368
H     1.0135629   -5.8763865    0.3280486
C    -1.2274689   -2.2867230   -1.7014296
N    -1.2664130   -0.9306584   -1.6524133
N    -2.1911351   -0.5680375   -2.5614141
H    -2.3959947    0.4159304   -2.7049155
C    -2.7436220   -1.6369888   -3.1883432
H    -3.5096978   -1.5195079   -3.9480272
C    -2.1416601   -2.7693695   -2.6597668
H    -2.3472313   -3.7970412   -2.9352947
N    -0.3664567    2.0874561    0.0152616
C     0.3008084    2.9501312   -0.7857140
C     0.0868627    4.3292198   -0.7009046
H     0.6246254    5.0142357   -1.3548544
C    -0.8307890    4.8055648    0.2396368
H    -1.0135629    5.8763865    0.3280486
C     1.2274689    2.2867230   -1.7014296
N     1.2664130    0.9306584   -1.6524133
N     2.1911351    0.5680375   -2.5614141
H     2.3959947   -0.4159304   -2.7049155
C     2.7436220    1.6369888   -3.1883432
H     3.5096978    1.5195079   -3.9480272
C     2.1416601    2.7693695   -2.6597668
H     2.3472313    3.7970412   -2.9352947
C     1.2641247   -2.5416697    0.9202883
C     1.5169295   -3.9097835    1.0635321
H     2.2377527   -4.2649452    1.7986126
C     1.9080001   -1.4716760    1.6788918
N     1.5395643   -0.2045611    1.3667044
N     2.2638930    0.5878306    2.1767473
H     2.1548597    1.5954586    2.1194239
C     3.0846302   -0.1223926    2.9924276
H     3.7430949    0.3647983    3.7042737
C     2.8798146   -1.4626634    2.7007382
H     3.3736146   -2.3067939    3.1675078
C    -1.2641247    2.5416697    0.9202883
C    -1.5169295    3.9097835    1.0635321
H    -2.2377527    4.2649452    1.7986126
C    -1.9080001    1.4716760    1.6788918
N    -1.5395643    0.2045611    1.3667044
N    -2.2638930   -0.5878306    2.1767473
H    -2.1548597   -1.5954586    2.1194239
C    -3.0846302    0.1223926    2.9924276
H    -3.7430949   -0.3647983    3.7042737
C    -2.8798146    1.4626634    2.7007382
H    -3.3736146    2.3067939    3.1675078
```

```
51
[Fe(3bpp)2]2+ BP-D3/def2TZVP COSMO acetone, singl
Fe     0.0000000    0.0000000    0.0000000
N      0.0000000   -0.0000000   -1.9155716
C     -0.8385194   -0.8385194   -2.5845213
C     -0.8585952   -0.8585952   -3.9804596
H     -1.5324380   -1.5324380   -4.5070917
C      0.0000000   -0.0000000   -4.6749132
H     -0.0000000    0.0000000   -5.7643756
C     -1.6235615   -1.6235615   -1.6510002
N     -1.3493441   -1.3493441   -0.3476786
N     -2.1466102   -2.1466102    0.3790564
H     -2.1165566   -2.1165566    1.3935842
C     -2.9276100   -2.9276100   -0.4139950
H     -3.6313414   -3.6313414    0.0167344
C     -2.6188124   -2.6188124   -1.7307041
H     -3.0545842   -3.0545842   -2.6219172
N      0.0000000    0.0000000    1.9155716
C     -0.8385194    0.8385194    2.5845213
C     -0.8585952    0.8585952    3.9804596
H     -1.5324380    1.5324380    4.5070917
C      0.0000000    0.0000000    4.6749132
H     -0.0000000   -0.0000000    5.7643756
C     -1.6235615    1.6235615    1.6510002
N     -1.3493441    1.3493441    0.3476786
N     -2.1466102    2.1466102   -0.3790564
H     -2.1165566    2.1165566   -1.3935842
C     -2.9276100    2.9276100    0.4139950
H     -3.6313414    3.6313414   -0.0167344
C     -2.6188124    2.6188124    1.7307041
H     -3.0545842    3.0545842    2.6219172
C      0.8385194    0.8385194   -2.5845213
C      0.8585952    0.8585952   -3.9804596
H      1.5324380    1.5324380   -4.5070917
C      1.6235615    1.6235615   -1.6510002
N      1.3493441    1.3493441   -0.3476786
N      2.1466102    2.1466102    0.3790564
H      2.1165566    2.1165566    1.3935842
C      2.9276100    2.9276100   -0.4139950
H      3.6313414    3.6313414    0.0167344
C      2.6188124    2.6188124   -1.7307041
H      3.0545842    3.0545842   -2.6219172
C      0.8385194   -0.8385194    2.5845213
C      0.8585952   -0.8585952    3.9804596
H      1.5324380   -1.5324380    4.5070917
C      1.6235615   -1.6235615    1.6510002
N      1.3493441   -1.3493441    0.3476786
N      2.1466102   -2.1466102   -0.3790564
H      2.1165566   -2.1165566   -1.3935842
C      2.9276100   -2.9276100    0.4139950
H      3.6313414   -3.6313414   -0.0167344
C      2.6188124   -2.6188124    1.7307041
H      3.0545842   -3.0545842    2.6219172
```

```
51
[Fe(3bpp)2]2+ BP-D3/def2TZVP COSMO acetone, quint
Fe    -0.0000699   -0.0000052   -0.3231387
N      0.3103188   -2.0761255    0.0210468
C     -0.3612675   -2.9777227   -0.7290829
C     -0.2152308   -4.3508055   -0.5127264
H     -0.7601590   -5.0677450   -1.1250275
C      0.6426315   -4.7756738    0.5060570
H      0.7716959   -5.8404025    0.6988436
C     -1.2166219   -2.3581308   -1.7371931
N     -1.1935068   -1.0023195   -1.8034392
N     -2.0565685   -0.6740956   -2.7798812
H     -2.2094667    0.3028267   -3.0143370
C     -2.6311767   -1.7641023   -3.3412813
H     -3.3550716   -1.6690912   -4.1435258
C     -2.1097994   -2.8776125   -2.6944046
H     -2.3497201   -3.9159441   -2.8911323
N     -0.3103220    2.0761103    0.0210512
C      0.3613857    2.9776677   -0.7290145
C      0.2155353    4.3507547   -0.5125585
H      0.7605697    5.0676632   -1.1248016
C     -0.6422678    4.7756673    0.5062566
H     -0.7711808    5.8403997    0.6991243
C      1.2166562    2.3580330   -1.7371712
N      1.1934015    1.0022271   -1.8034798
N      2.0563761    0.6739643   -2.7799849
H      2.2091553   -0.3029595   -3.0145133
C      2.6310580    1.7639391   -3.3413702
H      3.3548115    1.6688851   -4.1437397
C      2.1098327    2.8774712   -2.6944063
H      2.3498323    3.9157888   -2.8911114
C      1.1512019   -2.4807212    0.9988953
C      1.3378266   -3.8389189    1.2748891
H      2.0134162   -4.1527440    2.0692821
C      1.8075492   -1.3709302    1.6818830
N      1.5208631   -0.1304359    1.2180485
N      2.2213560    0.7155855    1.9887289
H      2.1665897    1.7163128    1.8208648
C      2.9552116    0.0658599    2.9256133
H      3.5846928    0.6070471    3.6237793
C      2.7115973   -1.2914781    2.7611519
H      3.1314763   -2.1028497    3.3441637
C     -1.1511311    2.4807495    0.9989411
C     -1.3375798    3.8389525    1.2750322
H     -2.0131184    4.1528105    2.0694553
C     -1.8076017    1.3710025    1.6818828
N     -1.5211241    0.1304928    1.2179626
N     -2.2216899   -0.7154520    1.9886679
H     -2.1671808   -1.7161738    1.8207292
C     -2.9553936   -0.0656657    2.9256362
H     -3.5848907   -0.6067881    3.6238387
C     -2.7115910    1.2916366    2.7612108
H     -3.1313107    2.1030456    3.3442851
```

4.4 $[Fe(tacn)_2]^{3+}$

```
49
[Fe(tacn)2]3+ BP-D3/def2TZVP vacuum, sextet
Fe   -0.0000000    0.0000000    0.0000296
N    -0.4994447   -1.4246572    1.6115187
N    -2.0220774   -0.6320938   -0.6205681
N     0.4540386   -1.9208498   -0.9911013
C    -0.0498458   -2.8216829    1.2649640
C     0.9571695   -2.7896253    0.1215766
C    -0.7515881   -2.4569523   -1.7211184
C    -1.7918281   -1.3593723   -1.9105850
C    -1.9787495   -1.2628097    1.7889294
C    -2.6949610   -1.4456536    0.4562117
H     0.3996104   -3.3026766    2.1440982
H    -1.4387210   -0.6168065   -2.6428367
H    -2.7301229   -1.7829920   -2.3024225
H    -2.6249579    0.1729142   -0.8186969
H     1.9121452   -2.3599703    0.4617959
H    -0.9305130   -3.4193884    1.0033342
H    -3.7469762   -1.1457878    0.5541284
H    -0.4529795   -2.8601527   -2.6981021
H    -0.0486890   -1.1679460    2.4956768
H    -2.7018285   -2.4977186    0.1489846
H     1.1674396   -3.8108645   -0.2337804
H     1.2093792   -1.8230053   -1.6772163
H    -2.3706495   -1.9712654    2.5358783
H    -1.1608092   -3.2995996   -1.1521070
H    -2.1491205   -0.2482815    2.1814236
N     0.4994447    1.4246572    1.6115187
N     2.0220774    0.6320938   -0.6205681
N    -0.4540386    1.9208498   -0.9911013
C     0.0498458    2.8216829    1.2649640
C     1.9787495    1.2628097    1.7889294
H     0.0486890    1.1679460    2.4956768
C     1.7918281    1.3593723   -1.9105850
C     2.6949610    1.4456536    0.4562117
H     2.6249579   -0.1729142   -0.8186969
C    -0.9571695    2.7896253    0.1215766
C     0.7515881    2.4569523   -1.7211184
H    -1.2093792    1.8230053   -1.6772163
H    -0.3996104    3.3026766    2.1440982
H     0.9305130    3.4193884    1.0033342
H     2.3706495    1.9712654    2.5358783
H     2.1491205    0.2482815    2.1814236
H     1.4387210    0.6168065   -2.6428367
H     2.7301229    1.7829920   -2.3024225
H     3.7469762    1.1457878    0.5541284
H     2.7018285    2.4977186    0.1489846
H    -1.9121452    2.3599703    0.4617959
H    -1.1674396    3.8108645   -0.2337804
H     0.4529795    2.8601527   -2.6981021
H     1.1608092    3.2995996   -1.1521070
```

```
49
[Fe(tacn)2]3+ BP-D3/def2TZVP vacuum, doublet
Fe    0.0000000    0.0000000    0.0061598
N     0.1045370   -1.5174484    1.3566248
N    -1.9902741   -0.4157292    0.0312783
N     0.0485283   -1.4815533   -1.3828318
C     0.3707617   -2.8348633    0.6488646
C     0.8730383   -2.5796652   -0.7648504
C    -1.3457054   -1.9364111   -1.7743447
C    -2.3605584   -0.8904004   -1.3450041
C    -1.1930648   -1.5090926    2.1153479
C    -2.3350028   -1.4181924    1.1162035
H     1.0957103   -3.4296254    1.2200156
H    -2.3529991   -0.0180360   -2.0127163
H    -3.3835027   -1.2968099   -1.3647990
H    -2.5386031    0.4323856    0.2170282
H     1.9226394   -2.2549492   -0.7724412
H    -0.5626249   -3.4091273    0.6356293
H    -3.2720465   -1.1345929    1.6133297
H    -1.3931467   -2.1154442   -2.8565089
H     0.8578566   -1.3768909    2.0394792
H    -2.5172959   -2.3878474    0.6386493
H     0.8226514   -3.4964324   -1.3723330
H     0.5299714   -1.1885533   -2.2404752
H    -1.2877241   -2.4073550    2.7448806
H    -1.5423556   -2.8996745   -1.2895536
H    -1.1752105   -0.6465874    2.7954479
N    -0.1045370    1.5174484    1.3566248
N     1.9902741    0.4157292    0.0312783
N    -0.0485283    1.4815533   -1.3828318
C    -0.3707617    2.8348633    0.6488646
C     1.1930648    1.5090926    2.1153479
H    -0.8578566    1.3768909    2.0394792
C     2.3605584    0.8904004   -1.3450041
C     2.3350028    1.4181924    1.1162035
H     2.5386031   -0.4323856    0.2170282
C    -0.8730383    2.5796652   -0.7648504
C     1.3457054    1.9364111   -1.7743447
H    -0.5299714    1.1885533   -2.2404752
H    -1.0957103    3.4296254    1.2200156
H     0.5626249    3.4091273    0.6356293
H     1.2877241    2.4073550    2.7448806
H     1.1752105    0.6465874    2.7954479
H     2.3529991    0.0180360   -2.0127163
H     3.3835027    1.2968099   -1.3647990
H     3.2720465    1.1345929    1.6133297
H     2.5172959    2.3878474    0.6386493
H    -1.9226394    2.2549492   -0.7724412
H    -0.8226514    3.4964324   -1.3723330
H     1.3931467    2.1154442   -2.8565089
H     1.5423556    2.8996745   -1.2895536
```

49

[Fe(tacn)2]3+ BP-D3/def2TZVP COSMO methanol, sextet

Fe	-0.0000000	0.0000000	-0.0075486
N	-0.5197701	-1.4009771	1.6064701
N	-2.0030097	-0.6333332	-0.6491774
N	0.4672389	-1.9253725	-0.9682871
C	-0.0814757	-2.7957528	1.2734000
C	0.9522484	-2.7698670	0.1603163
C	-0.7285525	-2.4733271	-1.6882143
C	-1.7525880	-1.3751663	-1.9179351
C	-1.9927920	-1.2285976	1.7574004
C	-2.6861752	-1.4329399	0.4203430
H	0.3419098	-3.2736391	2.1636755
H	-1.3769147	-0.6483200	-2.6507370
H	-2.6872071	-1.7973261	-2.3154362
H	-2.6122383	0.1567621	-0.8691377
H	1.8910853	-2.3264511	0.5192506
H	-0.9594942	-3.3824817	0.9834590
H	-3.7355383	-1.1252360	0.4958422
H	-0.4194327	-2.9008406	-2.6483211
H	-0.0848323	-1.1533997	2.4981549
H	-2.6813058	-2.4890431	0.1300801
H	1.1751881	-3.7911362	-0.1818765
H	1.2242298	-1.8534562	-1.6519585
H	-2.3937631	-1.9250204	2.5083982
H	-1.1534213	-3.2915957	-1.0971860
H	-2.1643248	-0.2078863	2.1252515
N	0.5197701	1.4009771	1.6064701
N	2.0030097	0.6333332	-0.6491774
N	-0.4672389	1.9253725	-0.9682871
C	0.0814757	2.7957528	1.2734000
C	1.9927920	1.2285976	1.7574004
H	0.0848323	1.1533997	2.4981549
C	1.7525880	1.3751663	-1.9179351
C	2.6861752	1.4329399	0.4203430
H	2.6122383	-0.1567621	-0.8691377
C	-0.9522484	2.7698670	0.1603163
C	0.7285525	2.4733271	-1.6882143
H	-1.2242298	1.8534562	-1.6519585
H	-0.3419098	3.2736391	2.1636755
H	0.9594942	3.3824817	0.9834590
H	2.3937631	1.9250204	2.5083982
H	2.1643248	0.2078863	2.1252515
H	1.3769147	0.6483200	-2.6507370
H	2.6872071	1.7973261	-2.3154362
H	3.7355383	1.1252360	0.4958422
H	2.6813058	2.4890431	0.1300801
H	-1.8910853	2.3264511	0.5192506
H	-1.1751881	3.7911362	-0.1818765
H	0.4194327	2.9008406	-2.6483211
H	1.1534213	3.2915957	-1.0971860

49

[Fe(tacn)2]3+ BP-D3/def2TZVP COSMO methanol, doublet

Fe	-0.0000000	0.0000000	0.0003120
N	0.1273411	-1.4938118	1.3443395
N	-1.9724126	-0.3937943	0.0359830
N	0.0539268	-1.4557482	-1.3882459
C	0.3738784	-2.8026275	0.6332019
C	0.8818479	-2.5434144	-0.7748507
C	-1.3354192	-1.9168392	-1.7552273
C	-2.3444512	-0.8673822	-1.3315483
C	-1.1565235	-1.4720950	2.1100818
C	-2.3044994	-1.3885312	1.1200308
H	1.0913239	-3.4034705	1.2017165
H	-2.3274088	0.0003166	-2.0018828
H	-3.3665421	-1.2709981	-1.3430770
H	-2.5077037	0.4592874	0.2274793
H	1.9271238	-2.2118133	-0.7727454
H	-0.5686771	-3.3595561	0.6094182
H	-3.2335155	-1.0957642	1.6216588
H	-1.3895540	-2.1070837	-2.8321704
H	0.8949454	-1.3485037	2.0086440
H	-2.4819666	-2.3603250	0.6469662
H	0.8326378	-3.4559698	-1.3850346
H	0.5224909	-1.1493267	-2.2472667
H	-1.2456372	-2.3649787	2.7445412
H	-1.5260749	-2.8683878	-1.2476170
H	-1.1312544	-0.6003036	2.7754494
N	-0.1273411	1.4938118	1.3443395
N	1.9724126	0.3937943	0.0359830
N	-0.0539268	1.4557482	-1.3882459
C	-0.3738784	2.8026275	0.6332019
C	1.1565235	1.4720950	2.1100818
H	-0.8949454	1.3485037	2.0086440
C	2.3444512	0.8673822	-1.3315483
C	2.3044994	1.3885312	1.1200308
H	2.5077037	-0.4592874	0.2274793
C	-0.8818479	2.5434144	-0.7748507
C	1.3354192	1.9168392	-1.7552273
H	-0.5224909	1.1493267	-2.2472667
H	-1.0913239	3.4034705	1.2017165
H	0.5686771	3.3595561	0.6094182
H	1.2456372	2.3649787	2.7445412
H	1.1312544	0.6003036	2.7754494
H	2.3274088	-0.0003166	-2.0018828
H	3.3665421	1.2709981	-1.3430770
H	3.2335155	1.0957642	1.6216588
H	2.4819666	2.3603250	0.6469662
H	-1.9271238	2.2118133	-0.7727454
H	-0.8326378	3.4559698	-1.3850346
H	1.3895540	2.1070837	-2.8321704
H	1.5260749	2.8683878	-1.2476170

4.5 $[Co(en)_3]^{3+}$

```
37
[Co(en)3]3+ singlet, PBE0-D3(BJ)/def2-TZVP in vacuum
Co   -0.0000000    0.0000000    0.0000000
C     2.7683108    0.0791472   -0.7472552
C     2.7683108   -0.0791472    0.7472552
H     1.5813038    1.7377300   -1.0024991
H     3.6186704    0.6706982   -1.0933173
H     1.3354840    0.6165095   -2.1240514
H     2.8240196   -0.8882957   -1.2514732
H     1.5813038   -1.7377300    1.0024991
H     2.8240196    0.8882957    1.2514732
H     1.3354840   -0.6165095    2.1240514
H     3.6186704   -0.6706982    1.0933173
N     1.4777780    0.7306557   -1.1211866
N     1.4777780   -0.7306557    1.1211866
N    -1.3716554    0.9144655   -1.1211866
N    -0.1061226   -1.6451211   -1.1211866
N    -0.1061226    1.6451211    1.1211866
N    -1.3716554   -0.9144655    1.1211866
C    -1.4526989    2.3578539   -0.7472552
H    -2.2955702    0.5005843   -1.0024991
H    -1.2016548    0.8483083   -2.1240514
C    -1.3156119   -2.4370011   -0.7472552
H     0.7142664   -2.2383143   -1.0024991
H    -0.1338291   -1.4648178   -2.1240514
C    -1.3156119    2.4370011    0.7472552
H     0.7142664    2.2383143    1.0024991
H    -0.1338291    1.4648178    2.1240514
C    -1.4526989   -2.3578539    0.7472552
H    -2.2955702   -0.5005843    1.0024991
H    -1.2016548   -0.8483083    2.1240514
H    -2.3901768    2.7985114   -1.0933173
H    -0.6427231    2.8898206   -1.2514732
H    -1.2284935   -3.4692096   -1.0933173
H    -2.1812965   -2.0015248   -1.2514732
H    -2.1812965    2.0015248    1.2514732
H    -1.2284935    3.4692096    1.0933173
H    -0.6427231   -2.8898206    1.2514732
H    -2.3901768   -2.7985114    1.0933173
```

```
37
[Co(en)3]3+ singlet, PBE0-D3(BJ)/def2-TZVP COSMO
Co    0.0000000    0.0000000    0.0000000
C     2.7147372    0.0609051   -0.7481082
C     2.7147372   -0.0609051    0.7481082
H     1.5570644    1.7232406   -1.0199120
H     3.5681428    0.6335522   -1.1101085
H     1.2724169    0.5808242   -2.1154442
H     2.7412655   -0.9228818   -1.2167971
H     1.5570644   -1.7232406    1.0199120
H     2.7412655    0.9228818    1.2167971
H     1.2724169   -0.5808242    2.1154442
H     3.5681428   -0.6335522    1.1101085
N     1.4436769    0.7183876   -1.1232060
N     1.4436769   -0.7183876    1.1232060
N    -1.3439804    0.8910671   -1.1232060
N    -0.0996965   -1.6094547   -1.1232060
N    -0.0996965    1.6094547    1.1232060
N    -1.3439804   -0.8910671    1.1232060
C    -1.4101140    2.3205788   -0.7481082
H    -2.2709023    0.4868371   -1.0199120
H    -1.1392169    0.8115333   -2.1154442
C    -1.3046232   -2.3814840   -0.7481082
H     0.7138379   -2.2100776   -1.0199120
H    -0.1332000   -1.3923575   -2.1154442
C    -1.3046232    2.3814840    0.7481082
H     0.7138379    2.2100776    1.0199120
H    -0.1332000    1.3923575    2.1154442
C    -1.4101140   -2.3205788    0.7481082
H    -2.2709023   -0.4868371    1.0199120
H    -1.1392169   -0.8115333    2.1154442
H    -2.3327437    2.7733263   -1.1101085
H    -0.5713936    2.8354464   -1.2167971
H    -1.2353992   -3.4068784   -1.1101085
H    -2.1698718   -1.9125646   -1.2167971
H    -2.1698718    1.9125646    1.2167971
H    -1.2353992    3.4068784    1.1101085
H    -0.5713936   -2.8354464    1.2167971
H    -2.3327437   -2.7733263    1.1101085
```

4.6 $[Co(en)_3]^{3+}$ and $\{[Co(en)_3]Cl_9\}^{3-}$ from crystal structure

```
37
[Co(en)3]3+ from IRIRAC01, X-H distances scaled by 1.1
    Co      0.0000000000000      0.0000000000000      0.0000000000000
     N     -1.5261512000000     -0.5368425000000     -1.1202023000000
     N      1.2279948000000     -1.0532645000000     -1.1202023000000
     N      0.2981564000000      1.5901069000000     -1.1202023000000
     N     -1.3306897000000      0.9130083000000      1.1206673000000
     N     -0.1253436000000     -1.6089152000000      1.1206673000000
     N      1.4560333000000      0.6959069000000      1.1206673000000
     C     -2.7026435000000      0.2746011000000     -0.7541373000000
     C     -2.6914742000000      0.4487122000000      0.7488680000000
     C      1.1135102000000     -2.4778584000000     -0.7541373000000
     C      0.9571410000000     -2.5552411000000      0.7488680000000
     C      1.5891333000000      2.2032573000000     -0.7541373000000
     C      1.7343332000000      2.1065290000000      0.7488680000000
     H     -3.6179618600000     -0.2254845300000     -1.0671369100000
     H     -2.6565703300000      1.2458077100000     -1.2444350200000
     H     -3.4368342000000      1.1828804700000      1.0499339300000
     H     -2.9167203200000     -0.4958941000000      1.2408705000000
     H     -1.7278488500000     -1.5186891900000     -0.9793866800000
     H      2.0042563200000     -3.0205045700000     -1.0671369100000
     H      0.2493840800000     -2.9235612400000     -1.2444350200000
     H      0.6940125300000     -3.5678259700000      1.0499339300000
     H      1.8878171200000     -2.2780068900000      1.2408705000000
     H     -1.3019289600000     -0.3967474900000     -2.0977291800000
     H      0.9945578600000     -0.9291297200000     -2.0977291800000
     H      0.3073709900000      1.3258773300000     -2.0977291800000
     H      2.1791478600000     -0.7370164800000     -0.9793866800000
     H     -1.1545881700000      0.7096638400000      2.0970007900000
     H     -0.0372927800000     -1.3547345700000      2.0970007900000
     H      1.1918809500000      0.6450707300000      2.0970007900000
     H     -1.2620919400000      1.9137708100000      0.9888869700000
     H     -1.0263281900000     -2.0498891400000      0.9888869700000
     H      2.2884201300000      0.1361183300000      0.9888869700000
     H      1.6137055400000      3.2459892100000     -1.0671369100000
     H      2.4071862500000      1.6777536400000     -1.2444350200000
     H      2.7428216700000      2.3849454900000      1.0499339300000
     H      1.0289033100000      2.7739009800000      1.2408705000000
     H     -0.4512989000000      2.2557055700000     -0.9793866800000

additional Cl ions for {[Co(en)3]Cl9}6- cluster
    Cl     -1.7824855728873     -1.3228146079995      3.8931227200000
    Cl     -2.8482166079891     -3.1687149079995      0.1791580360000
    Cl     -1.7824855728873      1.3228146080005     -3.8559272800000
    Cl      2.0368338414679     -0.8822704839995      3.8931227200000
    Cl      4.1682959116715     -0.8822704839995      0.1791580360000
    Cl     -0.2543482685815     -2.2050850919995     -3.8559272800000
    Cl     -0.2543482685815      2.2050850920005      3.8931227200000
    Cl     -1.3200793036833      4.0509853920005      0.1791580360000
    Cl      2.0368338414679      0.8822704840005     -3.8559272800000
```

5 Optimized crystal structures

5.1 $[Fe(1\text{-}bpp)_2](BF_4)_2$

```
! [Fe(1-bpp)2](BF4)2, singl state

CELL_PARAMETERS (alat= 15.98239649)
   1.004907447   0.000000000  -0.007569165
   0.000000000   1.011416423   0.000000000
  -0.330927204   0.000000000   2.133066800

ATOMIC_POSITIONS (angstrom)
Fe            4.0597890660        7.1839193763       13.4286821316
Fe            1.6404098841        2.9068820645        4.5477961130
N             4.2808720816        7.3541189920       11.5684057752
N             1.4193268685        3.0770816802        6.4080724694
C             3.2911827964        7.8727106460       10.8177838684
C             2.4090161538        3.5956733342        7.1586943762
C             3.3989823667        8.0015498052        9.4420371792
C             2.3012165835        3.7245124935        8.5344410654
H             2.5823860809        8.4268022414        8.8598644975
H             3.1178128692        4.1497649296        9.1166137472
C             4.5865943409        7.5671927078        8.8517976323
C             1.1136046018        3.2901553960        9.1246816034
H             4.7139051401        7.6546841663        7.7704314464
H             0.9862928052        3.3776468546       10.2060468058
C             5.6201753545        7.0173643535        9.6127235233
C             0.0800235882        2.7403270417        8.3637557124
H             6.5419926072        6.6653106286        9.1491349775
H            -0.8417946619        2.3882733168        8.8273432747
C             5.4140052522        6.9224106525       10.9813176851
C             0.2861926931        2.6453733408        6.9951605671
N             2.2060835067        8.2275816457       11.6187030424
N             3.4941154360        3.9505443339        6.3577761933
N             2.3417486618        7.9835324020       12.9733473958
N             3.3584502884        3.7064950903        5.0031308489
C             1.1963228324        8.3898724028       13.5340487195
C             4.5038761178        4.1128350910        4.4424295251
H             1.0349715922        8.2760943837       14.6070406797
H             4.6652273505        3.9990570719        3.3694385559
C             0.3265149903        0.3482528555       12.5457509013
C             5.3736839524        4.6252901672        5.4307283343
H            -0.6701123008        0.7535531133       12.6912818644
H             6.3703112510        5.0305904250        5.2851963803
C             0.9904608063        0.2267728776       11.3406461050
C             4.7097371315        4.5038101894        6.6358331383
H             0.6938524346        0.4512753652       10.3182743275
H             5.0063455032        4.7283126770        7.6582049157
N             6.2765478867        6.3816503132       11.9332424047
N            -0.5763489366        2.1046130015        6.0432358399
N             5.8393669311        6.4359315767       13.2420412329
N            -0.1391679809        2.1588942649        4.7344370118
C            -1.7060007792        5.8490101257       14.0331405837
C             7.4061997219        1.5719728140        3.9433386520
H            -1.8000897311        5.7983571221       15.1158313041
H             7.5002886813        1.5213198104        2.8606469406
C            -0.6602048145        5.4010102877       13.1990773063
C             6.3604037647        1.1239729759        4.7774009384
H             0.2451574440        4.8915197299       13.5158605551
H             5.4550415061        0.6144824182        4.4606176895
C            -1.0138266764        5.7518978483       11.9112847313
C             6.7140246142        1.4748605365        6.0651945120
H            -0.5102217234        5.6424080178       10.9527723391
H             6.2104206736        1.3653707061        7.0237059055
N             3.8155596224        6.9700659281       15.2822034800
N             1.8846383154        2.6930286164        2.6942757632
C             4.1764051870        7.9491870159       16.1315512589
C             1.5237937556        3.6721497041        1.8449279768
C             4.0225761701        7.8300076172       17.5046927530
C             1.6776227726        3.5529703054        0.4717864826
H             7.1106846393        8.6395956374        0.1327884871
H            -1.4104856891        4.3625583256       17.8436897575
C             3.4711989854        6.6408267745       17.9833165371
C             2.2289989598        2.3637894628       -0.0068382849
H             6.1118813463        6.5088045766        1.0148856650
H            -0.4116834010        2.2317672648       16.9615925872
C             3.1027880691        5.6090041801       17.1182441760
C             2.5974108811        1.3319668683        0.8582340686
H             2.6604871191        4.6875734091       17.4939372443
H             3.0397118236        0.4105360974        0.4825419913
C             3.2897124872        5.8266736435       15.7626279050
C             2.4104864630        1.5496363317        2.2138503397
N             4.7109486110        0.4744612616       15.4284055646
N             0.9892503392        4.7514985734        2.5480726800
N             4.7841647324        0.3312414579       14.0548448065
N             0.9160342178        4.6082787696        3.9216334381
C             5.3871997172        1.4369817321       13.6078546567
C             0.3129992330        5.7140190439        4.3686235880
H             5.5443055466        1.5848228984       12.5406780988
H             0.1558923986        5.8618602102        5.4358001534
C             5.7037108707        2.2917651919       14.6857074916
C            -0.0035119205        6.5688025036        3.2907707530
H             6.1880057887        3.2621727858       14.6226316835
H            -0.4878068385        7.5392100976        3.3538465611
C             5.2567028654        1.6579911504       15.8287258218
C             0.4434950724        5.9350284622        2.1477534215
H             5.2516012591        1.9500526688       16.8778225768
H             0.4485976911        6.2270899806        1.0986556678
N             2.9887929535        4.9533634761       14.7160245054
N             2.7114059967        0.6763261643        3.2604537392
N             3.3057637429        5.3988087057       13.4485393742
N             2.3944352073        1.1217713939        4.5279388705
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C	2.9982689833	4.3939161531	12.6220904505
C	2.7019299669	0.1168788413	5.3543877941
H	3.2015880376	4.4805970027	11.5577296887
H	2.4986109051	0.2035596909	6.4187495469
C	2.4657161754	3.3089130683	13.3477595723
C	3.2344827672	7.5859503801	4.6287196633
H	2.1340256663	2.3584106835	12.9422349762
H	3.5661732839	6.6354479953	5.0342432684
C	2.4738023893	3.6886714442	14.6769864006
C	3.2263965609	7.9657087560	3.2994918440
H	2.1946440290	3.1719292688	15.5939813306
H	3.5055549211	7.4489665806	2.3824969140
B	5.2173370854	2.6150088938	10.0247899602
B	0.4828618573	6.8920462056	7.9516892754
F	4.0897328635	2.1636448104	10.7474045257
F	1.6104660867	6.4406821221	7.2290737190
F	5.1617001794	2.1365415098	8.6905632309
F	0.5384987633	6.4135788215	9.2859160048
F	5.2161829072	4.0364619582	10.0035938845
F	0.4840160430	8.3134992700	7.9728843601
F	6.4048748461	2.1466681739	10.6455794128
F	-0.7046769008	6.4237054857	7.3308988394
B	5.8666388844	2.3451162429	0.8644294190
B	-0.1664399417	6.6221535546	17.1120498167
F	2.5957495264	2.2603721370	17.5717301058
F	3.1044494162	6.5374094487	0.4047491299
F	5.4511152700	1.2165638526	1.6078990699
F	0.2490836727	5.4936011643	16.3685801658
F	7.2973403257	2.3650504022	0.8400671483
F	-1.5971413755	6.6420877139	17.1364110963
F	5.3904507396	3.5309323208	1.4676484369
F	0.3097482031	7.8079696326	16.5088307988

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! [Fe(1-bpp)2](BF4)2, quint state

CELL_PARAMETERS (alat= 15.98239649)
   1.010818890   0.000000000  -0.003940476
   0.000000000   0.995217455   0.000000000
  -0.325474585   0.000000000   2.191423076

ATOMIC_POSITIONS (angstrom)
Fe            4.3663536555        7.1737256363       13.8124515757
Fe            1.4299572010        2.9651898727        4.6882668500
N             4.4620500649        7.1259050488       11.7115450472
N             1.3342607916        2.9173692852        6.7891733784
C             3.4339425584        7.5537616169       10.9678151722
C             2.3623682980        3.3452258533        7.5329032534
C             3.4785538252        7.6039527193        9.5797969454
C             2.3177570313        3.3954169557        8.9209214803
H             2.6247495805        7.9480253480        8.9962577837
H             3.1715612760        3.7394895844        9.5044606420
C             4.6648614239        7.1998237355        8.9689702315
C             1.1314494285        2.9912879719        9.5317492128
H             4.7470828936        7.2262648764        7.8794118348
H             1.0492269520        3.0177291128       10.6213065949
C             5.7509171848        6.7560459645        9.7234207761
C             0.0453936675        2.5475102009        8.7772986682
H             6.6822701926        6.4436865762        9.2495555845
H            -0.8859603470        2.2351508126        9.2511628451
C             5.5868953550        6.7261179153       11.1029223623
C             0.2094144907        2.5175821517        7.3977960673
N             2.3223556188        7.9290238808       11.7364575781
N             3.4739552336        3.7204881172        6.7642618663
N             2.4138397479        7.8358156760       13.0999760079
N             3.3824711086        3.6272799124        5.4007424178
C             1.2382094914        8.2742236417       13.5697090686
C             4.5581013650        4.0656878781        4.9310093571
H             1.0419703747        8.2628466964       14.6437759752
H             4.7543404777        4.0543109328        3.8569434692
C             0.3960981735        0.2549194064       12.5092080873
C             5.4002126788        4.4634551700        5.9915113571
H            -0.6102906046        0.6599812078       12.5645633820
H             6.4066014610        4.8685169714        5.9361550437
C             1.1126241590        0.0115325427       11.3529342234
C             4.6836856825        4.2200683063        7.1477852249
H             0.8521894534        0.1202083617       10.3022142369
H             4.9441203882        4.3287441253        8.1985052115
N             6.5532292441        6.2564361709       12.0047856292
N            -0.7569183877        2.0479004073        6.4959327965
N             6.3253943467        6.4462384026       13.3425787139
N            -0.5290834902        2.2377026390        5.1581397118
C            -1.2350457650        5.8014927034       14.0034520584
C             7.0313566174        1.5929569398        4.4972673860
H            -1.1738795529        5.8234092048       15.0892142086
H             6.9701904094        1.6148734412        3.4115042171
C            -0.3725786290        5.1859789012       13.0754775512
C             6.1688894854        0.9774431376        5.4252408745
H             0.5153948775        4.5990229659       13.2949209373
H             5.2809159790        0.3904872023        5.2057974884
C            -0.8831177357        5.4952410080       11.8296143339
C             6.6794275773        1.2867052444        6.6711051144
H            -0.5439952659        5.2580821151       10.8244440439
H             6.3403061223        1.0495463515        7.6762743818
N             3.9490487968        6.9895118338       15.8649618858
N             1.8472610447        2.7809760702        2.6357575625
C             4.2828475896        7.9689250904       16.7154224659
C             1.5134632627        3.7603893268        1.7852969785
C             4.0671661744        7.8861777789       18.0850847938
C             1.7291446780        3.6776420153        0.4156346506
H             7.0911360781        8.7027099805        0.2194225407
H            -1.2948252217        4.4941742169       18.2812958850
C             3.4839368612        6.7148239913       18.5659205512
C             2.3123729844        2.5062882277       -0.0652021216
H             6.0377064442        6.6032882580        1.0995601513
H            -0.2413965985        2.3947524944       17.4011582783
C             3.1589058375        5.6684691202       17.7047202491
C             2.6374050190        1.4599333566        0.7959981766
H             2.7141984691        4.7475268475       18.0789598798
H             3.0821123833        0.5389910839        0.4217595646
C             3.4128314809        5.8618113744       16.3538138983
C             2.3834793756        1.6532756108        2.1469045274
N             4.8796374255        0.6506920741       16.0755484766
N             0.9166734309        4.8592278377        2.4251699491
N             5.1076161479        0.5694303806       14.7262364460
N             0.6886947086        4.7779661442        3.7744819797
C             5.7214943482        1.7132902442       14.3967308749
C             0.0748165083        5.9218260078        4.1039875508
H             5.9969382608        1.9016748873       13.3593972747
H            -0.2006284152        6.1102106509        5.1413211549
C             5.8946166967        2.5287899391       15.5321359662
C            -0.0983058402        6.7373257027        2.9685824594
H             6.3556496387        3.5123099723       15.5735404060
H            -0.5593387822        7.7208457359        2.9271780197
C             5.3454600856        1.8240615029       16.5879230402
C             0.4508497559        6.0325972665        1.9127964081
H             5.2297092999        2.0700689423       17.6424569552
H             0.5666015566        6.2786047059        0.8582614705
N             3.1560469955        4.9047437623       15.3580083021
N             2.6402638609        0.6962079987        3.1427101236
N             3.5602068555        5.1870740063       14.0823287078
N             2.2361040010        0.9785382427        4.4183897179
C             3.2400584285        4.1126986162       13.3543557757
C             2.5562524280       -0.0958371474        5.1463626500
H             3.4941464851        4.0774086038       12.2965571138
H             2.3021643673       -0.1311271598        6.2041623306
C             2.6186541032        3.1364933345       14.1583523033
C             3.1776567492        7.3450290981        4.3423671411
H             2.2674389447        2.1574787369       13.8474567508
H             3.5288719118        6.3660145005        4.6532616749
C             2.5780620479        3.6710677604       15.4331695133
C             3.2182488086        7.8796035240        3.0675489124
H             2.2196003633        3.2739927873       16.3801566100
H             3.5767104932        7.4825285509        2.1205618157
B             5.2814841740        2.4303114463       10.6562362500
B             0.5148266783        6.6388472099        7.8444831944
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F	4.2157779608	1.8845641815	11.3994805267	B	-0.1222128962	6.7194333646	17.3201791885
F	1.5805328956	6.0930999451	7.1012378990	F	2.7361568095	2.4880781601	18.3635550930
F	5.2902837803	1.8950306924	9.3452352410	F	3.0601540429	6.6966139237	0.1371643513
F	0.5060270720	6.1035664560	9.1554842033	F	5.4455090671	1.3561253276	1.8518625222
F	5.1130763165	3.8428871319	10.5696557763	F	0.3508017853	5.5646610912	16.6488569221
F	0.6832345400	8.0514228955	7.9310626493	F	7.3457631835	2.4881772000	1.2081959273
F	6.5185587930	2.1405812592	11.2892313148	F	-1.5494523270	6.6967129636	17.2925224984
F	-0.7222489474	6.3491170228	7.2114871149	F	5.4455677221	3.6782890232	1.8177593862
B	5.9185237485	2.5108976010	1.1805402559	F	0.3507431302	7.8868247868	16.6829600582

5.2 $[Fe(1\text{-}bpp)_2](PF_6)_2$

```
! [Fe(1-bpp)2](PF6)2], singl state

CELL_PARAMETERS (alat= 26.92443988)
   0.558498136  -0.321820502   0.024209965
   0.558498136   0.321820502   0.024209965
  -0.189971375  -0.000000000   1.378017308

ATOMIC_POSITIONS (crystal)
Fe            0.2255903489        0.7744096511        0.2500000000
Fe            0.7744096511        0.2255903489        0.7500000000
P             0.2165311208        0.2254270292        0.4215952741
P             0.7745729708        0.7834688792        0.0784047259
P             0.7834688792        0.7745729708        0.5784047259
P             0.2254270292        0.2165311208        0.9215952741
F             0.2915037987        0.1161712217        0.3504698864
F             0.8838287783        0.7084962013        0.1495301136
F             0.7084962013        0.8838287783        0.6495301136
F             0.1161712217        0.2915037987        0.8504698864
F             0.1441467321        0.3328711012        0.4928035709
F             0.6671288988        0.8558532679        0.0071964291
F             0.8558532679        0.6671288988        0.5071964291
F             0.3328711012        0.1441467321        0.9928035709
F             0.3638791950        0.2786787264        0.4254028476
F             0.7213212736        0.6361208050        0.0745971524
F             0.6361208050        0.7213212736        0.5745971524
F             0.2786787264        0.3638791950        0.9254028476
F             0.3394358697        0.0582923043        0.4640759073
F             0.9417076957        0.6605641303        0.0359240927
F             0.6605641303        0.9417076957        0.5359240927
F             0.0582923043        0.3394358697        0.9640759073
F             0.0673554149        0.1742894765        0.4154358193
F             0.8257105235        0.9326445851        0.0845641807
F             0.9326445851        0.8257105235        0.5845641807
F             0.1742894765        0.0673554149        0.9154358193
F             0.0911425369        0.3938305939        0.3787532028
F             0.6061694061        0.9088574631        0.1212467972
F             0.9088574631        0.6061694061        0.6212467972
F             0.3938305939        0.0911425369        0.8787532028
N             0.2487540076        0.7667140924        0.3498979078
N             0.2332859076        0.7512459924        0.1501020922
N             0.7512459924        0.2332859076        0.6501020922
N             0.7667140924        0.2487540076        0.8498979078
N             0.9660702658        0.8631945544        0.3545312360
N             0.1368054456        0.0339297342        0.1454687640
N             0.0339297342        0.1368054456        0.6454687640
N             0.8631945544        0.9660702658        0.8545312360
N             0.9576388153        0.8769135029        0.2856464045
N             0.1230864971        0.0423611847        0.2143535955
N             0.0423611847        0.1230864971        0.7143535955
N             0.8769135029        0.9576388153        0.7856464045
N             0.5219614039        0.6842179621        0.3326433497
N             0.3157820379        0.4780385961        0.1673566503
N             0.4780385961        0.3157820379        0.6673566503
N             0.6842179621        0.5219614039        0.8326433497
N             0.4661893434        0.7125380701        0.2658281861
N             0.2874619299        0.5338106566        0.2341718139
N             0.5338106566        0.2874619299        0.7341718139
N             0.7125380701        0.4661893434        0.7658281861
C             0.1226433601        0.7985477191        0.3893024254
C             0.2014522809        0.8773566399        0.1106975746
C             0.8773566399        0.2014522809        0.6106975746
C             0.7985477191        0.1226433601        0.8893024254
C             0.1467634633        0.7728643478        0.4585191376
C             0.2271356522        0.8532365367        0.0414808624
C             0.8532365367        0.2271356522        0.5414808624
C             0.7728643478        0.1467634633        0.9585191376
C             0.3081684426        0.7165392339        0.4874171672
C             0.2834607661        0.6918315574        0.0125828328
C             0.6918315574        0.2834607661        0.5125828328
C             0.7165392339        0.3081684426        0.9874171672
C             0.4405251964        0.6853239693        0.4479536426
C             0.3146760307        0.5594748036        0.0520463574
C             0.5594748036        0.3146760307        0.5520463574
C             0.6853239693        0.4405251964        0.9479536426
C             0.4040805676        0.7113592054        0.3792563626
C             0.2886407946        0.5959194324        0.1207436374
C             0.5959194324        0.2886407946        0.6207436374
C             0.7113592054        0.4040805676        0.8792563626
C             0.7937525681       -0.0324130310        0.2685192325
C             1.0324130310        0.2062474319        0.2314807675
C             0.2062474319        1.0324130310        0.7314807675
C            -0.0324130310        0.7937525681        0.7685192325
C             0.6958565026        0.0119229709        0.3261002863
C             0.9880770291        0.3041434974        0.1738997137
C             0.3041434974        0.9880770291        0.6738997137
C             0.0119229709        0.6958565026        0.8261002863
C             0.8088785543        0.9433924500        0.3800864968
C             0.0566075500        0.1911214457        0.1199135032
C             0.1911214457        0.0566075500        0.6199135032
C             0.9433924500        0.8088785543        0.8800864968
C             0.6004556722        0.6809186846        0.2323639640
C             0.3190813154        0.3995443278        0.2676360360
C             0.3995443278        0.3190813154        0.7676360360
C             0.6809186846        0.6004556722        0.7323639640
C             0.7424147457        0.6325975075        0.2774772530
C             0.3674024925        0.2575852543        0.2225227470
C             0.2575852543        0.3674024925        0.7225227470
C             0.6325975075        0.7424147457        0.7774772530
C             0.6890371316        0.6356332636        0.3408037795
C             0.3643667364        0.3109628684        0.1591962205
C             0.3109628684        0.3643667364        0.6591962205
C             0.6356332636        0.6890371316        0.8408037795
H             0.0434156803        0.7955790184        0.4891273678
H             0.2044209816        0.9565843197        0.0108726322
H             0.9565843197        0.2044209816        0.5108726322
H             0.7955790184        0.0434156803        0.9891273678
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H	0.3313497170	0.6981211674	0.5418410191
H	0.3018788326	0.6686502830	0.9581589809
H	0.6686502830	0.3018788326	0.4581589809
H	0.6981211674	0.3313497170	0.0418410191
H	0.5659493476	0.6466578904	0.4706044777
H	0.3533421096	0.4340506524	0.0293955223
H	0.4340506524	0.3533421096	0.5293955223
H	0.6466578904	0.5659493476	0.9706044777
H	0.7530223417	-0.0057569738	0.2156666105
H	1.0057569738	0.2469776583	0.2843333895
H	0.2469776583	1.0057569738	0.7843333895
H	-0.0057569738	0.7530223417	0.7156666105
H	0.5599067540	0.0809719073	0.3288786095
H	0.9190280927	0.4400932460	0.1711213905
H	0.4400932460	0.9190280927	0.6711213905
H	0.0809719073	0.5599067540	0.8288786095
H	0.7894578922	0.9440582166	0.4335707372
H	0.0559417834	0.2105421078	0.0664292628
H	0.2105421078	0.0559417834	0.5664292628
H	0.9440582166	0.7894578922	0.9335707372
H	0.5898915101	0.6951962047	0.1779420035
H	0.3048037953	0.4101084899	0.3220579965
H	0.4101084899	0.3048037953	0.8220579965
H	0.6951962047	0.5898915101	0.6779420035
H	0.8675216142	0.6038605481	0.2654965897
H	0.3961394519	0.1324783858	0.2345034103
H	0.1324783858	0.3961394519	0.7345034103
H	0.6038605481	0.8675216142	0.7654965897
H	0.7554517351	0.6100016364	0.3902553671
H	0.3899983636	0.2445482649	0.1097446329
H	0.2445482649	0.3899983636	0.6097446329
H	0.6100016364	0.7554517351	0.8902553671

```
! [Fe(1-bpp)2](PF6)2], quint state

CELL_PARAMETERS (alat= 26.92443988)
   0.497922288  -0.335237770  -0.000645845
   0.497922288   0.335237770  -0.000645845
  -0.234581399   0.000000000   1.435197202

ATOMIC_POSITIONS (crystal)
Fe            0.1806940667        0.8193059333        0.2500000000
Fe            0.8193059333        0.1806940667        0.7500000000
P             0.1969190238        0.2520208079        0.4171259047
P             0.7479791921        0.8030809762        0.0828740953
P             0.8030809762        0.7479791921        0.5828740953
P             0.2520208079        0.1969190238        0.9171259047
F             0.2377702933        0.1401500923        0.3462206428
F             0.8598499077        0.7622297067        0.1537793572
F             0.7622297067        0.8598499077        0.6537793572
F             0.1401500923        0.2377702933        0.8462206428
F             0.1578902915        0.3631958396        0.4878791435
F             0.6368041604        0.8421097085        0.0121208565
F             0.8421097085        0.6368041604        0.5121208565
F             0.3631958396        0.1578902915        0.9878791435
F             0.3609753548        0.3070706797        0.4149414942
F             0.6929293203        0.6390246452        0.0850585058
F             0.6390246452        0.6929293203        0.5850585058
F             0.3070706797        0.3609753548        0.9149414942
F             0.3170303987        0.0859894374        0.4549860269
F             0.9140105626        0.6829696013        0.0450139731
F             0.6829696013        0.9140105626        0.5450139731
F             0.0859894374        0.3170303987        0.9549860269
F             0.0311509318        0.1990815758        0.4175686126
F             0.8009184242        0.9688490682        0.0824313874
F             0.9688490682        0.8009184242        0.5824313874
F             0.1990815758        0.0311509318        0.9175686126
F             0.0755747487        0.4193440849        0.3791126625
F             0.5806559151        0.9244252513        0.1208873375
F             0.9244252513        0.5806559151        0.6208873375
F             0.4193440849        0.0755747487        0.8791126625
N             0.2432826897        0.7774375730        0.3537185305
N             0.2225624270        0.7567173103        0.1462814695
N             0.7567173103        0.2225624270        0.6462814695
N             0.7774375730        0.2432826897        0.8537185305
N             0.9570480488        0.8818771395        0.3613887179
N             0.1181228605        0.0429519512        0.1386112821
N             0.0429519512        0.1181228605        0.6386112821
N             0.8818771395        0.9570480488        0.8613887179
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N             0.9146077037        0.9423588028        0.7976390420
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N             0.4785293413        0.3032582777        0.6656998666
N             0.6967417223        0.5214706587        0.8343001334
N             0.4610167543        0.7517786473        0.2737034135
N             0.2482213527        0.5389832457        0.2262965865
N             0.5389832457        0.2482213527        0.7262965865
N             0.7517786473        0.4610167543        0.7737034135
C             0.1200688624        0.8064631474        0.3922100277
C             0.1935368526        0.8799311376        0.1077899723
C             0.8799311376        0.1935368526        0.6077899723
C             0.8064631474        0.1200688624        0.8922100277
C             0.1515897382        0.7694056344        0.4570985541
C             0.2305943656        0.8484102618        0.0429014459
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C             0.7694056344        0.1515897382        0.9570985541
C             0.3204235939        0.7064607748        0.4823815144
C             0.2935392252        0.6795764061        0.0176184856
C             0.6795764061        0.2935392252        0.5176184856
C             0.7064607748        0.3204235939        0.9823815144
C             0.4509440192        0.6807335388        0.4438241724
C             0.3192664612        0.5490559808        0.0561758276
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C             0.8047686229        0.9540564996        0.3877144282
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H	0.7340654297	0.0481355225	0.2351306228	H	0.4161143367	0.2592960272	0.8090331181
H	0.9518644775	0.2659345703	0.2648693772	H	0.7407039728	0.5838856633	0.6909668819
H	0.2659345703	0.9518644775	0.7648693772	H	0.8769231892	0.5834275399	0.2681380963
H	0.0481355225	0.7340654297	0.7351306228	H	0.4165724601	0.1230768108	0.2318619037
H	0.5533168156	0.1066791797	0.3435819721	H	0.1230768108	0.4165724601	0.7318619037
H	0.8933208203	0.4466831844	0.1564180279	H	0.5834275399	0.8769231892	0.7681380963
H	0.4466831844	0.8933208203	0.6564180279	H	0.7659459649	0.5708921646	0.3849198460
H	0.1066791797	0.5533168156	0.8435819721	H	0.4291078354	0.2340540351	0.1150801540
H	0.7915713003	0.9419133308	0.4381271211	H	0.2340540351	0.4291078354	0.6150801540
H	0.0580866692	0.2084286997	0.0618728789	H	0.5708921646	0.7659459649	0.8849198460
H	0.2084286997	0.0580866692	0.5618728789				
H	0.9419133308	0.7915713003	0.9381271211				

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