Electronic Supporting Information

An aqueous non heme Fe(IV)oxo complex with a basic group in the second coordination sphere

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Syntheses

The synthesis of $[(tpenaH)_2Fe_2O](ClO_4)_4(H_2O)_2$ (**3**$(ClO_4)_4(H_2O)_2$) is reported[1]. *Perchlorate salts of metal complexes are potentially explosive and should be handled with caution in small quantities.*

$[V(O)(tpenaH)](ClO_4)_2\cdot 2H_2O$, (**4**$(ClO_4)_2\cdot 2H_2O$)

A mixture of tpenaH (84 mg, 0.22 mmol), $VOSO_4\cdot 2H_2O$ (55 mg, 0.3 mmol) and triethylamine (28 mg, 0.3 mmol) in water (15 ml) was heated under reflux for 30 minutes before $NaClO_4\cdot H_2O$ (36 mg, 0.3 mmol) was added. A small amount of a fine brown powder was filtered off and discarded. Overnight pale purple crystals of $[(V{=}O)(tpenaH)](ClO_4)_2\cdot 2H_2O$ (15 mg, 12%) were deposited. ESI MS (MeCN) *m/z*: 458.1 ($[VO(tpena)]^+$, 100%). *Anal. calcd. (%) for* $C_{22}H_{29}N_5O_{13}Cl_2V$; C: 38.09, H: 4.22, N: 10.10. *Found;* C: 38.09, H: 3.72 N: 10.09.

UV-Visible spectra of the aqueous solution containing $[Fe(O)(tpenaH)]^{2+}$ (**1**)

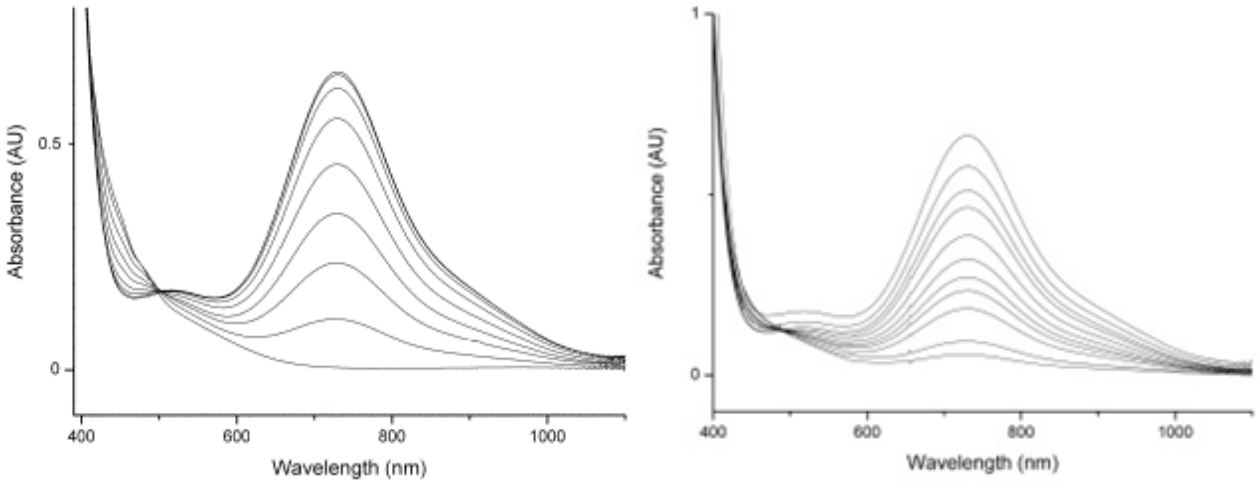

Figure S1. UV-Visible spectra of (left) the reaction between **3**$\cdot(ClO_4)_4(H_2O)_2$ [1.6 mM] and $(NH_4)_2[Ce(NO_3)_6]$ (CAN) added as a solid in water at ambient temperature to give **1**. The bottom

line shows the initial spectrum; the other spectra shows the increase in intensity at 730 nm on addition of eight consecutive equivalents of CAN added over 10 minutes and (right) the decay of **1** at ambient temperature recorded 2, 14, 23, 36, 46, 55, 62, 73, 92, 105 and 129 minutes after the addition of 7 eq. of CAN. UV-Vis spectra were recorded on an Agilent G1103A/8453 spectrophotometer.

Details and description of crystal structure of 1b

CIF file is submitted to the Cambridge Data Base and has been assigned deposit no. CCDC 879468. Diffraction data for $[V(O)(tpenaH)](ClO_4)_2 \cdot 2H_2O$ (**4**) were collected using a Bruker-Nonius X8 APEX-II instrument. Structures were solved using SIR-92[2] and refined using SHELXL-97.[3] All non-H atoms were refined anisotropically. A semi-empirical absorption correction was applied using the SADABS-program. Carbon bonded H-atoms were placed in calculated positions and refined using a riding model. The H-O distances in the co-crystallized water molecules were restrained using the DFIX command in SHELXL. The Flack parameter indicated racemic twinning, which was modelled using the TWIN and BASF commands in SHELXL, which indicated that 65% of the major enantiomorph was present in the crystal. Diagrams were drawn using ORTEP-3[4] for Windows. SIR-92, SHELXL, and ORTEP-3 operated under the WinGX program suit.[5]

Table S1. Crystal and refinement data for **4**.

Parameter	
Empirical formula	$C_{22}H_{29}Cl_2N_5O_{13}V$
M	693.34
T(K)	120(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	13.5030(8)
b/Å	14.0714(9)
c/Å	14.6794(9)
α/°	90
β/°	90
γ/°	90
V/Å^3	2789.2(3)
Z	4
D_c/g cm^{-3}	1.651
μ(Mo Kα)/mm^{-1}	0.623
Crystal size/mm^3	0.15 × 0.15 × 0.15
θ Range/°	3.55 to 26.00
Reflections collected	84571
Unique reflections; R_{int}	5451; 0.0540
No. of parameters	409
Final $R_1(F)^a (I > 2\sigma(I))$; $wR_2(F^2)^b$	0.0285; 0.0646

R_1[a]; $wR_2(F^2)$[b] (all data)	0.0348; 0.0679
Largest diff. peak and hole/eÅ^{-3}	0.533; -0.305
Flack parameter	0.351(18)

[a] $R_1(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{½}$

Table S2. Selected bond lengths [Å] and angles [°] for **4**.

O(1)-V(1)	1.9774(17)
O(3)-V(1)	1.5947(16)
V(1)-N(5)	2.115(2)
V(1)-N(4)	2.1190(19)
V(1)-N(2)	2.1770(19)
V(1)-N(1)	2.2661(19)
O(3)-V(1)-O(1)	105.42(8)
O(3)-V(1)-N(5)	104.40(8)
O(1)-V(1)-N(5)	84.56(7)
O(3)-V(1)-N(4)	93.94(8)
O(1)-V(1)-N(4)	159.87(7)
N(5)-V(1)-N(4)	96.10(7)
O(3)-V(1)-N(2)	101.97(8)
O(1)-V(1)-N(2)	80.72(7)
N(5)-V(1)-N(2)	152.40(7)
N(4)-V(1)-N(2)	90.05(7)
O(3)-V(1)-N(1)	169.95(8)
O(1)-V(1)-N(1)	84.46(7)
N(5)-V(1)-N(1)	74.23(7)
N(4)-V(1)-N(1)	76.43(7)
N(2)-V(1)-N(1)	81.18(7)

Electrospray Ionization Mass spectra of **3**$(ClO_4)_4 \cdot (H_2O)_2$

ESI MS were recorded on a Bruker micrOTOF-Q II mass spectrometer.

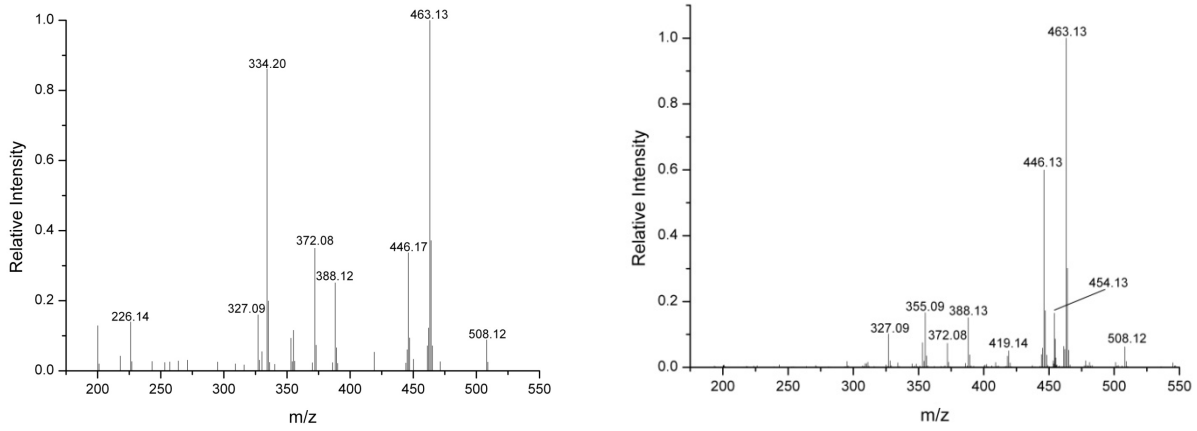

Figure S2. ESI Mass spectrum of **3**$(ClO_4)_4\cdot(H_2O)_2$ in H_2O (left) before and (right) after 21 hours the addition of 1 eq. of CAN. Assignments: 463.13, $[Fe^{III}(OH)(tpena)]^+$ (**5**); 454.13 $[Fe_2(tpena)_2O]^{2+}$ (**3**); 446.17 $[Fe^{II}(tpena)]^+$; 419.14 $[Fe^{III}(OH)(tpena\text{-}CO_2)]^+$; 388.12, $[Fe^{II}(tpena\text{-}CH_2CO_2)]^+$; 372.08, $[Fe^{III}(OH)(tpena\text{-}CH_2C_5H_4N+H)]^+$; 334.20, $\{(tpenaH\text{-}CH_2CO_2+H)\}^+$.

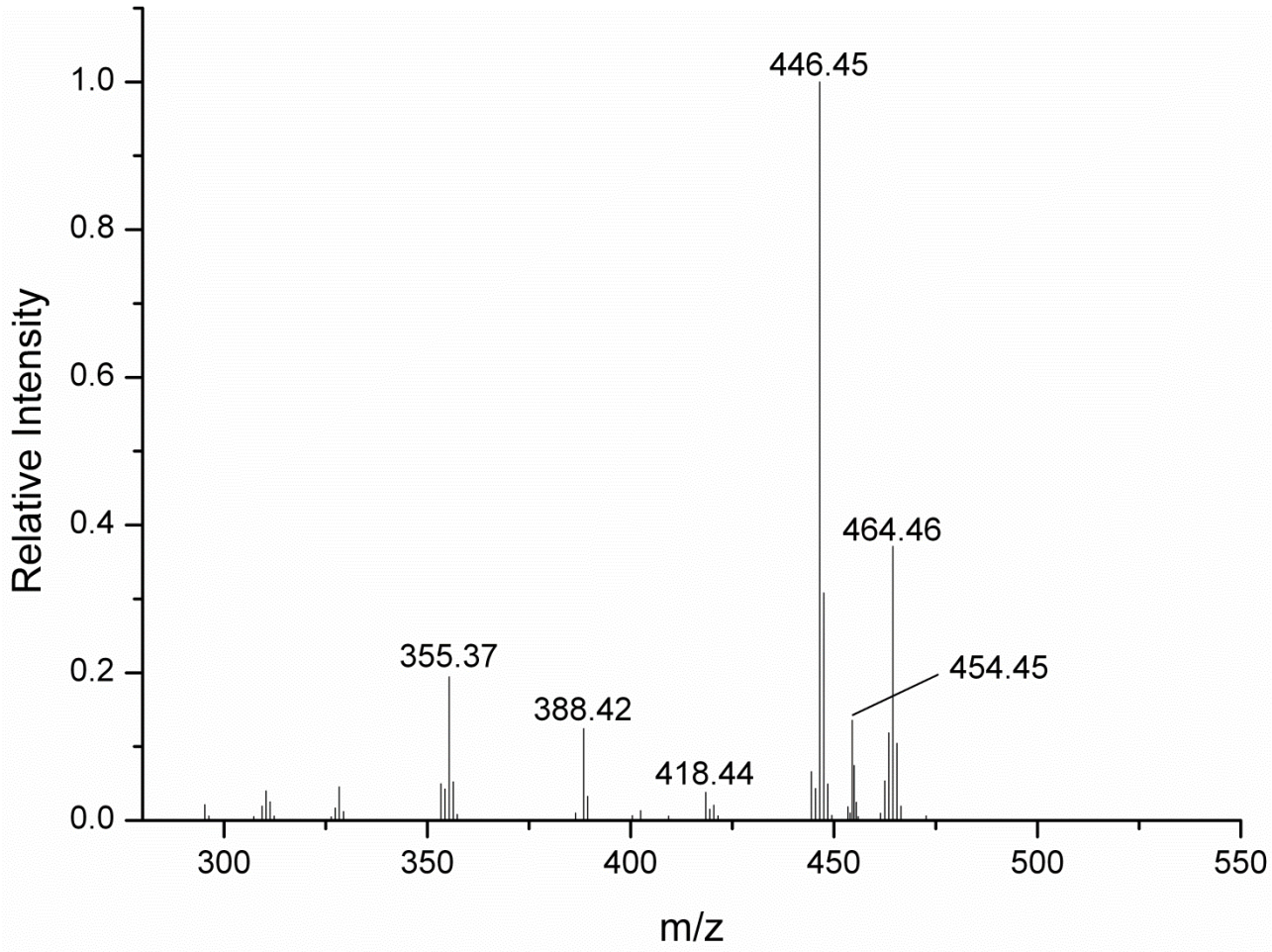

Figure S3. ESI Mass spectrum of **3**$(ClO_4)_4 \cdot (H_2O)_2$ in D_2O. Assignments: 464.46, $[Fe^{III}(OD)(tpena)]^+$ (**5**); 454.45 $[Fe_2(tpena)_2O]^{2+}$ (**3**); 446.45 $[Fe^{II}(tpena)]^+$; 388.42, $[Fe^{II}(tpena\text{-}CH_2CO_2)]^+$; 355.37, $[Fe^{II}(tpena\text{-}CH_2C_5H_4N{+}H)]^+$.

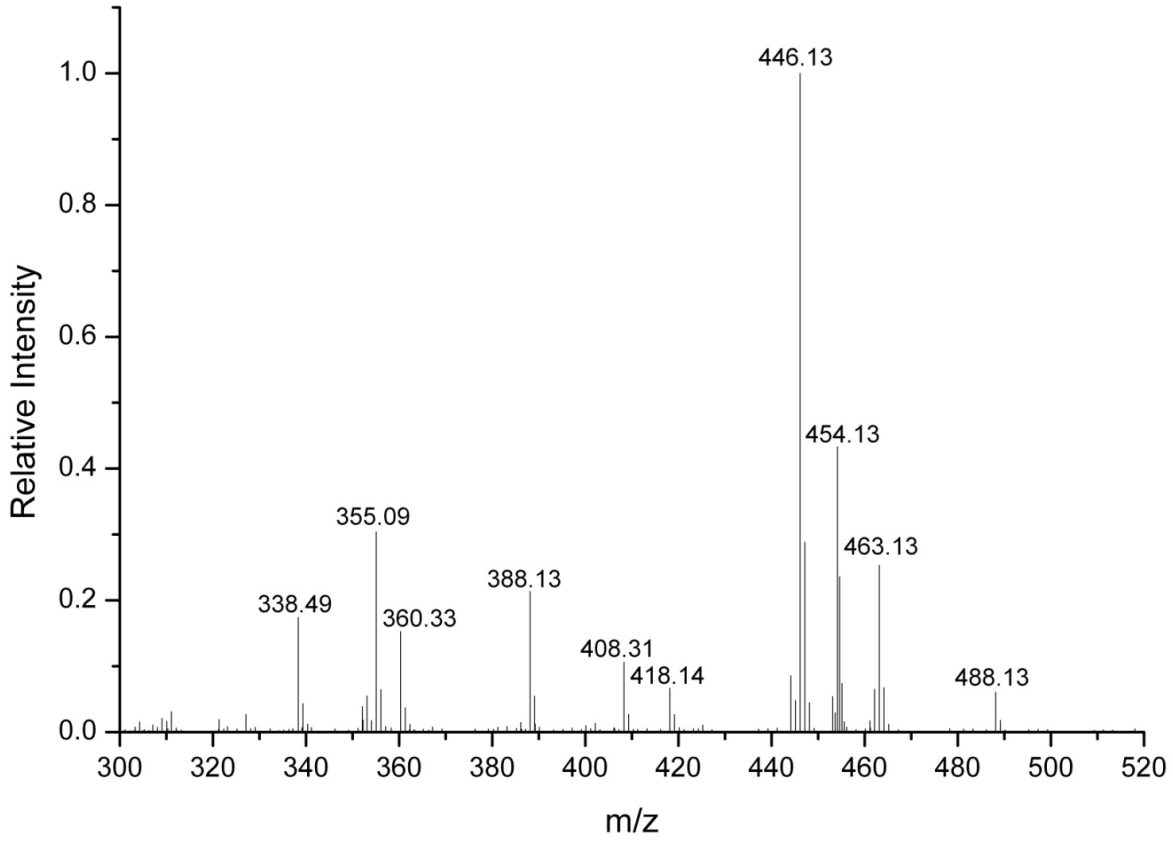

Figure S4. ESI Mass spectrum of **3**$(ClO_4)_4 \cdot (H_2O)_2$ in MeCN. Assignments: 463.13, $[Fe^{III}(OH)(tpena)]^+$ (**5**); 454.13, $[Fe_2(tpena)_2O]^{2+}$ (**3**-$2H^+$); 446.13, $[Fe^{II}(tpena)]^+$; 418.14, $[Fe^{II}(tpena\text{-}CO_2{+}O)]^+$; 388.12, $[Fe^{II}(tpena\text{-}CH_2CO_2)]^+$; 355.09, $[Fe^{II}(tpena\text{-}CH_2C_5H_4N{+}H)]^+$.

Mössbauer Spectroscopy

The Mössbauer spectra were obtained with conventional constant acceleration spectrometers with sources of ^{57}Co in rhodium. The spectrometers were calibrated using a 12.5 μm foil of α-Fe. Spectra were obtained at 22-27 K using a closed cycle helium refrigerator from APD Cryogenics. [^{57}Fe-**3**]$(ClO_4)_4(H_2O)_2$ was prepared from perchloric acid digestion of powdered ^{57}Fe purchased from Chemotrade. Sample solutions were injected into 4 mm thick plastic holders and frozen by immersion in liquid nitrogen.

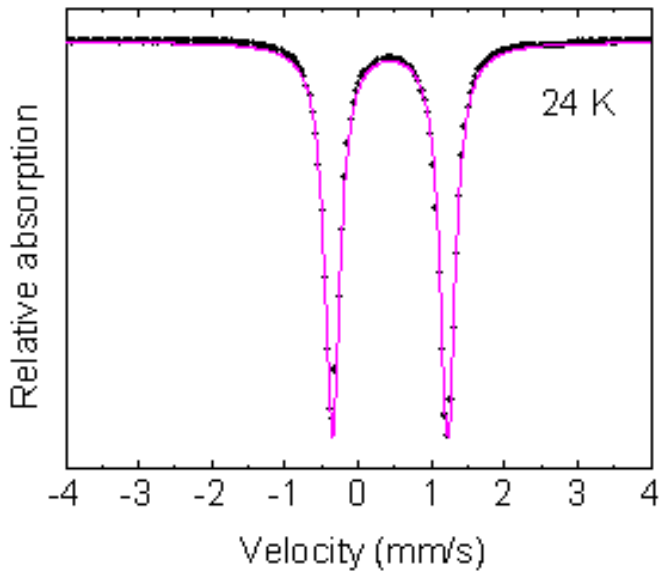

Figure S5 Mössbauer spectrum of solid state $[(tpenaH)_2Fe_2(\mu\text{-}O)](ClO_4)_4 \cdot 2H_2O$ (**3**$(ClO_4)_4 \cdot 2H_2O$) obtained at 24 K shows an isomer shift of δ=0.44 mm/s and a quadrupole splitting of ΔE_Q = 1.57 mm/s.

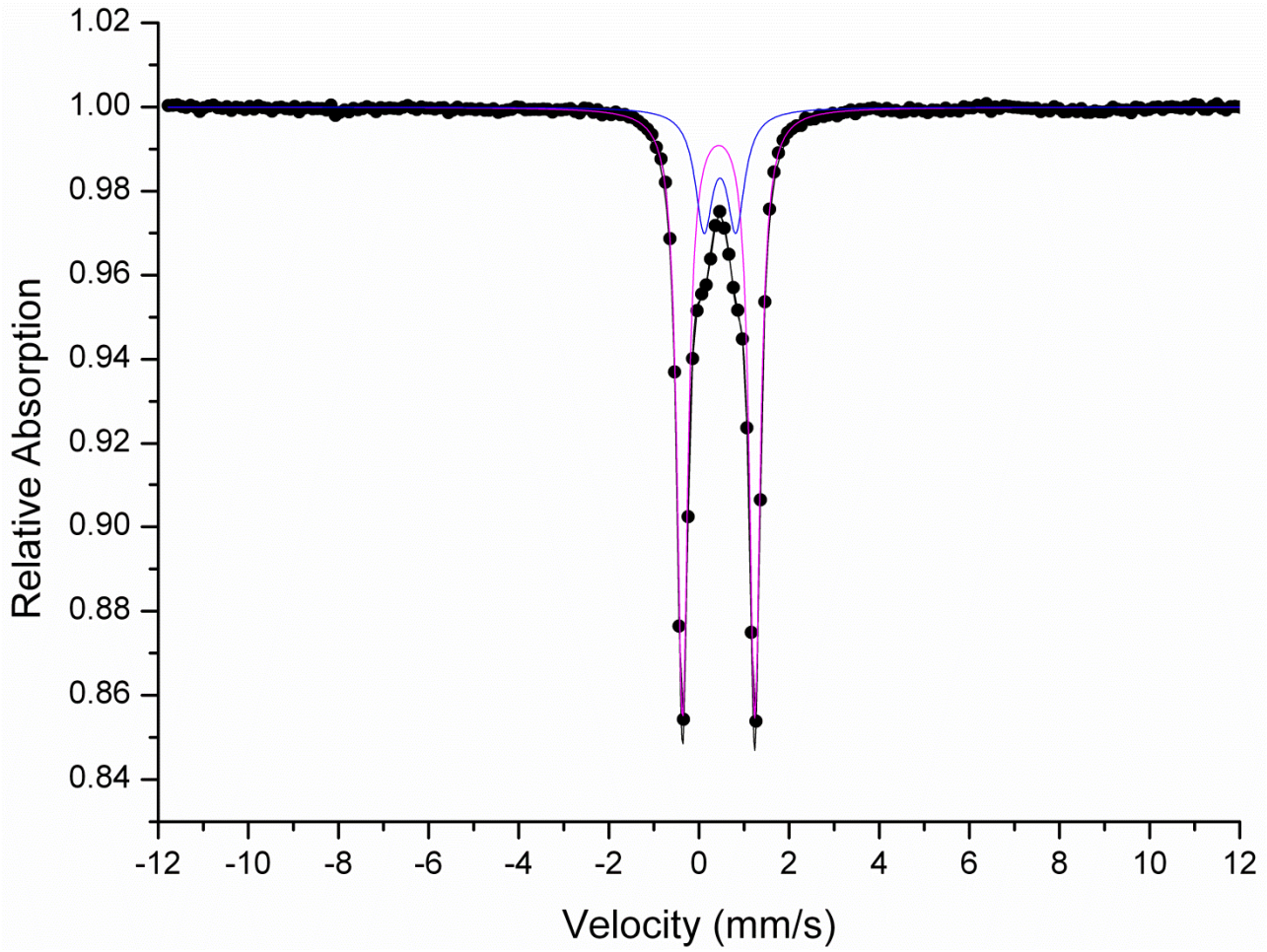

Figure S6 Mössbauer spectrum of aqueous solutions of ^{57}Fe labeled **3** at 50 K in water with 1 eq. of NaOH. [^{57}Fe-**3**](ClO$_4$)$_4$ (8.2 mg, 6.1 μmol) dissolved in 2.296 ml water was added 86.9 μl of 0.1405 M NaOH . The signal for ^{57}Fe-**3** (magenta) amounts to 76% of the total Fe content (δ=0.44 mm/s and a quadrupole splitting of ΔE_Q = 1.60 mm/s). The signal for ^{57}Fe-**5** (blue) account for 24% of the total Fe content (δ=0.46 mm/s and a quadrupole splitting of ΔE_Q = 0.71 mm/s).

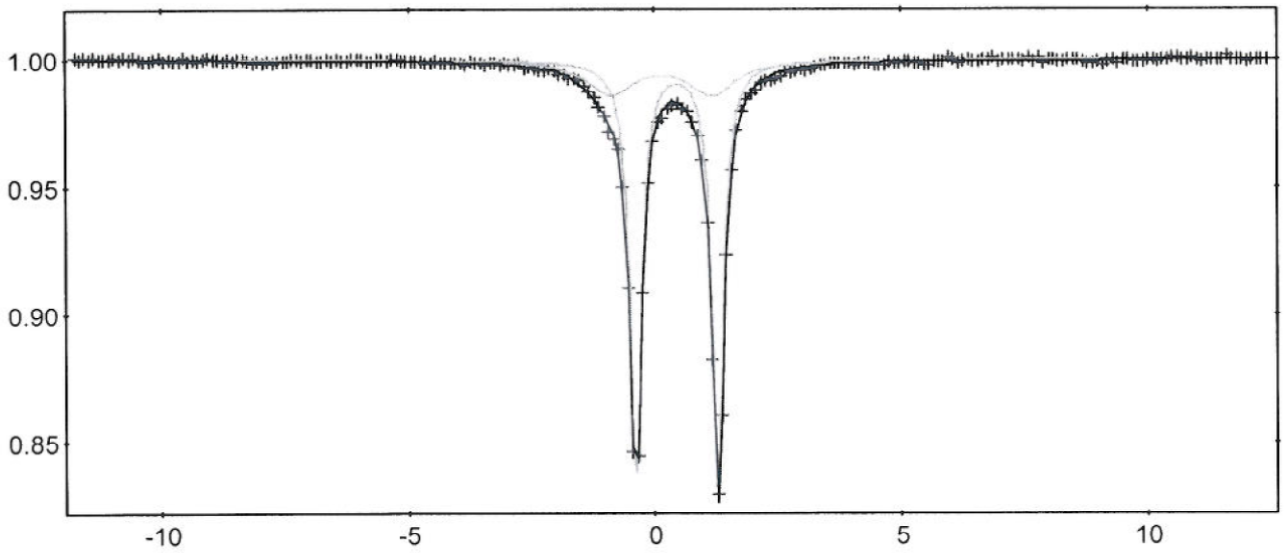

Figure S7. Mössbauer spectrum of aqueous solution of ^{57}Fe labeled **3** at T = 19 K. The spectrum of ^{57}Fe-**3** (3.6 mM) dissolved in water and frozen after approx. 30 second and stored at 70 K for 4 months and then thawed to room temperature and left for 30 min. and then frozen again. The absorption for ^{57}Fe-**3** (δ=0.45 mm/s and a quadrupole splitting of ΔE_Q = 1.67 mm/s) account for 75% of the total iron content and the absorption due to ^{57}Fe-**2** (δ=0.14 mm/s and a quadrupole splitting of ΔE_Q = 2.08 mm/s) account for 25% of the total iron content.

EPR spectroscopy

The EPR spectra (Figure 3a) were recorded at X-band with a Bruker EMX Plus CW spectrometer at T = 10 K with a conversion time of 48.04 ms, a time constant of 10.24 ms, a modulation amplitude of 5.0 Gauss and a microwave frequencies of 9.378571 GHz and 9.377329 GHz for the spectrum with and without base respectively.

ENDOR and HYSCORE spectroscopy

HYSCORE and ENDOR spectroscopy support that the low Fe(III) species (**2**) observed upon dissolution of **3**(ClO$_4$)$_4$·2H$_2$O in water is [Fe^{III}(OH)(tpenaH)]$^{2+}$ with a dangling pyridinium arm and not [Fe^{III}(tpena)]$^{2+}$ or [Fe^{III}(OH)(tpenaH)]$^{2+}$ with a dangling carboxylic acid arm. The signal for **2** relaxes very fast and even at T = 3.5 K most of the magnetisation is lost during the pulse sequence. This demanded a very long measurement time to acquire a decent signal-to-noise ratio. Despite this,

major relaxation features can be recorded with a measurement time of 24 hours. ^{1}H-ENDOR spectra were recorded in both H_2O and D_2O solutions (Figure S8). By ESI mass spectrometry we have observed that the proton in the hydroxo ligand of $[Fe^{III}(OH)(tpena)]^{+}$ is replaced with deuterium in D_2O solutions (Figure S3), but no difference was observable in the ^{1}H-ENDOR spectra. Considering the close proximity of the iron atom and its associated unpaired electrons, the components of the hyperfine coupling tensor for the proton nucleus of the hydroxo ligand (A_{OH}) is expected to have large dipole contributions. Further large anisotropy makes it likely that a signal from a Fe(III) coordinated hydroxo hydrogen would be broad and thus extremely difficult to detected in this ENDOR spectrum given the signal-to-noise ratio that we achieved in the measurement.

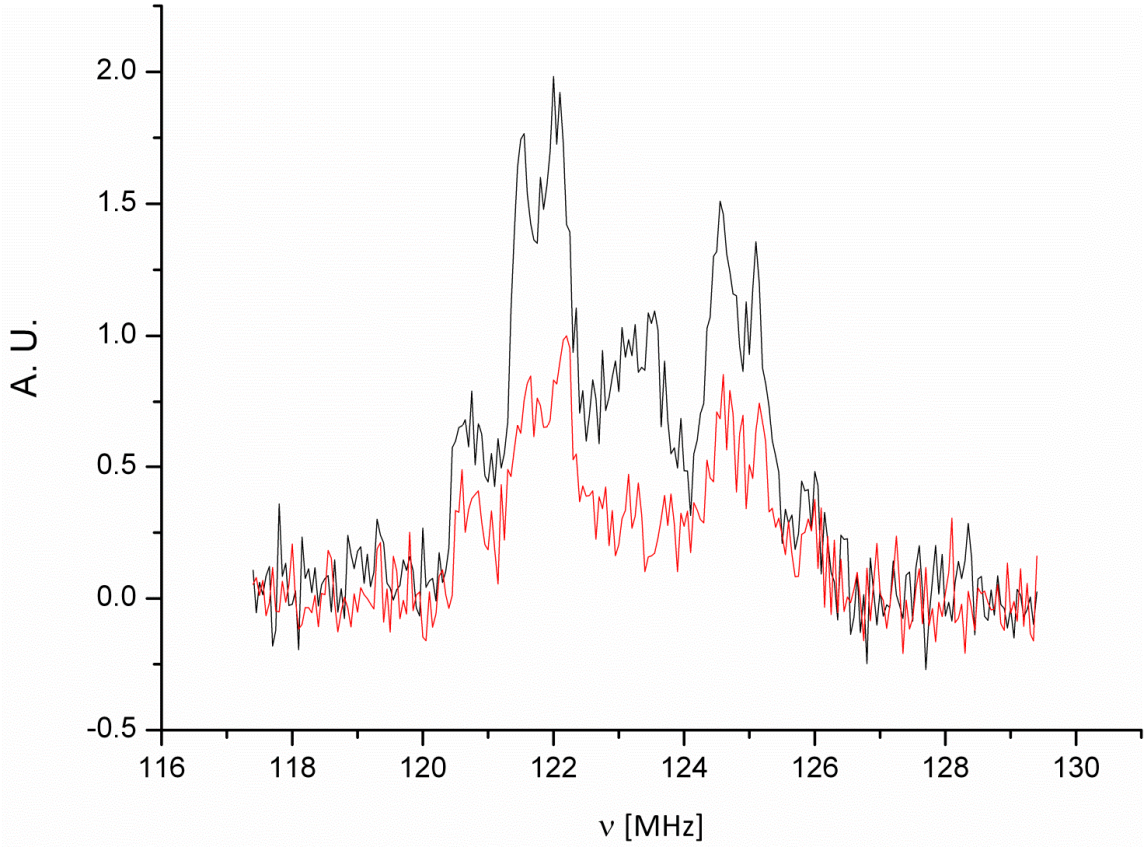

Figure S8 Pulse W-band ENDOR spectra recorded at T = 3.5 K and at the maximum intensity of the EPR signal at a magnetic field strength of 28984 Gauss. The spectra is recorded on 5 mM solutions of **3**$(ClO_4)_4 \cdot 2H_2O$ in (black) H_2O and (red) D_2O. The spectrum in H_2O is an average of 9805 scans recorded with a microwave frequency of 93.89846 GHz, and the spectrum in D_2O is an average of 6600 scans recorded with a microwave frequency of 93.9027 GHz. The data show ^{1}H hyperfine couplings less than *ca*. 7 MHz.

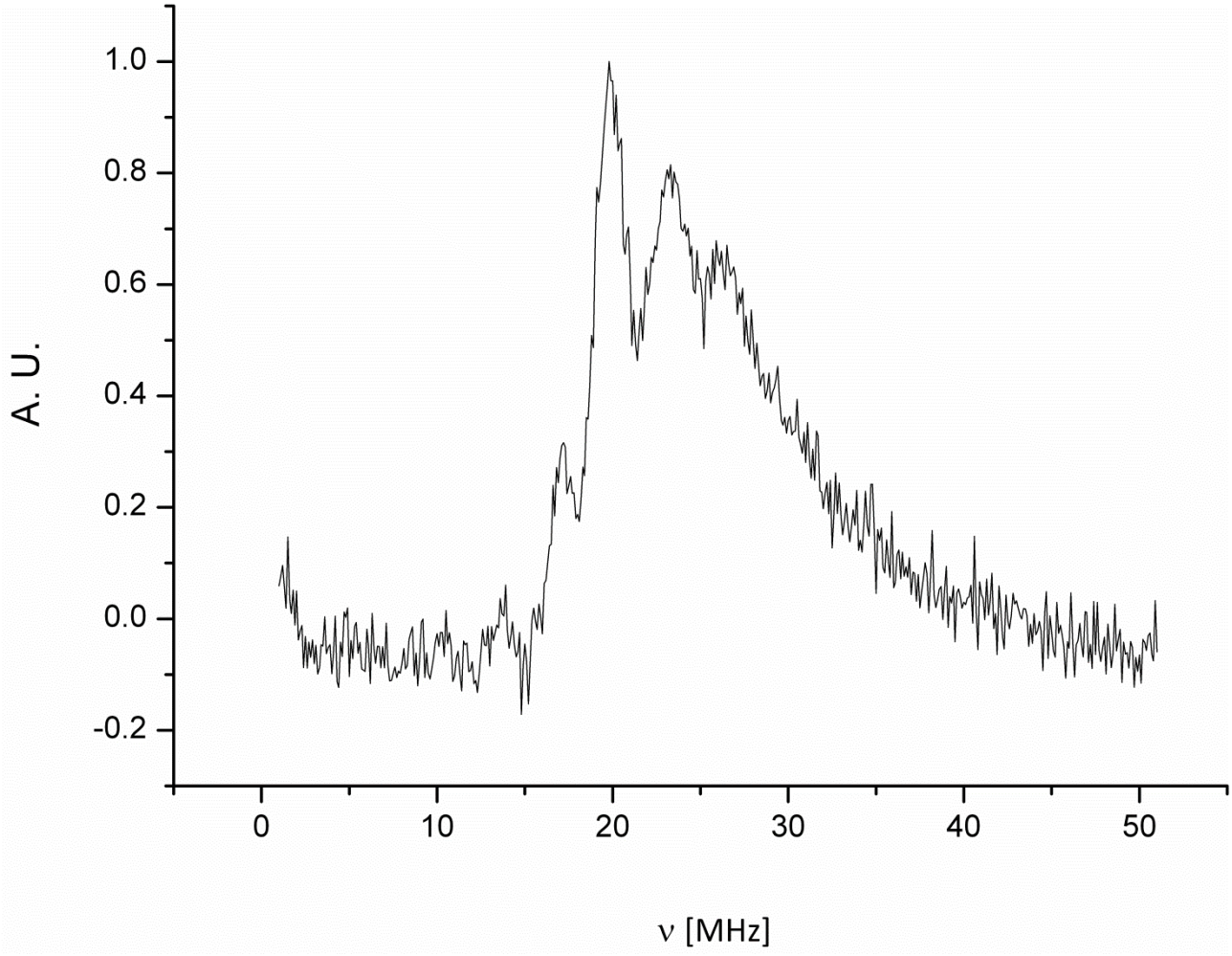

Figure S9. Davies ENDOR spectra recorded at T = 6 K and at the maximum intensity of the EPR signal at a magnetic field strength of 2968 Gauss. The spectra is recorded on 5 mM solutions of **3**$(ClO_4)_4 \cdot 2H_2O$ in H_2O. The spectrum is an average of 39 scans recorded with a microwave frequency of 9.732613 GHz.

An X-band Davies ENDOR spectrum (Figure S9) with a hard inversion pulse (to suppress the smaller proton couplings observed in Figure S8) covering a larger frequency range, shows that **2** contains nitrogen nuclei with large hyperfine coupling constants of ca. $A(^{14}N)$=20-30 MHz. To a first-order approximation, strong coupled nitrogen signals are centred around the hyperfine coupling A and split by twice the nuclear Zeeman frequency ($\nu(^{14}N)$ = 0.9 MHz) and also by the quadruple coupling which is expected to be a few MHz in magnitude. Note the proton signals, which to a first-order approximation, are centred around the proton Larmor frequency of 12.6 MHz at this field, are largely suppressed. A HYSCORE spectrum (Figure S10) shows that **2** simultaneously contains at least one nitrogen nucleus with a very small hyperfine coupling constant; the strong peak at (6.4, 6.4) MHz results from double-quantum transitions from very weakly coupled ^{14}N. Note that no

proton signals are observed, probably as a result of fast relaxation.

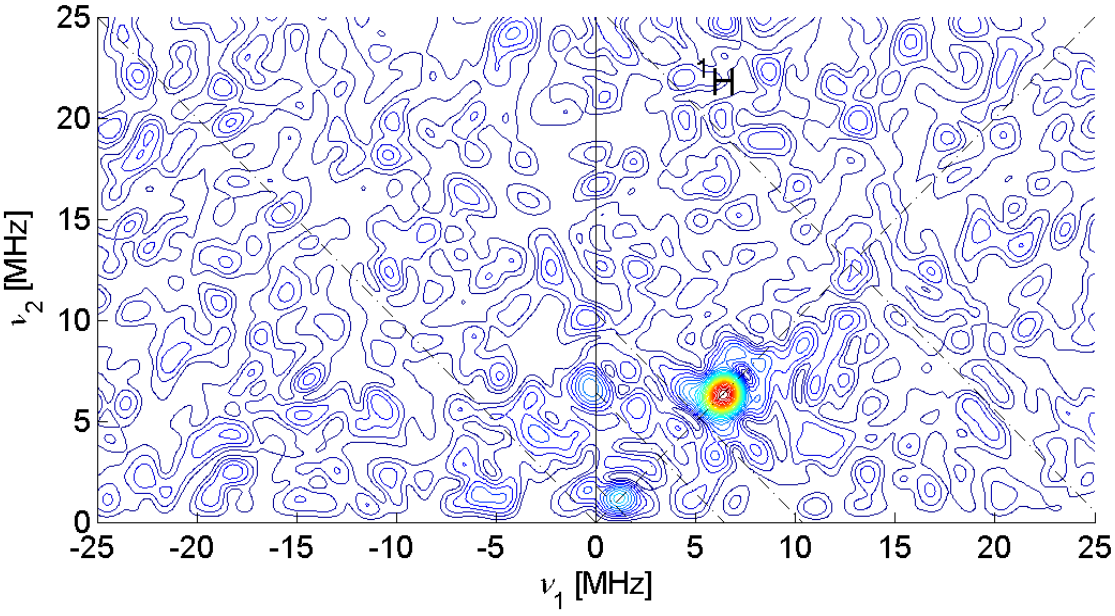

Figure S10 HYSCORE spectrum of a 5 mM solution of **3**$(ClO_4)_4 \cdot 2H_2O$ in H_2O at T = 6 K and a magnetic field strength of 2979 Gauss and a microwave frequency of 9.754215 GHz.

DFT calculations of Mössbauer parameters

The isomer shift and the quadrupole splitting for ^{57}Fe were calculated following a procedure published by Neese and co-workers.[6,7] A calibration curve correlating the isomer shift to the electron density at the iron nucleus were constructed as a linear least square fit to the data from eight Fe(IV)-oxo complexes Table S1 and Figure S11. The linear fit is described by the equation:

$$\delta = -0.4261194661 \frac{\text{mm}\cdot\text{au}^3}{\text{s}} \cdot \rho(\mathbf{0}) + 5037.1839327717 \frac{\text{mm}}{\text{s}} \qquad \text{Eq. S1}$$

Table S1 Calculated values for the electron density at the iron nucleus and the quadrupole splitting and the experimental values for the isomer shift and the quadrupole splitting for a test set of Fe(IV)-oxo complexes.

Complex[a]	Calculated		Experimental		Ref.
	$\rho(\mathbf{0})$[au^{-3}]	ΔE_Q[mm/s]	δ[mm/s]	ΔE_Q[mm/s]	
$[Fe(O)(TPA)(MeCN)]^{2+}$	11821.0497	0.60	0.01	0.92	8
$[Fe(O)(TCMPy)]^{2+}$	11820.6497	0.94	0.18	1.08	9
$[Fe(O)(N4Py)]^{2+}$	11821.1522	0.66	-0.04	0.93	10
$[Fe(O)(bztpen)]^{2+}$	11821.0480	0.68	0.01	0.87	10
$[Fe(O)(N2Py3)]^{2+}$	11821.0271	0.52	0.015	0.68	11

$[Fe(O)(TCM)(MeCN)]^{2+}$	11820.6488	1.06	0.17	1.24	12
$[Fe(O)(BPMCN)]^{2+}$	11820.9301	-0.57	0.07	1.02	13
$[Fe(O)(acetate\text{-}cyclam)]^{2+}$	11820.9801	0.80	0.01	1.37	14

[a] TPA = tris(2-pyridylmethyl)amine
TCMPy = 1-(2'-pyridylmethyl)-4,8,11-trimethyl -1,4,8,11-tetraazacyclotetradecane
N4Py = bis(2-pyridylmethyl)-bis(2-pyridyl)methylamine
Bztpen = *N*-benzyl-*N*,*N'*,*N'*-tris(2-pyridylmethyl)ethylenediamine
N2Py3 = 3-methyl-7-(2-methylpyridyl)-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]-nonane-1,5-dicarboxylate methyl ester
TCM = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
BPMCN = *N*,*N*-bis(2-pyridylmethyl)-*N*,*N*-dimethyltrans-1,2-diaminocyclohexane
cyclam-acetate = 1,4,8,11-tetraazacyclotetradecane-1-acetate

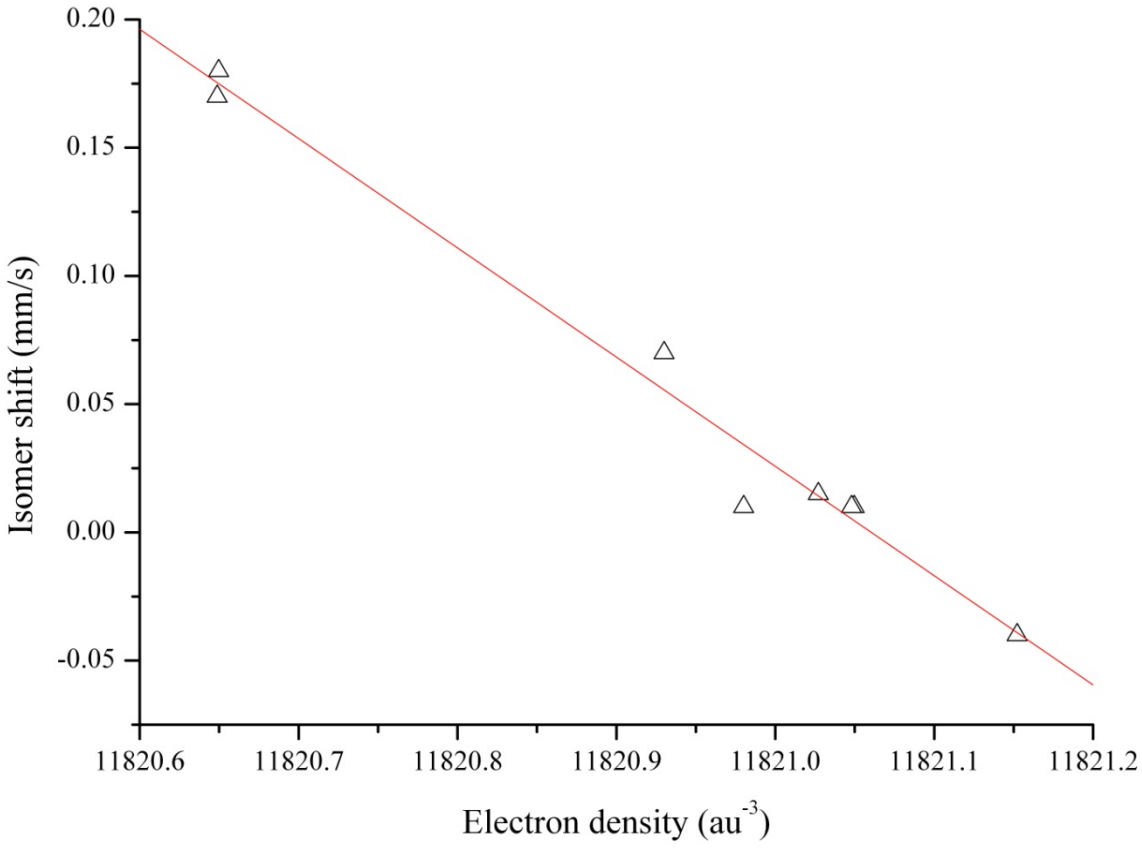

Figure S11 Calibration curve for the correlation between the electron density at the iron nucleus and the isomer shift for a test set of eight Fe(IV)-oxo complexes. The coefficient of determination, $R^2 = 0.98$.

All complexes were optimised at TPSS/TZVP level of theory using the program Gaussian09.[15,16] The electron density and the electric field gradient at the iron nucleus were calculated with the

program suite ORCA[17] at TPSSh/TZVP level of theory with the basis set CP(PPP) on iron.[16,18] The basis set CP(PPP) is build to describe the electron density in the core region with high accuracy. It is based on the double zeta (DZ) basis by Ahlrichs and co-worker taken from the Turbomole basis set library[19]. The s-part is uncontracted and three steep s-functions are added with exponents of 2.5, 6.25 and 15.625 times the largest exponent in the unchanged basis set. Two polarising p-functions with Wachters exponents[20] are added to the valence region together with a polarising f-function from the Turbomole basis set library. The narrow gaussians in the CP(PPP) basis set require a very fine radial integration grid at the iron nucleus in the DFT procedure. Following the procedure of Neese and co-workers[18] the numerical tolerance was therefore lowered to $\varepsilon = 10^{-7}$ when defining the number of radial similarly to Krack and Koster[21]

$$n_A^r = -5(3log\epsilon - t_A + 8)$$

where n_A^r is the number of radial shells and t_A is the period in the table of elements to which the element in question belongs. All single point calculations were done with the COSMO model simulating an aqueous environment.

The quadrupole splitting can be obtain from the electric field gradient tensor at the iron nucleus as

$$\Delta E_{\mathrm{Q}} = \frac{1}{2}\mathrm{eQV_Z}\sqrt{1+\frac{1}{3}\eta^2}$$

where e is the elemental charge, Q is the quadrupolar moment (in this study 0.16 barn, for ^{57}Fe) and $\eta = \frac{V_x - V_y}{V_z}$, where V_x, V_y and V_z are the principal components of the electric field gradient tensor in a coordinate system where $|V_z| \geq |V_y| \geq |V_x|$. If V_x is close to zero small errors in the calculation might flip the sign of the quadropolar splitting as $V_z + V_y + V_x = 0$. This can be seen for $[Fe(O)(BPMCN)]^{2+}$ where $|V_z| \approx -|V_y| \approx -10|V_x|$. The average absolute deviation between the experimental and the calculated quadrupole splittings in Table S1 omitting the result for $[Fe(O)(BPMCN)]^{2+}$ is 0.26 mm/s with the maximum deviation of 0.57 mm/s for $[Fe(O)(cyclam)]^{2+}$ showing that carefulness has to be practised when interpreting the results of calculated quadrupole splittings.

Optimised Structures used for the calculations of Mössbauer parameters.

Table S4. Calculated Mössbauer parameters for Fe^{IV} oxo/hydroxo complexes of $tpena^-$ with different protonation sites. The table contains an extra entry compared to the same table in the manuscript: An alternative structure for **2** in which the dangling arm is the carboxylic acid rather than a pyridinium.

Complex	δ (mm/s)	ΔE_Q (mm/s)
$[Fe(O)(tpenaH)]^{2+}$	0.004	0.82
$[Fe(OH)(tpenaH)]^{3+}$	-0.032	2.25
[a]$[Fe(O)(tpena\cdots H)]^{2+}$	-0.006	1.19
$[Fe(OH)(tpena)]^{2+}$	-0.035	2.41
[b]$[Fe(O)(tpenaH)]^{2+}$	0.010	0.64
$[Fe(O)(tpena)]^{+}$	-0.003	0.91

[a] In this structure the protonated dangling pyridyl arm is intramolecularly hydrogen bonding to the oxo group. [b] The dangling decoordinated arm is the carboxylic acid.

$[Fe(O)(tpenaH)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(tpenaH)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2616.85754151 Hartree, $\langle S^2 \rangle$ = 2.017.

C	0.522890	-2.809445	0.008323
C	1.704996	-1.844602	-0.153818
H	2.567823	-2.186308	0.427051
H	1.952379	-1.837825	-1.219376
C	1.276817	-0.227545	1.711575
H	1.298964	0.856069	1.878026
H	2.158014	-0.676080	2.190112
C	0.005460	-0.811206	2.333817
H	-0.016484	-1.897055	2.232405
H	-0.019172	-0.572653	3.405171
C	-2.401040	-1.143268	1.723304
H	-2.944643	-0.971349	2.659206
H	-2.047771	-2.177949	1.697810
C	-3.274617	-0.914568	0.512010
C	-4.648119	-1.136742	0.496799
H	-5.159905	-1.418489	1.412137
C	-5.345127	-1.011009	-0.706085
H	-6.415680	-1.189259	-0.738719
C	-4.648477	-0.663231	-1.863104
H	-5.152194	-0.568107	-2.819258
C	-3.278996	-0.436444	-1.786789
H	-2.676204	-0.174113	-2.649047
C	-1.510080	1.148999	2.050741
H	-2.564177	1.193846	2.345118
H	-0.927797	1.407362	2.943618
C	-1.268695	2.152796	0.947739
C	-1.477968	3.519884	1.133861
H	-1.788482	3.891936	2.106257
C	-1.304300	4.389369	0.059052

H	-1.472239	5.455152	0.182214
C	-0.927835	3.864256	-1.179646
H	-0.798647	4.502524	-2.047690
C	-0.726459	2.496239	-1.299352
H	-0.445400	2.017642	-2.232339
C	2.172951	0.560406	-0.496044
H	1.864461	0.509335	-1.544320
H	1.922791	1.555093	-0.114385
C	3.669594	0.325994	-0.422788
C	4.388419	-0.360689	-1.397607
H	3.861565	-0.752319	-2.261566
C	5.771062	-0.528165	-1.274878
H	6.321080	-1.062818	-2.044136
C	6.445464	-0.899000	-0.169010
H	7.517811	-0.112004	-0.049652
C	5.721598	0.693953	0.782508
H	6.158644	1.155710	1.660992
N	-2.614210	-0.553964	-0.619289
N	-0.883413	1.652438	-0.249517
N	1.307398	-0.442687	0.220553
N	-1.190296	-0.255072	1.625212
N	4.379512	0.833313	0.628792
O	-0.648663	-2.226469	-0.182337
O	0.682283	-3.983958	0.268848
O	-0.239825	-0.246682	-2.004856
Fe	-0.677805	-0.341871	-0.411914
H	3.879654	1.374477	1.332992

$[Fe(OH)(tpenaH)]^{3+}$

Cartesian coordinate of the gas phase structure of $[Fe(OH)(tpenaH)]^{3+}$ optimised at TPSS/TZVP level of theory, E = -2617.04177787 Hartree, $\langle S^2 \rangle$ = 2.028.

C	0.454530	-2.840514	-0.043352
C	1.682373	-1.929890	-0.081695
H	2.444779	-2.295979	0.612221
H	2.078759	-1.988846	-1.099484
C	1.284261	-0.204283	1.683376
H	1.281096	0.885017	1.794104
H	2.177100	-0.608905	2.175892
C	0.029882	-0.795520	2.312184
H	0.018114	-1.885206	2.235624
H	-0.024549	-0.538172	3.376261
C	-2.381584	-1.176103	1.739387
H	-2.858855	-1.004216	2.709789
H	-2.027080	-2.209715	1.695419
C	-3.305884	-0.908592	0.583420
C	-4.681418	-1.110489	0.610176
H	-5.160899	-1.441912	1.526875
C	-5.425563	-0.890721	-0.551788

H	-6.499503	-1.053879	-0.552575
C	-4.773906	-0.455005	-1.705978
H	-5.316072	-0.269387	-2.628002
C	-3.397731	-0.255176	-1.677125
H	-2.845516	0.086178	-2.545273
C	-1.535016	1.148766	1.998041
H	-2.611731	1.175606	2.195379
H	-1.032158	1.384827	2.942099
C	-1.211432	2.157406	0.926892
C	-1.361457	3.529329	1.124433
H	-1.660595	3.908397	2.097858
C	-1.148846	4.398348	0.054052
H	-1.273978	5.469567	0.184802
C	-0.790497	3.869478	-1.188628
H	-0.632536	4.509107	-2.051402
C	-0.641920	2.495161	-1.322357
H	-0.374801	2.027277	-2.263886
C	2.234184	0.453622	-0.549063
H	1.983061	0.339569	-1.605816
H	1.960910	1.468448	-0.246749
C	3.734775	0.237474	-0.395445
C	4.492295	-0.528692	-1.273570
H	4.005934	-1.025421	-2.107090
C	5.880899	-0.640632	-1.111059
H	6.464000	-1.239309	-1.809289
C	6.517176	0.029511	-0.064575
H	7.590994	-0.030322	0.082814
C	5.752776	0.810143	0.788586
H	6.162353	1.388956	1.610217
N	-2.685166	-0.486776	-0.552660
N	-0.840871	1.654060	-0.276107
N	1.316282	-0.499091	0.201117
N	-1.177300	-0.266198	1.581100
N	4.410181	0.888120	0.602736
O	-0.710510	-2.186837	-0.274788
O	0.499073	-4.029123	0.132055
O	-0.331316	-0.239257	-2.139417
Fe	-0.714048	-0.355423	-0.410726
H	-0.440143	-1.067429	-2.650110
H	3.893326	1.505945	1.227627

$[Fe(O)(tpena\cdots H)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(tpena\cdots H)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2616.87707350 Hartree, $\langle S^2 \rangle$ = 2.021. Figure S12.

C	-0.689508	-2.662456	-0.866110
C	-1.739648	-1.649992	-1.335642
H	-2.057439	-1.877571	-2.358198
H	-2.606789	-1.764724	-0.682152

C	-0.557540	0.158764	-2.536177
H	-0.406137	1.242546	-2.507078
H	-1.227677	-0.069966	-3.374438
C	0.772758	-0.565217	-2.699986
H	0.638029	-1.649161	-2.708805
H	1.243419	-0.279486	-3.648591
C	2.703079	-1.249486	-1.241102
H	3.569092	-1.125900	-1.901016
H	2.262352	-2.235524	-1.409803
C	3.076427	-1.121646	0.215942
C	4.307294	-1.503518	0.739947
H	5.086015	-1.869635	0.077603
C	4.515703	-1.421910	2.117805
H	5.466866	-1.723829	2.545750
C	3.487562	-0.952682	2.935007
H	3.608199	-0.881660	4.010888
C	2.281856	-0.573186	2.356274
H	1.438273	-0.214459	2.934971
C	2.281845	1.138851	-1.687084
H	3.320548	1.063440	-1.347027
H	2.311864	1.423403	-2.745145
C	1.591238	2.184528	-0.852667
C	1.875745	3.544380	-0.977507
H	2.557453	3.885054	-1.751578
C	1.292299	4.446610	-0.090461
H	1.505189	5.508663	-0.167182
C	0.444720	3.958053	0.906371
H	-0.013848	4.621471	1.632408
C	0.189148	2.594862	0.966353
H	-0.448973	2.149709	1.722107
C	-2.340459	0.759574	-0.991534
H	-1.869556	1.682182	-0.637418
H	-2.820439	0.974398	-1.953156
C	-3.443949	0.346093	-0.038125
C	-4.786872	0.417439	-0.395168
H	-5.060683	0.720862	-1.400628
C	-5.775194	0.096113	0.542372
H	-6.823590	0.152719	0.264188
C	-5.409477	-0.302239	1.828854
H	-6.151807	-0.564145	2.575007
C	-4.059856	-0.368622	2.145792
H	-3.684433	-0.678008	3.115360
N	2.089627	-0.652592	1.024087
N	0.740435	1.719136	0.091428
N	-1.224099	-0.238222	-1.235280
N	1.648742	-0.216899	-1.535606
N	-3.129935	-0.038777	1.225975
O	0.289997	-2.137426	-0.135630

O	-0.767865	-3.840582	-1.136615
O	-0.577663	-0.127781	1.494544
Fe	0.373212	-0.276466	0.123773
H	-2.071614	-0.110373	1.464290

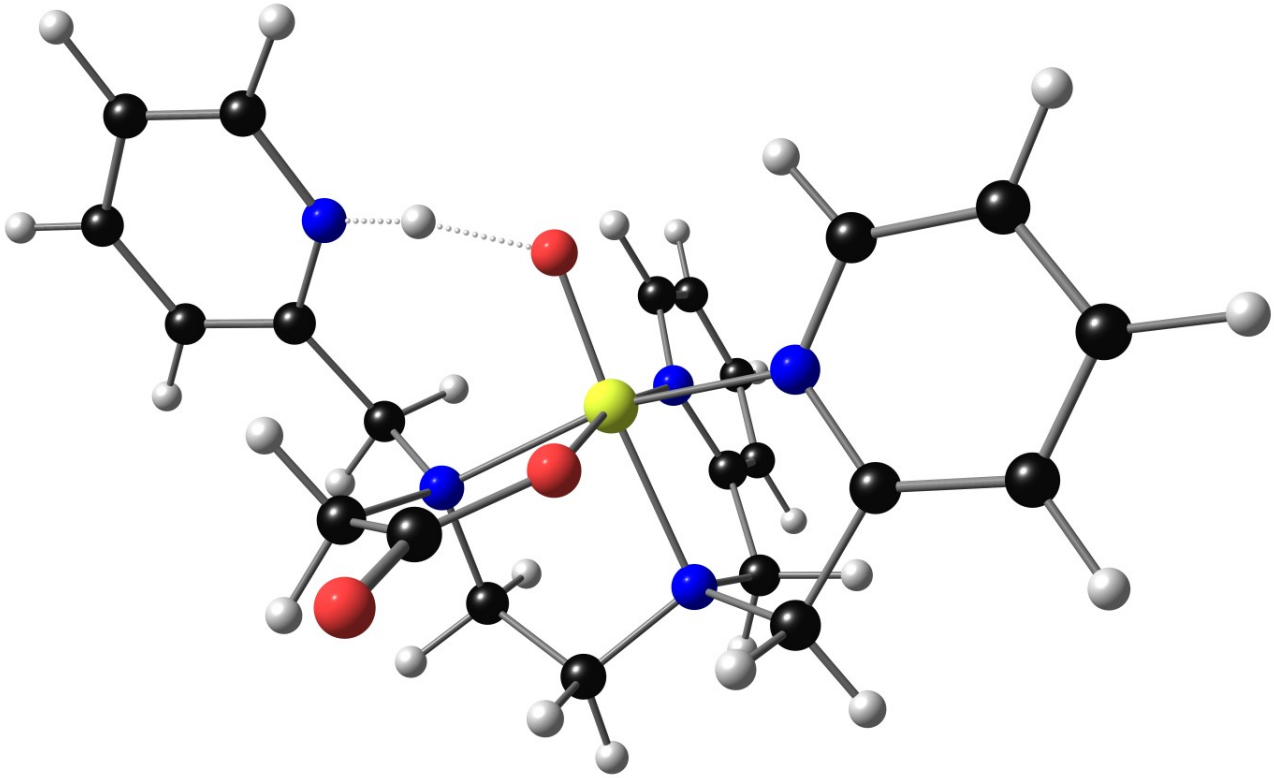

Figure S12. The gas phase structure of $[Fe(O)(tpena\cdots H)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2616.87707350 Hartree, $<S^2> = 2.021$.

$[Fe(OH)(tpena)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(OH)(tpena)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2616.85862431 Hartree, $<S^2> = 2.026$.

C	0.530768	-2.781621	-0.234174
C	1.721732	-1.836551	-0.171470
H	2.467994	-2.198175	0.539838
H	2.183868	-1.819719	-1.163765
C	1.266534	-0.205070	1.666704
H	1.226163	0.877484	1.817283
H	2.210557	-0.556996	2.094637
C	0.046719	-0.874540	2.264069
H	0.063296	-1.957593	2.121239
H	-0.025073	-0.678350	3.340035
C	-2.358451	-1.266485	1.663139
H	-2.841502	-1.153816	2.639707
H	-1.988470	-2.290850	1.564884
C	-3.289065	-0.956218	0.521029
C	-4.661686	-1.179467	0.540741
H	-5.134056	-1.566299	1.438759

C	-5.410526	-0.907935	-0.606036
H	-6.482041	-1.083787	-0.613993
C	-4.766294	-0.404674	-1.736218
H	-5.313025	-0.177930	-2.645670
C	-3.393020	-0.189786	-1.695118
H	-2.841907	0.202269	-2.542566
C	-1.549871	1.046904	2.030424
H	-2.638541	1.072881	2.148453
H	-1.112315	1.221229	3.019078
C	-1.147852	2.116077	1.049464
C	-1.208441	3.474693	1.353151
H	-1.485171	3.795351	2.353325
C	-0.923109	4.406484	0.355709
H	-0.967776	5.469979	0.570888
C	-0.590026	3.952101	-0.921956
H	-0.372679	4.643579	-1.729441
C	-0.528564	2.585105	-1.158893
H	-0.267988	2.169376	-2.126320
C	2.206722	0.568237	-0.507901
H	1.937525	0.573974	-1.565638
H	1.966505	1.545393	-0.079388
C	3.690375	0.266047	-0.350662
C	4.540029	0.380398	-1.455290
H	4.147308	0.631839	-2.436991
C	5.910064	0.183660	-1.263830
H	6.598807	0.276092	-2.098614
C	6.374092	-0.137879	0.009465
H	7.429266	-0.307047	0.199533
C	5.446551	-0.258184	1.048055
H	5.763255	-0.528594	2.052257
N	-2.673584	-0.466843	-0.587395
N	-0.796412	1.684149	-0.184210
N	1.291526	-0.437282	0.170532
N	-1.172791	-0.338778	1.552818
N	4.130943	-0.055641	0.877154
O	-0.658457	-2.146642	-0.415493
O	0.596516	-3.982868	-0.166059
O	-0.340348	-0.086050	-2.169570
Fe	-0.685120	-0.312156	-0.438268
H	-0.390428	-0.906760	-2.698303

$[Fe(O)(tpena)]^+$

Cartesian coordinate of the gas phase structure of $[Fe(O)(tpena)]^+$ optimised at TPSS/TZVP level of theory, E = -2616.57699197 Hartree, $<S^2> = 2.018$.

C	0.472052	-2.836309	-0.122062
C	1.661758	-1.890694	-0.281486
H	2.521852	-2.236804	0.298256
H	1.929027	-1.880284	-1.342356

C	1.319749	-0.273851	1.592113
H	1.385976	0.805503	1.757194
H	2.229675	-0.712243	2.012241
C	0.075123	-0.845664	2.260508
H	0.020613	-1.929351	2.147094
H	0.090642	-0.617661	3.334778
C	-2.363098	-1.108735	1.746969
H	-2.865105	-0.938623	2.707324
H	-2.037786	-2.151596	1.690604
C	-3.281569	-0.842742	0.577485
C	-4.662113	-1.016554	0.620063
H	-5.142794	-1.293385	1.553603
C	-5.405484	-0.846120	-0.548581
H	-6.482472	-0.984075	-0.537299
C	-4.745794	-0.504483	-1.729056
H	-5.286068	-0.374479	-2.660834
C	-3.366576	-0.329782	-1.706357
H	-2.786362	-0.075645	-2.587077
C	-1.396484	1.150861	2.044785
H	-2.452247	1.242069	2.324249
H	-0.810803	1.372156	2.945226
C	-1.094931	2.156165	0.958562
C	-1.168318	3.531577	1.180397
H	-1.406585	3.906545	2.171734
C	-0.939438	4.406003	0.120695
H	-0.992564	5.479782	0.273329
C	-0.648443	3.877248	-1.138633
H	-0.471593	4.520534	-1.994312
C	-0.578526	2.499716	-1.292020
H	-0.352093	2.015249	-2.236669
C	2.180454	0.497563	-0.619886
H	1.919578	0.413690	-1.677064
H	1.907637	1.493016	-0.261833
C	3.664700	0.273723	-0.408749
C	4.484375	-0.153375	-1.458353
H	4.063612	-0.353169	-2.440483
C	5.852054	-0.307693	-1.224118
H	6.514174	-0.633134	-2.021464
C	6.348527	-0.034608	0.048523
H	7.405106	-0.138358	0.275919
C	5.453615	0.383046	1.036499
H	5.802992	0.607635	2.042177
N	-2.655695	-0.488606	-0.572944
N	-0.790468	1.651311	-0.258074
N	1.281021	-0.487008	0.096846
N	-1.139046	-0.257933	1.606137
N	4.138199	0.543287	0.824872
O	-0.701833	-2.228730	-0.243112

O	0.599585	-4.028601	0.085131
O	-0.377422	-0.247703	-2.074884
Fe	-0.687497	-0.343700	-0.451272

$[Fe(O)(TPA)(MeCN)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(TPA)(MeCN)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2387.68504791 Hartree, $\langle S^2 \rangle$ = 2.015.

Fe	-0.113828	-0.157240	0.388034
O	-0.083198	0.551471	-1.108430
N	-0.901405	-1.803946	-0.374610
N	-0.084837	-0.906009	2.332734
N	1.683586	-0.998583	0.328451
N	-1.924136	0.444754	0.937983
N	0.667570	1.439708	1.231285
C	0.785106	-2.128398	2.271055
C	1.951912	-1.853501	1.351302
C	3.194240	-2.468402	1.466726
C	4.171887	-2.212926	0.502122
C	3.877626	-1.348731	-0.552155
C	2.622985	-0.750123	-0.608127
C	-1.519118	-1.206567	2.660338
C	-2.392091	-0.115669	2.085160
C	-3.621339	0.258158	2.618092
C	-4.390965	1.212655	1.948675
C	-3.907979	1.765995	0.763147
C	-2.664401	1.365213	0.285175
C	0.487258	0.126009	3.275362
C	0.876712	1.398413	2.566454
C	1.426248	2.484735	3.245662
C	1.765853	3.633631	2.534777
C	1.545621	3.665481	1.156454
C	0.995634	2.554099	0.533780
H	0.180021	-2.937919	1.849312
H	1.115234	-2.437359	3.269131
H	3.391614	-3.140913	2.296267
H	5.147358	-2.684564	0.574116
H	4.607807	-1.129969	-1.324390
H	2.332446	-0.068625	-1.400591
H	-1.668749	-1.323583	3.739468
H	-1.770849	-2.157471	2.178944
H	-3.973009	-0.194745	3.540356
H	-5.353942	1.516470	2.348102
H	-4.478703	2.505215	0.210702
H	-2.232511	1.757783	-0.629269
H	1.361339	-0.304000	3.779158
H	-0.253165	0.346038	4.051688
H	1.584166	2.426108	4.318776
H	2.194915	4.489180	3.047624

H	1.794777	4.538851	0.562816
H	0.799046	2.513099	-0.532278
C	-1.347644	-2.636081	-1.044566
C	-1.905442	-3.668976	-1.897449
H	-1.232562	-4.532070	-1.929681
H	-2.882825	-3.983006	-1.516842
H	-2.025793	-3.268863	-2.910359

$[Fe(O)(TCMPy)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(TCMPy)]^{2+}$ optimised at TPSS/TZVP level of theory, E =-2357.94278104 Hartree, $<S^2> = 2.020$.

Fe	0.428977	0.159207	0.151629
O	1.624742	0.891484	1.028551
N	-0.983150	0.760280	1.544722
C	-0.616533	2.119053	2.099705
H	0.354630	2.257000	2.582981
H	-1.363600	2.375021	2.863109
C	-0.563645	3.245661	1.062967
H	-0.263466	4.144191	1.616503
H	-1.565766	3.479995	0.685638
C	0.429214	3.109836	-0.092778
H	0.377583	4.020106	-0.705343
H	1.443521	3.356000	0.293010
N	0.180439	1.936181	-1.019538
C	1.265268	1.911611	-2.076734
H	0.824376	1.497094	-2.986559
H	1.571721	2.939581	-2.303873
C	2.447214	1.090076	-1.630403
H	2.921508	1.529709	-0.752182
H	3.189356	1.017211	-2.435967
N	1.991042	-0.292983	-1.237161
C	3.187077	-0.959496	-0.596382
H	3.631353	-0.222193	0.076003
H	3.904423	-1.172673	-1.399458
C	2.874975	-2.223879	0.192891
H	2.324033	-2.964669	-0.397462
H	3.835644	-2.696875	0.428547
C	2.194718	-1.916374	1.520010
H	2.715500	-1.087965	2.005398
H	2.234043	-2.789438	2.184236
N	0.745023	-1.510854	1.410647
C	0.356360	-0.956417	2.756766
H	0.320074	-1.766609	3.496419
H	1.133783	-0.248273	3.046901
C	-0.985145	-0.274129	2.655757
H	-1.251059	0.211482	3.601467
H	-1.769477	-0.999459	2.425075
C	-1.090308	2.176740	-1.781019

H	-0.962586	3.062768	-2.414337
H	-1.925014	2.358196	-1.109491
H	-1.310392	1.314244	-2.409967
C	1.651948	-1.061988	-2.474062
H	2.506398	-1.043600	-3.161135
H	0.787485	-0.627502	-2.975858
H	1.444223	-2.100727	-2.213216
C	-0.059167	-2.740990	1.121584
H	0.217434	-3.141990	0.146520
H	-1.123276	-2.513095	1.119438
H	0.149250	-3.495660	1.888895
C	-2.363374	0.787338	0.974833
H	-2.547751	1.768513	0.534335
H	-3.101561	0.662879	1.776236
C	-2.515329	-0.281053	-0.069992
C	-3.773136	-0.774345	-0.417052
H	-4.654115	-0.411858	0.104893
C	-3.884059	-1.724604	-1.429302
H	-4.854653	-2.118036	-1.716581
C	-2.717317	-2.164644	-2.054268
H	-2.742948	-2.911236	-2.841449
C	-1.497537	-1.642242	-1.644725
H	-0.581102	-1.989356	-2.099183
N	-1.371677	-0.702993	-0.674537

$[Fe(O)(N4Py)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(N4Py)]^{2+}$ optimised at TPSS/TZVP level of theory, E =-2502.07764310 Hartree, $<S^2> = 2.015$.

O	-2.299381	-0.198266	0.000000
Fe	-0.652578	-0.064062	0.000000
N	1.402043	0.098389	0.000000
C	1.465875	1.616753	0.000000
C	0.672651	2.072214	1.214686
C	1.007089	3.116982	2.065986
C	0.102636	3.469369	3.074228
C	-1.098487	2.774000	3.191810
C	-1.368452	1.723219	2.312392
N	-0.491873	1.385183	1.348195
C	1.940524	-0.534537	-1.253046
H	2.928200	-0.968013	-1.067150
H	2.066899	0.252438	-2.004765
C	0.975791	-1.570215	-1.786323
C	1.352359	-2.555952	-2.694516
C	0.380341	-3.414698	-3.209683
C	-0.945119	-3.262325	-2.801164
C	-1.259147	-2.269123	-1.880952
N	-0.313945	-1.439900	-1.385119
C	0.672651	2.072214	-1.214686

C	1.007089	3.116982	-2.065986
C	0.102636	3.469369	-3.074228
C	-1.098487	2.774000	-3.191810
C	-1.368452	1.723219	-2.312392
N	-0.491873	1.385183	-1.348195
C	1.940524	-0.534537	1.253046
H	2.928200	-0.968013	1.067150
H	2.066899	0.252438	2.004765
C	0.975791	-1.570215	1.786323
C	1.352359	-2.555952	2.694516
C	0.380341	-3.414698	3.209683
C	-0.945119	-3.262325	2.801164
C	-1.259147	-2.269123	1.880952
N	-0.313945	-1.439900	1.385119
H	-1.827070	3.027516	3.953559
H	-2.286635	1.146556	2.347336
H	0.334492	4.283241	3.754698
H	1.946924	3.647226	1.945042
H	1.946924	3.647226	-1.945042
H	0.334492	4.283241	-3.754698
H	-1.827070	3.027516	-3.953559
H	-2.286635	1.146556	-2.347336
H	2.391608	-2.645824	-2.997145
H	0.655161	-4.189312	-3.919279
H	-1.731432	-3.906904	-3.180035
H	-2.267421	-2.103579	-1.515946
H	2.391608	-2.645824	2.997145
H	0.655161	-4.189312	3.919279
H	-1.731432	-3.906904	3.180035
H	-2.267421	-2.103579	1.515946
H	2.490329	2.002607	0.000000

$[Fe(O)(bztpen)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(bztpen)]^{2+}$ optimised at TPSS/TZVP level of theory, E =-2659.38801560 Hartree, $\langle S^2 \rangle$ = 2.016.

Fe	0.652073	0.098518	-0.392851
N	2.636560	0.016920	-0.444950
N	1.022547	-0.179475	1.655450
N	0.617977	-1.890376	-0.382745
N	-1.330511	0.272447	0.140506
N	0.634477	2.105518	-0.231376
O	0.387441	0.173166	-2.025010
C	3.360313	-0.202706	-1.564792
H	2.790759	-0.275012	-2.485518
C	4.746420	-0.313648	-1.523626
H	5.295455	-0.484569	-2.443850
C	5.401452	-0.205943	-0.296629
H	6.481865	-0.297504	-0.237104

C	4.649373	0.020057	0.859071
H	5.130087	0.110710	1.828715
C	3.266725	0.134596	0.756595
C	2.351580	0.460167	1.914037
H	2.775329	0.139357	2.872527
H	2.193074	1.542897	1.965762
C	1.072005	-1.647800	1.996278
H	0.340695	-1.859530	2.784643
H	2.056985	-1.878997	2.415538
C	0.822869	-2.523876	0.794622
C	0.824012	-3.915945	0.881096
H	0.986701	-4.397723	1.841118
C	0.621542	-4.671096	-0.272163
H	0.620501	-5.755936	-0.224694
C	0.428131	-4.009699	-1.486918
H	0.272815	-4.557212	-2.410735
C	0.430124	-2.622209	-1.508573
H	0.278762	-2.046293	-2.415619
C	-0.126566	0.506991	2.332206
H	0.030047	1.584144	2.244764
H	-0.166811	0.253885	3.399623
C	-1.407229	0.062618	1.636746
H	-1.557839	-1.009271	1.792112
H	-2.280701	0.578474	2.048756
C	-1.738904	1.664271	-0.249051
H	-2.015085	1.621279	-1.308418
H	-2.625468	1.976295	0.311628
C	-0.607992	2.637998	-0.118743
C	-0.807748	4.013793	-0.012304
H	-1.815840	4.404710	0.087319
C	0.291986	4.868063	-0.057725
H	0.157562	5.943107	0.016244
C	1.565145	4.318737	-0.218192
H	2.448086	4.946121	-0.281785
C	1.698865	2.939176	-0.298406
H	2.669172	2.476676	-0.429482
C	-2.267823	-0.718079	-0.577669
H	-2.012548	-0.621788	-1.635771
H	-1.970039	-1.709057	-0.230860
C	-3.742625	-0.486156	-0.346678
C	-4.495088	0.248050	-1.278185
H	-4.017234	0.638110	-2.175344
C	-5.862084	0.450531	-1.085507
H	-6.435206	1.008695	-1.820098
C	-6.495411	-0.082635	0.039719
H	-7.560960	0.068055	0.186210
C	-5.762830	-0.833838	0.962332
H	-6.259625	-1.274973	1.821605

C	-4.396832	-1.039015	0.766997
H	-3.847755	-1.661102	1.471515

$[Fe(O)(N2Py3)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(N2Py3)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -3073.81162314 Hartree, $<S^2> = 2.015$.

Fe	-1.232519	-0.209000	0.854991
O	3.250166	3.095283	0.930556
O	2.966517	2.791843	-1.307743
O	3.251166	-3.094338	0.930480
O	2.967504	-2.790932	-1.307818
O	-2.198374	-0.356000	2.196832
N	-0.114459	-0.022000	-0.869891
N	0.586507	0.014000	1.935063
N	-1.168904	-1.962817	0.588768
N	-1.169393	1.962429	0.588828
N	-2.780613	-0.369000	-0.389918
C	0.664391	1.302416	-0.833842
C	1.864513	1.264785	0.161840
C	1.428637	1.206053	1.642951
C	1.429009	-1.205765	1.642914
C	1.864854	-1.264342	0.161789
C	0.664735	-1.302267	-0.833861
C	2.691120	0.350000	-0.130954
C	-1.026881	-0.108000	-2.082103
C	-0.313658	2.371059	-0.387397
C	-2.006869	2.851307	1.163627
C	-2.016027	4.189824	0.782212
C	-1.159322	4.614381	-0.233013
C	-0.293120	3.690596	-0.825406
C	2.771759	2.506515	-0.012000
C	3.963514	3.845004	-1.577565
H	3.659242	4.770431	-1.086166
H	3.970444	3.944954	-2.660854
H	4.932418	3.514614	-1.201393
C	0.298463	-0.056000	3.414565
C	2.772564	-2.505736	-0.012071
C	3.964986	-3.843643	-1.577644
H	4.933738	-3.512780	-1.201492
H	3.971948	-3.943603	-2.660932
H	3.661147	-4.769202	-1.086230
C	-0.313046	-2.371178	-0.387459
C	-2.006131	-2.851937	1.163544
C	-2.014902	-4.190456	0.782116
C	-1.158047	-4.614760	-0.233085
C	-0.292103	-3.690712	-0.825454
C	-2.489079	-0.308000	-1.708905
C	-4.072294	-0.501000	0.014502

C	-5.118520	-0.593000	-0.898136
C	-4.828742	-0.546000	-2.264247
C	-3.496631	-0.399000	-2.673033
H	1.068669	1.524826	-1.825995
H	0.877490	2.103783	1.921914
H	2.329028	1.169398	2.267488
H	2.329404	-1.168842	2.267425
H	0.878130	-2.103657	1.921895
H	1.069063	-1.524550	-1.826021
H	-0.799159	0.879011	-2.693884
H	-0.798901	-0.879084	-2.693994
H	-2.657886	2.455184	1.936132
H	-2.694025	4.879824	1.273919
H	-1.160548	5.650218	-0.558939
H	0.396525	3.987925	-1.608948
H	1.248950	0.075000	3.960383
H	-0.280096	0.887931	3.665417
H	-0.279834	-0.888223	3.665386
H	-2.657276	-2.456018	1.936047
H	-2.692715	-4.880649	1.273806
H	-1.158952	-5.650599	-0.559009
H	0.397672	-3.987825	-1.608963
H	-4.224234	-0.553000	1.088565
H	-6.141720	-0.694000	-0.536974
H	-5.627718	-0.635000	-2.999610
H	-3.237558	-0.343000	-3.727980
O	3.840677	0.495000	-0.497808

$[Fe(O)(TCM)(MeCN)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(TCM)(MeCN)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2243.55348723 Hartree, $\langle S^2 \rangle$ = 2.020.

Fe	0.024256	0.014000	-0.187757
O	0.024280	0.099000	-1.834903
N	1.414807	-1.575733	-0.330269
N	-1.445684	-1.548189	-0.176355
N	-1.445733	1.548164	-0.176188
N	1.414762	1.575831	-0.330131
C	0.624766	-2.635253	-1.057494
H	1.199693	-3.570103	-1.083054
H	0.487120	-2.278878	-2.079478
C	-0.702443	-2.853958	-0.373704
H	-0.560747	-3.302971	0.612307
H	-1.326288	-3.541683	-0.956368
C	-2.349787	-1.308862	-1.369255
H	-3.059064	-2.146681	-1.405201
H	-1.719941	-1.343094	-2.259091
C	-3.141383	0.011000	-1.326145
H	-3.770149	0.046000	-2.225177

H	-3.849600	-0.058000	-0.490711
C	-2.349851	1.308932	-1.369110
H	-1.720018	1.343292	-2.258951
H	-3.059166	2.146721	-1.404940
C	-0.702531	2.853976	-0.373413
H	-1.326410	3.541744	-0.955989
H	-0.560828	3.302887	0.612644
C	0.624667	2.635376	-1.057260
H	1.199563	3.570245	-1.082775
H	0.486992	2.279053	-2.079258
C	2.606182	1.262637	-1.203200
H	3.268340	2.137378	-1.167935
H	2.228049	1.158315	-2.222818
C	3.366987	0.095000	-0.821602
H	3.679592	0.064000	0.228433
H	4.296704	0.130000	-1.402629
C	2.606218	-1.262442	-1.203300
H	2.228096	-1.158048	-2.222916
H	3.268394	-2.137170	-1.168087
C	1.919779	-2.121828	0.968905
H	2.561664	-2.988258	0.771937
H	1.089173	-2.429054	1.602837
H	2.499084	-1.357261	1.486326
C	-2.305099	-1.765547	1.032896
H	-2.938143	-2.645234	0.865752
H	-2.947707	-0.909537	1.217608
H	-1.674824	-1.942410	1.903598
C	-2.305178	1.765417	1.033067
H	-2.938091	2.645224	0.866056
H	-1.674943	1.942001	1.903851
H	-2.947934	0.909474	1.217580
C	1.919715	2.121821	0.969090
H	2.561464	2.988374	0.772219
H	2.499145	1.357266	1.486388
H	1.089084	2.428831	1.603093
N	0.071431	-0.120000	1.877102
C	0.093098	-0.175000	3.036803
C	0.120674	-0.283000	4.488113
H	-0.902214	-0.014937	4.880037
H	0.630875	0.899007	4.850400
H	0.656193	-0.884993	4.849769

$[Fe(O)(BPMCN)]^{2+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(BPMCN)]^{2+}$ optimised at TPSS/TZVP level of theory, E = -2469.94768 Hartree, $\langle S^2 \rangle$ = 2.016.

Fe	-0.557068	-0.203907	-0.700537
N	-1.373015	-1.996177	-0.850204
O	-1.052348	0.082812	-2.261267

N	0.045230	-0.571613	1.304625
N	1.333892	-0.801458	-1.208342
N	-2.189957	0.433451	0.226604
N	0.278709	1.618441	-0.695858
C	1.553118	-0.376812	1.293203
H	1.702693	0.698890	1.157663
C	2.272896	-0.810989	2.583663
H	2.099425	-1.878347	2.765533
H	1.862978	-0.260782	3.438889
C	3.789791	-0.577972	2.468763
H	3.999530	0.496241	2.377890
H	4.274834	-0.917390	3.389013
C	4.356838	-1.325435	1.256411
H	4.242002	-2.408465	1.395558
H	5.428986	-1.132364	1.152709
C	3.643474	-0.884884	-0.035675
H	4.047131	-1.430206	-0.896181
H	3.843520	0.182906	-0.191212
C	2.127550	-1.119061	0.078627
H	1.961523	-2.191757	0.226839
C	-0.354949	-1.910382	1.844142
H	-0.080170	-1.989523	2.900121
H	0.129837	-2.706830	1.279767
H	-1.436759	-2.013380	1.749802
C	1.381692	-1.993841	-2.119982
H	2.406994	-2.156254	-2.470205
H	0.726410	-1.803928	-2.971320
H	1.042151	-2.876473	-1.579039
C	-0.670436	0.469525	2.110925
H	-0.123277	1.413458	2.008764
H	-0.688171	0.208186	3.174839
C	1.866879	0.364828	-1.992088
H	1.388481	0.307025	-2.976893
H	2.947751	0.288652	-2.133902
C	-2.070742	0.632674	1.567487
C	-3.166811	1.019330	2.333818
H	-3.053196	1.165564	3.403901
C	-4.400318	1.218047	1.709372
H	-5.265380	1.521743	2.291425
C	-4.506124	1.019042	0.332142
H	-5.445634	1.168566	-0.189846
C	-3.381915	0.620808	-0.382699
C	1.458593	1.660948	-1.367019
C	2.154059	2.853959	-1.546892
H	3.098550	2.850275	-2.082503
C	1.612143	4.040466	-1.055602
H	2.134379	4.982673	-1.192348
C	0.378654	3.997654	-0.405240

H	-0.093417	4.898439	-0.027189
C	-0.258995	2.773886	-0.243625
H	-1.223923	2.705289	0.242628
H	-3.394400	0.452263	-1.454458
C	-1.976922	-2.943191	-1.131291
C	-2.729658	-4.131119	-1.492246
H	-3.599896	-4.235218	-0.835944
H	-3.069699	-4.043504	-2.529853
H	-2.097624	-5.020042	-1.395264

$[Fe(O)(cyclam\text{-}acetate)]^{+}$

Cartesian coordinate of the gas phase structure of $[Fe(O)(cyclam\text{-}acetate)]^{+}$ optimised at TPSS/TZVP level of theory, E = -2181.16326939 Hartree, $\langle S^2 \rangle$ = 2.015.

Fe	1.944595	1.791137	-2.399958
N	0.029632	2.498792	-2.364680
H	-0.257185	2.186583	-1.431845
N	1.376238	-0.090703	-2.904821
H	1.102911	-0.475252	-1.995373
N	3.841254	1.082650	-2.514302
H	4.157993	1.368510	-3.447006
N	2.527740	3.736360	-2.147023
O	1.861043	1.469801	-0.761870
O	2.039841	2.196378	-4.291482
O	2.235340	3.882094	-5.783919
C	-0.940629	1.982993	-3.375350
H	-0.602849	2.337135	-4.353255
H	-1.926491	2.419611	-3.168314
C	-1.029689	0.458215	-3.364314
H	-1.849070	0.170283	-4.032349
H	-1.308206	0.092650	-2.365686
C	0.236974	-0.236967	-3.860343
H	0.043860	-1.307603	-4.008087
H	0.564513	0.196203	-4.809112
C	2.593738	-0.817263	-3.379954
H	2.434345	-1.901861	-3.359742
H	2.767600	-0.508073	-4.415065
C	3.753539	-0.409258	-2.489668
H	3.571443	-0.700838	-1.450837
H	4.693954	-0.863220	-2.823810
C	4.787542	1.599972	-1.483907
H	4.383970	1.292624	-0.515158
H	5.766185	1.123840	-1.629110
C	4.935014	3.117856	-1.548966
H	5.329450	3.421500	-2.527463
H	5.703225	3.405797	-0.821896
C	3.669952	3.894950	-1.181477
H	3.297184	3.541911	-0.215954
H	3.901950	4.965819	-1.103006

C	1.314378	4.399879	-1.559298
H	1.444210	5.489528	-1.556171
H	1.228489	4.045744	-0.528193
C	0.091469	3.991299	-2.359541
H	-0.820633	4.420612	-1.928290
H	0.160894	4.324802	-3.399288
C	2.839728	4.318493	-3.498370
H	3.924068	4.393728	-3.612462
H	2.434605	5.331448	-3.582636
C	2.320436	3.439162	-4.654481

Optimised structures and free energies used to determine the spin state of the Fe(IV) complex of tpena$^-$.

The free energy of both the triplet and quintet state of $[Fe(O)(tpenaH)]^{2+}$ were calculated with two different functionals TPSSh and PBE for both functionals the triplet state had the lowest energy by 24.9 kJ/mol and 34.7 kJ/mol respectively.

$[Fe(O)(tpenaH)]^{2+}$, TPSSh, S = 1.

Cartesian coordinate of the gas phase structure of $[Fe(O)(tpenaH)]^{2+}$ optimised at TPSSh/TZVP level of theory, G = -2615.398918 Hartree, $\langle S^2 \rangle$ = 2.020.

C	0.514906	-2.792369	0.016392
C	1.694535	-1.830849	-0.153506
H	2.567938	-2.176946	0.419835
H	1.933115	-1.827007	-1.226870
C	1.262915	-0.220919	1.709508
H	1.282547	0.867643	1.878346
H	2.147678	-0.666071	2.197611
C	-0.005746	-0.804653	2.329780
H	-0.022475	-1.897354	2.236845
H	-0.031756	-0.564345	3.406463
C	-2.401202	-1.151398	1.711338
H	-2.952346	-0.990723	2.651529
H	-2.044357	-2.190799	1.682194
C	-3.272619	-0.923043	0.499912
C	-4.648367	-1.148078	0.482683
H	-5.162888	-1.441392	1.399439
C	-5.345438	-1.011688	-0.721878
H	-6.421605	-1.192195	-0.757687
C	-4.646969	-0.647963	-1.875500
H	-5.151129	-0.541783	-2.836887
C	-3.275138	-0.421675	-1.790683
H	-2.668577	-0.146030	-2.653156
C	-1.534084	1.137210	2.038877
H	-2.604038	1.182790	2.296026
H	-0.988973	1.397950	2.961248
C	-1.261525	2.148276	0.952569

C	-1.448590	3.519519	1.152913
H	-1.758557	3.889118	2.132498
C	-1.255038	4.396492	0.084525
H	-1.405117	5.469942	0.216983
C	-0.880083	3.874871	-1.158577
H	-0.734438	4.520732	-2.025735
C	-0.701709	2.501350	-1.285185
H	-0.419425	2.023345	-2.224636
C	2.168039	0.566042	-0.483033
H	1.855658	0.534627	-1.536429
H	1.930632	1.565195	-0.089339
C	3.663133	0.320816	-0.421352
C	4.376984	-0.337007	-1.422776
H	3.845579	-0.697362	-2.304804
C	5.761204	-0.519392	-1.304492
H	6.311034	-1.034174	-2.095865
C	6.438347	-0.036166	-0.177982
H	7.515625	-0.160083	-0.058418
C	5.712213	0.628857	0.797582
H	6.152287	1.056464	1.698998
N	-2.615349	-0.549726	-0.625684
N	-0.878131	1.656356	-0.244946
N	1.303888	-0.433452	0.223950
N	-1.200692	-0.259923	1.622374
N	4.375373	0.782005	0.645666
O	-0.650296	-2.213354	-0.199754
O	0.674335	-3.957290	0.305911
O	-0.246963	-0.238316	-1.995144
Fe	-0.679321	-0.340943	-0.417906
H	3.879099	1.298459	1.373059

$[Fe(O)(tpenaH)]^{2+}$, TPSSh, S = 2.

Cartesian coordinate of the gas phase structure of $[Fe(O)(tpenaH)]^{2+}$ optimised at TPSSh/TZVP level of theory, G = -2615.389452 Hartree, $\langle S^2 \rangle$ = 6.051.

C	0.504869	-2.789790	-0.047278
C	1.735040	-1.878674	-0.151018
H	2.545940	-2.278570	0.479440
H	2.048508	-1.920123	-1.204941
C	1.278064	-0.189252	1.626180
H	1.296005	0.904833	1.756218
H	2.116415	-0.617801	2.208003
C	-0.023788	-0.749623	2.205538
H	-0.036293	-1.844400	2.132849
H	-0.076628	-0.495757	3.278271
C	-2.408017	-1.146228	1.676050
H	-2.839585	-1.032057	2.683835
H	-2.040092	-2.177411	1.566602
C	-3.432642	-0.893348	0.594774

C	-4.796531	-1.131936	0.762690
H	-5.184786	-1.452509	1.731180
C	-5.649062	-0.969343	-0.335094
H	-6.719539	-1.158103	-0.230811
C	-5.116085	-0.566905	-1.562774
H	-5.748668	-0.437718	-2.442003
C	-3.745398	-0.332523	-1.652336
H	-3.267854	-0.021934	-2.583034
C	-1.589013	1.162271	1.888212
H	-2.688452	1.228693	1.928517
H	-1.224556	1.380816	2.905572
C	-1.116565	2.197325	0.898445
C	-1.124576	3.565991	1.182259
H	-1.396519	3.916763	2.179770
C	-0.808900	4.471206	0.165580
H	-0.822232	5.545370	0.362672
C	-0.491402	3.985478	-1.108363
H	-0.259032	4.661113	-1.932877
C	-0.483178	2.609881	-1.316202
H	-0.250134	2.154082	-2.280642
C	2.319837	0.477858	-0.540273
H	2.064148	0.418698	-1.607783
H	2.094848	1.500269	-0.200416
C	3.808296	0.205673	-0.404201
C	4.557767	-0.482017	-1.358753
H	4.066603	-0.832982	-2.267605
C	5.925941	-0.706502	-1.159436
H	6.504471	-1.243283	-1.914893
C	6.551812	-0.238209	0.002972
H	7.615703	-0.395626	0.185557
C	5.791613	0.453649	0.932042
H	6.191292	0.870866	1.856781
N	-2.930088	-0.488652	-0.594211
N	-0.780252	1.739239	-0.327708
N	1.416660	-0.462708	0.172190
N	-1.231075	-0.234520	1.489401
N	4.471274	0.648781	0.701065
O	-0.621883	-2.182963	-0.363261
O	0.605567	-3.949258	0.287615
O	-0.425351	-0.181181	-2.188654
Fe	-0.813833	-0.311316	-0.605831
H	3.949310	1.183338	1.396480

[Fe(O)(tpenaH)]$^{2+}$, PBE, S = 1.

Cartesian coordinate of the gas phase structure of [Fe(O)(tpenaH)]$^{2+}$ optimised at PBE/TZVP level of theory, G = -2613.454004, Hartree, <S^2> =2.019.

C	0.496717	-2.819037	0.012750
C	1.688665	-1.861518	-0.142888

H	2.558120	-2.222321	0.443797
H	1.942984	-1.877183	-1.221077
C	1.271576	-0.227909	1.701565
H	1.300289	0.869869	1.862750
H	2.161213	-0.673048	2.200688
C	0.598000	-0.796047	2.336367
H	-0.022709	-1.898310	2.257626
H	-0.009500	-0.550437	3.421370
C	-2.408230	-1.128712	1.732432
H	-2.962815	-0.968713	2.681133
H	-2.061111	-2.181069	1.705739
C	-3.284120	-0.901857	0.522530
C	-4.667984	-1.112509	0.513540
H	-5.182843	-1.391898	1.444514
C	-5.374471	-0.981991	-0.691751
H	-6.460854	-1.153190	-0.719139
C	-4.676216	-0.635584	-1.857221
H	-5.188041	-0.532920	-2.824575
C	-3.296607	-0.420052	-1.784054
H	-2.687838	-0.155679	-2.659642
C	-1.516381	1.156582	2.040122
H	-2.592049	1.219918	2.307264
H	-0.967188	1.426821	2.967817
C	-1.241164	2.158865	0.944883
C	-1.407005	3.538698	1.141264
H	-1.701624	3.917931	2.131399
C	-1.214684	4.413526	0.064230
H	-1.349339	5.497573	0.195652
C	-0.862001	3.878748	-1.185565
H	-0.717744	4.523029	-2.064722
C	-0.702933	2.497308	-1.310300
H	-0.436336	2.007767	-2.258916
C	2.178856	0.534071	-0.504079
H	1.863875	0.483609	-1.566465
H	1.926846	1.547838	-0.133228
C	3.673873	0.304878	-0.429328
C	4.401724	-0.403048	-1.395952
H	3.873002	-0.811876	-2.269054
C	5.790398	-0.570943	-1.261513
H	6.352694	-1.125050	-2.029097
C	6.460537	-0.023482	-0.153333
H	7.546445	-0.134049	-0.021018
C	5.722562	0.689348	0.786750
H	6.159972	1.170294	1.673087
N	-2.628236	-0.544828	-0.617421
N	-0.877084	1.653619	-0.261185
N	1.313686	-0.457132	0.217468
N	-1.200275	-0.249411	1.640857

N	4.381101	0.826089	0.620041
O	-0.671958	-2.235304	-0.209705
O	0.643352	-3.995553	0.292993
O	-0.257381	-0.248315	-2.017099
Fe	-0.694490	-0.341149	-0.425258
H	3.872601	1.379966	1.320285

$[Fe(O)(tpenaH)]^{2+}$, PBE, S = 2.

Cartesian coordinate of the gas phase structure of $[Fe(O)(tpenaH)]^{2+}$ optimised at PBE/TZVP level of theory, G = -2613.440801 *Hartree,* $<S^2> = 6.034$.

C	0.448886	-2.811386	-0.064099
C	1.709193	-1.930629	-0.158484
H	2.503501	-2.358875	0.489994
H	2.037080	-2.008832	-1.214746
C	1.299779	-0.195480	1.582170
H	1.331164	0.908973	1.690964
H	2.141392	-0.618206	2.181141
C	-0.005133	-0.728103	2.187898
H	-0.028867	-1.832683	2.138531
H	-0.031825	-0.461118	3.267745
C	-2.407831	-1.106596	1.704902
H	-2.823797	-0.990605	2.728881
H	-2.054931	-2.152881	1.595671
C	-3.456746	-0.855655	0.643509
C	-4.823814	-1.084107	0.846740
H	-5.193383	-1.393476	1.835606
C	-5.704987	-0.927287	-0.235468
H	-6.781899	-1.110067	-0.102147
C	-5.198041	-0.538203	-1.484403
H	-5.855912	-0.412598	-2.356086
C	-3.823036	-0.311243	-1.609764
H	-3.361285	-0.008819	-2.561659
C	-1.555798	1.195811	1.871539
H	-2.662648	1.289532	1.894687
H	-1.208149	1.422498	2.902713
C	-1.051997	2.216204	0.880724
C	-1.002931	3.589145	1.168340
H	-1.247556	3.949066	2.178923
C	-0.668756	4.488755	0.145553
H	-0.638755	5.570338	0.347185
C	-0.388737	3.993270	-1.138998
H	-0.142911	4.666957	-1.972398
C	-0.434743	2.613192	-1.351233
H	-0.232305	2.145005	-2.327158
C	2.347638	0.408464	-0.602557
H	2.107357	0.303950	-1.679820
H	2.106577	1.453256	-0.316935
C	3.833601	0.154262	-0.422655

C	4.603906	-0.625575	-1.296864
H	4.126516	-1.057626	-2.188264
C	5.970252	-0.836465	-1.048110
H	6.567262	-1.445099	-1.744860
C	6.575669	-0.263513	0.084848
H	7.642965	-0.407425	0.305862
C	5.796944	0.516226	0.933606
H	6.183605	1.019253	1.831140
N	-2.981190	-0.464299	-0.566999
N	-0.750906	1.748777	-0.357615
N	1.437615	-0.503323	0.136455
N	-1.224065	-0.212303	1.492988
N	4.478532	0.694945	0.656112
O	-0.661461	-2.179668	-0.413434
O	0.511905	-3.976828	0.284853
O	-0.504093	-0.169446	-2.244535
Fe	-0.857447	-0.299003	-0.637678
H	3.939822	1.297988	1.289842

Optimised structures and free energies used in attempt to determine if the carboxylate arm or a pyridyl arm is decoordinated in 2.

Structures in which either a pyridyl or the carboxylate arm is decoordinated were optimised in the gas phase and their free energy calculated. As the charge distribution in the two complexes are very different a single point calculation with a pcm solvent model[22] was performed to account for the very different interactions expected for these two structures with the aqueous environment. The outcome was that the free energy in solution was only 2 kJ/mol lower for the configuration with the pyridyl arm decoordinated. This difference is within the error margin of DFT and hence no conclusion regarding which arm is decoordinated can be made based on the calculated free energies.

The calculated values for the Mössbauer parameters for the structure of **2** with a dangling pyridyl arm (δ = 0.004 mm/s and ΔE_q = 0.82) are closer to the experimental values of δ = 0.0 mm/s and ΔE_q = 0.8 than the values for the configuration with a dangling carboxylate (δ = 0.010 mm/s and ΔE_q = 0.64).

[Fe(O)(tpena-danglingCH$_2$COOH)]$^{2+}$, TPSS, S = 1.

Cartesian coordinates of the gas phase structure of [Fe(O)(tpenaH)]$^{2+}$, in a configuration where the carboxylate is dangling, optimised at TPSS/TZVP level of theory followed by a frequency calculation and a single point calculation including a pcm model, G(aq, solution) = -6870346.67 kJ/mol, <S^2> =2.017.

6	-1.183018000	2.600728000	-0.232366000
6	-2.295045000	1.600621000	-0.300104000
1	-3.171052000	1.904759000	0.277798000
1	-2.597212000	1.514065000	-1.350668000
6	-1.916441000	0.055341000	1.644967000
1	-2.033236000	-1.016499000	1.832414000

1	-2.810537000	0.551278000	2.029894000
6	-0.652017000	0.572143000	2.314907000
1	-0.540469000	1.650631000	2.184709000
1	-0.683359000	0.361996000	3.391591000
6	1.829292000	0.607836000	1.897034000
1	2.263420000	0.343903000	2.867962000
1	1.629557000	1.684972000	1.902934000
6	2.757845000	0.269714000	0.753971000
6	4.143960000	0.216133000	0.859758000
1	4.619245000	0.366373000	1.824677000
6	4.906267000	-0.025085000	-0.286195000
1	5.989490000	-0.069128000	-0.223379000
6	4.258105000	-0.208632000	-1.507898000
1	4.814998000	-0.392341000	-2.420942000
6	2.868763000	-0.157273000	-1.553511000
1	2.304785000	-0.288773000	-2.470916000
6	0.630366000	-1.542044000	2.072276000
1	1.609466000	-1.712136000	2.532392000
1	-0.117067000	-1.753198000	2.845490000
6	0.455363000	-2.477589000	0.903728000
6	0.551031000	-3.862570000	1.043066000
1	0.739906000	-4.295309000	2.021457000
6	0.409940000	-4.672949000	-0.081125000
1	0.484566000	-5.752695000	0.007500000
6	0.181181000	-4.072693000	-1.321806000
1	0.076799000	-4.664511000	-2.225414000
6	0.088778000	-2.690303000	-1.396591000
1	-0.085259000	-2.160648000	-2.327744000
6	-2.698675000	-0.793375000	-0.556154000
1	-2.510148000	-0.695838000	-1.630552000
1	-2.369954000	-1.788280000	-0.242631000
6	-4.201077000	-0.647672000	-0.237785000
8	-5.029092000	-1.444926000	-0.940769000
1	-4.568777000	-1.981790000	-1.612392000
7	2.135426000	0.076916000	-0.442658000
7	0.213932000	-1.904010000	-0.297771000
7	-1.843058000	0.226631000	0.134657000
7	0.525807000	-0.093352000	1.665748000
8	-4.629987000	0.110093000	0.600533000
7	0.073559000	2.098266000	-0.324040000
6	-1.422990000	3.973708000	-0.190428000
8	-0.125173000	0.072767000	-2.023645000
26	0.155882000	0.088366000	-0.392314000
6	-0.349029000	4.856376000	-0.281144000
6	0.939263000	4.336322000	-0.418519000
6	1.113434000	2.959250000	-0.432431000
1	-2.442152000	4.338284000	-0.103662000
1	-0.514519000	5.929365000	-0.257606000

1	1.803926000	4.984866000	-0.513489000
1	2.097230000	2.520605000	-0.541671000

[Fe(O)(tpena-danglingCH$_2$PyH)]$^{2+}$, TPSS, S = 1.

Cartesian coordinate of the gas phase structure of [Fe(O)(tpenaH)]$^{2+}$, in a configuration where the pyridyl arm is dangling, optimised at TPSS/TZVP level of theory followed by a frequency calculation and a single point calculation including a pcm model, G(aq, solution) = -6870348.975 kJ/mol, <S^2> = 2.017.

C	0.522890	-2.809445	0.008323
C	1.704996	-1.844602	-0.153818
H	2.567823	-2.186308	0.427051
H	1.952379	-1.837825	-1.219376
C	1.276817	-0.227545	1.711575
H	1.298964	0.856069	1.878026
H	2.158014	-0.676080	2.190112
C	0.005460	-0.811206	2.333817
H	-0.016484	-1.897055	2.232405
H	-0.019172	-0.572653	3.405171
C	-2.401040	-1.143268	1.723304
H	-2.944643	-0.971349	2.659206
H	-2.047771	-2.177949	1.697810
C	-3.274617	-0.914568	0.512010
C	-4.648119	-1.136742	0.496799
H	-5.159905	-1.418489	1.412137
C	-5.345127	-1.011009	-0.706085
H	-6.415680	-1.189259	-0.738719
C	-4.648477	-0.663231	-1.863104
H	-5.152194	-0.568107	-2.819258
C	-3.278996	-0.436444	-1.786789
H	-2.676204	-0.174113	-2.649047
C	-1.510080	1.148999	2.050741
H	-2.564177	1.193846	2.345118
H	-0.927797	1.407362	2.943618
C	-1.268695	2.152796	0.947739
C	-1.477968	3.519884	1.133861
H	-1.788482	3.891936	2.106257
C	-1.304300	4.389369	0.059052
H	-1.472239	5.455152	0.182214
C	-0.927835	3.864256	-1.179646
H	-0.798647	4.502524	-2.047690
C	-0.726459	2.496239	-1.299352
H	-0.445400	2.017642	-2.232339
C	2.172951	0.560406	-0.496044
H	1.864461	0.509335	-1.544320
H	1.922791	1.555093	-0.114385
C	3.669594	0.325994	-0.422788
C	4.388419	-0.360689	-1.397607
H	3.861565	-0.752319	-2.261566

C	5.771062	-0.528165	-1.274878
H	6.321080	-1.062818	-2.044136
C	6.445464	-0.899000	-0.169010
H	7.517811	-0.112004	-0.049652
C	5.721598	0.693953	0.782508
H	6.158644	1.155710	1.660992
N	-2.614210	-0.553964	-0.619289
N	-0.883413	1.652438	-0.249517
N	1.307398	-0.442687	0.220553
N	-1.190296	-0.255072	1.625212
N	4.379512	0.833313	0.628792
O	-0.648663	-2.226469	-0.182337
O	0.682283	-3.983958	0.268848
O	-0.239825	-0.246682	-2.004856
Fe	-0.677805	-0.341871	-0.411914
H	3.879654	1.374477	1.332992

Potentiometric titration of $3(ClO_4)_4 \cdot 2H_2O$

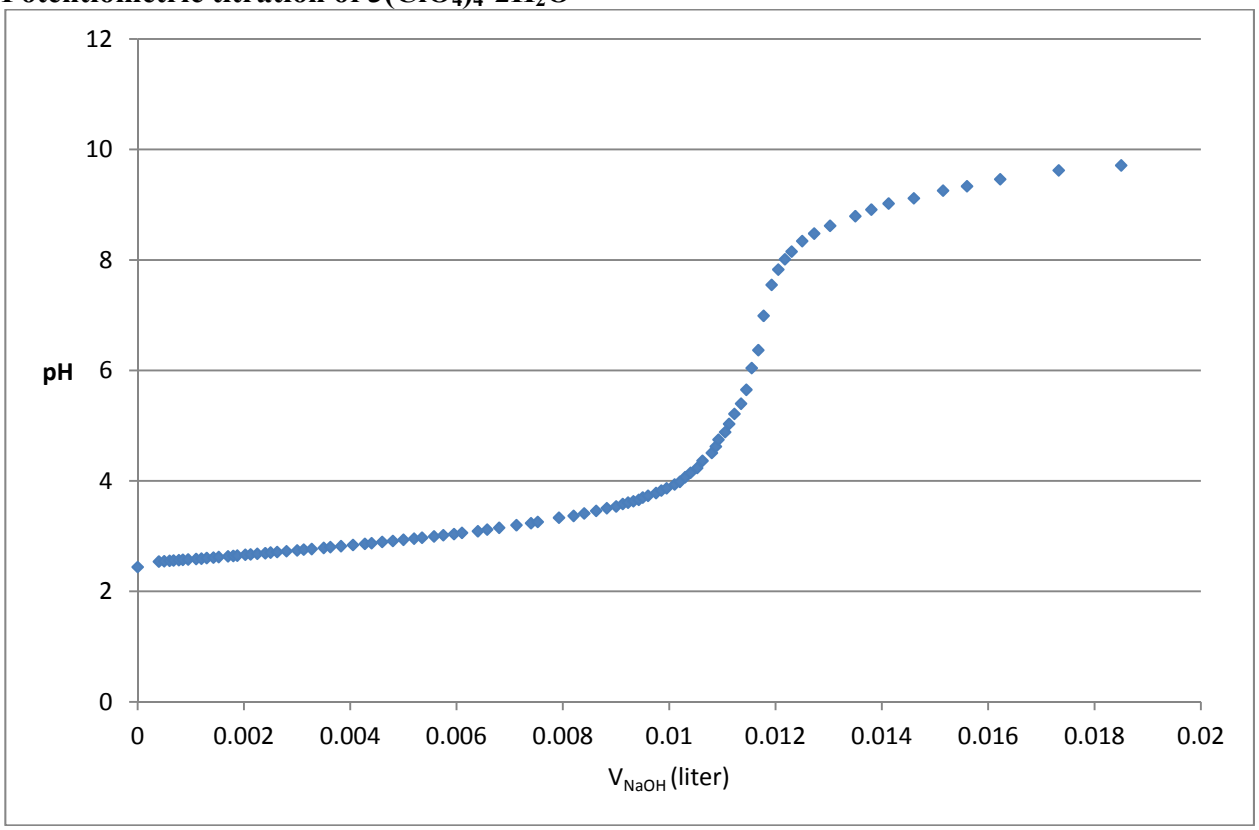

Figure S13. 69.2 mg of **3**$(ClO_4)_4 \cdot 2H_2O$ was added to 15 ml of water. This solution was titrated with 0.0101 M NaOH while the pH was measured by a pH electrode from Metrohm product number 6.0220.100 monitored on a PHM 240 PH/ION meter from Meterlab, Radiometer Copenhagen.

Optimised structures and free energies used to assign the spin state of 2

DFT calculations have been used to address whether or not it is reasonable to assign the low spin signal observed in both EPR and Mössbauer spectroscopy to a species formulated as

$[Fe(OH)(tpenaH)]^{2+}$ (dangling pyridinium arm). For two different functionals, TPSS and TPSSh, $[Fe(OH)(tpenaH)]^{2+}$, the low spin ground state was favoured by 69.6 kJ/mol and 28.4 kJ/mol respectively, compared the high spin state.

$[Fe(OH)(tpenaH)]^{2+}$, TPSS, S = 0.5.

Cartesian coordinates of the gas phase structure of $[Fe(OH)(tpenaH)]^{2+}$, optimised at TPSS/TZVP, E = -6871478.69 kJ/mol, $\langle S^2 \rangle$ =0.773.

6	0.449358000	-2.818780000	0.016058000
6	1.651072000	-1.874035000	-0.120676000
1	2.490576000	-2.228361000	0.486800000
1	1.929605000	-1.892158000	-1.178132000
6	1.253150000	-0.199296000	1.694892000
1	1.274951000	0.887998000	1.833307000
1	2.131116000	-0.635547000	2.191431000
6	-0.019380000	-0.769236000	2.326624000
1	-0.038833000	-1.857533000	2.247613000
1	-0.053178000	-0.507325000	3.391937000
6	-2.426515000	-1.131642000	1.732165000
1	-2.953639000	-0.955159000	2.676716000
1	-2.067991000	-2.164012000	1.704672000
6	-3.312256000	-0.892045000	0.534007000
6	-4.688970000	-1.092949000	0.536585000
1	-5.188413000	-1.403778000	1.449351000
6	-5.408029000	-0.900089000	-0.644137000
1	-6.481595000	-1.060744000	-0.664747000
6	-4.728430000	-0.492483000	-1.791748000
1	-5.250055000	-0.326349000	-2.728468000
6	-3.353887000	-0.293904000	-1.727957000
1	-2.778983000	0.034234000	-2.587328000
6	-1.554606000	1.176898000	2.000250000
1	-2.636915000	1.236961000	2.158085000
1	-1.081948000	1.416102000	2.960154000
6	-1.172203000	2.174346000	0.932403000
6	-1.276349000	3.551702000	1.122701000
1	-1.578086000	3.944468000	2.089641000
6	-1.013311000	4.408516000	0.054304000
1	-1.099829000	5.483739000	0.179175000
6	-0.656732000	3.859629000	-1.179735000
1	-0.463059000	4.489633000	-2.041877000
6	-0.555069000	2.479986000	-1.302553000
1	-0.289030000	1.981592000	-2.229736000
6	2.166584000	0.507277000	-0.532379000
1	1.866663000	0.412558000	-1.580946000
1	1.923629000	1.518076000	-0.190898000
6	3.657814000	0.262948000	-0.425017000
6	4.390187000	-0.480484000	-1.347531000
1	3.877697000	-0.906585000	-2.203561000

6	5.766504000	-0.659464000	-1.184110000
1	6.326876000	-1.237789000	-1.913169000
6	6.423407000	-0.087057000	-0.089373000
1	7.490962000	-0.206509000	0.060343000
6	5.688260000	0.663475000	0.808788000
1	6.111478000	1.162952000	1.673244000
7	-2.656252000	-0.499460000	-0.591124000
7	-0.796468000	1.648403000	-0.259083000
7	1.280491000	-0.455604000	0.213473000
7	-1.220661000	-0.236557000	1.602251000
7	4.351919000	0.812353000	0.616651000
8	-0.714667000	-2.218567000	-0.182349000
8	0.593462000	-4.000210000	0.255751000
8	-0.187217000	-0.297679000	-2.117476000
26	-0.715444000	-0.335554000	-0.369352000
1	-0.632936000	-0.969470000	-2.664217000
1	3.843056000	1.395246000	1.279798000

$[Fe(OH)(tpenaH)]^{2+}$, TPSS, S = 2.5.

Cartesian coordinates of the gas phase structure of $[Fe(OH)(tpenaH)]^{2+}$, optimised at TPSS/TZVP level of theory, E = -6871403.987 kJ/mol, $\langle S^2 \rangle$ = 8.757.

6	0.490130000	-2.872973000	0.010321000
6	1.737826000	-1.970191000	-0.075597000
1	2.494211000	-2.315564000	0.638973000
1	2.129021000	-2.097887000	-1.090172000
6	1.302655000	-0.150911000	1.553906000
1	1.293814000	0.944616000	1.604998000
1	2.167462000	-0.521148000	2.126391000
6	0.030833000	-0.702979000	2.209879000
1	0.024800000	-1.794494000	2.163306000
1	0.037159000	-0.422999000	3.273208000
6	-2.366330000	-1.117916000	1.743024000
1	-2.794987000	-1.001811000	2.746872000
1	-2.001387000	-2.144897000	1.637542000
6	-3.415525000	-0.872418000	0.679514000
6	-4.775252000	-1.074617000	0.902846000
1	-5.126815000	-1.368620000	1.887444000
6	-5.670215000	-0.903774000	-0.155106000
1	-6.733541000	-1.063596000	-0.002543000
6	-5.183853000	-0.523280000	-1.406628000
1	-5.848882000	-0.379451000	-2.251679000
6	-3.816666000	-0.325963000	-1.559908000
1	-3.379759000	-0.025841000	-2.507469000
6	-1.539254000	1.193805000	1.910664000
1	-2.631289000	1.268030000	1.976597000
1	-1.147708000	1.433533000	2.908405000
6	-1.080478000	2.222571000	0.895449000
6	-1.104483000	3.588508000	1.186173000

1	-1.379254000	3.928659000	2.180915000
6	-0.798761000	4.502408000	0.178891000
1	-0.824753000	5.569329000	0.381278000
6	-0.476169000	4.027881000	-1.095542000
1	-0.251741000	4.708072000	-1.910817000
6	-0.451257000	2.655841000	-1.311446000
1	-0.218153000	2.212792000	-2.275705000
6	2.317246000	0.364012000	-0.663714000
1	2.106694000	0.185805000	-1.721494000
1	2.041586000	1.400627000	-0.443620000
6	3.804013000	0.159349000	-0.426477000
6	4.614007000	-0.649622000	-1.219434000
1	4.178295000	-1.152469000	-2.076319000
6	5.972578000	-0.799459000	-0.928077000
1	6.594521000	-1.429345000	-1.557775000
6	6.532773000	-0.133720000	0.167216000
1	7.584345000	-0.229168000	0.414948000
6	5.720829000	0.677397000	0.937575000
1	6.066928000	1.247759000	1.792447000
7	-2.950961000	-0.499773000	-0.538004000
7	-0.739767000	1.767983000	-0.328893000
7	1.404533000	-0.527592000	0.114729000
7	-1.198446000	-0.205847000	1.534631000
7	4.405219000	0.796623000	0.621746000
8	-0.610149000	-2.266471000	-0.403425000
8	0.572651000	-4.021326000	0.392230000
8	-0.413085000	-0.067915000	-2.503820000
26	-0.834878000	-0.378927000	-0.723619000
1	-0.419439000	-0.759798000	-3.184986000
1	3.838445000	1.422226000	1.192793000

$[Fe(OH)(tpenaH)]^{2+}$, TPSSh, S = 0.5.

Cartesian coordinates of the gas phase structure of $[Fe(OH)(tpenaH)]^{2+}$, optimised at TPSSh/TZVP level of theory, E = -6871716.241 kJ/mol, $\langle S^2 \rangle$ =0.780.

6	0.464682000	-2.795826000	0.026964000
6	1.657701000	-1.844448000	-0.103664000
1	2.495289000	-2.195273000	0.504317000
1	1.939462000	-1.861240000	-1.157737000
6	1.237893000	-0.183852000	1.705049000
1	1.253528000	0.900617000	1.847987000
1	2.109810000	-0.617013000	2.209725000
6	-0.034245000	-0.759201000	2.324707000
1	-0.045502000	-1.845209000	2.245571000
1	-0.075063000	-0.500658000	3.387975000
6	-2.424211000	-1.132253000	1.718989000
1	-2.958113000	-0.959058000	2.657414000
1	-2.063894000	-2.161485000	1.694185000
6	-3.304242000	-0.902607000	0.517727000

6	-4.674889000	-1.118172000	0.515688000
1	-5.174885000	-1.431163000	1.424418000
6	-5.386832000	-0.936785000	-0.666689000
1	-6.456267000	-1.108328000	-0.692522000
6	-4.707977000	-0.527655000	-1.809498000
1	-5.225406000	-0.371211000	-2.747294000
6	-3.339465000	-0.315882000	-1.737452000
1	-2.763056000	0.012748000	-2.592683000
6	-1.571286000	1.169746000	1.990575000
1	-2.652881000	1.227458000	2.137324000
1	-1.111164000	1.412327000	2.952970000
6	-1.185807000	2.170713000	0.931026000
6	-1.299280000	3.543177000	1.126574000
1	-1.611293000	3.930545000	2.089587000
6	-1.031601000	4.401264000	0.065692000
1	-1.124914000	5.473358000	0.192880000
6	-0.661274000	3.861417000	-1.164074000
1	-0.463879000	4.494609000	-2.019820000
6	-0.551692000	2.486086000	-1.288293000
1	-0.276267000	1.991362000	-2.212083000
6	2.160099000	0.525626000	-0.504146000
1	1.856500000	0.448424000	-1.550466000
1	1.932006000	1.533837000	-0.152170000
6	3.649514000	0.268669000	-0.413772000
6	4.367990000	-0.423880000	-1.378257000
1	3.847825000	-0.802237000	-2.248986000
6	5.741530000	-0.616238000	-1.234426000
1	6.293116000	-1.156827000	-1.995028000
6	6.405941000	-0.108131000	-0.118364000
1	7.471482000	-0.239481000	0.017780000
6	5.680216000	0.592808000	0.821236000
1	6.110659000	1.040611000	1.707307000
7	-2.651400000	-0.508071000	-0.599853000
7	-0.797976000	1.656603000	-0.253155000
7	1.281581000	-0.434917000	0.230664000
7	-1.229253000	-0.235010000	1.597779000
7	4.348698000	0.756382000	0.646643000
8	-0.694234000	-2.208813000	-0.184187000
8	0.622751000	-3.967368000	0.278016000
8	-0.175077000	-0.282484000	-2.107668000
26	-0.708239000	-0.332704000	-0.368812000
1	-0.586656000	-0.969656000	-2.652342000
1	3.848111000	1.300208000	1.343438000

[Fe(OH)(tpenaH)]$^{2+}$, TPSSh, S = 2.5.

Cartesian coordinates of the gas phase structure of [Fe(OH)(tpenaH)]$^{2+}$, optimised at TPSSh/TZVP level of theory, E = -6871687.8 kJ/mol, $\langle S^2 \rangle$ =8.758.

6	0.486332000	-2.856336000	0.019999000

6	1.726761000	-1.953039000	-0.077931000
1	2.490773000	-2.296034000	0.625743000
1	2.106306000	-2.077783000	-1.094774000
6	1.292579000	-0.149415000	1.554177000
1	1.285102000	0.943373000	1.612835000
1	2.155388000	-0.523042000	2.122301000
6	0.023925000	-0.701601000	2.205687000
1	0.019904000	-1.790666000	2.159753000
1	0.026457000	-0.423447000	3.266655000
6	-2.361777000	-1.115650000	1.732846000
1	-2.794536000	-0.997217000	2.731755000
1	-1.999163000	-2.141083000	1.631236000
6	-3.403360000	-0.873627000	0.665889000
6	-4.759570000	-1.078590000	0.882100000
1	-5.114731000	-1.374011000	1.862180000
6	-5.646509000	-0.908775000	-0.177768000
1	-6.707983000	-1.070706000	-0.031614000
6	-5.155757000	-0.526823000	-1.422828000
1	-5.814838000	-0.383750000	-2.269439000
6	-3.791851000	-0.327726000	-1.567076000
1	-3.351986000	-0.026602000	-2.510199000
6	-1.541189000	1.186806000	1.904996000
1	-2.630852000	1.261147000	1.968611000
1	-1.153526000	1.425346000	2.901576000
6	-1.082789000	2.215486000	0.895486000
6	-1.102057000	3.576347000	1.190615000
1	-1.374558000	3.913448000	2.184236000
6	-0.794210000	4.489280000	0.188374000
1	-0.816123000	5.553383000	0.393300000
6	-0.474539000	4.018876000	-1.084201000
1	-0.248214000	4.699014000	-1.895637000
6	-0.455761000	2.651132000	-1.302873000
1	-0.224687000	2.210936000	-2.266153000
6	2.303091000	0.371925000	-0.651082000
1	2.090623000	0.206095000	-1.708108000
1	2.037577000	1.407158000	-0.423680000
6	3.787392000	0.157963000	-0.421678000
6	4.588246000	-0.635784000	-1.230794000
1	4.147922000	-1.124574000	-2.090340000
6	5.945088000	-0.790144000	-0.949972000
1	6.561600000	-1.409929000	-1.590907000
6	6.510335000	-0.143034000	0.148686000
1	7.560925000	-0.242053000	0.388520000
6	5.704037000	0.653796000	0.933113000
1	6.055049000	1.209341000	1.792810000
7	-2.935385000	-0.500043000	-0.543867000
7	-0.745919000	1.765853000	-0.325681000
7	1.392261000	-0.516773000	0.118292000

7	-1.198791000	-0.206424000	1.528987000
7	4.391721000	0.776841000	0.628061000
8	-0.611918000	-2.261129000	-0.392508000
8	0.575708000	-3.993923000	0.414733000
8	-0.393238000	-0.067601000	-2.482916000
26	-0.823367000	-0.377405000	-0.714322000
1	-0.410707000	-0.747324000	-3.169112000
1	3.829722000	1.390161000	1.211234000

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