Supporting Information

for

^{57}Fe Mössbauer and DFT study of the electronic and spatial structure of the iron(II) (pseudo)clathrochelates: the effect of a ligand field strength

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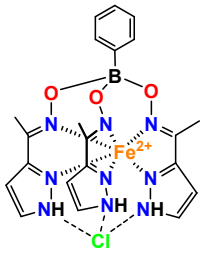


Chemical drawing

Experimental ^{57}Fe Mössbauer data:

δ (Isomer shift, IS, relative to α-Fe) = 0.99 mm/s

ΔE_q (Quadrupole splitting, QS) = 3.55 mm/s

Fe^{2+}@**L1**

X-Ray

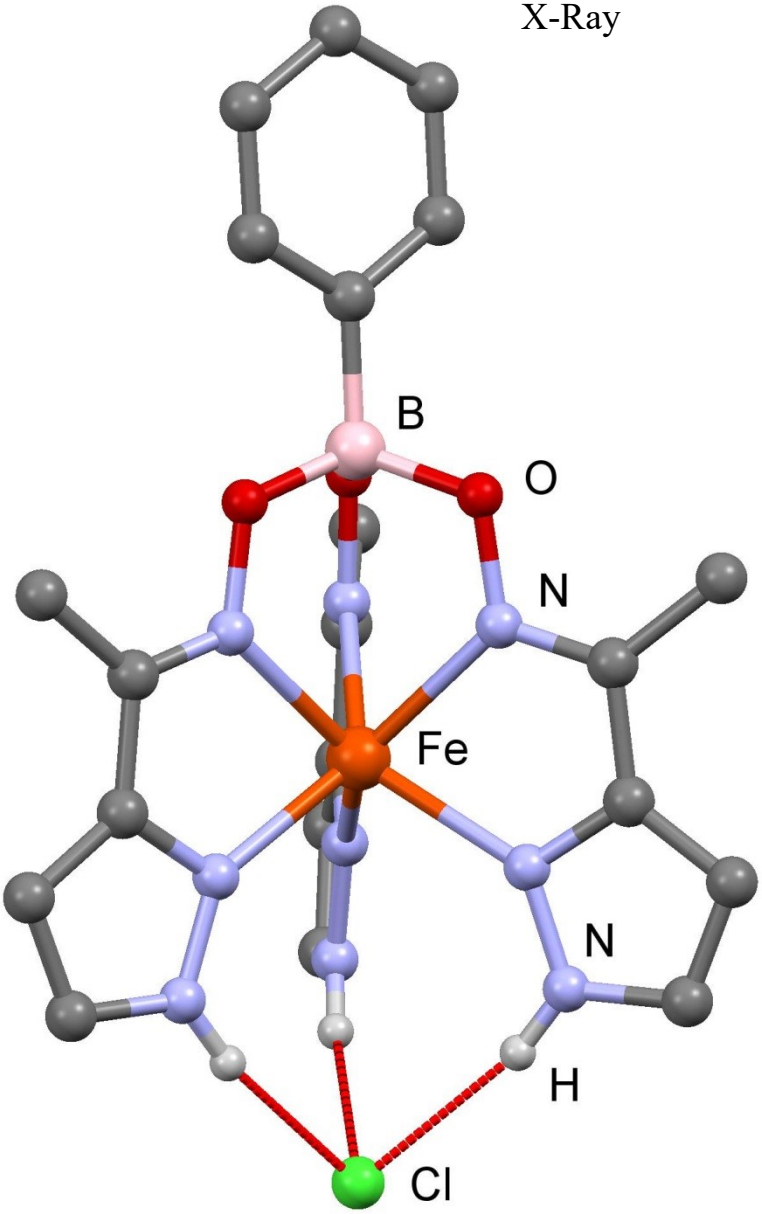
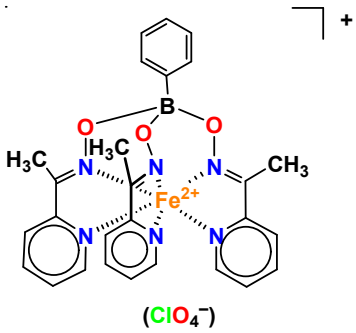


Figure S1. General view of the molecule $Fe(PzOx)_3(BC_6H_5)Cl$
High-spin iron(II) complex



Chemical drawing

Experimental ^{57}Fe Mössbauer data:

δ (Isomer shift, IS, relative to α-Fe) = 0.19 mm/s

ΔE_q (Quadrupole splitting, QS) = 0.0 mm/s

Fe^{2+}@**L2**

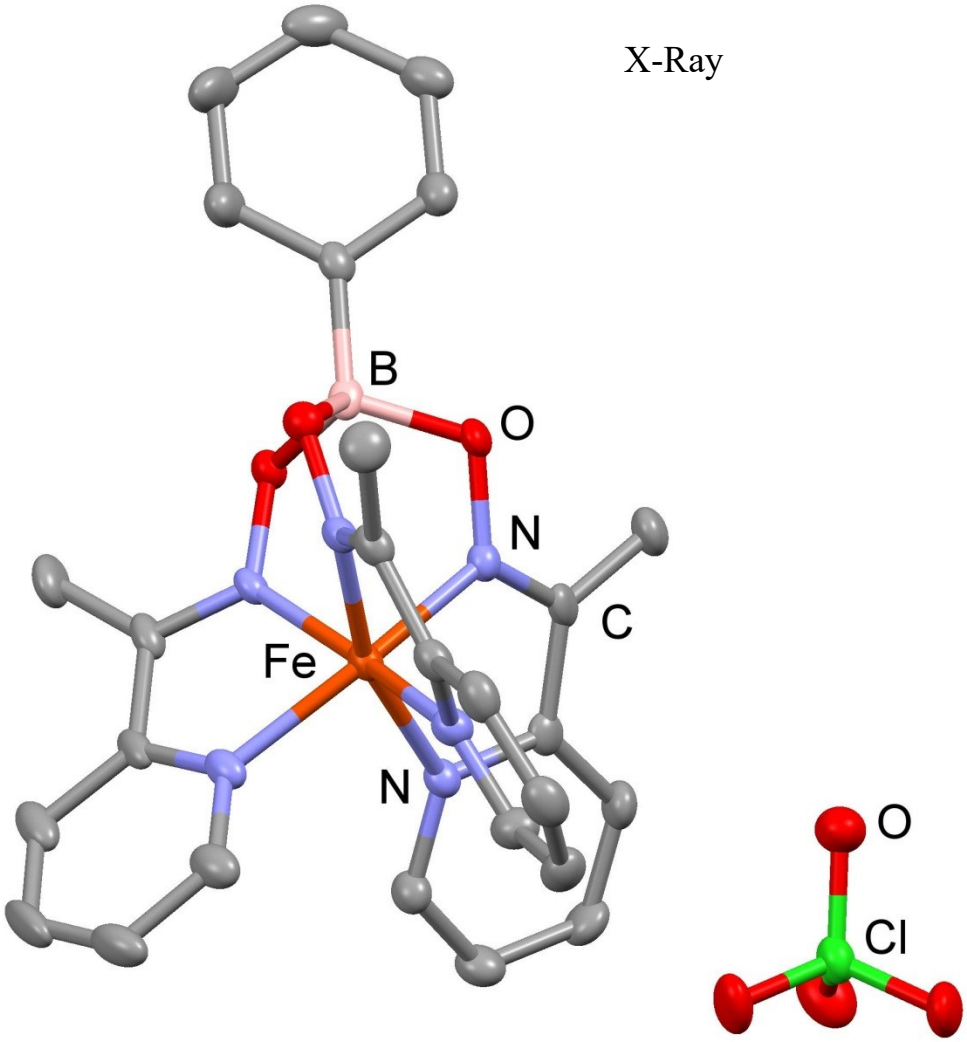
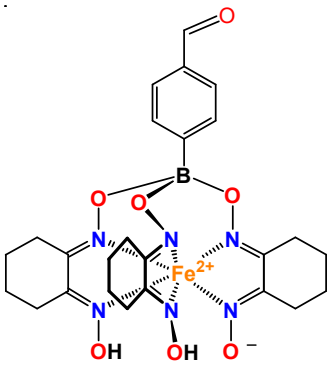


Figure S2. General view of the molecule $[Fe(AcPyOx)_3(BC_6H_5)](ClO_4)$

Low-spin iron(II) complex



Chemical drawing

Experimental ^{57}Fe Mössbauer data:

δ (Isomer shift, IS, relative to α-Fe) = 0.13 mm/s

ΔE_q (Quadrupole splitting, QS) = 0.56 mm/s

Fe^{2+}@**L3**

X-Ray

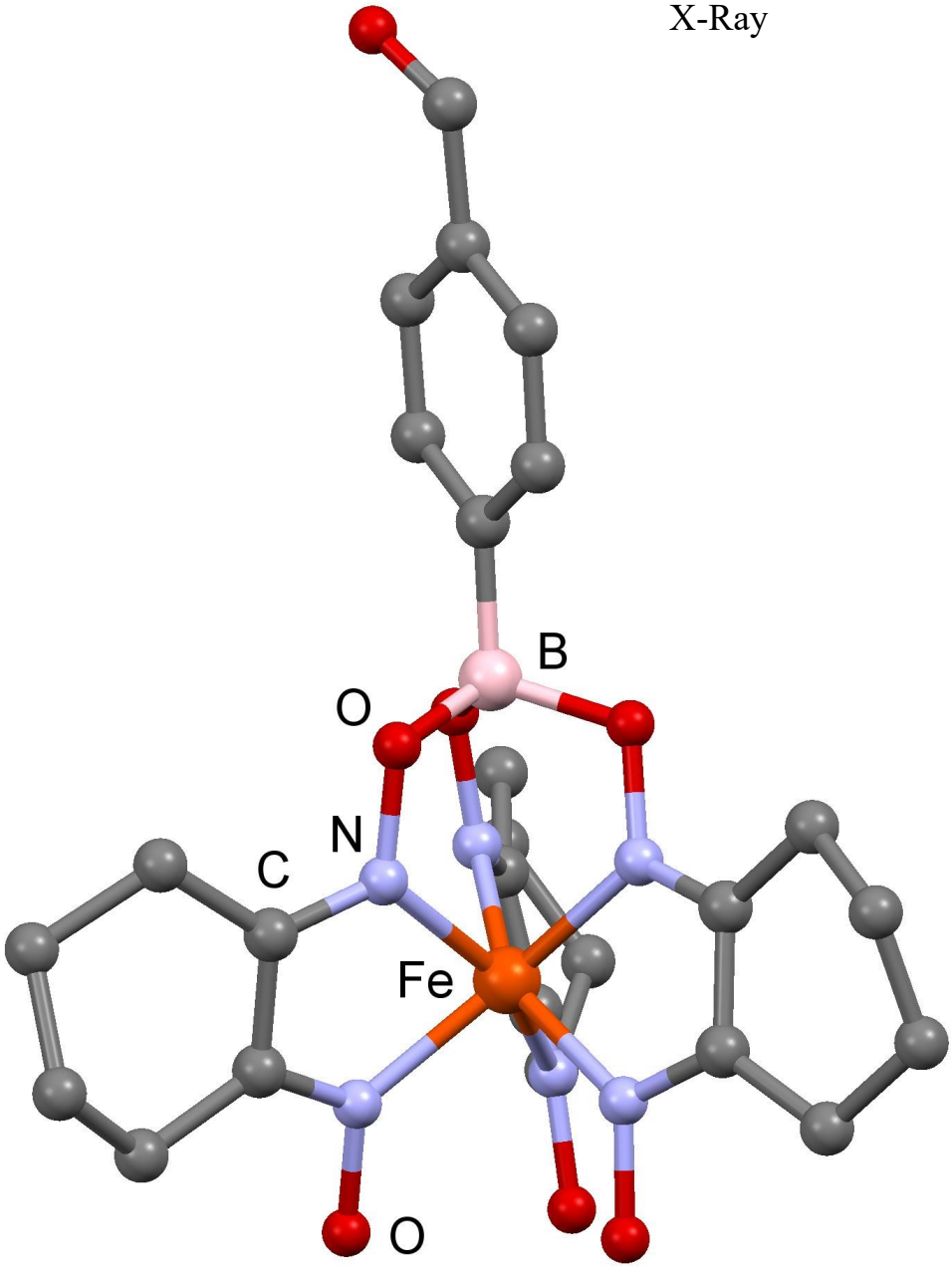
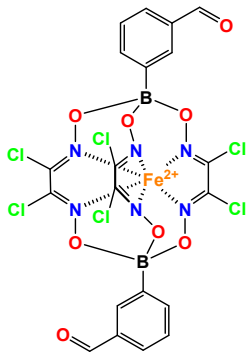


Figure S3. General view of the molecule FeNx(HNx)$_2$(B4-C_6H_4CHO)

Low-spin iron(II) complex



Chemical drawing

Experimental ^{57}Fe Mössbauer data:

δ (Isomer shift, IS, relative to α-Fe) = 0.13 mm/s

ΔE_q (Quadrupole splitting, QS) = 0.71 mm/s

Fe^{2+}@**L4**

X-Ray

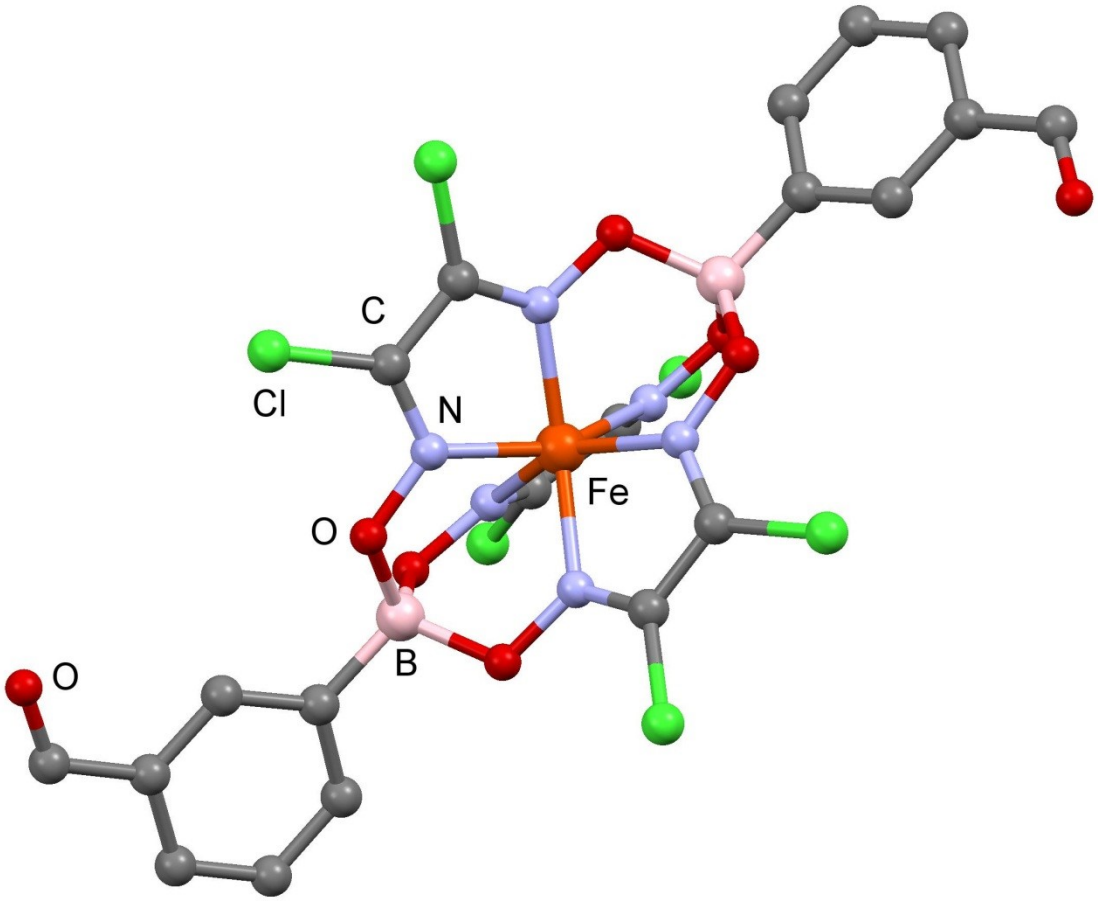
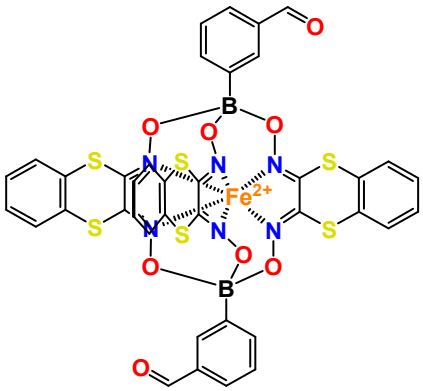


Figure S4. General view of the molecule $Fe(Cl_2Gm)_3(B3\text{-}C_6H_4CHO)_2$

Low-spin iron(II) complex



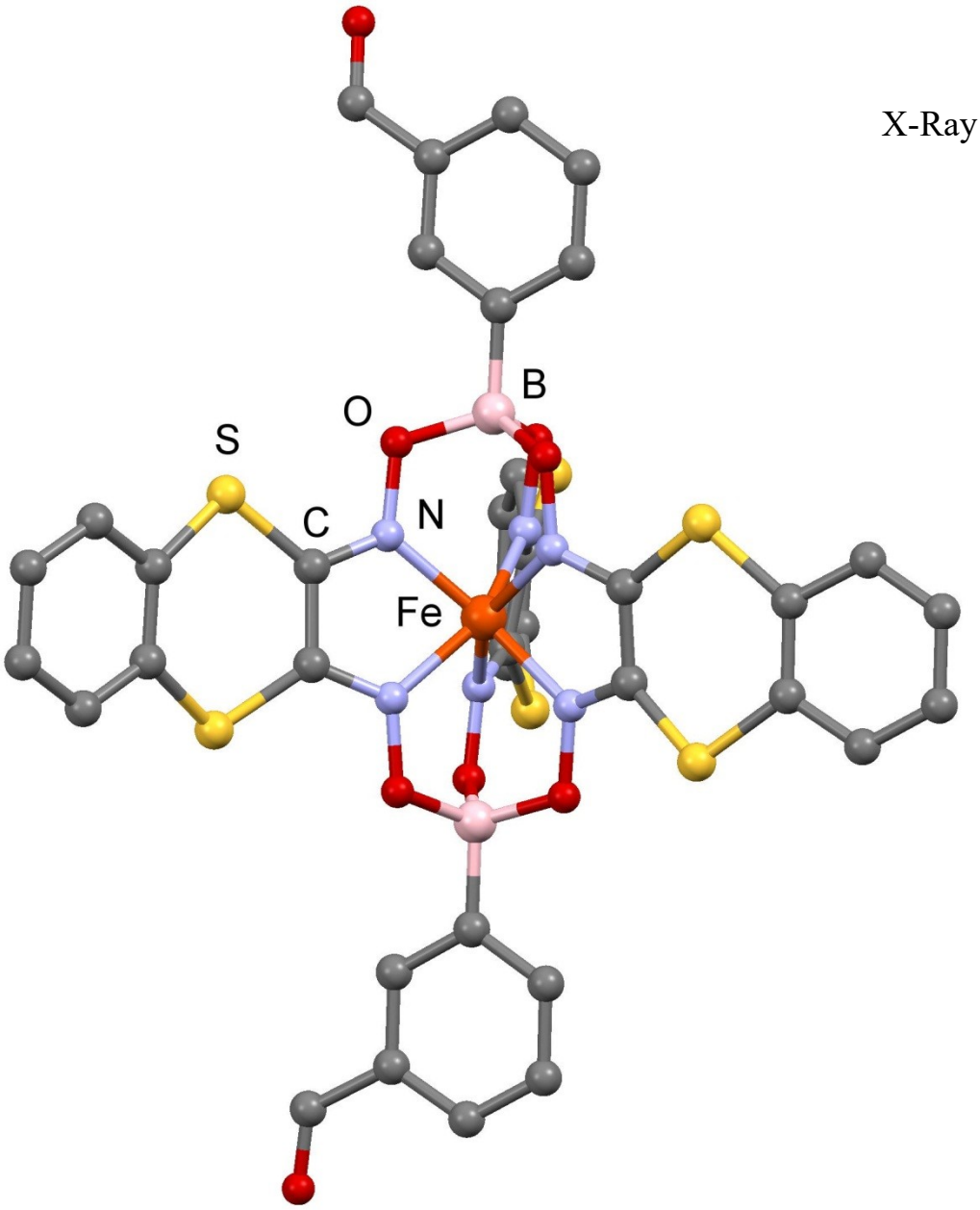
Chemical drawing

Experimental ^{57}Fe Mössbauer data:

δ (Isomer shift, IS, relative to α-Fe) = 0.09 mm/s

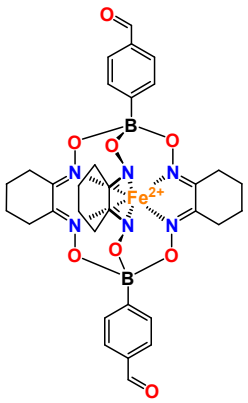
ΔE_q (Quadrupole splitting, QS) = 0.70 mm/s

Fe^{2+}@**L5**



X-Ray

Figure S5. General view of the molecule $Fe(S_2\text{-}C_6H_4Gm)_3(B3\text{-}C_6H_4CHO)_2$ Low-spin iron(II) complex



Chemical drawing

Experimental ^{57}Fe Mössbauer data:

δ (Isomer shift, IS, relative to α-Fe) = 0.03 mm/s

ΔE_q (Quadrupole splitting, QS) = 0.65 mm/s

Fe^{2+}@**L6**

X-Ray

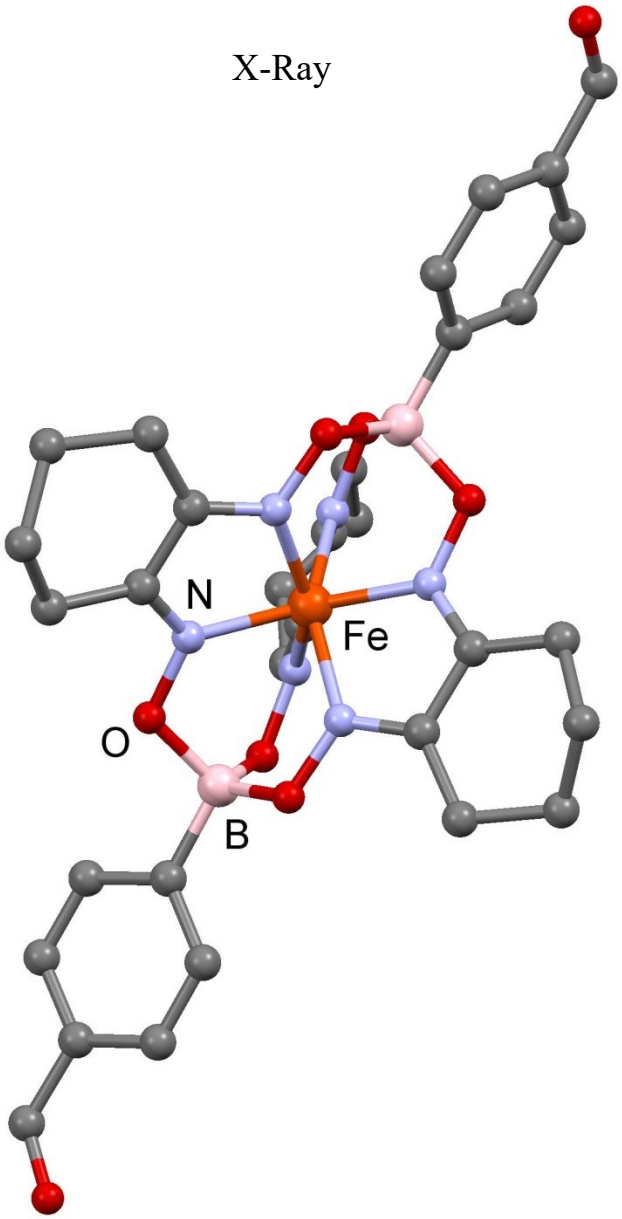


Figure S6. General view of the molecule $FeNx_3(B4\text{-}C_6H_4CHO)_2$

Low-spin iron(II) complex

DFT calculation of QS values

Regarding the quadrupolar splitting, it should be said that the potential caused by a point charge at a certain distance r from a nucleus is given by $\mathbf{V}(\mathbf{r}) = q/\mathbf{r}$. The electric field is the gradient of the potential, taken with a negative sign, i.e. $E = -\nabla V$, and the gradient of the electric field is known as the electric field gradient (EFG), which may be expressed as $EFG = -\nabla^2 V$. The EFG may be written in matrix form, according to Eq. S1.

$$EFG = -\nabla^2 V = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \quad \text{(S1)},$$

where $V_{ij} = \partial^2 V / \partial r_i \partial r_j$, where i and j stand for combinations of the Cartesian coorinates x, y or z.

The hyperfine quadrupole splitting is originated from the coupling of a nuclear electric quadrupole moment (Q) for nuclei with nuclear spin $I > 1/2$ and a non-zero EFG. In the case of the ^{57}Fe nucleus, the nuclear transition $I = 1/2 \leftrightarrow I = 3/2$ occurs at 14.41 eV. The spectral difference between the $I = 3/2$ Kramers doublet $M_I = \pm 3/2$ and $M_I = \pm 1/2$ may be expressed according to Eq. S2.

$$\Delta E_Q = \frac{eQV_{zz}}{2}\sqrt{\left(1 + \frac{\eta^2}{3}\right)} \quad \text{(S2)}$$

where $\eta = (V_{xx} - V_{yy})/(V_{zz})$ is an asymmetry parameter reflecting the asymmetry in the distribution of the electrons around the nucleus; each component is taken as $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. For the calculation of ΔE_Q it is worth to consider that $e = 1.602 \cdot 10^{-19} C$, for ^{57}Fe $Q = 150 - 160\, mb$ (where $1 mb = 10^{-31} m^2$) and V_{zz} is calculated in atomic units ($a.u.$) via DFT (where $1\, a.u. = 9.717365 \cdot 10^{21} V/m^2$). The product eQV_{zz} has conventional units of $[C][m^2][V/m^2] = [J]$ while $1 J = 6.242 \cdot 10^{18} eV$ and $1\, mm/s = 4.805 \cdot 10^{-8} eV$.

Table S1. Calculation of an electron density at the ^{57}Fe nucleus in the complex (Fe^{2+})@**L4** using the different convergence criteria; B3LYP functional; NRAD = 300

Electron density	Convergence
11578.995020	1.00E-05
11578.995008	1.00E-06
11578.995009	1.00E-07

Table S2. Calculation of an electron density at the ^{57}Fe nucleus in the complex (Fe^{2+})@**L4** using the different NRAD values; B3LYP functional; convergence = 1d-06

Electron density	Convergence
11578.995075	100
11578.995010	200
11578.995008	300
11578.995008	400
11578.995010	500

Table S3. Calculation of an electron density at the ^{57}Fe nucleus in the complex (Fe^{2+})@**L4** using the experimental XRD and DFT-optimized geometries

Method	Electrond density
XRD	11578.995010
DFT	11578.995015

Table S4. The calculated QS values (mm/s) which were obtained using various DFT functionals

Functional	Compound	Vzz (a.u.)	Vyy (a.u.)	Vxx (a.u.)	η	QS_{calcd}	QS_{exp}
B3LYP	(Fe^{2+})@**L1**	1.08	–0.82	–0.26	0.525	1.761	3.55
	(Fe^{2+})@**L2**	0.06	–0.05	–0.01	0.632	0.096	0.00
	(Fe^{2+})@**L3**	0.31	–0.27	–0.04	0.762	0.531	0.56
	(Fe^{2+})@**L4**	–0.55	0.31	0.24	0.115	–0.867	0.71
	(Fe^{2+})@**L5**	–0.16	0.13	0.03	0.592	–0.265	0.70
	(Fe^{2+})@**L6**	–0.35	0.31	0.04	0.766	–0.604	0.65
BP86	(Fe^{2+})@**L1**	–0.88	0.82	0.06	0.854	–1.541	3.55
	(Fe^{2+})@**L2**	0.28	–0.15	–0.13	0.089	0.434	0.00
	(Fe^{2+})@**L3**	0.18	–0.16	–0.024	0.740	0.313	0.56
	(Fe^{2+})@**L4**	–0.22	0.14	0.08	0.292	–0.342	0.71
	(Fe^{2+})@**L5**	–0.10	0.08	0.02	0.589	–0.166	0.70
	(Fe^{2+})@**L6**	0.11	–0.10	–0.005	0.898	0.189	0.65
OLYP	(Fe^{2+})@**L1**	–0.81	0.63	0.18	0.553	–1.328	3.55
	(Fe^{2+})@**L2**	0.28	–0.15	–0.13	0.082	0.439	0.00
	(Fe^{2+})@**L3**	0.18	–0.16	–0.03	0.716	0.309	0.56
	(Fe^{2+})@**L4**	–0.10	0.08	0.02	0.617	–0.162	0.71
	(Fe^{2+})@**L5**	–0.85	0.79	0.06	0.855	–1.487	0.70
	(Fe^{2+})@**L6**	0.11	–0.10	–0.007	0.865	0.189	0.65
RPBE	(Fe^{2+})@**L1**	–0.85	0.79	0.06	0.855	–1.487	3.55
	(Fe^{2+})@**L2**	0.28	–0.15	–0.13	0.086	0.446	0.00
	(Fe^{2+})@**L3**	0.18	–0.15	–0.025	0.720	0.302	0.56
	(Fe^{2+})@**L4**	–0.20	0.13	0.07	0.298	–0.322	0.71
	(Fe^{2+})@**L5**	–0.10	0.077476	0.02	0.609	–0.160	0.70
	(Fe^{2+})@**L6**	0.01	–0.092	–0.008	0.833	0.174	0.65
TPSS	(Fe^{2+})@**L1**	0.89	–0.73	–0.15	0.654	1.487	3.55
	(Fe^{2+})@**L2**	0.22	–0.12	–0.10	0.125	0.343	0.00
	(Fe^{2+})@**L3**	0.19	–0.17	–0.023	0.764	0.333	0.56
	(Fe^{2+})@**L4**	–0.26	0.15	0.10	0.202	–0.407	0.71
	(Fe^{2+})@**L5**	–0.11	0.083918	0.02	0.590	–0.175	0.70
	(Fe^{2+})@**L6**	0.14	–0.13	–0.007	0.900	0.245	0.65

Table S5. The calculated QS values (mm/s) for the complex (Fe^{2+})@**L4** which were obtained using various basis sets

Basis set	Vzz (a.u.)	Vyy (a.u.)	Vxx (a.u.)	η	QS_{calcd}	QS_{exp}
STO-6G	–0.29	0.17	0.12	0.19	–0.454	0.71
631-G	–0.38	0.22	0.16	0.15	–0.595	
CCT	–0.44	0.25	0.19	0.13	–0.685	
TZV	–0.55	0.31	0.24	0.11	–0.867	
SPKrTZV	–0.45	0.26	0.20	0.13	–0.713	