

Supporting Information

**Robust magnetic anisotropy of a monolayer of hexacoordinate Fe(II) complexes assembled on Cu(111)**

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## 1. X-rays analysis

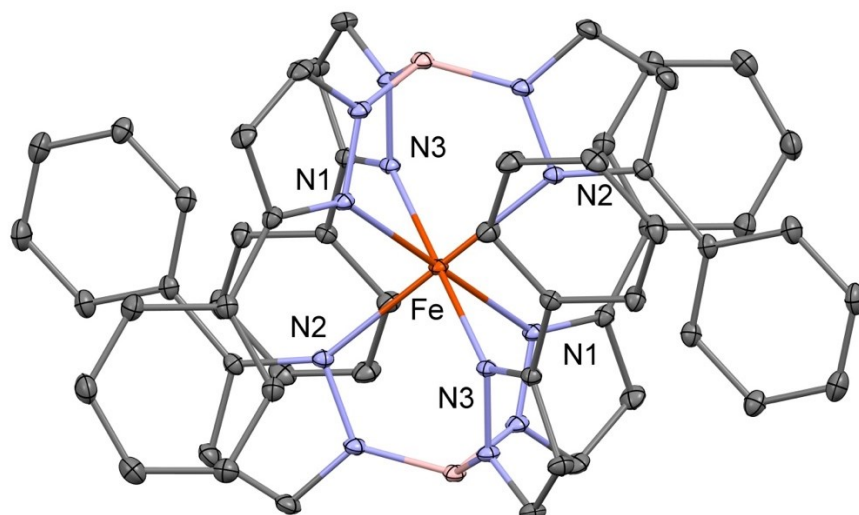


Figure S1. An ORTEP drawing of **2**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity.

X-ray diffraction data for compound **2** were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated  $\text{Mo}_{K\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. For compounds, the temperature of the crystal was maintained at the selected value by means of a 700 series Cryostream cooling device to within an accuracy of  $\pm 1\text{K}$ . The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97<sup>1</sup> and refined against  $F^2$  by full-matrix least-squares techniques using SHELXL-2018<sup>2</sup> with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.<sup>3</sup>

The iron atom, located on an inversion center, is octahedrally coordinated by six N from two ligands.

The crystal data collection and refinement parameters are given in Table S1.

CCDC 2022479 contains the supplementary crystallographic data for this paper. these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

Table S1. Crystallographic data and structure refinement details.

<b>Compound</b>	<b>2</b>
CCDC	2022479
Empirical Formula	$\text{C}_{54} \text{H}_{44} \text{B}_2 \text{Fe} \text{N}_{12}$
$M_r$	938.48
Crystal size, $\text{mm}^3$	0.28 x 0.19 x 0.05
Crystal system	triclinic
Space group	$P - 1$
a, $\text{\AA}$	10.5020(6)
b, $\text{\AA}$	10.6260(7)
c, $\text{\AA}$	12.0360(8)
$\alpha$ , $^\circ$	66.8390(10)
$\beta$ , $^\circ$	82.0480(10)

$\gamma$ , °	64.0010(10)
Cell volume, Å <sup>3</sup>	1108.98(12)
Z ; Z'	1 ; 1/2
T, K	100(1)
Radiation type ; wavelength Å	MoK $\alpha$ ; 0.71073
F <sub>000</sub>	488
$\mu$ , mm <sup>-1</sup>	0.396
range, °	1.842 - 31.052
Reflection collected	17 434
Reflections unique	6 582
R <sub>int</sub>	0.0177
GOF	1.050
Refl. obs. ( $I > 2(I)$ )	5 881
Parameters	310
wR <sub>2</sub> (all data)	0.0870
R value ( $I > 2(I)$ )	0.0331
Largest diff. peak and hole (e <sup>-</sup> ·Å <sup>-3</sup> )	0.449 ; -0.263

Table S2. Selected bond length (Å) and angles (°) of 1 and 2. Symmetry code: i = -x, -y, -z

Compounds	<b>2</b>	<b>1</b>	Fe(ptz) <sub>6</sub> <sup>2+</sup> (from ref. <sup>4</sup> )
bond distances			
Fe-N1	2.2271(9)	2.189(2)	2.183 <sup>a</sup>
Fe-N2	2.2750(9)	2.185(2)	
Fe-N3	2.2098(9)	2.160(2)	
angles			
N1FeN2	90.81(3)	87.51(3)	89.07
N1FeN3	86.41(3)	86.22(3)	
N2FeN3	92.18(3)	86.30(3)	
N1FeN2 <sup>(i)</sup>	89.19(3)	92.49(3)	90.93
N1FeN3 <sup>(i)</sup>	93.59(3)	93.78(3)	
N2FeN3 <sup>(i)</sup>	87.82(3)	93.70(3)	
BFeN1	54.39(3)	52.36(3)	55.40
BFeN2	54.67(3)	52.10(3)	
BFeN3	54.82(3)	52.82(3)	
torsion angles ( $\psi$ )			
BFeN1N	5.33(6)	5.69 (6)	63.25 <sup>b</sup>
BFeN2N	3.92(6)	1.34(6)	
BFeN3N	1.65 (6)	3.23(6)	

<sup>a</sup>all the the six Fe-N distances are equal, <sup>b</sup>measured between the three-fold axis of the complex and the tetrazole ring

## 2. Magnetic data of complex **2**

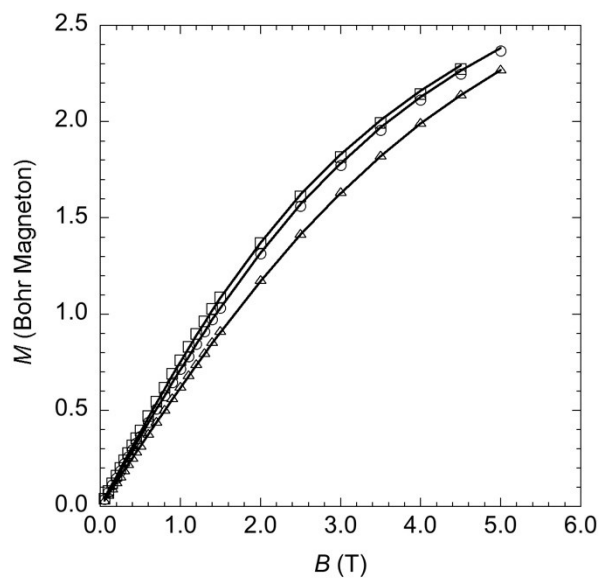


Figure S2.  $M = f(B)$  for **2** at  $T = 2$  (●), 4 (○) and 6 (□) K.

Energy of the  $M_S$  sub-levels of a  $S = 2$  spin state split by the axial ( $D$ ) and rhombic ( $E$ ) anisotropy parameters

$$E_0 = -\text{sign}(D)2\sqrt{D^2 + 3E^2}$$

$$E_{1-} = -D - 3E$$

$$E_{1+} = -D + 3E$$

$$E_{2-} = 2D$$

$$E_{2+} = \text{sign}(D)2\sqrt{D^2 + 3E^2}$$

Where  $\text{sign}(D)$  is + or - for cases with positive and negative  $D$  values respectively

### 3. X-ray Absorption Spectroscopy data

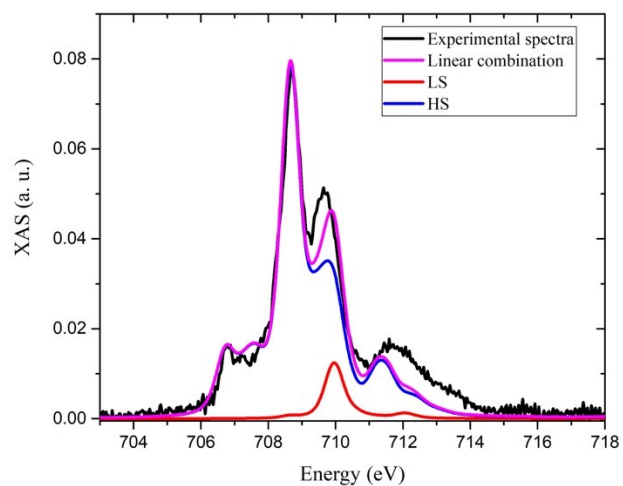


Figure S3. XAS spectrum of **1** on Cu(111) with deconvolution after 2 hours irradiation with X-rays and deconvolution corresponding to 90% of HS proportion.

#### 4. Magnetic data of **1** on Cu(111) from X-ray Magnetic Circular Dichroism measurements

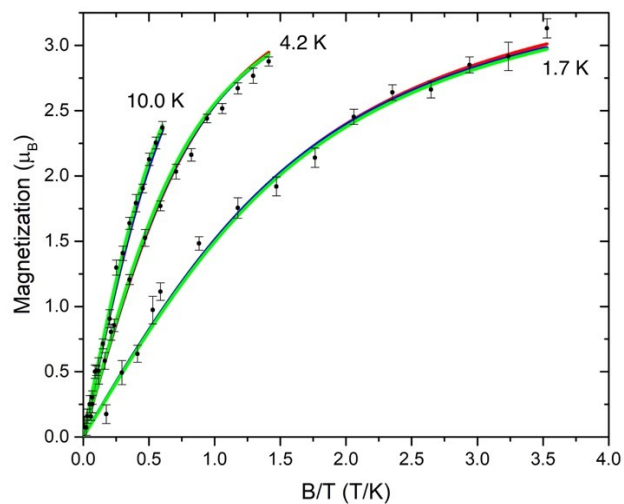


Figure S4. Simulated magnetization data for **1**/Cu(111), with  $g_{1/Cu} = 2.12$ ,  $D_{1/Cu} = 7.5 \text{ cm}^{-1}$ ,  $\theta = 50^\circ$  (red),  $g_{1/Cu} = 2.04$ ,  $D_{1/Cu} = 7.9 \text{ cm}^{-1}$ ,  $\theta = 55^\circ$  (blue) and  $g_{1/Cu} = 2.00$ ,  $D_{1/Cu} = 8.6 \text{ cm}^{-1}$ ,  $\theta = 60^\circ$  (green)

## 5. Theoretical studies

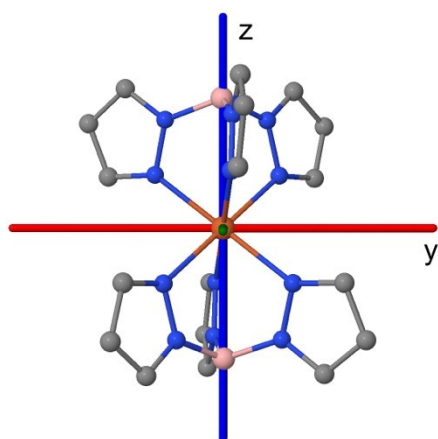


Figure S5. Orientation of the  $D$  tensor axes for **2**, the Ph groups were removed for clarity.

Table S3. Composition and energy of the one electron AILFT MOs for **2** and **1** at the NEVPT2 level

<b>2</b>	MO composition for <b>2</b>	$E$ (cm <sup>-1</sup> )
MO1	$z^2$	0
MO2	$-0.73xy+0.68yz-0.05xz-0.06(x^2-y^2)$	1753.8
MO3	$-0.06xy+0.04yz+0.61xz+0.79(x^2-y^2)$	2209.5
MO4	$-0.09xy-0.08yz+0.78xz-0.61(x^2-y^2)$	9175.8
MO5	$-0.68xy-0.72yz-0.1xz+0.06(x^2-y^2)$	10288.0
<b>1</b>	MO composition for <b>1</b>	$E$ (cm <sup>-1</sup> )
MO1	$z^2$	0
MO2	$0.08xy+0.59yz-0.80(x^2-y^2)$	1526.5
MO3	$-0.84xy-0.54xz+0.08(x^2-y^2)$	1766.2
MO4	$0.53xy+0.08yz-0.83xz+0.10(x^2-y^2)$	10962.6
MO5	$0.10xy-0.80yz-0.08xz+0.58(x^2-y^2)$	11615.1

Table S4. Contribution of the quintet and the three triplet states to the axial parameter  $D$  for **2** and **1**.

<b>2</b>			<b>1</b>		
State	contribution to $D_2$	composition of the state	State	contribution to $D_1$	composition of the state
Q0	-	$ xy,yz,xz,x^2-y^2 $	Q0	-	$ xy,yz,xz,x^2-y^2 $
Q1	3.78	$0.52 yz,z^2,xz,x^2-y^2 ,$ $0.47 xy,z^2,xz,x^2-y^2 $	Q1	2.51	$0.64 xy,yz,z^2,xz ,$ $0.35 xy,z^2,xz,x^2-y^2 $
Q2	2.37	$0.61 xy,yz,z^2,xz ,$ $0.39 xy,yz,z^2,x^2-y^2 $	Q2	1.88	$0.70 yz,z^2,xz,x^2-y^2 ,$ $0.28 xy,yz,z^2,x^2-y^2 $
Q3	1.02	$0.60 xy,yz,z^2,x^2-y^2 ,$ $0.38 xy,yz,z^2,xz $	Q3	0.78	$0.70 xy,yz,z^2,x^2-y^2 ,$ $0.28 yz,z^2,xz,x^2-y^2 $
Q4	0.77	$0.52 xy,z^2,xz,x^2-y^2 ,$ $0.47 yz,z^2,xz,x^2-y^2 $	Q4	0.73	$0.64 xy,z^2,xz,x^2-y^2 ,$ $0.34 xy,yz,z^2,xz $
T0	2.26		T0	3.54	
T16	0.90		T14	0.73	
T20	1.22		T20	0.86	

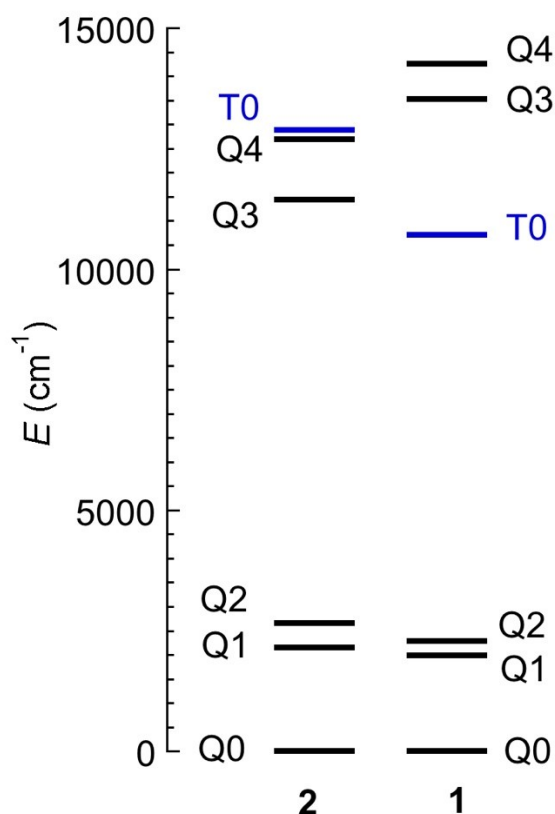


Figure S6. NEVPT2 energy of the electronic states before spin-orbit coupling for **1** and **2**.

For an  $S = 2$  state, there are 5 quintet and 45 triplet states. The calculations show that the four quintet and the first triplet excited states all contribute positively to  $D$  and account almost for the major contributions to the overall  $D$  values for the two compounds (Table S4). The wave functions of the ground states for **1** and **2** are a single determinant in the frame of the magnetic axes and are identical for the two complexes with two electrons in the  $d_{z^2}$  orbital ( $|xy, yz, xz, x^2-y^2|$  in the hole formalism). Therefore, all the (four) quintet excited states are obtained by excitations from the  $d_{z^2}$  orbital ( $m_l = 0$ ) to one of the other four ones ( $m_l = \pm 1$  or  $\pm 2$ ) with, therefore, a change of the value of  $|m_l|$  by 1 or 2. It is worth reminding that, for states with the same spin multiplicity, two determinants are coupled by the spin-orbit operator if the excitation involves  $|\Delta m_l| = 0$  or 1 (and not 2), with a negative contribution to  $D$  when  $|\Delta m_l| = 0$  (involving therefore  $\hat{l}_z \hat{s}_z$  term of the SOC operator) and a positive one when  $|\Delta m_l| = \pm 1$  (involving the  $\frac{1}{2}(\hat{l}_+ \hat{s}_- + \hat{l}_- \hat{s}_+)$  of SOC).<sup>5, 6</sup> While two determinants with an electronic excitation involving  $|\Delta m_l| = 2$  cannot be coupled by the spin-orbit operator. Here for **1** and **2**, the excitations from the ground to the four excited quintet states never involve a  $|\Delta m_l| = 0$ , rationalizing the fact that all the quintet excited states bring only positive contributions to  $D$ . For example (we consider the case of **1**), the first excited quintet state is composed by:  $0.64 |xy, yz, z^2, xz|$  and  $0.35 |xy, z^2, xz, x^2-y^2|$  due to excitation from the  $d_{z^2}$  to the  $x^2-y^2$  and  $yz$  orbitals respectively. The first excitation cannot couple the two determinants by SOC ( $|\Delta m_l| = 2$ ), while the second brings a positive contribution to  $D$  ( $|\Delta m_l| = 1$ ). Examining the remaining three quintet excited states leads to the same result (Table S4). The first excited triplet state (T1) has a non-negligible positive contribution to  $D$  (around  $3 \text{ cm}^{-1}$ , Table S4), the same type of analysis can be made as for the quintet state. The energy of the two first excited quintet states (Q1 and Q2) are relatively close to the ground state, within less than  $3000 \text{ cm}^{-1}$ , while Q3 and Q4 have much higher energy (Figure S6). This is consistent with the larger contribution to  $D$  from Q1 and Q2 than Q3 and Q4 since  $D$  is (within the frame of second order perturbation theory) inversely proportional to the energy separation between the ground and the excited states with which it is coupled by SOC.



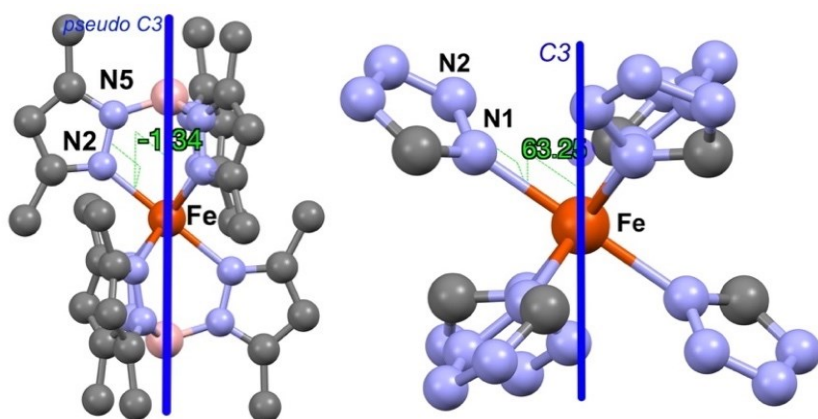


Figure S7. View of the crystal structure of **1** and  $\text{Fe}(\text{ptz})_6]^{2+}$  showing the change of the torsion angle from  $1.34^\circ$  to  $63.25^\circ$ .

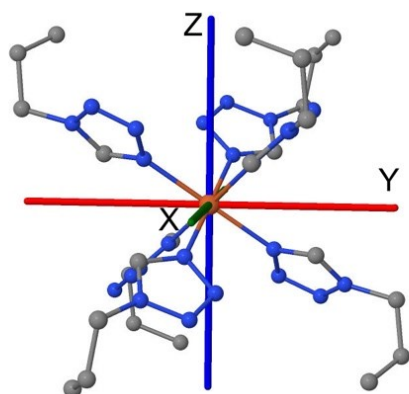


Figure S8. Orientation of the **D** tensor axes for  $\text{Fe}(\text{ptz})_6]^{2+}$ .

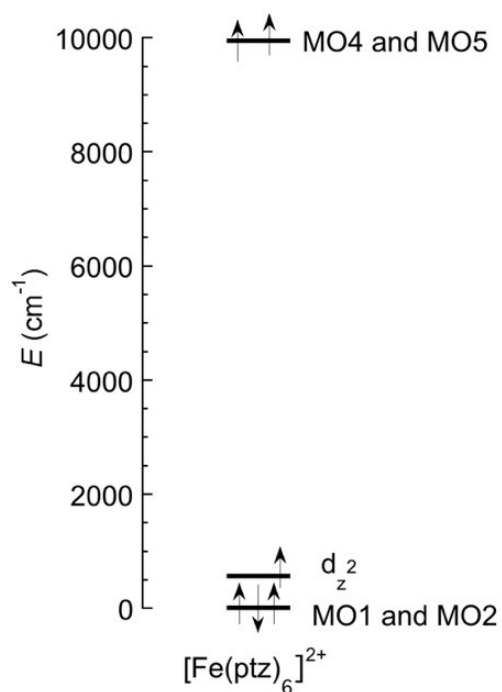


Figure S9. Energy diagram of the one electron molecular orbitals for  $[\text{Fe}(\text{ptz})_6]^{2+}$  obtained from ab initio ligand field theory (AIFLT) calculations by ORCA. The MO1 and MO2 on one hand and the MO4 and MO5 on the other hand are almost degenerate.

Table S5. Composition and energy of the one electron AILFT MOs for  $[\text{Fe}(\text{ptz})_6]^{2+}$  at the NEVPT2 level

	MO composition for $[\text{Fe}(\text{ptz})_6]^{2+}$	$E$ ( $\text{cm}^{-1}$ )
MO1	$0.11xy+0.33yz+0.47xz+0.81(x^2-y^2)$	0
MO2	$-0.80xy+0.48yz-0.34xz+0.11(x^2-y^2)$	3.6
MO3	$z^2$	561.5
MO4	$0.56xy+0.73yz-0.36xz-0.16(x^2-y^2)$	9941.4
MO5	$0.17xy-0.37yz-0.73xz+0.55(x^2-y^2)$	9945.2

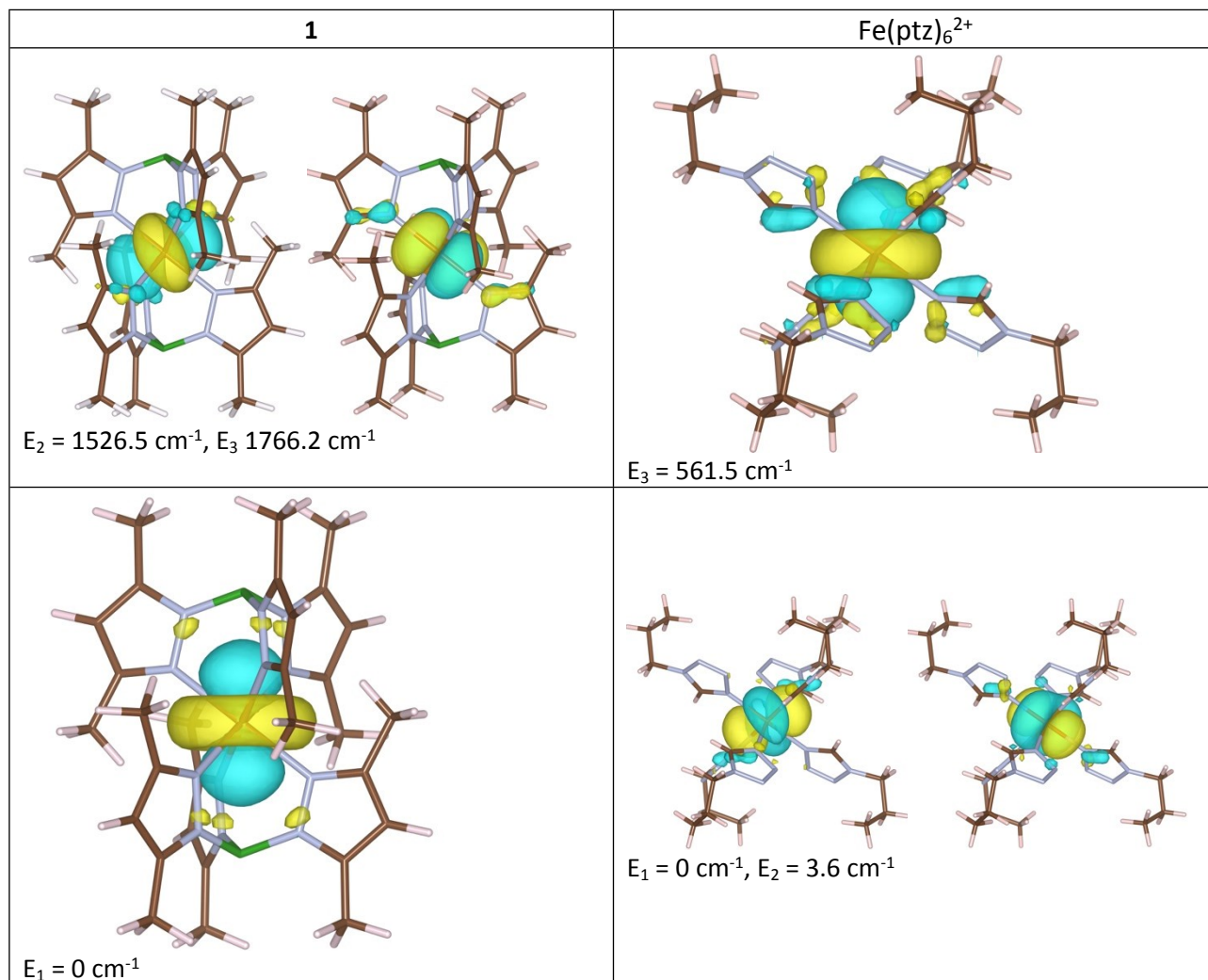


Figure S10. View of the three low-lying MOs of **1** and  $\text{Fe}(\text{ptz})_6^{2+}$ .

## Uncategorized References

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