“Synthesis, Characterization and Study of Octanuclear Iron-Oxo Clusters Containing a Redox-Active Fe_4O_4-Cubane Core”.

Peter Baran,[a,b] Roman Boča,[c] Indranil Chakraborty,[a] John Giapintzakis,[d] Radovan Herschel,[e,f] Qing Huang,[a] John E. McGrady,[g] Raphael G. Raptis,[a] Yiannis Sanakis[h], Athanasios Simopoulos[h]

Supplementary Information

S1. Infrared Spectra.

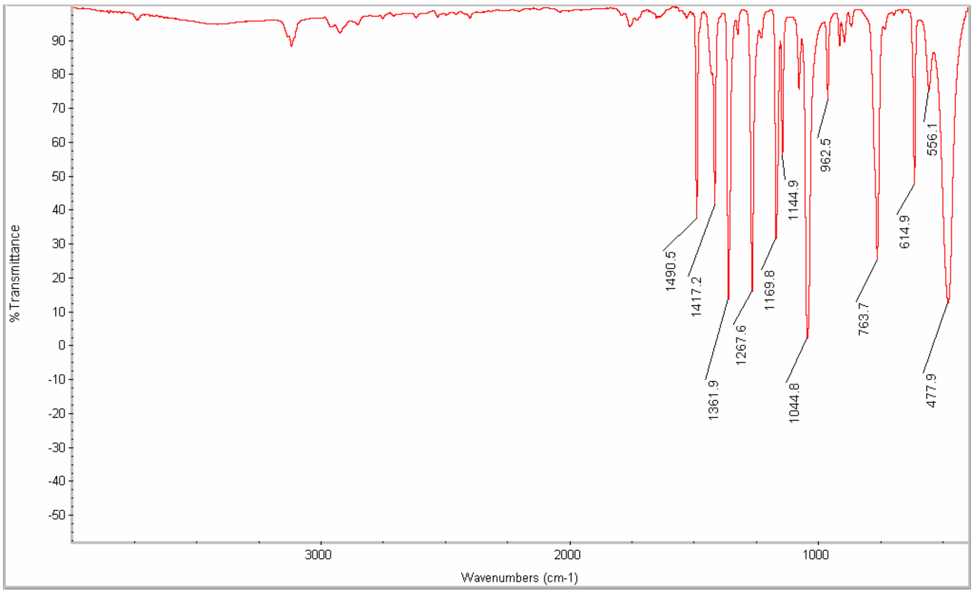

Figure 1. Infrared spectrum of **1**

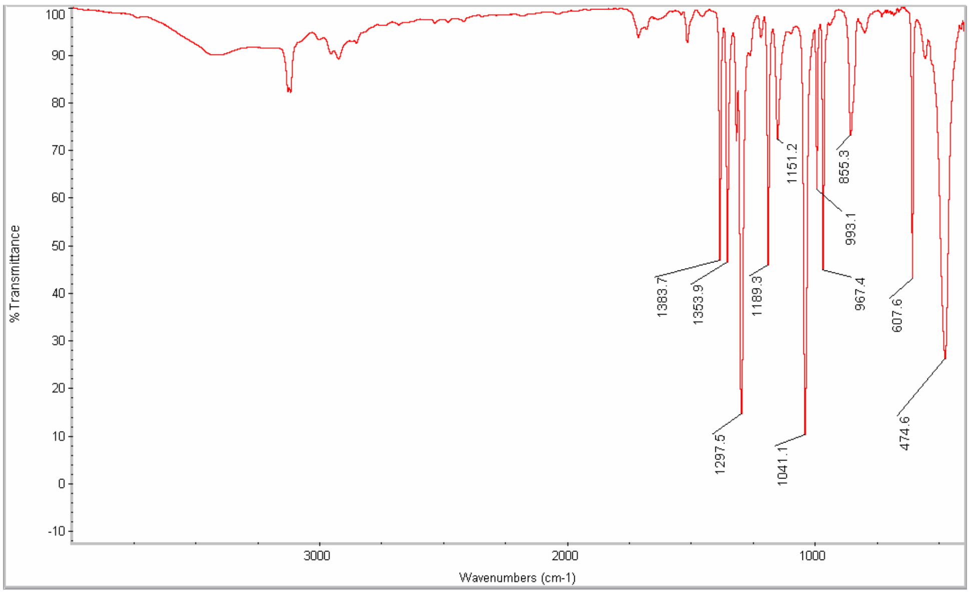

Figure 2. Infrared spectrum of **2**

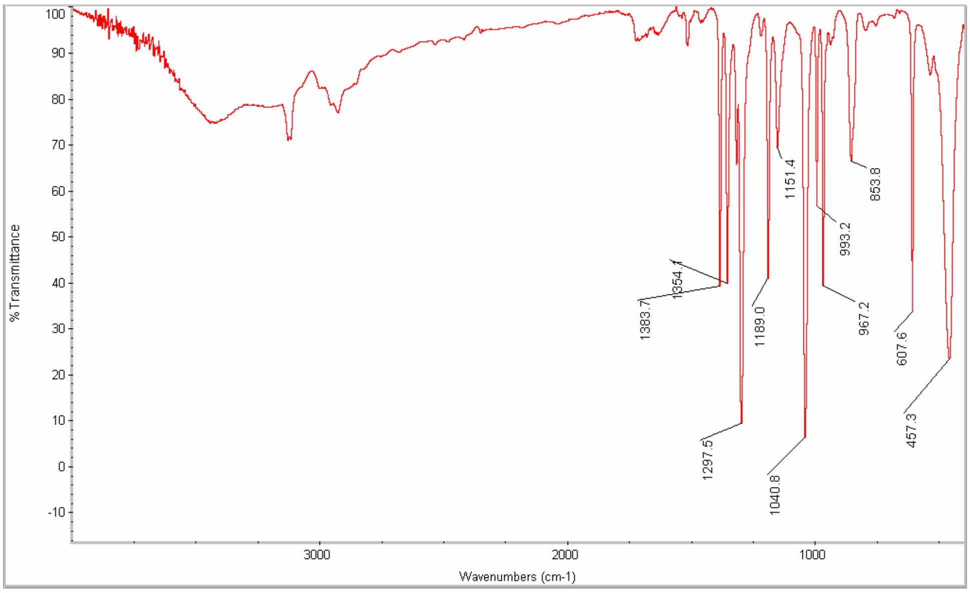

Figure 3. Infrared spectrum of **2** (O^{18} labeled)

S2. Resonance Raman Spectra.

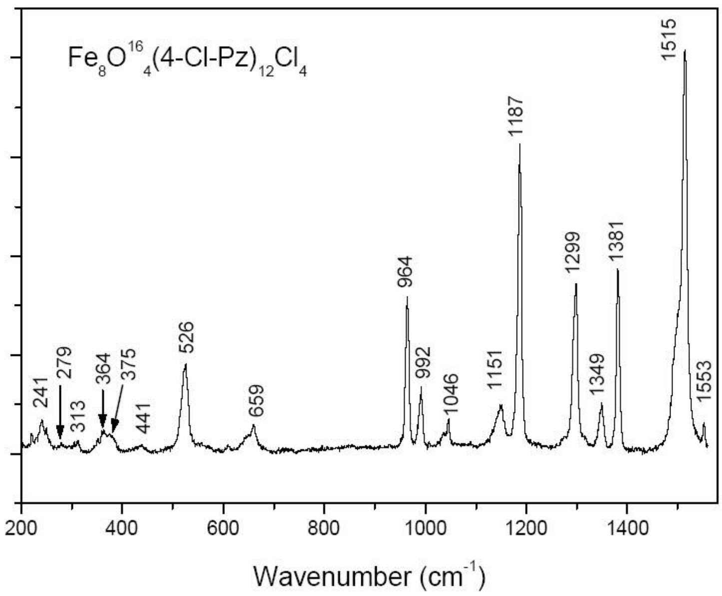

Figure 4. Resonance Raman spectrum of **2**

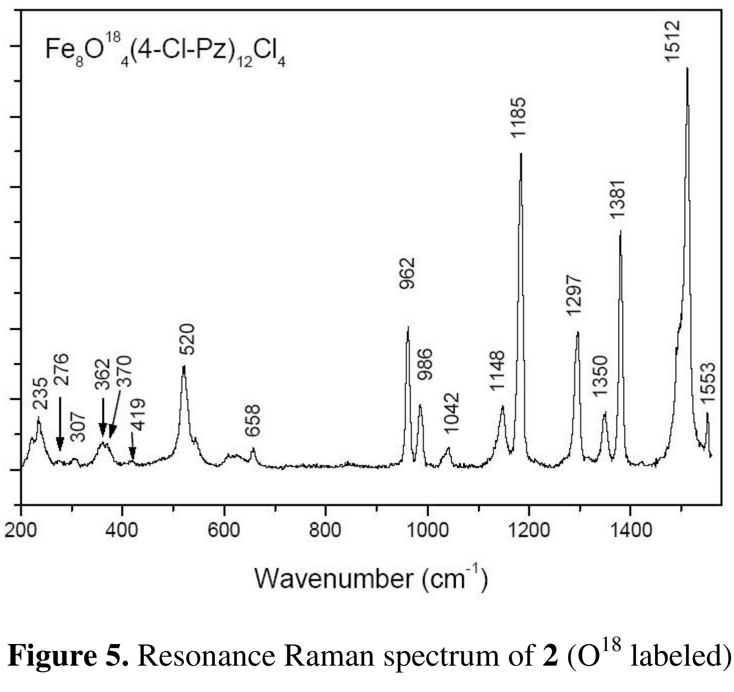

Figure 5. Resonance Raman spectrum of **2** (O^{18} labeled)

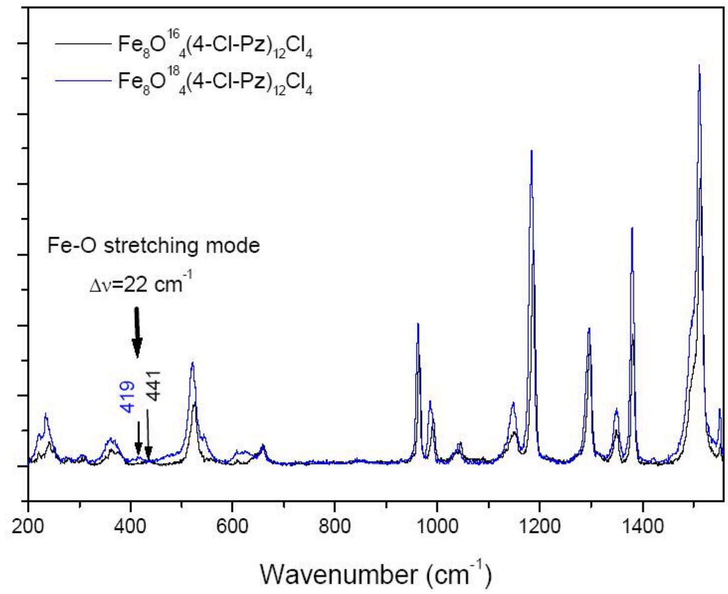

Figure 6. Comparative resonance Raman spectra for **2** (O^{16} in black and O^{18} in blue)

S3. Details of magnetic susceptibility fitting.

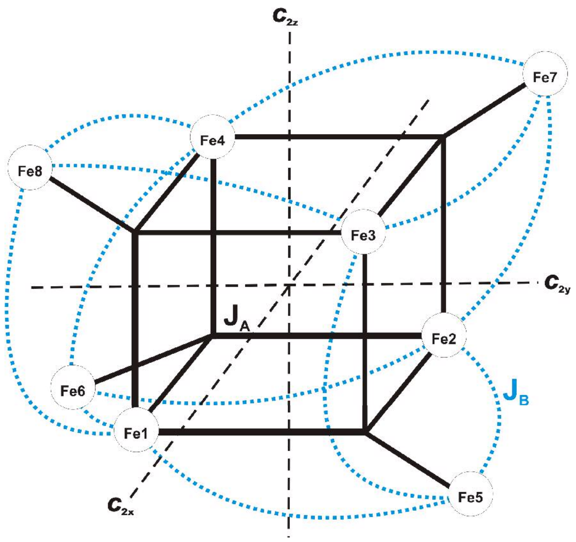

Figure 7. Schematic structure of the complex core for **1** showing the super-exchange interaction pathways: J_A – an interaction through (μ_4-O) (black bold line), J_B – an interaction through (μ-pz) (blue dashed line). According eq.1 J_1 represents the isotropic exchange interactions in $Fe^{III}{}_4O_4$-cubane core mediated only through (μ_4-O) bridges (labeled as J_A in this scheme), J_2 represents the isotropic exchange interactions mediated through (μ_4-O) and (μ-pz) bridges among each apical Fe(III) center and the triangular base of the inner tetrahedron to which it lies closest (labeled as J_A and J_B). Symmetry operations for D_2 point group are depicted.

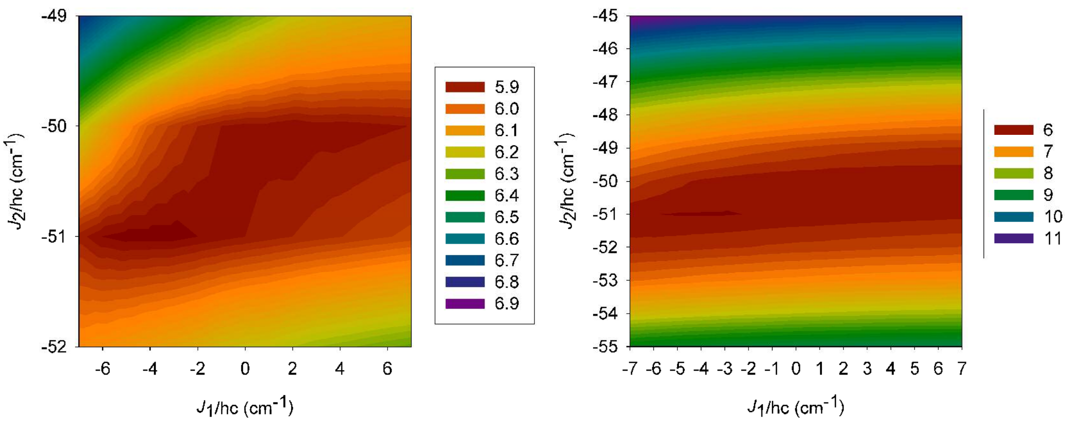

Figure 8. Contour graph for error functional depicting the area of the possible solutions. The dark red color represent the lowest minima of the error functional R, defined as $R = 100/N \times \sum_{i}^{N} \left(1 - \mu^{c}_{eff,i} / \mu^{o}_{eff,i}\right)$, where $\mu^{c}_{eff,i}$ is calculated and $\mu^{o}_{eff,i}$ is observed effective magnetic moment and N is number of experimental points.

Table 1. Classification of spin states in zero magnetic field according to D_2 point symmetry group.

S	A_1	B_1	B_2	B_3	Total
0	776	630	630	630	2666
1	1820	1960	1960	1960	7700
2	3080	2940	2940	2940	11900
3	3625	3750	3750	3750	14875
4	4201	4076	4076	4076	16429
5	4066	4170	4170	4170	16576
6	3958	3854	3854	3854	15520
7	3340	3420	3420	3420	13600
8	2860	2780	2780	2780	11200
9	2128	2184	2184	2184	8680
10	1624	1568	1568	1568	6328
11	1057	1092	1092	1092	4333
12	721	686	686	686	2779
13	400	420	420	420	1660
14	244	224	224	224	916
15	108	118	118	118	462
16	60	50	50	50	210
17	18	22	22	22	84
18	10	6	6	6	28
19	1	2	2	2	7
20	1	0	0	0	1

Details about the factorization procedure according to the irreducible representation of D_2 symmetry point group

D_2	E	$C_2(z)$	$C_2(x)$	$C_2(y)$
A_1	+1	+1	+1	+1
B_1	+1	+1	–1	–1
B_2	+1	–1	–1	+1
B_3	+1	–1	+1	–1

A details about the general procedure are published in ref 41: Waldmann, O., Symmetry and energy spectrum of high-nuclearity spin clusters. *Phys. Rev. B* **2000,** 61, 6138.

Symmetry operation		Centers								Clebsh-Gordon coefficients				
		1	2	3	4	5	6	7	8	<1,2,12>	<3,4,34>	<5,6,56>	<7,8,78>	<12,34,1234>
O(12345678)	E	1	2	3	4	5	6	7	8	<1,2,12>	<3,4,34>	<5,6,56>	<7,8,78>	<12,34,1234>
O(21436587)	$C_2(z)$	2	1	4	3	6	5	8	7	<2,1,12>	<4,3,34>	<6,5,56>	<8,7,78>	<12,34,1234>
O(34128765)	$C_2(x)$	3	4	1	2	8	7	6	5	<3,4,34>	<1,2,12>	<8,7,78>	<6,5,56>	<34,12,1234>
O(43217856)	$C_2(y)$	4	3	2	1	7	8	5	6	<4,3,34>	<2,1,12>	<7,8,78>	<5,6,56>	<34,12,1234>

Generator for A_1 spin states functions

$$\left|\mathrm{A}_1; S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle =$$

$$= \frac{1}{4}\left(O(12345678) + O(21436587) + O(43217856) + O(34128765)\right)\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle =$$

$$= \frac{1}{4}\Big[+1\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$+(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_5+S_6-S_{56}+S_7+S_8-S_{78}}\left|S_2S_1S_{12}S_4S_3S_{34}S_6S_5S_{56}S_8S_7S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$+(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_4S_3S_{34}S_2S_1S_{12}S_7S_8S_{78}S_5S_6S_{56}S_{1234}S_{5678}SM\right\rangle$$
$$+(-1)^{S_5+S_6-S_{56}+S_7+S_8-S_{78}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_3S_4S_{34}S_1S_2S_{12}S_8S_7S_{78}S_6S_5S_{56}S_{1234}S_{5678}SM\right\rangle\Big]$$

Generator for B_1 spin states functions

$$\left|B_1; S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle =$$

$$= \frac{1}{4}\left(O(12345678) + O(21436587) - O(43217856) - O(34128765)\right)\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle$$

$$= \frac{1}{4}\Big[+1\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$+(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_5+S_6-S_{56}+S_7+S_8-S_{78}}\left|S_2S_1S_{12}S_4S_3S_{34}S_6S_5S_{56}S_8S_7S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$-(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_4S_3S_{34}S_2S_1S_{12}S_7S_8S_{78}S_5S_6S_{56}S_{1234}S_{5678}SM\right\rangle$$
$$-(-1)^{S_5+S_6-S_{56}+S_7+S_8-S_{78}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_3S_4S_{34}S_1S_2S_{12}S_8S_7S_{78}S_6S_5S_{56}S_{1234}S_{5678}SM\right\rangle\Big]$$

Generator for B_2 spin states functions

$$\left|B_2; S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle =$$

$$= \frac{1}{4}\left(O(12345678) - O(21436587) + O(43217856) - O(34128765)\right)\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle$$

$$= \frac{1}{4}\Big[+1\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$-(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_5+S_6-S_{56}+S_7+S_8-S_{78}}\left|S_2S_1S_{12}S_4S_3S_{34}S_6S_5S_{56}S_8S_7S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$+(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_4S_3S_{34}S_2S_1S_{12}S_7S_8S_{78}S_5S_6S_{56}S_{1234}S_{5678}SM\right\rangle$$
$$-(-1)^{S_5+S_6-S_{56}+S_7+S_8-S_{78}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_3S_4S_{34}S_1S_2S_{12}S_8S_7S_{78}S_6S_5S_{56}S_{1234}S_{5678}SM\right\rangle\Big]$$

Generator for B_3 spin states functions

$$\left|B_3;S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle =$$
$$=\frac{1}{4}\big(O(12345678)-O(21436587)-O(43217856)+O(34128765)\big)\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle =$$
$$=\frac{1}{4}\Big[+1\left|S_1S_2S_{12}S_3S_4S_{34}S_5S_6S_{56}S_7S_8S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$-(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_5+S_6-S_{56}+S_7+S_8-S_{78}}\left|S_2S_1S_{12}S_4S_3S_{34}S_6S_5S_{56}S_8S_7S_{78}S_{1234}S_{5678}SM\right\rangle$$
$$-(-1)^{S_1+S_2-S_{12}+S_3+S_4-S_{34}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_4S_3S_{34}S_2S_1S_{12}S_7S_8S_{78}S_5S_6S_{56}S_{1234}S_{5678}SM\right\rangle$$
$$+(-1)^{S_5+S_6-S_{56}+S_7+S_8-S_{78}+S_{34}+S_{12}-S_{1234}+S_{78}+S_{56}-S_{5678}}\left|S_3S_4S_{34}S_1S_2S_{12}S_8S_7S_{78}S_6S_5S_{56}S_{1234}S_{5678}SM\right\rangle\Big]$$

Example of usage:

$$\left|\mathrm{A}_1;5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle =$$
$$=\frac{1}{4}\big(O(12345678)+O(21436587)+O(43217856)+O(34128765)\big)\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle =$$
$$=\frac{1}{4}\Big[+1\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle$$
$$+(-1)^{2}\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle$$
$$+(-1)^{16}\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle$$
$$+(-1)^{18}\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle\Big]$$
$$=\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,4,1,1,1,M\right\rangle$$

$$\left|B_3;5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle =$$
$$=\frac{1}{4}\big(O(12345678)-O(21436587)-O(43217856)+O(34128765)\big)\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle =$$
$$=\frac{1}{4}\Big[+1\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle$$
$$-(-1)^{1}\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle$$
$$-(-1)^{0}\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,5,10,9,19,M\right\rangle$$
$$+(-1)^{1}\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,5,10,9,19,M\right\rangle\Big]$$
$$=\frac{1}{2}\Big[\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle-\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,5,10,9,19,M\right\rangle\Big]$$

This function must be normalized. As a result we obtain

$$\left|B_3;5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle =$$
$$=\frac{1}{\sqrt{2}}\Big[\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,10,9,19,M\right\rangle-\left|5/2,5/2,5,5/2,5/2,5,5/2,5/2,4,5/2,5/2,5,10,9,19,M\right\rangle\Big]$$

S4. Mössbauer spectra. Deconvolution with crossed-model.

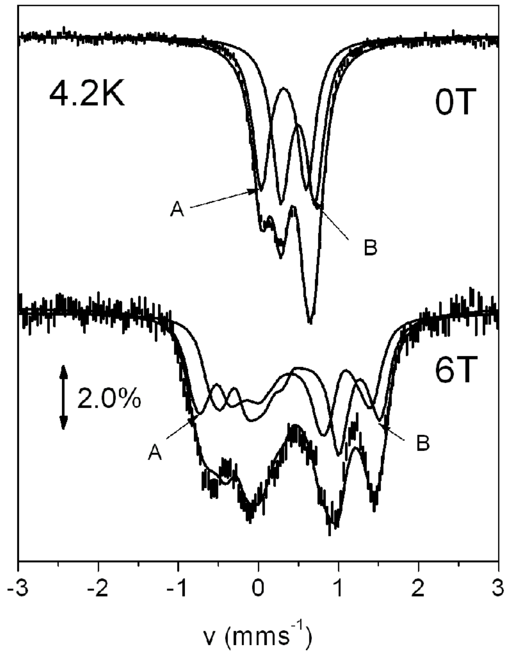

Figure 9. Mössbauer spectra from powdered samples of 1 in the absence or presence of an external magnetic field of 6T applied perpendicular to the γ-rays. Solid lines are theoretical simulations assuming two species A, B with the parameters quoted in Table 6 (crossed model).

S5. ***Full Gaussian 03*** **reference (Reference 27).**

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004