

Supplementary Information (SI)

Ferromagnetically coupled tetranuclear Ni(II)-2-oxy-aceto or benzo-phenonates complexes

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Dedicated in memory of Professor ABP Lever, Department of Chemistry, York University, Toronto, Canada.

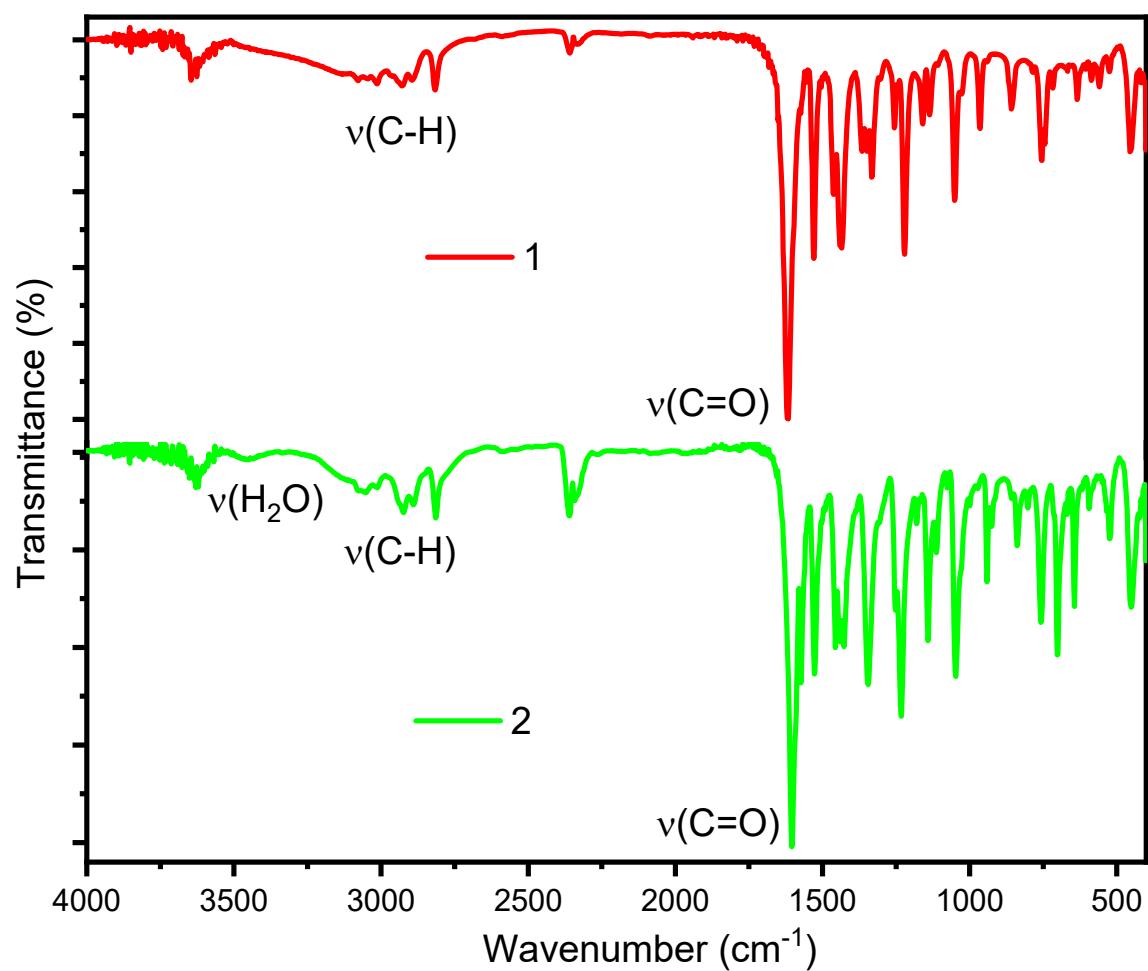


Fig. S1. FT-IR (KBr, cm^{-1}) for complexes **1** and **2**.

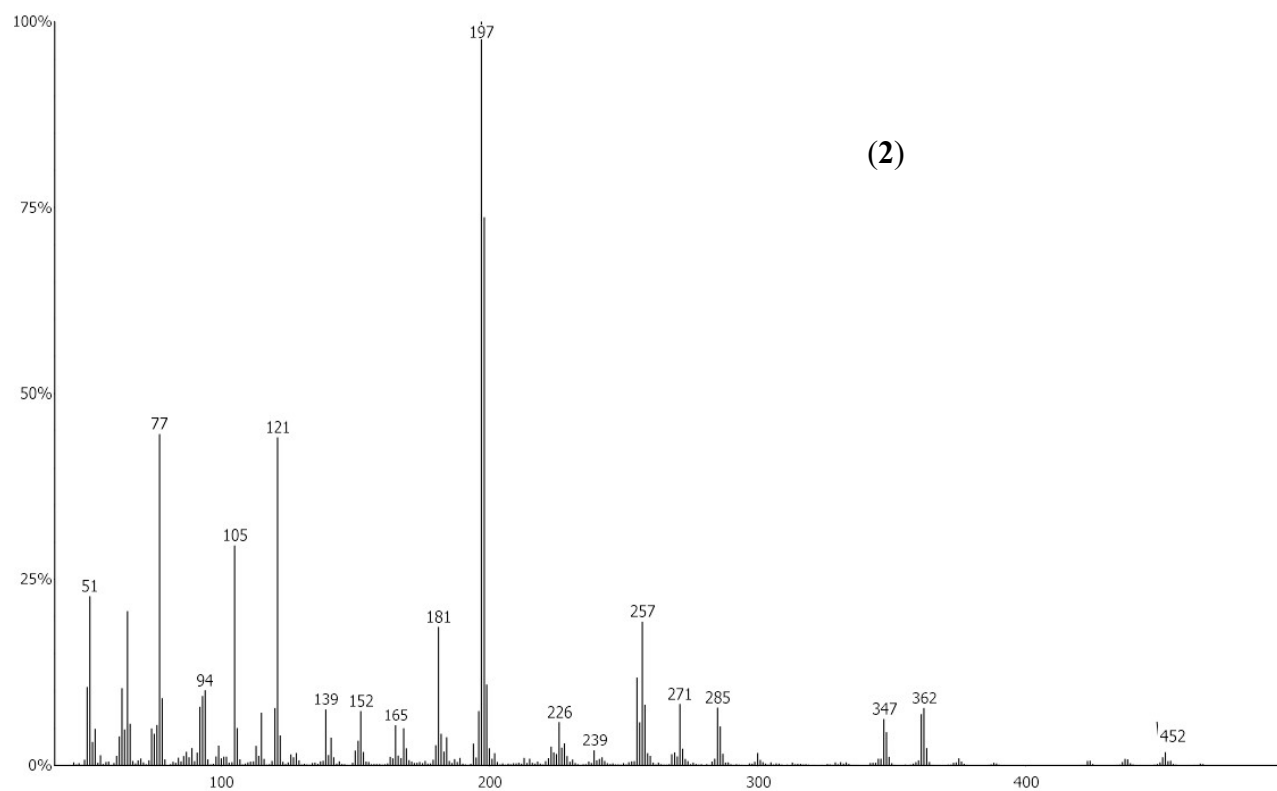
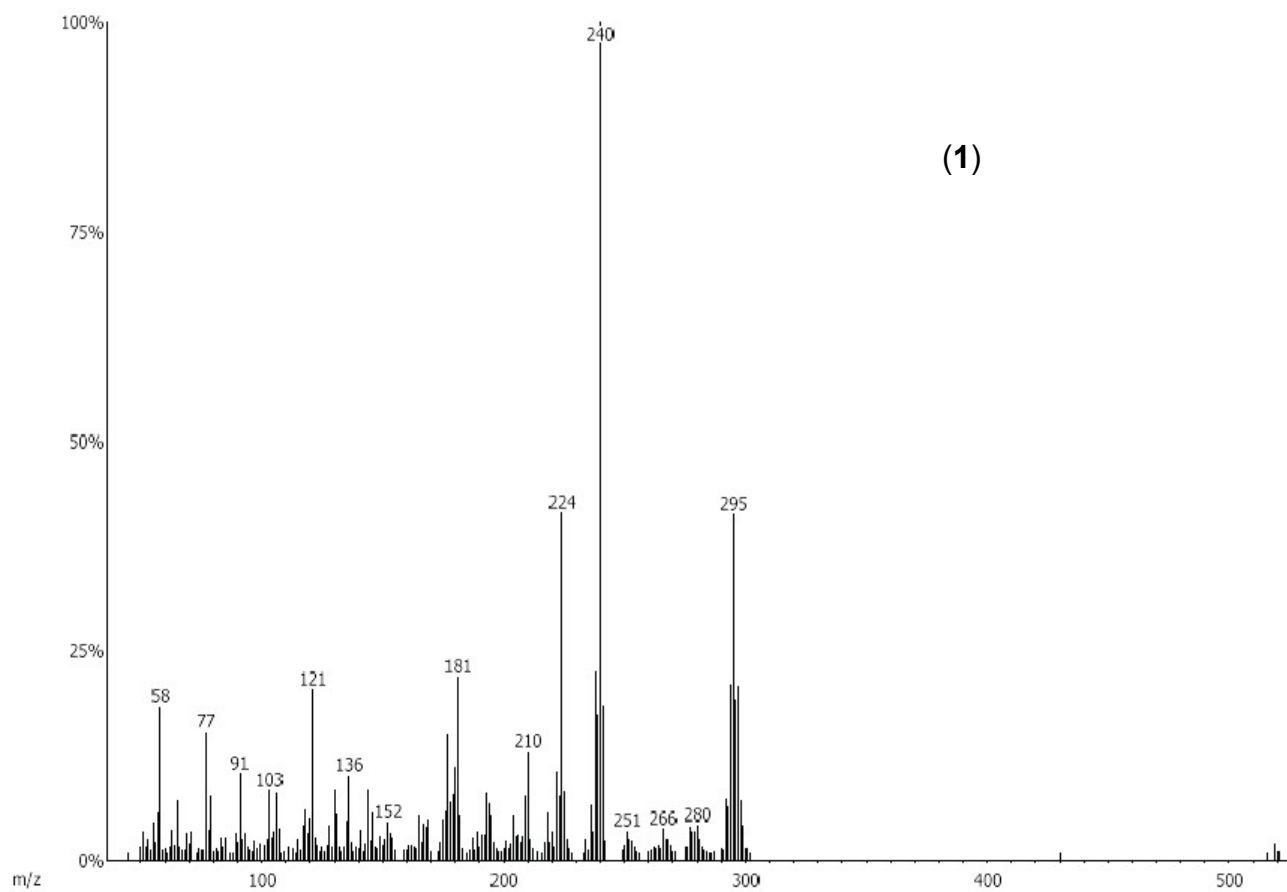


Fig. S2. EI-mass spectrum for complexes **1** and **2** (monoligated species).

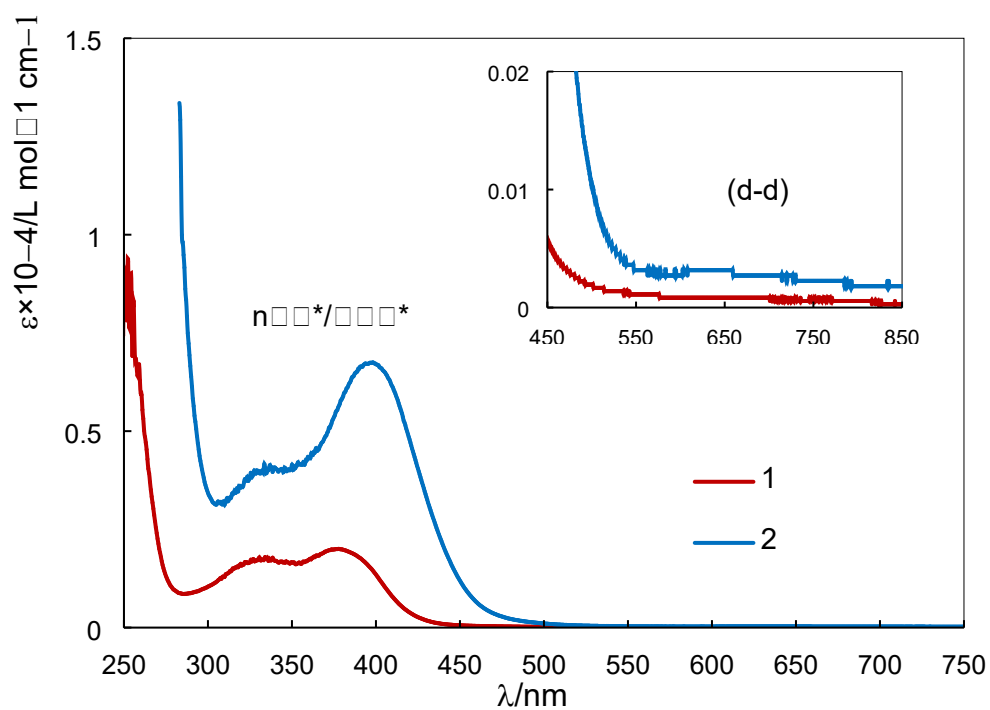


Fig. S3. Electronic absorption spectra for **1** (0.36 mM) and **2** (0.22 mM) in chloroform at 25 °C.

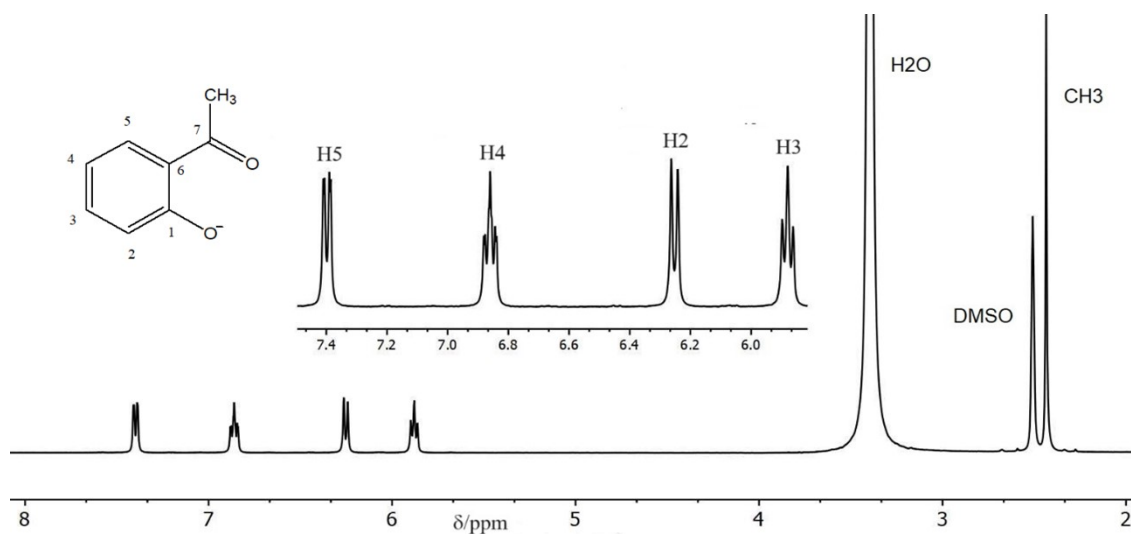


Fig. S4. ^1H NMR spectrum for HL (isolated *via* decomplexation of **1** with NaCN) in DMSO- d_6 at 20 °C.

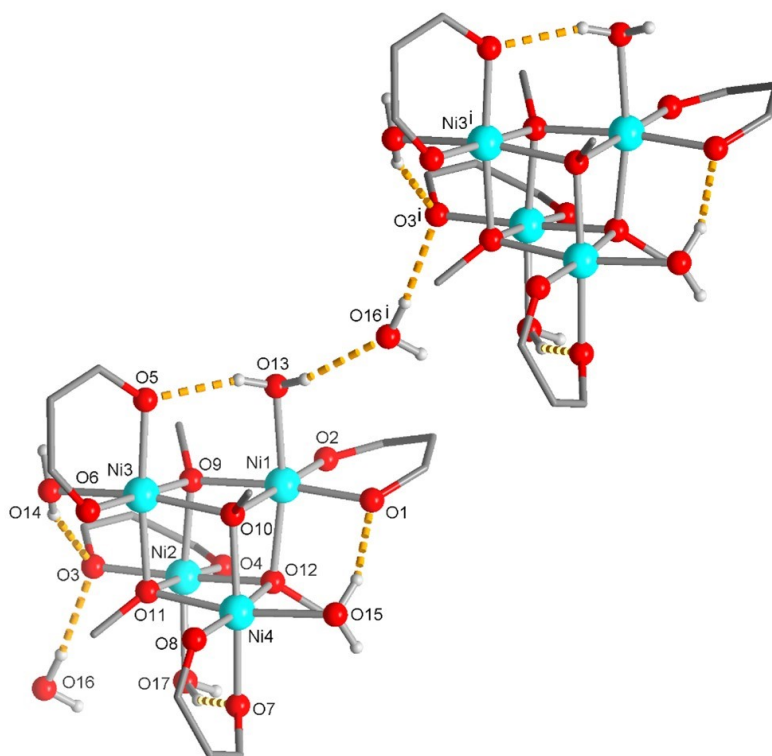
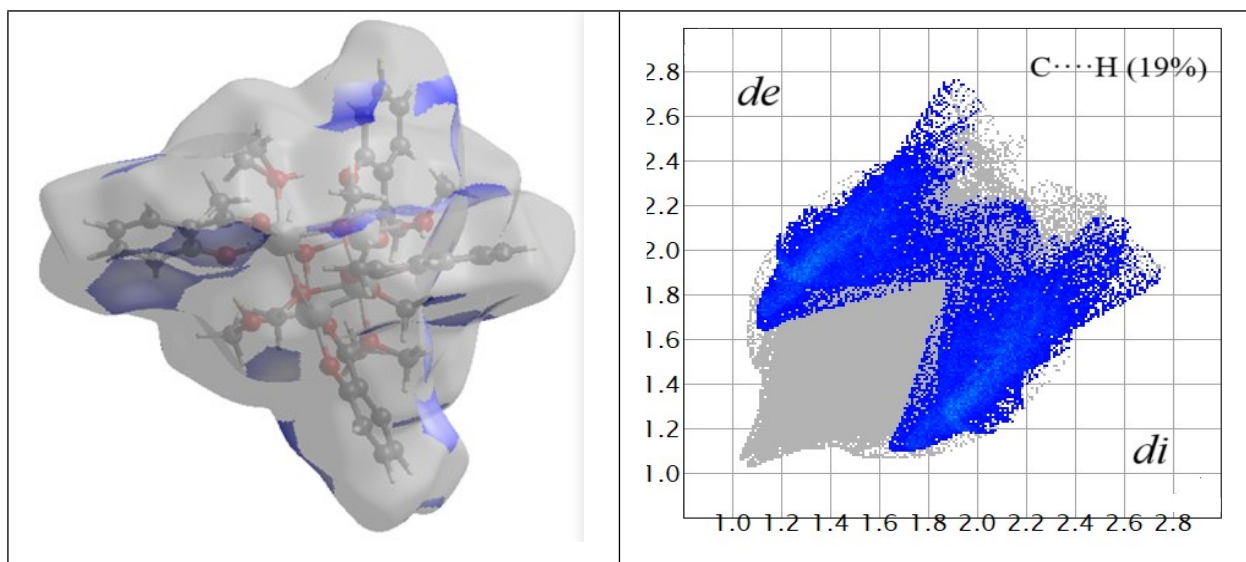


Fig. S5. Illustration of intra- and inter-molecular hydrogen bonds (dashed orange lines) in **2** between the symmetry related complexes and the lattice water molecule (for details and symmetry operations see Tables S2). For clarity, the remaining carbon atoms of the six-membered chelate ring and the methoxy group are depicted in wireframe mode. Note that from the water molecules with O14, O15, O16 and O17 only one H-atom participates in H-bonding. The other H-atom is without an acceptor.



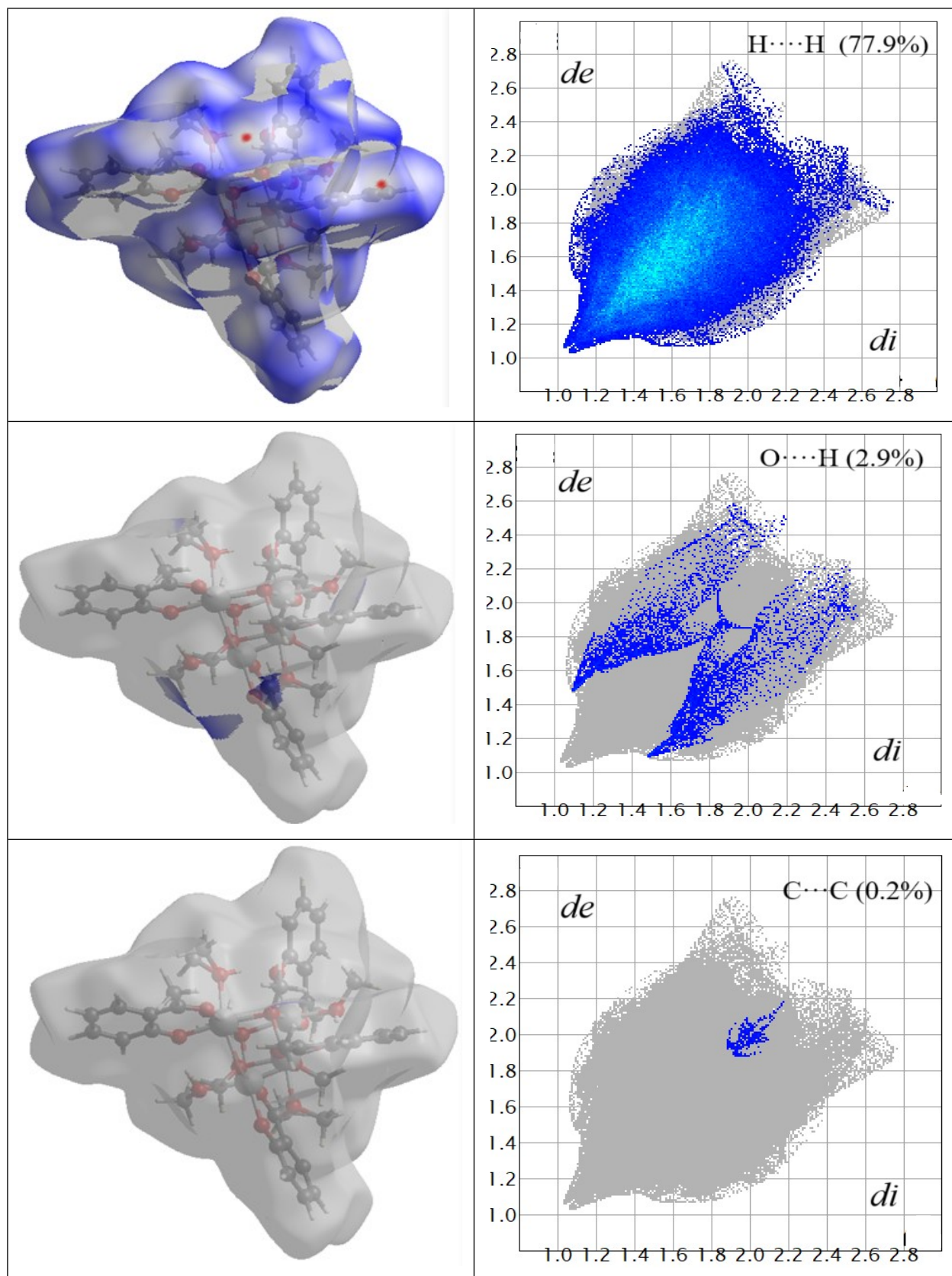
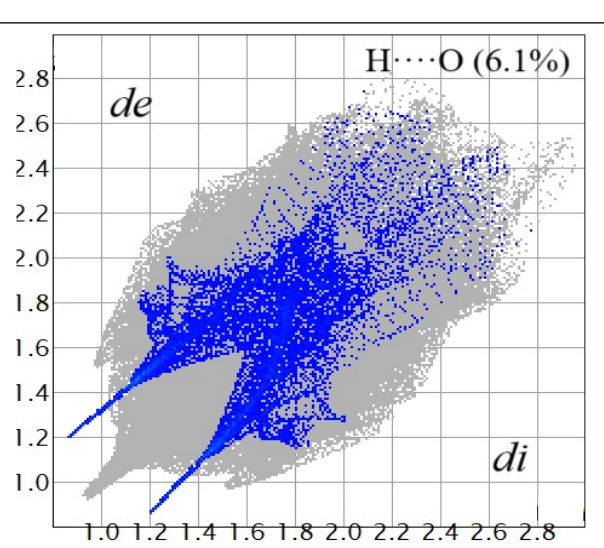
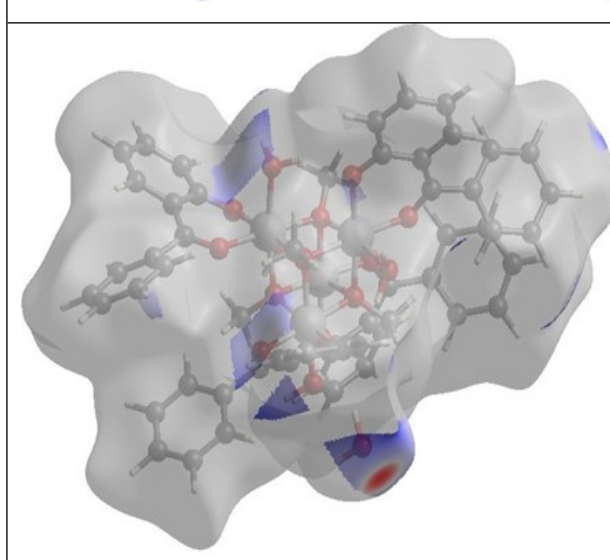
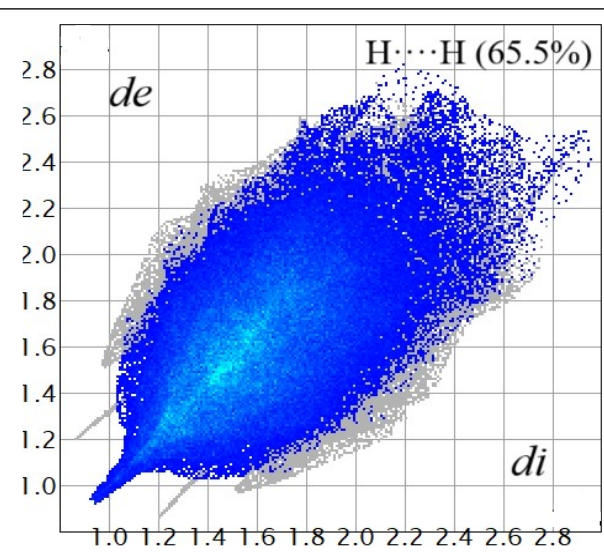
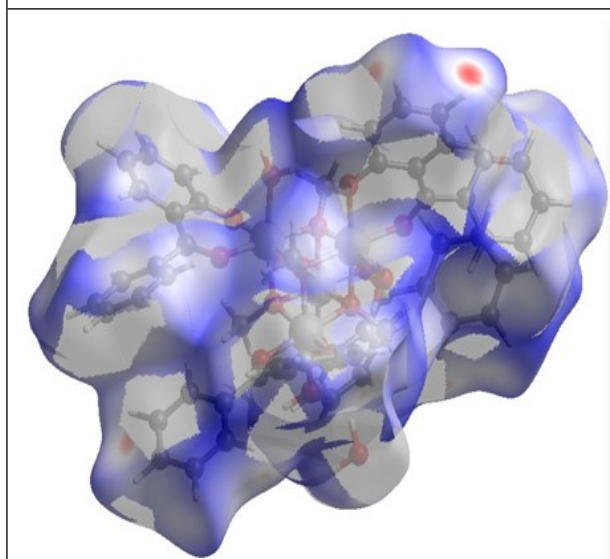
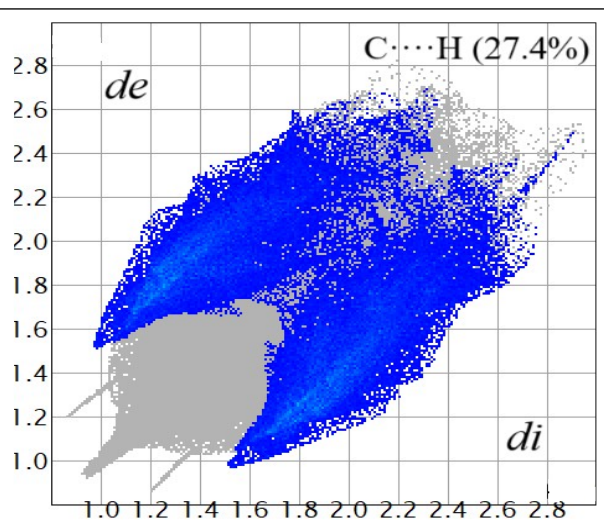
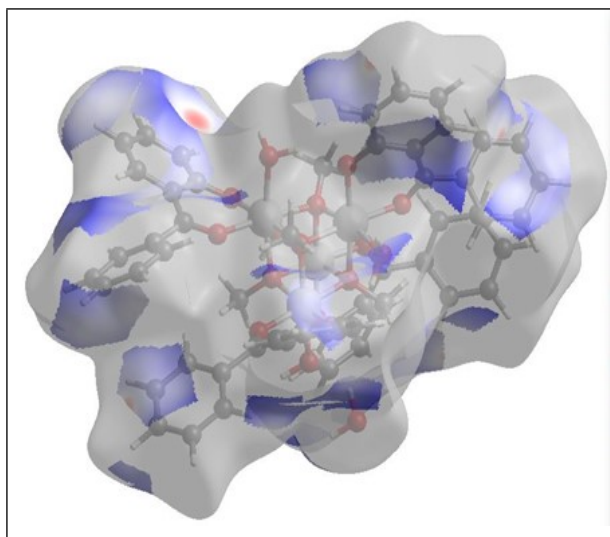


Fig. S6. Hirshfeld surface mapped with the d-norm property (left side) and 2D fingerprint plot (right side), showing details breakdown of all relative contributions to Hirshfeld surface from closest contacts for compound **1**.



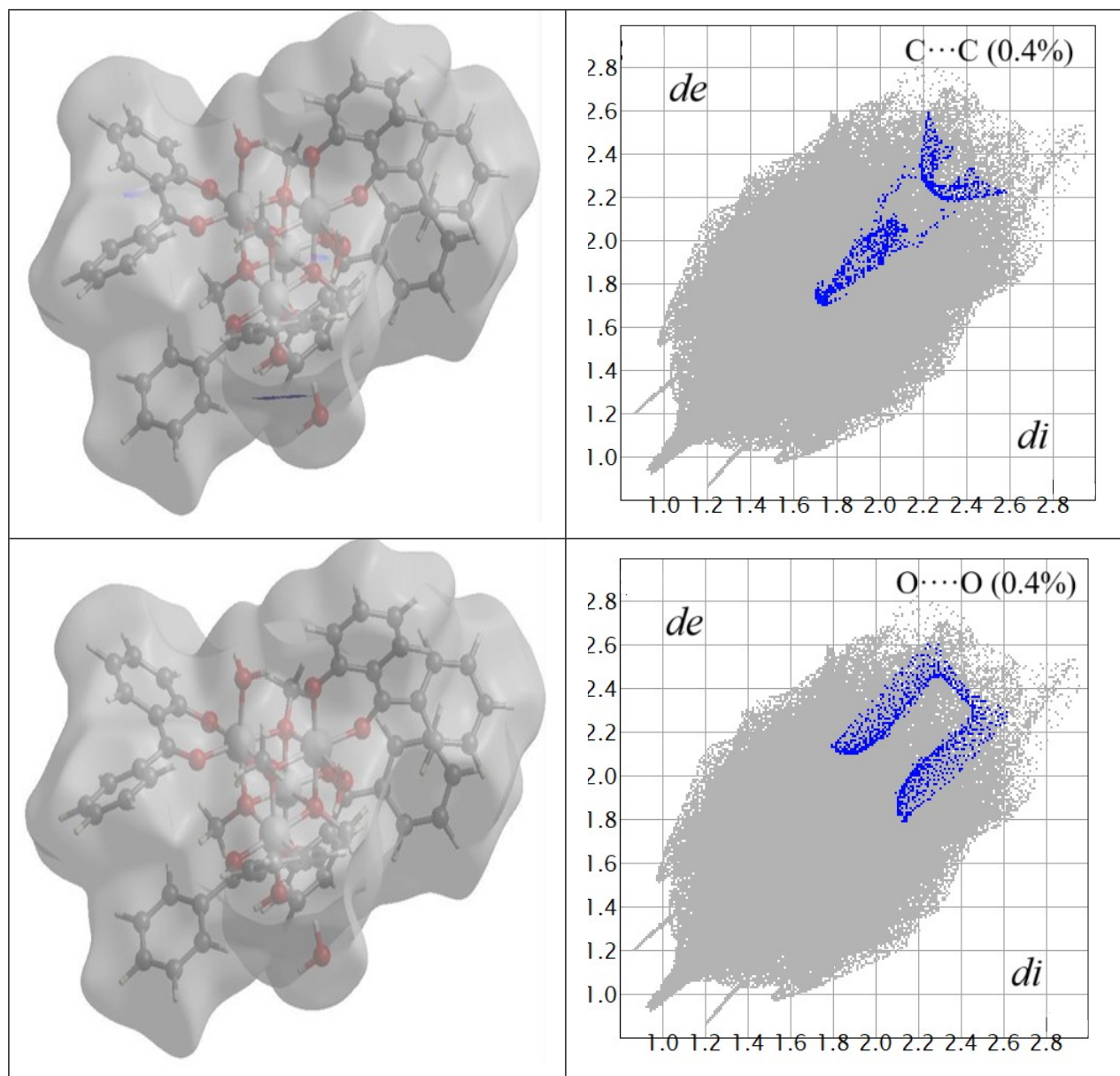
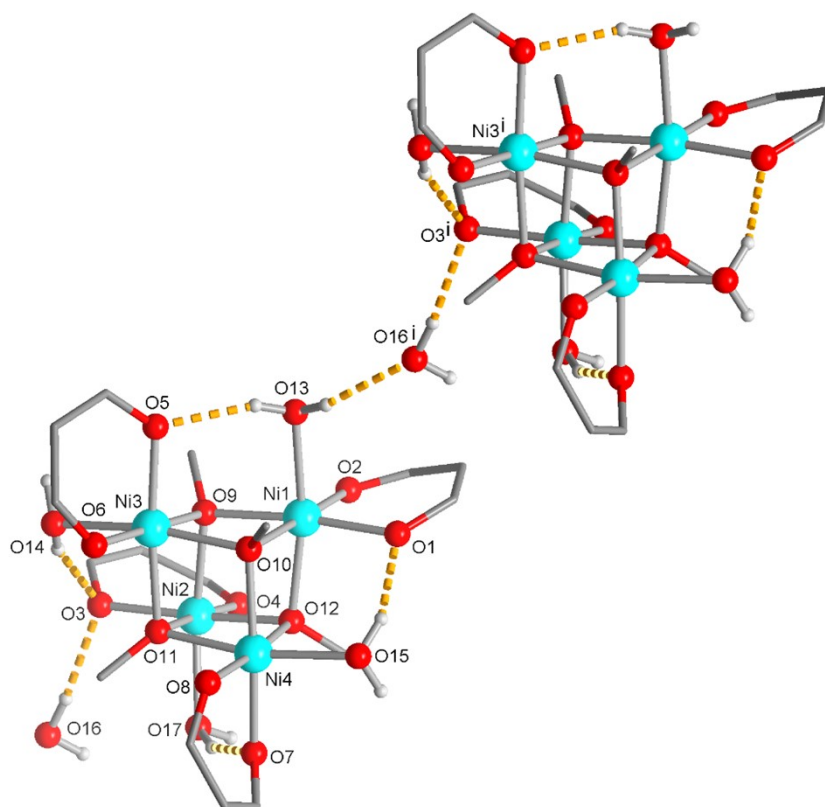


Fig. S7. Hirshfeld surface mapped with the d-norm property (left side) and 2D fingerprint plot (right side), showing details breakdown of all relative contributions to Hirshfeld surface from closest contacts for compound **2**.

Table S1. Hydrogen-bond geometry (Å, °) for **1**

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O10–H10 \cdots O11	0.91 (4)	1.80 (4)	2.686 (2)	164 (4)
O7–H7 \cdots O8	0.96 (2)	1.78 (2)	2.704 (2)	162 (5)
O13–H13 \cdots O14	0.86 (5)	1.82 (5)	2.663 (2)	166 (5)
O16–H16 \cdots O5	0.82 (6)	1.96 (6)	2.745 (2)	160 (6)

Table S2. Hydrogen-bond geometry (Å, °) for **2**.



$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O13-H13A \cdots O5	0.87	1.97	2.776 (3)	154
O13-H13B \cdots O16 ⁱ	0.87	2.19	3.017(3)	160
O14-H14A \cdots O3	0.87	1.97	2.806 (3)	160
O15-H15A \cdots O1	0.87	1.93	2.749 (3)	157
O17-H17A \cdots O7	0.87	1.88	2.701 (3)	157
O16-H16A \cdots O3	0.87	2.10	2.969(3)	174

Symmetry transformation: $i = 1+x, y, z$

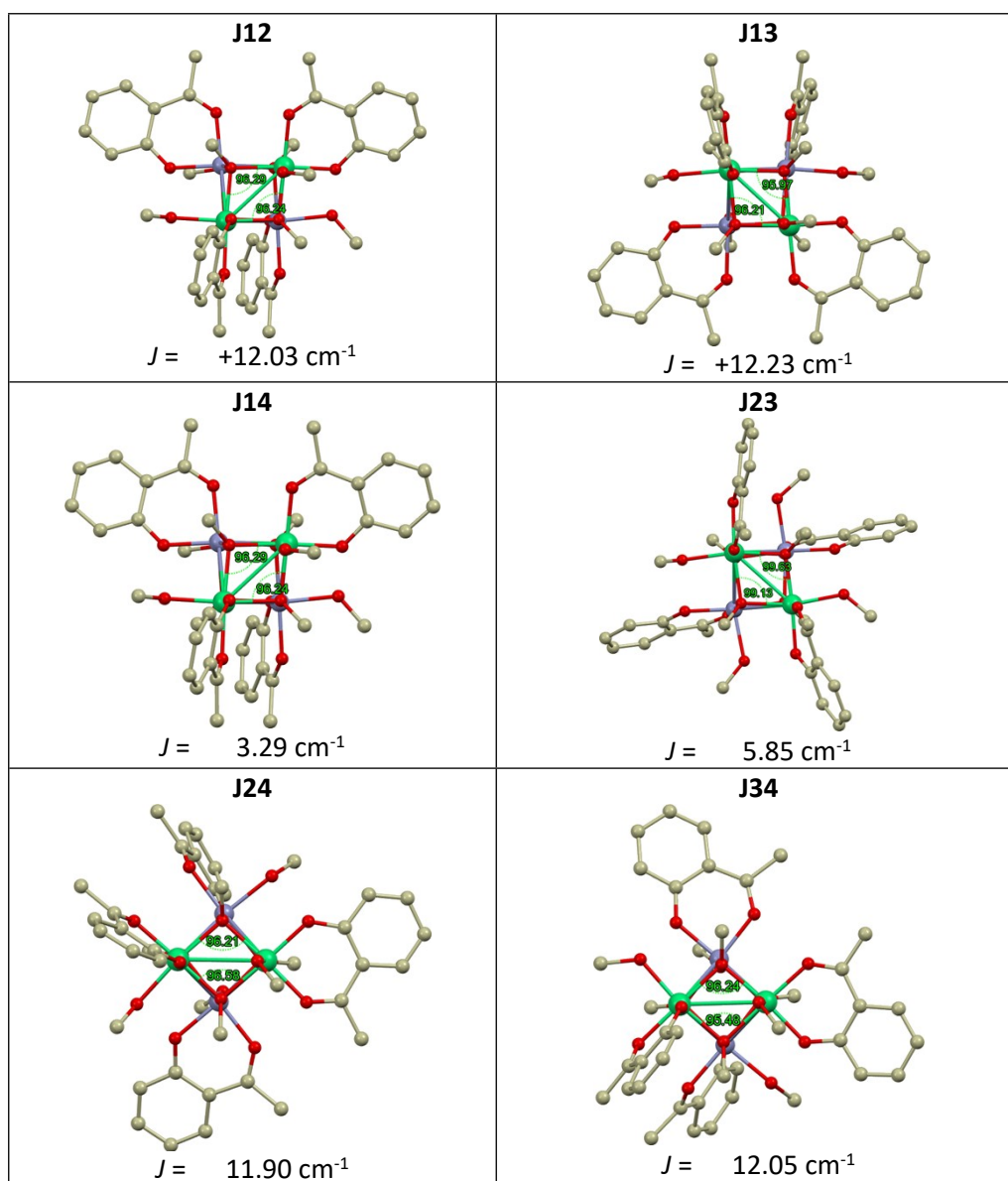
Note that from the water molecules with O14, O15, O16 and O17 only one H-atom participates in H-bonding. The other H-atom is without an acceptor.

BS-DFT studies

The positions of the hydrogen atoms were normalized. The BS-DFT calculations were performed for all six pairs of the Ni atoms within the cubane core, resulting in six calculations. In each case, two Ni atoms were substituted with diamagnetic d^{10} Zn(II) atoms to obtain the pair isotropic exchange interaction constant J_{ij} (e.g. for J_{12} the fragment containing NiNiZnZn atoms) using the following spin Hamiltonian for two paramagnetic centers A and B: $\hat{H}_i = JS_A S_B$. The energies of high spin (HS, $A\uparrow B\uparrow$) and broken symmetry states (BS, $A\uparrow B\downarrow$) were evaluated using Ruiz approach to calculate the

J values.¹ The BS-DFT calculations were performed using Orca 4.2.1 software² package and we used hybrid functional B3LYP³ and with Ahlrichs's triple- ζ basis sets def2-TZVP.⁴

Acetophenone based complex 1:

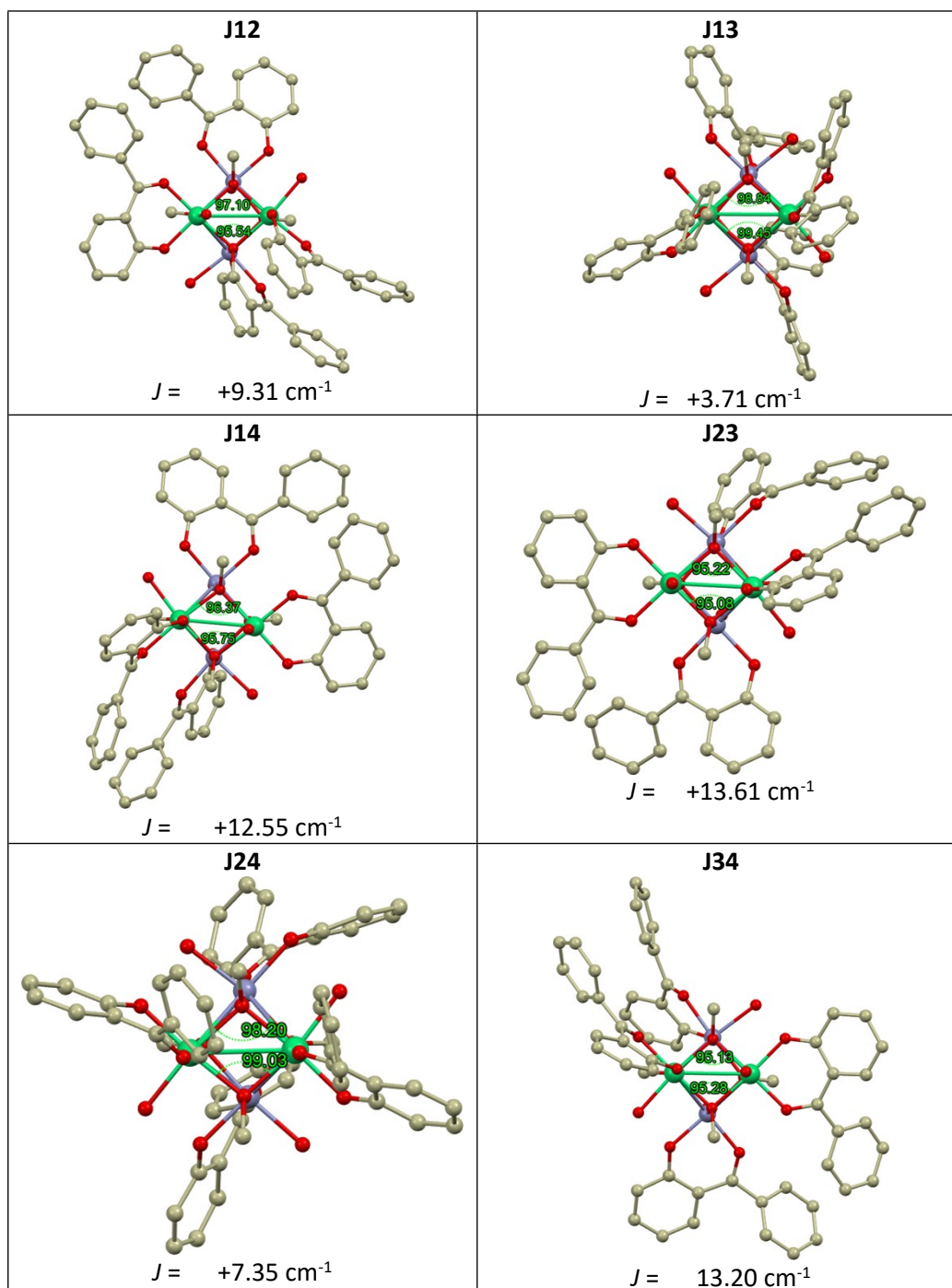


Coupling scheme for fitting of magnetic data:

$$J1 = J12 = J13 = J24 = J34$$

$$J2 = J14, J3 = J23$$

Benzophenone based complex 2:



Coupling scheme for fitting of magnetic data:

$$J1 = J12 = J24$$

$$J2 = J13, J3 = J14 = J23 = J34$$

Magnetic data fitting

The magnetic data following isotropic exchange spin Hamiltonians for fitting of the magnetic data measured for **1** and **2** (3J model):

$$\hat{H}_{iso} = -J_1(\vec{S}_1\vec{S}_2 + \vec{S}_1\vec{S}_3 + \vec{S}_2\vec{S}_4 + \vec{S}_3\vec{S}_4) - J_2(\vec{S}_1\vec{S}_4) - J_3(\vec{S}_2\vec{S}_3) \quad (1) \quad \text{for } \mathbf{1} \text{ and,}$$

$$\hat{H}_{iso} = -J_1(\vec{S}_1\vec{S}_2 + \vec{S}_2\vec{S}_4) - J_2(\vec{S}_1\vec{S}_3) - J_3(\vec{S}_1\vec{S}_4 + \vec{S}_2\vec{S}_3 + \vec{S}_3\vec{S}_4) \quad (2) \quad \text{for } \mathbf{2}, \text{ respectively.}$$

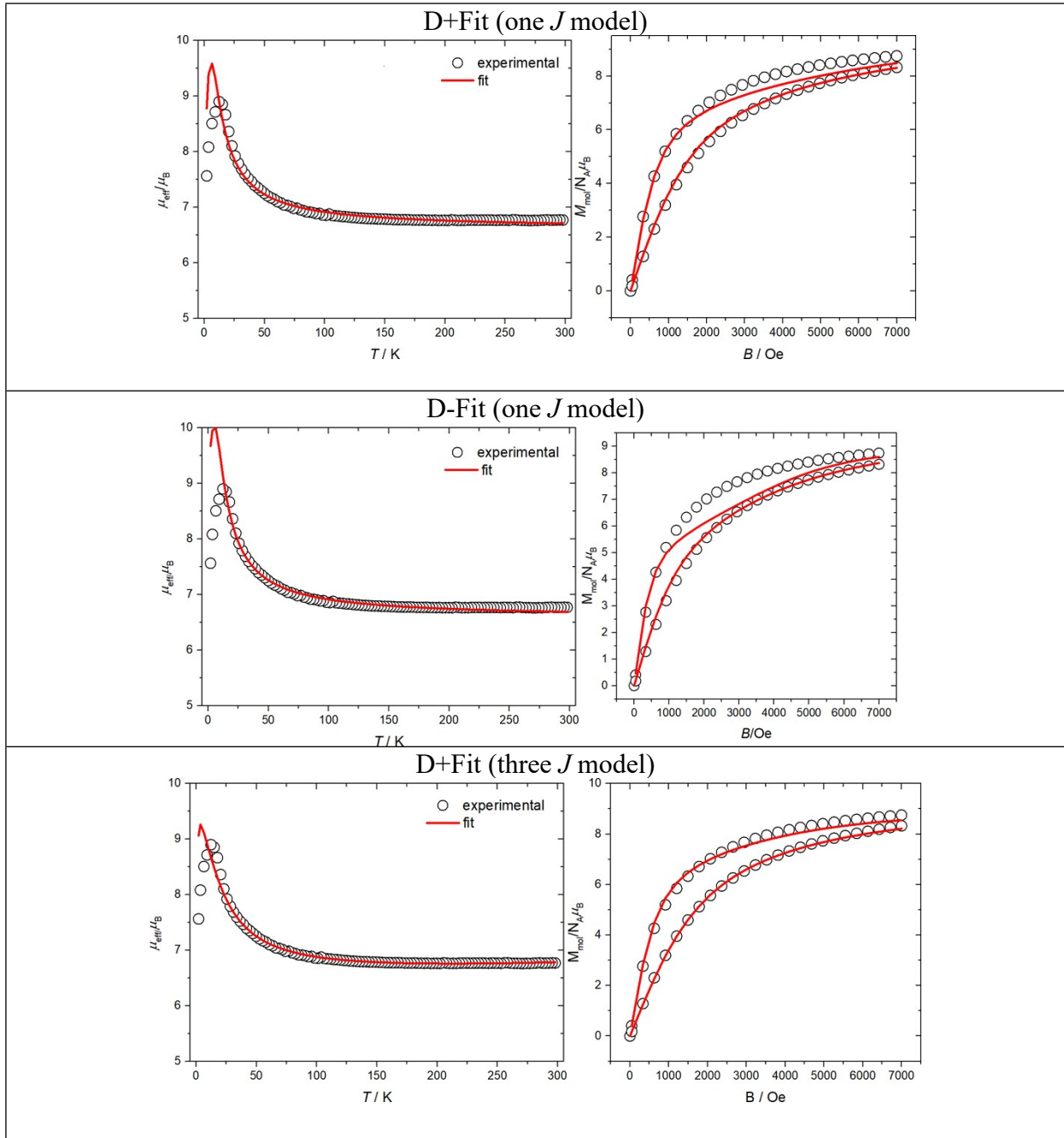
Then, the overall spin Hamiltonian including axial parameter of magnetic anisotropy D then reads:

$$\hat{H} = \hat{H}_{iso} + \sum_{i=1}^4 D_i(\hat{S}_z^2 - \hat{S}^2) + \mu_B B_a \sum_{i=1}^4 g\hat{S}_i \quad (3)$$

where a-direction of the magnetic field is defined as $B_a = B(\sin(\theta)\cos(\varphi), \sin(\theta)\sin(\varphi), \cos(\theta))$.

In the case of the 1J model the following spin Hamiltonian for isotropic exchange was used:

$$\hat{H}_{iso} = -J_1(\vec{S}_1\vec{S}_2 + \vec{S}_1\vec{S}_3 + \vec{S}_1\vec{S}_4 + \vec{S}_2\vec{S}_3 + \vec{S}_2\vec{S}_4 + \vec{S}_3\vec{S}_4) \quad (4)$$



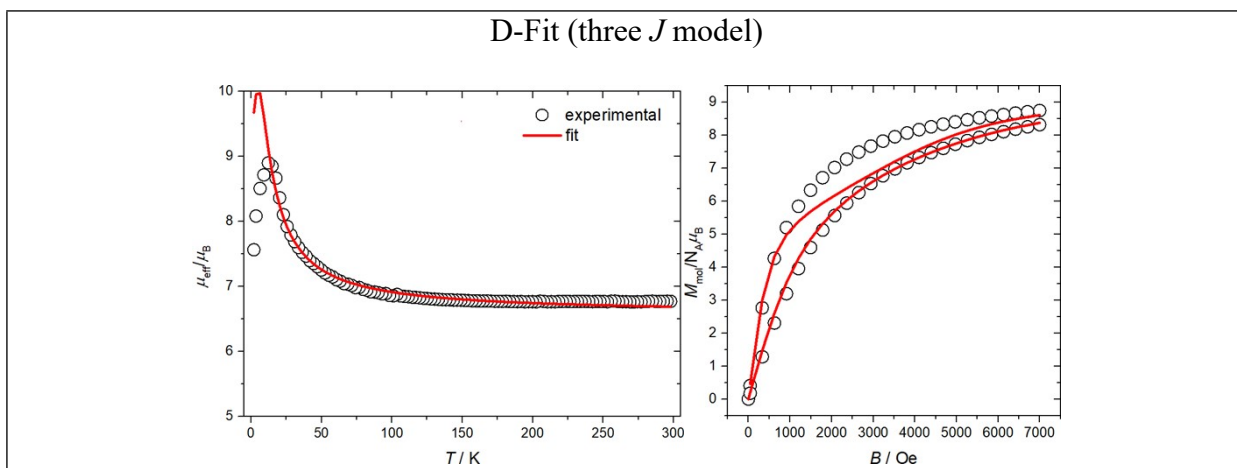
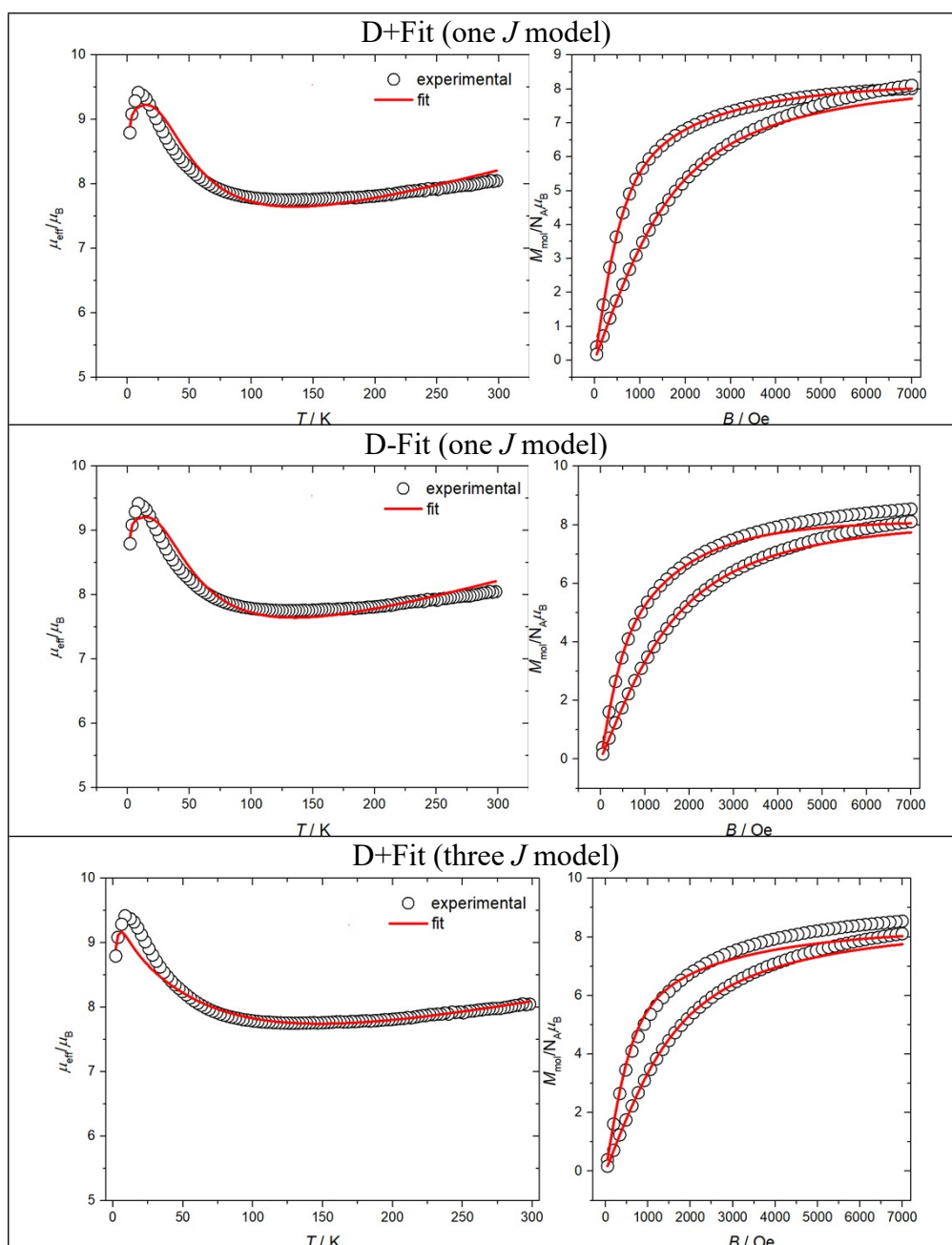


Fig. S8. Fits of the magnetic data for compound **1** using Eq. 1 or Eq. 3.



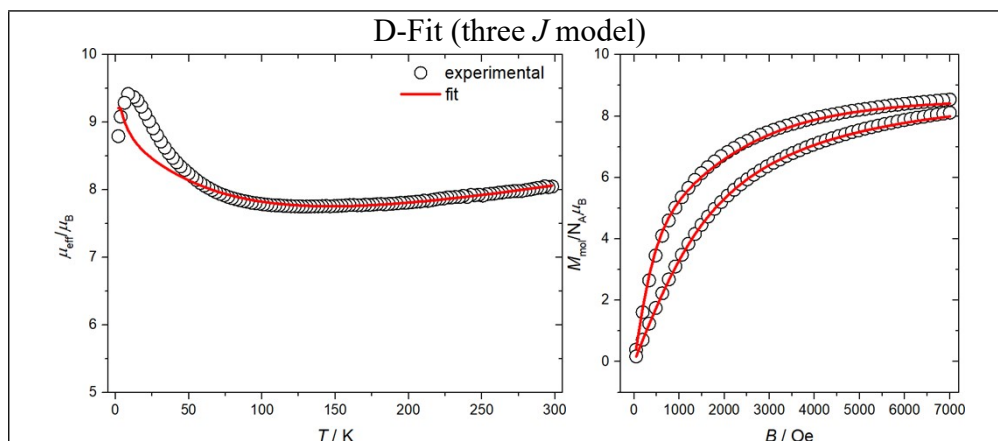


Fig. S9. Fits of the magnetic data for compound **2** using Eq. 1 or Eq. 3.

Table S3. The fitted spin Hamiltonian parameters for compound **1**.

1	g_{iso}	D/cm^{-1}	J_1/cm^{-1}	J_2/cm^{-1}	J_3/cm^{-1}	χ_{TIP}
1J model $+D_I$	2.335	+7.8	+3.2	—	—	0
1J model $-D_I$	2.324	-7.6	+3.5	—	—	0
3J model $+D$	2.329	+6.8	+1.1	-4.7	+12.1	0
3J model $-D$	2.324	-7.5	+2.9	+3.8	+5.6	0

Table S4. The fitted spin Hamiltonian parameters for compound **2**.

2	g_{iso}	D/cm^{-1}	J_1/cm^{-1}	J_2/cm^{-1}	J_3/cm^{-1}	χ_{TIP}
1J model $+D_I$	2.054	3.7	+14.3	—	—	150.7
1J model $-D_I$	2.045	-2.7	+14.5	—	—	152.2
3J model $+D$	2.084	+4.7	-5.7	-1.1	+46.6	124.6
3J model $-D$	2.161	-3.9	-8.8	-1.0	+43.6	111.1

References

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