Supporting Information

Rigorous extraction of the anisotropic multispin Hamiltonian in bimetallic complexes from the exact electronic Hamiltonian

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Matrix elements of the coupled spin Hamiltonian in the $|M_{S_A}, M_{S_B}\rangle$ basis in an arbitrary coordinate frame.

$$\begin{aligned}
\langle -1, -1 | \hat{H}_{mod} | -1, -1 \rangle &= D_a^{11} + D_a^{22} + 2D_a^{33} + D_{ab}^{33} + J \\
\langle -1, -1 | \hat{H}_{mod} | -1, 0 \rangle &= -\frac{1}{2}\sqrt{2} ((D_a^{13} + D_{ab}^{13}) + i(D_a^{23} + D_{ab}^{23})) \\
\langle -1, -1 | \hat{H}_{mod} | 0, -1 \rangle &= -\frac{1}{2}\sqrt{2} ((D_a^{13} + D_{ab}^{13}) + i(D_a^{23} + D_{ab}^{23})) \\
\langle -1, -1 | \hat{H}_{mod} | -1, 1 \rangle &= \frac{1}{2}(D_a^{11} - D_a^{22} + 2iD_a^{12}) \\
\langle -1, -1 | \hat{H}_{mod} | 0, 0 \rangle &= \frac{1}{2}(D_{ab}^{11} - D_{ab}^{22} + 2iD_{ab}^{12}) \\
\langle -1, -1 | \hat{H}_{mod} | 1, -1 \rangle &= \frac{1}{2}(D_a^{11} - D_a^{22} + 2iD_a^{12}) \\
\langle -1, -1 | \hat{H}_{mod} | 1, 0 \rangle &= 0 \\
\langle -1, -1 | \hat{H}_{mod} | 0, 1 \rangle &= 0 \\
\langle -1, -1 | \hat{H}_{mod} | 1, 1 \rangle &= 0 \\
\\
\langle -1, 0 | \hat{H}_{mod} | -1, 0 \rangle &= \frac{3}{2}(D_a^{11} + D_a^{22}) + D_a^{33} \\
\langle -1, 0 | \hat{H}_{mod} | 0, -1 \rangle &= \frac{1}{2}(D_{ab}^{11} + D_{ab}^{22}) + J \\
\langle -1, 0 | \hat{H}_{mod} | -1, 1 \rangle &= \frac{1}{2}\sqrt{2} ((D_a^{13} - D_{ab}^{13}) + i(D_a^{23} - D_{ab}^{23})) \\
\langle -1, 0 | \hat{H}_{mod} | 0, 0 \rangle &= -\frac{1}{2}\sqrt{2}(D_a^{13} + iD_a^{23}) \\
\langle -1, 0 | \hat{H}_{mod} | 1, -1 \rangle &= 0 \\
\langle -1, 0 | \hat{H}_{mod} | 1, 0 \rangle &= \frac{1}{2}(D_a^{11} - D_a^{22} + 2iD_a^{12}) \\
\langle -1, 0 | \hat{H}_{mod} | 0, 1 \rangle &= \frac{1}{2}(D_{ab}^{11} - D_{ab}^{22} + 2iD_{ab}^{12}) \\
\langle -1, 0 | \hat{H}_{mod} | 1, 1 \rangle &= 0 \\
\\
\langle 0, -1 | \hat{H}_{mod} | 0, -1 \rangle &= \frac{3}{2}(D_a^{11} + D_a^{22}) + D_a^{33} \\
\langle 0, -1 | \hat{H}_{mod} | -1, 1 \rangle &= 0 \\
\langle 0, -1 | \hat{H}_{mod} | 0, 0 \rangle &= -\frac{1}{2}\sqrt{2}(D_a^{13} + iD_a^{23}) \\
\langle 0, -1 | \hat{H}_{mod} | 1, -1 \rangle &= \frac{1}{2}\sqrt{2} ((D_a^{13} - D_{ab}^{13}) + i(D_a^{23} - D_{ab}^{23})) \\
\langle 0, -1 | \hat{H}_{mod} | 1, 0 \rangle &= \frac{1}{2}(D_{ab}^{11} - D_{ab}^{22} + 2iD_{ab}^{12}) \\
\langle 0, -1 | \hat{H}_{mod} | 0, 1 \rangle &= \frac{1}{2}(D_a^{11} - D_a^{22} + 2iD_a^{12}) \\
\langle 0, -1 | \hat{H}_{mod} | 1, 1 \rangle &= 0 \\
\\
\langle -1, 1 | \hat{H}_{mod} | -1, 1 \rangle &= D_a^{11} + D_a^{22} + 2D_a^{33} - D_{ab}^{33} - J \\
\langle -1, 1 | \hat{H}_{mod} | 0, 0 \rangle &= \frac{1}{2}(D_{ab}^{11} + D_{ab}^{22}) + J \\
\langle -1, 1 | \hat{H}_{mod} | 1, -1 \rangle &= 0 \\
\langle -1, 1 | \hat{H}_{mod} | 1, 0 \rangle &= 0 \\
\langle -1, 1 | \hat{H}_{mod} | 0, 1 \rangle &= -\frac{1}{2}\sqrt{2} ((D_a^{13} - D_{ab}^{13}) + i(D_a^{23} - D_{ab}^{23})) \\
\langle -1, 1 | \hat{H}_{mod} | 1, 1 \rangle &= \frac{1}{2}(D_a^{11} - D_a^{22} + 2iD_a^{12})
\end{aligned}$$

$$\begin{aligned}
\langle 0, 0 | \hat{H}_{mod} | 0, 0 \rangle &= 2(D_a^{11} + D_a^{22}) \\
\langle 0, 0 | \hat{H}_{mod} | 1, -1 \rangle &= \frac{1}{2}(D_{ab}^{11} + D_{ab}^{22}) + J \\
\langle 0, 0 | \hat{H}_{mod} | 1, 0 \rangle &= \frac{1}{2}\sqrt{2}(D_a^{13} + iD_a^{23}) \\
\langle 0, 0 | \hat{H}_{mod} | 0, 1 \rangle &= \frac{1}{2}\sqrt{2}(D_a^{13} + iD_a^{23}) \\
\langle 0, 0 | \hat{H}_{mod} | 1, 1 \rangle &= \frac{1}{2}(D_{ab}^{11} - D_{ab}^{22} + 2iD_{ab}^{12}) \\
\\
\langle 1, -1 | \hat{H}_{mod} | 1, -1 \rangle &= D_a^{11} + D_a^{22} + 2D_a^{33} - D_{ab}^{33} - J \\
\langle 1, -1 | \hat{H}_{mod} | 1, 0 \rangle &= -\frac{1}{2}\sqrt{2}(D_a^{13} - D_{ab}^{13} + i(D_a^{23} - D_{ab}^{23})) \\
\langle 1, -1 | \hat{H}_{mod} | 0, 1 \rangle &= 0 \\
\langle 1, -1 | \hat{H}_{mod} | 1, 1 \rangle &= \frac{1}{2}(D_a^{11} - D_a^{22} + 2iD_a^{12}) \\
\\
\langle 1, 0 | \hat{H}_{mod} | 1, 0 \rangle &= \frac{3}{2}(D_a^{11} + D_a^{22}) + D_a^{33} \\
\langle 1, 0 | \hat{H}_{mod} | 0, 1 \rangle &= \frac{1}{2}(D_{ab}^{11} + D_{ab}^{22}) + J \\
\langle 1, 0 | \hat{H}_{mod} | 1, 1 \rangle &= \frac{1}{2}\sqrt{2}(D_a^{13} + D_{ab}^{13} + i(D_a^{23} + D_{ab}^{23})) \\
\\
\langle 0, 1 | \hat{H}_{mod} | 0, 1 \rangle &= \frac{3}{2}(D_a^{11} + D_a^{22}) + D_a^{33} \\
\langle 0, 1 | \hat{H}_{mod} | 1, 1 \rangle &= \frac{1}{2}\sqrt{2}(D_a^{13} + D_{ab}^{13} + i(D_a^{23} + D_{ab}^{23})) \\
\\
\langle 1, 1 | \hat{H}_{mod} | 1, 1 \rangle &= D_a^{11} + D_a^{22} + 2D_a^{33} + D_{ab}^{33} + J
\end{aligned}$$

Table 1: Numerical matrix elements of the effective Hamiltonian in the coupled $|S, M_S\rangle$ basis in the magnetic proper axes frame.

H^{eff}	$ 2, 2\rangle$	$ 2, 1\rangle$	$ 2, 0\rangle$	$ 2, -1\rangle$	$ 2, -2\rangle$	$ 1, 1\rangle$	$ 1, 0\rangle$	$ 1, -1\rangle$	$ 0, 0\rangle$
$\langle 2, 2 $	1.670	0.001+0.003 <i>i</i>	1.616	0.000	0.002	0.000	0.000	0.000	-2.367+0.020 <i>i</i>
$\langle 2, 1 $	0.001-0.003 <i>i</i>	10.742	0.000	1.989	0.000	0.000	0.000	0.000	-0.024-0.086 <i>i</i>
$\langle 2, 0 $	1.616	0.000	13.793	0.000	1.616	0.000	0.000	0.000	9.057-0.001 <i>i</i>
$\langle 2, -1 $	0.000	1.989	0.000	10.742	-0.001-0.003 <i>i</i>	0.000	0.000	0.000	0.024-0.086 <i>i</i>
$\langle 2, -2 $	0.002	0.000	1.616	-0.001+0.003 <i>i</i>	1.670	0.000	0.000	0.000	-2.366-0.020 <i>i</i>
$\langle 1, 1 $	0.000	0.000	0.000	0.000	0.000	21.814	0.020+0.070 <i>i</i>	-2.095+0.025 <i>i</i>	0.000
$\langle 1, 0 $	0.000	0.000	0.000	0.000	0.000	0.020-0.070 <i>i</i>	12.021	-0.021-0.070 <i>i</i>	0.000
$\langle 1, -1 $	0.000	0.000	0.000	0.000	0.000	-2.095-0.025 <i>i</i>	-0.021+0.070 <i>i</i>	21.814	0.000
$\langle 0, 0 $	-2.367-0.020 <i>i</i>	-0.024+0.086 <i>i</i>	9.057+0.001 <i>i</i>	0.024+0.086 <i>i</i>	-2.366+0.020 <i>i</i>	0.000	0.000	0.000	24.125

SO-SI spectrum of $[\text{Ni}_2(\text{en})_4\text{Cl}_2]^{2+}$ as function of the spin-free isotropic exchange J used in the SO-RASSI calculation. CASPT2 energies are used for the excited states. The parameters of the standard spin coupled Hamiltonian extracted from each spectrum are listed in the Table (in cm^{-1}).

	-3.0 cm^{-1}	-6.0 cm^{-1}	-9.0 cm^{-1}	-12.0 cm^{-1}
J	-2.48	-5.41	-8.33	-11.25
D_a	-9.429	-9.436	-9.443	-9.449
D_{ab}	0.356	0.363	0.370	0.376
E_a	2.040	2.041	2.041	2.044
E_{ab}	-0.051	-0.052	-0.052	-0.055

Orthonormalized projections of the *ab initio* wave functions on the $|S, M_S\rangle$ model space.

	$ 2, 2\rangle$	$ 2, 1\rangle$	$ 2, 0\rangle$	$ 2, -1\rangle$	$ 2, -2\rangle$	$ 1, 1\rangle$	$ 1, 0\rangle$	$ 1, -1\rangle$	$ 0, 0\rangle$
Ψ_1	0.428+i0.488	-0.001+i0.002	-0.205-i0.236	-0.002+i0.001	0.424+i0.491	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.161+i0.185
Ψ_2	-0.707-i0.003	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.707+i0.009	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000
Ψ_3	-0.003-i0.003	0.479+i0.520	-0.006-i0.006	-0.479-i0.520	-0.002-i0.003	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.004+i0.004
Ψ_4	-0.143-i0.237	-0.016+i0.000	-0.417-i0.697	-0.008+i0.014	-0.141-i0.238	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.221+i0.370
Ψ_5	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.007+i0.006	-0.765+i0.644	0.004+i0.008	0.000+i0.000
Ψ_6	-0.002-i0.003	0.556-i0.436	-0.012-i0.015	0.556-i0.436	-0.002-i0.003	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.002+i0.003
Ψ_7	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.674+i0.212	0.004-i0.012	0.672+i0.220	0.000+i0.000
Ψ_8	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.646-i0.287	0.002-i0.001	-0.649+i0.280	0.000+i0.000
Ψ_9	-0.012+i0.044	-0.004+i0.000	0.139-i0.471	-0.004-i0.002	-0.013+i0.043	0.000+i0.000	0.000+i0.000	0.000+i0.000	0.246-i0.833

Table 2: Numerical matrix elements of the effective Hamiltonian in the uncoupled $|M_{S_a}, M_{S_b}\rangle$ basis obtained with the CASSCF spin-free energies on the diagonal of the spin-orbit matrix.

H^{eff}	$ -1, -1\rangle$	$ -1, 0\rangle$	$ 0, -1\rangle$	$ -1, 1\rangle$	$ 0, 0\rangle$	$ 1, -1\rangle$	$ 1, 0\rangle$	$ 0, 1\rangle$	$ 1, 1\rangle$
$\langle -1, -1 $	1.362	-0.067+0.126 <i>i</i>	-0.067+0.126 <i>i</i>	-0.450+0.040 <i>i</i>	1.785-0.175 <i>i</i>	-0.450+0.040 <i>i</i>	0.000	0.000	0.001
$\langle -1, 0 $	-0.067-0.126 <i>i</i>	11.003	-2.520	-0.022+0.042 <i>i</i>	0.017-0.022 <i>i</i>	-0.079+0.127 <i>i</i>	1.345-0.130 <i>i</i>	-0.006-0.006 <i>i</i>	0.000
$\langle 0, -1 $	-0.067-0.126 <i>i</i>	-2.520	11.003	-0.079+0.127 <i>i</i>	0.017-0.022 <i>i</i>	-0.022+0.042 <i>i</i>	-0.006-0.006 <i>i</i>	1.345-0.130 <i>i</i>	0.000
$\langle -1, 1 $	-0.450-0.040 <i>i</i>	-0.022-0.042 <i>i</i>	-0.079-0.127 <i>i</i>	12.569	0.820	6.412	0.079-0.127 <i>i</i>	0.022-0.042 <i>i</i>	-0.450+0.040 <i>i</i>
$\langle 0, 0 $	1.785+0.175 <i>i</i>	0.017+0.022 <i>i</i>	0.017+0.022 <i>i</i>	0.820	5.175	0.820	-0.017+0.022 <i>i</i>	-0.017+0.022 <i>i</i>	1.785-0.175 <i>i</i>
$\langle 1, -1 $	-0.450-0.040 <i>i</i>	-0.079-0.127 <i>i</i>	-0.022-0.042 <i>i</i>	6.412	0.820	12.569	0.022-0.042 <i>i</i>	0.079-0.127 <i>i</i>	-0.450+0.040 <i>i</i>
$\langle 1, 0 $	0.000	1.345+0.130 <i>i</i>	-0.006+0.006 <i>i</i>	0.079+0.127 <i>i</i>	-0.017-0.022 <i>i</i>	0.022+0.042 <i>i</i>	11.003	-2.520	0.067-0.126 <i>i</i>
$\langle 0, 1 $	0.000	-0.006+0.006 <i>i</i>	1.345+0.130 <i>i</i>	0.022+0.042 <i>i</i>	-0.017-0.022 <i>i</i>	0.079+0.127 <i>i</i>	-2.520	11.003	0.067-0.126 <i>i</i>
$\langle 1, 1 $	0.001	0.000	0.000	-0.450-0.040 <i>i</i>	1.785+0.175 <i>i</i>	-0.450-0.040 <i>i</i>	0.067+0.126 <i>i</i>	0.067+0.126 <i>i</i>	1.362

Coupled spin Hamiltonian matrix extended with fourth-order interaction in the proper magnetic axes frame.

$ M_{S_a}, M_{S_b}\rangle$	$ -1, 1\rangle$	$ -1, 0\rangle$	$ 0, -1\rangle$	$ -1, 1\rangle$	$ 0, 0\rangle$	$ 1, -1\rangle$	$ 1, 0\rangle$	$ 0, 1\rangle$	$ 1, 1\rangle$
$\langle -1, 1 $	$J + \frac{2}{3}(D_a + D_{ab})$ + (1)	0	0	$E_a + (2)$	$E_{ab} + (3)$	$E_a + (2)$	0	0	$0 + (4)$
$\langle -1, 0 $	0	$-\frac{1}{3}D_a + (5)$	$J - \frac{1}{3}D_{ab}$ + (6)	0	0	0	$E_a + (7)$	$E_{ab} - (3)$	0
$\langle 0, -1 $	0	$J - \frac{1}{3}D_{ab}$ + (6)	$-\frac{1}{3}D_a + (5)$	0	0	0	$E_{ab} - (3)$	$E_a + (7)$	0
$\langle -1, 1 $	$E_a + (2)$	0	0	$-J + \frac{2}{3}(D_a - D_{ab})$ + (1)	$J - \frac{1}{3}D_{ab}$ - (6)	$0 + (8)$	0	0	$E_a + (2)$
$\langle 0, 0 $	$E_{ab} + (3)$	0	0	$J - \frac{1}{3}D_{ab}$ - (6)	$-\frac{4}{3}D_a$ + (9)	$J - \frac{1}{3}D_{ab}$ - (6)	0	0	$E_{ab} + (3)$
$\langle 1, -1 $	$E_a + (2)$	0	0	$0 + (8)$	$J - \frac{1}{3}D_{ab}$ - (6)	$-J + \frac{2}{3}(D_a - D_{ab})$ + (1)	0	0	$E_a + (2)$
$\langle 1, 0 $	0	$E_a + (7)$	$E_{ab} - (3)$	0	0	0	$-\frac{1}{3}D_a + (5)$	$J - \frac{1}{3}D_{ab}$ + (6)	0
$\langle 0, 1 $	0	$E_{ab} - (3)$	$E_a + (7)$	0	0	0	$J - \frac{1}{3}D_{ab}$ + (6)	$-\frac{1}{3}D_a + (5)$	0
$\langle 1, 1 $	$0 + (4)$	0	0	$E_a + (2)$	$E_{ab} + (3)$	$E_a + (2)$	0	0	$J + \frac{2}{3}(D_a + D_{ab})$ + (1)

$$(1) = \frac{1}{4}(D_{xxxx} + D_{yyyy}) + \frac{1}{2}D_{xxyy} + D_{xxzz} + D_{yyzz} + D_{zzzz}$$

$$(2) = \frac{1}{4}(D_{xxxx} - D_{yyyy}) + \frac{1}{2}(D_{xxzz} - D_{yyzz})$$

$$(3) = \frac{1}{2}(D_{xxzz} - D_{yyzz})$$

$$(4) = \frac{1}{4}(D_{xxxx} + D_{yyyy}) - \frac{1}{2}D_{xxyy} - D_{xyxy}$$

$$(5) = \frac{1}{2}(D_{xxxx} + D_{yyyy}) + D_{xxyy} + D_{xxzz} + D_{yyzz}$$

$$(6) = \frac{1}{2}(D_{xxzz} + D_{yyzz})$$

$$(7) = \frac{1}{2}(D_{xxxx} - D_{yyyy})$$

$$(8) = \frac{1}{4}(D_{xxxx} + D_{yyyy}) + D_{xyxy} - \frac{1}{2}D_{xxyy}$$

$$(9) = D_{xxxx} + D_{yyyy} + 2D_{xxyy}$$