Supplementary Information

Orthogonal magnetic orbitals in high spin Cu-VO units: structure, magnetism and EPR study of anisotropic heterometallic complexes

Qing-Song Deng,[a] Yu-Shuang Zhang,[a] Ye-Xin Wang,[b] Yi Xie,[a] Peng-Xiang Fu,[c] Song Gao,[a,d] Zheng Liu*[d] and Shang-Da Jiang*[a]

a. Spin-X Institute, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 511442, China. E-mail: jiangsd@scut.edu.cn

b. Quantum Science Center of Guangdong-Hong Kong-Macao Greater Bay Area, Shenzhen, 518045, China. E-mail: wangyexin@quantumsc.cn

c. Beijing National Laboratory of Molecular Science, Beijing Key Laboratory of Magnetoelectric Materials and Devices, College of Chemistry and Molecular Engineering, Peking University, Beijing (China)

d. Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, LIFM, School of Chemistry, IGCME, Sun Yat-Sen University, Guangzhou 510275, China. E-mail: liuzh363@mail.sysu.edu.cn

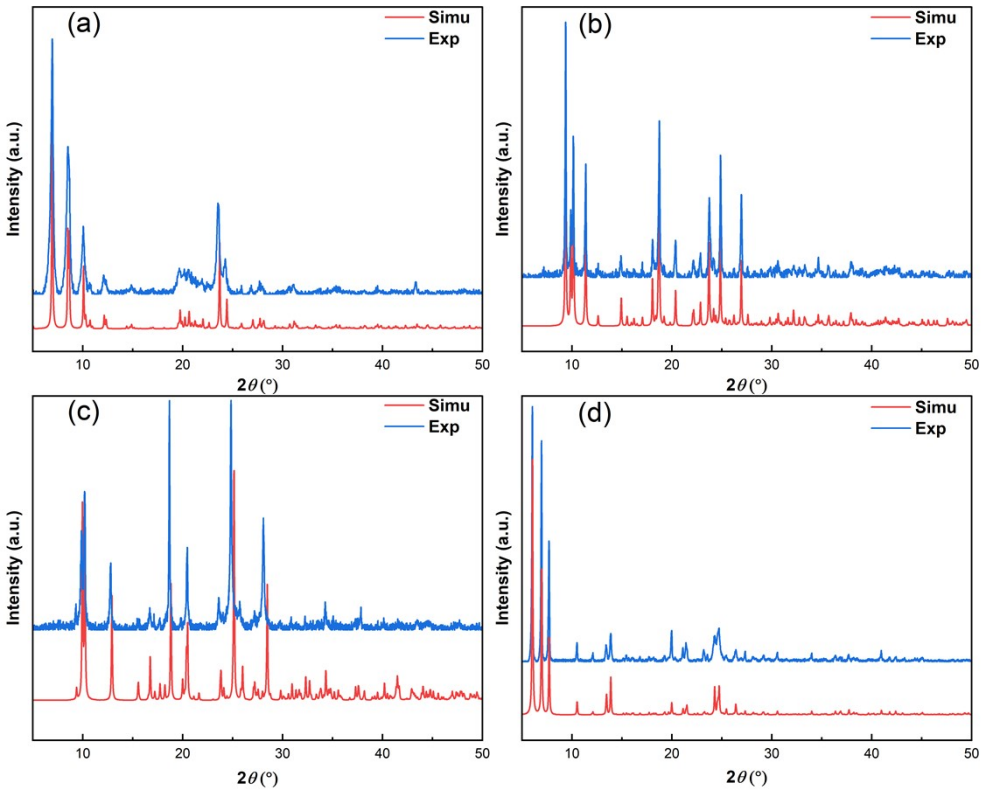

Figure S1. PXRD patterns of **1a** (a), **2a** (b), **2b** (c), **2c** (d). The simulated one based on their single crystal structures.

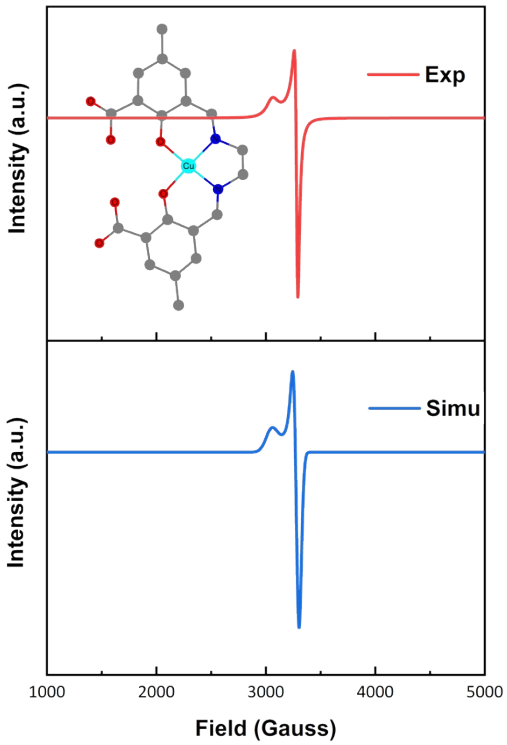

Figure S2. 9.388 GHz EPR spectrum of mononuclear Cu^{II} complex at 10 K. The inset shows the corresponding molecular structure. The Hamiltonian is: $\hat{H} = \mu_B \vec{B}^T \bar{\bar{g}}_{cu} \hat{S}$. The principal values of $\bar{\bar{g}}_{Cu}$ obtained from the simulation is [2.04 2.04 2.22].

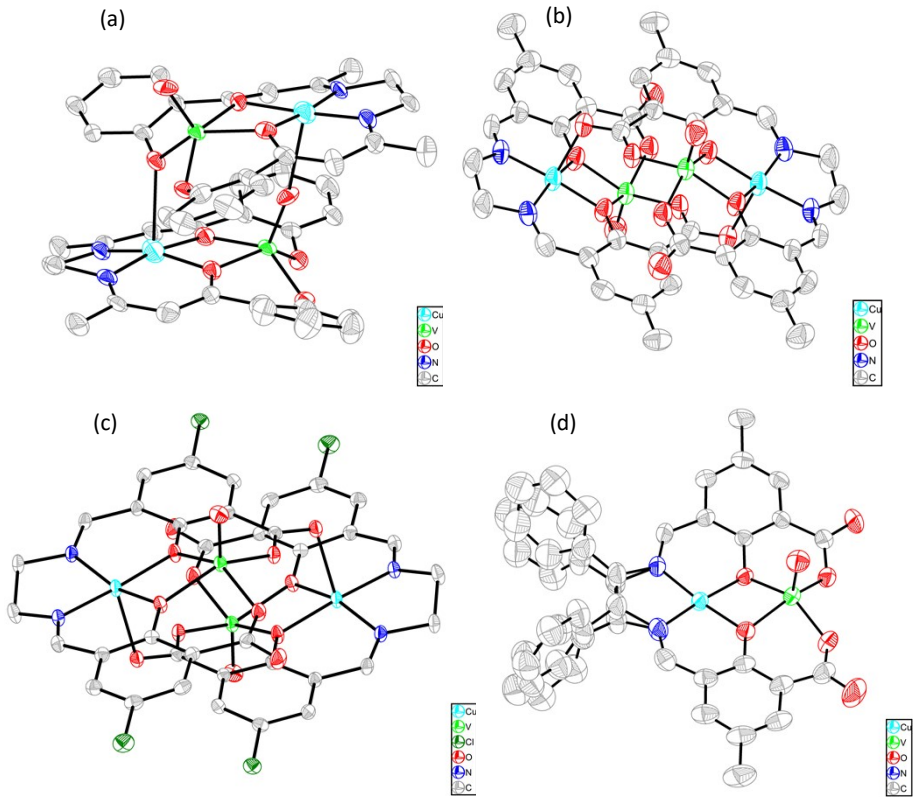

Figure S3. Structural representation of **1a** (a), **2a** (b), **2b** (c) and **2c** (d) with hydrogen atoms omitted (50% probability thermal ellipsoids).

Table S1. Crystallographic data of **1a**, **2a**, **2b** and **2c**

	1a	**2a**	**2b**	**2c**
Formula	$C_{44}H_{40}Cu_2N_4O_{10}V_2$	$C_{40}H_{32}Cu_2N_4O_{14}V_2$	$C_{36}H_{20}Cl_4Cu_2N_4O_{14}V_2$	$C_{32}H_{24}CuN_2O_7V$
FW (g mol^{-1})	1013.76	1021.65	1103.32	663.01
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	*P*-1	*C*2/*c*	*P*-1	*P*-1
a (Å)	9.0873(2)	20.1187(8)	9.6581(2)	7.3860(2)
b (Å)	13.3569(3)	10.8875(4)	10.7180(3)	13.3981(4)
c (Å)	17.7604(3)	18.4955(7)	10.7586(3)	15.4197(4)
α (°)	86.312(2)	90	114.387(3)	71.938(2)
β (°)	80.406(1)	109.576(4)	94.858(2)	84.339(2)
γ (°)	72.478(2)	90	111.117(2)	83.891(2)
V (Å3)	2026.72(8)	3817.1(3)	909.78(5)	1438.99(7)
ρ_{cacd} (g.cm^{-3})	1.661	1.778	2.014	1.530
μ (mm^{-1})	1.55	1.653	2.026	1.116
F (000)	1032.0	2064.0	548.0	676.0
Collected reflections	38210	14216	24914	21737
Independent reflections	7386	4840	4859	7306
R_{int}	0.122	0.0262	0.0314	0.0261

R_1 [$I > 2\sigma(I)$]	0.068	0.0390	0.0262	0.0793
wR_2 (all data)	0.174	0.1088	0.0712	0.2426
GOF	1.076	1.017	1.070	1.092

Table S2. Selected bond lengths [Å] and angles [°] for **1a**, **2a**, **2b** and **2c**

1a					
Cu1—O4	1.937 (7)	V1—O4	2.025 (7)	Cu2—O2	1.929 (8)
Cu1—O5	1.933 (8)	V1—O5	2.025 (8)	Cu2—N1	1.906 (9)
Cu1—O9	2.401 (7)	V1—O6	1.908 (8)	Cu2—N2	1.902 (10)
Cu1—N3	1.898 (9)	V1—O8	1.599 (7)	V2—O7	1.918 (8)
Cu1—N4	1.892 (10)	V2—O1	1.994 (8)	V2—O9	1.578 (8)
Cu2—O1	1.932 (8)	V2—O2	2.037 (8)	V2—O10	1.899 (8)
V1—O3	1.930 (7)				
O4—Cu1—O9	81.8 (3)	O6—V1—O4	145.4 (3)	O10—V2—O1	142.4 (3)
O5—Cu1—O4	80.6 (3)	O6—V1—O5	87.4 (3)	O10—V2—O2	84.8 (3)
O5—Cu1—O9	84.8 (3)	O8—V1—O3	108.1 (4)	O10—V2—O7	90.7 (3)
N3—Cu1—O4	95.6 (4)	O8—V1—O4	107.5 (4)	Cu2—O1—V2	102.9 (4)
N3—Cu1—O5	174.5 (4)	O8—V1—O5	107.1 (4)	Cu2—O2—V2	101.4 (4)
N3—Cu1—O9	98.6 (3)	O8—V1—O6	106.4 (4)	Cu1—O4—V1	100.7 (3)
N4—Cu1—O4	174.3 (4)	O1—V2—O2	75.4 (3)	V2—O9—Cu1	169.9 (5)
N4—Cu1—O5	95.9 (4)	O7—V2—O1	85.2 (3)	N2—Cu2—O1	161.9 (4)
N4—Cu1—O9	102.4 (3)	O7—V2—O2	140.6 (3)	N2—Cu2—O2	95.0 (4)
N4—Cu1—N3	87.6 (4)	O9—V2—O1	109.2 (4)	N2—Cu2—N1	87.6 (4)
O2—Cu2—O1	79.4 (3)	O9—V2—O2	110.1 (4)	O3—V1—O4	87.2 (3)
N1—Cu2—O1	95.2 (4)	O9—V2—O7	108.6 (4)	O3—V1—O5	144.2 (3)
N1—Cu2—O2	169.7 (4)	O9—V2—O10	107.6 (4)	O5—V1—O4	76.3 (3)
O6—V1—O3	88.8 (3)				
2a					
Cu1—V1	3.0231 (5)	V1—O3	1.9484 (17)	V1—O4	1.928 (2)
Cu1—O1	1.9059 (17)	V1—O1	1.9802 (18)	V1—O7	1.579 (2)
Cu1—O2	1.9241 (18)	V1—O2	1.9753 (18)	Cu1—N2	1.897 (2)
Cu1—O5^{i}	2.349 (2)	Cu1—N1	1.900 (2)		
O1—Cu1—V1	39.82 (5)	O3—V1—O1	84.17 (7)	N2—Cu1—V1	133.43 (7)
O1—Cu1—O2	79.46 (7)	O3—V1—O2	143.78 (8)	N2—Cu1—O1	169.82 (9)
O1—Cu1—O5^{i}	93.30 (8)	O1—V1—Cu1	38.05 (5)	N2—Cu1—O2	94.90 (9)
O2—Cu1—V1	39.79 (5)	O2—V1—Cu1	38.56 (5)	N2—Cu1—O5^{i}	95.48 (9)
O2—Cu1—O5^{i}	93.11 (8)	O2—V1—O1	76.47 (7)	N2—Cu1—N1	87.73 (10)
O5i—Cu1—V1	96.85 (5)	O4—V1—Cu1	120.52 (6)	O7—V1—O3	107.06 (10)
N1—Cu1—V1	131.62 (8)	O4—V1—O3	92.42 (8)	O7—V1—O1	108.27 (11)
N1—Cu1—O1	95.16 (9)	O4—V1—O1	144.89 (9)	O7—V1—O2	107.97 (10)
N1—Cu1—O2	162.43 (10)	O4—V1—O2	86.55 (8)	O7—V1—O4	106.13 (11)
N1—Cu1—O5^{i}	103.95 (9)	O7—V1—Cu1	110.77 (8)	Cu1—O1—V1	102.12 (8)
Cu1—O2—V1	101.65 (8)				
Symmetry code: (i) −x+1, −y+1, −z+1.					
2b					
Cu1—V1	3.0259 (4)	V1—O3	1.9566 (13)	V1—O7	1.5890 (14)
Cu1—O1	1.9127 (12)	V1—O1	1.9858 (12)	Cu1—N1	1.9096 (15)
Cu1—O2	1.9258 (12)	V1—O2	1.9855 (12)	Cu1—N2	1.8952 (15)
Cu1—O5^{i}	2.3311 (13)	V1—O4	1.9269 (13)		
O1—Cu1—V1	39.97 (4)	O3—V1—O1	84.53 (5)	O7—V1—O3	107.29 (7)
O1—Cu1—O2	79.81 (5)	O3—V1—O2	143.96 (6)	O7—V1—O1	108.19 (7)
O1—Cu1—O5^{i}	92.44 (5)	O1—V1—Cu1	38.22 (4)	O7—V1—O2	107.70 (7)
O2—Cu1—V1	40.04 (4)	O2—V1—Cu1	38.61 (4)	O7—V1—O4	105.78 (7)
O2—Cu1—O5^{i}	94.21 (5)	O2—V1—O1	76.64 (5)	Cu1—O1—V1	101.81 (6)
O5—Cu1—V1	97.49 (3)	O4—V1—Cu1	120.88 (4)	Cu1—O2—V1	101.35 (6)
N1—Cu1—V1	131.81 (5)	O4—V1—O3	92.20 (6)	N2—Cu1—V1	134.33 (5)
N1—Cu1—O1	95.08 (6)	O4—V1—O1	145.28 (6)	N2—Cu1—O1	171.92 (6)
N1—Cu1—O2	163.61 (6)	O4—V1—O2	86.52 (5)	N2—Cu1—O2	95.30 (6)

N1—Cu1—O5^{i}	101.60 (6)	O7—V1—Cu1	110.14 (5)	N2—Cu1—O5^{i}	94.33 (5)
N2—Cu1—N1	87.85 (6)	O3—V1—Cu1	118.56 (4)		
Symmetry code: (i) −x+1, −y+1, −z+1.					
2c					
Cu1—V1	2.9612 (9)	V1—O2	1.923 (4)	V1—O3	1.586 (4)
Cu1—O5	1.914 (3)	V1—O4	1.947 (3)	Cu1—N2	1.897 (4)
Cu1—O6	1.922 (3)	V1—O5	1.961 (3)	Cu1—O3^{i}	2.438 (4)
Cu1—N1	1.895 (4)	V1—O6	1.998 (3)		
O5—Cu1—V1	40.76 (10)	O2—V1—O4	93.82 (16)	N2—Cu1—V1	134.61 (16)
O5—Cu1—O6	80.65 (14)	O2—V1—O5	86.68 (16)	N2—Cu1—O5	95.32 (19)
O5—Cu1—O3^{i}	93.38 (15)	O2—V1—O6	146.25 (16)	N2—Cu1—O6	175.54 (18)
O6—Cu1—V1	41.92 (10)	O4—V1—Cu1	123.97 (11)	N2—Cu1—O3^{i}	92.7 (2)
O6—Cu1—O3^{i}	89.41 (15)	O4—V1—O5	148.39 (16)	O3i—Cu1—V1	81.87 (10)
N1—Cu1—V1	134.76 (13)	O4—V1—O6	84.89 (14)	O2—V1—Cu1	124.72 (13)
N1—Cu1—O5	174.17 (18)	O5—V1—Cu1	39.58 (10)	O3—V1—O2	107.4 (2)
N1—Cu1—O6	96.18 (16)	O5—V1—O6	77.65 (13)	O3—V1—O4	103.4 (2)
N1—Cu1—N2	88.0 (2)	O6—V1—Cu1	40.00 (9)	O3—V1—O5	106.6 (2)
N1—Cu1—O3^{i}	81.65 (18)	O3—V1—Cu1	101.44 (16)	O3—V1—O6	105.71 (18)
Cu1—O5—V1	99.66 (15)	Cu1—O6—V1	98.08 (14)		
Symmetry code: (i) −x+1, −y+2, −z.					

Compound	*J* / cm-1	φ / °	θ / °	*R* / Å	*R*' / Å	Ref
2c	-132.66	1.6	98.08, 99.66	2.096	3.86	This work
D	-91.20	6.41	101.8, 101.86	3.089	3.98	1
2a	-122.40	8.9	102.12, 101.66	3.023	3.88	This work
2b	-117.85	9.2	101.81, 101.35	3.026	3.9	This work
C	-118	9.8	99.21, 98.47	2.989	3.92	2
1a	-94	27.5	102.16, 100.68	3.054	3.94	This work
B	-85	31.97	97.51, 98.02	3.067	4.06	3
A	-85	31.43	106.34, 94.37	3.131	3.92	4

Table S3. Coupling constant and structural parameters.

References

1 T. Glaser, H. Theil, I. Liratzis, T. Weyhermüller and E. Bill, *Inorganic Chemistry*, 2006, **45**, 4889-4891.

2 O. Kahn, J. Galy, Y. Journaux, J. Jaud and I. Morgenstern-Badarau, *Journal of the American Chemical Society*, 1982, **104**, 2165-2176.

3 S. Mohanta, K. K. Nanda, L. K. Thompson, U. Flörke and K. Nag, *Inorganic Chemistry*, 1998, **37**, 1465-1472.

4 A. Bencini, C. Benelli, A. Dei and D. Gatteschi, *Inorganic Chemistry*, 1985, **24**, 695-699.

Relationship between J_{23} in four *S* = 1/2 spins coupled model and J_{iso} in two *S* = 1 spins coupled model

The energy gaps between different spin multiplicities is relevant for isotropic exchange interactions, and based on symmetry consideration, these energy gaps in "multi-spin" system can be obtained by diagonalizing the Hamiltonian as follow.

$$\hat{H} = J_1\hat{S}_1^T\hat{S}_2 + J_2\hat{S}_2^T\hat{S}_3 + J_1\hat{S}_3^T\hat{S}_4 + J_2\hat{S}_4^T\hat{S}_1 \#(1)$$

Table S4. Eigenvalues of the 16 × 16 Hamiltonian matrix.

eigenvalue	spin multiplicity
$-\frac{J_1+J_2}{2}$	3
$\frac{J_1-J_2}{2}$	3
$-\frac{J_1-J_2}{2}$	3
$\frac{J_1+J_2}{2}$	5
$-\frac{J_1+J_2+2\sqrt{J_1^2-J_1J_2+J_2^2}}{2}$	1
$-\frac{J_1+J_2-2\sqrt{J_1^2-J_1J_2+J_2^2}}{2}$	1

The nine lowest energy levels of the system contain a quintet, a triplet, and a singlet, with energy gaps E_1 for the quintet and triplet and E_2 for the triplet and singlet.

$$E_1 = J_2 \#(2)$$

$$E_2 = \left|J_1 + \sqrt{J_1^2 - J_1J_2 + J_2^2}\right| \#(3)$$

When J_2/J_1 tends to 0,

$$\lim_{\frac{J_2}{J_1}\to 0} \left|J_1 + \sqrt{J_1^2 - J_1J_2 + J_2^2}\right| = \left|\frac{J_2}{2}\right| \#(4)$$

Based on the interactions obtained from the magnetic data, the electronic structure of **2b** and **2c** at low energy can also be approximated by the "giant-spin" Hamiltonian. The coupling between two *S* = 1 spins is denoted by J_{iso},

$$\hat{H} = J_{iso}\hat{S}_a^T\hat{S}_b \#(5)$$

The eigenvalues of this 9 × 9 Hamiltonian matrix as shown in Table S5.

Table S5. Eigenvalues of the 9 × 9 Hamiltonian matrix.

eigenvalue	spin multiplicity
$-2J_{iso}$	1
$-J_{iso}$	3
J_{iso}	5

The energy gap between the quintet and triplet is E_1', and the energy gap between the triplet and singlet is E_2'.

$$E_1' = 2J_{iso} \#(6)$$

$$E_2' = J_{iso} \#(7)$$

Comparing Equation (2), Equation (4) and Equation (6), Equation (7), a following relationship exists when J_2/J_1 tends to 0,

$$J_{iso} = \frac{J_2}{2} \#(8)$$

Table S6. Hamiltonian parameters used for calculation.

EPR parameters	2b	2c
$g_{i\parallel}$	2.08	2.08
$g_{i\perp}$	2.00	2.00
D_{ixx} / cm^{-1}	0.063	0.067
D_{iyy} / cm^{-1}	-0.141	-0.174
D_{izz} / cm^{-1}	0.078	0.107
J_{iso} / cm^{-1}	-0.373	5.18
D_{abxx} / cm^{-1}	-0.165	-0.267
D_{abyy} / cm^{-1}	-0.140	-0.133
D_{abzz} / cm^{-1}	0.305	0.400

Table S7. Matrix elements calculated with the following spin Hamiltonian and basis sets at zero field of effective model containing two S = 1 spins.

$$\hat{H} = \sum_{i=a}^{b} \mu_B \vec{B}^T \bar{\bar{g}}_i \hat{S}_i + \sum_{i=a}^{b} \hat{S}_i^T \bar{\bar{D}}_i \hat{S}_i + J \hat{S}_a^T \hat{S}_b + \hat{S}_a^T \bar{\bar{D}}_{ab} \hat{S}_b \#(9)$$

	$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$	$\|0,1\rangle$	$\|0,0\rangle$	$\|0,-1\rangle$	$\|-1,1\rangle$	$\|-1,0\rangle$	$\|-1,-1\rangle$
$\langle 1,1\|$	$\frac{2D}{3}+\frac{2D_{ab}}{3}+J$	0	E	0	E_{ab}	0	E	0	0
$\langle 1,0\|$	0	$\frac{-D}{3}$	0	$\frac{-D_{ab}}{3}+J$	0	E_{ab}	0	E	0
$\langle 1,-1\|$	E	0	$\frac{2D}{3}-\frac{2D_{ab}}{3}-J$	0	$\frac{-D_{ab}}{3}+J$	0	0	0	E
$\langle 0,1\|$	0	$\frac{-D_{ab}}{3}+J$	0	$\frac{-D}{3}$	0	E	0	E_{ab}	0
$\langle 0,0\|$	E_{ab}	0	$\frac{-D_{ab}}{3}+J$	0	$\frac{-4D}{3}$	0	$\frac{-D_{ab}}{3}+J$	0	E_{ab}
$\langle 0,-1\|$	0	E_{ab}	0	E	0	$\frac{-D}{3}$	0	$\frac{-D_{ab}}{3}+J$	0
$\langle -1,1\|$	E	0	0	0	$\frac{-D_{ab}}{3}+J$	0	$\frac{2D}{3}-\frac{2D_{ab}}{3}-J$	0	E
$\langle -1,0\|$	0	E	0	E_{ab}	0	$\frac{-D_{ab}}{3}+J$	0	$\frac{-D}{3}$	0
$\langle -1,-1\|$	0	0	E	0	E_{ab}	0	E	0	$\frac{2D}{3}+\frac{2D_{ab}}{3}+J$

$D = \frac{3}{2}D_{zz}$, $E = \frac{1}{2}\left(D_{xx} - D_{yy}\right)$. D_{xx}, D_{yy} and D_{zz} are principal values of $\bar{D}_i$.

$D_{ab} = \frac{3}{2}D_{abzz}$, $E_{ab} = \frac{1}{2}\left(D_{abxx} - D_{abyy}\right)$. D_{abxx}, D_{abyy} and D_{abzz} are principal values of $\bar{D}_{ab}$.

Table S8. Energy level results obtained and corresponding state compositions of **2b**.

Energy / GHz	Expression	State composition								
		$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$	$\|0,1\rangle$	$\|0,0\rangle$	$\|0,-1\rangle$	$\|-1,1\rangle$	$\|-1,0\rangle$	$\|-1,-1\rangle$
-23.402	(Complicated)	-0.105	0	0.451	0	0.755	0	0.451	0	-0.105
-19.606	$(2D+2D_{ab}+3J)/3$	0	-0.500	0	-0.500	0	0.500	0	0.500	0
-14.240	$(-D-D_{ab}+3E+3E_{ab}+3J)/3$	0	-0.500	0	-0.500	0	-0.500	0	-0.500	0
-0.294	$(-D+D_{ab}-3E+3E_{ab}-3J)/3$	0.683	0	-0.051	0	0.250	0	-0.051	0	0.683
0.300	(Complicated)	-0.707	0	0	0	0	0	0	0	0.707
4.337	$(-D-D_{ab}-3E-3E_{ab}+3J)/3$	0	0	0.707	0	0	0	-0.707	0	0
11.152	$(2D-2D_{ab}-3J)/3$	0	0.500	0	-0.500	0	0.500	0	-0.500	0
18.018	$(-D+D_{ab}+3E-3E_{ab}-3J)/3$	0	0.500	0	-0.500	0	-0.500	0	0.500	0
23.696	(Complicated)	0.151	0	0.542	0	-0.606	0	0.542	0	0.151

Table S9. Energy level results obtained and corresponding state compositions of **2c**.

Energy / GHz	Expression	State composition								
		$\|1,1\rangle$	$\|1,0\rangle$	$\|1,-1\rangle$	$\|0,1\rangle$	$\|0,0\rangle$	$\|0,-1\rangle$	$\|-1,1\rangle$	$\|-1,0\rangle$	$\|-1,-1\rangle$
-310.670	(Complicated)	0.011	0	-0.581	0	0.570	0	-0.581	0	0.011
-163.777	$(-D+D_{ab}-3E+3E_{ab}-3J)/3$	0	0	-0.707	0	0	0	0.707	0	0
-154.303	$(2D-2D_{ab}-3J)/3$	0	-0.500	0	0.500	0	-0.500	0	0.500	0
-147.798	$(-D+D_{ab}+3E-3E_{ab}-3J)/3$	0	-0.500	0	0.500	0	0.500	0	-0.500	0
139.429	(Complicated)	0.041	0	-0.402	0	-0.821	0	-0.402	0	0.041
144.470	$(2D+2D_{ab}+3J)/3$	0	0.500	0	0.500	0	-0.500	0	-0.500	0
150.616	$(-D-D_{ab}+3E+3E_{ab}+3J)/3$	0	0.500	0	0.500	0	0.500	0	0.500	0
170.792	$(-D-D_{ab}-3E-3E_{ab}+3J)/3$	-0.707	0	0	0	0	0	0	0	0.707
171.241	(Complicated)	-0.706	0	-0.033	0	-0.039	0	-0.033	0	-0.706