supporting information

Ligand Field Fine-tuning on Modulation of Magnetic Properties and

Relaxation Dynamics for Dysprosium (III) Single-Ion Magnets

(SIMs): Synthesis, Structure, Magnetism and Ab Initio Calculations

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| Compound | 1 | 2 | 3 | 4 |
|--|----------------------------------|------------------|---------------------|------------------|
| Emminical formaulo | $C_{41.33}H_{25.67}DyF_{12}$ | $C_{42}H_{23}Dy$ | $C_{43}H_{32}Dy \\$ | $C_{45}H_{36}Dy$ |
| Empirical formula | N ₂ O _{6.33} | $F_{12}N_2O_6$ | $F_9N_2O_6$ | $F_9N_2O_7$ |
| Formula weight | 1042.14 | 1042.12 | 1006.21 | 1050.26 |
| Temperature | 296(2) K | 296(2) K | 293(2) | 296(2) K |
| Crystal system | Trigonal | Triclinic | Triclinic | Triclinic |
| space group | <i>P</i> -3 | <i>P</i> -1 | <i>P</i> -1 | <i>P</i> -1 |
| <i>a</i> (Å) | 26.791(4) | 10.273(2) | 12.429(3) | 10.8160(11) |
| <i>b</i> (Å) | 26.791(4) | 13.625(3) | 17.651(4) | 10.9937(11) |
| <i>c</i> (Å) | 10.119(2) | 15.204(3) | 21.655(5) | 18.5997(18) |
| α (°) | 90 | 83.405(4) | 87.902(5) | 81.692(2) |
| eta (°) | 90 | 87.777(4) | 74.279(5) | 86.565(2) |
| γ (°) | 120 | 76.586(4) | 71.393(4) | 84.476(2) |
| $V(Å^3)$ | 6289.8(19) | 2056.1(7) | 4327.5(18) | 2166.2(4) |
| Ζ | 6 | 2 | 2 | 2 |
| F(000) | 3074 | 1022 | 1996 | 1046 |
| Goodness of fit (F ²) | 1.022 | 1.051 | 1.099 | 1.082 |
| $\Gamma' = 1 D' = 1$ $\Gamma = 2 C = -1$ | R1 = 0.0652 | R1 = 0.0637 | R1 = 0.1032 | R1 = 0.0359 |
| Final R indices [1>2sigma(1)] | $wR_2 = 0.1243$ | $wR_2 = 0.1391$ | $wR_2 = 0.2068$ | $wR_2 = 0.1052$ |
| | R1 = 0.1382 | R1 = 0.1739 | R1 = 0.1225 | R1 = 0.0400 |
| k indices (all data) | $wR_2 = 0.1415$ | $wR_2 = 0.1905$ | $wR_2 = 0.2561$ | $wR_2 = 0.1150$ |
| CCDC | 1446105 | 1445984 | 1518734 | 1518732 |

 Table S1. Crystallographic Data for the compounds 1-4.

Table S2. Selected bond lengths (Å) and angles (°) for 1-4.

| | | 1 | | | |
|-----------------|----------|-----------------|----------|-----------------|----------|
| Dy(1)-O(1) | 2.290(7) | O(1)-Dy(1)-O(5) | 82.1(3) | O(1)-Dy(1)-O(3) | 142.0(3) |
| Dy(1)-O(4) | 2.295(7) | O(4)-Dy(1)-O(5) | 75.0(2) | O(4)-Dy(1)-O(3) | 73.1(3) |
| Dy(1)-O(2) | 2.301(7) | O(2)-Dy(1)-O(5) | 148.8(3) | O(2)-Dy(1)-O(3) | 74.7(2) |
| Dy(1)-O(3) | 2.326(7) | O(3)-Dy(1)-O(5) | 118.2(3) | O(1)-Dy(1)-O(6) | 143.1(3) |
| Dy(1)-O(6) | 2.341(7) | O(6)-Dy(1)-O(5) | 70.2(3) | O(4)-Dy(1)-O(6) | 111.4(3) |
| Dy(1)-O(5) | 2.381(8) | O(1)-Dy(1)-N(2) | 111.0(3) | O(2)-Dy(1)-O(6) | 139.8(2) |
| Dy(1)-N(2) | 2.529(9) | O(4)-Dy(1)-N(2) | 149.3(3) | O(1)-Dy(1)-N(1) | 74.4(3) |
| Dy(1)-N(1) | 2.558(8) | O(2)-Dy(1)-N(2) | 75.7(3) | O(4)-Dy(1)-N(1) | 146.9(3) |
| O(1)-Dy(1)-O(4) | 83.1(3) | O(3)-Dy(1)-N(2) | 80.0(3) | O(2)-Dy(1)-N(1) | 112.3(2) |
| O(1)-Dy(1)-O(2) | 73.3(3) | O(6)-Dy(1)-N(2) | 74.2(3) | O(3)-Dy(1)-N(1) | 138.0(3) |
| O(4)-Dy(1)-O(2) | 83.0(3) | O(5)-Dy(1)-N(2) | 132.4(3) | O(6)-Dy(1)-N(1) | 76.4(3) |

| O(3)-Dy(1)-O(6) | 74.4(2) | N(2)-Dy(1)-N(1) | 63.4(3) | O(5)-Dy(1)-N(1) | 78.2(3) |
|---------------------|-----------|--------------------------|-------------|--------------------------|----------|
| $D_{\rm W}(1) O(2)$ | 7706101 | $2 = 0(3) D_{y}(1) O(1)$ | 71 7(2) | $O(3)$ $D_{2}(1)$ $O(5)$ | 142 7(2) |
| Dy(1)-O(3) | 2.280(8) | O(3)-Dy(1)-O(1) | (1.)(3) | O(3)-Dy(1)-O(3) | 142.7(2) |
| Dy(1)-O(0) | 2.302(9) | O(0)-Dy(1)-O(1) | 138.8(3) | O(0)-Dy(1)-O(3) | 72.0(2) |
| Dy(1)-O(2) | 2.307(8) | O(2)-Dy(1)-O(1) | 1/2.7(3) | O(2)-Dy(1)-O(3) | 75.0(5) |
| Dy(1)-O(5) | 2.311(8) | O(5)-Dy(1)-O(1) | 142.6(3) | O(3)-Dy(1)-O(4) | /1.5(3) |
| Dy(1)-O(4) | 2.327(7) | O(4)- $Dy(1)$ - $O(1)$ | 115.3(3) | O(6)-Dy(1)-O(4) | 87.8(2) |
| Dy(1)-O(1) | 2.334(10) | O(3)-Dy(1)-N(2) | 138.0(3) | O(2)-Dy(1)-O(4) | 81./(3) |
| Dy(1)-N(2) | 2.553(10) | O(6)-Dy(1)-N(2) | 93.7(3) | O(5)-Dy(1)-O(4) | 77.5(2) |
| Dy(1)-N(1) | 2.605(9) | O(2)-Dy(1)-N(2) | 81.3(3) | O(3)-Dy(1)-N(1) | 76.0(4) |
| O(3)-Dy(1)-O(6) | 85.7(3) | O(5)-Dy(1)-N(2) | 74.9(3) | O(6)-Dy(1)-N(1) | 71.2(3) |
| O(3)-Dy(1)-O(2) | 119.2(3) | O(4)-Dy(1)-N(2) | 150.5(4) | O(2)-Dy(1)-N(1) | 131.9(3) |
| O(6)-Dy(1)-O(2) | 147.4(3) | O(1)-Dy(1)-N(2) | 82.1(3) | O(5)-Dy(1)-N(1) | 122.2(3) |
| O(4)-Dy(1)-N(1) | 142.3(4) | O(1)-Dy(1)-N(1) | 70.2(3) | O(3)-Dy(1)-O(1) | 71.7(3) |
| | | 3 | | | |
| Dy(1)-O(2) | | 2.28(3) | O(6-Dy(1)- | ·O(3) 1. | 39.5(9) |
| Dy(1)-O(6) | | 2.30(3) | O(6)-Dy(1) | -N2) 7 | 2.7(9) |
| Dy(1)-O(5) | | 2.33(3) | O(5)-Dy(1) | -N(1) 1. | 36.8(8) |
| Dy(1)-O(4) | | 2.34(3) | O(5)-Dy(1) | -O(4) 7' | 7.3(10) |
| Dy(1)-O(3) | | 2.36(2) | O(5)-Dy(1) | -O(3) 14 | 45.2(9) |
| Dy(1)-O(1) | | 2.28(2) | O(5)-Dy(1) | -N(2) 8 | 0.7(9) |
| N(1)-Dy(1)-N2 |) | 64.1(9) | O(4)-Dy(1) | -N(1) 1 | 14.1(9) |
| O(2)-Dy(1)-N(1 | .) | 80.2(8) | O4)-Dy(1)- | ·O(3) 7 | 1.3(9) |
| O(2)-Dy(1)-O(6 | 5) | 79.5(9) | O(4)-Dy(1) | -N(2) 7 | 5.2(9) |
| O(2)-Dy(1)-O(5 | 5) | 119.3(10) | O(3)-Dy(1) | -N(1) 7 | 2.0(8) |
| O(2)-Dy(1)-O(4 | ł) | 139.5(9) | O(3)-Dy(1) | -N(2) 10 | 04.9(9) |
| O(2)-Dy(1)-O(3 | 3) | 78.6(9) | O(1)-Dy(1) | -N(1) 14 | 45.9(8) |
| O(2)-Dy(1)-O(1 |) | 73.6(8) | O(1)-Dy(1) | -O(6) 12 | 23.5(9) |
| O(2)-Dy(1)-N(2 | 2) | 140.1(9) | O(1)- Dy(1) | -O(5) 7 | 6.4(9) |
| O(6)-Dy(1)-N(1 |) | 71.0(9) | O(1)- Dy(1) | -O(4) 7 | 5.7(9) |
| O(6)-Dy(1)-O(5 | 5) | 75.3(10) | O1)- Dy(1)- | -O(3) 8 | 1.6(8) |
| O(6)-Dy(1)-O(4 | ł) | 140.4(9) | O(1)- Dy(1) | -N(2) 14 | 46.1(9) |
| N(1)-Dy(1) | | 2.477(18) | Dy(1)-N | (2) 2 | .53(3) |
| | | 4 | | | |
| Dy(1)-O(5) | | 2.307(3) | O(3)-Dy(1) | -O(2) 75 | .07(12) |
| Dy(1)-O(6) | | 2.315(3) | O(5)-Dy(1) | -O(4) 77 | .71(11) |
| Dy(1)-O(1) | | 2.319(3) | O(6)-Dy(1) | -O(4) 141 | .62(11) |
| Dy(1)-O(3) | | 2.333(3) | O(1)-Dy(1) | -O(4) 75 | .78(11) |
| | | | | | |

| Dy(1)-O(2) | 2.336(3) | O(3)-Dy(1)-O(4) | 71.75(11) |
|-----------------|------------|-----------------|------------|
| Dy(1)-O(4) | 2.359(3) | O(2)-Dy(1)-O(4) | 136.13(11) |
| Dy(1)-N(1) | 2.544(4) | O(5)-Dy(1)-N(1) | 134.04(11) |
| Dy(1)-N(2) | 2.554(4) | O(6)-Dy(1)-N(1) | 72.13(11) |
| O(5)-Dy(1)-O(6) | 73.26(10) | O(1)-Dy(1)-N(1) | 150.50(12) |
| O(5)-Dy(1)-O(1) | 74.08(11) | O(3)-Dy(1)-N(1) | 74.74(12) |
| O(6)-Dy(1)-O(1) | 118.28(11) | O(2)-Dy(1)-N(1) | 82.83(12) |
| O(5)-Dy(1)-O(3) | 145.59(11) | O(4)-Dy(1)-N(1) | 114.31(12) |
| O(6)-Dy(1)-O(3) | 141.11(11) | O(5)-Dy(1)-N(2) | 79.56(12) |
| O(1)-Dy(1)-O(3) | 83.26(11) | O(6)-Dy(1)-N(2) | 75.90(12) |
| O(5)-Dy(1)-O(2) | 120.27(11) | O(1)-Dy(1)-N(2) | 143.73(12) |
| O(6)-Dy(1)-O(2) | 81.12(11) | O(3)-Dy(1)-N(2) | 106.53(12) |
| O(1)-Dy(1)-O(2) | 72.54(11) | O(2)-Dy(1)-N(2) | 143.50(12) |

Table S3. Dy^{III} ion geometry analysis of 1-4 by SHAPE 2.1 software.

 Dy^{III} ion geometry analysis of 1

| HPP-8 3 Deh Heragonal bipyramid SAPR-8 5 Did4 Square antiprism TD-8 6 D22 Triangular dodecahedron JGEP-8 7 D24 Johnson syrobifastigium J26 JGEP-8 10 C22 Biaugemented trigonal prism J50 BTPR-8 0 C22 Biaugemented trigonal prism JSD-8 11 D22 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JETEP-8 BTPR-8 ABOXIT , 16.036, 9.293, 0.511, 2.267, 15.933, 226.208, 2.818, 2.207, Dy ^{III} ion geometry analysis of 2 HEPY-8 3 Deh Heragonal bipyramid CU-8 SAPR-8 5 Did4 Square antiprism JGEP-8 7 D24 Johnson gorobifastigium J26 JGEP-8 7 D24 Johnson gorobifastigium J26 JGEP-8 11 D22 Snub diphenoid J84 Structure [ML8] MEY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JETEP-8 STPR-8 SAPR-8 5 D4d Square antiprism JGEP-8 7 D24 Johnson gorobifastigium J26 JGEP-8 11 D22 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JETEP-8 JSD-8 ADOXIT J D28 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JETEP-8 JSD-8 ADOXIT J D28 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JETEP-8 JSD-8 ADOXIT J D28 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JSTPR-8 JSD-8 ADOXIT J D28 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JSTPR-8 JSD-8 ADOXIT J D29 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JSTPR-8 JSD-8 ADOXIT J D29 Snub diphenoid J84 Structure [ML8] HEPY-8 CU-8 SAPR-8 TDD-8 JGER-8 JETEPY-8 JSTPR-8 JSD-8 ADOXIT J T CONTINUOUS Shape Measures calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona Contact: Hunell&bu.edu T | Dy ^{III} ion (SHAPE (c) 2013 E1 | v2.1 Lectronic Tres 3 Dé 4 Of 5 DJ 6 D2 7 D2 7 D2 7 D2 8 D3 9 C2 10 C2 11 D2 | Structure (sontact: 11) bh Hexagon d Cube d Square a d Triangu d Johnson tu Biaugmen tu Biaugmen d Snub di | al bipyramic antiprism Lar dodecahe gyrobifasti elongated t nted trigona nted J84 | I gium J26 riangular b I prism J50 I prism | ipyramid J1 | 4 | | | | | |
|--|--|---|--|--|--|----------------------|-------------------|---------------------|------------------|------------------|------------------|----------------|
| HEPP-8 3 06h Heragonal bipyramid SAFR-8 5 144 Square antiprism TDD-8 6 1224 Triangular dodecahedron JGEF-8 7 1224 Johnson syrobifastigium J26 JGEF-8 7 1224 Johnson syrobifastigium J26 JETFF-8 9 C2+ Biaugemented trigonal prism J50 EFFR-8 10 C2+ Biaugemented trigonal prism JSD-8 11 D24 Snub diphenoid J84 Structure [UL8] HEPY-8 C1-8 SAFR-8 TDD-8 JGEF-8 JETEFY-8 JBTFR-8 BTFR-8 ABOXIY , 16.036, 9.293, 0.511, 2.267, 15.933, 28.208, 2.818, 2.207, Dy ^{UII} ion geometry analysis of 2 HEPY-8 3 D6h Heragonal bipyramid C1-8 4 0h Cube SAFR-8 5 D44 Square antiprism TDD-8 6 D24 Triangular dodecahedron JETFR-8 10 C2+ Biaugemented trigonal prism JSD-8 11 D24 Snub diphenoid J84 Structure [UL8] HEPY-8, C1-8 SAFR-8 TDD-8 JGEF-8 JETEFY-8 JBTFR-8 BTFR-8 JSD-8 10 D4 Square antiprism TDD-8 6 D24 Graumented trigonal prism JSD-8 11 D24 Snub diphenoid J84 Structure [UL8] HEPY-8, C1-8 SAFR-8 TDD-8 JGEF-8 JETEFY-8 JBTFR-8 JSD-8 ABOXIY , 15.550, 10.541, 1.344, 1.509, 14.497, 28.104, 1.785, 1.314, 4.070 Dy ^{III} ion geometry analysis of 3 Structure [UL8] HEPY-8 C1-8 SAFR-8 TDD-8 JGEF-8 JETEFY-8 JETFR-8 JSD-8 ABOXIY , 15.550, 10.541, 1.344, 1.509, 14.497, 28.104, 1.785, 1.314, 4.070 Dy ^{III} ion geometry analysis of 3 Structure Foug, Universitat de Barcelona Contact: 1 luneIldw.edu | Dy ^{III} ion { SH A P E (c) 2013 E1 PtL4 structu HBPY-8 CU-8 SAPR-8 JETBPY-8 JETBPY-8 JETBPY-8 | v2.1 Lectronic (3 Dé 4 Of 5 DJ 6 D2 7 D2 8 D3 9 C5 | Structure (contact: 1) h Hexagona h Cube id Square a d Triangu d Johnson h Johnson h Johnson | al bipyramic al bipyramic antiprism Lar dodecahe gyrobifasti elongated t elongated t | I I gium J26 riangular b I nrism J50 | ipyramid J1 | 4 | | | | | |
| HEPT-8 3 D6h Hexagonal bipyramid SAPR-8 5 D4d Square antiprism TDD-8 6 D2d Triangular dodecahedron JGEP-8 7 D2d Johnson elongated triangular bipyramid J14 JETEPT-8 9 C2v Biaugmented trigonal prism JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 ETER-8 ABOXIY , 16.036, 9.293, 0.511, 2.267, 15.933, 28.208, 2.818, 2.207, DyIII ion geometry analysis of 2 HEPT-8 3 D6h Hexagonal bipyramid CU-8 4 0h Cube Stress 10 C2v Biaugmented trigonal prism JETER-8 9 C2v. DyIII ion geometry analysis of 2 HEPT-8 3 D6h Hexagonal bipyramid CU-8 4 0h Cube Stress 10 C2v Biaugmented trigonal prism DEFR-8 9 C2v Biaugmented trigonal prism DEFR-8 9 C2v Biaugmented trigonal prism JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 STER-8 JSD-8 JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 JSD-8 JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 JSD-8 JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 JSD-8 JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 JSD-8 JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 JSD-8 JSD-8 11 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JETER-8 JSD-8 JSD-8 10 C2v Biaugmented trigonal prism JSD-8 10 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JSTPR-8 JSD-8 JSD-8 10 D2d Snub diphenoid J84 Structure [UL8] HEPT-8 CU-8 SAPR-8 TDD-8 JGEP-8 JETEPT-8 JSTPR-8 JSD-8 JSD-8 10 D2d Snub diphenoid J84 Structure STURE S | Dy ^{III} ion { SH A P E (c) 2013 E1 PtL4 structu HBPY-8 CU-8 SAPR-8 TDD-8 JGBF-8 | v2.1 Lectronic Ires 3 Dé 4 Of 5 DJ 6 D2 7 D2 | : Structure (contact: 11) in Hexagona n Cube id Square a 2d Triangu 2d Johnson | al bipyramic al bipyramic antiprism Lar dodecahe gyrobifasti | ı I gium J26 | | | | | | | |
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| Structure | [ML8] | HBPY-8 | CU-8 | SAPR-8 | TDD-8 | JGBF-8 | JETBP' | Y-8 | JBTPR-8 | |
| ABOXIY 2.135, | JSD-8 4.959 | 16.139, | 9.026, | 0.557, | 1.994, | 16.464, | 27. | 854, | 2.664 | , |
| | C | C 4 | | | ABOXIY, | ABO | KIY, | ABO | XIY, | ABOXIY, |
| | C | onfigurati | on | | 1 | 2 | | 3 | 3 | 4 |
| | Hexagor | al bipyrai | nid (D_{6h}) | | 16.036 | 15.5 | 50 | 15. | 510 | 16.139 |
| | | Cube (O _h) |) | | 9.293 | 10.5 | 41 | 10. | 186 | 9.026 |
| | Square | e antiprisr | n (D _{4d}) | | 0.511 | 1.34 | 14 | 0.8 | 34 | 0.557 |
|] | Friangular | dodecahe | edron (D_{2d}) |) | 2.267 | 1.50 |)9 | 2.3 | 00 | 1.994 |
| Jo | hnson gyr | obifastigi | um J26 (D2 | _{2d}) | 15.933 | 14.4 | 97 | 14. | 919 | 16.464 |
| Johnso | n elongate | ed triangut (D_{3h}) | lar bipyran | nid J14 | 28.208 | 28.1 | 04 | 27. | 555 | 27.845 |
| Biau | ugmented | trigonal p | rism J50 (| C_{2v}) | 2.818 | 1.78 | 35 | 2.3 | 42 | 2.664 |
| Bi | iaugmente | ed trigonal | prism (C_2 | v) | 2.207 | 1.3 | 14 | 1.7 | 30 | 2.135 |
| | Snub si | phenoid J | 84 (D _{2d}) | | 5.166 | 4.07 | 70 | 4.8 | 886 | 4.959 |

S H A P E v2.1 Continuous Shape Measures calculation (c) 2013 Electronic Structure Group, Universitat de Barcelona



Figure S1. Packing arrangement between two neutral in 3.



Figure S2. Packing arrangement between two neutral in 4.



Figure S4. Relaxation time of the magnetization for **1** extracted from the temperature-dependent data under zero-DC field. The red solid lines represent the fitting by the Arrhenius law for high temperature region.



Figure S5. Relaxation time of the magnetization for **1** (a)-**4** (d) extracted from the temperaturedependent data under an applied dc field of 1200 Oe. The red solid lines represent the fitting by the Arrhenius law for high temperature region.



Figure S6. Relaxation time of the magnetization for **3** (a) and **4** (b) extracted from the frequencydependent data , by fitting the χ''_{M} vs. frequency curves based on the Debye model, under 1200 Oe-DC field. The red solid lines represent the fitting by the Arrhenius law for high temperature region.





Figure S7. Simulations of dynamical susceptibility $\chi(\omega)$ of 1 ranging from 4 to 15 K in a Cole-Cole diagram. Red lines were performed using the sum of two modified Debye functions with the fitting parameters in Table S4.









Figure S8. Simulations of dynamical susceptibility $\chi(\omega)$ of **2** ranging from 2.8 to 13 K in a Cole-Cole diagram. Redlines were performed using the sum of two modified Debye functions with the fitting parameters in Table S5.





Figure S9. Simulations of dynamical susceptibility $\chi(\omega)$ of **3** ranging from 4.6 to 11 K in a Cole-Cole diagram. Redlines were performed using the sum of two modified Debye functions with the fitting parameters in Table S6.







Figure S10. Simulations of dynamical susceptibility $\chi(\omega)$ of **4** ranging from 2.0 to 14 K in a Cole-Cole diagram. Redlines were performed using the sum of two modified Debye functions with the fitting parameters in Table S7.

The magnetic susceptibility data were described by the modified Debye functions:¹

$$\chi'(\omega) = \chi_{\rm S} + (\chi_{\rm T} - \chi_{\rm S}) \frac{1 + (\omega\tau)^{1-\alpha} \sin(\frac{\pi}{2}\alpha)}{1 + 2(\omega\tau)^{1-\alpha} \sin(\frac{\pi}{2}\alpha) + (\omega\tau)^{(2-2\alpha)}}$$
$$\chi''(\omega) = (\chi_{\rm T} - \chi_{\rm S}) \frac{(\omega\tau)^{1-\alpha} \cos(\frac{\pi}{2}\alpha)}{1 + 2(\omega\tau)^{1-\alpha} \sin(\frac{\pi}{2}\alpha) + (\omega\tau)^{(2-2\alpha)}}$$
$$\chi''_{\omega=\tau^{-1}} = (\chi_{\rm T} - \chi_{\rm S}) \frac{\cos(\frac{\pi}{2}\alpha)}{2 + 2\sin(\frac{\pi}{2}\alpha)} = \frac{1}{2} (\chi_{\rm T} - \chi_{\rm S}) \tan\frac{\pi}{4} (1-\alpha)$$

1. F. Habib, G. Brunet, V. Vieru, I. Korobkov, L. F. Chibotaru, M. Murugesu, J. Am. Chem. Soc. 2013, 135, 13242.

| <i>T</i> (K) | $\Delta \chi_1$ (cm ³ mol ⁻¹) | $\Delta \chi_2$ (cm ³ mol ⁻¹) | α_1 |
|--------------|---|---|------------|
| 4 | 3.336 | 0.059 | 0.408 |
| 6 | 2.041 | 0.089 | 0.278 |
| 8 | 1.492 | 0.125 | 0.180 |
| 10 | 1.190 | 0.167 | 0.105 |
| 10.5 | 1.134 | 0.171 | 0.097 |
| 11 | 1.084 | 0.177 | 0.091 |
| 11.5 | 1.038 | 0.190 | 0.082 |
| 12 | 0.999 | 0.199 | 0.077 |
| 12.5 | 0.961 | 0.202 | 0.086 |
| 13 | 0.926 | 0.194 | 0.106 |
| 13.5 | 0.890 | 0.289 | 0.034 |
| 14 | 0.858 | 0.285 | 0.055 |
| 15 | 0.806 | 0.304 | 0.053 |

Table S4. Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for **1**.

Table S5. Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for **2**.

| <i>T</i> (K) | $T(K) \qquad \qquad \frac{\Delta \chi_1}{(cm^3 mol^{-1})}$ | | α_1 |
|--------------|--|-------|------------|
| 2.8 | 4.848 | 0.065 | 0.038 |
| 3.0 | 3.256 | 0.062 | 0.054 |
| 3.2 | 2.885 | 0.046 | 0.190 |
| 3.4 | 2.542 | 0.045 | 0.155 |
| 3.8 | 1.588 | 0.041 | 0.115 |
| 4.2 | 1.199 | 0.046 | 0.037 |
| 4.6 | 1.094 | 0.041 | 0.035 |
| 5.0 | 1.011 | 0.037 | 0.035 |
| 5.5 | 0.912 | 0.036 | 0.022 |
| 5.7 | 0.893 | 0.032 | 0.040 |
| 6.0 | 0.846 | 0.031 | 0.032 |
| 6.5 | 0.784 | 0.029 | 0.029 |
| 7.0 | 0.729 | 0.028 | 0.027 |
| 7.5 | 0.682 | 0.026 | 0.026 |
| 8.0 | 0.641 | 0.025 | 0.028 |
| 8.5 | 0.604 | 0.023 | 0.029 |
| 9.0 | 0.571 | 0.022 | 0.026 |
| 10 | 0.514 | 0.023 | 0.016 |
| 11 | 0.468 | 0.026 | 0.011 |
| 12 | 0.430 | 0.021 | 0.040 |
| 13 | 0.398 | 0.021 | 0.029 |

| <i>T</i> (K) | $\Delta \chi_1 \text{ (cm}^3 \text{mol}^{-1}\text{)}$ | $\Delta \chi_2 \text{ (cm}^3 \text{mol}^{-1}\text{)}$ | α_1 |
|--------------|---|---|------------|
| 4.6 | 0.879 | 0.108 | 0.272 |
| 5.0 | 0.867 | 0.099 | 0.284 |
| 5.5 | 0.869 | 0.085 | 0.322 |
| 5.7 | 0.853 | 0.080 | 0.336 |
| 6.0 | 0.818 | 0.077 | 0.327 |
| 6.5 | 0.757 | 0.070 | 0.329 |
| 7.0 | 0.701 | 0.066 | 0.319 |
| 7.5 | 0.651 | 0.062 | 0.307 |
| 8.0 | 0.603 | 0.058 | 0.292 |
| 8.5 | 0.567 | 0.055 | 0.275 |
| 9.0 | 0.533 | 0.051 | 0.269 |
| 10 | 0.457 | 0.062 | 0.179 |
| 11 | 0.436 | 0.054 | 0.211 |

Table S6. Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for **3**.

Table S7. Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for 4.

| <i>T</i> (K) | $\Delta \chi_1 \text{ (cm}^3 \text{mol}^{-1}\text{)}$ | $\Delta \chi_2 \text{ (cm}^3 \text{mol}^{-1}\text{)}$ | α_1 |
|--------------|---|---|------------|
| 2.0 | 7.226 | 0.686 | 0.146 |
| 2.2 | 6.634 | 0.658 | 0.138 |
| 2.4 | 6.044 | 0.584 | 0.140 |
| 2.6 | 5.550 | 0.556 | 0.128 |
| 2.8 | 5.182 | 0.511 | 0.125 |
| 3.0 | 4.833 | 0.485 | 0.121 |
| 3.2 | 4.408 | 0.377 | 0.137 |
| 3.4 | 4.257 | 0.451 | 0.111 |
| 3.6 | 3.996 | 0.418 | 0.110 |
| 3.8 | 3.804 | 0.417 | 0.102 |
| 4.0 | 3.591 | 0.403 | 0.098 |
| 4.2 | 3.433 | 0.363 | 0.108 |
| 4.5 | 3.214 | 0.357 | 0.101 |
| 5.0 | 2.894 | 0.338 | 0.091 |
| 5.5 | 2.629 | 0.318 | 0.089 |
| 6.0 | 2.411 | 0.289 | 0.086 |
| 7.0 | 2.065 | 0.265 | 0.074 |
| 8.0 | 1.809 | 0.239 | 0.067 |
| 9.0 | 1.610 | 0.209 | 0.063 |
| 10 | 1.450 | 0.191 | 0.050 |
| 12 | 1.212 | 0.171 | 0.018 |
| 14 | 1.042 | 0.084 | 0.035 |



Figure S11. The orientation of the easy axis (g_Z) of the ground KD of 2 obtained from *ab initio* calculations





Figure S12. The orientation of the easy axis (g_Z) of the ground KD of 3 obtained from *ab initio* calculations.



Figure S13. The orientation of the easy axis (g_Z) of the ground KD of 4 obtained from *ab initio* calculations.

| | | Wavefunction composition |
|---|--------------------|---|
| 1 | KD ₀ -1 | 91.57% $\left \frac{15}{2}\right\rangle$ +7.19% $\left \frac{11}{2}\right\rangle$ |
| | KD ₀ -2 | 91.57% $\left \frac{15}{2} \right\rangle$ +7.19% $\left \frac{-11}{2} \right\rangle$ |
| 2 | KD ₁ -1 | 85.20% $\left \frac{-15}{2} \right\rangle + 13.57\% \left \frac{-11}{2} \right\rangle$ |
| | KD ₁ -2 | 85.20% $\left \frac{15}{2}\right\rangle$ +13.57% $\left \frac{11}{2}\right\rangle$ |
| 3 | KD ₁ -1 | 78.93% $\left -\frac{15}{2} \right\rangle$ + 1.87% $\left -\frac{13}{2} \right\rangle$ + 11.87% $\left -\frac{11}{2} \right\rangle$ + 2.98% $\left -\frac{9}{2} \right\rangle$ + 2.57% $\left -\frac{5}{2} \right\rangle$ |
| | KD ₁ -2 | 78.93% $\binom{15}{2}$ + 1.87% $\binom{13}{2}$ + 11.87% $\binom{11}{2}$ + 2.98% $\binom{9}{2}$ + 2.57% $\binom{5}{2}$ |
| 4 | KD ₀ -1 | 93.88% $\left \frac{15}{2} \right\rangle + 5.53\% \left \frac{11}{2} \right\rangle$ |
| | KD ₀ -2 | 93.88% $\left \frac{15}{2} \right\rangle$ +5.53% $\left \frac{11}{2} \right\rangle$ |

Table S8. Decomposition of the wavefunctions of ground KDs of 1-4 into componentscorresponding to the lowest atomic multiplet J=15/2, | JM >

Table S9 Coplanarity of the first-sphere atoms at the equatorial positions for 1-4

| 2 | 03 | 06 | N8 | N9 | average |
|------------------------|---------|--------|---------|--------|---------|
| Deviation from average | -0.3287 | 0.3889 | -0.2061 | 0.2001 | 0.2810 |
| Z_coordinate | -0.5099 | 0.2617 | -0.3333 | 0.0729 | -0.1272 |
| 1 | O4 | 05 | N8 | N9 | average |

| Z_coordinate | 0.4058 | -0.7206 | 0.1072 | -0.1350 | -0.0856 |
|------------------------|--------|---------|---------|---------|---------|
| Deviation from average | 0.4914 | -0.6350 | 0.1928 | -0.0494 | 0.3422 |
| 3 | O4 | 07 | N8 | N9 | average |
| Z_coordinate | 0.1245 | -0.3376 | 0.4724 | -0.6438 | -0.0961 |
| Deviation from average | 0.2206 | 0.1299 | 0.5685 | -0.5477 | 0.3667 |
| 4 | 02 | 03 | N8 | N9 | average |
| Z_coordinate | 0.0003 | -0.4184 | -0.2432 | 0.4225 | -0.0597 |
| Deviation from average | 0.0600 | -0.3587 | -0.1835 | 0.4822 | 0.2711 |