**Supporting Information**

**Uniaxial Negative Thermal Expansion Induced by Molecular Rotation in One-Dimensional Supramolecular Assembly with Associated Peculiar Magnetic Behavior**

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Table of Contents

**§1. Crystal data, Crystal Data, Data Collection, and Reduction Parameter.**

**§2. Crystallographically independent molecules with atom numbering**

**§3. Input and output file of PASCal Calculation**

**§4 Differential scanning calorimetry (DSC) for crystal 1**

**§5 Temperature-dependence of structural change between PD1B•••DB2 and PD1B•••PD2.**

**§6 Transfer integrals (t) between [Ni(dmit)2]– anions and their temperature dependence.**

**§7 Expanded χm*T* versus *T* plot of Figure 5.**

**§1. Crystal data, Crystal Data, Data Collection, and Reduction Parameter.**

The Flack parameter analyzed for *P2*1 was 0.320(11) at 118 K. Relatively large Flack parameter suggests that the inverted domain, where dipole moment of **PD2** are aligned anti-parallel to the first domain, are included in the crystal **1**. It is because crystal structure of **1** can be refined by assuming inversion twin and BASF commands in shelx refinement, where volume ratio of twin domains were 0.680(11):0.320(11) at 118 K.

**Table S1.** Crystal Data, Data Collection, and Reduction Parameter for crystal **1**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **1** |  |  |  |
| *Temperature* / K | 118 | 135 | 151 | 169 |
| *Crystal Dimensions* / mm3 | 0.6×0.6×0.6 | | | |
| *Chemical formula* | C92H106N4Ni2O24S20 |  |  |  |
| *Formula weight* | 2410.42 |  |  |  |
| *Crystal System* | Monoclinic |  |  |  |
| *Space group* | *P*21 |  |  |  |
| *a /* Å | 13.0944(2) | 13.1146(2) | 13.1390(2) | 13.1620(3) |
| *b /* Å | 21.8192(3) | 21.8149(3) | 21.8050(3) | 21.7862(3) |
| *c /* Å | 18.0486(3) | 18.0621(3) | 18.0856(3) | 18.1119(3) |
| *β /* deg | 94.6070(15) | 94.502(2) | 94.4155(16) | 94.3187(16) |
| *V /* Å3 | 5139.99(14) | 5151.51(14) | 5166.08(15) | 5178.82(15) |
| *Z* | 2 | 2 | 2 | 2 |
| *Dcalc /* g∙cm-3 | 1.557 | 1.554 | 1.550 | 1.546 |
| *μ*(Mo Kα) */* cm-1 | 0.847 | 0.845 | 0.843 | 0.840 |
| 2*θ*max */* deg | 62.5200 | 61.8940 | 62.1320 | 61.586 |
| *Reflections measured* | 77144 | 78128 | 77762 | 80139 |
| *Independent reflections* | 26132 | 25961 | 25989 | 26243 |
| *Reflections used* | 26132 | 25961 | 25989 | 26243 |
| *R1 a* | 0.0350 | 0.0357 | 0.0364 | 0.0374 |
| *Rw(F2)a* | 0.0803 | 0.0833 | 0.0861 | 0.0888 |
| *GOF* | 1.026 | 1.034 | 1.041 | 1.039 |
| *Flack Parameter* | 0.320(11) | 0.334(11) | 0.318(11) | 0.315(11) |
| *CCDC No.* | 2163119 | 2163120 | 2163121 | 2163122 |

*a* *R*1 = ||*F*o| - |*F*c|| / |*F*o| and *R*w = (|*F*o| - |*F*c|)2 / *F*o2)1/2.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | **1** |  |  |  |  |
| *Temperature* / K | 177 | 186 | 194 | 202 | 221 |
| *Crystal Dimensions* / mm3 | 0.6×0.6×0.6 | | | | |
| *Chemical formula* | C92H106N4Ni2O24S20 |  |  |  |  |
| *Formula weight* | 2410.42 |  |  |  |  |
| *Crystal System* | Monoclinic |  |  |  |  |
| *Space group* | *P*21 |  |  |  |  |
| *a /* Å | 13.19743(18) | 13.1936(3) | 13.2130(3) | 13.2325(3) | 13.2688(3) |
| *b /* Å | 21.7622(2) | 21.7511(3) | 21.7297(3) | 21.7185(3) | 21.6763(3) |
| *c /* Å | 18.1487(2) | 18.1553(3) | 18.1815(3) | 18.1943(3) | 18.2309(3) |
| *β /* deg | 94.1520(11) | 94.2038(17) | 94.1495(18) | 94.039(2) | 93.8703(18) |
| *V /* Å3 | 5198.74(11) | 5196.10(16) | 5206.48(17) | 5215.87(16) | 5231.59(17) |
| *Z* | 2 | 2 | 2 | 2 | 2 |
| *Dcalc /* g∙cm-3 | 1.540 | 1.541 | 1.538 | 1.535 | 1.530 |
| *μ*(Mo Kα) */* cm-1 | 0.837 | 0.838 | 0.836 | 0.834 | 0.832 |
| 2*θ*max */* deg | 62.3520 | 61.878 | 60.702 | 61.526 | 61.938 |
| *Reflections measured* | 97567 | 83480 | 79833 | 82353 | 87510 |
| *Independent reflections* | 26744 | 26486 | 26365 | 26375 | 26468 |
| *Reflections used* | 26744 | 26486 | 26365 | 26375 | 26468 |
| *R1 a* | 0.0333 | 0.0381 | 0.0390 | 0.0379 | 0.0369 |
| *Rw(F2)a* | 0.0806 | 0.0900 | 0.0913 | 0.0895 | 0.0851 |
| *GOF* | 1.018 | 1.042 | 1.031 | 1.021 | 1.027 |
| *Flack Parameter* | 0.356(10) | 0.319(11) | 0.309(12) | 0.323(11) | 0.276(11) |
| *CCDC No.* | 2163123 | 2163124 | 2163125 | 2163126 | 2163127 |

*a* *R*1 = ||*F*o| - |*F*c|| / |*F*o| and *R*w = (|*F*o| - |*F*c|)2 / *F*o2)1/2.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **1** |  |  |  |
| *Temperature* / K | 237 | 254 | 272 | 282 |
| *Crystal Dimensions* / mm3 | 0.6×0.6×0.6 | | | |
| *Chemical formula* | C92H106N4Ni2O24S20 |  |  |  |
| *Formula weight* | 2410.42 |  |  |  |
| *Crystal System* | Monoclinic |  |  |  |
| *Space group* | *P*21 |  |  |  |
| *a /* Å | 13.3027(3) | 13.3375(3) | 13.3760(3) | 13.3988(3) |
| *b /* Å | 21.6453(4) | 21.6167(4) | 21.5994(4) | 21.5792(4) |
| *c /* Å | 18.2686(4) | 18.3081(4) | 18.3362(4) | 18.3596(4) |
| *β /* deg | 93.655(2) | 93.505(2) | 93.373(2) | 93.338(2) |
| *V /* Å3 | 5249.58(19) | 5268.58(19) | 5288.40(19) | 5299.40(19) |
| *Z* | 2 | 2 | 2 | 2 |
| *Dcalc /* g∙cm-3 | 1.525 | 1.519 | 1.514 | 1.511 |
| *μ*(Mo Kα) */* cm-1 | 0.829 | 0.826 | 0.823 | 0.821 |
| 2*θ*max */* deg | 61.4080 | 61.8740 | 61.9860 | 62.5520 |
| *Reflections measured* | 82444 | 85675 | 84884 | 70798 |
| *Independent reflections* | 26609 | 26960 | 26919 | 21627 |
| *Reflections used* | 26609 | 26960 | 26919 | 21627 |
| *R1 a* | 0.0382 | 0.0383 | 0.0391 | 0.0350 |
| *Rw(F2)a* | 0.0903 | 0.0879 | 0.1171 | 0.0839 |
| *GOF* | 0.934 | 1.018 | 0.902 | 1.018 |
| *Flack Parameter* | 0.321(12) | 0.337(11) | 0.299(12) | 0.248(13) |
|  | 2163128 | 2163129 | 2163130 | 2163131 |

*a* *R*1 = ||*F*o| - |*F*c|| / |*F*o| and *R*w = (|*F*o| - |*F*c|)2 / *F*o2)1/2.



**Figure S1.** Temperature-dependence of *β* in unit cell.



**Figure S2.** Temperature dependence of cell parameters normalized at 118 K.

**§2. Crystallographically independent molecules with atom numbering**

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**Figure S3.** Crystallographically independent molecular structure in the crystal **1** at 118 K with atomic number. (a) Molecular structure of **DB3**. Disordered carbon atoms depicted as yellow and blue colors. (b) molecular structures of **PD2** and **DB2**. (c) Molecular structures of **DB1**, **PD1A**, and **PD1B**. (d) Atom numbering for [Ni(dmit)2]­ in the packing with crystallographically independent supramolecular cations.

The length of covalent bonds between the nitrogen atoms in the typical pdazH+ cations are longer than those between the nitrogen and carbon atoms. We could not assign nitrogen atoms next to N1A and N1B from the lengths of C-C and C-N bond within **PD1A** and **PD1B** due to the disorder of pdazH+. However, if we place the nitrogen atoms other than N2A and N2B, as described in Figure 2b, we could not solve the structure without using restrained commands for bond distance on Shelx refinement. On the other hand, the distance between N3 and N4 atoms in **PD2** was 1.307(5) Å whereas those between N3 or N4 and adjacent carbon atoms were 1.302(6) and 1.276(6) Å, respectively. Therefore, we could safely assign the position of N4 atom of the **PD2** in crystal **1**. The assignment of N4 atom in **PD2** is reasonable because N4 atom in **PD2** contacts C-H bond in **PD1A** and **PD1B** and forms a C-H•••N interaction (Figure 2c, see also Table S3 for the details of C-H•••N4 interactions).

**Table S2.** Temperature-dependent C•••O distance and C-H•••O angles between **PD1A**•••**DB3A**, and **PD1B**•••**DB3B**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **PD1A**•••**DB3A** |  | **PD1B**•••**DB3B** |  |
| *T* / K | C15A•••O16A  distance / Å | C15A-H@•••O16A  angle / ° | C13B•••O16B  distance / Å | C13B•••O16B  angle / ° |
| 118 | 3.154 | 134.16 | 3.322 | 153.76 |
| 135 | 3.126 | 136.24 | 3.418 | 152.91 |
| 151 | 3.132 | 134.01 | 3.409 | 154.05 |
| 169 | 3.101 | 135.80 | 3.392 | 155.84 |
| 186 | 3.089 | 133.53 | 3.410 | 152.97 |
| 194 | 3.037 | 135.47 | 3.445 | 153.81 |
| 202 | 3.031 | 134.52 | 3.451 | 154.01 |
| 221 | 3.031 | 132.98 | 3.438 | 151.70 |
| 237 | 3.035 | 132.29 | 3.364 | 141.17 |
| 254 | 3.025 | 131.19 | 3.400 | 142.78 |
| 272 | 3.084 | 130.60 | 3.380 | 139.94 |
| 282 | 3.047 | 128.51 | 3.337 | 139.23 |

**Table S3.** Temperature-dependent C•••N distances, and C-H•••N angles between **PD1A**•••**PD2**, and **PD1B**•••**PD2**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **PD1A**•••**PD2** |  | **PD1B**•••**PD2** | |
| *T* / K | C13A•••N4  distance / Å | C13A-H@•••N4  angle / ° | C16B•••N4 distance / Å | C16B-H•••N4  angle / ° |
| 118 | 3.426 | 165.05 | 3.430 | 120.16 |
| 135 | 3.415 | 166.59 | 3.462 | 120.05 |
| 151 | 3.439 | 166.13 | 3.463 | 120.30 |
| 169 | 3.536 | 163.54 | 3.431 | 120.90 |
| 186 | 3.532 | 166.32 | 3.472 | 120.34 |
| 194 | 3.531 | 166.09 | 3.487 | 120.81 |
| 202 | 3.578 | 165.91 | 3.467 | 122.87 |
| 221 | 3.588 | 165.89 | 3.541 | 120.80 |
| 237 | 3.621 | 165.86 | 3.557 | 119.83 |
| 254 | 3.600 | 164.95 | 3.790 | 118.94 |
| 272 | 3.640 | 162.61 | 3.843 | 116.02 |
| 282 | 3.684 | 164.80 | 3.719 | 118.41 |

**Table S3.** Temperature dependence of the parameters for N-H•••O hydrogen bonds (N•••O distance and N-H•••O angle) between **PD1A**•••**DB1**, **PD1B**•••**DB1**, and **PD2**•••**DB2**.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | N-H•••O hydrogen bond | |  |  |  |  |
|  | **PD1A**•••**DB1** | | **PD1B**•••**DB1** | | **PD2**•••**DB2** | |
| *T* / K | N1A•••O20  distance / Å | N1A-H1A•••O16  angle / ° | N1B-O24  distance / Å | N1B-H1B•••O24  angle / ° | N3•••O4  distance / Å | N3-H3•••O4  angle / ° |
| 118 | 2.806 | 172.03 | 2.932 | 170.89 | 2.814 | 170.45 |
| 135 | 2.804 | 171.12 | 2.914 | 171.28 | 2.814 | 169.79 |
| 151 | 2.831 | 171.57 | 2.911 | 171 | 2.816 | 169.85 |
| 169 | 2.793 | 168.83 | 2.912 | 172.16 | 2.818 | 168.57 |
| 186 | 2.798 | 169.97 | 2.912 | 170.83 | 2.827 | 167.07 |
| 194 | 2.806 | 169.38 | 2.92 | 168.51 | 2.83 | 166.68 |
| 202 | 2.81 | 167.66 | 2.916 | 174.45 | 2.832 | 165.48 |
| 221 | 2.81 | 168.14 | 2.922 | 172.7 | 2.847 | 164.54 |
| 237 | 2.806 | 168.41 | 2.919 | 166.59 | 2.853 | 163.28 |
| 254 | 2.817 | 169.19 | 2.983 | 171.32 | 2.865 | 161.69 |
| 272 | 2.813 | 169.66 | 2.955 | 166.01 | 2.884 | 161.11 |
| 282 | 2.824 | 168.64 | 2.907 | 166.33 | 2.88 | 160.99 |

**Table S5.** Temperature dependence of O•••π distances between **DB1**•••**PD1A** and **DB2**•••**PD2**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **DB1**•••**PD1A** | | | |
|  | Interatomic Distance / Å | | | |
| *T* / K | O18•••C13A | O18•••C14A | O22•••C13A | O22•••C14A |
| 118 | 2.999 | 3.022 | 2.908 | 3.057 |
| 135 | 2.969 | 3.038 | 2.941 | 3.036 |
| 151 | 2.984 | 3.038 | 2.936 | 3.048 |
| 169 | 2.979 | 3.039 | 2.929 | 3.058 |
| 186 | 3.021 | 3.054 | 2.902 | 3.054 |
| 194 | 3.027 | 3.016 | 2.901 | 3.112 |
| 202 | 3.026 | 3.045 | 2.901 | 3.083 |
| 221 | 3.048 | 3.053 | 2.894 | 3.081 |
| 237 | 3.031 | 3.019 | 2.92 | 3.124 |
| 254 | 3.052 | 3.022 | 2.93 | 3.132 |
| 272 | 3.091 | 3.019 | 2.91 | 3.143 |
| 282 | 3.055 | 3.028 | 2.937 | 3.125 |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **DB2**•••**PD2**. | | | |
|  | Interatomic Distance / Å | | | |
| *T* / K | O6•••C17 | O6•••N3 | O2•••C20 | O7•••C20 |
| 118 | 3.192 | 3.092 | 3.057 | 3.192 |
| 135 | 3.202 | 3.096 | 3.055 | 3.194 |
| 151 | 3.19 | 3.092 | 3.054 | 3.197 |
| 169 | 3.202 | 3.083 | 3.049 | 3.195 |
| 186 | 3.212 | 3.075 | 3.047 | 3.19 |
| 194 | 3.22 | 3.073 | 3.041 | 3.188 |
| 202 | 3.224 | 3.068 | 3.045 | 3.187 |
| 221 | 3.237 | 3.059 | 3.046 | 3.174 |
| 237 | 3.241 | 3.054 | 3.045 | 3.177 |
| 254 | 3.247 | 3.042 | 3.05 | 3.17 |
| 272 | 3.25 | 3.038 | 3.048 | 3.176 |
| 282 | 3.259 | 3.038 | 3.053 | 3.17 |

**§3. Input and output file of PASCal Calculation, and indicatrix plots**

**Table S6.** Input and output file of PASCal Calculation for structural data of **1** between 118 and 169 K.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| input | *T* / K | *σ*T | *a* / Å | *b* / Å | *c* / Å | *α* / ° | *β* / ° | *γ* / ° |
|  | 169 | 5 | 13.162 | 21.7862 | 18.1119 | 90 | 94.3187 | 90 |
|  | 151 | 5 | 13.139 | 21.805 | 18.0856 | 90 | 94.4155 | 90 |
|  | 135 | 5 | 13.1146 | 21.8149 | 18.0621 | 90 | 94.502 | 90 |
|  | 118 | 5 | 13.0944 | 21.8192 | 18.0486 | 90 | 94.607 | 90 |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| output |  |  |  |  | Direction |  |
|  | Axes | *α* / MK–1 | σα / MK–1 | *a* | *b* | *c* |
|  | *X*1 | -29.6503 | 4.1985 | 0 | 1 | 0 |
|  | *X*2 | 38.0421 | 3.9509 | -0.6675 | 0 | 0.7446 |
|  | *X*2 | 142.2858 | 1.4664 | 0.8931 | 0 | 0.4499 |
|  | *V* | 151.2583 | 2.7976 |  |  |  |
|  | % change in length | | | | | | |
|  | *T* / K | *X*1 | *X*2 | *X*2 | *X*1,calc | *X*2,calc | *X*3,calc |
|  | 118 | 0 | 0 | 0 | 0.0159 | -0.0179 | -0.0069 |
|  | 135 | -0.0197 | 0.0215 | 0.2221 | -0.0345 | 0.0468 | 0.235 |
|  | 151 | -0.0651 | 0.1047 | 0.4674 | -0.082 | 0.1077 | 0.4626 |
|  | 169 | -0.1512 | 0.1865 | 0.72 | -0.1354 | 0.1761 | 0.7188 |
|  | Volume |  |  |
|  | *T* / K | *V* / Å3 | Vlin / Å3 |
|  | 118 | 5139.993 | 5139.4723 |
|  | 135 | 5151.509 | 5152.6892 |
|  | 151 | 5166.071 | 5165.1287 |
|  | 169 | 5178.84 | 5179.1231 |

**Table S7.** Input and output file of PASCal Calculation for structural data of **1** between 186 and 282 K.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| input | *T* / K | *σ*T | *a* / Å | *b* / Å | *c* / Å | *α* / ° | *β* / ° | *γ* / ° |
|  | 282 | 5 | 13.3988 | 21.5792 | 18.3596 | 90 | 93.338 | 90 |
|  | 272 | 5 | 13.376 | 21.5994 | 18.3362 | 90 | 93.373 | 90 |
|  | 254 | 5 | 13.3375 | 21.6167 | 18.3081 | 90 | 93.505 | 90 |
|  | 237 | 5 | 13.3027 | 21.6453 | 18.2686 | 90 | 93.655 | 90 |
|  | 221 | 5 | 13.2688 | 21.6763 | 18.2309 | 90 | 93.8703 | 90 |
|  | 202 | 5 | 13.2325 | 21.7185 | 18.1943 | 90 | 94.039 | 90 |
|  | 194 | 5 | 13.213 | 21.7297 | 18.1815 | 90 | 94.1495 | 90 |
|  | 186 | 5 | 13.1936 | 21.7511 | 18.1553 | 90 | 94.2038 | 90 |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| output |  |  |  |  | Direction |  |
|  | Axes | *α* / MK–1 | σα / MK–1 | *a* | *b* | *c* |
|  | *X*1 | -81.2513 | 2.7 | 0 | 1 | 0 |
|  | *X*2 | 55.4528 | 3.149 | -0.738 | 0 | 0.6749 |
|  | *X*2 | 230.0634 | 3.3742 | 0.859 | 0 | 0.512 |
|  | *V* | 204.178 | 1.9955 |  |  |  |
|  | % change in length | | | | | | |
|  | *T* / K | *X*1 | *X*2 | *X*2 | *X*1,calc | *X*2,calc | *X*3,calc |
|  | 186 | 0 | 0 | 0 | -0.0324 | 0.018 | 0.028 |
|  | 194 | -0.0984 | 0.1015 | 0.1967 | -0.0974 | 0.0624 | 0.2121 |
|  | 202 | -0.1499 | 0.1152 | 0.4153 | -0.1624 | 0.1068 | 0.3961 |
|  | 221 | -0.3439 | 0.2107 | 0.817 | -0.3168 | 0.2121 | 0.8333 |
|  | 237 | -0.4864 | 0.2644 | 1.2529 | -0.4468 | 0.3008 | 1.2014 |
|  | 254 | -0.6179 | 0.3778 | 1.6376 | -0.5849 | 0.3951 | 1.5925 |
|  | 272 | -0.6974 | 0.4775 | 1.9988 | -0.7312 | 0.4949 | 2.0066 |
|  | 282 | -0.7903 | 0.5935 | 2.1883 | -0.8124 | 0.5504 | 2.2367 |
|  | Volume |  |  |
|  | *T* / K | *V* / Å3 | Vlin / Å3 |
|  | 186 | 5196.1057 | 5196.7608 |
|  | 194 | 5206.4888 | 5205.2482 |
|  | 202 | 5215.8741 | 5213.7356 |
|  | 221 | 5231.5855 | 5233.8933 |
|  | 237 | 5249.5783 | 5250.8682 |
|  | 254 | 5268.5849 | 5268.904 |
|  | 272 | 5288.3999 | 5288.0008 |
|  | 282 | 5299.4039 | 5298.6101 |

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**Figure S4.** Indicatrix plots for structural data of **1** between (a) 118 and 169 K and (b) 186 and 282 K.

PASCal Indicatrix Plotter was used to plot the data. The software was obtained from the web site: https://cliffe.nottingham.ac.uk/programs/

**§4 Differential scanning calorimetry (DSC) for crystal 1**

**Figure S5.** Differential scanning calorimetry from 150 to 290 K. Red and blue allows indicate the heating and cooling processes, respectively.

**§5 Temperature-dependence of structural change between PD1B•••DB3B and PD1B•••PD2.**

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**Figure S6.** Schematic of selected parameters in supramolecular cation structure. The atoms are displayed using the thermal ellipsoid model. (a) Schematic of the interaction (purple) between C16B in **PD1B** and N4 in **PD2** (*d*C-N). (b) Temperature dependences of *Ψ*PD1B (Green), and *d*C-N (purple). The dashed line corresponds to the phase transition temperature of 183 K.

**§6 Transfer integrals (t) between [Ni(dmit)2]– anions and their temperature dependence.**

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**Figure S7.** Transfer integrals (*t*) between [Ni(dmit)2]– anions and their temperature dependence. (a) Arrangement of [Ni(dmit)2]– and corresponding *t* (*t*intra, *t*2, *t*3, and *t*4), where *t*intra represents *t* in intradimer. (b) Temperature-dependent *t*. Each *t* corresponds to those in (a).

**§6 Expanded *χ*m*T* versus *T* plot of Figure 5.**

**Figure S8.** Expanded χm*T* *versus* *T* plot of Figure 5 with the left axis expanded from 0.65 to 1.0 cm3 K mol–1. Black and blue lines represent the singlet-triplet (S-T) thermal excitation models explained in the main text.

Singlet-triplet (S-T) thermal excitation model is described as follows S1:

where *N*A, *μ*B, *g*, and *k*B are Avogadro number, Bohr magneton, Landé g-factor, and Boltzmann constant, respectively. In the modified model, *J*/*k*B = *c*0 *T* + *c*1 are used, where *c*0 and *c*1 are constant.

References

[S1] B. Bleaney, K. D. Bowers, *Proc. R. Soc. Lond.* *A*, **1952**, *214*, 451–465.