- Supporting Information -

Insights into D_{4h}@Metal-Symmetry Single-Molecule Magnetism: The Case of a Dysprosium-bis(Boryloxide) Complex

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Experimental

General

All manipulations were carried out under an inert atmosphere of dry nitrogen or argon using standard Schlenk techniques, or an MBraun UniLab glovebox operating under an atmosphere of dry nitrogen with H_2O and O_2 at less than 0.1 ppm. All glassware was silylated following the procedure outlined in reference[1] and then dried by flame-drying with subsequent cooling under 10^{-3} mbar vacuum, followed by repeated alternate evacuation and purging with nitrogen. THF, pentane and toluene were dried by passage through activated alumina, degassed prior to use, and stored over activated 3Å molecular sieves (THF), a potassium mirror (pentane and toluene). C_6H_6 and C_6D_6 were stored over NaK_2 and the latter was degassed by three freeze-pump-thaw cycles, distilled and stored under nitrogen. $Ln(BH_4)_3(THF)_3$,[2] [$(HCDippN)_2BOK$)] (BOK),[3] $[Ph_3C][BPh_4]$,[4] and $[HNMe_3][BPh_4]$[5] were prepared using published procedures. Martin Jennings and Anne Davies at The University of Manchester carried out elemental microanalyses. FTIR spectra were recorded on a Bruker Alpha spectrometer with a Platinum-ATR module in the glove box. Magnetic data were recorded on a Quantum Design MPMS3 SQUID Magnetometer. Samples were immobilised in an eicosane matrix to prevent sample reorientation during measurements. Specifically, 27.8 mg of finely ground $[Dy(BO)_2(THF)_4][BPh_4]$ was immobilised in a matrix of 26.5 mg of eicosane within a 4 mm diameter tube sealed under vacuum.

Preparation of $[Dy\{OB(NArCH)_2\}_2(BH_4)(THF)_2]$ (1Dy)

Toluene (15 ml) was added to a pre-cooled (−78 °C) mixture of [$(HCDippN)_2BOK$)] (0.442 g, 1.00 mmol) and $Dy(BH_4)_3(THF)_3$ (0.212 g, 0.50 mmol) and slowly warmed to room temperature to give a pale yellow solution with a white precipitate. After stirring overnight, volatiles were removed *in vacuo* to give a white solid which was then re-extracted in toluene (15 ml) and pentane (10 ml) and filtered to give a pale yellow solution. Volatiles were removed *in vacuo* to give a white powder. Colourless crystals of **1Dy** were isolated following slow evaporation of a C_6H_6 solution. Yield: 0.21

g, 86%. Anal. Calcd for $C_{60}H_{92}B_3DyN_4O_4$: C, 63.87; H, 8.22; N, 4.97%. Found: C, 64.11; H, 8.67; N, 4.58%. FTIR v/cm^{-1} (ATR): 2961 (m), 2867 (w), 2466 (vw), 1580 (vw), 1440 (s), 1376 (vs), 1327 (m), 1272 (m), 1254 (m), 1176 (w), 1111 (m), 1070 (m), 1021 (m), 934 (w), 877 (m), 803 (m), 756 (vs), 705 (m), 648 (vs), 495 (vw).

Preparation of [Y{OB(NArCH)$_2$}$_2$(BH$_4$)(THF)$_2$] (1Y)

Prepared as **1Dy**, with $Y(BH_4)_3(THF)_3$ (0.140 g, 0.40 mmol) and [(HCDippN)$_2$BOK)] (0.354 g, 0.80 mmol). Colourless crystals of **1Y** were obtained following slow evaporation of volatiles from a C_6H_6 solution. Yield: 0.13 g, 91% Anal. Calcd for $C_{60}H_{92}B_3N_4O_4Y$: C, 68.32; H, 8.79; N, 5.31%. Found: C, 68.58; H, 8.95; N, 5.88%. FTIR v/cm^{-1} (ATR): 2959 (m), 2927 (w), 2869 (w), 2470 (vw), 1578 (vw), 1452 (s), 1393 (vs), 1322 (m), 1276 (m), 1255 (m), 1181 (vw), 1128 (w), 1064 (m), 1016 (m), 895 (vw), 864 (m), 803 (m), 746 (vs), 697 (m), 653 (vs), 601 (vw), 444 (vw); ^{1}H NMR (C_6D_6, 298 K): δ 0.98 (m, 8H, OCH$_2$C*H*$_2$), 1.19 (m, 4H, BH$_4$), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 1.34 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 3.02 (m, 8H, C*H*(CH$_3$)$_2$), 3.53 (m, 8H, OC*H*$_2$CH$_2$), 5.89 (s, 4H, NC*H*), 7.06 (m, 12H, Dipp-C*H*); ^{11}B{^{1}H} NMR (C_6D_6, 298 K): δ -28.42 (BH$_4$), 21.50 (BO); ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ = 23.6 (CH(*C*H$_3$)$_2$), 24.8 (OCH$_2$*C*H$_2$), 24.9 (CH(*C*H$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 70.6 (O*C*H$_2$CH$_2$), 116.9 (N*C*H), 123.3 (Dipp-*m*-*C*H), 126.1 (Dipp-*p*-*C*H), 141.2 (Dipp-*i*-*C*), 146.0 (Dipp-*o*-*C*).

Preparation of [Dy{OB(NArCH)$_2$}$_2$(THF)$_4$][BPh$_4$] (2Dy)

Method A: THF (15 ml) was distilled on to **1Dy** (0.360 g, 0.30 mmol) and [Ph$_3$C][BPh$_4$] (0.70 g, 0.30 mmol) at 77 K in the absence of light and warmed slowly to room temperature. After stirring overnight, a pale yellow solution with white precipitate was produced. Volatiles were removed *in vacuo* to give a white precipitate which was washed thoroughly with toluene (3 × 10 ml). After dissolving this white powder in THF (2 ml), adding toluene (0.5 ml) and cooling to –30 °C, colourless crystals of **2Dy** were produced. Yield: 0.38 g, 77%. *Method B:* THF (15 ml) was distilled on to **1Dy**

(0.360 g, 0.30 mmol) and [$HNMe_3$][BPh_4] (0.89 g, 0.30 mmol) at 77 K and warmed slowly to room temperature to give a clear pale yellow solution. After stirring overnight, volatiles were removed *in vacuo* to give a white powder. After washing with pentane (10 ml) and dissolving in THF (2 ml), toluene (0.5 ml) was added and cooled to −30 °C to produce colourless crystals of **2Dy**. Yield: 0.46 g, 94 %. Anal. Calcd for $C_{98}H_{130}B_3DyN_4O_6$: C, 71.12; H, 7.92; N, 3.39%. Found: C, 71.23; H, 8.15; N, 3.20%. FTIR v/cm^{-1} (ATR): 3033 (vw), 2959 (w), 2923 (w), 2863 (vw), 1580 (vw), 1458 (m), 1372 (s), 1254 (w), 1113 (m), 1009 (m), 854 (m), 803 (m), 738 (s), 699 (s), 656 (s), 601 (m), 469 (w).

Preparation [Y{OB(NArCH)$_2$}$_2$(THF)$_4$][BPh$_4$] (2Y)

Prepared as **2Dy**, with **1Y** (0.092 g, 0.08 mmol) and [Ph_3C][BPh_4] (0.46 g, 0.08 mmol) or [$HNMe_3$][BPh_4] (0.024 g, 0.08 mmol). Colourless crystals of **2Y** were obtained after dissolving in THF (5 ml), adding toluene (0.5 ml) and cooling to −30 °C. Yield: 0.12 / 0.14 g, 81 / 96 %. Anal. Calcd for $C_{98}H_{130}B_3N_4O_6Y$: C, 74.43; H, 8.29; N, 3.54%. Found: C, 4.74; H, 8.07; N, 3.68%. FTIR v/cm^{-1} (ATR): 2962 (w), 2934 (w), 2872 (vw), 1580 (w), 1450 (m), 1360 (vs), 1244 (w), 1127 (m), 1001 (s), 832 (w), 789 (m), 746 (s), 716 (s), 671 (s), 592 (s); ^{1}H NMR (d^8-THF, 298 K): δ 1.12 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.17 (d, $^3J_{HH}$ = 7.0 Hz, 24H, CH(CH_3)$_2$), 1.78 (m, 16H, OCH$_2$CH_2), 3.21 (m, 8H, CH(CH$_3$)$_2$), 3.62 (m, 16H, OCH_2CH$_2$), 5.72 (s, 4H, NCH), 6.72 (m, 4H, BPh_4), 6.86 (m, 8H, BPh_4), 7.17 (m, 12H, Dipp-CH), 7.29 (m, 8H, BPh_4); ^{11}B{^{1}H} NMR (d_8-THF, 298 K): δ -6.52 (*B*Ph_4), 21.60 (*B*O); ^{13}C{^{1}H} NMR (d^8-THF, 298 K): δ = 23.1 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 25.1 (OCH$_2$*C*H$_2$), 27.7 (*C*H(CH$_3$)$_2$), 30.5 (*C*H(CH$_3$)$_2$), 68.8 (O*C*H$_2$CH$_2$), 117.0 (N*C*H), 121.2 (s, *m*-BPh_4), 122.8 (*p*-BPh_4), 123.4 (Dipp-*m*-*C*H), 126.5 (Dipp-*p*-*C*H), 127.0 (*o*-BPh_4), 135.3 (*i*-BPh_4), 141.0 (Dipp-*i*-*C*), 146.0 (Dipp-*o*-*C*).

NMR spectra

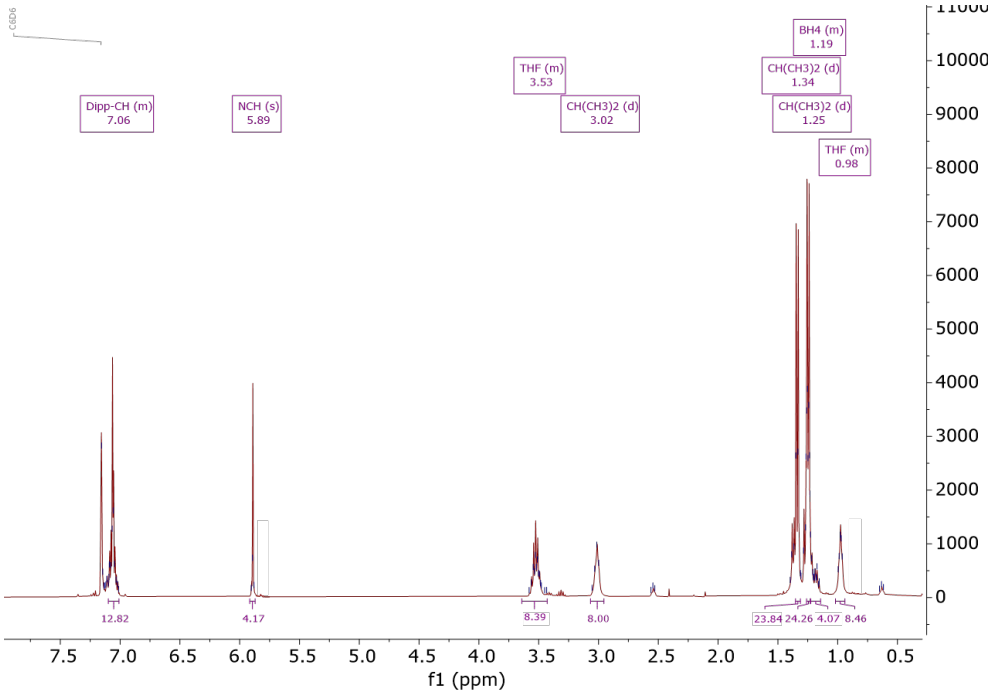

Figure 1. ^{1}H NMR of **1Y**.

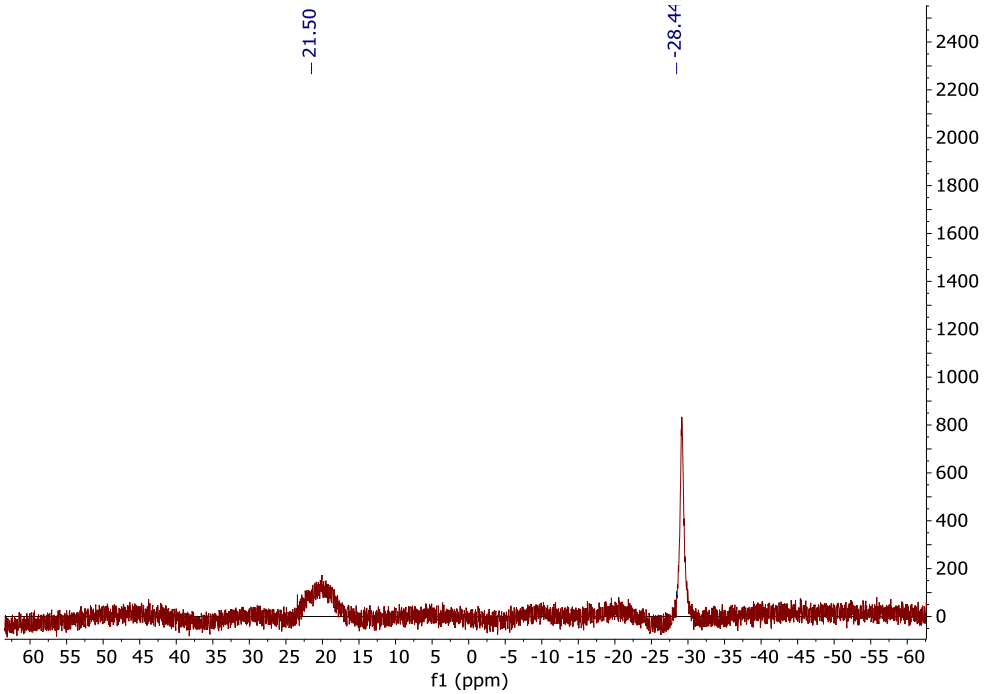

Figure 2. ^{11}B{^{1}H} NMR of **1Y**.

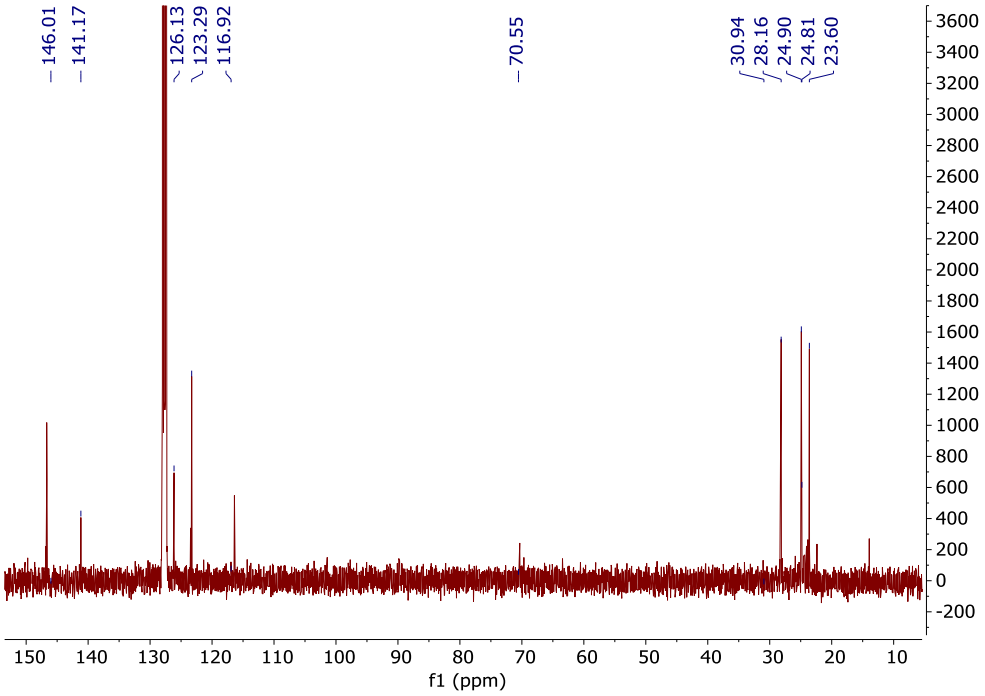

Figure 3. $^{13}C\{^{1}H\}$ NMR of **1Y**.

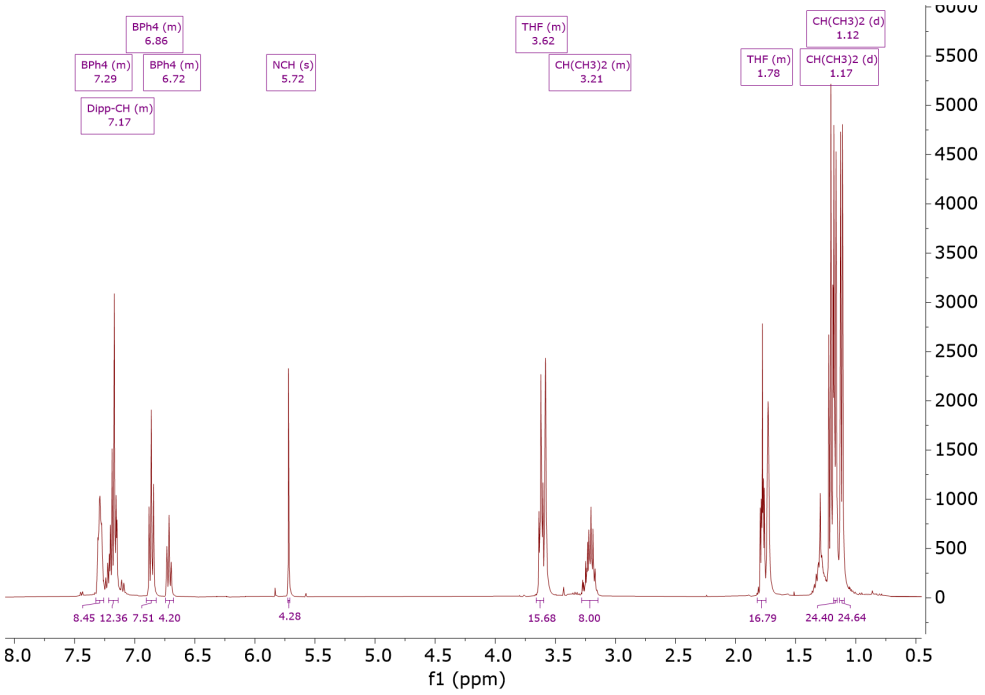

Figure 4. ^{1}H NMR of **2Y**.

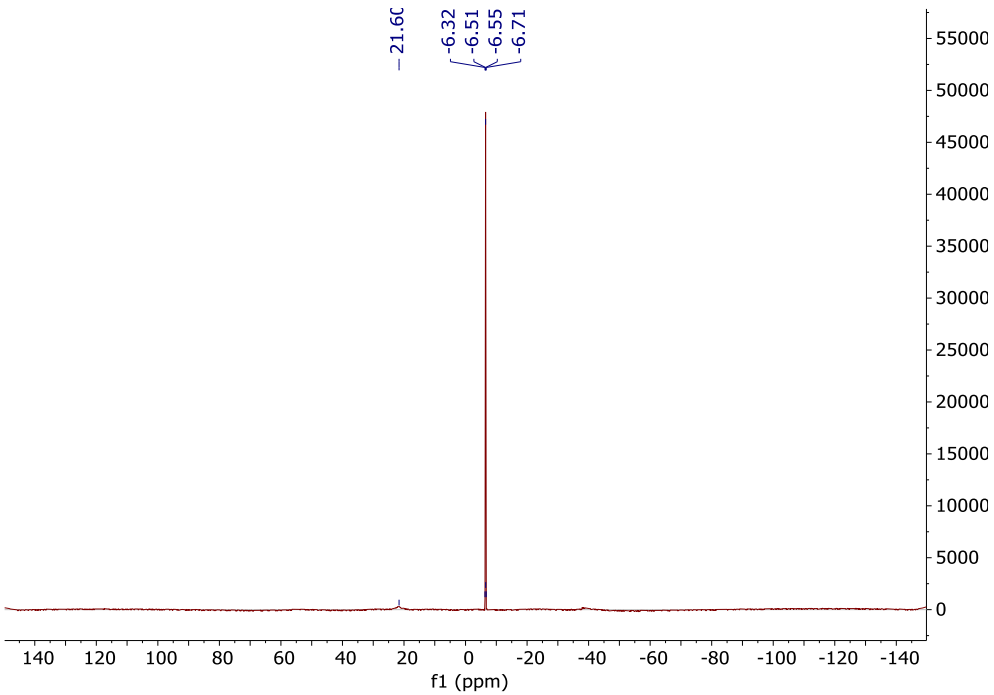

Figure 5. $^{11}B\{^{1}H\}$ NMR of **2Y**.

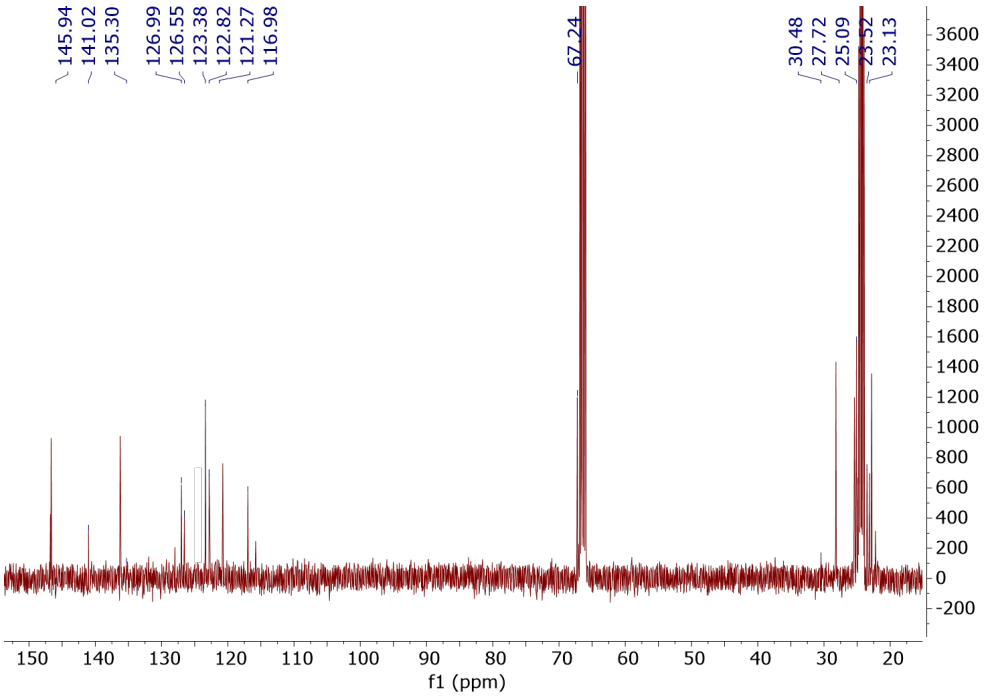

Figure 6. $^{13}C\{^{1}H\}$ NMR of **2Y**.

Crystallography

Crystals were examined using an Agilent Supernova diffractometer, equipped with an Eos CCD area detector and a Microfocus source with Mo Kα radiation (λ = 0.71073 Å). Intensities were integrated from data recorded on narrow (0.5°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Gaussian grid face-indexed absorption corrections with a beam profile correction were applied. The structures were solved either by direct, heavy or iterative methods using ShelXS[6] or ShelXT[7] and all non-hydrogen atoms were refined by full-matrix least-squares on all unique F2 values with anisotropic displacement parameters with exceptions noted in the respective cif files. Except where noted, Hydrogen atoms were refined with constrained geometries and riding thermal parameters. CrysAlisPro[8] was used for control and integration, and SHELXL[9] and Olex2[10] were employed for structure refinement. ORTEP-3[11] and POV-Ray[12] were employed for molecular graphics.

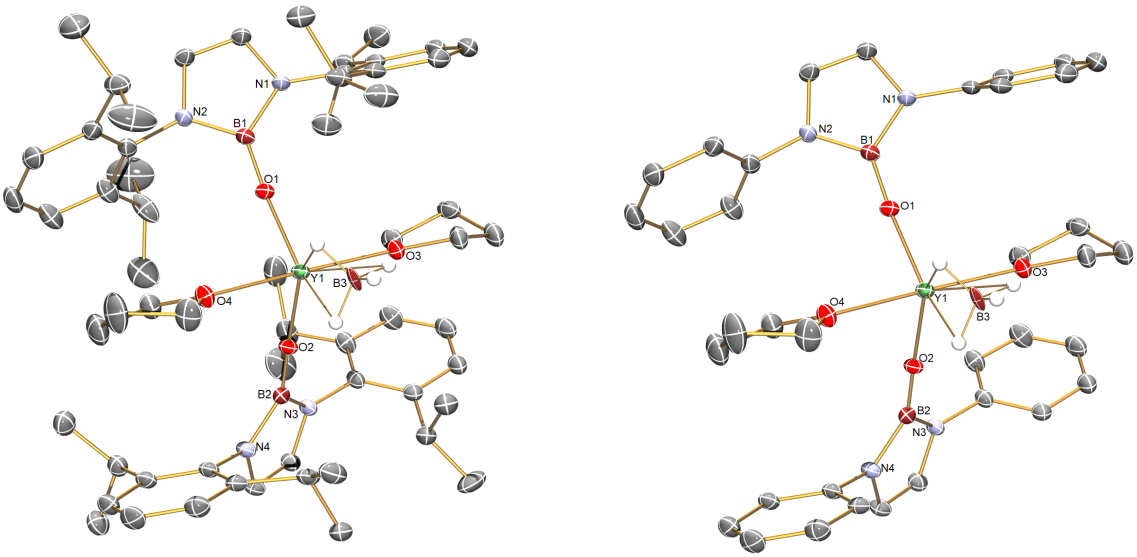

Figure 7. Solid state structure of **1Y** at 150K. Thermal ellipsoids are set at 30% probability and hydrogen atoms, disordered components and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1-O1 2.085(2), Y1-O2 2.093(2), Y1-O3 2.340(2), Y1-O4 2.352(2), O1-B1 1.340(4), O2-B2 1.336(4), N1-B1 1.457(4), N2-B1 1.455(5), N3-B2 1.461(5), N4-B2 1.458(5), O1-Y1-O2 113.01(9), B1-O1-Y1 171.1(2), B2-O2-Y1 175.1(2).

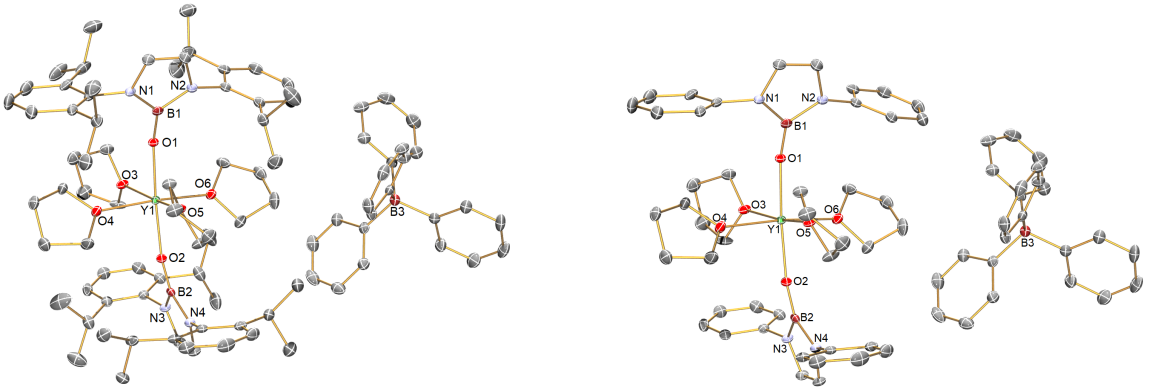

Figure 7. Solid state structure of **2Y** at 150K. Thermal ellipsoids are set at 30% probability with hydrogen atoms and disordered components omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1-O1 2.1415(17), Y1-O2 2.1503(18), Y1-O3 2.3325(18), Y1-O4 2.3256(17), Y1-O5 2.3268(17), Y1-O6 2.3284(17), O1-B1 1.344(3), O2-B2 1.346(3), N1-B1 1.469(4), N2-B1 1.466(4), N3-B2 1.460(4), N4-B2 1.465(4), O1-Y1-O2 173.46(7), O4-Y1-O6 173.19(7), O5-Y1-O3 167.17(6), B1-O1-Y1 158.11(17), B2-O2-Y1 168.53(17).

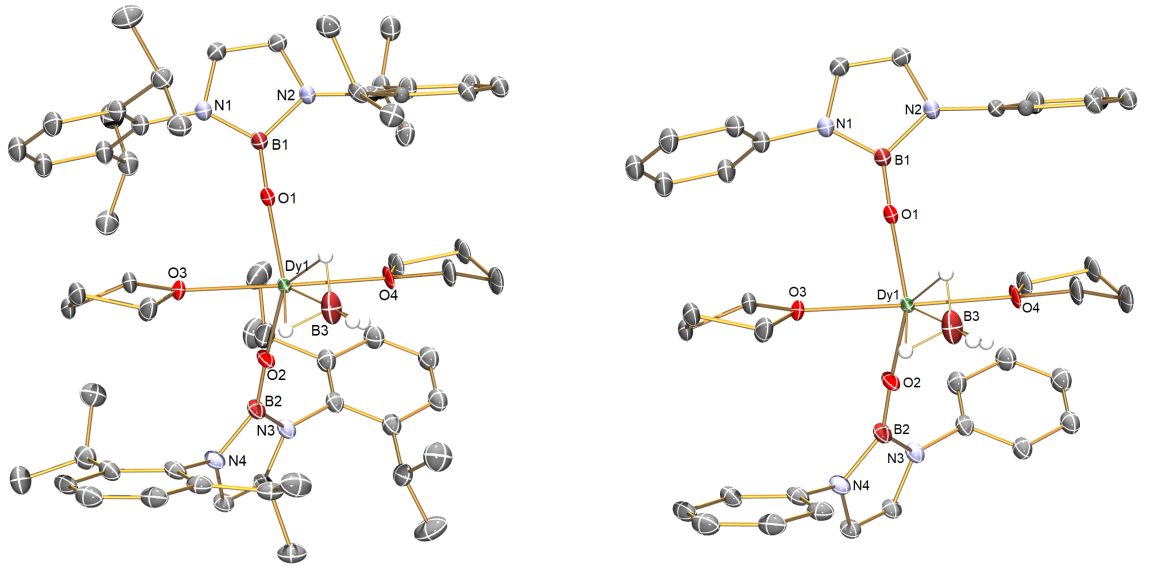

Figure 9. Solid state structure of **1Dy** at 150K. Thermal ellipsoids are set at 30% probability and hydrogen atoms, disordered components and lattice solvent are omitted for clarity. Selected bond lengths [Å] and angles [°]:Dy1-O1 2.113(11), Dy1-O2 2.089(10), Dy1-O3 2.381(10), Dy1-O4 2.372(10), O1-B1 1.34(2), O2-B2 1.33(2), N1-B1 1.44(2), N2-B1 1.49(2), N3-B2 1.47(2), N4-B2 1.46(2), O1-Dy1-O2 115.5(4), B1-O1- Dy1 176.4(11), B2-O2- Dy1 171.9(12).

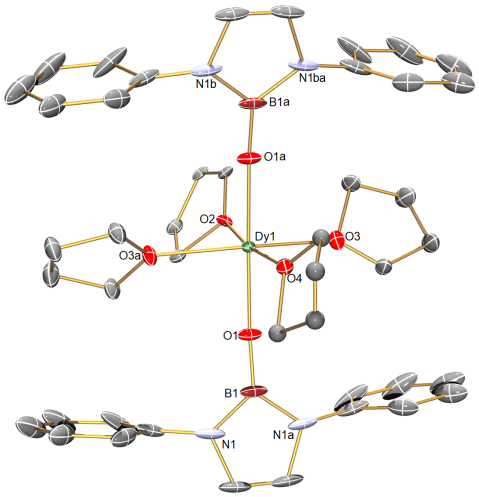

Figure 8. Solid state structure of **2Dy** at 150K. Thermal ellipsoids are set at 30% probability, with iPr groups, hydrogen atoms, BPh_4, lattice solvent and disordered components omitted for clarity. Selected bond lengths [Å] and angles [°]: Dy1-O1 2.136(5), Dy1-O2 2.346(9), Dy1-O3 2.347(6), Dy1-O4 2.365(8), O1-B1 1.367(10), N1-B1 1.457(8), O1-Dy1-O1 175.9(3), O1-Dy1-O2 89.6(7), O1-Dy1-O2 94.5(7), O1-Dy1-O2 94.5(7), O1-Dy1-O3 87.8(6), O1-Dy1-O4 86.2(7), O1-Dy1-O4 89.7(8), B1-O1-Dy1 169.7(5).

Table 1. Single Crystal X-ray diffraction data for compounds **1Ln** and **2 Ln**.

Compound	1Y	2Y	1Dy	2Dy
Formula	$C_{96}H_{121}B_3N_5O_5Y$	$C_{92}H_{124}B_3N_4O_6Y$	$C_{66}H_{98}B_3DyN_4O_4$	$C_{98}H_{130}B_3DyN_4O_6$
Fw, g mol^{-1}	1546.31	1503.28	1206.41	1654.98
Cryst size, mm	0.196 x 0.137 x 0.135	0.262 x 0.187 x 0.116	0.175 x 0.228 x 0.341	0.295 x 0.198 x 0.185
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group	C2/c	$P2_1/n$	P-1	Cmcm
Collection Temp. (K)	150(2)	150(2)	150(2)	150(2)
a, (Å)	19.238(5)	12.9871(5)	12.7769(7)	23.5114(3)
b, (Å)	18.3930(18)	27.1689(11)	13.6689(7)	19.5012(3)
c, (Å)	25.674(4)	24.3048(11)	19.8264(15)	19.8810(3)
α, (°)	90	90	107.413(6)	90
β, (°)	90.25(2)	93.672(4)	92.621(5)	90
γ, (°)	90	90	98.825(4)	90
V, (Å^3)	9085(3)	8558.2(6)	3249.4(4)	9115.5(2)
Z	4	4	2	4
ρ_{calc} g cm^{-3}	1.131	1.167	1.233	1.206
μ, mm^{-1}	0.694	0.735	1.197	0.873
# reflections measured	11671	74428	11803	54368
# unique reflections, Rint	7395, 0.0649	18769, 0.0842	11803, 0.1044	4264, 0.0305
# reflections with $F^2 > 2s(F^2)$	3495	11827	9412	3872
Transmission coefficient range	0.699-1.000	0.690-1.000	0.565-1.000	0.553-1.000
R, $R_w{}^a$ ($F^2 > 2\sigma(F^2)$)	0.1173, 0.2759	0.0593, 0.0987	0.1325, 0.3221	0.0629, 0.1322
R, $R_w{}^a$ (all data)	0.2244, 0.3384	0.1170, 0.1153	0.1541, 0.3354	0.0672, 0.1342
S^a	1.043	1.040	1.078	1.224
Parameters, Restraints	552, 781	1003, 1	727, 1088	350, 536
Max.,min. difference map, e Å^{-3}	0.650, -0.340	0.317, -0.443	4.601, -4.057	0.888, -0.926

IR spectra

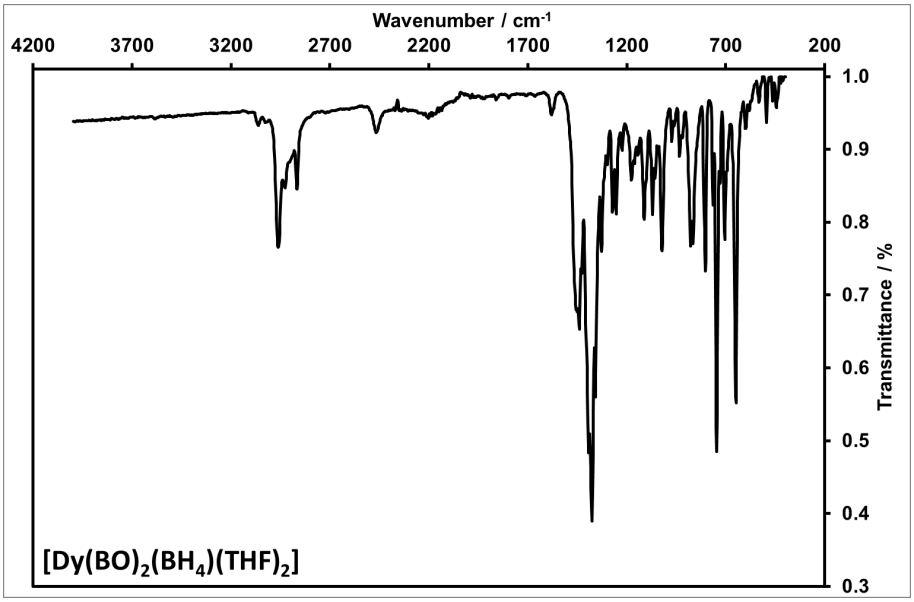

Figure 11. IR spectrum of **1Dy**.

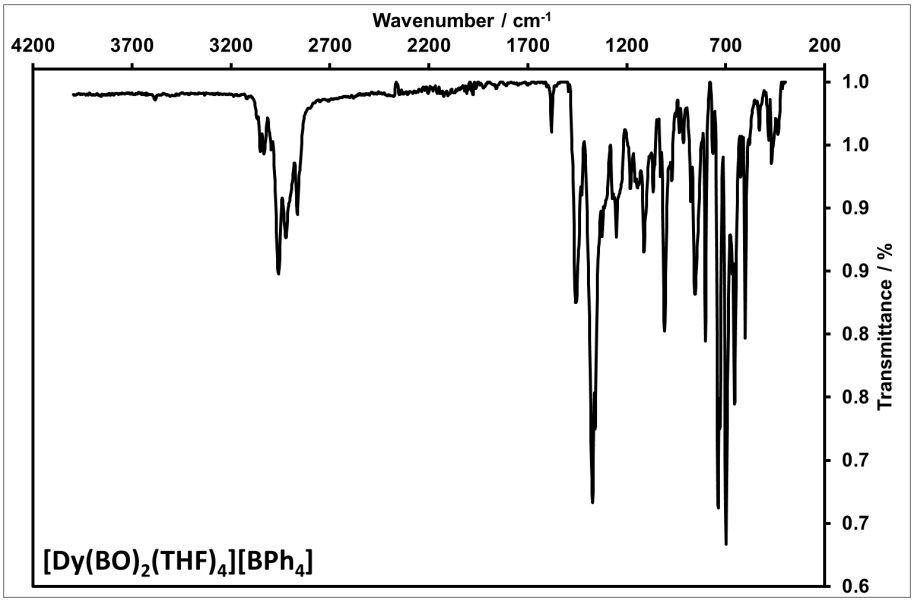

Figure 12. IR spectrum of **2Dy**.

Magnetometry

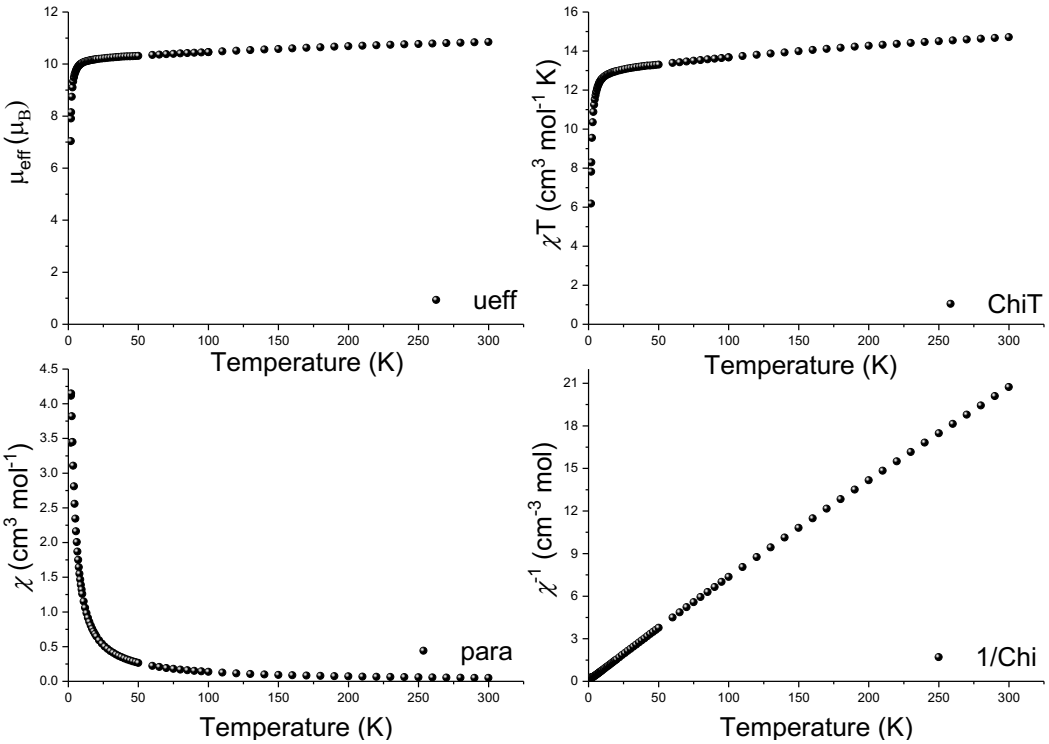

Figure 13. Variable temperature magnetic susceptibility measurements of **2Dy** performed with a 1000 Oe applied field in the temperature range 1.8 to 300 K.

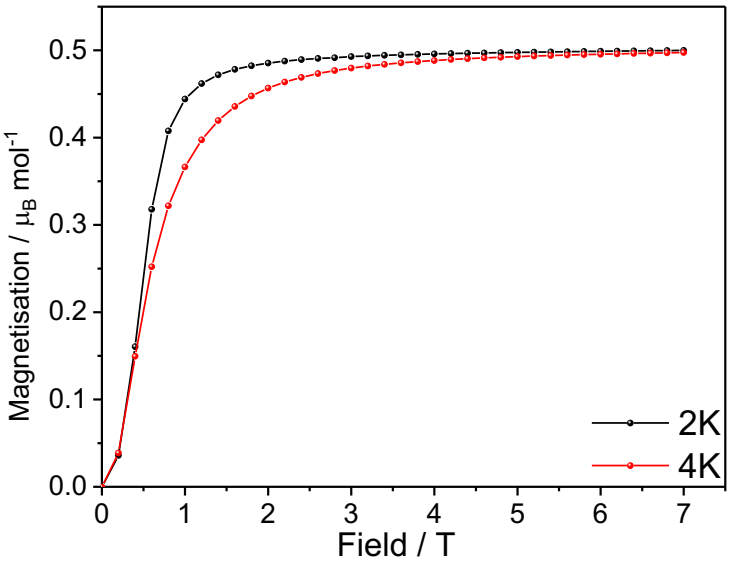

Figure 14. Magnetisation vs Field measurements for **2Dy** with a line to guide the eye.

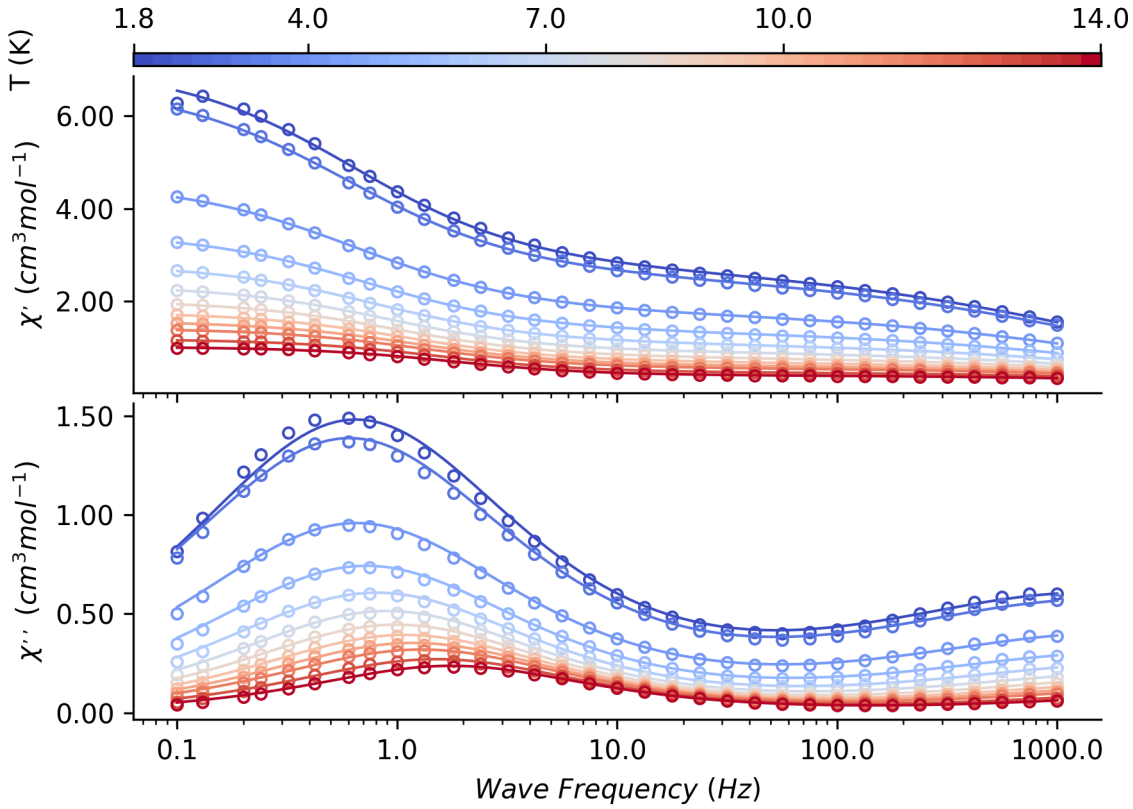

Figure 15. Alternating-current susceptibility data for **2Dy** between 1.8 and 14 K.

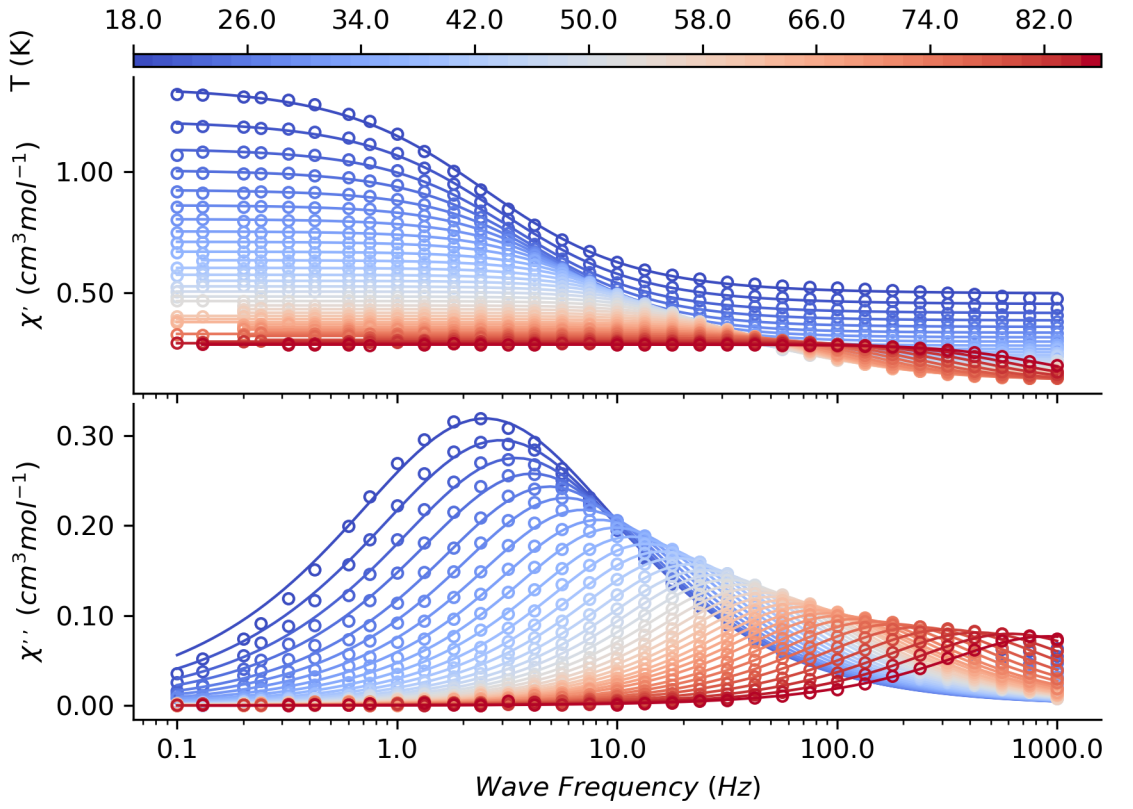

Figure 16. Alternating-current susceptibility data for **2Dy** between 18 and 86 K.

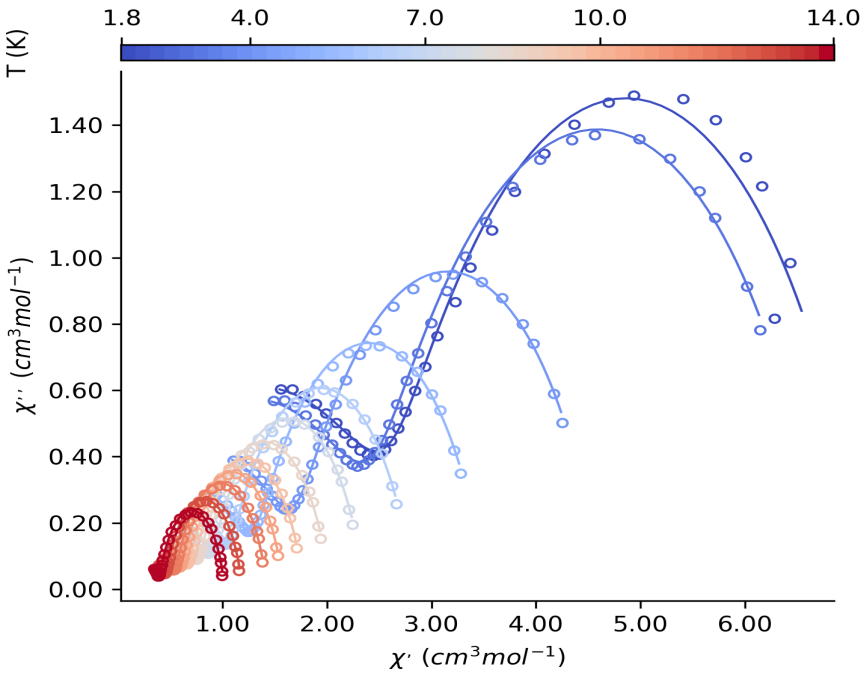

Figure 17. Alternating-current susceptibility data as a Cole-Cole plot for **2Dy** between 1.8 and 14 K.

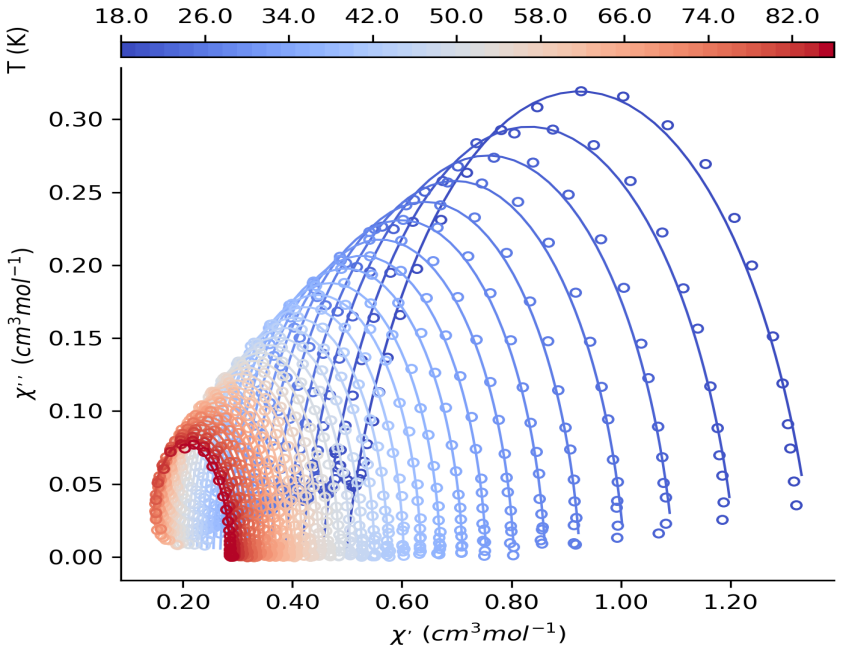

Figure 18. Alternating-current susceptibility data as a Cole-Cole plot for **2Dy** between 18 and 86 K.

Table 2. Electronic structure of the cation in **2Dy** determined with CASSCF-SO methods. CF wavefunctions shown with components ≥10%, rounded to the nearest percent.

Energy / K	g_x	g_y	g_z	Angle / °	CF wavefunction
0.0	0.00	0.00	19.86	--	97% |±15/2⟩
763.0	0.05	0.06	16.83	2.3	70%|±13/2⟩ +28%|∓13/2⟩
1308.9	0.63	1.08	13.15	7.7	87% |±11/2⟩
1535.8	3.53	6.79	11.18	84.1	28%|±1/2⟩ +26%|∓1/2⟩ +18%|±9/2⟩ +11%|∓9/2⟩
1684.1	0.37	1.80	16.49	73.1	30%|±3/2⟩ +14%|±9/2⟩ +14%|±7/2⟩ +14%|±5/2⟩
1754.5	1.85	4.40	10.42	74.2	27%|±3/2⟩ +18%|±9/2⟩ +15%|∓9/2⟩ +13%|±1/2⟩
1840.9	1.54	5.27	12.51	75.7	36%|±7/2⟩ +19%|∓5/2⟩ +17%|±5/2⟩
1956.0	0.50	1.31	18.42	86.3	26%|±7/2⟩ +23%|∓5/2⟩ +15%|∓1/2⟩ +14%|±3/2⟩

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