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Supporting Information

Exchange Interactions Switch Tunneling: A Comparative Experimental and Theoretical Study on Relaxation Dynamics by Targeted Metal Ion Replacement

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Supporting Information

1 Structural and magnetic data

2 Ab initio calculations

1. Structural and magnetic data

Table S1. Structural data of H_2opch, **1** and **2**.

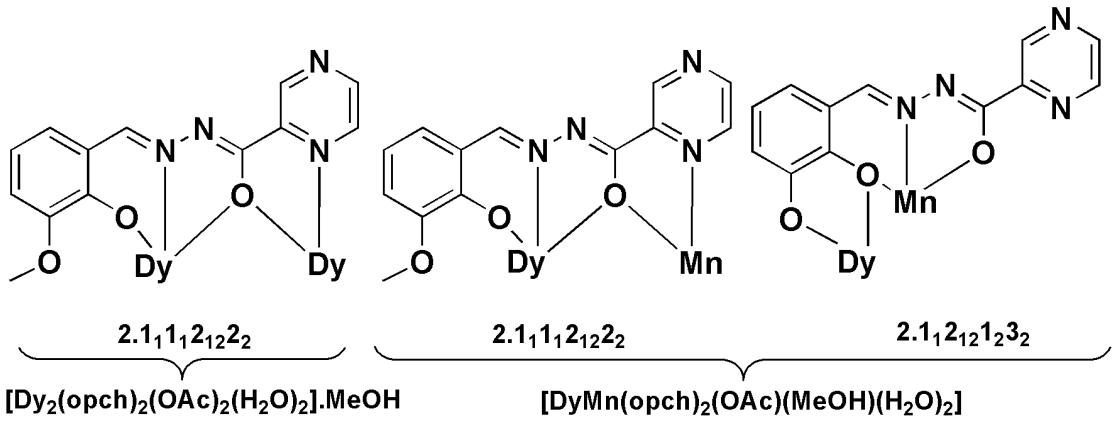
Compound	**H_2opch**	**1**	**2**
fromula	$C_{13}H_{12}N_4O_3$	$C_{32}H_{38}Dy_2N_8O_{14}$	$C_{29}H_{31}DyMnN_8O_{11}$
M_r	272.27	1083.70	886.07
Crystal size	0.30×0.30×0.20	0.30×0.25×0.21	0.25×0.25×0.30
color	orange blocks	yellow blocks	red blocks
T [K]	293	293	273(2)
λ [Å]	0.71073	0.71073	0.71073
crystal syst	monoclinic	triclinic	monoclinic
space group	C2/c	P-1	P2(1)/c
a [Å]	16.984(17)	9.5758(12)	13.8079(6)
b [Å]	11.257(11)	9.6249(13)	20.2511(9)
c [Å]	15.463(16)	11.8364(15)	15.7731(7)
α [deg]	90	108.715(2)	90.00
β [deg]	97.034(17)	92.964(2)	106.494(1)
γ [deg]	90	103.950(2)	90.00
V [$Å^3$]	2934(5)	992.8(2)	4229.1(3)
Z	8	1	4
ρ[g cm^{-3}]	1.233	1.813	1.392
F(000)	1136	530	1760
reflns collected	2555	3195	7445
unique reflns	1925	2442	5840
R_{int}	0.0298	0.0553	0.0446
GOF	0.991	0.9189	0.999
R1 [I > 2σ(I)]	0.0549	0.0718	0.0708
*w*R2 (all data)	0.1673	0.1346	0.1525
$(\Delta\rho)_{max}$,$(\Delta\rho)_{min}$/[e$Å^3$]	2.42, -1.23	1.83, -1.01	2.11, -1.39

Table S2. Selected bond lengths (Å) and angles (º) in compounds **1** and **2**.

Compound 1			
Dy1–O3	2.324(1)	Dy1–O3a	2.338(1)
Dy1–O4	2.419(1)	Dy1–N3	2.566(2)
Dy1–O5	2.363(1)	Dy1–N1a	2.478(2)
Dy1–O6	2.362(1)	Dy1⋯Dy1a	3.891(2)
Dy1–O2a	2.145(1)	Dy1–O3–Dy1a	113.1(2)
Compound 2			
Mn1–O3	2.188(1)	Dy1–O4	2.429(1)
Mn1–O5	2.314(1)	Dy1–O5	2.335(1)
Mn1–O6	2.313(1)	Dy1–O7	2.466(1)
Mn1–O9	2.242(1)	Dy1–O8	2.404(1)
Mn1–O10	2.079(1)	Dy1–O11	2.382(1)
Mn1–N4	2.422(1)	Dy1–N1	2.455(2)
Mn1–N5	2.354(2)	Mn1⋯Dy1	3.727(2)
Dy1–O2	2.171(1)	Mn1–O3–Dy1	112.5(1)
Dy1–O3	2.295(1)	Mn1–O5–Dy1	106.6(1)

Table S3. The geometry analysis for compounds **1** and **2** by SHAPE software.

Compound		**Square antiprism** (D_{4d})	**Triangular dodecahedron** (D_{2d})	**Pentagonal bipyramid** (D_{5h})
1	Dy	5.711	3.281	
2	Dy	3.434	2.781	
	Mn			0.647



Scheme S1. Binding modes of the H_2opch ligands observed in compounds **1** and **2**.

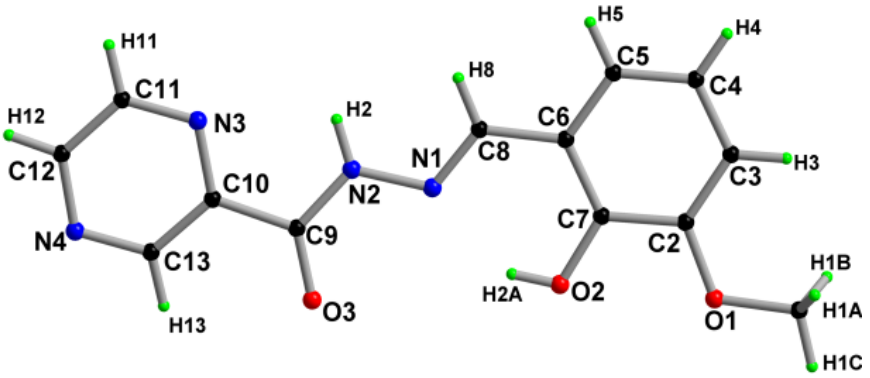


Figure S1. The molecular structure of H_2opch.

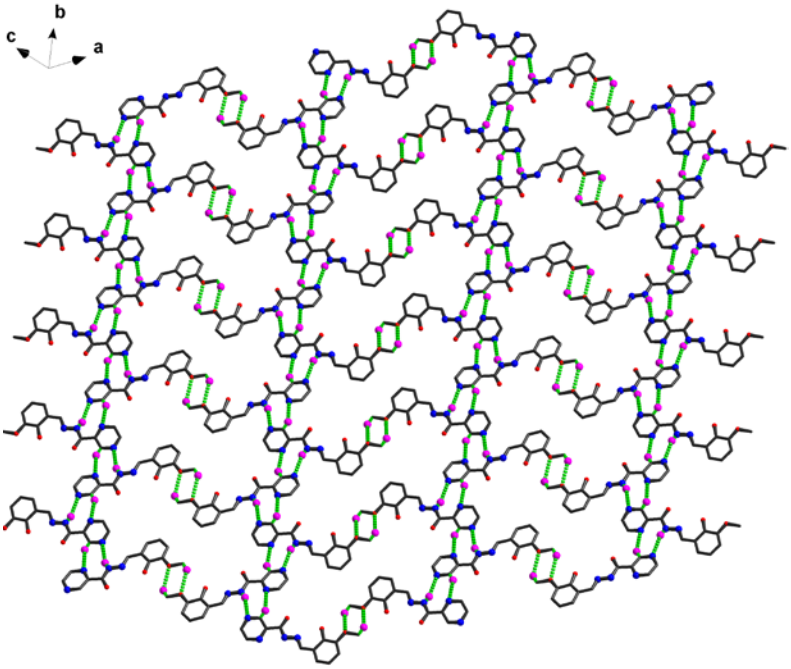


Figure S2. Illustration showing the hydrogen-bonding interactions (bright green lines) and the two-dimensional supramolecular arrangement of the molecules in the **H_2opch** ligand.

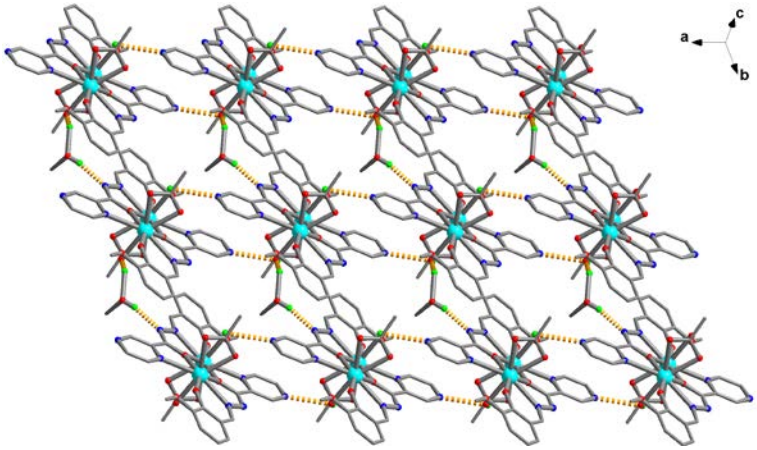


Figure S3. Illustration showing the hydrogen-bonding interactions (light orange lines) and the two-dimensional supramolecular plane arrangement of the molecules in compound **1**.

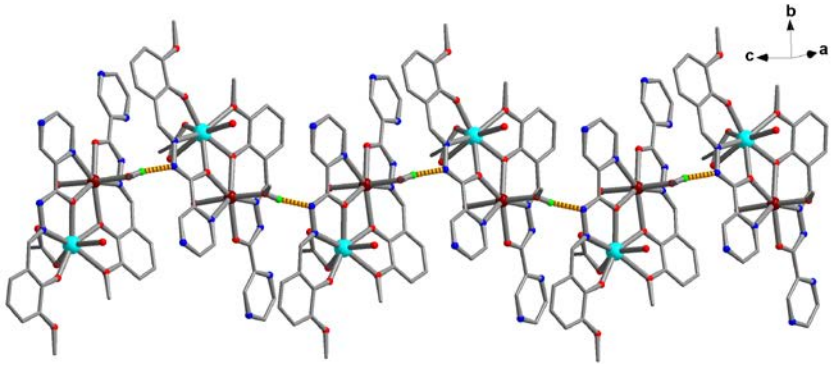


Figure S4. Illustration showing the hydrogen-bonding interactions (light orange lines) and the one-dimensional zigzag chain arrangement of the molecules in compound **2**.

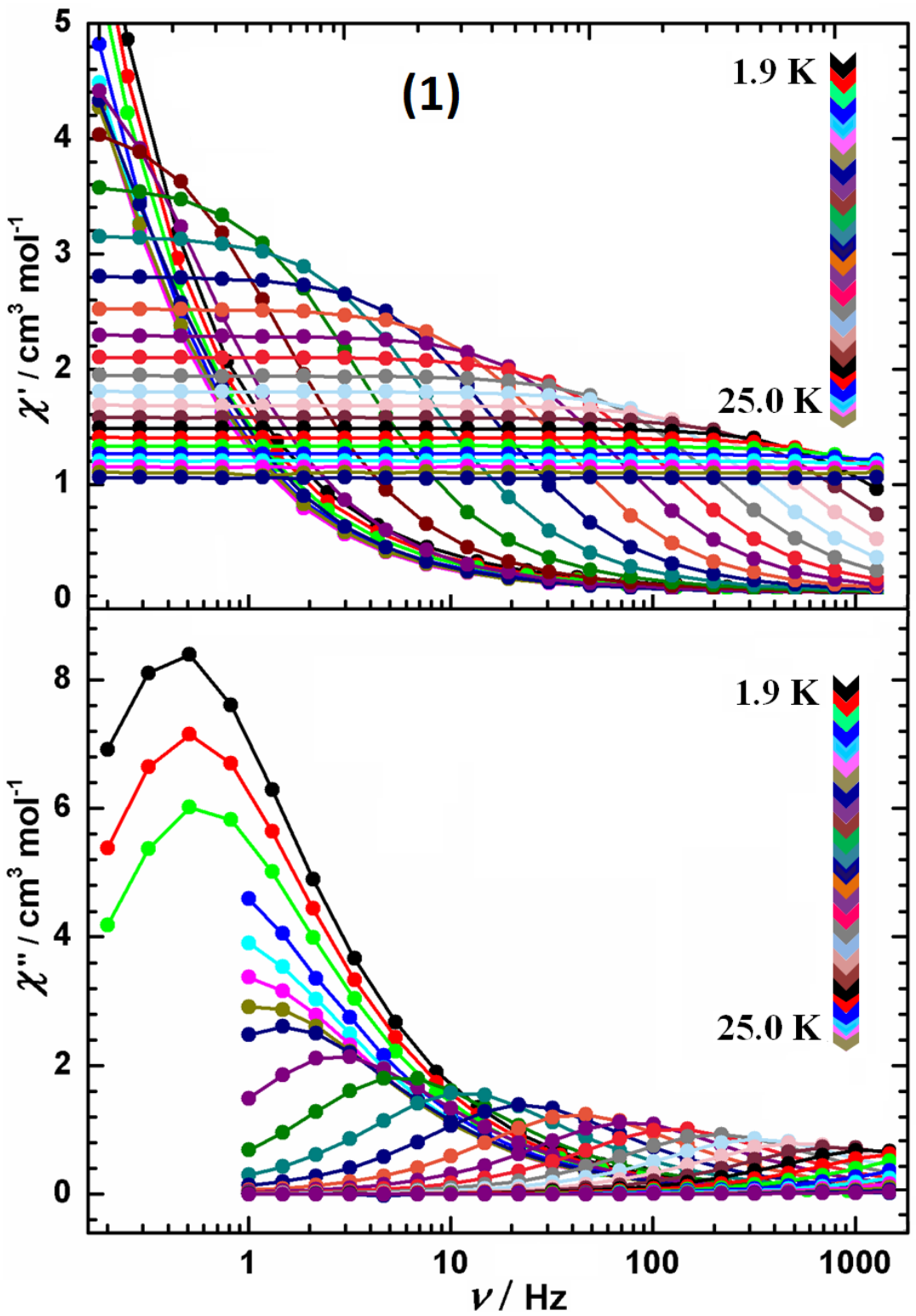


Figure S5. Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility of compound **1** under zero-dc field.

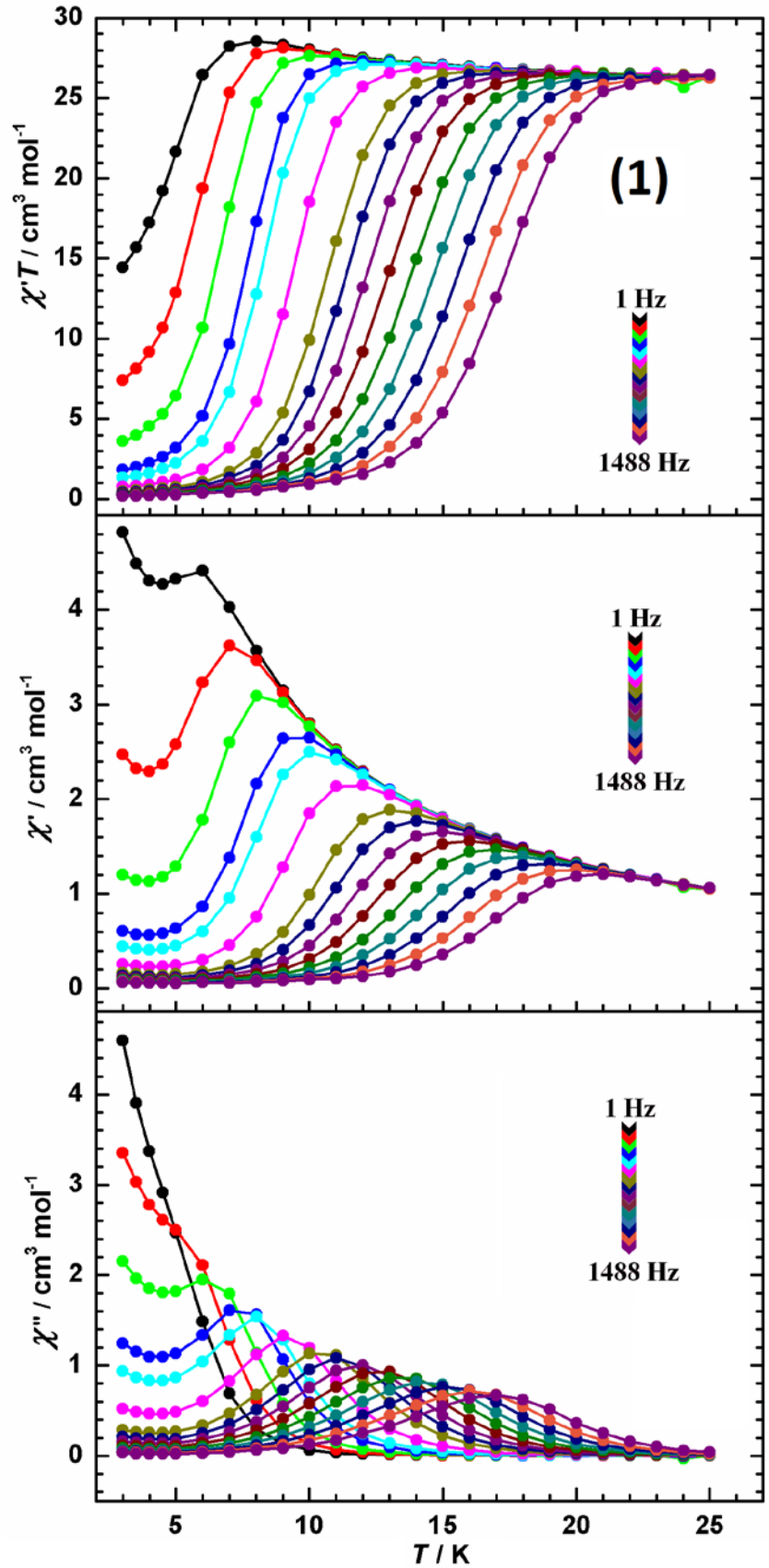


Figure S6. Temperature dependence of the $\chi'T$ product (top), χ' (middle) and χ'' (bottom) under zero-dc field for **1**.

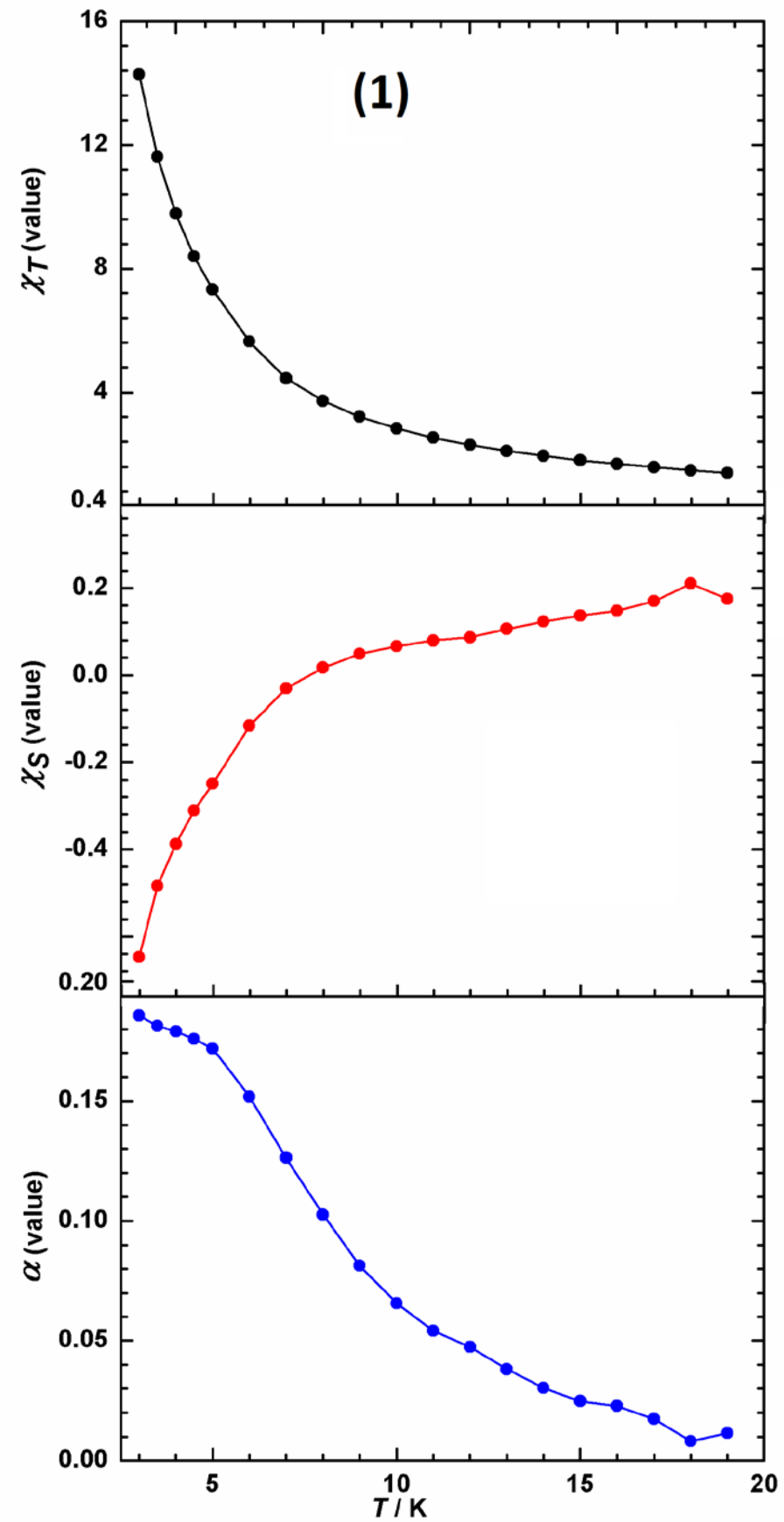


Figure S7. The obtained χ_T (top), χ_S (middle) and α (bottom) values from the fit using a generalized Debye model for compound **1**.

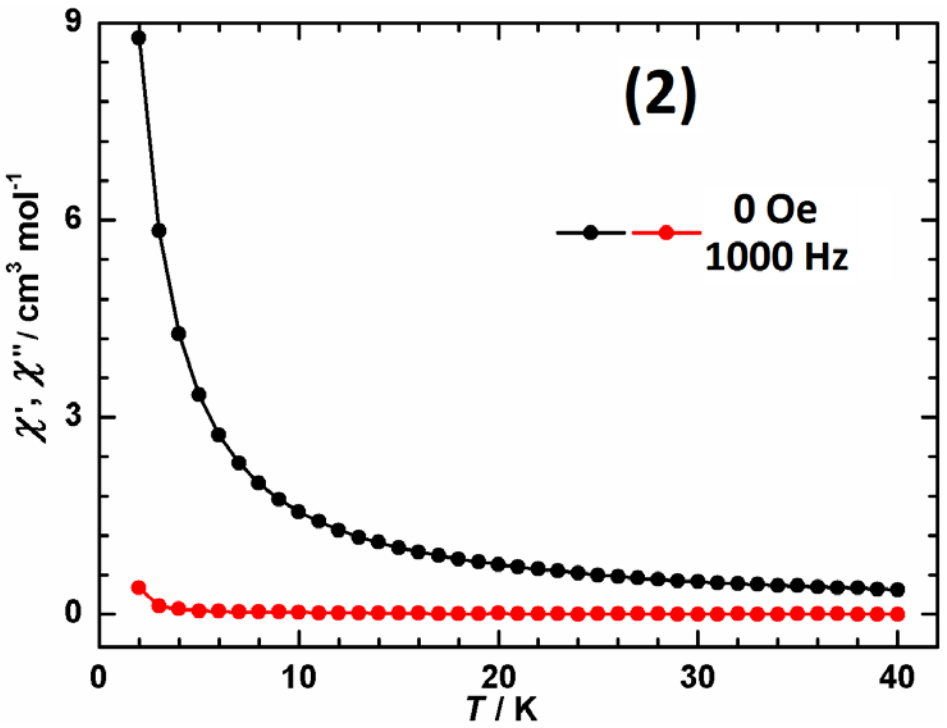


Figure S8. Temperature dependence of in-phase (black) and out-of-phase (red) *ac* susceptibility under zero-dc field for compound **2**.

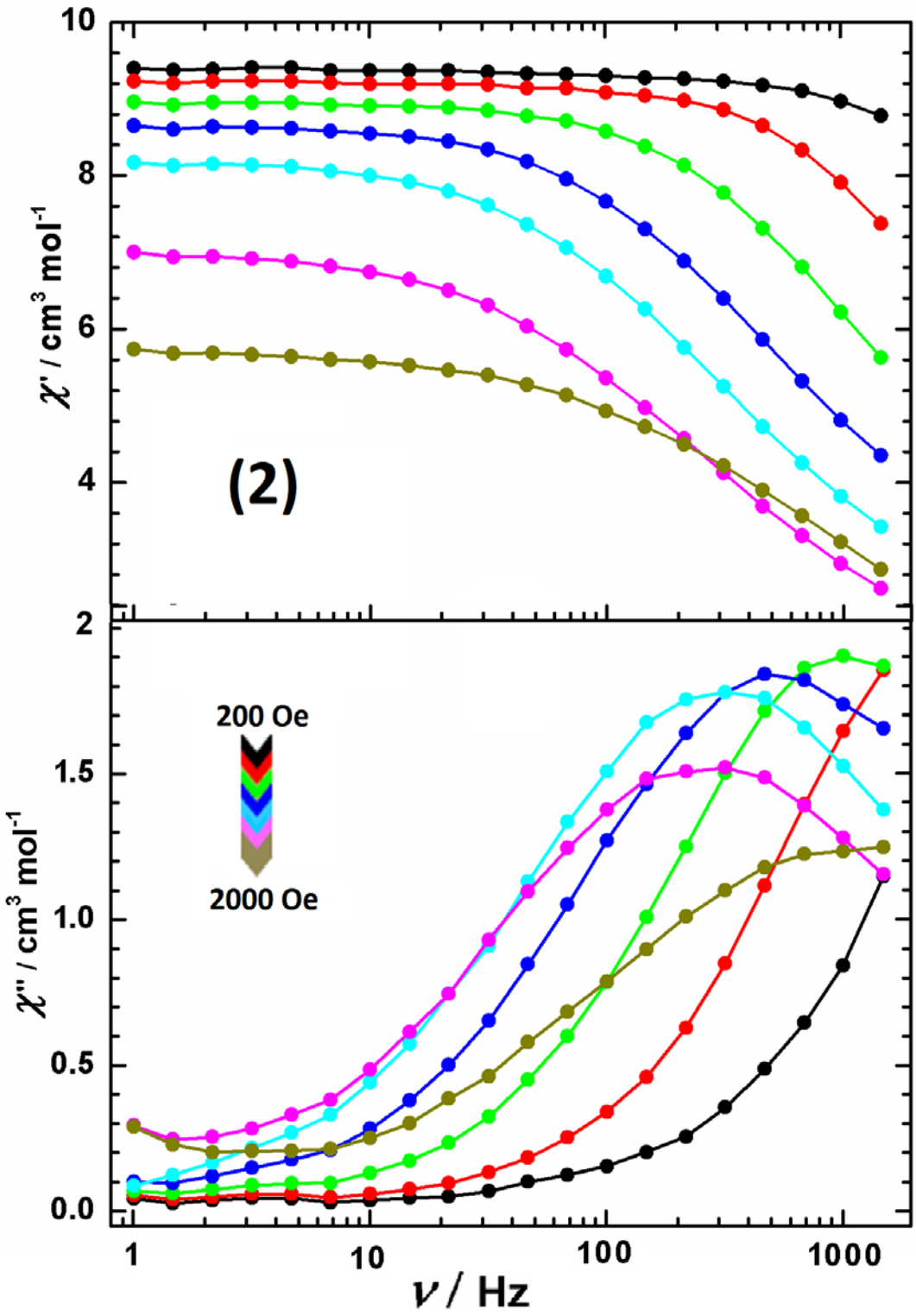


Figure S9. Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility of compound **2** under various applied dc fields at 1.9 K.

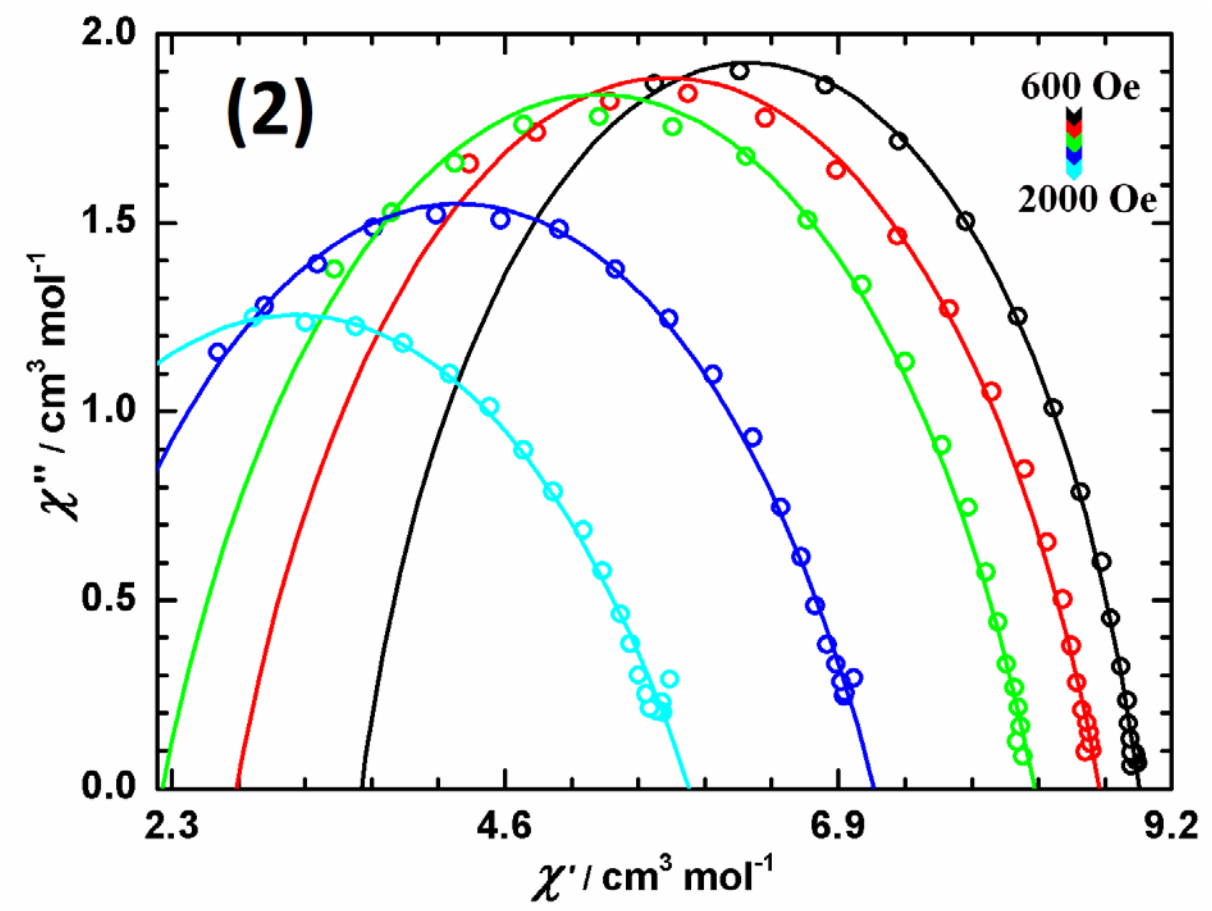


Figure S10. Cole-Cole plots under variable static fields at 1.9 K for compound **2**. The solid lines are the best fits to the experimental data.

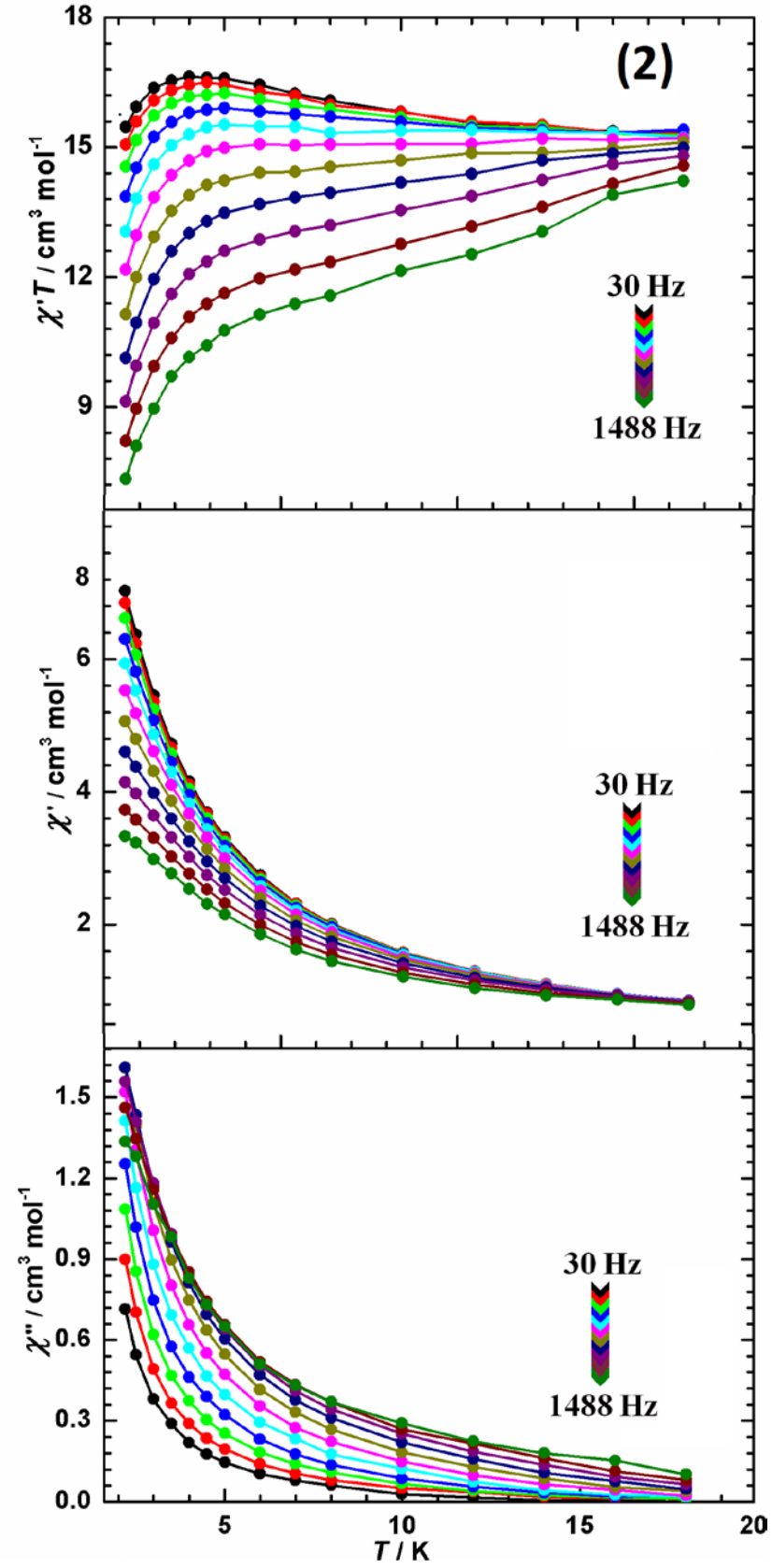


Figure S11. Temperature dependence of the $\chi'T$ product (top), χ' (middle) and χ'' (bottom) under 1000 Oe dc field for **2**.

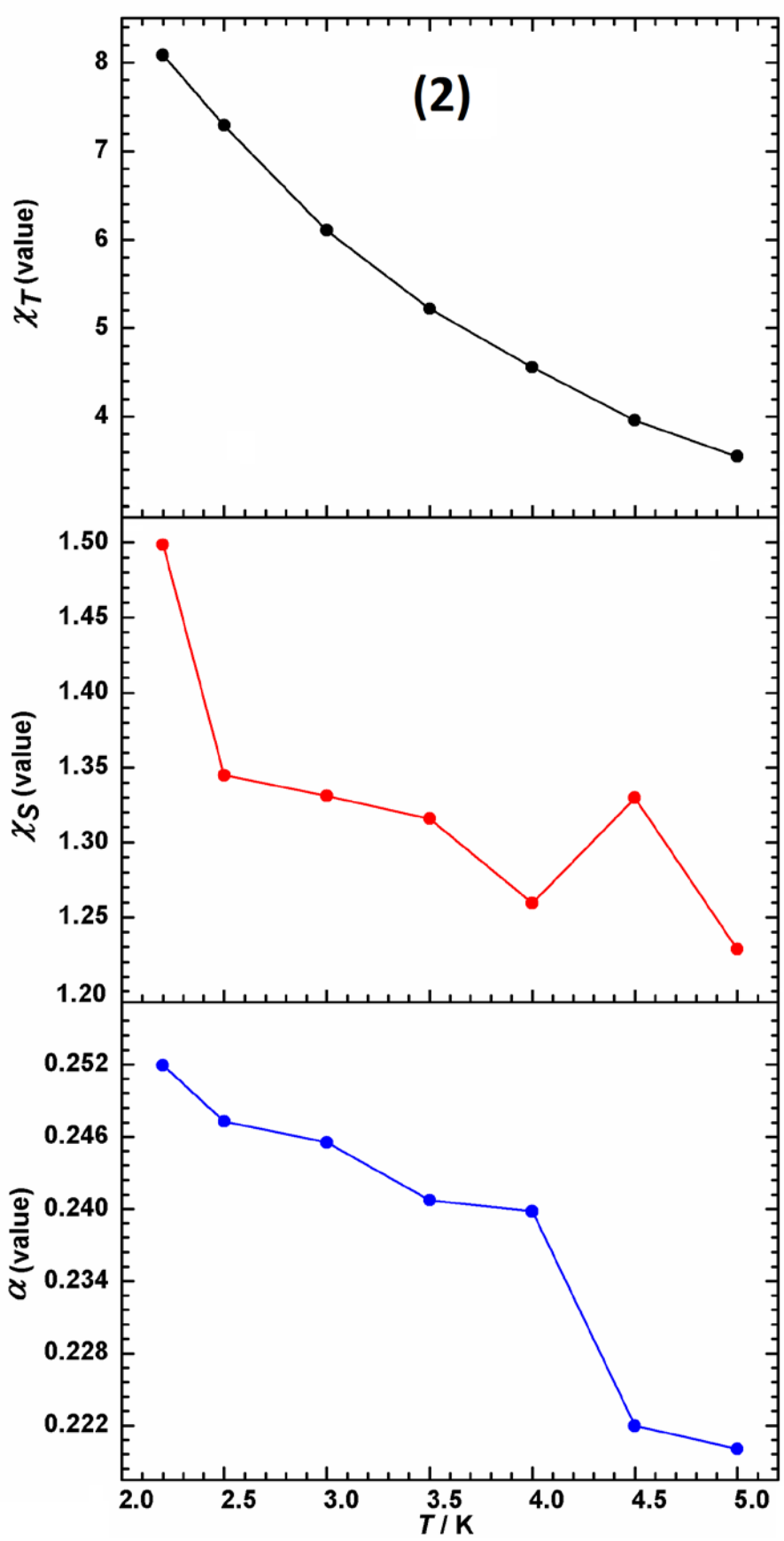


Figure S12. The obtained χ_T (top), χ_S (middle) and α (bottom) values from the fit using a generalized Debye model for compound **1**.

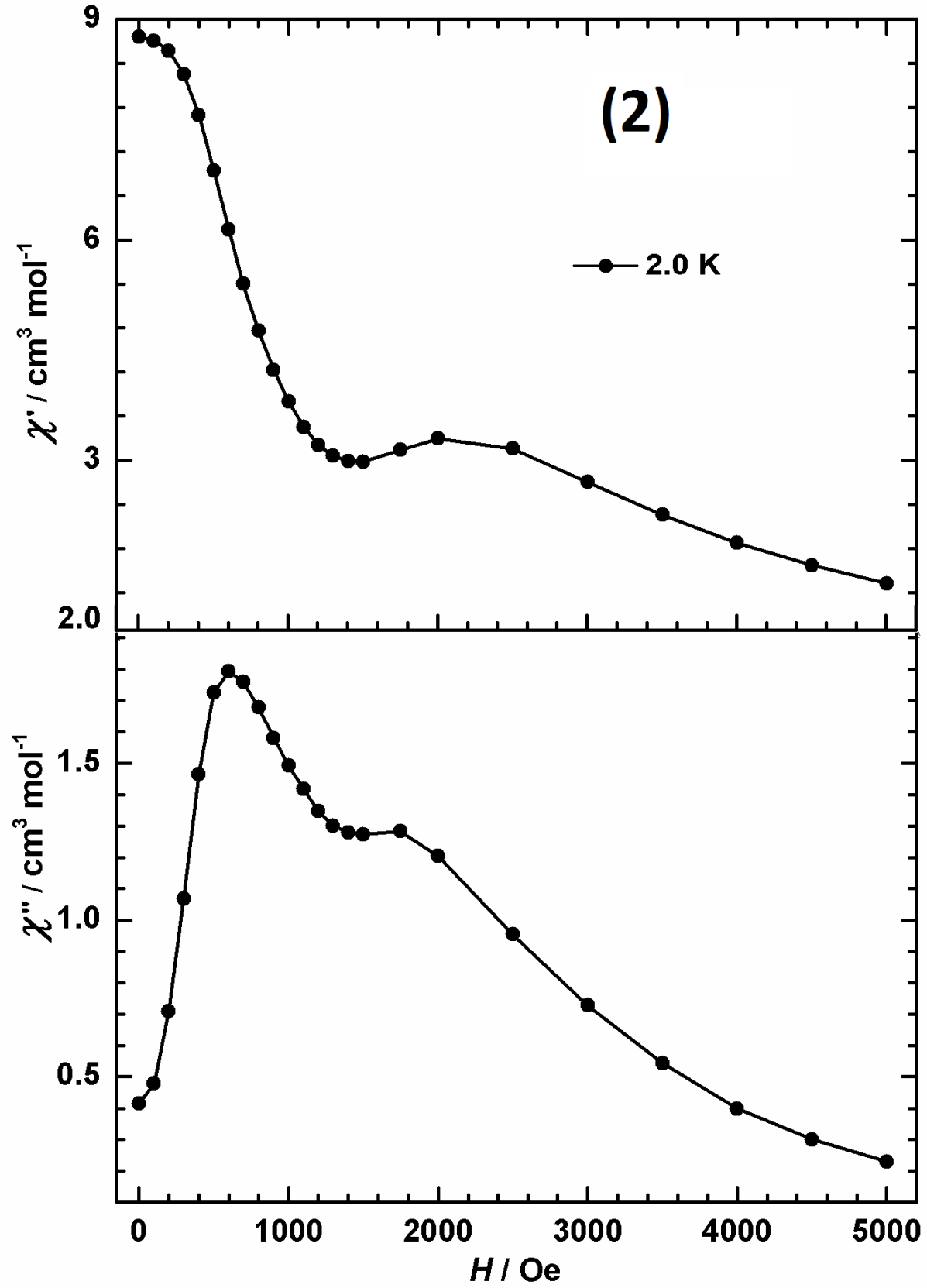


Figure S13. Field dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility of compound **2** at 1000 Hz and 2 K.

2 Ab initio calculations

Computational details

Table S4. Contractions of the employed basis sets.

Basis 1	Basis 2
Ln.ANO-RCC...7s6p4d2f1g	Ln.ANO-RCC...8s7p5d4f2g1h
N.ANO-RCC...3s2p	N.ANO-RCC...4s3p1d
C.ANO-RCC...3s2p	C.ANO-RCC...4s3p1d. (close)
H.ANO-RCC...2s	C.ANO-RCC...3s2p. (distant)
	H.ANO-RCC...2s

Table S5. Energy of the lowest spin-orbit Kramers doublets (cm^{-1}) on Dy sites in the investigated compounds

Dy in Dy_2 (compound 1)		Dy in DyMn (compound 2)	
Basis 1	**Basis 2**	**Basis 1**	**Basis 2**
0.000	0.000	0.000	0.000
187.784	191.727	202.174	204.075
327.356	333.817	355.074	365.896
351.336	353.559	422.331	423.700
426.082	415.434	540.913	537.958
484.460	442.544	611.520	585.852
535.436	513.722	687.177	671.784
615.540	579.318	766.976	754.154
3661.005	3658.616	3658.229	3655.805
3785.400	3785.036	3818.658	3820.552
3833.297	3834.210	3902.598	3903.714
3907.244	3899.588	3984.211	3981.442
3958.852	3940.007	4060.038	4049.401
4020.338	3994.949	4148.997	4131.900
4079.953	4034.503	4247.985	4228.245
6252.704	6247.162	6275.833	6272.087
6315.043	6312.209	6360.427	6359.264
6357.580	6351.206	6427.300	6422.842
6424.104	6406.783	6514.181	6506.734
6499.606	6478.499	6608.441	6596.767

	6594.406	6555.363	6752.472	6731.399
	8227.489	8218.258	8274.409	8269.011
	8268.900	8261.686	8331.052	8326.572
	8329.713	8318.848	8398.095	8392.477
	8422.203	8401.285	8518.682	8507.044
	8525.633	8491.280	8670.967	8651.591
	9754.421	9746.509	9808.253	9802.773
	9811.134	9799.441	9877.351	9871.888
	9895.265	9880.373	9978.146	9969.184
	10052.409	10018.202	10193.593	10175.181
	…	…	…	…

Table S6. *g* tensors of the low-lying Kramers doublets (KD) of individual Dy sites in compounds **1** and **2** obtained within basis set 1 model.

KD		Dy in Dy_2 (compound 1)		Dy in DyMn (compound 2)	
		Basis 1	**Basis 2**	**Basis 1**	**Basis 2**
1	g_x	0.00879	0.00656	0.00465	0.00377
	g_y	0.01780	0.01297	0.00939	0.00746
	g_z	19.43683	19.47883	19.58761	19.60838
2	g_x	0.25267	0.20683	0.13141	0.09764
	g_y	0.31210	0.24975	0.20370	0.14829
	g_z	16.57562	16.64449	16.63121	16.68307
3	g_x	1.31070	1.73682	2.29743	2.43880
	g_y	1.73405	3.00333	3.12829	4.01876
	g_z	17.68043	15.63005	16.27305	15.24130
4	g_x	2.50815	1.66865	9.06333	8.30491
	g_y	5.20984	5.31728	5.17572	5.18753
	g_z	11.45500	11.80336	0.14775	1.34074
5	g_x	2.54586	1.44494	8.81253	8.37729
	g_y	4.36105	3.80855	6.46103	6.74977
	g_z	10.44753	12.14542	3.44147	2.28868
6	g_x	0.40583	1.19377	1.46439	1.92027
	g_y	0.89745	2.07300	1.98905	3.15284
	g_z	17.76346	16.24514	15.56897	15.15655
7	g_x	0.37824	0.44372	0.32006	0.30107
	g_y	0.78228	1.15980	0.61862	0.52062
	g_z	16.04755	15.03593	17.38576	17.15311
8	g_x	0.17755	0.23857	0.11603	0.12276
	g_y	0.34932	0.53052	0.14246	0.14069
	g_z	18.50217	18.07661	19.35562	19.33366

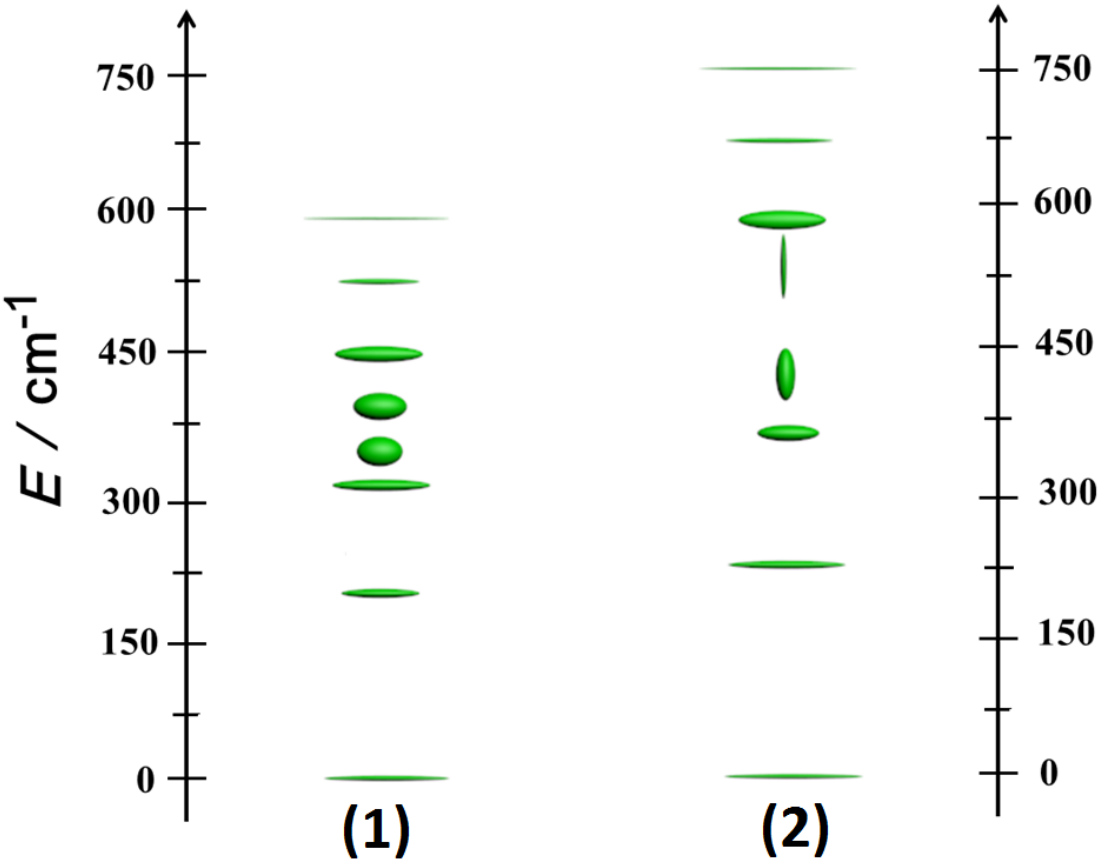


Figure S14. Approximative depictions of *g* tensors of the lowest Kramers doublets (KD) in compounds **1** and **2**.

Table S7. Ab initio calculated LoProp atomic charges in Dy_2 (compound 1). Atomic labels are those form the crystallographic CIF file. Atoms from the first coordination sphere are highlighted yellow.

	Atomic coordinates			LoProp Charges	
	x	y	z	Basis 1	Basis 2
Dy1	-0.928236	-3.109502	4.053765	2.4902	2.5231
Dy1 (Lu)	0.316194	-0.955784	7.045750	1.4120	1.3957
O1	2.866798	1.741215	9.859698	-0.3853	-0.3856
O2	1.101899	0.625736	8.263588	-0.6549	-0.6536
O3	-1.311733	-1.249525	5.393254	-0.7720	-0.7877
O4	-0.909357	-1.507874	2.239882	-0.6790	-0.7068
O5	0.969155	-2.430407	2.820387	-0.7885	-0.8129
O6	-2.035930	-4.146671	5.863873	-0.7199	-0.7298
O1	-3.478841	-5.806501	1.239816	-0.3885	-0.3973
O2	-1.713941	-4.691023	2.835926	-0.8876	-0.9102
O3	0.699690	-2.815762	5.706260	-0.7639	-0.7821
O4	0.297314	-2.557412	8.859632	-0.5694	-0.5680
O5	-1.581198	-1.634879	8.279128	-0.6647	-0.6619
O6	1.423887	0.081384	5.235641	-0.5965	-0.5977

N1	-1.278963	0.921728	6.779583	-0.2023	-0.1965
N2	-2.450866	0.660729	6.035916	-0.3152	-0.3325
N3	-3.291343	-2.117434	3.934778	-0.2726	-0.3055
N4	-5.799344	-0.938069	3.935888	-0.1955	-0.2233
N1	0.666921	-4.987014	4.319931	-0.3108	-0.3384
N2	1.838824	-4.726016	5.063598	-0.3168	-0.3341
N3	2.679301	-1.947852	7.164736	-0.1745	-0.1764
N4	5.187302	-3.127217	7.163626	-0.1961	-0.1969
C1	3.784121	2.294974	10.773188	-0.1736	-0.1735
C2	1.796474	2.508769	9.503404	0.1681	0.1682
C3	1.604671	3.807190	9.906316	-0.1853	-0.1873
C4	0.477469	4.526846	9.476765	-0.1806	-0.1811
C5	-0.421879	3.936630	8.639862	-0.1343	-0.1355
C6	-0.260557	2.621206	8.199211	-0.1100	-0.1078
C7	0.880478	1.898713	8.611003	0.2735	0.2731
C8	-1.259117	2.075265	7.343439	0.0841	0.0775
C9	-2.375173	-0.481571	5.395474	0.3861	0.4232
C10	-3.523712	-0.973725	4.609628	0.0804	0.0952
C11	-4.774890	-0.412891	4.590759	-0.0267	0.0007
C12	-5.554677	-2.061185	3.253268	-0.0462	-0.0212
C13	-4.299142	-2.629517	3.228849	-0.0180	0.0009
C14	0.296297	-1.537617	2.165515	0.5799	0.6310
C15	1.110660	-0.511879	1.336382	-0.4512	-0.4531
C1	-4.396164	-6.360260	0.326326	-0.1736	-0.1730
C2	-2.408516	-6.574055	1.596110	0.1618	0.1802
C3	-2.216714	-7.872476	1.193198	-0.1861	-0.1853
C4	-1.089512	-8.592133	1.622749	-0.1817	-0.1879
C5	-0.190163	-8.001917	2.459652	-0.1352	-0.1336
C6	-0.351485	-6.686492	2.900303	-0.1086	-0.1138
C7	-1.492520	-5.963999	2.488511	0.2820	0.3072
C8	0.647074	-6.140551	3.756076	0.0777	0.0989
C9	1.763131	-3.583715	5.704040	0.3825	0.4307
C10	2.911669	-3.091562	6.489886	0.0792	0.0775
C11	4.162847	-3.652396	6.508755	-0.0286	-0.0309
C12	4.942635	-2.004101	7.846247	-0.0470	-0.0488
C13	3.687099	-1.435769	7.870666	-0.0109	-0.0109
C14	-0.908339	-2.527669	8.933999	0.5586	0.5639
C15	-1.722702	-3.553407	9.763133	-0.4398	-0.4410
H1A	4.257965	3.016576	10.353627	0.1309	0.1308
H1B	4.408627	1.619681	11.048456	0.1588	0.1586
H1C	3.312321	2.624559	11.541275	0.1311	0.1310
H3	2.225130	4.213324	10.467952	0.1456	0.1450
H4	0.345928	5.401308	9.762023	0.1471	0.1466
H5	-1.161781	4.423156	8.354604	0.1448	0.1442

H8	-1.989780	2.624417	7.170286	0.1482	0.1461
H6A	-1.696712	-3.876936	6.596441	0.1751	0.1678
H6B	-1.940149	-4.988478	5.800606	0.1643	0.1566
H11	-4.911811	0.377394	5.062488	0.1820	0.1736
H12	-6.247830	-2.469180	2.785978	0.1644	0.1643
H13	-4.152877	-3.385629	2.707172	0.1541	0.1512
H15A	1.281551	-0.871034	0.462850	0.1498	0.1473
H15B	1.944332	-0.334598	1.778142	0.3738	0.3715
H15C	0.610690	0.303378	1.255355	0.3749	0.3768
H1A	-4.870008	-7.081862	0.745887	0.1311	0.1323
H1B	-5.020669	-5.684968	0.051058	0.1583	0.1569
H1C	-3.924363	-6.689845	-0.441761	0.1313	0.1327
H3	-2.837173	-8.278610	0.631562	0.1450	0.1410
H4	-0.957971	-9.466595	1.337491	0.1467	0.1447
H5	0.549739	-8.488443	2.744910	0.1446	0.1417
H8	1.377738	-6.689703	3.929228	0.1462	0.1399
H11	4.299769	-4.442681	6.037026	0.1755	0.1751
H12	5.635787	-1.596106	8.313536	0.1648	0.1642
H13	3.540835	-0.679658	8.392343	0.1852	0.1862
H15A	-1.893594	-3.194253	10.636664	0.1659	0.1668
H15B	-2.556374	-3.730688	9.321372	0.1558	0.1556
H15C	-1.222733	-4.368665	9.844159	0.1522	0.1521
H6A	1.084670	-0.188350	4.503073	0.3667	0.3700
H6B	1.328107	0.923191	5.298908	0.3615	0.3643

Table S8. Ab initio calculated LoProp atomic charges in DyMn (compound 2). Atomic labels are those form the crystallographic CIF file. Atoms from the first coordination sphere are highlighted yellow.

	Atomic coordinates			**LoProp Charges**	
	x	**y**	**z**	**Basis 1**	**Basis 2**
Dy1	1.171877	8.089970	8.419985	2.5058	2.5361
Mn1	1.506943	4.686510	6.937241	1.5704	1.5618
O1	1.006272	12.533406	9.807933	-0.3886	-0.4043
O2	1.225221	9.931139	9.567460	-0.8350	-0.8586
O3	1.756525	5.892058	8.747738	-0.8571	-0.8794
O4	1.601351	9.511942	6.501820	-0.4745	-0.5015
O5	1.211595	6.917776	6.400489	-0.9082	-0.9290
O6	1.004775	2.531388	6.268910	-0.7422	-0.7422
O7	-0.985836	6.970429	8.846044	-0.7597	-0.7828
O8	-0.995092	8.807203	7.664858	-0.7247	-0.7539
O9	-0.632019	4.601050	7.599824	-0.6956	-0.6959
O10	3.448997	4.651678	6.184215	-0.5902	-0.5884
O11	3.548529	8.266499	8.324265	-0.7234	-0.7344

N23	0.085576	0.931551	3.241079	-0.1687	-0.1694
N25	0.141742	-1.328472	4.865400	-0.2224	-0.2225
N1	1.586653	7.464555	10.757722	-0.3562	-0.3853
N2	1.789891	6.091531	11.069277	-0.3337	-0.3457
N3	2.443565	1.929930	11.249252	-0.2002	-0.1981
N4	2.051044	3.307005	8.853606	-0.2456	-0.2616
N5	0.896773	4.623326	4.665763	-0.2556	-0.2600
N6	0.652671	3.341432	4.198430	-0.4001	-0.4007
C1	1.002914	13.948958	9.847255	-0.1730	-0.1838
C2	1.197569	11.844868	10.961896	0.1620	0.1818
C3	1.266312	12.383548	12.212653	-0.2015	-0.2033
C4	1.445107	11.545152	13.357542	-0.1838	-0.1876
C5	1.591620	10.236931	13.207814	-0.1359	-0.1361
C6	1.526049	9.639524	11.895048	-0.1388	-0.1455
C7	1.305420	10.417166	10.756209	0.3180	0.3461
C8	1.681295	8.217896	11.855726	0.0884	0.1100
C9	1.858519	5.402993	9.956148	0.3670	0.4047
C10	2.064443	3.942889	10.034793	0.0660	0.0944
C11	2.270182	3.256377	11.209930	-0.0371	-0.0508
C12	2.410499	1.298096	10.083190	-0.0560	-0.0620
C13	2.239503	1.986633	8.879317	-0.0177	-0.0132
C14	1.827391	10.917368	6.563828	-0.1664	-0.1404
C15	1.438827	8.940861	5.208715	0.1568	0.1744
C16	1.500737	9.712428	4.062314	-0.1742	-0.1748
C17	1.344483	9.076543	2.859954	-0.1699	-0.1714
C18	1.099560	7.725795	2.796433	-0.1418	-0.1411
C19	1.063698	6.950178	3.976107	-0.0563	-0.0474
C20	1.232119	7.592137	5.202666	0.2422	0.2601
C21	0.843369	5.558927	3.768908	0.0106	0.0062
C22	0.718801	2.347102	5.075624	0.3818	0.3825
C24	-0.182261	-0.293641	2.741986	-0.0703	-0.0705
C26	0.422566	-0.117456	5.320633	-0.0408	-0.0407
C27	-1.608125	7.814899	8.117066	0.6089	0.6600
C28	-2.992498	7.656941	7.793412	-0.4547	-0.4566
C29	4.688015	4.842038	6.910169	-0.1600	-0.1589
C1A	0.404204	0.988254	4.543258	0.0468	0.0472
C1B	-0.126356	-1.409477	3.551122	-0.0564	-0.0569
H1A	1.075199	14.293226	8.954937	0.1565	0.1623
H1B	1.746862	14.256774	10.370546	0.1285	0.1355
H1C	0.184143	14.256774	10.243505	0.1362	0.1428
H3	1.196787	13.304973	12.321546	0.1432	0.1418
H4	1.458095	11.917772	14.209025	0.1441	0.1441
H5	1.737201	9.698252	13.951916	0.1429	0.1424
H8	1.861881	7.782498	12.658812	0.1484	0.1426

H11	2.292388	3.732278	12.006966	0.1754	0.1733
H12	2.502415	0.372620	10.066553	0.1639	0.1623
H13	2.258236	1.514782	8.079256	0.1777	0.1772
H14A	2.552081	11.152281	5.977016	0.1270	0.1225
H14B	2.052498	11.166457	7.463708	0.1775	0.1701
H14C	1.032578	11.383143	6.291596	0.1502	0.1443
H16	1.643780	10.629802	4.106174	0.1493	0.1481
H17	1.406580	9.568645	2.071992	0.1461	0.1461
H18	0.956069	7.320773	1.970661	0.1472	0.1464
H21	0.640616	5.293638	2.900789	0.1394	0.1453
H24	-0.405054	-0.386796	1.843619	0.1607	0.1605
H26	0.643978	-0.022276	6.219001	0.1679	0.1680
H28A	-3.075160	7.268120	6.920755	0.1621	0.1621
H28B	-3.423230	8.515588	7.802486	0.1658	0.1640
H28C	-3.409234	7.083835	8.440720	0.1570	0.1546
H29A	5.403562	4.402589	6.442836	0.1451	0.1454
H29B	4.604124	4.465368	7.790387	0.1587	0.1594
H29C	4.878676	5.779664	6.979739	0.1467	0.1459
H1BA	-0.281789	-2.245847	3.176046	0.1600	0.1598
H9A	-1.132761	4.434991	6.931342	0.3495	0.3505
H9B	-0.850631	5.352366	7.937090	0.3571	0.3598
H10	3.635739	4.414740	5.385667	0.3557	0.3566
H11A	4.092188	7.940456	8.894441	0.3766	0.3788
H11B	3.986276	8.669496	7.713255	0.3753	0.3768

Table S9. Angles between the main magnetic axes of the lowest Kramers doublet obtained in different computational approximations (degrees).

	Compound Dy2		**Compound DyMn**	
	Basis 1	**Basis 2**	**Basis 1**	**Basis 2**
Basis 1	0.000	0.786	0.000	0.310
Basis 2	0.786	0.786	0.310	0.000

Table S10. Angles between the main magnetic axes of the lowest and first excited Kramers doublet obtained in different computational approximations (degrees).

Compound Dy2		**Compound DyMn**	
Basis 1	**Basis 2**	**Basis 1**	**Basis 2**
19.849	20.423	8.805	8.658

Table S11. Exchange interactions between Dy^{III} ions in the compounds Dy_2 and DyMn.

Lines parameters (cm^{-1})				
	Compound Dy2		Compound DyMn	
	Basis 1	**Basis 2**	**Basis 1**	**Basis 2**
J_{exch}	-0.039	-0.023	0.136	0.330
$J_{dipolar}$	0.206	0.208	0.111	0.124
$J_{total} = J_{exch} + J_{dipolar}$	0.167	0.185	0.247	0.454

Table S12. Exchange interactions between magnetic sites ions in the compounds Dy_2 and DyMn obtained within BS-DFT calculations. These parameters are to be compared with the Lines parameters in Table S8.

basis set employed	Compound Dy2	Compound DyMn
SVP	-0.06	0.49
def2-TZVP	-0.06	0.54
def2-TZVPP	-0.06	0.54