CrystEngComm/RSC
Supporting information

Mononuclear complexes of dysprosium with 2,6-diacetylpyridine bis(isonicotinoylhydrazone): synthesis, crystal structure, magnetic properties

V.A. Kopotkov,[a*] L.V. Zorina,[b*] S.V. Simonov,[b] D.V. Korchagin,[a] M.V. Zhidkov,[a] A.I. Dmitriev,[a] G. Mahmoudi,[c,d,e] E.B. Yagubskii[a*]

[a]*Federal Research Centre of Problems of Chemical Physics and Medicinal Chemistry, FRC PCP MC RAS, 1 ac. Semenov av., 142432 Chernogolovka, Russian Federation.*
[b]*Osipyan Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russian Federation*
[c]*Department of Chemistry, Faculty of Science, University of Maragheh, P.O. Box 55136-83111, Maragheh, Iran*
[d]*Chemistry Department, Faculty of Engineering and Natural Sciences, Istinye University, Sarıyer, Istanbul 34396, Turkey*
[e]*Department of Technical Sciences, Western Caspian University, Baku 1001, Azerbaijan*

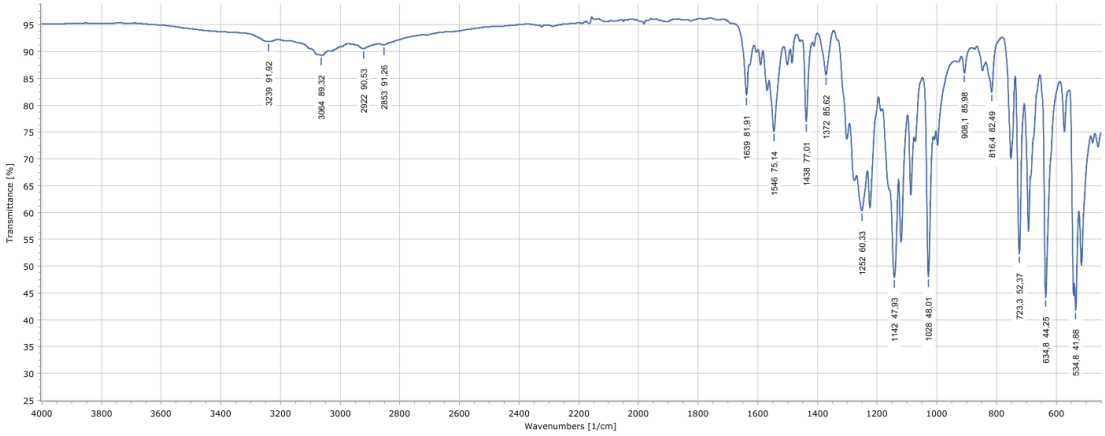


Figure S1. IR spectrum of complex **1**.

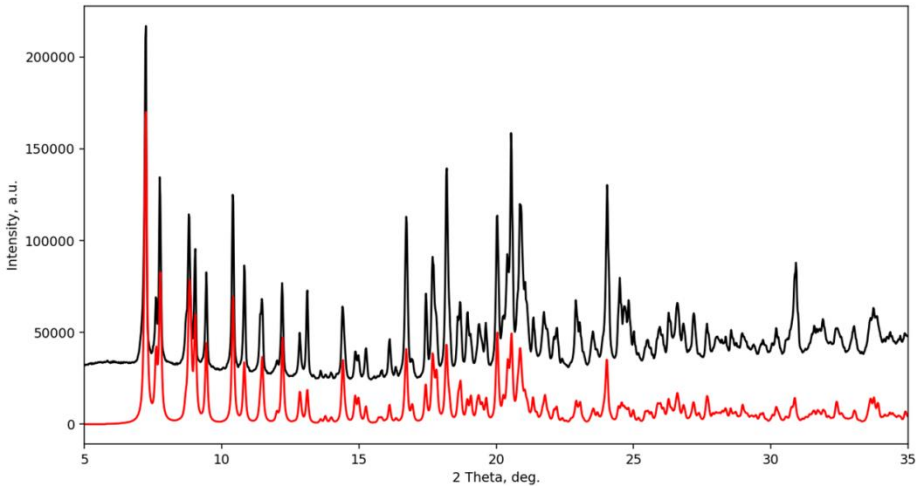


Figure S2. Powder X-ray diffraction pattern of polycrystalline samples of **1**: experimental (black), and calculated from single crystal data (red).

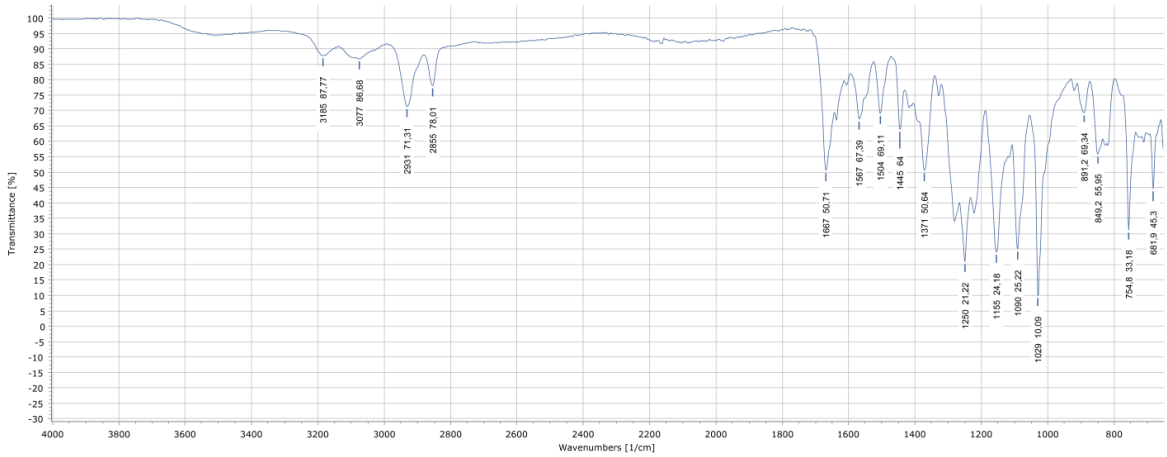


Figure S3. IR spectrum of complex **3**.

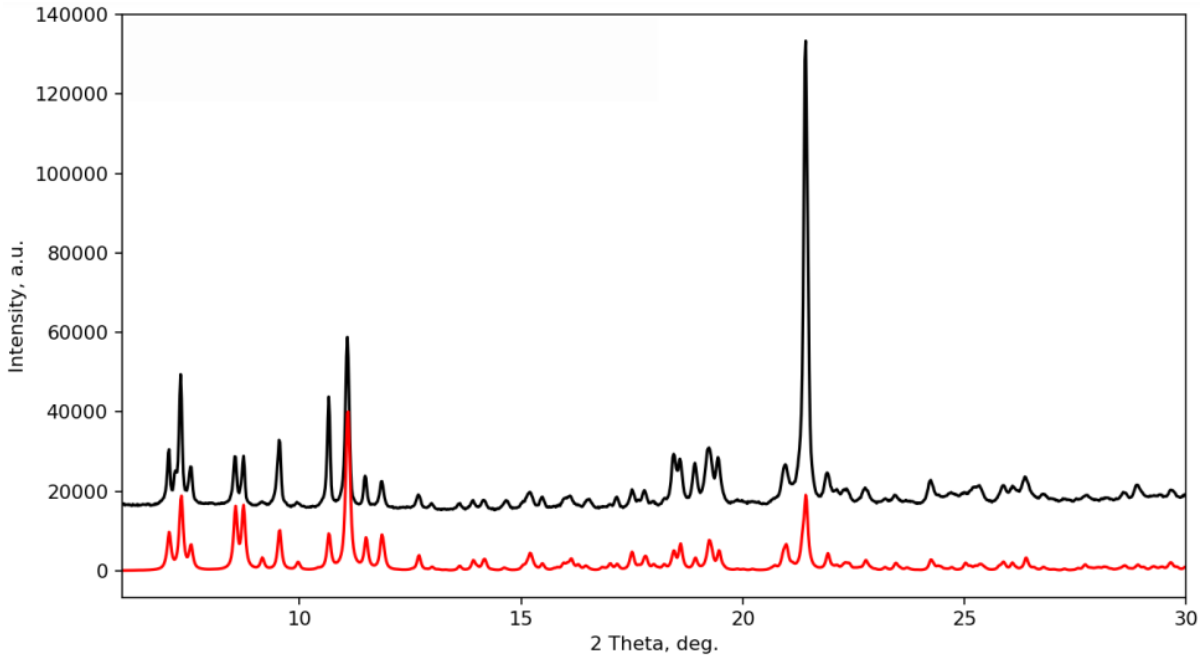


Figure S4. Powder X-ray diffraction pattern of polycrystalline samples of **3**: experimental (black), and calculated from single crystal data (red).

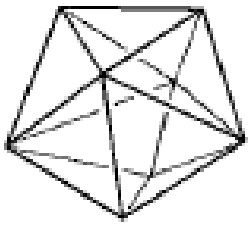
Table S1. SHAPE* analysis of the Dy-complexes with 8-vertex polyhedra in **1** and **2**.

Complex	Polyhedra [ML8]						
	OP-8	HPY-8	HBPY-8	CU-8	SAPR-8	**TDD-8**	
1	34.080	21.194	5.809	6.357	5.862	**5.680**	
2, cation I	32.038	21.807	8.786	8.962	4.767	**4.007**	
2, cation II	33.612	21.481	8.322	8.694	5.103	4.615	
	JGBF-8	JETBPY-8	JBTPR-8	**BTPR-8**	JSD-8	TT-8	ETBPY-8
1	6.989	22.123	6.140	5.904	6.859	7.196	19.485
2, cation I	7.602	23.606	4.641	4.353	4.771	9.816	20.428
2, cation II	7.228	23.405	4.699	**4.292**	5.477	9.512	20.120

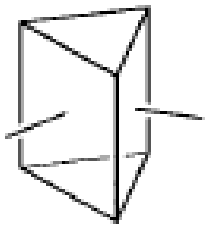
OP-8 - Octagon (D_{8h}); HPY-8 - Heptagonal pyramid (C_{7v}); HBPY-8 - Hexagonal bipyramid (D_{6h}); CU-8 - Cube (O_h); SAPR-8 - Square antiprism (D_{4d}); **TDD-8 - Triangular dodecahedron (D_{2d})**; JGBF-8 - Johnson gyrobifastigium J26 (D_{2d}); JETBPY-8 - Johnson elongated triangular

bipyramid J14 (D_{3h}); JBTPR-8 - Biaugmented trigonal prism J50 (C_{2v}); **BTPR-8 - Biaugmented trigonal prism (C_{2v})**; JSD-8 - Snub disphenoid J84 (D_{2d}); TT-8 - Triakis tetrahedron (T_d); ETBPY-8 - Elongated trigonal bipyramid (D_{3h})

***** [M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, 'SHAPE: Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools', Version 2.1, 2013, Barcelona]



Triangular dodecahedron (D_{2d})



Biaugmented trigonal prism (C_{2v})

Table S2. The N-C and O-C bond lengths (Å) in five-membered $DyN_2(H)CO$ heterocycles of the pentadentate ligands in complexes **1-4**.

Complex (ligand)	Bond	Bond length in 3 types of 5-membered heterocycle of the ligand		
		(a) N-N(H)-C(Py)=O^0	(b) N-N=C(PyH^+)-O^-	(c) N-N=C(Py)-O^-
1 $(H_2dapin)^0$	N(1)-C	1.350(4)		
	O(1)=C	1.232(3)		
	N(5)=C		1.313(4)	
	O(2)-C		1.278(3)	
2, Cation I $(Hdapin)^-$	N(1)=C		1.323(4)	
	O(1)-C		1.265(4)	
	N(5)=C			1.321(4)
	O(2)-C			1.276(4)
2, Cation II $(Hdapin)^-$	N(8)=C		1.320(4)	
	O(6)-C		1.277(4)	
	N(12)=C			1.317(4)
	O(7)-C			1.266(4)
3, Cation I $(Hdapin)^-$	N(1)=C		1.323(8)	
	O(1)-C		1.273(7)	
	N(5)=C			1.312(8)
	O(2)-C			1.267(7)
3, Cation II $(Hdapin)^-$	N(8)=C			1.310(9)
	O(5)-C			1.291(8)
	N(12)=C		1.315(8)	
	O(6)-C		1.288(8)	
4, Cation I $(dapin)^{2-}$	N(1)=C			1.322(5)
	O(1)-C			1.279(5)
	N(5)=C			1.312(5)
	O(2)-C			1.293(5)
4, Cation II $(Hdapin)^-$	N(8)=C			1.320(6)
	O(5)-C			1.274(6)
	N(12)=C		1.326(6)	
	O(6)-C		1.283(6)	

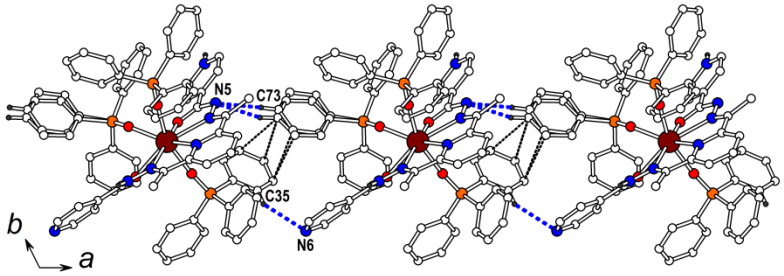


Figure S5. The chains of the cation complexes in the structure **1**. C-H...N hydrogen bonds (blue dashed lines) and C...C contacts < 3.6 A (black dotted lines) are shown.

Table S3. Hydrogen bond geometry in complex **1**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, Å
N1	H1N	O14	x-1, y, z	0.82(3)	2.59(3)	3.019(4)	159.9
N7	H7N	O11	1-x, 2-y, -z	0.80(4)	2.02(4)	2.687(5)	140.5
N7	H7N	O9a	1-x, 2-y, -z	0.80(4)	2.10(4)	2.892(8)	167.6
C1	H1	O14	x-1, y, z	0.95	2.30	3.239(4)	170.4
C3	H3	O9	-x, 1-y, -z	0.95	2.54	3.482(5)	170.7
C3	H3	O9a	-x, 1-y, -z	0.95	2.21	3.090(9)	154.1
C7	H7a	O7	x-1, y, z	0.98	2.52	3.308(4)	137.1
C7	H7a	O14	x-1, y, z	0.98	2.50	3.312(4)	140.2
C10	H10	O13	1-x, 1-y, 1-z	0.95	2.48	3.391(4)	160.0
C11	H11	O12	1-x, 1-y, 1-z	0.95	2.60	3.392(4)	140.6
C12	H12	F8a	x, y, z	0.95	2.58	3.30(3)	132.8
C15	H15c	O6	x, y+1, z	0.98	2.52	3.428(4)	153.4
C20	H20	O8	x, y+1, z	0.95	2.37	3.091(4)	132.8
C21	H21	O6	x, y+1, z	0.95	2.60	3.534(4)	166.1
C23	H23	O1	x-1, y, z	0.95	2.65	3.422(4)	138.4
C23	H23	F1	x+1, y, z	0.95	2.59	3.309(4)	132.9
C25	H25	O11a	x-1, y-1, z	0.95	2.15	2.945(10)	140.7
C25	H25	F6	x-1, y-1, z	0.95	2.61	3.231(6)	123.7
C35	H35	N6	x+1, y, z	0.95	2.61	3.394(4)	139.7
C38	H38	O10a	x, y, z	0.95	2.23	3.040(9)	143.1
C39	H39	O2	x, y, z	0.95	2.54	3.376(3)	146.9
C41	H41	F7	x-1, y, z	0.95	2.56	3.500(5)	172.6
C41	H41	F7a	x-1, y, z	0.95	2.55	3.402(17)	149.1
C43	H43	O7	1-x, 1-y, 1-z	0.95	2.58	3.505(4)	165.3
C47	H47	O5	x, y, z	0.95	2.50	3.437(3)	171.3
C53	H53	F9a	1-x, 2-y, 1-z	0.95	2.51	3.31(2)	143.0
C55	H55	O14	x, y+1, z	0.95	2.60	3.519(4)	164.2
C57	H57	N4	x, y, z	0.95	2.66	3.497(4)	147.8
C57	H57	N5	x, y, z	0.95	2.52	3.380(4)	149.9
C61	H61	F4	1-x, 2-y, -z	0.95	2.55	3.319(8)	138.2
C61	H61	F4a	1-x, 2-y, -z	0.95	2.56	3.195(17)	124.2
C65	H65	O2	x, y, z	0.95	2.46	3.322(4)	151.7
C73	H73	N5	x-1, y, z	0.95	2.49	3.442(6)	175.2
C73a	H73a	N5	x-1, y, z	0.95	2.46	3.382(14)	163.1

Table S4. Hydrogen bond geometry in complex **2**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, Å
N6	H6N	O36	1-x, 1-y, 1-z	0.88	1.84	2.698(5)	164.4
N13	H13N	N7	x, y, z	0.88	1.89	2.763(4)	174.9
C2	H2	O26a	1-x, 1-y, 1-z	0.95	2.60	3.433(16)	146.0
C2	H2	O33	1-x, 1-y, 1-z	0.95	2.43	3.308(6)	152.9
C11	H11	O13	x, y-1, z	0.95	2.48	3.187(5)	131.6
C15	H15a	O19	x, y, z	0.98	2.65	3.280(5)	122.0
C20	H20	O15	x, y, z	0.95	2.59	3.233(5)	125.1
C21	H21	O21	x, y, z	0.95	2.45	3.325(6)	152.5
C24	H24	O11	x, y, z	0.95	2.48	3.277(6)	141.1
C30	H30	O19	x, y, z	0.95	2.48	3.232(6)	136.4
C31	H31	O26a	x, y-1, z	0.95	2.54	3.444(17)	159.3
C32	H32	O24	x, y-1, z	0.95	2.65	3.380(6)	133.7
C38	H38	O13	1-x, 1-y, 1-z	0.95	2.54	3.383(6)	148.2
C39	H39	O1	x, y, z	0.95	2.29	3.235(4)	174.6
C43	H43	O12	x, y-1, z	0.95	2.52	3.251(5)	133.9
C47	H47	N5	x, y, z	0.95	2.53	3.461(5)	165.3
C57	H57	O5	x, y, z	0.95	2.63	3.566(4)	170.0
C63	H63	O2	x, y, z	0.95	2.42	3.301(5)	154.8
C68	H68	O24	1-x, 1-y, 1-z	0.95	2.55	3.434(6)	155.2
C68	H68	O23	1-x, 1-y, 1-z	0.95	2.65	3.338(6)	129.3
C91	H91	O16	x, y+1, z	0.95	2.59	3.324(5)	134.1
C104	H104	O20	x+1, y+1, z	0.95	2.56	3.355(5)	142.0
C105	H105	O22	x+1, y+1, z	0.95	2.60	3.483(6)	154.2
C107	H107	O26	x+1, y, z	0.95	2.61	3.318(6)	131.4
C112	H112	O17	x, y, z	0.95	2.56	3.505(6)	175.3
C112	H112	O18	x, y, z	0.95	2.64	3.346(5)	131.7
C118	H118	O16	2-x, 1-y, -z	0.95	2.63	3.462(6)	146.4
C119	H119	O7	x, y, z	0.95	2.33	3.268(4)	170.2
C122	H122	O16	x, y+1, z	0.95	2.63	3.249(5)	123.3
C123	H123	O15	x, y+1, z	0.95	2.61	3.329(5)	132.5
C127	H127	N8	x, y, z	0.95	2.53	3.450(5)	162.2
C129	H129	O33	x, y, z	0.95	2.36	3.112(6)	135.5
C137	H137	O10	x, y, z	0.95	2.59	3.532(4)	170.0
C145	H145	O6	x, y, z	0.95	2.64	3.439(5)	142.5
C146	H146	O17	x, y, z	0.95	2.58	3.210(6)	123.9
C154	H154	O20	1-x, 1-y, -z	0.95	2.35	3.259(6)	160.3
O26a	H26a	O31a	x, y, z	0.84	2.51	3.07(2)	125.2
C158	H15j	O31a	x, y, z	0.99	2.16	2.89(3)	129.3
O27	H27a	O21	x, y, z	0.84	1.94	2.752(6)	162.0

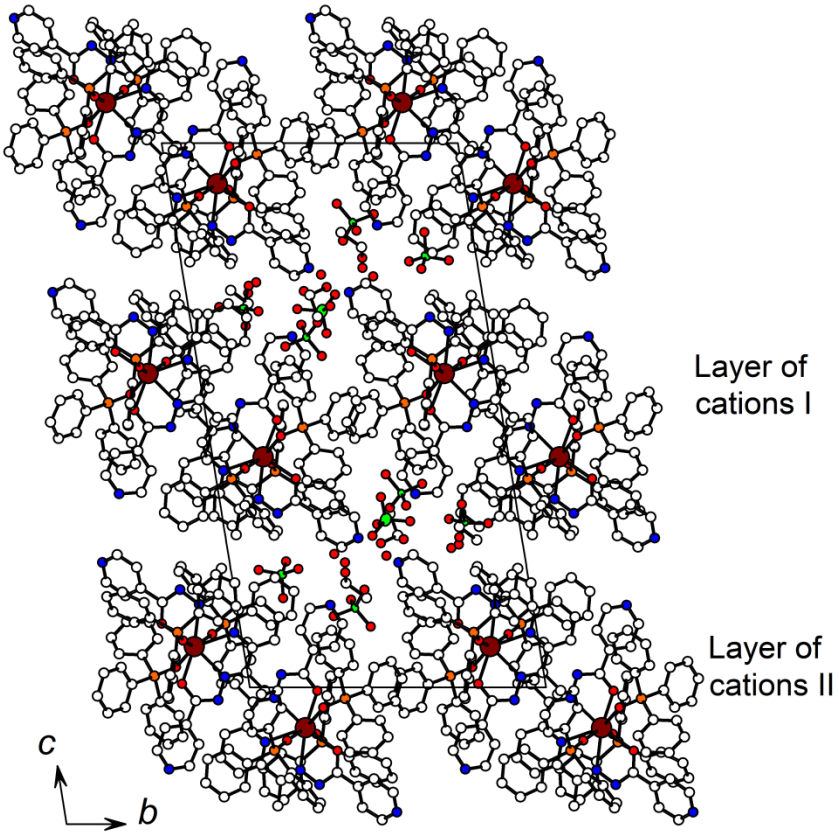


Figure S6. Projection of structure **2** along the *a*-axis. Hydrogen atoms are omitted for clarity. Layers of cations I and cations II alternate along *c*.

Table S5. SHAPE* analysis of the Dy-complexes with 7-vertex polyhedra in **3** and **4**.

Structure	HP-7	HPY-7	**PBPY-7**	COC-7	CTPR-7	JPBPY-7	JETPY-7
3, cation I	31.387	19.696	**1.545**	7.454	6.029	4.177	20.547
3, cation II	31.465	20.850	**1.287**	8.059	6.530	3.994	21.203
4, cation I	31.375	20.366	**1.455**	8.031	6.392	3.916	20.410
4, cation II	32.037	20.474	**1.615**	7.846	5.871	4.324	18.411

HP-7 - Heptagon (D_{7h}); HPY-7 - Hexagonal pyramid (C_{6v}); **PBPY-7 - Pentagonal bipyramid (D_{5h})**; COC-7 - Capped octahedron (C_{3v}); CTPR-7 - Capped trigonal prism (C_{2v}); JPBPY-7 - Johnson pentagonal bipyramid J13 (D_{5h}); JETPY-7 - Johnson elongated triangular pyramid J7 (C_{3v})

***** [M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, 'SHAPE: Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape Measures and Associated Tools', Version 2.1, 2013, Barcelona]

Table S6. Hydrogen bond geometry in complex **3**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, Å
N6	H6	N13	1-x, 1-y, -z	0.88	1.80	2.677(8)	174.5
N14	H14	N7	2-x, 1-y, 1-z	0.88	1.82	2.695(7)	171.2
C2	H2	O10	1-x, 1-y, -z	0.95	2.42	3.208(9)	139.8
C2	H2	O11	1-x, 1-y, -z	0.95	2.57	3.429(9)	151.0
C3	H3	O20	x, y, z	0.95	2.25	3.15(4)	158.6
C3	H3	O18a	x, y, z	0.95	2.47	3.19(2)	132.6
C3	H3	O19a	x, y, z	0.95	2.22	3.14(4)	163.7
C10	H10	O11	x-1, y-1, z	0.95	2.60	3.520(8)	163.5
C12	H12	O13	x-1, y-1, z	0.95	2.42	3.35 (1)	168.6
C15	H15a	O13	x-1, y-1, z	0.98	2.65	3.36 (1)	130.2
C19	H19	O17	x, y, z	0.95	2.31	3.21 (1)	158.0
C19	H19	O17a	x, y, z	0.95	2.20	3.01(2)	143.1
C20	H20	O12	2-x, 1-y, 1-z	0.95	2.47	3.31 (1)	147.3
C23	H23a	O2	x, y, z	0.99	2.54	3.53(1)	171.7
C31	H31b	F12	1-x, -y, -z	0.99	2.55	3.33(2)	135.7
C40	H40	O17a	x-1, y, z	1.00	2.27	3.23(2)	161.4
C47	H47a	O2	x, y, z	0.99	2.54	3.512(9)	166.4
C51	H51a	O15a	x-1, y, z	0.99	2.40	3.27(2)	145.3
C53	H53a	O1	x, y, z	0.99	2.64	3.62(2)	166.8
C52a	H52a	O16a	x-1, y, z	1.00	2.56	3.48(4)	153.7
C62	H62	O20	1-x, 1-y, -z	0.95	2.34	3.19(5)	148.4
C62	H62	O19a	1-x, 1-y, -z	0.95	2.35	3.23(5)	153.0
C63	H63	O10	x, y, z	0.95	2.23	3.12(1)	155.7
C67	H67a	F10a	x-1, y, z	0.98	2.60	3.37(1)	135.0
C70	H70	O18	x-1, y, z	0.95	2.56	3.48(1)	163.8
C70	H70	O19	x-1, y, z	0.95	2.45	3.08(1)	123.7
C70	H70	O20a	x-1, y, z	0.95	2.54	3.13(2)	120.5
C71	H71	O16	x, y, z	0.95	2.50	3.15(2)	125.7
C72	H72	O15	x-1, y, z	0.95	2.37	3.31(2)	174.2
C72	H72	O15a	x-1, y, z	0.95	2.48	3.41(2)	167.5
C79	H79	O12	x, y, z	0.95	2.20	3.13(1)	163.2
C80	H80	O17	2-x, 1-y, 1-z	0.95	2.30	3.21(2)	159.3
C80	H80	O17a	2-x, 1-y, 1-z	0.95	2.38	3.21(2)	145.7
C83	H83a	O6	x, y, z	0.99	2.59	3.56(1)	166.1
C94	H94	O19	x, y, z	1.00	2.25	3.22(2)	162.9
C97	H97b	F7a	x+1, y, z	0.99	2.23	3.13(2)	150.5
C100	H100	O12	x, y, z	1.00	2.55	3.55(1)	176.2
C107	H10k	O6	x, y, z	0.99	2.61	3.58(1)	168.9
C113	H11e	O5	x, y, z	0.99	2.48	3.44(2)	161.4

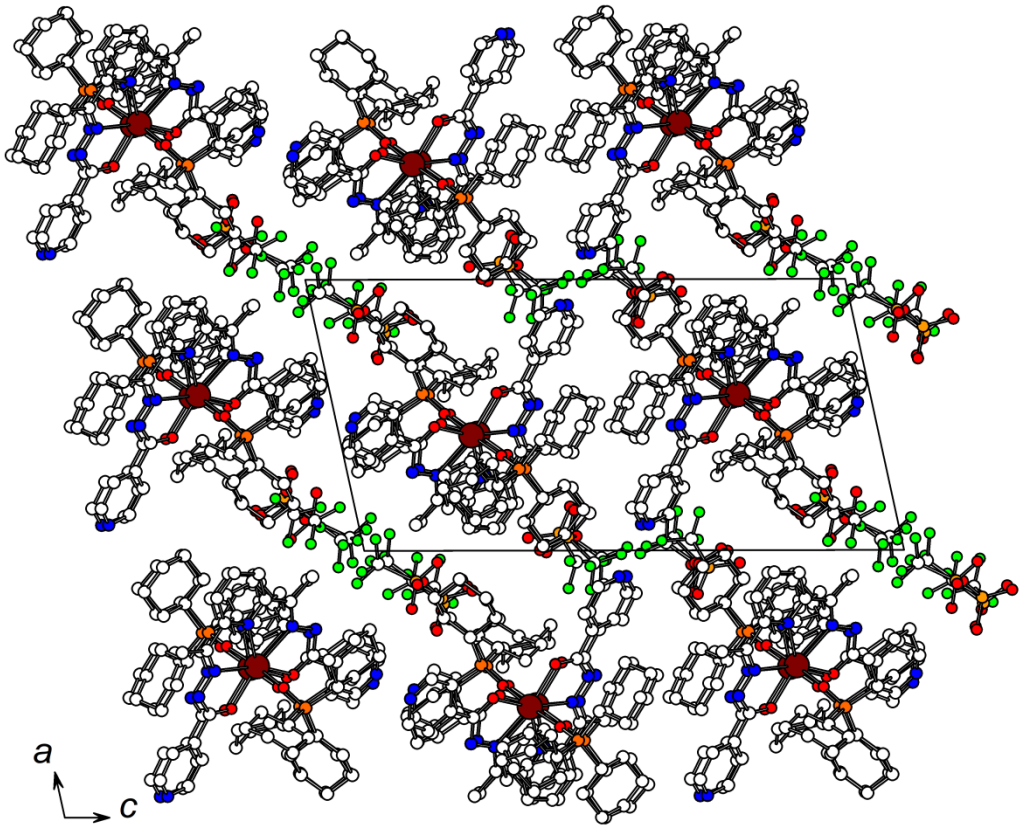


Figure S7. Projection of structure **3** along the *b*-axis. Hydrogen atoms are omitted for clarity. Cationic and anionic layers alternate along *a*.

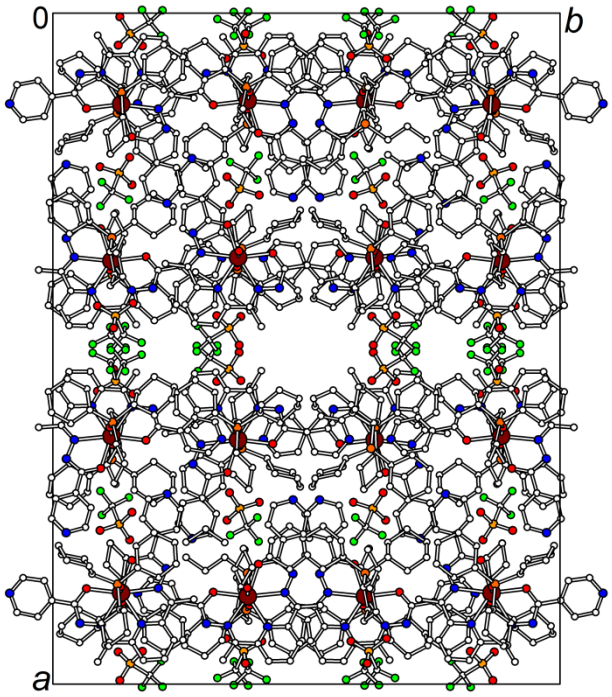


Figure S8. Projection of structure **4** along the *c*-axis. Hydrogen atoms are omitted for clarity. An open channel along *c* is visible in the center of the drawn lattice.

Table S7. Hydrogen bond geometry in complex **4**.

D	H	A	Symmetry code for A	D-H, Å	H…A, Å	D…A, Å	D-H…A, Å
N14	H14N	N6	x, y, z	0.88	1.88	2.738(5)	164.3
C2	H2	O13	1-x, 1-y, 1-z	0.95	2.52	3.175(6)	126.0
C4	H4	O15	1-x, 1-y, 1-z	0.95	2.53	3.469(6)	170.5
C10	H10b	O13	1-x, 1-y, 1-z	0.98	2.34	3.258(6)	155.5
C13	H13	N13	0.5-x, y+0.5, 0.5-z	0.95	2.67	3.549(5)	153.9
C14	H14	O11	x, y, z	0.95	2.36	3.313(5)	176.5
C15	H15	O12	x, y, z	0.95	2.35	3.287(5)	167.0
C19	H19	O9	0.5-x, y+0.5, 0.5-z	0.95	2.52	3.379(5)	150.5
C43	H43	O14	x, 1-y, z-0.5	1.00	2.49	3.327(5)	141.3
C56	H56a	O14	x, 1-y, z-0.5	0.99	2.56	3.538(6)	169.0
C62	H62a	O1	x, y, z	0.99	2.64	3.610(5)	166.3
C66	H66b	F3	x, 1-y, z+0.5	0.99	2.60	3.490(5)	149.7
C23	H23	O16	x, y, z	0.95	2.43	3.374(5)	172.9
C25	H25	O17	1-x, -y, 1-z	0.95	2.42	3.359(5)	160.1
C31	H31b	O16	x, y, z	0.98	2.62	3.346(6)	130.7
C31	H31c	F7a	x, y, z	0.98	2.62	3.49(2)	147.8
C34	H34	N7	0.5-x, y-0.5, 0.5-z	0.95	2.52	3.389(5)	152.2
C35	H35	O9	x, y, z	0.95	2.17	3.099(5)	165.3
C36	H36	O12	x, y, z	0.95	2.43	3.200(5)	138.1
C36	H36	O14	x, y, z	0.95	2.51	3.168(5)	126.2
C37	H37	O14	x, y, z	0.95	2.64	3.227(5)	120.2
C39	H39	F1	0.5-x, y-0.5, 0.5-z	0.95	2.61	3.351(5)	135.6
C40	H40	O11	0.5-x, y-0.5, 0.5-z	0.95	2.30	3.239(5)	170.0
C80	H80b	O5	x, y, z	0.99	2.62	3.566(4)	160.8
C91	H91	O16	1-x, y, 0.5-z	1.00	2.61	3.596(5)	168.0
C96	H96a	N11	x, y, z	0.99	2.64	3.455(5)	140.0
C98	H98a	N9	x, y, z	0.99	2.67	3.593(5)	155.2
C114	H11l	F1	0.5-x, 0.5-y, 1-z	0.99	2.47	3.274(5)	138.0

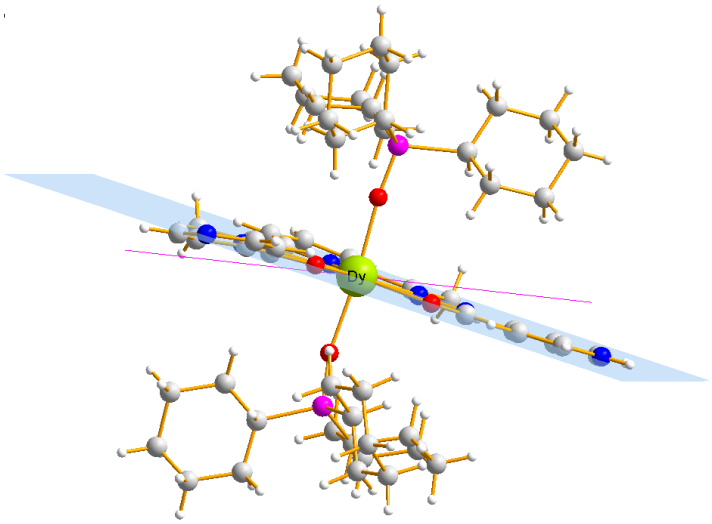


Figure S9. The main magnetic axis of ground KD of **3** orientation (magenta) obtained within the *ab initio* SA-CASSCF/RASSI-SO/SINGLE_ANISO calculation. Color code: green = Dy, magenta = P, red = O, blue = N, gray = C, white = H.

Table S8. The computed energy levels (cm^{-1}) with the associated g-tensors of the eight lowest KDs for **1** and **3**.

Complex	**1**				**3**			
KD	*Energy*	g_x	g_y	g_z	*Energy*	g_x	g_y	g_z
1	0.0	0.305	0.822	19.144	0.0	0.024	0.042	19.907
2	105.4	2.447	4.127	12.487	307.2	11.776	6.981	1.569
3	134.3	2.210	3.545	15.006	351.3	10.020	7.390	0.912
4	177.9	0.040	3.432	12.869	424.1	11.046	7.218	2.629
5	211.8	0.988	2.694	10.088	486.2	9.950	7.775	1.440
6	327.7	0.094	4.322	11.657	556.9	8.027	6.505	2.691
7	372.4	0.538	3.026	14.519	625.2	2.067	3.995	12.309
8	395.9	0.332	1.339	17.388	804.4	0.122	0.229	18.532

Table S9. SINGLE_ANISO computed wave function decomposition analysis for lowest KDs of Dy(III) ion in **1** and **3**.

	wave function decomposition analysis (main (> 10%) contributio ns)	
KD	**1**	**3**
1	0.918 |±15/2›	0.996 |±15/2›
2	0.265 |±13/2› + 0.281 |±1/2› + 0.109 |±5/2› + 0.101 |±3/2›	0.430 |±13/2› + 0.387 |±1/2› + 0.124 |±3/2›
3	0.322 |±3/2› + 0.222 |±5/2› + 0.127 |±1/2› + 0.105 |±9/2› + 0.103 |±7/2›	0.462 |±13/2› + 0.185 |±5/2› + 0.140 |±3/2› + 0.117 |±1/2›
4	0.312 |±1/2› + 0.173 |±13/2› + 0.157 |±5/2› + 0.129 |±7/2› + 0.109 |±3/2›	0.435 |±3/2› + 0.185 |±1/2› + 0.167 |±11/2› + 0.113 |±9/2›
5	0.289 |±13/2› + 0.214 |±3/2› + 0.141 |±11/2› + 0.109 |±5/2› + 0.106 |±7/2›	0.358 |±5/2› + 0.215 |±7/2› + 0.133 |±1/2›
6	0.500 |±11/2› + 0.201 |±9/2› + 0.122 |±13/2›	0.564 |±11/2› + 0.182 |±5/2› + 0.143 |±7/2›
7	0.373 |±9/2› + 0.193 |±7/2› + 0.141 |±11/2› + 0.113 |±5/2›	0.556 |±9/2› + 0.284 |±7/2› + 0.123 |±11/2›
8	0.328 |±9/2› + 0.268 |±5/2› + 0.152 |±9/2› + 0.133 |±3/2›	0.238 |±7/2› + 0.200 |±9/2› + 0.205 |±5/2› + 0.159 |±3/2› + 0.120 |±1/2›

Figure S10. Computed possible magnetization relaxation pathways for **1** (a) and **3** (b). The red arrows show the QTM and TA-QTM via ground and higher excited KD, respectively. The blue arrow shows the Orbach process for the relaxation. The green arrows show the mechanism of magnetic relaxation.