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Supporting Information

Synthesis, structure, magnetic and magnetocaloric properties of a series of $\{Cr_4^{III}Ln^{III}\}$ complexes

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1. Selected bond lengths and angles

Table S1. Selected bond lengths (Å) and angles (°) for **1a**.

Bonds	**Length ranges (Å)**	**Bonds**	**Length ranges (Å)**
d(Cr···O)	1.923(2)-1.982(2)	**d(Cr···N)**	2.041(3)-2.079(3)
d(Dy···O)	2.348(2)-2.431(2)		
Interatomic distances (Å)		**Selected angles (°)**	
Cr···Cr	5.2198(7)-7.8419(8)	**Dy1–O7–Cr2**	133.57(10)
Cr···Dy	3.4399(5)-3.9809(7)	**Dy1–O17–Cr4**	132.35(11)
Selected angles (°)		**Dy1–O3–Cr1**	105.681(8)
Cr2···Dy1···Cr4	162.923(14)	**Dy1–O18–Cr1**	102.86(8)
Cr1···Dy1···Cr3	110.041(16)	**Dy1–O8–Cr3**	103.62(9)
		Dy1–O13–Cr3	105.40(9)

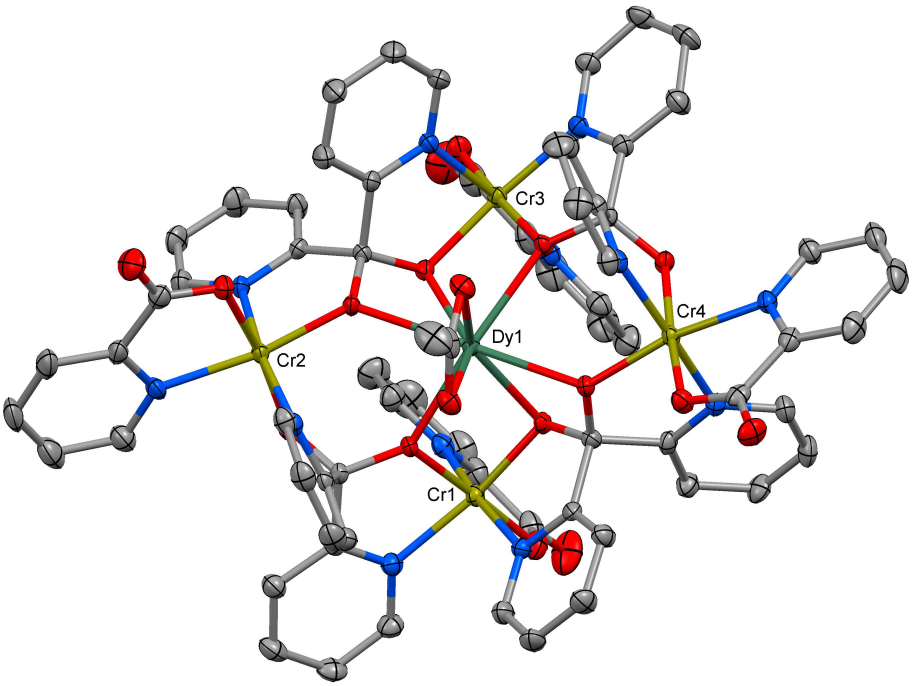

Figure S1. Ellipsoidal representation of **1a**, with a probability of the ellipsoids of 50%.

Table S2. Selected bond lengths (Å) and angles (°) for **1b**.

Bonds	**Length ranges (Å)**	**Bonds**	**Length ranges (Å)**
d(Cr···O)	1.911(2)-1.980(3)	**d(Cr···N)**	2.038(3)-2.080(3)
d(Dy···O)	2.348(2)-2.431(2)		
Interatomic distances (Å)		**Selected angles (°)**	
Cr···Cr	5.1764(7)-7.8872(9)	**Dy1–O7–Cr2**	132.2(1)
Cr···Dy	3.4479(6)-3.9837(8)	**Dy1–O17–Cr4**	132.5(1)
Selected angles (°)		**Dy1–O3–Cr1**	106.6(1)
Cr2···Dy1···Cr4	165.96(2)	**Dy1–O18–Cr1**	104.2(1)
Cr1···Dy1···Cr3	117.20(2)	**Dy1–O8–Cr3**	104.5(1)
		Dy1–O13–Cr3	105.4(1)

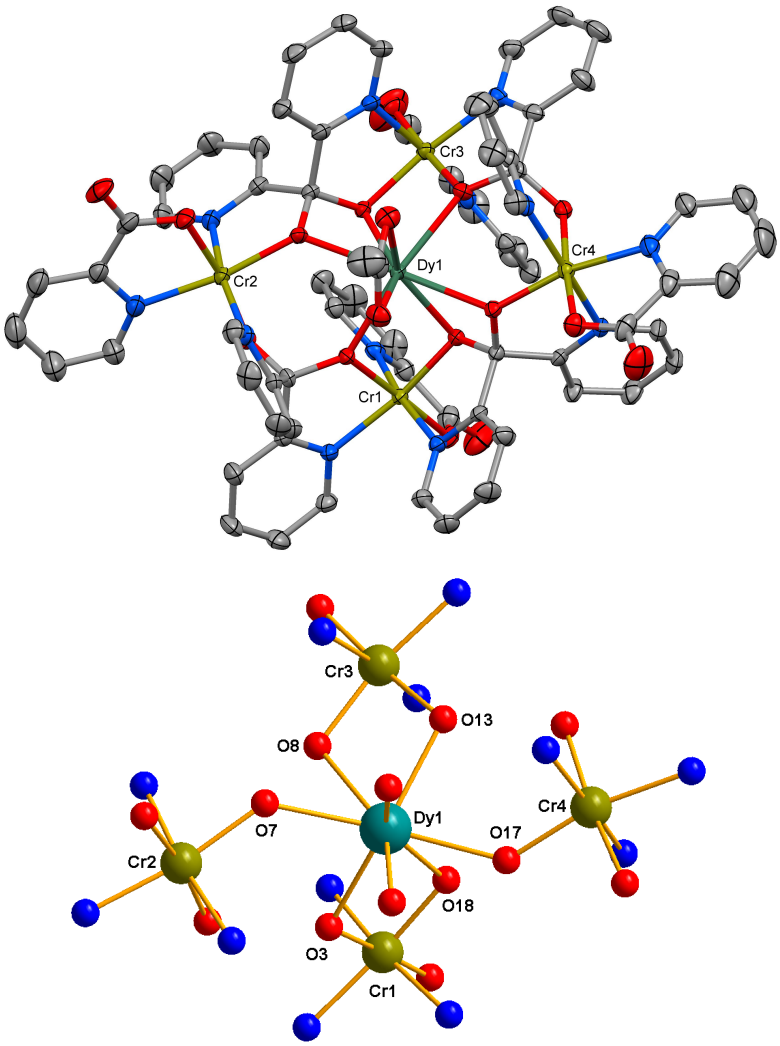

Figure S2. Top: Ellipsoidal representation of **1b**, with a probability of the ellipsoids of 50%. Bottom: Ball and stick representation with labelled atoms of the central metal core of complexes **1a** and **1b**.

Table S3. Selected bond lengths (Å) and angles (°) for **2**.

Bonds	**Length ranges (Å)**	**Bonds**	**Length ranges (Å)**
d(Cr···O)	1.916(5)-1.981(5)	**d(Cr···N)**	2.032(7)-2.086(7)
d(Tb···O)	2.358(5)- 2.426(4)		
Interatomic distances (Å)		**Selected angles (°)**	
Cr···Cr	5.1824(16)-7.8924(17)	**Tb1–O7–Cr2**	131.88(22)
Cr···Tb	3.4553(13)-3.8949(12)	**Tb1–O17–Cr4**	131.61(22)
Selected angles (°)		**Tb1–O3–Cr1**	106.98(20)
Cr2···Tb1···Cr4	166.187(27)	**Tb1–O18–Cr1**	104.02(19)
Cr1···Tb1···Cr3	106.992(29)	**Tb1–O8–Cr3**	104.11(19)
		Tb1–O13–Cr3	105.39(20)

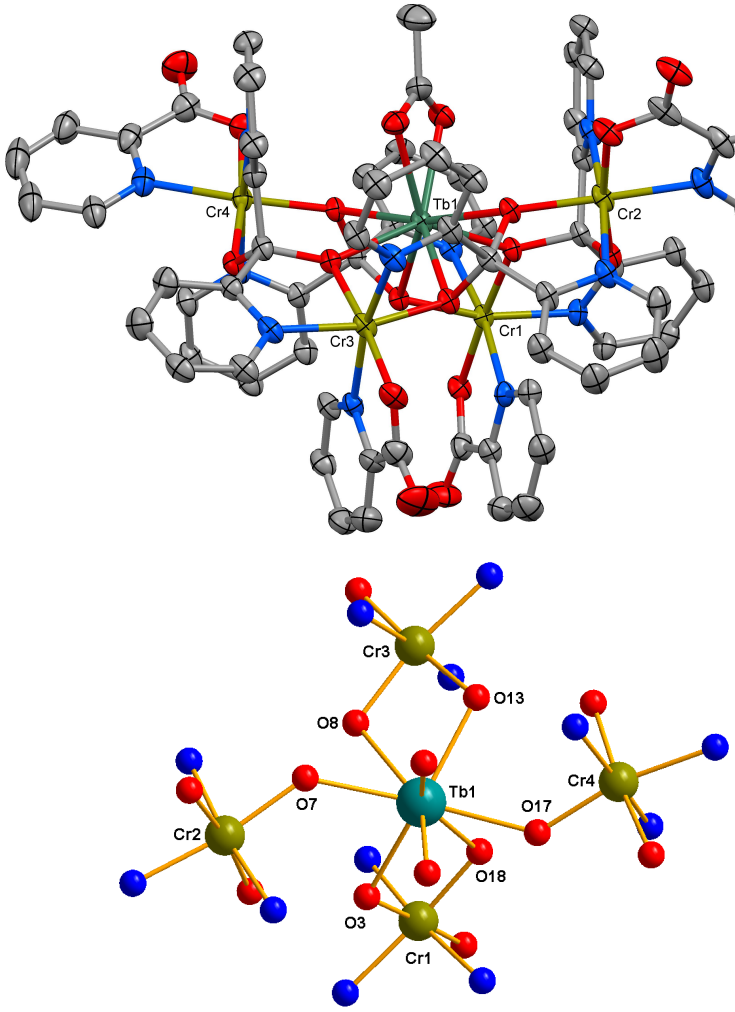

Figure S3. Top: Ellipsoidal representation of **2**, with a probability of the ellipsoids of 30%. Bottom: Ball and stick representation with labelled atoms of the central metal core of complexes **2**.

Table S4. Selected bond lengths (Å) and angles (°) for **3**.

Bonds	**Length ranges (Å)**	**Bonds**	**Length ranges (Å)**
d(Cr···O)	1.911(3)-1.979(3)	**d(Cr···N)**	2.044(3)-2.081(4)
d(Gd···O)	2.384(3)-2.449(3)		
Interatomic distances (Å)		**Selected angles (°)**	
Cr···Cr	5.1863(9)-7.9177(10)	**Gd1–O4–Cr1**	131.63(13)
Cr···Gd	3.4553(13)-3.8949(12)	**Gd1–O13–Cr4**	131.49(13)
Selected angles (°)		**Gd1–O11–Cr3**	105.68(12)
Cr1···Gd1···Cr4	167.254(19)	**Gd1–O12–Cr3**	103.98(11)
Cr2···Gd1···Cr3	106.971(19)	**Gd1–O5–Cr2**	103.86(11)
		Gd1–O8–Cr2	106.87(12)

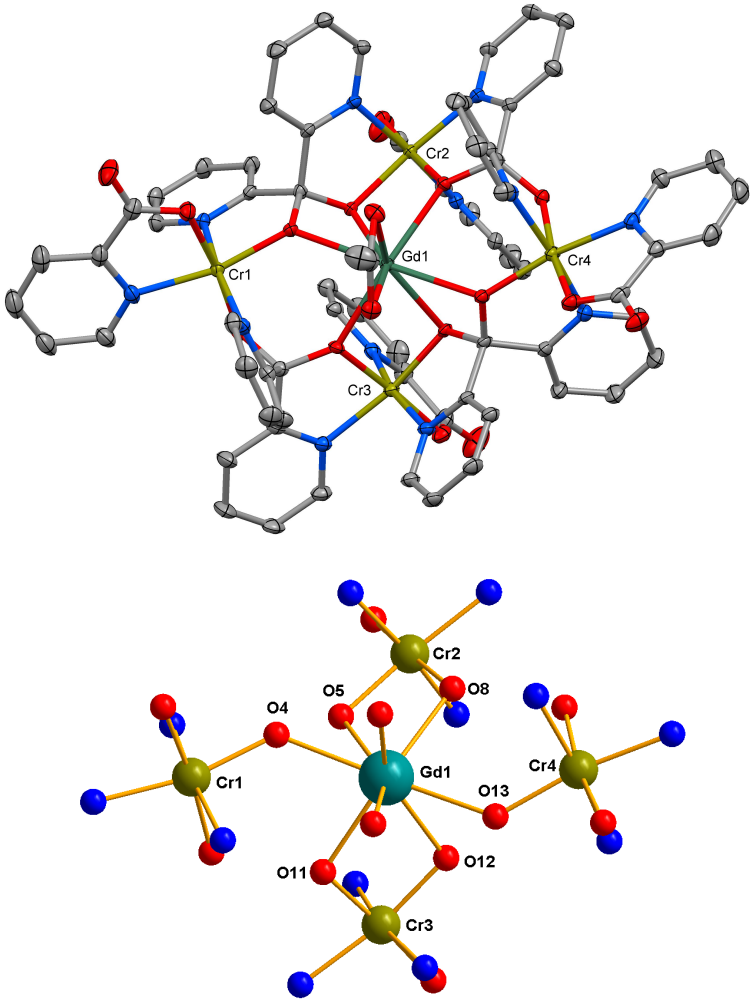

Figure S4. Top: Ellipsoidal representation of **3**, with a probability of the ellipsoids of 30%. Bottom: Ball and stick representation with labelled atoms of the central metal core of complexes **3**.

2. Crystal packing and crystal structure representation

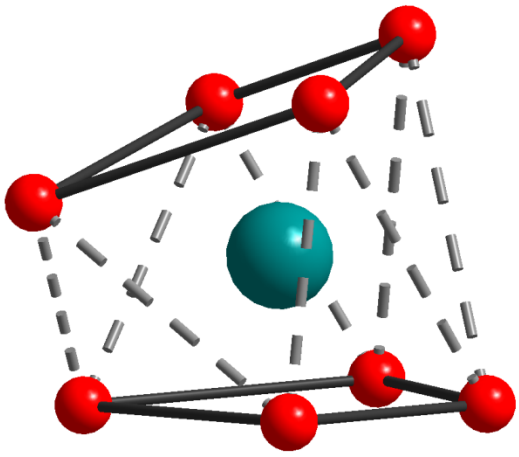

Figure S5. Representation of the highly distorted square anti-prism geometry around Dy1. Colour code: Dy: teal, O: Red.

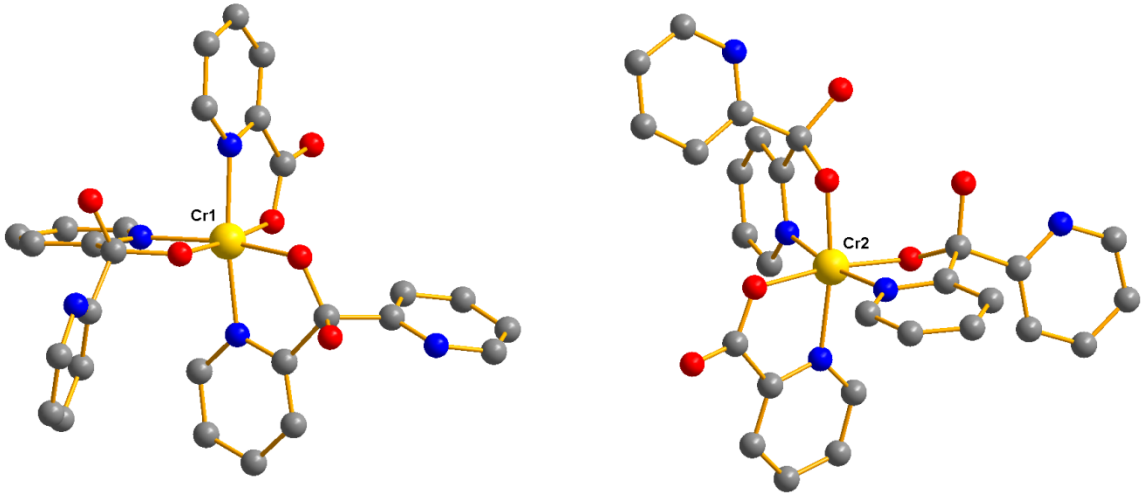

Figure S6. Ball and stick representations of the octahedral Cr1 (left) and Cr2 (right) closed environment, in complexes **1a**, **1b**, and **2**. Colour code: Cr: yellow, O: red, N: blue, C: grey.

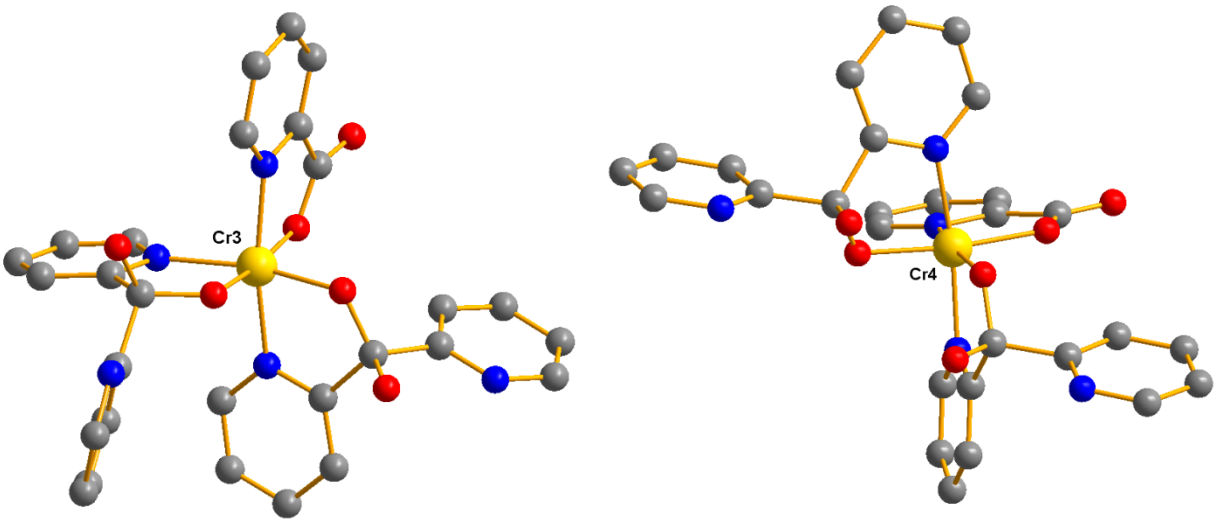

Figure S7. Ball and stick representations of the octahedral Cr2 (left) and Cr3 (right) closed environment, in complexes **1a**, **1b**, and **2**. Colour code: Cr: yellow, O: red, N: blue, C: grey.

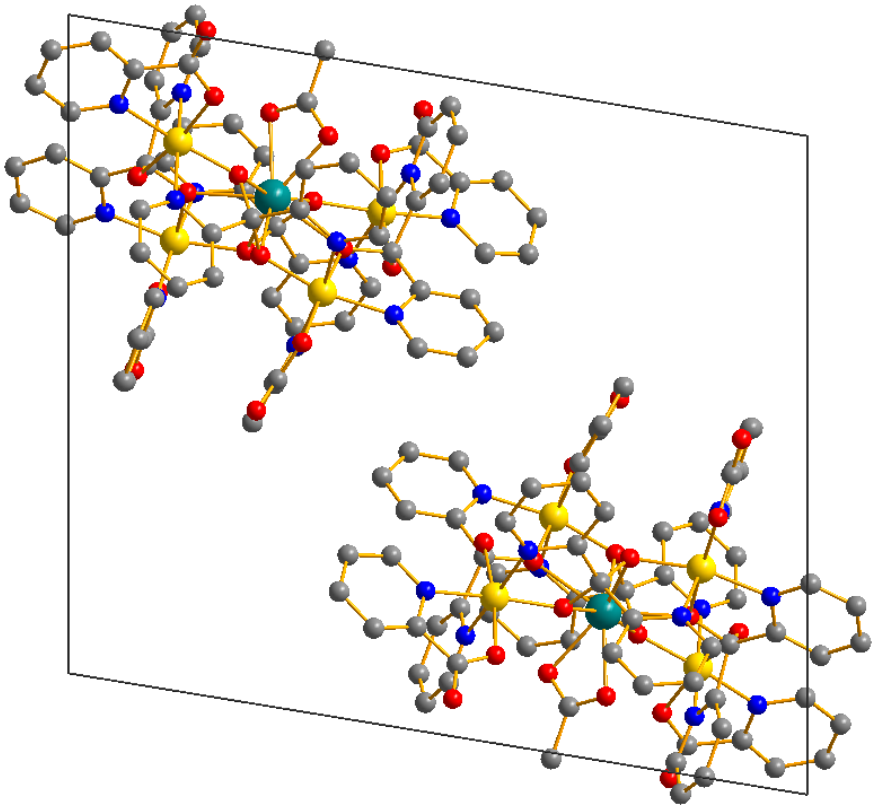

Figure S8. Ball and stick representation of the unit cell of complex **1a** (along a axis). Nitrate anions and water molecules are omitted for clarity, as well as the H atoms. C atoms are represented as sticks for clarity. Cr^{III}: yellow, Dy^{III}: teal, O: red, N: blue, C: grey.

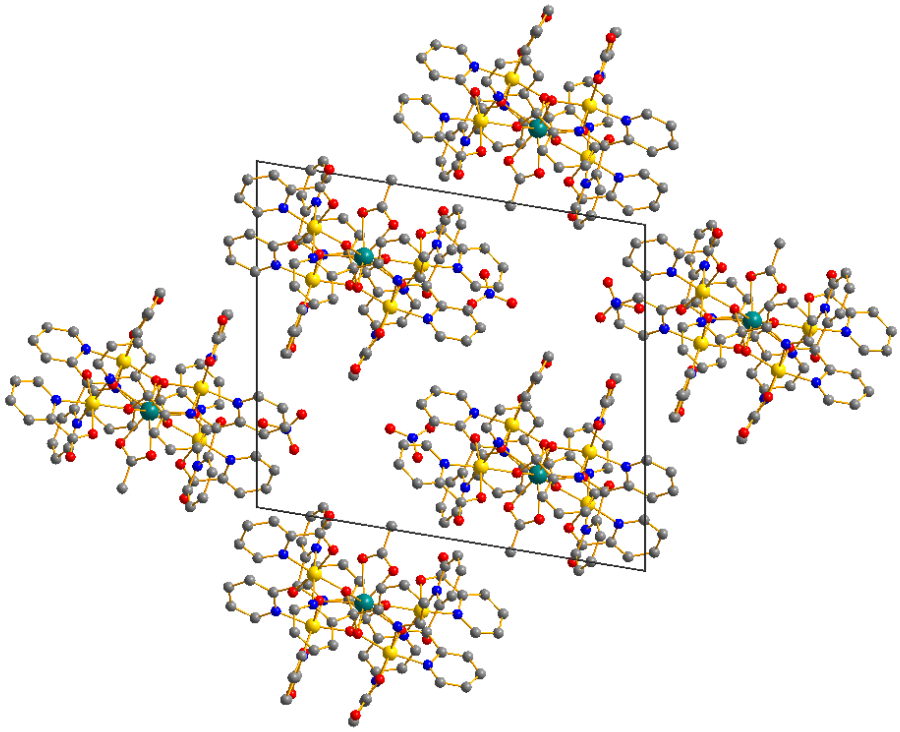

Figure S9. Ball and stick representation of an extended unit cell of complex **1a** (along a axis). Nitrate anions and water molecules are omitted for clarity, as well as the H atoms. C atoms are represented as sticks for clarity. Cr^{III}: yellow, Dy^{III}: teal, O: red, N: blue, C: grey.

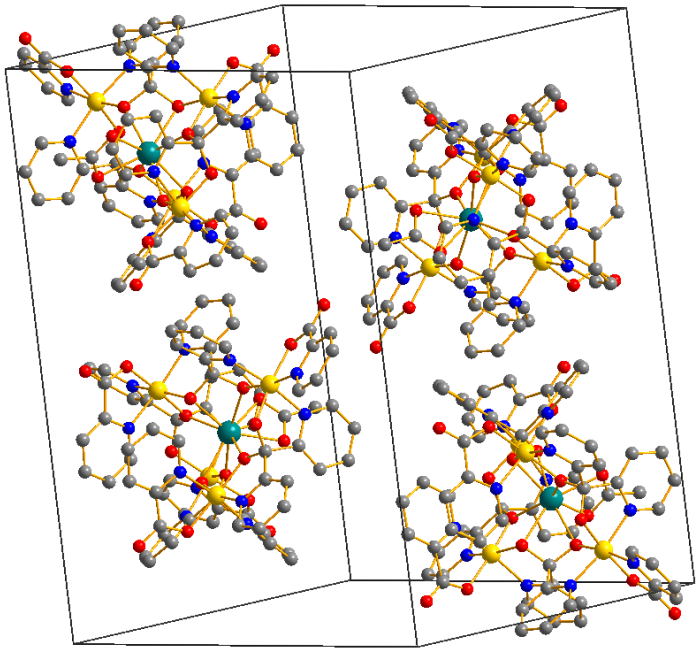

Figure S10. Ball and stick representation of the unit cell of complex **1b**. Nitrate anions and water molecules are omitted for clarity, as well as the H atoms. C atoms are represented as sticks for clarity. Cr^{III}: yellow, Dy^{III}: teal, O: red, N: blue, C: grey.

3. Coordination geometry of Dy(III) ion

Results of Continuous Shape measurements for LnCr4 complexes. Legend and corresponding symmetry: HPY: C7v Heptagonal pyramid; HBPY: D6h Hexagonal bipyramid; CU: Oh, Cube; SAPR: D4d Square antiprism; TDD: D2d, Triangular dodecahedron; JGBF: D2d, Johnson gyrobifastigium; JETBPY: D3h, Johnson elongated triangular bipyramid; JBTPR: C2v, Biaugmented trigonal prism J50; BTPR: C2v, Biaugmented trigonal prism; JSD: D2d, Snub diphenoid; TT: Td, Triakis tetrahedron; ETBPY: D3h, Elongated trigonal bipyramid

Table S5 (two parts). Results of Continuous Shape measurements for Dy(III) ions in complex **1a**.

HPY	HBPY	CU	SAPR	TDD	JGBF
19.595	12.811	6.340	4.092	3.921	15.579

JETBPY	JBTPR	BTPR	JSD	TT	ETBPY
23.226	6.321	5.726	8.109	7.189	20.569