Supporting Information

Synthesis and magneto-structural studies on a new family of carbonato bridged 3d-4f complexes featuring a [CoII3LnIII3(CO3)] (Ln = La, Gd, Tb, Dy and Ho) core: slow magnetic relaxation displayed by the cobalt(II)-dysprosium(III) analogue

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CONTENT:

Table S1 Selected Bond Distances (Å) and Angles (deg) for **1** – **5**

		Bond Distances (Å)			
Parameters	**1**	**2**	**3**	**4**	**5**
Ln1—O3	2.448(8)	2.334(10)	2.321(8)	2.290(9)	2.296(8)
Ln1—O1	2.473(8)	2.353(10)	2.336(8)	2.305(9)	2.320(8)
Ln1—O7^{i}	2.479(7)	2.358(9)	2.362(8)	2.347(8)	2.338(8)
Ln1—O7	2.465(7)	2.367(10)	2.358(8)	2.326(8)	2.322(8)
Ln1—O4	2.577(9)	2.465(11)	2.467(8)	2.446(10)	2.440(9)
Ln1—O9	2.575(10)	2.468(11)	2.476(8)	2.443(11)	2.437(9)
Ln1—O8	2.569(7)	2.470(9)	2.453(7)	2.442(9)	2.447(9)
Ln1—O8^{i}	2.648(7)	2.569(10)	2.558(8)	2.555(9)	2.55(1)
Ln1—O2	2.686(8)	2.64(1)	2.634(8)	2.63(1)	2.664(9)
Co1—O5	1.970(8)	1.943(9)	1.947(7)	1.926(10)	1.956(8)
Co1—O3^{ii}	1.991(8)	1.978(10)	1.962(8)	1.976(9)	1.978(8)
Co1—O1	1.992(8)	1.982(11)	1.985(8)	1.984(9)	1.990(8)
Co1—O7	2.157(9)	2.132(13)	2.131(9)	2.125(11)	2.127(10)
Co1—N1	2.135(10)	2.136(12)	2.12(1)	2.118(13)	2.121(10)
		Bond angles (deg)			
O3—Ln1—O1	135.0(3)	132.5(4)	132.8(3)	131.9(4)	131.4(3)
O3—Ln1—O7^{i}	71.7(3)	73.5(4)	73.4(3)	74.4(4)	74.0(3)
O1—Ln1—O7^{i}	150.7(3)	150.5(4)	150.4(3)	150.2(3)	151.0(3)
O3—Ln1—O7	153.6(3)	153.4(4)	152.9(3)	153.1(3)	153.2(3)
O1—Ln1—O7	69.1(3)	71.2(4)	71.5(3)	71.9(4)	72.3(3)
O7^{i}—Ln1—O7	82.5(4)	80.7(6)	80.4(4)	79.7(5)	80.2(5)
O3—Ln1—O4	62.4(3)	65.6(3)	66.2(3)	65.9(3)	66.7(3)
O1—Ln1—O4	85.7(3)	82.1(3)	81.9(3)	81.7(3)	80.7(3)
O7^{i}—Ln1—O4	122.6(3)	126.5(4)	126.7(3)	127.1(3)	127.3(3)
O7—Ln1—O4	141.4(3)	138.7(4)	138.4(3)	138.6(3)	138.0(3)
O3—Ln1—O9	89.8(3)	89.3(3)	89.3(3)	89.4(3)	89.1(3)
O1—Ln1—O9	94.2(3)	92.1(3)	92.1(3)	91.8(3)	91.8(3)
O7^{i}—Ln1—O9	70.8(3)	72.2(4)	72.3(3)	72.4(3)	72.7(3)
O7—Ln1—O9	75.9(3)	76.4(4)	76.3(3)	76.1(3)	76.1(3)
O4—Ln1—O9	136.9(3)	136.9(4)	137.3(3)	137.2(4)	137.3(3)
O3—Ln1—O8	123.6(3)	124.8(4)	124.5(3)	124.2(4)	125.7(3)
O1—Ln1—O8	77.6(3)	78.0(4)	78.1(3)	78.8(4)	77.8(3)
O7^{i}—Ln1—O8	97.6(3)	98.6(4)	98.5(3)	98.0(3)	98.9(4)
O7—Ln1—O8	64.8(3)	65.1(4)	65.4(3)	65.9(3)	65.1(3)
O4—Ln1—O8	81.9(3)	79.1(4)	78.4(3)	78.3(3)	78.4(3)
O9—Ln1—O8	140.2(3)	141.4(4)	141.7(3)	142.0(3)	141.2(3)
O3—Ln1—O8^{i}	77.0(3)	77.1(4)	76.9(3)	77.5(4)	76.8(3)
O1—Ln1—O8^{i}	126.0(3)	127.9(4)	127.8(3)	127.9(4)	128.9(3)
O7^{i}—Ln1—O8^{i}	63.4(3)	63.6(3)	63.8(3)	63.8(3)	63.2(3)
O7—Ln1—O8^{i}	97.2(3)	97.5(4)	97.5(3)	97.2(3)	98.1(3)
O4—Ln1—O8^{i}	73.9(3)	74.4(4)	74.1(3)	74.3(3)	74.4(3)
O9—Ln1—O8^{i}	134.2(3)	135.8(3)	136.0(3)	136.2(3)	135.8(3)

O8—Ln1—O8^{i}	50.7(4)	52.5(6)	52.3(4)	51.6(5)	53.9(5)
O3—Ln1—O2	78.9(2)	74.6(3)	74.2(3)	73.8(3)	73.3(3)
O1—Ln1—O2	60.7(3)	62.0(4)	62.8(3)	62.2(4)	62.2(3)
O7^{i}—Ln1—O2	130.7(3)	129.0(4)	128.3(3)	129.0(4)	128.6(3)
O7—Ln1—O2	115.5(3)	118.8(4)	119.4(3)	119.5(3)	119.7(3)
O4—Ln1—O2	72.2(3)	71.1(4)	71.6(3)	71.2(4)	71.1(3)
O9—Ln1—O2	70.4(3)	68.6(4)	68.1(3)	68.5(4)	68.3(3)
O8—Ln1—O2	131.7(3)	132.4(4)	133.1(3)	132.9(4)	132.4(3)
O8^{i}—Ln1—O2	144.7(3)	142.0(4)	141.8(3)	141.8(4)	141.0(3)
O5—Co1—O3^{ii}	110.1(3)	109.5(4)	110.1(3)	108.9(5)	108.8(4)
O5—Co1—O1	126.3(4)	127.1(4)	127.2(4)	128.0(5)	127.1(4)
O3^{ii}—Co1—O1	122.5(4)	122.2(5)	121.4(4)	121.7(5)	122.6(4)
O5—Co1—O7	87.1(3)	89.4(4)	89.1(3)	89.9(4)	89.7(4)
O3^{ii}—Co1—O7	88.1(3)	86.1(4)	86.0(3)	86.2(3)	85.5(3)
O1—Co1—O7	84.8(3)	83.8(4)	83.5(3)	82.9(3)	83.3(3)
O5—Co1—N1	94.4(4)	94.7(5)	94.7(4)	94.8(5)	95.3(4)
O3^{ii}—Co1—N1	92.4(4)	92.8(5)	93.1(4)	93.6(4)	93.6(3)
O1—Co1—N1	93.4(4)	93.4(5)	93.7(4)	93.1(4)	93.1(4)
O7—Co1—N1	178.1(4)	175.9(5)	176.1(4)	175.1(4)	174.9(4)

Table S2 Summary of Magnetic Data for the Complex **1 – 5**

Complex [$Co^{II}_3Ln^{III}_3$]	**$^{2s+1}L_J$ (Ln^{III})**	**$\chi_M T$calcd (cm^3 mole^{-1} K)**	**$\chi_M T$ at 300k (cm^3 mole^{-1} K)**	**Wiss const [θ](K)**	**Magnetization at 2 K and 5 T ($N\beta$)**
Co_3La_3 (**1**)	$^1S_0$	5.63	6.41	-4.92	2.10
Co_3Gd_3 (**2**)	$^8S_{7/2}$	29.25	29.01	+0.12	25.11
Co_3Tb_3 (**3**)	$^7F_6$	41.06	38.3	-1.58	18.6
Co_3Dy_3 (**4**)	$^6H_{15/2}$	42.9	44.4	-0.17	19.6
Co_3Ho_3 (**5**)	$^5I_8$	42.7	44.3	-2.32	16.8

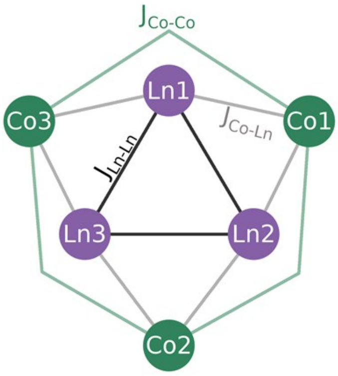
DFT computations

Although in this section of the Supporting Information results for all the members of the $Co^{II}_3Ln^{III}_3$ series are reported, one has to keep in mind that for $Co^{II}_3Tb^{III}_3$, $Co^{II}_3Dy^{III}_3$ and $Co^{II}_3Ho^{III}_3$ strong magnetic anisotropy on the Ln sites is induced by the crystal field splitting of their atomic J multiplets and to describe this effect multiconfigurational *ab initio* methods should be used rather than DFT.

To estimate exchange coupling constants the Heisenberg-Dirac-van Vleck Hamiltonian was used:

$$\hat{H} = -2J\sum J_{ij}\hat{S}_i\hat{S}_j \qquad (1)$$

where $\hat{S}$ are the local spin operators for each paramagnetic centre and J are the Heisenberg exchange coupling constants between two paramagnetic centres. Except for $\mathrm{Co^{II}_3La^{III}_3}$, in the $\mathrm{Co^{II}_3Ln^{III}_3}$ series three different magnetic exchange interactions can be distinguished:



that is $\mathrm{Co^{II} - Co^{II}}$, $\mathrm{Co^{II} - Ln^{III}}$ and $\mathrm{Ln^{III} - Ln^{III}}$. Hence, the Heisenberg-Dirac-van Vleck Hamiltonian can be rewritten as:

$$\begin{aligned}\hat{H} = -2J_{\mathrm{Ln-Ln}}\left(\hat{S}_{\mathrm{Ln1}}\hat{S}_{\mathrm{Ln2}} + \hat{S}_{\mathrm{Ln1}}\hat{S}_{\mathrm{Ln3}} + \hat{S}_{\mathrm{Ln2}}\hat{S}_{\mathrm{Ln3}}\right)\\ -2J_{\mathrm{Ln}-Co}\left(\hat{S}_{\mathrm{Ln1}}\hat{S}_{\mathrm{Co1}} + \hat{S}_{\mathrm{Ln1}}\hat{S}_{\mathrm{Co3}} + \hat{S}_{\mathrm{Ln2}}\hat{S}_{\mathrm{Co1}} + \hat{S}_{\mathrm{Ln2}}\hat{S}_{\mathrm{Co2}} + \hat{S}_{\mathrm{Ln3}}\hat{S}_{\mathrm{Co2}} + \hat{S}_{\mathrm{Ln3}}\hat{S}_{\mathrm{Co3}}\right)\\ -2J_{\mathrm{Co-Co}}\left(\hat{S}_{\mathrm{Co1}}\hat{S}_{\mathrm{Co2}} + \hat{S}_{\mathrm{Co1}}\hat{S}_{\mathrm{Co3}} + \hat{S}_{\mathrm{Co2}}\hat{S}_{\mathrm{Co3}}\right)\end{aligned} \quad (2)$$

For $\mathrm{Co^{II}_3La^{III}_3}$, which can be considered a trinuclear $\mathrm{Co^{II}}$ cluster from the magnetochemical point of view, Equation 1 can be rewritten as:

$$\hat{H} = -2J_{\mathrm{Co-Co}}\left(\hat{S}_{\mathrm{Co1}}\hat{S}_{\mathrm{Co2}} + \hat{S}_{\mathrm{Co1}}\hat{S}_{\mathrm{Co3}} + \hat{S}_{\mathrm{Co2}}\hat{S}_{\mathrm{Co3}}\right) (3)$$

Hence, the theoretical investigation of $\mathrm{Co^{II}_3La^{III}_3}$ implies to consider only two different spin configurations that correspond to the HS configuration and to one BS solutions (spin flipped on only one $\mathrm{Co^{II}}$). Applying the Hamiltonian from Eq. 3 to both of these single determinant wavefunctions gives the following expression of the energies:

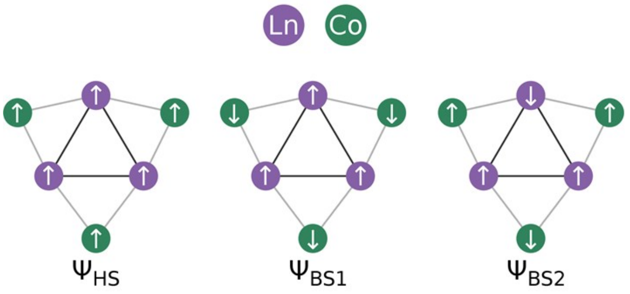
$$E_{HS} = -13\frac{1}{2}J_{Co-Co} \qquad (4)$$

$$E_{BS} = 4\frac{1}{2}J_{Co-Co} \qquad (5)$$

The analytic expression of the exchange coupling constant $J_{Co\text{-}Co}$ is then derived from Eqs. 4 and 5:

$$J_{Co-Co} = -\frac{E_{HS} - E_{BS}}{18} \qquad (6)$$

The $J_{Co\text{-}Ln}$ and $J_{Ln\text{-}Ln}$ constants were calculated likewise $J_{Co\text{-}Co}$, but in order to simplify the calculations $J_{Co\text{-}Co}$ in Eq. 2 was assumed to equal to the one obtained from Eq. 6. In consequence, $J_{Co\text{-}Ln}$ and $J_{Ln\text{-}Ln}$ were calculated from three different spin configurations:



Applying the Hamiltonian from Eq. 2 to the three of the single determinant wavefunctions shown above gives the following expression of the energies:

$$E_{HS} = -3J_{\mathrm{Ln-Ln}}\frac{N_{\mathrm{Ln}}{}^{2}}{2} - 3J_{\mathrm{Co-Ln}}N_{\mathrm{Ln}}N_{Co} - 3J_{\mathrm{Co-Co}}\frac{N_{\mathrm{Co}}{}^{2}}{2} \tag{7}$$

$$E_{BS1} = -3J_{\mathrm{Ln-Ln}}\frac{N_{\mathrm{Ln}}{}^{2}}{2} + 3J_{\mathrm{Co-Ln}}N_{\mathrm{Ln}}N_{Co} - 3J_{\mathrm{Co-Co}}\frac{N_{\mathrm{Co}}{}^{2}}{2} \tag{8}$$

$$E_{BS2} = J_{\mathrm{Ln-Ln}}\frac{N_{\mathrm{Ln}}{}^{2}}{2} + J_{\mathrm{Co-Ln}}N_{\mathrm{Ln}}N_{Co} + J_{\mathrm{Co-Co}}\frac{N_{\mathrm{Co}}{}^{2}}{2} \tag{9}$$

where N_i is the number of unpaired electrons on the metal site. From Eqs. 7-9 the expressions of $J_{Co\text{-}Ln}$ and $J_{Ln\text{-}Ln}$ can be obtained:

$$J_{\mathrm{Co-Ln}} = -\frac{E_{HS} - E_{BS1}}{6N_{\mathrm{Ln}}N_{Co}} \tag{10}$$

$$J_{\mathrm{Ln-Ln}} = -\frac{E_{HS} - E_{BS2} + 4J_{Co-\mathrm{Ln}}N_{Co}N_{\mathrm{Ln}} + 2J_{Co-Co}N_{Co}{}^{2}}{2N_{\mathrm{Ln}}^{2}} \tag{11}$$

Table S3 Exchange coupling constants, total energies of spin states used in these calculations and expectations values of total square spin operators

		1		**2**	
		B3LYP	**TPSS0**	**B3LYP**	**TPSS0**
HS	***E [a.u.]***	-35512.802051	-35511.133148	-44150.912498	-44148.849325
	<S2>	24.7701	24.7701	240.0366	240.0377
BS1	***E [a.u.]***	-35512.802080	-35511.133199	-44150.912440	-44148.849266
	<S2>	6.77	6.77	51.0333	51.0364
BS2	***E [a.u.]***	-	-	-44150.912485	-44148.849311
	<S2>	-	-	40.0342	40.0368
$J_{Ln\text{-}Ln}$ [cm^{-1}]		-	-	-0.01	-0.03
$J_{Co\text{-}Ln}$ [cm^{-1}]		-	-	0.10	0.10
$J_{Co\text{-}Co}$ [cm^{-1}]		-0.35	-0.62	-	-

Table S4 Löwdin populations computed at the **UB3LYP** theory level

spin population on	**1**	**2**
Co	2.655	2.653
Ln	0.001	7.015
oxygen atoms of $OH^–$	0.037	0.034
hydroxyl oxygen atoms of $[L]^{3–}$	0.057	0.059
oxygen atoms of CO_3^{2-}	0	-0.004

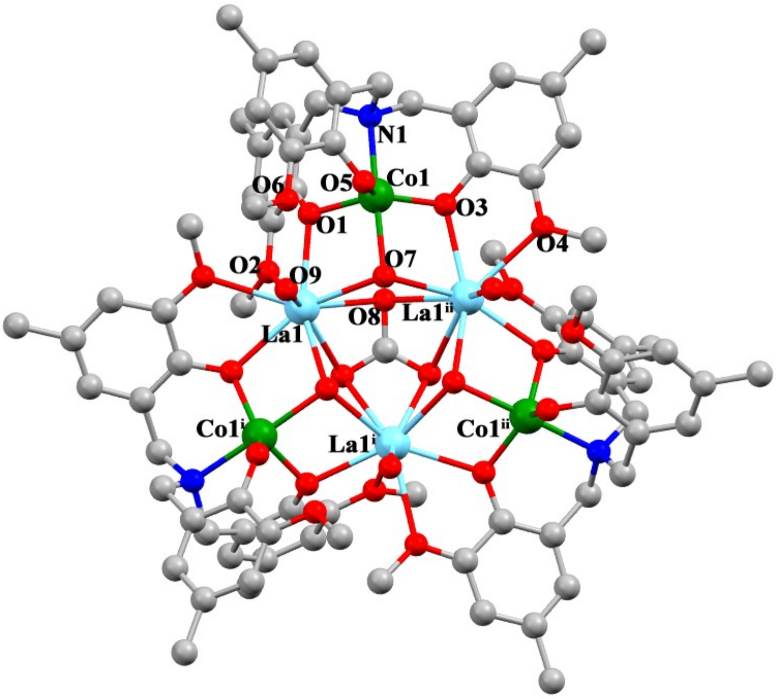


Fig. S1 Partially labeled POV-Ray (in ball and stick form) diagram showing the atom-labeling scheme for the complex **1**

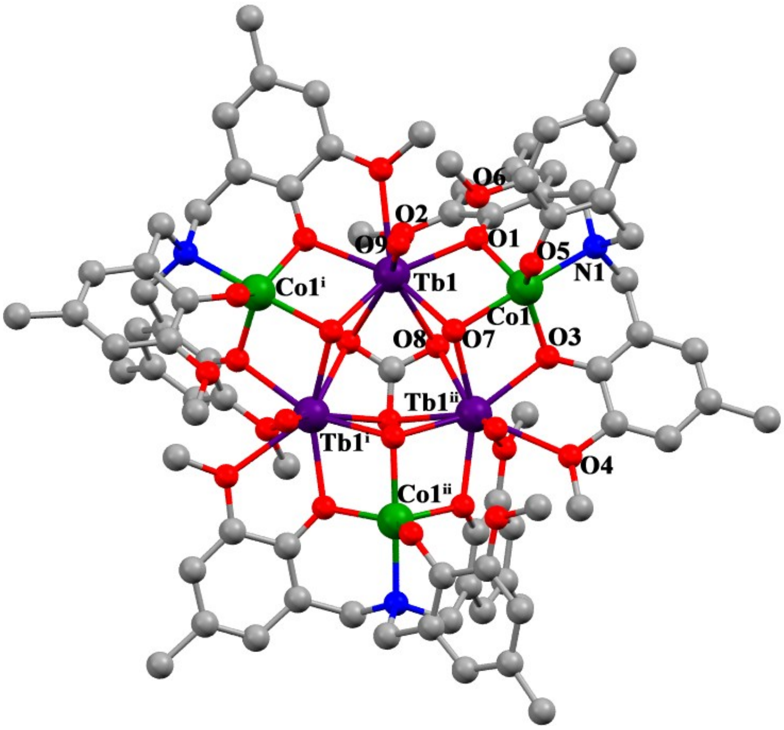


Fig. S2 Partially labeled POV-Ray (in ball and stick form) diagram showing the atom-labeling scheme for the complex **3**

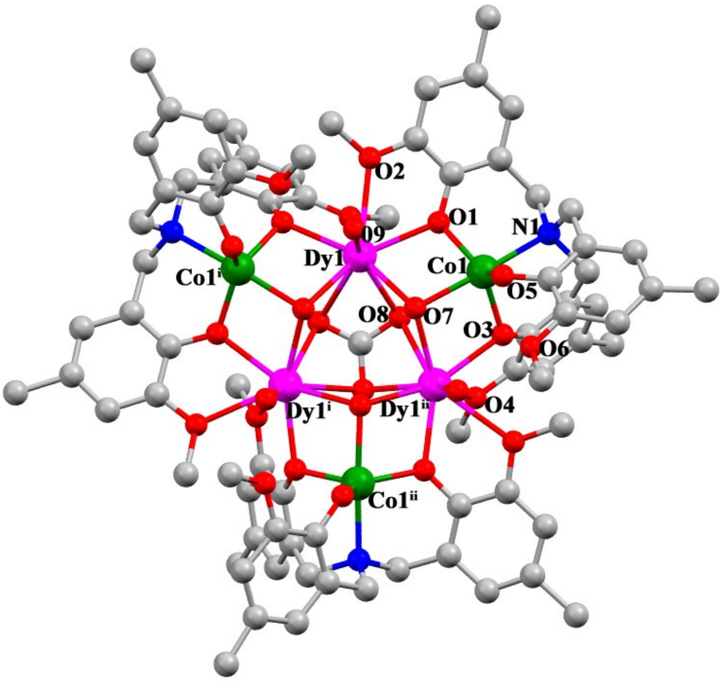


Fig. S3 Partially labeled POV-Ray (in ball and stick form) diagram showing the atom-labeling scheme for the complex **4**

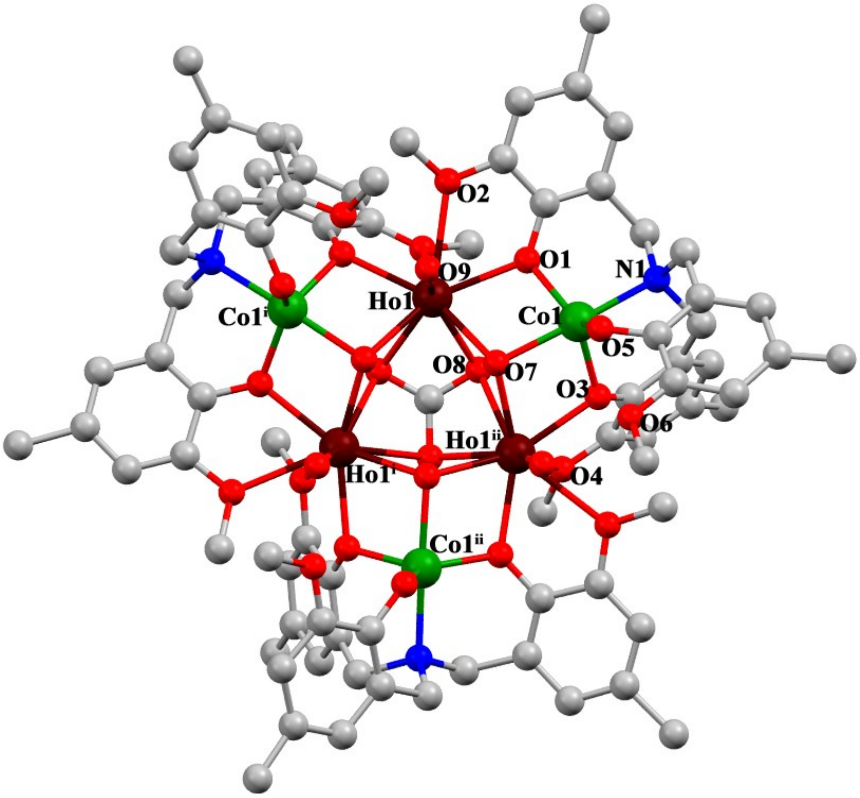


Fig. S4 Partially labeled POV-Ray (in ball and stick form) diagram showing the atom-labeling scheme for the complex **5**

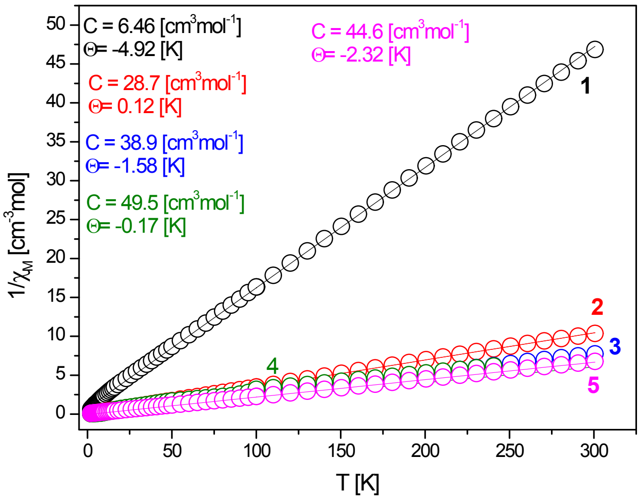


Fig. S5 Thermal dependence of inverse magnetic susceptibility for (○) - 1, (○) - 2, (○) – 3, (○) – 4, (○) – 5.

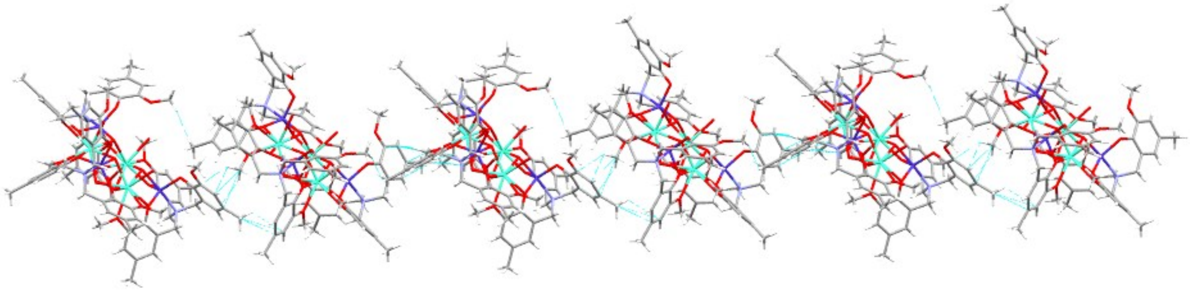


Fig. S6 H···H and C–H···π interactions between the cations of complex **2** generating an oligumeric structure. Solvent molecules are omitted for clarity.