

## ***Electronic supplementary information***

**for**

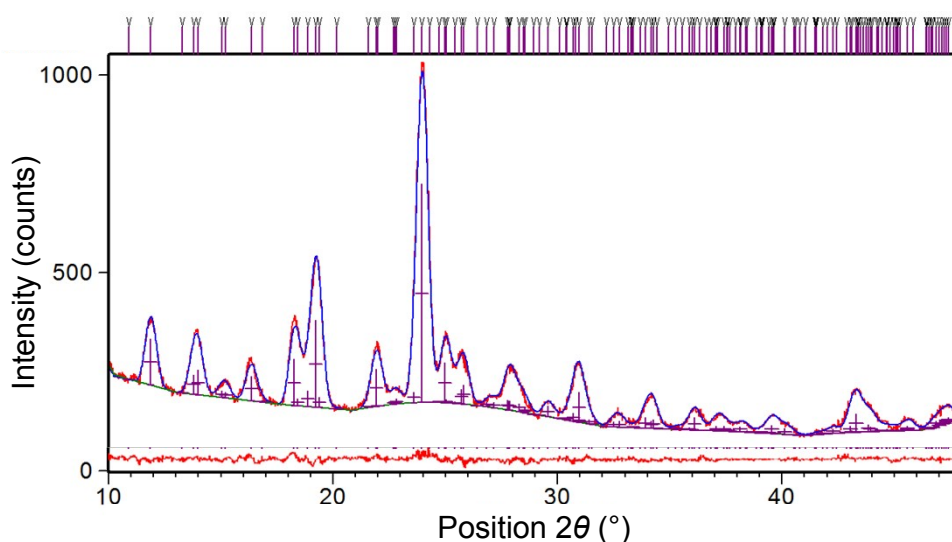
# **From square core to square opening: Structural diversity and magnetic properties of the oxo-bridged [Cr<sup>III</sup>Nb<sup>V</sup>] complexes**

*Marijana Jurić,<sup>\*a</sup> Lidija Androš Dubraja,<sup>a</sup> Jasminka Popović,<sup>a</sup> Krešimir*

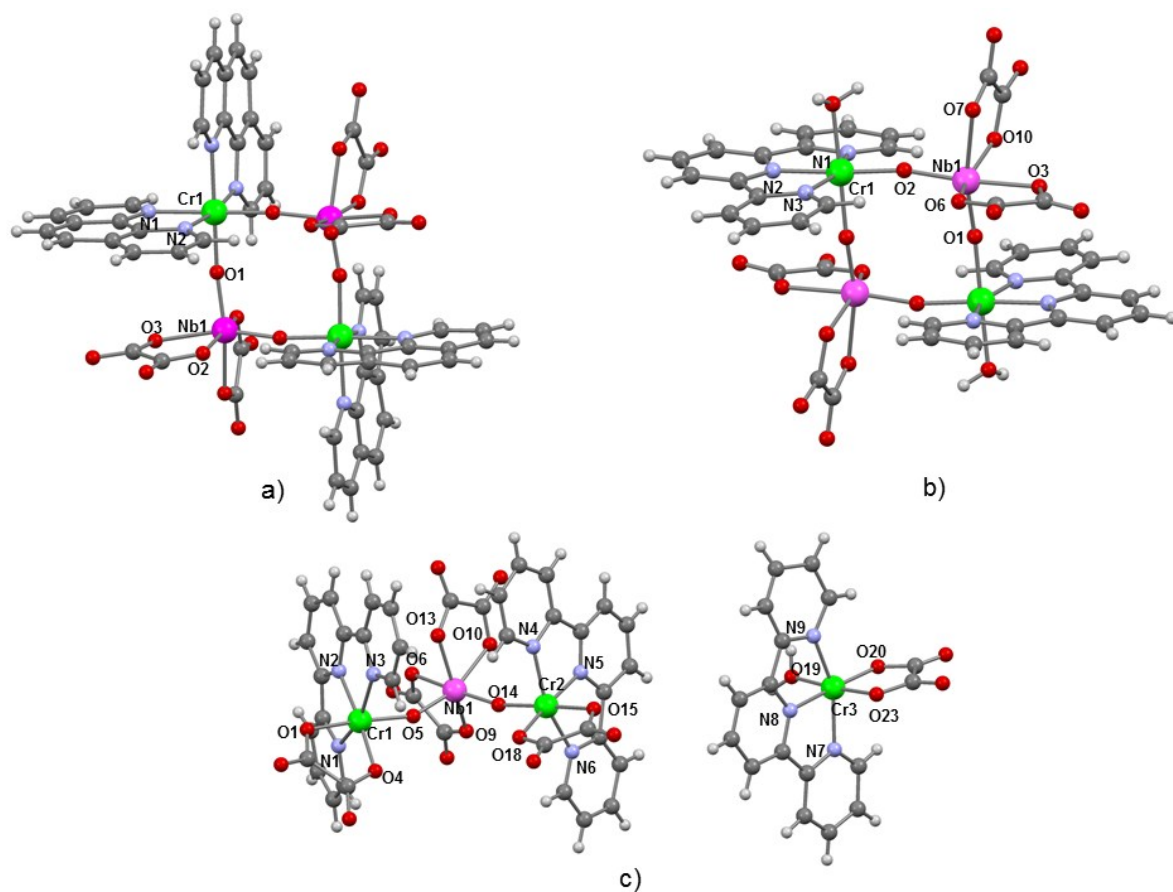
*Molčanov,<sup>a</sup> Filip Torić,<sup>b</sup> Damir Pajić<sup>b</sup> and Ivor Lončarić<sup>a</sup>*

<sup>a</sup>Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

<sup>b</sup>Department of Physics, Faculty of Science, University of Zagreb, Bijenička cesta 32, 10000 Zagreb, Croatia



**Fig. S1** Final Rietveld refinement for powder sample **1**. The experimental data are given in red, the calculated pattern in blue, while the difference between experimental and calculated curve is given below. The purple vertical marks represent the diffraction lines of [Cr<sub>2</sub>(phen)<sub>4</sub>(μ-O)<sub>4</sub>Nb<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>]·2H<sub>2</sub>O.



**Fig. S2** The molecular structure with the atom-numbering scheme of: (a) tetranuclear unit  $[\text{Cr}_2(\text{phen})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]$  in **1**; (b) tetranuclear unit  $[\text{Cr}_2(\text{terpy})_2(\text{H}_2\text{O})_2(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]$  in **2**; (c) complex anion  $[\text{Cr}_2(\text{terpy})_2(\text{C}_2\text{O}_4)_2(\mu\text{-O})_2\text{Nb}(\text{C}_2\text{O}_4)_2]$  and cation  $[\text{Cr}(\text{terpy})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$  in **3**.

**Table S1** Selected bond distances (Å) and angles (°) for compounds [Cr<sub>2</sub>(phen)<sub>4</sub>(μ-O)<sub>4</sub>Nb<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>4</sub>] $\cdot$ 2H<sub>2</sub>O (**1**), [Cr<sub>2</sub>(terpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(μ-O)<sub>4</sub>Nb<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] $\cdot$ 4HO (**2**) and [Cr(terpy)(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)][Cr<sub>2</sub>(terpy)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(μ-O)<sub>2</sub>Nb(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>] $\cdot$ 3H<sub>2</sub>O (**3**)

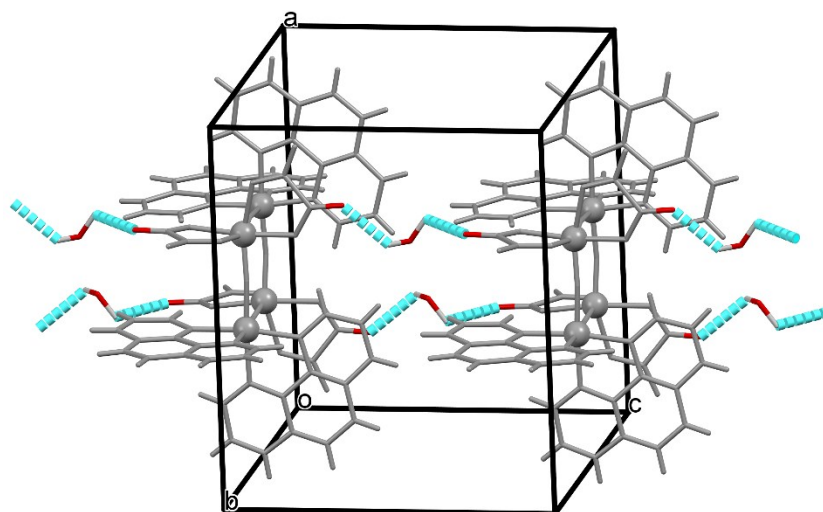
<b>1</b>		<b>2</b>		<b>3</b>	
Nb1–O1	1.782(5)	Nb1–O1	1.787(2)	Nb1–O14	1.791(2)
Nb1–O2	2.055(6)	Nb1–O2	1.794(2)	Nb1–O5	1.808(2)
Nb1–O3	2.140(6)	Nb1–O3	2.207(2)	Nb1–O6	2.218(2)
Cr1–O1	1.885(5)	Nb1–O6	2.042(2)	Nb1–O9	2.073(2)
Cr1–N1	2.069(6)	Nb1–O7	2.202(2)	Nb1–O10	2.152(2)
Cr1–N2	2.044(8)	Nb1–O10	2.042(2)	Nb1–O13	2.054(2)
O1–Nb1–O2	100.3(3)	Cr1–O1 <sup>c</sup>	1.908(2)	Cr1–N1	2.084(3)
O1–Nb1–O3	91.9(3)	Cr1–O2	1.912(2)	Cr1–N2	1.983(3)
O1–Nb1–O1 <sup>a</sup>	102.2(3)	Cr1–O11	1.987(2)	Cr1–N3	2.104(3)
O1–Nb1–O2 <sup>a</sup>	87.9(3)	Cr1–N1	2.077(3)	Cr1–O1	1.981(2)
O1–Nb1–O3 <sup>a</sup>	159.3(3)	Cr1–N2	1.993(3)	Cr1–O4	1.942(2)
O2–Nb1–O3	74.5(2)	Cr1–N3	2.052(3)	Cr1–O5	1.927(2)
O2–Nb1–O2 <sup>a</sup>	167.1(3)	O1–Nb1–O2	102.14(10)	Cr2–N4	2.090(3)
O2–Nb1–O3 <sup>a</sup>	95.3(3)	O1–Nb1–O10	96.85(10)	Cr2–N5	1.996(3)
O3–Nb3–O3 <sup>a</sup>	79.1(3)	O2–Nb1–O10	100.37(9)	Cr2–N6	2.078(3)
O1–Cr1–N1	88.5(2)	O1–Nb1–O6	101.17(10)	Cr2–O14	1.923(2)
O1–Cr1–N2	90.9(3)	O2–Nb1–O6	95.29(9)	Cr2–O15	1.962(3)
O1–Cr1–O1 <sup>b</sup>	93.0(3)	O10–Nb1–O6	153.03(9)	Cr2–O18	1.941(3)
O1–Cr1–N1 <sup>b</sup>	175.4(3)	O1–Nb1–O7	167.01(9)	Cr3–O19	1.975(3)
O1–Cr1–N2 <sup>b</sup>	95.3(3)	O2–Nb1–O7	89.64(9)	Cr3–O20	1.950(3)
N1–Cr1–N2	80.3(3)	O10–Nb1–O7	75.39(9)	Cr3–O23	1.932(3)
N1–Cr1–O1 <sup>b</sup>	175.4(3)	O6–Nb1–O7	82.95(9)	Cr3–N7	2.086(3)
N1–Cr1–N1 <sup>b</sup>	90.3(2)	O1–Nb1–O3	87.91(9)	Cr3–N8	1.986(3)
N1–Cr1–N2 <sup>b</sup>	93.3(3)	O2–Nb1–O3	167.22(9)	Cr3–N9	2.058(4)
N2–Cr1–N2 <sup>b</sup>	171.0(3)	O10–Nb1–O3	86.05(8)	O14–Nb1–O5	103.86(10)
Nb1–O1–Cr1	170.4(4)	O6–Nb1–O3	74.81(8)	O14–Nb1–O13	102.57(10)
		O7–Nb1–O3	81.25(8)	O5–Nb1–O13	91.14(10)
		O1–Cr1–O2 <sup>c</sup>	91.46(9)	O14–Nb1–O9	95.50(10)
		O1–Cr1–O11 <sup>c</sup>	177.37(10)	O5–Nb1–O9	100.08(10)
		O2–Cr1–O11	90.08(10)	O13–Nb1–O9	155.81(9)
		O1–Cr1–N2 <sup>c</sup>	91.85(10)	O14–Nb1–O10	90.87(10)
		O2–Cr1–N2	176.66(10)	O5–Nb1–O10	161.59(9)
		O11–Cr1–N2	86.63(10)	O13–Nb1–O10	74.68(9)
		O1–Cr1–N3 <sup>c</sup>	89.39(10)	O9–Nb1–O10	89.24(9)
		O2–Cr1–N3	100.59(10)	O14–Nb1–O6	165.76(10)
		O11–Cr1–N3	92.42(10)	O5–Nb1–O6	87.51(9)
		N2–Cr1–N3	78.97(11)	O13–Nb1–O6	85.48(9)
		O1–Cr1–N1 <sup>c</sup>	89.61(10)	O9–Nb1–O6	73.78(8)
		O2–Cr1–N1	101.99(10)	O10–Nb1–O6	79.84(9)
		O11–Cr1–N1	87.99(10)	O5–Cr1–O4	91.53(10)
		N2–Cr1–N1	78.51(11)	O5–Cr1–O1	173.53(10)
		N3–Cr1–N1	157.42(11)	O4–Cr1–O1	82.68(10)
		Nb1–O1–Cr1 <sup>c</sup>	167.60(13)	O5–Cr1–N2	92.22(10)
		Nb1–O2–Cr1	164.73(14)	O4–Cr1–N2	175.90(11)
				O1–Cr1–N2	93.66(10)
				O5–Cr1–N1	89.41(10)
				O4–Cr1–N1	99.00(11)

	O1–Cr1–N1	94.31(11)
	N2–Cr1–N1	79.38(12)
	O5–Cr1–N3	89.75(11)
	O4–Cr1–N3	88.91(11)
	O1–Cr1–N3	104.21(11)
	N2–Cr1–N3	77.48(11)
	N1–Cr1–N3	156.79(11)
	O14–Cr2–O18	93.97(11)
	O14–Cr2–O15	177.98(11)
	O18–Cr2–O15	84.02(12)
	O14–Cr2–N5	94.53(11)
	O18–Cr2–N5	71.41(12)
	O15–Cr2–N5	87.49(12)
	O14–Cr2–N6	90.62(11)
	O18–Cr2–N6	102.28(13)
	O15–Cr2–N6	89.58(11)
	N5–Cr2–N6	78.83(14)
	O14–Cr2–N4	89.97(10)
	O18–Cr2–N4	100.60(12)
	O15–Cr2–N4	90.63(11)
	N5–Cr2–N4	78.22(13)
	N6–Cr2–N4	157.02(13)
	O23–Cr3–O20	81.52(13)
	O23–Cr3–O19	175.08(13)
	O20–Cr3–O19	94.04(14)
	O23–Cr3–N8	94.09(12)
	O20–Cr3–N8	175.59(13)
	O19–Cr3–N8	90.36(13)
	O23–Cr3–N9	90.12(13)
	O20–Cr3–N9	101.24(15)
	O19–Cr3–N9	88.66(12)
	N8–Cr3–N9	79.18(15)
	O23–Cr3–N7	93.09(12)
	O20–Cr3–N7	101.06(14)
	O19–Cr3–N7	89.83(12)
	N8–Cr3–N7	78.58(15)
	N9–Cr3–N7	157.69(15)
	Nb1–O5–Cr1	156.80(13)
	Nb1–O14–Cr2	163.81(15)

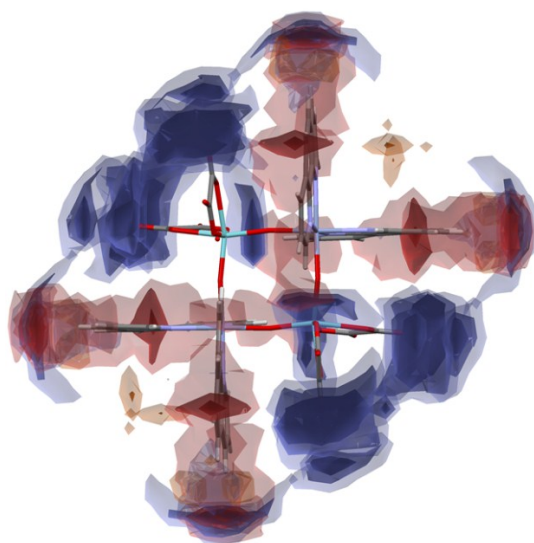
<sup>a</sup>Symmetry operator: (i)  $y, x, 2-z$

<sup>b</sup>Symmetry operator: (ii)  $1-y, 1-x, 2-z$

<sup>c</sup>Symmetry operator: (ii)  $1-x, -y, 1-z$



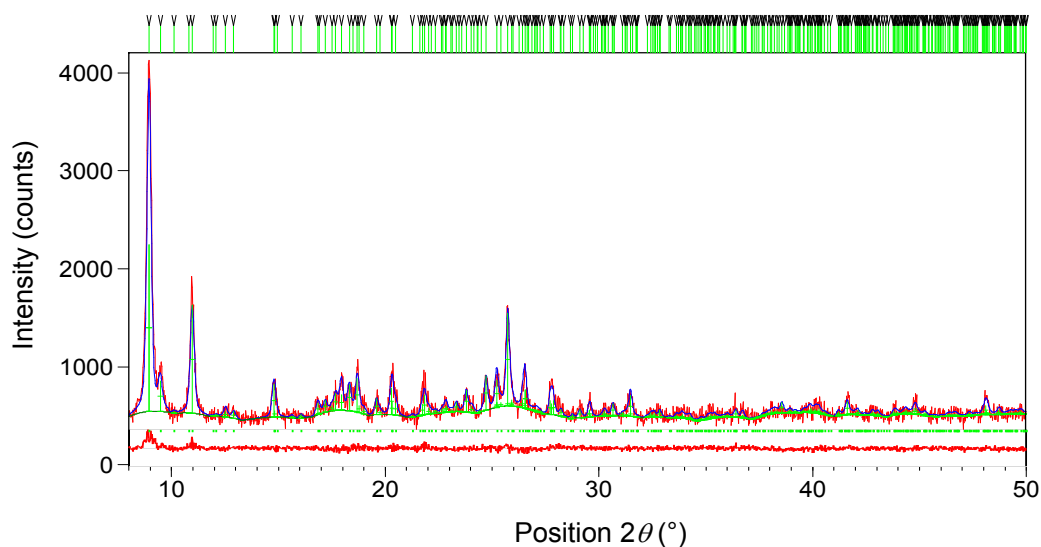
**Fig. S3** The one-dimensional hydrogen-bonding pattern in the crystal packing of  $[\text{Cr}_2(\text{phen})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]\cdot 2\text{H}_2\text{O}$  (**1**).



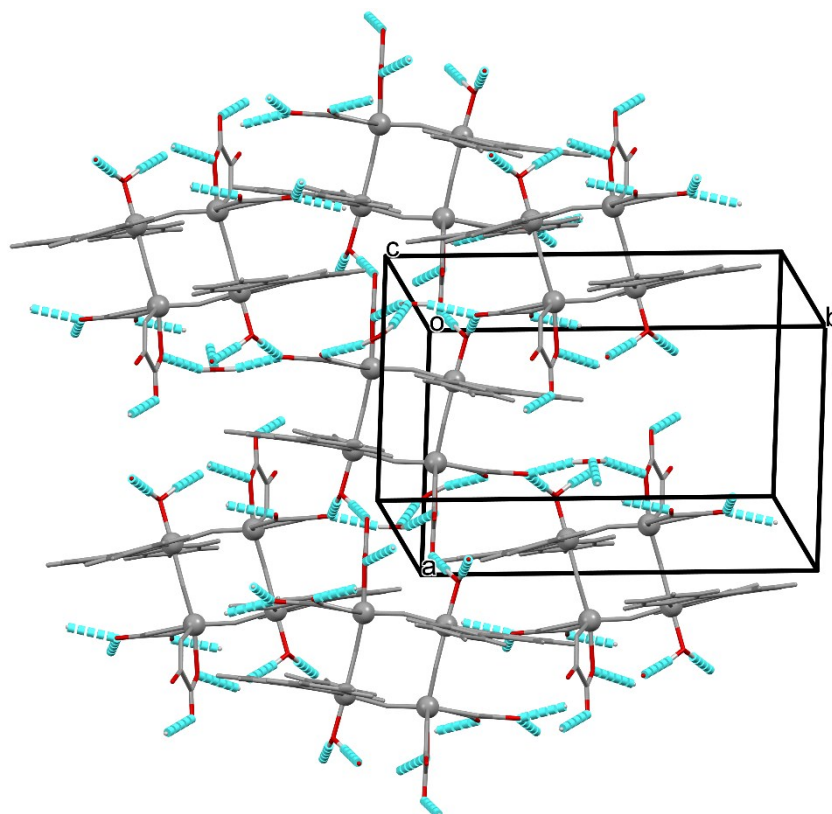
**Fig. S4** Full interaction map showing interaction preferences of the tetranuclear  $[\text{Cr}_2(\text{phen})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]$  unit in **1**.

**Table S2** Hydrogen-bonding geometry in compounds **1–3**. Interatomic distances involving the water molecules without located hydrogen atoms are given.

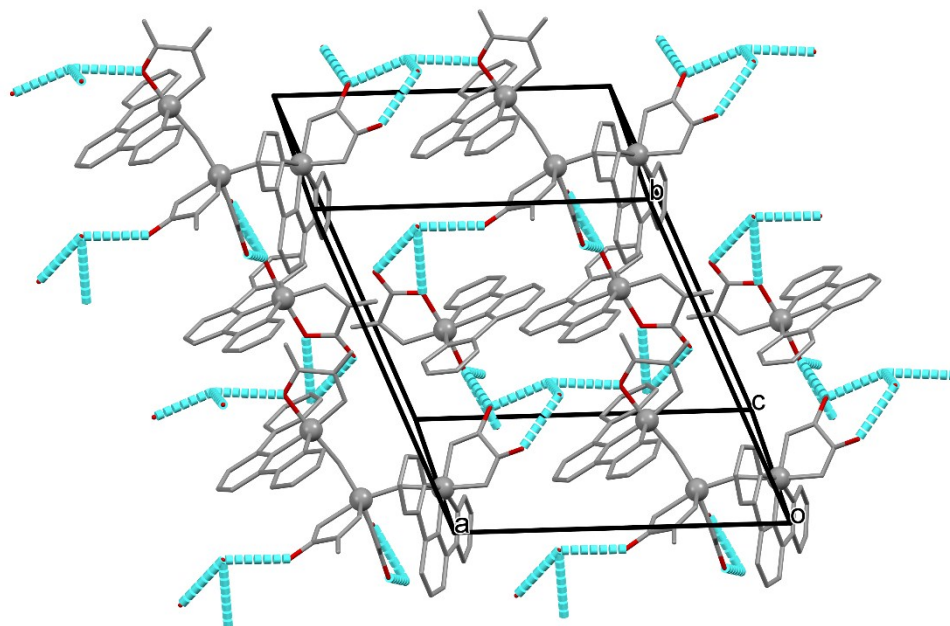
Compound	<i>D</i> –H... <i>A</i>	<i>D</i> –H/Å	H... <i>A</i> /Å	<i>D</i> ... <i>A</i> /Å	<i>D</i> –H... <i>A</i> /°	Symm. op. on <i>A</i>
<b>1</b>	O6–H6A...O4	0.8(2)	2.4(6)	2.938(14)	123(1)	<i>x, y, –1 + z</i>
	O11–H11A...O4	0.851(18)	1.809(18)	2.659(3)	178(4)	$3/2 - x, -1/2 + y, 1/2 - z$
<b>2</b>	O11–H11B...O8	0.84(3)	1.89(2)	2.688(3)	158(2)	$2 - x, -y, 1 - z$
	O12–H12A...O5	0.87(2)	2.17(2)	3.022(4)	167(3)	<i>x, y, z</i>
	O12–H12B...O13	0.87(2)	1.95(2)	2.789(5)	163(2)	<i>x, y, z</i>
	O13–H13A...O7	0.86(2)	2.29(2)	3.108(4)	159(3)	<i>x, y, z</i>
	O13–H13B...O4	0.857(11)	2.196(15)	3.025(4)	163(3)	$3/2 - x, -1/2 + y, 1/2 - z$
<b>3</b>	O19–H19A...O3	0.84(3)	1.92(4)	2.754(4)	179(5)	$1 + x, y, z$
	O19–H19B...O7	0.84(3)	1.91(2)	2.740(4)	166(4)	$1 - x, -y, 1 - z$
	O24...O22			2.789(16)		$x, -1 + y, z$
	O24...O11			2.906(17)		<i>x, y, z</i>
	O25...O3			2.819(11)		<i>x, y, z</i>
	O25...O15			2.957(10)		$-1 + x, y, z$
	O26...O2			2.847(8)		$-x, 1 + y, -z$
	O26...O25			2.904(14)		$-x, 1 + y, -z$



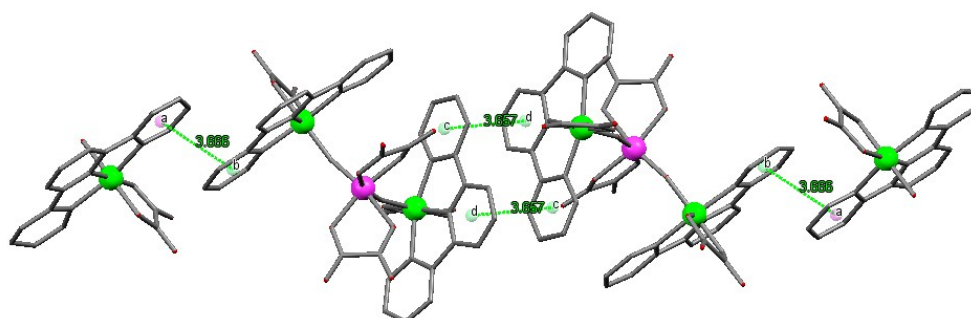
**Fig. S5** Final Rietveld refinement for powder sample of **2**. The experimental data are given in red, the calculated pattern in blue, while the difference between experimental and calculated curve is given below. The green vertical marks represent the diffraction position of  $[\text{Cr}_2(\text{terpy})_2(\text{H}_2\text{O})_2(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]\cdot 4\text{H}_2\text{O}$ .



**Fig. S6** The three-dimensional hydrogen-bonding pattern in the crystal packing of  $[\text{Cr}_2(\text{terpy})_2(\text{H}_2\text{O})_2(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]\cdot 4\text{H}_2\text{O}$  (**2**).



**Fig. S7** The hydrogen bonding pattern in the crystal packing of  $[\text{Cr}(\text{terpy})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})][\text{Cr}_2(\text{terpy})_2(\text{C}_2\text{O}_4)_2(\mu\text{-O})_2\text{Nb}(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$  (**3**).



**Fig. S8** The  $\pi$ -stacked tetramers in  $[\text{Cr}(\text{terpy})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})][\text{Cr}_2(\text{terpy})_2(\text{C}_2\text{O}_4)_2(\mu\text{-O})_2\text{Nb}(\text{C}_2\text{O}_4)_2]\cdot 3\text{H}_2\text{O}$  (**3**).



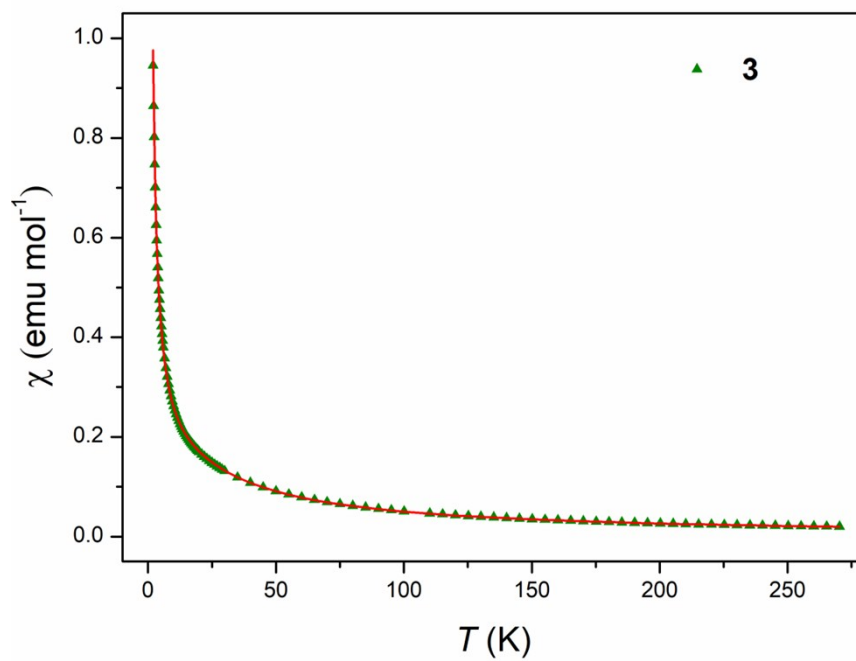
**Table S3** Geometric parameters of the aromatic stacking interactions in compound **3**

Compound	Cg(i)⋯Cg(j)	Cg(i)⋯Cg(j)/Å <sup>a</sup>	α/° <sup>b</sup>	β/° <sup>c</sup>	Cg(i)⋯plane [Cg(j)]/Å <sup>d</sup>	Symmetry operator
<b>3</b>	(N2→C10)⋯(N3→C15)	3.647(3)	0.9(2)	22.0	3.3748(16)	-x, -y, -z
	(N6→C30)⋯(N7→C35)	3.695(4)	5.8(3)	20.9	3.501(2)	1 - x, 1 - y, 1 - z

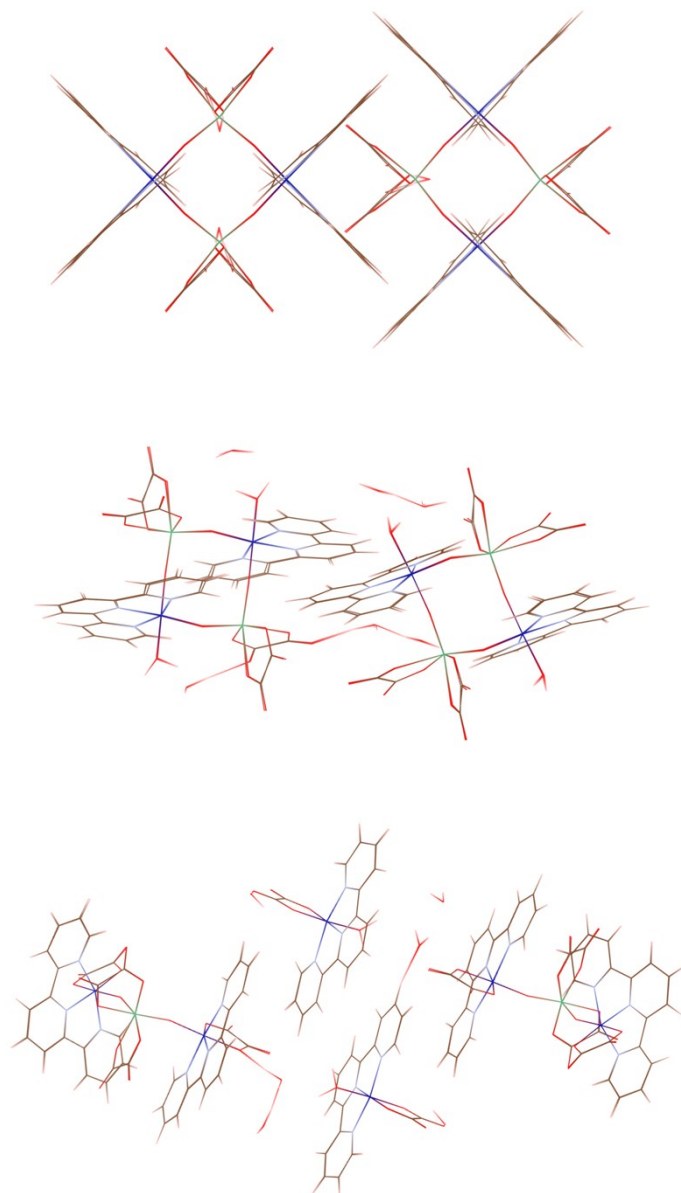
<sup>a</sup> Cg = centre of gravity of the aromatic ring. <sup>b</sup> α = angle between the planes of two aromatic rings. <sup>c</sup> β = angle between the Cg⋯Cg line and the normal to the plane of the first aromatic ring

**Table S4** Intra and shortest intermolecular distances (Å) between metal centres in compounds **1–3**

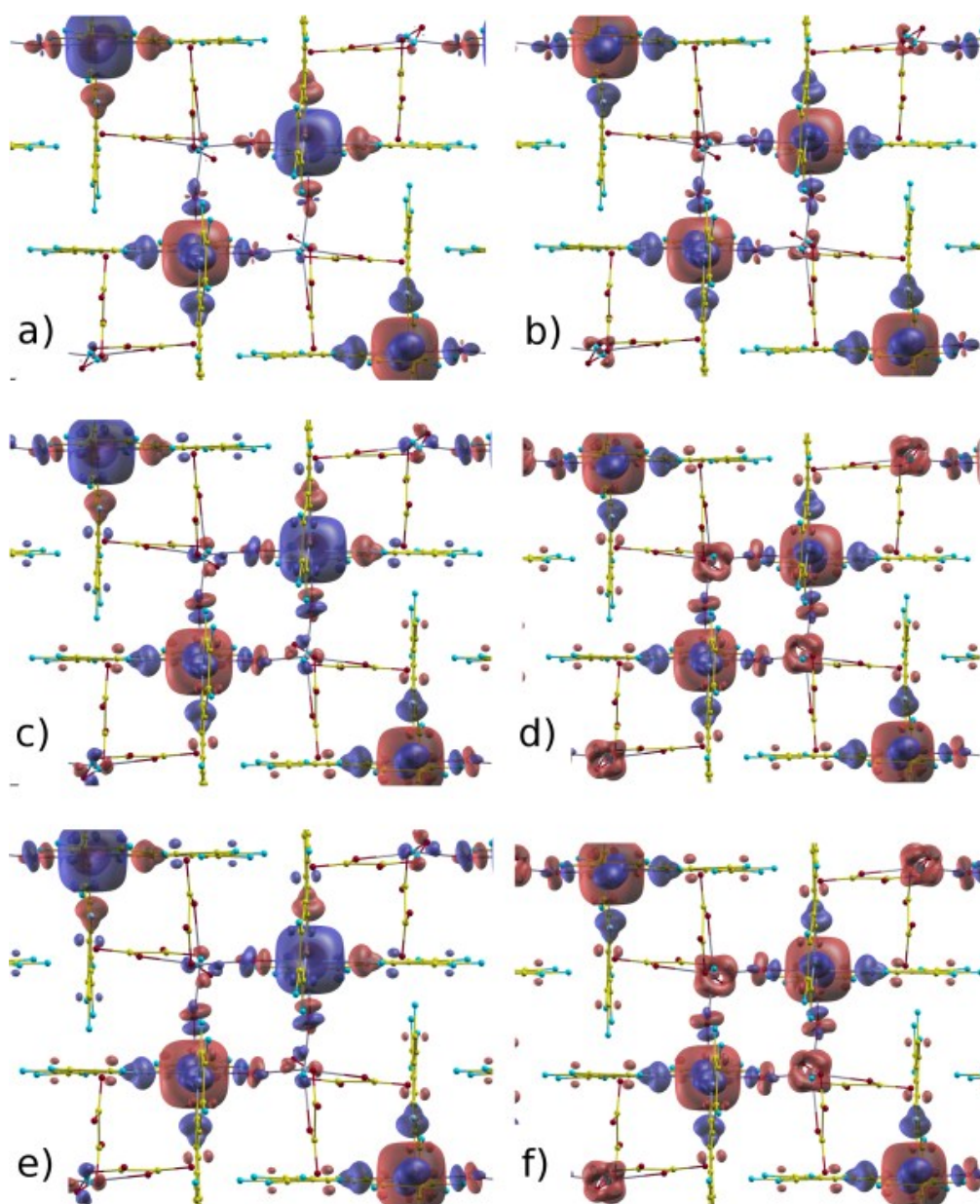
Compound	[Cr⋯Cr] <sub>intra</sub>	Cr–O–Nb–O–Cr	Cr⋯Cr	Cr⋯Nb
<b>1</b>	5.359	7.332	10.346	8.214
<b>2</b>	5.411	7.400	9.121	7.369
<b>3</b>	6.089	7.407	6.936	8.025



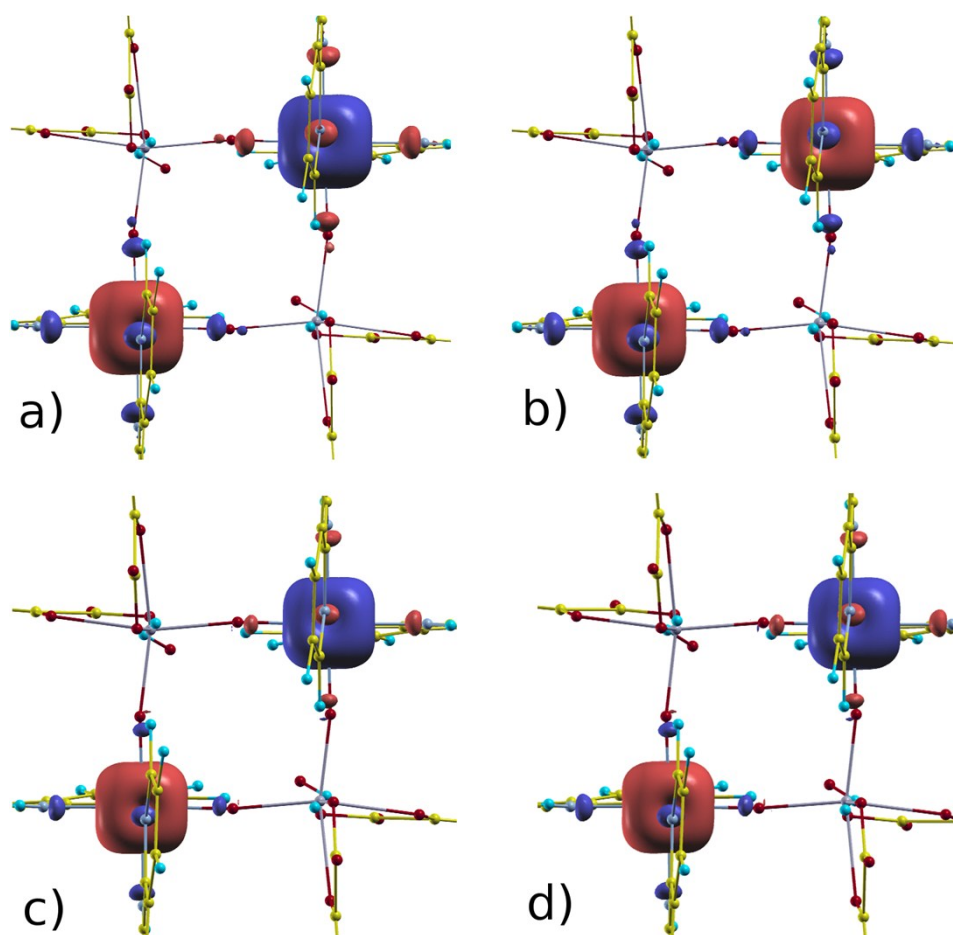
**Fig. S9** Temperature dependence of the molar magnetic susceptibility for compound **3**. The red solid line represents the best-fitted model curve.



**Fig. S10** Overlayered relaxed structures of **1–3** calculated with three different density functionals: PBE,<sup>1</sup> GGA+U,<sup>2</sup> and vdW-DF-cx.<sup>3</sup> All three functionals predict very similar geometries with only subtle differences showing that it is not very important to account for vdW forces for these compounds.



**Fig. S11** Isosurface plots (iso value is 0.003 electrons/a.u.<sup>3</sup>) of magnetic polarization density (difference of spin up and spin down electron density) for compound **1**: (a) antiferromagnetic solution obtained with GGA+U;<sup>2</sup> (b) ferromagnetic solution obtained with GGA+U;<sup>2</sup> (c) antiferromagnetic solution obtained with PBE;<sup>14</sup> (d) ferromagnetic solution obtained with PBE;<sup>1</sup> (e) antiferromagnetic solution obtained with vdW-DF-cx;<sup>3</sup> f) ferromagnetic solution obtained with vdW-DF-cx.<sup>3</sup>



**Fig. S12** Isosurface plots (iso value is 0.01 electrons/a.u.<sup>3</sup>) of magnetic polarization density (difference of spin up and spin down electron density) for compound **1**: (a) antiferromagnetic solution obtained with GGA+U;<sup>2</sup> (b) ferromagnetic solution obtained with GGA+U;<sup>2</sup> (c) antiferromagnetic solution obtained with PBE;<sup>1</sup> (d) antiferromagnetic solution obtained with vdW-DF-cx.<sup>3</sup>

**Table S6** Magnetic and structural properties obtained from DFT calculations

Compound	1			2			3		
	PBE	$U = 3.5$ eV	vdW-DF-cx	PBE	$U = 3.5$ eV	vdW-DF-cx	PBE	$U = 3.5$ eV	vdW-DF-cx
$\Delta E$ (mV)	-52.11	-11.02	-65.75	-53.09	-12.73	-61.26	-33.86	-11.06	-40.09
$J$ (cm <sup>-1</sup> )	-5.79	-1.22	-7.31	-5.90	-1.41	-6.81	-3.76	-1.23	-4.45
Cr–O–Nb–O–Cr (Å)	7.41	7.47	7.38	7.41	7.48	7.40	7.43	7.50	7.41
Cr···Cr (Å)	5.42	5.45	5.37	5.44	5.48	5.41	6.20	6.23	6.20
Cr–O–Nb (deg)	171.4	170.7	171.5	168.5	167.1	168.7	155.7	155.3	155.3
Cr–O–Nb <sub>2</sub> (deg)	171.8	171.2	172.0	165.0	163.6	165.7	168.1	169.0	168.2

## References:

1. J. P. Perdew, K.; Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
2. M. Cococcioni and S. de Gironcoli, *Phys. Rev. B*, 2005, **71**, 035105.
3. K. Berland and P. Hyldgaard, *Phys. Rev. B*, 2014, **89**, 035412.