Electronic Supplementary Information

for

The ladder-like [CrCu] coordination polymers containing unique bridging modes of $[Cr(C_2O_4)_3]^{3-}$ and $Cr_2O_7^{2-}$

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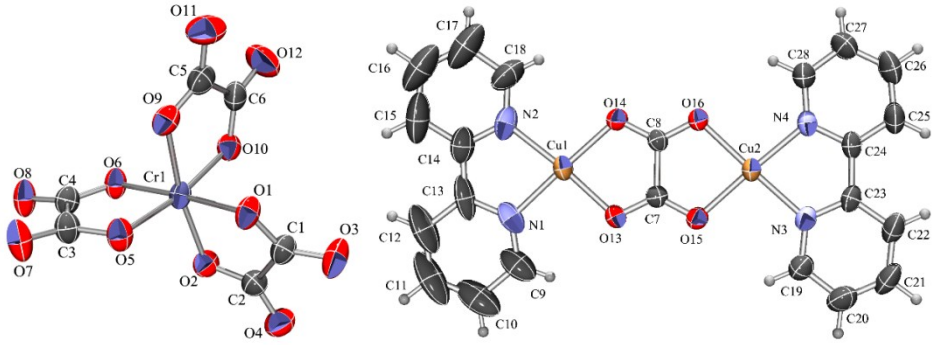
Table S1. Selected bond lengths (Å) and angles (°) in compounds **1**–**3**

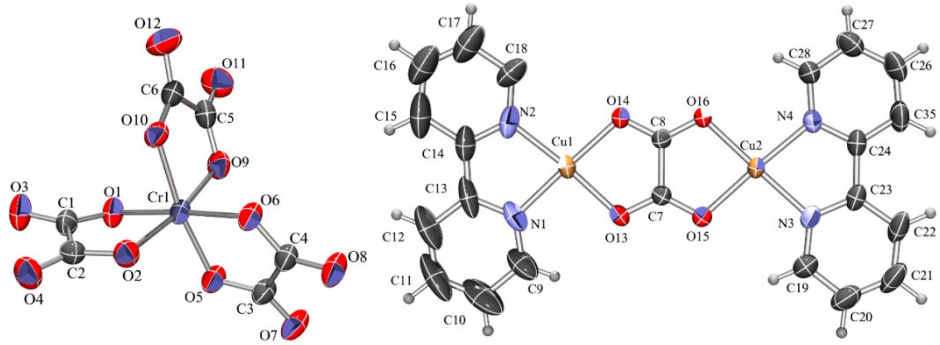
Compounds	**1**	**2**	**3**	
Cr1–O1	1.973(3)	1.9816(18)	Cr1–O1	1.623(3)
Cr1–O2	1.966(3)	1.971(2)	Cr1–O2	1.602(5)
Cr1–O5	1.967(3)	1.9685(18)	Cr1–O3	1.783(9)
Cr1–O6	1.970(3)	1.9637(18)	Cr1–O4A	1.702(9)
Cr1–O9	1.966(3)	1.980(2)	Cr1–O4B	1.516(9)
Cr1–O10	1.989(3)	1.9939(18)	Cu1–N1	2.005(4)
Cu1–O1	2.760(4)	2.7166(19)	Cu1–N2	1.983(4)
Cu1–O10[a]	2.602(3)	2.6351(19)	Cu1–O1	2.244(3)
Cu1–O13	1.963(3)	1.9596(19)	Cu1–O4A[c]	2.571(9)
Cu1–O14	1.986(3)	1.9760(18)	Cu1–O4B[c]	2.584(4)
Cu1–N1	1.973(5)	1.958(3)	Cu1–O5	1.978(4)
Cu1–N2	1.980(5)	1.976(3)	Cu1–O6	1.982(3)
Cu2–O7	2.465(4)	2.471(2)		
Cu2–O8[a]	2.597(4)	2.584(2)		
Cu2–O15	1.989(3)	1.9722(19)		
Cu2–O16	1.976(3)	1.9887(18)		
Cu2–N3	1.986(4)	1.973(2)		
Cu2–N4	1.988(4)	1.988(2)		

K1–O1	2.750(4)
K1–O3[b]	2.627(4)
K1–O4[b]	2.929(4)
K1–O11	2.888(5)
K1–O14	2.955(4)
K1–O16	2.912(3)
K1–O17	3.048(12)

[a]Symmetry operator: (*i*) 1 + *x*, *y*, *z*
[b]Symmetry operator: (*ii*) *x*, 1 + *y*, *z*
[c]Symmetry operator: (*iii*) –1 + *x*, *y*, *z*



a)



b)

Fig. S1 ORTEP-3[1] drawings of $[Cr(C_2O_4)_3]^{3-}$ (left) and $[Cu(C_2O_4)(bpy)_2]^{2+}$ (right) moieties in a) compound **1** and b) compound **2** with atom numbering scheme. Displacement ellipsoids have been drawn for the probability of 50 % and hydrogen atoms are shown as spheres of arbitrary radii.

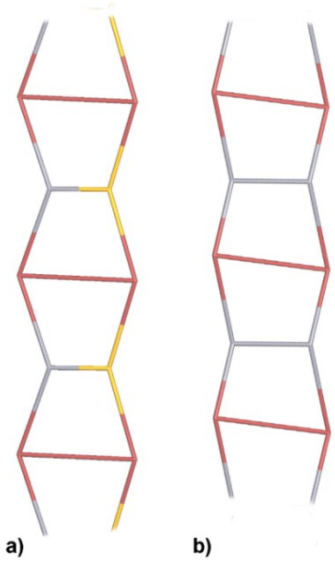


Fig. S2 Topological representation of 1D ladder-like chains in a) **1** and **2** and b) **3**. Brown nodes correspond to Cu atoms, gray nodes to Cr atoms and yellow nodes to oxalate moieties bridging three metal centres.[2]

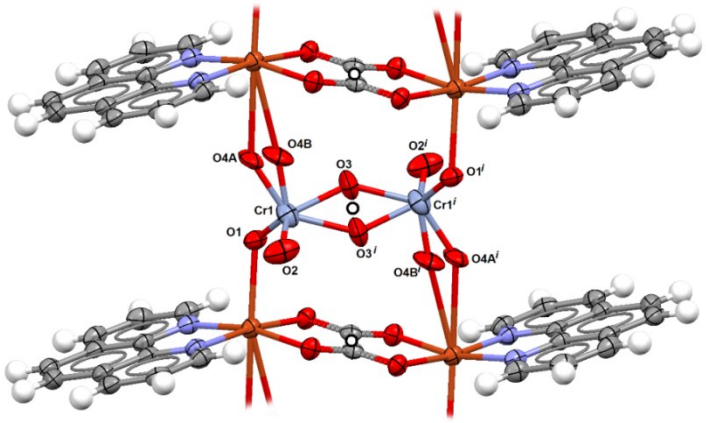


Fig. S3 Disorder of dichromate moieties in **3**: the dichromates are disordered about an inversion center (shown as black circles). Thus, occupancy of atom O3 disordered over two symmetry-equivalent positions, O3 and O3^{i}, which have occupancies of 0.5; O4 is disordered over two symmetry-independent positions, O4A and O4B, with respective occupancies of 0.5. At RT, the two positions could not be resolved, so ellipsoids of O3 and O4 were unrealistically elongated. Symmetry operator: (*i*) 1–*x*, –*y*, 1–*z*.

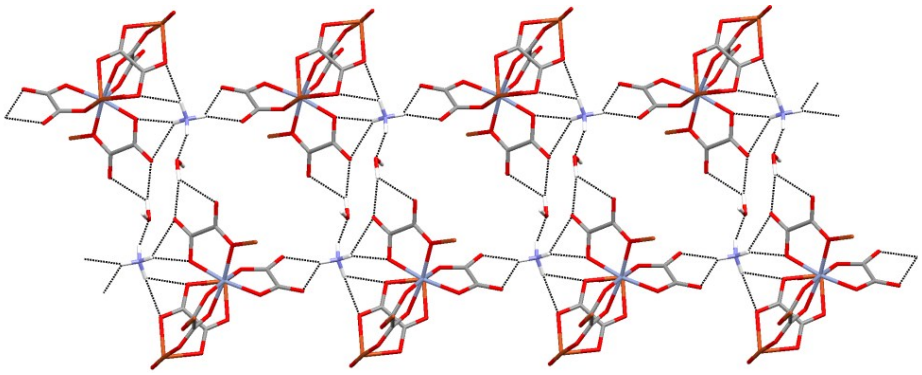


Fig. S4 The ladder-like hydrogen bonding pattern along *b* axis in compound **2**. Molecules of 2,2′-bipyridine are omitted for clarity.

Table S2 Hydrogen-bonding geometry in compounds **1** and **2**

Compound	*D*–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)	Symm. op. on
1	O17–H17A···O11	0.84	2.28	2.9719(19	140	1 – *x*,1 – *y*,1 –
2	N5–H1N···O3	0.94(3)	1.93(3)	2.776(4)	150(4)	x, y, z
	N5–H1N···O4	0.94(3)	2.50(4)	3.220(4)	134(3)	x, y, z
	N5–H2N···O14	0.92(5)	2.43(5)	3.054(4)	125(4)	*x*, –1 + y, z
	N5–H2N···O16	0.92(5)	2.15(5)	3.065(4)	168(5)	*x*, –1 + y, z
	N5–H3N···O9	0.93(5)	2.12(6)	2.962(4)	149(5)	*x*, –1 + y, z
	N5–H3N···O11	0.93(5)	2.32(7)	3.024(5)	132(7)	*x*, –1 + *y*, *z*
	N5–H4N···O17	0.92(5)	2.19(6)	3.076(6)	161(6)	–*x*, –*y*, –*z*
	O17–H17B···O11	0.96(5)	2.04(7)	2.906(5)	149(14)	*x*, *y*, *z*
	O17–H17B···O12	0.96(5)	2.5(3)	3.238(5)	133(1)	*x*, *y*, *z*

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

Cg(*i*)···Cg(*j*)	Cg(*i*)···Cg(*j*) (Å)[b]	*α* (°)[b]	*β* (°)[c]	Cg(*i*)···plane [Cg(*j*)] (Å)	Symmetry operator
(N2→C7)···(C5→C12)	3.707(3)	0.1(2)	18.9	3.506(2)	1 – *x*, 1 – *y*, 2 – *z*
(C5→C12)···(C5→C12)	3.610(3)	0.0(2)	19.6	3.401(3)	*x*, 1 + *y*, *z*
(C5→C12)···(C5→C12)	3.707(3)	0.0(2)	19.3	3.500(2)	1 – *x*, 1 – *y*, 2 – *z*

[a]Cg = center of gravity of the aromatic ring; [b]*α* = angle between the planes of two aromatic rings.
[c]*β* = angle between the Cg···Cg line and the normal to the plane of the first aromatic ring.

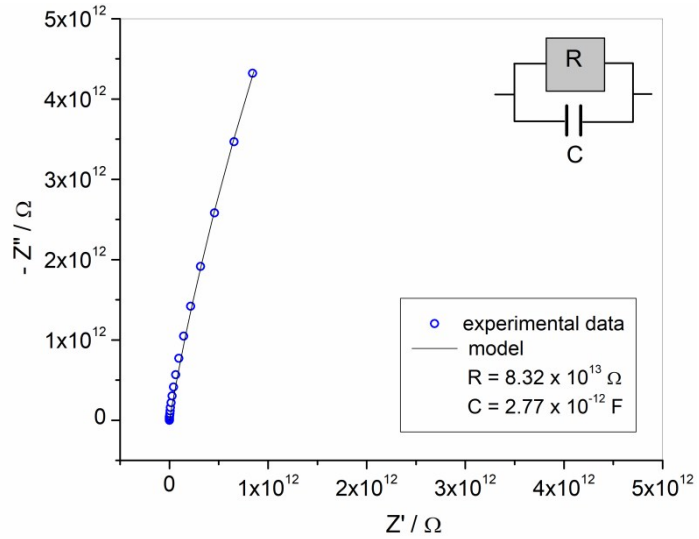


Fig. S5 Complex impedance plot and corresponding equivalent circuit for compound **2** at 20 °C.

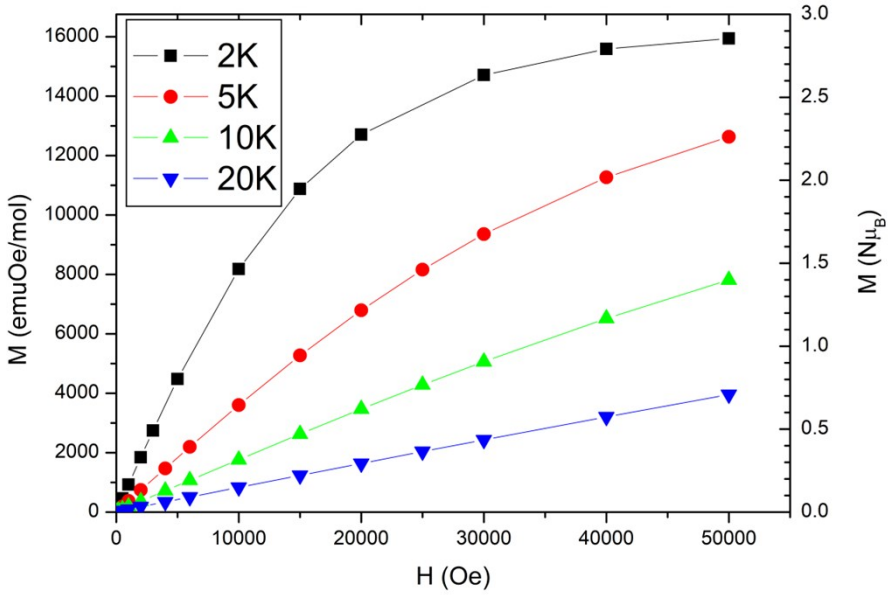


Fig. S6 The *M*(*H*) curves for compound **1** measured at 2, 5, 10 and 20 K.

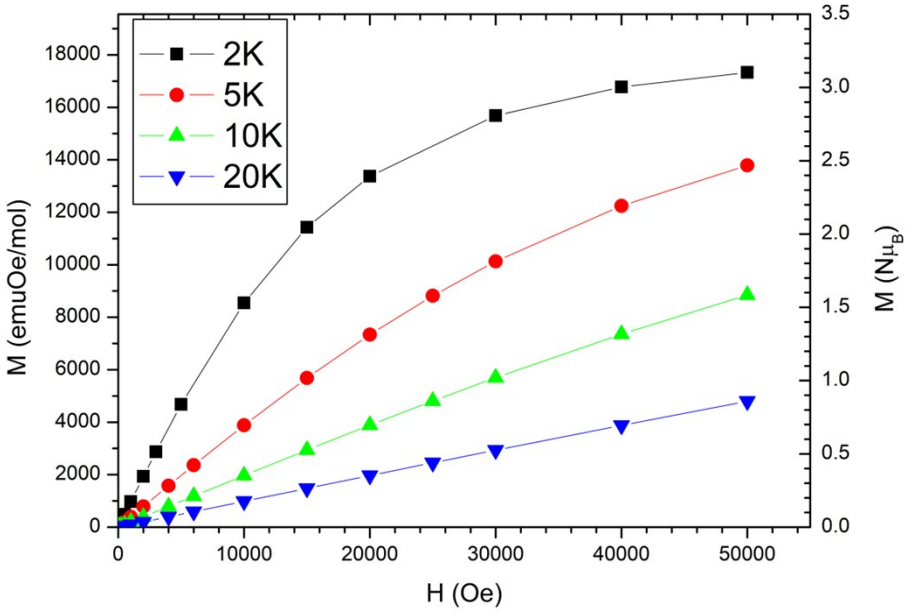


Fig. S7 The *M(H)* curves for compound **2** measured at 2, 5, 10 and 20 K.

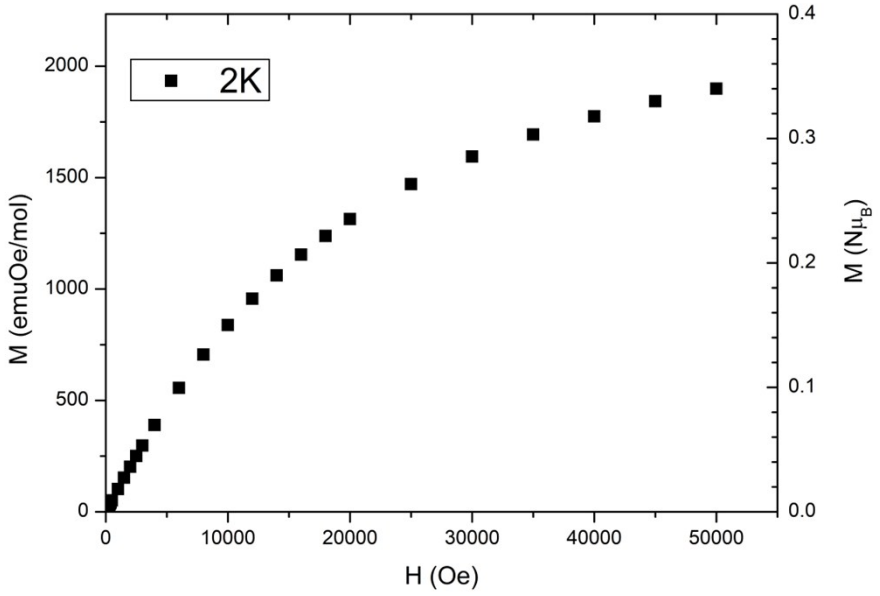


Fig. S8 The *M(H)* curve for compound **3** measured at 2 K.

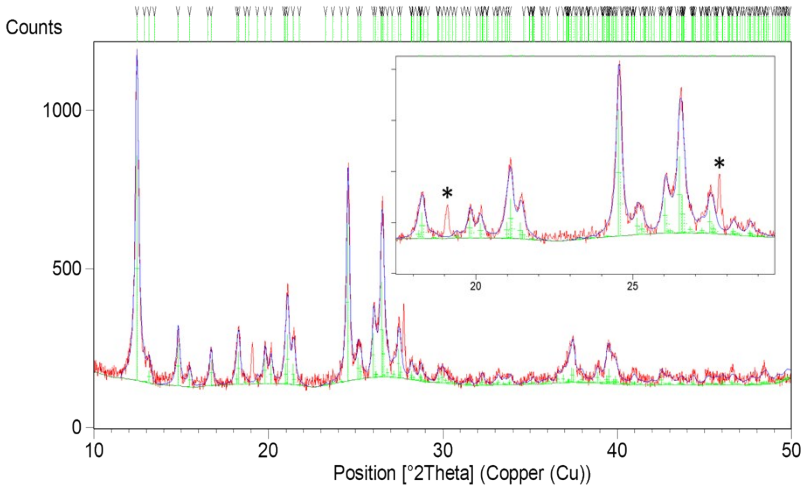


Fig. S9 Graphical results of the final Rietveld refinement for powder sample **3** used for magnetic measurements. The experimental data are given in red, the calculated pattern in blue. The green vertical marks represent the diffraction lines of $[(Cr_2O_7)Cu_2(C_2O_4)(phen)_2]_n$ (**3**). Inset: Diffraction lines of unidentified phases are indicated by asterisks.

Table S4 Selected magneto-structural parameters for oxalate-bridged copper(II) complexes of the type $[Cu(L)(\mu\text{-}C_2O_4)Cu(L)]^{2+}$

L[a]	Donor set	φ[b]	h_{Cu}[c]	$d_{Cu\cdots Cu}$[d]	J[e]	Ref.
bpy	O_2N_2/O_2	4.6	0.11	5.143	–382	3
bpy	O_2N_2/O	3.2	0.16	5.154(1)	–386	4
bpy	O_2N_2/O	12.0	0.18	5.150(1)	–376	4b
bpy	O_2N_2/O	10.4	0.16	5.144(1)	–378	4b
phen	O_2N_2/O	16.9	0.27	5.158(1)	–330	5
bpy	O_2N_2/Cl	16.9	0.40	5.227(2)	–295	6
bpy (**1**)	O_2N_2/O_2	5.88/2.81	0.0737(8)/0.0256(7)	5.1392(14)	–343	This work
bpy (**2**)	O_2N_2/O_2	6.21/2.04	0.0572(5)/0.0248(5)	5.1350(6)	–371	This work
phen (**3**)	O_2N_2/O_2	12.53	0.1373(8)	5.1315(14)	–340 (from DFT)	This work

[a]Abbreviations: bpy = 2,2-bipyridine; phen = 1,10-phenanthroline; [b]Dihedral angle (°) angle between the plane of the oxalate ligand and the mean basal plane; [c]Amount of the out-of-plane displacement of the copper(II) ions (Å); [d]Cu···Cu separation across the bridging oxalate (Å). [e]Magnetic coupling in cm^{-1}.

References

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