Electronic Supplementary Information for

Influence of the metal centres on the exchange interaction in heterometallic complexes with oxalate-bridged cations

Lidija Androš Dubraja,[a] Marijana Jurić,[a] Filip Torić[b] and Damir Pajić[b]

[a]*Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*

[b]*Department of Physics, Faculty of Science, University of Zagreb, Bijenička cesta 32, 10000 Zagreb, Croatia*

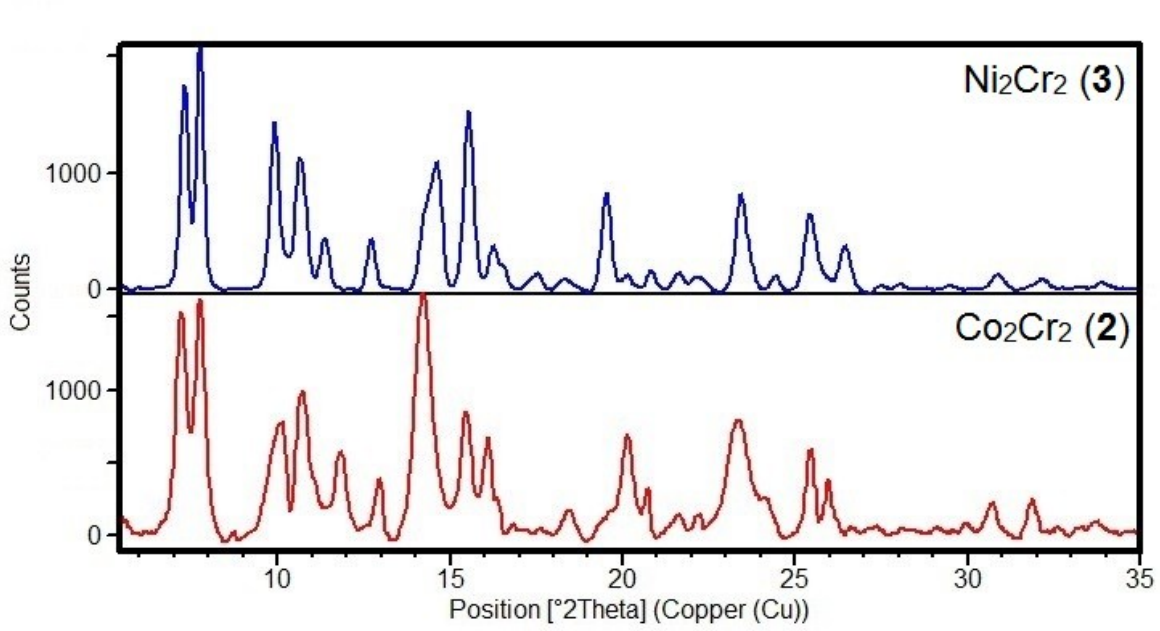

Figure S1 The X-ray powder diffraction patterns of Co_2Cr_2 (**2**) and Ni_2Cr_2 (**3**) were recorded on an Oxford Xcalibur Nova R diffractometer with a micro-focus tube using CuKα radiation. The samples were placed in a 0.3 mm diameter capillary.

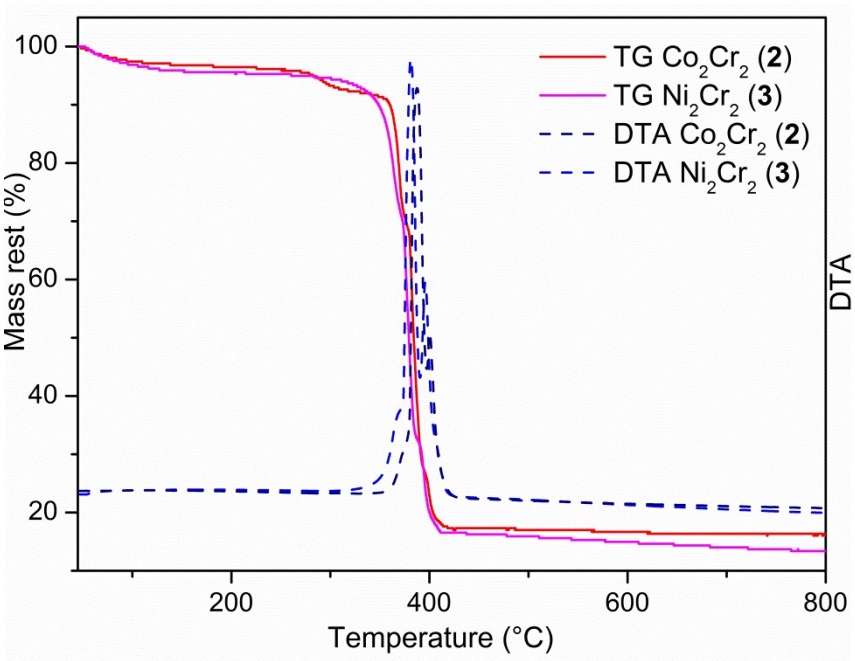

Figure S2 The TG and DTA curves for compounds Co_2Cr_2 (**2**) and Ni_2Cr_2 (**3**) measured in the synthetic air atmosphere

Table S1. Thermoanalytical data for compounds Co_2Cr_2 (**2**) and Ni_2Cr_2 (**3**)

Compound	Δ*t* (°C)	*Mass loss* (%)			*t*(DTA_{max}) (°C)
		exp.	*calc.*	*elimination*	
Co_2Cr_2 (**2**)	60–140	3.81	3.97	$2H_2O$	-
	140–390	59.05	59.56	3phen	387 egzo
	390–600	20.64	19.83	$2.5CO_2$	400 egzo
	residue	16.50	16.64	$CoO + 1/2Cr_2O_3$	-
Ni_2Cr_2 (**3**)	60–150	3.56	3.97	$2H_2O$	-
	150–385	60.52	59.58	3phen	381 egzo
	385–600	18.76	19.84	$2.5CO_2$	396 egzo
	residue	16.16	16.61	$NiO + 1/2Cr_2O_3$	-

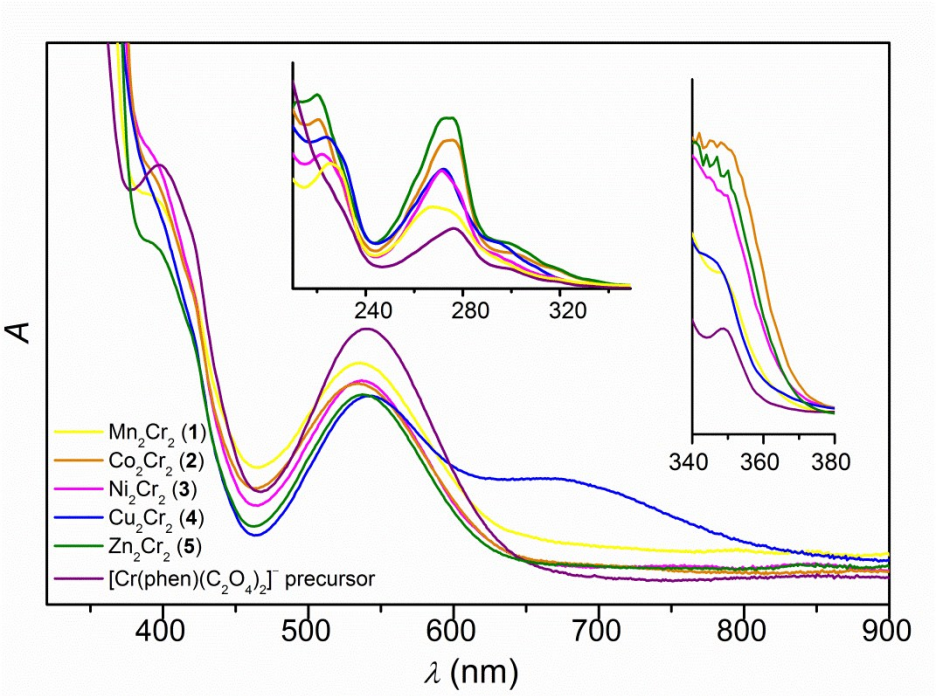

Figure S3. Electronic spectra of compounds **1**–**5** and $[Cr(phen)(C_2O_4)_2]^-$ precursor complex obtained from aqueous solutions for $c(Cr^{3+}) = 1 \times 10^{-3}$ (main plot, visible light region), 1×10^{-4} (right inset, 340–380 nm region) and 1×10^{-5} (left inset; 220–320 nm region) mol dm^{-3}.

Elemental analysis data and absorption bands in the IR spectrum:

Anal. Calcd for $C_{41}H_{28}MnCrN_6O_{12}$; Mn_2Cr_2 (**1**): C, 54.50; H, 3.12; N, 9.30. Found: C, 54.37; H, 3.02; N, 9.11%.
IR (KBr, cm^{-1}): 3446 (m, br), 3061 (w), 2925 (w), 1715 (vs), 1705 (vs), 1681 (vs), 1642 (vs), 1516 (m), 1425 (s), 1376 (m), 1361 (s), 1224 (m), 1145 (w), 1101 (w), 854 (m), 806 (m), 793 (m), 725 (s), 668 (m), 549 (m), 437 (w), 416 (m), 395 (m).

Anal. Calcd for $C_{41}H_{28}CoCrN_6O_{12}$; Co_2Cr_2 (**2**): C, 54.26; H, 3.11; N, 9.26. Found: C, 54.57; H, 3.12; N, 9.01%.
IR (KBr, cm^{-1}): 3446 (m, br), 3061 (w), 2925 (w), 1715 (vs), 1705 (vs), 1681 (vs), 1642 (vs), 1516 (m), 1425 (s), 1376 (m), 1361 (s), 1224 (m), 1145 (w), 1101 (w), 854 (m), 806 (m), 793 (m), 725 (s), 668 (m), 549 (m), 437 (w), 416 (m), 395 (m).

Anal. Calcd for $C_{41}H_{28}NiCrN_6O_{12}$; Ni_2Cr_2 (**3**): C, 54.27; H, 3.11; N, 9.26. Found: C, 54.88; H, 3.07; N, 9.16%.
IR (KBr, cm^{-1}): 3446 (m, br), 3061 (w), 2924 (w), 1714 (vs), 1705 (vs), 1681 (vs), 1639 (vs), 1517 (m), 1426 (s), 1377 (m), 1361 (s), 1224 (m), 1144 (w), 1105 (w), 854 (m), 806 (m), 799 (m), 726 (s), 644 (m), 549 (m), 437 (w), 415 (m), 393 (m).

Anal. Calcd for $C_{41}H_{28}CuCrN_6O_{12}$; Cu_2Cr_2 (**4**): C, 53.98; H, 3.09; N, 9.21. Found: C, 54.41; H, 3.02; N, 9.44%.
IR (KBr, cm^{-1}): 3443 (vs, br), 3058 (w), 2921 (w), 1715 (vs), 1704 (vs), 1680 (vs), 1632 (vs), 1518 (m), 1428 (s), 1376 (m), 1361 (s), 1224 (m), 1144 (w), 1105 (w), 854 (m), 806 (m), 793 (m), 724 (s), 655 (w), 548 (m), 435 (w), 415 (m), 396 (m).

Anal. Calcd for $C_{41}H_{28}ZnCrN_6O_{12}$; Zn_2Cr_2 (**5**): C, 53.87; H, 3.11; N, 9.26. Found: C, 54.21; H, 3.22; N, 9.56%.
IR (KBr, cm^{-1}): 3442 (vs, br), 3058 (w), 2922 (M), 1715 (vs), 1705 (vs), 1680 (vs), 1642 (vs), 1517 (m), 1427 (s), 1383 (m), 1360 (s), 1224 (m), 1144 (w), 1104 (w), 855 (m), 807 (m), 793 (m), 725 (s), 642 (w), 549 (m), 438 (w), 413 (W), 393 (m).

Table S2. Selected absorption bands in the IR spectra of compounds **1**–**5**

Compound	*bidentate oxalate group*			*bis(bidentate) oxalate group*		
	ν_{as}(CO)	ν_s(CO)	δ(OCO)	ν_{as}(CO)	ν_s(CO)	δ(OCO)
Mn_2Cr_2 (**1**)	1715, 1705, 1681	1376	806	1642	1361	793
Co_2Cr_2 (**2**)	1715, 1705, 1681	1376	806	1642	1361	793
Ni_2Cr_2 (**3**)	1714, 1705, 1681	1377	806	1639	1361	799
Cu_2Cr_2 (**4**)	1715, 1704, 1680	1376	806	1632	1361	793
Zn_2Cr_2 (**5**)	1715, 1705, 1680	1383	807	1642	1360	793

Table S3 Selected bond lengths (Å) and angles (°) for the $[\{M(phen)_2\}_2(\mu\text{-}C_2O_4)]^{2+}$ cations in compounds Mn_2Cr_2 (**1**), Co_2Cr_2 (**2**), Cu_2Cr_2 (**4**) and Zn_2Cr_2 (**5**)

	Mn_2Cr_2 (**1**)	Co_2Cr_2 (**2**)	Cu_2Cr_2 (**4**)	Zn_2Cr_2 (**5**)
M1–N1	2.240(5)	2.125(3)	2.023(4)	2.138(3)
M1–N2	2.211(5)	2.118(2)	2.086(2)	2.139(2)
M1–N3	2.231(6)	2.126(3)	2.021(3)	2.134(3)
M1–N4	2.225(5)	2.136(3)	2.228(3)	2.153(3)
M1–O1	2.135(4)	2.093(2)	2.032(3)	2.084(2)
M1–O2^i	2.168(4)[b]	2.105(3)[a]	2.270(3)[b]	2.123(2)[c]
O1–M1–O2	77.43(15)	79.42(7)	77.21(9)	79.38(8)
O1–M1–N1	94.89(16)	96.01(10)	94.29(11)	94.71(10)
O1–M1–N2	161.30(14)	166.74(9)	165.64(9)	165.62(9)
O1–M1–N3	94.82(15)	90.96(10)	91.47(10)	93.27(10)
O1–M1–N4	99.39(17)	96.66(8)	97.23(10)	96.65(9)
O2–M1–N1	99.86(17)	94.93(10)	94.55(11)	96.35(11)
O2–M1–N2	88.82(17)	89.01(8)	89.77(9)	88.94(9)
O2–M1–N3	92.73(17)	93.95(10)	94.15(10)	93.29(10)
O2–M1–N4	166.70(17)	171.20(9)	170.94(9)	169.91(10)
N1–M1–N2	74.82(17)	78.39(10)	80.57(11)	78.13(11)
N1–M1–N3	165.52(17)	169.58(10)	170.44(11)	168.37(10)
N1–M1–N4	93.3(2)	93.31(11)	92.98(12)	93.20(11
N2–M1–N3	98.48(17)	96.34(10)	95.54(11)	95.81(11)
N2–M1–N4	96.80(18)	95.67(9)	96.43(10)	96.20(10)
N3–M1–N4	74.6(2)	78.16(11)	78.72(11)	77.46(11)

[a] Symmetry operator (*i*) 2 – *x*, – *y*, 1 – *z*. [b] Symmetry operator: *i*) 1 – *x*, – *y*, 2 – *z*. [c] Symmetry operator: *i*) 1 – *x*, 2– *y*, 1 – *z*.

Table S4 Selected bond lengths (Å) and angles (°) for the $[Cr(phen)(C_2O_4)_2]^-$ anions in compounds Mn_2Cr_2 (**1**), Co_2Cr_2 (**2**), Cu_2Cr_2 (**4**) and Zn_2Cr_2 (**5**)

	Mn_2Cr_2 (**1**)	Co_2Cr_2 (**2**)	Cu_2Cr_2 (**4**)	Zn_2Cr_2 (**5**)
Cr1–N5	2.066(4)	2.076(2)	2.074(3)	2.077(2)
Cr1–N6	2.080(5)	2.079(3)	2.078(3)	2.085(3)
Cr1–O3	1.953(5)	1.952(2)	1.956(3)	1.952(2)
Cr1–O6	1.945(4)	1.961(3)	1.960(2)	1.961(3)
Cr1–O7	1.951(4)	1.946(2)	1.950(2)	1.952(2)
Cr1–O10	1.939(4)	1.951(3)	1.949(2)	1.954(3)
O3–Cr1–O6	82.63(16)	82.69(9)	82.71(9)	82.67(9)
O3–Cr1–O7	96.68(15)	96.06(10)	96.16(10)	95.81(10)
O3–Cr1–O10	95.09(17)	95.09(10)	94.98(10)	94.96(10)
O3–Cr1–N5	91.89(15)	92.05(9)	92.02(9)	92.15(9)
O3–Cr1–N6	169.17(16)	168.81(10)	168.91(10)	169.10(9)
O6–Cr1–O7	93.29(17)	93.95(10)	93.50(10)	93.96(10)
O6–Cr1–O10	176.11(13)	176.05(9)	175.75(9)	175.77(9)
O6–Cr1–N5	93.62(16)	93.82(9)	94.17(9)	93.80(9)
O6–Cr1–N6	90.81(16)	89.93(9)	90.12(9)	90.20(9)
O7–Cr1–O10	83.83(16)	83.01(9)	83.18(9)	82.77(9)
O7–Cr1–N5	169.62(15)	169.41(10)	169.43(9)	169.52(10)
O7–Cr1–N6	92.28(15)	92.82(10)	92.71(10)	92.88(10)
O10–Cr1–N5	89.59(16)	89.52(9)	89.47(9)	89.78(9)
O10–Cr1–N6	91.91(16)	92.73(10)	92.68(10)	92.64(10)
N5–Cr1–N6	79.89(15)	80.01(10)	80.02(9)	80.07(9)

Table S5 Geometric parameters of the aromatic stacking interactions for compounds Mn_2Cr_2 (**1**), Co_2Cr_2 (**2**), Cu_2Cr_2 (**4**) and Zn_2Cr_2 (**5**)

Compound	Cg(*i*)···Cg(*j*)	Cg(*i*)···Cg(*j*)/Å[a]	*α*/°[b]	*β*/°[c]	Cg(*i*)···plane [Cg(*j*)]/Å[d]	Symmetry operator
Mn_2Cr_2 (**1**)	(N2→C11)···(N2→C11)	3.610(5)	0	19.0	3.414(2)	1 – *x*, –*y*, 1 – *z*
	(N6→C35)···(C4→C12)	3.773(6)	19.0(3)	7.8	3.737(2)	*x*, –1 + *y*, *z*
	(N5→C36)···(C28→C36)	3.589(5)	2.8(2)	20.4	3.3646(19)	1 – *x*, 1 – *y*, 2 – *z*
	(C28→C36)···(C28→C36)	3.670(5)	0	23.0	3.3785(19)	1 – *x*, 1 – *y*, 2 – *z*
Co_2Cr_2 (**2**)	(N2→C11)···(N2→C11)	3.646(2)	0.03(18)	18.6	3.4562(15)	2 – *x*, 1 – *y*, 1 – *z*
	(N6→C35)···(C4→C12)	3.795(2)	17.6(2)	22.5	3.7294(14)	2 – *x*, 1 – *y*, 1 – *z*
	(N5→C36)···(C28→C36)	3.674(2)	3.07(16)	23.8	3.3612(13)	2 – *x*, 2 – *y*, –*z*
	(C28→C36)···(C28→C36)	3.6527(19)	0.03(16)	20.1	3.4298(14)	2 – *x*, 2 – *y*, –*z*
Cu_2Cr_2 (**4**)	(N2→C11)···(N2→C11)	3.661(3)	0	18.1	3.4790(15)	1 – *x*, –*y*, 1 – *z*
	(N6→C35)···(C4→C12)	3.795(3)	17.1(2)	23.3	3.7169(13)	*x*, 1 + *y*, *z*
	(N5→C36)···(C28→C36)	3.680(2)	3.06(14)	21.1	3.3688(12)	1 – *x*, 1 – *y*, 2 – *z*
	(C28→C36)···(C28→C36)	3.647(2)	0.00	19.6	3.4364(11)	1 – *x*, 1 – *y*, 2 – *z*
Zn_2Cr_2 (**5**)	(N2→C11)···(N2→C11)	3.672(3)	0.00(19)	18.9	3.4753(16)	1 – *x*, 1 – *y*, 1 –*z*
	(N6→C35)···(C4→C12)	3.776(3)	16.2(2)	22.1	3.7036(13)	*x*, *y*, *z*
	(N5→C36)···(C28→C36)	3.676(2)	2.99(14)	21.2	3.3630(12)	1 – *x*, 2 – *y*, –*z*
	(C28→C36)···(C28→C36)	3.656(2)	0.00(13)	20.3	3.4291(12)	1 – *x*, 2 – *y*, –*z*

[a] Cg = centre 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.

Table S6 Hydrogen-bonding geometry in compounds Mn_2Cr_2 (**1**), Co_2Cr_2 (**2**), Cu_2Cr_2 (**4**) and Zn_2Cr_2 (**5**). Interatomic distances involving the water molecules without located hydrogen atoms are given. For the disordered water molecules only position 'A' is included.

Compound	*D*−H···*A*	*D*−H/Å	H···*A*/Å	*D*···*A*/Å	*D*−H···*A*/°	Symm. op. on *A*
Mn_2Cr_2 (**1**)	O11−H11A···O5	0.85(12)	2.03(13)	2.877(9)	176(18)	*x*, *y*, *z*
	O11−H11B···O8	0.85(8)	2.07(9)	2.904(10)	169(10)	2 – *x*, 1 – *y*, 2 – *z*
	O12A ···O9			2.993(16)		2 – *x*, 1 – *y*, 1 – *z*
	O12A ···O3			3.133(16)		*x*, *y*, *z*
Co_2Cr_2 (**2**)	O11−H11A···O8	0.86(10)	2.15(6)	2.975(6)	160(13)	2 – *x*, 1 – *y*, 1 – *z*
	O11−H11B···O5	0.87(11)	2.18(13)	2.903(7)	141(15)	–1 + *x*, –1 + *y*, 1 + *z*
	O12A−H12A···O9	0.9(2)	1.97(16)	2.824(15)	177(1)	3 – *x*, 1 – *y*, – *z*
	O12A−H12B···O3	0.9(2)	2.6(2)	3.055(14)	150(1)	*x*, *y*, *z*
Cu_2Cr_2 (**4**)	O11−H11A···O5	0.85(18)	2.1(2)	2.896(6)	164(1)	*x, y, z*
	O11−H11B···O8	0.86(13)	2.15(14)	2.957(7)	157(1)	2 – *x*, 1 – *y*, 2 –*z*
	O12A···O9			2.833(8)		2 – *x*, 1 – *y*, 1 –*z*
	O12A···O3			3.081(8)		*x*, *y*, *z*
Zn_2Cr_2 (**5**)	O11−H11A···O5	0.87(10)	2.40(13)	2.899(8)	117(8)	1 – *x*, 2 – *y*, –*z*
	O11−H11B···O8	0.86(8)	2.11(7)	2.926(7)	158(13)	–1 + *x*, *y*, *z*
	O12a···O9			2.876(11)		2 – *x*, 1 – *y*, 1 – *z*
	O12a···O3			3.026(11)		*x*, *y*, 1 + *z*