Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Informations

For

Syntheses, crystal structures, magnetic properties and ESI-MS studies of a series of trinuclear $Cu^{II}M^{II}Cu^{II}$ compounds (M = Cu, Ni, Co, Fe, Mn, Zn)

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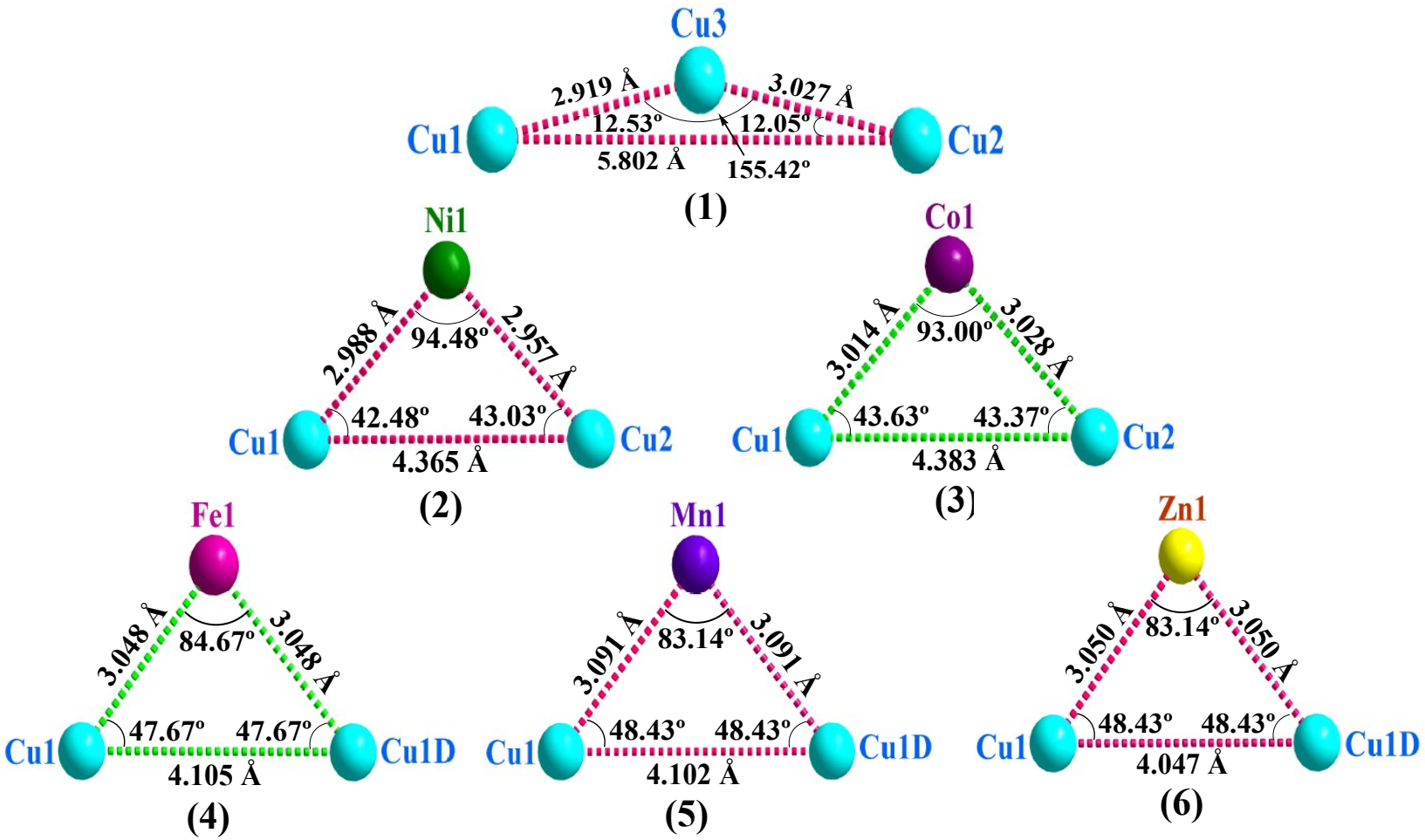


Scheme S1 The triangular arrangement of the three metal ions in all of **1**–**6**; isosceles in **4**–**6** and closely isosceles in **1**–**3**.

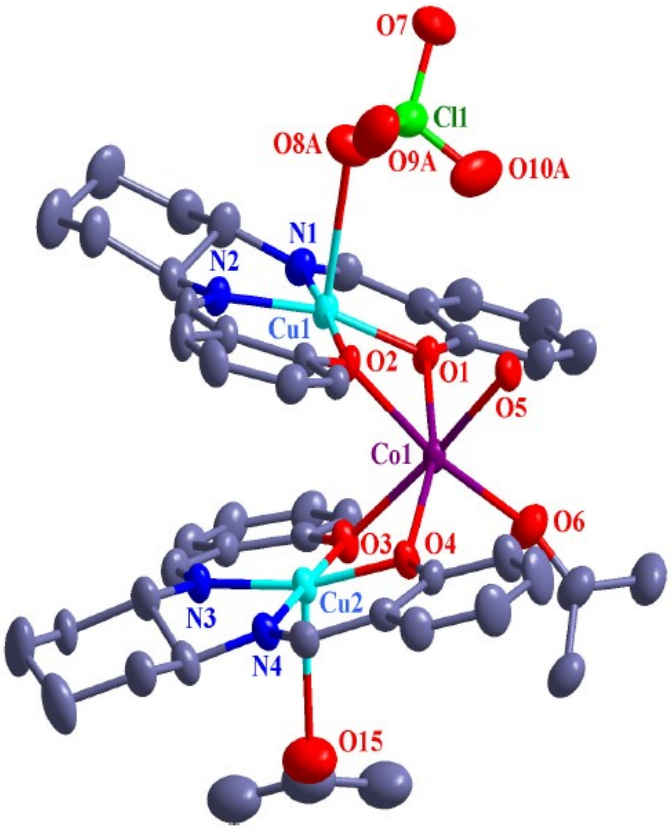


Fig. S1 ORTEP drawing (ellipsoid probability at 30%) of the structure of $[\{Cu^{II}L(ClO_4)\}\{Co^{II}(CH_3COCH_3)(H_2O)\}\{Cu^{II}L(CH_3COCH_3\}]ClO_4$ (**3**). All hydrogen atoms, and one perchlorate anion, are omitted for clarity.

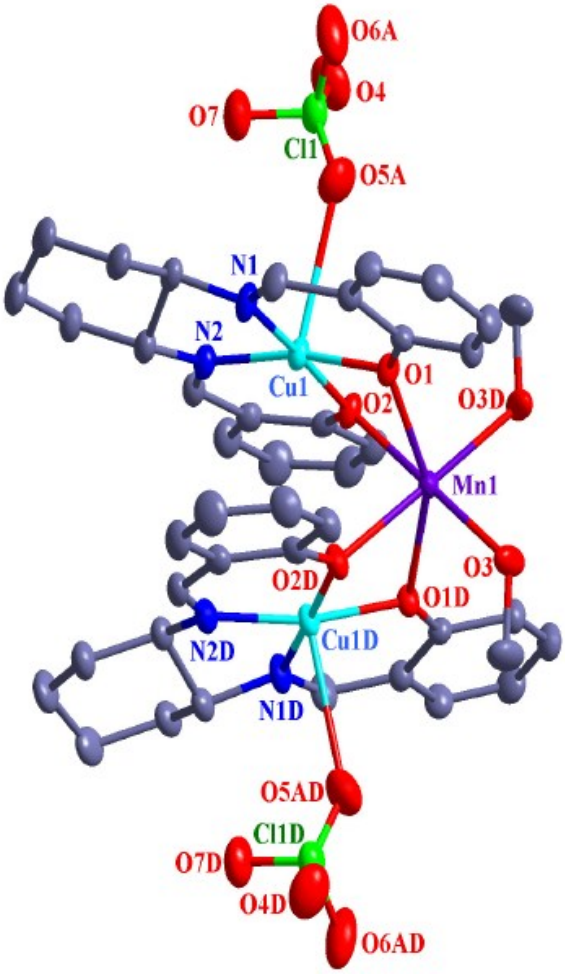


Fig. S2 ORTEP drawing (ellipsoid probability at 30%) of the structure of $[\{Cu^{II}L(ClO_4)\}_2Mn^{II}(CH_3OH)_2]$ (**5**). All hydrogen atoms are omitted for clarity. Symmetry code: D, 2–x, y, 0.5–z.

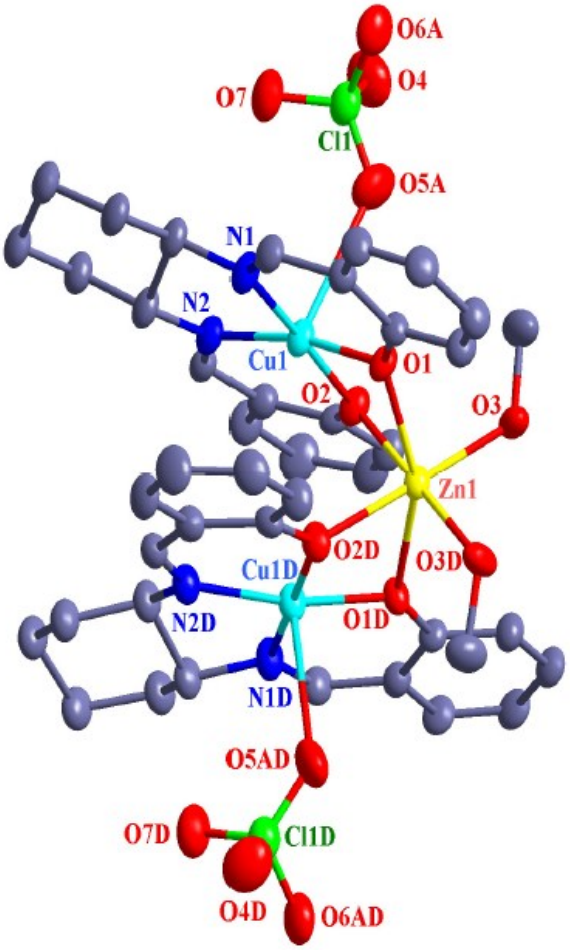


Fig. S3 ORTEP drawing (ellipsoid probability at 30%) of the structure of $[\{Cu^{II}L(ClO_4)\}_2Zn^{II}(CH_3OH)_2]$ (**6**). All hydrogen atoms are omitted for clarity. Symmetry code: D, 2–x, y, 0.5–z.

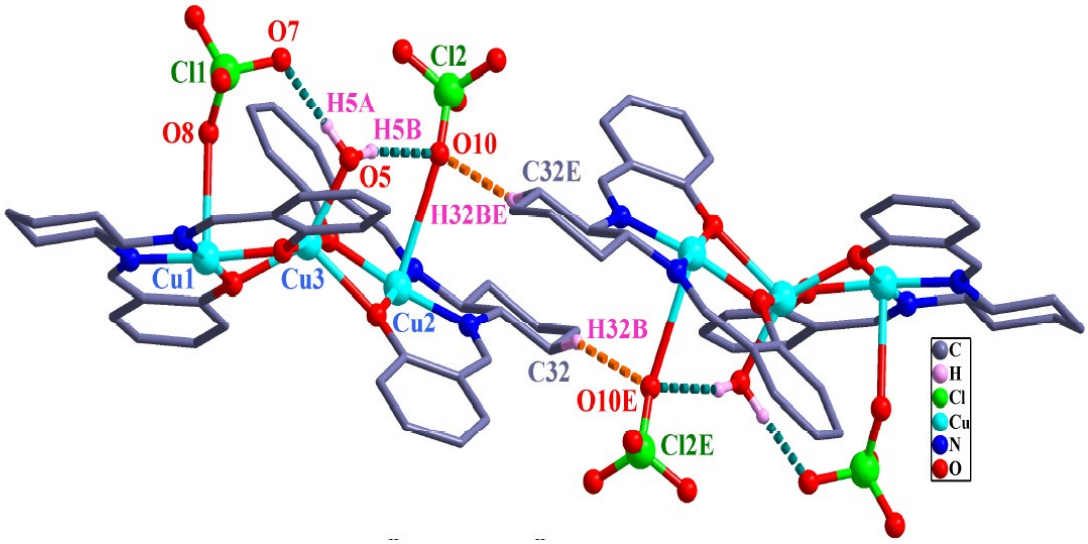


Fig. S4 Perspective view of $[\{Cu^{II}L(ClO_4)\}_2Cu^{II}(H_2O)]\cdot 2H_2O$ (**1**), showing the dimer-of-trinuclear type self-assembly. Only those hydrogen atoms which participate in hydrogen bonding interactions are shown. Symmetry: E, 1–x, 2–y, 1–z.

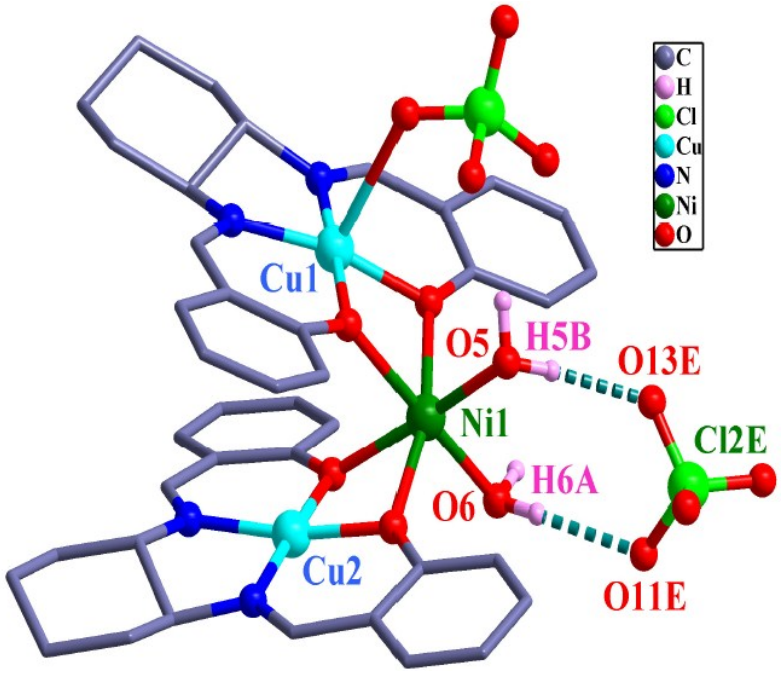


Fig. S5 Perspective view of $[\{Cu^{II}L(ClO_4)\}\{Ni^{II}(H_2O)_2\}\{Cu^{II}L\}]ClO_4\cdot CH_3COCH_3$ (**2**), showing the hydrogen bonding interactions. Only those hydrogen atoms which participate in hydrogen bonding interactions are shown. Symmetry: E, 1–x, y, z.

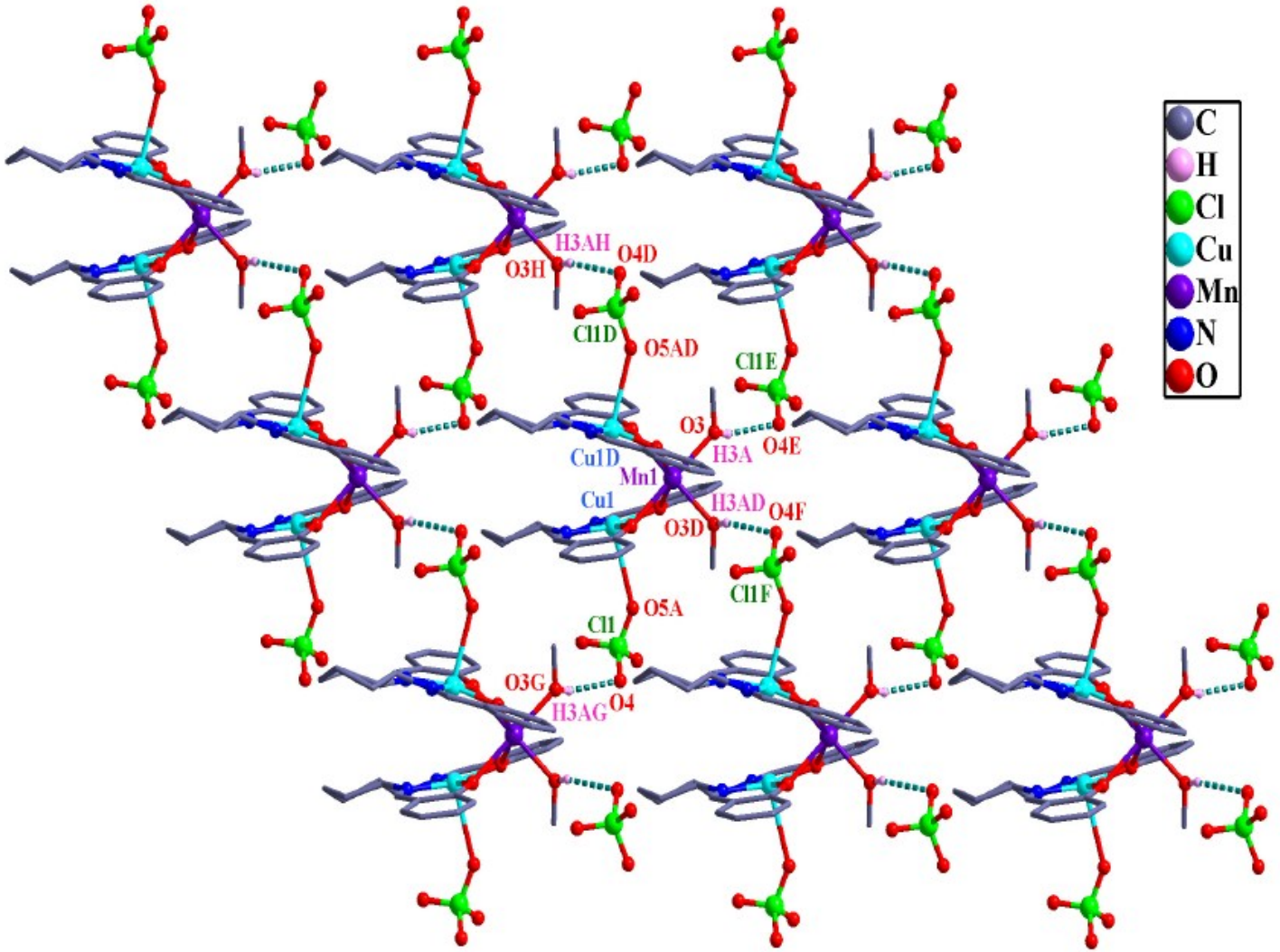


Fig. S6 Perspective view of the two–dimensional self-assembly in the crystallographic *ab* plane of $[\{Cu^{II}L(ClO_4)\}_2Mn^{II}(CH_3OH)_2]$ (**5**). Only the hydrogen atoms participating in hydrogen bonding interactions are shown. Symmetry: D, 2–x, y, 0.5–z; E, 0.5+x, –0.5+y, z; F, 1.5–x, –0.5+y, 0.5–z; G, –0.5+x, 0.5+y, z; H, 2.5–x, 0.5+y, 0.5–z.

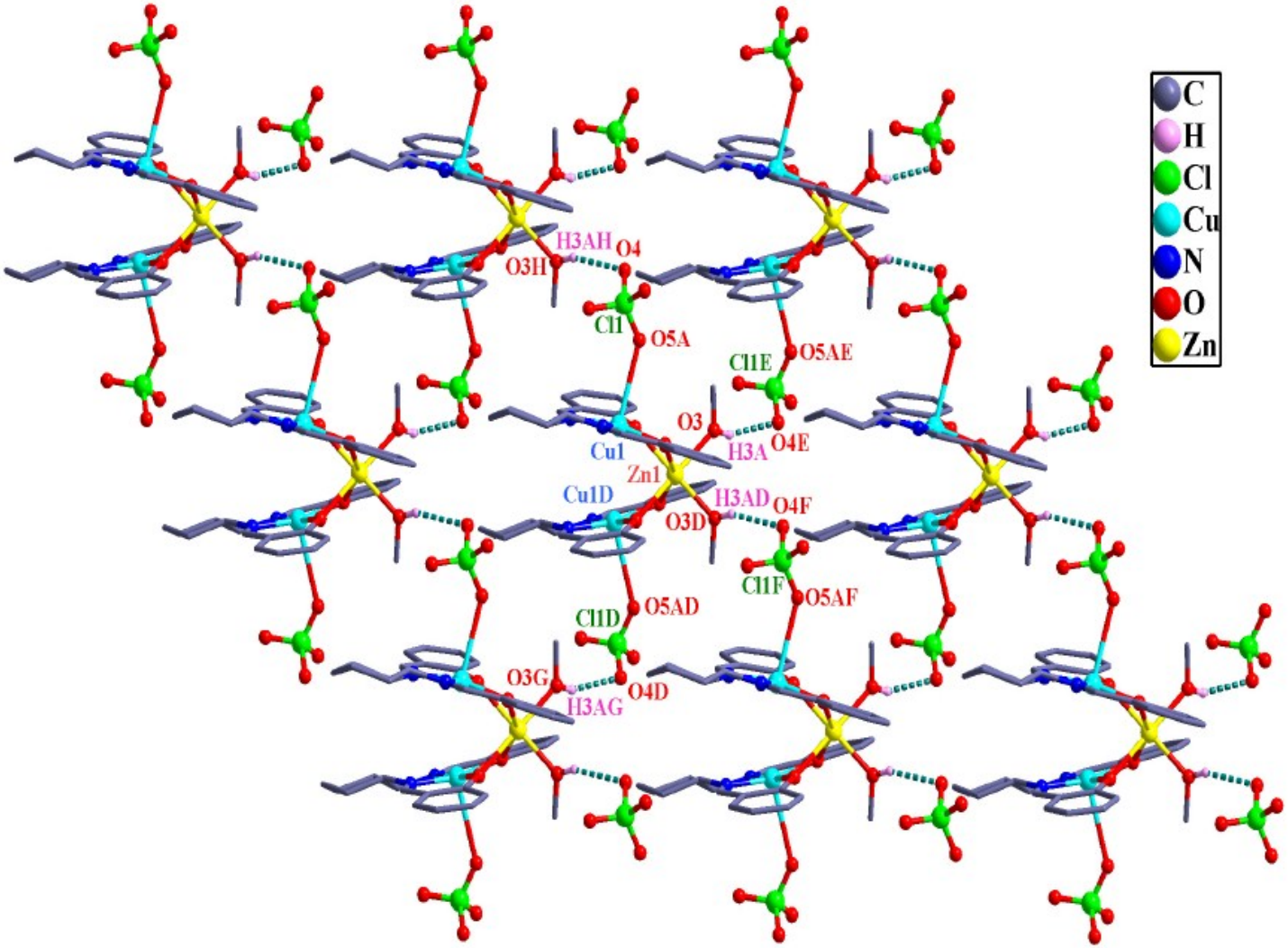


Fig. S7 Perspective view of the two–dimensional self-assembly in the crystallographic *ab* plane of $[\{Cu^{II}L(ClO_4)\}_2Zn^{II}(CH_3OH)_2]$ (**6**). Only the hydrogen atoms participating in hydrogen bonding interactions are shown. Symmetry: D, 2–x, y, 0.5–z; E, 1.5–x, –0.5+y, 0.5–z; F, 0.5+x, –0.5+y, z; G, 0.5+x, 0.5+y, z; H, 1.5–x, 0.5+y, 0.5–z.

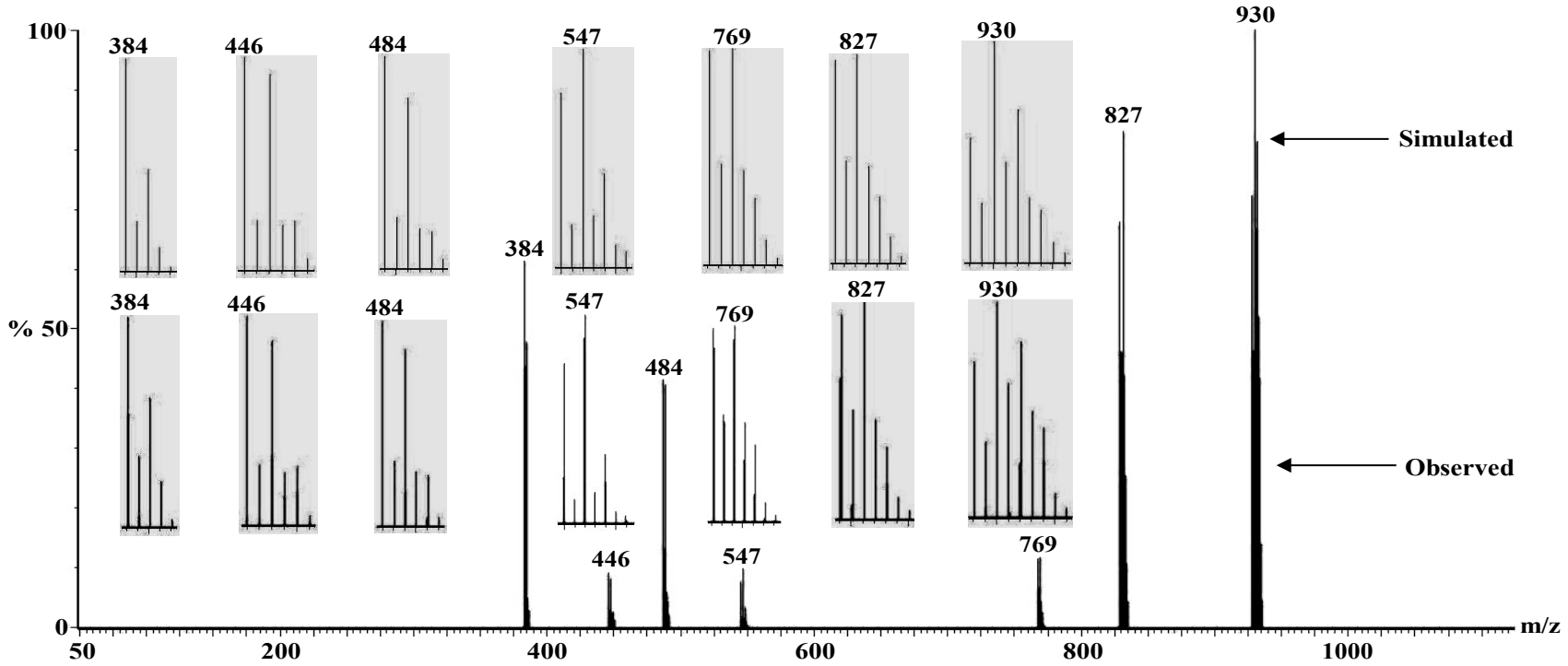


Fig. S8 Electrospray ionization mass spectrum in positive mode (ESI-MS positive) of $[\{Cu^{II}L(ClO_4)\}_2Cu^{II}(H_2O)]\cdot 2H_2O$ (**1**) in methanol, showing observed and simulated isotopic distribution patterns.

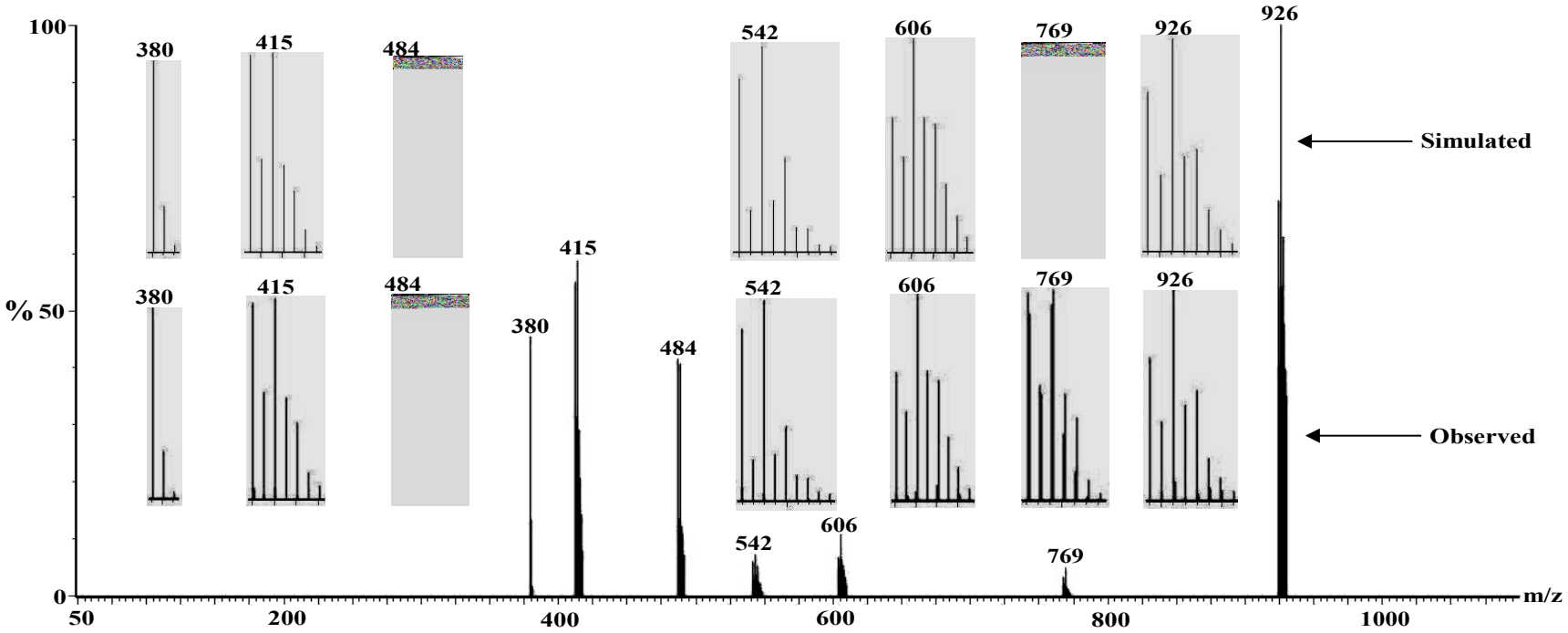


Fig. S9 Electrospray ionization mass spectrum in positive mode (ESI-MS positive) of $[\{Cu^{II}L(ClO_4)\}\{Co^{II}(CH_3COCH_3)(H_2O)\}\{Cu^{II}L(CH_3COCH_3\}]ClO_4$ (**3**) in acetonitrile, showing observed and simulated isotopic distribution patterns.

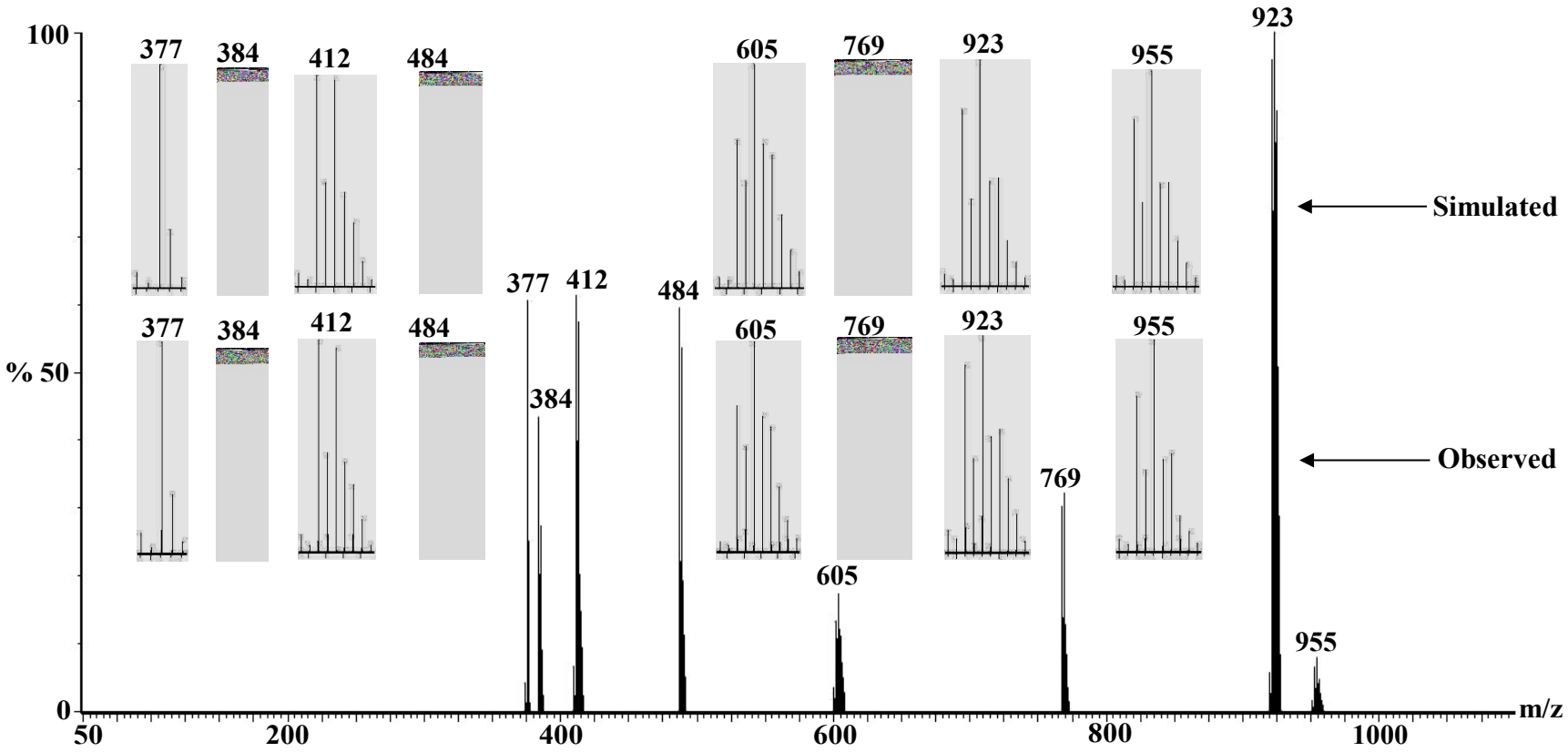


Fig. S10 Electrospray ionization mass spectrum in positive mode (ESI-MS positive) of $[\{Cu^{II}L(ClO_4)\}_2Fe^{II}(CH_3OH)_2]$ (**4**) in acetonitrile, showing observed and simulated isotopic distribution patterns.

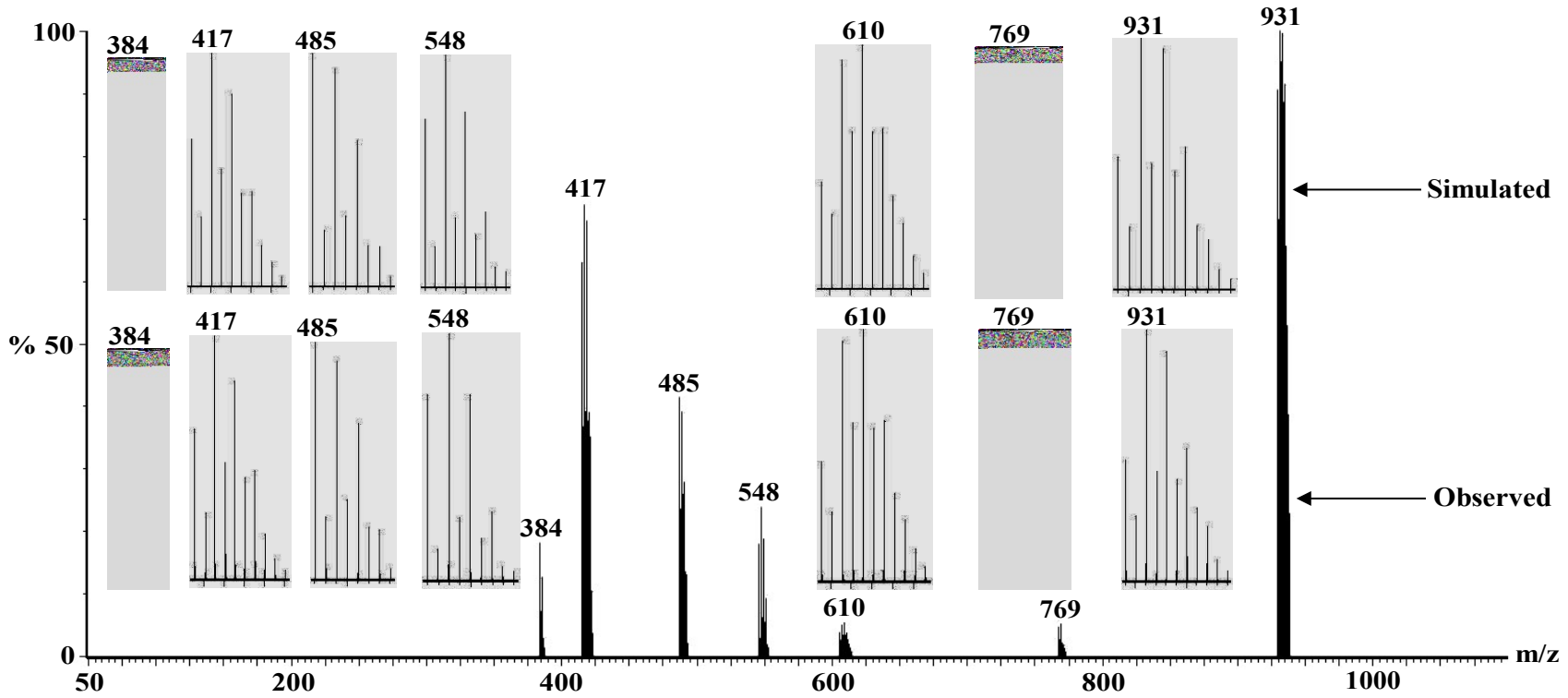


Fig. S11 Electrospray ionization mass spectrum in positive mode (ESI-MS positive) of $[\{Cu^{II}L(ClO_4)\}_2Zn^{II}(CH_3OH)_2]$ (**6**) in acetonitrile, showing observed and simulated isotopic distribution patterns.

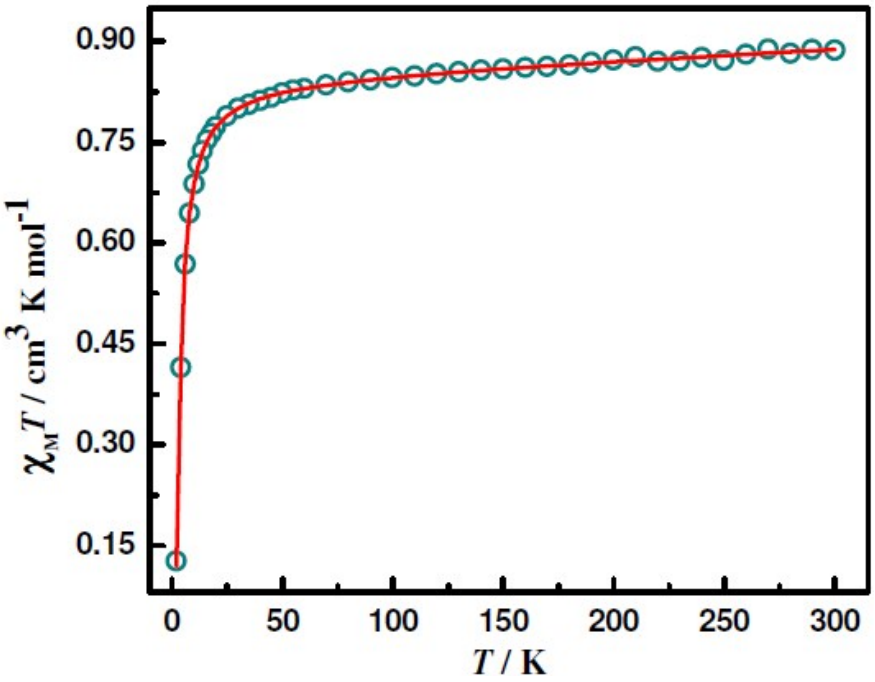


Fig. S12 Fitting of $\chi_M T$ versus T of [{$Cu^{II}L(ClO_4)$}$_2$$Zn^{II}(CH_3OH)_2$] (**6**) between 2 and 300 K. The experimental data are shown in symbols and the solid lines correspond to the fitted values.

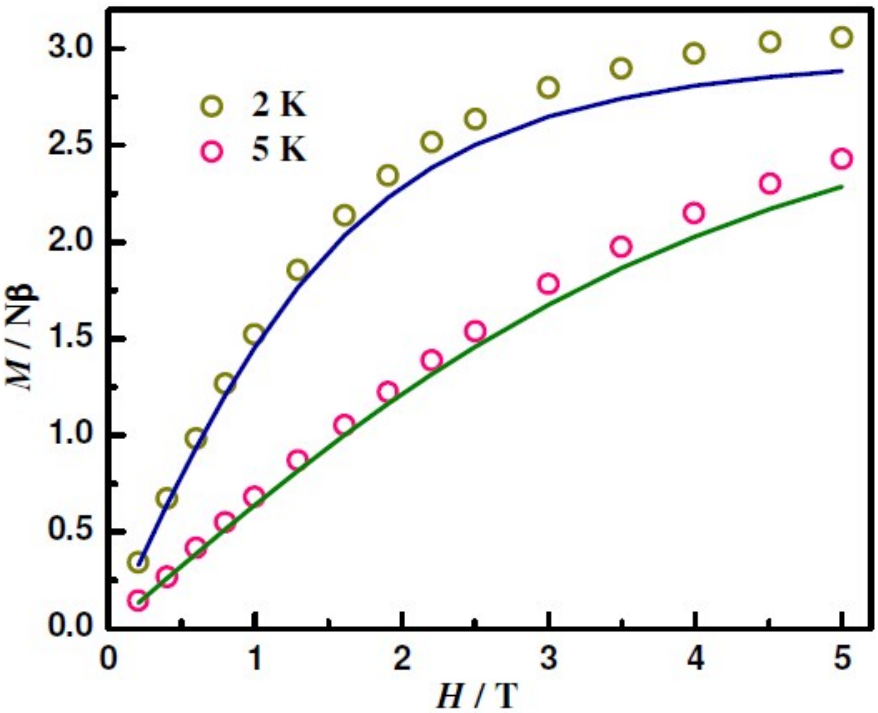


Fig. S13 Magnetization of [{$Cu^{II}L(ClO_4)$}$_2$$Mn^{II}(CH_3OH)_2$] (**5**) at the indicated temperatures. The symbols are the experimental data, while the solid lines represent the fitted curves.

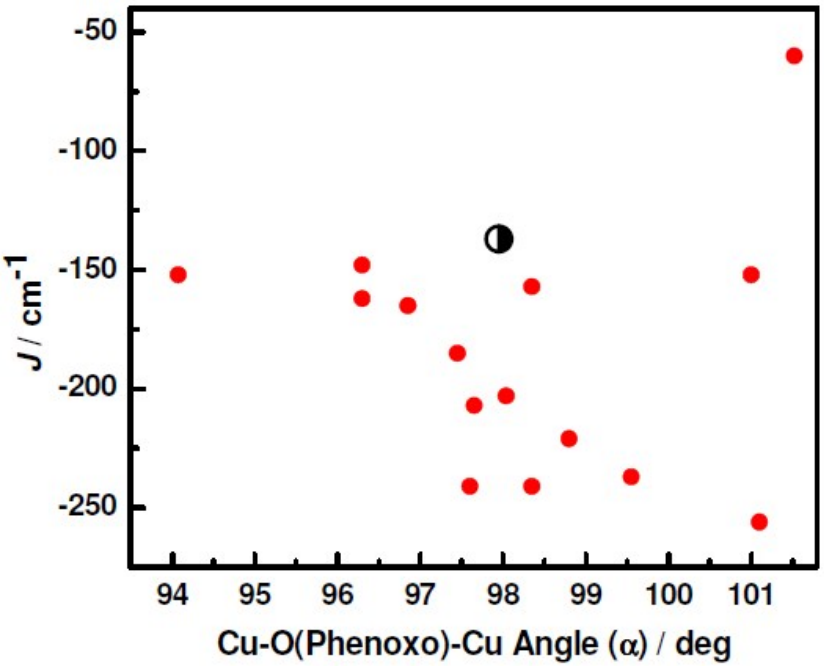


Fig. S14 *J* versus Cu–O(Phenoxo)–Cu bridge angle (α) in the trinuclear $Cu^{II}Cu^{II}Cu^{II}$ compounds where the two copper(II) centres in a $Cu^{II}\cdots Cu^{II}$ pair are bridged by solely bis(μ_2–phenoxo) moiety (Table S5): No straightforward correlation is possible. Red filled circles: Data of previous compounds. Black-white half-filled circle: Data of compound **1**.

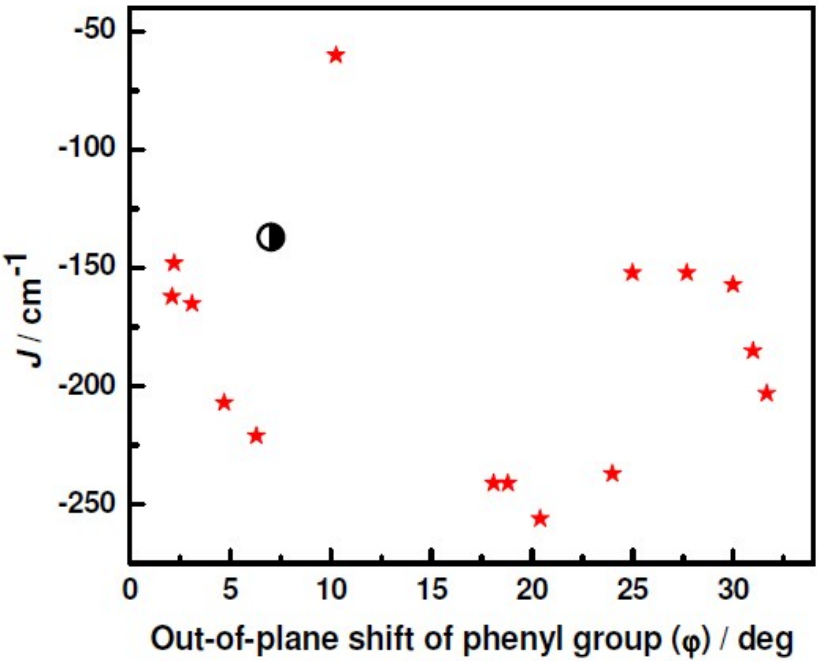


Fig. S15 *J* versus Out–of–plane shift of phenyl group (φ) in the trinuclear $Cu^{II}Cu^{II}Cu^{II}$ compounds where the two copper(II) centres in a $Cu^{II}\cdots Cu^{II}$ pair are bridged by solely bis(μ_2–phenoxo) moiety (Table S5): No straightforward correlation is possible. Red filled stars: Data of previous compounds. Black-white half-filled circle: Data of compound **1**.

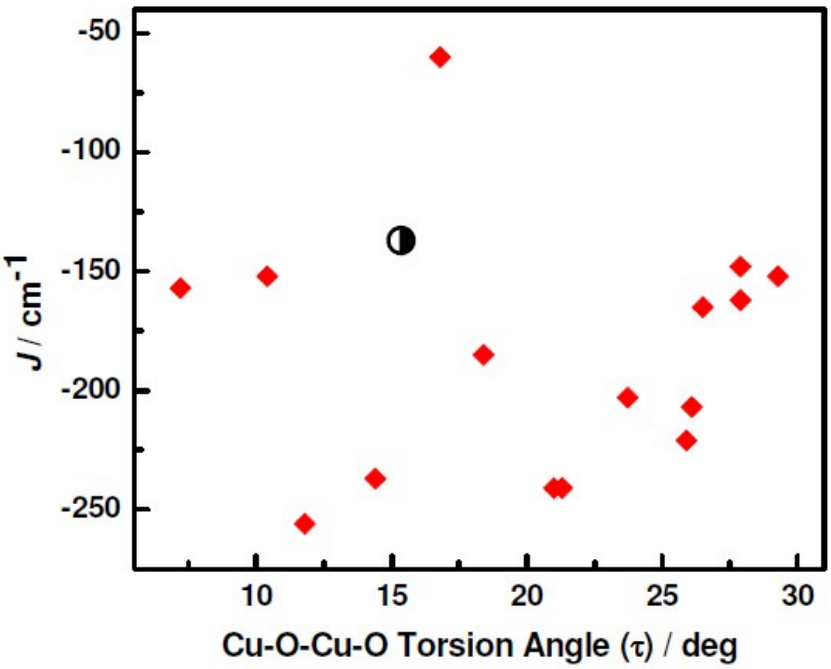


Fig. S16 *J* versus Cu–O–Cu–O torsion angle (τ) in the trinuclear $Cu^{II}Cu^{II}Cu^{II}$ compounds where the two copper(II) centres in a $Cu^{II}\cdots Cu^{II}$ pair are bridged by solely bis(μ_2–phenoxo) moiety (Table S5): No straightforward correlation is possible. Red filled squares: Data of previous compounds. Black-white half-filled circle: Data of compound **1**.

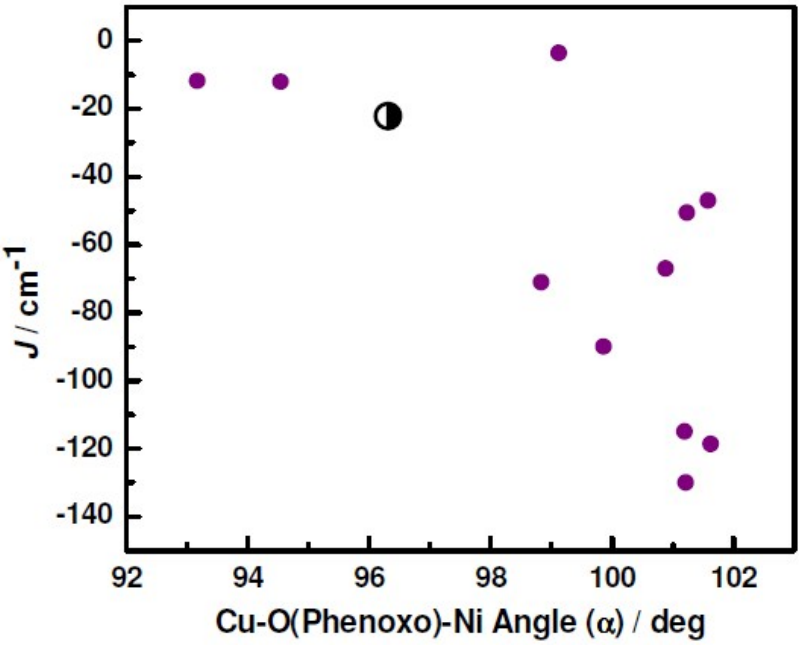


Fig. S17 *J* versus Cu–O(Phenoxo)–Ni bridge angle (α) in the compounds where copper(II) and nickel(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S6): No straightforward correlation is possible. Violet filled circles: Data of previous compounds. Black-white half-filled circle: Data of compound **2**.

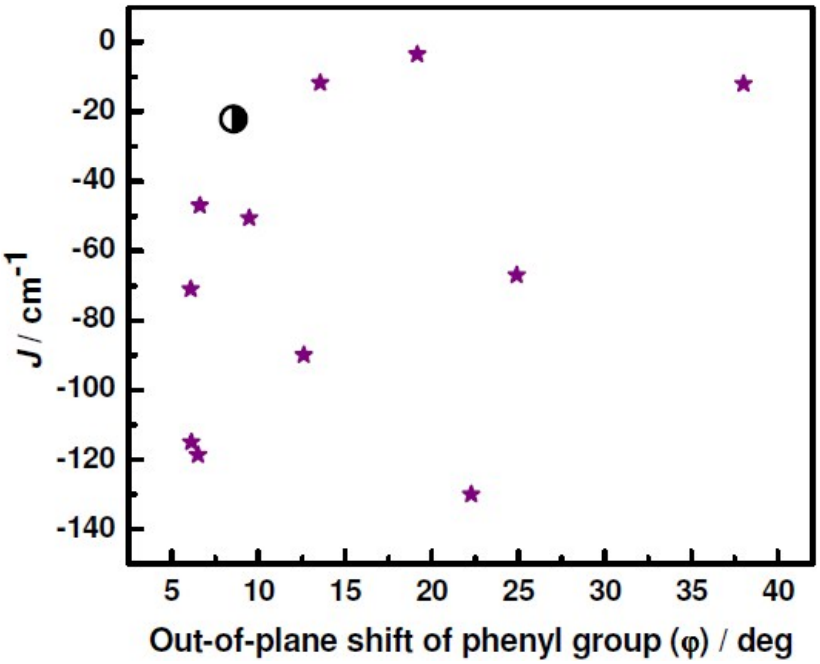


Fig. S18 *J* versus Out–of–plane shift of phenyl group (φ) in the compounds where copper(II) and nickel(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S6): No straightforward correlation is possible. Violet filled stars: Data of previous compounds. Black-white half-filled circle: Data of compound **2**.

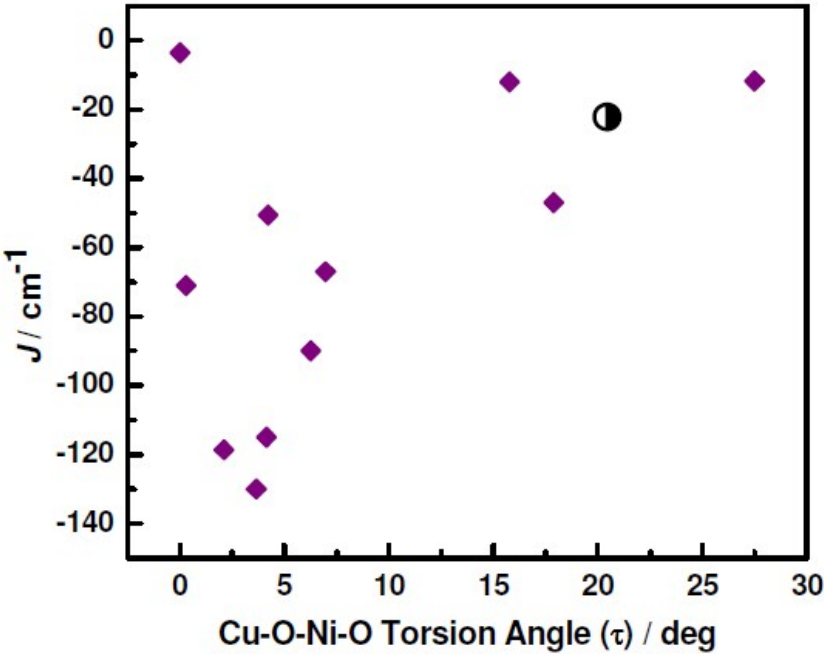


Fig. S19 *J* versus Cu–O–Ni–O torsion angle (τ) in the compounds where copper(II) and nickel(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S6): No straightforward correlation is possible. Violet filled squares: Data of previous compounds. Black-white half-filled circle: Data of compound **2**.

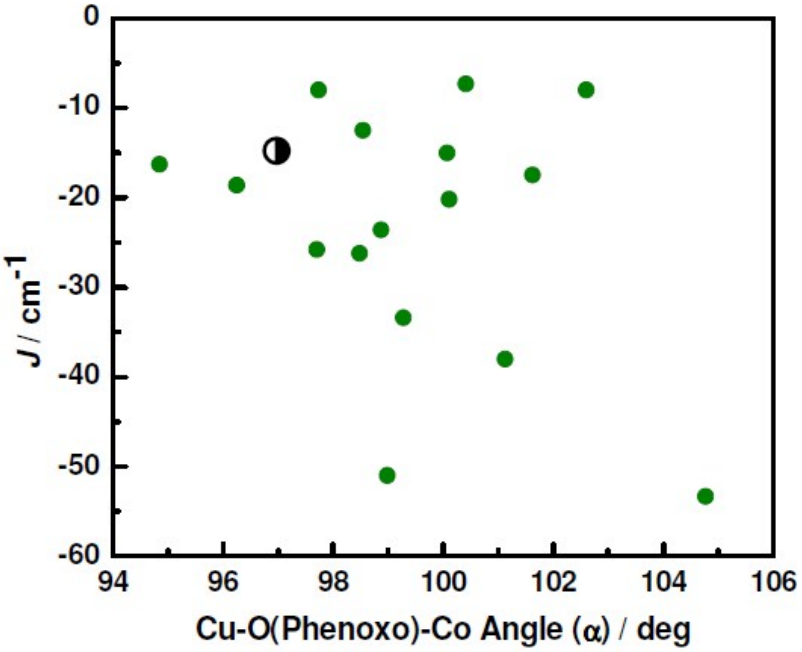


Fig. S20 *J* versus Cu–O(Phenoxo)–Co bridge angle (α) in the compounds where copper(II) and cobalt(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S7): No straightforward correlation is possible. Green filled circles: Data of previous compounds. Black-white half-filled circle: Data of compound **3**.

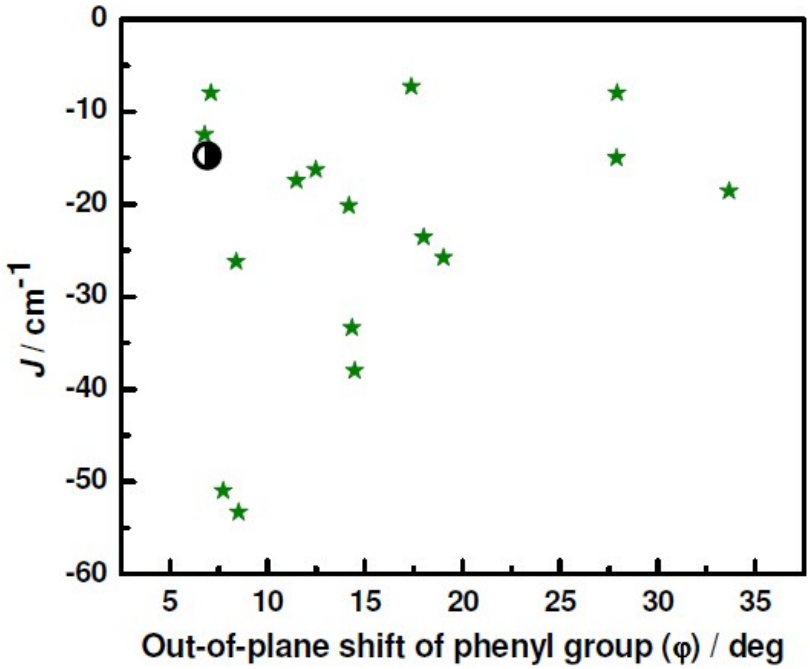


Fig. S21 *J* versus Out–of–plane shift of phenyl group (φ) in the compounds where copper(II) and cobalt(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S7): No straightforward correlation is possible. Green filled stars: Data of previous compounds. Black-white half-filled circle: Data of compound **3**.

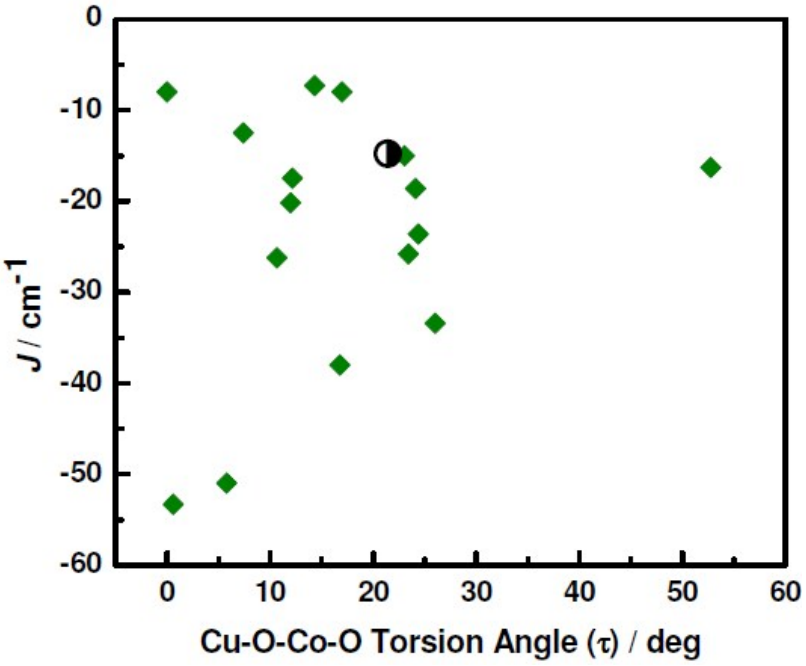


Fig. S22 *J* versus Cu–O–Co–O torsion angle (τ) in the compounds where copper(II) and cobalt(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S7): No straightforward correlation is possible. Green filled squares: Data of previous compounds. Black-white half-filled circle: Data of compound **3**.

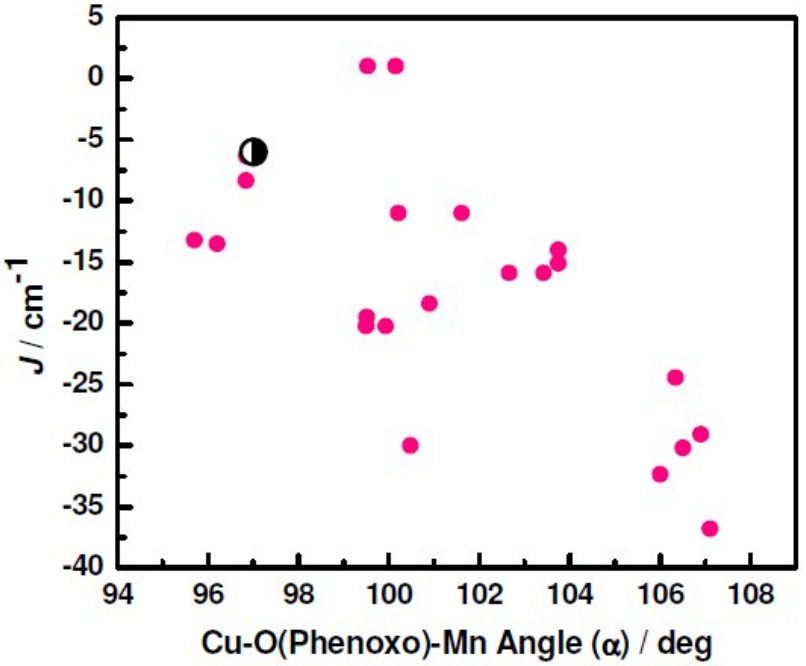


Fig. S23 *J* versus Cu–O(Phenoxo)–Mn bridge angle (α) in the compounds where copper(II) and manganese(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S8): No straightforward correlation is possible. Pink filled circles: Data of previous compounds. Black-white half-filled circle: Data of compound **5**.

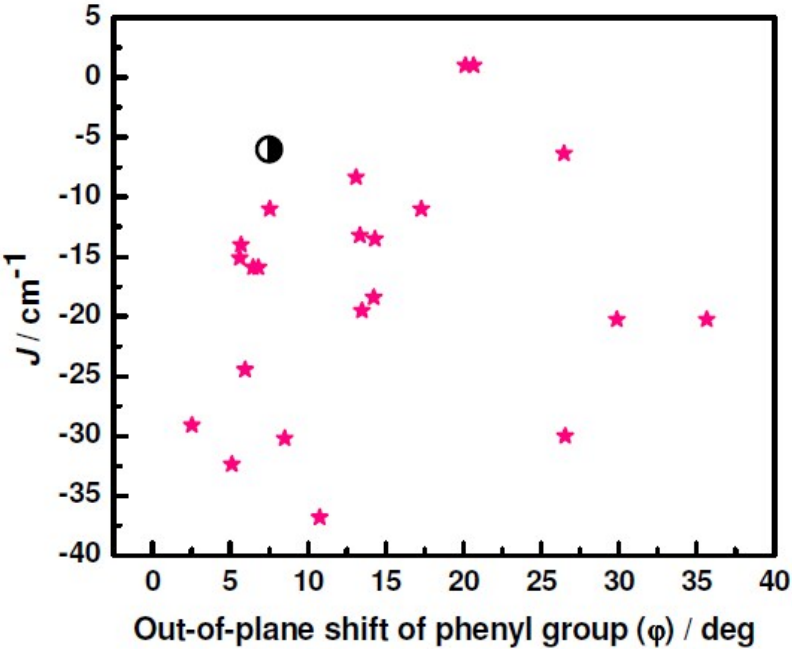


Fig. S24 *J* versus Out–of–plane shift of phenyl group (φ) in the compounds where copper(II) and manganese(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S8): No straightforward correlation is possible. Pink filled stars: Data of previous compounds. Black-white half-filled circle: Data of compound **5**.

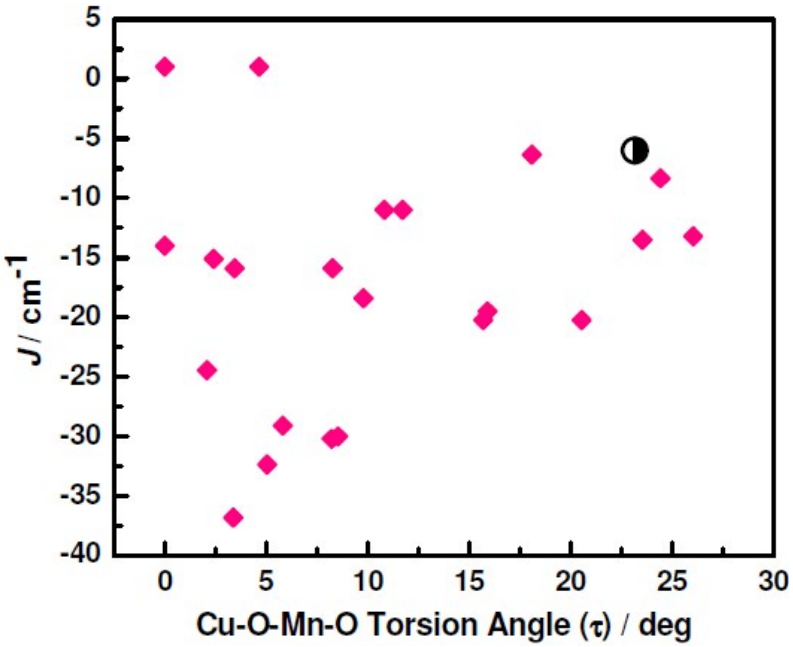


Fig. S25 *J* versus Cu–O–Mn–O torsion angle (τ) in the compounds where copper(II) and manganese(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table S8): No straightforward correlation is possible. Pink filled squares: Data of previous compounds. Black-white half-filled circle: Data of compound **5**.

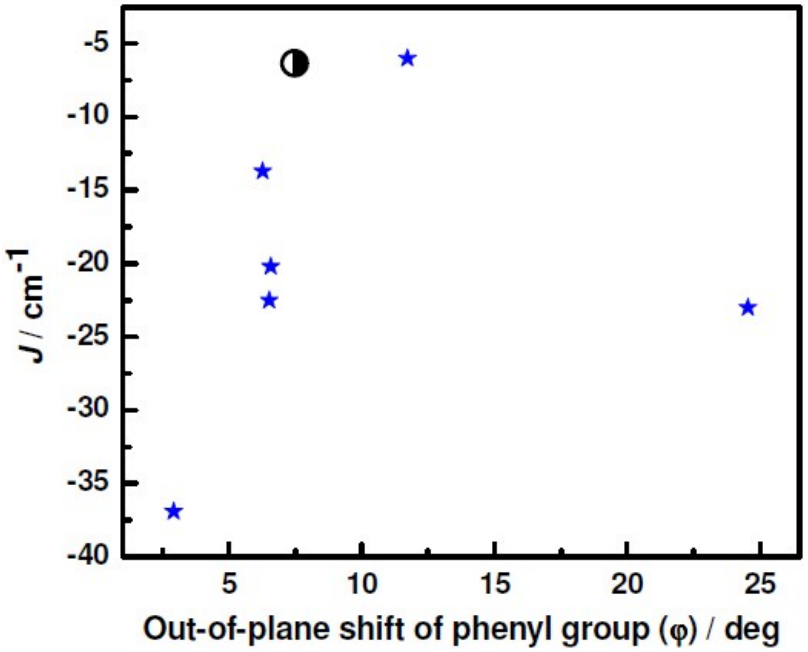


Fig. S26 *J* versus Out–of–plane shift of phenyl group (φ) in the compounds where copper(II) and iron(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table 5 in the text): No straightforward correlation is possible. Blue filled stars: Data of previous compounds. Black-white half-filled circle: Data of compound **4**.

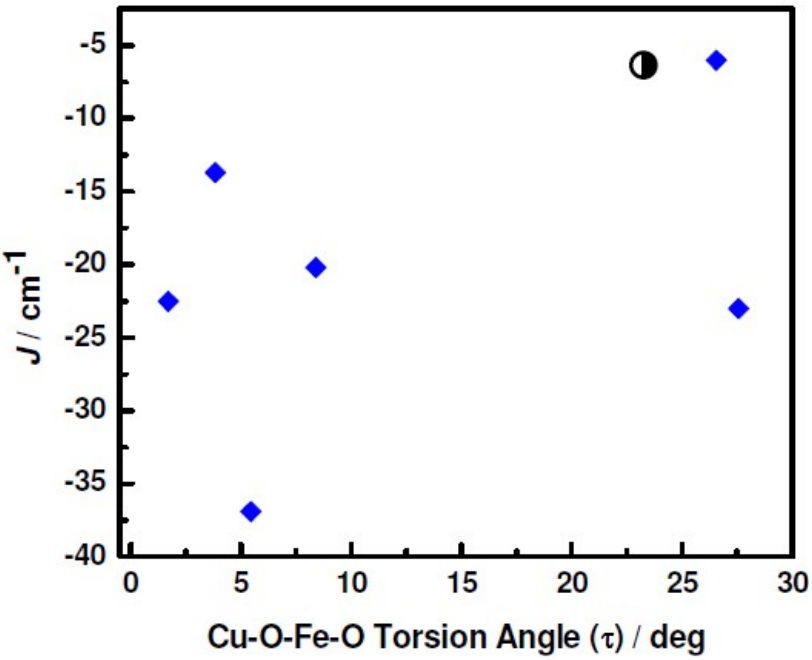


Fig. S27 *J* versus Cu–O–Fe–O torsion angle (τ) in the compounds where copper(II) and iron(II) centres are bridged by solely bis(μ_2–phenoxo) moiety (Table 5 in the text): No straightforward correlation is possible. Blue filled squares: Data of previous compounds. Black-white half-filled circle: Data of compound **4**.

Table S1 Some structural parameters (lengths in Å and angles in º) around Cu1 and Cu2 centres in **1–6**

		$Cu^{II}Cu^{II}Cu^{II}$ (1)	**$Cu^{II}Ni^{II}Cu^{II}$ (2)**	**$Cu^{II}Co^{II}Cu^{II}$ (3)**	**$Cu^{II}Fe^{II}Cu^{II}$ (4)**	**$Cu^{II}Mn^{II}Cu^{II}$ (5)**	**$Cu^{II}Zn^{II}Cu^{II}$ (6)**
Bond Lengths	Cu1–O1	1.910(5)	1.906(2)	1.916(4)	1.915(2)	1.920(2)	1.928(5)
	Cu1–O2	1.912(5)	1.909(3)	1.908(5)	1.908(2)	1.912(2)	1.920(5)
	Cu1–O5A/O8/O8A	2.596(6)	2.644(13)	2.597(45)	2.749(9)	2.723(14)	2.802(16)
	Cu1–N1	1.906(6)	1.911(3)	1.932(6)	1.918(3)	1.920(3)	1.935(7)
	Cu1–N2	1.902(6)	1.917(4)	1.928(6)	1.930(3)	1.929(3)	1.942(7)
	Cu2–O3	1.916(5)	1.901(3)	1.906(5)	–	–	–
	Cu2–O4	1.895(5)	1.906(3)	1.918(4)	–	–	–
	Cu2–O10	2.868(7)	–	–	–	–	–
	Cu2–O15	–	–	2.671(12)	–	–	–
	Cu2–N3	1.889(6)	1.910(3)	1.925(6)	–	–	–
	Cu2–N4	1.896(6)	1.906(3)	1.914(5)	–	–	–
Bond Angles	O2–Cu1–N1	175.3(3)	177.02(14)	175.2(3)	176.98(13)	177.24(11)	177.7(3)
	O1–Cu1–N2	175.6(3)	167.02(16)	166.4(3)	168.16(12)	168.57(10)	168.8(3)
	O1–Cu1–O2	81.3(2)	83.87(11)	83.79(18)	83.28(10)	84.10(18)	83.2(2)
	O1–Cu1– O5A/O8/O8A	89.947(222)	91.441(291)	104.169(679)	92.124(217)	88.852(419)	89.491(462)
	O1–Cu1–N1	96.3(2)	95.53(13)	95.0(2)	95.74(11)	95.27(10)	95.8(2)
	O2–Cu1– O5A/O8/O8A	87.465(200)	88.608(288)	88.095(738)	84.967(247)	99.855(622)	87.259(535)
	O2–Cu1–N2	96.4(2)	94.40(13)	94.2(2)	94.68(11)	94.72(10)	94.8(2)
	O5A/O8/O8A–Cu1–N1	88.457(233)	94.326(293)	96.66(74)	97.937(249)	82.818(621)	94.862(548)
	O5A/O8/O8A–Cu1–N2	93.717(249)	101.409(297)	89.127(624)	99.348(225)	102.545(433)	101.449(491)
	N1–Cu1– N2	86.2(3)	85.53(15)	85.9(3)	85.70(13)	85.36(11)	85.8(3)
	O3–Cu2–N4	173.1(3)	176.07(14)	178.6(3)	–	–	–
	O4–Cu2–N3	172.4(3)	170.07(14)	167.9(3)	–	–	–
	O3–Cu2–O4	84.1(2)	84.08(11)	83.05(19)	–	–	–
	O3–Cu2–O10	81.410(192)	–	–	–	–	–
	O3–Cu2–O15	–	–	88.041(303)	–	–	–
	O3–Cu2–N3	95.4(2)	95.16(13)	95.5(2)	–	–	–
	O4–Cu2–O10	104.947(219)	–	–	–	–	–
	O4–Cu2–O15	–	–	105.51(30)	–	–	–
	O4–Cu2–N4	95.4(3)	95.59(13)	96.2(2)	–	–	–
	O10–Cu2–N3	82.378(247)	–	–	–	–	–
	O10–Cu2–N4	92.100(251)	–	–	–	–	–
	O15–Cu2– N3	–	–	86.412(304)	–	–	–
	O15–Cu2– N4	–	–	91.051(308)	–	–	–
	N3–Cu2– N4	86.0(3)	85.84(15)	85.5(2)	–	–	–
Discrimination parameter (τ)	Cu1	0.005	0.1667	0.147	0.147	0.144	0.148
	Cu2	0.012	–	0.179	–	–	–

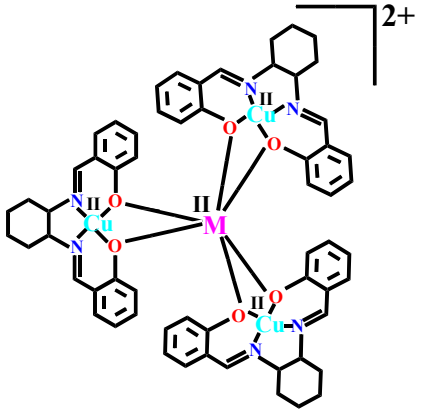
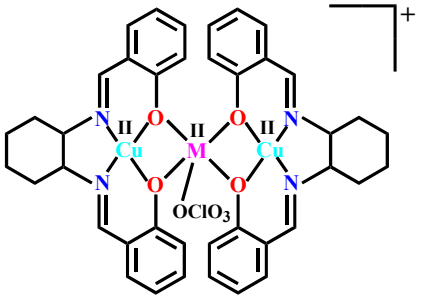
Table S2 The geometries of the hydrogen bonds in $[\{Cu^{II}L(ClO_4)\}_2Cu^{II}(H_2O)]\cdot 2H_2O$ (**1**) and $[\{Cu^{II}L(ClO_4)\}\{Ni^{II}(H_2O)_2\}\{Cu^{II}L\}]ClO_4\cdot CH_3COCH_3$ (**2**) (distances in Å and angles in º). Symmetry for **1**: E, 1–x, 2–y, 1–z. Symmetry for **2**: E, 2–x, 1–y, 1–z.

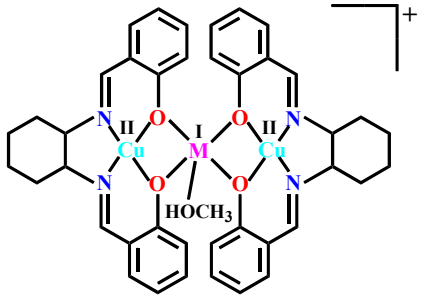
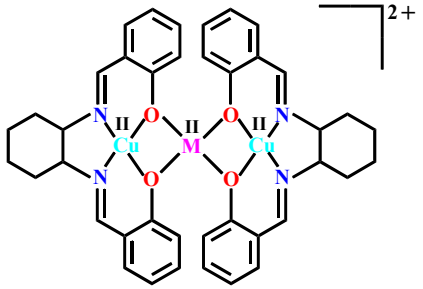
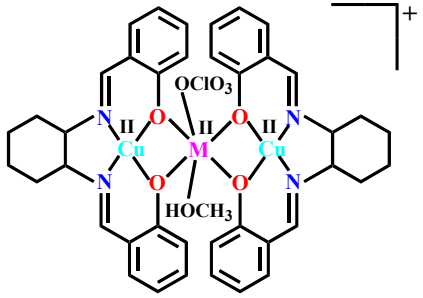
D–H···A	H···A		D···A		D–H···A	
	1	**2**	**1**	**2**	**1**	**2**
C32–H32B···O10E	2.512	–	3.382	–	148.33	–
O5–H5A···O7	1.917	–	2.707	–	153.94	–
O5–H5B···O10	2.089	–	2.919	–	162.57	–
O5–H5B···O13E	–	1.909	–	2.779	–	171.25
O6–H6A···O11E	–	2.017	–	2.841	–	157.28

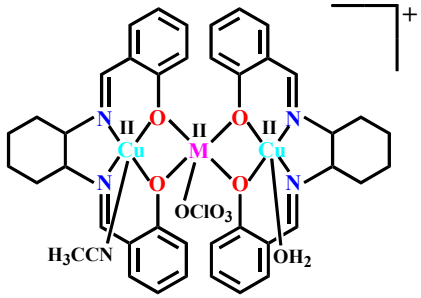
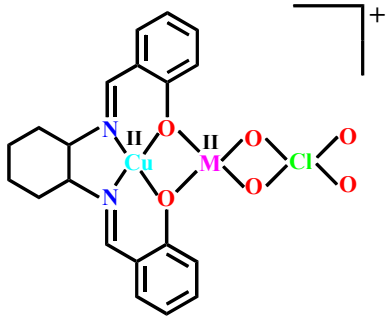
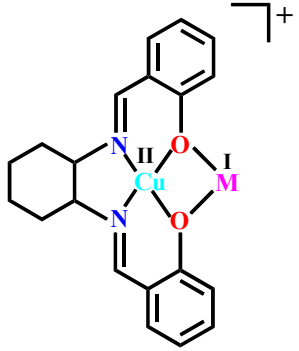
Table S3 The geometries of the hydrogen bonds in $[\{Cu^{II}L(ClO_4)\}_2Fe^{II}(CH_3OH)_2]$ (**4**), $[\{Cu^{II}L(ClO_4)\}_2Mn^{II}(CH_3OH)_2]$ (**5**) and $[\{Cu^{II}L(ClO_4)\}_2Zn^{II}(CH_3OH)_2]$ (**6**) (distances in Å and angles in º). Symmetry for **4**: E, 0.5–x, –0.5+y, 0.5–z. Symmetry for **5**: E, 0.5+x, –0.5+y, z. Symmetry for **6**: E, 1.5–x, –0.5+y, 0.5–z.

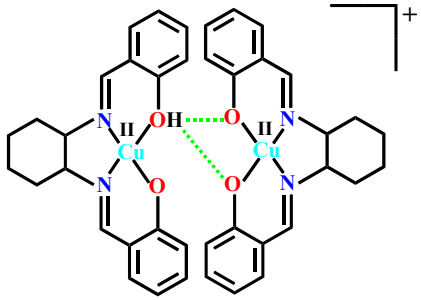
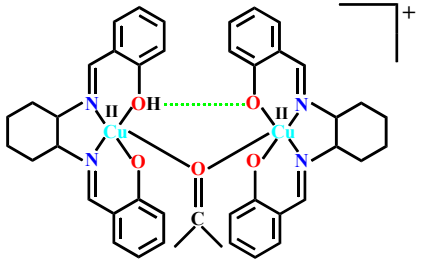
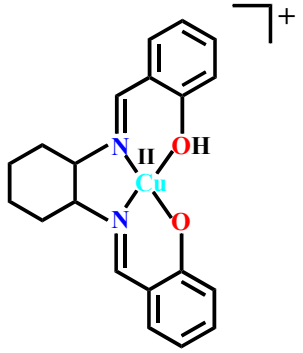
D–H···A	H···A			D···A			D–H···A		
	4	**5**	**6**	**4**	**5**	**6**	**4**	**5**	**6**
O3–H3A···O4E	2.074	2.081	2.104	2.878	2.849	2.899	159.70	151.69	156.52

Table S4 The composition (with drawing), peak position and relative peak intensity of the species in the ESI–MS positive spectra of **1** in MeOH and **2**–**6** in MeCN

Ions in ESI–MS	**Line–to–line m/z gap**	**1** (M = Cu^{II})		**2** (M = Ni^{II})		**3** (M = Co^{II})		**4** (M = Fe^{II})		**5** (M = Mn^{II})		**6** (M = Zn^{II})	
		Intensity	**m/z**	**Intensity**	**m/z**	**Intensity**	**m/z**	**Intensity**	**m/z**	**Intensity**	**m/z**	**Intensity**	**m/z**
 $[(Cu^{II}L)_3M^{II}]^{2+}$ (**I**; $C_{60}H_{60}N_6O_6Cu^{II}_3M^{II}$)	0.5	–	–	37%	606	12%	606	28%	605	6%	604	7%	610
 $[(Cu^{II}L)M^{II}(ClO_4)(Cu^{II}L)]^{+}$ (**II**; $C_{40}H_{40}N_4O_8ClCu^{II}_2M^{II}$)	1.0	100%	930	100%	925	100%	926	100%	923	–	–	100%	931

 $[(Cu^{II}L)M^{I}(CH_3OH)(Cu^{II}L)]^{+}$ (**III**; $C_{41}H_{44}N_4O_5Cu^{II}_2M^{I}$)	1.0	–	–	–	–	–	–	–	–	100%	855	–	–
 $[(Cu^{II}L)M^{II}(Cu^{II}L)]^{2+}$ (**IV**; $C_{40}H_{40}N_4O_4Cu^{II}_2M^{II}$)	0.5	–	–	58%	414	59%	415	61%	412	12%	413	73%	417
 $[(Cu^{II}L)M^{II}(ClO_4)(CH_3OH)(Cu^{II}L)]^{+}$ (**V**; $C_{41}H_{44}N_4O_9ClCu^{II}_2M^{II}$)	1.0	–	–	–	–	–	–	9%	955	–	–	–	–

 $[(Cu^{II}L)(CH_3CN)M^{II}(ClO_4)(Cu^{II}L)(H_2O)]^+$ (**VI**; $C_{42}H_{45}N_5O_9ClCu^{II}_2M^{II}$)	1.0	–	–	–	–	–	–	–	–	23%	981	–	–
 $[(Cu^{II}L)M^{II}(ClO_4)]^+$ (**VII**; $C_{20}H_{20}N_2O_6ClCu^{II}M^{II}$)	1.0	9%	547	21%	542	8%	542	–	–	–	–	24%	548
 $[(Cu^{II}L)M^{I}]^+$ (**VIII**; $C_{20}H_{20}N_2O_2Cu^{II}M^{I}$)	1.0	9%	446	–	–	–	–	–	–	–	–	–	–

 $[\{Cu^{II}(HL)\}(Cu^{II}L)]^+$ (**IX**; $C_{40}H_{41}N_4O_4Cu^{II}_2$)	1.0	12%	769	7%	769	5%	769	32%	769	–	–	7%	769
 $[\{Cu^{II}(HL)\}(Cu^{II}L)(CH_3COCH_3)]^+$ (**X**; $C_{43}H_{47}N_4O_5Cu^{II}_2$)	1.0	83%	827	9%	827	–	–	–	–	–	–	–	–
 $[Cu^{II}(HL)]^+$ (**XI**; $C_{20}H_{21}N_2O_2Cu^{II}$)	1.0	62%	384	–	–	–	–	43%	384	–	–	19%	384

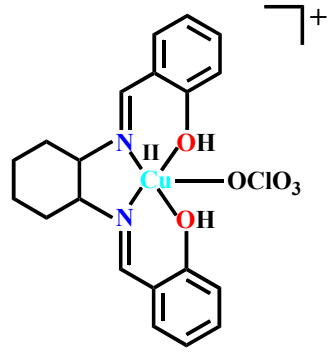
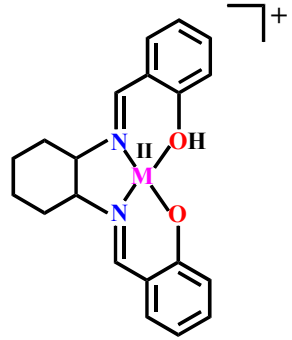
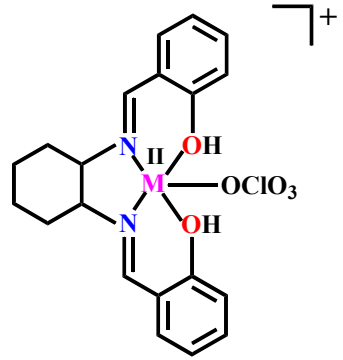
 $[Cu^{II}(H_2L)(ClO_4)]^+$ (**XII**; $C_{20}H_{22}N_2O_6ClCu^{II}$)	1.0	42%	484	33%	484	42%	484	60%	484	–	–	–	–
 $[M^{II}(HL)]^+$ (**XIII**; $C_{20}H_{21}N_2O_2M^{II}$)	1.0	–	–	47%	379	46%	380	61%	377	63%	376	–	–
 $[M^{II}(H_2L)(ClO_4)]^+$ (**XIV**; $C_{20}H_{22}N_2O_6ClM^{II}$)	1.0	–	–	–	–	–	–	–	–	44%	476	42%	485

Table S5 Magnetic exchange integral and some relevant structural parameters of the trinuclear $Cu^{II}Cu^{II}Cu^{II}$ compounds where the two copper(II) centres in a $Cu^{II}\cdots Cu^{II}$ pair are bridged by solely bis(μ_2–phenoxo) moiety:

Compound No.	CSD Code	J (cm^{-1})	Average Cu–O(Phenoxo)–Cu bridge angle (α) (deg)	Out–of–plane shift of phenyl group (φ) (deg)	Cu–O–Cu–O torsion angle (τ) (deg)	Reference
1	DAHVEP02	–152	94.07	27.70	29.28	1(*a*)
2	ITIFOH	–203	98.04	31.67	23.73	1(*b*)
3	WUYFUS	–60	101.52	10.25	16.79	1(*c*)
4	LIFSAV	–185	97.45	31.0	18.4	1(*d*)
5	IBERIQ	–241	97.6	18.1	21.3	1(*e*)
6	FIDZUO	–241	98.35	18.8	21.0	1(*f*)
7	FEZTEK	–157	98.35	30.0	7.2	1(*g*)
8	VAVQOZ	–237	99.55	24.0	14.4	1(*h*)
9	IKOQUU	–256	101.1	20.4	11.8	1(*i*)
10	FIDZOI	–152	101.0	25.0	10.4	1(*f*)
11	RAJNAT	–148	96.3	2.2	27.9	1(*j*)
12	RAJNEX	–162	96.3	2.1	27.9	1(*j*)
13	RAJNIB	–165	96.85	3.1	26.5	1(*j*)
14	RAJNOH	–207	97.65	4.7	26.1	1(*j*)
15	RAJNUN	–221	98.8	6.3	25.9	1(*j*)
16	----------	–137	97.97	6.88	15.43	This work

Table S6 Magnetic exchange integral and some relevant structural parameters of the systems where copper(II) and nickel(II) centres are bridged by solely bis(μ_2–phenoxo) moiety

Compound No.	CSD Code	J (cm^{-1})	Average Cu–O(Phenoxo)–Ni bridge angle (α) (deg)	Out–of–plane shift of phenyl group (φ) (deg)	Cu–O–Ni–O torsion angle (τ) (deg)	Reference
1	KAJFEG	–130	101.21	22.28	3.65	2(*a*)
2	GIWYEQ	–118.6	101.62	6.5	2.11	2(*b*)
3	KAHVAQ	–115.0	101.19	6.12	4.14	2(*a*)
4	LINWIO	–47.0	101.58	6.6	17.88	2(*c*)
5	IXAZUC	–50.6	101.23	9.46	4.22	2(*d*)
6	UKIPOT	–67.0	100.88	24.91	6.97	2(*e*)
7	ZOJFEJ	–90.0	99.86	12.6	6.27	2 (*f*)
8	BIHZEX	–71.0	98.83	6.08	0.28	2(*g*)
9	UDUWEV	–12.0	94.54	38.01	15.78	2(*h*)
10	DEWPAW	–11.8	93.17	13.55	27.49	2(*i*)
11	YOXKED	–3.53	99.12	19.17	0.00	2(*j*)
12	----------	–22.16	96.32	8.587	20.39	This work

Table S7 Magnetic exchange integral and some relevant structural parameters of the systems where copper(II) and cobalt(II) centres are bridged by solely bis(μ_2–phenoxo) moiety

Compound No.	**CSD Code**	***J* (cm^{-1})**	**Average Cu–O(Phenoxo)–Co bridge angle (α) (deg)**	**Out–of–plane shift of phenyl group (φ) (deg)**	**Cu–O–Co–O torsion angle (τ) (deg)**	**Reference**
1	CEPLEP	–12.5	98.54	6.78	7.38	3(*a*)
2	CPRECO	–16.3	94.84	12.48	52.76	3(*b*)
3	DEXRAA	–8	102.60	7.11	0.00	3(*c*)
4	FIHFIL	–15	100.07	27.88	23.03	3(*d*)
5	ILAKIP	–20.2	100.11	14.17	11.97	3(*e*)
6	IXAZOW	–26.2	98.48	8.41	10.64	2(*d*)
7	MUQNES	–51	98.98	7.74	5.78	3(*f*)
8	QADWUN	–7.3	100.41	17.38	14.33	3(*g*)
9	TEGCOY	–53.3	104.77	8.53	0.59	3(*h*)
10	UDUWAR	–8	97.73	27.92	16.98	3(*i*)
11	UDUWIZ	–38	101.12	14.48	16.76	3(*i*)
12	WIVHAM	–18.6	96.25	33.66	24.10	3(*j*)
13	WIVHEQ	–25.8	97.70	19.03	23.42	3(*j*)
14	WIVHEQ01	–23.6	98.87	18.00	24.36	3(*j*)
15	YEHVEN	–17.45	101.62	11.49	12.15	3(*k*)
16	ZOJQEW	–33.4	99.28	14.34	26.02	3(*l*)
17	----------	–14.78	96.99	6.86	21.36	This work

Table S8 Magnetic exchange integral and some relevant structural parameters of the systems where copper(II) and manganese(II) centres are bridged by solely bis(μ_2–phenoxo) moiety

Compound No.	CSD Code	J (cm^{-1})	Average Cu–O(Phenoxo)–Mn bridge angle (α) (deg)	Out–of–plane shift of phenyl group (φ) (deg)	Cu–O–Mn–O torsion angle (τ) (deg)	Reference
1	GAJYOH	–36.8	107.11	10.75	3.36	4(*a*)
2	VOBLAA	–32.35	106.00	5.1	5.04	4(*b*)
3	VOBLII	–30.2	106.51	8.51	8.21	4(*b*)
4	BICCAT	–29.1	106.9	2.54	5.82	4(*c*)
5	VOBKUT	–24.45	106.34	5.96	2.07	4(*b*)
6	DEXQUT	–14.0	103.75	5.69	0.0	3(*c*)
7	YUVRAJ	–15.1	103.75	5.62	2.41	4(*d*)
8	MIXLEL	–15.9	103.42	6.47	3.43	4(*e*)
9	BICBIA	–15.9	102.66	6.8	8.27	4(*c*)
10	ILAKOV	–11.0	101.61	7.55	11.72	3(*e*)
11	QEKFIW	–18.4	100.9	14.23	9.79	4(*f*)
12	LEGJAI	–11.0	100.21	17.29	10.82	4(*g*)
13	UKIPEJ	–30.0	100.48	26.55	8.53	2(*e*)
14	HETZIQ	–19.5	99.51	13.48	15.91	4(*h*)
15	YADNIB	–8.35	96.84	13.1	24.43	4(*i*)
16	WATGON	–13.5	96.2	14.31	23.54	4(*j*)
17	FAEPCU	–13.2	95.7	13.34	26.05	3(*b*)
18	FANHUZ	–20.25, –20.25, –6.35,	99.5, 99.93, 96.85,	29.88, 35.65, 26.48,	20.54, 15.69, 18.09,	4(*k*)
19	YOXKAZ	1.02	100.15, 99.53	21.67, 20.13	4.62, 0.00	2(*j*)
20	–	–6.02	97.08	7.46	23.12	This work

References

1 (*a*) S. Saha, A. Sasmal, C. Roy Choudhury, C. J. Gómez-Garcia, E. Garribba and S. Mitra, *Polyhedron*, 2014, **69**, 262; (*b*) P. Talukder, S. Shit, A. Sasmal, S. R. Batten, B. Moubaraki, K. S. Murray and S. Mitra, *Polyhedron*, 2011, **30**, 1767; (*c*) S. Thakurta, C. Rizzoli, R. J. Butcher, C. J. Gómez-García, E, Garribba and S. Mitra, *Inorg*. *Chim*. *Acta*, 2010, **363**, 1395; (*d*) Y.-F. Song, G. A. van Albada, J. Tang, I. Mutikainen, U. Turpeinen, C. Massera, O. Roubeau, J. S. Costa, P. Gamez, and J. Reedijk, *Inorg*. *Chem*., 2007, **46**, 4944; (*e*) X.-H. Bu, M. Du, Z.-L. Shang, R.-H. Zhang, D.-Z. Liao, M. Shionoya and T. Clifford, *Inorg*. *Chem*., 2000, **39**, 4190; (*f*) Y. Song, P. Gamez, O. Roubeau, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg*. *Chim*. *Acta*, 2005, **358**, 109; (*g*) M. Du, X.-J. Zhao, J.-H. Guo, X.-H. Bu and J. Ribas, *Eur*. *J*. *Inorg*. *Chem*., 2005, 294; (*h*) Y. F. Song, G. A. van Albada, M. Quesada, I. Mutikainen, U. Turpeinen and J. Reedijk, *Inorg*. *Chem*. *Commun*., 2005, **8**, 975; (*i*) Y. Song, P. Gamez, O. Roubeau, M. Lutz, A. L. Spek and J. Reedijk, *Eur*. *J*. *Inorg*. *Chem*., 2003, 2924; (*j*) L. Botana, J. Ruiz, J. M. Seco, A. J. Mota, A. Rodríguez-Di´eguez, R. Sillanpää and E. Colacio, *Dalton Trans*., 2011, **40**, 12462.

2 (*a*) C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill and P. Chaudhuri, *J*. *Chem*. *Soc*., *Dalton Trans*., 2000, 251; (*b*) C. N. Verani, T. Weyhermüller, E. Rentschler, E. Bill and P. Chaudhuri, *Chem*. *Commun*., 1998, 2475; (*c*) M. Yonemura, M. Ohba, K. Takahashi, H. Ōkawa and D. E. Fenton, *Inorg*. *Chim*. *Acta*, 1998, **283**, 79; (*d*) R.-J. Tao, C.-Z. Mei, S.-Q. Zang, Q.-L. Wang, J.-Y. Niu and D.-Z. Liao, *Inorg*. *Chim*. *Acta*, 2004, **357**, 1985; (*e*) A. Hori, Y. Mitsuka, M. Ohba and H. Ōkawa, *Inorg*. *Chim*. *Acta*, 2002, **337**, 113; (*f*) T. Aono, H. Wada, Y.-I. Aratake, N. Matsumoto, H. Ōkawa and Y. Matsuda, *Dalton Trans*, 1996, 25; (*g*) I. Morgenstern-Badarau, M. Rerat, O. Khan, J. Jaud and J. Galy, *Inorg*. *Chem*., 1982, **21**, 3050; (*h*) M. Yonemura, K. Arimura, K. Inoue, N. Usuki, M. Ohba and H. Ōkawa, *Inorg*. *Chem*., 2002, **41**, 582; (*i*) Y. Journaux, O. Kahn, I. Morgenstern-Badarau, J. Galy, J. Jaud, A. Bencini and D. Gatteschi, *J*. *Am*. *Chem*. *Soc*., 1985, **107**, 6305; (*j*) S. Mondal, S. Mandal, L. Carrella, A. Jana, M. Fleck, A. Köhn, E. Rentschler and S. Mohanta, *Inorg*. *Chem*., 2015, **54**, 117.

3 (*a*) R.-J. Tao, F.-A. Li, S.-Q. Zang, Y.-X. Cheng, Q.-L. Wang, J.-Y. Niu and D.-Z. Liao, *Polyhedron*, 2006, **25**, 2153; (*b*) C. J. O'connor, D. P. Freyberg and E. Sinn, *Inorg*. *Chem*., 1979, **18**, 1077; (*c*) M. Nayak, R. Koner, H.-H. Lin, U. Flörke, H.-H. Wei, and S. Mohanta, *Inorg*. *Chem*., 2006, **45**, 10764; (*d*) G. A. Brewer and E. Sinn, *Inorg*. *Chem*., 1987, **26**, 1529; (*e*) S. Osa, Y. Sunatsuki, Y. Yamamoto, M. Nakamura, T. Shimamoto, N. Matsumoto, and N. Re, *Inorg*. *Chem*., 2003, **42**, 5507; (*f*) A. Gutiérrez, M. F. Perpiñán, A. E. Sánchez, M. C. Torralba and M. R. Torres, *Inorg*. *Chim*. *Acta*, 2010, **363**, 1837; (*g*) Y. Sunatsuki, T. Matsuo, M. Nakamura, F. Kai, N. Matsumoto and J.-P. Tuchagues, *Bull*. *Chem*. *Soc*. *Jpn*., 1998, **71**, 2611; (*h*) J.-P. Costes, R. Gheorghe, M.

Andruh, S. Shovac and J.-M. C. Juand, *New J. Chem*., 2006, **30**, 572; (*i*) M. Yonemura, K. Arimura, K. Inoue, N. Usuki, M. Ohba and H. Ohkawa, *Inorg. Chem*., 2002, **41**, 582; (*j*) S. Biswas, C. J. Gómez-García, J. M. Clemente-Juan, S. Benmansour and A. Ghosh, *Inorg. Chem*., 2014, **53**, 2441; (*k*) R.-J. Tao, F.-A. Li, S.-Q. Zang, Y.-X. Cheng, Q.-L. Wang, J.-Y. Niu and D.-Z. Liao, *J. Coord. Chem*., 2006, **59**, 901; (*l*) S. Ghosh, G. Aromí, P. Gamez and A. Ghosh, *Eur. J. Inorg. Chem*., 2014, 3341.

4 (*a*) D. G. Branzea, A. M. Madalan, S. Ciattini, N. Avarvari, A. Caneschi and M. Andruh, *New J. Chem*., 2010, **34**, 2479; (*b*) D. G. Branzea, A. Guerri, O. Fabelo, C. Ruiz-Pérez, L.-M. Chamoreau, C. Sangregorio, A. Caneschi and M. Andruh, *Cryst. Growth Des.*, 2008, **8**, 941; (*c*) A. Biswas, L. Mandal, S. Mondal, C. R. Lucas and S. Mohanta, *CrystEngComm.*, 2013, **15**, 5888; (*d*) A. Biswas, M. Ghosh, P. Lemoine, S. Sarkar, S. Hazra and S. Mohanta, *Eur. J. Inorg. Chem*., 2010, 3125; (*e*) M. Nayak, S. Hazra, P. Lemoine, R. Koner, C. R. Lucas and S. Mohanta, *Polyhedron*, 2008, **27**, 1201; (*f*) L. Bo, Z. Hong, P. Zhi-Quan, S. You, W. Cheng-Gang, Z. Han-Ping, H. Jing-Dong and C. Ru-An, *J. Coord. Chem*., 2006, **59**, 1271; (*g*) R. Ruiz, F. Lloret, M. Julve and J. Faus, *Inorg. Chim. Acta*, 1993, **213**, 261; (*h*) D. Visinescu, J.-P. Sutter, C. Ruiz-Pérez and M. Andruh, *Inorg. Chim. Acta*, 2006, **359**, 433; (*i*) M. Pascu, F. Lloret, N. Avarvari, M. Julve and M. Andruh, *Inorg. Chem*., 2004, **43**, 5189; (*j*) H. Ōkawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida and D. E. Fenton, *Inorg. Chem*., 1993, **32**, 2949; (*k*) S. Biswas, S. Naiya, C. J. Gomez-Garcia and A. Ghosh, *Dalton Trans*., 2012, **41**, 462.