Supporting Information file

Hetero Triply-bridged Dinuclear Copper(II) Compounds with Ferromagnetic Coupling: A Challenge for Current Density Functionals

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Synthesis conditions and procedure for compounds 2 to 7

*[Cu_2(4,4′-dmbpy)$_2$(μ-OH)(μ-OH_2)(μ-O_2CH)](ClO_4)$_2$ (**2**)*

A warmed methanol solution (10 ml) of 4,4′-dmbpy (0.184 g, 1.0 mmol) was added to a warmed aqueous solution (20 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol). Then an aqueous solution (5 ml) of NaO_2CH (0.204 g, 3.0 mmol) was slowly added. The mixture was warmed with adding DMF (2 ml), yielding a clear dark blue solution. On slow evaporation at room temperature for 5 days, the product **2** was isolated as dark blue block-shaped crystals. The crystals were filtered off, washed with the mother liquid and air-dried. Yield: ca. 53%. Anal. Calc. for $C_{25}H_{28}Cl_2Cu_2N_4O_{12}$: C, 38.84; H, 3.26; N, 7.01. Found: C, 38.76; H, 3.62; N, 7.23%.

*[Cu_2(4,4′-dmbpy)$_2$(μ-OH)(μ-OH_2)(μ-O_2CCH_3)](ClO_4)$_2$ (**3**)*

A warmed methanol solution (10 ml) of 4,4′-dmbpy (0.184 g, 1.0 mmol) was added to a warmed aqueous solution (20 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol). Then an aqueous solution (5 ml) of NaO_2CCH_3 (0.204 g, 3.0 mmol) was slowly added. The mixture was warmed with adding DMF (2 ml), yielding a clear dark blue solution. On slow evaporation at room temperature for 5 days, the product **3** was isolated as blue block-shaped crystals. The crystals were filtered off, washed with the mother liquid and air-dried. Yield: ca. 46%. Anal. Calc. for $C_{26}H_{30}Cl_2Cu_2N_4O_{12}$: C, 39.57; H, 3.84; N, 7.10. Found: C, 39.92; H, 3.88; N, 7.57%.

*[Cu_2(5,5′-dmbpy)$_2$(μ-OH)(μ-OH_2)(μ-O_2CCH_3)](ClO_4)$_2$ (**4**)*

A warmed methanol solution (10 ml) of 5,5′-dmbpy (0.184 g, 1.0 mmol) was added to a warmed aqueous solution (20 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol). Then solid NaO_2CCH_3 (0.204 g, 3.0 mmol) was slowly added. The mixture was warmed with adding DMF (2 ml), yielding a clear dark blue solution. On slow evaporation at room temperature for 5 days, the product **4** was isolated as blue block-shaped crystals. The crystals were filtered off, washed with the mother liquid and air-dried. Yield: ca. 42%. Anal. Calc. for $C_{26}H_{30}Cl_2Cu_2N_4O_{12}$: C, 39.57; H, 3.84; N, 7.10. Found: C, 39.83; H, 3.16; N, 7.51%.

*[Cu_2(5,5′-dmbpy)$_2$(μ-OH)(μ-OH_2)(μ- $O_2CC(CH_3)_3$)](ClO_4)$_2$ (**5**)*

A warmed methanol solution (10 ml) of 5,5′-dmbpy (0.184 g, 1.0 mmol) was added to a warmed aqueous solution (20 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol). Then solid $NaO_2CC(CH_3)_3$ (0.204 g, 3.0 mmol) was slowly added. The mixture was warmed with adding DMF (2 ml), yielding a clear dark blue solution. On slow evaporation at room temperature for a week, the product **5** was isolated as dark blue block-shaped crystals. The crystals were

filtered off, washed with the mother liquid and air-dried. Yield: ca. 30%. Anal. Calc. for $C_{29}H_{36}Cl_2Cu_2N_4O_{12}$: C, 41.90; H, 4.38; N, 6.74. Found: C, 41.75; H, 4.40; N, 6.73%.

$[Cu_2(5,5'\text{-dmbpy})_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](CF_3SO_3)_2$ ***(6)***

A warmed methanol solution (10 ml) of 5,5′-dmbpy (0.184 g, 1.0 mmol) was added to a warmed aqueous solution (20 ml) of $Cu(CF_3SO_3)_2$ (0.361 g, 1.0 mmol). Then solid NaO_2CCH_3 (0.204 g, 3.0 mmol) was slowly added. The mixture was warmed with adding DMF (2 ml), yielding a clear dark blue solution. On slow evaporation at room temperature for 7 days, the product **6** was isolated as dark blue block-shaped crystals. The crystals were filtered off, washed with the mother liquid and air-dried. Yield: ca. 40%. Anal. Calc. for $C_{28}H_{30}Cu_2F_6N_4O_{10}S_2$: C, 37.86; H, 3.41; N, 6.31. Found: C, 37.70; H, 3.17; N, 6.51%.

$[Cu_2(5,5'\text{-dmbpy})_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_2CH_3)](CF_3SO_3)_2$ ***(7)***

A warmed methanol solution (10 ml) of 5,5′-dmbpy (0.184 g, 1.0 mmol) was added to a warmed aqueous solution (20 ml) of $Cu(CF_3SO_3)_2$ (0.361 g, 1.0 mmol). Then solid $NaO_2CCH_2CH_3$ (0.204 g, 3.0 mmol) was slowly added. The mixture was warmed with adding DMF (2 ml), yielding a clear dark blue solution. On slow evaporation at room temperature for 6 days, the product **7** was isolated as violet block-shaped crystals. The crystals were filtered off, washed with the mother liquid and air-dried. Yield: ca. 30%. Anal. Calc. for $C_{29}H_{32}Cu_2F_6N_4O_{10}S_2$: C, 38.60; H, 3.58; N, 6.21. Found: C, 38.73; H, 3.50; N, 6.34%.

T**able S1.** Crystallographic and refinement data for compounds **1-7**

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{24}H_{22}Cu_2F_6N_4O_{10}S_2$	$C_{25}H_{28}Cl_2Cu_2N_4O_{12}$	$C_{26}H_{30}Cl_2Cu_2N_4O_{12}$	$C_{26}H_{30}Cl_2Cu_2N_4O_{12}$	$C_{29}H_{36}Cl_2Cu_2N_4O_{12}$	$C_{28}H_{30}Cu_2F_6N_4O_{10}S_2$	$C_{29}H_{32}Cu_2F_6N_4O_{10}S_2$
Formula weight	831.66	774.49	788.52	788.52	830.59	887.76	901.79
T/K	100(2)	100(2)	150(2)	100(2)	173(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	P -1	P -1	P -1	$P2_1/n$	P -1	$P2_1/n$	P -1
a (Å)	8.3587(5)	8.0321(6)	8.4364(5)	8.2136(3)	8.6600(10)	9.1312(6)	9.1519(6)
b (Å)	11.3580(6)	11.1208(8)	11.0080(7)	16.5961(6)	12.712(2)	17.4262(11)	12.2550(8)
c (Å)	16.6543(9)	16.9976(12)	17.0555(10)	22.9861(9)	16.826(2)	22.0653(14)	16.5318(10)
α (°)	71.2370(10)	87.467(4)	94.2320(10)	90.00	71.420(10)	90.00	104.155(2)
β (°)	81.4730(10)	88.341(4)	92.7770(10)	95.8280(10)	89.940(10)	90.562(3)	92.966(2)
γ (°)	86.1070(10)	79.509(4)	95.2800(10)	90.00	75.560(10)	90.00	97.551(2)
V ($Å^3$)	1480.21(14)	1491.11(19)	1570.45(16)	3117.1(2)	1694.1(4)	3510.9(4)	1775.5(2)
Z	2	2	2	4	2	4	2
D_{calc} (g cm^{-3})	1.866	1.725	1.668	1.680	1.626	1.680	1.687
μ (mm^{-1})	1.679	1.675	1.592	1.604	1.480	1.422	1.407
F(000)	836	788	804	1608	850	1800	916
Crystal size (mm)	0.09×0.21×0.22	0.20×0.22×0.46	0.13×0.15×0.28	0.08×0.16×0.40	0.08×0.10×0.30	0.04×0.32×0.38	0.30×0.40×0.48
Number of reflection collected	19850	22123	21625	42942	21277	27236	21801
Number of unique reflections (R_{int})	7106 (0.0368)	11199 (0.0372)	7591 (0.0250)	7717 (0.0190)	5938 (0.0534)	6182 (0.0623)	10807 (0.0239)
Data/restraints/ parameter	7106/0/521	11199/0/518	7591/0/535	7717/0/432	5938/86/486	6182/27/540	10807/0/584
Goodness-of-fit	1.064	1.099	1.046	1.049	1.267	1.147	
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0325 wR_2 = 0.0871	R_1 = 0.0283 wR_2 = 0.0827	R_1 = 0.0301 wR_2 = 0.0811	R_1 = 0.0292 wR_2 = 0.0785	R_1 = 0.0778 wR_2 = 0.1758	R_1 = 0.0652 wR_2 = 0.1436	R_1 = 0.0424 wR_2 = 0.1197
R indices (all data)	R_1 = 0.0368 wR_2 = 0.0894	R_1 = 0.0356 wR_2 = 0.0953	R_1 = 0.0333 wR_2 = 0.0832	R_1 = 0.0325 wR_2 = 0.0806	R_1 = 0.0900 wR_2 = 0.1835	R_1 = 0.0810 wR_2 = 0.1534	R_1 = 0.0476 wR_2 = 0.1265
Largest difference in peak and hole (e^3)	0.930 and -0.805	0.630 and -0.538	0.946 and -0.608	1.134 and -0.504	2.715 and -1.414	0.911 and -0.594	3.581 and -1.316
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$, $R_w = [\Sigma w\{\|\|F_o\|-\|F_c\|\|\}^2/\Sigma w\|F_o\|^2]^{1/2}$.							

Table S2. Selected bond lengths (Å) and bond angles (deg) with e.s.d.s. in parentheses for compound **1**: $[Cu_2(bpy)_2(\mu\text{-}OH)(\mu\text{-}OH_2)(\mu\text{-}O_2CCH_3)](CF_3SO_3)_2$

Bond Lengths			
Cu(1)-O(1)	1.931(1)	Cu(2)-O(1)	1.921(1)
Cu(1)-O(2)	2.394(1)	Cu(2)-O(2)	2.323(1)
Cu(1)-O(3)	1.942(1)	Cu(2)-O(4)	1.956(1)
Cu(1)-N(1)	1.994(1)	Cu(2)-N(3)	2.009(1)
Cu(1)-N(2)	2.004(1)	Cu(2)-N(4)	1.998(1)
Bond Angles			
O(1)-Cu(1)-N(2)	176.69(6)	O(1)-Cu(2)-N(4)	174.14(6)
O(3)-Cu(1)-N(1)	162.05(6)	O(4)-Cu(2)-N(3)	159.20(6)

Table S3. Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for compound **2**: $[Cu_2(4,4'\text{-dmbpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CH})](ClO_4)_2$

Bond Lengths			
Cu(1)-O(1)	1.914(1)	Cu(2)-O(1)	1.908(1)
Cu(1)-O(2)	2.324(1)	Cu(2)-O(2)	2.409(1)
Cu(1)-O(3)	1.959(1)	Cu(2)-O(4)	1.983(1)
Cu(1)-N(1)	1.999(1)	Cu(2)-N(3)	1.978(1)
Cu(1)-N(2)	1.996(1)	Cu(2)-N(4)	1.995(1)
Bond Angles			
O(1)-Cu(1)-N(2)	173.61(4)	O(1)-Cu(2)-N(3)	173.12(5)
O(3)-Cu(1)-N(1)	167.39(5)	O(4)-Cu(2)-N(4)	150.49(5)

Table S4. Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for compound **3**: $[Cu_2(4,4'\text{-dmbpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2CCH_3)](ClO_4)_2$

Bond Lengths			
Cu(1)-O(1)	1.918(1)	Cu(2)-O(1)	1.918(1)
Cu(1)-O(2)	2.323(1)	Cu(2)-O(2)	2.442(1)
Cu(1)-O(3)	1.945(1)	Cu(2)-O(4)	1.958(1)
Cu(1)-N(1)	1.996(1)	Cu(2)-N(3)	1.985(1)
Cu(1)-N(2)	1.999(1)	Cu(2)-N(4)	1.993(1)
Bond Angles			
O(1)-Cu(1)-N(1)	173.22(6)	O(1)-Cu(2)-N(3)	171.86(6)
O(3)-Cu(1)-N(2)	166.68(6)	O(4)-Cu(2)-N(4)	153.99(6)

Table S5. Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for compound **4**: $[Cu_2(5,5'\text{-dmbpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2CCH_3)](ClO_4)_2$

Bond Lengths			
Cu(1)-O(1)	1.937(1)	Cu(2)-O(1)	1.929(1)
Cu(1)-O(2)	2.329(1)	Cu(2)-O(2)	2.346(1)
Cu(1)-O(4)	1.947(1)	Cu(2)-O(4)	1.950(1)
Cu(1)-N(1)	1.996(1)	Cu(2)-N(3)	1.991(1)
Cu(1)-N(2)	1.986(1)	Cu(2)-N(4)	2.003(1)
Bond Angles			
O(1)-Cu(1)-N(1)	175.54(6)	O(1)-Cu(2)-N(3)	175.16(6)
O(4)-Cu(1)-N(2)	162.83(6)	O(3)-Cu(2)-N(4)	162.19(6)

Table S6. Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for compound **5**: $[Cu_2(5,5'\text{-dmbpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2CC(CH_3)_3](ClO_4)_2$

Bond Lengths			
Cu(1)-O(1)	1.938(5)	Cu(2)-O(1)	1.921(5)
Cu(1)-O(2)	2.320(5)	Cu(2)-O(2)	2.333(5)
Cu(1)-O(32)	1.960(5)	Cu(2)-O(31)	1.970(5)
Cu(1)-N(11)	2.002(6)	Cu(2)-N(21)	2.012(6)
Cu(1)-N(112)	2.000(6)	Cu(2)-N(212)	1.995(6)
Bond Angles			
O(1)-Cu(1)-N(112)	175.20(2)	O(1)-Cu(2)-N(212)	174.6(2)
O(32)-Cu(1)-N(11)	165.00(2)	O(31)-Cu(2)-N(21)	163.2(2)

Table S7. Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for compound **6**: $[Cu_2(5,5'\text{-dmbpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2CCH_3)](CF_3SO_3)_2$

Bond Lengths			
Cu(1)-O(1)	1.964(4)	Cu(2)-O(2)	1.958(4)
Cu(1)-O(3)	1.923(4)	Cu(2)-O(3)	1.931(4)
Cu(1)-O(4)	2.310(4)	Cu(2)-O(4)	2.323(4)
Cu(1)-N(11)	1.999(5)	Cu(2)-N(21)	2.003(5)
Cu(1)-N(112)	1.985(5)	Cu(2)-N(212)	1.993(5)
Bond Angles			
O(1)-Cu(1)-N(11)	155.80(18)	O(2)-Cu(2)-N(21)	157.33(19)
O(3)-Cu(1)-N(112)	176.46(18)	O(3)-Cu(2)-N(212)	176.05(17)

Table S8. Selected bond lengths (Å) and angles (deg) with e.s.d.s. in parentheses for compound **7**: $[Cu_2(5,5'\text{-dmbpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2CCH_2CH_3)](CF_3SO_3)_2$

Bond Lengths			
Cu(1)-O(1)	1.934(1)	Cu(2)-O(1)	1.931(1)
Cu(1)-O(2)	2.339(1)	Cu(2)-O(2)	2.321(1)
Cu(1)-O(3)	1.944(1)	Cu(2)-O(4)	1.941(1)
Cu(1)-N(1)	1.988(1)	Cu(2)-N(3)	1.992(1)
Cu(1)-N(2)	1.988(1)	Cu(2)-N(4)	1.996(1)
Bond Angles			
O(1)-Cu(1)-N(1)	175.80(7)	O(1)-Cu(2)-N(3)	176.27(7)
O(3)-Cu(1)-N(2)	162.20(7)	O(4)-Cu(2)-N(4)	159.94(7)

Table S9. Details about the best fit of the $\chi_M T$ versus T curves to Eq. 3 (g_{iso}, J_{exp} and θ) for compounds **1-7**. The last column reports the measured $\chi_M T$ values at room temperature (298 K) with the values calculated from the fit given in parenthesis.

Compound	g_{iso}	J_{exp} (cm^{-1})	θ (K)	$N\alpha(\times 10^{-6})$	R ($\times 10^{-4}$)	$(\chi_M T)_{RT}$
1	2.194±0.004	102.4±7.5	-0.39±0.02	30	2.4	1.007 (1.007)
2	2.163±0.006	72.6±6.1	-0.73±0.03	90	3.6	0.965 (0.970)
3	2.177±0.005	90.2±7.5	-0.58±0.03	60	3.3	0.987 (0.992)
4	2.167±0.003	104.3±6.0	-0.33±0.01	110	1.4	1.007 (1.008)
5	2.178±0.004	98.7±6.6	-0.31±0.02	50	2.1	0.998 (0.998)
6	2.196±0.005	92.1±7.4	-0.55±0.02	60	3.1	1.003 (1.009)
7	2.162±.004	103.1±7.6	-0.38±0.02	4.±4.	2.3	0.981 (0.981)

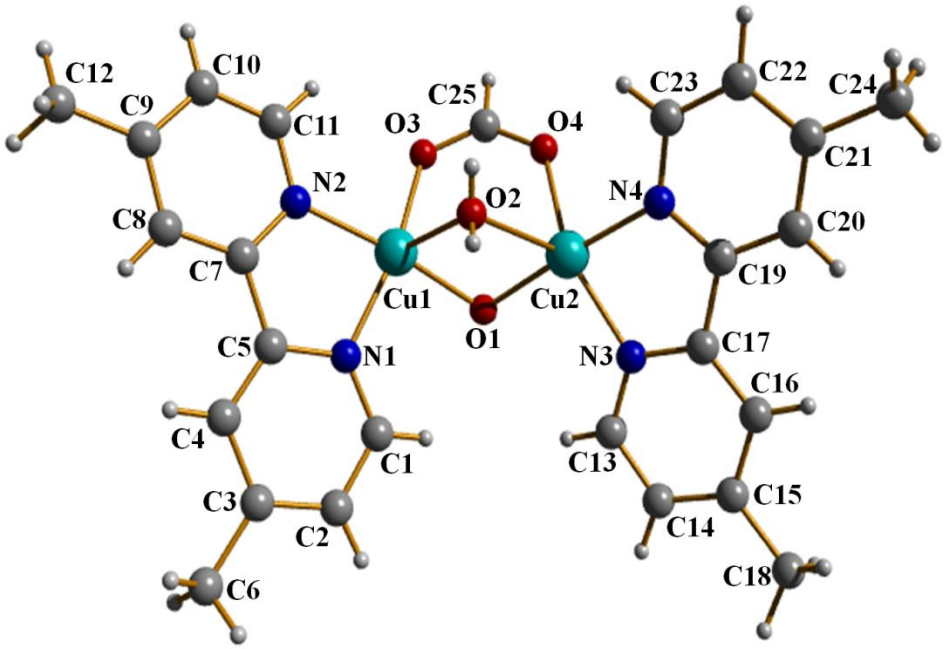

Figure S1. Molecular structure and atomic numbering scheme for compound **2**. Perchlorate counteranions are omitted for clarity.

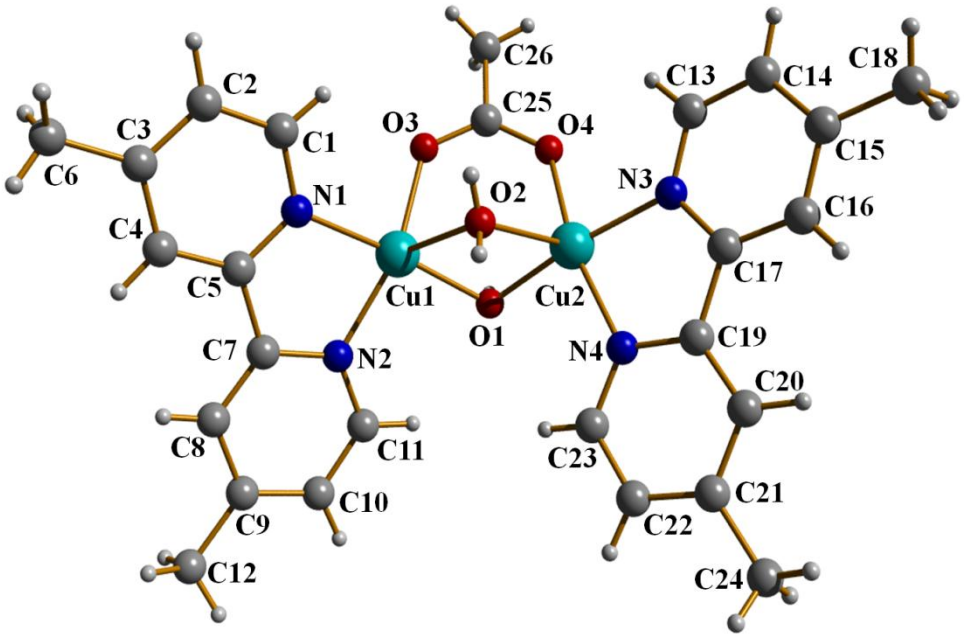

Figure S2. Molecular structure and atomic numbering scheme for compound **3**. Perchlorate counteranions are omitted for clarity.

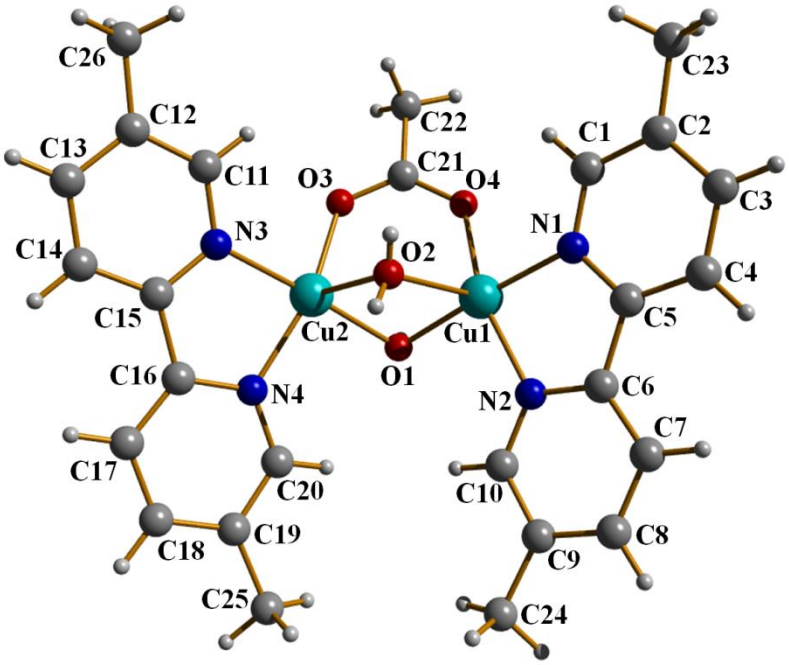

Figure S3. Molecular structure and atomic numbering scheme for compound **4**. Perchlorate counteranions are omitted for clarity.

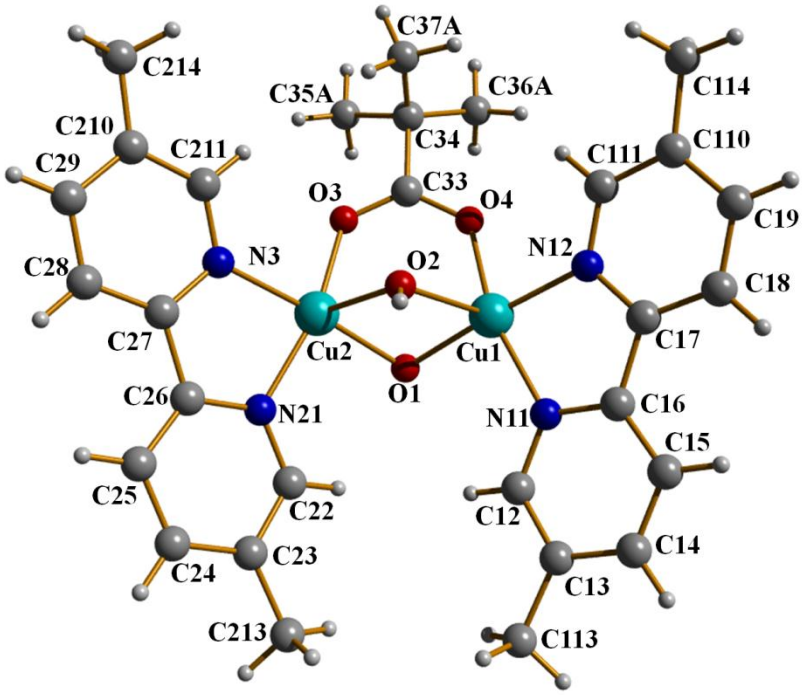

Figure S4. Molecular structure and atomic numbering scheme for compound **5**. Perchlorate counteranions are omitted for clarity.

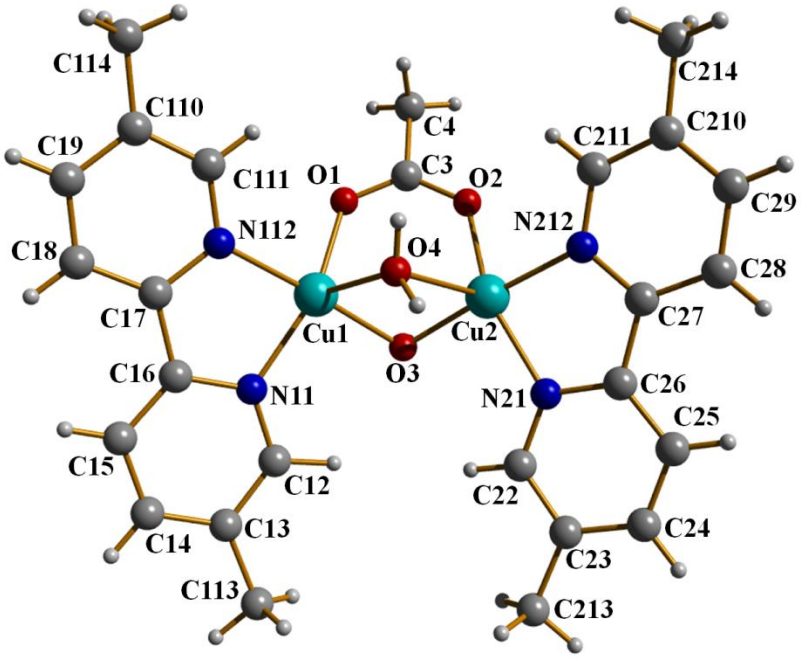

Figure S5. Molecular structure and atomic numbering scheme for compound **6**. Trifluoromethanesulfonate counteranions are omitted for clarity.

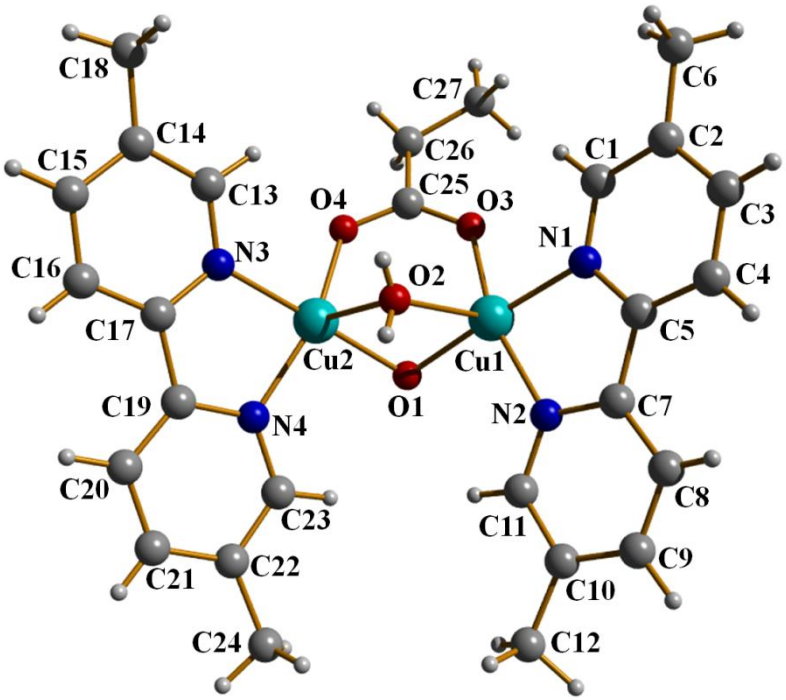

Figure S6. Molecular structure and atomic numbering scheme for compound **7**. Triflate counteranions are omitted for clarity.

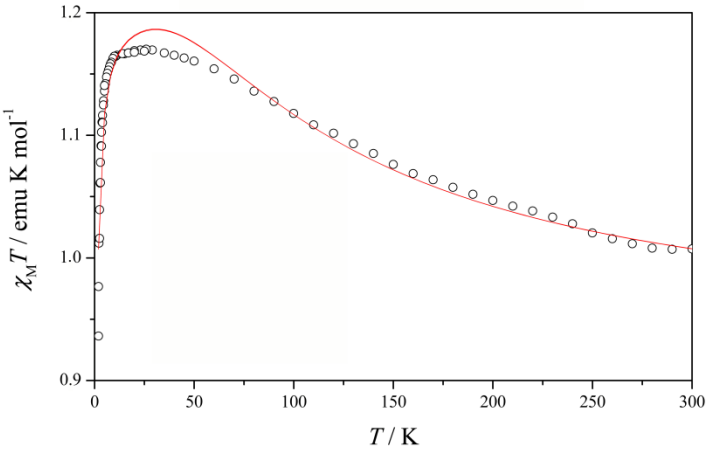

Figure S7. Plot of magnetic susceptibility-temperature product ($\chi_M T$) versus temperature (T) for compound **1**.

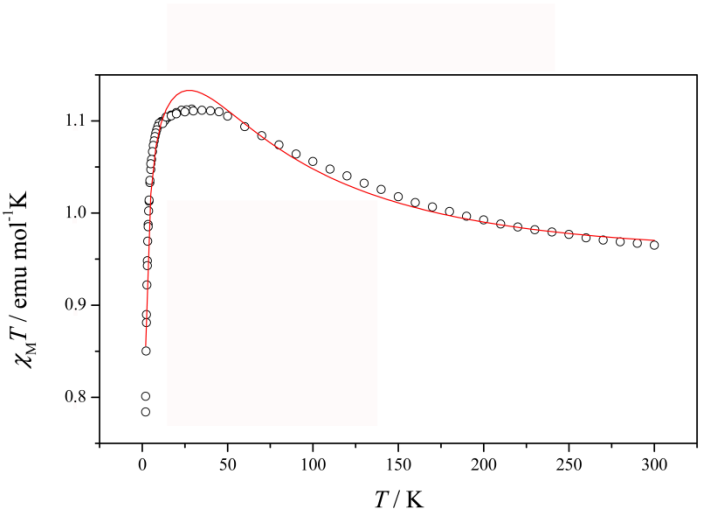

Figure S8. Plot of magnetic susceptibility-temperature product ($\chi_M T$) versus temperature (T) for compound **2**.

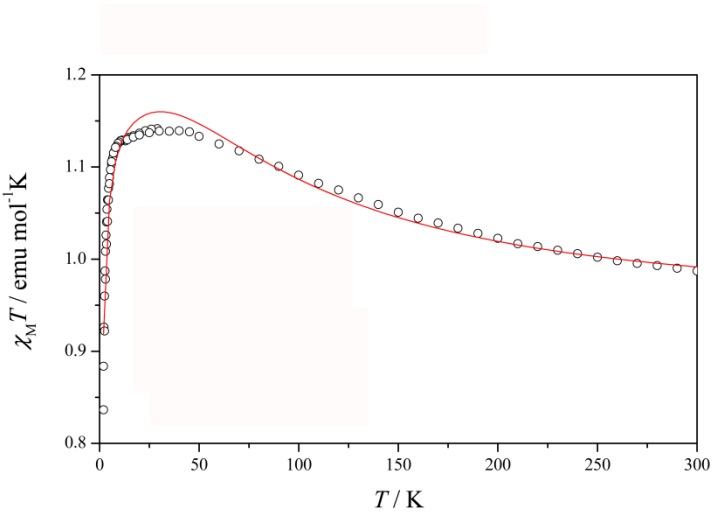

Figure S9. Plot of magnetic susceptibility-temperature product ($\chi_M T$) versus temperature (T) for compound **3**.

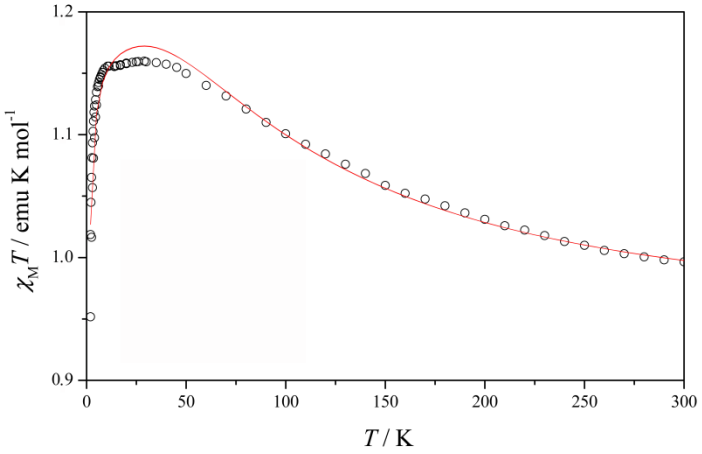

Figure S10. Plot of magnetic susceptibility-temperature product ($\chi_M T$) versus temperature (T) for compound **5**.

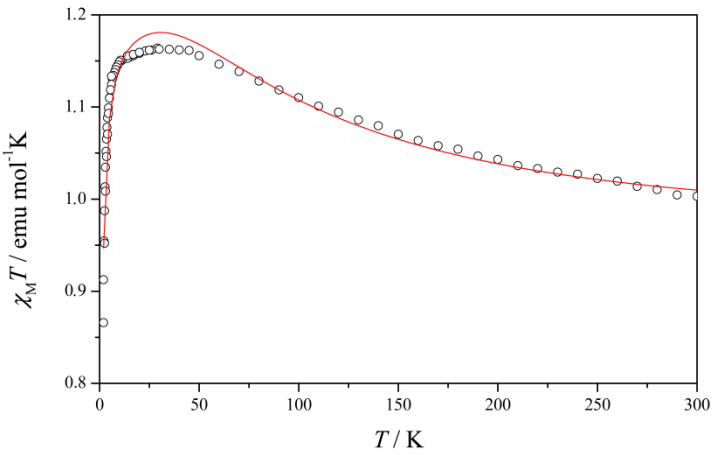

Figure S11. Plot of magnetic susceptibility-temperature product ($\chi_M T$) versus temperature (T) for compound **6**.

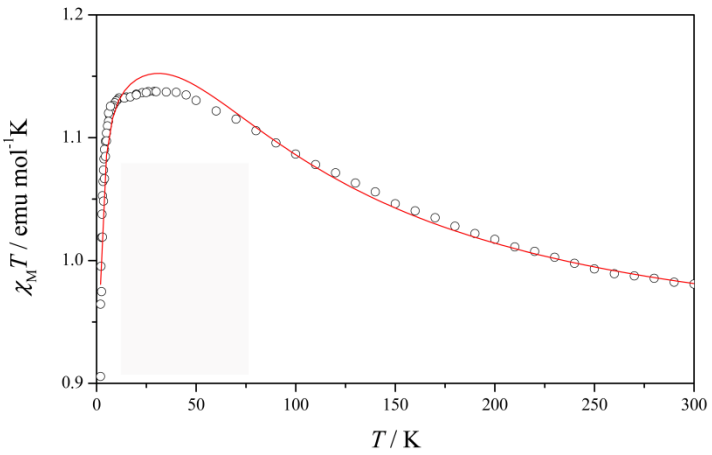

Figure S12. Plot of magnetic susceptibility-temperature product ($\chi_M T$) versus temperature (T) for compound **7**.