Supporting Information

Turning a "useless" ligand into a "useful" ligand: a magneto-structural study of an unusual family of Cu^{II} wheels derived from functionalised phenolic oximes

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Experimental Procedures:

¹H and ¹³C NMR spectra were recorded on an ava 500 MHz spectrometer. 1-3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylsalicylaldoxime was prepared by a previously published procedure.¹ Solvents and reagents were used as received from commercial suppliers.

Synthesis of {1-3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-methylpropiophenoneoxime (H₄L₂)

3-((bis(2-hydroxyethyl)amino)methyl)-2-hydroxy-5-propiophenone (10.0 g, 35 mmol), hydroxylamine hydrochloride (3.5 g, 50 mmol) and sodium acetate (4.14 g, 50 mmol) were dissolved in 400 mL of ethanol. The mixture was refluxed under N₂ for 24 h. A white precipitate was filtered off from the warm ethanol solution. The solvent is evaporated to dryness, CH₂Cl₂ is added and a white product collected after filtration (9.14 g, 84%). ¹H NMR (500 MHz, DMSO): δ 7.12 (bs, 1H), 7.05 (bs, 1H), 3.60 (s, 2H), 3.54 (t, *J*=6.2 Hz, 4H), 2.53 (t, *J*= 6.2 Hz, 4H), 2.23 (s, 3H), 2.22 (s, 3H).¹³C NMR (500 MHz, DMSO): δ 157.28 (1C, *C*_{ar}OH), 153.86 (1C, *C*NOH), 131.34 (1C, *C*H), 127.61 (1C, *C*H), 126.99 (1C, *C*), 124.34 (1C, *C*), 121.01 (1C, *C*), 59.14 (2C, *C*H₂), 56.51 (2C, *C*H₂), 54.78 (1C, *C*H₂), 21.69 (1C, *C*H₃), 12.73 (1C, CH₃).

	1	2	3	4	5	
Empirical formula	C ₅₈ H ₈₃ Cl ₄ Cu ₈ N ₈ O ₁₈	C ₅₆ H ₇₆ Cl _{0.79} Cu8N _{11.21} O _{25.62}	C ₆₉ H ₁₀₈ Cu ₈ N ₈ O ₂₉	C _{90.78} H _{129.13} B ₂ Cu ₈ F ₈ N ₁₂ O _{24.78}	C ₆₇ H ₁₂₀ Cu ₈ N ₂₀ O ₂₇	
Formula weight	1830.44	1852.53	2021.95	2467.01	2146.17	
Temperature, K	170	170	120	120.0	120.0	
Wavelength, Å	Μο Κα (0.71073)	Μο Κα (0.71073)	Cu Kα (1.54184)	Μο Κα (0.71073)	Cu Ka (1.54184)	
Crystal system	Orthorhombic	Hexagonal	Cubic	Monoclinic	Orthorhombic	
Space group	Pbca	P62	Pn-3n	C2/c	Pbca	
a, Å	25.5938(6)	20.2162(4)	37.57080(16)	a = 23.3511(4)	25.2990(5)	
			, í			
b, Å	19.9423(4)	20.2162(4)	37.57080(16)	17.1783(2)	20.7375(4)	
c, Å	32.2211(6)	16.8492(3)	37.57080(16)	26.2510(5)	32.5445(8)	
a, °	90	90	90	90	90	
b, °	90	90	90	101.0240(17)	90	
g, °	90	120	90	90	90	
Volume, Å3	16445.6(6)	5963.6(3)	53033.6(7)	10335.8(3)	17074.1(6)	
Ζ	8	3	24	4	8	
ρ (calc), Mg/m ³	1.479	1.547	1.519	1.585	1.670	
μ, mm ⁻¹	2.219	2.199	2.726	1.704	2.883	
Measd/indep. reflns	97866/10680	74631/5175	232108/9253	72031/15269	87780/17342	
$R(_{\rm int})$	0.0818	0.0695	0.0729	0.0390	0.0744	
Goodness-of-fit on F ²	1.070	1.089	1.063	1.037	1.070	
<i>R</i> 1	0.0748	0.0378	0.0467	0.0410	0.0956	
wR2	0.2016	0.1126	0.1404	0.1035	0.2636	
Δ0	2.823 and -0.641	0.878, -0.353	1.266, -0.741	0.877, -0.748	2.987, -0.819	
	6	7	8	9		
Empirical formula	$\frac{6}{C_{68}H_{104}Cl_4Cu_8N_8O_{18}}$	$\frac{7}{C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}}$	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆	9 C _{58 50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18 50}	-	
Empirical formula Formula weight	6 C ₆₈ H ₁₀₄ Cl ₄ Cu ₈ N ₈ O ₁₈ 1971.71	$\frac{7}{C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}}}$ 4224.97	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆ 1498.48	9 <u>C_{58,50} H₈₄Cu₄N₈Na₂O_{18,50} 1495.47</u>		
Empirical formula Formula weight Temperature, K	6 C ₆₈ H ₁₀₄ Cl ₄ Cu ₈ N ₈ O ₁₈ 1971.71 200.0	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0 \end{array}$	8 <u>C₅₆H₇₆Cu₆N₈O₁₆ 1498.48 120.0</u>	9 C _{58.50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18.50} 1495.47 120.0	-	
Empirical formula Formula weight Temperature, K Wavelength, Å	6 C ₆₈ H ₁₀₄ Cl ₄ Cu ₈ N ₈ O ₁₈ 1971.71 200.0 Cu Kα (1.54184)	7 C ₁₃₂ H ₁₉₈ Br ₈ Cu ₁₆ N ₁₆ O ₃₅ 4224.97 120.0 Cu Kα (1.54184)	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆ 1498.48 120.0 Cu Kα (1.54184)	9 C _{58.50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18.50} 1495.47 120.0 Μο Κα (0.71073)	-	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system	6 C ₆₈ H ₁₀₄ Cl ₄ Cu ₈ N ₈ O ₁₈ 1971.71 200.0 Cu Kα (1.54184) Monoclinic	7 C ₁₃₂ H ₁₉₈ Br ₈ Cu ₁₆ N ₁₆ O ₃₅ 4224.97 120.0 Cu Kα (1.54184) Monoclinic	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆ 1498.48 120.0 Cu Kα (1.54184) Monoclinic	9 C _{58.50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18.50} 1495.47 120.0 Μο Κα (0.71073) Monoclinic	-	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group	6 C ₆₈ H ₁₀₄ Cl ₄ Cu ₈ N ₈ O ₁₈ 1971.71 200.0 Cu Kα (1.54184) Monoclinic <i>I</i> 2/a	7 C ₁₃₂ H ₁₉₈ Br ₈ Cu ₁₆ N ₁₆ O ₃₅ 4224.97 120.0 Cu Kα (1.54184) Monoclinic <i>I</i> 2/ <i>a</i>	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆ 1498.48 120.0 Cu Kα (1.54184) Monoclinic C2/c	9 C _{58,50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo Kα (0.71073) Monoclinic C2/c	- - - -	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å	6 C ₆₈ H ₁₀₄ Cl ₄ Cu ₈ N ₈ O ₁₈ 1971.71 200.0 Cu Kα (1.54184) Monoclinic <i>I</i> 2/ <i>a</i> 15.74110(10)	7 $C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$ 4224.97 120.0 $Cu K\alpha (1.54184)$ Monoclinic $12/a$ $15.8200(4)$	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆ 1498.48 120.0 Cu Kα (1.54184) Monoclinic C2/c 14.5984(3)	9 C _{58,50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo Kα (0.71073) Monoclinic C2/c 15.2213(3)	-	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å	$\begin{array}{c} 6 \\ \hline \\ \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \\ \mathbf{Cu}\ \mathbf{K\alpha}\ (1.54184) \\ \hline \\ \mathbf{Monoclinic} \\ 12/a \\ 15.74110(10) \\ 20.12890(10) \\ \end{array}$	7 $C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$ 4224.97 120.0 $Cu K\alpha (1.54184)$ Monoclinic $12/a$ $15.8200(4)$ $20.0425(4)$	8 C ₅₆ H ₇₆ Cu ₆ N ₈ O ₁₆ 1498.48 120.0 Cu Kα (1.54184) Monoclinic C2/c 14.5984(3) 26.6204(7)	9 C _{58,50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo Kα (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6)	- - - - - - - -	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathbf{Cu}\ \mathbf{K\alpha}\ (1.54184) \\ \hline \mathbf{Monoclinic} \\ 12/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \end{array}$	7 $C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$ 4224.97 120.0 $Cu K\alpha (1.54184)$ Monoclinic $12/a$ $15.8200(4)$ $20.0425(4)$ $51.3059(14)$	$\frac{8}{C_{56}H_{76}Cu_6N_8O_{16}}$ 1498.48 120.0 Cu K α (1.54184) Monoclinic C2/c 14.5984(3) 26.6204(7) 18.8428(4)	9 $C_{58,50}$ H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4)	- - - - - - - - -	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, °	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathbf{Cu} \ \mathbf{K\alpha} \ (1.54184) \\ \hline \mathbf{Monoclinic} \\ 12/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu K\alpha (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90 \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu K\alpha (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ \hline 90 \\ \end{array}$	$\begin{array}{c} \textbf{9} \\ \hline C_{58,50} H_{84} Cu_4 N_8 Na_2 O_{18,50} \\ \hline 1495.47 \\ \hline 120.0 \\ Mo K\alpha (0.71073) \\ Monoclinic \\ \hline C2/c \\ \hline 15.2213(3) \\ \hline 26.3669(6) \\ \hline 17.2409(4) \\ \hline 90 \end{array}$	- - - - - - - - - - -	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, °	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ \hline 1971.71 \\ 200.0 \\ \hline \mathbf{Cu}\ \mathbf{K\alpha}\ (1.54184) \\ \hline \mathbf{Monoclinic} \\ \hline \mathbf{12/a} \\ \hline \mathbf{15.74110(10)} \\ 20.12890(10) \\ \hline \mathbf{51.7316(5)} \\ 90 \\ \hline \mathbf{93.2820(10)} \\ \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu K\alpha (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90\\ \hline 93.223(2)\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu K\alpha (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ \end{array}$	$\begin{array}{c} \textbf{9} \\ \hline C_{58,50} H_{84} Cu_4 N_8 Na_2 O_{18,50} \\ \hline 1495,47 \\ \hline 120.0 \\ \hline Mo K\alpha (0.71073) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 15.2213(3) \\ \hline 26.3669(6) \\ \hline 17.2409(4) \\ \hline 90 \\ \hline 93.295(2) \\ \end{array}$	- - - - - - - - - - - -	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, °	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68} \mathrm{H}_{104} \mathrm{Cl}_4 \mathrm{Cu}_8 \mathrm{N}_8 \mathrm{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathrm{Cu} \ \mathrm{Ka} \ (1.54184) \\ \mathrm{Monoclinic} \\ \hline 12/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \\ \hline 93.2820(10) \\ 90 \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu \ K\alpha \ (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90\\ \hline 93.223(2)\\ \hline 90\\ \hline \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu \ K\alpha \ (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline \end{array}$	9 C _{58,50} H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo Kα (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90	- - - - - - - - - - - - - -	
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ \hline 1971.71 \\ 200.0 \\ \hline \mathbf{Cu} \ \mathbf{Ka} \ (1.54184) \\ \hline \mathbf{Monoclinic} \\ \hline \mathbf{12/a} \\ \hline 15.74110(10) \\ 20.12890(10) \\ \hline 51.7316(5) \\ 90 \\ \hline 90 \\ \hline 93.2820(10) \\ 90 \\ \hline 16364 \ \mathbf{3(2)} \ \mathbf{\hat{s}}^3 \end{array}$	7 $C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$ 4224.97 120.0 Cu Ka (1.54184) Monoclinic <i>12/a</i> 15.8200(4) 20.0425(4) 51.3059(14) 90 93.223(2) 90 16242.0(7) Å ³	8 $C_{56}H_{76}Cu_6N_8O_{16}$ 1498.48 120.0 Cu Ka (1.54184) Monoclinic C2/c 14.5984(3) 26.6204(7) 18.8428(4) 90 104.153(2) 90 7100.3(3) δ^3	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) δ^3		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ \hline 1971.71 \\ \hline 200.0 \\ \hline \mathbf{Cu}\ \mathbf{K\alpha}\ (1.54184) \\ \hline \mathbf{Monoclinic} \\ \hline \mathbf{12/a} \\ \hline \mathbf{15.74110(10)} \\ \hline \mathbf{20.12890(10)} \\ \hline \mathbf{51.7316(5)} \\ \hline 90 \\ \hline 90 \\ \hline \mathbf{93.2820(10)} \\ \hline 90 \\ \hline \mathbf{16364.3(2)}\ \mathbf{\mathring{A}}^3 \\ 8 \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu K\alpha (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90\\ \hline 93.223(2)\\ \hline 90\\ \hline 16242.0(7) Å^3\\ \hline 4 \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu \ K\alpha \ (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) \ \text{\AA}^3 \\ \hline 4 \end{array}$	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z o (calc) Mø/m³	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ \hline 1971.71 \\ \hline 200.0 \\ \hline \mathbf{Cu} \ \mathbf{Ka} \ (1.54184) \\ \hline \mathbf{Monoclinic} \\ \hline \mathbf{12/a} \\ \hline 15.74110(10) \\ \hline 20.12890(10) \\ \hline 51.7316(5) \\ \hline 90 \\ \hline 93.2820(10) \\ \hline 90 \\ \hline 16364.3(2) \ \mathbb{A}^3 \\ \hline 8 \\ \hline 1 \ 601 \\ \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu K\alpha (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90\\ \hline 93.223(2)\\ \hline 90\\ \hline 16242.0(7) Å^3\\ \hline 4\\ \hline 1728\\ \hline \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu \ K\alpha \ (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) \ \text{\AA}^3 \\ \hline 4 \\ \hline 1402 \\ \end{array}$	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1 438		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z ρ (calc), Mg/m³ u, umr¹	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ \hline 1971.71 \\ \hline 200.0 \\ \hline \mathbf{Cu} \ \mathbf{Ka} \ (1.54184) \\ \hline \mathbf{Monoclinic} \\ \hline \mathbf{12/a} \\ \hline 15.74110(10) \\ \hline 20.12890(10) \\ \hline 51.7316(5) \\ 90 \\ \hline 90 \\ \hline 93.2820(10) \\ 90 \\ \hline 16364.3(2) \ \mathbb{A}^3 \\ 8 \\ \hline 1.601 \\ \hline 3.997 \\ \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu K\alpha (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ 90\\ \hline 93.223(2)\\ 90\\ \hline 16242.0(7) Å^3\\ \hline 4\\ \hline 1.728\\ \hline 5.106\\ \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu \ K\alpha \ (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) \ \text{\AA}^3 \\ \hline 4 \\ \hline 1.402 \\ \hline 2.487 \\ \hline \end{array}$	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z ρ (calc), Mg/m ³ μ, mm ⁻¹ Measd/indep_reflux	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68} \mathrm{H}_{104} \mathrm{Cl}_4 \mathrm{Cu}_8 \mathrm{N}_8 \mathrm{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathrm{Cu} \ \mathrm{K\alpha} \ (1.54184) \\ \hline \mathrm{Monoclinic} \\ \hline I2/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \\ 93.2820(10) \\ 90 \\ 16364.3(2) \ \mathrm{\AA}^3 \\ 8 \\ 1.601 \\ 3.997 \\ 200377/17064 \\ \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu K\alpha (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ 90\\ \hline 93.223(2)\\ 90\\ \hline 16242.0(7) Å^3\\ \hline 4\\ \hline 1.728\\ \hline 5.106\\ \hline 125018/14848\\ \hline \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu Ka (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) Å^3 \\ \hline 4 \\ \hline 1.402 \\ \hline 2.487 \\ \hline 44755/7393 \\ \hline \end{array}$	9 $C_{58,50}$ H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo Ka (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299 57914/8317		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z ρ (calc), Mg/m ³ μ, mm ⁻¹ Measd/indep. reflns <i>B</i> (init)	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68} \mathrm{H}_{104} \mathrm{Cl}_4 \mathrm{Cu}_8 \mathrm{N}_8 \mathrm{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathrm{Cu} \ \mathrm{K\alpha} \ (1.54184) \\ \hline \mathrm{Monoclinic} \\ \hline I2/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \\ 93.2820(10) \\ 90 \\ 93.2820(10) \\ 90 \\ 16364.3(2) \ \mathrm{\AA}^3 \\ 8 \\ 1.601 \\ 3.997 \\ 200377/17064 \\ 0.0503 \\ \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu \ K\alpha \ (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90\\ \hline 93.223(2)\\ \hline 90\\ \hline 16242.0(7) \ Å^3\\ \hline 4\\ \hline 1.728\\ \hline 5.106\\ \hline 125018/14848\\ \hline 0 \ 1203\\ \hline \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu Ka (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) Å^3 \\ \hline 4 \\ \hline 1.402 \\ \hline 2.487 \\ \hline 44755/7393 \\ \hline 0.0474 \\ \end{array}$	9 $C_{58,50}$ H ₈₄ Cu ₄ N ₈ Na ₂ O _{18,50} 1495.47 120.0 Mo Ka (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299 57914/8317 0 0792		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z ρ (calc), Mg/m ³ μ , mm ⁻¹ Measd/indep. reflns $R(_{ini})$ Goodness-of-fit on F ²	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68} \mathrm{H}_{104} \mathrm{Cl}_4 \mathrm{Cu}_8 \mathrm{N}_8 \mathrm{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathrm{Cu} \ \mathrm{K\alpha} \ (1.54184) \\ \hline \mathrm{Monoclinic} \\ \hline I2/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \\ 93.2820(10) \\ 90 \\ 16364.3(2) \ \mathrm{\AA}^3 \\ 8 \\ 1.601 \\ 3.997 \\ 200377/17064 \\ 0.0503 \\ 1.134 \\ \end{array}$	$\begin{array}{c} 7\\ \hline C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline 4224.97\\ \hline 120.0\\ \hline Cu \ K\alpha \ (1.54184)\\ \hline Monoclinic\\ \hline 12/a\\ \hline 15.8200(4)\\ \hline 20.0425(4)\\ \hline 51.3059(14)\\ \hline 90\\ \hline 93.223(2)\\ \hline 90\\ \hline 16242.0(7) \ Å^3\\ \hline 4\\ \hline 1.728\\ \hline 5.106\\ \hline 125018/14848\\ \hline 0.1203\\ \hline 1066\\ \hline \end{array}$	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu Ka (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) Å^3 \\ \hline 4 \\ \hline 1.402 \\ \hline 2.487 \\ \hline 44755/7393 \\ \hline 0.0474 \\ \hline 1.056 \\ \hline \end{array}$	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299 57914/8317 0.0792 1.045		
Empirical formulaFormula weightTemperature, KWavelength, ÅCrystal systemSpace groupa, Åb, Åc, Åa, °b, °g, °VolumeZ ρ (calc), Mg/m³ μ , mm¹Measd/indep. reflns $R(_{int})$ Goodness-of-fit on F² $R1$	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68} \mathrm{H}_{104} \mathrm{Cl}_4 \mathrm{Cu}_8 \mathrm{N}_8 \mathrm{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathrm{Cu} \ \mathrm{K\alpha} \ (1.54184) \\ \hline \mathrm{Monoclinic} \\ \hline I2/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \\ 93.2820(10) \\ 90 \\ 16364.3(2) \ \mathrm{\AA}^3 \\ 8 \\ 1.601 \\ 3.997 \\ 200377/17064 \\ 0.0503 \\ 1.134 \\ 0.0588 \\ \end{array}$	7 $C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$ 4224.97 120.0 Cu Ka (1.54184) Monoclinic $I2/a$ 15.8200(4) 20.0425(4) 51.3059(14) 90 16242.0(7) Å ³ 4 1.728 5.106 125018/14848 0.1203 1.066 0 0769	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu Ka (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) Å^3 \\ \hline 4 \\ \hline 1.402 \\ \hline 2.487 \\ \hline 44755/7393 \\ \hline 0.0474 \\ \hline 1.056 \\ \hline 0.0486 \\ \end{array}$	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299 57914/8317 0.0792 1.045 0 0494		
Empirical formulaFormula weightTemperature, KWavelength, ÅCrystal systemSpace groupa, Åb, Åc, Åa, °b, °g, °VolumeZ ρ (calc), Mg/m³ μ , mm¹Measd/indep. reflns $R(_{int})$ Goodness-of-fit on F² $R1$ $wR2$	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68} \mathrm{H}_{104} \mathrm{Cl}_4 \mathrm{Cu}_8 \mathrm{N}_8 \mathrm{O}_{18} \\ 1971.71 \\ 200.0 \\ \hline \mathrm{Cu} \ \mathrm{K\alpha} \ (1.54184) \\ \hline \mathrm{Monoclinic} \\ \hline I2/a \\ 15.74110(10) \\ 20.12890(10) \\ 51.7316(5) \\ 90 \\ 93.2820(10) \\ 90 \\ 16364.3(2) \ \mathrm{\AA}^3 \\ 8 \\ 1.601 \\ 3.997 \\ 200377/17064 \\ 0.0503 \\ 1.134 \\ 0.0588 \\ 0.2016 \\ \end{array}$	7 $C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$ 4224.97 120.0 Cu Ka (1.54184) Monoclinic $I2/a$ 15.8200(4) 20.0425(4) 51.3059(14) 90 16242.0(7) Å ³ 4 1.728 5.106 125018/14848 0.1203 1.066 0.0769 0.2205	$\begin{array}{c} \textbf{8} \\ \hline C_{56}H_{76}Cu_6N_8O_{16} \\ \hline 1498.48 \\ \hline 120.0 \\ \hline Cu Ka (1.54184) \\ \hline Monoclinic \\ \hline C2/c \\ \hline 14.5984(3) \\ \hline 26.6204(7) \\ \hline 18.8428(4) \\ 90 \\ \hline 104.153(2) \\ 90 \\ \hline 7100.3(3) Å^3 \\ \hline 4 \\ \hline 1.402 \\ \hline 2.487 \\ \hline 44755/7393 \\ \hline 0.0474 \\ \hline 1.056 \\ \hline 0.0486 \\ \hline 0 1410 \\ \hline \end{array}$	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo K α (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299 57914/8317 0.0792 1.045 0.0494 0 1242		
Empirical formula Formula weight Temperature, K Wavelength, Å Crystal system Space group a, Å b, Å c, Å a, ° b, ° g, ° Volume Z ρ (calc), Mg/m³ μ , mm¹ Measd/indep. reflns $R(imt)$ Goodness-of-fit on F² $R1$ $wR2$ χ -3	$\begin{array}{c} 6 \\ \hline \mathbf{C}_{68}\mathbf{H}_{104}\mathbf{Cl}_4\mathbf{Cu}_8\mathbf{N}_8\mathbf{O}_{18} \\ \hline 1971.71 \\ \hline 200.0 \\ \hline \mathbf{Cu}\ \mathbf{K\alpha}\ (1.54184) \\ \hline \text{Monoclinic} \\ \hline 12/a \\ \hline 15.74110(10) \\ \hline 20.12890(10) \\ \hline 51.7316(5) \\ \hline 90 \\ \hline 93.2820(10) \\ \hline 90 \\ \hline 16364.3(2)\ \text{Å}^3 \\ \hline 8 \\ \hline 1.601 \\ \hline 3.997 \\ \hline 200377/17064 \\ \hline 0.0503 \\ \hline 1.134 \\ \hline 0.0588 \\ \hline 0.2016 \\ \hline 1913 - 0.820 \\ \hline \end{array}$	$\begin{array}{c} 7\\ \hline \\ C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}\\ \hline \\ 4224.97\\ \hline \\ 120.0\\ \hline \\ Cu \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	8 $C_{56}H_{76}Cu_6N_8O_{16}$ 1498.48 120.0 Cu Ka (1.54184) Monoclinic C2/c 14.5984(3) 26.6204(7) 18.8428(4) 90 104.153(2) 90 7100.3(3) Å ³ 4 1.402 2.487 44755/7393 0.0474 1.056 0.0486 0.1410 1.116 -0.769	9 $C_{58,50} H_{84}Cu_4N_8Na_2O_{18,50}$ 1495.47 120.0 Mo Ka (0.71073) Monoclinic C2/c 15.2213(3) 26.3669(6) 17.2409(4) 90 93.295(2) 90 6908.0(3) Å ³ 4 1.438 1.299 57914/8317 0.0792 1.045 0.0494 0.1242 0.810 -0.503		

Table S1: A selection of crystallographic data for complexes 1-9 pertinent to the discussion in the main body.

	Co	omplex1		Comp	lex2		Comp	olex3		Com	plex4		Com	plex5			Com	plex6	
Configu	HS	BS1	BS2	HS	BS1	BS	HS	BS1	BS2	HS	BS1	BS2	HS	BS1	BS2	BS3	HS	BS1	BS2
rations						2													
Cu1	▲		↑	↑	↓	↑			↑					↑	↑	≜		┢	
Cu2	♠	▲	↑	▲	•		♠	1		•	↑	↑		1		1		1	
Cu3	1	1	↑	1	↑		♠	▲	▲	↑	▲	1		1	♠	1		↓	
Cu4	1	1	1	1	↓		1	•	•	1	1	1	1	1	1	1	1	A	•
Cu5	1	1	1	1	•	1	1	l ↓		1	↓	1	1	↓	↓	•			
Cu6	1	1	1	1	l ↓	1	1	•	1	1		1	1	1	1	•			
Cu7	1	1	•	1	1		1	•	I ↓	1	Î	•							
Cu8	1	1	↓	1	•		1	1	•	1	↑								

Table S2. The different spin configurations employed in the calculations of the magnetic exchange.

Complex Name	$J_{1\rm DFT}$	$J_{\rm 2DFT}$	$J_{\rm 3DFT}$	$J_{I \to p}$	$J_{2\text{Exp}}$
$[Cu_8(HL)_4(Cl)_4](1)$	-44.97	-320.49		-460.23	+17.53
$[Cu_8(HL)_4(NO_3)_4](2)$	-46.61	-278.27		-389.65	-219.22
[Cu ₆ (HL) ₄](8)	5.53	-25.9	-120.6		
$[Cu_4Na_2(HL)_2(H_2L)_2](9)$	-95.78	0.08		-271.31	N/A

 Table S3. DFT computed exchange constants for 1, 2, 8 and 9.



Figure S2: Packing of molecules of 1 as viewed down the *b*-axis of the crystal. H-atoms omitted for clarity.



Figure S3: Packing of molecules of 8 as viewed down the *a*-axis of the crystal. H-atoms omitted for clarity.



Figure S4: Packing of molecules of 9 as viewed down the *a*-axis of the crystal. H-atoms omitted for clarity.



Figure S5: Packing of molecules of 9 as viewed down the c-axis of the crystal. H-atoms omitted for clarity.

Figure S6 Representative MO diagram depicting the symmetric combinations of the dx^2-y^2 orbitals of complex 1.

Figure S7 Computed spin density plot of complex 2.



Figure S8 Representative MO diagrams employed to calculate the overlap integrals in complex 9.

References

 S. Sanz, J. M. Frost, T. Rajeshkumar, S. J. Dalgarno, W. Wernsdorfer, J. Schnack, P. J. Lusby and E. K. Brechin, *Chem. Eur. J.*, 2014, 20, 3010.