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:

^{1}H and ^{13}C 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 (H_4L_2)

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 N_2 for 24 h. A white precipitate was filtered off from the warm ethanol solution. The solvent is evaporated to dryness, CH_2Cl_2 is added and a white product collected after filtration (9.14 g, 84%). ^{1}H 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).^{13}C 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, CH_2), 56.51 (2C, CH_2), 54.78 (1C, CH_2), 21.69 (1C, CH_3), 12.73 (1C, CH_3).

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{58}H_{83}Cl_4Cu_8N_8O_{18}$	$C_{56}H_{76}Cl_{0.79}Cu8N_{11.21}O_{25.62}$	$C_{69}H_{108}Cu_8N_8O_{29}$	$C_{90.78}H_{129.13}B_2Cu_8F_8\ N_{12}O_{24.78}$	$C_{67}H_{120}Cu_8N_{20}O_{27}$
Formula weight	1830.44	1852.53	2021.95	2467.01	2146.17
Temperature, K	170	170	120	120.0	120.0
Wavelength, Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Cu Kα (1.54184)	Mo Kα (0.71073)	Cu Kα (1.54184)
Crystal system	Orthorhombic	Hexagonal	Cubic	Monoclinic	Orthorhombic
Space group	*Pbca*	*P*62	*Pn*-3*n*	*C*2/*c*	*Pbca*
a, Å	25.5938(6)	20.2162(4)	37.57080(16)	a = 23.3511(4)	25.2990(5)
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)
Z	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
$R_{(int)}$	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
*R*1	0.0748	0.0378	0.0467	0.0410	0.0956
*wR*2	0.2016	0.1126	0.1404	0.1035	0.2636
$\Delta\rho_{max, min}$, e.Å^{-3}	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	$C_{68}H_{104}Cl_4Cu_8N_8O_{18}$	$C_{132}H_{198}Br_8Cu_{16}N_{16}O_{35}$	$C_{56}H_{76}Cu_6N_8O_{16}$	$C_{58.50}H_{84}Cu_4N_8Na_2O_{18.50}$	
Formula weight	1971.71	4224.97	1498.48	1495.47	
Temperature, K	200.0	120.0	120.0	120.0	
Wavelength, Å	Cu Kα (1.54184)	Cu Kα (1.54184)	Cu Kα (1.54184)	Mo Kα (0.71073)	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	
Space group	*I*2/*a*	*I*2/*a*	*C*2/*c*	*C*2/*c*	
a, Å	15.74110(10)	15.8200(4)	14.5984(3)	15.2213(3)	
b, Å	20.12890(10)	20.0425(4)	26.6204(7)	26.3669(6)	
c, Å	51.7316(5)	51.3059(14)	18.8428(4)	17.2409(4)	
a, °	90	90	90	90	
b, °	93.2820(10)	93.223(2)	104.153(2)	93.295(2)	
g, °	90	90	90	90	
Volume	16364.3(2) Å^3	16242.0(7) Å^3	7100.3(3) Å^3	6908.0(3) Å^3	
Z	8	4	4	4	
ρ (calc), Mg/m^3	1.601	1.728	1.402	1.438	
μ, mm^{-1}	3.997	5.106	2.487	1.299	
Measd/indep. reflns	200377/17064	125018/14848	44755/7393	57914/8317	
$R_{(int)}$	0.0503	0.1203	0.0474	0.0792	
Goodness-of-fit on F^2	1.134	1.066	1.056	1.045	
*R*1	0.0588	0.0769	0.0486	0.0494	
*wR*2	0.2016	0.2205	0.1410	0.1242	
$\Delta\rho_{max, min}$, e.Å^{-3}	1.913, -0.820	1.451,-2.800	1.116, -0.769	0.810, -0.503	

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

	Complex1			Complex2			Complex3			Complex4			Complex5				Complex6		
Configurations	HS	BS1	BS2	HS	BS1	BS 2	HS	BS1	BS2	HS	BS1	BS2	HS	BS1	BS2	BS3	HS	BS1	BS2
Cu1	↑	↓	↑	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↓	↑
Cu2	↑	↑	↑	↑	↑	↓	↑	↑	↓	↑	↑	↑	↑	↑	↓	↑	↑	↑	↓
Cu3	↑	↑	↑	↑	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↓	↑
Cu4	↑	↑	↑	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↓
Cu5	↑	↑	↑	↑	↑	↑	↑	↓	↓	↑	↓	↑	↑	↓	↓	↓			
Cu6	↑	↑	↑	↑	↓	↑	↑	↑	↑	↑	↑	↑	↑	↑	↑	↓			
Cu7	↑	↑	↓	↑	↑	↑	↑	↓	↓	↑	↑	↓							
Cu8	↑	↑	↓	↑	↓	↑	↑	↑	↓	↑	↑	↓							

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

Complex Name	J_{1DFT}	J_{2DFT}	J_{3DFT}	J_{1Exp}	J_{2Exp}
$[Cu_8(HL)_4(Cl)_4]$(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**.

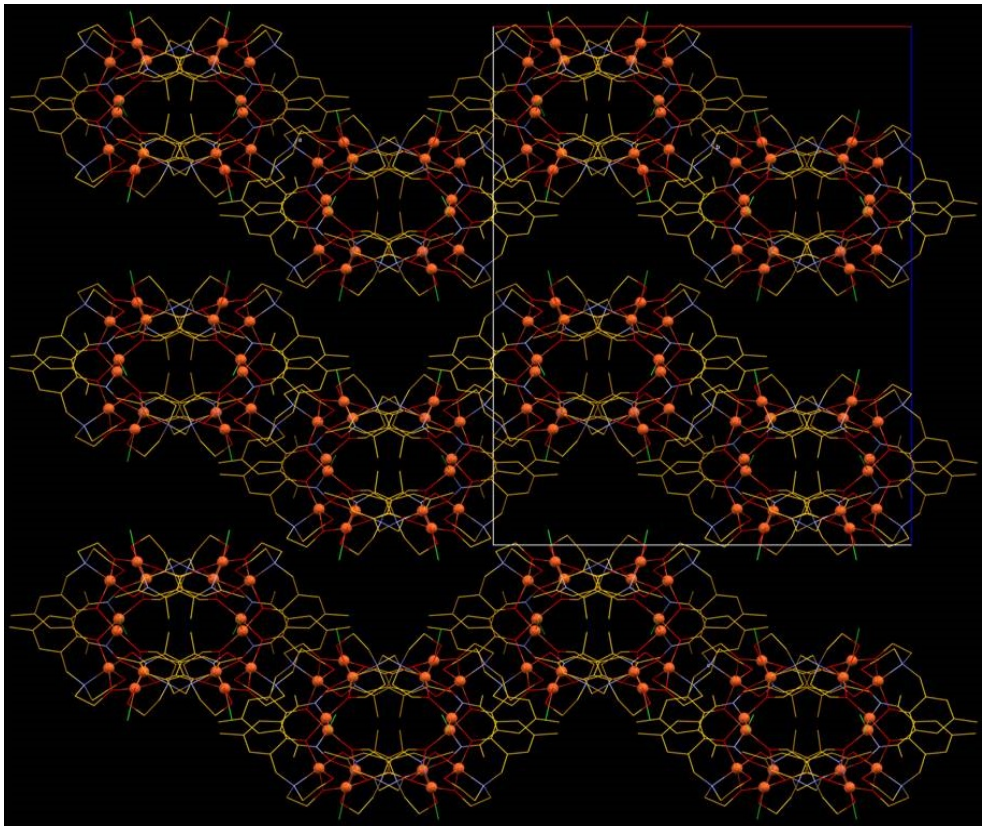

Figure S2: Packing of molecules of **1** as viewed down the *b*-axis of the crystal. H-atoms omitted for clarity.

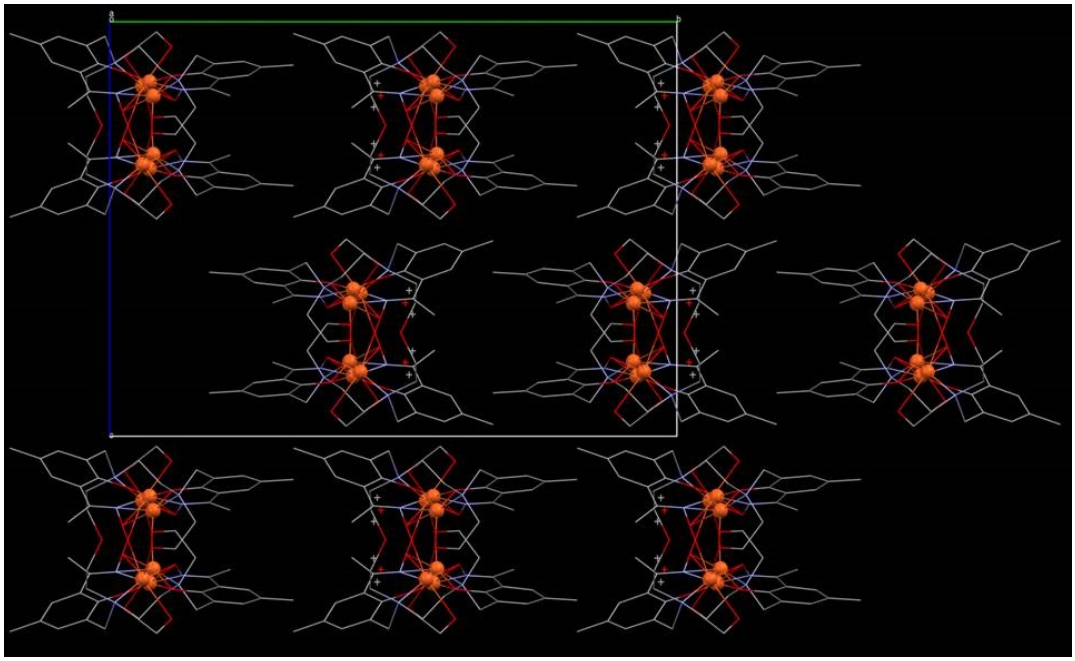

Figure S3: Packing of molecules of **8** as viewed down the *a*-axis of the crystal. H-atoms omitted for clarity.

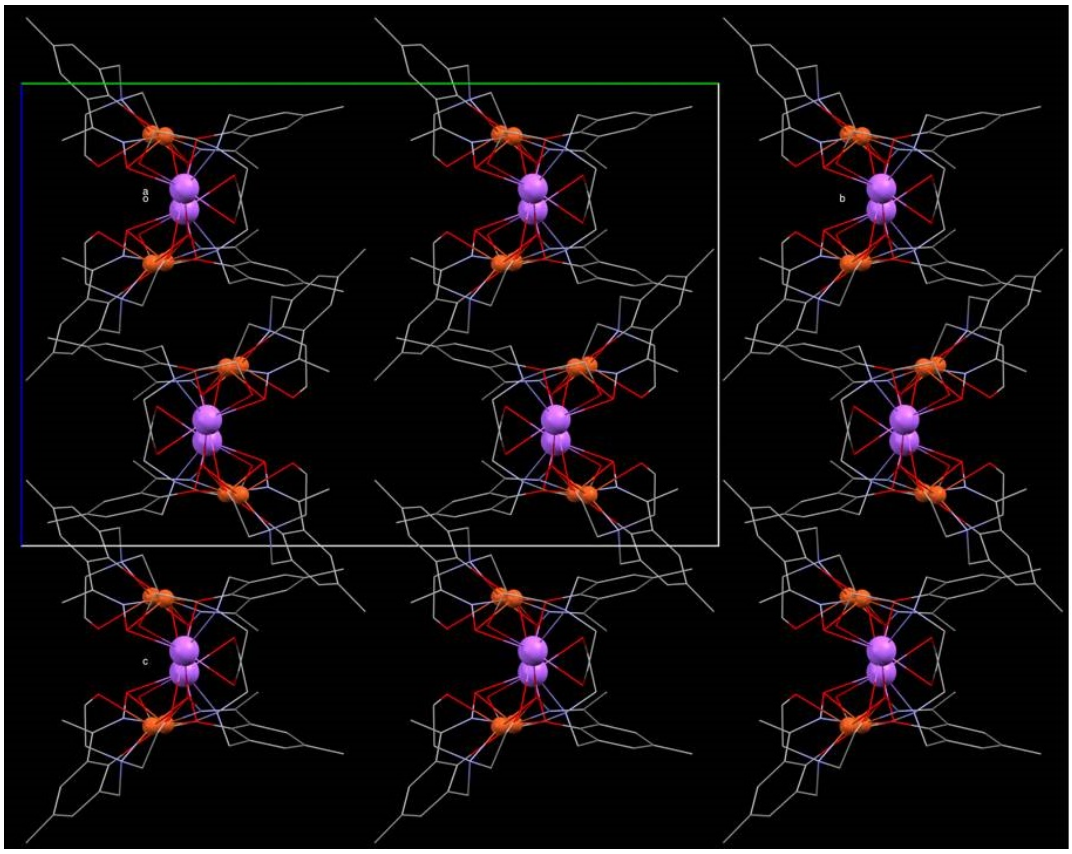

Figure S4: Packing of molecules of **9** as viewed down the *a*-axis of the crystal. H-atoms omitted for clarity.

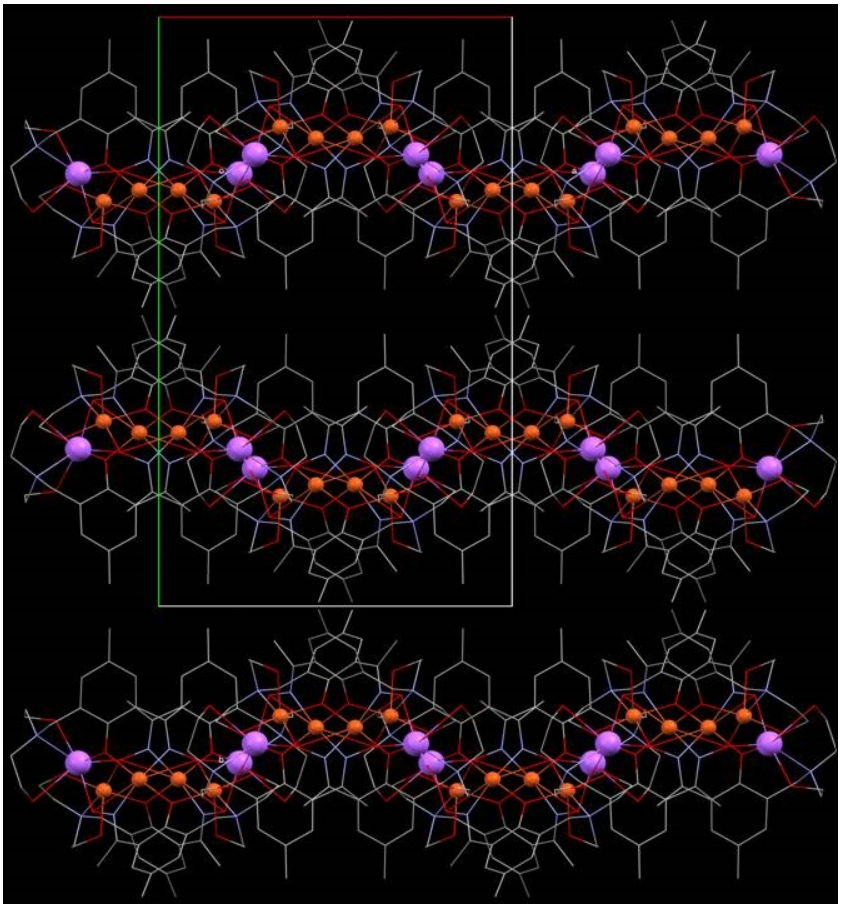

Figure S5: Packing of molecules of **9** as viewed down the c-axis of the crystal. H-atoms omitted for clarity.

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**.

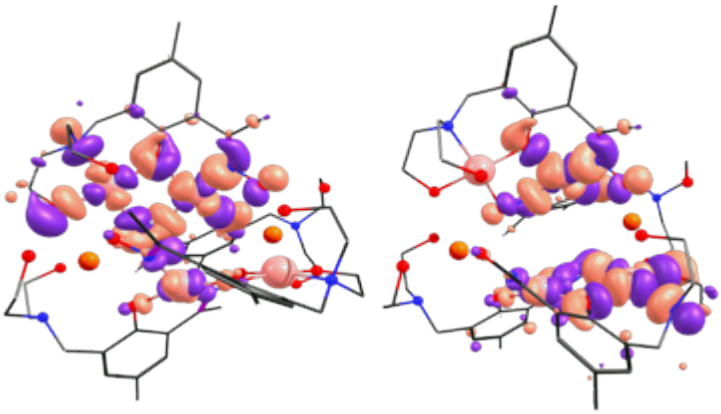

Figure S8 Representative MO diagrams employed to calculate the overlap integrals in complex **9.**

References

1. 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.