

Supporting Information

The Role of Halogen Bonding in Controlling Assembly and Organization of Cu(II)-Acac Based Coordination Complexes

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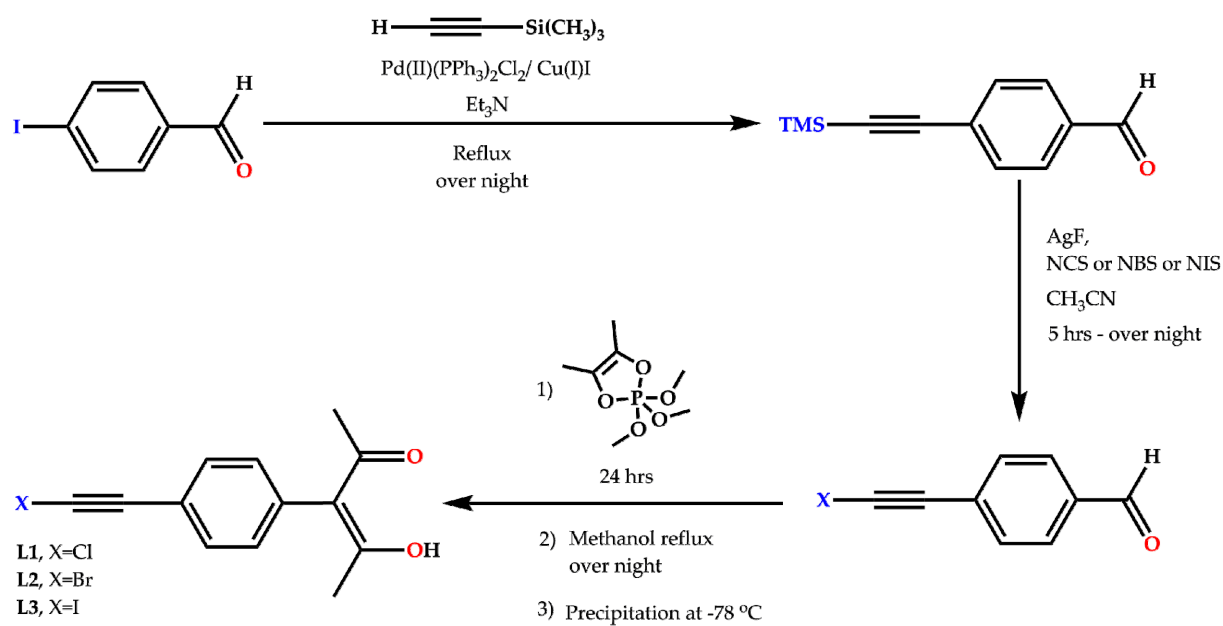
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Scheme S1. Synthesis pathway to ligands **L1-3**.

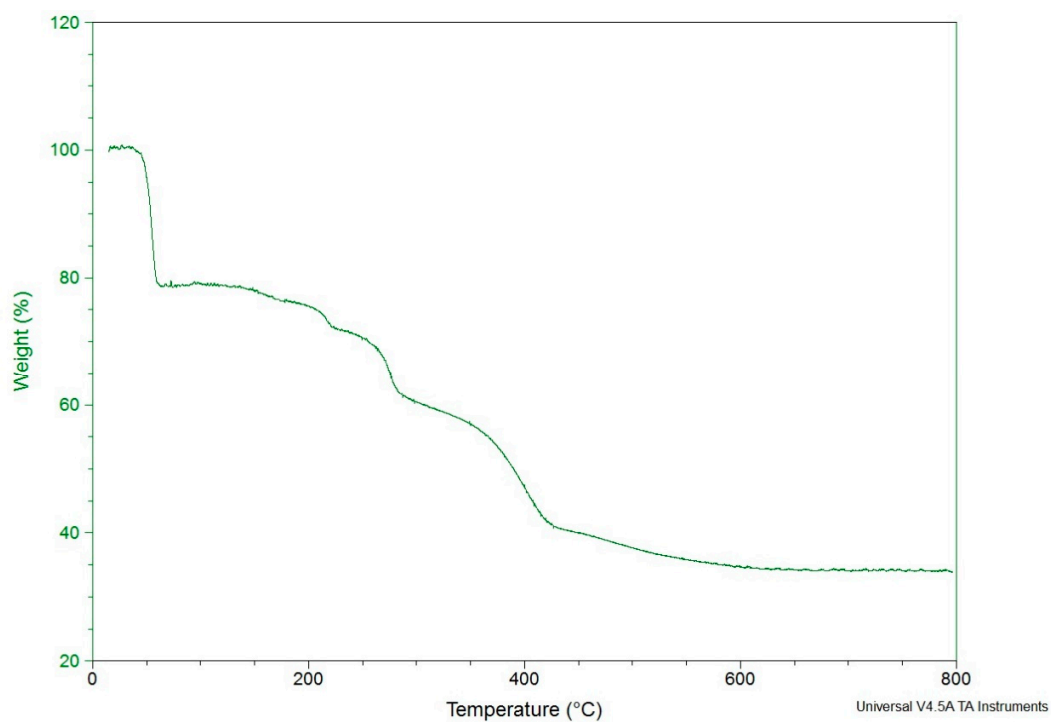


Figure S1. TGA trace of $[\text{Cu}(\text{L2})_2] \cdot 2\text{C}_4\text{H}_8\text{O}_2$.

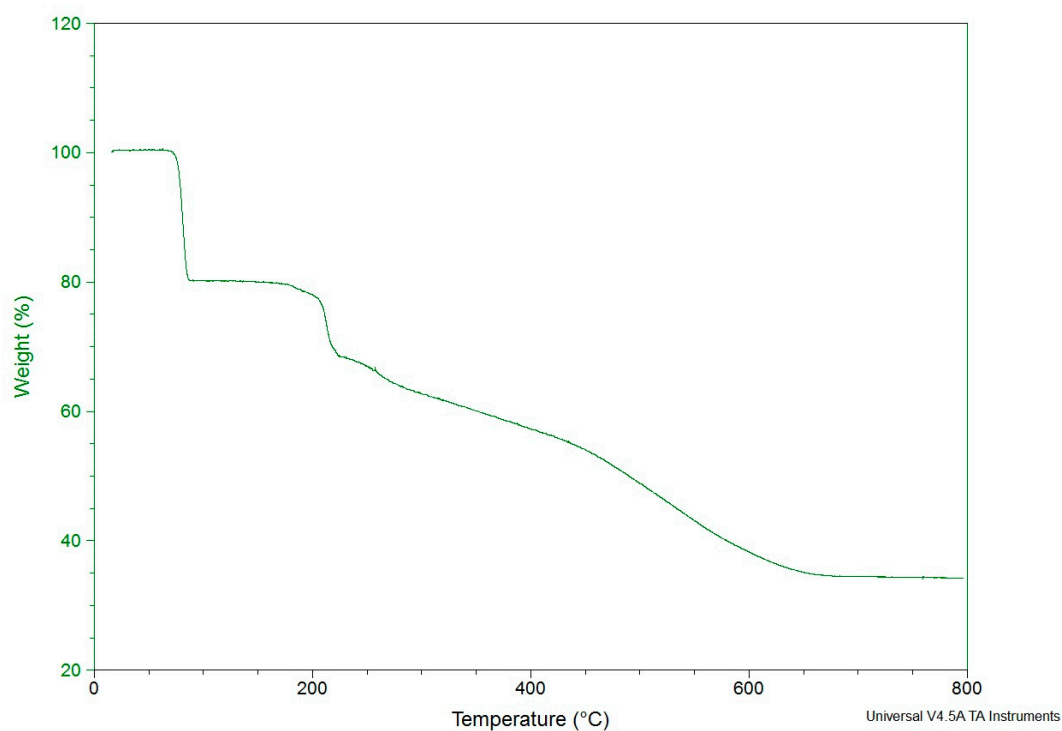


Figure S2. TGA trace of $[\text{Cu}(\text{L2})_2] \cdot 2\text{C}_4\text{H}_8\text{O}_2$.

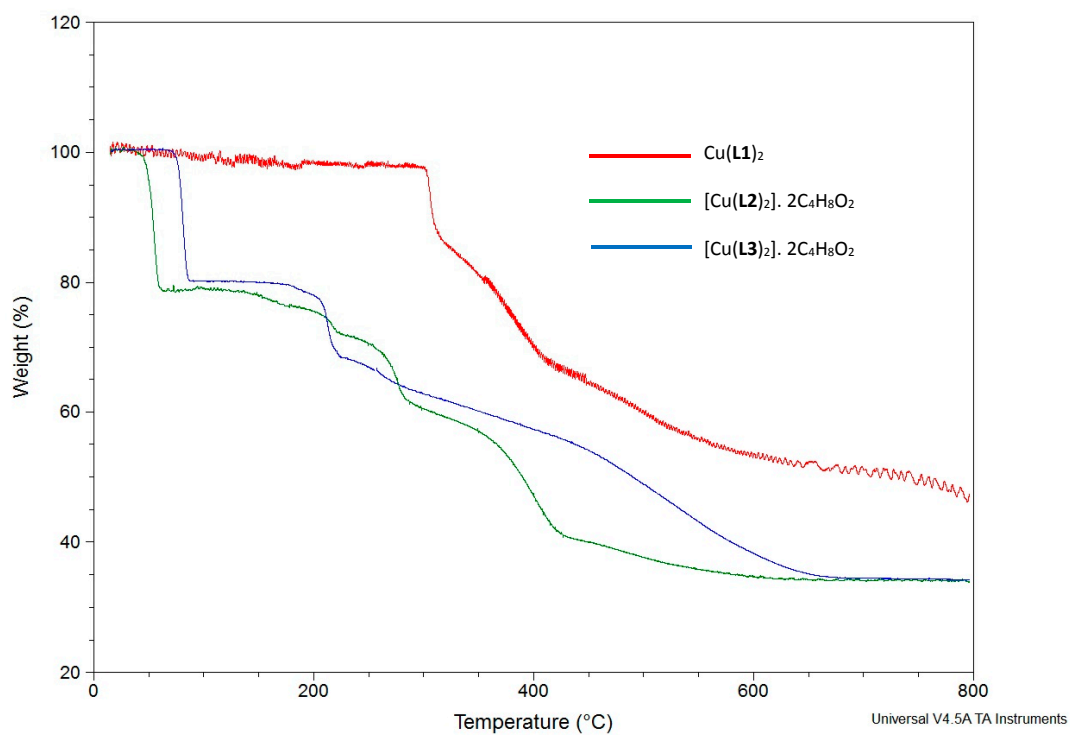


Figure S3. TGA traces comparison, $[\text{Cu}(\text{L2})_2] \cdot 2\text{C}_4\text{H}_8\text{O}_2$ and $[\text{Cu}(\text{L3})_2] \cdot 2\text{C}_4\text{H}_8\text{O}_2$ with $\text{Cu}(\text{L1})_2$

Table S1. Crystallographic data for the ligands and their metal complexes

Code	L1	L2	L3	[Cu(L1) ₂]	[Cu(L2) ₂].2CH ₃ CN
Formula moiety	C ₁₃ H ₁₁ ClO ₂	C ₁₃ H ₁₁ BrO ₂	C ₁₃ H ₁₁ IO ₂	(C ₁₃ H ₁₀ ClO ₂) ₂ , Cu	(C ₁₃ H ₁₀ BrO ₂) ₂ , Cu, (C ₂ H ₃ N) ₂
Empirical formula	C ₁₃ H ₁₁ ClO ₂	C ₁₃ H ₁₁ BrO ₂	C ₁₃ H ₁₁ IO ₂	C ₂₆ H ₂₀ Cl ₂ CuO ₄	C ₃₀ H ₂₆ Br ₂ CuN ₂ O ₄
Molecular weight	234.67	279.13	326.12	530.87	701.89
Color, Habit	Colorless, Prism	Brown, Prism	Yellow, Plate	Green, Needles	Green, Plate
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group, Z	C2/c, 4	P2(1)/n, 4	Pnma, 4	P2(1)/c, 2	P $\bar{1}$, 1
a, Å	9.704(5)	7.0148(7)	12.5746(13)	12.112(4)	8.0843(8)
b, Å	13.620(6)	12.2169(12)	7.2883(9)	12.704(4)	9.2352(10)
c, Å	8.810(5)	13.5874(13)	13.9188(7)	7.622(3)	10.8870(12)
α , °	90	90	90	90	92.144(4)
β , °	99.138(12)	91.691(4)	90	100.46(2)	99.260(3)
γ , °	90	90	90	90	100.990(3)
Volume, Å ³	1149.6(10)	1163.9(2)	1275.6(2)	1153.3(6)	785.57(14)
Density, g/cm ³	1.356	1.593	1.698	1.529	1.484
T, °K	120(2)	120(2)	296(2)	130(2)	120(2)
Crystal size, min x mid x max	0.120 x 0.220 x 0.380	0.160 x 0.440 x 0.480	0.100 x 0.330 x 0.590	0.048 x 0.242 x 0.368	0.060 x 0.320 x 0.400
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ , mm ⁻¹	0.313	3.513	2.493	1.210	3.273
Trans min / max	0.89 / 0.96	0.28 / 0.60	0.54 / 1.00	0.66 / 0.94	0.35 / 0.83
θ_{min} , °	2.99	2.24	4.36	1.71	1.90
θ_{max} , °	32.16	31.00	26.99	25.55	32.55
Reflections					
collected	5953	24368	5677	31884	19718
independent	1770	3637	1482	2127	5127
observed	1306	2859	1085	1743	2577
R _{int}	0.0399	0.0516	0.0288	0.0730	0.0488
Threshold expression	> 2 $\sigma(I)$	> 2 $\sigma(I)$	> 2 $\sigma(I)$	> 2 $\sigma(I)$	> 2 $\sigma(I)$
No. parameters	80	145	94	153	180
No. restraints	0	0	0	0	0
R ₁ (observed)	0.0496	0.0748	0.0418	0.0310	0.0519
wR ₂ (all)	0.1492	0.2238	0.0891	0.0872	0.1584
Goodness of fit (all)	1.093	1.068	1.074	1.072	0.932
ρ_{max} , ρ_{min} , e Å ⁻³	0.374, -0.250	4.819, -0.768	0.529, -0.450	0.340, -0.378	0.718, -0.945
Completeness to 2 θ limit	0.972	0.981	0.994	0.985	0.900

Code	[Cu(L2) ₂].2C ₄ H ₈ O ₂	[Cu(L2) ₂].2CH ₃ NO ₂	[Cu(L3) ₂].4CH ₃ CN	[Cu(L3) ₂].2C ₄ H ₈ O ₂	[Cu(L3) ₂]
Formula moiety	(C ₁₃ H ₁₀ BrO ₂) ₂ , Cu, (C ₄ H ₈ O ₂) ₂	(C ₁₃ H ₁₀ BrO ₂) ₂ , Cu, (CH ₃ NO ₂) ₂	(C ₁₃ H ₁₀ IO ₂) ₂ , Cu, (C ₂ H ₃ N) ₄	(C ₁₃ H ₁₀ IO ₂) ₂ , Cu, (C ₄ H ₈ O ₂) ₂	(C ₁₃ H ₁₀ IO ₂) ₂ , Cu
Empirical formula	C ₃₄ H ₃₆ Br ₂ CuO ₈	C ₂₈ H ₂₆ Br ₂ CuN ₂ O ₈	C ₃₄ H ₃₂ CuI ₂ N ₄ O ₄	C ₃₄ H ₃₆ CuI ₂ O ₈	C ₂₆ H ₂₀ CuI ₂ O ₄
Molecular weight	795.99	741.87	877.98	889.98	713.77
Color, Habit	Blue, Prism	Green, Plate	Blue, Plate	Green, Needles	Green, Plates
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group, Z	<i>P</i> 2(1)/ <i>c</i> , 2	<i>P</i> ₁ , 1	<i>P</i> ₁ , 1	<i>P</i> 2(1)/ <i>c</i> , 2	<i>P</i> 2(1)/ <i>n</i> , 6
<i>a</i> , Å	8.0238(9)	7.9062(13)	8.2630(4)	8.242(2)	21.351(4)
<i>b</i> , Å	13.8635(15)	8.9753(15)	10.6819(6)	14.206(4)	7.2561(13)
<i>c</i> , Å	15.3770(16)	11.2457(19)	11.4576(6)	15.472(4)	25.317(5)
α , °	90	85.197(7)	92.134(3)	90	90
β , °	102.274(4)	80.067(6)	104.211(2)	102.722(12)	112.809(10)
γ , °	90	76.761(6)	107.705(3)	90	90
Volume, Å ³	1671.4(3)	764.3(2)	927.04(8)	1767.1(8)	3615.5(12)
Density, g/cm ³	1.582	1.612	1.573	1.673	1.967
<i>T</i> , °K	120(2)	120(2)	120(2)	130(2)	130(2)
Crystal size, min x mid x max	0.320 x 0.400 x 0.440	0.100 x 0.320 x 0.440	0.060 x 0.320 x 0.400	0.122 x 0.356 x 0.578	0.055 x 0.232 x 0.356
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ , mm ⁻¹	3.094	3.378	2.293	2.412	3.499
Trans min / max	0.34 / 0.44	0.32 / 0.73	0.46 / 0.87	0.34 / 0.76	0.37 / 0.83
θ_{min} , °	2.00	1.84	1.85	1.97	1.06
θ_{max} , °	32.60	33.02	32.61	25.71	25.34
Reflections					
collected	22675	27759	19909	49520	35365
independent	5919	5266	6249	3335	6499
observed	5026	3837	3322	3037	4692
<i>R</i> _{int}	0.0264	0.0364	0.0527	0.0607	0.0647
Threshold expression	> 2 σ (<i>I</i>)	> 2 σ (<i>I</i>)	> 2 σ (<i>I</i>)	> 2 σ (<i>I</i>)	> 2 σ (<i>I</i>)
No. parameters	209	192	202	209	454
No. restraints	0	15	9	0	0
<i>R</i> ₁ (observed)	0.0279	0.0576	0.0506	0.0232	0.0438
<i>wR</i> ₂ (all)	0.0699	0.1744	0.1425	0.0564	0.1344
Goodness of fit (all)	1.031	1.090	1.055	1.048	1.083
ρ_{max} , ρ_{min} , e Å ⁻³	0.532, -0.365	1.640, -1.156	0.840, -0.790	0.381, -0.401	1.765, -1.133
Completeness to 2 θ limit	0.976	0.987	0.921	0.994	0.982