Supramolecular Assemblies of Trinuclear Copper(II)-Pyrazolato Units; A Structural, Magnetic and EPR Study

Kaige Shi, Logesh Mathivathanan, Radovan Herchel, Athanassios K. Boudalis, and Raphael G. Raptis

Table S1. Crystallographic and refinement data for [**1**] and [**2**].

	[**1**], CCDC2005300	[**2**], CCDC2005301
Empirical formula	$C_{170}H_{148}Cl_8Cu_7N_{26}O_2P_4$	$C_{45}H_{40}Cu_3N_{16}OP_2$
Formula weight	3439.40	1073.49
Temperature/K	293(2)	200(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	14.161(7)	8.6121(9)
b/Å	17.814(8)	17.034(2)
c/Å	18.173(9)	32.237(3)
α/°	80.66(1)	90
β/°	68.33(1)	96.493(2)
γ/°	85.25(1)	90
Volume/Å$_3$	4202(4)	4698.8(8)
Z	1	4
ρ_{calc}g/cm$_3$	1.359	1.517
μ/mm^{-1}	1.093	1.468
F(000)	1765.0	2188.0
Crystal size/mm$_3$	0.246 × 0.168 × 0.146	0.359 × 0.07 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.64 to 52.76	6.12 to 50.054
Index ranges	-17 ≤ h ≤ 17, -22 ≤ k ≤ 22, 0 ≤ l ≤ 22	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -38 ≤ l ≤ 38
Reflections collected	52608	78661
Independent reflections	17116 [R_{int} = 0.0692, R_{sigma} = 0.0894]	8296 [R_{int} = 0.1467, R_{sigma} = 0.0715]
Data/restraints/parameters	17116/33/985	5601/852/623
Goodness-of-fit on F_2	1.020	0.987
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1345	R_1 = 0.0662, wR_2 = 0.1637

Final R indexes [all data]	R_1 = 0.1132, wR_2 = 0.1543	R_1 = 0.1053, wR_2 = 0.1916
Largest diff. peak/hole / e Å^{-3}	0.63/-0.48	1.50/-1.08

Table S2. Selected interatomic distances (Å) and angles (°) for [**1**].

Cu1···Cu2	3.451(2)	Cu1O1Cu2	118.34(15)
Cu2···Cu3	3.417(1)	Cu3O1Cu1	108.47(14)
Cu3···Cu1	3.243(1)	Cu3O1Cu2	117.23(15)
Cu1···Cu4	5.228(3)	Cl1Cu1Cl4	110.08(5)
Cu1-Cl1	2.307(2)	O1Cu1Cl1	162.63(10)
Cu1-Cl4	2.744(2)	N4Cu1N5	175.51(15)
Cu1-O1	2.007(3)	N5Cu1Cl4	94.90(11)
Cu1-N4	1.948(4)	O1Cu2Cl2	167.44(10)
Cu1-N5	1.950(4)	N6Cu2N1	160.43(14)
Cu2-Cl2	2.258(1)	O1Cu3Cl3	169.34(10)
Cu2-O1	2.012(3)	N3Cu3N2	163.27(15)
Cu2-N1	1.951(3)	N7Cu4N7$_1$	180.0
Cu2-N6	1.949(3)	N9Cu4N9$_1$	91.62(14)
Cu3-Cl3	2.251(2)		
Cu3-O1	1.990(3)		
Cu3-N2	1.957(3)		
Cu3-N3	1.953(4)		
Cu4-N7	2.017(4)		
Cu4-N9	2.019(3)		
Cu4-Cl4	2.792(2)		

$_1$-*x*, 2-*y*, 1-*z*

Table S3. Selected interatomic distances (Å) and angles (°) for [**2**].

Cu1···Cu2	3.386(1)	Cu1O1Cu2	116.79(18)
Cu2···Cu3	3.470(1)	Cu1O1Cu3	115.8(2)
Cu3···Cu1	3.389(1)	Cu2O1Cu3	119.10(18)
Cu1-O1	1.976(4)	O1Cu1N13	174.73(19)
Cu1-N1	1.941(5)	N1Cu1N13	90.9(2)
Cu1-N12	1.935(5)	N12Cu1N1	171.0(2)
Cu1-N13	1.982(5)	N12Cu1N13	92.5(2)
Cu2-O1	2.000(4)	O1Cu2N13$_1$	110.69(18)

Cu2-N2	1.943(5)	N2Cu2N3	92.6(2)
Cu2-N3	2.002(6)	N2Cu2N6	174.9(2)
Cu2-N6	1.963(5)	N2Cu2N13$_1$	89.01(19)
Cu2-N13$_1$	2.322(5)	N3Cu2N13$_1$	100.2(2)
Cu3-O1	2.024(4)	N6Cu2N3	92.2(2)
Cu3-N3$_2$	2.422(5)	N6Cu2N13$_1$	91.74(19)
Cu3-N7	1.974(5)	N7Cu3N3$_2$	91.59(19)
Cu3-N8	1.974(6)	N8Cu3N3$_2$	100.8(2)
Cu3-N11	1.948(5)	N8Cu3N7	92.1(2)
		N11Cu3N3$_2$	90.59(19)
		N11Cu3N7	173.6(2)
		N11Cu3N8	93.4(2)

$_1$1-*x*,2-*y*,1-*z*; $_2$2-*x*,2-*y*,1-*z*

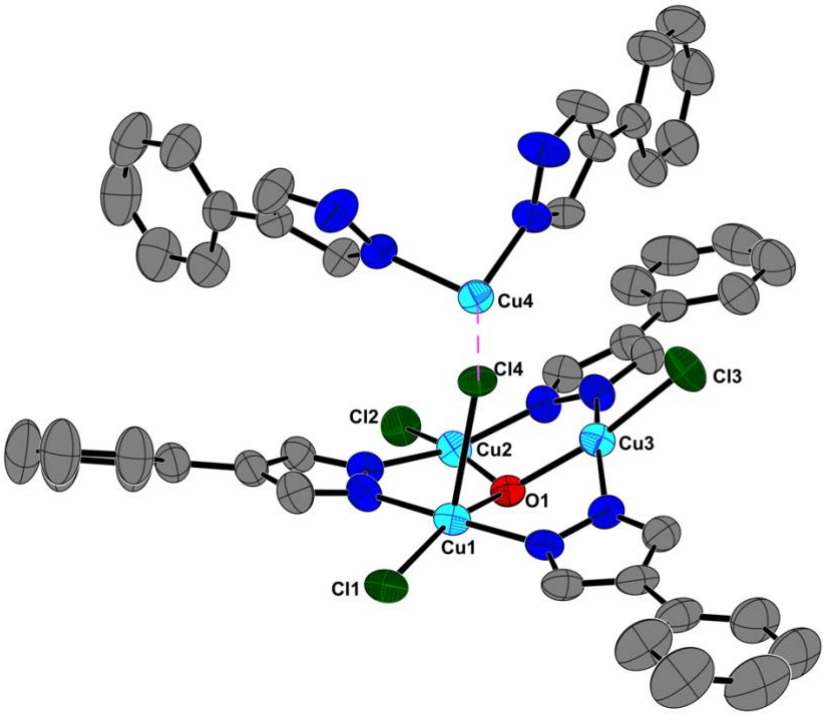

Figure S1. Asymmetric unit of [**1**] showing partial atom labeling scheme; thermal ellipsoids are drawn at 50% probability level. H-atoms, PPN counterion and interstitial solvents are not shown.

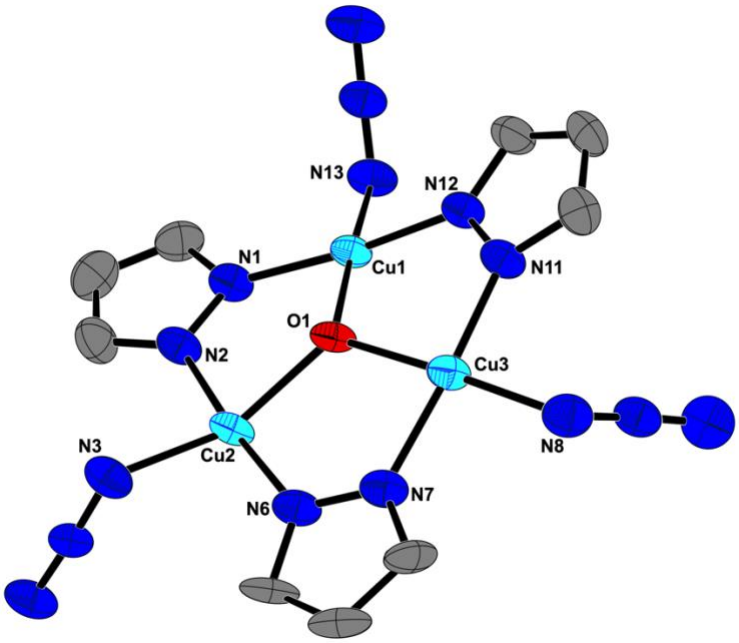

Figure S2. Molecular structure of [**2**] showing partial atom labeling scheme; thermal ellipsoids are drawn at 50% probability level. Azide disorder, H-atoms and PPN counterions are not shown for clarity.

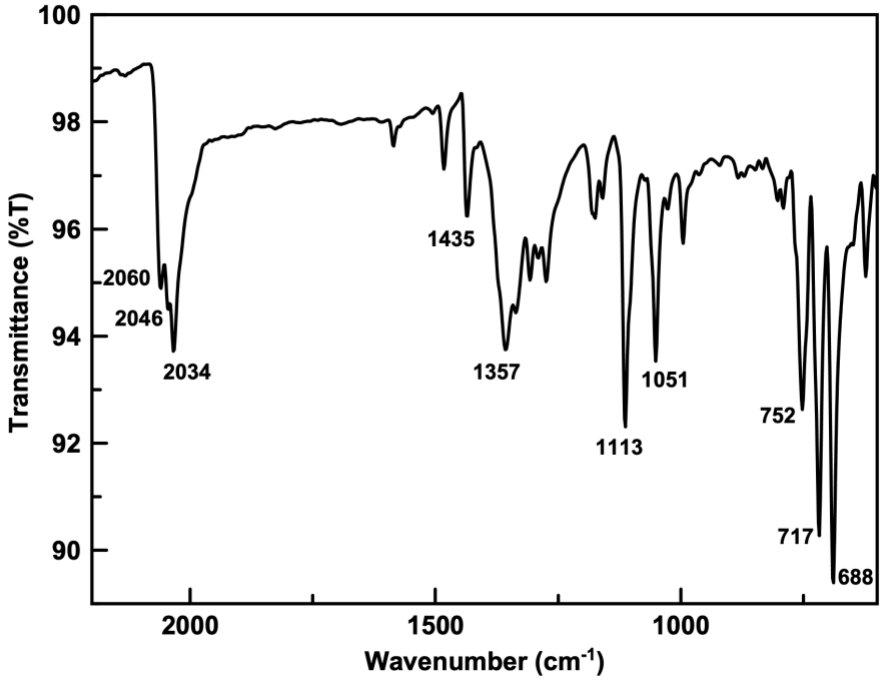

Figure S3. Infrared spectrum of [**2**] recorded in ATR mode.

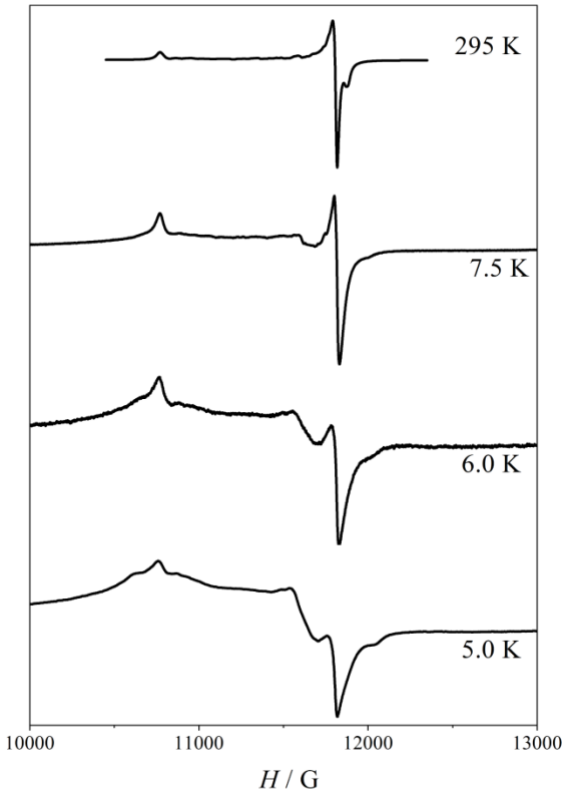

Figure S4. Solid-state X-band EPR spectra of [**1**] between 5 and 295 K.

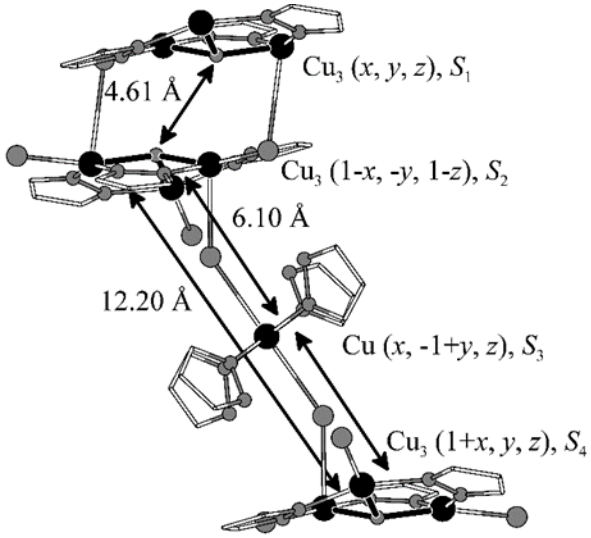

Figure S5. Dipolar exchange scheme indicating the symmetry codes of the spins S_i (i = 1-4) and the main intermolecular distances of [**1**].