Electronic Supporting Information

N9 Substituent Mediated Structural Tuning of Copper-Purine Complexes: Chelate Effect and Thin Film Studies

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General Experimental Information

Identification code	L1	L3	L4
Empirical formula	$C_{16}H_{18}Cl_2N_8$	$C_{12}H_9Cl_1N_4$	$C_{11}H_8Cl_1N_5$
Mr	393.28	244.68	245.67
crystal system	Orthorhombic	Monoclinic	Orthorhombic
space group	<i>P</i> b c a	P1 21/n 1	P 21 21 21
a(Á)	15.60(1)	4.8996(8)	4.12060(10)
$b(\text{\AA})$	6.591(4)	24.168(4)	12.0535(4)
c(Å)	16.80(1)	9.3291(15)	21.2191(7)
α (deg)	90.000	90.000	90.000
β (deg)	90.000	93.474(3)	90.000
γ (deg)	90.000	90.000	90.000

Volume (Å ³⁾	1728(2)	1102.6(3)	1053.90(6)
Z	4	4	4
<i>Dx</i> (Mg m ⁻³)	1.512	1.474	1.548
F(000)	816	504	504
μ (mm ⁻¹)	0.395	0.326	0.344
θ range for data collection(deg)	4.14-25.03	2.34-28.31	2.56-28.34
	-18→h→18	-6→h→6,	-5→h→5,
Limiting indices	-5→k→7	-32→k→30,	-15→k→15,
	-20→l→17	-9→l→12	-15→l→28
Reflections collected	7935	7161	10771
unique reflections	1508	2710	2623
R(int)	0.0662	0.0369	0.0458
Completeness to θ	= 25.03, 99.1	= 28.31, 98.2	= 28.34, 99.4
T _{max} / T _{min}	0.9322/ 0.9180	0.9619 / 0.9376	0.9406/ 0.9281
Data / restraints / parameters	1508/0/119	2710/0/154	2623/0/154
GOF on F^2	1.041	1.057	1.104
R1 and R2 [$I > 2\sigma(I)$]	0.0517, 0.1306	0.0590, 0.1519	0.0354, 0.0772
R1 and R2 (all data)	0.0655, 0.1424	0.0387, 0.0728	0.0428, 0.0806
Largest diff. peak and hole(e.A ⁻³)	0.633 and -0.444	0.503 and -0.468	0.215 and -0.318

Crystal structure analysis:

Crystal structure analysis of N9-propyl-6-chloropurine (L1):

Diffraction quality, block-type, colorless crystals were grown by slow evaporation of methanolic solution of L1. Refinement data suggest that L1 crystallized in orthorhombic unit cell (P b c a) comprising of a single molecule in the asymmetric unit. Figure S1.

Crystal structure analysis of N9-benzyl-6-chloropurine (L3):

Colorless needle-like crystals were obtained on slow evaporation of a solution of L3 in methanol which on crystallographic study revealed that the crystal acquired monoclinic system with space group " $P \ 1 \ 21/n1$ ". Figure S1.

Crystal structure analysis of N9-pyridin-2-ylmethyl-6-chloropurine (L4):

Methanolic solution of L4 on slow evaporation led to the formation of colorless needle-like crystals suitable for X-ray crystallography. L4 crystallized in orthorhombic unit cell (*P* 21 21 21) with one molecule in its asymmetric unit. Figure S1.



Figure S1: Crystal structures of ligands L1, L3 and L4.



Figure S2: Part of lattice of 4 displaying pi-pi stacking as well as two H-bonding interactions.



Figure S3: EDX images for thin films of **3** on quartz at 650 $^{\circ}$ C in (a) air and (b) in inert cond. (under N₂); (c) and (d) show expansions of (a) and (b) respectively.





Figure S4: EDX images for thin films of 3 on Si(111) at 650 $^{\circ}$ C in (a) air and (b) in inert cond. (under N₂); (c) and (d) show expansions of (a) and (b) respectively.

¹HNMR of L4:



¹³CNMR of L4:



HRMS of L4:



HRMS of complex 1:



HRMS of complex 2:



HRMS of complex 3:





HRMS of complex 4:



HRMS of complex 5:



HRMS of complex 6:



 Table S2: Selected Bond Lengths (Å) and Bond Angles (°) for complexes 1-6

Bond lengths (Å)		
Cu1–N7A	1.975	
Cu1–N7B	1.978	
Cu1–Cl3	2.246	
Cu1–Cl2	2.266	
Bond Angles (°)		
N7A–Cu1–Cl2	93.837	
Cl2–Cu1–N7B	92.575	
N7B–Cu1–Cl3	91.765	
Cl3–Cu1–N7A	98.931	

Complex 1

Bond lengths (Å)		
Cu1–N1	2.037	
Cu1–Cl _{b1}	2.281	
Cu1–Cl _{b2}	2.309	
Cu1–Cl _{b3}	2.280	
Cu1–Cl _{b4}	2.604	
Cu2–N7	1.984	

Cu2–Cl _{b1}	2.287
Cu2–Cl _{b2}	2.321
Cu2–Cl _{b3}	2.577
Cu2–Cl _{b4}	2.301
Bond	Angles (°)
Cu1–Cl _{b1} –Cu2	95.486
Cl _{b1} -Cu2-Cl _{b2}	84.979
Cu2–Cl _{b2} –Cu1	93.804
Cl _{b2} -Cu1-Cl _{b1}	85.385
N1–Cu1–Cl _{b1}	90.532
N1–Cu1–Cl _{b3}	91.107
Cl _{b3} -Cu1-Cl _{b4}	91.757
Cl _{b2} -Cu1-Cl _{b4}	98.632
Cl _{b1} -Cu2-Cl _{b3}	96.717
Cl _{b3} -Cu2-Cl _{b4}	91.975
Cl _{b4} –Cu2–N7	88.586
N7–Cu2–Cl _{b2}	89.957

Bond lengths (Å)		
Cu–Cl _{b1}	2.280	

Cl _{b2} –Cu	2.574
Cu–N7A	2.014
Cu–O1A	1.984
Cu–Cl3	2.265
Bond A	ngles (°)
N7A–Cu–O1A	88.340
O1A–Cu–Cl _{b1}	88.357
O1A–Cu–Cl3	91.140
Cl3–Cu–Cl _{b1}	91.296
Cl _{b1} –Cu–N7A	90.023
Cl _{b2} –Cu–Cl _{b1}	89.748
Cl _{b2} –Cu–O1A	88.357
Cl _{b2} –Cu–N7A	100.197
Cl _{b2} –Cu–Cl3	105.421

Bond lengths (Å)		
Cu1A–N3A	2.034	
Cu1A–N12A	2.012	
Cu1A–O2A	1.964	
Cu1A–O1W	2.232	

Bond Angles (°)		
N12A–Cu1A–N3A	92.403	
N3A–Cu1A–O1A	87.130	
O1A–Cu1A–O2A	88.898	
O2A–Cu1A–N12A	91.388	
O2A–Cu1A–O1W	83.458	
O1A–Cu1A–O1W	85.374	
N3A–Cu1A–O1W	98.360	
N12A–Cu1A–O1W	99.110	

Bond lengths (Å)		
Cu1–N12	2.242	
Cu1–O3	1.960	
Cu1–O2	1.975	
Cu1–O4	1.966	
Cu1–O1	1.966	
Bond Angles (°)		
O2–Cu1–O3	88.257	

O3–Cu1–O1	90.996
O1–Cu1–O4	89.35
O4–Cu1–O2	89.167
N12–Cu1–O2	94.975
N12-Cu1-O3	99.862
N12-Cu1-O1	96.261
N12-Cu1-O4	91.465

Bond lengths (Å)				
Cu1–N7A	1.997			
Cu1–Cl1	2.258			
Cu1–Cl5	2.282			
Cu1–Cl _{b1}	2.716			
Cu1–O2S	1.965			
Cu2–Cl _{b1}	2.311			
Cu2–Cl4	2.247			
Cu2–N12A	2.026			
Cu2–N3A	2.031			

Cu2–Cl _{b2}	2.740				
Bond Angles (°)					
N7A–Cu1–Cl5	92.539				
N7A–Cu1–Cl1	89.443				
Cl1–Cu1–O2S	87.225				
O2S–Cu1–Cl5	90.881				
Cl5–Cu1–Cl _{b1}	94.466				
N7A–Cu1–Cl _{b1}	87.854				
Cl1–Cu1–Cl _{b1}	98.371				
O2S–Cu1–Cl _{b1}	91.865				
Cl4–Cu2–Cl _{b2}	94.674				
Cl4–Cu2–N12A	88.817				
N12A–Cu2–N3A	89.771				
N3A–Cu2–Cl _{b2}	88.836				
Cl _{b1} –Cu2–Cl _{b2}	79.596				
Cl _{b2} –Cu2–N3A	97.282				
Cl _{b2} –Cu2–N12A	95.429				
Cl _{b2} –Cu2–Cl4	101.668				
Cu2–Cl2–Cu1	103.484				

Cu2–Cl _{b1} –Cu2	100.404
Cu1–Cl _{b1} –Cu2	103.484

Table S3: Hydrogen bonding Table for complexes **3** and $4^{\#}$

D-HA	Symmetry of A	D-H	HA	D-A	∠D—H…A		
Complex 3							
O(1A)—H(1W)Cl(5)	-1+x,1+y,z	0.85	2.57	3.269	140		
O(1A)—H(2W)Cl(3)	-1-x,1-y,-z	0.85	2.35	3.165	162		
O(1B)—H(3W)Cl(3)	1+x,y,z	0.88	2.60	3.355	143		
O(1B)—H(4W)Cl(5)	2-x,-y,-z	0.88	2.36	3.167	153		
Complex 4							
O(2W)—H(1W)N(7B)	1+x,y,z	0.67	2.29	2.957	177		
O(2W)—H(2W)O(4C)	x,1/2-y,1/2+z	0.85	1.98	2.780	157		
O(1W)—H(3W)N(7A)	-1+x,y,z	0.77	2.07	2.838	177		
O(1W)—H(4W)O(1B)	-x,-y,2-z	0.71	2.38	3.076	171		

Where D is donor and A is acceptor, the bond lengths are in Å and angles are in deg.

Electron Paramagnetic Resonance (EPR):





PXRD:

Figure S6. The simulated (blue) and experimental (black) PXRD patterns for six complexes 1-6.

Photoluminescence:

Both L1 and 1 when excited at 266 nm exhibited emission at 294 nm along with another small peak at 362 nm. L3 and 3 showed emission peaks at 298 nm and 318 nm respectively. Here, again an additional peak for both ligand and metal complex was observed at 361 nm. The emission maxima exhibited by the ligand L4 and its complexes 4-6 at 295 nm indicate no significant change in the values but different fluorescent intensities.



Figure S7. Absorption spectra illustrating photoluminescence intensities of ligands L1-L4 along with their complexes 1-6.



Figure S8. Emission spectra illustrating photoluminescence intensities of ligands L1-L4 along with their complexes 1-6.



Figure S9. 3D image and diameter-height profile of thin films 3Si in (a) air and (b) in inert cond. (under N_2) (Scale in nm).



Figure S10. (i) AFM images of thin films **3q** in (a) air and (b) in inert cond. (under N₂); (ii) 3D image and diameter-height profile of corresponding films (Scale in nm).