Supporting Information

Is Crystal Engineering Approach Useful in Designing Metallogels? – A Case Study

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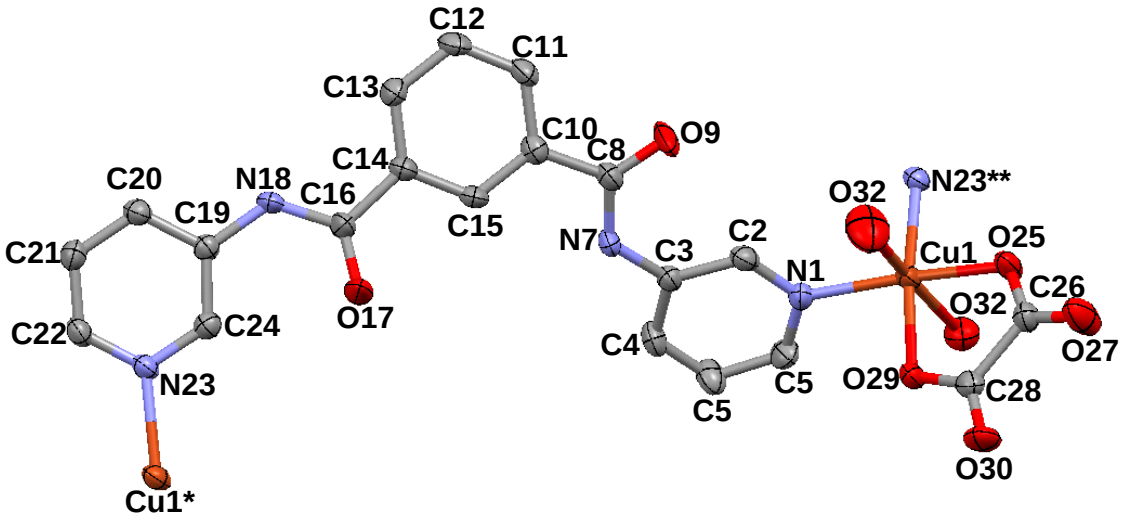
Molecular Plots and Hydrogen Bonding Parameters for compounds 1a - 7

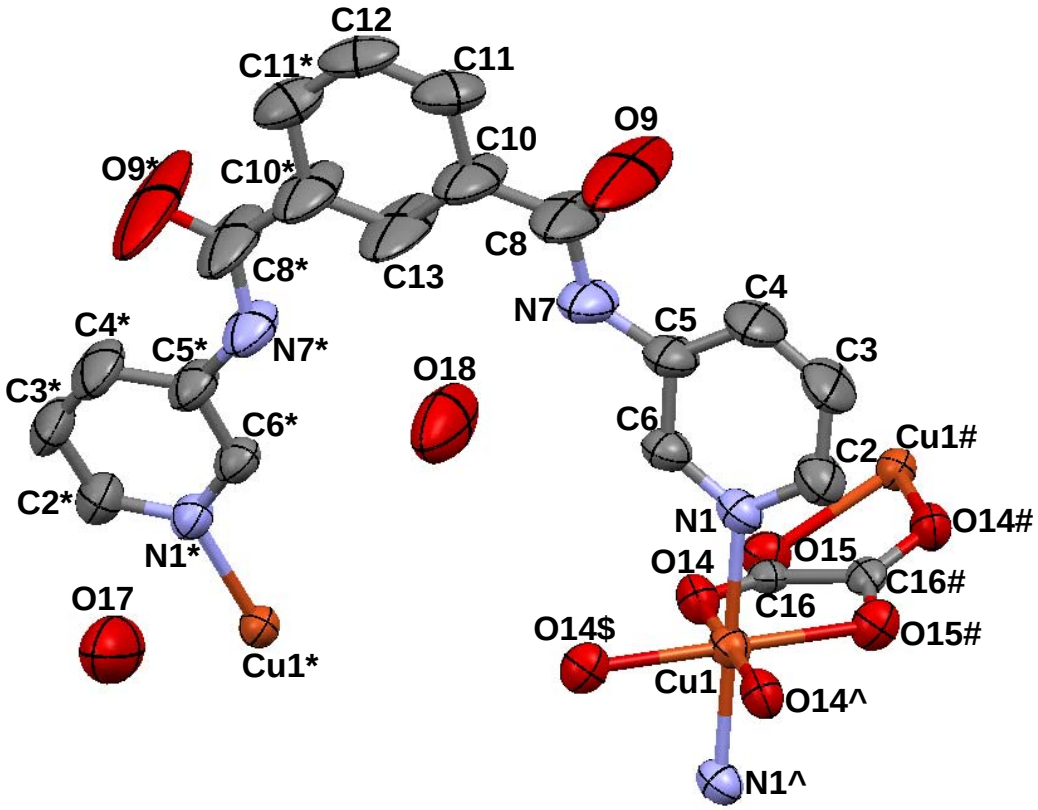
Compound 1a



***** -1/2+x, 1.5-y, 1/2 + z; ** 1/2+x, 1.5-y, -1/2+z

Hydrogen bonding parameters of **1a**					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(29)	0.86	2.19	2.982(4)	153.5	1-x, 1-y, 2-z
N(18)–H(18)•••O(30)	0.86	2.10	2.934(4)	161.6	-1+x, 1+y, z
O(17)•••O(31)			2.753(5)		1-x, 1-y, 2-z
O(25)•••O(32)			2.924(5)		3/2-x, -1/2+y, 3/2-z
O(27)•••O(32)			2.902(5)		3/2-x, -1/2+y, 3/2-z
O(27)•••O(31)			3.037(5)		3/2-x, 1/2+y, 3/2-z

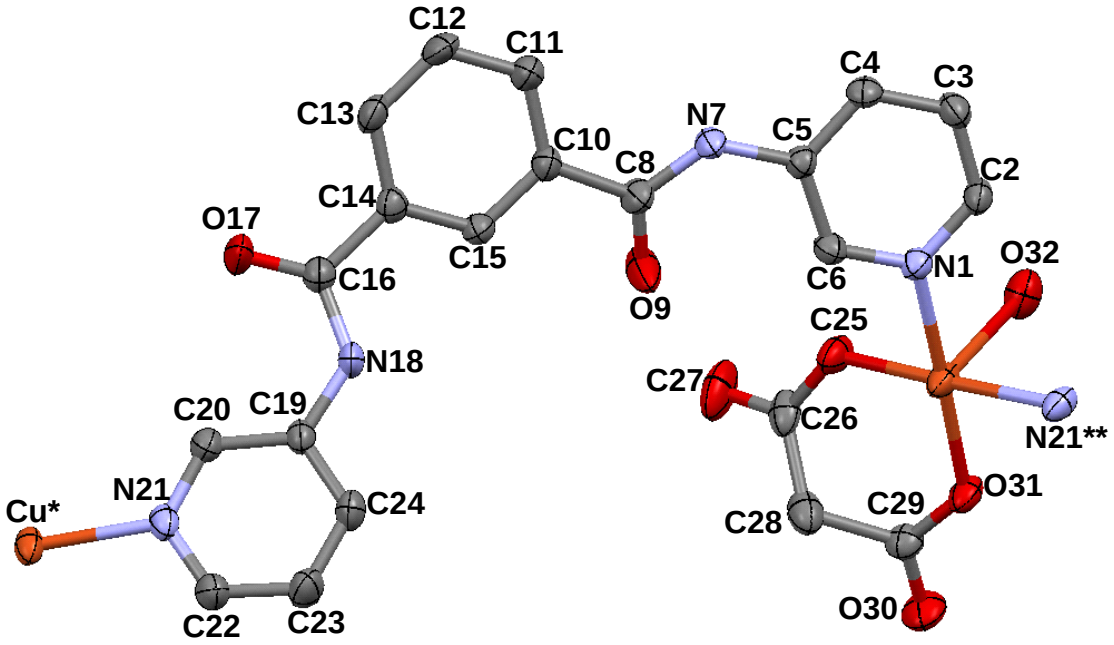
Compound 1b



* 1-x, y, 1/2-z; # -x, y, 1/2-z; ^ 1/2-x, 1/2-y, 2-z; $ 1/2+x, 1/2-y, 1/2+z ;

Hydrogen bonding parameters **1b**					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(18)	0.86	2.22	3.053(9)	162.1	x, y, z
O(15)•••O(17)			2.796(11)		1-x, y, 1/2-z
O(14)•••O(17)			2.998(11)		-1/2+x, 1/2-y, 1/2+z
O(17)•••O(18)			2.701(12)		1/2+x, 1/2-y, -1/2+z
O(17)•••O(18)			2.701(12)		3/2-x, 1/2-y, 1-z

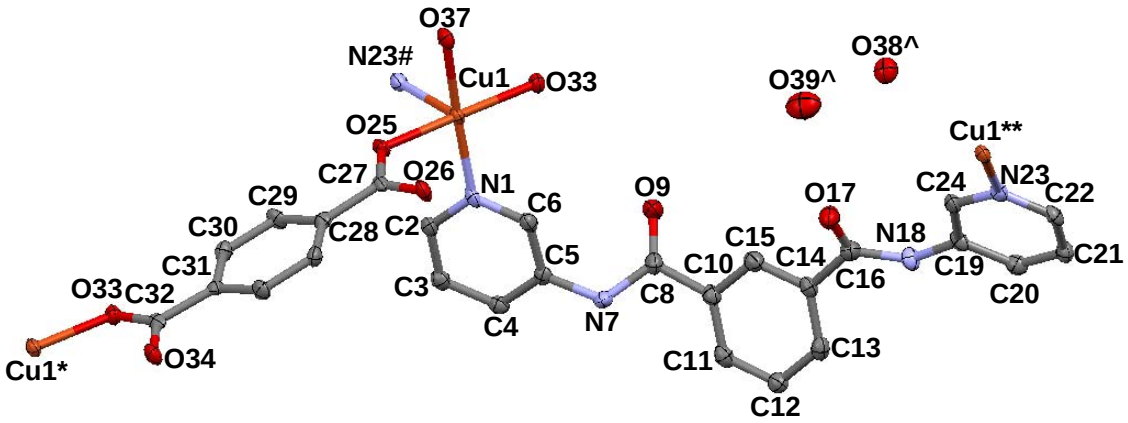
Compound 2



* 1/2+x, -1/2-y, -1/2+z; ** -1/2+x, -1/2-y, 1/2+z

Compound 2					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(30)	0.86	2.19	3.010(4)	158.2	x-1/2, -y+1/2, z-1/2
N(18)–H(18)•••O(31)	0.86	2.45	3.244(4)	153.5	-x+3/2, y-1/2, -z+3/2
O(9)•••O(32)			2.848(4)		3/2-x, -1/2+y, 3/2-z
O(27)•••O(32)			2.934(5)		3/2-x, -1/2+y, 3/2-z

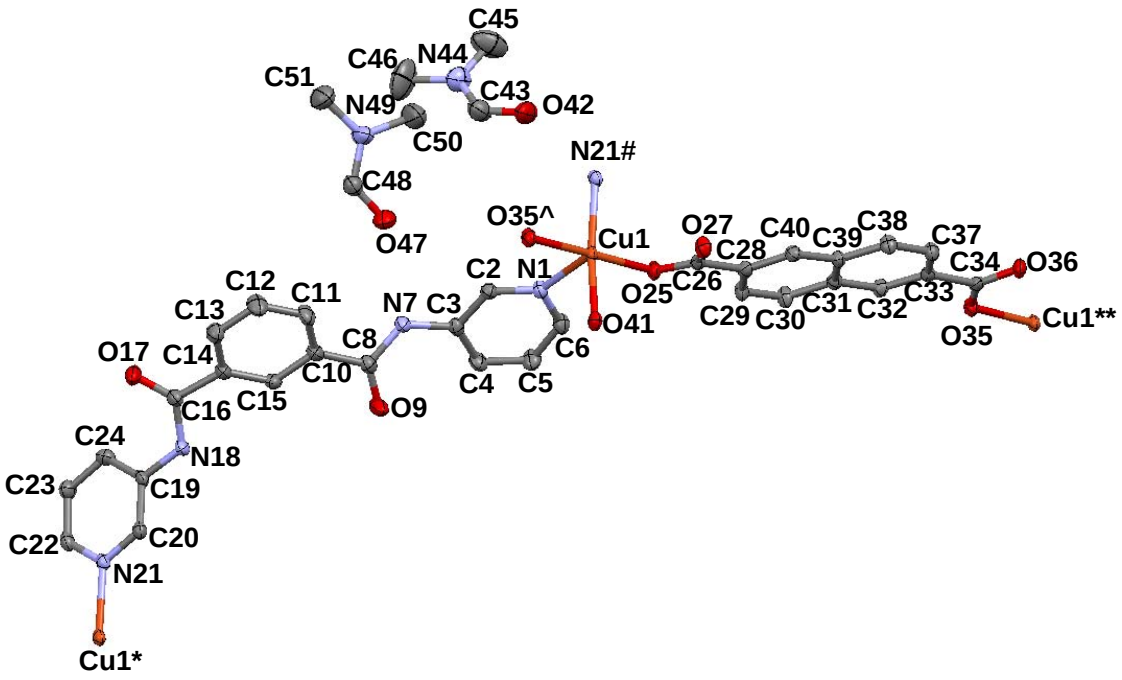
Compound 3



* -1+x, y, z; ** 2.5-x, -1/2+y, 1.5-z; # 2.5-x, 1/2+y, 1.5-z; ^ 1+x, -1+y, z

Hydrogen bonding parameters for **3**					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(17)	0.86	2.22	2.915(4)	137.5	-x+2, -y, -z+1
N(18)–H(18)•••O(38)	0.86	1.93	2.783(4)	168.8	-x+2, -y+1, -z+1
O(37)–H(37A)•••O(26)	0.79(6)	1.93(6)	2.702(4)	165(6)	-x+2, -y, -z+2
O(37)–H(37B)•••O(34)	0.86(5)	1.78(5)	2.624(4)	166(4)	-x+1, -y, -z+2
O(38)–H(38A)•••O(26)	0.90(6)	1.86(6)	2.764(5)	173(5)	x, y+1, z
O(38)–H(38B)•••O(39)	0.86(7)	2.02(7)	2.872(5)	170(6)	x, y, z
O(39)–H(39A)•••O(9)	0.87(5)	2.21(6)	3.026(5)	158(5)	-x+3/2, y+1/2, -z+3/2
O(39)–H(39B)•••O(17)	0.99(5)	2.07(5)	2.862(4)	136(4)	x-1, y+1, z

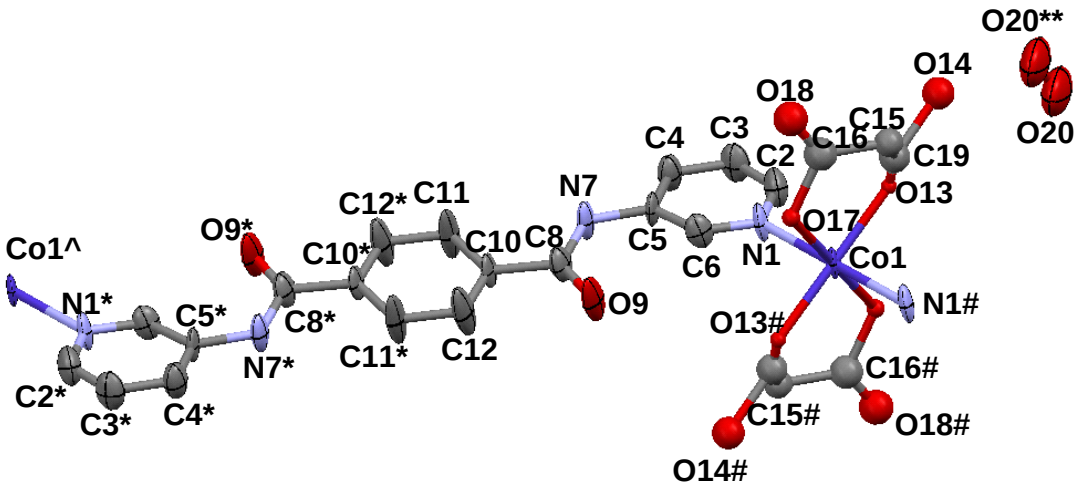
Compound 4



* x, -1+y, -1+z; ** x, 1+y, z; # x, 1+y, 1+z; ^ x, -1+y, z

Hydrogen bonding parameters for **4**					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(18)–H(18)•••O(42)	0.86	2.00	2.820(3)	158.2	-x+1, -y+1, -z
N(7)–H(7)•••O(47)	0.86	2.014	2.850	163.87	x, y, z
O(41)–H(41A)•••O(27)	0.85(3)	1.81(3)	2.665(3)	178(3)	-x+2, -y+2, -z+1
O(41)–H(41B)•••O(36)	0.77(3)	1.93(3)	2.679(3)	163(3)	-x+2, -y+3, -z+1

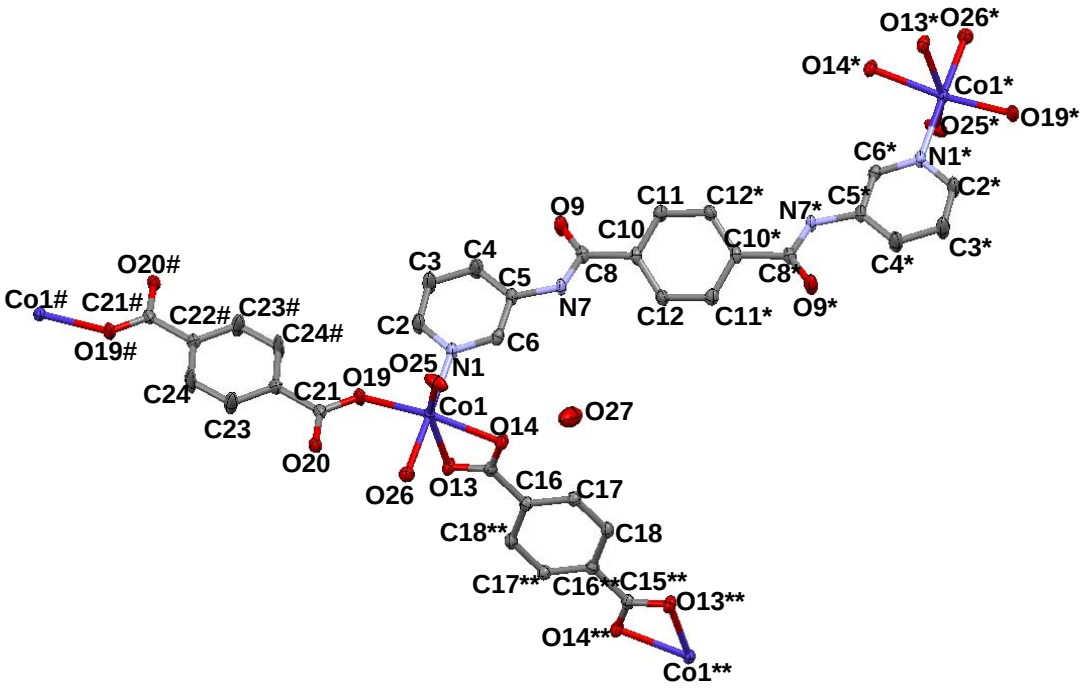
Compound 6



* -x, 1-y, 1-z; # 2-x, 2-y, -z; ** 3-x, 2-y, -1-z; ^ -2+x, -1+y, 1+z

Hydrogen bonding parameters for **6**					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(14)	0.86	2.11	2.95(3)	163.5	2-x, 1-y, -z
O(17)•••O(17)			2.71(2)		1-x, 2-y, -z
O(14)•••O(20)			2.71(5)		x, y, z
O(9)•••O(20)			2.94(4)		2-x, 2-y, -z

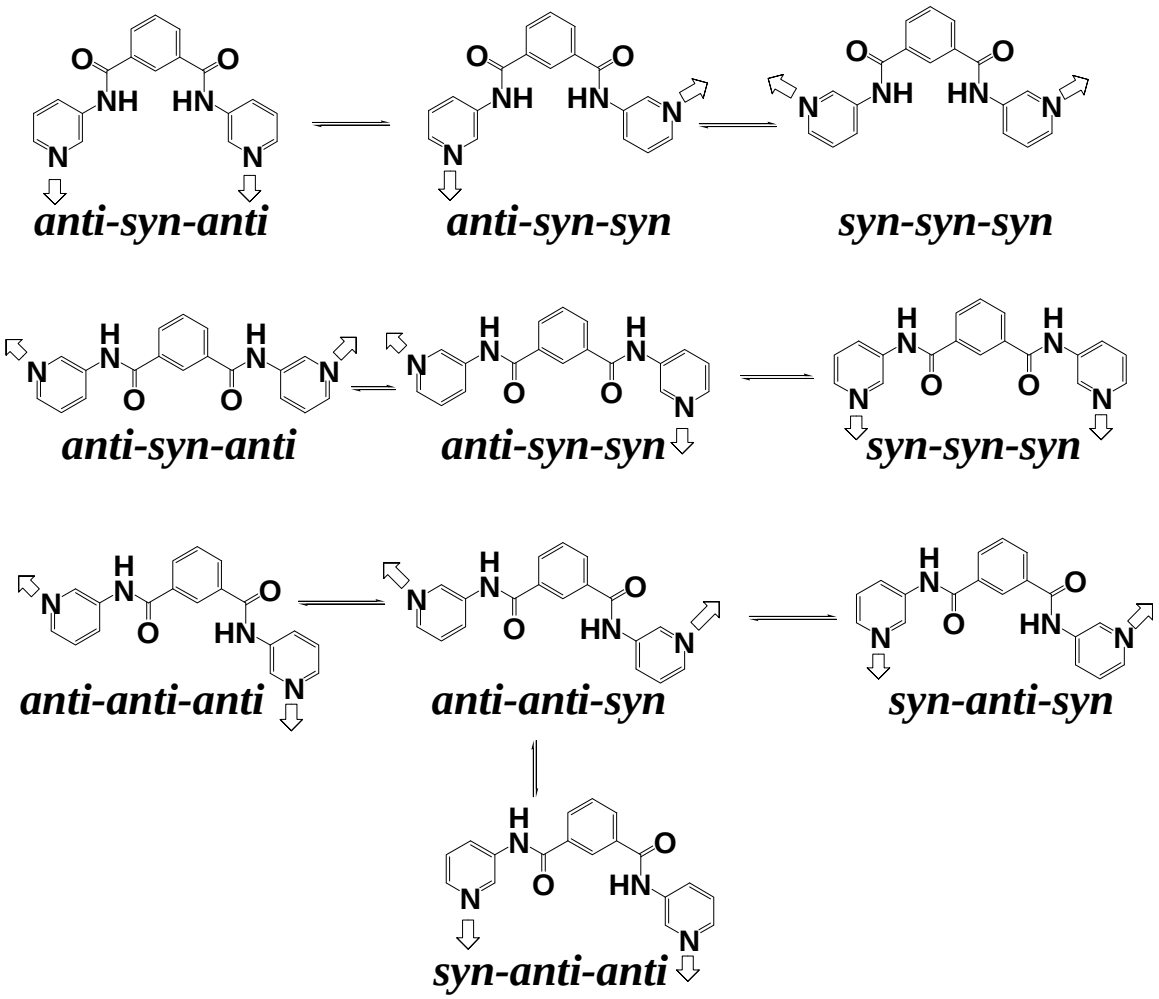
Compound 7



* -x, 2-y, 2-z; ** 2-x, 1-y, 2-z; # 3-x, 2-y, 1-z;

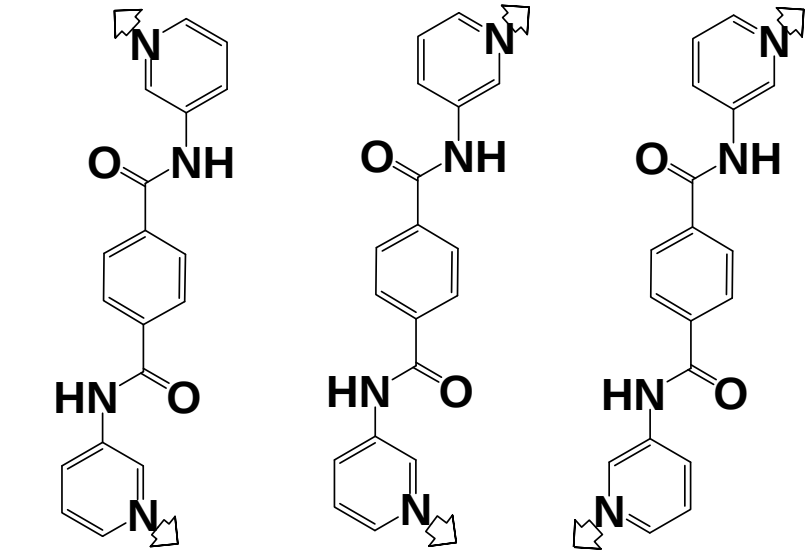
Hydrogen bonding parameters for **7**					
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(13)	0.86	2.02	2.818(3)	154.3	x-1, y, z
O(25)–H(25A)•••O(20)	0.869(10)	1.859(13)	2.709(3)	166(3)	-x+2, -y+1, -z+1
O(25)–H(25B)•••O(20)	0.870(10)	1.844(12)	2.708(3)	172(4)	x-1, y, z
O(26)–H(26A)•••O(20)	0.881(10)	1.857(18)	2.703(3)	160(4)	x, y, z
O(26)–H(26B)•••O(27)	0.898(10)	1.784(11)	2.681(3)	176(4)	x+1, y, z
O(27)–H(27A)•••O(9)	0.889(10)	1.944(18)	2.797(3)	161(4)	x, y-1, z
O(27)–H(27B)•••O(14)	0.886(11)	1.948(17)	2.818(3)	167(5)	x, y, z

Various conformations of L1

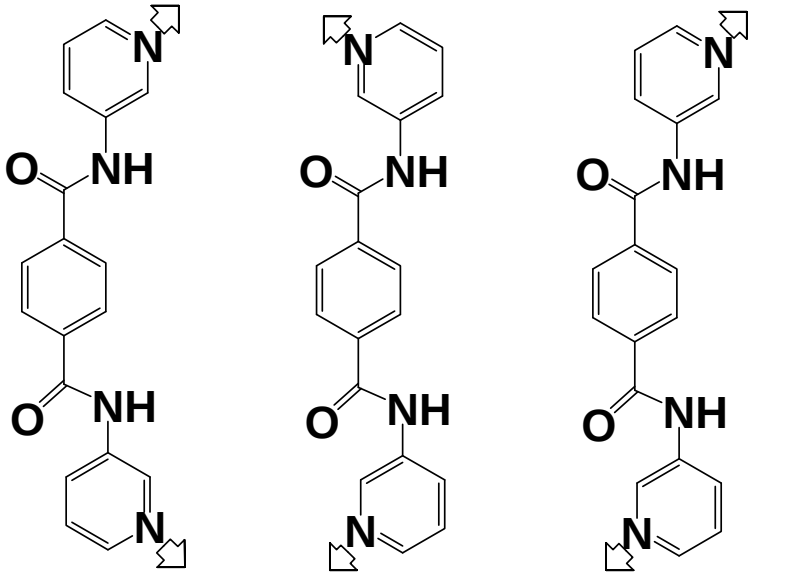


Scheme S1

Various conformations of L2



syn-anti-syn *syn-anti-anti* *anti-anti-anti*



anti-syn-anti *syn-syn-syn* *syn-syn-anti*

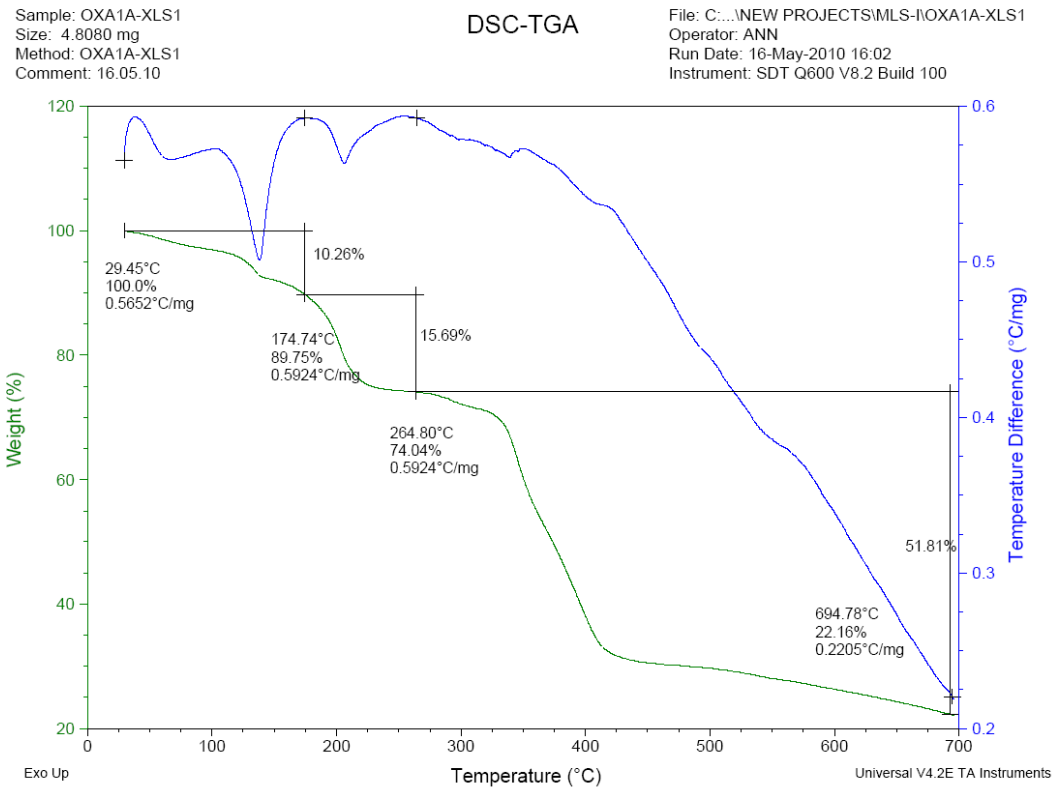
Scheme S2

Table S1: Various torsion angles in **L1** and **L2** as observed in the corresponding coordination polymers

	Torsion angle between terminal pyridyl planes (°)	Torsion angle between terminal pyridyl and central aromatic plane (°)
	L1	
1a	37.7 (3)	19.2 (3)
1b	23.3 (3)	11.8 (12)
2	39.8 (3)	37.7 (13)
3	22.4 (2)	38.4 (11)
4	68.4 (1)	70.3 (12)
	L2	
6	0.00 (1)	11.7 (13)
7	0.00 (1)	21.7 (2)

TGA of Compounds 1b – 6

Compound 1b



Unit cell contents = 4 Ligand + 4 Cu(II) + 6 H_2O (water of solvation)

Monoclinic C2/c space group, Z = 4

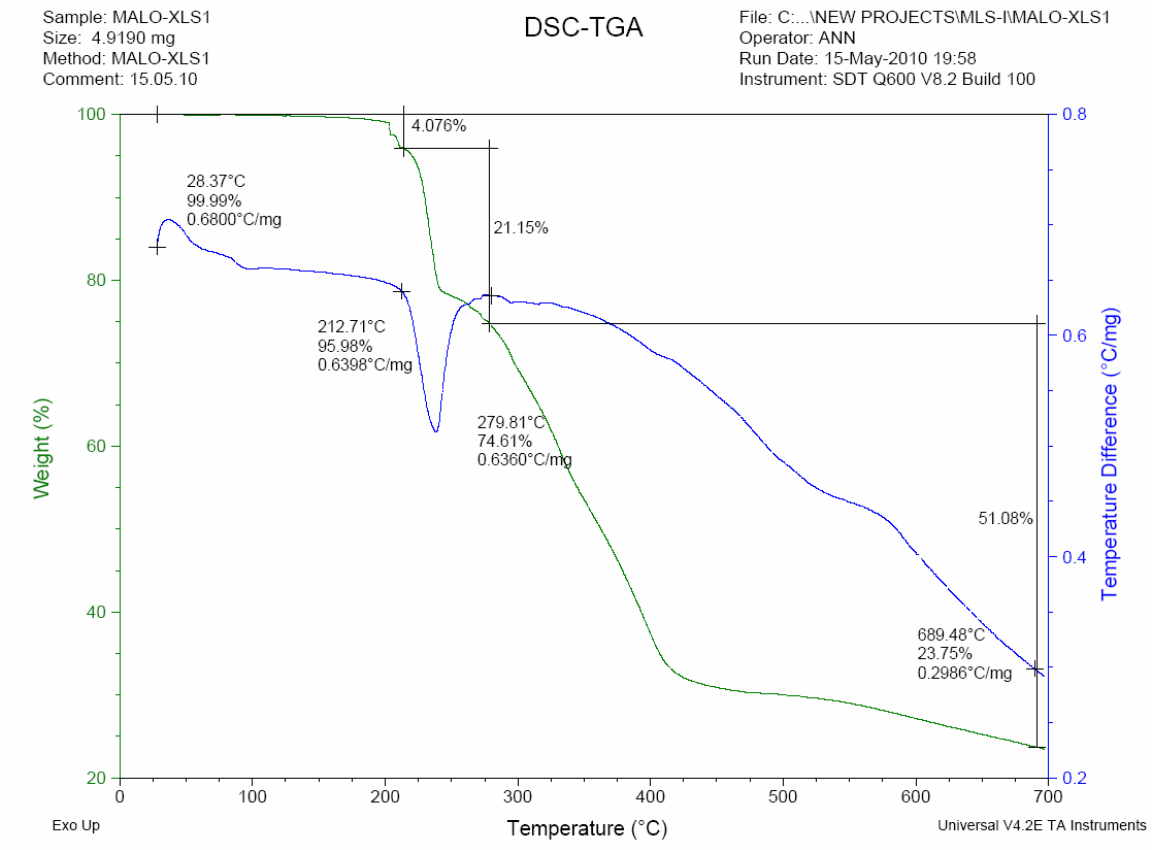
Therefore FW = Unitcell contents/Z

= 1 Ligand + 1 Cu(II) + 3 H_2O (water of solvation)

Weight loss for 3 H_2O = 54/541 X 100

= 9.98 % (Experimental = 10.26 %)

Compound 2



Unit cell contents = 4 Ligand + 4 Cu(II) + 4 Maloante + 4 H_2O (coordinated)

Monoclinic $P2_1/n$ space group, Z = 4

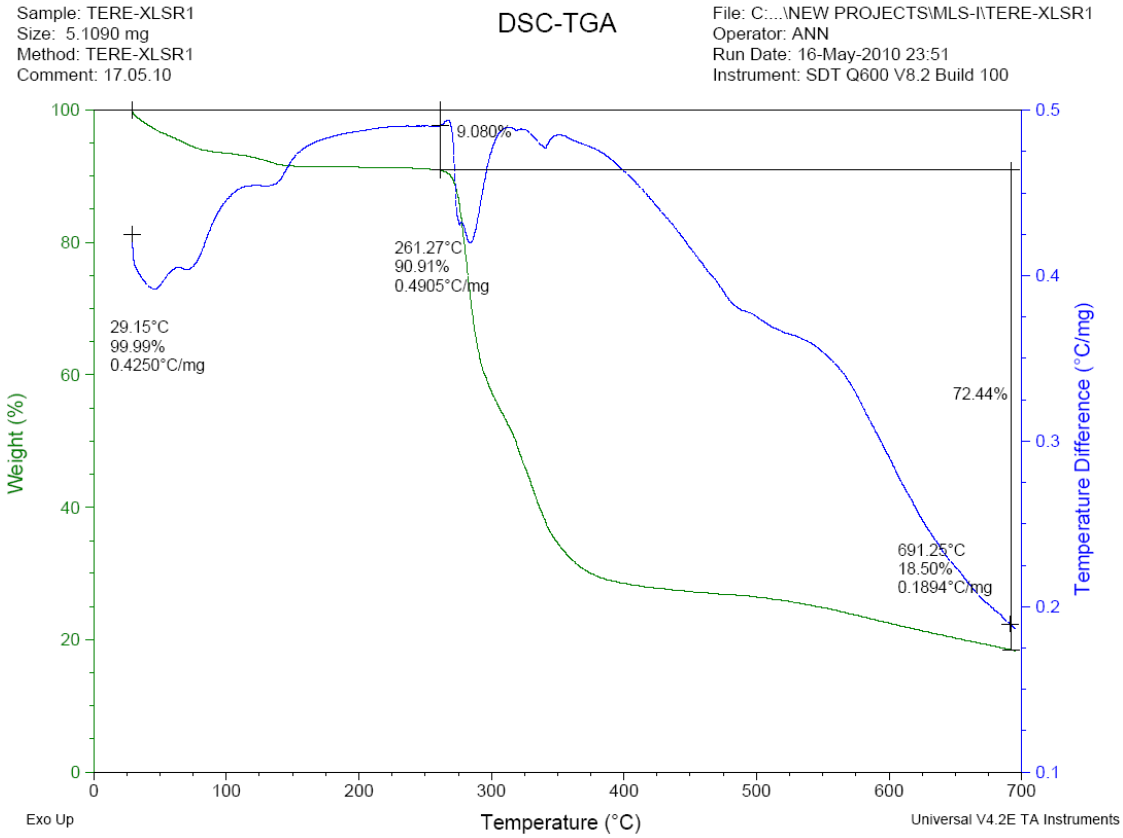
Therefore FW = Unitcell contents/Z

= 1 Ligand + 1 Cu(II) + 1 Malonate + 1 H_2O (coordinated)

Weight loss for 1 H_2O = 18/501X 100

= 3.6 % (Experimental = 4.0%)

Compound 3



Unit cell contents = 4 Ligand + 4 Cu(II) + 4 Terephthalate + 4 H_2O (coordinated) + 8 H_2O (water of solvation)

Monoclinic $P2_1/n$ space group, Z = 4

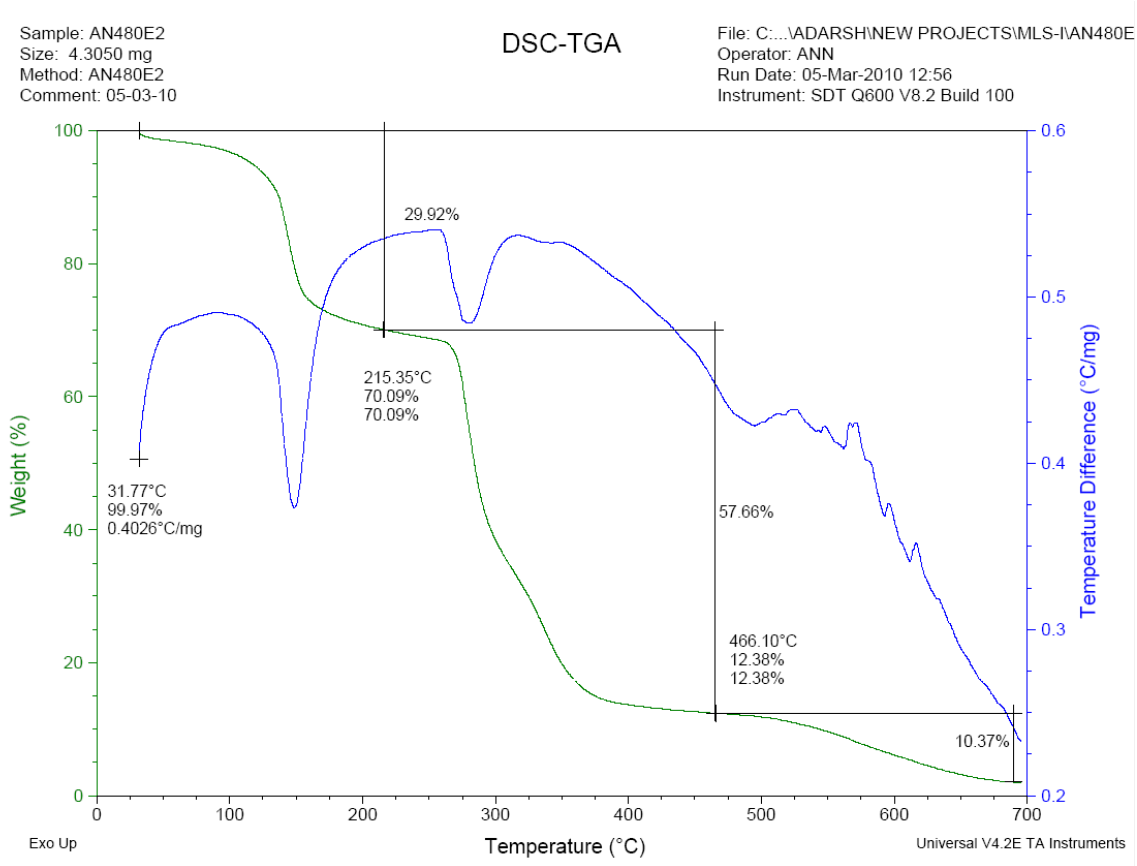
Therefore FW = Unitcell contents/Z

= 1 Ligand + 1 Cu(II) + 1 Terephthalate + 1 H_2O (coordinated) + 2 H_2O (water of solvation)

Weight loss for 3 H_2O = 54/600 X 100

= 9.0 % (Experimental = 9.1%)

Compound 4



Unit cell contents = 2 Ligand + 2 Cu(II) + 2 Naphthalate + 2 H_2O (coordinated) + 4 DMF (solvated) + ~ 6 H_2O [64 electron (SQUEEZE result)]

Monoclinic $P2_1/n$ space group, Z = 4

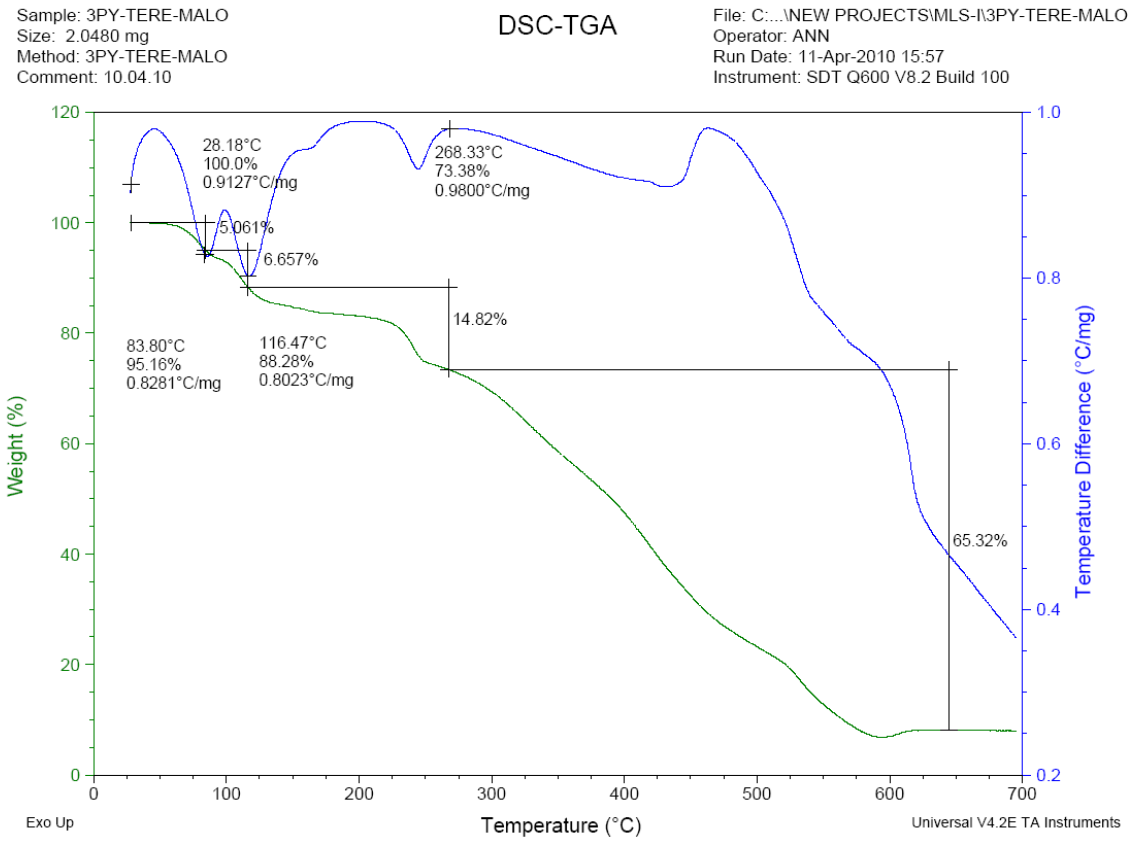
Therefore FW = Unitcell contents/Z

= 1 Ligand + 1 Cu(II) + 1 Naphthalate+ 1 H_2O (coordinated) + 2 DMF (solvated) + ~ 3 H_2O [32 electron (SQUEEZE result)]

Weight loss for 4 H_2O + 2 DMF = 218/814 X 100

= 26.8 % (Experimental = 30.0%)

Compound 5



Unit cell contents = 1 Ligand + 1 Co(II) + 2 Malonate + 1 H_2O (solvated)

Triclinic *P*-1 space group, Z = 1

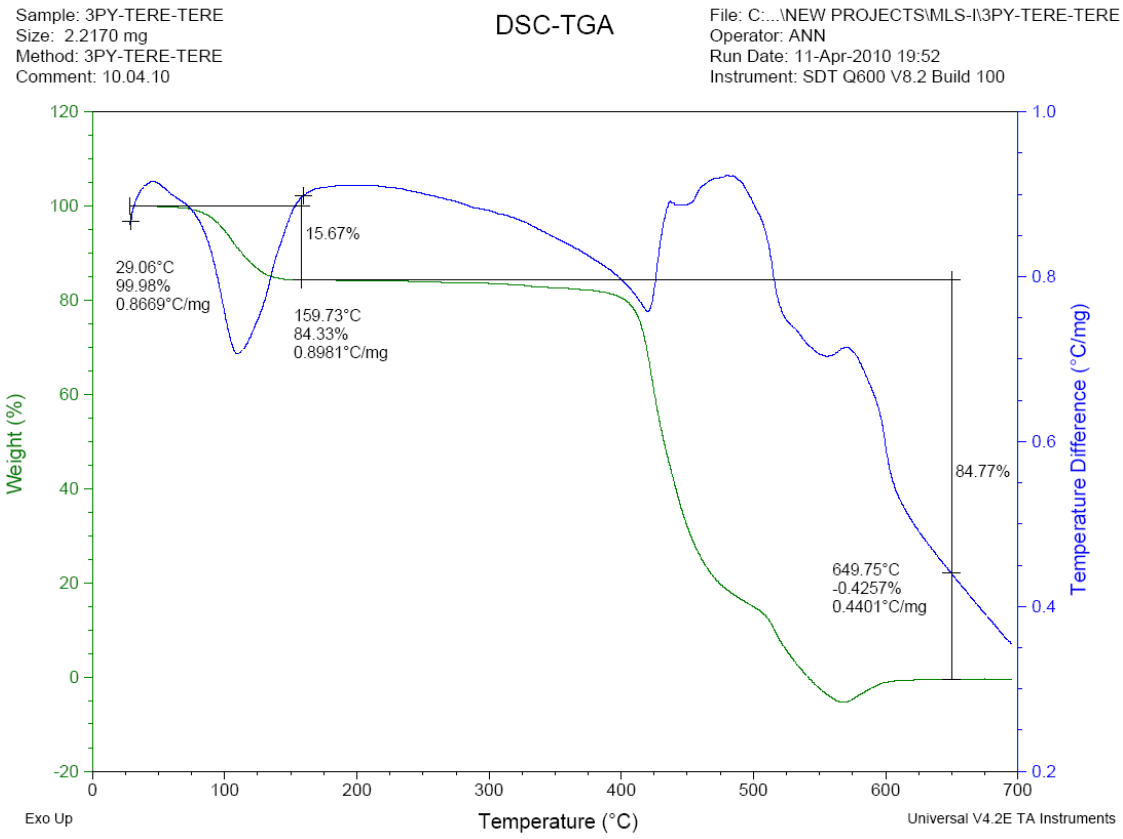
Therefore FW = Unitcell contents/Z

= 1 Ligand + 1 Co(II) + 2 Malonate + 1 H_2O (solvated)

Weight loss for 1 H_2O = 18/599.37 X 100

= 3.0 % (Experimental = 5.0%)

Compound 6



Unit cell contents = 1 Ligand + 2 Co(II) + 2 Terephthalate + 4 H_2O (coordinated) $2H_2O$ (solvated)

Triclinic *P*-1 space group, Z = 2

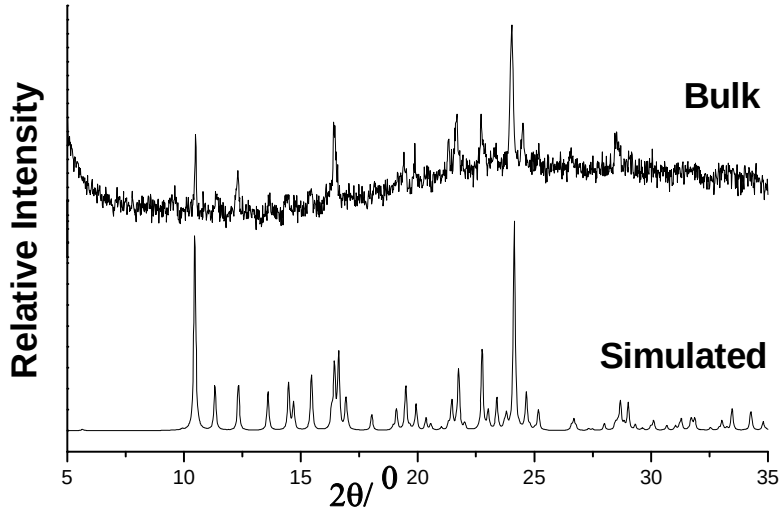
Therefore FW = Unitcell contents/Z

= 1/2 Ligand + 1 Co(II) + 1 Terephthalate + 2 H_2O (coordinated) + 1 H_2O (solvated)

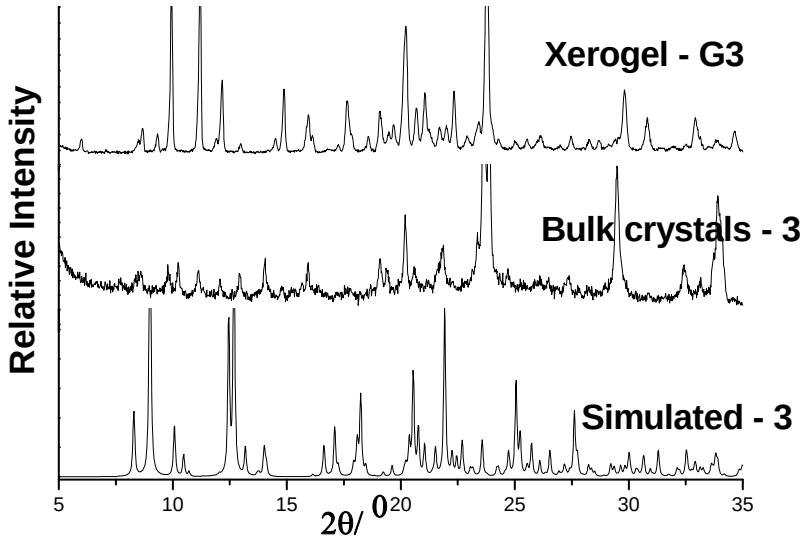
Weight loss for 3 H_2O = 54/436.26 X 100

= 12.4 % (Experimental = 15.6%)

XRPD comparison plot of Compound 6 (Non-gelator)



XRPD comparison plot of Compound 3 (Gelator)



Gelation Studies of L1 and L2

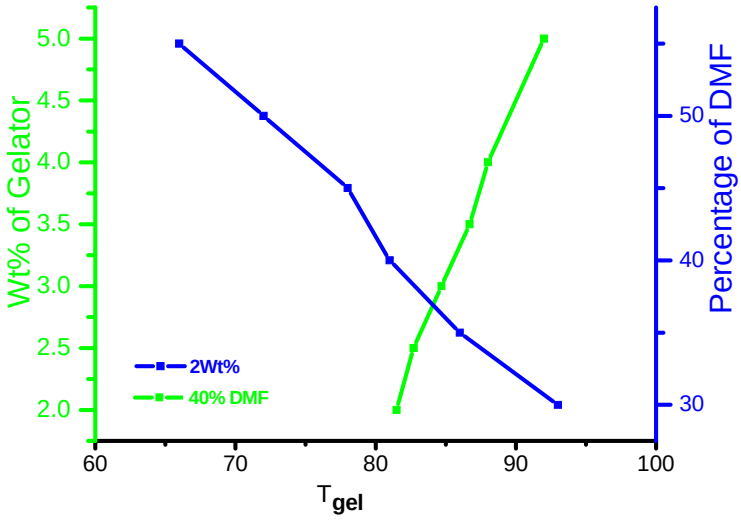
It was observed that both **L1** and **L2** were capable of gelling DMF/water mixture. While the gel derived from **L1** was thermoreversible, the corresponding gel from **L2** did not display thermoreversiblity because of its poor solubility in water. Gel formation was confirmed by tube inversion test. The gel derived from **L1** was characterized by SEM, FT-IR, PXRD and elemental analysis. These results are given below. Since **L2** did not give thermoreversible gel, further characterization was not performed.

I) Gelation data*

Wt% of the gelator	**L1**
1.0	Precipitate
1.5	Precipitate
2.0	Gel
2.5	Gel
3.0	Gel
3.5	Gel
4.0	Gel
5.0	Gel

* Gelation experiments were carried out in 40% DMF in H_2O; in the case of **L2**, the concentration of the gelator was 2.0 wt %.

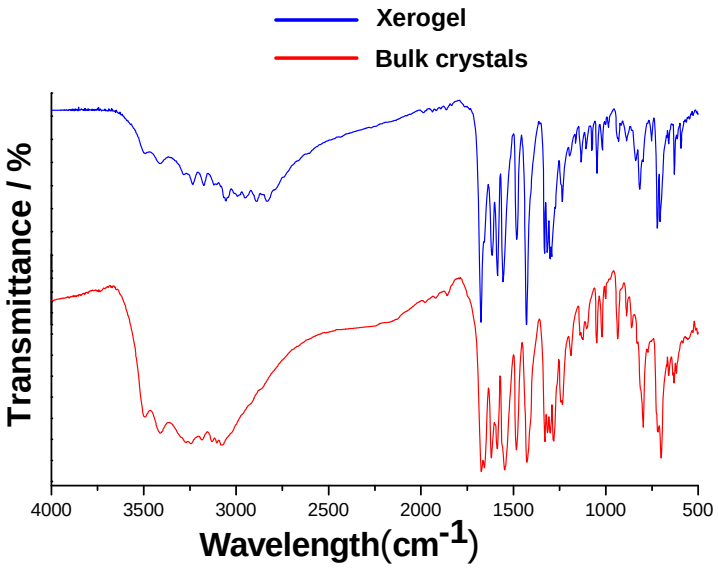
II) T_{gel} vs. **[L1]** and T_{gel} vs. [DMF] concentration in water (v/v) at a fixed concentration of 2 wt % gelator (blue color). gel prepared in 40% DMF/H_2O (v/v) (green color)



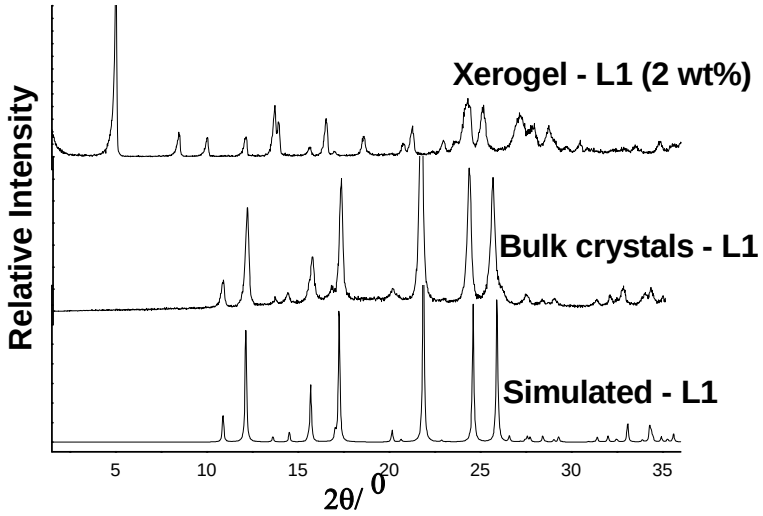
III) Elemental Analysis data

Gelator	Bulk Ctystals	Xerogel
L1	$C_{18}H_{14}N_4O_2$ Calcd. C, 67.91; H, 4.43; N, 17.60. Found: C, 67.74; H, 4.22; N, 17.65.	$C_{18}H_{14}N_4O_2$ Calcd. C, 67.91; H, 4.43; N, 17.60. Found: C, 68.24; H, 4.02; N, 17.55

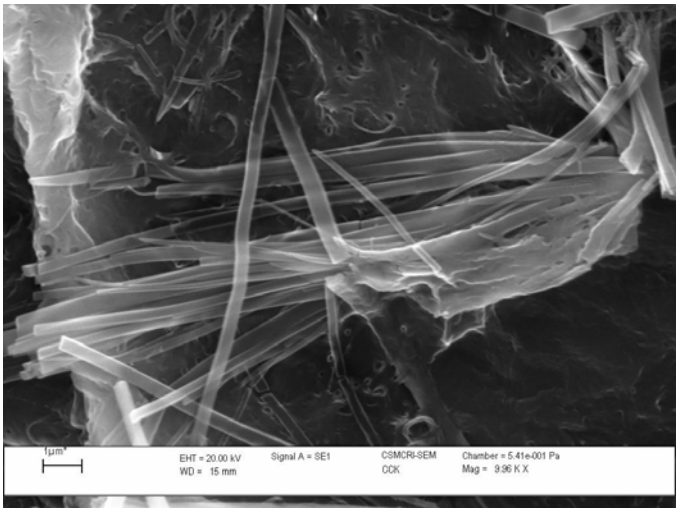
IV) FT-IR comparison plot of hydrogelator L1 at various conditions



V) PXRD comparison plot of hydrogelator L1 at various conditions



VI) FE-SEM of Xerogel of L1 [concentration of gelator = 2.5% (w/v)]



FT-IR comparison plots of the metallogelators

Compound 1b

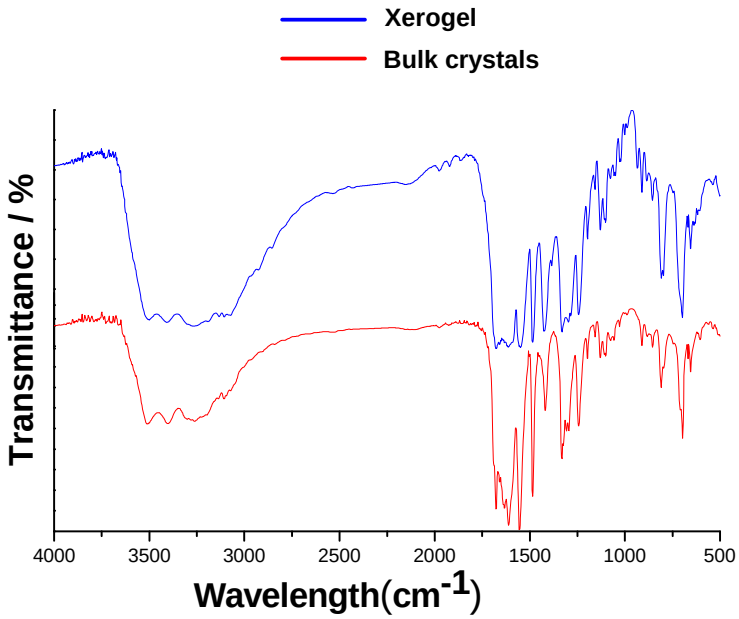


Figure S1

Compound 2

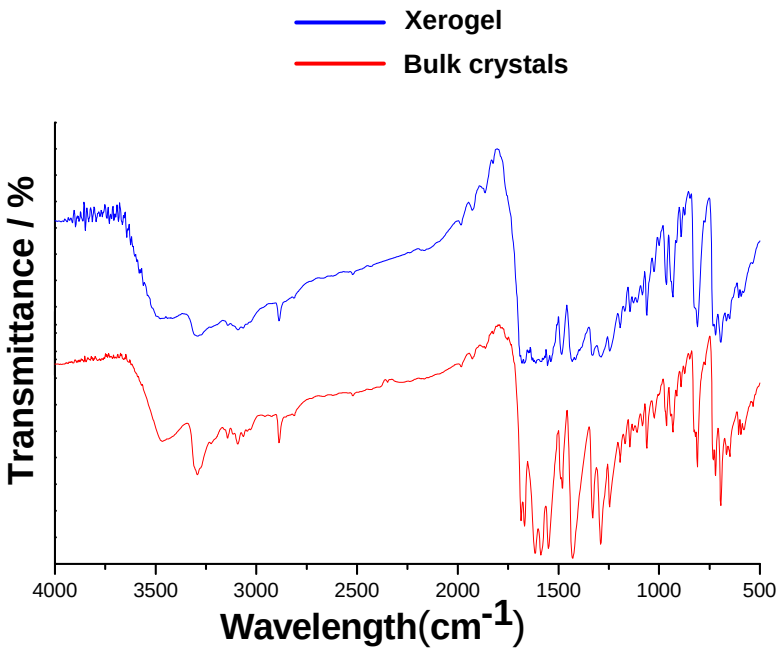


Figure S2

Compound 3

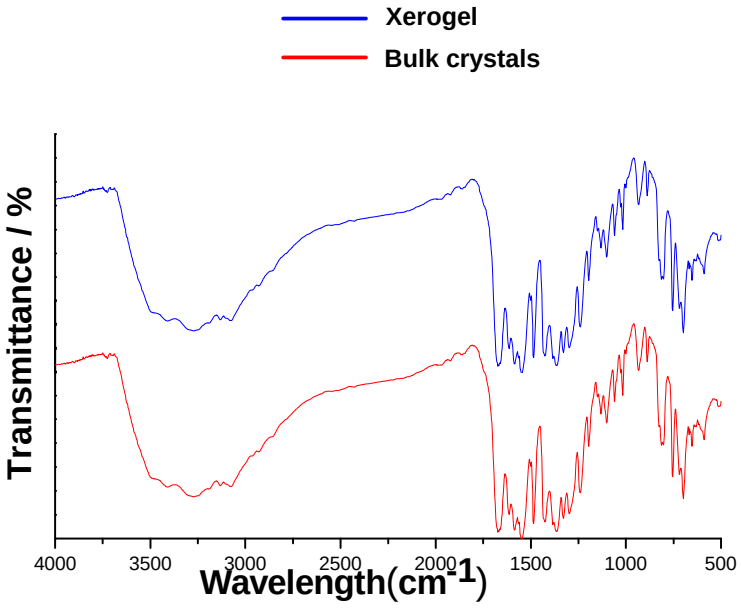


Figure S3

Compound 4

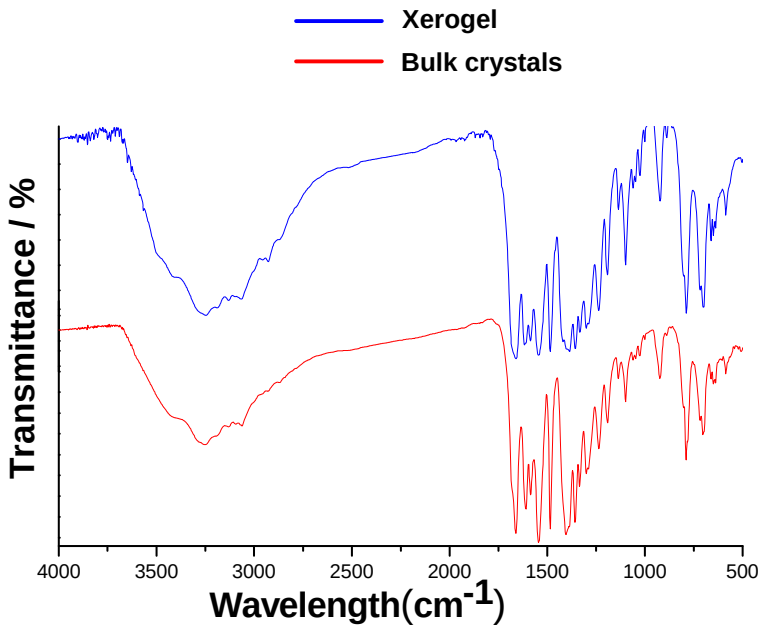


Figure S4

Compound 5

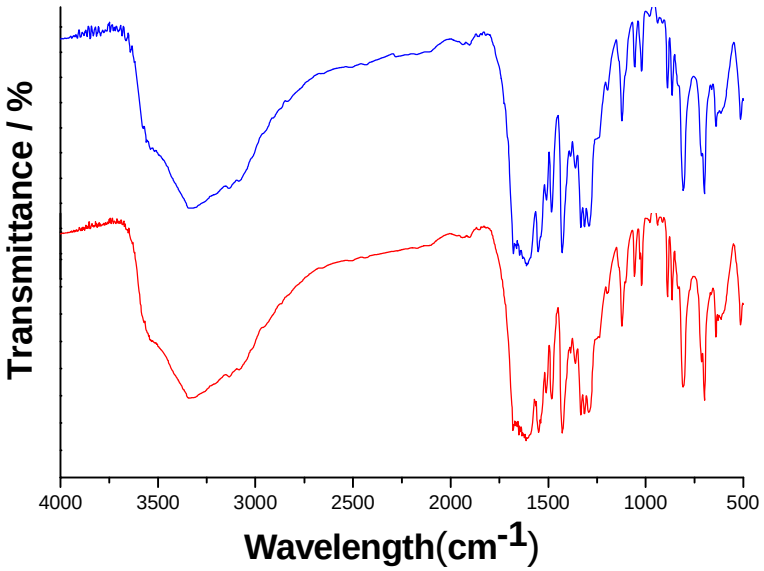


Figure S5

Compound 7

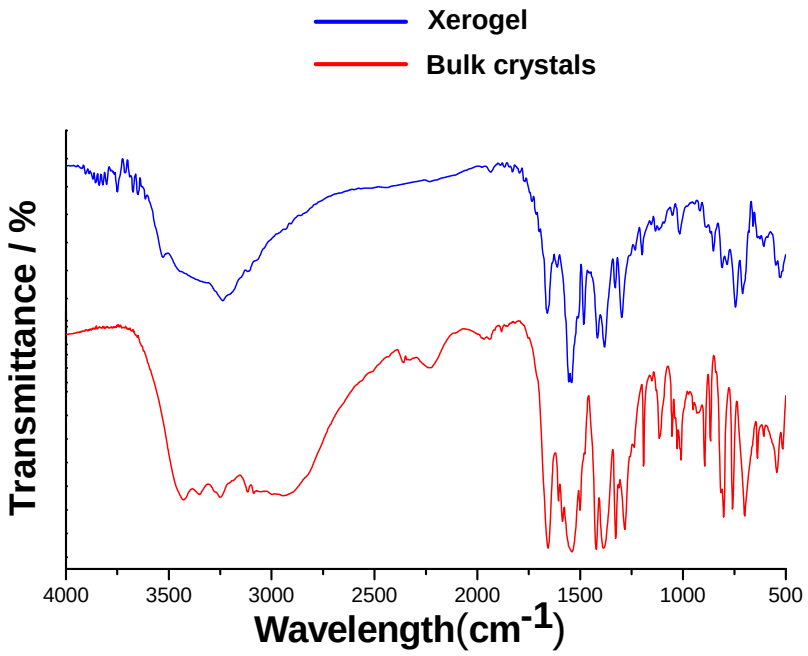


Figure S6

Compound 8

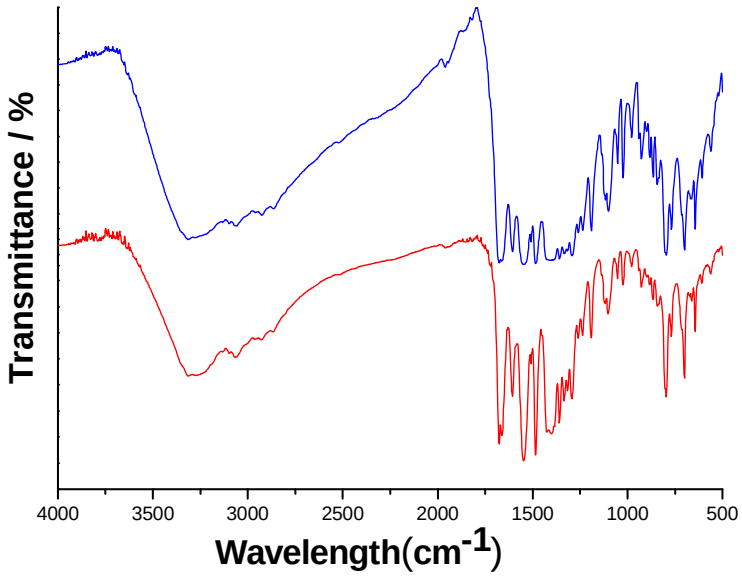


Figure S7

Table S2: Elemental Analysis data

Gelator	Bulk Ctystals	Xerogel
1b	$C_{20}H_{14}N_4O_6Cu.3H_2O$: Calcd. C, 45.85; H, 3.85; N, 10.69. Found: C, 45.36; H, 3.34; N, 10.48.	$C_{20}H_{14}N_4O_6Cu.3H_2O$: Calcd. C, 45.85; H, 3.85; N, 10.69. Found: C, 45.67; H, 3.46; N, 10.78.
2	$C_{21}H_{18}N_4O_7Cu$: Calcd. C, 50.25; H, 3.61; N, 11.16. Found: C, 49.76; H, 4.20; N, 11.18.	$C_{21}H_{18}N_4O_7Cu$: Calcd. C, 50.25; H, 3.61; N, 11.16. Found: C, 50.60; H, 4.28; N, 11.22.
3	$C_{26}H_{20}N_4O_7Cu.2H_2O$: Calcd. C, 52.04; H, 4.03; N, 9.34. Found: C, 52.28; H, 4.10; N, 10.12.	$C_{26}H_{20}N_4O_7Cu.2H_2O$: Calcd. C, 52.04; H, 4.03; N, 9.34. Found: C, 52.20; H, 4.08; N, 10.22.
4	$C_{30}H_{22}N_4O_7Cu.3H_2O.2DMF$: Calcd. C, 53.10; H, 5.20; N, 10.32. Found: C, 53.56; H, 5.42; N, 10.30.	$C_{30}H_{22}N_4O_7Cu.3H_2O.2DMF$: Calcd. C, 53.10; H, 5.20; N, 10.32. Found: C, 53.66; H, 5.20; N, 10.30.
5	$C_{20}H_{14}N_4O_6Co.2H_2O$: Calcd. C, 47.92; H, 3.62; N, 11.18. Found: C, 47.80; H, 3.34; N, 8.94.	$C_{22}H_{14}N_4O_{10}Co.2H_2O$: Calcd. C, 47.92; H, 3.62; N, 11.18. Found: C, 47.34; H, 3.48; N, 11.12.
7	$C_{17}H_{15}N_2O_7Co.H_2O$: Calcd. C, 46.80; H, 3.93; N, 6.42. Found: C, 46.90; H, 3.77; N, 6.98.	$C_{17}H_{15}N_2O_7Co.H_2O$: Calcd. C, 46.80; H, 3.93; N, 6.42. Found: C, 46.76; H, 4.21; N, 6.40.
8	$C_{30}H_{20}N_4O_6Co.5H_2O$: Calcd. C, 52.87; H, 4.44; N, 8.22. Found: C, 52.90; H, 4.40; N, 8.36.	$C_{30}H_{20}N_4O_6Co.5H_2O$: Calcd. C, 52.87; H, 4.44; N, 8.22. Found: C, 52.66; H, 4.42; N, 8.21.