

Studying fluororous interactions in a series of coordination compounds derived from mono-pyridyl ligands equipped with hydrogen bonding functionality: exploiting anion... π_F interaction in separating ClO_4^- anion from a competing mixture of anions

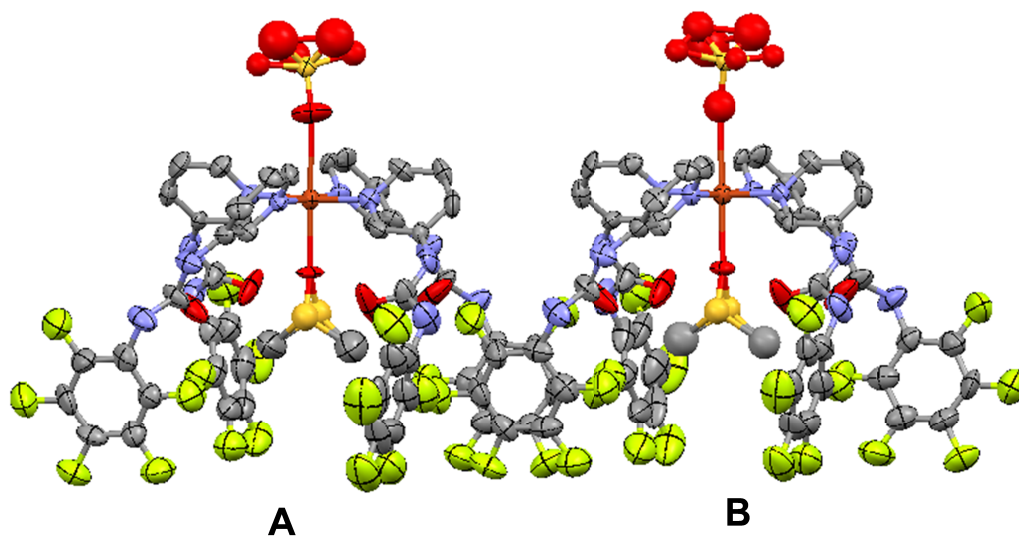
Subhabrata Banerjee and Parthasarathi Dastidar*

*Departement of Organic Chemistry, Indian Association for the Cultivation of Science, 2A&2B
Raja S. C. Mullick Road, Jadavpur, Kolkata – 700032, West Bengal, India;*

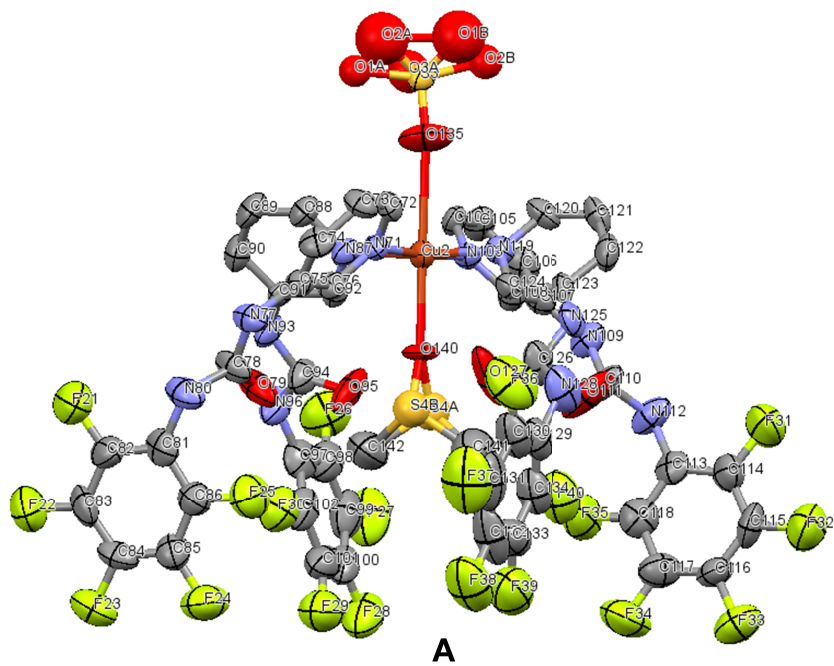
E-mail: ocpd@iacs.res.in; parthod123@rediffmail.com;

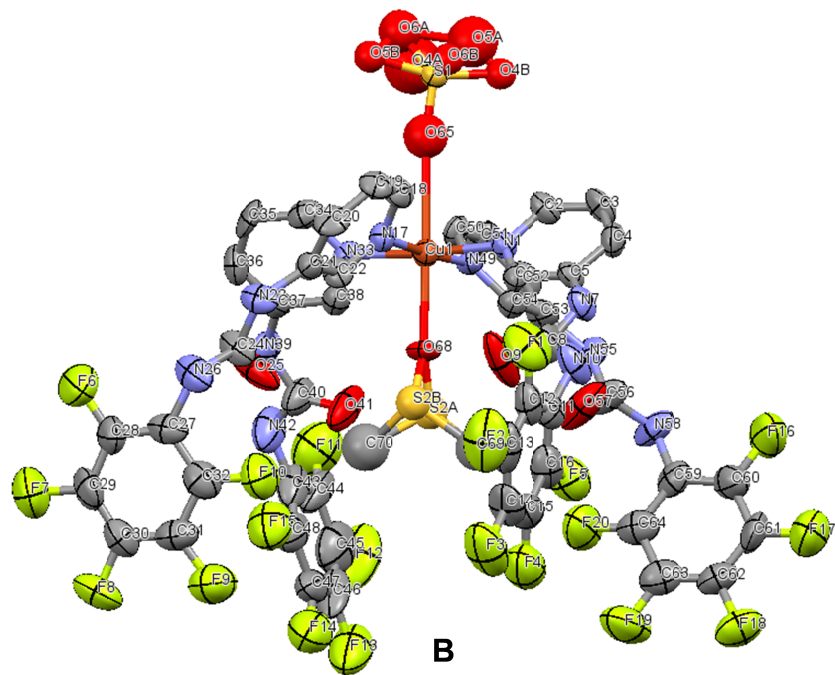
<u>Contents</u>	<u>Page No</u>
1. Ortep diagram and hydrogen bonding parameters of compounds CC1 – CC9, CP1,CP2	S1-S12
2. Bulk vs Simulated PXRD plots of CC1-CC9, CP1, CP2	S13-S17
3. TGAs of compounds	S18-23

CC1



A and B are two crystallographically independent molecules in the asymmetric unit

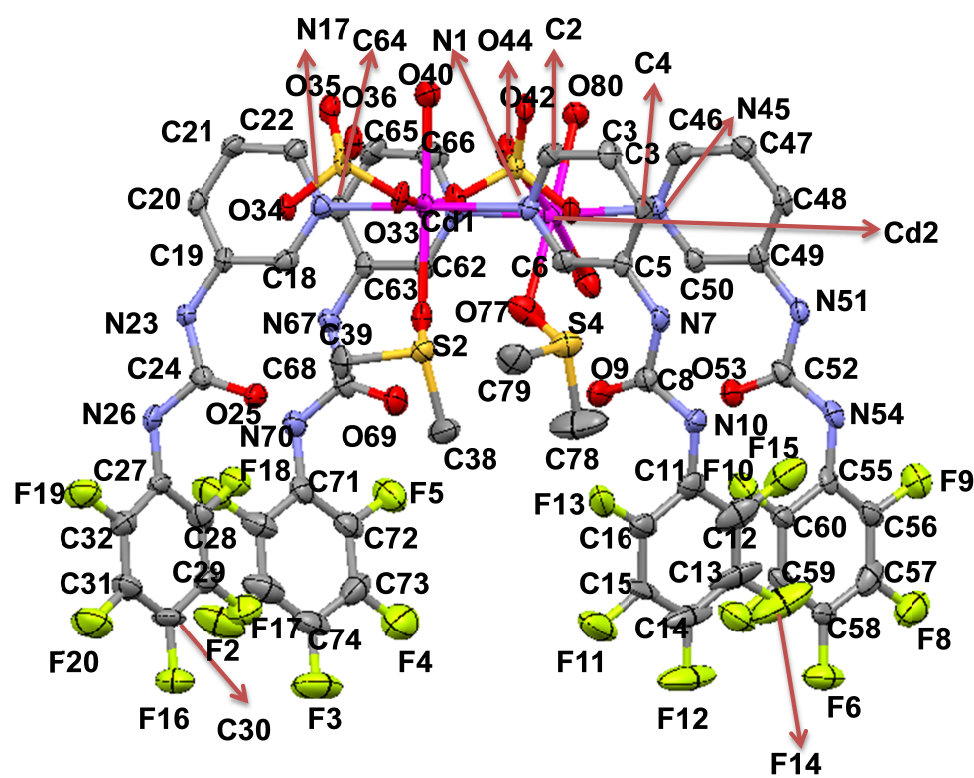




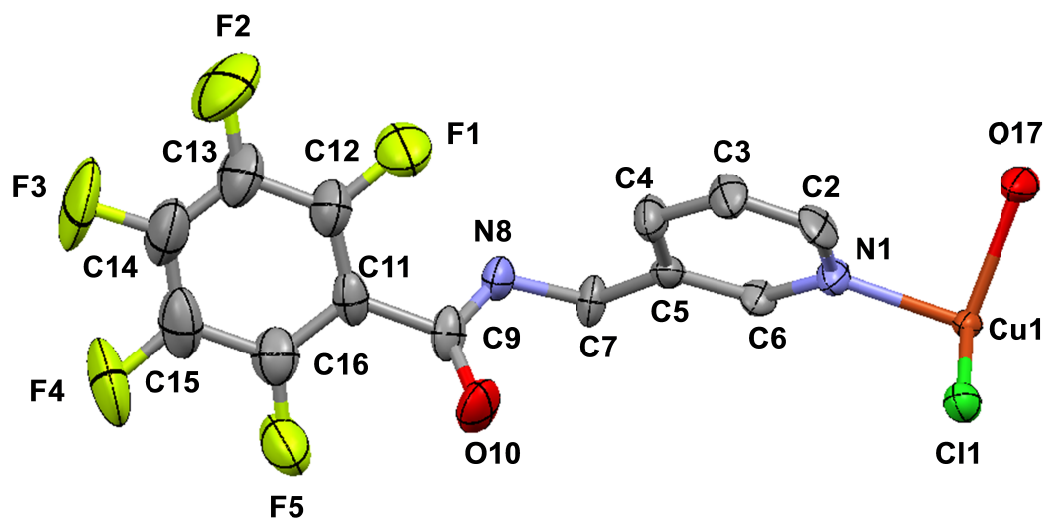
Molecules A and B in the asymmetric unit are shown separately with the atom numbering scheme

Hydrogen bonding parameters for CC1					
D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry operation for A
N(7)–H(7)···O(6B)	0.86	2.101	2.938(12)	163.3	-x+1, -y+2, -z+1
N(7)–H(7)···O(4B)	0.86	2.51	3.192(15)	137.0	-x+1, -y+2, -z+1
N(10)–H(10)···O(4B)	0.86	2.04	2.827(15)	151.6	-x+1, -y+2, -z+1
N(10)–H(10)···O(5A)	0.86	2.07	2.94(2)	177.50	-x+1, -y+2, -z+1
N(39)–H(39)···O(4A)	0.86	2.07	2.872(16)	154.3	-x+1, -y+1, -z+1
N(39)–H(39)···O(5B)	0.86	2.101	2.876(16)	149.8	-x+1, -y+1, -z+1
N(39)–H(39)···O(6A)	0.86	2.169	2.965	153.78	-x+1, -y+1, -z+1
N(42)–H(42)···O(5B)	0.86	1.999	2.784	151.33	-x+1, -y+1, -z+1
N(42)–H(42)···O(6A)	0.86	2.092	2.86(3)	148.95	-x+1, -y+1, -z+1
N(55)–H(55)···O(2B)	0.86	2.126	2.907(17)	150.74	x-1, y, z
N(55)–H(55)···O(3A)	0.86	2.24	3.013(11)	149.33	x-1, y, z
N(58)–H(58)···O(3A)	0.86	2.217	2.910	151.24	x-1, y, z
N(77)–H(77)···O(6B)	0.86	2.231	3.011(12)	151.32	-x+2, -y+1, -z+1
N(77)–H(77)···O(5B)	0.86	2.232	2.996(16)	147.69	-x+2, -y+1, -z+1
N(80)–H(80)···O(6B)	0.86	2.199	2.972(13)	149.8	-x+2, -y+1, -z+1
N(93)–H(93)···O(3A)	0.86	2.093	2.916(11)	160.19	x, y-1, z
N(93)–H(93)···O(1A)	0.86	2.453	3.156(15)	139.9	x, y-1, z
N(96)–H(96)···O(2A)	0.86	2.04	2.90(3)	178.24	x, y-1, z
N(96)–H(96)···O(1A)	0.86	2.043	2.830 (17)	151.64	x, y-1, z
N(109)–H(109)···O(4B)	0.86	1.997	2.797(14)	155.21	-x+1, -y+1, -z+1
N(109)–H(109)···O(5A)	0.86	2.13	2.94(2)	155.81	-x+1, -y+1, -z+1
N(109)–H(109)···O(4A)	0.86	2.398	3.13(2)	144.5	-x+1, -y+1, -z+1
N(112)–H(112)···O(4A)	0.86	2.040	2.83(2)	152.1	-x+1, -y+1, -z+1
N(112)–H(112)···O(5A)	0.86	2.308	3.053	145.08	-x+1, -y+1, -z+1
N(112)–H(112)···O(6A)	0.86	2.486	3.34(3)	174.6	-x+1, -y+1, -z+1

CC2

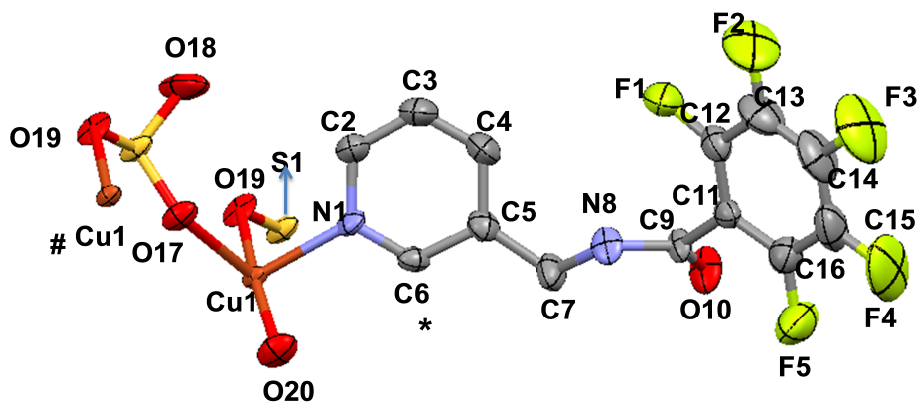


CC3



Hydrogen bonding parameters for CC3					
D–H⋯A	D–H (Å)	H⋯A (Å)	D⋯A (Å)	D–H⋯A (°)	Symmetry operation for A
N(7)–H(7)⋯O(35)	0.86	2.38	3.156(9)	150.9	-x+2, -y+1, -z+1

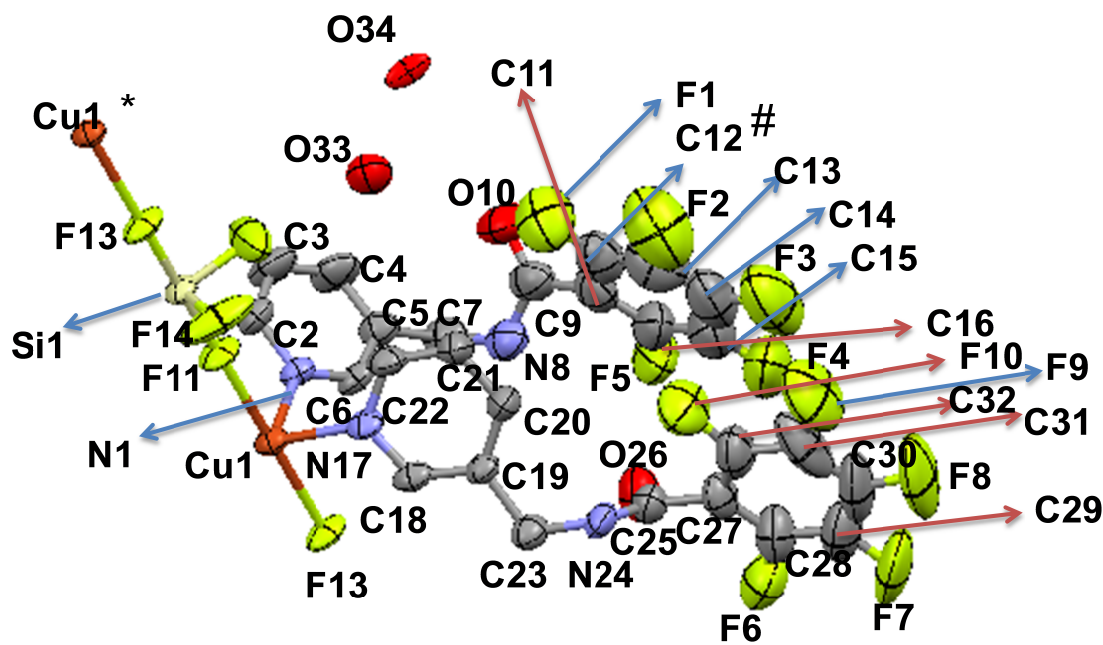
CP1



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

Hydrogen bonding parameters for CP1					
D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symmetry operation for A
N(8)-H(8)...O(10)	0.86	2.015	2.874(13)	178.2	x+1, y, z

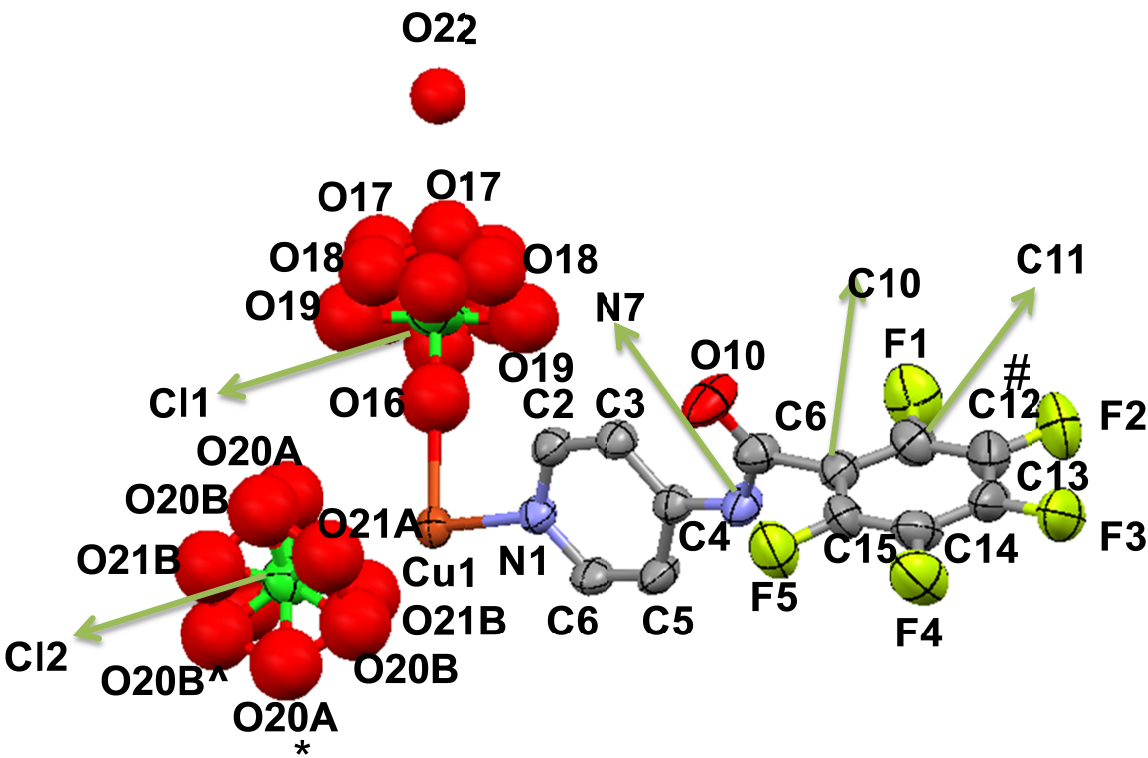
CP2



*x, -1+y, z # 1-x, y, 1.5-z

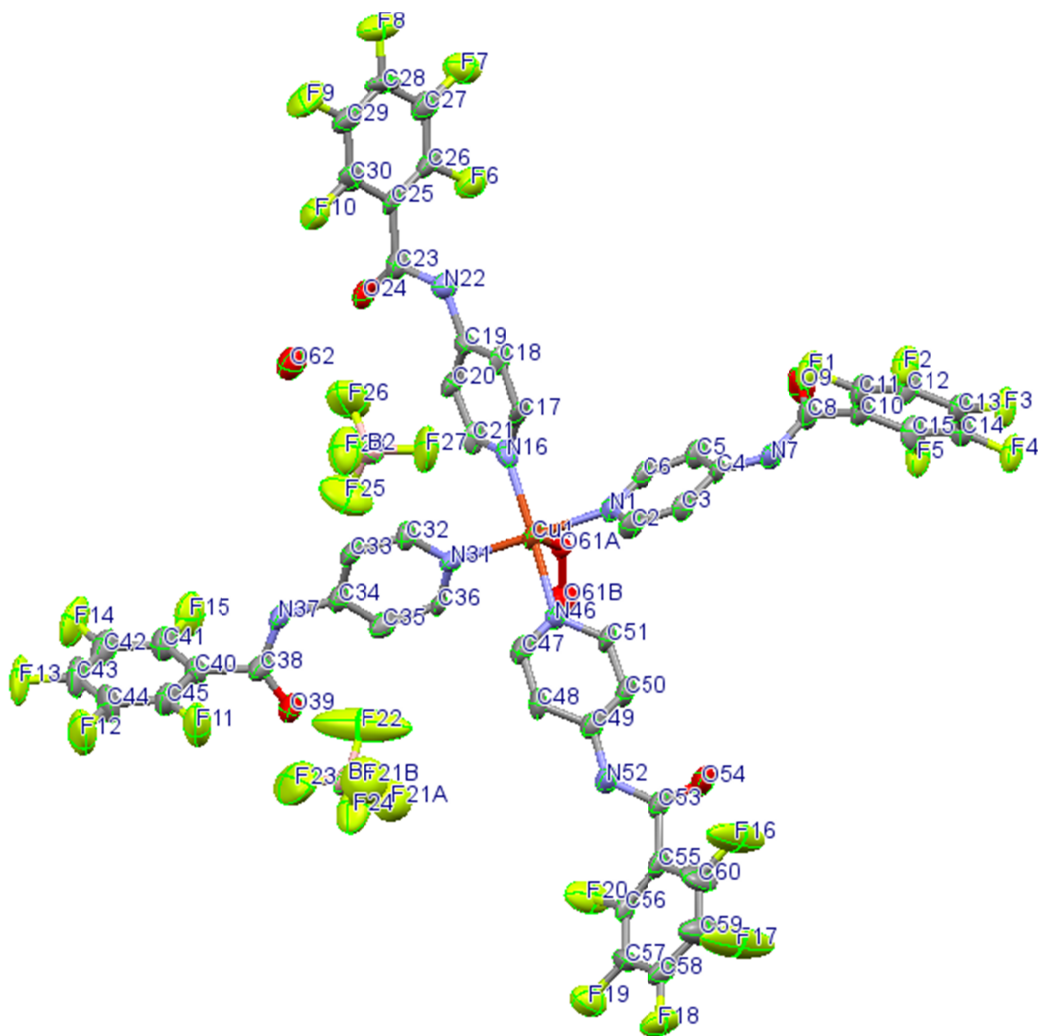
Hydrogen bonding parameters for CP2					
D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symmetry operation for A
N(8)-H(8)...O(33)	0.86	2.015	2.853(13)	164.4	-x+1, y+1, -z+3/2
N(24)-H(24)...O(34)	0.86	1.954	2.762(4)	158.2	x, y, z+1

CC4



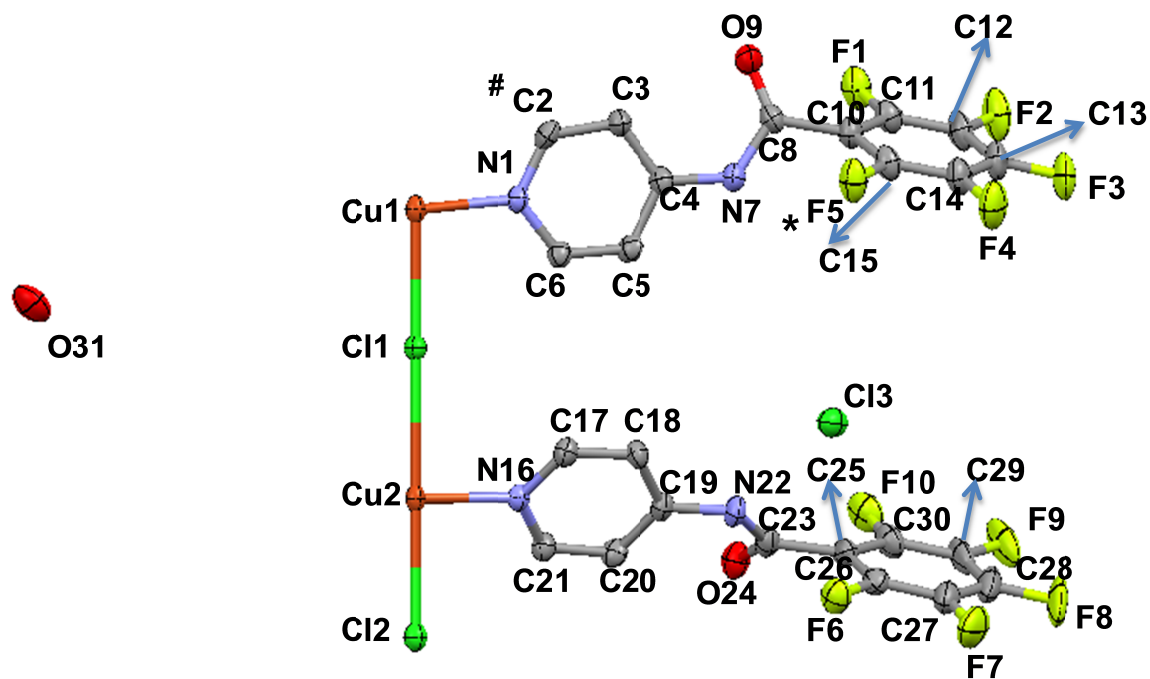
1-x, y, 1/2-z *-1/2+ y, 1/2 +x, 1/2-z ^ 1-y, 1-x, 1/2-z

CC5



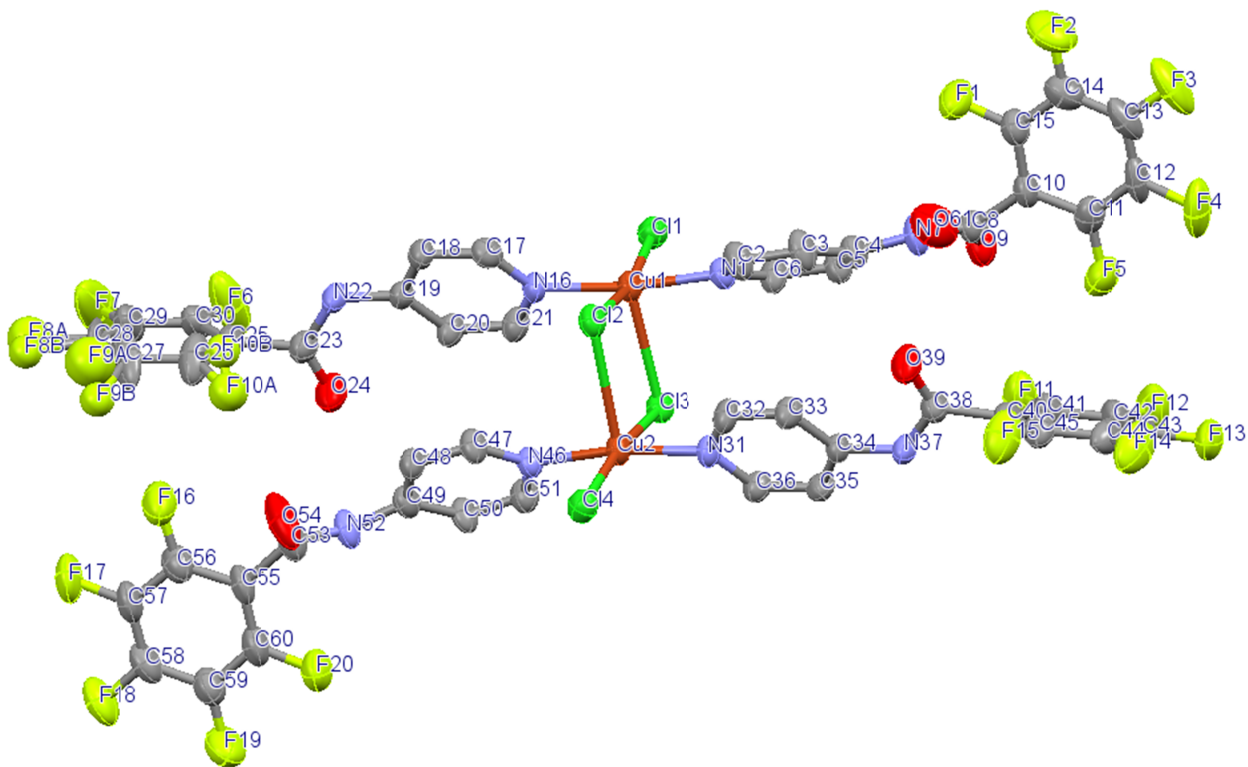
Hydrogen bonding parameters for CC5					
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)	Symmetry operation for A
N(22)–H(22)...F(27)	0.86	2.10	2.887(14)	151.1	-x, 1/2+y, 3/2-z
N(37)–H(37)...F(23)	0.86	2.02	2.876(14)	172.2	1-x, 1-y, 1-z
N(52)–H(52)...F(25)	0.86	1.92	2.751(14)	161.6	1-x, 1/2+y, 3/2-z

CC6



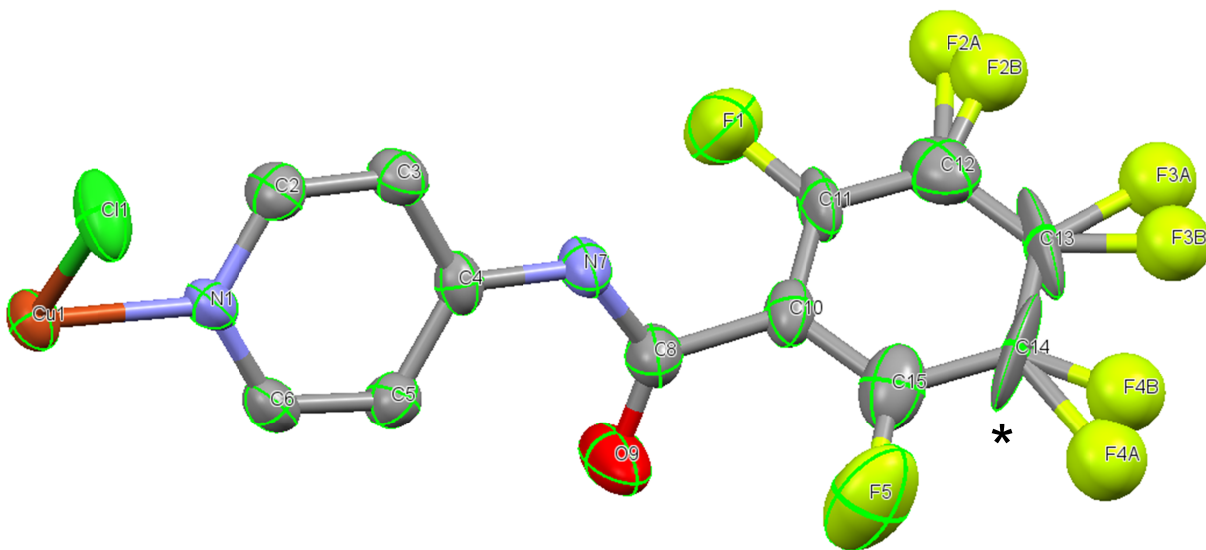
1/2- y , x , z *1/2- x , 1/2 - y , z

Hydrogen bonding parameters for CC6					
D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A ($^{\circ}$)	Symmetry operation for A
N(7)-H(7)...O(31)	0.86	1.90	2.745(8)	166.5	x, y, z
N(22)-H(22)...Cl(27)	0.86	2.21	3.050(7)	165.3	x, y, z



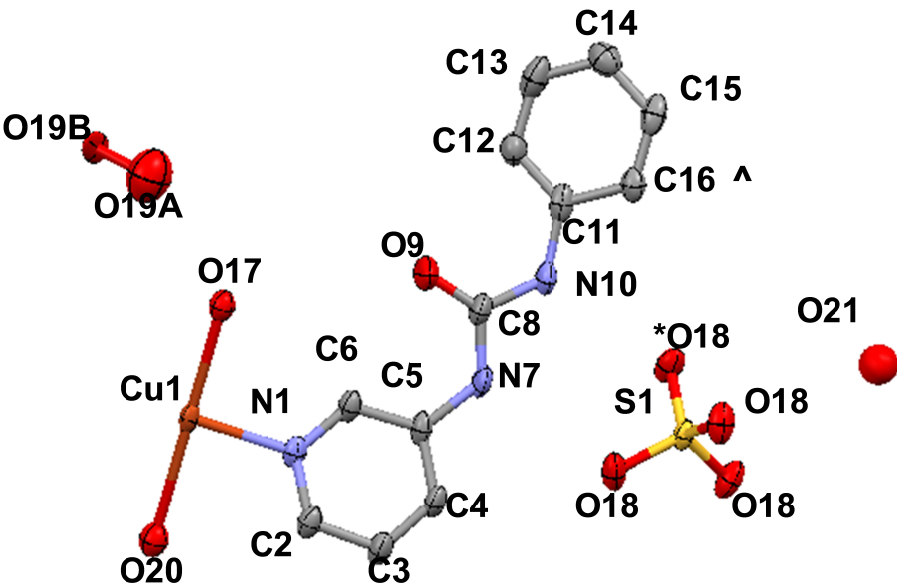
S10

CC8



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

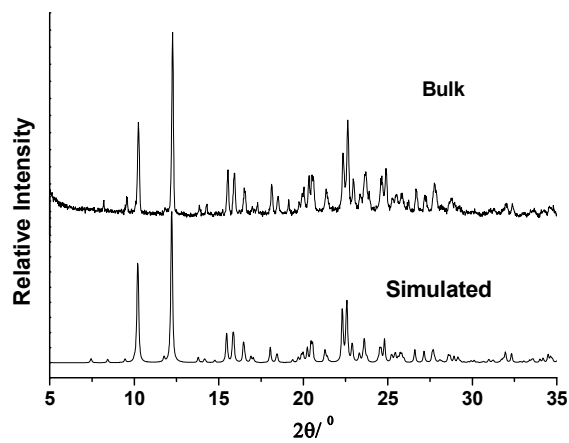
Hydrogen bonding parameters for CC8					
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)	Symmetry operation for A
N(7)–H(7)...Cl(11)	0.86	2.50	3.287(4)	152.4	x, -y+3/2, z-1/2



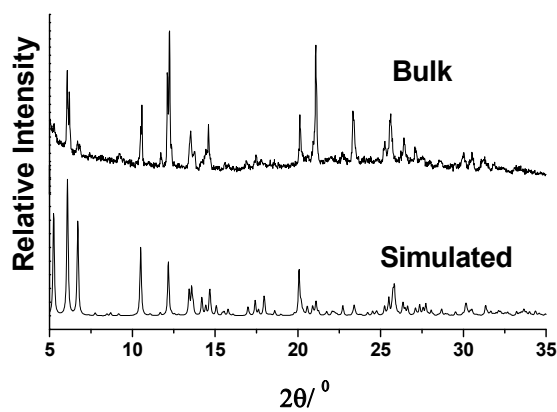
$*1/2+y, 1-x, 1-z \quad ^y, 1/2-x, z$

Hydrogen bonding parameters for CC9					
D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)	Symmetry operation for A
N(10)–H(10)...O(18)	0.86	1.98	2.828(7)	168.4	-y+1/2, x, z
N(7)–H(7)...O(18)	0.86	2.19	2.982(6)	152.8	-x+1, -y+1, -z+1

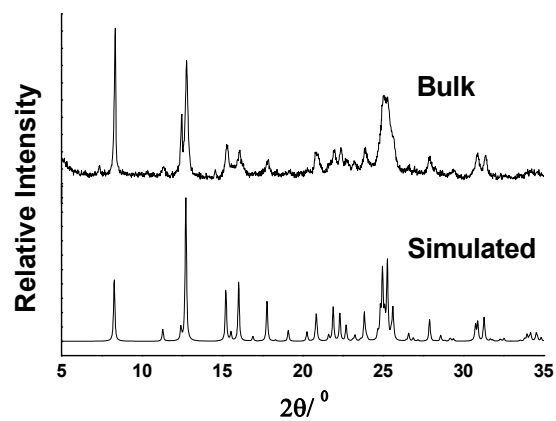
CC1



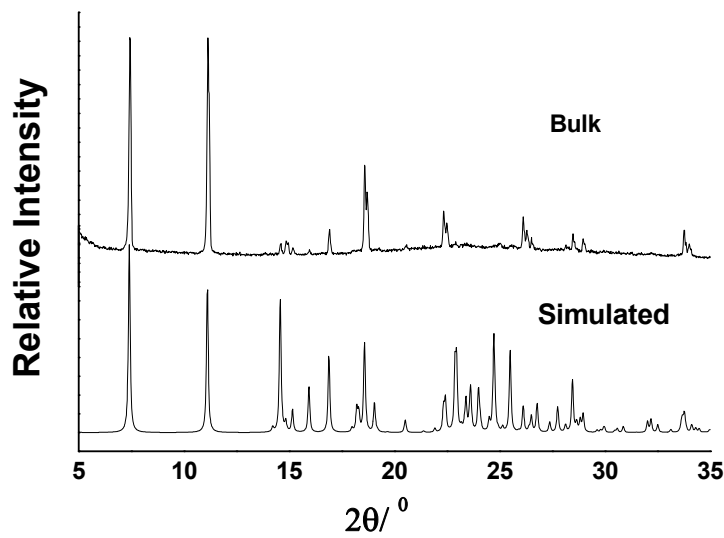
CC2



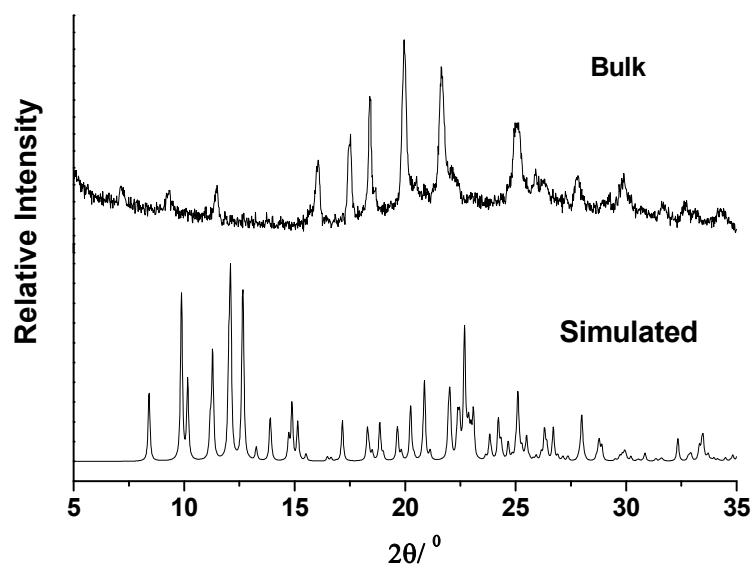
CC3



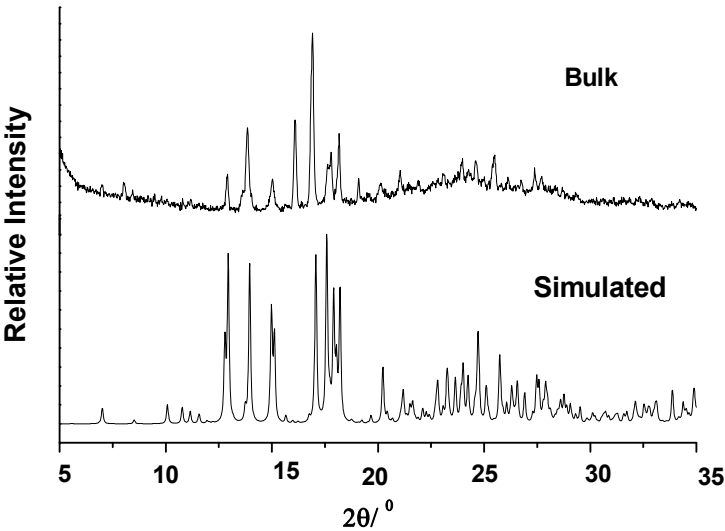
CP1



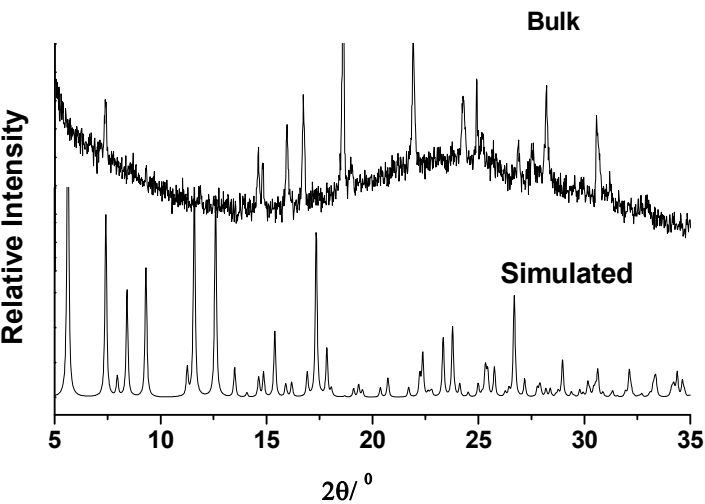
CP2



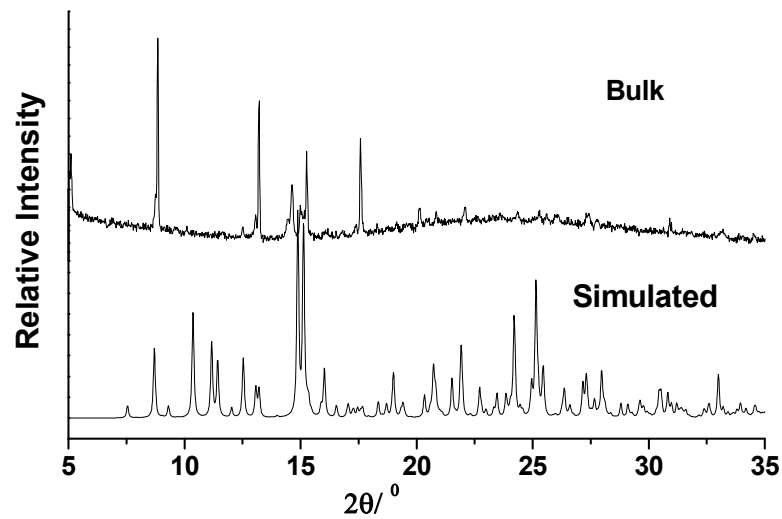
CC5



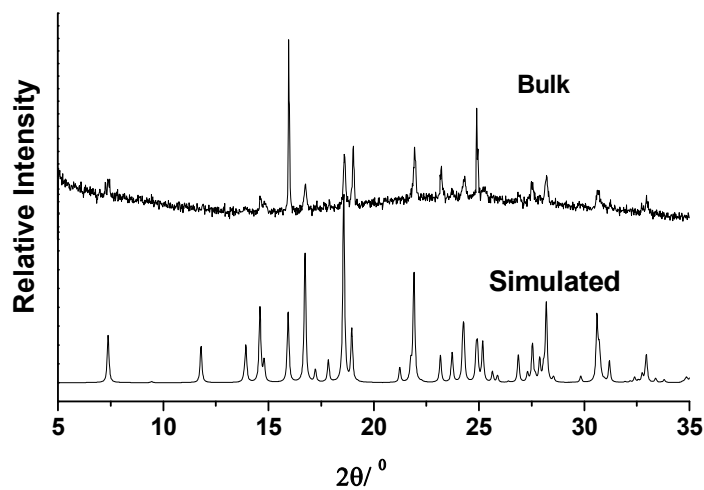
CC6



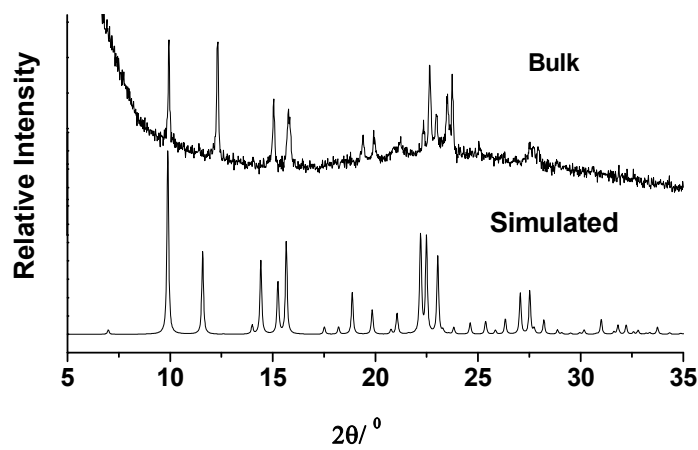
CC7



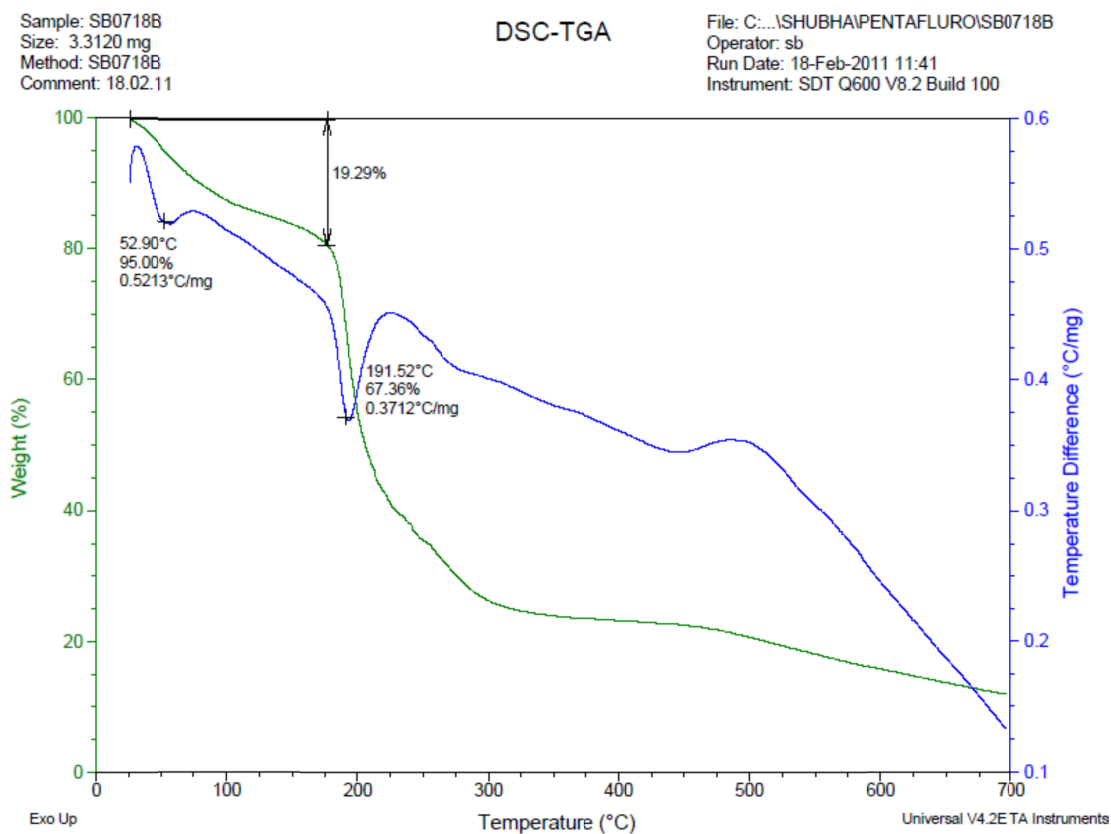
CC8



CC9



CC1



Unit cell contents= 16 Ligands+4CuSO₄+4 DMSO

Z=1

Therefore FW=Unit cell contents/4

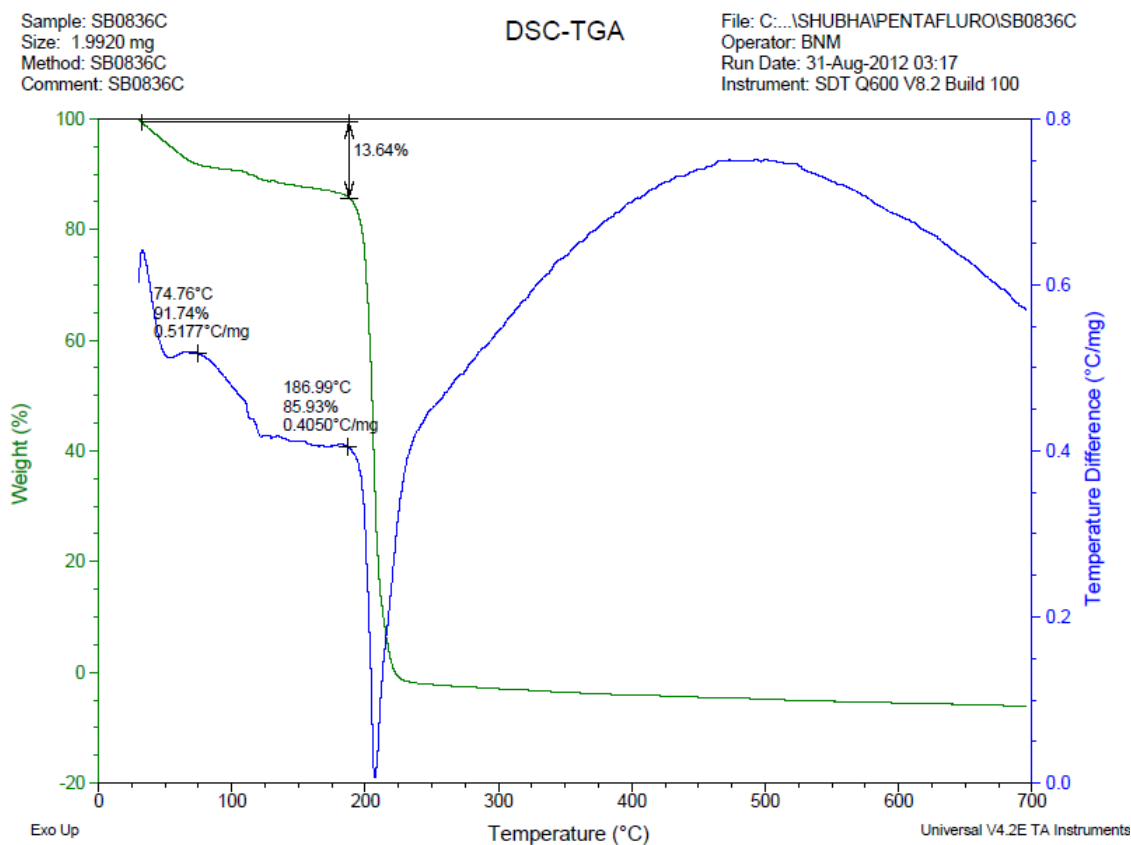
= 4 Ligands+1CuSO₄+1DMSO

=4 X 303.04+1X 158.88 +1X78.01

=1449.05

Weight loss for 1 DMSO= 78.01/1449.05=5.37%(experimental 19.29%)

CC2



Unit cell contents = 8Ligands+4CdSO₄+4DMSO+6H₂O+13.6H₂O (SQUEEZE results of 136 electrons) (solvent of inclusion)

$$Z=2$$

Therefore FW= Unit cell contents/2

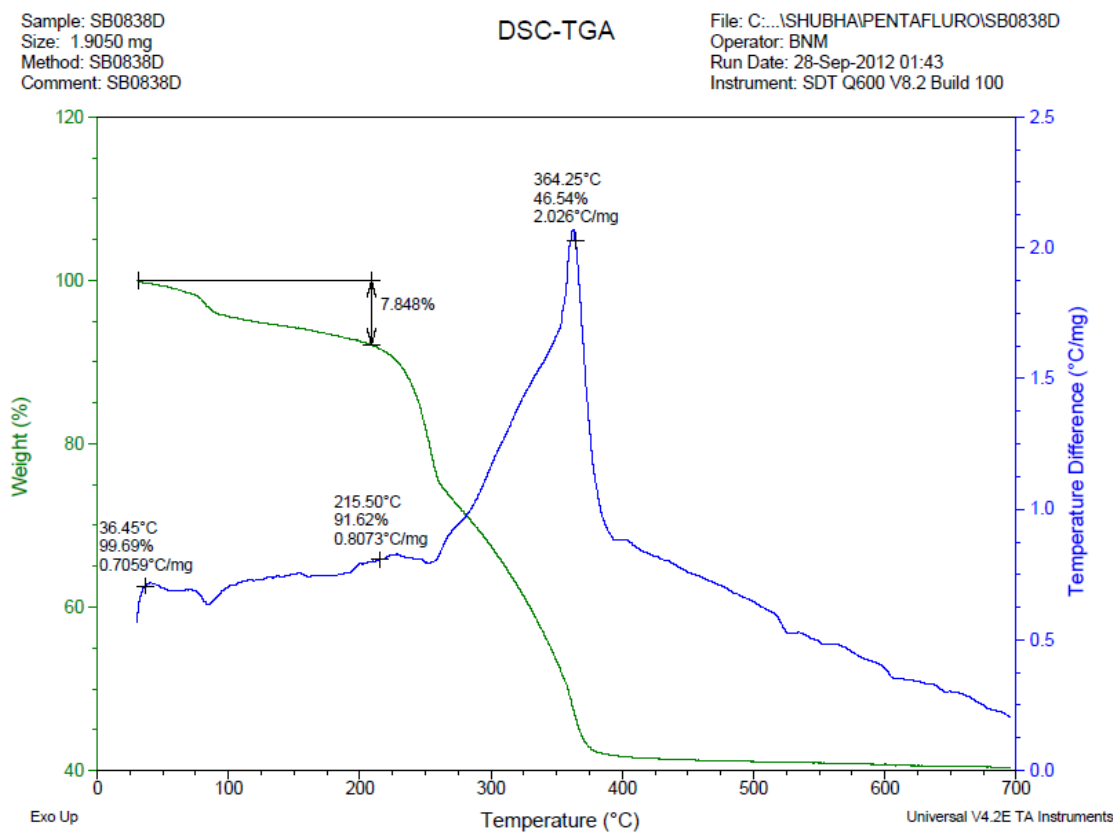
$$= 4 \text{ Ligands} + 2\text{CdSO}_4 + 2\text{DMSO} + 6.8\text{H}_2\text{O}$$

$$= 4 \times 303.04 + 2 \times 208.86 + 2 \times 78.01 + 6.8 \times 18.03$$

$$= 1907.27$$

Weight loss for DMSO and H₂O = $278.51/1907.27 = 14.6\%$ (experimental 13.64%)

CP2



Unit cell contents= 16 Ligands+4CuSiF₆+8H₂O+4H₂O (SQUEEZE results of 32 electrons) (solvent of inclusion)

$$Z=4$$

Therefore FW=Unit cell contents/Z

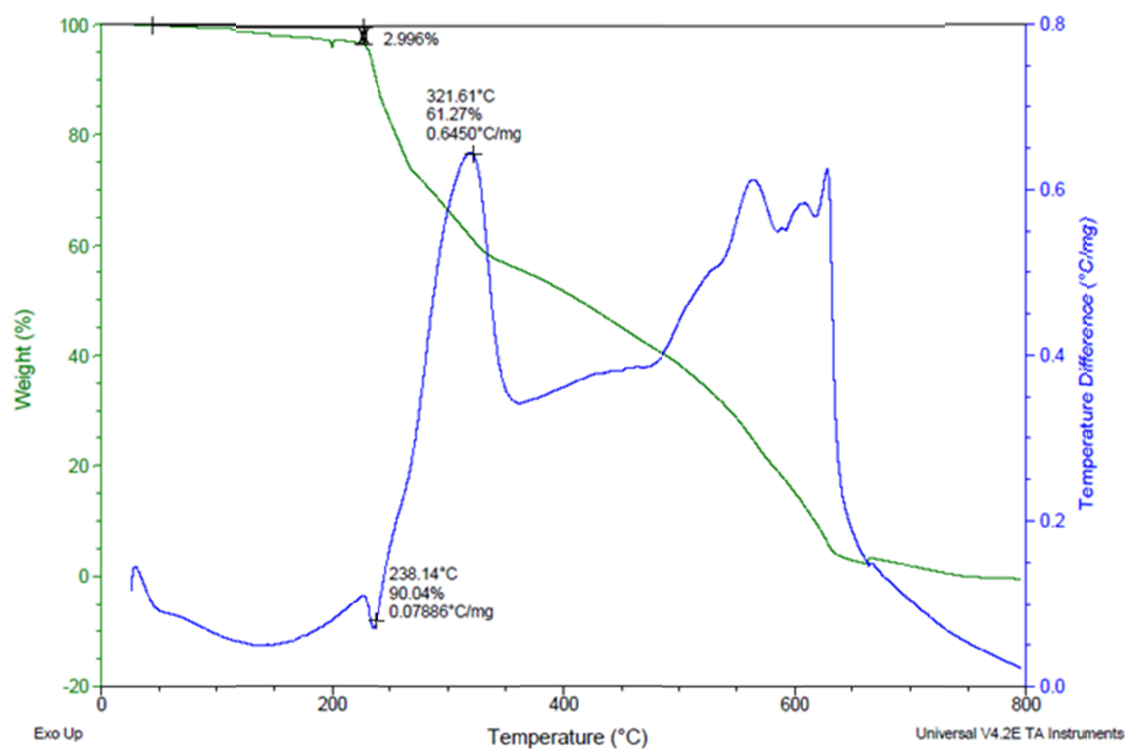
$$= 4\text{Ligands} + 1 \text{ CuSiF}_6 + 2\text{H}_2\text{O} + 1\text{H}_2\text{O}$$

$$= 4 \times 302.05 + 1 \times 204.45 + 2 \times 18.01 + 1 \times 18.01$$

$$= 1470.52$$

Weight loss for 3 H₂O = $3 \times 18.01 / 1470.52 = 54.03 / 1470.52 = 3.67\%$ (experimental 7.85%)

CC4



Unit cell contents=16 Ligands+4Cu(ClO₄)₂+4H₂O

$$Z=4$$

Therefore FW= Unitcell contents/Z

$$=4\text{Ligands}+ 1\text{Cu}(\text{ClO}_4)_2+1\text{H}_2\text{O}$$

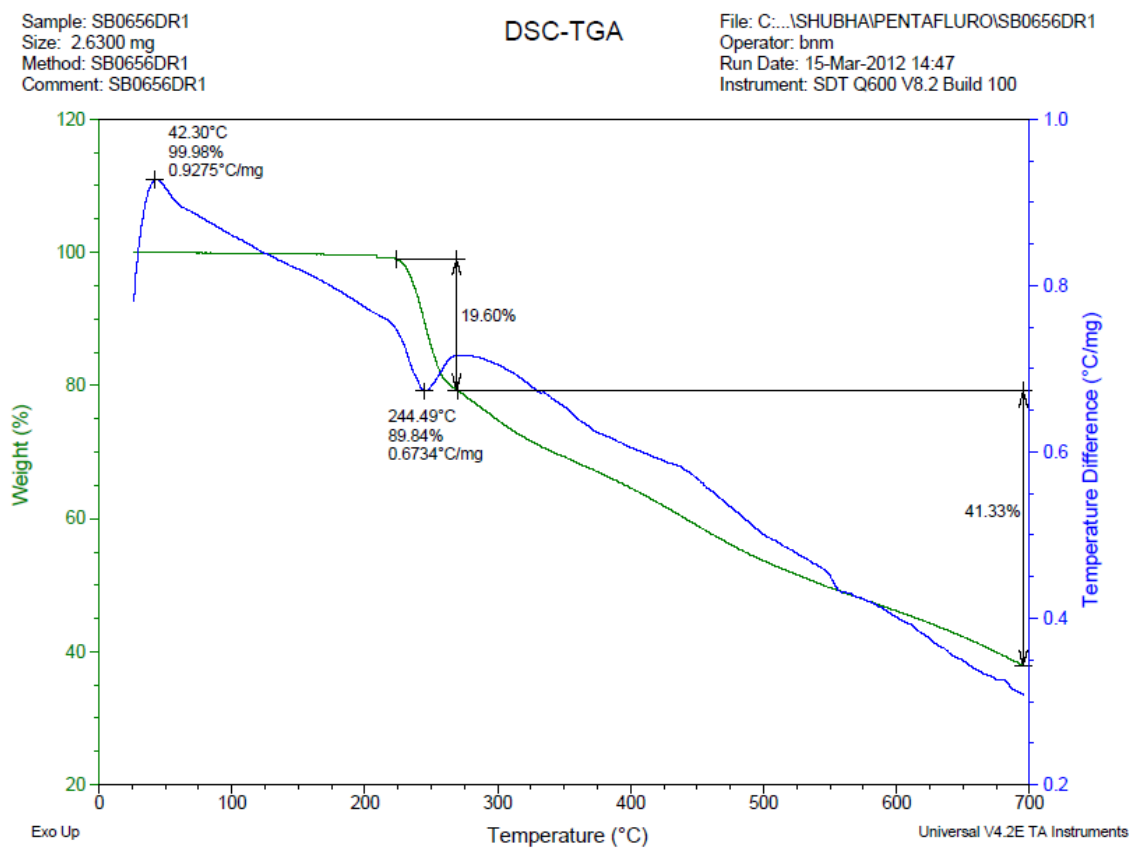
$$=4 \times 288.17+1 \times 260.83+1 \times 18.01$$

$$=1152.68+260.83+18.01$$

$$=1431.52$$

Weight loss for 1 H₂O=18x18.01/1431.52=270.15/1431.52=1.25% (experimental 2.9%)

CC6



Unit cell contents = 16 Ligands+4CuCl₂+8H₂O+22H₂O (SQUEEZE results of 223 electrons) (solvent of inclusión)

$$Z=2$$

Therefore FW=Unit cell contents/Z

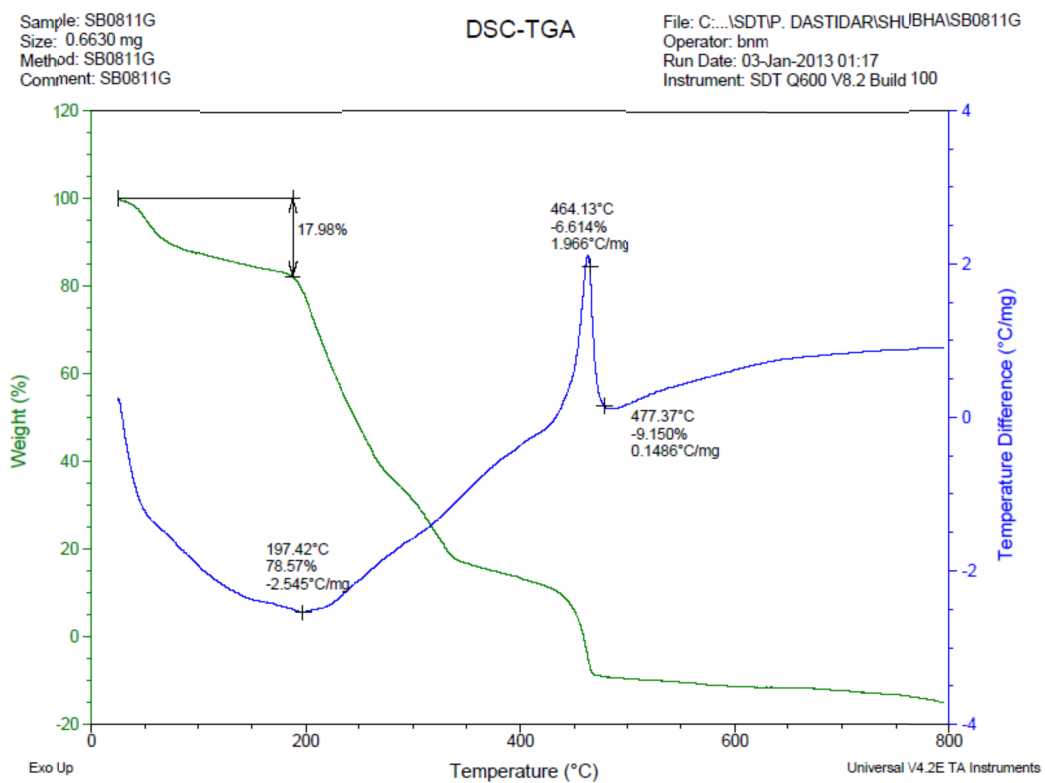
$$= 8\text{Ligands}+ 2\text{CuCl}_2+4\text{H}_2\text{O}+11\text{H}_2\text{O}$$

$$=8 \times 288.17+2 \times 132.45+4 \times 18.01+11 \times 18.01$$

$$=2840.4$$

Weight loss for 15 H₂O=15x18.01/2840.4=270.15/2840.4=9.50%(experimental 19.6%)

CC9



Unit cell contents = 8 Ligands + 2CuSO₄ + 14H₂O

$$Z=2$$

Therefore FW=Unit cell contents /Z

$$= 4 \text{ Ligands} + 1 \text{ CuSO}_4 + 7 \text{ H}_2\text{O}$$

$$= 4 \times 213.09 + 1 \times 158.61 + 7 \times 18.01$$

$$= 1136.56$$

Weight loss for 7 H₂O = $7 \times 18.01 / 1136.56 = 126.07 / 1136.56 = 11.09\%$ (experimental 17.9%)