Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplimentary Information

Metalla-macro-tricyclic Cryptands: Anion Encapsulation and Selective Separation of Sulfate via in situ Crystallization

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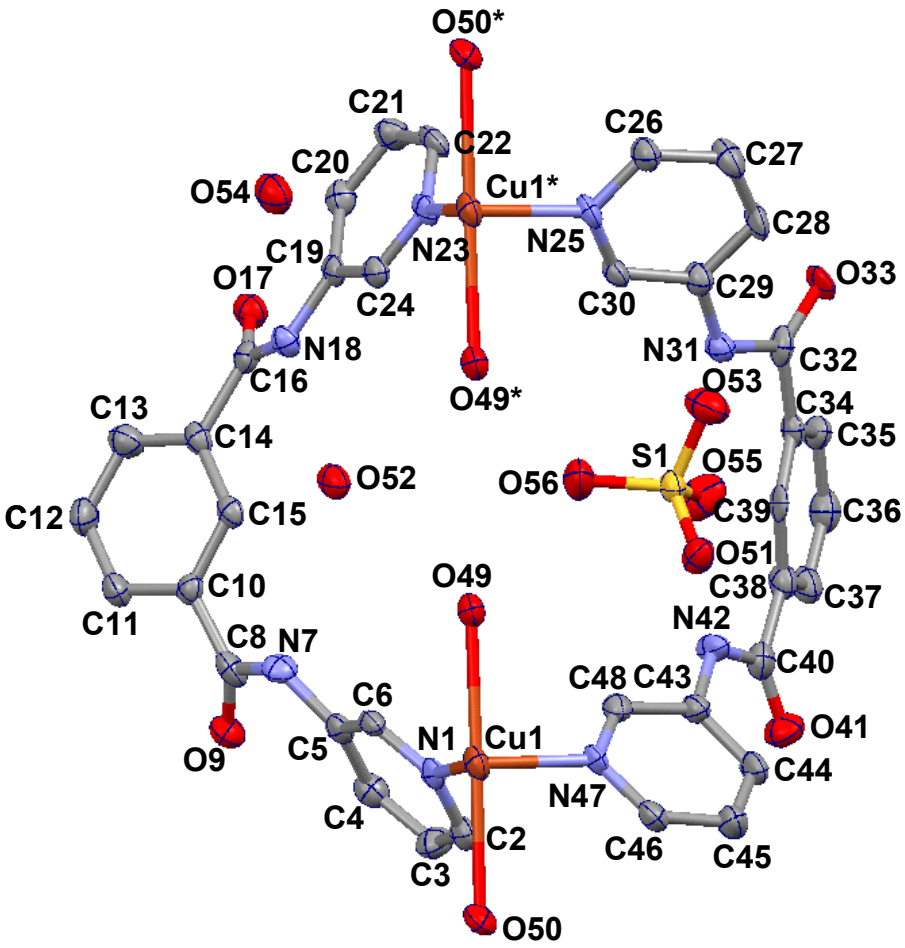
Molecular Plots and Hydrogen Bonding Parameters for 1a, 1b, 2, 3, 4a, 5 and 6

Molecular Plot of 1a

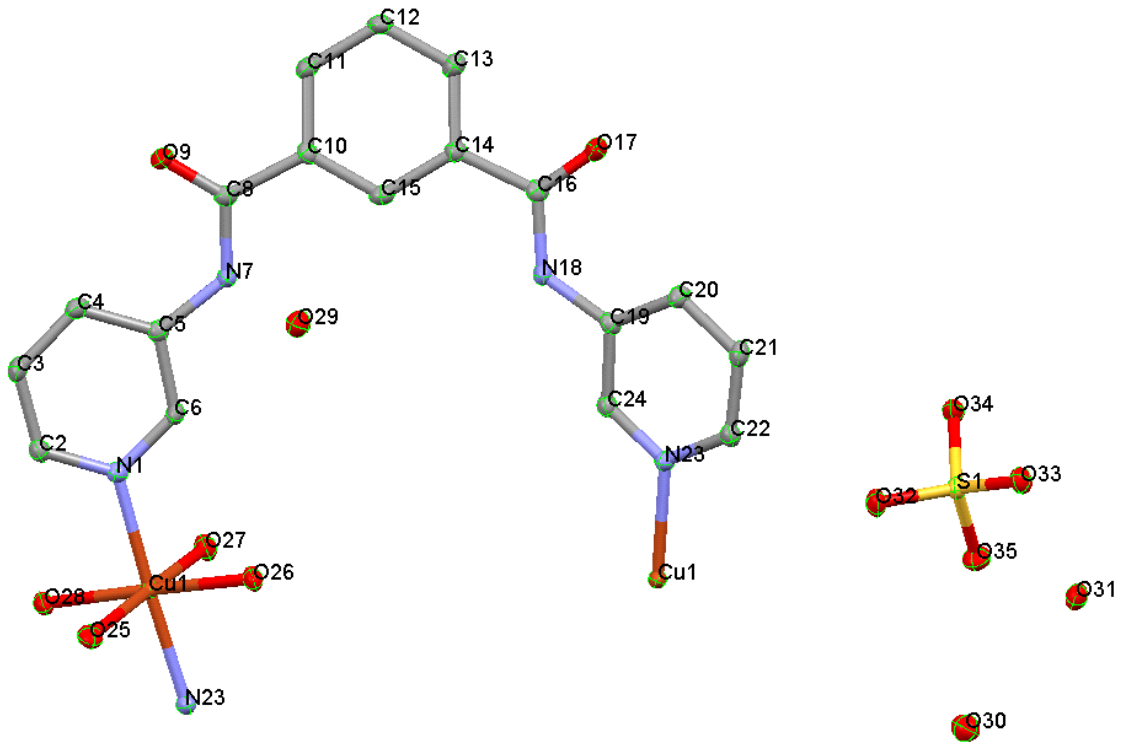


* 1-x, 2-y, 2-z

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(53)	0.86	1.95	2.768(6)	157.6	x, y+1, z
N(18)–H(18)•••O(51)	0.86	1.99	2.780(5)	153.1	x, y+1, z
N(31)–H(31)•••O(52)	0.86	2.07	2.918(5)	170.7	x, y, z
N(42)–H(42)•••O(52)	0.86	2.11	2.955(5)	165.8	x, y, z
O(49)–H(49A)•••O(55)	0.801(11)	2.025(19)	2.025(19)	164(6)	-x+1, -y+1, -z+2
O(50)–H(50B)•••O(9)	0.801(11)	1.976(15)	2.768(5)	170(5)	-x+1, -y+2, -z+1
O(49)–H(49B)•••O(55)	0.798(11)	2.00(2)	2.765(6)	162(5)	x, y+1, z
O(52)•••O(56)			2.656(6)		x, 1+y, z
O(52)•••O(54)			2.732(6)		x, -1+y, z
O(54)•••O(55)			2.781(6)		1-x, 2-y, 2-z
O(17)•••O(54)			2.822(5)		x, y, z

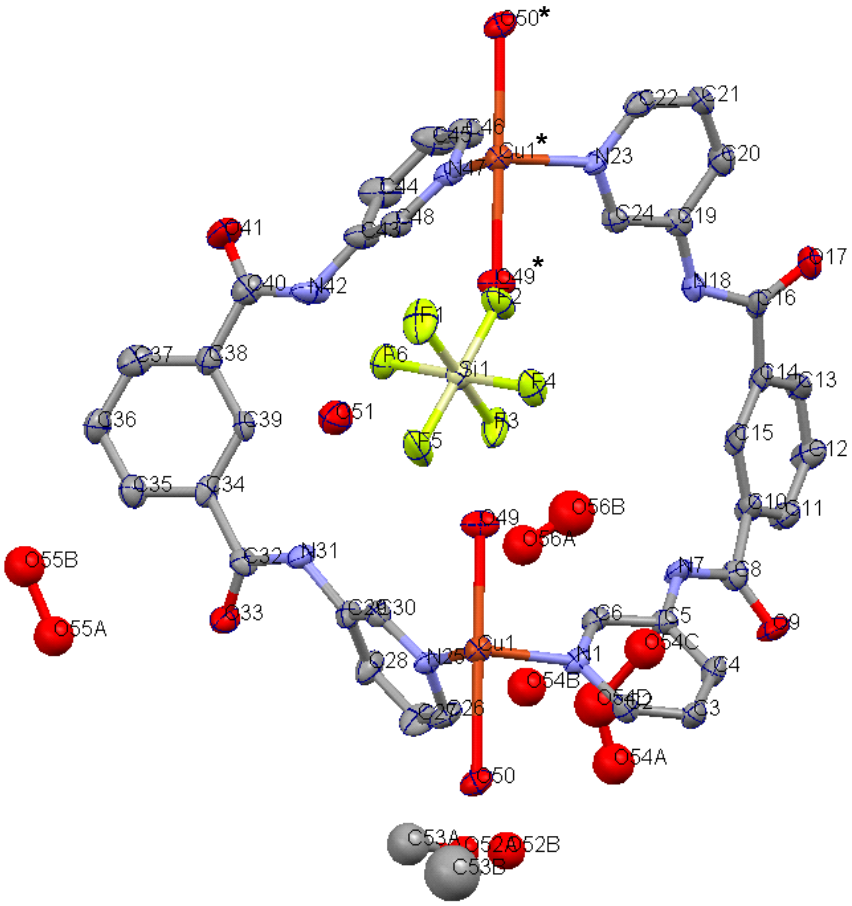
Molecular Plot of 1b



Hydrogen bonding parameters of 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(35)	0.86	2.49	3.315(2)	161.4	x, y, z
N(18)–H(18)•••O(35)	0.86	2.25	3.095(2)	168.9	x, y, z
O(25)–H(25A)•••O(33)	0.81(3)	1.93(3)	2.723(2)	169(3)	-x, 1/2+y, 1/2-z
O(25)–H(25B)•••O(9)	0.80(3)	1.99(3)	2.783(2)	179(2)	-x, 1-y, 1-z
O(26)–H(26A)•••O(29)	0.78(3)	1.86(3)	2.626(2)	170(3)	-1+x, y, z
O(26)–H(26B)•••O(34)	0.70(3)	2.01(3)	2.701(2)	172(3)	x, y, z
O(27)–H(27A)•••O(25)	0.78(3)	2.27(3)	3.039(3)	171(3)	1+x, y, z
O(27)–H(27B)•••O(32)	0.80(3)	1.93(3)	2.726(2)	169(2)	x, y, z
O(28)–H(28A)•••O(34)	0.81(3)	1.90(3)	2.712(2)	176(3)	-x, 1/2+y, 1/2-z
O(28)–H(28B)•••O(31)	0.73(3)	1.95(3)	2.677(2)	175(3)	1-x, 1/2+y, 1/2-z
O(29)–H(29A)•••O(32)	0.81(3)	1.92(3)	2.722(2)	171(2)	x, y, z
O(29)–H(29B)•••O(30)	0.74(3)	2.04(3)	2.781(3)	174(3)	x, y, z
O(30)–H(30A)•••O(35)	0.83(3)	1.95(3)	2.770(3)	171(3)	1+x, y, z
O(30)–H(30B)•••O(31)	0.78(3)	2.04(3)	2.806(3)	170(3)	x, y, z
O(31)–H(31A)•••O(17)	0.74(3)	2.01(3)	2.743(2)	169(3)	1-x, -y, 1-z
O(31)–H(31B)•••O(33)	0.84(3)	1.83(3)	2.651(2)	168(3)	x, y, z

Molecular Plot of 2

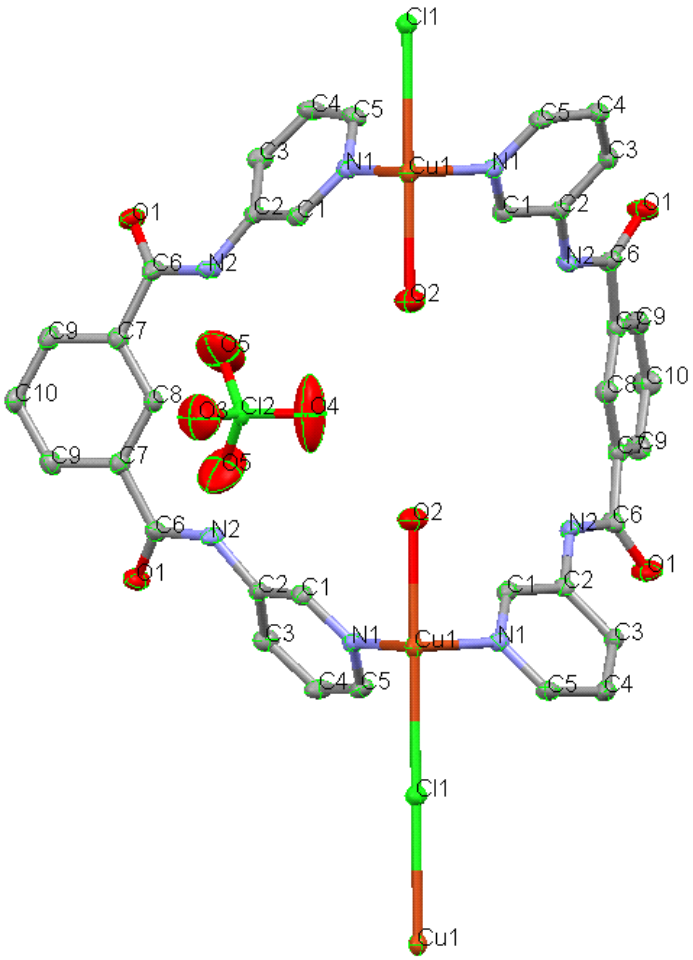


* 1-x, 2-y, 2-z

Hydrogen bonding parameters of 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)•••F(6)	0.86	2.11	2.903(7)	153.5	x, 1+y, z
N(7)–H(7)•••F(1)	0.86	2.37	3.104(7)	142.9	x, 1+y, z
N(18)–H(18)•••F(5)	0.86	2.02	2.831(7)	157.9	x, 1+y, z
N(31)–H(31)•••O(51)	0.86	2.10	2.961(8)	174.7	x, y, z
N(42)–H(42)•••O(51)	0.86	2.12	2.969(8)	167.8	x, y, z
O(49)–H(49A)•••F(3)	0.798(11)	1.862(15)	2.656(7)	173(7)	1-x, 1-y, 2-z
O(49)–H(49B)•••F(2)	0.797(11)	1.99(3)	2.739(7)	155(7)	x, 1+y, z
O(50)–H(50A)•••O(52A)	0.800(11)	1.99(3)	2.754(11)	161(8)	x, y, z
O(50)–H(50B)•••O(9)	0.798(11)	1.983(17)	2.775(7)	171(8)	1-x, 2-y, 1-z
O(51)•••O(55A)			2.687(14)		x, y, 1+z
O(51)•••O(55B)			2.576(15)		x, y, 1+z
O(56A)•••O(54B)			2.624(18)		x, y, z
O(56A)•••O(54C)			2.82(2)		x, y, z
O(33)•••O(54B)			2.727(15)		-x, 1-y, 1-z
O(51)•••F(3)			2.783(7)		x, -1+y, z
O(56A)•••F(1)			2.737(13)		x, -1+y, z
O(56B)•••F(1)			2.651(17)		x, -1+y, z
O(49)•••F(3)			2.657(7)		1-x, 1-y, 2-z
O(55A)•••F(6)			2.616(13)		1-x, 1-y, 1-z
O(55B)•••F(6)			2.802(13)		1-x, 1-y, 1-z

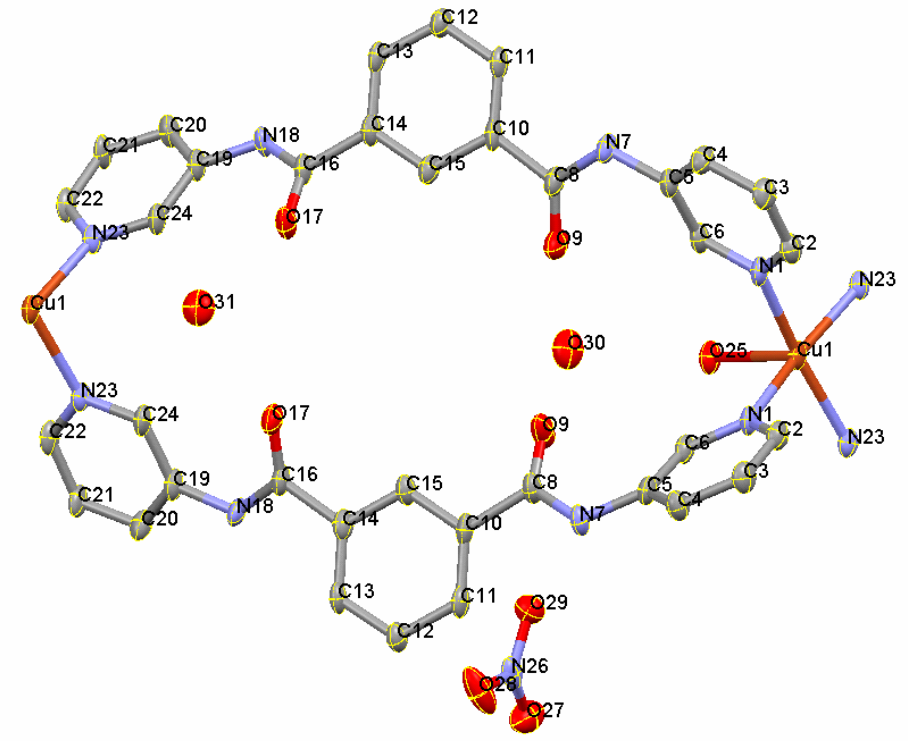
Molecular Plot of 3



Hydrogen bonding parameters of 3

D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(2)–H(1N)•••O(5)	0.76(5)	2.36(5)	3.030(7)	148(5)	x, y, z
O(2)–H(2O)•••O(4)	0.88(8)	2.10(9)	2.978(8)	175(15)	x, y, z

Molecular plot of 4a

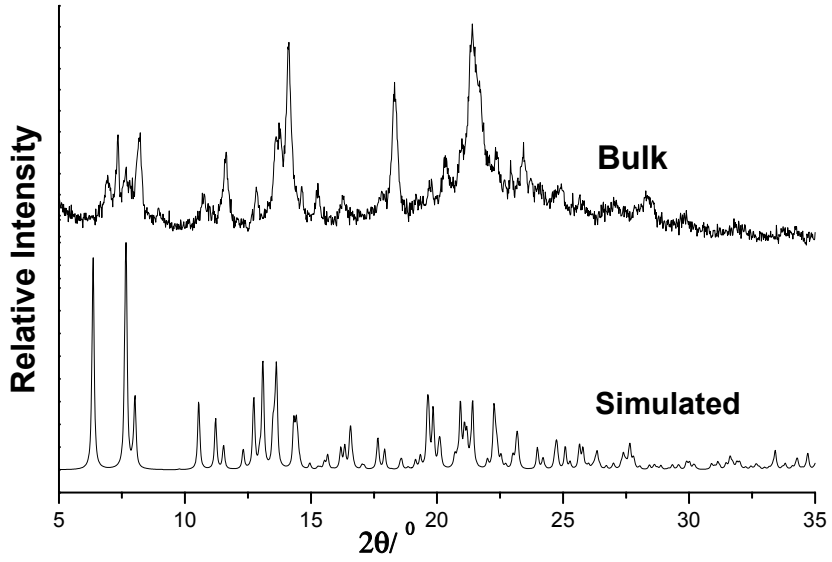


Hydrogen bonding parameters of 4a

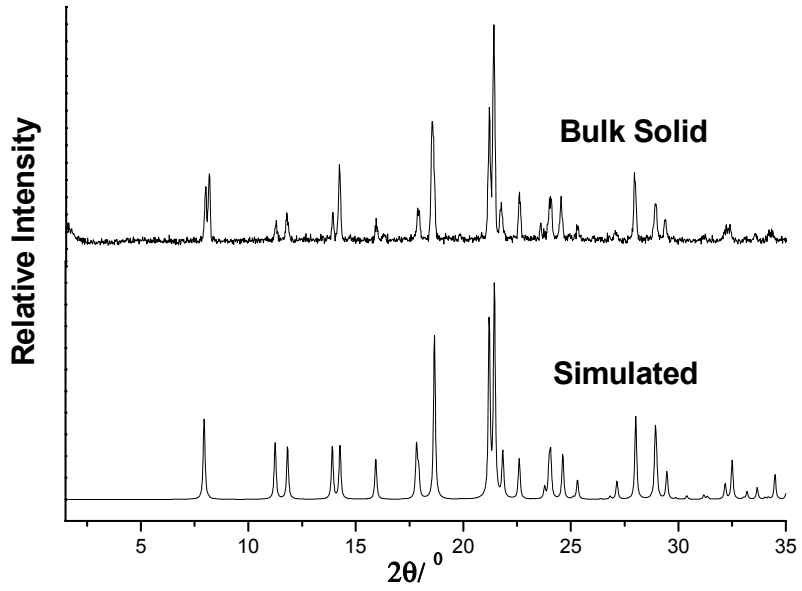
D–H•••A	D–H (Å)	H•••A (Å)	D•••A (Å)	D–H•••A (^{0})	Symmetry operation for A
N(7)–H(7)•••O(29)	0.86	2.05	2.801(5)	145.3	x, y, z
N(18)–H(18)•••O(29)	0.86	2.07	2.870(5)	154.9	x, y, -1+z
O(17)•••O(31)			2.790(7)		1/2+x, 1/2-y, 1+z
O(25)•••O(31)			2.723(10)		-1/2+x, 1/2-y, z
O(31)•••O(17)			2.790(7)		-1/2+x, 1/2-y, -1+z
O(30)•••O(9)			2.704(7)		x, y, z
O(25)•••O(30)			2.691(8)		x, 1-y, z

X-ray Powder Diffraction (XRPD) – Simulated and Bulk solid comparison plot

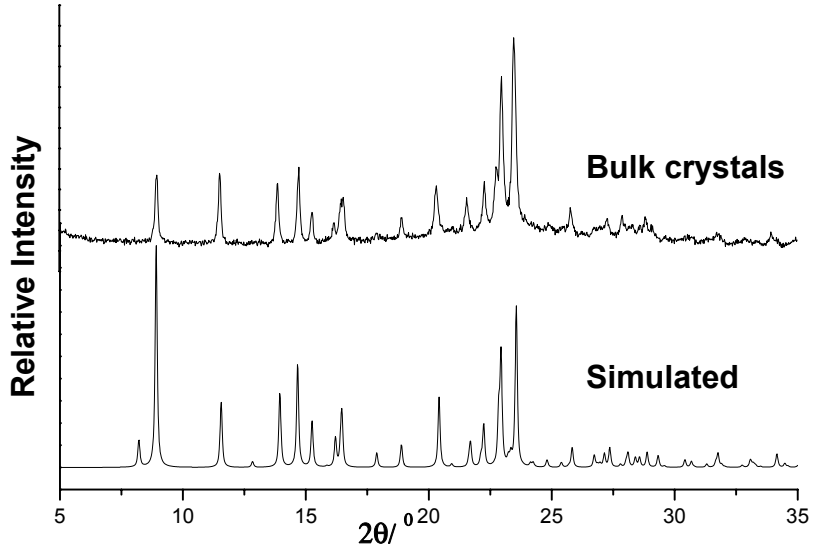
Compound 2



Compound 3



Compound 4a



TGA of Compound 1a, 2 and 4a

Compound 1a

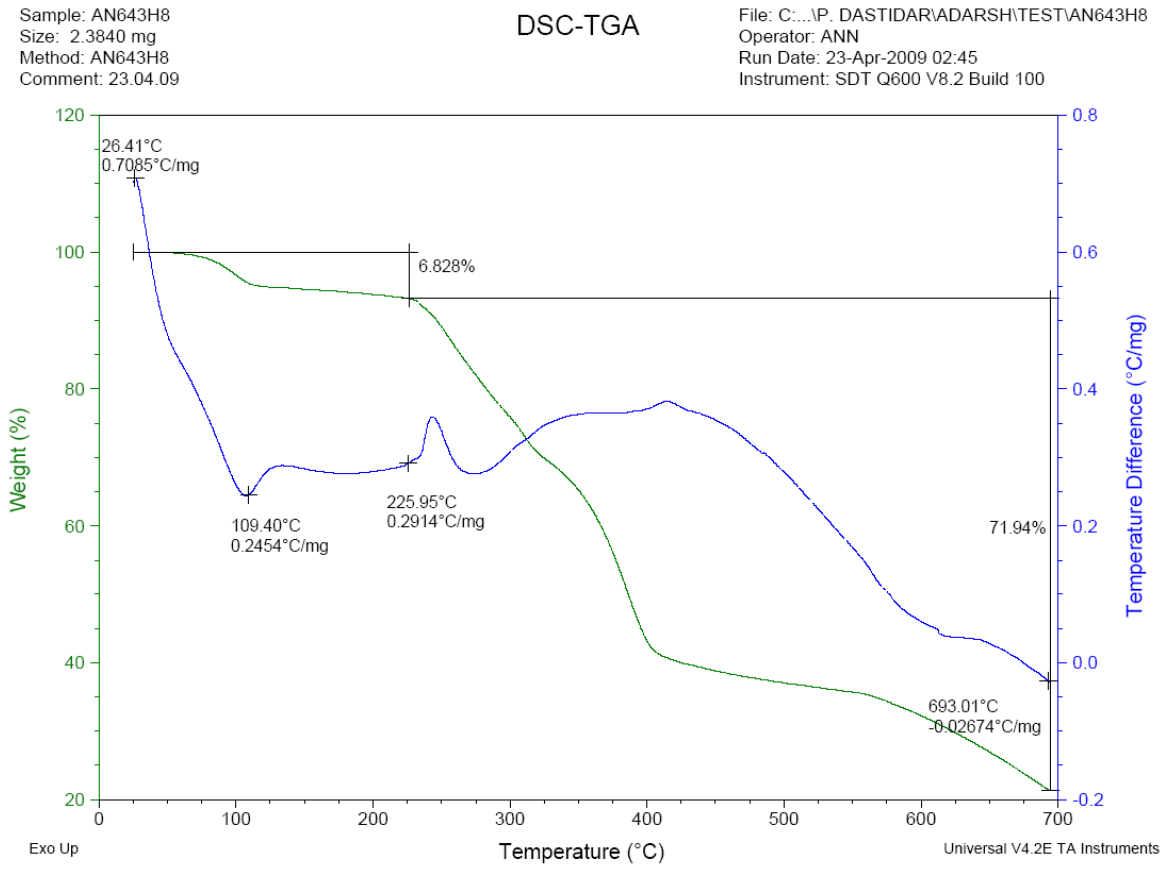


Figure S1

Unit cell contents = 4 Ligand + 2 $CuSO_4$+ 18 H_2O
[(4 solvated H_2O + 4 coordinated H_2O) + ~ 10 H_2O (97 electron SQEEZE result)]

Triclinic *P-1* spacegroup, Z = 2

Therefore FW = Unit cell contents/Z
= 2 Ligand + $CuSO_4$ + 9 H_2O [(2 solvated H_2O + 2 coordinated H_2O) + ~ 5 H_2O (48.5 electron SQEEZE result)]

= 958 g

Weight loss for 9 H_2O = 9 X 18/958 X 100 = 17 % (experimental 9.05 %)

Compound 2

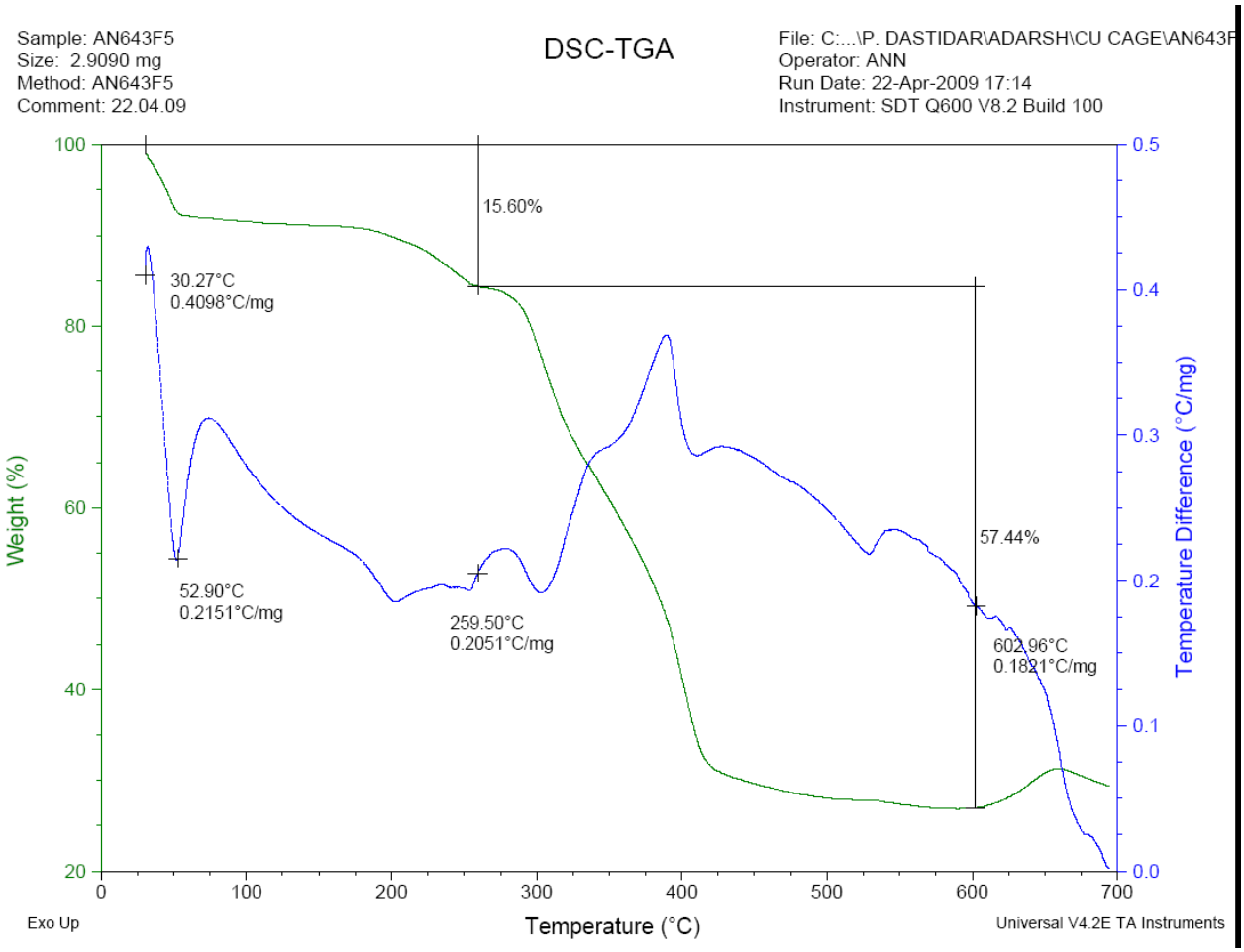


Figure S2

Unit cell contents = 4 Ligand + 2 $CuSiF_6$ + 12 H_2O
[(8 solvated + 4 coordinated)] + 2 MeOH

Triclinic *P-1* spacegroup, Z = 2

Therefore FW = Unitcell contents/Z

= 2 Ligand + $CuSiF_6$ + 6 H_2O + 1 MeOH

= 982.4 g

Weight loss for 6 H_2O + 1 MeOH = 140.13/982.4 X 100

= 14.26 % (experimental 15.6 %)

Compound 4a

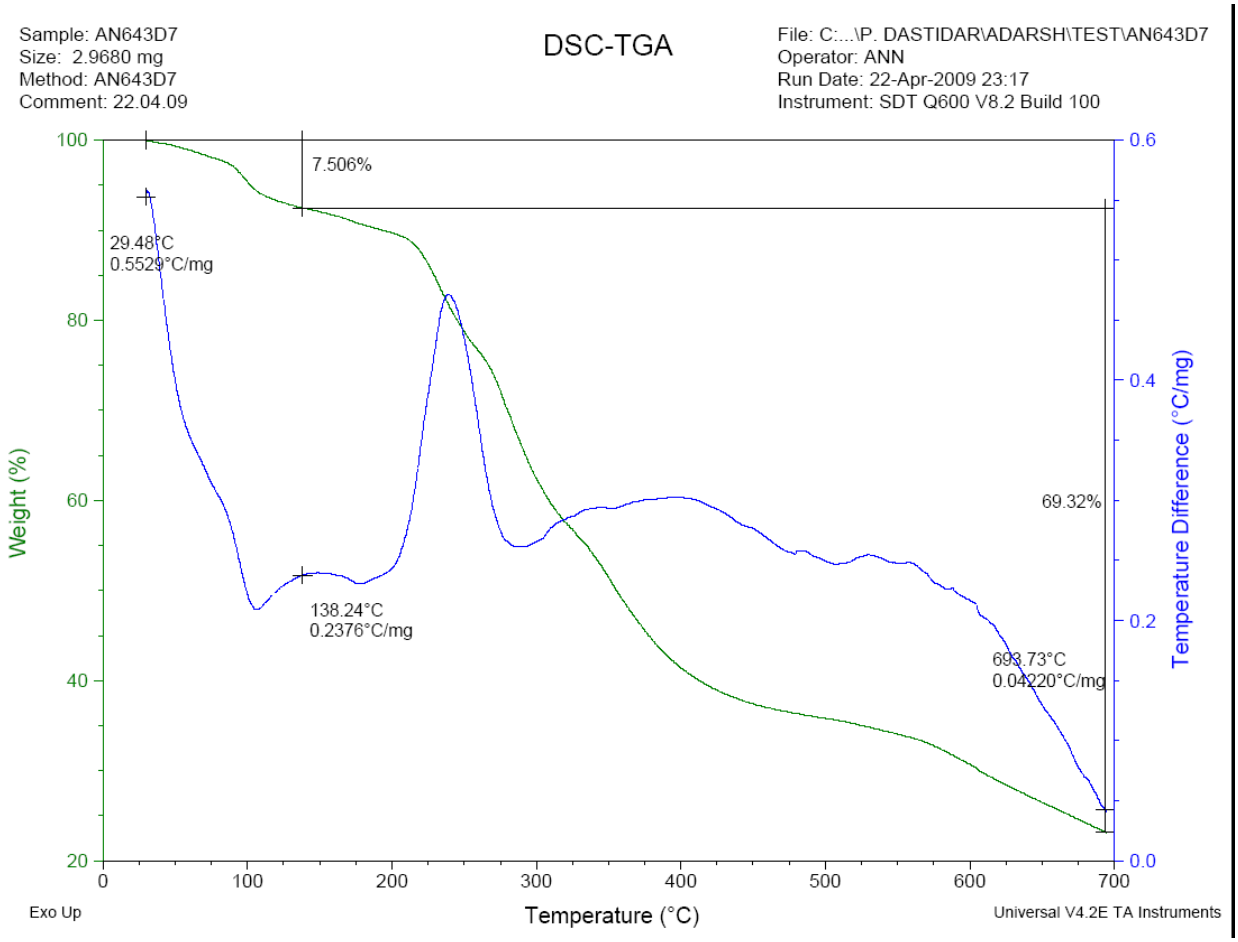


Figure S3

Unit cell contents = 4 Ligand + 2 $Cu(NO_3)_2$+ 12 H_2O
[(4 solvated H_2O + 2 coordinated H_2O) + ~ 6 H_2O
(54 electron SQEEZE result)]

Monoclinic *Cm* spacegroup, Z = 2

Therefore FW = Unitcell contents/Z = 2 Ligand + $Cu(NO_3)_2$+ 6 H_2O
[(2 solvated H_2O + 1 coordinated H_2O) + 3 H_2O (27
electron SQEEZE result)]
= 932.3 g

Weight loss for 6 H_2O = 6 X 18/932.3 X 100
= 11.6 % (experimental 7.5 %)

Anion binding property

Condition 1: To a 10 ml aqueous ethanolic solution of $CuSO_4.5H_2O$ (16 mg, 0.064 mmol), a methanolic solution of **L1** (40mg, 0.126 mmol) was layered carefully and kept undisturbed. After three days, deep blue colored crystals, pale green colored crystals and pale blue colored precipitate were harvested separately. Both the crystals and the powder were washed with water and then with methanol and characterized by Elemental analysis, X-ray powder diffraction (XRPD) and FT-IR.
Yield: 20 mg, 15 % (deep blue colored crystals); 30 mg (pale blue powder)

Condition 2: To an aqueous ethanolic solution (10 ml) containing $CuSO_4.5H_2O$ (16 mg, 0.064 mmol), $NaClO_4$ (8mg, 0.064 mmol) and $NaNO_3$ (5.5 mg, 0.064 mmol), a methanolic solution of **L1** (40mg, 0.126 mml) was layered carefully and kept undisturbed. After three days, deep blue colored crystals and pale blue colored precipitate, thus obtained, were harvested separately and washed with water and then with methanol, and characterized by elemental analysis, X-ray powder diffraction (XRPD) and FT-IR.
Yield: 20 mg, 15 % (deep blue colored crystals); 30 mg (pale blue powder)

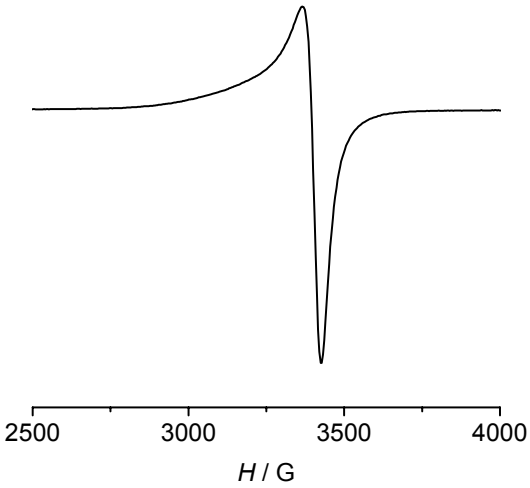
Condition 3: To an aqueous ethanolic solution (10 ml) containing $Cu(ClO_4)_2.6H_2O$ (23 mg, 0.064 mmol), Na_2SO_4 (9 mg, 0.064 mmol) and $NaNO_3$ (5.5 mg, 0.064 mmol), a methanolic solution of **L1** (40 mg, 0.126 mmol) was layered carefully and kept undisturbed. After three days, deep blue colored crystals and pale blue colored precipitate were harvested separately, washed with water and then with methanol, and characterized by elemental analysis, X-ray powder diffraction (XRPD) and FT-IR.
Yield: 20 mg, 15 % (deep blue colored crystals); 30 mg (pale blue powder)

Condition 4: To an aqueous ethanolic solution (10 ml) containing $Cu(NO_3)_2.3H_2O$ (15 mg, 0.062 mmol), Na_2SO_4 (9 mg, 0.064 mmol) and $NaClO_4$ (8 mg, 0.064 mmol), a methanolic solution of **L1** (40 mg, 0.126 mmol) was layered carefully and kept undisturbed. After three days, deep blue colored crystals and pale blue colored precipitate were harvested separately, washed with water and then with methanol and characterized by elemental analysis, X-ray powder diffraction (XRPD) and FT-IR.
Yield: 20 mg, 15 % (deep blue colored crystals); 30 mg (pale blue powder)

FT-IR (KBr pellet) (Table S1)

Various crystallization condition	**Characteristic IR frequencies for Deep blue colored crystals (KBr pellet cm^{-1})**	**Characteristic IR frequencies for Pale blue colored powder (KBr pellet cm^{-1})**	**Characteristic IR frequencies for Pale blue colored crystals (KBr pellet cm^{-1})**
Compound 1a/1b crystallization (non competitive condition)	3248 (w, water ν O-H), 3188 (m, amide ν N-H), 3076 (m, aromatic ν C-H), 1674 (s, amide ν C=O),	3390 (w, water ν O-H), 3281 (m, amide ν N-H), 3076 (m, aromatic ν C-H), 1672 (s, amide ν C=O),	3334 (s, water O-H stretch), 3097 (s, amide N-H stretch), 2925 (s, aromatic C-H stretch), 1670 (s, amide C=O stretch),
Condition 1	1614 (s, amide δ N-H), 1101 (s, SO_4^{2-} ν_{asymm} S-O), 918 (w, SO_4^{2-} ν_{symm} S-O), 617 (m, SO_4^{2-} δ O-S-O) cm^{-1}	1620 (s, amide δ N-H), 1111 (sb, SO_4^{2-} ν_{asymm} S-O), 964 (s, SO_4^{2-} ν_{symm} S-O), 615 (m, SO_4^{2-} δ O-S-O) cm^{-1}	1616 (s, amide N-H bend) 1103 (sb, SO_4^{2-} ν_{asymm} S-O), 962 (s, SO_4^{2-} ν_{symm} S-O), 619 (m, SO_4^{2-} δ O-S-O) cm^{-1}
Condition 2	3250 (w, water ν O-H), 3188 (m, amide ν N-H), 3074 (m, aromatic ν C-H), 1672 (s, amide ν C=O), 1612 (s, amide δ N-H), 1103 (s, SO_4^{2-} ν_{asymm} S-O), 920 (w, SO_4^{2-} ν_{symm} S-O), 617 (m, SO_4^{2-} δ O-S-O) cm^{-1}	3398 (w, water ν O-H), 3284 (m, amide ν N-H), 3076 (m, aromatic ν C-H), 1672 (s, amide ν C=O), 1620 (s, amide δ N-H), 1116 (s, SO_4^{2-} ν_{asymm} S-O), 964 (s, SO_4^{2-} ν_{symm} S-O), 617 (m, SO_4^{2-} δ O-S-O) cm^{-1}	
Condition 3	3250 (w, water ν O-H), 3188 (m, amide ν N-H), 3074 (m, aromatic ν C-H), 1676 (s, amide ν C=O), 1614 (s, amide δ N-H), 1103 (s, SO_4^{2-} ν_{asymm} S-O), 918 (m, SO_4^{2-} ν_{symm} S-O) 617 (s, SO_4^{2-} δ O-S-O) cm^{-1}	3390 (w, water ν O-H), 3284 (m, amide ν N-H), 3076 (m, aromatic ν C-H), 1672 (s, amide ν C=O), 1620 (s, amide δ N-H), 1116 (s, SO_4^{2-} ν_{asymm} S-O), 964 (s, SO_4^{2-} ν_{symm} S-O), 615 (m, SO_4^{2-} δ O-S-O) cm^{-1}	
Condition 4	3246 (w, water ν O-H), 3198 (m, amide ν N-H), 3072 (m, aromatic ν C-H), 1676 (s, amide ν C=O), 1614 (s, amide δ N-H), 1103 (s, SO_4^{2-} ν_{asymm} S-O), 918 (w, SO_4^{2-} ν_{symm} S-O), 617 (m, SO_4^{2-} δ O-S-O) cm^{-1}	3390 (w, water ν O-H), 3288 (m, amide ν N-H), 3086 (m, aromatic ν C-H), 1678 (s, amide ν C=O), 1618 (s, amide δ N-H), 1116 (s, SO_4^{2-} ν_{asymm} S-O), 964 (s, SO_4^{2-} ν_{symm} S-O), 617 (m, SO_4^{2-} δ O-S-O) cm^{-1}	

EPR spectra for compound 3



$g_{par} = 2.17$; $g_{perp} = 2.06$; $g_{average} = 2.10$

Figure S4