Electronic Supplementary Material (ESI) for CrystEngComm.
This journal is © The Royal Society of Chemistry 2014

Electroactive Tetrathiafulvalene Based Pyridine-mono and -bis(1,2,3-triazoles) Click Ligands: Synthesis, Crystal Structures and Coordination Chemistry

Thomas Biet and Narcis Avarvari*

SUPPORTING INFORMATION

X-Ray structures of the ligands

Compound **2**

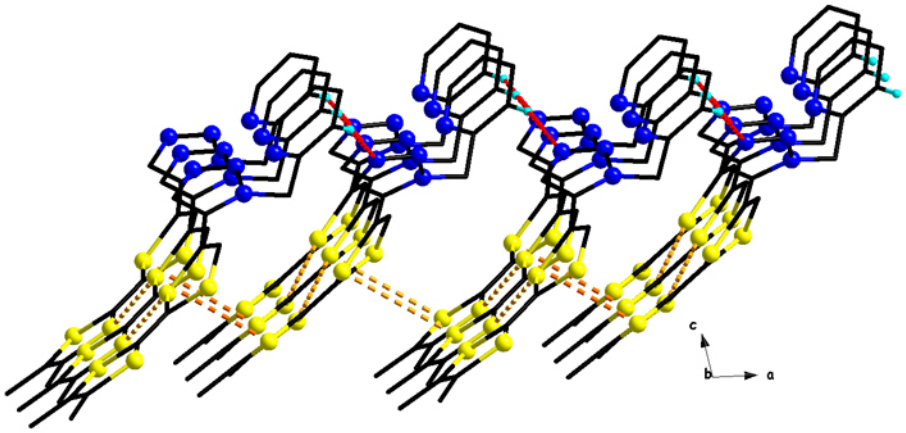


Figure S1. Packing diagram for **2** in the *ac* plane with S···S and N···H intermolecular contacts. S2···S1 3.90 Å and S2···S3 3.94 Å; N3···H13 2.67 Å.

Table S1. Selected lengths (Å) and angles (º) for **2**

Distances (Å)		Torsion Angle (º) (calc)		Dihedral Angle between two planes(º) (calc)
C(3)-C(4)	1.337(5)	C(6)-C(5)-C(7)-C(8)	42.72	S(2)-C(4)-S(4)-C(5)-C(6) & C(7)-N(3)-N(1)-N(2)-C(8) 41.12
S-C int.	1.763(4)	C(6)-C(5)-C(7)-N(1)	45.75	
C(1)-C(2)	1.325(5)			
C(5)-C(6)	1.3335)			
C(7)-C(8)	1.366(5)			
C(.)-N_{trz}(.)	1.355(5)			
N(1)-N(2)	1.351(4)			
N(2)-N(3)	1.319(5)			

Intermolecular contacts: S2-S3: 3.94 Å; S2-S1: 3.90 Å; N3-H13: 2.67 Å.

Compound **3**

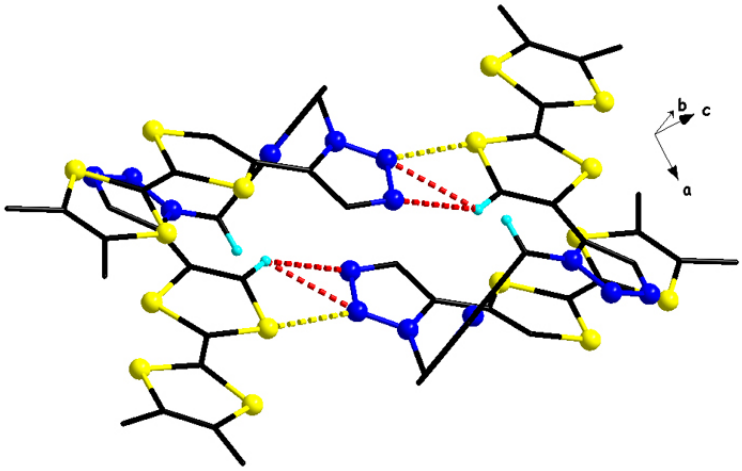


Figure S2. Packing diagram for **3** with N···S and N···H intermolecular contacts. S2···S4 3.24 Å; N2···H6 2.68 Å and N3···H6 2.60 Å.

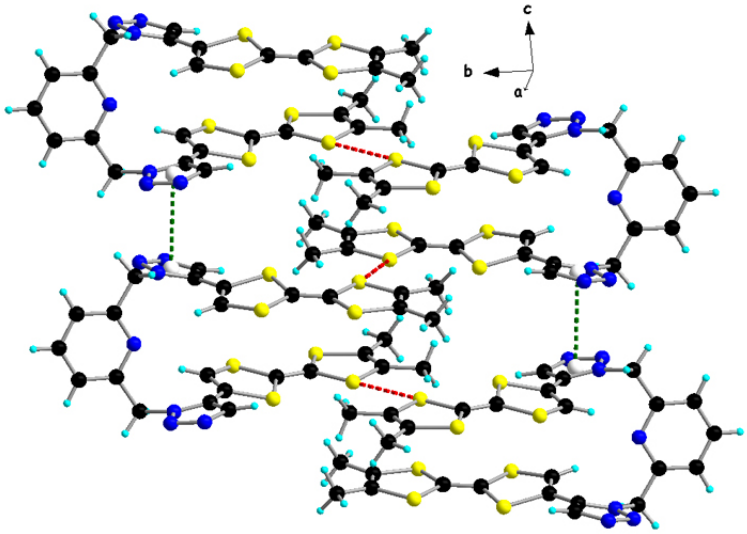


Figure S3. Packing diagram for **3** with S···S and triazole···triazole intermolecular contacts. S1···S1 3.59 Å; trz···trz 3.59 Å.

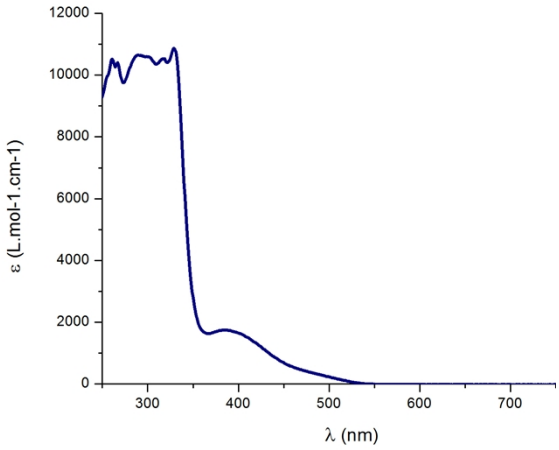
Table S2. Selected lengths (Å) and angles (º) for **3**

Distances (Å)		Torsion Angle (º) (calc)		Dihedral Angle between two planes(º) (calc)
C(3)-C(4)	1.351(6)	C(6)-C(5)-C(7)-C(8)	18.39	S(3)-C(4)-S(4)-C(5)-C(6) & C(7)-N(3)-N(1)-N(2)-C(8) 20.18
S-C int.	1.754(4)	C(6)-C(5)-C(7)-N(1)	22.25	
C(1)-C(2)	1.334(6)			
C(5)-C(6)	1.334(5)			
C(7)-C(8)	1.366(6)			
C(.)-N_{trz}(.)	1.351(6)			
N(1)-N(2)	1.349(5)			
N(2)-N(3)	1.316(5)			

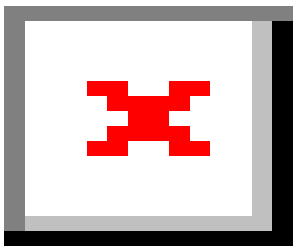
Intermolecular contacts: S1-S1: 3.59 Å; N2-S4: 3.24 Å; N2-H6: 2.68 Å; N3-H6 : 2.60 Å.

UV-Vis spectra of CH_2Cl_2 solutions

2 (10^{-4} M)



3 (10^{-4} M)



4 (10^{-4} M)

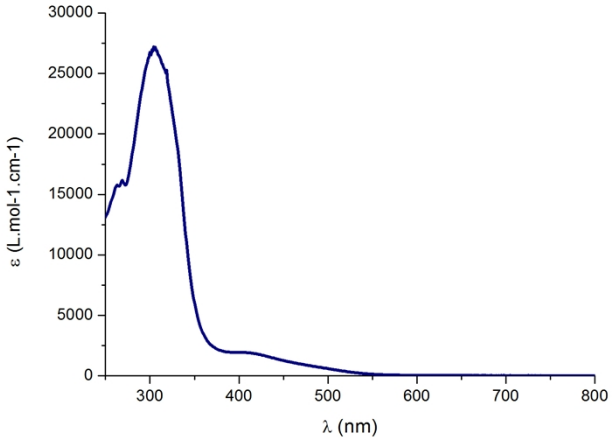


Figure S4. UV-Vis spectra.

Table S3. UV-Vis data.

compound	λ_{max} (nm)	ε (L.mol^{-1}.cm^{-1})
2	386	1759
3	397	3480
4	405	1980

Electrochemical studies. Cyclic voltammetry measurements were performed using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/Ag^+ pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a 0.1 $mol.L^{-1}$ solution of $(n\text{-}Bu)_4NPF_6$ in CH_2Cl_2. All experiments have been performed at room temperature at 0.1 $V \cdot s^{-1}$. Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.

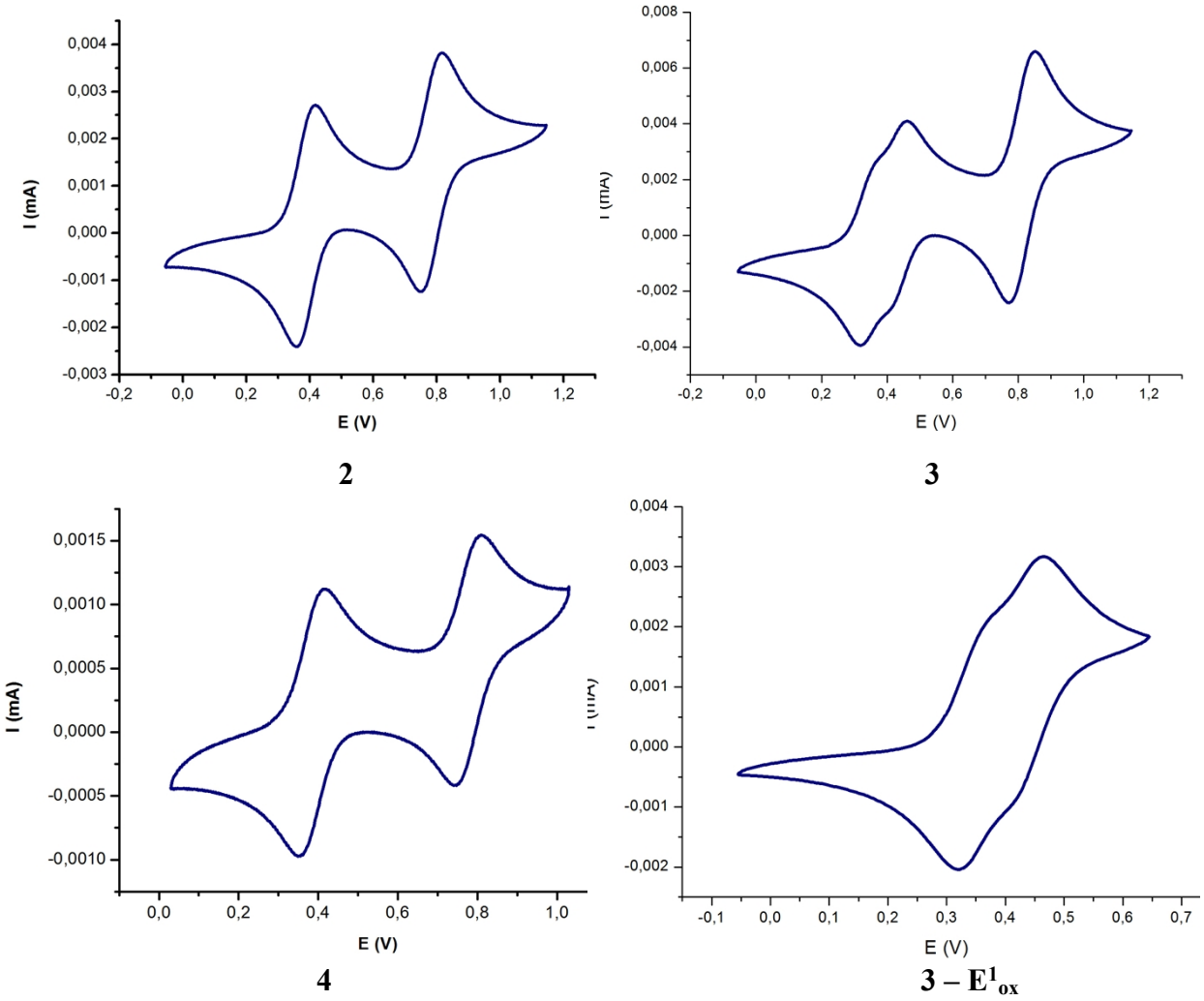


Figure S5. Cyclic voltammograms.

Table S4. Oxidation potentials from cyclic voltammetry data. Measurements have been performed in CH_2Cl_2 in the presence of $(n\text{-}Bu_4N)PF_6$ (0.1 M) at a scan rate of 0.1 $V \cdot s^{-1}$.

compound	$E^1_{1/2}$ (V)	$E^2_{1/2}$ (V)
2	0.38	0.78
3	0.34 + 0.44	0.81
4	0.38	0.78

X-Ray structures of the complexes

Complex **4**

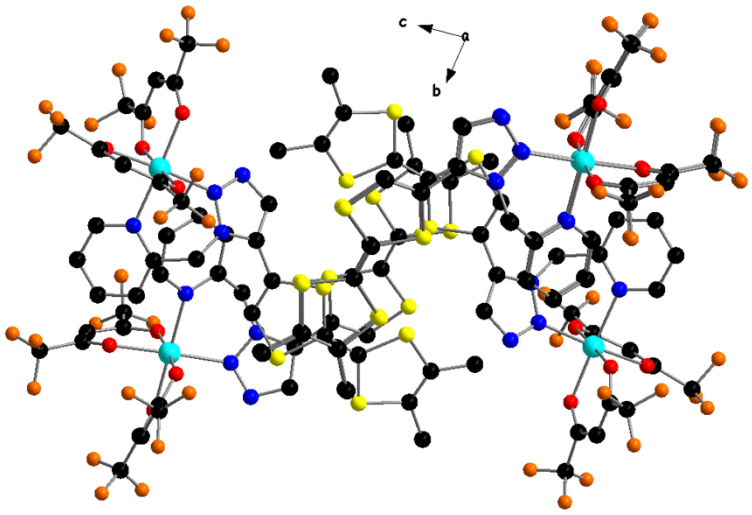


Figure S6. Packing diagram for **4**.

Table S5. Selected lengths (Å) and angles (º) for **4**.

Distances (Å) *s-cis*/*s-trans*		Angles (º) (calc)	
C(3)-C(4) / C(31)-C(32)	1.349(13) / 1.346(12)	O3—Co1—O4	88.2(3)
C(7)-N(1) / C(35)-N(5)	1.376(11) / 1.352(10)	O2—Co1—N2	91.9(3)
C(8)-N(3) / C(36)-N(7)	1.344(12) / 1.356(12)	O4—Co1—N4	93.6(3)
N(3)-N(2) / N(7)-N(6)	1.330(1) / 1.317(10)	N2—Co1—N4	88.4(3)
N(2)-N(1) / N(6)-N(5)	1.333(10) / 1.360(1)	O4—Co1—N2	178.0(3)
		O8—Co2—O6	87.7(3)
$Co(1)-N_{moy}$ / $Co(2)-N_{moy}$	2.149(8) / 2.160(8)	O6—Co2—N8	91.5(3)
$Co(1)-O_{moy}$ / $Co(2)-O_{moy}$	2.068(7) / 2.061(7)	O8—Co2—N6	95.1(3)
		N6—Co2—N8	85.9(3)
		O6—Co2—N6	175.3(3)

Torsion Angle (º) (calc)		Dihedral Angle between two planes(º) (calc)
C(6)-C(5)-C(7)-C(8)	30.34	S(3)-C(4)-S(4)-C(5)-C(6) & C(7)-N(3)-N(1)-N(2)-C(8) 36.55
C(6)-C(5)-C(7)-N(1)	26.83	
C(33)-C(34)-C(35)-C(36)	51.85	
C(33)-C(34)-C(35)-N(5)	46.13	S(5)-C(32)-S(6)-C(33)-C(34) & C(35)-N(5)-N(6)-N(7)-C(36) 48.37

Complex **5**

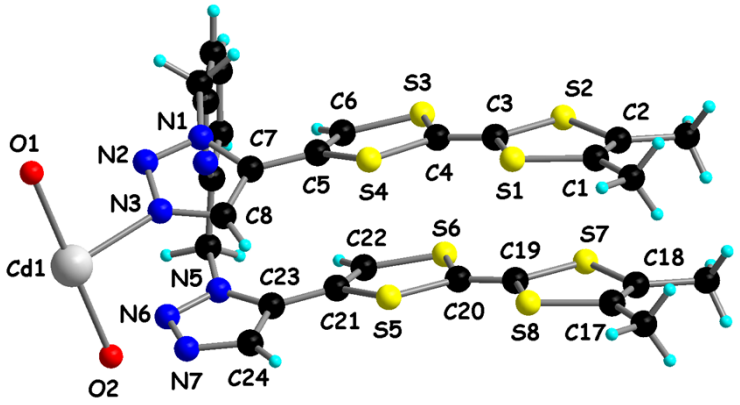


Figure S7. Molecular structure for **5**.

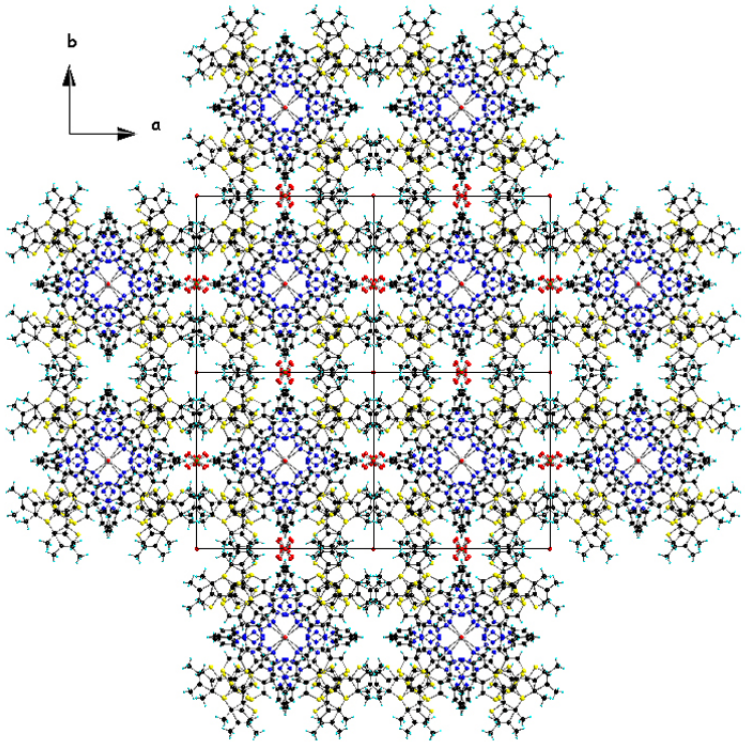


Figure S8. Packing diagram for **5**.

Table S6. Selected lengths (Å) and angles (°) for **5**

Distances (Å)			
"Coordinated triazole moiety"		"Free triazole moiety"	
C(3)-C(4)	1.334(8)	C(19)-C(20)	1.318(9)
S-C int.	1.760(6)	S-C int.	1.764(7)
C(1)-C(2)	1.309(10)	C(17)-C(18)	1.299(12)
C(5)-C(6)	1.341(8)	C(21)-C(22)	1.337(8)
C(7)-C(8)	1.373(7)	C(23)-C(24)	1.358(8)

C(.)-N_{trz}(.)	1.338(7)	C(.)-N_{trz}(.)	1.350(9)
N(1)-N(2)	1.337(6)	N(5)-N(6)	1.349(7)
N(2)-N(3)	1.331(6)	N(6)-N(7)	1.290(9)

Distances (Å)		Angles (º) (calc)	
Cd(1)-O(1)	2.328(8)	O1—Cd1—O2	180.0(3)
Cd(1)-O(2)	2.267(9)	O2—Cd1—N3	89.4(15)
Cd(1)-N(3)	2.330(4)	O1—Cd1—N3	90.6(15)

Torsion Angle (º) (calc)		Dihedral Angle between two planes(º) (calc)
C(6)-C(5)-C(7)-C(8)	37.02	S(3)-C(4)-S(4)-C(5)-C(6) & C(7)-N(3)-N(1)-N(2)-C(8) 37.93
C(6)-C(5)-C(7)-N(1)	39.31	
C(22)-C(21)-C(23)-C(24)	21.04	
C(22)-C(21)-C(23)-N(5)	19.64	S(5)-C(20)-S(6)-C(21)-C(22) & C(23)-N(5)-N(6)-N(7)-C(24) 19.27

Intermolecular contacts: N5-H11B: 2.58 Å; N6-H11B: 2.84 Å.
Intramolecular contacts: N7-O2: 3.09 Å.

Complex **6**

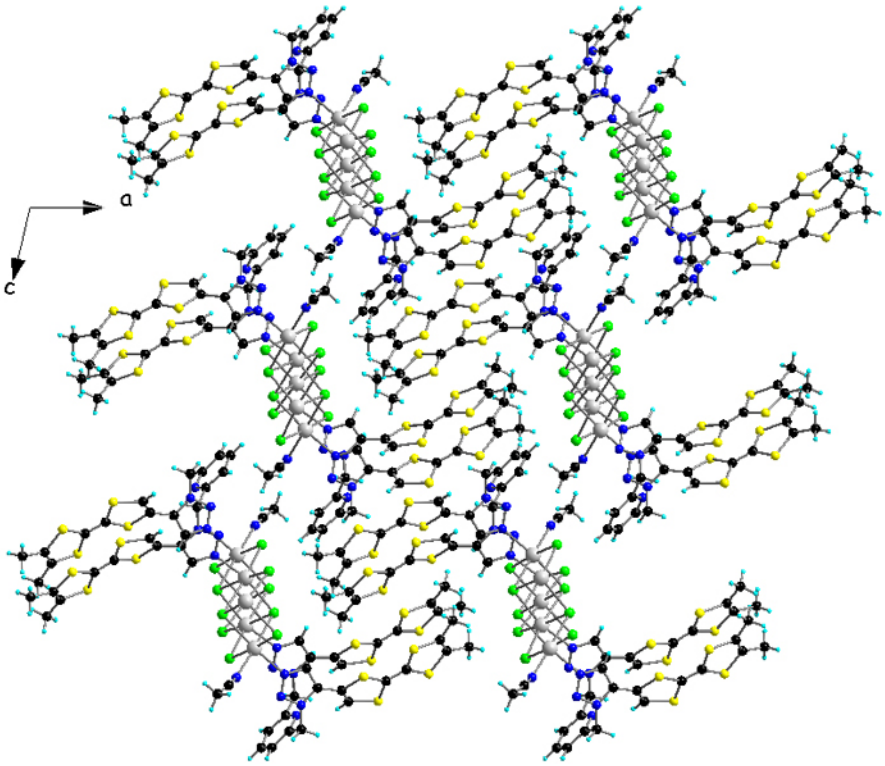


Figure S9. Packing diagram for **6**.

Table S7. Selected lengths (Å) and angles (º) for **6**

Distances (Å)			
C(3)-C(4)	1.337(6)	C(19)-C(20)	1.331(5)
S-C int.	1.757(5)	S-C int.	1.761(5)
C(1)-C(2)	1.327(7)	C(17)-C(18)	1.336(8)
C(5)-C(6)	1.344(6)	C(21)-C(22)	1.346(6)
C(7)-C(8)	1.378(6)	C(23)-C(24)	1.373(6)
C(.)-N_{trz}(.)	1.349(6)	C(.)-N_{trz}(.)	1.355(6)
N(1)-N(2)	1.350(5)	N(5)-N(6)	1.341(5)
N(2)-N(3)	1.323(5)	N(6)-N(7)	1.315 (5)

Distances (Å)		Angles (º) (calc)	
Cd(1)-N(3)	2.379(4)	N3—Cd1—N8	92.5(17)
Cd(1)-O(2)	2.384(5)	N3—Cd1—Cl3	92.8(9)
Cd(3)-N(7)	2.323(4)	N8—Cd1—Cl3	88.0(14)
Cd(1)-$Cl_{min/max}$	2.523(12) / 2.781(11)	N3—Cd1—Cl2	89.6(10)
Cd(2)-$Cl_{min/max}$	2.610(11) / 2.712(12)	N8—Cd1—Cl4	94.2(15)
Cd(3)-$Cl_{min/max}$	2.537(12) / 2.828(11)	$N7^{i}$—Cd3—$Cl2^{i}$	87.92(9)
		$N7^{i}$—Cd3—$Cl1^{i}$	93.7(10)

(i) -x, 1-y, -z

Torsion Angle (º) (calc)		Dihedral Angle between two planes(º) (calc)
C(6)-C(5)-C(7)-C(8)	44.29	S(3)-C(4)-S(4)-C(5)-C(6) & C(7)-N(3)-N(1)-N(2)-C(8) 42.62
C(6)-C(5)-C(7)-N(1)	45.89	
C(22)-C(21)-C(23)-C(24)	37.54	
C(22)-C(21)-C(23)-N(5)	34.16	S(5)-C(20)-S(6)-C(21)-C(22) &

	C(23)-N(5)-N(6)-N(7)-C(24) 32.11

Intermolecular contacts: N6-H29B: 2.96 Å; S2-S8: 3.96 Å; S4-S6: 3.76 Å.