Electronic Supplementary Material (ESI) for *CrystEngComm*

Robust Hydrogen Bonding Synthon in One-dimensional and Two-dimensional Coordination Polymers of Pyridine Appended Reverse Amides and Amides

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Supporting information

Synthesis of coordination polymers, elemental analysis TGA and crystallographic parameters

{Cu $(2a)_2$ $(SCN)_2$]·2·di-iodobenzene} (3a)

65.2mg (2mmol) of **1a** & 1,4-Di-iodobenzene (330mg 5mmol) dissolved in 3ml DMF and to it was added a methanolic solution of $Cu(SCN)_2$, formed by addition of a MeOH (0.5 mL) solution of $Cu(NO_3)_2$ (24.16 mg, 1mmol) to a MeOH (0.5 mL) solution of NaSCN (16.21mg, 2mmol). After a week green color crystals were formed.

Yield: 62% Anal.Calcd. for $C_{50}H_{52}N_{10}O_4S_2I_4Cu$ C, 40.22%; H, 3.49%; N, 9.39%; Found: C, 40.85%; H, 3.64%; N, 9.74%.

Similar procedure was adopted for the synthesis of complexes **3d, 4a-b**.

{Cu $(2a)_2$ $(SCN)_2$]·2·phenanthrene} (3d): Yield: 65% Anal.Calcd. for $C_{66}H_{64}N_{10}O_4S_2Cu$ C, 66.69%; H, 5.38%; N, 11.79%; Found: C, 67.30%; H, 5.33%; N, 11.95%.

{Cu $(1a)_2$ $(SCN)_2$]·2·di-bromobenzene} (4a): Yield: 46% Anal.Calcd. for $C_{50}H_{52}N_{10}O_4S_2Br_4Cu$ C, 48.40 %; H, 4.19 %; N, 11.29 %; Found: C, 48.07 %; H, 4.62 %; N, 10.94 %.

{Cu $(1a)_2$ $(SCN)_2$]·2·phenanthrene} (4b): Yield: 44% Anal.Calcd. for $C_{66}H_{64}N_{10}O_4S_2Cu$ C,66.69 %; H, 5.38 %; N, 11.79 %; Found: C, 66.68 %; H, 5.31 %; N, 12.08 %.

Good quality crystals of **3b** & **3c** were obtained by dissolving complex **3d** with di-bromobenzene or pyrene guest molecules.

{Cu $(2a)_2$ $(SCN)_2$]·2·di-bromobenzene} (3b): Yield: 52% Anal.Calcd. for $C_{50}H_{52}N_{10}O_4S_2Br_4Cu$ C, 48.40 %; H, 4.19 %; N 11.29, %; Found: C, 47.95 %; H, 3.78 %; N, 10.69 %.

{Cu $(2a)_2$ $(SCN)_2$]·2·pyrene} (3c): Yield: 43% Anal.Calcd. for $C_{70}H_{68}N_{10}O_4S_2Cu$ C, 67.98%; H, 5.18%; N, 11.33%; Found: C, 68.13 %; H, 5.24 %; N, 11.62 %.

For complex **5** layering technique applied in which metal in methanol layered over the mixture of DMF-Benzonitrile solution.

{$(Cu(2b)_2(SCN)_2)$.2·benzonitrile} (5): Yield: 33% Anal.Calcd. for $C_{66}H_{64}N_{10}O_4S_2Cu$ C, 61.08%; H, 3.72%; N, 16.44%; Found: C, 60.42%; H, 3.53%; N, 16.31%.

Crystal data for **3a**: Triclinic, P-1, a = 9.008(4)Å, b = 10.139(5)Å, c = 16.671(8)Å, α= 92.822(15)°, β= 104.167(15)°, γ = 109.238(14)°, V = 1379.7(11)$Å^3$, Z = 1 , Dc = 1.796 g cm^{-3}, 4446 reflections out of 9735 unique reflections with $I > 2\sigma(I)$, $1.27<\theta<25°$, final R-factors R_1 = 0.0539, wR_2 =0.1694. Yield: 62% Elemental analysis**:** Anal.Calcd. for $C_{50}H_{52}N_{10}O_4S_2I_4Cu$ C, 40.22%; H, 3.49%; N, 9.39%; Found: C, 40.85%; H, 3.64%; N, 9.74%.CCDC-720551

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Crystal data for **3b**: Triclinic, P-1, a = 9.1064(12)Å, b = 10.0279(12)Å, c = 16.012(2)Å , α= 94.197(4)°, *β*= 102.983(4)°,γ = 108.093(4)°, V = 1338.1(3)Å^3, Z = 1, Dc = 1.619 g cm^{-3}, 5184 reflections out of 16657 unique reflections with I > 2σ(I), 2.16< θ<26°, final R-factors R_1 = 0.0654, wR_2 =0.1358. Yield: 52% Elemental analysis: Anal.Calcd. for $C_{50}H_{52}N_{10}O_4S_2Br_4Cu$ C, 48.40 %; H, 4.19 %; N 11.29, %; Found: C, 47.95 %; H, 3.78 %; N, 10.69 %.CCDC.720552

Crystal data for **3c**: Monoclinic, $P2_1/n$, a = 10.1435(4)Å, b = 14.9724(7)Å,c = 20.3506(9)Å, *β*= 101.111(10)°, V = 3032.8(2)Å^3 , Z = 6, Dc = 1.355 g cm^{-3}, 6054 reflections out of 38303 unique reflections with I > 2σ(I), 1.70< θ<26.17°, final R-factors R_1 = 0.0448, wR_2 = 0.1338. Yield: 43% Elemental analysis: Anal.Calcd. for $C_{70}H_{68}N_{10}O_4S_2Cu$ C, 67.98%; H, 5.18%; N, 11.33%; Found: C, 68.13 %; H, 5.24 %; N, 11.62 %.CCDC.720553

Crystal data for **3d**: Monoclinic, $P2_1/n$, a = 9.9865(14)Å, b = 14.840(2)Å, c= 20.416(3), *β*= 100.363(4)°, V = 2976.4(7)Å^3, Z =2 , Dc = 1.322g cm^{-3}, 5838 reflections out of 37212 unique reflections with I > 2σ(I), 1.71< θ<26°, final R-factors R_1 =0.0436, wR_2 =0.1242. Yield: 65% Elemental analysis: Anal.Calcd. for $C_{66}H_{64}N_{10}O_4S_2Cu$ C, 66.69%; H, 5.38%; N, 11.79%; Found: C, 67.30%; H, 5.33%; N, 11.95%.CCDC.720554

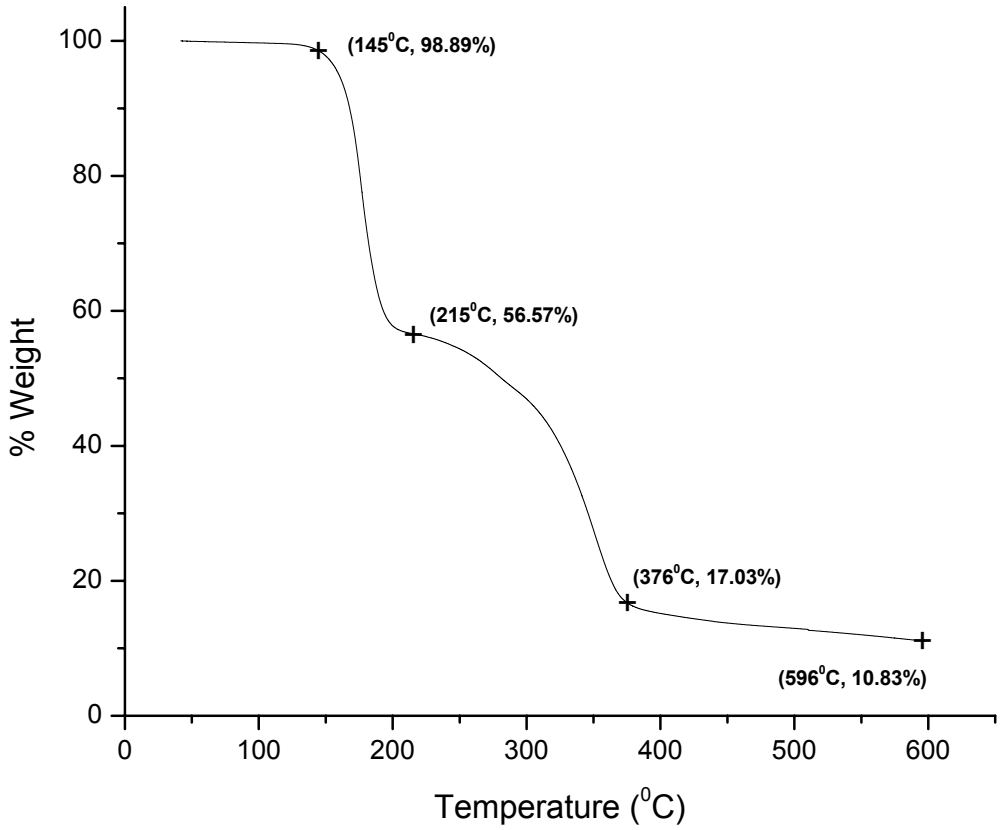
Crystal data for **4a**: Triclinic, P-1, a = 9.210(6)Å, b = 10.155(7)Å , c = 15.921(11)Å, α= 93.77(2)°, *β*= 104.08(2)°, γ = 109.20(2)°, V = 1346.6(16)Å^3 , Z = 2, Dc = 1.608g cm^{-3}, 5224reflections out of 17079 unique reflections with I > 2σ(I), 1.34< θ<25.99°, final R-factors R_1 = 0.0515, wR_2 = 0.1333. Yield: 46% Elemental analysis: Anal.Calcd. for $C_{50}H_{52}N_{10}O_4S_2Br_4Cu$ C, 48.40 %; H, 4.19 %; N, 11.29 %; Found: C, 48.07 %; H, 4.62 %; N, 10.94 %.CCDC.720555

Crystal data for **4b**: Monoclinic, $P2_1/n$, a = 10.1605(10)Å, b = 15.0606(15)Å, c= 20.010(2)Å, *β*= 100.338(3)°, V = 3012.4(5)Å^3, Z = 6, Dc = 1.306 g cm^{-3}, 5918 reflections out of 37053 unique reflections with I > 2σ(I), 1.70< θ<26°, final R-factors R_1 = 0.0618, wR_2 =0.1507. Yield: 44% Elemental analysis: Anal.Calcd. for $C_{66}H_{64}N_{10}O_4S_2Cu$ C,66.69 %; H, 5.38 %; N, 11.79 %; Found: C, 66.68 %; H, 5.31 %; N, 12.08 %.CCDC.720556

Crystal data for **5**: Triclinic, P-1, a = 8.1942(7)Å, b = 10.0010(9)Å, c= 14.8220(13)Å, α= 75.664(3)°, *β*= 85.553(3)°, γ = 85.294(3)°, V = 1170.81(18)Å^3, Z= 1, Dc = 1.450 g cm^{-3}, 4555 reflections out of 14887 unique reflections with I > 2σ(I), 1.42< θ<26°, final R-factors R_1 = 0.0441, wR_2 =0.1016. Yield: 33% Elemental analysis: Anal.Calcd. for $C_{66}H_{64}N_{10}O_4S_2Cu$ C, 61.08%; ,3.72%;N,16.44%; Found: C, 60.42%; H, 3.53%; N, 16.31%. CCDC.720557

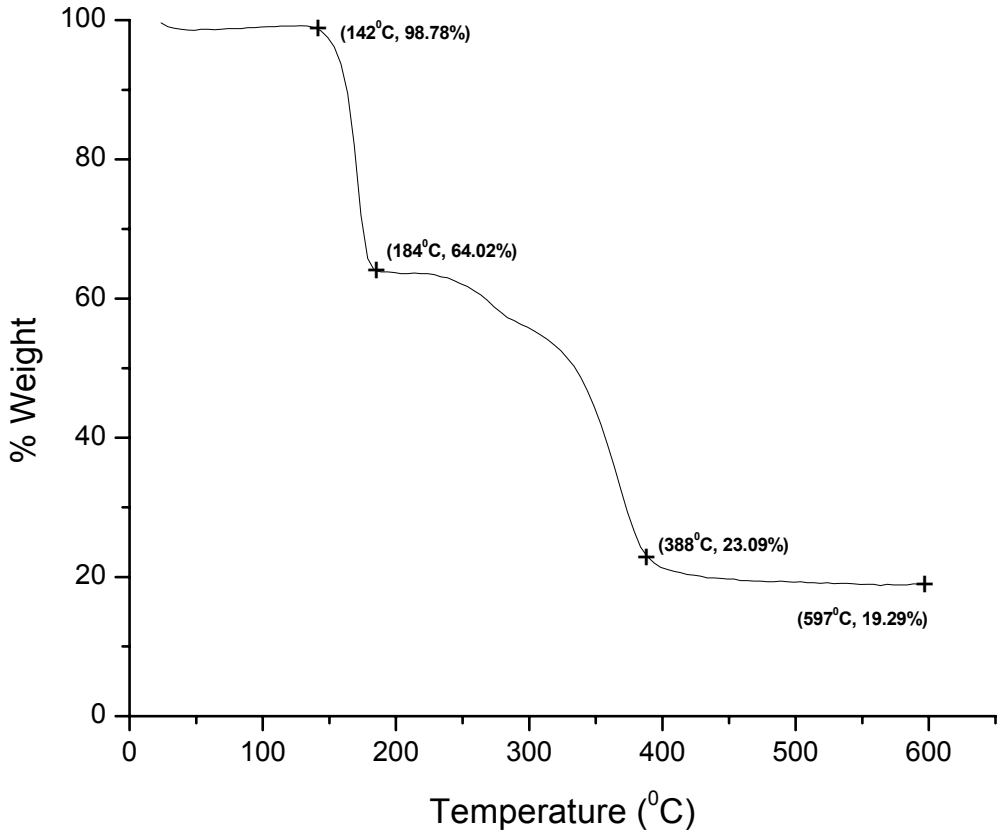
TGA Study:

Complex (3a): {[Cu(**2a**)$_2$(SCN)$_2$]·2·di-iodobenzene}



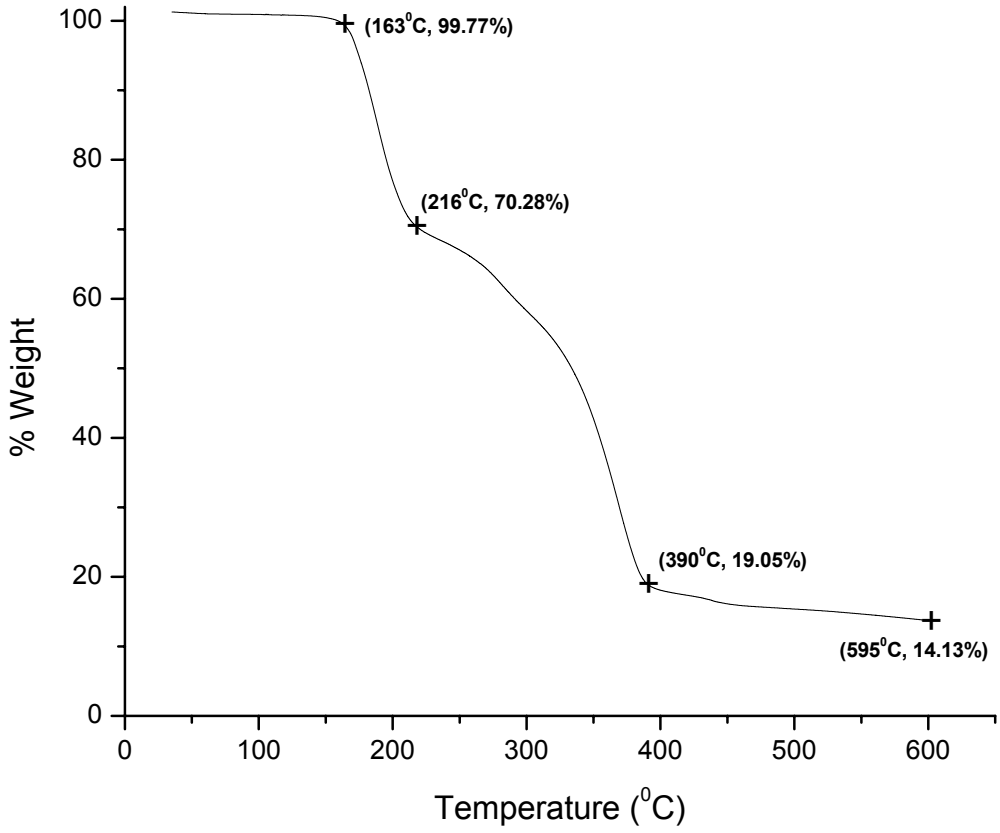
At 215˚C 43.43% weight loss corresponds to loss of two 1,4-di-iodobenzene molecules (Cal: 44.24%) whereas from 215˚C onwards ligand degradation starts.

Complex (3b): {[Cu(**2a**)$_2$(SCN)$_2$]·2·di-bromobenzene}



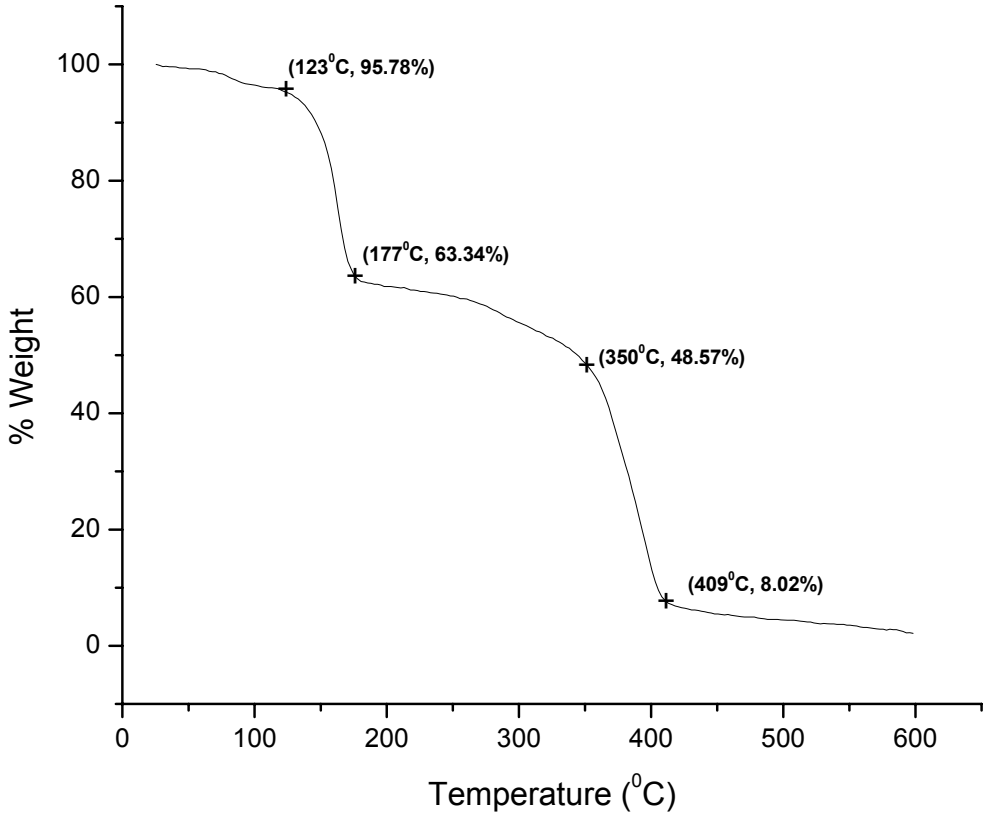
At 184˚C 35.98% weight loss corresponds to loss of two 1,4-dibromobenzene molecules (Cal: 38.04%) whereas from 184˚C onwards ligand degradation starts.
Suberic Acid+3-Ampy-CuSCN-BR

Complex (3d): {[Cu(**2a**)$_2$(SCN)$_2$]·2·phenanthrene}



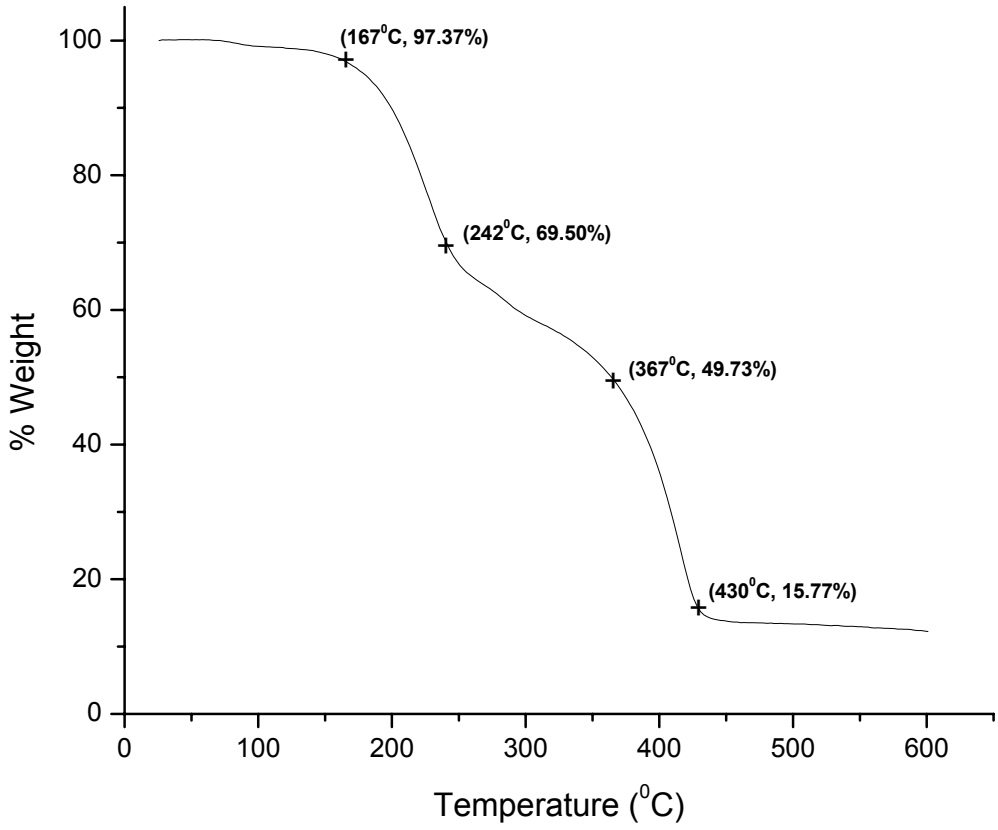
At 216˚C 29.72% weight loss corresponds to loss of two phenanthrene molecules (Cal: 29.98%) whereas from 216˚C onwards ligand degradation starts.

Complex (4a): {[Cu(**1a**)$_2$(SCN)$_2$]·2·di-bromobenzene}



At 177˚C 36.66% weight loss corresponds to loss of two 1,4-di-bromobenzene molecules (Cal: 36.11%) whereas from 177˚C onwards ligand degradation starts.

Complex (4b): {[Cu(**1a**)$_2$(SCN)$_2$]·2·phenanthrene}



At 242˚C 30.50% weight loss corresponds to loss of two phenanthrene molecules (Cal: 29.98%) whereas from 242˚C onwards ligand degradation starts.

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Table 1. Crystal data and structure refinement for (**3a**).

Identification code	3a	
Empirical formula	C50 H52 Cu I4 N10 O4 S2	
Formula weight	1492.28	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.008(4) Å	α= 92.822(15)°.
	b = 10.139(5) Å	β= 104.167(15)°.
	c = 16.671(8) Å	γ = 109.238(14)°.
Volume	1379.7(11) $Å^3$	
Z	1	
Density (calculated)	1.796 gm/cm^3	
Absorption coefficient	2.761 mm^{-1}	
F(000)	727	
Crystal size	0.15 x 0.12 x 0.08 mm^3	
Theta range for data collection	1.27 to 25.00°.	
Index ranges	-10<=h<=7, -11<=k<=12, -19<=l<=15	
Reflections collected	9735	
Independent reflections	4446 [R(int) = 0.0452]	
Completeness to theta = 25.00°	91.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.802 and 0.679	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4446 / 0 / 322	
Goodness-of-fit on F^2	0.784	
Final R indices [I>2sigma(I)]	R1 = 0.0539, wR2 = 0.1694	
R indices (all data)	R1 = 0.1001, wR2 = 0.2020	
Largest diff. peak and hole	0.882 and -1.242 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (3a). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	0	0	41(1)
I(1)	4258(1)	1980(1)	4567(1)	63(1)
I(2)	10002(1)	5443(1)	8304(1)	112(1)
S(100)	784(4)	310(4)	2880(2)	78(1)
N(100)	-200(9)	-88(7)	1157(4)	47(2)
C(100)	206(10)	72(8)	1873(5)	39(2)
N(11)	1687(8)	2037(6)	390(4)	36(2)
N(21)	5203(9)	4041(6)	2136(4)	47(2)
N(31)	17768(9)	10987(7)	9625(4)	43(2)
O(21)	6112(8)	6435(6)	2327(4)	65(2)
O(28)	14283(8)	8629(6)	7537(4)	61(2)
C(11)	4021(11)	3782(8)	1366(5)	42(2)
C(12)	2854(10)	2426(7)	1112(5)	34(2)
C(13)	1626(12)	3009(9)	-114(6)	52(3)
C(14)	2714(14)	4363(10)	96(7)	76(4)
C(15)	3939(14)	4755(10)	821(6)	73(4)
N(22)	14324(9)	10835(7)	7841(4)	45(2)
C(21)	6193(11)	5354(8)	2572(5)	40(2)
C(22)	7374(12)	5303(9)	3378(6)	54(3)
C(23)	8331(12)	6749(9)	3887(6)	53(3)
C(24)	9508(11)	6685(8)	4707(5)	48(2)
C(25)	10526(12)	8138(9)	5209(6)	54(3)
C(26)	11671(11)	8124(8)	6020(5)	40(2)
C(27)	12792(11)	9579(9)	6461(5)	48(2)
C(28)	13841(11)	9602(9)	7327(5)	45(2)
C(31)	15342(10)	11105(7)	8666(5)	38(2)
C(32)	16790(10)	10837(8)	8846(5)	36(2)
C(33)	17253(12)	11459(8)	10253(5)	48(2)
C(34)	15891(12)	11819(8)	10132(6)	49(2)
C(35)	14891(12)	11612(9)	9325(6)	53(2)
C(41)	5991(12)	2993(9)	5710(6)	52(2)

C(42)	6313(14)	4396(10)	5946(6)	66(3)
C(43)	7494(14)	5099(10)	6682(7)	70(3)
C(44)	8249(13)	4351(11)	7198(6)	63(3)
C(45)	7959(14)	2947(11)	6956(7)	68(3)
C(46)	6794(14)	2254(10)	6208(6)	66(3)

Table 3. Bond lengths [Å] and angles [°] for (**3a**).

Cu(1)-N(100)#1	1.984(7)	C(27)-C(28)	1.514(11)
Cu(1)-N(100)	1.984(7)	C(31)-C(32)	1.383(11)
Cu(1)-N(11)	2.077(6)	C(31)-C(35)	1.392(12)
Cu(1)-N(11)#1	2.077(6)	C(33)-C(34)	1.363(13)
I(1)-C(41)	2.103(10)	C(34)-C(35)	1.385(12)
I(2)-C(44)	2.084(10)	C(41)-C(46)	1.379(13)
S(100)-C(100)	1.611(9)	C(41)-C(42)	1.371(12)
N(100)-C(100)	1.146(10)	C(42)-C(43)	1.386(14)
N(11)-C(13)	1.332(10)	C(43)-C(44)	1.376(13)
N(11)-C(12)	1.330(9)	C(44)-C(45)	1.380(14)
N(21)-C(21)	1.379(10)	C(45)-C(46)	1.391(14)
N(21)-C(11)	1.401(10)		
N(31)-C(32)	1.348(10)	N(100)#1-Cu(1)-N(100)	180.0(5)
N(31)-C(33)	1.369(11)	N(100)#1-Cu(1)-N(11)	91.1(3)
O(21)-C(21)	1.206(9)	N(100)-Cu(1)-N(11)	88.9(3)
O(28)-C(28)	1.216(10)	N(100)#1-Cu(1)-N(11)#1	88.9(3)
C(11)-C(15)	1.382(11)	N(100)-Cu(1)-N(11)#1	91.1(3)
C(11)-C(12)	1.396(11)	N(11)-Cu(1)-N(11)#1	180.0
C(13)-C(14)	1.366(13)	C(100)-N(100)-Cu(1)	158.3(8)
C(14)-C(15)	1.358(13)	N(100)-C(100)-S(100)	179.6(9)
N(22)-C(28)	1.357(10)	C(13)-N(11)-C(12)	117.8(7)
N(22)-C(31)	1.409(10)	C(13)-N(11)-Cu(1)	118.6(6)
C(21)-C(22)	1.511(11)	C(12)-N(11)-Cu(1)	123.7(5)
C(22)-C(23)	1.517(13)	C(21)-N(21)-C(11)	125.6(6)
C(23)-C(24)	1.530(11)	C(32)-N(31)-C(33)	115.3(7)
C(24)-C(25)	1.524(12)	C(15)-C(11)-C(12)	116.8(7)
C(25)-C(26)	1.490(11)	C(15)-C(11)-N(21)	125.2(8)
C(26)-C(27)	1.511(12)	C(12)-C(11)-N(21)	118.0(7)

N(11)-C(12)-C(11)	123.9(7)	C(32)-C(31)-C(35)	118.2(7)
N(11)-C(13)-C(14)	121.7(8)	C(32)-C(31)-N(22)	121.1(7)
C(15)-C(14)-C(13)	120.8(8)	C(35)-C(31)-N(22)	120.7(8)
C(14)-C(15)-C(11)	119.0(9)	N(31)-C(32)-C(31)	124.2(8)
C(28)-N(22)-C(31)	124.0(6)	C(34)-C(33)-N(31)	124.6(8)
O(21)-C(21)-N(21)	122.6(7)	C(33)-C(34)-C(35)	118.4(8)
O(21)-C(21)-C(22)	123.7(7)	C(34)-C(35)-C(31)	119.2(8)
N(21)-C(21)-C(22)	113.6(6)	C(46)-C(41)-C(42)	120.8(9)
C(21)-C(22)-C(23)	112.7(6)	C(46)-C(41)-I(1)	120.2(7)
C(22)-C(23)-C(24)	112.3(7)	C(42)-C(41)-I(1)	119.0(7)
C(25)-C(24)-C(23)	112.8(7)	C(41)-C(42)-C(43)	120.0(9)
C(26)-C(25)-C(24)	114.7(7)	C(44)-C(43)-C(42)	119.2(9)
C(25)-C(26)-C(27)	113.6(7)	C(43)-C(44)-C(45)	121.0(10)
C(26)-C(27)-C(28)	114.6(7)	C(43)-C(44)-I(2)	118.0(7)
O(28)-C(28)-N(22)	122.3(8)	C(45)-C(44)-I(2)	120.8(7)
O(28)-C(28)-C(27)	123.3(8)	C(44)-C(45)-C(46)	119.3(9)
N(22)-C(28)-C(27)	114.3(7)	C(41)-C(46)-C(45)	119.4(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**3a**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	41(1)	38(1)	31(1)	-2(1)	-2(1)	5(1)
I(1)	69(1)	53(1)	57(1)	-5(1)	6(1)	18(1)
I(2)	105(1)	121(1)	82(1)	-31(1)	-37(1)	56(1)
S(100)	83(2)	112(2)	34(1)	0(1)	9(1)	37(2)
N(100)	44(5)	56(4)	33(4)	4(3)	6(3)	13(4)
C(100)	32(5)	38(4)	42(5)	1(3)	7(4)	11(4)
N(11)	33(4)	36(3)	35(3)	2(3)	5(3)	8(3)
N(21)	47(5)	26(3)	53(4)	4(3)	-10(3)	12(3)
N(31)	40(5)	39(4)	41(4)	-3(3)	-6(3)	16(3)
O(21)	76(5)	28(3)	67(4)	7(3)	-18(3)	14(3)
O(28)	67(5)	40(3)	60(4)	-2(3)	-17(3)	26(3)

C(11)	44(6)	36(4)	40(4)	0(3)	0(4)	16(4)
C(12)	32(5)	29(4)	37(4)	3(3)	3(4)	9(4)
C(13)	52(7)	40(5)	51(5)	18(4)	2(5)	4(4)
C(14)	81(9)	46(5)	67(7)	24(5)	-14(6)	1(5)
C(15)	78(8)	42(5)	62(6)	17(4)	-23(6)	0(5)
N(22)	50(5)	35(3)	48(4)	4(3)	-5(3)	27(3)
C(21)	35(6)	30(4)	45(5)	0(3)	2(4)	5(4)
C(22)	58(7)	44(5)	49(5)	2(4)	-14(4)	27(5)
C(23)	49(7)	35(4)	59(6)	-4(4)	-9(5)	14(4)
C(24)	46(6)	38(4)	42(5)	2(4)	-8(4)	9(4)
C(25)	54(7)	49(5)	45(5)	-7(4)	-14(4)	20(5)
C(26)	39(6)	32(4)	44(5)	11(3)	6(4)	7(4)
C(27)	43(6)	41(5)	47(5)	5(4)	-12(4)	14(4)
C(28)	39(6)	39(4)	48(5)	3(4)	-1(4)	11(4)
C(31)	36(6)	22(3)	43(5)	5(3)	-1(4)	3(3)
C(32)	29(5)	35(4)	40(4)	6(3)	11(4)	4(4)
C(33)	54(7)	38(4)	41(5)	1(4)	0(4)	11(4)
C(34)	59(7)	38(4)	57(6)	4(4)	22(5)	23(5)
C(35)	45(7)	54(5)	57(6)	-7(4)	0(5)	28(5)
C(41)	39(6)	48(5)	60(6)	-1(4)	9(5)	8(4)
C(42)	91(9)	50(5)	52(6)	8(4)	-2(5)	32(6)
C(43)	75(9)	45(5)	72(7)	-7(5)	-9(6)	23(5)
C(44)	57(8)	68(6)	59(6)	1(5)	-2(5)	30(6)
C(45)	73(9)	65(6)	68(7)	7(5)	7(6)	34(6)
C(46)	85(9)	40(5)	71(7)	2(4)	6(6)	32(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (**3a**).

	x	y	z	U(eq)
H(21)	5321	3319	2355	56
H(12)	2895	1753	1469	41
H(13)	821	2759	-622	63
H(14)	2615	5024	-261	91
H(15)	4710	5665	948	88
H(22)	13989	11491	7653	54
H(22A)	8134	4891	3249	65
H(22B)	6769	4697	3710	65
H(23A)	7572	7167	4010	63
H(23B)	8949	7352	3559	63
H(24A)	8883	6111	5044	57
H(24B)	10236	6231	4584	57
H(25A)	11156	8702	4871	65
H(25B)	9790	8595	5318	65
H(26A)	12331	7581	5920	49
H(26B)	11037	7653	6384	49
H(27A)	12132	10152	6504	58
H(27B)	13504	10009	6121	58
H(32)	17108	10535	8402	43
H(33)	17875	11540	10800	58
H(34)	15641	12195	10580	59
H(35)	13930	11810	9226	63
H(42)	5739	4875	5613	79
H(43)	7773	6065	6826	84
H(45)	8537	2470	7289	82
H(46)	6559	1299	6047	79

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Table 1. Crystal data and structure refinement for (**3b**).

Identification code	3b	
Empirical formula	C50 H52 Br4 Cu N10 O4 S2	
Formula weight	1304.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.1064(12) Å	α= 94.197(4)°.
	b = 10.0279(12) Å	β= 102.983(4)°.
	c = 16.012(2) Å	γ = 108.093(4)°.
Volume	1338.1(3) $Å^3$	
Z	1	
Density (calculated)	1.619 gm/cm^3	
Absorption coefficient	3.526 mm^{-1}	
F(000)	655	
Crystal size	0.16 x 0.13 x 0.08 mm^3	
Theta range for data collection	2.16 to 26.00°.	
Index ranges	-11<=h<=11, -12<=k<=12, -18<=l<=19	
Reflections collected	16657	
Independent reflections	5184 [R(int) = 0.1094]	
Completeness to theta = 26.00°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.754 and 0.583	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5184 / 0 / 322	
Goodness-of-fit on F^2	0.874	
Final R indices [I>2sigma(I)]	R1 = 0.0654, wR2 = 0.1358	
R indices (all data)	R1 = 0.1991, wR2 = 0.1607	
Largest diff. peak and hole	0.480 and -0.890 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**3b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	0	5000	41(1)
Br(2)	-9457(1)	-12089(1)	292(1)	80(1)
Br(1)	-14925(1)	-15376(1)	-3260(1)	115(1)
C(100)	4671(7)	-163(7)	3063(5)	41(2)
N(100)	5121(6)	44(6)	3799(4)	48(2)
S(100)	3952(3)	-457(2)	2004(1)	76(1)
C(1)	-11025(8)	-13032(8)	-751(5)	58(2)
C(2)	-11444(9)	-14441(9)	-982(5)	70(2)
C(3)	-12597(9)	-15156(8)	-1721(5)	69(2)
C(4)	-13308(8)	-14405(9)	-2239(5)	59(2)
C(5)	-12930(9)	-12964(9)	-2020(5)	69(2)
C(6)	-11786(9)	-12265(8)	-1266(5)	67(2)
N(11)	3396(5)	-2052(5)	4638(3)	40(1)
N(12)	-142(5)	-4081(5)	2908(3)	43(1)
C(11)	1082(7)	-3811(7)	3679(4)	40(2)
C(12)	2221(6)	-2456(6)	3921(4)	37(2)
C(13)	3521(8)	-3009(7)	5153(4)	57(2)
C(14)	2459(9)	-4367(7)	4957(5)	75(3)
C(15)	1207(8)	-4800(7)	4205(5)	72(3)
O(21)	-1093(6)	-6473(5)	2735(3)	74(2)
O(22)	-9306(5)	-8572(5)	-2533(3)	59(1)
C(21)	-1144(7)	-5375(8)	2478(4)	48(2)
C(22)	-2321(7)	-5315(7)	1667(4)	51(2)
C(23)	-3345(7)	-6757(7)	1165(4)	49(2)
C(24)	-4528(7)	-6693(7)	349(4)	46(2)
C(25)	-5557(7)	-8138(7)	-168(4)	48(2)
C(26)	-6688(7)	-8087(7)	-1013(4)	45(2)
C(27)	-7784(7)	-9543(7)	-1459(4)	48(2)
C(28)	-8869(7)	-9554(7)	-2343(4)	43(2)
N(31)	-12775(5)	-10992(5)	-4666(3)	38(1)
N(32)	-9344(5)	-10804(5)	-2886(3)	43(1)

C(31)	-10371(7)	-11082(6)	-3732(4)	36(2)
C(32)	-11795(7)	-10808(6)	-3873(4)	42(2)
C(33)	-12343(7)	-11489(7)	-5330(4)	45(2)
C(34)	-11003(8)	-11863(6)	-5246(4)	43(2)
C(35)	-9977(7)	-11633(6)	-4437(4)	42(2)

Table 3. Bond lengths [Å] and angles [°] for (**3b**).

Cu(1)-N(100)	1.954(6)	C(25)-C(26)	1.520(8)
Cu(1)-N(100)#1	1.954(6)	C(26)-C(27)	1.503(8)
Cu(1)-N(11)	2.069(5)	C(27)-C(28)	1.531(8)
Cu(1)-N(11)#1	2.069(5)	C(28)-N(32)	1.359(7)
Br(2)-C(1)	1.892(7)	N(31)-C(33)	1.328(8)
Br(1)-C(4)	1.893(7)	N(31)-C(32)	1.340(7)
C(100)-N(100)	1.137(7)	N(32)-C(31)	1.414(7)
C(100)-S(100)	1.643(7)	C(31)-C(32)	1.381(8)
C(1)-C(2)	1.343(10)	C(31)-C(35)	1.385(8)
C(1)-C(6)	1.385(10)	C(33)-C(34)	1.366(8)
C(2)-C(3)	1.366(10)	C(34)-C(35)	1.372(8)
C(3)-C(4)	1.352(10)		
C(4)-C(5)	1.376(10)	N(100)-Cu(1)-N(100)#1	180.000(2)
C(5)-C(6)	1.376(10)	N(100)-Cu(1)-N(11)	89.3(2)
N(11)-C(12)	1.318(7)	N(100)#1-Cu(1)-N(11)	90.7(2)
N(11)-C(13)	1.325(8)	N(100)-Cu(1)-N(11)#1	90.7(2)
N(12)-C(21)	1.357(7)	N(100)#1-Cu(1)-N(11)#1	89.3(2)
N(12)-C(11)	1.410(7)	N(11)-Cu(1)-N(11)#1	180.0(3)
C(11)-C(15)	1.361(9)	N(100)-C(100)-S(100)	177.7(6)
C(11)-C(12)	1.392(8)	C(100)-N(100)-Cu(1)	157.4(5)
C(13)-C(14)	1.369(9)	C(2)-C(1)-C(6)	119.7(7)
C(14)-C(15)	1.392(9)	C(2)-C(1)-Br(2)	120.7(6)
O(21)-C(21)	1.214(7)	C(6)-C(1)-Br(2)	119.5(6)
O(22)-C(28)	1.206(7)	C(1)-C(2)-C(3)	122.1(8)
C(21)-C(22)	1.506(8)	C(4)-C(3)-C(2)	118.3(7)
C(22)-C(23)	1.504(8)	C(3)-C(4)-C(5)	121.4(7)
C(23)-C(24)	1.515(8)	C(3)-C(4)-Br(1)	119.1(6)
C(24)-C(25)	1.516(8)	C(5)-C(4)-Br(1)	119.5(6)

C(6)-C(5)-C(4)	119.5(7)	C(22)-C(23)-C(24)	113.1(5)
C(5)-C(6)-C(1)	118.9(7)	C(25)-C(24)-C(23)	113.7(5)
C(12)-N(11)-C(13)	117.7(5)	C(24)-C(25)-C(26)	114.2(5)
C(12)-N(11)-Cu(1)	123.1(4)	C(27)-C(26)-C(25)	112.0(5)
C(13)-N(11)-Cu(1)	119.2(4)	C(26)-C(27)-C(28)	114.0(5)
C(21)-N(12)-C(11)	126.4(5)	O(22)-C(28)-N(32)	123.0(6)
C(15)-C(11)-C(12)	118.2(6)	O(22)-C(28)-C(27)	123.6(6)
C(15)-C(11)-N(12)	123.6(6)	N(32)-C(28)-C(27)	113.4(6)
C(12)-C(11)-N(12)	118.3(6)	C(33)-N(31)-C(32)	117.2(5)
N(11)-C(12)-C(11)	124.4(6)	C(28)-N(32)-C(31)	124.0(5)
N(11)-C(13)-C(14)	121.4(6)	C(32)-C(31)-C(35)	118.5(6)
C(13)-C(14)-C(15)	121.2(7)	C(32)-C(31)-N(32)	120.4(6)
C(11)-C(15)-C(14)	117.1(6)	C(35)-C(31)-N(32)	121.1(5)
O(21)-C(21)-N(12)	122.5(6)	N(31)-C(32)-C(31)	122.8(6)
O(21)-C(21)-C(22)	123.6(6)	N(31)-C(33)-C(34)	124.0(6)
N(12)-C(21)-C(22)	113.9(6)	C(33)-C(34)-C(35)	118.6(6)
C(23)-C(22)-C(21)	113.2(6)	C(34)-C(35)-C(31)	118.8(6)

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**3b**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	32(1)	39(1)	34(1)	-3(1)	-6(1)	-1(1)
Br(2)	66(1)	82(1)	69(1)	-12(1)	-5(1)	15(1)
Br(1)	100(1)	125(1)	84(1)	-24(1)	-38(1)	42(1)
C(100)	32(4)	44(4)	49(5)	5(4)	12(3)	12(3)
N(100)	47(3)	48(4)	40(4)	2(3)	-2(3)	13(3)
S(100)	85(2)	96(2)	37(1)	-1(1)	-2(1)	33(1)
C(1)	42(4)	58(5)	66(5)	-5(4)	10(4)	12(4)
C(2)	63(5)	65(6)	73(6)	7(5)	-9(4)	28(4)
C(3)	65(5)	54(5)	76(6)	4(4)	2(5)	17(4)
C(4)	48(4)	66(6)	48(5)	-5(4)	-10(4)	19(4)
C(5)	67(5)	76(6)	67(6)	16(5)	8(4)	31(5)

C(6)	59(5)	53(5)	81(6)	5(5)	12(5)	12(4)
N(11)	32(3)	37(3)	34(3)	-4(3)	-12(2)	6(2)
N(12)	38(3)	28(3)	45(3)	-3(3)	-18(2)	5(2)
C(11)	34(4)	37(4)	43(4)	0(3)	-3(3)	14(3)
C(12)	30(3)	28(4)	47(4)	4(3)	3(3)	6(3)
C(13)	55(4)	45(5)	39(4)	4(4)	-22(3)	0(4)
C(14)	81(6)	44(5)	59(5)	18(4)	-28(4)	-5(4)
C(15)	65(5)	32(4)	78(6)	11(4)	-27(4)	-7(4)
O(21)	75(4)	29(3)	80(4)	1(3)	-41(3)	10(3)
O(22)	61(3)	39(3)	61(3)	-7(2)	-22(2)	25(3)
C(21)	34(4)	46(5)	49(4)	-2(4)	-7(3)	6(3)
C(22)	40(4)	42(4)	48(4)	-3(3)	-16(3)	5(3)
C(23)	39(4)	45(4)	48(4)	-2(3)	-7(3)	10(3)
C(24)	36(4)	44(4)	43(4)	-5(3)	-11(3)	12(3)
C(25)	42(4)	48(4)	44(4)	2(3)	1(3)	11(3)
C(26)	31(3)	49(4)	40(4)	3(3)	-10(3)	9(3)
C(27)	36(4)	42(4)	49(4)	4(3)	-17(3)	9(3)
C(28)	24(3)	40(4)	52(4)	-7(4)	1(3)	2(3)
N(31)	27(3)	43(3)	36(3)	-1(3)	-4(2)	8(2)
N(32)	34(3)	41(3)	45(3)	1(3)	-8(3)	14(3)
C(31)	30(3)	26(3)	42(4)	2(3)	-2(3)	5(3)
C(32)	33(3)	47(4)	36(4)	-11(3)	-2(3)	11(3)
C(33)	37(4)	42(4)	35(4)	-7(3)	-9(3)	-2(3)
C(34)	52(4)	36(4)	39(4)	-1(3)	11(3)	14(3)
C(35)	32(3)	39(4)	54(5)	-1(3)	12(3)	10(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (**3b**).

	x	y	z	U(eq)
H(2)	-10932	-14946	-628	84
H(3)	-12886	-16135	-1864	83
H(5)	-13444	-12466	-2380	83
H(6)	-11528	-11293	-1105	81
H(12)	-266	-3354	2687	52
H(12A)	2147	-1792	3552	44
H(13)	4349	-2752	5658	68
H(14)	2575	-5014	5333	90
H(15)	486	-5724	4067	86
H(22A)	-3009	-4824	1823	61
H(22B)	-1739	-4768	1297	61
H(23A)	-3928	-7304	1535	58
H(23B)	-2658	-7248	1008	58
H(24A)	-5219	-6208	508	55
H(24B)	-3944	-6135	-16	55
H(25A)	-6183	-8676	188	57
H(25B)	-4863	-8643	-297	57
H(26A)	-7324	-7515	-894	53
H(26B)	-6066	-7636	-1397	53
H(27A)	-8447	-9965	-1086	58
H(27B)	-7141	-10130	-1536	58
H(32)	-8999	-11465	-2704	52
H(32A)	-12087	-10483	-3398	50
H(33)	-12993	-11589	-5885	54
H(34)	-10791	-12266	-5727	51
H(35)	-9034	-11842	-4363	51

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Table 1. Crystal data and structure refinement for (**3c**).

Identification code	3c	
Empirical formula	C70 H64 Cu N10 O4 S2	
Formula weight	1236.97	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.1435(4) Å	α= 90°.
	b = 14.9724(7) Å	β= 101.1110(10)°.
	c = 20.3506(9) Å	γ = 90°.
Volume	3032.8(2) $Å^3$	
Z	2	
Density (calculated)	1.355 gm/cm^3	
Absorption coefficient	0.489 mm^{-1}	
F(000)	1294	
Crystal size	0.15 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.70 to 26.17°.	
Index ranges	-12<=h<=12, -18<=k<=18, -25<=l<=25	
Reflections collected	38303	
Independent reflections	6054 [R(int) = 0.0466]	
Completeness to theta = 26.17°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.952 and 0.929	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6054 / 0 / 395	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1338	
R indices (all data)	R1 = 0.0680, wR2 = 0.1536	
Largest diff. peak and hole	0.458 and -0.357 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**3c**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	0	0	42(1)
S(100)	5841(1)	-2816(1)	1010(1)	90(1)
N(100)	5381(2)	-1103(1)	524(1)	48(1)
C(100)	5576(2)	-1810(2)	727(1)	43(1)
N(11)	6807(2)	755(1)	-9179(1)	45(1)
C(11)	8119(2)	859(2)	-8070(1)	40(1)
C(12)	7243(2)	418(2)	-8571(1)	43(1)
C(13)	7302(3)	1545(2)	-9315(1)	51(1)
C(14)	8241(3)	1998(2)	-8863(1)	57(1)
C(15)	8644(2)	1660(2)	-8223(1)	53(1)
N(21)	8480(2)	497(1)	-7421(1)	45(1)
N(22)	6680(2)	-620(1)	-2304(1)	43(1)
O(21)	6390(2)	127(1)	-7287(1)	60(1)
O(22)	8685(2)	-746(2)	-2621(1)	68(1)
C(20)	7599(2)	167(2)	-7063(1)	41(1)
C(21)	8223(2)	-135(2)	-6366(1)	46(1)
C(22)	7257(3)	-185(2)	-5895(1)	49(1)
C(23)	7927(3)	-409(2)	-5179(1)	52(1)
C(24)	6966(3)	-515(2)	-4703(1)	50(1)
C(25)	7675(2)	-569(2)	-3975(1)	47(1)
C(26)	6734(2)	-669(2)	-3489(1)	42(1)
C(27)	7466(2)	-677(2)	-2772(1)	39(1)
N(31)	6441(2)	-354(1)	-555(1)	41(1)
C(31)	7105(2)	-594(2)	-1608(1)	37(1)
C(32)	6169(2)	-383(2)	-1222(1)	39(1)
C(33)	7695(3)	-539(2)	-244(1)	50(1)
C(34)	8689(3)	-728(2)	-589(1)	59(1)
C(35)	8411(3)	-763(2)	-1278(1)	53(1)
C(1A)	4161(4)	-2659(3)	-2622(2)	96(1)
C(2A)	4539(4)	-2636(3)	-1950(2)	92(1)
C(3A)	6234(4)	-2843(2)	-922(2)	77(1)

C(4A)	7523(4)	-3045(2)	-627(2)	82(1)
C(5A)	8476(4)	-3241(2)	-1006(2)	71(1)
C(6A)	9077(3)	-3429(2)	-2121(2)	68(1)
C(7A)	8736(3)	-3401(2)	-2793(2)	66(1)
C(8A)	7033(4)	-3191(2)	-3815(2)	72(1)
C(9A)	5720(4)	-3020(2)	-4121(2)	84(1)
C(10A)	4757(4)	-2857(2)	-3743(2)	82(1)
C(11A)	5086(3)	-2849(2)	-3049(2)	68(1)
C(12A)	5841(3)	-2836(2)	-1622(2)	63(1)
C(13A)	8138(3)	-3234(2)	-1703(1)	56(1)
C(14A)	7407(3)	-3204(2)	-3128(1)	56(1)
C(15A)	6431(3)	-3032(2)	-2731(1)	51(1)
C(16A)	6808(3)	-3035(2)	-2016(1)	52(1)

Table 3. Bond lengths [Å] and angles [°] for (**3c**).

Cu(1)-N(100)	1.964(2)	C(22)-C(23)	1.522(3)
Cu(1)-N(100)#1	1.964(2)	C(23)-C(24)	1.509(3)
Cu(1)-N(31)	2.0801(19)	C(24)-C(25)	1.519(3)
Cu(1)-N(31)#1	2.0801(19)	C(25)-C(26)	1.509(3)
S(100)-C(100)	1.617(3)	C(26)-C(27)	1.505(3)
N(100)-C(100)	1.139(3)	N(31)-C(33)	1.337(3)
N(11)-C(12)	1.332(3)	N(31)-C(32)	1.334(3)
N(11)-C(13)	1.334(3)	C(31)-C(35)	1.389(3)
C(11)-C(15)	1.373(3)	C(31)-C(32)	1.379(3)
C(11)-C(12)	1.383(3)	C(33)-C(34)	1.366(4)
C(11)-N(21)	1.410(3)	C(34)-C(35)	1.376(3)
C(13)-C(14)	1.370(4)	C(1A)-C(2A)	1.347(5)
C(14)-C(15)	1.383(4)	C(1A)-C(11A)	1.425(5)
N(21)-C(20)	1.350(3)	C(2A)-C(12A)	1.393(5)
N(22)-C(27)	1.357(3)	C(3A)-C(4A)	1.363(5)
N(22)-C(31)	1.400(3)	C(3A)-C(12A)	1.404(4)
O(21)-C(20)	1.225(3)	C(4A)-C(5A)	1.378(5)
O(22)-C(27)	1.221(3)	C(5A)-C(13A)	1.394(4)
C(20)-C(21)	1.507(3)	C(6A)-C(7A)	1.344(4)
C(21)-C(22)	1.498(3)	C(6A)-C(13A)	1.424(4)

C(7A)-C(14A)	1.420(4)	C(26)-C(25)-C(24)	113.8(2)
C(8A)-C(14A)	1.377(4)	C(25)-C(26)-C(27)	112.38(19)
C(8A)-C(9A)	1.381(5)	O(22)-C(27)-N(22)	122.2(2)
C(9A)-C(10A)	1.376(5)	O(22)-C(27)-C(26)	122.1(2)
C(10A)-C(11A)	1.388(5)	N(22)-C(27)-C(26)	115.71(19)
C(11A)-C(15A)	1.420(4)	C(33)-N(31)-C(32)	117.8(2)
C(12A)-C(16A)	1.412(4)	C(33)-N(31)-Cu(1)	120.01(15)
C(13A)-C(16A)	1.409(4)	C(32)-N(31)-Cu(1)	122.18(16)
C(14A)-C(15A)	1.417(4)	C(35)-C(31)-C(32)	117.6(2)
C(15A)-C(16A)	1.431(4)	C(35)-C(31)-N(22)	124.2(2)
		C(32)-C(31)-N(22)	118.10(19)
N(100)-Cu(1)-N(100)#1	180.00(12)	N(31)-C(32)-C(31)	123.9(2)
N(100)-Cu(1)-N(31)	89.73(8)	N(31)-C(33)-C(34)	122.0(2)
N(100)#1-Cu(1)-N(31)	90.27(8)	C(33)-C(34)-C(35)	120.4(2)
N(100)-Cu(1)-N(31)#1	90.27(8)	C(34)-C(35)-C(31)	118.3(2)
N(100)#1-Cu(1)-N(31)#1	89.73(8)	C(2A)-C(1A)-C(11A)	122.1(4)
N(31)-Cu(1)-N(31)#1	180.00(14)	C(1A)-C(2A)-C(12A)	122.6(3)
C(100)-N(100)-Cu(1)	168.6(2)	C(4A)-C(3A)-C(12A)	120.6(3)
N(100)-C(100)-S(100)	179.5(3)	C(3A)-C(4A)-C(5A)	121.2(3)
C(12)-N(11)-C(13)	117.2(2)	C(4A)-C(5A)-C(13A)	120.4(3)
C(15)-C(11)-C(12)	118.1(2)	C(7A)-C(6A)-C(13A)	122.0(3)
C(15)-C(11)-N(21)	120.4(2)	C(6A)-C(7A)-C(14A)	122.0(3)
C(12)-C(11)-N(21)	121.4(2)	C(14A)-C(8A)-C(9A)	120.9(3)
N(11)-C(12)-C(11)	123.8(2)	C(10A)-C(9A)-C(8A)	120.5(3)
N(11)-C(13)-C(14)	122.7(2)	C(9A)-C(10A)-C(11A)	120.9(3)
C(13)-C(14)-C(15)	119.5(2)	C(10A)-C(11A)-C(1A)	124.4(3)
C(11)-C(15)-C(14)	118.4(2)	C(10A)-C(11A)-C(15A)	118.9(3)
C(20)-N(21)-C(11)	124.50(19)	C(1A)-C(11A)-C(15A)	116.6(3)
C(27)-N(22)-C(31)	127.19(19)	C(2A)-C(12A)-C(3A)	123.0(3)
O(21)-C(20)-N(21)	122.4(2)	C(2A)-C(12A)-C(16A)	118.1(3)
O(21)-C(20)-C(21)	123.0(2)	C(3A)-C(12A)-C(16A)	118.8(3)
N(21)-C(20)-C(21)	114.5(2)	C(5A)-C(13A)-C(16A)	119.2(3)
C(22)-C(21)-C(20)	114.1(2)	C(5A)-C(13A)-C(6A)	123.0(3)
C(21)-C(22)-C(23)	113.4(2)	C(16A)-C(13A)-C(6A)	117.7(3)
C(24)-C(23)-C(22)	114.4(2)	C(8A)-C(14A)-C(15A)	119.3(3)
C(23)-C(24)-C(25)	112.9(2)	C(8A)-C(14A)-C(7A)	122.8(3)

C(15A)-C(14A)-C(7A)	117.8(3)	C(13A)-C(16A)-C(12A)	119.8(3)
C(14A)-C(15A)-C(11A)	119.4(3)	C(13A)-C(16A)-C(15A)	120.4(2)
C(14A)-C(15A)-C(16A)	120.0(3)	C(12A)-C(16A)-C(15A)	119.8(3)
C(11A)-C(15A)-C(16A)	120.6(3)		

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**3c**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	59(1)	44(1)	28(1)	6(1)	19(1)	7(1)
S(100)	93(1)	58(1)	123(1)	38(1)	30(1)	7(1)
N(100)	65(1)	45(1)	36(1)	8(1)	15(1)	3(1)
C(100)	39(1)	52(2)	38(1)	1(1)	10(1)	-4(1)
N(11)	53(1)	56(1)	28(1)	-1(1)	12(1)	-2(1)
C(11)	34(1)	56(1)	32(1)	3(1)	11(1)	2(1)
C(12)	49(1)	50(1)	31(1)	0(1)	12(1)	-4(1)
C(13)	56(2)	64(2)	36(1)	10(1)	13(1)	-1(1)
C(14)	58(2)	60(2)	55(2)	11(1)	12(1)	-14(1)
C(15)	45(1)	65(2)	47(2)	2(1)	7(1)	-11(1)
N(21)	35(1)	68(1)	30(1)	4(1)	5(1)	-5(1)
N(22)	37(1)	63(1)	29(1)	1(1)	10(1)	4(1)
O(21)	40(1)	101(2)	38(1)	11(1)	8(1)	-13(1)
O(22)	40(1)	133(2)	33(1)	7(1)	11(1)	7(1)
C(20)	43(1)	53(1)	29(1)	-2(1)	8(1)	-3(1)
C(21)	48(1)	59(2)	32(1)	4(1)	10(1)	2(1)
C(22)	48(1)	71(2)	29(1)	4(1)	9(1)	-5(1)
C(23)	52(1)	72(2)	32(1)	6(1)	10(1)	3(1)
C(24)	50(1)	70(2)	31(1)	2(1)	9(1)	-2(1)
C(25)	46(1)	67(2)	29(1)	1(1)	11(1)	6(1)
C(26)	44(1)	55(1)	29(1)	-2(1)	10(1)	-1(1)
C(27)	39(1)	52(1)	29(1)	1(1)	12(1)	2(1)
N(31)	54(1)	44(1)	29(1)	1(1)	15(1)	4(1)
C(31)	41(1)	43(1)	29(1)	1(1)	11(1)	3(1)

C(32)	42(1)	48(1)	31(1)	5(1)	11(1)	0(1)
C(33)	61(2)	62(2)	27(1)	3(1)	7(1)	11(1)
C(34)	54(2)	86(2)	35(1)	2(1)	4(1)	20(1)
C(35)	48(1)	78(2)	36(1)	2(1)	11(1)	16(1)
C(1A)	66(2)	109(3)	115(3)	14(3)	21(2)	11(2)
C(2A)	85(3)	95(3)	108(3)	10(2)	50(2)	16(2)
C(3A)	109(3)	63(2)	68(2)	-3(2)	43(2)	-2(2)
C(4A)	126(3)	71(2)	50(2)	-5(2)	18(2)	-20(2)
C(5A)	82(2)	64(2)	64(2)	5(2)	4(2)	-11(2)
C(6A)	60(2)	60(2)	83(2)	-2(2)	13(2)	-6(1)
C(7A)	64(2)	62(2)	76(2)	-8(2)	25(2)	1(1)
C(8A)	96(2)	69(2)	55(2)	-16(2)	23(2)	-4(2)
C(9A)	112(3)	83(2)	52(2)	-12(2)	2(2)	-14(2)
C(10A)	76(2)	86(2)	77(2)	6(2)	-7(2)	-11(2)
C(11A)	62(2)	66(2)	75(2)	4(2)	14(2)	2(1)
C(12A)	74(2)	52(2)	69(2)	4(1)	28(2)	7(1)
C(13A)	68(2)	44(1)	55(2)	1(1)	12(1)	-7(1)
C(14A)	70(2)	46(1)	55(2)	-7(1)	20(1)	-6(1)
C(15A)	64(2)	38(1)	54(2)	-4(1)	15(1)	-2(1)
C(16A)	67(2)	38(1)	54(2)	-3(1)	20(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (**3c**).

	x	y	z	U(eq)
H(12)	6942	-146	-8477	51
H(13)	6998	1798	-9734	61
H(14)	8604	2529	-8985	69
H(15)	9257	1969	-7904	63
H(21)	9319	485	-7240	53
H(22)	5827	-599	-2452	51
H(21A)	8620	-720	-6393	55
H(21B)	8941	274	-6183	55
H(22A)	6584	-636	-6056	59

H(22B)	6799	384	-5898	59
H(23A)	8430	-960	-5182	62
H(23B)	8563	60	-5013	62
H(24A)	6441	-1054	-4818	60
H(24B)	6351	-13	-4758	60
H(25A)	8287	-1073	-3922	56
H(25B)	8207	-32	-3864	56
H(26A)	6233	-1221	-3584	51
H(26B)	6095	-179	-3553	51
H(32)	5298	-253	-1441	47
H(33)	7897	-538	222	60
H(34)	9559	-834	-358	71
H(35)	9082	-896	-1516	64
H(1A)	3267	-2547	-2813	115
H(2A)	3906	-2481	-1695	110
H(3A)	5610	-2709	-657	92
H(4A)	7764	-3051	-163	99
H(5A)	9349	-3378	-794	85
H(6A)	9954	-3579	-1923	81
H(7A)	9391	-3515	-3045	79
H(8A)	7673	-3298	-4077	86
H(9A)	5485	-3014	-4586	101
H(10A)	3874	-2751	-3956	99

Electronic Supplementary Material (ESI) for *CrystEngComm*

Table 1. Crystal data and structure refinement for (**3d**).

Identification code	3d	
Empirical formula	C66 H60 Cu N10 O4 S2	
Formula weight	1184.90	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.9865(14) Å	α= 90°.
	b = 14.840(2) Å	β= 100.363(4)°.
	c = 20.416(3) Å	γ = 90°.
Volume	2976.4(7) $Å^3$	
Z	2	
Density (calculated)	1.322 gm/cm^3	
Absorption coefficient	0.495 mm^{-1}	
F(000)	1238	
Crystal size	0.14 x 0.13 x 0.09 mm^3	
Theta range for data collection	1.71 to 26.00°.	
Index ranges	-12<=h<=11, -18<=k<=18, -25<=l<=25	
Reflections collected	37212	
Independent reflections	5838 [R(int) = 0.0403]	
Completeness to theta = 26.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.956 and 0.933	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5838 / 0 / 395	
Goodness-of-fit on F^2	0.827	
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.1242	
R indices (all data)	R1 = 0.0631, wR2 = 0.1368	
Largest diff. peak and hole	0.602 and -0.492 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**3d**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	0	0	43(1)
S(100)	5918(1)	-2754(1)	1130(1)	123(1)
N(100)	5415(2)	-1103(1)	521(1)	49(1)
C(100)	5626(2)	-1782(2)	774(1)	49(1)
N(11)	6813(2)	797(1)	-9180(1)	47(1)
C(11)	8028(2)	931(2)	-8062(1)	42(1)
C(12)	7237(2)	456(2)	-8573(1)	44(1)
C(13)	7223(3)	1619(2)	-9299(1)	54(1)
C(14)	8060(3)	2119(2)	-8834(1)	71(1)
C(15)	8464(3)	1775(2)	-8198(1)	64(1)
N(21)	8395(2)	554(1)	-7420(1)	46(1)
N(22)	6733(2)	-580(1)	-2301(1)	44(1)
O(21)	6292(2)	135(1)	-7290(1)	63(1)
O(22)	8750(2)	-767(2)	-2635(1)	67(1)
C(20)	7505(2)	191(2)	-7069(1)	44(1)
C(21)	8147(3)	-131(2)	-6386(1)	51(1)
C(22)	7188(3)	-150(2)	-5894(1)	47(1)
C(23)	7898(3)	-398(2)	-5193(1)	51(1)
C(24)	6949(2)	-494(2)	-4698(1)	50(1)
C(25)	7697(2)	-563(2)	-3983(1)	48(1)
C(26)	6759(2)	-653(2)	-3482(1)	44(1)
C(27)	7522(2)	-669(2)	-2775(1)	42(1)
N(31)	6480(2)	-325(1)	-555(1)	42(1)
C(31)	7173(2)	-559(2)	-1607(1)	39(1)
C(32)	6214(2)	-344(2)	-1220(1)	41(1)
C(33)	7745(3)	-516(2)	-251(1)	51(1)
C(34)	8760(3)	-707(2)	-602(1)	56(1)
C(35)	8489(3)	-736(2)	-1286(1)	53(1)
C(1A)	4981(4)	2869(3)	3059(2)	91(1)
C(2A)	5268(4)	2886(3)	3754(2)	101(1)
C(3A)	4268(5)	3022(3)	4122(2)	93(1)

C(4A)	2968(4)	3165(2)	3807(2)	83(1)
C(5A)	1624(5)	3185(2)	989(2)	91(1)
C(6A)	2581(6)	2996(2)	610(2)	98(1)
C(7A)	3887(5)	2812(3)	918(2)	96(1)
C(8A)	4258(5)	2814(2)	1608(2)	90(1)
C(11A)	2643(4)	3168(2)	3118(2)	73(1)
C(12A)	3639(4)	3017(2)	2732(2)	73(1)
C(13A)	3304(4)	3005(2)	2005(2)	75(1)
C(14A)	1971(4)	3185(2)	1689(2)	76(1)
C(9A)	1398(5)	3352(3)	2764(2)	60(1)
C(10A)	1098(4)	3379(3)	2098(2)	60(1)
C(15A)	5718(8)	2739(6)	2597(6)	87(3)
C(16A)	5366(10)	2692(7)	1948(6)	83(3)

Table 3. Bond lengths [Å] and angles [°] for (**3d**).

Cu(1)-N(100)#1	1.9557(19)	C(22)-C(23)	1.523(3)
Cu(1)-N(100)	1.9557(19)	C(23)-C(24)	1.511(3)
Cu(1)-N(31)#1	2.0746(18)	C(24)-C(25)	1.518(3)
Cu(1)-N(31)	2.0746(18)	C(25)-C(26)	1.514(3)
S(100)-C(100)	1.617(3)	C(26)-C(27)	1.505(3)
N(100)-C(100)	1.135(3)	N(31)-C(33)	1.333(3)
N(11)-C(13)	1.324(3)	N(31)-C(32)	1.336(3)
N(11)-C(12)	1.336(3)	C(31)-C(32)	1.384(3)
C(11)-C(15)	1.371(4)	C(31)-C(35)	1.384(3)
C(11)-C(12)	1.384(3)	C(33)-C(34)	1.371(3)
C(11)-N(21)	1.410(3)	C(34)-C(35)	1.376(3)
C(13)-C(14)	1.366(4)	C(1A)-C(15A)	1.311(10)
C(14)-C(15)	1.386(4)	C(1A)-C(2A)	1.397(5)
N(21)-C(20)	1.351(3)	C(1A)-C(12A)	1.403(5)
N(22)-C(27)	1.361(3)	C(2A)-C(3A)	1.369(6)
N(22)-C(31)	1.406(2)	C(3A)-C(4A)	1.358(5)
O(21)-C(20)	1.217(3)	C(4A)-C(11A)	1.386(4)
O(22)-C(27)	1.217(3)	C(5A)-C(6A)	1.363(6)
C(20)-C(21)	1.505(3)	C(5A)-C(14A)	1.408(5)
C(21)-C(22)	1.508(3)	C(6A)-C(7A)	1.370(6)

C(7A)-C(8A)	1.392(5)	C(26)-C(25)-C(24)	113.49(19)
C(8A)-C(16A)	1.210(10)	C(27)-C(26)-C(25)	112.42(18)
C(8A)-C(13A)	1.387(5)	O(22)-C(27)-N(22)	122.17(19)
C(11A)-C(9A)	1.349(5)	O(22)-C(27)-C(26)	122.87(19)
C(11A)-C(12A)	1.394(5)	N(22)-C(27)-C(26)	114.95(19)
C(12A)-C(13A)	1.461(4)	C(33)-N(31)-C(32)	117.81(19)
C(13A)-C(14A)	1.397(5)	C(33)-N(31)-Cu(1)	120.24(14)
C(14A)-C(10A)	1.343(5)	C(32)-N(31)-Cu(1)	121.94(15)
C(9A)-C(10A)	1.339(6)	C(32)-C(31)-C(35)	117.98(19)
C(15A)-C(16A)	1.309(14)	C(32)-C(31)-N(22)	117.22(19)
		C(35)-C(31)-N(22)	124.81(19)
N(100)#1-Cu(1)-N(100)	180.00(18)	N(31)-C(32)-C(31)	123.6(2)
N(100)#1-Cu(1)-N(31)#1	90.04(8)	N(31)-C(33)-C(34)	121.9(2)
N(100)-Cu(1)-N(31)#1	89.96(8)	C(33)-C(34)-C(35)	120.5(2)
N(100)#1-Cu(1)-N(31)	89.96(8)	C(34)-C(35)-C(31)	118.1(2)
N(100)-Cu(1)-N(31)	90.04(8)	C(15A)-C(1A)-C(2A)	134.0(6)
N(31)#1-Cu(1)-N(31)	180.00(13)	C(15A)-C(1A)-C(12A)	107.0(5)
C(100)-N(100)-Cu(1)	174.1(2)	C(2A)-C(1A)-C(12A)	119.0(4)
N(100)-C(100)-S(100)	179.5(3)	C(3A)-C(2A)-C(1A)	121.6(4)
C(13)-N(11)-C(12)	117.5(2)	C(4A)-C(3A)-C(2A)	119.5(3)
C(15)-C(11)-C(12)	118.2(2)	C(3A)-C(4A)-C(11A)	120.7(4)
C(15)-C(11)-N(21)	120.8(2)	C(6A)-C(5A)-C(14A)	120.4(4)
C(12)-C(11)-N(21)	121.1(2)	C(5A)-C(6A)-C(7A)	119.1(4)
N(11)-C(12)-C(11)	123.4(2)	C(6A)-C(7A)-C(8A)	121.5(4)
N(11)-C(13)-C(14)	123.0(2)	C(16A)-C(8A)-C(13A)	110.4(6)
C(13)-C(14)-C(15)	119.3(3)	C(16A)-C(8A)-C(7A)	129.1(7)
C(11)-C(15)-C(14)	118.5(2)	C(13A)-C(8A)-C(7A)	120.4(4)
C(20)-N(21)-C(11)	124.40(18)	C(9A)-C(11A)-C(4A)	124.7(4)
C(27)-N(22)-C(31)	127.08(19)	C(9A)-C(11A)-C(12A)	114.4(3)
O(21)-C(20)-N(21)	122.4(2)	C(4A)-C(11A)-C(12A)	120.9(3)
O(21)-C(20)-C(21)	123.5(2)	C(11A)-C(12A)-C(1A)	118.3(3)
N(21)-C(20)-C(21)	114.04(19)	C(11A)-C(12A)-C(13A)	121.3(3)
C(20)-C(21)-C(22)	114.0(2)	C(1A)-C(12A)-C(13A)	120.4(3)
C(21)-C(22)-C(23)	112.7(2)	C(14A)-C(13A)-C(8A)	117.8(3)
C(24)-C(23)-C(22)	114.1(2)	C(14A)-C(13A)-C(12A)	119.5(3)
C(23)-C(24)-C(25)	112.9(2)	C(8A)-C(13A)-C(12A)	122.7(4)

C(10A)-C(14A)-C(13A)	115.2(3)	C(14A)-C(10A)-C(9A)	125.0(4)
C(10A)-C(14A)-C(5A)	124.2(4)	C(16A)-C(15A)-C(1A)	130.7(8)
C(13A)-C(14A)-C(5A)	120.6(4)	C(8A)-C(16A)-C(15A)	128.6(9)
C(11A)-C(9A)-C(10A)	124.5(4)		

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**3d**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	59(1)	45(1)	27(1)	7(1)	17(1)	7(1)
S(100)	104(1)	88(1)	187(1)	85(1)	50(1)	22(1)
N(100)	64(1)	49(1)	35(1)	10(1)	13(1)	5(1)
C(100)	40(1)	59(2)	49(1)	9(1)	12(1)	-1(1)
N(11)	57(1)	57(1)	27(1)	-1(1)	9(1)	0(1)
C(11)	36(1)	60(1)	31(1)	1(1)	8(1)	-2(1)
C(12)	48(1)	52(1)	32(1)	-1(1)	9(1)	-3(1)
C(13)	57(2)	65(2)	40(1)	14(1)	10(1)	-5(1)
C(14)	78(2)	68(2)	64(2)	18(1)	1(2)	-23(2)
C(15)	64(2)	71(2)	52(2)	3(1)	-4(1)	-24(1)
N(21)	35(1)	73(1)	30(1)	3(1)	3(1)	-7(1)
N(22)	34(1)	71(1)	27(1)	-1(1)	7(1)	2(1)
O(21)	37(1)	113(2)	38(1)	13(1)	5(1)	-10(1)
O(22)	38(1)	130(2)	35(1)	3(1)	10(1)	7(1)
C(20)	38(1)	64(2)	31(1)	-1(1)	8(1)	-2(1)
C(21)	45(1)	75(2)	33(1)	6(1)	9(1)	2(1)
C(22)	48(1)	63(2)	32(1)	1(1)	8(1)	-2(1)
C(23)	49(1)	75(2)	31(1)	5(1)	9(1)	4(1)
C(24)	47(1)	73(2)	30(1)	1(1)	8(1)	-1(1)
C(25)	44(1)	70(2)	30(1)	2(1)	10(1)	7(1)
C(26)	39(1)	63(1)	30(1)	-2(1)	8(1)	0(1)
C(27)	38(1)	58(1)	31(1)	1(1)	10(1)	-1(1)
N(31)	54(1)	45(1)	28(1)	2(1)	12(1)	2(1)
C(31)	43(1)	47(1)	28(1)	1(1)	9(1)	-1(1)

C(32)	41(1)	52(1)	30(1)	3(1)	9(1)	1(1)
C(33)	63(2)	60(2)	29(1)	3(1)	5(1)	11(1)
C(34)	52(2)	77(2)	36(1)	2(1)	-1(1)	16(1)
C(35)	48(1)	76(2)	35(1)	2(1)	10(1)	14(1)
C(1A)	95(3)	89(3)	91(3)	1(2)	22(2)	-13(2)
C(2A)	88(3)	106(3)	98(3)	2(2)	-9(2)	-19(2)
C(3A)	118(3)	90(3)	65(2)	-19(2)	3(2)	-20(2)
C(4A)	108(3)	76(2)	65(2)	-16(2)	16(2)	-1(2)
C(5A)	119(3)	73(2)	78(2)	5(2)	9(2)	-11(2)
C(6A)	160(4)	73(2)	63(2)	-6(2)	27(3)	-13(2)
C(7A)	140(4)	75(2)	85(3)	-1(2)	51(3)	-3(2)
C(8A)	128(4)	66(2)	82(2)	2(2)	32(2)	-6(2)
C(11A)	95(2)	54(2)	71(2)	-8(1)	13(2)	-3(2)
C(12A)	102(3)	49(2)	67(2)	-4(1)	11(2)	-14(2)
C(13A)	111(3)	46(2)	68(2)	-2(1)	16(2)	-8(2)
C(14A)	112(3)	49(2)	70(2)	0(1)	22(2)	-7(2)
C(9A)	52(3)	53(2)	78(3)	-5(2)	19(2)	1(2)
C(10A)	45(2)	53(3)	83(3)	2(2)	13(2)	-3(2)
C(15A)	37(4)	96(7)	131(9)	11(6)	24(5)	5(4)
C(16A)	59(5)	94(7)	102(7)	22(6)	29(5)	16(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (**3d**).

	x	y	z	U(eq)
H(12)	6988	-131	-8489	53
H(13)	6927	1868	-9718	65
H(14)	8356	2684	-8943	86
H(15)	9019	2109	-7871	77
H(21)	9243	555	-7241	55
H(22)	5870	-531	-2441	52
H(21A)	8909	259	-6214	61
H(21B)	8504	-733	-6423	61
H(22A)	6470	-584	-6042	57

H(22B)	6768	438	-5883	57
H(23A)	8379	-963	-5212	62
H(23B)	8569	61	-5034	62
H(24A)	6394	-1028	-4806	60
H(24B)	6344	23	-4738	60
H(25A)	8299	-1081	-3944	57
H(25B)	8257	-30	-3878	57
H(26A)	6124	-153	-3535	52
H(26B)	6236	-1205	-3570	52
H(32)	5337	-204	-1435	49
H(33)	7944	-520	212	61
H(34)	9638	-818	-375	67
H(35)	9171	-870	-1527	63
H(2A)	6160	2802	3972	121
H(3A)	4477	3018	4585	111
H(4A)	2288	3262	4056	99
H(5A)	735	3313	784	110
H(6A)	2350	2993	147	118
H(7A)	4541	2684	659	116
H(9A)	700	3469	2998	72
H(10A)	217	3543	1904	73
H(15A)	6645	2668	2756	104
H(16A)	6061	2545	1719	100

Electronic Supplementary Material (ESI) for *CrystEngComm*

Table 1. Crystal data and structure refinement for 4a.

Identification code	4a	
Empirical formula	C50 H52 Br4 Cu N10 O4 S2	
Formula weight	1304.32	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.210(6) Å	α= 93.77(2)°.
	b = 10.155(7) Å	β= 104.08(2)°.
	c = 15.921(11) Å	γ = 109.20(2)°.
Volume	1346.6(16) Å^3	
Z	1	
Density (calculated)	1.608 Mg/m^3	
Absorption coefficient	3.504 mm^{-1}	
F(000)	655	
Crystal size	0.18 x 0.17 x 0.10 mm^3	
Theta range for data collection	1.34 to 25.99°.	
Index ranges	-11<=h<=9, -12<=k<=12, -19<=l<=19	
Reflections collected	17079	
Independent reflections	5224 [R(int) = 0.0545]	
Completeness to theta = 25.99°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.704 and 0.538	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5224 / 0 / 322	
Goodness-of-fit on F^2	0.878	
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1333	
R indices (all data)	R1 = 0.1148, wR2 = 0.1566	
Largest diff. peak and hole	0.825 and -0.735 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 4a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	5000	0	41(1)
Br(2)	10498(1)	12840(1)	5322(1)	79(1)
Br(1)	4967(1)	9670(1)	1678(1)	111(1)
C(1)	6617(7)	10618(7)	2726(3)	63(2)
C(2)	6970(7)	12015(6)	2983(4)	68(2)
C(3)	8145(7)	12692(6)	3749(4)	64(2)
C(4)	8901(6)	11927(6)	4245(3)	56(1)
C(5)	8521(7)	10523(6)	3977(4)	73(2)
C(6)	7358(8)	9859(6)	3219(4)	74(2)
S(100)	6098(2)	5395(2)	3004(1)	79(1)
C(100)	5353(6)	5068(5)	1951(3)	41(1)
N(100)	4845(5)	4836(4)	1197(2)	47(1)
O(11)	10577(4)	7616(3)	2439(2)	51(1)
N(11)	6637(4)	7025(4)	425(2)	40(1)
C(11)	9036(5)	8613(4)	1456(3)	37(1)
C(12)	7837(5)	7314(4)	1153(3)	36(1)
C(13)	6593(6)	8072(5)	-34(3)	52(1)
C(14)	7736(6)	9413(5)	226(3)	63(2)
C(15)	8964(6)	9689(5)	980(3)	55(1)
C(16)	10374(5)	8693(5)	2249(3)	38(1)
O(21)	18906(4)	17294(3)	7765(2)	63(1)
N(21)	22745(4)	15975(4)	9671(2)	41(1)
C(21)	20423(5)	16329(4)	8791(3)	37(1)
C(22)	21757(5)	15951(4)	8893(3)	40(1)
C(23)	22399(6)	16411(5)	10383(3)	45(1)
C(24)	21123(6)	16840(5)	10346(3)	48(1)
C(25)	20120(6)	16799(4)	9541(3)	43(1)
C(26)	19343(5)	16291(4)	7910(3)	40(1)
N(31)	11259(4)	9968(4)	2712(2)	43(1)
N(32)	18882(5)	15133(4)	7319(2)	46(1)
C(31)	12539(6)	10115(4)	3497(3)	46(1)

C(32)	13387(6)	11635(5)	3936(3)	45(1)
C(33)	14676(5)	11788(4)	4775(3)	44(1)
C(34)	15607(6)	13295(5)	5208(3)	44(1)
C(35)	16816(5)	13452(5)	6076(3)	45(1)
C(36)	17788(6)	14958(5)	6452(3)	51(1)

Table 3. Bond lengths [Å] and angles [°] for 4a.

Cu(1)-N(100)	1.959(4)	C(21)-C(25)	1.381(6)
Cu(1)-N(100)#1	1.959(4)	C(21)-C(26)	1.498(6)
Cu(1)-N(11)	2.059(4)	C(23)-C(24)	1.371(7)
Cu(1)-N(11)#1	2.059(4)	C(24)-C(25)	1.375(6)
Br(2)-C(4)	1.905(5)	C(26)-N(32)	1.334(5)
Br(1)-C(1)	1.901(5)	N(31)-C(31)	1.455(5)
C(1)-C(2)	1.357(8)	N(32)-C(36)	1.459(5)
C(1)-C(6)	1.356(8)	C(31)-C(32)	1.511(6)
C(2)-C(3)	1.374(8)	C(32)-C(33)	1.516(6)
C(3)-C(4)	1.372(7)	C(33)-C(34)	1.505(6)
C(4)-C(5)	1.363(8)	C(34)-C(35)	1.510(6)
C(5)-C(6)	1.359(8)	C(35)-C(36)	1.489(6)
S(100)-C(100)	1.615(5)		
C(100)-N(100)	1.155(6)	N(100)-Cu(1)-N(100)#1	180.0(2)
O(11)-C(16)	1.213(5)	N(100)-Cu(1)-N(11)	90.21(15)
N(11)-C(12)	1.331(5)	N(100)#1-Cu(1)-N(11)	89.79(15)
N(11)-C(13)	1.335(6)	N(100)-Cu(1)-N(11)#1	89.79(15)
C(11)-C(15)	1.381(6)	N(100)#1-Cu(1)-N(11)#1	90.21(15)
C(11)-C(12)	1.375(6)	N(11)-Cu(1)-N(11)#1	180.0
C(11)-C(16)	1.510(6)	C(2)-C(1)-C(6)	121.8(5)
C(13)-C(14)	1.380(7)	C(2)-C(1)-Br(1)	119.4(5)
C(14)-C(15)	1.373(6)	C(6)-C(1)-Br(1)	118.8(5)
C(16)-N(31)	1.331(5)	C(3)-C(2)-C(1)	119.3(5)
O(21)-C(26)	1.228(5)	C(2)-C(3)-C(4)	119.0(5)
N(21)-C(23)	1.336(6)	C(5)-C(4)-C(3)	120.7(5)
N(21)-C(22)	1.340(5)	C(5)-C(4)-Br(2)	119.7(4)
C(21)-C(22)	1.381(6)	C(3)-C(4)-Br(2)	119.6(4)

C(6)-C(5)-C(4)	120.0(6)	C(22)-C(21)-C(25)	117.5(4)
C(5)-C(6)-C(1)	119.2(6)	C(22)-C(21)-C(26)	122.9(4)
N(100)-C(100)-S(100)	178.9(5)	C(25)-C(21)-C(26)	119.6(4)
C(100)-N(100)-Cu(1)	153.7(4)	N(21)-C(22)-C(21)	124.2(4)
C(12)-N(11)-C(13)	117.5(4)	N(21)-C(23)-C(24)	123.3(4)
C(12)-N(11)-Cu(1)	120.3(3)	C(25)-C(24)-C(23)	119.1(4)
C(13)-N(11)-Cu(1)	122.0(3)	C(24)-C(25)-C(21)	119.2(4)
C(15)-C(11)-C(12)	117.5(4)	O(21)-C(26)-N(32)	123.1(4)
C(15)-C(11)-C(16)	126.2(4)	O(21)-C(26)-C(21)	119.7(4)
C(12)-C(11)-C(16)	116.2(4)	N(32)-C(26)-C(21)	117.2(4)
N(11)-C(12)-C(11)	124.3(4)	C(16)-N(31)-C(31)	119.7(4)
N(11)-C(13)-C(14)	122.2(4)	C(26)-N(32)-C(36)	121.9(4)
C(15)-C(14)-C(13)	119.4(4)	N(31)-C(31)-C(32)	111.8(3)
C(14)-C(15)-C(11)	119.2(4)	C(31)-C(32)-C(33)	112.0(4)
O(11)-C(16)-N(31)	123.6(4)	C(34)-C(33)-C(32)	113.6(4)
O(11)-C(16)-C(11)	119.5(4)	C(33)-C(34)-C(35)	114.0(4)
N(31)-C(16)-C(11)	116.9(4)	C(36)-C(35)-C(34)	112.3(4)
C(23)-N(21)-C(22)	116.6(4)	N(32)-C(36)-C(35)	112.9(4)

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 4a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	41(1)	33(1)	27(1)	-3(1)	-6(1)	-3(1)
Br(2)	75(1)	80(1)	57(1)	-2(1)	-1(1)	13(1)
Br(1)	105(1)	112(1)	75(1)	-18(1)	-28(1)	31(1)
C(1)	56(4)	70(4)	49(3)	-6(3)	0(3)	17(3)
C(2)	73(4)	66(4)	63(4)	14(3)	7(3)	31(3)
C(3)	66(4)	51(3)	72(4)	5(3)	12(3)	21(3)
C(4)	52(3)	56(3)	46(3)	1(2)	4(2)	11(3)
C(5)	76(4)	64(4)	68(4)	9(3)	-6(3)	31(3)
C(6)	87(5)	52(3)	69(4)	-4(3)	-2(3)	27(3)
S(100)	88(1)	102(1)	33(1)	-3(1)	-1(1)	31(1)
C(100)	42(3)	35(3)	43(3)	2(2)	9(2)	11(2)
N(100)	51(3)	44(2)	30(2)	0(2)	-1(2)	7(2)
O(11)	57(2)	26(2)	50(2)	-2(1)	-17(2)	14(2)
N(11)	36(2)	32(2)	36(2)	-4(2)	-5(2)	5(2)
C(11)	38(3)	29(2)	34(2)	-3(2)	-3(2)	11(2)
C(12)	35(3)	27(2)	35(2)	-1(2)	-4(2)	7(2)
C(13)	51(3)	37(3)	44(3)	6(2)	-17(2)	7(2)
C(14)	68(4)	30(3)	57(3)	11(2)	-20(3)	-1(3)
C(15)	51(3)	30(3)	56(3)	-2(2)	-14(2)	3(2)
C(16)	37(3)	33(3)	30(2)	-7(2)	-4(2)	7(2)
O(21)	72(3)	31(2)	63(2)	-7(2)	-24(2)	23(2)
N(21)	36(2)	41(2)	38(2)	-1(2)	-1(2)	13(2)
C(21)	35(3)	20(2)	42(2)	-2(2)	-4(2)	4(2)
C(22)	43(3)	32(2)	35(2)	-3(2)	4(2)	9(2)
C(23)	50(3)	37(3)	32(2)	0(2)	-8(2)	12(2)
C(24)	60(3)	40(3)	40(3)	-3(2)	7(2)	19(3)
C(25)	45(3)	26(2)	53(3)	1(2)	8(2)	13(2)
C(26)	39(3)	23(2)	43(2)	-1(2)	-5(2)	5(2)
N(31)	44(2)	24(2)	41(2)	-6(2)	-14(2)	11(2)
N(32)	49(2)	28(2)	44(2)	-3(2)	-17(2)	15(2)
C(31)	46(3)	27(2)	44(3)	-4(2)	-15(2)	8(2)

C(32)	44(3)	36(3)	39(2)	-6(2)	-10(2)	12(2)
C(33)	46(3)	28(2)	39(2)	-2(2)	-10(2)	5(2)
C(34)	44(3)	33(2)	42(2)	-5(2)	-8(2)	14(2)
C(35)	42(3)	33(2)	42(3)	-3(2)	-13(2)	11(2)
C(36)	51(3)	38(3)	40(3)	0(2)	-16(2)	8(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 4a.

	x	y	z	U(eq)
H(2)	6423	12508	2645	81
H(3)	8422	13654	3928	77
H(5)	9057	10019	4312	88
H(6)	7073	8896	3040	89
H(12)	7868	6590	1478	43
H(13)	5766	7892	-546	63
H(14)	7676	10123	-107	76
H(15)	9737	10590	1168	66
H(22)	21986	15660	8390	48
H(23)	23057	16425	10932	54
H(24)	20939	17154	10858	58
H(25)	19247	17084	9502	51
H(31)	11074	10701	2548	51
H(32)	19241	14469	7454	55
H(31A)	13308	9754	3341	55
H(31B)	12096	9554	3906	55
H(32A)	12610	12008	4069	54
H(32B)	13869	12188	3535	54
H(33A)	14180	11269	5184	53
H(33B)	15414	11363	4645	53
H(34A)	14860	13739	5300	53
H(34B)	16163	13796	4814	53
H(35A)	16258	13015	6487	53
H(35B)	17524	12959	5995	53
H(36A)	18402	15375	6058	61
H(36B)	17073	15465	6491	61

Electronic Supplementary Material (ESI) for *CrystEngComm*

Table 1. Crystal data and structure refinement for 4b.

Identification code	4b	
Empirical formula	C66 H60 Cu N10 O4 S2	
Formula weight	1184.90	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.1605(10) Å	α= 90°.
	b = 15.0606(15) Å	β= 100.338(3)°.
	c = 20.010(2) Å	γ = 90°.
Volume	3012.4(5) $Å^3$	
Z	2	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.489 mm^{-1}	
F(000)	1238	
Crystal size	0.14 x 0.13 x 0.09 mm^3	
Theta range for data collection	1.70 to 26.00°.	
Index ranges	-12<=h<=12, -18<=k<=18, -24<=l<=24	
Reflections collected	37053	
Independent reflections	5918 [R(int) = 0.1041]	
Completeness to theta = 26.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.957 and 0.934	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5918 / 0 / 394	
Goodness-of-fit on F^2	0.965	
Final R indices [I>2sigma(I)]	R1 = 0.0618, wR2 = 0.1507	
R indices (all data)	R1 = 0.1498, wR2 = 0.1730	
Largest diff. peak and hole	0.521 and -0.457 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 4b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	0	0	50(1)
S(100)	5636(2)	2661(1)	1203(1)	140(1)
N(100)	5508(3)	1064(2)	532(2)	55(1)
C(100)	5572(4)	1721(3)	817(2)	55(1)
O(16)	5143(3)	-433(2)	2658(1)	73(1)
N(11)	3679(3)	-320(2)	629(1)	47(1)
C(11)	3276(3)	-540(3)	1762(2)	42(1)
C(12)	4077(4)	-316(3)	1301(2)	47(1)
C(13)	2405(4)	-545(3)	394(2)	57(1)
C(14)	1527(4)	-759(3)	817(2)	66(1)
C(15)	1964(4)	-756(3)	1509(2)	56(1)
C(16)	3916(4)	-539(3)	2498(2)	48(1)
O(26)	-186(2)	622(2)	7274(1)	68(1)
N(21)	3086(3)	803(2)	9217(1)	52(1)
C(21)	1652(3)	977(3)	8135(2)	43(1)
C(22)	2527(4)	491(3)	8606(2)	49(1)
C(23)	2753(4)	1612(3)	9372(2)	62(1)
C(24)	1855(5)	2126(3)	8948(3)	83(2)
C(25)	1289(5)	1801(3)	8324(2)	72(1)
C(26)	1031(4)	608(3)	7458(2)	46(1)
N(31)	3139(3)	-647(2)	2954(1)	48(1)
N(32)	1864(3)	297(2)	7071(1)	49(1)
C(31)	3667(4)	-650(3)	3679(2)	53(1)
C(32)	2552(4)	-593(3)	4083(2)	51(1)
C(33)	3067(4)	-508(3)	4841(2)	56(1)
C(34)	1969(4)	-390(3)	5256(2)	52(1)
C(35)	2478(4)	-145(3)	5990(2)	53(1)
C(36)	1369(4)	-30(3)	6387(2)	54(1)
C(1A)	3360(8)	1794(4)	4070(5)	124(2)
C(2A)	2356(12)	1989(5)	4477(4)	131(3)
C(3A)	1088(10)	2172(4)	4139(4)	116(2)

C(4A)	-463(9)	2003(5)	1291(5)	135(3)
C(5A)	500(12)	1851(5)	883(4)	134(3)
C(6A)	1795(10)	1741(4)	1214(4)	119(2)
C(7A)	2953(9)	1785(4)	3353(4)	101(2)
C(8A)	1641(9)	1960(4)	3047(4)	104(2)
C(9A)	744(10)	2165(4)	3454(4)	112(2)
C(10A)	-49(9)	2060(4)	2016(4)	110(2)
C(11A)	1287(8)	1925(4)	2289(3)	95(2)
C(12A)	2201(9)	1773(4)	1895(4)	109(2)
C(13A)	-847(12)	2218(9)	2434(10)	111(4)
C(14A)	-452(14)	2286(8)	3072(9)	98(4)
C(13')	3386(13)	1632(8)	2311(9)	95(4)
C(14')	3704(13)	1596(8)	2957(9)	98(4)

Table 3. Bond lengths [Å] and angles [°] for 4b.

Cu(1)-N(100)#1	1.941(4)	C(3A)-C(9A)	1.353(9)
Cu(1)-N(100)	1.941(4)	C(4A)-C(5A)	1.400(10)
Cu(1)-N(11)	2.056(3)	C(4A)-C(10A)	1.440(10)
Cu(1)-N(11)#1	2.056(3)	C(5A)-C(6A)	1.372(10)
S(100)-C(100)	1.608(5)	C(6A)-C(12A)	1.352(9)
N(100)-C(100)	1.139(5)	C(7A)-C(14')	1.229(13)
O(16)-C(16)	1.240(4)	C(7A)-C(8A)	1.389(9)
N(11)-C(12)	1.331(4)	C(8A)-C(9A)	1.362(9)
N(11)-C(13)	1.339(5)	C(8A)-C(11A)	1.495(9)
C(11)-C(12)	1.378(4)	C(9A)-C(14A)	1.327(14)
C(11)-C(15)	1.376(5)	C(10A)-C(13A)	1.287(14)
C(11)-C(16)	1.499(5)	C(10A)-C(11A)	1.384(9)
C(13)-C(14)	1.374(5)	C(11A)-C(12A)	1.342(8)
C(14)-C(15)	1.376(5)	C(12A)-C(13')	1.352(14)
C(16)-N(31)	1.320(4)	C(13A)-C(14A)	1.273(17)
O(26)-C(26)	1.226(4)	C(13')-C(14')	1.276(16)
N(21)-C(23)	1.315(5)		
N(21)-C(22)	1.339(4)	N(100)#1-Cu(1)-N(100)	180.0(2)
C(21)-C(25)	1.367(6)	N(100)#1-Cu(1)-N(11)	90.19(12)
C(21)-C(22)	1.383(5)	N(100)-Cu(1)-N(11)	89.81(12)
C(21)-C(26)	1.496(5)	N(100)#1-Cu(1)-N(11)#1	89.81(12)
C(23)-C(24)	1.368(6)	N(100)-Cu(1)-N(11)#1	90.19(12)
C(24)-C(25)	1.369(6)	N(11)-Cu(1)-N(11)#1	180.0(2)
C(26)-N(32)	1.330(4)	C(100)-N(100)-Cu(1)	168.0(4)
N(31)-C(31)	1.454(4)	N(100)-C(100)-S(100)	178.3(4)
N(32)-C(36)	1.458(4)	C(12)-N(11)-C(13)	117.1(3)
C(31)-C(32)	1.508(5)	C(12)-N(11)-Cu(1)	120.2(3)
C(32)-C(33)	1.519(5)	C(13)-N(11)-Cu(1)	122.7(2)
C(33)-C(34)	1.515(5)	C(12)-C(11)-C(15)	117.5(3)
C(34)-C(35)	1.513(5)	C(12)-C(11)-C(16)	116.9(3)
C(35)-C(36)	1.501(5)	C(15)-C(11)-C(16)	125.6(3)
C(1A)-C(7A)	1.419(9)	N(11)-C(12)-C(11)	124.4(4)
C(1A)-C(2A)	1.446(10)	N(11)-C(13)-C(14)	122.5(3)
C(2A)-C(3A)	1.371(10)	C(13)-C(14)-C(15)	119.4(4)

C(14)-C(15)-C(11)	119.1(3)	C(5A)-C(4A)-C(10A)	119.2(8)
O(16)-C(16)-N(31)	122.4(3)	C(6A)-C(5A)-C(4A)	116.7(7)
O(16)-C(16)-C(11)	119.5(3)	C(12A)-C(6A)-C(5A)	125.0(8)
N(31)-C(16)-C(11)	118.1(3)	C(14')-C(7A)-C(8A)	114.6(10)
C(23)-N(21)-C(22)	117.0(4)	C(14')-C(7A)-C(1A)	123.6(12)
C(25)-C(21)-C(22)	117.7(4)	C(8A)-C(7A)-C(1A)	121.8(8)
C(25)-C(21)-C(26)	119.8(4)	C(9A)-C(8A)-C(7A)	118.1(8)
C(22)-C(21)-C(26)	122.3(4)	C(9A)-C(8A)-C(11A)	123.3(8)
N(21)-C(22)-C(21)	123.5(4)	C(7A)-C(8A)-C(11A)	118.6(8)
N(21)-C(23)-C(24)	123.3(4)	C(14A)-C(9A)-C(3A)	128.7(11)
C(23)-C(24)-C(25)	119.2(4)	C(14A)-C(9A)-C(8A)	109.3(9)
C(21)-C(25)-C(24)	119.1(4)	C(3A)-C(9A)-C(8A)	121.9(9)
O(26)-C(26)-N(32)	123.0(3)	C(13A)-C(10A)-C(11A)	117.3(11)
O(26)-C(26)-C(21)	120.3(3)	C(13A)-C(10A)-C(4A)	124.2(12)
N(32)-C(26)-C(21)	116.7(3)	C(11A)-C(10A)-C(4A)	118.5(7)
C(16)-N(31)-C(31)	122.1(3)	C(12A)-C(11A)-C(10A)	121.7(7)
C(26)-N(32)-C(36)	121.1(3)	C(12A)-C(11A)-C(8A)	122.4(8)
N(31)-C(31)-C(32)	110.9(3)	C(10A)-C(11A)-C(8A)	115.8(8)
C(31)-C(32)-C(33)	112.5(3)	C(11A)-C(12A)-C(6A)	118.7(8)
C(34)-C(33)-C(32)	113.6(3)	C(11A)-C(12A)-C(13')	107.4(9)
C(33)-C(34)-C(35)	113.8(3)	C(6A)-C(12A)-C(13')	133.8(11)
C(36)-C(35)-C(34)	112.6(3)	C(14A)-C(13A)-C(10A)	123.0(13)
N(32)-C(36)-C(35)	111.8(3)	C(13A)-C(14A)-C(9A)	131.1(13)
C(7A)-C(1A)-C(2A)	117.7(8)	C(14')-C(13')-C(12A)	131.7(13)
C(3A)-C(2A)-C(1A)	117.3(7)	C(7A)-C(14')-C(13')	124.8(14)
C(9A)-C(3A)-C(2A)	123.2(8)		

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for kblr080. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	64(1)	62(1)	28(1)	-9(1)	19(1)	-15(1)
S(100)	150(2)	100(1)	172(2)	-78(1)	32(1)	-5(1)
N(100)	67(2)	64(2)	36(2)	-7(2)	16(2)	-9(2)
C(100)	44(2)	74(3)	46(2)	-6(2)	8(2)	-2(2)
O(16)	35(2)	149(3)	36(2)	-1(2)	9(1)	-8(2)
N(11)	53(2)	61(2)	28(2)	-4(1)	14(2)	-8(2)
C(11)	38(2)	63(3)	27(2)	-5(2)	8(2)	-2(2)
C(12)	44(2)	71(3)	28(2)	-4(2)	12(2)	-5(2)
C(13)	61(3)	82(3)	28(2)	-6(2)	6(2)	-17(2)
C(14)	50(3)	112(4)	34(2)	-9(2)	3(2)	-25(3)
C(15)	46(2)	95(3)	30(2)	-7(2)	12(2)	-21(2)
C(16)	38(2)	78(3)	28(2)	0(2)	9(2)	-5(2)
O(26)	26(2)	139(3)	37(2)	-8(2)	4(1)	2(2)
N(21)	60(2)	67(2)	28(2)	-2(2)	4(2)	0(2)
C(21)	31(2)	72(3)	28(2)	0(2)	9(2)	5(2)
C(22)	52(2)	65(3)	30(2)	-5(2)	7(2)	4(2)
C(23)	58(3)	85(3)	41(2)	-20(2)	5(2)	0(3)
C(24)	81(4)	81(4)	77(3)	-25(3)	-8(3)	26(3)
C(25)	65(3)	79(3)	63(3)	-8(3)	-13(2)	23(3)
C(26)	36(2)	76(3)	26(2)	5(2)	7(2)	-1(2)
N(31)	31(2)	92(3)	23(2)	-3(2)	6(1)	-5(2)
N(32)	30(2)	87(2)	29(2)	-5(2)	3(1)	2(2)
C(31)	43(2)	91(3)	24(2)	2(2)	6(2)	4(2)
C(32)	41(2)	85(3)	27(2)	-1(2)	9(2)	-5(2)
C(33)	47(2)	96(3)	25(2)	4(2)	8(2)	6(2)
C(34)	39(2)	91(3)	27(2)	-2(2)	7(2)	-3(2)
C(35)	40(2)	88(3)	32(2)	-5(2)	9(2)	3(2)
C(36)	46(2)	88(3)	30(2)	-11(2)	8(2)	-6(2)
C(1A)	124(6)	79(4)	150(7)	5(5)	-23(6)	-15(4)
C(2A)	206(10)	89(5)	91(5)	-8(4)	8(6)	-34(6)
C(3A)	155(7)	97(5)	101(6)	-8(4)	41(5)	-16(5)

C(4A)	131(7)	122(6)	136(7)	21(5)	-17(6)	-29(5)
C(5A)	187(9)	125(6)	79(5)	-6(4)	-3(6)	-17(6)
C(6A)	169(8)	107(5)	84(5)	-15(4)	30(5)	1(5)
C(7A)	132(7)	78(4)	91(5)	-2(4)	17(5)	-20(4)
C(8A)	135(7)	52(3)	116(6)	-2(3)	0(5)	-18(4)
C(9A)	166(8)	74(4)	99(5)	-7(4)	34(6)	-15(4)
C(10A)	133(7)	87(4)	116(6)	11(4)	37(6)	-7(4)
C(11A)	116(6)	60(3)	99(5)	0(3)	-8(5)	-8(3)
C(12A)	138(7)	85(4)	103(6)	-10(4)	18(6)	-7(4)
C(13A)	50(7)	122(11)	163(14)	13(10)	27(10)	12(7)
C(14A)	69(9)	99(9)	120(11)	-5(8)	1(8)	14(7)
C(13')	80(9)	87(8)	114(11)	-7(8)	7(9)	-14(7)
C(14')	80(9)	84(8)	135(12)	-13(8)	29(10)	-15(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for kblr080.

	x	y	z	U(eq)
H(12)	4956	-150	1470	56
H(13)	2104	-556	-73	68
H(14)	645	-906	638	79
H(15)	1381	-897	1802	67
H(22)	2738	-83	8491	59
H(23)	3148	1846	9790	74
H(24)	1631	2688	9083	99
H(25)	666	2137	8032	86
H(31)	2293	-718	2818	58
H(32)	2709	288	7228	59
H(31A)	4267	-149	3791	63
H(31B)	4176	-1190	3798	63
H(32A)	2000	-1121	3999	61
H(32B)	1994	-84	3929	61
H(33A)	3579	-1035	4998	67
H(33B)	3668	-3	4920	67

H(34A)	1464	-939	5242	62
H(34B)	1362	70	5047	62
H(35A)	3080	-605	6201	64
H(35B)	2982	404	6006	64
H(36A)	716	385	6151	65
H(36B)	924	-595	6414	65
H(1A)	4241	1677	4270	148
H(2A)	2562	1991	4949	158
H(3A)	432	2307	4393	139
H(4A)	-1360	2066	1095	162
H(5A)	274	1826	412	161
H(6A)	2443	1636	949	143
H(13A)	-1755	2285	2262	133
H(14A)	-1117	2450	3313	118
H(13')	4100	1546	2085	114
H(14')	4566	1412	3141	118

Electronic Supplementary Material (ESI) for *CrystEngComm*

Table 1. Crystal data and structure refinement for (**5**).

Identification code	5	
Empirical formula	C52 H38 Cu N12 O4 S2	
Formula weight	1022.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1942(7) Å	α= 75.664(3)°.
	b = 10.0010(9) Å	β= 85.553(3)°.
	c = 14.8220(13) Å	γ = 85.294(3)°.
Volume	1170.81(18) $Å^3$	
Z	1	
Density (calculated)	1.450 gm/cm^3	
Absorption coefficient	0.618 mm^{-1}	
F(000)	527	
Crystal size	0.13 x 0.13 x 0.09 mm^3	
Theta range for data collection	1.42 to 26.00°.	
Index ranges	-10<=h<=9, -12<=k<=12, -18<=l<=18	
Reflections collected	14887	
Independent reflections	4555 [R(int) = 0.0496]	
Completeness to theta = 26.00°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.946 and 0.923	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4555 / 0 / 322	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1016	
R indices (all data)	R1 = 0.0833, wR2 = 0.1127	
Largest diff. peak and hole	0.322 and -0.405 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**5**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5000	0	5000	38(1)
S(100)	6679(1)	1259(1)	1911(1)	70(1)
N(100)	6095(3)	-49(3)	3778(2)	42(1)
C(100)	6351(3)	494(3)	2998(2)	37(1)
N(11)	2917(3)	-697(2)	4613(1)	32(1)
N(12)	814(3)	-361(2)	2473(1)	32(1)
C(11)	1131(3)	-801(2)	3432(2)	29(1)
C(12)	2504(3)	-361(3)	3720(2)	32(1)
C(13)	1937(3)	-1522(3)	5240(2)	37(1)
C(14)	547(3)	-1994(3)	5000(2)	39(1)
C(15)	116(3)	-1625(3)	4081(2)	36(1)
O(20)	252(3)	-2443(2)	2278(1)	46(1)
C(20)	421(3)	-1208(3)	1958(2)	30(1)
C(21)	221(3)	-550(2)	942(2)	27(1)
C(22)	1130(3)	521(3)	443(2)	32(1)
C(23)	-905(3)	-1073(3)	491(2)	32(1)
N(31)	4019(3)	2582(2)	4296(2)	41(1)
N(32)	1790(3)	4655(2)	2293(1)	34(1)
C(31)	2455(3)	4229(3)	3182(2)	31(1)
C(32)	3449(3)	3022(3)	3448(2)	36(1)
C(33)	3669(4)	3381(3)	4886(2)	48(1)
C(34)	2761(4)	4610(3)	4671(2)	56(1)
C(35)	2127(4)	5045(3)	3806(2)	47(1)
O(40)	1554(3)	2534(2)	2048(1)	50(1)
C(40)	1356(3)	3797(3)	1790(2)	33(1)
C(41)	632(3)	4463(3)	873(2)	30(1)
C(42)	980(3)	5782(3)	359(2)	35(1)
C(43)	-347(3)	3694(3)	506(2)	35(1)
N(200)	7885(5)	4469(4)	3196(2)	90(1)
C(200)	7123(5)	5199(4)	2649(2)	63(1)
C(201)	6216(4)	6141(3)	1937(2)	47(1)

C(202)	6106(4)	5843(4)	1090(2)	60(1)
C(203)	5316(4)	6797(4)	390(2)	67(1)
C(204)	4614(4)	8006(4)	549(3)	62(1)
C(205)	4704(4)	8288(4)	1401(3)	66(1)
C(206)	5500(4)	7372(4)	2090(2)	61(1)

Table 3. Bond lengths [Å] and angles [°] for (**5**).

Cu(1)-N(100)#1	1.968(2)	O(40)-C(40)	1.226(3)
Cu(1)-N(100)	1.968(2)	C(40)-C(41)	1.501(4)
Cu(1)-N(11)	2.067(2)	C(41)-C(43)	1.382(3)
Cu(1)-N(11)#1	2.067(2)	C(41)-C(42)	1.390(4)
S(100)-C(100)	1.616(3)	C(42)-C(43)#3	1.382(4)
N(100)-C(100)	1.160(3)	C(43)-C(42)#3	1.382(4)
N(11)-C(13)	1.342(3)	N(200)-C(200)	1.136(4)
N(11)-C(12)	1.346(3)	C(200)-C(201)	1.438(5)
N(12)-C(20)	1.345(3)	C(201)-C(202)	1.372(4)
N(12)-C(11)	1.418(3)	C(201)-C(206)	1.382(4)
C(11)-C(15)	1.376(3)	C(202)-C(203)	1.385(5)
C(11)-C(12)	1.375(3)	C(203)-C(204)	1.363(5)
C(13)-C(14)	1.372(4)	C(204)-C(205)	1.369(5)
C(14)-C(15)	1.385(4)	C(205)-C(206)	1.360(5)
O(20)-C(20)	1.223(3)		
C(20)-C(21)	1.503(3)	N(100)#1-Cu(1)-N(100)	180.0
C(21)-C(22)	1.379(3)	N(100)#1-Cu(1)-N(11)	90.22(9)
C(21)-C(23)	1.385(3)	N(100)-Cu(1)-N(11)	89.78(9)
C(22)-C(23)#2	1.379(3)	N(100)#1-Cu(1)-N(11)#1	89.78(9)
C(23)-C(22)#2	1.379(3)	N(100)-Cu(1)-N(11)#1	90.22(9)
N(31)-C(33)	1.324(3)	N(11)-Cu(1)-N(11)#1	180.0
N(31)-C(32)	1.333(3)	C(100)-N(100)-Cu(1)	148.9(2)
N(32)-C(40)	1.351(3)	N(100)-C(100)-S(100)	179.2(3)
N(32)-C(31)	1.418(3)	C(13)-N(11)-C(12)	117.3(2)
C(31)-C(35)	1.375(4)	C(13)-N(11)-Cu(1)	121.39(17)
C(31)-C(32)	1.389(4)	C(12)-N(11)-Cu(1)	121.31(17)
C(33)-C(34)	1.363(4)	C(20)-N(12)-C(11)	124.1(2)
C(34)-C(35)	1.377(4)	C(15)-C(11)-C(12)	119.1(2)

C(15)-C(11)-N(12)	122.9(2)	N(31)-C(33)-C(34)	123.6(3)
C(12)-C(11)-N(12)	118.0(2)	C(33)-C(34)-C(35)	119.1(3)
N(11)-C(12)-C(11)	123.3(2)	C(31)-C(35)-C(34)	118.5(3)
N(11)-C(13)-C(14)	122.4(2)	O(40)-C(40)-N(32)	122.8(2)
C(13)-C(14)-C(15)	119.9(3)	O(40)-C(40)-C(41)	120.5(2)
C(11)-C(15)-C(14)	118.0(3)	N(32)-C(40)-C(41)	116.7(2)
O(20)-C(20)-N(12)	123.3(2)	C(43)-C(41)-C(42)	119.0(2)
O(20)-C(20)-C(21)	121.0(2)	C(43)-C(41)-C(40)	118.1(2)
N(12)-C(20)-C(21)	115.7(2)	C(42)-C(41)-C(40)	122.9(2)
C(22)-C(21)-C(23)	119.3(2)	C(43)#3-C(42)-C(41)	120.0(2)
C(22)-C(21)-C(20)	122.9(2)	C(41)-C(43)-C(42)#3	121.0(2)
C(23)-C(21)-C(20)	117.8(2)	N(200)-C(200)-C(201)	177.8(4)
C(21)-C(22)-C(23)#2	120.2(2)	C(202)-C(201)-C(206)	119.6(3)
C(22)#2-C(23)-C(21)	120.5(2)	C(202)-C(201)-C(200)	120.0(3)
C(33)-N(31)-C(32)	117.4(2)	C(206)-C(201)-C(200)	120.3(3)
C(40)-N(32)-C(31)	125.3(2)	C(201)-C(202)-C(203)	119.5(3)
C(35)-C(31)-C(32)	118.3(2)	C(204)-C(203)-C(202)	120.3(3)
C(35)-C(31)-N(32)	119.2(2)	C(203)-C(204)-C(205)	119.9(3)
C(32)-C(31)-N(32)	122.5(2)	C(206)-C(205)-C(204)	120.5(3)
N(31)-C(32)-C(31)	122.9(2)	C(205)-C(206)-C(201)	120.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x,-y,-z #3 -x,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	37(1)	58(1)	19(1)	-8(1)	-5(1)	-10(1)
S(100)	81(1)	86(1)	33(1)	2(1)	12(1)	2(1)
N(100)	40(1)	60(2)	25(1)	-9(1)	-4(1)	-6(1)
C(100)	29(2)	50(2)	33(2)	-15(1)	-4(1)	1(1)
N(11)	35(1)	39(1)	20(1)	1(1)	-7(1)	-4(1)
N(12)	45(1)	26(1)	22(1)	2(1)	-15(1)	-3(1)
C(11)	33(1)	29(1)	22(1)	-2(1)	-7(1)	2(1)
C(12)	33(2)	36(2)	22(1)	2(1)	-5(1)	-4(1)

C(13)	45(2)	41(2)	22(1)	1(1)	-5(1)	-8(1)
C(14)	43(2)	48(2)	25(1)	-2(1)	-1(1)	-14(1)
C(15)	33(2)	42(2)	33(2)	-9(1)	-6(1)	-6(1)
O(20)	78(2)	28(1)	30(1)	2(1)	-15(1)	-7(1)
C(20)	34(2)	30(2)	27(1)	-4(1)	-8(1)	0(1)
C(21)	33(1)	27(1)	21(1)	-3(1)	-7(1)	4(1)
C(22)	37(2)	34(2)	26(1)	-5(1)	-13(1)	-4(1)
C(23)	38(2)	32(1)	25(1)	-3(1)	-6(1)	-7(1)
N(31)	44(1)	47(1)	31(1)	-8(1)	-14(1)	4(1)
N(32)	51(1)	25(1)	24(1)	1(1)	-12(1)	-1(1)
C(31)	37(2)	33(1)	23(1)	-2(1)	-6(1)	-5(1)
C(32)	39(2)	41(2)	30(2)	-11(1)	-9(1)	6(1)
C(33)	61(2)	53(2)	30(2)	-8(1)	-22(1)	-2(2)
C(34)	90(3)	48(2)	34(2)	-18(2)	-19(2)	7(2)
C(35)	69(2)	35(2)	38(2)	-9(1)	-19(2)	10(2)
O(40)	80(2)	26(1)	45(1)	-1(1)	-33(1)	1(1)
C(40)	36(2)	33(2)	28(1)	-5(1)	-8(1)	0(1)
C(41)	36(2)	30(1)	24(1)	-6(1)	-6(1)	2(1)
C(42)	43(2)	32(2)	31(2)	-8(1)	-10(1)	-7(1)
C(43)	47(2)	28(1)	27(1)	-1(1)	-7(1)	-3(1)
N(200)	112(3)	80(2)	63(2)	11(2)	-15(2)	4(2)
C(200)	75(3)	61(2)	48(2)	-2(2)	1(2)	-6(2)
C(201)	46(2)	54(2)	36(2)	0(2)	2(1)	-7(2)
C(202)	64(2)	61(2)	59(2)	-25(2)	-8(2)	9(2)
C(203)	61(2)	94(3)	51(2)	-24(2)	-12(2)	1(2)
C(204)	48(2)	72(2)	60(2)	-3(2)	-15(2)	3(2)
C(205)	62(2)	62(2)	74(3)	-17(2)	-9(2)	13(2)
C(206)	68(2)	70(2)	46(2)	-22(2)	-1(2)	5(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for (**5**).

	x	y	z	U(eq)
H(12)	876	502	2204	38
H(12A)	3181	196	3275	38
H(13)	2210	-1783	5859	44
H(14)	-106	-2562	5453	47
H(15)	-831	-1925	3909	43
H(22)	1898	871	738	38
H(23)	-1513	-1803	822	38
H(32)	1653	5529	2054	41
H(32A)	3729	2497	3014	44
H(33)	4063	3087	5479	57
H(34)	2573	5147	5103	67
H(35)	1489	5873	3646	56
H(42)	1640	6312	596	41
H(43)	-583	2810	845	42
H(202)	6559	5007	986	72
H(203)	5265	6610	-191	81
H(204)	4074	8640	79	74
H(205)	4218	9111	1509	79
H(206)	5562	7575	2665	73