Electronic Supplementary Information for Dalton Transactions

Supporting Information

Asymmetric Dinuclear Copper(I) Complexes of bis-(2-(2-pyridyl)ethyl)-2-(N-toluenesulfonylamino)ethylamine with Short Copper-Copper Distances.

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Table D.1.1. Crystal data and structure refinement for Cu(PETAEA)-CuCl.

Identification code	mn1530	
Empirical formula	C23 H27 Cl Cu2 N4 O2 S	
Formula weight	586.08	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.1111(6) Å	α= 68.776(3)°.
	b = 10.8627(7) Å	β= 84.102(3)°.
	c = 13.4127(9) Å	γ = 87.524(3)°.
Volume	1230.86(14) $Å^3$	
Z	2	
Density (calculated)	1.581 Mg/m^3	
Absorption coefficient	1.949 mm^{-1}	
F(000)	600	
Crystal size	0.34 x 0.10 x 0.06 mm^3	
Crystal color and habit	pale-yellow needle	
Diffractometer	Bruker SMART 1000	
Θ range for data collection	1.64 to 27.48°.	
Index ranges	-11≤h≤11, -12≤k≤14, -17≤l≤17	
Reflections collected	13798	
Independent reflections	5612 [R(int) = 0.0232]	
Observed reflections (I > 2σ(I))	4922	
Completeness to Θ = 27.48°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.892 and 0.557	
Solution method	SHELXS-97 (Sheldrick, 1990)	
Refinement method	SHELXL-97 (Sheldrick, 1997)	
Data / restraints / parameters	5612 / 0 / 299	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2σ(I)]	R1 = 0.0241, wR2 = 0.0599	
R indices (all data)	R1 = 0.0307, wR2 = 0.0646	
Largest diff. peak and hole	0.503 and -0.321 $e.Å^{-3}$	

Table D.1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Cu(PETAEA)-CuCl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	3820(1)	4455(1)	3148(1)	13(1)
Cu(2)	6489(1)	4386(1)	2106(1)	14(1)
Cl(1)	7978(1)	2837(1)	2136(1)	21(1)
S(1)	5812(1)	7015(1)	2240(1)	14(1)
O(1)	4657(1)	7918(1)	2364(1)	20(1)
O(2)	6678(1)	6378(1)	3135(1)	18(1)
N(1)	3782(2)	2554(1)	4035(1)	15(1)
N(2)	2564(2)	4477(1)	1854(1)	14(1)
N(3)	2366(2)	5447(1)	3866(1)	15(1)
N(4)	5181(2)	5852(1)	1924(1)	13(1)
C(1)	3713(2)	2165(2)	5116(2)	19(1)
C(2)	3317(2)	909(2)	5800(2)	27(1)
C(3)	2965(3)	-2(2)	5360(2)	35(1)
C(4)	3038(3)	381(2)	4255(2)	30(1)
C(5)	3451(2)	1664(2)	3601(2)	18(1)
C(6)	3510(2)	2121(2)	2395(2)	18(1)
C(7)	2284(2)	3112(2)	1911(2)	18(1)
C(8)	1151(2)	5201(2)	1846(1)	17(1)
C(9)	391(2)	4906(2)	2982(1)	17(1)
C(10)	962(2)	5682(2)	3594(1)	15(1)
C(11)	57(2)	6586(2)	3887(2)	19(1)
C(12)	583(2)	7229(2)	4502(2)	21(1)
C(13)	1990(2)	6939(2)	4827(2)	20(1)
C(14)	2846(2)	6062(2)	4481(1)	17(1)
C(15)	3545(2)	5172(2)	879(1)	15(1)
C(16)	4297(2)	6337(2)	982(1)	15(1)
C(17)	7028(2)	7942(2)	1117(1)	15(1)
C(18)	6672(2)	9235(2)	509(2)	22(1)
C(19)	7587(2)	9925(2)	-408(2)	25(1)
C(20)	8867(2)	9354(2)	-716(2)	18(1)
C(21)	9222(2)	8064(2)	-76(2)	17(1)
C(22)	8305(2)	7354(2)	830(1)	16(1)

C(23)	9835(2)	10098(2)	-1720(2)	25(1)

Table D.1.3. Bond lengths [Å] and angles [°] for Cu(PETAEA)-CuCl.

Cu(1)-N(1)	1.9755(15)	C(2)-C(3)	1.386(3)
Cu(1)-N(3)	2.0517(15)	C(3)-C(4)	1.383(3)
Cu(1)-N(4)	2.1158(14)	C(4)-C(5)	1.395(3)
Cu(1)-N(2)	2.1671(15)	C(5)-C(6)	1.506(3)
Cu(1)-Cu(2)	2.6903(3)	C(6)-C(7)	1.539(3)
Cu(2)-N(4)	1.9054(15)	C(8)-C(9)	1.534(2)
Cu(2)-Cl(1)	2.1060(5)	C(9)-C(10)	1.511(2)
S(1)-O(2)	1.4456(13)	C(10)-C(11)	1.393(3)
S(1)-O(1)	1.4454(13)	C(11)-C(12)	1.387(3)
S(1)-N(4)	1.6148(14)	C(12)-C(13)	1.383(3)
S(1)-C(17)	1.7788(18)	C(13)-C(14)	1.383(3)
N(1)-C(1)	1.350(2)	C(15)-C(16)	1.520(2)
N(1)-C(5)	1.355(2)	C(17)-C(18)	1.389(3)
N(2)-C(15)	1.477(2)	C(17)-C(22)	1.390(3)
N(2)-C(8)	1.478(2)	C(18)-C(19)	1.395(3)
N(2)-C(7)	1.488(2)	C(19)-C(20)	1.393(3)
N(3)-C(14)	1.347(2)	C(20)-C(21)	1.397(3)
N(3)-C(10)	1.355(2)	C(20)-C(23)	1.508(3)
N(4)-C(16)	1.487(2)	C(21)-C(22)	1.392(2)
C(1)-C(2)	1.379(3)		

N(1)-Cu(1)-N(3)	109.29(6)	Cl(1)-Cu(2)-Cu(1)	132.872(16)
N(1)-Cu(1)-N(4)	140.05(6)	O(2)-S(1)-O(1)	117.83(8)
N(3)-Cu(1)-N(4)	108.60(6)	O(2)-S(1)-N(4)	106.49(8)
N(1)-Cu(1)-N(2)	100.75(6)	O(1)-S(1)-N(4)	111.67(8)
N(3)-Cu(1)-N(2)	99.48(6)	O(2)-S(1)-C(17)	108.12(8)
N(4)-Cu(1)-N(2)	85.04(5)	O(1)-S(1)-C(17)	106.27(8)
N(1)-Cu(1)-Cu(2)	95.31(4)	N(4)-S(1)-C(17)	105.80(8)
N(3)-Cu(1)-Cu(2)	147.84(4)	C(1)-N(1)-C(5)	118.36(15)
N(4)-Cu(1)-Cu(2)	44.76(4)	C(1)-N(1)-Cu(1)	119.84(12)
N(2)-Cu(1)-Cu(2)	95.77(4)	C(5)-N(1)-Cu(1)	119.71(12)
N(4)-Cu(2)-Cl(1)	174.18(5)	C(15)-N(2)-C(8)	110.27(14)
N(4)-Cu(2)-Cu(1)	51.43(4)	C(15)-N(2)-C(7)	109.95(14)

C(8)-N(2)-C(7)	109.85(14)	N(2)-C(8)-C(9)	112.07(14)
C(15)-N(2)-Cu(1)	103.30(10)	C(10)-C(9)-C(8)	114.99(15)
C(8)-N(2)-Cu(1)	112.10(11)	N(3)-C(10)-C(11)	121.41(17)
C(7)-N(2)-Cu(1)	111.20(11)	N(3)-C(10)-C(9)	117.79(16)
C(14)-N(3)-C(10)	118.10(16)	C(11)-C(10)-C(9)	120.78(16)
C(14)-N(3)-Cu(1)	120.49(12)	C(12)-C(11)-C(10)	119.51(18)
C(10)-N(3)-Cu(1)	120.54(12)	C(13)-C(12)-C(11)	119.11(18)
C(16)-N(4)-S(1)	113.83(11)	C(12)-C(13)-C(14)	118.37(18)
C(16)-N(4)-Cu(2)	120.19(11)	N(3)-C(14)-C(13)	123.36(18)
S(1)-N(4)-Cu(2)	114.28(8)	N(2)-C(15)-C(16)	111.35(14)
C(16)-N(4)-Cu(1)	105.04(10)	N(4)-C(16)-C(15)	109.15(14)
S(1)-N(4)-Cu(1)	115.63(8)	C(18)-C(17)-C(22)	120.26(17)
Cu(2)-N(4)-Cu(1)	83.81(5)	C(18)-C(17)-S(1)	119.87(14)
N(1)-C(1)-C(2)	123.32(17)	C(22)-C(17)-S(1)	119.83(13)
C(1)-C(2)-C(3)	118.58(19)	C(17)-C(18)-C(19)	119.37(18)
C(4)-C(3)-C(2)	118.72(19)	C(20)-C(19)-C(18)	121.37(18)
C(3)-C(4)-C(5)	120.25(19)	C(19)-C(20)-C(21)	118.19(17)
N(1)-C(5)-C(4)	120.77(17)	C(19)-C(20)-C(23)	121.01(17)
N(1)-C(5)-C(6)	117.61(16)	C(21)-C(20)-C(23)	120.80(18)
C(4)-C(5)-C(6)	121.60(17)	C(22)-C(21)-C(20)	121.10(17)
C(5)-C(6)-C(7)	113.89(16)	C(17)-C(22)-C(21)	119.68(16)
N(2)-C(7)-C(6)	113.53(14)		

Table D.1.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Cu(PETAEA)-CuCl. 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)	14(1)	14(1)	12(1)	-5(1)	-1(1)	-2(1)
Cu(2)	13(1)	14(1)	16(1)	-5(1)	-1(1)	1(1)
Cl(1)	19(1)	18(1)	25(1)	-7(1)	-1(1)	4(1)
S(1)	13(1)	15(1)	15(1)	-6(1)	0(1)	-1(1)
O(1)	18(1)	18(1)	25(1)	-10(1)	3(1)	0(1)
O(2)	19(1)	22(1)	15(1)	-7(1)	-3(1)	-2(1)
N(1)	15(1)	15(1)	15(1)	-6(1)	-1(1)	0(1)
N(2)	14(1)	16(1)	13(1)	-6(1)	1(1)	-2(1)
N(3)	15(1)	16(1)	13(1)	-5(1)	1(1)	-1(1)
N(4)	13(1)	13(1)	13(1)	-5(1)	-2(1)	0(1)
C(1)	23(1)	19(1)	17(1)	-8(1)	-3(1)	-1(1)
C(2)	40(1)	22(1)	15(1)	-4(1)	-2(1)	-3(1)
C(3)	61(2)	18(1)	23(1)	-2(1)	-2(1)	-12(1)
C(4)	50(1)	17(1)	23(1)	-8(1)	-2(1)	-8(1)
C(5)	21(1)	17(1)	18(1)	-7(1)	-2(1)	0(1)
C(6)	23(1)	16(1)	16(1)	-8(1)	0(1)	-3(1)
C(7)	20(1)	20(1)	16(1)	-8(1)	-2(1)	-5(1)
C(8)	14(1)	23(1)	14(1)	-7(1)	-2(1)	-1(1)
C(9)	14(1)	23(1)	15(1)	-7(1)	0(1)	-2(1)
C(10)	16(1)	16(1)	11(1)	-2(1)	2(1)	-2(1)
C(11)	18(1)	19(1)	16(1)	-2(1)	2(1)	1(1)
C(12)	28(1)	15(1)	18(1)	-5(1)	6(1)	1(1)
C(13)	28(1)	17(1)	16(1)	-8(1)	4(1)	-5(1)
C(14)	18(1)	19(1)	14(1)	-5(1)	1(1)	-4(1)
C(15)	16(1)	19(1)	12(1)	-6(1)	0(1)	-3(1)
C(16)	14(1)	16(1)	13(1)	-4(1)	-2(1)	-1(1)
C(17)	14(1)	15(1)	15(1)	-6(1)	-2(1)	-3(1)
C(18)	19(1)	17(1)	28(1)	-7(1)	1(1)	2(1)
C(19)	27(1)	15(1)	26(1)	0(1)	-2(1)	1(1)
C(20)	22(1)	18(1)	17(1)	-6(1)	-2(1)	-7(1)
C(21)	14(1)	19(1)	18(1)	-8(1)	0(1)	-1(1)
C(22)	16(1)	14(1)	17(1)	-5(1)	-2(1)	-1(1)

C(23)	31(1)	22(1)	20(1)	-3(1)	3(1)	-8(1)

Table D.1.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for Cu(PETAEA)-CuCl.

	x	y	z	U(eq)
H(1)	3948	2789	5420	23
H(2)	3287	674	6556	32
H(3)	2679	-873	5810	42
H(4)	2805	-232	3939	36
H(6A)	3436	1342	2186	22
H(6B)	4479	2536	2083	22
H(7A)	2179	3132	1178	22
H(7B)	1338	2802	2351	22
H(8A)	486	4953	1411	20
H(8B)	1337	6161	1503	20
H(9A)	-678	5089	2929	21
H(9B)	508	3952	3400	21
H(11)	-913	6760	3667	23
H(12)	-15	7859	4696	25
H(13)	2359	7333	5278	24
H(14)	3822	5883	4688	21
H(15A)	2961	5490	250	18
H(15B)	4304	4548	757	18
H(16A)	4948	6785	321	18
H(16B)	3546	6981	1078	18
H(18)	5813	9646	716	26
H(19)	7332	10803	-832	30
H(21)	10104	7665	-262	20
H(22)	8550	6471	1249	19
H(23A)	9234	10739	-2237	38
H(23B)	10294	9475	-2037	38
H(23C)	10604	10563	-1539	38

Table D.2.1. Crystal data and structure refinement for Cu(PEMAEA)-CuCl.

Identification code	mn1588	
Empirical formula	C23 H27 Cl Cu2 N4 O3 S	
Formula weight	602.08	
Temperature	133(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.5617(12) Å	α= 92.187(8)°.
	b = 9.9875(10) Å	β= 91.981(9)°.
	c = 13.4720(12) Å	γ = 108.049(8)°.
Volume	1220.9(2) $Å^3$	
Z	2	
Density (calculated)	1.638 Mg/m^3	
Absorption coefficient	4.233 mm^{-1}	
F(000)	616	
Crystal size	0.56 x 0.40 x 0.08 mm^3	
Crystal color and habit	yellow plate	
Diffractometer	Siemens P4	
Θ range for data collection	3.29 to 56.09°.	
Index ranges	-2<=h<=10, -10<=k<=10, -14<=l<=14	
Reflections collected	4351	
Independent reflections	3203 [R(int) = 0.0479]	
Observed reflections (I > 2σ(I))	3044	
Completeness to Θ = 56.09°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7282 and 0.2003	
Solution method	SHELXS97 (Sheldrick, 1990)	
Refinement method	SHELXL97 (Sheldrick, 1997)	
Data / restraints / parameters	3203 / 0 / 309	
Goodness-of-fit on F^2	1.108	
Final R indices [I>2σ(I)]	R1 = 0.0628, wR2 = 0.1676	
R indices (all data)	R1 = 0.0643, wR2 = 0.1700	
Extinction coefficient	0.0086(10)	
Largest diff. peak and hole	1.642 and -1.446 $e.Å^{-3}$	

Table D.2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Cu(PEMAEA)-CuCl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	3924(1)	2456(1)	2208(1)	18(1)
Cu(2)	2836(1)	3628(1)	3672(1)	20(1)
Cl(1)	2584(1)	3217(1)	5181(1)	30(1)
S(1)	1263(1)	3779(1)	1814(1)	19(1)
O(1)	1243(3)	3636(3)	750(2)	28(1)
O(2)	272(3)	2648(3)	2318(2)	26(1)
O(3)	-18(4)	9136(3)	2627(3)	33(1)
N(1)	4649(4)	1275(4)	3126(3)	20(1)
N(2)	5925(4)	4158(4)	2046(3)	21(1)
N(3)	3632(4)	1559(4)	791(3)	24(1)
N(4)	2882(4)	4050(4)	2308(3)	19(1)
C(1)	4038(5)	-143(5)	3076(3)	24(1)
C(2)	4674(5)	-1035(5)	3534(4)	29(1)
C(3)	6013(6)	-475(5)	4029(4)	32(1)
C(4)	6664(5)	968(5)	4075(4)	30(1)
C(5)	5954(5)	1835(5)	3633(3)	21(1)
C(6)	6609(5)	3404(5)	3703(3)	26(1)
C(7)	7143(5)	4065(5)	2734(4)	26(1)
C(8)	6359(5)	4184(5)	1006(3)	24(1)
C(9)	6246(5)	2722(5)	556(4)	30(1)
C(10)	4735(5)	1836(5)	160(3)	25(1)
C(11)	4494(6)	1314(5)	-815(4)	33(1)
C(12)	3121(7)	489(5)	-1160(4)	40(1)
C(13)	2002(6)	178(5)	-506(4)	36(1)
C(14)	2294(5)	729(5)	453(4)	27(1)
C(15)	5524(5)	5430(4)	2320(3)	21(1)
C(16)	3980(5)	5304(5)	1919(3)	21(1)
C(17)	850(4)	5372(4)	2101(3)	19(1)
C(18)	499(5)	6120(5)	1327(3)	21(1)
C(19)	191(5)	7354(5)	1532(3)	23(1)
C(20)	236(5)	7864(5)	2512(4)	23(1)
C(21)	565(5)	7118(5)	3293(3)	23(1)

C(22)	854(4)	5853(4)	3072(3)	19(1)
C(23)	146(6)	9788(5)	3611(4)	32(1)

Table D.2.3. Bond lengths [Å] and angles [°] for Cu(PEMAEA)-CuCl.

Cu(1)-N(1)	1.990(4)	C(7)-H(7B)	0.9900
Cu(1)-N(3)	2.050(4)	C(8)-C(9)	1.530(7)
Cu(1)-N(4)	2.126(3)	C(8)-H(8A)	0.9900
Cu(1)-N(2)	2.154(3)	C(8)-H(8B)	0.9900
Cu(1)-Cu(2)	2.6572(8)	C(9)-C(10)	1.508(7)
Cu(2)-N(4)	1.900(3)	C(9)-H(9A)	0.9900
Cu(2)-Cl(1)	2.0960(12)	C(9)-H(9B)	0.9900
S(1)-O(1)	1.434(3)	C(10)-C(11)	1.380(7)
S(1)-O(2)	1.440(3)	C(11)-C(12)	1.370(8)
S(1)-N(4)	1.602(3)	C(11)-H(11)	0.9500
S(1)-C(17)	1.786(4)	C(12)-C(13)	1.377(8)
O(3)-C(20)	1.370(6)	C(12)-H(12)	0.9500
O(3)-C(23)	1.436(6)	C(13)-C(14)	1.370(7)
N(1)-C(5)	1.348(6)	C(13)-H(13)	0.9500
N(1)-C(1)	1.353(6)	C(14)-H(14)	0.9500
N(2)-C(15)	1.474(6)	C(15)-C(16)	1.519(6)
N(2)-C(8)	1.475(6)	C(15)-H(15A)	0.9900
N(2)-C(7)	1.491(6)	C(15)-H(15B)	0.9900
N(3)-C(10)	1.345(6)	C(16)-H(16A)	0.9900
N(3)-C(14)	1.344(6)	C(16)-H(16B)	0.9900
N(4)-C(16)	1.489(6)	C(17)-C(22)	1.376(6)
C(1)-C(2)	1.376(7)	C(17)-C(18)	1.396(6)
C(1)-H(1)	0.9500	C(18)-C(19)	1.373(7)
C(2)-C(3)	1.366(7)	C(18)-H(18)	0.9500
C(2)-H(2)	0.9500	C(19)-C(20)	1.391(7)
C(3)-C(4)	1.379(8)	C(19)-H(19)	0.9500
C(3)-H(3)	0.9500	C(20)-C(21)	1.393(7)
C(4)-C(5)	1.393(7)	C(21)-C(22)	1.398(6)
C(4)-H(4)	0.9500	C(21)-H(21)	0.9500
C(5)-C(6)	1.495(7)	C(22)-H(22)	0.9500
C(6)-C(7)	1.518(7)	C(23)-H(23A)	0.9800
C(6)-H(6A)	0.9900	C(23)-H(23B)	0.9800
C(6)-H(6B)	0.9900	C(23)-H(23C)	0.9800
C(7)-H(7A)	0.9900		

N(1)-Cu(1)-N(3)	109.96(14)	S(1)-N(4)-Cu(2)	112.00(19)
N(1)-Cu(1)-N(4)	137.90(14)	C(16)-N(4)-Cu(1)	103.7(2)
N(3)-Cu(1)-N(4)	109.94(14)	S(1)-N(4)-Cu(1)	120.5(2)
N(1)-Cu(1)-N(2)	100.50(14)	Cu(2)-N(4)-Cu(1)	82.39(13)
N(3)-Cu(1)-N(2)	99.39(15)	N(1)-C(1)-C(2)	123.1(4)
N(4)-Cu(1)-N(2)	85.75(13)	N(1)-C(1)-H(1)	118.5
N(1)-Cu(1)-Cu(2)	92.87(10)	C(2)-C(1)-H(1)	118.5
N(3)-Cu(1)-Cu(2)	147.76(11)	C(3)-C(2)-C(1)	118.9(4)
N(4)-Cu(1)-Cu(2)	45.14(9)	C(3)-C(2)-H(2)	120.5
N(2)-Cu(1)-Cu(2)	98.38(10)	C(1)-C(2)-H(2)	120.5
N(4)-Cu(2)-Cl(1)	174.12(11)	C(2)-C(3)-C(4)	118.8(4)
N(4)-Cu(2)-Cu(1)	52.46(10)	C(2)-C(3)-H(3)	120.6
Cl(1)-Cu(2)-Cu(1)	132.48(4)	C(4)-C(3)-H(3)	120.6
O(1)-S(1)-O(2)	117.30(19)	C(3)-C(4)-C(5)	120.3(5)
O(1)-S(1)-N(4)	111.89(19)	C(3)-C(4)-H(4)	119.8
O(2)-S(1)-N(4)	107.48(18)	C(5)-C(4)-H(4)	119.8
O(1)-S(1)-C(17)	106.12(19)	N(1)-C(5)-C(4)	120.6(4)
O(2)-S(1)-C(17)	108.90(19)	N(1)-C(5)-C(6)	118.0(4)
N(4)-S(1)-C(17)	104.35(19)	C(4)-C(5)-C(6)	121.4(4)
C(20)-O(3)-C(23)	118.0(4)	C(5)-C(6)-C(7)	115.0(4)
C(5)-N(1)-C(1)	118.2(4)	C(5)-C(6)-H(6A)	108.5
C(5)-N(1)-Cu(1)	119.5(3)	C(7)-C(6)-H(6A)	108.5
C(1)-N(1)-Cu(1)	120.5(3)	C(5)-C(6)-H(6B)	108.5
C(15)-N(2)-C(8)	110.4(3)	C(7)-C(6)-H(6B)	108.5
C(15)-N(2)-C(7)	109.6(3)	H(6A)-C(6)-H(6B)	107.5
C(8)-N(2)-C(7)	110.8(3)	N(2)-C(7)-C(6)	113.2(4)
C(15)-N(2)-Cu(1)	103.7(2)	N(2)-C(7)-H(7A)	108.9
C(8)-N(2)-Cu(1)	110.2(3)	C(6)-C(7)-H(7A)	108.9
C(7)-N(2)-Cu(1)	111.9(3)	N(2)-C(7)-H(7B)	108.9
C(10)-N(3)-C(14)	118.2(4)	C(6)-C(7)-H(7B)	108.9
C(10)-N(3)-Cu(1)	121.7(3)	H(7A)-C(7)-H(7B)	107.7
C(14)-N(3)-Cu(1)	120.0(3)	N(2)-C(8)-C(9)	113.0(4)
C(16)-N(4)-S(1)	112.3(3)	N(2)-C(8)-H(8A)	109.0
C(16)-N(4)-Cu(2)	123.1(3)	C(9)-C(8)-H(8A)	109.0

N(2)-C(8)-H(8B)	109.0	N(4)-C(16)-C(15)	110.6(3)
C(9)-C(8)-H(8B)	109.0	N(4)-C(16)-H(16A)	109.5
H(8A)-C(8)-H(8B)	107.8	C(15)-C(16)-H(16A)	109.5
C(10)-C(9)-C(8)	115.8(4)	N(4)-C(16)-H(16B)	109.5
C(10)-C(9)-H(9A)	108.3	C(15)-C(16)-H(16B)	109.5
C(8)-C(9)-H(9A)	108.3	H(16A)-C(16)-H(16B)	108.1
C(10)-C(9)-H(9B)	108.3	C(22)-C(17)-C(18)	120.0(4)
C(8)-C(9)-H(9B)	108.3	C(22)-C(17)-S(1)	120.7(3)
H(9A)-C(9)-H(9B)	107.4	C(18)-C(17)-S(1)	119.2(3)
N(3)-C(10)-C(11)	121.1(4)	C(19)-C(18)-C(17)	120.1(4)
N(3)-C(10)-C(9)	117.9(4)	C(19)-C(18)-H(18)	119.9
C(11)-C(10)-C(9)	121.0(4)	C(17)-C(18)-H(18)	119.9
C(12)-C(11)-C(10)	120.4(5)	C(18)-C(19)-C(20)	120.0(4)
C(12)-C(11)-H(11)	119.8	C(18)-C(19)-H(19)	120.0
C(10)-C(11)-H(11)	119.8	C(20)-C(19)-H(19)	120.0
C(11)-C(12)-C(13)	118.4(5)	O(3)-C(20)-C(19)	115.0(4)
C(11)-C(12)-H(12)	120.8	O(3)-C(20)-C(21)	124.5(4)
C(13)-C(12)-H(12)	120.8	C(19)-C(20)-C(21)	120.5(4)
C(14)-C(13)-C(12)	119.0(5)	C(20)-C(21)-C(22)	118.8(4)
C(14)-C(13)-H(13)	120.5	C(20)-C(21)-H(21)	120.6
C(12)-C(13)-H(13)	120.5	C(22)-C(21)-H(21)	120.6
N(3)-C(14)-C(13)	122.9(5)	C(17)-C(22)-C(21)	120.5(4)
N(3)-C(14)-H(14)	118.5	C(17)-C(22)-H(22)	119.7
C(13)-C(14)-H(14)	118.5	C(21)-C(22)-H(22)	119.7
N(2)-C(15)-C(16)	111.3(4)	O(3)-C(23)-H(23A)	109.5
N(2)-C(15)-H(15A)	109.4	O(3)-C(23)-H(23B)	109.5
C(16)-C(15)-H(15A)	109.4	H(23A)-C(23)-H(23B)	109.5
N(2)-C(15)-H(15B)	109.4	O(3)-C(23)-H(23C)	109.5
C(16)-C(15)-H(15B)	109.4	H(23A)-C(23)-H(23C)	109.5
H(15A)-C(15)-H(15B)	108.0	H(23B)-C(23)-H(23C)	109.5

Table D.2.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Cu(PEMAEA)-CuCl. 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)	16(1)	20(1)	18(1)	1(1)	1(1)	4(1)
Cu(2)	21(1)	22(1)	16(1)	2(1)	2(1)	6(1)
Cl(1)	46(1)	27(1)	17(1)	4(1)	5(1)	12(1)
S(1)	17(1)	21(1)	19(1)	-2(1)	-3(1)	6(1)
O(1)	33(2)	33(2)	22(2)	-8(1)	-7(1)	16(2)
O(2)	17(2)	23(2)	36(2)	1(1)	-3(1)	1(1)
O(3)	47(2)	24(2)	32(2)	-5(1)	-5(2)	17(2)
N(1)	22(2)	25(2)	15(2)	-2(2)	0(2)	7(2)
N(2)	12(2)	22(2)	27(2)	1(2)	3(2)	4(2)
N(3)	30(2)	24(2)	19(2)	0(2)	4(2)	12(2)
N(4)	18(2)	22(2)	19(2)	2(2)	-1(2)	8(2)
C(1)	25(2)	26(3)	19(2)	-4(2)	7(2)	4(2)
C(2)	37(3)	23(2)	28(3)	2(2)	9(2)	10(2)
C(3)	45(3)	33(3)	26(3)	6(2)	4(2)	23(2)
C(4)	29(3)	39(3)	23(3)	3(2)	0(2)	13(2)
C(5)	19(2)	29(2)	16(2)	2(2)	2(2)	9(2)
C(6)	23(2)	26(2)	28(3)	-3(2)	-9(2)	8(2)
C(7)	14(2)	26(2)	38(3)	1(2)	-1(2)	6(2)
C(8)	18(2)	25(2)	26(3)	6(2)	9(2)	2(2)
C(9)	29(3)	33(3)	30(3)	1(2)	11(2)	13(2)
C(10)	33(3)	23(2)	23(3)	2(2)	8(2)	16(2)
C(11)	51(3)	26(3)	25(3)	5(2)	15(2)	16(2)
C(12)	69(4)	31(3)	23(3)	-3(2)	-2(3)	22(3)
C(13)	44(3)	33(3)	36(3)	-6(2)	-12(2)	21(2)
C(14)	25(2)	26(2)	29(3)	-10(2)	-5(2)	6(2)
C(15)	19(2)	17(2)	23(2)	3(2)	3(2)	2(2)
C(16)	24(2)	20(2)	22(2)	3(2)	5(2)	10(2)
C(17)	11(2)	21(2)	21(2)	-3(2)	0(2)	1(2)
C(18)	16(2)	22(2)	23(2)	-1(2)	-2(2)	1(2)
C(19)	19(2)	24(2)	23(2)	5(2)	-6(2)	3(2)
C(20)	13(2)	18(2)	35(3)	2(2)	0(2)	1(2)
C(21)	15(2)	26(2)	24(2)	-2(2)	3(2)	3(2)

C(22)	14(2)	23(2)	22(2)	5(2)	2(2)	6(2)
C(23)	35(3)	24(3)	38(3)	-2(2)	10(2)	9(2)

Table D.2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for Cu(PEMAEA)-CuCl.

	x	y	z	U(eq)
H(1)	3128	-543	2708	29
H(2)	4190	-2023	3505	35
H(3)	6487	-1070	4337	38
H(4)	7601	1372	4409	36
H(6A)	7450	3660	4199	31
H(6B)	5863	3816	3954	31
H(7A)	7833	5026	2885	31
H(7B)	7692	3502	2396	31
H(8A)	7386	4807	975	29
H(8B)	5720	4588	601	29
H(9A)	6929	2841	6	36
H(9B)	6588	2197	1070	36
H(11)	5286	1528	-1250	39
H(12)	2944	141	-1834	48
H(13)	1042	-410	-717	43
H(14)	1515	515	899	33
H(15A)	6238	6263	2049	25
H(15B)	5576	5572	3053	25
H(16A)	3737	6166	2120	25
H(16B)	3940	5216	1184	25
H(18)	473	5775	658	26
H(19)	-53	7859	1005	27
H(21)	593	7462	3963	27
H(22)	1056	5321	3597	23
H(23A)	-40	10697	3584	48
H(23B)	1149	9936	3883	48
H(23C)	-561	9174	4038	48

Table D.3.1. Crystal data and structure refinement for Cu(PENAEA)-CuCl.

Identification code	mn1643	
Empirical formula	C22 H24 Cl Cu2 N5 O4 S	
Formula weight	617.05	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.9933(9) Å	α= 94.085(3)°.
	b = 10.8437(11) Å	β= 98.630(4)°.
	c = 26.491(3) Å	γ = 92.039(3)°.
Volume	2544.9(4) $Å^3$	
Z	4	
Density (calculated)	1.611 Mg/m^3	
Absorption coefficient	1.897 mm^{-1}	
F(000)	1256	
Crystal size	0.64 x 0.13 x 0.06 mm^3	
Crystal color and habit	red-brown needle	
Diffractometer	Bruker SMART 1000	
Θ range for data collection	1.56 to 27.48°.	
Index ranges	-11≤h≤11, -14≤k≤14, -34≤l≤34	
Reflections collected	28321	
Independent reflections	11643 [R(int) = 0.0251]	
Observed reflections (I > 2σ(I))	9820	
Completeness to Θ = 27.5°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.895 and 0.377	
Solution method	SHELXS97 (Sheldrick, 1990)	
Refinement method	SHELXL97 (Sheldrick, 1997) Full-matrix least-squares on F^2	
Data / restraints / parameters	11643 / 0 / 631	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2σ(I)]	R1 = 0.0270, wR2 = 0.0657	
R indices (all data)	R1 = 0.0366, wR2 = 0.0707	
Largest diff. peak and hole	0.510 and -0.339 $e.Å^{-3}$	

Table D.3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Cu(PENAEA)-CuCl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	2220(1)	5810(1)	1000(1)	14(1)
Cu(2)	-106(1)	6091(1)	1512(1)	14(1)
Cl(1)	-1401(1)	7656(1)	1588(1)	23(1)
S(1)	222(1)	3470(1)	1152(1)	14(1)
O(1)	1263(2)	2560(1)	1024(1)	21(1)
O(2)	-802(2)	3918(1)	739(1)	18(1)
O(3)	-4023(2)	-134(1)	2367(1)	27(1)
O(4)	-5359(2)	1488(2)	2276(1)	27(1)
N(1)	2021(2)	7540(2)	814(1)	14(1)
N(2)	3894(2)	6029(2)	1672(1)	14(1)
N(3)	3190(2)	4662(2)	521(1)	15(1)
N(4)	1052(2)	4663(2)	1484(1)	13(1)
N(5)	-4213(2)	925(2)	2242(1)	21(1)
C(1)	1562(2)	7778(2)	323(1)	19(1)
C(2)	1568(3)	8961(2)	158(1)	24(1)
C(3)	2066(3)	9947(2)	511(1)	25(1)
C(4)	2555(3)	9713(2)	1015(1)	21(1)
C(5)	2523(2)	8503(2)	1159(1)	15(1)
C(6)	3026(2)	8223(2)	1706(1)	16(1)
C(7)	4347(2)	7360(2)	1787(1)	16(1)
C(8)	5213(2)	5306(2)	1585(1)	17(1)
C(9)	5601(2)	5360(2)	1042(1)	18(1)
C(10)	4678(2)	4478(2)	640(1)	17(1)
C(11)	5350(3)	3520(2)	392(1)	21(1)
C(12)	4486(3)	2756(2)	7(1)	23(1)
C(13)	2976(3)	2976(2)	-129(1)	21(1)
C(14)	2376(2)	3926(2)	138(1)	18(1)
C(15)	3198(2)	5544(2)	2095(1)	15(1)
C(16)	2213(2)	4381(2)	1915(1)	16(1)
C(17)	-947(2)	2721(2)	1541(1)	15(1)
C(18)	-1026(3)	1431(2)	1523(1)	21(1)
C(19)	-2073(3)	833(2)	1769(1)	22(1)

C(20)	-3003(2)	1549(2)	2025(1)	17(1)
C(21)	-2901(2)	2826(2)	2069(1)	19(1)
C(22)	-1855(2)	3414(2)	1818(1)	18(1)
Cu(3)	2900(1)	10499(1)	3975(1)	13(1)
Cu(4)	5305(1)	10616(1)	3515(1)	13(1)
Cl(2)	6752(1)	12156(1)	3456(1)	20(1)
S(2)	4730(1)	8119(1)	3863(1)	13(1)
O(5)	3599(2)	7233(1)	3964(1)	19(1)
O(6)	5724(2)	8726(1)	4297(1)	18(1)
O(7)	10240(2)	5994(2)	2702(1)	31(1)
O(8)	9465(2)	4263(2)	2959(1)	30(1)
N(6)	3159(2)	12297(2)	4160(1)	14(1)
N(7)	1277(2)	10434(2)	3289(1)	13(1)
N(8)	1825(2)	9533(2)	4449(1)	15(1)
N(9)	4033(2)	9178(2)	3522(1)	12(1)
N(10)	9353(2)	5371(2)	2900(1)	21(1)
C(23)	3505(2)	12728(2)	4658(1)	19(1)
C(24)	3403(3)	13949(2)	4825(1)	23(1)
C(25)	2932(3)	14788(2)	4468(1)	23(1)
C(26)	2571(2)	14360(2)	3957(1)	20(1)
C(27)	2692(2)	13114(2)	3811(1)	15(1)
C(28)	2297(2)	12617(2)	3258(1)	15(1)
C(29)	916(2)	11705(2)	3152(1)	16(1)
C(30)	-101(2)	9735(2)	3371(1)	15(1)
C(31)	-518(2)	10009(2)	3906(1)	17(1)
C(32)	318(2)	9303(2)	4323(1)	15(1)
C(33)	-450(2)	8466(2)	4581(1)	21(1)
C(34)	338(3)	7874(2)	4978(1)	23(1)
C(35)	1872(2)	8143(2)	5116(1)	18(1)
C(36)	2561(2)	8964(2)	4841(1)	17(1)
C(37)	1976(2)	9782(2)	2879(1)	15(1)
C(38)	2880(2)	8713(2)	3081(1)	15(1)
C(39)	5933(2)	7250(2)	3507(1)	14(1)
C(40)	6184(2)	6030(2)	3621(1)	18(1)
C(41)	7286(3)	5394(2)	3412(1)	21(1)
C(42)	8086(2)	5996(2)	3087(1)	17(1)

C(43)	7780(2)	7168(2)	2937(1)	16(1)
C(44)	6694(2)	7803(2)	3156(1)	14(1)

Table D.3.3. Bond lengths [Å] and angles [°] for Cu(PENAEA)-CuCl.

Cu(1)-N(1)	1.9797(17)	C(7)-H(7A)	0.9900
Cu(1)-N(3)	2.0264(17)	C(7)-H(7B)	0.9900
Cu(1)-N(2)	2.1456(16)	C(8)-C(9)	1.533(3)
Cu(1)-N(4)	2.1980(16)	C(8)-H(8A)	0.9900
Cu(1)-Cu(2)	2.6730(4)	C(8)-H(8B)	0.9900
Cu(2)-N(4)	1.8988(17)	C(9)-C(10)	1.508(3)
Cu(2)-Cl(1)	2.1068(6)	C(9)-H(9A)	0.9900
S(1)-O(1)	1.4417(15)	C(9)-H(9B)	0.9900
S(1)-O(2)	1.4456(15)	C(10)-C(11)	1.393(3)
S(1)-N(4)	1.6039(17)	C(11)-C(12)	1.386(3)
S(1)-C(17)	1.791(2)	C(11)-H(11A)	0.9500
O(3)-N(5)	1.228(2)	C(12)-C(13)	1.386(3)
O(4)-N(5)	1.228(2)	C(12)-H(12A)	0.9500
N(1)-C(1)	1.351(3)	C(13)-C(14)	1.379(3)
N(1)-C(5)	1.354(3)	C(13)-H(13A)	0.9500
N(2)-C(15)	1.482(2)	C(14)-H(14A)	0.9500
N(2)-C(8)	1.482(3)	C(15)-C(16)	1.520(3)
N(2)-C(7)	1.483(3)	C(15)-H(15A)	0.9900
N(3)-C(14)	1.350(3)	C(15)-H(15B)	0.9900
N(3)-C(10)	1.354(3)	C(16)-H(16A)	0.9900
N(4)-C(16)	1.485(2)	C(16)-H(16B)	0.9900
N(5)-C(20)	1.471(3)	C(17)-C(22)	1.385(3)
C(1)-C(2)	1.384(3)	C(17)-C(18)	1.394(3)
C(1)-H(1B)	0.9500	C(18)-C(19)	1.390(3)
C(2)-C(3)	1.385(3)	C(18)-H(18A)	0.9500
C(2)-H(2B)	0.9500	C(19)-C(20)	1.380(3)
C(3)-C(4)	1.384(3)	C(19)-H(19A)	0.9500
C(3)-H(3A)	0.9500	C(20)-C(21)	1.380(3)
C(4)-C(5)	1.392(3)	C(21)-C(22)	1.391(3)
C(4)-H(4A)	0.9500	C(21)-H(21A)	0.9500
C(5)-C(6)	1.509(3)	C(22)-H(22A)	0.9500
C(6)-C(7)	1.537(3)	Cu(3)-N(6)	1.9730(17)
C(6)-H(6A)	0.9900	Cu(3)-N(8)	2.0223(16)
C(6)-H(6B)	0.9900	Cu(3)-N(7)	2.1485(16)

Cu(3)-N(9)	2.1800(16)	C(29)-H(29A)	0.9900
Cu(3)-Cu(4)	2.6395(4)	C(29)-H(29B)	0.9900
Cu(4)-N(9)	1.9030(16)	C(30)-C(31)	1.532(3)
Cu(4)-Cl(2)	2.1100(6)	C(30)-H(30A)	0.9900
S(2)-O(5)	1.4418(15)	C(30)-H(30B)	0.9900
S(2)-O(6)	1.4488(15)	C(31)-C(32)	1.512(3)
S(2)-N(9)	1.5998(16)	C(31)-H(31A)	0.9900
S(2)-C(39)	1.788(2)	C(31)-H(31B)	0.9900
O(7)-N(10)	1.227(2)	C(32)-C(33)	1.397(3)
O(8)-N(10)	1.227(2)	C(33)-C(34)	1.388(3)
N(6)-C(23)	1.354(3)	C(33)-H(33A)	0.9500
N(6)-C(27)	1.358(2)	C(34)-C(35)	1.389(3)
N(7)-C(30)	1.482(2)	C(34)-H(34A)	0.9500
N(7)-C(37)	1.484(2)	C(35)-C(36)	1.377(3)
N(7)-C(29)	1.485(2)	C(35)-H(35A)	0.9500
N(8)-C(36)	1.346(3)	C(36)-H(36A)	0.9500
N(8)-C(32)	1.356(3)	C(37)-C(38)	1.522(3)
N(9)-C(38)	1.486(2)	C(37)-H(37A)	0.9900
N(10)-C(42)	1.476(3)	C(37)-H(37B)	0.9900
C(23)-C(24)	1.376(3)	C(38)-H(38A)	0.9900
C(23)-H(23A)	0.9500	C(38)-H(38B)	0.9900
C(24)-C(25)	1.390(3)	C(39)-C(44)	1.391(3)
C(24)-H(24A)	0.9500	C(39)-C(40)	1.396(3)
C(25)-C(26)	1.386(3)	C(40)-C(41)	1.386(3)
C(25)-H(25A)	0.9500	C(40)-H(40A)	0.9500
C(26)-C(27)	1.391(3)	C(41)-C(42)	1.385(3)
C(26)-H(26A)	0.9500	C(41)-H(41A)	0.9500
C(27)-C(28)	1.509(3)	C(42)-C(43)	1.383(3)
C(28)-C(29)	1.539(3)	C(43)-C(44)	1.389(3)
C(28)-H(28A)	0.9900	C(43)-H(43A)	0.9500
C(28)-H(28B)	0.9900	C(44)-H(44A)	0.9500

N(1)-Cu(1)-N(3)	116.30(7)	N(1)-Cu(1)-N(4)	133.03(6)
N(1)-Cu(1)-N(2)	101.77(7)	N(3)-Cu(1)-N(4)	107.91(6)
N(3)-Cu(1)-N(2)	102.61(7)	N(2)-Cu(1)-N(4)	82.60(6)

N(1)-Cu(1)-Cu(2)	88.58(5)	C(2)-C(1)-H(1B)	118.5
N(3)-Cu(1)-Cu(2)	145.34(5)	C(1)-C(2)-C(3)	118.7(2)
N(2)-Cu(1)-Cu(2)	94.70(4)	C(1)-C(2)-H(2B)	120.7
N(4)-Cu(1)-Cu(2)	44.57(4)	C(3)-C(2)-H(2B)	120.7
N(4)-Cu(2)-Cl(1)	176.67(5)	C(4)-C(3)-C(2)	118.8(2)
N(4)-Cu(2)-Cu(1)	54.33(5)	C(4)-C(3)-H(3A)	120.6
Cl(1)-Cu(2)-Cu(1)	128.351(19)	C(2)-C(3)-H(3A)	120.6
O(1)-S(1)-O(2)	117.88(9)	C(3)-C(4)-C(5)	119.9(2)
O(1)-S(1)-N(4)	112.53(9)	C(3)-C(4)-H(4A)	120.0
O(2)-S(1)-N(4)	106.98(9)	C(5)-C(4)-H(4A)	120.0
O(1)-S(1)-C(17)	105.42(9)	N(1)-C(5)-C(4)	121.29(18)
O(2)-S(1)-C(17)	105.47(9)	N(1)-C(5)-C(6)	117.67(17)
N(4)-S(1)-C(17)	107.95(9)	C(4)-C(5)-C(6)	121.04(18)
C(1)-N(1)-C(5)	118.27(17)	C(5)-C(6)-C(7)	115.22(16)
C(1)-N(1)-Cu(1)	120.18(14)	C(5)-C(6)-H(6A)	108.5
C(5)-N(1)-Cu(1)	120.99(13)	C(7)-C(6)-H(6A)	108.5
C(15)-N(2)-C(8)	109.99(15)	C(5)-C(6)-H(6B)	108.5
C(15)-N(2)-C(7)	110.70(15)	C(7)-C(6)-H(6B)	108.5
C(8)-N(2)-C(7)	110.47(15)	H(6A)-C(6)-H(6B)	107.5
C(15)-N(2)-Cu(1)	106.85(12)	N(2)-C(7)-C(6)	113.75(16)
C(8)-N(2)-Cu(1)	109.45(11)	N(2)-C(7)-H(7A)	108.8
C(7)-N(2)-Cu(1)	109.31(12)	C(6)-C(7)-H(7A)	108.8
C(14)-N(3)-C(10)	118.27(18)	N(2)-C(7)-H(7B)	108.8
C(14)-N(3)-Cu(1)	122.40(14)	C(6)-C(7)-H(7B)	108.8
C(10)-N(3)-Cu(1)	118.41(13)	H(7A)-C(7)-H(7B)	107.7
C(16)-N(4)-S(1)	114.64(13)	N(2)-C(8)-C(9)	113.20(16)
C(16)-N(4)-Cu(2)	122.20(13)	N(2)-C(8)-H(8A)	108.9
S(1)-N(4)-Cu(2)	115.74(9)	C(9)-C(8)-H(8A)	108.9
C(16)-N(4)-Cu(1)	105.88(12)	N(2)-C(8)-H(8B)	108.9
S(1)-N(4)-Cu(1)	110.45(8)	C(9)-C(8)-H(8B)	108.9
Cu(2)-N(4)-Cu(1)	81.10(6)	H(8A)-C(8)-H(8B)	107.8
O(3)-N(5)-O(4)	124.41(18)	C(10)-C(9)-C(8)	115.19(17)
O(3)-N(5)-C(20)	117.83(18)	C(10)-C(9)-H(9A)	108.5
O(4)-N(5)-C(20)	117.74(17)	C(8)-C(9)-H(9A)	108.5
N(1)-C(1)-C(2)	123.00(19)	C(10)-C(9)-H(9B)	108.5
N(1)-C(1)-H(1B)	118.5	C(8)-C(9)-H(9B)	108.5

H(9A)-C(9)-H(9B)	107.5	C(18)-C(19)-H(19A)	121.0
N(3)-C(10)-C(11)	121.31(19)	C(19)-C(20)-C(21)	123.42(19)
N(3)-C(10)-C(9)	117.95(18)	C(19)-C(20)-N(5)	118.44(18)
C(11)-C(10)-C(9)	120.73(19)	C(21)-C(20)-N(5)	118.08(19)
C(12)-C(11)-C(10)	119.5(2)	C(20)-C(21)-C(22)	117.86(19)
C(12)-C(11)-H(11A)	120.3	C(20)-C(21)-H(21A)	121.1
C(10)-C(11)-H(11A)	120.3	C(22)-C(21)-H(21A)	121.1
C(13)-C(12)-C(11)	119.2(2)	C(17)-C(22)-C(21)	120.06(19)
C(13)-C(12)-H(12A)	120.4	C(17)-C(22)-H(22A)	120.0
C(11)-C(12)-H(12A)	120.4	C(21)-C(22)-H(22A)	120.0
C(14)-C(13)-C(12)	118.3(2)	N(6)-Cu(3)-N(8)	114.99(7)
C(14)-C(13)-H(13A)	120.8	N(6)-Cu(3)-N(7)	101.45(6)
C(12)-C(13)-H(13A)	120.8	N(8)-Cu(3)-N(7)	102.90(7)
N(3)-C(14)-C(13)	123.3(2)	N(6)-Cu(3)-N(9)	134.58(7)
N(3)-C(14)-H(14A)	118.3	N(8)-Cu(3)-N(9)	107.56(6)
C(13)-C(14)-H(14A)	118.3	N(7)-Cu(3)-N(9)	83.32(6)
N(2)-C(15)-C(16)	111.55(15)	N(6)-Cu(3)-Cu(4)	89.46(5)
N(2)-C(15)-H(15A)	109.3	N(8)-Cu(3)-Cu(4)	144.65(5)
C(16)-C(15)-H(15A)	109.3	N(7)-Cu(3)-Cu(4)	96.19(4)
N(2)-C(15)-H(15B)	109.3	N(9)-Cu(3)-Cu(4)	45.28(4)
C(16)-C(15)-H(15B)	109.3	N(9)-Cu(4)-Cl(2)	175.86(5)
H(15A)-C(15)-H(15B)	108.0	N(9)-Cu(4)-Cu(3)	54.48(5)
N(4)-C(16)-C(15)	108.76(15)	Cl(2)-Cu(4)-Cu(3)	129.130(19)
N(4)-C(16)-H(16A)	109.9	O(5)-S(2)-O(6)	117.75(9)
C(15)-C(16)-H(16A)	109.9	O(5)-S(2)-N(9)	112.53(9)
N(4)-C(16)-H(16B)	109.9	O(6)-S(2)-N(9)	107.28(8)
C(15)-C(16)-H(16B)	109.9	O(5)-S(2)-C(39)	105.26(9)
H(16A)-C(16)-H(16B)	108.3	O(6)-S(2)-C(39)	105.08(9)
C(22)-C(17)-C(18)	120.78(18)	N(9)-S(2)-C(39)	108.35(9)
C(22)-C(17)-S(1)	119.92(15)	C(23)-N(6)-C(27)	118.06(18)
C(18)-C(17)-S(1)	119.07(15)	C(23)-N(6)-Cu(3)	120.06(13)
C(19)-C(18)-C(17)	119.7(2)	C(27)-N(6)-Cu(3)	120.44(13)
C(19)-C(18)-H(18A)	120.2	C(30)-N(7)-C(37)	110.36(15)
C(17)-C(18)-H(18A)	120.2	C(30)-N(7)-C(29)	110.47(15)
C(20)-C(19)-C(18)	118.09(19)	C(37)-N(7)-C(29)	109.98(15)
C(20)-C(19)-H(19A)	121.0	C(30)-N(7)-Cu(3)	108.98(11)

C(37)-N(7)-Cu(3)	106.50(12)	N(7)-C(29)-H(29A)	109.0
C(29)-N(7)-Cu(3)	110.48(12)	C(28)-C(29)-H(29A)	109.0
C(36)-N(8)-C(32)	118.25(17)	N(7)-C(29)-H(29B)	109.0
C(36)-N(8)-Cu(3)	122.78(14)	C(28)-C(29)-H(29B)	109.0
C(32)-N(8)-Cu(3)	118.31(13)	H(29A)-C(29)-H(29B)	107.8
C(38)-N(9)-S(2)	114.06(13)	N(7)-C(30)-C(31)	113.37(16)
C(38)-N(9)-Cu(4)	123.18(12)	N(7)-C(30)-H(30A)	108.9
S(2)-N(9)-Cu(4)	115.94(9)	C(31)-C(30)-H(30A)	108.9
C(38)-N(9)-Cu(3)	105.46(11)	N(7)-C(30)-H(30B)	108.9
S(2)-N(9)-Cu(3)	110.87(8)	C(31)-C(30)-H(30B)	108.9
Cu(4)-N(9)-Cu(3)	80.24(6)	H(30A)-C(30)-H(30B)	107.7
O(7)-N(10)-O(8)	124.10(19)	C(32)-C(31)-C(30)	115.37(17)
O(7)-N(10)-C(42)	117.94(18)	C(32)-C(31)-H(31A)	108.4
O(8)-N(10)-C(42)	117.95(18)	C(30)-C(31)-H(31A)	108.4
N(6)-C(23)-C(24)	123.16(19)	C(32)-C(31)-H(31B)	108.4
N(6)-C(23)-H(23A)	118.4	C(30)-C(31)-H(31B)	108.4
C(24)-C(23)-H(23A)	118.4	H(31A)-C(31)-H(31B)	107.5
C(23)-C(24)-C(25)	118.9(2)	N(8)-C(32)-C(33)	121.19(18)
C(23)-C(24)-H(24A)	120.5	N(8)-C(32)-C(31)	118.01(17)
C(25)-C(24)-H(24A)	120.5	C(33)-C(32)-C(31)	120.77(19)
C(26)-C(25)-C(24)	118.6(2)	C(34)-C(33)-C(32)	119.5(2)
C(26)-C(25)-H(25A)	120.7	C(34)-C(33)-H(33A)	120.2
C(24)-C(25)-H(25A)	120.7	C(32)-C(33)-H(33A)	120.2
C(25)-C(26)-C(27)	119.97(19)	C(33)-C(34)-C(35)	119.09(19)
C(25)-C(26)-H(26A)	120.0	C(33)-C(34)-H(34A)	120.5
C(27)-C(26)-H(26A)	120.0	C(35)-C(34)-H(34A)	120.5
N(6)-C(27)-C(26)	121.32(18)	C(36)-C(35)-C(34)	118.29(19)
N(6)-C(27)-C(28)	117.45(18)	C(36)-C(35)-H(35A)	120.9
C(26)-C(27)-C(28)	121.23(17)	C(34)-C(35)-H(35A)	120.9
C(27)-C(28)-C(29)	114.12(16)	N(8)-C(36)-C(35)	123.63(19)
C(27)-C(28)-H(28A)	108.7	N(8)-C(36)-H(36A)	118.2
C(29)-C(28)-H(28A)	108.7	C(35)-C(36)-H(36A)	118.2
C(27)-C(28)-H(28B)	108.7	N(7)-C(37)-C(38)	111.18(15)
C(29)-C(28)-H(28B)	108.7	N(7)-C(37)-H(37A)	109.4
H(28A)-C(28)-H(28B)	107.6	C(38)-C(37)-H(37A)	109.4
N(7)-C(29)-C(28)	112.85(16)	N(7)-C(37)-H(37B)	109.4

C(38)-C(37)-H(37B)	109.4	C(39)-C(40)-H(40A)	120.1
H(37A)-C(37)-H(37B)	108.0	C(42)-C(41)-C(40)	118.14(19)
N(9)-C(38)-C(37)	109.69(16)	C(42)-C(41)-H(41A)	120.9
N(9)-C(38)-H(38A)	109.7	C(40)-C(41)-H(41A)	120.9
C(37)-C(38)-H(38A)	109.7	C(43)-C(42)-C(41)	123.27(19)
N(9)-C(38)-H(38B)	109.7	C(43)-C(42)-N(10)	118.16(18)
C(37)-C(38)-H(38B)	109.7	C(41)-C(42)-N(10)	118.55(18)
H(38A)-C(38)-H(38B)	108.2	C(42)-C(43)-C(44)	117.85(18)
C(44)-C(39)-C(40)	120.71(18)	C(42)-C(43)-H(43A)	121.1
C(44)-C(39)-S(2)	120.86(15)	C(44)-C(43)-H(43A)	121.1
C(40)-C(39)-S(2)	118.23(15)	C(43)-C(44)-C(39)	120.02(18)
C(41)-C(40)-C(39)	119.70(19)	C(43)-C(44)-H(44A)	120.0
C(41)-C(40)-H(40A)	120.1	C(39)-C(44)-H(44A)	120.0

Table D.3.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Cu(PENAEA)-CuCl. 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)	14(1)	14(1)	14(1)	0(1)	1(1)	-1(1)
Cu(2)	13(1)	12(1)	17(1)	0(1)	3(1)	1(1)
Cl(1)	21(1)	17(1)	30(1)	-2(1)	4(1)	6(1)
S(1)	16(1)	12(1)	15(1)	-1(1)	6(1)	-1(1)
O(1)	22(1)	15(1)	29(1)	-2(1)	13(1)	1(1)
O(2)	21(1)	19(1)	15(1)	-1(1)	2(1)	-3(1)
O(3)	38(1)	19(1)	23(1)	7(1)	4(1)	-9(1)
O(4)	18(1)	37(1)	27(1)	8(1)	5(1)	-4(1)
N(1)	12(1)	16(1)	15(1)	0(1)	3(1)	0(1)
N(2)	12(1)	17(1)	13(1)	0(1)	4(1)	0(1)
N(3)	17(1)	17(1)	13(1)	1(1)	4(1)	-1(1)
N(4)	13(1)	12(1)	14(1)	1(1)	2(1)	1(1)
N(5)	22(1)	25(1)	14(1)	4(1)	0(1)	-8(1)
C(1)	18(1)	21(1)	17(1)	-2(1)	2(1)	1(1)
C(2)	31(1)	24(1)	18(1)	6(1)	2(1)	7(1)
C(3)	32(1)	18(1)	27(1)	6(1)	6(1)	6(1)
C(4)	24(1)	16(1)	23(1)	-1(1)	5(1)	1(1)
C(5)	13(1)	15(1)	18(1)	-2(1)	4(1)	1(1)
C(6)	17(1)	15(1)	14(1)	-4(1)	3(1)	-1(1)
C(7)	15(1)	17(1)	15(1)	-1(1)	1(1)	-2(1)
C(8)	13(1)	20(1)	17(1)	-1(1)	1(1)	2(1)
C(9)	13(1)	23(1)	18(1)	-1(1)	6(1)	-1(1)
C(10)	17(1)	19(1)	15(1)	2(1)	6(1)	-2(1)
C(11)	20(1)	26(1)	18(1)	2(1)	5(1)	4(1)
C(12)	31(1)	20(1)	19(1)	-3(1)	10(1)	2(1)
C(13)	26(1)	21(1)	14(1)	-4(1)	5(1)	-7(1)
C(14)	18(1)	21(1)	16(1)	1(1)	5(1)	-4(1)
C(15)	14(1)	20(1)	12(1)	1(1)	3(1)	1(1)
C(16)	17(1)	17(1)	16(1)	4(1)	3(1)	1(1)
C(17)	12(1)	15(1)	18(1)	2(1)	3(1)	-2(1)
C(18)	24(1)	14(1)	25(1)	-1(1)	9(1)	1(1)
C(19)	29(1)	13(1)	26(1)	3(1)	7(1)	-1(1)

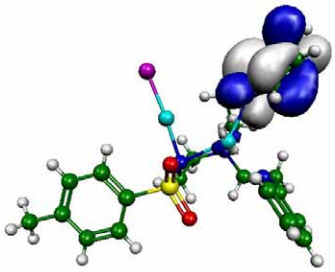
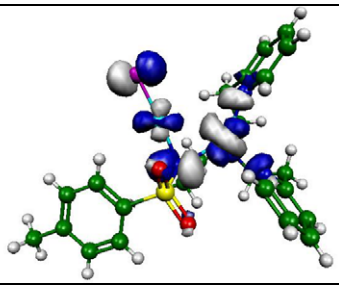
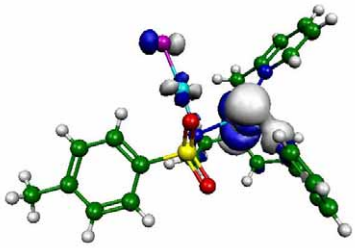
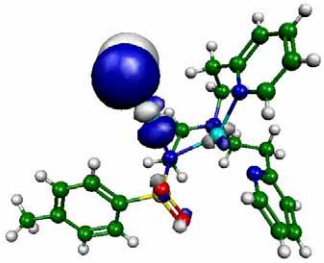
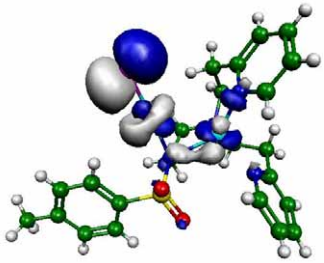
C(20)	16(1)	17(1)	16(1)	5(1)	1(1)	-4(1)
C(21)	19(1)	18(1)	20(1)	4(1)	7(1)	2(1)
C(22)	21(1)	11(1)	23(1)	2(1)	8(1)	1(1)
Cu(3)	13(1)	13(1)	13(1)	1(1)	1(1)	1(1)
Cu(4)	13(1)	12(1)	16(1)	2(1)	2(1)	0(1)
Cl(2)	19(1)	16(1)	25(1)	5(1)	2(1)	-3(1)
S(2)	14(1)	12(1)	14(1)	3(1)	4(1)	3(1)
O(5)	19(1)	15(1)	25(1)	4(1)	10(1)	2(1)
O(6)	20(1)	18(1)	14(1)	2(1)	1(1)	5(1)
O(7)	25(1)	34(1)	38(1)	2(1)	17(1)	7(1)
O(8)	30(1)	21(1)	39(1)	-1(1)	8(1)	12(1)
N(6)	13(1)	15(1)	15(1)	2(1)	3(1)	0(1)
N(7)	12(1)	14(1)	13(1)	0(1)	3(1)	2(1)
N(8)	15(1)	15(1)	14(1)	0(1)	3(1)	2(1)
N(9)	12(1)	12(1)	13(1)	2(1)	1(1)	0(1)
N(10)	18(1)	25(1)	20(1)	-4(1)	2(1)	5(1)
C(23)	19(1)	19(1)	17(1)	3(1)	1(1)	-3(1)
C(24)	30(1)	21(1)	17(1)	-3(1)	4(1)	-7(1)
C(25)	29(1)	14(1)	26(1)	-2(1)	6(1)	-2(1)
C(26)	23(1)	16(1)	21(1)	4(1)	3(1)	0(1)
C(27)	12(1)	16(1)	17(1)	3(1)	3(1)	0(1)
C(28)	17(1)	15(1)	15(1)	3(1)	3(1)	3(1)
C(29)	15(1)	16(1)	16(1)	1(1)	1(1)	5(1)
C(30)	13(1)	18(1)	15(1)	2(1)	1(1)	0(1)
C(31)	13(1)	22(1)	17(1)	2(1)	4(1)	3(1)
C(32)	16(1)	18(1)	13(1)	-2(1)	4(1)	2(1)
C(33)	18(1)	25(1)	21(1)	1(1)	5(1)	-2(1)
C(34)	27(1)	22(1)	22(1)	4(1)	9(1)	-2(1)
C(35)	23(1)	19(1)	15(1)	3(1)	5(1)	5(1)
C(36)	16(1)	20(1)	14(1)	-2(1)	4(1)	3(1)
C(37)	15(1)	19(1)	13(1)	-1(1)	3(1)	2(1)
C(38)	15(1)	14(1)	16(1)	-2(1)	1(1)	2(1)
C(39)	13(1)	14(1)	15(1)	-1(1)	2(1)	2(1)
C(40)	20(1)	15(1)	20(1)	3(1)	7(1)	0(1)
C(41)	24(1)	13(1)	25(1)	3(1)	5(1)	4(1)
C(42)	14(1)	18(1)	17(1)	-4(1)	2(1)	4(1)

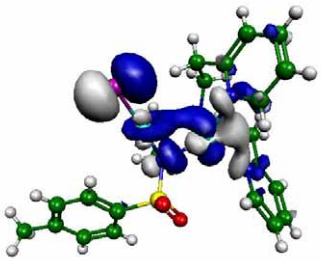
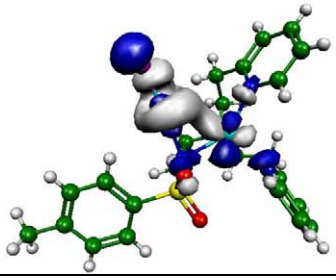
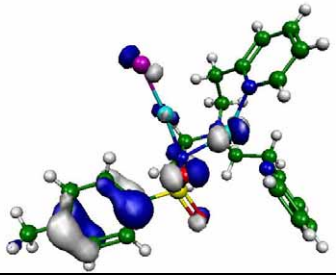
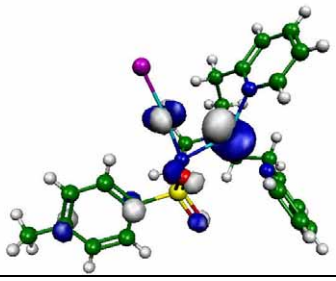
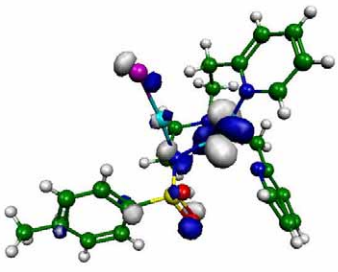
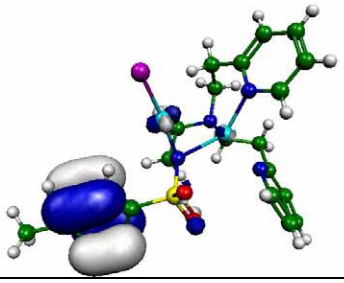
C(43)	15(1)	17(1)	16(1)	0(1)	4(1)	0(1)
C(44)	16(1)	11(1)	17(1)	2(1)	2(1)	1(1)

Table D.3.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Cu(PENAEA)-CuCl.

	x	y	z	U(eq)
H(1B)	1219	7104	80	23
H(2B)	1236	9094	-191	29
H(3A)	2073	10770	410	30
H(4A)	2912	10377	1262	25
H(6A)	2159	7842	1838	19
H(6B)	3319	9013	1913	19
H(7A)	5092	7588	1566	19
H(7B)	4846	7491	2147	19
H(8A)	5005	4431	1647	20
H(8B)	6096	5625	1835	20
H(9A)	5470	6213	938	21
H(9B)	6677	5183	1051	21
H(11A)	6391	3390	486	26
H(12A)	4925	2091	-161	28
H(13A)	2369	2484	-399	25
H(14A)	1337	4069	48	22
H(15A)	2580	6185	2233	18
H(15B)	3999	5355	2374	18
H(16A)	2836	3711	1802	20
H(16B)	1723	4099	2200	20
H(18A)	-367	965	1345	25
H(19A)	-2146	-45	1761	27
H(21A)	-3525	3289	2263	22
H(22A)	-1763	4293	1838	22
H(23A)	3833	12161	4904	22
H(24A)	3651	14213	5178	28
H(25A)	2860	15638	4572	28
H(26A)	2241	14916	3707	24
H(28A)	3174	12196	3154	18
H(28B)	2103	13322	3043	18
H(29A)	135	12012	3349	19
H(29B)	494	11676	2783	19

H(30A)	51	8838	3318	18
H(30B)	-951	9939	3113	18
H(31A)	-331	10906	4004	21
H(31B)	-1611	9821	3889	21
H(33A)	-1503	8304	4485	25
H(34A)	-167	7292	5153	27
H(35A)	2433	7770	5394	22
H(36A)	3613	9139	4933	20
H(37A)	2647	10373	2741	18
H(37B)	1179	9462	2596	18
H(38A)	2199	8082	3190	18
H(38B)	3379	8320	2806	18
H(40A)	5604	5638	3840	22
H(41A)	7485	4569	3489	25
H(43A)	8297	7527	2692	19
H(44A)	6470	8617	3067	17

	Orbital
LUMO	
HOMO	
HOMO-1	
HOMO-2	
HOMO-3	

HOMO-4	
HOMO-5	
HOMO-6	
HOMO-7	
HOMO-8	
HOMO-9	

HOMO-10