Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

A new Cu-Cysteamine Complex: Structure and Optical Properties

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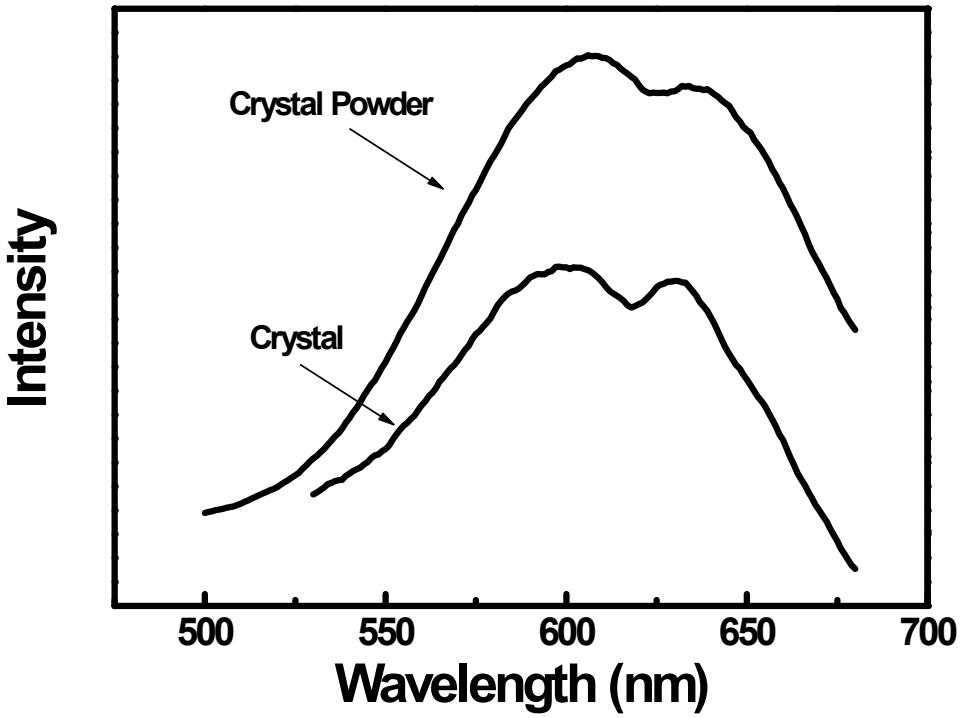

Figure S1. The photoluminescence spectra of crystal powders and large single crystals of $Cu_3Cl(SR)_2$ using excitation of 360 nm.

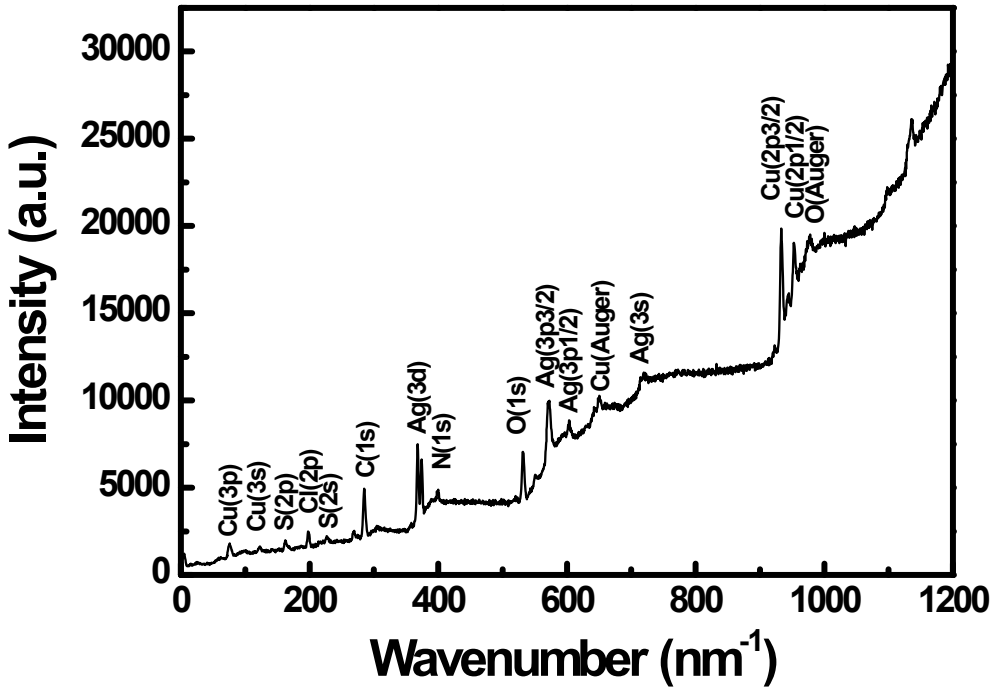

Figure S2. XPS spectrum of $Cu_3Cl(SR)_2$.

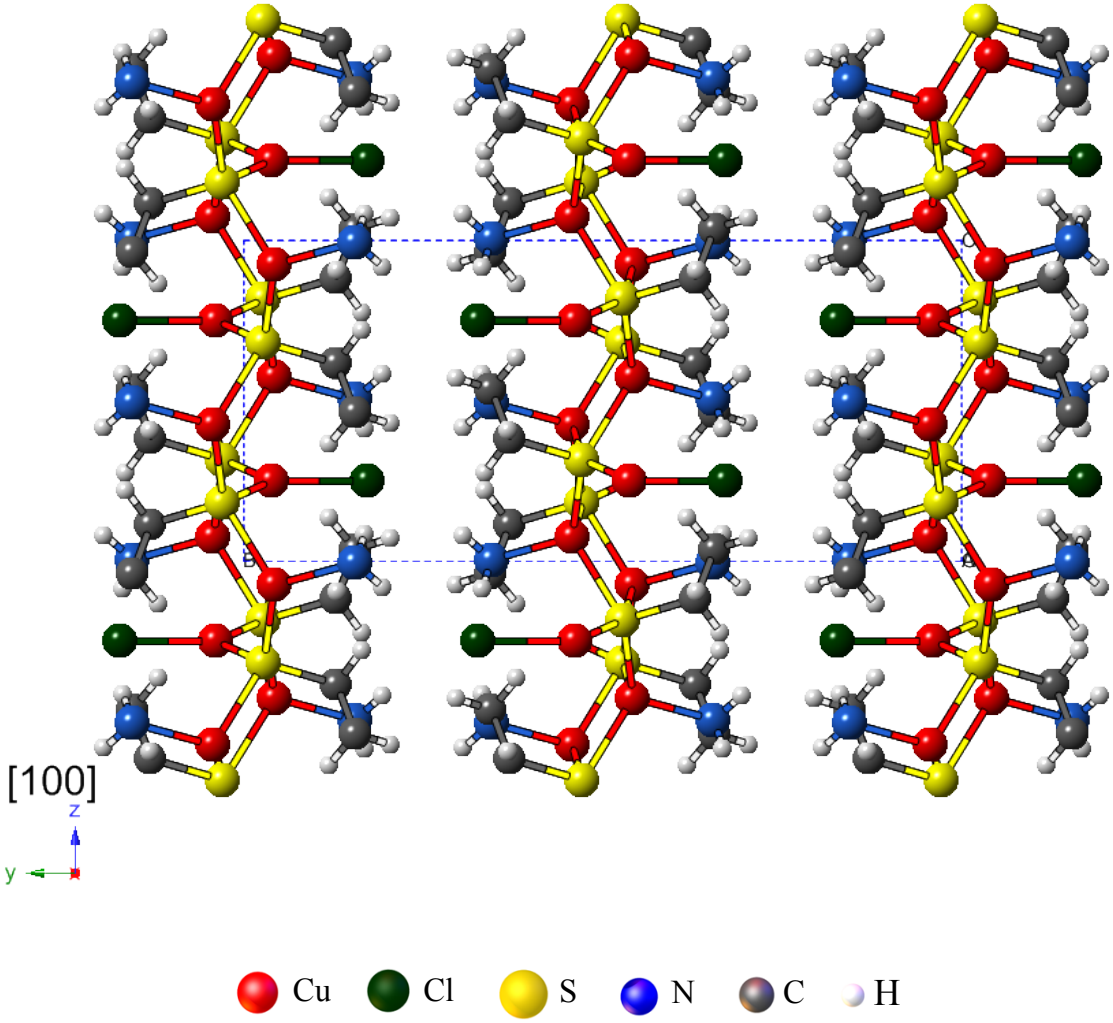

Figure S3. The packing diagram of $Cu_3Cl(SR)_2$ viewed along (100) direction.

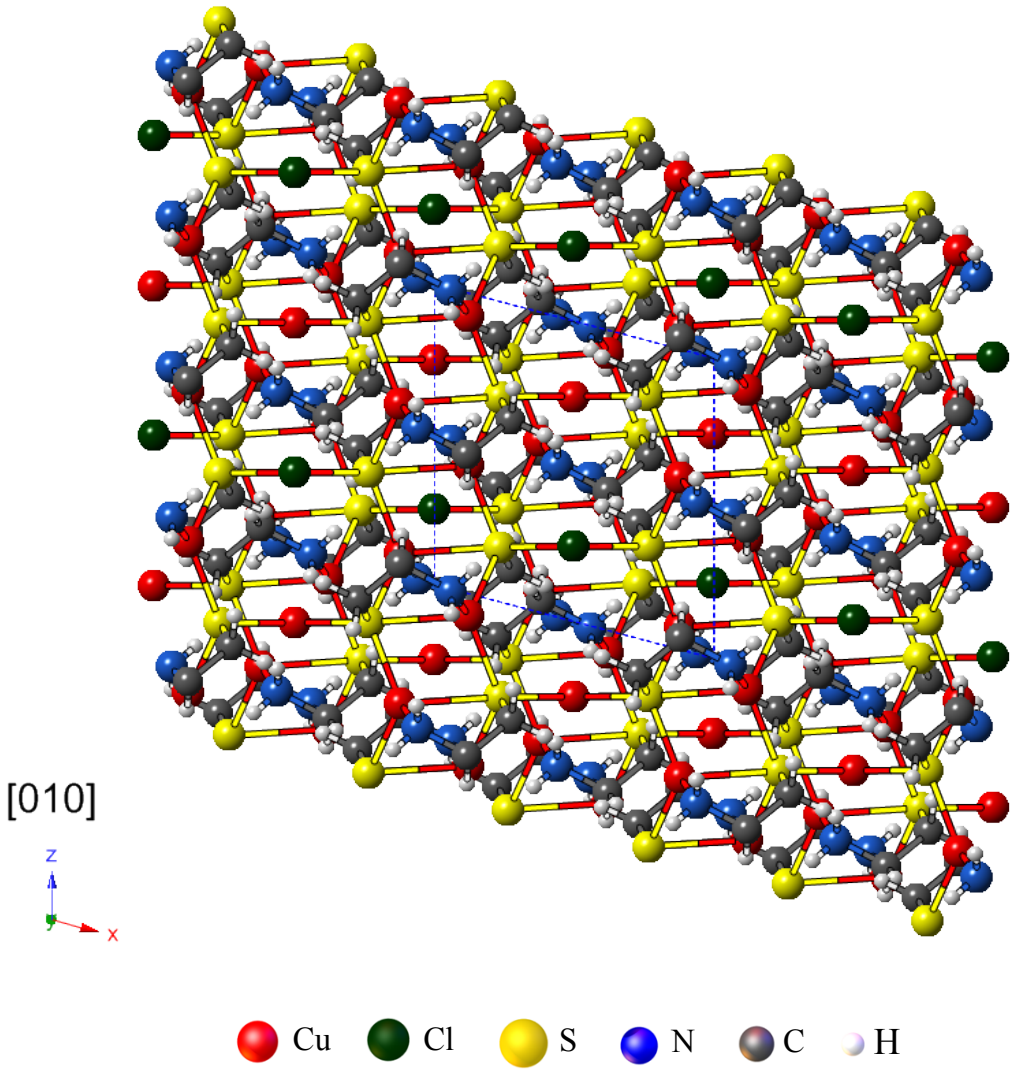

Figure S4. The packing diagram of $Cu_3Cl(SR)_2$ viewed along (010) direction.

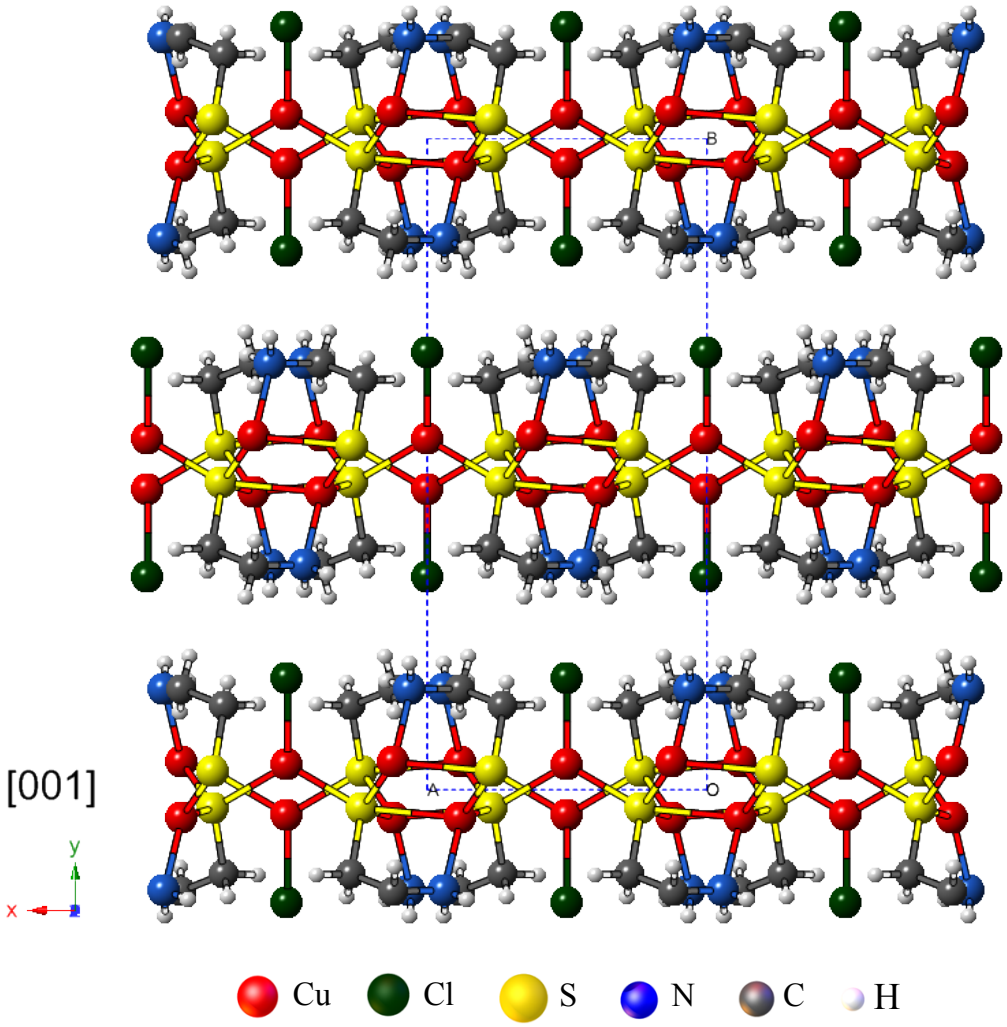

Figure S5. The packing diagram of $Cu_3Cl(SR)_2$ viewed along (001) direction.

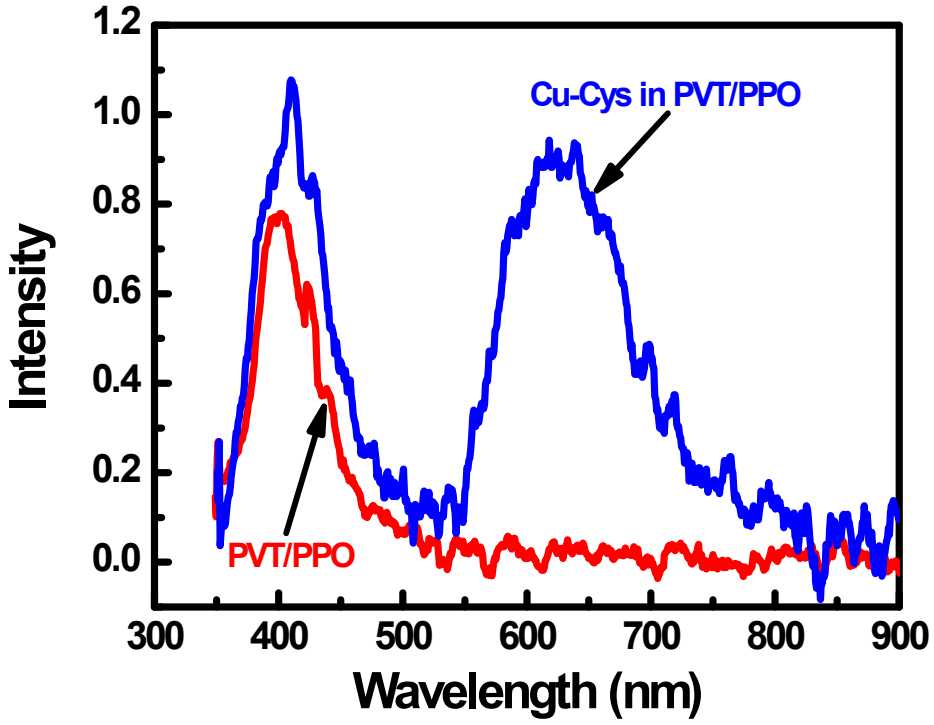

Figure S6. The X-ray luminescence spectra of $Cu_3Cl(SR)_2$ in PVT and PVT/PPO polymers.

Table S1. Crystal data and structure refinement of $Cu_3Cl(SR)_2$.

A. Crystal Data

Empirical formula	$C_4H_{12}Cl_1Cu_3N_2S_2$
Formula weight	378.38
Crystal Color, Habit	pale brown, rod-like
Crystal dimensions (mm)	0.10 × 0.03 × 0.03
Crystal system	monoclinic
Space group	*C*2/*c* [No. 15]
Unit cell parameters[a]	
a (Å)	7.5510(4)
b (Å)	16.9848(7)
c (Å)	7.8364(4)
α (°)	90
β (°)	104.798(3)
γ (°)	90
V (Å^3)	971.70(8)
Z[b]	4
F(000)	744
Density (ρ_{calcd})	2.586 Mg/m^3
Absorption coefficient (μ)	7.152 mm^{-1}

B. Data Collection and Refinement Conditions

Diffractometer	Nonius KappaCCD diffractometer[c]
Radiation	monochromated Mo Kα
Wavelength (Mo Kα)	0.71073 Å
Temperature	-100(2) °C [173(2) K]
Scan type	ω (2º per frame, 80 s exposure/frame)
Theta range for data collection	3.04 to 29.13°
Completeness to theta = 29.13°	99.8%
Reflections collected[d]	2516
Index ranges	$-10 \le h \le 10$, $-23 \le k \le 23$, $-10 \le l \le 10$
Independent reflections [$F_o^2 \ge -3\sigma(F_o^2)$][e]	1314 [$R_{int} = 0.0341$][f]
Observed reflections [$F_o^2 > 2\sigma(F_o^2)$][g]	1034
Absorption correction method	multi-scan [SCALEPACK]
Range of transmission factors (max./min.)	0.8140-0.5349 [from SHELXL-2012]
Anomalous Dispersion	For all non-hydrogen atoms
Structure solution method	Patterson method (SHELXS-97)[h]
Refinement method	Full-matrix least-squares on F^2 (SHELXL-2012)[i]
Function Minimized	$\Sigma w(\lvert F_o\rvert^2 - \lvert kF_c\rvert^2)^2$ (k: overall scale factor)
Weighing scheme, w	$w = [\sigma(F_o^2) + (0.0330\,P)^2 + (0.8292\,P)]^{-1}$

$w = [\sigma(F_o^2) + (a\,P)^2 + (b\,P)]^{-1}$

P-factor	$[\mathrm{Max}(F_o^2,0) + 2\,F_c^2]/3$
Data / restraints / parameters	1314 $[F_o^2 \geq -3\sigma(F_o^2)]$ / 0 / 80
Reflection (observed)/parameter ratio	13:1
Reflection (data)/parameter ratio	16:1
Goodness-of-fit[j] on F^2	1.063

$GooF = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/(n - p)\}^{1/2}$

n: number of reflections, *p*: number of parameters

Final *R* indices

$R_1 = [\Sigma\|\|F_o\|\text{-}\|F_c\|\|]/[\Sigma\|F_o\|]$ for $[F_o^2 > 2\sigma(F_o^2)]$[i]	0.0328
$wR_2 = \{[\Sigma w(F_o^2\text{-}F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ [all data]	0.0780
Max. Shift/Error in Final Cycle	0.000
Largest difference peak and hole	0.844 and -0.713 $e^-/Å^3$

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[a] Obtained from least-squares refinement of 1355 centered reflections with 1.00º < θ < 30.03º (mosaicity: 0.428(3)°).

[b] *Z* is the number of formula units per unit cell. Comparison of *Z* with the multiplicity of the general position n_a of the space group will then require that the asymmetric unit is Z/n_a times the formula unit. The asymmetric unit is the minimum group of atoms whose positions, together with those generated by the symmetry operations of the space group generate the complete contents of the unit cell.

[c] *KappaCCD*: 4-circle diffractometer; sealed Mo tube; *CCD*: Charge-coupled Device.

[d] Number of reflections after truncation or rejection (before merging).

[e] The criterion for the independent or unique reflections $[F_o^2 \geq -3\sigma(F_o^2)]$ was taken from:

G. M. Sheldrick, *SHELXL-93, Program for the Solution of Crystal Structures;* University of Göttingen: Göttingen, Germany 1993.

[f] $R_{int} = [\Sigma|F_o^2\text{-}F_o^2(\text{mean})|]/[\Sigma|F_o^2|]$

[g] The criterion for the observed reflections [$F_o^2 > 2\sigma(F_o^2)$] is equivalent to [$I > 2\sigma(I)$]: I is proportional to F_o^2.

[h] G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures;* University of Göttingen, Göttingen, Germany 1997. G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112–122.

[i] G. M. Sheldrick, *SHELXL-2012, Program for the Solution of Crystal Structures;* University of Göttingen, Göttingen, Germany 2013. G. M. Sheldrick, *Acta Cryst.* 2008, A64, 112–122.

Function minimized: $\Sigma w(|F_o|^2\text{-}|kF_c|^2)^2$; k: overall scale factor.

Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R-factors wR_2 and the values for *GooF* are based on F_o^2; conventional R-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. R-factors based on F_o^2 are statistically about twice as large as those based on F_o, and R-factors based on ALL data will be even larger.

[j] Standard deviation of an observation of unit weight (*goodness-of-fit* on F^2):

$$GooF = \{\Sigma[w(F_o^2\text{-}F_c^2)^2]/(n - p)\}^{1/2}$$

n: number of reflections, p: number of parameters

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and site occupancy factors for $Cu_3Cl(SR)_2$.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)	s.o.f.
Cu(1)	1212(1)	-426(1)	-743(1)	21(1)	1.00
Cu(2)	5000	-385(1)	2500	20(1)	0.50
Cl(1)	5000	-1724(1)	2500	22(1)	0.50
S(1)	2341(1)	282(1)	1833(1)	15(1)	1.00
N(1)	-595(4)	1548(2)	55(4)	18(1)	1.00
C(1)	2729(4)	1292(2)	1165(4)	18(1)	1.00
C(2)	1195(4)	1555(2)	-376(4)	19(1)	1.00

Table S3a. Interatomic Distances [Å] for $Cu_3Cl(SR)_2$.

Cu(1)-N(1)*	2.067(3)
Cu(1)-S(1)′	2.2852(9)
Cu(1)-S(1)	2.3167(9)
Cu(1)-S(1)*	2.6110(9)
Cu(1)-Cu(1)*	2.8076(8)
Cu(1)-Cu(1)#	2.8912(9)
Cu(2)-S(1)**	2.2474(8)
Cu(2)-S(1)	2.2474(8)
Cu(2)-Cl(1)	2.2739(12)
S(1)-C(1)	1.839(3)
S(1)-Cu(1)##	2.2852(9)
S(1)-Cu(1)*	2.6110(9)
N(1)-C(2)	1.475(4)
N(1)-Cu(1)*	2.067(3)
N(1)-H(1)	0.86(4)
N(1)-H(2)	0.90(5)
C(1)-C(2)	1.512(4)

Symmetry transformations used to generate equivalent atoms:

*: -x, -y, -z ′: x, -y, z - ½ #: -x , y, -z - ½ **: -x + 1, y, -z + ½ ##: x, -y, z + ½

$$r_{vdW}(Cu) + r_{vdW}(N) = (1.40 + 1.55)\ [Å] = 2.95\ [Å]\ (Bondi)^{1}$$

$$r_{vdW}(Cu) + r_{vdW}(S) = (1.40 + 1.80)\ [Å] = 3.20\ [Å]\ (Bondi)^{1}$$

Table S3b. Interatomic Angles [°] for $Cu_3Cl(SR)_2$.

N(1)*-Cu(1)-S(1)′	118.17(8)
N(1)*-Cu(1)-S(1)	107.97(9)
S(1)′-Cu(1)-S(1)	122.44(3)
N(1)*-Cu(1)-S(1)*	83.70(8)
S(1)′-Cu(1)-S(1)*	106.77(3)
S(1)-Cu(1)-S(1)*	110.83(3)
N(1)*-Cu(1)-Cu(1)*	98.77(8)
S(1)′-Cu(1)-Cu(1)*	135.31(3)
S(1)-Cu(1)-Cu(1)*	60.37(2)
S(1)*-Cu(1)-Cu(1)*	50.46(2)
N(1)*-Cu(1)-Cu(1)#	96.80(8)
S(1)′-Cu(1)-Cu(1)#	59.21(2)
S(1)-Cu(1)-Cu(1)#	146.37(2)
S(1)*-Cu(1)-Cu(1)#	48.75(2)
Cu(1)*-Cu(1)-Cu(1)#	94.24(3)
S(1)**-Cu(2)-S(1)	119.45(4)
S(1)**-Cu(2)-Cl(1)	120.27(2)
S(1)-Cu(2)-Cl(1)	120.27(2)
C(1)-S(1)-Cu(2)	109.81(11)
C(1)-S(1)-Cu(1)##	104.92(11)
Cu(2)-S(1)-Cu(1)##	111.19(4)
C(1)-S(1)-Cu(1)	106.60(11)
Cu(2)-S(1)-Cu(1)	92.83(3)
Cu(1)##-S(1)-Cu(1)	130.32(4)
C(1)-S(1)-Cu(1)*	92.56(10)
Cu(2)-S(1)-Cu(1)*	154.87(4)
Cu(1)##-S(1)-Cu(1)*	72.03(3)
Cu(1)-S(1)-Cu(1)*	69.17(3)
C(2)-N(1)-Cu(1)*	110.35(19)
C(2)-N(1)-H(1)	110(3)

C(2)-N(1)-H(2)	109(3)
H(1)-N(1)-H(2)	103(4)
C(2)-C(1)-S(1)	111.0(2)
N(1)-C(2)-C(1)	112.0(3)

Symmetry transformations used to generate equivalent atoms:

*: -x, -y, -z ′: x, -y, z - ½ #: -x , y, -z - ½ **: -x + 1, y, -z + ½ ##: x, -y, z + ½

NOTE:

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Cu_3Cl(SR)_2$.

The anisotropic displacement factor exponent takes the form:

$[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	27(1)	17(1)	23(1)	-2(1)	12(1)	-3(1)
Cu(2)	17(1)	17(1)	25(1)	0	7(1)	0
Cl(1)	21(1)	15(1)	30(1)	0	5(1)	0
S(1)	14(1)	16(1)	16(1)	0(1)	4(1)	0(1)
N(1)	17(2)	15(1)	19(2)	0(1)	2(1)	2(1)
C(1)	17(2)	18(2)	17(2)	2(1)	0(1)	-4(1)
C(2)	21(2)	17(2)	16(2)	4(1)	2(1)	-6(1)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Cu_3Cl(SR)_2$.

Atom	x	y	z	U(eq)
H(1)	-1440(60)	1680(20)	-850(60)	29(11)
H(2)	-620(60)	1940(30)	820(60)	35(12)
H(1A)	2866	1642	2221	29(11)
H(1B)	3960	1306	926	31(11)
H(2A)	1158	1191	-1346	14(9)
H(2B)	1508	2042	-716	26(10)

Table S6. Selected torsion angles [°] for $Cu_3Cl(SR)_2$.

Cu(2)-S(1)-C(1)-C(2)	139.7(2)
Cu(1)$^{\#\#}$-S(1)-C(1)-C(2)	-100.7(2)
Cu(1)-S(1)-C(1)-C(2)	40.4(2)
Cu(1)*-S(1)-C(1)-C(2)	-28.7(2)
Cu(1)*-N(1)-C(2)-C(1)	-60.1(3)
S(1)-C(1)-C(2)-N(1)	60.4(3)

Symmetry transformations used to generate equivalent atoms:

*: -x, -y, -z ′: x, -y, z - ½ $^{\#}$: -x , y, -z - ½ **: -x + 1, y, -z + ½ $^{\#\#}$: x, -y, z + ½

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S7. Intra- and Intermolecular N(H)···Cl contacts [Å] for $Cu_3Cl(SR)_2$.

D-H···A	***D-A***	***H···A***	***H···A***	***D-H···A***
N1-H1···Cl1*	0.86(4)	2.67(4)	3.429(3)	149(4)
N1-H2···Cl1″	0.90(5)	2.61(5)	3.471(3)	162(4)

Symmetry transformations used to generate equivalent atoms:

*: -x, -y, -z ″: - ½ + x, ½ + y, z

Table S8. Calculated values for elemental analysis for $Cu_3Cl(SR)_2$.

Formula weight: 378.38

Element	**Analysis [%] calcd. [atomic [%] in () with H atoms excluded]**
C	12.698 (33.33)
H	3.197
Cl	9.370 (8.33)
Cu	50.383 (25.00)
N	7.404 (16.67)
S	16.949 (16.67)

Table S9. Calculated powder diffraction (Source: X-ray tube, Cu radiation) for $Cu_3Cl(SR)_2$ (program: POUDRIX).

POUDRIX. Powder diffraction diagram (Source: X-ray tube)

2/7/2013 2:27:43 PM
C4H12ClCu3N2S2
Cell : 7.551 16.985 7.836 90.000 104.800 90.000
Lambda : 1.54180
S.Group: C2/C
Syst. : MONO
Bravais: C
Centro

Space group positions:

Asymetric unit content:

	x	y	z	B	Pop.	Mult.	Elem. Nb.
CU1	0.12117	-0.04255	-0.07430	1.69	1.000	1.000	1
CU2	0.50000	-0.03851	0.25000	1.54	1.000	0.500	1
CL1	0.50000	-0.17238	0.25000	1.78	1.000	0.500	2
S1	0.23415	0.02819	0.18333	1.18	1.000	1.000	3
N1	-0.05950	0.15475	0.00560	1.38	1.000	1.000	4
H1	-0.14300	0.16800	-0.08400	2.21	1.000	1.000	5
H2	-0.06300	0.19300	0.08200	2.76	1.000	1.000	5
C1	0.27310	0.12918	0.11670	1.40	1.000	1.000	6
H1A	0.28100	0.16530	0.21760	1.66	1.000	1.000	5
H1B	0.39080	0.13160	0.08330	1.66	1.000	1.000	5
C2	0.11950	0.15550	-0.03760	1.47	1.000	1.000	6
H2A	0.14550	0.20940	-0.07260	1.74	1.000	1.000	5
H2B	0.11430	0.12020	-0.13930	1.74	1.000	1.000	5

Atomic scattering factors

	f(0)	f'	f"
CU	28.9859	-1.9590	0.5910
CL	17.0005	0.3650	0.7040
S	15.9998	0.3340	0.5580
N	6.9946	0.0310	0.0180
H	0.9999	0.0000	0.0000
C	5.9992	0.0180	0.0090

Cromer Factors

	c	a1	b1	a2	b2	a3	b3	a4	b4
CU	1.1910	13.3380	3.5828	7.1676	0.2470	5.6158	11.3966	1.6735	64.8126
CL	-9.5574	11.4604	0.0104	7.1964	1.1662	6.2556	18.5194	1.6455	47.7784
S	0.8669	6.9053	1.4679	5.2034	22.2151	1.4379	0.2536	1.5863	56.1720
N	-11.5290	12.2126	0.0057	3.1322	9.8933	2.0125	28.9975	1.1663	0.5826
H	0.0030	0.4930	10.5109	0.3229	26.1257	0.1402	3.1424	0.0408	57.7997
C	0.2156	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512

The intensities were multiplied by: 4.8384E-0006

Results for lambda= 1.54180

Nb	h	k	l	2Theta	dhkl	N	LP	Intensity
1	0	2	0	10.416	8.4924	2	119.87	100.00
2	-1	1	0	13.200	6.7072	4	74.22	7.25
3	-1	1	1	15.453	5.7341	4	53.85	5.79
4	0	2	1	15.674	5.6535	4	52.31	0.05
5	1	1	1	19.628	4.5228	4	32.96	5.17
6	-1	3	0	19.844	4.4739	4	32.22	0.20
7	0	4	0	20.920	4.2462	2	28.89	2.49
8	-1	3	1	21.426	4.1471	4	27.49	10.42
9	0	0	2	23.483	3.7882	2	22.71	0.13
10	0	4	1	24.024	3.7041	4	21.65	5.01
11	-1	1	2	24.117	3.6901	4	21.47	19.84

12	2	0	0	24.384	3.6502	2	20.98	0.58
13	1	3	1	24.642	3.6127	4	20.53	1.24
14	0	2	2	25.750	3.4596	4	18.71	1.01
15	-2	2	1	26.419	3.3736	4	17.72	0.91
16	-2	2	0	26.579	3.3536	4	17.50	0.67
17	-1	3	2	28.388	3.1439	4	15.22	0.12
18	-1	5	0	28.991	3.0799	4	14.55	0.02
19	-2	0	2	29.321	3.0459	2	14.20	5.61
20	1	1	2	29.681	3.0098	4	13.84	12.33
21	-1	5	1	30.121	2.9669	4	13.41	11.84
22	-2	2	2	31.195	2.8671	4	12.43	2.15
23	0	6	0	31.605	2.8308	2	12.09	3.66
24	2	2	1	31.608	2.8306	4	12.09	10.49
25	0	4	2	31.652	2.8268	4	12.05	1.40
26	-2	4	1	32.207	2.7793	4	11.61	0.62
27	-2	4	0	32.341	2.7680	4	11.50	0.17
28	1	5	1	32.540	2.7516	4	11.35	0.06
29	1	3	2	33.297	2.6908	4	10.80	0.13
30	0	6	1	33.801	2.6517	4	10.45	0.29
31	-1	1	3	34.899	2.5708	4	9.75	0.03
32	-1	5	2	35.528	2.5267	4	9.38	1.37
33	-3	1	1	36.157	2.4842	4	9.02	2.38
34	-2	4	2	36.296	2.4750	4	8.95	0.19
35	2	4	1	36.658	2.4514	4	8.75	5.94
36	0	2	3	37.140	2.4207	4	8.51	3.71
37	-3	1	0	37.328	2.4089	4	8.41	7.74
38	-1	3	3	38.075	2.3633	4	8.05	1.28
39	2	0	2	38.366	2.3461	2	7.92	0.88
40	-3	1	2	38.902	2.3150	4	7.68	2.10
41	-1	7	0	39.121	2.3026	4	7.58	0.00
42	-3	3	1	39.246	2.2955	4	7.53	1.76
43	-2	2	3	39.301	2.2924	4	7.51	1.23
44	1	5	2	39.654	2.2728	4	7.36	0.86
45	0	6	2	39.749	2.2676	4	7.32	0.15
46	2	2	2	39.863	2.2614	4	7.27	1.04
47	-1	7	1	39.996	2.2542	4	7.22	8.35
48	-2	6	1	40.206	2.2429	4	7.14	0.01
49	-2	6	0	40.317	2.2370	4	7.09	0.10
50	-3	3	0	40.340	2.2357	4	7.08	1.62
51	1	1	3	41.037	2.1994	4	6.82	0.65
52	0	4	3	41.606	2.1706	4	6.61	2.77
53	-3	3	2	41.819	2.1600	4	6.54	1.09
54	1	7	1	41.916	2.1553	4	6.50	1.29
55	3	1	1	42.138	2.1444	4	6.43	0.00
56	0	8	0	42.581	2.1231	2	6.28	0.60
57	-2	4	3	43.582	2.0767	4	5.96	0.58
58	-2	6	2	43.650	2.0736	4	5.94	0.00
59	1	3	3	43.836	2.0652	4	5.88	0.15
60	-1	5	3	43.840	2.0650	4	5.88	2.08
61	2	6	1	43.961	2.0596	4	5.84	6.56
62	2	4	2	44.099	2.0535	4	5.80	0.08
63	0	8	1	44.307	2.0443	4	5.74	0.11
64	-1	7	2	44.361	2.0420	4	5.72	0.59
65	3	3	1	44.881	2.0195	4	5.58	0.78
66	-3	5	1	44.885	2.0193	4	5.58	0.45
67	-3	1	3	44.958	2.0162	4	5.55	0.39
68	-3	5	0	45.870	1.9783	4	5.31	0.90
69	-1	1	4	46.670	1.9462	4	5.10	6.77
70	-3	5	2	47.208	1.9253	4	4.97	0.00
71	-3	3	3	47.572	1.9114	4	4.89	1.38
72	1	7	2	47.853	1.9008	4	4.82	0.17
73	0	0	4	48.033	1.8941	2	4.78	0.24
74	-2	0	4	48.139	1.8902	2	4.76	0.02
75	0	6	3	48.293	1.8845	4	4.72	2.86
76	1	5	3	49.050	1.8572	4	4.56	0.01
77	0	8	2	49.195	1.8521	4	4.53	0.00
78	-1	3	4	49.214	1.8514	4	4.53	2.81
79	0	2	4	49.291	1.8487	4	4.51	0.01

80	-2	2	4	49.395	1.8450	4	4.49	0.51
81	-4	2	1	49.465	1.8426	4	4.47	0.07
82	-2	8	1	49.582	1.8385	4	4.45	0.27
83	-4	0	2	49.595	1.8381	2	4.45	3.22
84	-2	8	0	49.676	1.8352	4	4.43	0.57
85	3	1	2	49.724	1.8336	4	4.42	3.20
86	-1	9	0	49.911	1.8271	4	4.38	0.07
87	4	0	0	49.970	1.8251	2	4.37	0.04
88	3	5	1	50.010	1.8237	4	4.36	1.21
89	2	2	3	50.052	1.8223	4	4.35	0.17
90	-2	6	3	50.060	1.8221	4	4.35	1.88
91	2	6	2	50.526	1.8064	4	4.26	0.00
92	-1	9	1	50.636	1.8027	4	4.24	0.57
93	-4	2	2	50.824	1.7965	4	4.21	2.21
94	-4	2	0	51.192	1.7844	4	4.14	0.00
95	-1	7	3	51.509	1.7742	4	4.08	0.26
96	3	3	2	52.156	1.7537	4	3.96	0.34
97	1	9	1	52.245	1.7509	4	3.95	0.29
98	-3	7	1	52.437	1.7449	4	3.92	1.80
99	-3	5	3	52.501	1.7429	4	3.91	1.95
100	-2	8	2	52.540	1.7417	4	3.90	0.76
101	2	8	1	52.811	1.7334	4	3.85	4.36
102	0	4	4	52.931	1.7298	4	3.83	0.00
103	-2	4	4	53.029	1.7268	4	3.82	0.25
104	-4	4	1	53.096	1.7248	4	3.81	0.11
105	1	1	4	53.247	1.7203	4	3.78	0.29
106	-3	7	0	53.315	1.7182	4	3.77	0.04
107	-3	1	4	53.443	1.7144	4	3.75	0.55
108	2	4	3	53.655	1.7082	4	3.72	0.01
109	0	10	0	53.985	1.6985	2	3.67	1.74
110	-1	5	4	54.033	1.6971	4	3.66	1.00
111	-1	9	2	54.331	1.6885	4	3.61	0.40
112	-4	4	2	54.390	1.6868	4	3.60	0.79
113	-3	7	2	54.517	1.6832	4	3.58	0.01
114	-4	4	0	54.742	1.6768	4	3.55	0.01
115	-4	2	3	55.104	1.6666	4	3.50	0.07
116	0	10	1	55.439	1.6573	4	3.45	0.51
117	1	3	4	55.569	1.6538	4	3.43	0.14
118	-3	3	4	55.760	1.6485	4	3.41	0.01
119	4	2	1	55.800	1.6475	4	3.40	0.32
120	1	7	3	56.184	1.6371	4	3.35	0.41
121	0	8	3	56.636	1.6251	4	3.29	1.49
122	3	5	2	56.798	1.6209	4	3.27	0.38
123	3	7	1	57.060	1.6141	4	3.23	0.23
124	1	9	2	57.371	1.6060	4	3.19	2.16
125	-2	8	3	58.222	1.5846	4	3.09	1.03
126	-4	4	3	58.490	1.5780	4	3.06	1.04
127	0	6	4	58.642	1.5742	4	3.04	0.22
128	2	8	2	58.643	1.5742	4	3.04	0.00
129	-2	6	4	58.735	1.5720	4	3.03	0.10
130	-4	6	1	58.797	1.5704	4	3.02	0.22
131	4	4	1	59.160	1.5617	4	2.98	0.08
132	-1	1	5	59.282	1.5588	4	2.97	0.09
133	2	6	3	59.320	1.5578	4	2.96	0.29
134	3	1	3	59.335	1.5575	4	2.96	0.10
135	-3	7	3	59.345	1.5572	4	2.96	2.00
136	0	10	2	59.657	1.5498	4	2.92	0.07
137	-2	10	1	59.997	1.5419	4	2.89	0.04
138	-4	6	2	60.009	1.5416	4	2.89	0.35
139	1	5	4	60.034	1.5410	4	2.88	0.02
140	-2	10	0	60.080	1.5399	4	2.88	0.14
141	-3	5	4	60.216	1.5368	4	2.86	0.01
142	-4	6	0	60.339	1.5339	4	2.85	0.19
143	2	0	4	60.550	1.5291	2	2.83	1.86
144	-1	9	3	60.623	1.5274	4	2.82	0.40
145	-1	7	4	60.762	1.5243	4	2.81	0.04
146	-4	0	4	60.821	1.5229	2	2.80	0.32
147	-2	2	5	60.893	1.5213	4	2.79	0.28

148	-1	11	0	61.369	1.5107	4	2.75	0.19
149	-1	3	5	61.454	1.5088	4	2.74	0.02
150	-3	9	1	61.458	1.5087	4	2.74	0.42
151	3	3	3	61.507	1.5076	4	2.73	0.18
152	2	2	4	61.628	1.5049	4	2.72	0.87
153	-5	1	1	61.800	1.5011	4	2.70	0.05
154	4	0	2	61.801	1.5011	2	2.70	0.88
155	-4	2	4	61.897	1.4990	4	2.69	0.28
156	-1	11	1	62.002	1.4967	4	2.68	0.00
157	0	2	5	62.234	1.4917	4	2.66	0.07
158	-3	9	0	62.253	1.4913	4	2.66	0.72
159	-5	1	2	62.269	1.4910	4	2.66	0.44
160	-2	10	2	62.621	1.4834	4	2.63	0.55
161	2	10	1	62.863	1.4783	4	2.60	0.61
162	4	2	2	62.867	1.4782	4	2.60	0.45
163	3	7	2	63.339	1.4683	4	2.56	0.04
164	-3	9	2	63.345	1.4682	4	2.56	0.02
165	1	11	1	63.418	1.4667	4	2.55	0.06
166	-3	1	5	63.756	1.4597	4	2.52	0.05
167	-4	6	3	63.880	1.4572	4	2.51	0.51
168	-5	3	1	63.923	1.4563	4	2.51	0.07
169	-5	1	0	64.001	1.4547	4	2.50	0.92
170	-2	4	5	64.087	1.4530	4	2.50	0.25
171	-5	3	2	64.383	1.4470	4	2.47	0.06
172	4	6	1	64.517	1.4443	4	2.46	0.39
173	2	4	4	64.802	1.4387	4	2.44	0.11
174	1	9	3	64.869	1.4373	4	2.43	0.21
175	-4	4	4	65.063	1.4335	4	2.42	0.17
176	-1	11	2	65.272	1.4294	4	2.40	0.09
177	-5	1	3	65.375	1.4274	4	2.39	0.04
178	0	4	5	65.391	1.4271	4	2.39	0.07
179	-1	5	5	65.673	1.4217	4	2.37	0.01
180	3	9	1	65.674	1.4217	4	2.37	0.28
181	3	5	3	65.724	1.4207	4	2.36	0.22
182	-3	3	5	65.843	1.4184	4	2.35	0.01
183	0	12	0	66.002	1.4154	2	2.34	0.55
184	4	4	2	66.008	1.4153	4	2.34	0.10
185	-5	3	0	66.084	1.4138	4	2.34	0.01
186	0	8	4	66.108	1.4134	4	2.33	0.07
187	-2	8	4	66.194	1.4118	4	2.33	0.03
188	-4	8	1	66.252	1.4107	4	2.32	0.02
189	0	10	3	66.319	1.4094	4	2.32	0.11
190	1	1	5	66.357	1.4087	4	2.32	0.15
191	1	7	4	66.384	1.4082	4	2.31	0.04
192	-3	7	4	66.556	1.4050	4	2.30	0.02
193	2	8	3	66.741	1.4015	4	2.29	0.18
194	0	12	1	67.294	1.3913	4	2.25	0.01
195	-4	8	2	67.387	1.3896	4	2.24	0.26
196	-5	3	3	67.436	1.3887	4	2.24	0.20
197	-4	8	0	67.697	1.3840	4	2.22	0.05
198	-2	10	3	67.771	1.3827	4	2.21	0.04
199	-3	9	3	67.789	1.3824	4	2.21	0.52
200	1	11	2	68.014	1.3784	4	2.20	0.41
201	-5	5	1	68.058	1.3776	4	2.20	0.23
202	2	10	2	68.158	1.3758	4	2.19	0.14
203	1	3	5	68.403	1.3714	4	2.17	0.59
204	-5	5	2	68.504	1.3697	4	2.17	0.07
205	5	1	1	68.730	1.3657	4	2.15	0.04
206	-1	9	4	69.109	1.3592	4	2.13	0.52
207	-2	6	5	69.231	1.3571	4	2.12	0.50
208	2	6	4	69.919	1.3454	4	2.08	0.16
209	-3	5	5	69.921	1.3453	4	2.08	0.05

Table S10. Calculation of bond valences.

The valence V of an atom is the sum of the individual bond valences s_{ij} surrounding the atom:

$$V_i = \mathrm{S}\, s_{ij}$$

The individual bond valences s_{ij} are calculated from the observed bond lengths:

$$s_{ij} = \exp[(R_0 - R_{ij})/b]$$

R_{ij} is the observed bond length, R_0 is tabulated, and b is a constant, typically 0.37 Å.[2] The values for R_0 were taken from the file bvparm2011.cif published on the IUCr website (http://www.iucr.org/resources/data/datasets/bond-valence-parameters).

Bond Type	Bond distance R_0	Bond distance R_{ij}	b	Valence S_{ij}	Bond Valence Sum V_i
Cu(1)-S	1.898	2.2852	0.37	0.3512	
Cu(1)-S	1.898	2.3168	0.37	0.3224	
Cu(1)-S	1.898	2.611	0.37	0.1456	
Cu(1)-N	1.630	2.066	0.37	0.3078	
					1.1269
Cu(2)-S	1.898	2.2474	0.37	0.3889	
Cu(2)-S	1.898	2.2474	0.37	0.3889	
Cu(2)-Cl	1.890	2.2737	0.37	0.3545	
					1.1324
S(1)-Cu	1.898	2.2474	0.37	-0.3889	
S(1)-Cu	1.898	2.2852	0.37	-0.3512	
S(1)-Cu	1.898	2.3168	0.37	-0.3224	
S(1)-Cu	1.898	2.611	0.37	-0.1456	
S(1)-N	1.800	1.838	0.37	-0.9024	
					-2.1105
N(1)-C(2)	1.442	1.475	0.37	-0.9147	
N(1)-H(1)	1.014	0.84	0.41	-1.5240	
N(1)-H(2)	1.014	0.89	0.41	-1.3502	
N(1)-	1.630	2.066	0.37	-0.3078	
					-2.7464

In the following the constant *b* is set to 0.37 for the calculation of bond valences of the NH bonds.

Bond Type	Bond distance	Bond distance R_{ij}	*b*	Valence S_{ij}	Bond Valence Sum V_i
Cu(1)-S	1.898	2.2852	0.37	0.3512	
Cu(1)-S	1.898	2.3168	0.37	0.3224	
Cu(1)-S	1.898	2.611	0.37	0.1456	
Cu(1)-N	1.630	2.066	0.37	0.3078	
					1.1269
Cu(2)-S	1.898	2.2474	0.37	0.3889	
Cu(1)-S	1.898	2.2474	0.37	0.3889	
Cu(2)-Cl	1.890	2.2737	0.37	0.3545	
					1.1324
S(1)-Cu	1.898	2.2474	0.37	-0.3889	
S(1)-Cu	1.898	2.2852	0.37	-0.3512	
S(1)-Cu	1.898	2.3168	0.37	-0.3224	
S(1)-Cu	1.898	2.611	0.37	-0.1456	
S(1)-N	1.800	1.838	0.37	-0.9024	
					-2.1105
N(1)-C(2)	1.442	1.475	0.37	-0.9147	
N(1)-H(1)	1.014	0.84	*0.37*	-1.6004	
N(1)-H(2)	1.014	0.89	*0.37*	-1.3981	
N(1)-	1.630	2.066	0.37	-0.3078	
					-2.8229

The results show that Cu^{+} and not Cu^{2+} is present in structure.

Reference:

1. N. W. Alcock, Adv. Inorg. Chem. Radiochem. 1972, 15, 1.
2. I. D. Brown, Chem. Rev. 2009, 109, 6858–6919 and references therein.