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(μ_3-Trithiocyanurato-$\kappa^6N^1,S^2:N^3,S^4:N^5,S^6$)tris[(*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine-κ^3N,N',N'')copper(II)] tris(perchlorate)

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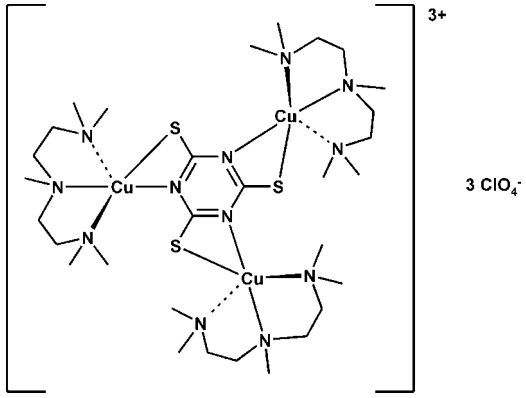
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.007 Å; disorder in main residue; R factor = 0.034; wR factor = 0.072; data-to-parameter ratio = 16.2.

In the title compound, $[Cu_3(C_9H_{23}N_3)_3(C_3N_3S_3)](ClO_4)_3$, the three Cu^{II} centres, related by the body-diagonal threefold rotation symmetry along [111], are bridged by a trithiocyanurate(3−) anion (ttc), with each centre having a considerably distorted trigonal–bipyramidal geometry and bonded to three N atoms of a tridentate *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine ligand, and one S and one N atoms of the ttc ligand. The secondary structure is stabilized by a variety of weak hydrogen bonds of the type C—H···O (H···A < 2.7 Å) connecting the cation and perchlorate anions.

Related literature

For related literature, see: Addison *et al.* (1984); Allen (2002); Desiraju (1996); Kar *et al.* (2004); Kopel *et al.* (2007); Marek *et al.* (2007).



Experimental

Crystal data

$[Cu_3(C_9H_{23}N_3)_3(C_3N_3S_3)](ClO_4)_3$
M_r = 1183.12
Cubic, $P2_13$
a = 17.3590 (4) Å
V = 5230.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.54 mm^{-1}
T = 120 (2) K
0.35 × 0.3 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.568, T_{max} = 0.680
38778 measured reflections
3461 independent reflections
2802 reflections with $I > 2\sigma(I)$
R_{int} = 0.095

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.072
S = 1.10
3460 reflections
213 parameters
53 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Absolute structure: Flack (1983), with 1556 Friedel pairs
Flack parameter: −0.050 (15)

Table 1
Selected geometric parameters (Å, °).

Cu—S	2.4824 (11)	Cu—N4	2.091 (11)
Cu—N1	2.118 (3)	S—C1	1.705 (4)
Cu—N2	2.074 (3)	N1—C1^{i}	1.346 (4)
Cu—N3	2.109 (3)	N1—C1	1.364 (5)
N1—Cu—S	67.95 (8)	N2—Cu—S	117.75 (10)
N1—Cu—N3	170.23 (12)	N4—Cu—S	109.46 (18)
N2—Cu—N4	132.8 (2)		

Symmetry code: (i) $-y+\frac{1}{2}, -z+1, x+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9*C*···O1	0.98	2.58	3.501 (7)	156
C3—H3*A*···O5^{i}	0.99	2.55	3.353 (5)	138
C3—H3*B*···O1^{ii}	0.99	2.62	3.310 (5)	127
C3—H3*A*···O5^{iii}	0.99	2.57	3.545 (6)	168
C4—H4*B*···O5^{iii}	0.99	2.52	3.502 (7)	170
C7—H7*C*···O5^{iii}	0.98	2.64	3.615 (6)	172
C9—H9*A*···O5^{iii}	0.98	2.70	3.669 (7)	170
C5*A*—H5*A*1···O5^{iii}	0.99	2.32	3.28 (2)	163
C4—H4*A*···O3^{iv}	0.99	2.57	3.476 (6)	153
C5*A*—H5*A*2···O1^{v}	0.99	2.47	3.247 (18)	135
C5—H5*B*···O3^{vi}	0.99	2.50	3.350 (6)	144
C8—H8*A*···O3^{vi}	0.98	2.69	3.466 (5)	137
C4*A*—H4*A*1···O3^{vi}	0.99	2.37	3.34 (4)	166
C10—H10*B*···O6^{vii}	0.98	2.68	2.983 (6)	99
C10—H10*B*···O6^{viii}	0.98	2.68	2.983 (6)	99
C10—H10*B*···O6^{ix}	0.98	2.68	2.983 (6)	99

Symmetry codes: (i) $-y+\frac{1}{2}, -z+1, x+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iii) $-z+\frac{1}{2}, -x+1, y+\frac{1}{2}$; (iv) y, z, x; (v) $-y+1, z+\frac{1}{2}, -x+\frac{1}{2}$; (vi) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (vii) $-y, z+\frac{1}{2}, -x+\frac{1}{2}$; (viii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (ix) $-z, x+\frac{1}{2}, -y+\frac{1}{2}$.

The measurement of low-angle reflection (112) was affected by shielding by the beam stop, therefore this reflection was removed from further calculations.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduc-

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tion: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *VMD 1.8.5* (Humphrey *et al.*, 1996) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997), *PLATON* (Spek, 2003), *PARST* (Nardelli, 1995) and *DIAMOND* (Brandenburg, 2006).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2015).

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supplementary materials

Acta Cryst. (2007). E**63**, m1742-m1743 [**doi:10.1107/S1600536807024026**]

(μ_3-Trithiocyanurato-$\kappa^6N^1,S^2:N^3,S^4:N^5,S^6$)tris[(*N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine-κ^3N,N',N'')copper(II)] tris(perchlorate)

Z. Trávnícek, J. Marek and S. Cermáková

Comment

This paper relates to our preceeding contributions describing X-ray structures of transition metal complexes bearing variously deprotonated trithiocyanuric acid ($ttcH_n$, n = 0–3) (see *e.g.* Marek *et al.*, 2007).

The molecular structure of the title compound, (I), is depicted in Fig. 1. The structure consists of a trinuclear Cu^{II} cation and three perchlorate anions. The three Cu^{II} metal centres are related by the body-diagonal threefold symmetry along [111] and bridged by an essentially planar [out-of-plane (C_3N_3) deviation is −0.009 (4) Å for C1 atom and 0.006 (3) Å for N1 atom (Brandenburg, 2006)] trithiocyanurate(3-) anion (ttc). Each Cu^{II} ion adopts a considerably distorted trigonal bipyramidal geometry (τ = 0.62) (Addison *et al.*, 1984) and is bonded by three N atoms of pmdien, and one S and one N atoms of the ttc ligand. For comparison, Zn^{II} ions in similar recently published trinuclear Zn complex (II) (Marek *et al.*, 2007) have τ=0.82. A different degree of the polyhedron deformation in (I) as compared to (II) can be also seen from the metal-S distances which differ significantly (Cu—S = 2.4824 (11) and Zn—S = 2.3793 (8) Å). The separation of Cu···Cu = 5.9235 (5) Å, while the distance of Zn···Zn = 6.0283 (5) Å in (II) and the Ru···Ru distances in a similar, but nonsymmetrical, trinuclear Ru complex bridged by the ttc (Kar *et al.*, 2004) are in the range of 5.838 (3)—5.894 (2) Å. The bond distances Cu—N are in the range of 2.073 (3)—2.118 (3) Å. The bond length C1—S = 1.705 (4) Å in (I), while the average value of a double C=S bond is 1.655 (11) Å (Cambridge Structural Database Version 5.27.1; Allen, 2002).

Mutual orientation of dinuclear cations and perchlorate anions causes the formation of the spherical voids in the crystal structure of (I) (Fig. 2). These cavities are in the distance of 3.84 Å from S1, and their volume is 63 (6) $Å^3$ (Spek, 2003). There is no evidence for presence of any molecules of the crystal water neither in peaks of difference electron density, nor in results of FT—IR spectroscopy (Kopel *et al.*, 2007). The secondary structure of the title compound (I) is stabilized by variety of interactions of the type C—H···O, connecting the cation and perchlorate anions [see Fig. 3 and Table 1 with the list prepared by *PARST*(Nardelli, 1995) and cut-off value H···*A=2.7* Å). These *non classic hydrogen bonds* (the term from Spek, 2003) could be probably classified as *weak hydrogen bonds* (using terminology of Desiraju, 1996).

Experimental

Crystals of (I) were prepared by a recently described method (Kopel *et al.*, 2007). **Safety note:** *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even a small amount of these materials should be handled with great caution.

Refinement

The measurement of low-angle reflection (112) was affected by shielding by the beam stopper, therefore this reflection was removed from further calculations. A part of pmdien ligand (namely atoms C4, C5, N4, C9 and C10) has been refined as disordered between two positions [the site occupancy factors refined to 0.792 (6) and 0.208 (6)] defined by approx. 25–40° angular rotation of disordered fragment around the Cu—N4 bond. All H atoms were located in a difference map and refined using the riding model with C–H distances of 0.98 (C_{methyl}) and 0.99 Å (CH_2), and with U_{iso}(H) values of 1.2U_{eq}(CH_2) or 1.5U_{eq}(C_{methyl}).

Figures

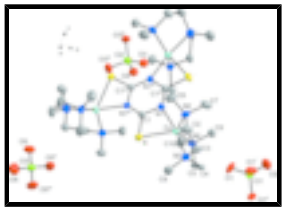

Fig. 1. : The molecular structure of the title compound (I). The non-H atoms are drawn as 50% probability displacement ellipsoids. The major part of the disordered fragment of pmdien ligand is shown only for better clarity. The H-atoms have been omitted for clarity. [Symmetry codes: (i) 1 − *y*, 1/2 + *z*, 1/2 − *x*; (ii) 1/2 − *z*, 1 − *x*, −1/2 + *y*; (iii) 1/2 − *y*, 1 − *z*, 1/2 + *x*; (iv) −1/2 + *z*, 1/2 − *x*, 1 − *y*; (v) *y*, *z*, *x*; (vi) *z*, *x* *y*].

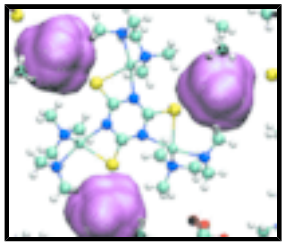

Fig. 2. : Part of the crystal structure of (I), showing the formation of voids. The cavities generated by VMD 1.8.5 (Humphrey *et al.*, 1996) and probe with radius 1.5 Å are demonstrated by mauve colour.

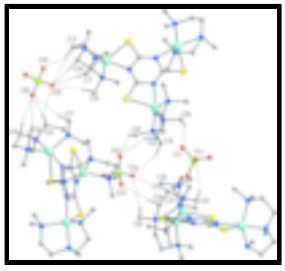

Fig. 3. : Part of the crystal structure of (I), showing C—H···O non-bonding interactions as dashed lines. Minor disordered pmdien fragments and H atoms not involved in hydrogen bonding have been omitted for clarity.

(μ$_3$-Trithiocyanurato-κ^6*N*^{1},*S*^{2}:*N*^{3},*S*^{4}:*N*^{5},*S*^{6})tris[(*N*,*N*,*N*′,*N*″,\ *N*″- pentamethyldiethylenetriamine-κ^3*N*,*N*′,*N*″)copper(II)] tris(perchlorate)

Crystal data

$[Cu_3(C_9H_{23}N_3)_3(C_3N_3S_3)](ClO_4)_3$	$Z = 4$
$M_r = 1183.12$	$F_{000} = 2460$
Cubic, $P2_13$	$D_x = 1.502$ Mg m^{-3}
Hall symbol: P 2ac 2ab 3	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 17.3590$ (4) Å	Cell parameters from 29540 reflections
$b = 17.3590$ (4) Å	θ = 2.6–31.9°

c = 17.3590 (4) Å
α = 90º
β = 90º
γ = 90º
V = 5230.9 (2) Å^3

μ = 1.54 mm^{-1}
T = 120 (2) K
Prism, blue
0.35 × 0.3 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur2 + CCD diffractometer
Radiation source: fine-focus sealed tube
Monochromator: Enhance (Oxford Diffraction)
Detector resolution: 8.3611 pixels mm^{-1}
T = 120(2) K
rotation method, ω–scan
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)
T_{min} = 0.568, T_{max} = 0.680
38778 measured reflections

3461 independent reflections
2802 reflections with $I > 2\sigma(I)$
R_{int} = 0.095
θ_{max} = 26.0º
θ_{min} = 2.6º
h = −21→21
k = −14→21
l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.072
S = 1.10
3460 reflections
213 parameters
53 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 1556 Friedel pairs
Flack parameter: −0.050 (15)

Special details

Geometry. 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu	0.19495 (2)	0.58035 (2)	0.52012 (2)	0.01962 (11)	
Cl1	0.06784 (5)	0.93216 (5)	0.43216 (5)	0.0264 (4)	
Cl2	0.20500 (5)	0.29500 (5)	0.70500 (5)	0.0288 (4)	
Cl3	0.15427 (6)	0.15427 (6)	0.15427 (6)	0.0304 (4)	
O1	0.02855 (15)	0.86131 (14)	0.41485 (18)	0.0390 (7)	
O2	0.02011 (16)	0.97989 (16)	0.47989 (16)	0.0502 (14)	
O3	0.26501 (16)	0.34143 (16)	0.73923 (16)	0.0351 (7)	
O4	0.15686 (15)	0.34314 (15)	0.65686 (15)	0.0336 (11)	
O5	0.17414 (18)	0.11298 (17)	0.22363 (16)	0.0433 (8)	
O6	0.10716 (18)	0.10716 (18)	0.10716 (18)	0.0575 (16)	
S	0.18225 (6)	0.46540 (5)	0.43600 (6)	0.0289 (2)	
N1	0.10373 (16)	0.50747 (17)	0.55558 (17)	0.0210 (7)	
N2	0.26446 (17)	0.57110 (19)	0.61687 (17)	0.0262 (7)	
N3	0.28906 (19)	0.63870 (18)	0.47013 (18)	0.0297 (8)	
C1	0.1078 (2)	0.4533 (2)	0.4988 (2)	0.0222 (8)	
C2	0.3432 (2)	0.5844 (3)	0.5876 (3)	0.0423 (11)	
H2A	0.3615	0.5375	0.5609	0.051*	
H2B	0.3782	0.5945	0.6314	0.051*	
C3	0.3456 (2)	0.6511 (3)	0.5331 (2)	0.0359 (10)	
H3A	0.3331	0.6993	0.5610	0.043*	
H3B	0.3980	0.6563	0.5112	0.043*	
N4	0.1269 (4)	0.6697 (5)	0.4766 (4)	0.0233 (11)	0.792 (6)
C4	0.2575 (5)	0.7153 (4)	0.4453 (3)	0.0280 (19)	0.792 (6)
H4A	0.2901	0.7369	0.4037	0.034*	0.792 (6)
H4B	0.2585	0.7516	0.4893	0.034*	0.792 (6)
C5	0.1761 (3)	0.7064 (3)	0.4167 (3)	0.0310 (13)	0.792 (6)
H5A	0.1548	0.7577	0.4034	0.037*	0.792 (6)
H5B	0.1758	0.6744	0.3695	0.037*	0.792 (6)
C9	0.1072 (4)	0.7230 (3)	0.5388 (4)	0.0352 (17)	0.792 (6)
H9A	0.1546	0.7439	0.5613	0.053*	0.792 (6)
H9B	0.0780	0.6956	0.5785	0.053*	0.792 (6)
H9C	0.0760	0.7653	0.5182	0.053*	0.792 (6)
C10	0.0541 (3)	0.6435 (3)	0.4398 (3)	0.0379 (15)	0.792 (6)
H10A	0.0292	0.6872	0.4142	0.057*	0.792 (6)
H10B	0.0196	0.6226	0.4792	0.057*	0.792 (6)
H10C	0.0656	0.6034	0.4017	0.057*	0.792 (6)
N4A	0.1346 (17)	0.673 (2)	0.4844 (15)	0.0233 (11)	0.208 (6)
C4A	0.260 (2)	0.7058 (18)	0.4241 (18)	0.0280 (19)	0.208 (6)
H4A1	0.2429	0.6892	0.3722	0.034*	0.208 (6)
H4A2	0.2997	0.7460	0.4186	0.034*	0.208 (6)
C5A	0.1920 (12)	0.7356 (11)	0.4703 (12)	0.0310 (13)	0.208 (6)
H5A1	0.2106	0.7559	0.5203	0.037*	0.208 (6)
H5A2	0.1670	0.7783	0.4421	0.037*	0.208 (6)
C9A	0.0754 (16)	0.7019 (16)	0.5375 (17)	0.0352 (17)	0.208 (6)
H9A1	0.0987	0.7121	0.5879	0.053*	0.208 (6)

H9A2	0.0348	0.6630	0.5432	0.053*	0.208 (6)
H9A3	0.0532	0.7495	0.5170	0.053*	0.208 (6)
C10A	0.0956 (13)	0.6583 (13)	0.4096 (14)	0.0379 (15)	0.208 (6)
H10D	0.0762	0.7069	0.3885	0.057*	0.208 (6)
H10E	0.0524	0.6228	0.4176	0.057*	0.208 (6)
H10F	0.1324	0.6354	0.3735	0.057*	0.208 (6)
C6	0.2592 (3)	0.4946 (3)	0.6536 (3)	0.0447 (12)	
H6A	0.2648	0.4545	0.6143	0.067*	
H6B	0.2090	0.4893	0.6788	0.067*	
H6C	0.3002	0.4893	0.6920	0.067*	
C7	0.2447 (2)	0.6301 (3)	0.6766 (2)	0.0417 (11)	
H7A	0.2795	0.6246	0.7207	0.063*	
H7B	0.1914	0.6226	0.6935	0.063*	
H7C	0.2503	0.6818	0.6545	0.063*	
C8	0.3237 (3)	0.5950 (2)	0.4064 (2)	0.0430 (11)	
H8A	0.2849	0.5858	0.3665	0.064*	
H8B	0.3429	0.5455	0.4257	0.064*	
H8C	0.3666	0.6245	0.3845	0.064*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0182 (2)	0.0188 (2)	0.0218 (2)	−0.00134 (19)	−0.00067 (19)	0.0043 (2)
Cl1	0.0264 (4)	0.0264 (4)	0.0264 (4)	−0.0045 (4)	−0.0045 (4)	0.0045 (4)
Cl2	0.0288 (4)	0.0288 (4)	0.0288 (4)	−0.0013 (4)	0.0013 (4)	−0.0013 (4)
Cl3	0.0304 (4)	0.0304 (4)	0.0304 (4)	0.0034 (5)	0.0034 (5)	0.0034 (5)
O1	0.0327 (16)	0.0213 (14)	0.0630 (19)	−0.0087 (13)	−0.0155 (16)	0.0091 (15)
O2	0.0502 (14)	0.0502 (14)	0.0502 (14)	0.0107 (16)	0.0107 (16)	−0.0107 (16)
O3	0.0312 (15)	0.0408 (17)	0.0331 (16)	−0.0108 (14)	−0.0046 (13)	−0.0004 (14)
O4	0.0336 (11)	0.0336 (11)	0.0336 (11)	0.0049 (13)	−0.0049 (13)	0.0049 (13)
O5	0.0482 (19)	0.0508 (19)	0.0309 (16)	0.0163 (16)	0.0076 (14)	0.0168 (14)
O6	0.0575 (16)	0.0575 (16)	0.0575 (16)	−0.0089 (17)	−0.0089 (17)	−0.0089 (17)
S	0.0283 (5)	0.0250 (5)	0.0333 (6)	−0.0017 (4)	0.0108 (4)	−0.0013 (4)
N1	0.0197 (16)	0.0210 (16)	0.0222 (16)	0.0015 (13)	0.0019 (13)	−0.0016 (13)
N2	0.0203 (16)	0.0294 (18)	0.0291 (18)	0.0009 (15)	0.0012 (14)	0.0085 (15)
N3	0.035 (2)	0.0268 (17)	0.0276 (18)	−0.0007 (15)	−0.0019 (16)	0.0042 (15)
C1	0.023 (2)	0.0214 (19)	0.022 (2)	0.0035 (16)	0.0009 (16)	0.0034 (16)
C2	0.021 (2)	0.068 (3)	0.037 (2)	−0.004 (2)	−0.004 (2)	0.013 (3)
C3	0.027 (2)	0.045 (3)	0.035 (2)	−0.011 (2)	−0.0054 (19)	0.009 (2)
N4	0.026 (2)	0.0246 (19)	0.020 (2)	0.0019 (16)	−0.0016 (19)	0.0021 (18)
C4	0.033 (2)	0.025 (3)	0.026 (4)	−0.005 (2)	0.001 (3)	0.006 (3)
C5	0.038 (3)	0.025 (3)	0.030 (3)	0.004 (2)	0.008 (3)	0.005 (2)
C9	0.048 (5)	0.028 (4)	0.029 (3)	0.013 (3)	−0.001 (3)	−0.001 (3)
C10	0.027 (3)	0.037 (3)	0.049 (4)	0.003 (3)	−0.013 (3)	0.006 (3)
N4A	0.026 (2)	0.0246 (19)	0.020 (2)	0.0019 (16)	−0.0016 (19)	0.0021 (18)
C4A	0.033 (2)	0.025 (3)	0.026 (4)	−0.005 (2)	0.001 (3)	0.006 (3)
C5A	0.038 (3)	0.025 (3)	0.030 (3)	0.004 (2)	0.008 (3)	0.005 (2)
C9A	0.048 (5)	0.028 (4)	0.029 (3)	0.013 (3)	−0.001 (3)	−0.001 (3)

C10A	0.027 (3)	0.037 (3)	0.049 (4)	0.003 (3)	−0.013 (3)	0.006 (3)
C6	0.039 (3)	0.046 (3)	0.049 (3)	0.002 (2)	−0.010 (2)	0.022 (2)
C7	0.035 (3)	0.065 (3)	0.025 (2)	−0.004 (2)	−0.001 (2)	0.000 (2)
C8	0.050 (3)	0.035 (2)	0.044 (3)	−0.006 (2)	0.010 (2)	−0.002 (2)

Geometric parameters (Å, °)

Cu—N4A	2.02 (4)	N4—C5	1.489 (8)
Cu—S	2.4824 (11)	C4—C5	1.507 (9)
Cu—N1	2.118 (3)	C4—H4A	0.9900
Cu—N2	2.074 (3)	C4—H4B	0.9900
Cu—N3	2.109 (3)	C5—H5A	0.9900
Cu—N4	2.091 (11)	C5—H5B	0.9900
Cl1—O2	1.435 (5)	C9—H9A	0.9800
Cl1—O1^{i}	1.438 (2)	C9—H9B	0.9800
Cl1—O1	1.438 (2)	C9—H9C	0.9800
Cl1—O1^{ii}	1.438 (2)	C10—H10A	0.9800
Cl2—O3	1.445 (3)	C10—H10B	0.9800
Cl2—O3^{iii}	1.445 (3)	C10—H10C	0.9800
Cl2—O3^{iv}	1.445 (3)	N4A—C9A	1.467 (18)
Cl2—O4	1.447 (5)	N4A—C10A	1.487 (18)
Cl3—O6	1.416 (6)	N4A—C5A	1.492 (18)
Cl3—O5^{v}	1.443 (3)	C4A—C5A	1.512 (18)
Cl3—O5^{vi}	1.443 (3)	C4A—H4A1	0.9900
Cl3—O5	1.443 (3)	C4A—H4A2	0.9900
S—C1	1.705 (4)	C5A—H5A1	0.9900
N1—C1^{iv}	1.346 (4)	C5A—H5A2	0.9900
N1—C1	1.364 (5)	C9A—H9A1	0.9800
N2—C6	1.475 (5)	C9A—H9A2	0.9800
N2—C2	1.476 (5)	C9A—H9A3	0.9800
N2—C7	1.497 (5)	C10A—H10D	0.9800
N3—C8	1.470 (5)	C10A—H10E	0.9800
N3—C3	1.484 (5)	C10A—H10F	0.9800
N3—C4	1.502 (6)	C6—H6A	0.9800
N3—C4A	1.503 (17)	C6—H6B	0.9800
C1—N1^{iii}	1.346 (4)	C6—H6C	0.9800
C2—C3	1.497 (6)	C7—H7A	0.9800
C2—H2A	0.9900	C7—H7B	0.9800
C2—H2B	0.9900	C7—H7C	0.9800
C3—H3A	0.9900	C8—H8A	0.9800
C3—H3B	0.9900	C8—H8B	0.9800
N4—C9	1.463 (7)	C8—H8C	0.9800
N4—C10	1.486 (7)		
N4A—Cu—N2	127.7 (7)	C9—N4—C10	108.2 (6)
N4A—Cu—N4	5.2 (8)	C9—N4—C5	112.2 (6)
N4A—Cu—N3	83.8 (7)	C10—N4—C5	108.6 (5)
N2—Cu—N3	85.39 (12)	C9—N4—Cu	109.5 (5)

N4—Cu—N3	86.1 (2)	C10—N4—Cu	114.1 (5)
N4A—Cu—N1	100.2 (6)	C5—N4—Cu	104.3 (5)
N2—Cu—N1	98.82 (12)	N3—C4—C5	110.2 (6)
N4—Cu—N1	97.22 (19)	N3—C4—H4A	109.6
N1—Cu—S	67.95 (8)	C5—C4—H4A	109.6
N1—Cu—N3	170.23 (12)	N3—C4—H4B	109.6
N2—Cu—N4	132.8 (2)	C5—C4—H4B	109.6
N4A—Cu—S	114.5 (7)	H4A—C4—H4B	108.1
N2—Cu—S	117.75 (10)	N4—C5—C4	110.6 (5)
N4—Cu—S	109.46 (18)	N4—C5—H5A	109.5
N3—Cu—S	102.29 (9)	C4—C5—H5A	109.5
O2—Cl1—O1^{i}	109.91 (14)	N4—C5—H5B	109.5
O2—Cl1—O1	109.91 (14)	C4—C5—H5B	109.5
O1^{i}—Cl1—O1	109.03 (14)	H5A—C5—H5B	108.1
O2—Cl1—O1^{ii}	109.91 (14)	C9A—N4A—C10A	107 (3)
O1^{i}—Cl1—O1^{ii}	109.03 (14)	C9A—N4A—C5A	109 (2)
O1—Cl1—O1^{ii}	109.03 (14)	C10A—N4A—C5A	107 (2)
O3—Cl2—O3^{iii}	109.57 (12)	C9A—N4A—Cu	116 (2)
O3—Cl2—O3^{iv}	109.57 (12)	C10A—N4A—Cu	111 (2)
O3^{iii}—Cl2—O3^{iv}	109.57 (12)	C5A—N4A—Cu	106 (2)
O3—Cl2—O4	109.37 (12)	N3—C4A—C5A	104.3 (15)
O3^{iii}—Cl2—O4	109.37 (12)	N3—C4A—H4A1	110.9
O3^{iv}—Cl2—O4	109.37 (13)	C5A—C4A—H4A1	110.9
O6—Cl3—O5^{v}	109.45 (15)	N3—C4A—H4A2	110.9
O6—Cl3—O5^{vi}	109.45 (15)	C5A—C4A—H4A2	110.9
O5^{v}—Cl3—O5^{vi}	109.49 (15)	H4A1—C4A—H4A2	108.9
O6—Cl3—O5	109.45 (15)	N4A—C5A—C4A	111 (2)
O5^{v}—Cl3—O5	109.49 (15)	N4A—C5A—H5A1	109.4
O5^{vi}—Cl3—O5	109.49 (15)	C4A—C5A—H5A1	109.4
C1—S—Cu	77.88 (13)	N4A—C5A—H5A2	109.4
C1^{iv}—N1—C1	117.9 (3)	C4A—C5A—H5A2	109.4
C1^{iv}—N1—Cu	142.5 (3)	H5A1—C5A—H5A2	108.0
C1—N1—Cu	99.4 (2)	N4A—C9A—H9A1	109.5
C6—N2—C2	110.3 (3)	N4A—C9A—H9A2	109.5
C6—N2—C7	107.6 (3)	H9A1—C9A—H9A2	109.5
C2—N2—C7	110.1 (3)	N4A—C9A—H9A3	109.5
C6—N2—Cu	112.5 (3)	H9A1—C9A—H9A3	109.5
C2—N2—Cu	104.3 (2)	H9A2—C9A—H9A3	109.5
C7—N2—Cu	112.0 (2)	N4A—C10A—H10D	109.5
C8—N3—C3	111.0 (3)	N4A—C10A—H10E	109.5
C8—N3—C4	113.0 (3)	H10D—C10A—H10E	109.5
C3—N3—C4	108.9 (4)	N4A—C10A—H10F	109.5
C8—N3—C4A	98.0 (12)	H10D—C10A—H10F	109.5
C3—N3—C4A	120.3 (18)	H10E—C10A—H10F	109.5
C8—N3—Cu	112.3 (2)	N2—C6—H6A	109.5

C3—N3—Cu	106.2 (2)	N2—C6—H6B	109.5
C4—N3—Cu	105.2 (4)	H6A—C6—H6B	109.5
C4A—N3—Cu	109.1 (13)	N2—C6—H6C	109.5
$N1^{iii}$—C1—N1	122.1 (3)	H6A—C6—H6C	109.5
$N1^{iii}$—C1—S	123.3 (3)	H6B—C6—H6C	109.5
N1—C1—S	114.6 (3)	N2—C7—H7A	109.5
N2—C2—C3	111.4 (3)	N2—C7—H7B	109.5
N2—C2—H2A	109.4	H7A—C7—H7B	109.5
C3—C2—H2A	109.4	N2—C7—H7C	109.5
N2—C2—H2B	109.4	H7A—C7—H7C	109.5
C3—C2—H2B	109.4	H7B—C7—H7C	109.5
H2A—C2—H2B	108.0	N3—C8—H8A	109.5
N3—C3—C2	109.6 (3)	N3—C8—H8B	109.5
N3—C3—H3A	109.8	H8A—C8—H8B	109.5
C2—C3—H3A	109.8	N3—C8—H8C	109.5
N3—C3—H3B	109.8	H8A—C8—H8C	109.5
C2—C3—H3B	109.8	H8B—C8—H8C	109.5
H3A—C3—H3B	108.2		
N4A—Cu—S—C1	−89.2 (7)	Cu—N2—C2—C3	44.3 (4)
N2—Cu—S—C1	90.77 (15)	C8—N3—C3—C2	−87.9 (4)
N4—Cu—S—C1	−87.8 (2)	C4—N3—C3—C2	147.1 (4)
N3—Cu—S—C1	−177.99 (15)	C4A—N3—C3—C2	158.7 (11)
N1—Cu—S—C1	2.27 (15)	Cu—N3—C3—C2	34.4 (4)
N4A—Cu—N1—$C1^{iv}$	−65.1 (8)	N2—C2—C3—N3	−55.0 (5)
N2—Cu—N1—$C1^{iv}$	66.0 (4)	N4A—Cu—N4—C9	−39 (9)
N4—Cu—N1—$C1^{iv}$	−69.5 (4)	N2—Cu—N4—C9	−22.4 (5)
S—Cu—N1—$C1^{iv}$	−177.6 (4)	N3—Cu—N4—C9	−102.4 (4)
N4A—Cu—N1—C1	109.6 (8)	N1—Cu—N4—C9	86.8 (4)
N2—Cu—N1—C1	−119.3 (2)	S—Cu—N4—C9	155.9 (4)
N4—Cu—N1—C1	105.3 (3)	N4A—Cu—N4—C10	−160 (10)
S—Cu—N1—C1	−2.81 (18)	N2—Cu—N4—C10	−143.8 (4)
N4A—Cu—N2—C6	143.0 (9)	N3—Cu—N4—C10	136.1 (5)
N4—Cu—N2—C6	141.2 (3)	N1—Cu—N4—C10	−34.7 (5)
N3—Cu—N2—C6	−138.4 (3)	S—Cu—N4—C10	34.4 (5)
N1—Cu—N2—C6	32.7 (3)	N4A—Cu—N4—C5	81 (9)
S—Cu—N2—C6	−37.0 (3)	N2—Cu—N4—C5	97.9 (4)
N4A—Cu—N2—C2	−97.4 (9)	N3—Cu—N4—C5	17.8 (4)
N4—Cu—N2—C2	−99.3 (4)	N1—Cu—N4—C5	−153.0 (4)
N3—Cu—N2—C2	−18.9 (3)	S—Cu—N4—C5	−83.9 (4)
N1—Cu—N2—C2	152.3 (3)	C8—N3—C4—C5	86.6 (5)
S—Cu—N2—C2	82.6 (3)	C3—N3—C4—C5	−149.6 (4)
N4A—Cu—N2—C7	21.7 (9)	C4A—N3—C4—C5	71 (7)
N4—Cu—N2—C7	19.8 (4)	Cu—N3—C4—C5	−36.2 (4)
N3—Cu—N2—C7	100.2 (3)	C9—N4—C5—C4	75.1 (8)
N1—Cu—N2—C7	−88.7 (3)	C10—N4—C5—C4	−165.3 (6)
S—Cu—N2—C7	−158.3 (2)	Cu—N4—C5—C4	−43.3 (5)
N4A—Cu—N3—C8	−118.2 (8)	N3—C4—C5—N4	55.8 (7)

N2—Cu—N3—C8	113.1 (3)	N2—Cu—N4A—C9A	−60.9 (19)
N4—Cu—N3—C8	−113.4 (3)	N4—Cu—N4A—C9A	104 (10)
S—Cu—N3—C8	−4.3 (3)	N3—Cu—N4A—C9A	−140.2 (18)
N4A—Cu—N3—C3	120.4 (8)	N1—Cu—N4A—C9A	48.8 (18)
N2—Cu—N3—C3	−8.4 (3)	S—Cu—N4A—C9A	119.1 (17)
N4—Cu—N3—C3	125.1 (3)	N2—Cu—N4A—C10A	176.5 (12)
S—Cu—N3—C3	−125.8 (2)	N4—Cu—N4A—C10A	−19 (9)
N4A—Cu—N3—C4	5.0 (8)	N3—Cu—N4A—C10A	97.2 (16)
N2—Cu—N3—C4	−123.7 (3)	N1—Cu—N4A—C10A	−73.8 (16)
N4—Cu—N3—C4	9.8 (4)	S—Cu—N4A—C10A	−3.5 (18)
S—Cu—N3—C4	118.8 (3)	N2—Cu—N4A—C5A	60.6 (19)
N4A—Cu—N3—C4A	−10.6 (18)	N4—Cu—N4A—C5A	−135 (11)
N2—Cu—N3—C4A	−139.4 (16)	N3—Cu—N4A—C5A	−18.7 (15)
N4—Cu—N3—C4A	−5.9 (16)	N1—Cu—N4A—C5A	170.3 (14)
S—Cu—N3—C4A	103.2 (16)	S—Cu—N4A—C5A	−119.4 (14)
C1^{iv}—N1—C1—N1^{iii}	2.1 (7)	C8—N3—C4A—C5A	153 (2)
Cu—N1—C1—N1^{iii}	−174.3 (3)	C3—N3—C4A—C5A	−86 (3)
C1^{iv}—N1—C1—S	−179.42 (16)	C4—N3—C4A—C5A	−41 (5)
Cu—N1—C1—S	4.2 (3)	Cu—N3—C4A—C5A	36 (3)
Cu—S—C1—N1^{iii}	174.8 (3)	C9A—N4A—C5A—C4A	173 (2)
Cu—S—C1—N1	−3.6 (2)	C10A—N4A—C5A—C4A	−72 (3)
C6—N2—C2—C3	165.3 (4)	Cu—N4A—C5A—C4A	47 (2)
C7—N2—C2—C3	−76.1 (4)	N3—C4A—C5A—N4A	−56 (3)

Symmetry codes: (i) −*z*+1/2, −*x*+1, *y*−1/2; (ii) −*y*+1, *z*+1/2, −*x*+1/2; (iii) *z*−1/2, −*x*+1/2, −*y*+1; (iv) −*y*+1/2, −*z*+1, *x*+1/2; (v) *y*, *z*, *x*; (vi) *z*, *x*, *y*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5A···O1	0.99	2.84	3.713 (6)	147
C5A—H5A2···O1	0.99	2.84	3.71 (2)	146
C9—H9C···O1	0.98	2.58	3.501 (7)	156
C3—H3A···O5^{iv}	0.99	2.55	3.353 (5)	138
C9A—H9A3···O1	0.98	2.66	3.59 (3)	157
C9A—H9A2···N1	0.98	2.96	3.42 (3)	110
C10—H10B···N1	0.98	2.81	3.218 (6)	106
C10A—H10D···O1	0.98	2.84	3.71 (2)	148
C5A—H5A2···O1	0.99	2.84	3.71 (2)	146
C5A—H5A2···O1	0.99	2.84	3.71 (2)	146
C9A—H9A2···N1	0.98	2.96	3.42 (3)	110
C9A—H9A3···O1	0.98	2.66	3.59 (3)	157
C6—H6C···O3	0.98	2.76	3.049 (5)	97
C6—H6B···O4	0.98	2.72	3.174 (5)	109
C6—H6C···O3	0.98	2.76	3.049 (5)	97
C6—H6B···O4	0.98	2.72	3.174 (5)	109
C6—H6B···N1	0.98	2.83	3.198 (5)	103
C6—H6C···O3	0.98	2.76	3.049 (5)	97
C2—H2B···O1^{vii}	0.99	2.84	3.354 (5)	113

C3—H3B···O1^{vii}	0.99	2.62	3.310 (5)	127
C2—H2A···O2^{vii}	0.99	2.86	3.472 (4)	121
C2—H2A···O2^{viii}	0.99	2.86	3.472 (4)	121
C2—H2A···O2^{ix}	0.99	2.86	3.472 (4)	121
C3—H3A···O5^{x}	0.99	2.57	3.545 (6)	168
C4—H4B···O5^{x}	0.99	2.52	3.502 (7)	170
C7—H7C···O5^{x}	0.98	2.64	3.615 (6)	172
C9—H9A···O5^{x}	0.98	2.70	3.669 (7)	170
C5A—H5A1···O5^{x}	0.99	2.32	3.28 (2)	163
C7—H7C···O5^{iv}	0.98	2.91	3.543 (6)	124
C4—H4A···O3^{v}	0.99	2.57	3.476 (6)	153
C8—H8C···O3^{v}	0.98	2.91	3.519 (5)	121
C5A—H5A2···O1^{ii}	0.99	2.47	3.247 (18)	135
C9—H9C···O1^{ii}	0.98	2.93	3.571 (7)	124
C5—H5B···O3^{xi}	0.99	2.50	3.350 (6)	144
C10A—H10F···O3^{xi}	0.98	2.96	3.82 (3)	147
C8—H8A···O3^{xi}	0.98	2.69	3.466 (5)	137
C4A—H4A1···O3^{xi}	0.99	2.37	3.34 (4)	166
C10—H10B···O6^{xii}	0.98	2.68	2.983 (6)	99
C10A—H10E···O6^{xii}	0.98	2.82	3.64 (2)	142
C10—H10B···O6^{xiii}	0.98	2.68	2.983 (6)	99
C10A—H10E···O6^{xiii}	0.98	2.82	3.64 (2)	142
C10—H10B···O6^{xiv}	0.98	2.68	2.983 (6)	99
C10A—H10E···O6^{xiv}	0.98	2.82	3.64 (2)	142

Symmetry codes: (iv) −*y*+1/2, −*z*+1, *x*+1/2; (vii) *x*+1/2, −*y*+3/2, −*z*+1; (viii) −*z*+1, *x*+1/2, −*y*+3/2; (ix) −*y*+3/2, −*z*+1, *x*+1/2; (x) −*z*+1/2, −*x*+1, *y*+1/2; (v) *y*, *z*, *x*; (ii) −*y*+1, *z*+1/2, −*x*+1/2; (xi) −*x*+1/2, −*y*+1, *z*−1/2; (xii) −*y*, *z*+1/2, −*x*+1/2; (xiii) −*x*, *y*+1/2, −*z*+1/2; (xiv) −*z*, *x*+1/2, −*y*+1/2.

Fig. 1

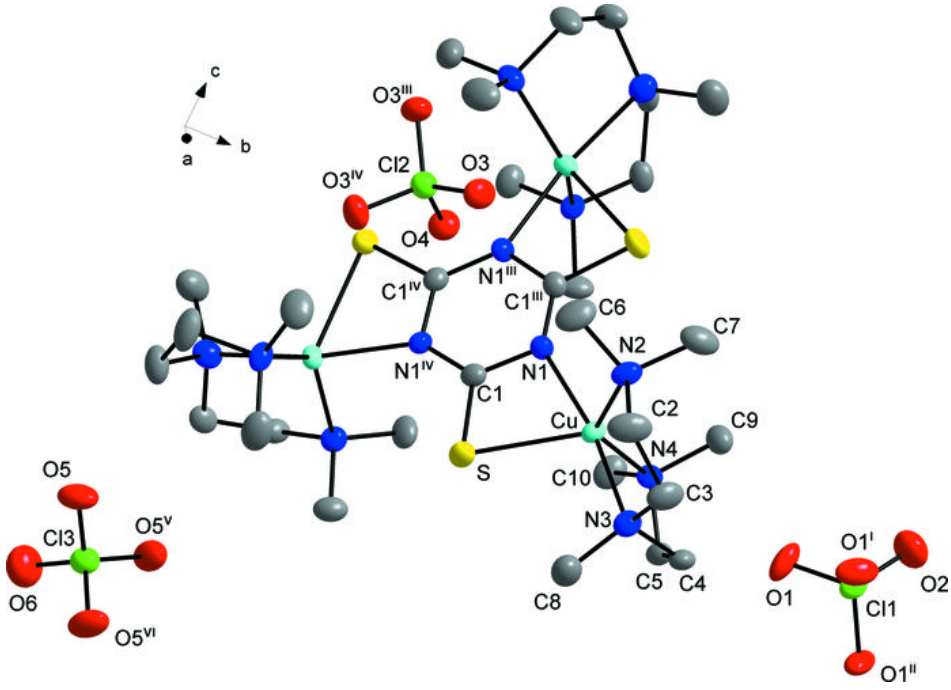
c
b
a
O3III
O3IV
Cl2
O3
O4
N1III
C1IV
C1III
C6
C7
N2
N1IV
N1
C1
Cu
C2
C9
N4
S
C10
C3
N3
C8
C5
C4
O5
Cl3
O5V
O6
O5VI
O1I
O1
O2
Cl1
O1II

Fig. 2

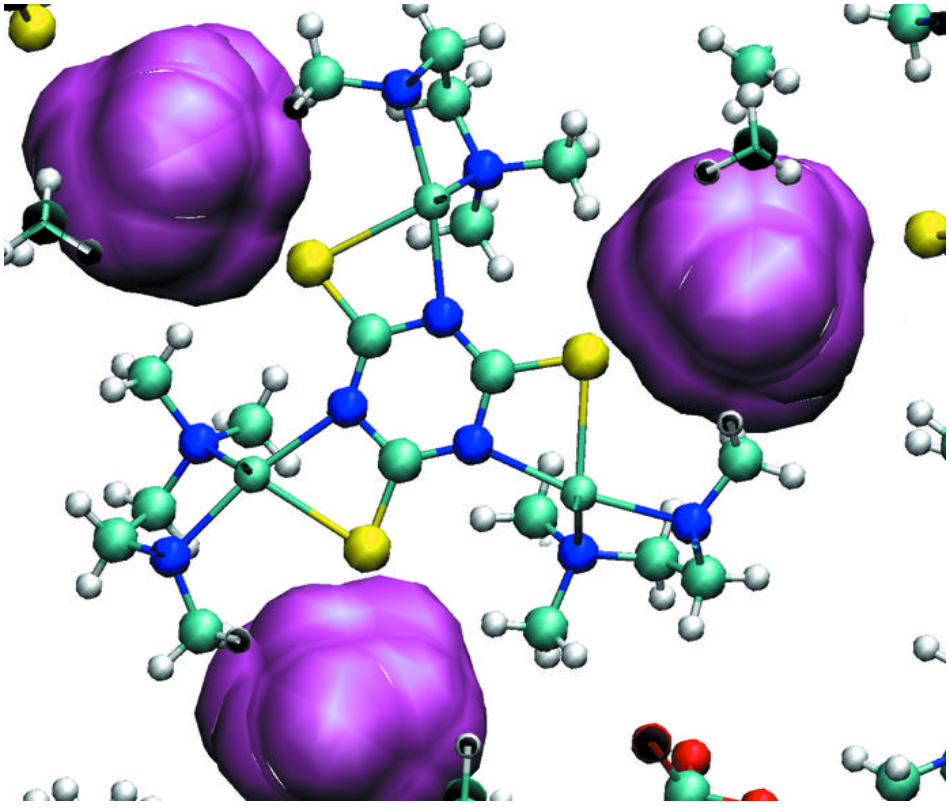

Fig. 3