

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Poly[[tris[μ -2,2'-(butane-1,4-diyl-dithio)-bis(1,3,4-thiadiazole)- κ^2 N⁴:N⁴]-copper(II)] bis(perchlorate)]

Pu-Zhou Hu,* Jian-Hua Qin and Jian-Ge Wang

College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, People's Republic of China

Correspondence e-mail: jh_q128105@126.com

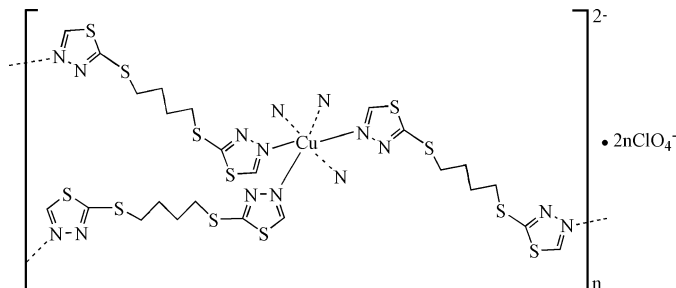
Received 11 February 2009; accepted 17 February 2009

 Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.047; wR factor = 0.133; data-to-parameter ratio = 18.6.

In the title compound, $[\{\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_4\text{S}_4)_3(\text{ClO}_4)_2\}]_n$, the Cu^{II} atom is located on a threefold inversion axis coordinated by six N atoms of symmetry-equivalent 2,2'-(butane-1,4-diyl-dithio)bis(1,3,4-thiadiazole) ligands in a slightly distorted octahedral geometry. Adjacent Cu^{II} atoms are linked by the bridging bidentate thiadiazole ligands, which are situated about inversion centers. This leads to the formation of a three-dimensional network structure.

Related literature

For copper(II) complexes involving the same ligand, see: Huang *et al.* (2009); Wang *et al.* (2008).



Experimental

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_{10}\text{N}_4\text{S}_4)_3(\text{ClO}_4)_2]$
 $M_r = 1133.76$
 Trigonal, $R\bar{3}$
 $a = 10.5455$ (6) Å
 $c = 33.728$ (4) Å
 $V = 3248.3$ (5) Å³

$Z = 3$
 Mo $K\alpha$ radiation
 $\mu = 1.27$ mm⁻¹
 $T = 291$ K
 $0.28 \times 0.21 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\text{min}} = 0.717$, $T_{\text{max}} = 0.839$

9432 measured reflections
 1673 independent reflections
 1320 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.133$
 $S = 1.05$
 1673 reflections

90 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.82$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The authors thank the Luoyang Normal University, for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2097).

References

- Bruker (1997). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Huang, H.-M., Ju, F.-Y., Wang, J.-G. & Qin, J.-H. (2009). *Acta Cryst.* E65, m80–m81.
 Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.
 Wang, J. G., Qin, J. H., Hu, P. Z. & Zhao, B. T. (2008). *Z. Kristallogr. New Cryst. Struct.* 223, 225–227.

supporting information

Acta Cryst. (2009). E65, m307 [doi:10.1107/S1600536809005625]

Poly[[tris[μ -2,2'-(butane-1,4-diylidithio)bis(1,3,4-thiadiazole)- $\kappa^2N^4:N^4'$]copper(II)] bis(perchlorate)]

Pu-Zhou Hu, Jian-Hua Qin and Jian-Ge Wang

S1. Comment

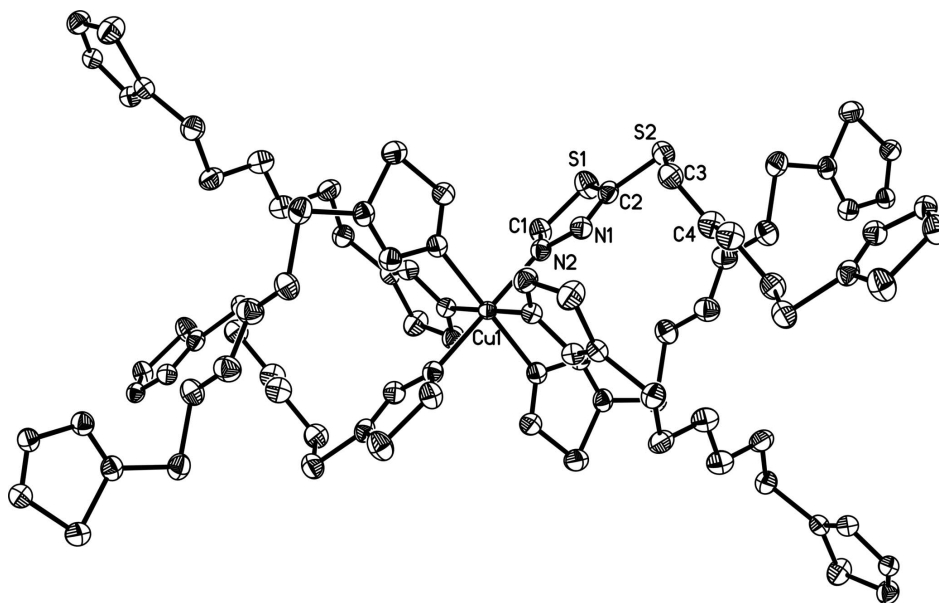
The asymmetric unit of the title compound consists of one sixth of a Cu^{II} atom, which is located on a three-fold inversion axis, half a 2,2'-(butane-1,4-diylidithio)bis(1,3,4-thiadiazole) ligand which possesses an inversion center, and one third of a perchlorate ion, which is situated on a three-fold rotation axis. As depicted in Fig. 1, the Cu^{II} atom is coordinated by six N atoms from six symmetry equivalent 2,2'-(butane-1,4-diylidithio)bis(1,3,4-thiadiazole) ligands, in a slightly distorted octahedral geometry of the central atom. The Cu—N bond distance is 2.149 (3) Å, within the range expected for such coordination bonds (Huang *et al.*, 2009; Wang *et al.*, 2008). The centrosymmetric 2,2'-(butane-1,4-diylidithio)bis(1,3,4-thiadiazole) ligand adopts a N,N'-bidentate bridging mode in a trans configuration and links the Cu^{II} atoms to form a three-dimensional network. The bridging Cu...Cu distance is 12.7854 (12) Å (Fig. 2).

S2. Experimental

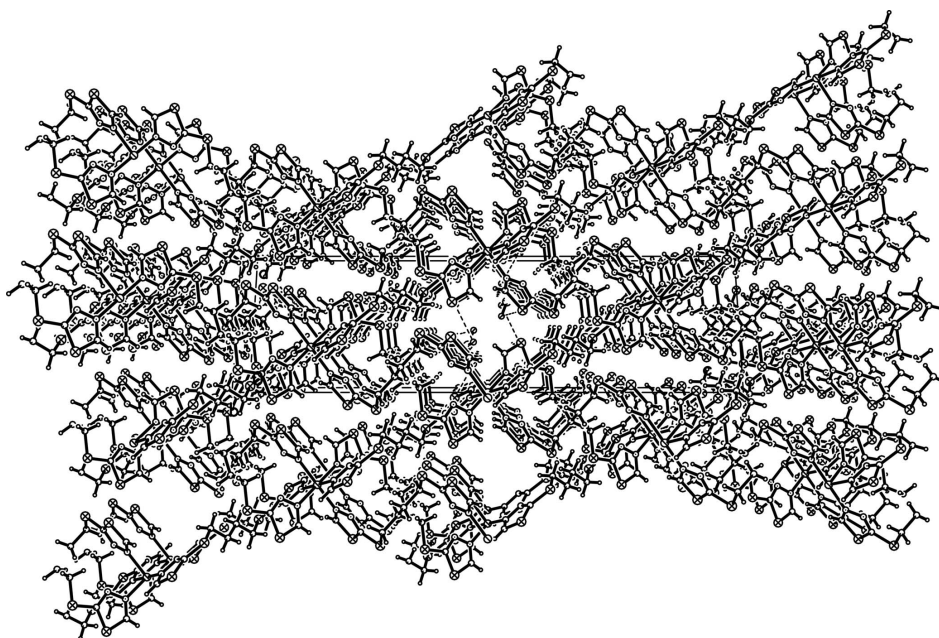
The reaction of 2,2'-(butane-1,4-diylidithio)bis(1,3,4-thiadiazole) (0.3 mmol) with Cu(ClO₄)₂ (0.1 mmol) in MeOH(10 ml) for a few minutes gave a light blue solid, which was filtered off, washed with acetone, and dried in air. Single crystals, suitable for X-ray analysis, were obtained by slow diffusion of Et₂O into an acetonitrile solution of the solid.

S3. Refinement

The H-atoms were positioned geometrically and treated as riding: C—H = 0.93 - 0.97 Å and U_{iso}(H) = 1.2U_{eq}(parent C-atom).

**Figure 1**

A view of the coordination around the Cu^{II} atom in the cation of the title compound. Displacement ellipsoids are drawn at the 30% probability level. The H atoms and perchlorate ion were omitted for clarity.

**Figure 2**

A view down the *b* axis of the crystal packing of the title compound.

Poly[[tris(μ -2,2'-(butane-1,4-diyl)dithio)bis(1,3,4-thiadiazole)- $\kappa^2N^4:N^4$]copper(II)] bis(perchlorate)]

Crystal data

[Cu(C₈H₁₀N₄S₄)₃](ClO₄)₂

M_r = 1133.76

Trigonal, *R* $\bar{3}$

Hall symbol: -R 3

a = 10.5455 (6) Å

c = 33.728 (4) Å

$V = 3248.3 (5) \text{ \AA}^3$
 $Z = 3$
 $F(000) = 1731$
 $D_x = 1.739 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 2638 reflections

$\theta = 2.3\text{--}24.5^\circ$
 $\mu = 1.27 \text{ mm}^{-1}$
 $T = 291 \text{ K}$
 Block, blue
 $0.28 \times 0.21 \times 0.14 \text{ mm}$

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 1997)
 $T_{\min} = 0.717$, $T_{\max} = 0.839$

9432 measured reflections
 1673 independent reflections
 1320 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.3^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -43 \rightarrow 43$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.133$
 $S = 1.05$
 1673 reflections
 90 parameters
 0 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
 $w = 1/[\sigma^2(F_o^2) + (0.0617P)^2 + 10.9603P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.82 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e \AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	1.0000	1.0000	0.5000	0.0338 (2)
Cl1	0.3333	0.6667	0.45984 (7)	0.0692 (5)
S1	0.94592 (14)	0.59055 (13)	0.43361 (3)	0.0702 (4)
S2	0.71904 (11)	0.56831 (12)	0.37580 (3)	0.0608 (3)
O1	0.3599 (4)	0.8063 (4)	0.47130 (14)	0.1084 (13)
O2	0.3333	0.6667	0.4165 (2)	0.124 (3)
N1	0.8519 (3)	0.7722 (3)	0.43379 (8)	0.0500 (7)
N2	0.9537 (3)	0.8133 (3)	0.46412 (8)	0.0461 (6)
C1	1.0099 (4)	0.7300 (4)	0.46704 (11)	0.0578 (9)
H1	1.0802	0.7448	0.4860	0.069*
C2	0.8366 (4)	0.6570 (4)	0.41560 (10)	0.0501 (8)
C3	0.6329 (4)	0.6782 (5)	0.36973 (12)	0.0615 (9)
H3A	0.5323	0.6158	0.3613	0.074*
H3B	0.6313	0.7208	0.3951	0.074*
C4	0.7119 (5)	0.8003 (5)	0.33947 (13)	0.0679 (11)
H4A	0.8032	0.8758	0.3508	0.082*
H4B	0.7351	0.7613	0.3163	0.082*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0332 (3)	0.0332 (3)	0.0350 (4)	0.01660 (15)	0.000	0.000
Cl1	0.0537 (6)	0.0537 (6)	0.1003 (14)	0.0269 (3)	0.000	0.000
S1	0.0854 (8)	0.0764 (7)	0.0679 (7)	0.0548 (6)	-0.0153 (5)	-0.0153 (5)
S2	0.0585 (6)	0.0671 (6)	0.0537 (6)	0.0292 (5)	-0.0048 (4)	-0.0096 (4)
O1	0.101 (3)	0.073 (2)	0.152 (4)	0.045 (2)	0.015 (3)	-0.023 (2)
O2	0.140 (4)	0.140 (4)	0.090 (5)	0.070 (2)	0.000	0.000
N1	0.0441 (15)	0.0547 (17)	0.0504 (16)	0.0242 (13)	-0.0014 (12)	-0.0007 (13)
N2	0.0424 (14)	0.0526 (16)	0.0430 (14)	0.0237 (12)	0.0009 (11)	0.0021 (12)
C1	0.063 (2)	0.067 (2)	0.053 (2)	0.040 (2)	-0.0060 (17)	-0.0057 (17)
C2	0.0449 (17)	0.059 (2)	0.0434 (17)	0.0241 (16)	0.0067 (13)	0.0052 (15)
C3	0.051 (2)	0.068 (2)	0.062 (2)	0.0271 (19)	-0.0115 (17)	-0.0019 (19)
C4	0.060 (2)	0.073 (3)	0.075 (3)	0.036 (2)	-0.004 (2)	-0.001 (2)

Geometric parameters (Å, °)

Cu1—N2 ⁱ	2.149 (3)	S2—C2	1.748 (4)
Cu1—N2	2.149 (3)	S2—C3	1.807 (4)
Cu1—N2 ⁱⁱ	2.149 (3)	N1—C2	1.298 (4)
Cu1—N2 ⁱⁱⁱ	2.149 (3)	N1—N2	1.386 (4)
Cu1—N2 ^{iv}	2.149 (3)	N2—C1	1.286 (4)
Cu1—N2 ^v	2.149 (3)	C1—H1	0.9300
Cl1—O1	1.409 (4)	C3—C4	1.523 (6)
Cl1—O1 ^{vi}	1.409 (4)	C3—H3A	0.9700
Cl1—O1 ^{vii}	1.409 (4)	C3—H3B	0.9700
Cl1—O2	1.463 (8)	C4—C4 ^{viii}	1.494 (8)
S1—C1	1.702 (4)	C4—H4A	0.9700
S1—C2	1.731 (4)	C4—H4B	0.9700
N2 ⁱ —Cu1—N2	91.39 (10)	C2—N1—N2	110.8 (3)
N2 ⁱ —Cu1—N2 ⁱⁱ	91.40 (10)	C1—N2—N1	113.1 (3)
N2—Cu1—N2 ⁱⁱ	91.39 (10)	C1—N2—Cu1	127.7 (2)
N2 ⁱ —Cu1—N2 ⁱⁱⁱ	88.61 (10)	N1—N2—Cu1	119.2 (2)
N2—Cu1—N2 ⁱⁱⁱ	88.61 (10)	N2—C1—S1	114.9 (3)
N2 ⁱⁱ —Cu1—N2 ⁱⁱⁱ	179.998 (1)	N2—C1—H1	122.6
N2 ⁱ —Cu1—N2 ^{iv}	88.61 (10)	S1—C1—H1	122.6
N2—Cu1—N2 ^{iv}	179.999 (2)	N1—C2—S1	114.7 (3)
N2 ⁱⁱ —Cu1—N2 ^{iv}	88.61 (10)	N1—C2—S2	125.9 (3)
N2 ⁱⁱⁱ —Cu1—N2 ^{iv}	91.39 (10)	S1—C2—S2	119.4 (2)
N2 ⁱ —Cu1—N2 ^v	179.999 (1)	C4—C3—S2	112.3 (3)
N2—Cu1—N2 ^v	88.61 (10)	C4—C3—H3A	109.1
N2 ⁱⁱ —Cu1—N2 ^v	88.60 (10)	S2—C3—H3A	109.1
N2 ⁱⁱⁱ —Cu1—N2 ^v	91.39 (10)	C4—C3—H3B	109.1
N2 ^{iv} —Cu1—N2 ^v	91.39 (10)	S2—C3—H3B	109.1
O1—Cl1—O1 ^{vi}	112.77 (18)	H3A—C3—H3B	107.9
O1—Cl1—O1 ^{vii}	112.77 (18)	C4 ^{viii} —C4—C3	111.9 (4)

O1 ^{vi} —C11—O1 ^{vii}	112.77 (18)	C4 ^{viii} —C4—H4A	109.2
O1—C11—O2	105.9 (2)	C3—C4—H4A	109.2
O1 ^{vi} —C11—O2	105.9 (2)	C4 ^{viii} —C4—H4B	109.2
O1 ^{vii} —C11—O2	105.9 (2)	C3—C4—H4B	109.2
C1—S1—C2	86.55 (18)	H4A—C4—H4B	107.9
C2—S2—C3	101.18 (18)		
C2—N1—N2—C1	0.6 (4)	Cu1—N2—C1—S1	179.51 (16)
C2—N1—N2—Cu1	-179.3 (2)	C2—S1—C1—N2	0.1 (3)
N2 ⁱ —Cu1—N2—C1	84.4 (4)	N2—N1—C2—S1	-0.6 (4)
N2 ⁱⁱ —Cu1—N2—C1	175.8 (3)	N2—N1—C2—S2	179.7 (2)
N2 ⁱⁱⁱ —Cu1—N2—C1	-4.2 (3)	C1—S1—C2—N1	0.3 (3)
N2 ^v —Cu1—N2—C1	-95.6 (4)	C1—S1—C2—S2	-179.9 (2)
N2 ⁱ —Cu1—N2—N1	-95.76 (17)	C3—S2—C2—N1	-0.8 (4)
N2 ⁱⁱ —Cu1—N2—N1	-4.3 (2)	C3—S2—C2—S1	179.4 (2)
N2 ⁱⁱⁱ —Cu1—N2—N1	175.7 (2)	C2—S2—C3—C4	93.0 (3)
N2 ^v —Cu1—N2—N1	84.24 (17)	S2—C3—C4—C4 ^{viii}	165.9 (4)
N1—N2—C1—S1	-0.4 (4)		

Symmetry codes: (i) $-y+2, x-y+1, z$; (ii) $-x+y+1, -x+2, z$; (iii) $x-y+1, x, -z+1$; (iv) $-x+2, -y+2, -z+1$; (v) $y, -x+y+1, -z+1$; (vi) $-x+y, -x+1, z$; (vii) $-y+1, x-y+1, z$; (viii) $-x+4/3, -y+5/3, -z+2/3$.