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(Thiocyanato-κN)(tris{2-[(3-phenylallylidene)amino]ethyl}amine-$\kappa^4 N,N',N'',N'''$)copper(II) perchlorate

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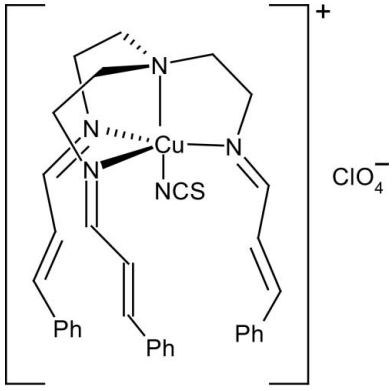
Key indicators: single-crystal X-ray study; T = 95 K; mean σ(C–C) = 0.007 Å; R factor = 0.060; wR factor = 0.168; data-to-parameter ratio = 16.1.

In the title compound, [Cu(NCS)(ca_3-tren)]ClO_4, [ca_3tren = tris(*trans*-cinnamaldehyde)tris(2-aminoethyl)amine, $C_{33}H_{36}N_4$], a tetradentate Schiff base ca_3tren ligand and a thiocyanate anion coordinate to a Cu^{II} ion, forming a CuN_5 distorted trigonal–bipyramidal geometry. Cohesion of the crystal structure is provided by weak intra- and intermolecular C—H···O and C—H···N hydrogen-bonding intractions.

Related literature

For related literature, see: Abdus & Aoki (2001); Alyea *et al.* (1990); Chen *et al.* (2000); Kickelbick *et al.* (2003); Kwak *et al.* (1999); Laskowski *et al.* (1975); Lu *et al.* (1996); Massoud *et al.* (1999); Patra & Goldberg (2003); Raab *et al.* (2001); Saha *et al.* (2003); Scarpellini *et al.* (2004); Su *et al.* (1999); Wei *et al.* (1994).



Experimental

Crystal data

$[Cu(NCS)(C_{33}H_{36}N_4)]ClO_4$
M_r = 709.73
Triclinic, $P\overline{1}$
a = 10.1328 (13) Å
b = 12.3212 (17) Å
c = 15.0666 (18) Å
α = 108.147 (10)°
β = 105.921 (10)°
γ = 91.638 (11)°
V = 1705.5 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.82 mm^{-1}
T = 95 (1) K
0.31 × 0.23 × 0.22 mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2005)
T_{min} = 0.773, T_{max} = 0.859
20318 measured reflections
6704 independent reflections
5751 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.168
S = 1.18
6704 reflections
416 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···O1^{i}	0.97	2.55	3.521 (5)	176
C21—H21A···O1^{ii}	0.97	2.49	3.320 (5)	143
C21—H21A···O2^{ii}	0.97	2.45	3.359 (5)	156
C32—H32B···O2^{iii}	0.97	2.55	3.362 (5)	141
C18—H18···O3^{iv}	0.93	2.48	3.091 (5)	123
C24—H24···N40	0.93	2.57	3.205 (5)	126
C34—H34···N40	0.93	2.58	3.240 (5)	128

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x, y, z-1$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y+1, z$.

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-RED32* (Stoe & Cie, 2005); data reduction: *X-RED32*; program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2374).

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supplementary materials

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(Thiocyanato-κN)(tris{2-[(3-phenylallylidene)amino]ethyl}amine-$\kappa^4 N,N',N'',N'''$)copper(II) perchlorate

A. D. Khalaji, M. Amirnasr and K. J. Schenk

Comment

Tripodal ligands generally coordinate to transition metal ions using all of their nitrogen atoms as donors (Scarpellini *et al.*, 2004; Abdus Salam & Aoki, 2001; Raab *et al.*, 2001; Chen *et al.*, 2000; Su *et al.*, 1999; Massoud *et al.*, 1999). Six coordinate octahedral complexes containing such ligands invariably display *cis* geometries (Kwak *et al.*, 1999; Saha *et al.*, 2003). The steric constraints imposed by such ligands often result in trigonal bipyramidal geometries for five coordinate systems (Chen *et al.*, 2000; Su *et al.*, 1999), while rare examples of four coordinate complexes containing tripodal ligands display distored tetrahedral geometries (Patra & Goldberg, 2003; Wei *et al.*, 1994; Alyea *et al.*, 1990). The pseudohalide, NCS, is known to coordinate to metals (Laskowski *et al.*, 1975; Kickelbick *et al.*, 2003) and act as terminal ligand in these complexes. In this context, we decided to examine the nature of the copper(II) complex formed with the tripodal Schiff base ligand *ca*$_3$-tren. Therefore, (I) has been synthesized and structurally investigated. Compound (I) is a monomeric complex (Fig. 1) in which the *ca*$_3$-tren ligand is tetradentate and the thiocyanate anion is monodentate. The Cu—N bond lengths in (I) are in good agreement with the corresponding distances in related complexes (Abdus Salam *et al.*, 2001; Chen *et al.*, 2000). The coordination geometry around the Cu^{II} ion in (I) can be described as grossly distorted trigonal bipyramid with approximate molecular C_s symmetry with respect to the N4—N1—Cu—N40—C40—S plane. The N2—Cu—N3 angle across this plane is much larger than the analoguous N2—Cu—N1 and N3—Cu—N1 angles. The Cu—N1 bond is, naturally, the longest equatorial bond, since it has to accommodate the thiocyanate. In the three legs all atoms except the α carbons are essentially co-planar, with atoms N4 and N40 being in one of the planes. The angles between the planes of the legs are 81.8 (1)° between 1 and 2, 79.5 (1)° between 1 and 3 and 9.7 (1)° between 2 and 3 (the plane number is realted to the N atom label contained within each plane *i.e.* N1 = plane 1). It is noteworthy, that at 95 K the perchlorate anion, a notorious troublemaker, is perfectly ordered,[Cu(*ca*3-tren)(NCS)]ClO4 whereas at room temperature it is distributed between the position shown in Fig.1 and one staggered about the O1—Cl bond.

The crystal packing of (I), shown in Fig. 2., demonstrates that the main cohesion of this structure is due to hydrogen bonding. Two planes may be preceived in the structure accross which a minimum of bonding (other than van der Waals) seem to exist: (02$\bar{3}$) and (010). Otherwise there exist C—H···O bonds along [100], [032] and [01$\bar{1}$]. This bonding seems to be weaker along the latter two directions than along the *a* axis. One might even say that (I) has some pseudo layer-character with respect to (02$\bar{3}$) and (010), especially at room temperature. From the observation of some arching in the (b*,c*) layer, we may conclude the strongest cohesion exists along [100] and that the real structure consists of slightly disoriented (~5°) blocks bounded by (100), (02$\bar{3}$) and (010). This conjecture is further confirmed by the observation that crystal of (I) crumble into many tiny pieces at room temperature upon even a very gentle attempt at cutting them with the blade of a scalpel·EDITORS: Please check name

[Cu(*ca*3-tren)(NCS)]ClO4 At 95 K, most atoms are fairly isotropic, but there exists a remnant of some more pronounced disorder in the phenyl ring C36 → C311, *i.e.* two slightly rotated positions of the ring. Another occurrence of dynamic

disorder has all but disappeared at 95 K; indeed at room temperature atoms C11, C21 and C31 were strongly elongated perpendicularly to the planes of the legs.

Experimental

The title compound was prepared by the reaction of $CuClO_4$ with *ca*$_3$-tren and KSCN (molar ratio 1:1:1) in a methanolic solution at 298 K. The blue precipitate was filtered and dried *in vacuo*. Turquoise crystals of (I) were obtained by slow diffusion of Et_2O vapour into a nitromethan solution of the complex at 298 K. The measured crystal was bounded by the {010}, {001}, {10$\bar{1}$}, {101} and {1$\bar{1}$1} pinacoids, the last two being of the bevel persuasion.

Refinement

H atoms were made to ride on their associated carrier atoms, their displacement parameters being coupled to those of the carrier atoms (U_{iso}(H)/U_{eq}(C) were 1.5 for methyl groups and 1.2 for all other H atoms; C—H were 0.99 Å for methylene and 0.95Å for aromatic H atoms).

A comparison between room and low temperature data shows the lattice constants at 293 K are: a=10.263 (2), b=12.415 (3), c=15.536 (3) Å, α=107.70 (3), β=105.38 (3) γ=91.67 (3)°, V=1805.4 (6) Å^3. Noteworthy the value of ε≃ 0.03. Unsurprisingly, the intramolecular distances and angles remain pratically the same, but there exist considerable variations in the intermolecular hydrogen bonds. Except for the C12—H12B···O1 bond they all shorten by between ~0.1 for the C18—H18···O3 bond and ~0.2Å for the C21—H21*a*···O3 bond.

Figures

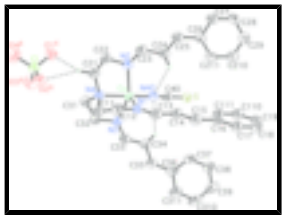


Fig. 1. The asymmetric unit of (I) with hydrogen bonds shown as dashed lines and displacement ellipsoids shown at the 70% probability level [symmetry code ($): *x*, *y*, −1 + *z*].

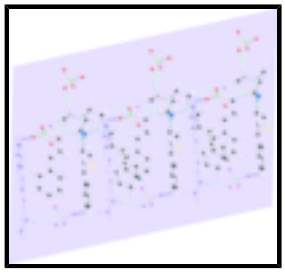


Fig. 2. Part of the crystal structure of (I) showing C—H···O hydrogen bonds (light blue) within the (02$\bar{3}$) plane in (I). Dark blue lines are hydrogen bonds between the (02$\bar{3}$) blocks.

(Thiocyanato-κ<it>*N*</it>)(tris{2-[(3-phenylallylidene)amino]ethyl}amine- κ^4<it>N</it>,<it>N</it>',<it>N</it>'',<it>N</it>''')copper(II) perchlorate

Crystal data

$[Cu(NCS)(C_{33}H_{36}N_4)]ClO_4$ $Z = 2$

M_r = 709.73

Triclinic, $P\bar{1}$

Hall symbol: -P 1

a = 10.1328 (13) Å

b = 12.3212 (17) Å

c = 15.0666 (18) Å

α = 108.147 (10)º

β = 105.921 (10)º

γ = 91.638 (11)º

V = 1705.5 (4) Å^3

F_{000} = 738

D_x = 1.382 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 65844 reflections

θ = 2.2–29.4º

μ = 0.82 mm^{-1}

T = 95 (1) K

Parallelepiped, blue

0.31 × 0.23 × 0.22 mm

Data collection

STOE IPDS II diffractometer

Radiation source: fine-focus sealed tube

Monochromator: plane graphite

Detector resolution: 6.67 pixels mm^{-1}

T = 95(1) K

rotation scans

Absorption correction: integration (X-RED32; Stoe & Cie, 2005)

T_{min} = 0.773, T_{max} = 0.859

20318 measured reflections

6704 independent reflections

5751 reflections with $I > 2\sigma(I)$

R_{int} = 0.068

θ_{max} = 26.0º

θ_{min} = 2.2º

h = −12→12

k = −15→15

l = −18→18

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.060

$wR(F^2)$ = 0.168

S = 1.18

6704 reflections

416 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 5.0438P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.67 e Å^{-3}

$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0171 (16)

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}
Cu	0.28977 (5)	0.83858 (4)	0.11201 (3)	0.02368 (18)
S	0.35163 (11)	1.24129 (10)	0.16514 (8)	0.0314 (3)
N40	0.3133 (4)	1.0030 (3)	0.1311 (3)	0.0306 (8)
C40	0.3308 (4)	1.1026 (4)	0.1440 (3)	0.0246 (8)
N4	0.2736 (3)	0.6623 (3)	0.0685 (2)	0.0249 (7)
C11	0.3412 (4)	0.6276 (4)	0.1561 (3)	0.0286 (9)
H11B	0.4409	0.6437	0.1730	0.034*
H11A	0.3178	0.5455	0.1405	0.034*
C12	0.2927 (4)	0.6933 (4)	0.2422 (3)	0.0281 (9)
H12B	0.1967	0.6657	0.2304	0.034*
H12A	0.3473	0.6802	0.3009	0.034*
N1	0.3067 (3)	0.8177 (3)	0.2564 (2)	0.0255 (7)
C13	0.3157 (4)	0.8858 (4)	0.3418 (3)	0.0287 (9)
H13	0.3167	0.8542	0.3905	0.034*
C14	0.3247 (4)	1.0100 (4)	0.3672 (3)	0.0265 (9)
H14	0.3239	1.0426	0.3190	0.032*
C15	0.3340 (4)	1.0790 (4)	0.4569 (3)	0.0285 (9)
H15	0.3335	1.0433	0.5029	0.034*
C16	0.3450 (4)	1.2056 (4)	0.4915 (3)	0.0249 (8)
C17	0.3537 (4)	1.2651 (4)	0.5892 (3)	0.0285 (9)
H17	0.3522	1.2241	0.6314	0.034*
C18	0.3644 (5)	1.3846 (4)	0.6240 (3)	0.0305 (9)
H18	0.3700	1.4226	0.6891	0.037*
C19	0.3667 (4)	1.4473 (4)	0.5623 (3)	0.0298 (9)
H19	0.3739	1.5272	0.5857	0.036*
C110	0.3581 (4)	1.3896 (4)	0.4651 (3)	0.0292 (9)
H110	0.3591	1.4313	0.4234	0.035*
C111	0.3480 (4)	1.2707 (4)	0.4300 (3)	0.0278 (9)
H111	0.3432	1.2334	0.3650	0.033*
C21	0.1245 (4)	0.6132 (4)	0.0255 (3)	0.0274 (9)
H21B	0.0858	0.6094	0.0767	0.033*
H21A	0.1152	0.5360	−0.0203	0.033*
C22	0.0480 (4)	0.6916 (4)	−0.0273 (3)	0.0284 (9)
H22B	0.0778	0.6877	−0.0840	0.034*
H22A	−0.0510	0.6685	−0.0487	0.034*
N2	0.0826 (3)	0.8097 (3)	0.0442 (2)	0.0246 (7)
C23	−0.0189 (4)	0.8687 (4)	0.0544 (3)	0.0269 (9)
H23	−0.1072	0.8346	0.0144	0.032*
C24	−0.0063 (4)	0.9828 (4)	0.1227 (3)	0.0267 (9)
H24	0.0794	1.0168	0.1673	0.032*

C25	−0.1167 (4)	1.0415 (4)	0.1232 (3)	0.0287 (9)
H25	−0.2004	1.0036	0.0778	0.034*
C26	−0.1197 (4)	1.1572 (4)	0.1865 (3)	0.0277 (9)
C27	−0.2479 (4)	1.2014 (4)	0.1804 (3)	0.0293 (9)
H27	−0.3285	1.1562	0.1362	0.035*
C28	−0.2550 (5)	1.3118 (4)	0.2399 (3)	0.0347 (10)
H28	−0.3399	1.3400	0.2354	0.042*
C29	−0.1353 (5)	1.3798 (4)	0.3059 (4)	0.0381 (11)
H29	−0.1395	1.4538	0.3453	0.046*
C210	−0.0096 (5)	1.3372 (4)	0.3128 (4)	0.0381 (11)
H210	0.0704	1.3828	0.3573	0.046*
C211	−0.0013 (5)	1.2273 (4)	0.2543 (4)	0.0358 (10)
H211	0.0842	1.2000	0.2602	0.043*
C31	0.3490 (4)	0.6274 (4)	−0.0061 (3)	0.0303 (9)
H31B	0.2927	0.6333	−0.0674	0.036*
H31A	0.3656	0.5478	−0.0171	0.036*
C32	0.4879 (4)	0.7047 (4)	0.0283 (3)	0.0313 (9)
H32B	0.5623	0.6649	0.0543	0.038*
H32A	0.5050	0.7210	−0.0268	0.038*
N3	0.4849 (4)	0.8142 (3)	0.1050 (2)	0.0261 (7)
C33	0.6033 (4)	0.8667 (4)	0.1633 (3)	0.0278 (9)
H33	0.6821	0.8366	0.1509	0.033*
C34	0.6215 (4)	0.9695 (4)	0.2467 (3)	0.0280 (9)
H34	0.5454	1.0056	0.2578	0.034*
C35	0.7497 (4)	1.0130 (4)	0.3085 (3)	0.0300 (9)
H35	0.8220	0.9726	0.2950	0.036*
C36	0.7862 (4)	1.1176 (4)	0.3947 (3)	0.0298 (9)
C37	0.6895 (4)	1.1914 (4)	0.4190 (3)	0.0303 (9)
H37	0.5981	1.1747	0.3794	0.036*
C38	0.7286 (5)	1.2892 (4)	0.5017 (3)	0.0330 (10)
H38	0.6632	1.3369	0.5177	0.040*
C39	0.8650 (5)	1.3156 (5)	0.5604 (3)	0.0389 (11)
H39	0.8910	1.3817	0.6153	0.047*
C310	0.9622 (5)	1.2448 (5)	0.5380 (4)	0.0446 (13)
H310	1.0533	1.2624	0.5781	0.054*
C311	0.9238 (5)	1.1464 (5)	0.4550 (3)	0.0376 (11)
H311	0.9900	1.0994	0.4395	0.045*
Cl	0.13292 (10)	0.33145 (9)	0.81496 (7)	0.0286 (3)
O1	0.0504 (3)	0.4218 (3)	0.8021 (2)	0.0361 (7)
O2	0.1788 (3)	0.3425 (3)	0.9181 (2)	0.0307 (7)
O3	0.2530 (4)	0.3409 (3)	0.7830 (3)	0.0443 (9)
O4	0.0522 (4)	0.2202 (3)	0.7606 (3)	0.0453 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0197 (3)	0.0303 (3)	0.0191 (3)	0.00149 (19)	0.00357 (18)	0.0075 (2)
S	0.0298 (6)	0.0329 (6)	0.0313 (6)	0.0005 (4)	0.0061 (4)	0.0134 (5)

N40	0.0212 (17)	0.041 (2)	0.0261 (19)	0.0015 (15)	0.0035 (14)	0.0094 (16)
C40	0.0189 (18)	0.037 (2)	0.0179 (19)	0.0012 (16)	0.0034 (15)	0.0104 (17)
N4	0.0188 (16)	0.0334 (19)	0.0223 (17)	0.0022 (14)	0.0061 (13)	0.0091 (15)
C11	0.027 (2)	0.034 (2)	0.025 (2)	0.0038 (17)	0.0051 (17)	0.0114 (18)
C12	0.029 (2)	0.031 (2)	0.024 (2)	0.0003 (17)	0.0037 (17)	0.0118 (18)
N1	0.0237 (17)	0.0317 (19)	0.0202 (17)	0.0024 (14)	0.0048 (13)	0.0090 (15)
C13	0.027 (2)	0.039 (2)	0.021 (2)	0.0046 (18)	0.0039 (16)	0.0137 (18)
C14	0.026 (2)	0.032 (2)	0.0201 (19)	0.0019 (17)	0.0049 (16)	0.0093 (17)
C15	0.029 (2)	0.037 (2)	0.022 (2)	0.0033 (18)	0.0069 (16)	0.0144 (18)
C16	0.0211 (19)	0.035 (2)	0.0188 (19)	0.0038 (16)	0.0048 (15)	0.0092 (17)
C17	0.030 (2)	0.038 (2)	0.020 (2)	0.0041 (18)	0.0079 (17)	0.0124 (18)
C18	0.032 (2)	0.038 (2)	0.022 (2)	0.0068 (18)	0.0073 (17)	0.0092 (18)
C19	0.029 (2)	0.031 (2)	0.031 (2)	0.0063 (17)	0.0094 (18)	0.0135 (19)
C110	0.029 (2)	0.037 (2)	0.024 (2)	0.0033 (18)	0.0060 (17)	0.0157 (19)
C111	0.025 (2)	0.041 (2)	0.0174 (19)	0.0045 (17)	0.0035 (16)	0.0122 (18)
C21	0.022 (2)	0.032 (2)	0.024 (2)	−0.0010 (16)	0.0062 (16)	0.0051 (18)
C22	0.024 (2)	0.035 (2)	0.022 (2)	−0.0006 (17)	0.0049 (16)	0.0050 (18)
N2	0.0240 (17)	0.0324 (19)	0.0187 (16)	0.0034 (14)	0.0071 (13)	0.0097 (14)
C23	0.024 (2)	0.038 (2)	0.0198 (19)	0.0023 (17)	0.0031 (16)	0.0142 (18)
C24	0.0219 (19)	0.036 (2)	0.024 (2)	0.0036 (17)	0.0061 (16)	0.0138 (18)
C25	0.024 (2)	0.036 (2)	0.025 (2)	0.0040 (17)	0.0043 (16)	0.0126 (18)
C26	0.023 (2)	0.037 (2)	0.028 (2)	0.0056 (17)	0.0081 (16)	0.0157 (19)
C27	0.026 (2)	0.037 (2)	0.027 (2)	0.0059 (17)	0.0062 (17)	0.0139 (19)
C28	0.025 (2)	0.044 (3)	0.040 (3)	0.0107 (19)	0.0123 (19)	0.017 (2)
C29	0.039 (3)	0.037 (3)	0.038 (3)	0.008 (2)	0.013 (2)	0.009 (2)
C210	0.028 (2)	0.041 (3)	0.041 (3)	0.0022 (19)	0.007 (2)	0.010 (2)
C211	0.022 (2)	0.044 (3)	0.039 (3)	0.0071 (19)	0.0052 (18)	0.012 (2)
C31	0.026 (2)	0.039 (2)	0.025 (2)	0.0031 (18)	0.0115 (17)	0.0070 (19)
C32	0.025 (2)	0.036 (2)	0.028 (2)	0.0042 (18)	0.0104 (17)	0.0026 (19)
N3	0.0254 (17)	0.0298 (19)	0.0214 (17)	0.0013 (14)	0.0067 (14)	0.0065 (14)
C33	0.022 (2)	0.033 (2)	0.029 (2)	0.0030 (17)	0.0093 (17)	0.0116 (18)
C34	0.025 (2)	0.032 (2)	0.026 (2)	0.0015 (17)	0.0056 (16)	0.0095 (18)
C35	0.022 (2)	0.041 (2)	0.029 (2)	0.0030 (17)	0.0051 (17)	0.0157 (19)
C36	0.027 (2)	0.037 (2)	0.025 (2)	−0.0007 (18)	0.0017 (17)	0.0153 (19)
C37	0.027 (2)	0.037 (2)	0.022 (2)	−0.0024 (18)	−0.0019 (17)	0.0120 (18)
C38	0.035 (2)	0.037 (2)	0.024 (2)	0.0014 (19)	0.0028 (18)	0.0113 (19)
C39	0.039 (3)	0.049 (3)	0.022 (2)	−0.010 (2)	0.0006 (19)	0.012 (2)
C310	0.025 (2)	0.070 (4)	0.026 (2)	−0.009 (2)	−0.0039 (18)	0.010 (2)
C311	0.025 (2)	0.054 (3)	0.029 (2)	0.000 (2)	0.0036 (18)	0.010 (2)
Cl	0.0292 (5)	0.0357 (6)	0.0209 (5)	0.0048 (4)	0.0082 (4)	0.0088 (4)
O1	0.0363 (17)	0.0405 (18)	0.0314 (17)	0.0103 (14)	0.0055 (14)	0.0155 (14)
O2	0.0293 (15)	0.0453 (18)	0.0212 (15)	0.0084 (13)	0.0086 (12)	0.0147 (14)
O3	0.044 (2)	0.063 (2)	0.042 (2)	0.0138 (17)	0.0288 (16)	0.0254 (18)
O4	0.054 (2)	0.0327 (18)	0.0364 (19)	−0.0031 (16)	0.0013 (16)	0.0043 (15)

Geometric parameters (Å, °)

Cu—N1	2.231 (3)	C24—C25	1.350 (6)
Cu—N2	2.033 (3)	C24—H24	0.9300

Cu—N3	2.035 (3)	C25—C26	1.454 (6)
Cu—N4	2.052 (4)	C25—H25	0.9300
Cu—N40	1.954 (4)	C26—C211	1.396 (6)
S—C40	1.634 (4)	C26—C27	1.413 (6)
N40—C40	1.180 (6)	C27—C28	1.394 (7)
N4—C31	1.489 (5)	C27—H27	0.9300
N4—C21	1.495 (5)	C28—C29	1.386 (7)
N4—C11	1.505 (5)	C28—H28	0.9300
C11—C12	1.517 (6)	C29—C210	1.381 (7)
C11—H11B	0.9700	C29—H29	0.9300
C11—H11A	0.9700	C210—C211	1.386 (7)
C12—N1	1.477 (5)	C210—H210	0.9300
C12—H12B	0.9700	C211—H211	0.9300
C12—H12A	0.9700	C31—C32	1.540 (6)
N1—C13	1.276 (6)	C31—H31B	0.9700
C13—C14	1.451 (6)	C31—H31A	0.9700
C13—H13	0.9300	C32—N3	1.486 (5)
C14—C15	1.330 (6)	C32—H32B	0.9700
C14—H14	0.9300	C32—H32A	0.9700
C15—C16	1.473 (6)	N3—C33	1.285 (5)
C15—H15	0.9300	C33—C34	1.444 (6)
C16—C17	1.403 (6)	C33—H33	0.9300
C16—C111	1.407 (6)	C34—C35	1.352 (6)
C17—C18	1.389 (6)	C34—H34	0.9300
C17—H17	0.9300	C35—C36	1.466 (6)
C18—C19	1.385 (6)	C35—H35	0.9300
C18—H18	0.9300	C36—C37	1.401 (7)
C19—C110	1.391 (6)	C36—C311	1.404 (6)
C19—H19	0.9300	C37—C38	1.388 (6)
C110—C111	1.384 (6)	C37—H37	0.9300
C110—H110	0.9300	C38—C39	1.387 (6)
C111—H111	0.9300	C38—H38	0.9300
C21—C22	1.533 (6)	C39—C310	1.377 (8)
C21—H21B	0.9700	C39—H39	0.9300
C21—H21A	0.9700	C310—C311	1.395 (7)
C22—N2	1.478 (6)	C310—H310	0.9300
C22—H22B	0.9700	C311—H311	0.9300
C22—H22A	0.9700	Cl—O3	1.440 (3)
N2—C23	1.293 (6)	Cl—O1	1.441 (3)
C23—C24	1.438 (6)	Cl—O4	1.445 (4)
C23—H23	0.9300	Cl—O2	1.456 (3)
N1—Cu—N2	103.32 (13)	N2—C23—C24	125.2 (4)
N1—Cu—N3	99.85 (13)	N2—C23—H23	117.4
N1—Cu—N4	81.66 (13)	C24—C23—H23	117.4
N1—Cu—N40	108.32 (14)	C25—C24—C23	121.1 (4)
N2—Cu—N3	149.09 (14)	C25—C24—H24	119.4
N2—Cu—N4	83.58 (14)	C23—C24—H24	119.4
N2—Cu—N40	96.97 (14)	C24—C25—C26	127.4 (4)
N3—Cu—N4	79.82 (14)	C24—C25—H25	116.3

N3—Cu—N40	94.85 (15)	C26—C25—H25	116.3
N4—Cu—N40	169.47 (15)	C211—C26—C27	117.9 (4)
C40—N40—Cu	178.4 (3)	C211—C26—C25	123.0 (4)
N40—C40—S	177.7 (4)	C27—C26—C25	119.1 (4)
C31—N4—C21	111.0 (3)	C28—C27—C26	120.8 (4)
C31—N4—C11	110.8 (3)	C28—C27—H27	119.6
C21—N4—C11	111.1 (3)	C26—C27—H27	119.6
C31—N4—Cu	105.8 (3)	C29—C28—C27	119.9 (4)
C21—N4—Cu	109.5 (3)	C29—C28—H28	120.0
C11—N4—Cu	108.5 (3)	C27—C28—H28	120.0
N4—C11—C12	110.0 (3)	C210—C29—C28	119.7 (5)
N4—C11—H11B	109.7	C210—C29—H29	120.1
C12—C11—H11B	109.7	C28—C29—H29	120.1
N4—C11—H11A	109.7	C29—C210—C211	120.9 (4)
C12—C11—H11A	109.7	C29—C210—H210	119.6
H11B—C11—H11A	108.2	C211—C210—H210	119.6
N1—C12—C11	110.2 (3)	C210—C211—C26	120.8 (4)
N1—C12—H12B	109.6	C210—C211—H211	119.6
C11—C12—H12B	109.6	C26—C211—H211	119.6
N1—C12—H12A	109.6	N4—C31—C32	110.6 (3)
C11—C12—H12A	109.6	N4—C31—H31B	109.5
H12B—C12—H12A	108.1	C32—C31—H31B	109.5
C13—N1—C12	116.6 (4)	N4—C31—H31A	109.5
C13—N1—Cu	135.1 (3)	C32—C31—H31A	109.5
C12—N1—Cu	108.2 (2)	H31B—C31—H31A	108.1
N1—C13—C14	123.6 (4)	N3—C32—C31	110.1 (3)
N1—C13—H13	118.2	N3—C32—H32B	109.6
C14—C13—H13	118.2	C31—C32—H32B	109.6
C15—C14—C13	122.2 (4)	N3—C32—H32A	109.6
C15—C14—H14	118.9	C31—C32—H32A	109.6
C13—C14—H14	118.9	H32B—C32—H32A	108.2
C14—C15—C16	127.2 (4)	C33—N3—C32	115.8 (4)
C14—C15—H15	116.4	C33—N3—Cu	131.2 (3)
C16—C15—H15	116.4	C32—N3—Cu	112.1 (2)
C17—C16—C111	117.9 (4)	N3—C33—C34	124.1 (4)
C17—C16—C15	119.7 (4)	N3—C33—H33	118.0
C111—C16—C15	122.5 (4)	C34—C33—H33	118.0
C18—C17—C16	121.0 (4)	C35—C34—C33	119.7 (4)
C18—C17—H17	119.5	C35—C34—H34	120.1
C16—C17—H17	119.5	C33—C34—H34	120.1
C19—C18—C17	120.4 (4)	C34—C35—C36	126.5 (4)
C19—C18—H18	119.8	C34—C35—H35	116.8
C17—C18—H18	119.8	C36—C35—H35	116.8
C18—C19—C110	119.4 (4)	C37—C36—C311	118.2 (4)
C18—C19—H19	120.3	C37—C36—C35	122.7 (4)
C110—C19—H19	120.3	C311—C36—C35	119.1 (4)
C111—C110—C19	120.6 (4)	C38—C37—C36	120.7 (4)
C111—C110—H110	119.7	C38—C37—H37	119.6
C19—C110—H110	119.7	C36—C37—H37	119.6

C110—C111—C16	120.7 (4)	C39—C38—C37	120.0 (5)
C110—C111—H111	119.6	C39—C38—H38	120.0
C16—C111—H111	119.6	C37—C38—H38	120.0
N4—C21—C22	108.0 (3)	C310—C39—C38	120.5 (5)
N4—C21—H21B	110.1	C310—C39—H39	119.8
C22—C21—H21B	110.1	C38—C39—H39	119.8
N4—C21—H21A	110.1	C39—C310—C311	119.8 (4)
C22—C21—H21A	110.1	C39—C310—H310	120.1
H21B—C21—H21A	108.4	C311—C310—H310	120.1
N2—C22—C21	106.5 (3)	C310—C311—C36	120.8 (5)
N2—C22—H22B	110.4	C310—C311—H311	119.6
C21—C22—H22B	110.4	C36—C311—H311	119.6
N2—C22—H22A	110.4	O3—Cl—O1	109.8 (2)
C21—C22—H22A	110.4	O3—Cl—O4	110.2 (2)
H22B—C22—H22A	108.6	O1—Cl—O4	110.2 (2)
C23—N2—C22	117.2 (3)	O3—Cl—O2	108.5 (2)
C23—N2—Cu	134.0 (3)	O1—Cl—O2	109.51 (19)
C22—N2—Cu	108.7 (2)	O4—Cl—O2	108.5 (2)
N40—Cu—N4—C31	18.8 (9)	N4—Cu—N2—C23	154.0 (4)
N2—Cu—N4—C31	112.4 (3)	N1—Cu—N2—C23	74.2 (4)
N3—Cu—N4—C31	−41.4 (2)	N40—Cu—N2—C22	147.5 (3)
N1—Cu—N4—C31	−143.0 (3)	N3—Cu—N2—C22	35.8 (4)
N40—Cu—N4—C21	−100.8 (8)	N4—Cu—N2—C22	−21.9 (3)
N2—Cu—N4—C21	−7.2 (3)	N1—Cu—N2—C22	−101.8 (3)
N3—Cu—N4—C21	−161.1 (3)	C22—N2—C23—C24	177.5 (4)
N1—Cu—N4—C21	97.3 (3)	Cu—N2—C23—C24	1.8 (6)
N40—Cu—N4—C11	137.8 (7)	N2—C23—C24—C25	174.8 (4)
N2—Cu—N4—C11	−128.6 (3)	C23—C24—C25—C26	−179.2 (4)
N3—Cu—N4—C11	77.5 (3)	C24—C25—C26—C211	3.8 (7)
N1—Cu—N4—C11	−24.1 (2)	C24—C25—C26—C27	−175.7 (4)
C31—N4—C11—C12	163.0 (3)	C211—C26—C27—C28	0.5 (6)
C21—N4—C11—C12	−73.2 (4)	C25—C26—C27—C28	180.0 (4)
Cu—N4—C11—C12	47.3 (4)	C26—C27—C28—C29	0.1 (7)
N4—C11—C12—N1	−50.0 (4)	C27—C28—C29—C210	−0.6 (7)
C11—C12—N1—C13	−156.8 (4)	C28—C29—C210—C211	0.3 (8)
C11—C12—N1—Cu	27.6 (4)	C29—C210—C211—C26	0.3 (8)
N40—Cu—N1—C13	7.1 (4)	C27—C26—C211—C210	−0.7 (7)
N2—Cu—N1—C13	−95.0 (4)	C25—C26—C211—C210	179.8 (4)
N3—Cu—N1—C13	105.6 (4)	C21—N4—C31—C32	163.3 (4)
N4—Cu—N1—C13	−176.3 (4)	C11—N4—C31—C32	−72.8 (4)
N40—Cu—N1—C12	−178.5 (2)	Cu—N4—C31—C32	44.6 (4)
N2—Cu—N1—C12	79.4 (3)	N4—C31—C32—N3	−20.4 (5)
N3—Cu—N1—C12	−80.0 (3)	C31—C32—N3—C33	156.1 (4)
N4—Cu—N1—C12	−1.9 (2)	C31—C32—N3—Cu	−14.0 (4)
C12—N1—C13—C14	−177.6 (4)	N40—Cu—N3—C33	52.3 (4)
Cu—N1—C13—C14	−3.5 (7)	N2—Cu—N3—C33	164.6 (3)
N1—C13—C14—C15	180.0 (4)	N4—Cu—N3—C33	−136.8 (4)
C13—C14—C15—C16	179.3 (4)	N1—Cu—N3—C33	−57.2 (4)
C14—C15—C16—C17	179.8 (4)	N40—Cu—N3—C32	−139.5 (3)

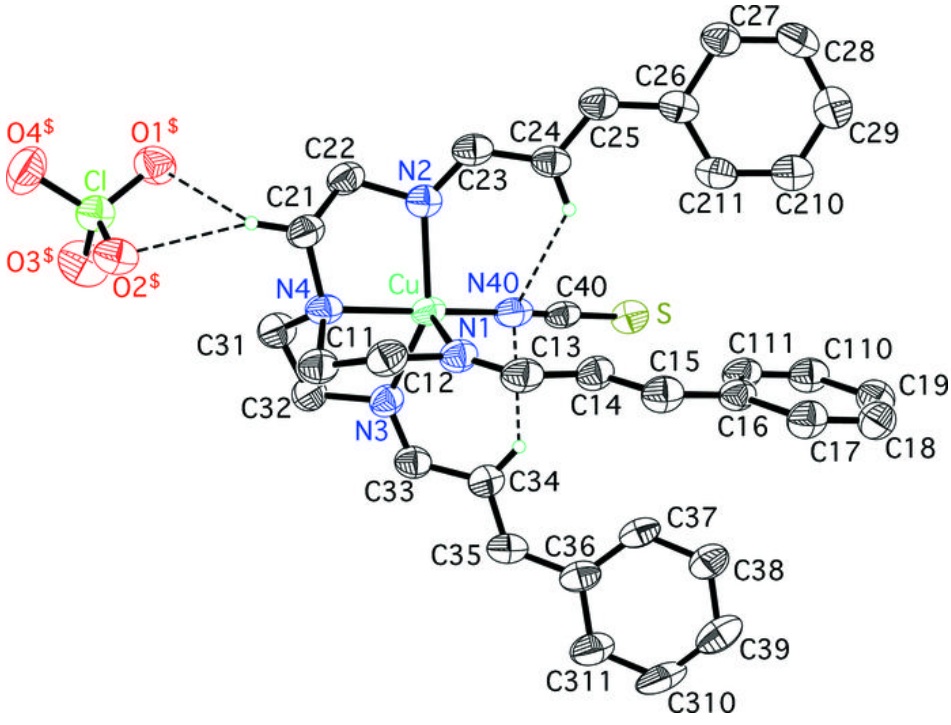
C14—C15—C16—C111	−0.5 (7)	N2—Cu—N3—C32	−27.2 (4)
C111—C16—C17—C18	0.2 (6)	N4—Cu—N3—C32	31.4 (3)
C15—C16—C17—C18	179.9 (4)	N1—Cu—N3—C32	111.0 (3)
C16—C17—C18—C19	0.0 (6)	C32—N3—C33—C34	−175.2 (4)
C17—C18—C19—C110	0.0 (7)	Cu—N3—C33—C34	−7.4 (6)
C18—C19—C110—C111	−0.4 (6)	N3—C33—C34—C35	174.4 (4)
C19—C110—C111—C16	0.6 (6)	C33—C34—C35—C36	178.4 (4)
C17—C16—C111—C110	−0.5 (6)	C34—C35—C36—C37	−5.1 (7)
C15—C16—C111—C110	179.8 (4)	C34—C35—C36—C311	175.7 (4)
C31—N4—C21—C22	−82.4 (4)	C311—C36—C37—C38	−1.1 (7)
C11—N4—C21—C22	153.9 (3)	C35—C36—C37—C38	179.7 (4)
Cu—N4—C21—C22	34.0 (4)	C36—C37—C38—C39	0.9 (7)
N4—C21—C22—N2	−52.5 (4)	C37—C38—C39—C310	−0.8 (7)
C21—C22—N2—C23	−130.9 (4)	C38—C39—C310—C311	0.9 (8)
C21—C22—N2—Cu	45.8 (3)	C39—C310—C311—C36	−1.1 (8)
N40—Cu—N2—C23	−36.6 (4)	C37—C36—C311—C310	1.2 (7)
N3—Cu—N2—C23	−148.3 (4)	C35—C36—C311—C310	−179.6 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12B···O1^{i}	0.97	2.55	3.521 (5)	176
C21—H21A···O1^{ii}	0.97	2.49	3.320 (5)	143
C21—H21A···O2^{ii}	0.97	2.45	3.359 (5)	156
C32—H32B···O2^{iii}	0.97	2.55	3.362 (5)	141
C18—H18···O3^{iv}	0.93	2.48	3.091 (5)	123
C24—H24···N40	0.93	2.57	3.205 (5)	126
C34—H34···N40	0.93	2.58	3.240 (5)	128

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

Fig. 1


C27
C28
C26
C29
C24
C25
O4$
O1$
C22
N2
C23
Cl
C21
C211
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O2$
N4
Cu
N40
C40
S
C31
C11
N1
C13
C111
C110
C15
C19
C12
C14
C32
C16
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C17
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C34
C37
C35
C36
C38
C39
C311
C310

Fig. 2