research communications

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Crystal structure of dichloridobis(dimethyl N-cyanodithioiminocarbonate)cobalt(II)
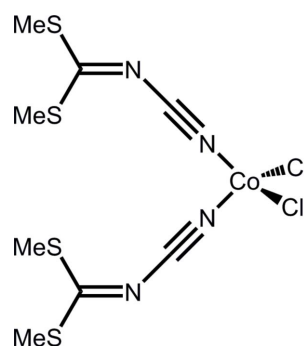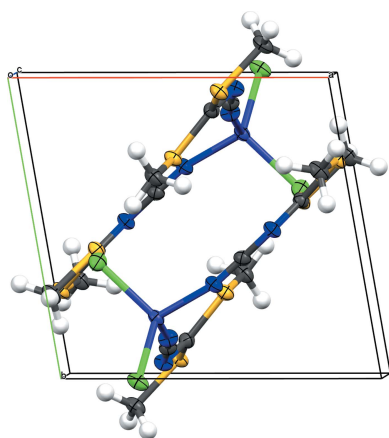
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The structure of the mononuclear title complex, $[\{(H_3CS)_2C=NC=N\}_2CoCl_2]$, consists of a Co^{II} atom coordinated in a distorted tetrahedral manner by two Cl^- ligands and the terminal N atoms of two dimethyl N-cyanodithioiminocarbonate ligands. The two organic ligands are almost coplanar, with a dihedral angle of 5.99 (6)° between their least-squares planes. The crystal packing features pairs of inversion-related complexes that are held together through C—H···Cl and C—H···S interactions and π–π stacking [centroid-to-centroid distance = 3.515 (su?) Å]. Additional C—H···Cl and C—H···S interactions, as well as Cl···S contacts < 3.6 Å, consolidate the crystal packing.

1. Chemical context

Dimethyl N-cyanodithioiminocarbonate with its two N and two S atoms has four possible coordination sites and hence should present a high coordination ability. The behaviour of N and S atoms according to Pearson's concept as hard and soft donors, respectively, may allow coordination to both hard and soft Lewis acids. Despite this coordination property, the ligand has scarcely been studied. Only one crystalline compound with dimethyl N-cyanodithioiminocarbonate as a ligand has been reported previously (Kojić-Prodić et al., 1992). The structure of this latter compound contains polymeric $[Cu^ICl]_n$ chains flanked by two N-coordinating ligands. Because of the scarcity of data on this ligand, we have initiated a study of the interactions between cobalt(II) chloride hexahydrate and dimethyl N-cyanodithioiminocarbonate which has yielded the title complex, $[\{(H_3CS)_2C=NC=N\}_2CoCl_2]$.

2. Structural commentary

The structure of the title complex consists of a Co^{II} atom coordinated in a distorted tetrahedral manner by two Cl^- ligands and the cyanide N atoms of two dimethyl N-cyano-

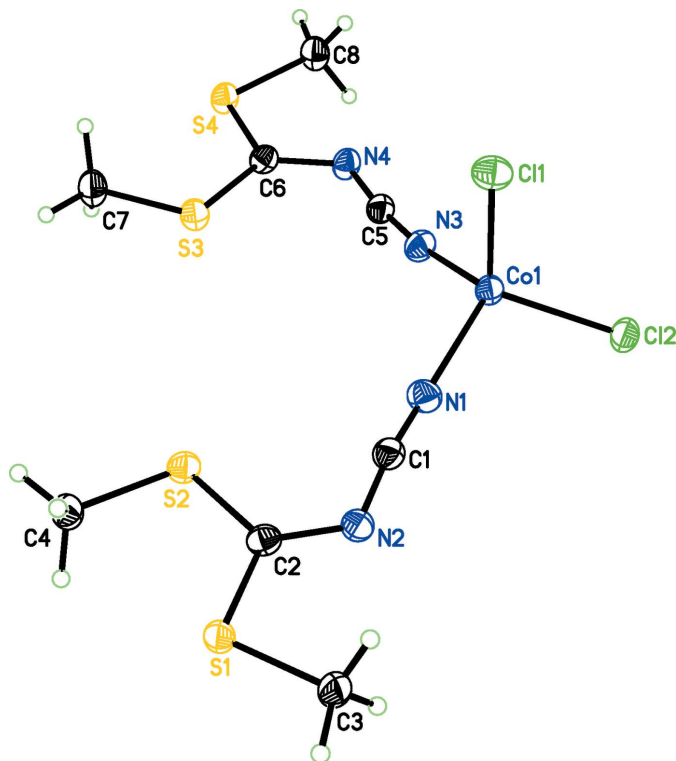OPEN ACCESS

Table 1
Selected geometric parameters (Å, °).

Co1—N3	1.9788 (18)	Co1—Cl2	2.2159 (6)
Co1—N1	1.9791 (19)	Co1—Cl1	2.2291 (6)
N3—Co1—N1	110.03 (8)	N1—Co1—Cl1	106.68 (6)
N3—Co1—Cl2	110.81 (6)	Cl2—Co1—Cl1	114.28 (2)
N1—Co1—Cl2	108.76 (6)	C1—N1—Co1	169.31 (18)
N3—Co1—Cl1	106.16 (6)	C5—N3—Co1	167.94 (18)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3A$\cdots$Cl2^{i}	0.98	2.88	3.538 (2)	125
C4—H4A$\cdots$Cl1^{ii}	0.98	2.85	3.602 (2)	135
C4—H4C$\cdots$Cl2^{iii}	0.98	2.74	3.714 (2)	177
C7—H7A$\cdots$Cl1^{ii}	0.98	2.80	3.592 (3)	138
C7—H7B$\cdots$Cl1^{iv}	0.98	2.87	3.590 (3)	131
C8—H8A$\cdots$Cl2^{v}	0.98	2.73	3.450 (2)	131
C8—H8B$\cdots$S4^{vi}	0.98	2.95	3.910 (2)	167
C8—H8C$\cdots$S1^{ii}	0.98	2.99	3.709 (3)	131

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

Table 3
Intermolecular contacts under 3.6 Å.

Atom 1$\cdots$Atom 2	Distance (Å)
Cl2$\cdots$S1^{i}	3.3742 (11)
Cl2$\cdots$S4^{ii}	3.3814 (10)
Cl1$\cdots$S2^{iii}	3.5945 (10)

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

carbonate ligands might be expected to enforce a higher distortion. The coordination of the ligand's nitrile nitrogen atoms to Co^{II} is slightly bent (Table 1). Despite this bending, the nitrile groups retain triple-bond character, with C1≡N1 and C5≡N3 bond lengths of 1.148 (3) and 1.147 (3) Å, respectively. The angular sums of the central C atoms of the ligands (C1, C5, 360.0 and 359.98°, respectively) show the expected trigonal–planar configuration. The least-squares planes of the two dimethyl N-cyanodithioiminocarbonate ligands are almost co-planar [dihedral angle = 5.99 (6)°]. The Co^{II} atom lies 0.437 (2) and 0.557 (2) Å from the mean planes of the two ligands.

3. Supramolecular features

The crystal packing features inversion-related pairs of complex molecules (Fig. 2). These pairs are arranged such that Cl1 is oriented between the H$_3$C—S groups of the adjacent molecule, presumably reducing steric interactions. Apart from C—H$\cdots$Cl and C—H$\cdots$S interactions (Table 2), π–π stacking

dithioiminocarbonate ligands (Fig. 1). Co—Cl and Co—N bond lengths are within expected ranges (Table 1). The Cl—Co—Cl angle is slightly larger than an ideal tetrahedral angle whereas three of the Cl—Co—N angles are smaller and the N—Co—N angle is very close to the ideal tetrahedral angle. This is remarkable because the bulky N-cyanodithioimino-

Figure 1
The molecular structure of the title compound, with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

Figure 2
Packing diagram of the title compound viewed approximately along the c axis. Displacement ellipsoids are as in Fig. 1.

Table 4
Experimental details.

Crystal data

Chemical formula	$[CoCl_2(C_4H_6N_2S_2)_2]$
M_r	422.29
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	120
a, b, c (Å)	8.8533 (10), 8.8722 (10), 11.2487 (14)
α, β, γ (°)	72.823 (3), 87.281 (4), 80.072 (3)
V (Å^3)	831.51 (17)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.85
Crystal size (mm)	$0.17 \times 0.15 \times 0.10$

Data collection

Diffractometer	Bruker Kappa X8 APEXII
Absorption correction	Numerical (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.757, 0.963
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12851, 4139, 3566
R_{int}	0.028
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.669

Refinement

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.033, 0.087, 1.09
No. of reflections	4139
No. of parameters	176
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.11, −0.50

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *XP* in *SHELXTL* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

with a centroid-to-centroid distance of 3.515 **(su?)** Å prevails within a pair of complex molecules. In the crystal, these pairs are arranged parallel to (110) (Fig. 2). Additional C—H···Cl and C—H···S interactions between individual pairs consolidate the crystal packing which might be influenced also by other weak contacts under 3.6 Å involving the Cl and S atoms (Table 3).

4. Synthesis and crystallization

All chemicals were purchased from Aldrich (Germany) and were used as received. The title compound was prepared by mixing of CoCl$_2$·6H$_2$O (1.665 g, 7 mmol) in acetonitrile (30 ml) and dimethyl *N*-cyanodithioiminocarbonate (1.023 g, 7 mmol) in acetonitrile (20 ml) at room temperature. The resulting blue solution was stirred for about 2 h. Blue crystals suitable for single-crystal X-ray diffraction were obtained after six days of slow solvent evaporation at room temperature (300 K).

Infra-red bands: ν(C≡N) 2224 cm^{-1}, ν(C=N) 1458 cm^{-1}, ν(CS$_2$) + rocking CH$_3$ 1024 and 962 cm^{-1}. Melting point 398 K. Elemental analyses of C$_8$H$_{12}$Cl$_2$CoN$_4$S$_4$: calculated (found): C 22.75 (21.91), H 2.86 (3.43), N 13.27 (12.63), S 30.37 (29.40).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. Methyl H atoms were allowed to rotate to maximize their contribution to the electron density and were modelled with C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C).

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supporting information

Crystal structure of dichloridobis(dimethyl *N*-cyanodithioimino-carbonate)cobalt(II)

Mouhamadou Birame Diop, Libasse Diop and Allen G. Oliver

Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Dichloridobis(dimethyl *N*-cyanodithioiminocarbonate)cobalt(II)

Crystal data

[CoCl$_2$(C$_4$H$_6$N$_2$S$_2$)$_2$]	$Z = 2$
$M_r = 422.29$	$F(000) = 426$
Triclinic, $P\bar{1}$	$D_x = 1.687$ Mg m^{-3}
$a = 8.8533$ (10) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.8722$ (10) Å	Cell parameters from 6476 reflections
$c = 11.2487$ (14) Å	$\theta = 2.3–28.4°$
$\alpha = 72.823$ (3)°	$\mu = 1.85$ mm^{-1}
$\beta = 87.281$ (4)°	$T = 120$ K
$\gamma = 80.072$ (3)°	Block, blue
$V = 831.51$ (17) Å^3	$0.17 \times 0.15 \times 0.10$ mm

Data collection

Bruker Kappa X8 APEXII diffractometer	12851 measured reflections
Radiation source: fine-focus sealed tube	4139 independent reflections
Graphite monochromator	3566 reflections with $I > 2\sigma(I)$
Detector resolution: 8.33 pixels mm^{-1}	$R_{int} = 0.028$
combination of ω and φ–scans	$\theta_{max} = 28.4°$, $\theta_{min} = 1.9°$
Absorption correction: numerical (*SADABS*; Krause *et al.*, 2015)	$h = -11\rightarrow11$
	$k = -11\rightarrow11$
$T_{min} = 0.757$, $T_{max} = 0.963$	$l = -14\rightarrow7$

Refinement

Refinement on F^2	Primary atom site location: real-space vector search
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.033$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.087$	
$S = 1.09$	Hydrogen site location: inferred from neighbouring sites
4139 reflections	
176 parameters	H-atom parameters constrained
0 restraints	

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.4168P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	$U_{iso}*/U_{eq}$
Co1	0.32319 (3)	0.80109 (3)	0.23799 (3)	0.01930 (9)
Cl1	0.16996 (6)	0.61729 (6)	0.29242 (6)	0.02787 (13)
Cl2	0.23586 (6)	1.01243 (6)	0.08085 (5)	0.02677 (13)
S1	0.35461 (6)	0.94916 (6)	0.80748 (5)	0.02145 (12)
S2	0.53818 (6)	0.72624 (6)	0.68536 (5)	0.02235 (12)
S3	0.83867 (6)	0.41595 (6)	0.37512 (5)	0.02199 (12)
S4	0.97640 (6)	0.27842 (6)	0.17733 (5)	0.02215 (12)
N1	0.3446 (2)	0.8728 (2)	0.38617 (18)	0.0247 (4)
N2	0.3115 (2)	0.9569 (2)	0.57616 (17)	0.0223 (4)
N3	0.5233 (2)	0.6904 (2)	0.19638 (19)	0.0242 (4)
N4	0.73672 (19)	0.5076 (2)	0.14206 (18)	0.0220 (4)
C1	0.3361 (2)	0.9056 (2)	0.4779 (2)	0.0217 (4)
C2	0.3924 (2)	0.8854 (2)	0.6783 (2)	0.0206 (4)
C3	0.1932 (3)	1.1047 (3)	0.7548 (2)	0.0266 (5)
H3A	0.1614	1.1553	0.8205	0.040*
H3B	0.1081	1.0588	0.7346	0.040*
H3C	0.2217	1.1849	0.6804	0.040*
C4	0.6032 (2)	0.6665 (3)	0.8441 (2)	0.0261 (4)
H4A	0.6846	0.5730	0.8579	0.039*
H4B	0.5173	0.6391	0.9001	0.039*
H4C	0.6429	0.7547	0.8608	0.039*
C5	0.6267 (2)	0.6032 (2)	0.1776 (2)	0.0208 (4)
C6	0.8401 (2)	0.4120 (2)	0.2233 (2)	0.0201 (4)
C7	1.0010 (3)	0.2699 (3)	0.4438 (2)	0.0288 (5)
H7A	1.0052	0.2589	0.5330	0.043*
H7B	1.0951	0.3042	0.4038	0.043*
H7C	0.9915	0.1667	0.4323	0.043*
C8	0.9185 (3)	0.3104 (3)	0.0198 (2)	0.0271 (5)
H8A	0.9860	0.2358	−0.0163	0.041*
H8B	0.9255	0.4205	−0.0290	0.041*
H8C	0.8125	0.2924	0.0188	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01959 (14)	0.02016 (14)	0.01816 (16)	0.00228 (10)	−0.00075 (11)	−0.00863 (11)

Cl1	0.0279 (3)	0.0291 (3)	0.0300 (3)	−0.0061 (2)	0.0048 (2)	−0.0138 (2)
Cl2	0.0319 (3)	0.0244 (2)	0.0215 (3)	0.00654 (19)	−0.0057 (2)	−0.0084 (2)
S1	0.0240 (2)	0.0225 (2)	0.0175 (3)	0.00254 (19)	−0.00157 (19)	−0.0087 (2)
S2	0.0242 (2)	0.0216 (2)	0.0215 (3)	0.00096 (19)	0.0012 (2)	−0.0095 (2)
S3	0.0212 (2)	0.0245 (2)	0.0197 (3)	0.00097 (18)	0.00047 (19)	−0.0084 (2)
S4	0.0208 (2)	0.0231 (2)	0.0210 (3)	0.00428 (18)	0.00045 (19)	−0.0086 (2)
N1	0.0309 (9)	0.0249 (9)	0.0192 (9)	−0.0058 (7)	0.0009 (7)	−0.0072 (7)
N2	0.0273 (9)	0.0222 (8)	0.0175 (9)	−0.0008 (7)	−0.0002 (7)	−0.0076 (7)
N3	0.0236 (8)	0.0217 (8)	0.0266 (10)	0.0018 (7)	−0.0005 (7)	−0.0088 (7)
N4	0.0210 (8)	0.0222 (8)	0.0211 (9)	0.0025 (6)	0.0004 (7)	−0.0070 (7)
C1	0.0249 (10)	0.0194 (9)	0.0202 (11)	−0.0039 (7)	−0.0002 (8)	−0.0047 (8)
C2	0.0214 (9)	0.0202 (9)	0.0208 (11)	−0.0032 (7)	0.0032 (8)	−0.0077 (8)
C3	0.0295 (11)	0.0250 (10)	0.0239 (11)	0.0063 (8)	−0.0046 (9)	−0.0105 (9)
C4	0.0246 (10)	0.0272 (10)	0.0259 (12)	0.0043 (8)	−0.0055 (9)	−0.0109 (9)
C5	0.0231 (9)	0.0195 (9)	0.0190 (10)	−0.0020 (7)	−0.0014 (8)	−0.0049 (8)
C6	0.0198 (9)	0.0197 (9)	0.0203 (10)	−0.0013 (7)	0.0020 (8)	−0.0067 (8)
C7	0.0282 (11)	0.0317 (11)	0.0235 (12)	0.0036 (9)	−0.0040 (9)	−0.0077 (9)
C8	0.0295 (11)	0.0309 (11)	0.0199 (11)	0.0046 (9)	−0.0007 (9)	−0.0113 (9)

Geometric parameters (Å, º)

Co1—N3	1.9788 (18)	N3—C5	1.147 (3)
Co1—N1	1.9791 (19)	N4—C5	1.306 (3)
Co1—Cl2	2.2159 (6)	N4—C6	1.321 (3)
Co1—Cl1	2.2291 (6)	C3—H3A	0.9800
S1—C2	1.708 (2)	C3—H3B	0.9800
S1—C3	1.793 (2)	C3—H3C	0.9800
S2—C2	1.726 (2)	C4—H4A	0.9800
S2—C4	1.798 (2)	C4—H4B	0.9800
S3—C6	1.718 (2)	C4—H4C	0.9800
S3—C7	1.793 (2)	C7—H7A	0.9800
S4—C6	1.714 (2)	C7—H7B	0.9800
S4—C8	1.795 (2)	C7—H7C	0.9800
N1—C1	1.148 (3)	C8—H8A	0.9800
N2—C1	1.310 (3)	C8—H8B	0.9800
N2—C2	1.314 (3)	C8—H8C	0.9800
N3—Co1—N1	110.03 (8)	H3B—C3—H3C	109.5
N3—Co1—Cl2	110.81 (6)	S2—C4—H4A	109.5
N1—Co1—Cl2	108.76 (6)	S2—C4—H4B	109.5
N3—Co1—Cl1	106.16 (6)	H4A—C4—H4B	109.5
N1—Co1—Cl1	106.68 (6)	S2—C4—H4C	109.5
Cl2—Co1—Cl1	114.28 (2)	H4A—C4—H4C	109.5
C2—S1—C3	100.97 (10)	H4B—C4—H4C	109.5
C2—S2—C4	103.59 (10)	N3—C5—N4	172.7 (2)
C6—S3—C7	103.88 (10)	N4—C6—S4	119.43 (16)
C6—S4—C8	101.50 (10)	N4—C6—S3	121.39 (15)
C1—N1—Co1	169.31 (18)	S4—C6—S3	119.16 (12)

C1—N2—C2	120.71 (18)	S3—C7—H7A	109.5
C5—N3—Co1	167.94 (18)	S3—C7—H7B	109.5
C5—N4—C6	120.10 (19)	H7A—C7—H7B	109.5
N1—C1—N2	172.7 (2)	S3—C7—H7C	109.5
N2—C2—S1	120.19 (15)	H7A—C7—H7C	109.5
N2—C2—S2	121.18 (16)	H7B—C7—H7C	109.5
S1—C2—S2	118.63 (13)	S4—C8—H8A	109.5
S1—C3—H3A	109.5	S4—C8—H8B	109.5
S1—C3—H3B	109.5	H8A—C8—H8B	109.5
H3A—C3—H3B	109.5	S4—C8—H8C	109.5
S1—C3—H3C	109.5	H8A—C8—H8C	109.5
H3A—C3—H3C	109.5	H8B—C8—H8C	109.5
C1—N2—C2—S1	−177.67 (16)	C5—N4—C6—S4	175.87 (16)
C1—N2—C2—S2	2.3 (3)	C5—N4—C6—S3	−2.8 (3)
C3—S1—C2—N2	2.6 (2)	C8—S4—C6—N4	−3.5 (2)
C3—S1—C2—S2	−177.38 (13)	C8—S4—C6—S3	175.25 (13)
C4—S2—C2—N2	−176.86 (18)	C7—S3—C6—N4	−178.88 (18)
C4—S2—C2—S1	3.11 (15)	C7—S3—C6—S4	2.43 (16)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3A⋯Cl2[i]	0.98	2.88	3.538 (2)	125
C4—H4A⋯Cl1[ii]	0.98	2.85	3.602 (2)	135
C4—H4C⋯Cl2[iii]	0.98	2.74	3.714 (2)	177
C7—H7A⋯Cl1[ii]	0.98	2.80	3.592 (3)	138
C7—H7B⋯Cl1[iv]	0.98	2.87	3.590 (3)	131
C8—H8A⋯Cl2[v]	0.98	2.73	3.450 (2)	131
C8—H8B⋯S4[vi]	0.98	2.95	3.910 (2)	167
C8—H8C⋯S1[ii]	0.98	2.99	3.709 (3)	131

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