The Crystal and Molecular Structure of Dichlorobis(pyridinium-2-thiolate)cobalt(II)

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Abstract

The crystal and molecular structure of $C_{10}H_{10}Cl_2$-CoN_2S_2, $Co(C_5H_5NS)_2Cl_2$, has been determined by single-crystal X-ray diffraction techniques using counter methods, and has been refined by full-matrix least-squares procedures using 1893 unique and significant (at the 3σ level) reflections. The complex crystallizes in the monoclinic space group $P2_1/c$ with unit-cell dimensions of $a = 9.353$ (1), $b = 11.463$ (2), $c = 13.599$ (2) Å, $\beta = 109.09$ (1)°, and with four molecules per unit cell. The Co^{II} ions have distorted tetrahedral geometry with mean Co^{II}–S and Co^{II}–Cl distances of 2.320 (1) and 2.265 (1) Å, respectively. Bond lengths indicate that coordination to the metal ion has changed the predominant character of the ligand from 2-pyridinethione to pyridinium-2-thiolate, the zwitterionic form. The H atoms on the N atoms are involved in intermolecular hydrogen bonding with Cl ions. Due to an initial inaccuracy of <0.1 Å in the Co^{II} position, the structure refined to a false minimum with $R_1 = 0.100$ and $R_2 = 0.137$. Correct positional coordinates for the Co^{II} ion led to successful convergence with $R_1 = 0.032$ and $R_2 = 0.034$.

Introduction

Crystallographic studies (Kadooka, Warner & Seff, 1976; Binamira-Soriaga, Lundeen & Seff, 1979) of Co^{II} complexes of organic dipyridyl disulfides have shown the preferential bonding of Co^{II} to the N rather than to the S atom of the disulfide ligand, with the remaining coordination requirements of Co^{II} satisfied by either Cl ions or water molecules. With the aim of synthesizing a Co^{II}–disulfide complex which demonstrates cobalt(II)–sulfur coordination, the title compound was prepared by reacting 2-pyridinethione (commonly known as 2-pyridinethiol) with $CoCl_2$. The structure shows that the next step, an attempt to oxidize the complexed thione to the disulfide, had been unsuccessful.

Experimental

Green crystals of dichlorobis(pyridinium-2-thiolate)-cobalt(II) were obtained by reacting 2-pyridinethione with analytical reagent grade $CoCl_2.6H_2O$ while passing air through the solution for a period of 48 h. The product has been characterized as $Co(2\text{-pySH})_2$-Cl_2 by Kennedy & Lever (1972), and by Evans & Wilkinson (1974). A few blue crystals of $Co(2,2'\text{-py}_2S_2)Cl_2$ (Kadooka, Warner & Seff, 1976), the corresponding disulfide, were also obtained.

A single crystal of approximate dimensions 0.16 × 0.32 × 0.14 mm was selected for X-ray diffraction study and was mounted along its longest dimension. A Syntex four-circle computer-controlled $P\bar{1}$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda = 0.70930$ Å; $K\alpha_2$, $\lambda = 0.71359$ Å) was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations (see Table 1) were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 24° ($K\alpha$, $\bar{\lambda} = 0.71073$ Å). The space group was assigned on the basis of the systematic absences, l odd for $h0l$ and k odd for $0k0$. The θ–2θ scan mode was used with a scan rate (ω) in 2θ of 2° min^{-1}. The total background time, equal to the scan time, was spent equally at each end of the scan range, from 0.8° in 2θ below the $K\alpha_1$ maximum to 0.8° above that of $K\alpha_2$. The intensities of three check reflections remeasured after every 97 reflections showed an average decrease in intensity of less than 1% during data collection, for which a correction using linear interpolation was applied.

Table 1. *Crystal data*

Dichlorobis(pyridinium-2-thiolate)cobalt(II)

$C_{10}H_{10}Cl_2CoN_2S_2$	FW 352.2
Monoclinic	$Z = 4$
Space group $P2_1/c$	Systematic absences: $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$
$a = 9.353$ (1) Å	$F(000) = 708$
$b = 11.463$ (2)	$D_x = 1.697$ Mg m^{-3}
$c = 13.599$ (2)	$D_m = 1.70$
$\beta = 109.09$ (1)°	$V = 1377.8$ (4) Å^3

Standard deviations were assigned according to the formula $\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2}$, where CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity I is given by $\omega(CT - B_1 - B_2)$. A value of 0·02 was assigned to the empirical parameter p (Peterson & Levy, 1957) to account for physical and instrumental inaccuracies. The weights (w) used in least-squares refinement of structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 3347 unique reflections measured, those for which $2\theta < 55°$, 1893 had intensities greater than three times their standard deviations, and only these were used in subsequent calculations. The intensities were corrected for Lorentz and polarization effects (Ottersen, 1976), and for absorption ($\mu = 1·905$ mm^{-1}) (*International Tables for X-ray Crystallography*, 1974*a*; Busing & Levy, 1957; Ottersen, 1974). The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction.

The atomic scattering factors for Co^{2+}, Cl$^-$, S^0, N^0, C^0, and H (bonded) were taken from *International Tables for X-ray Crystallography* (1974*b*) with modifications for the real part of the anomalous-dispersion correction for the first three atoms or ions.

Structure determination

The position of the Co^{II} ion was determined from a three-dimensional Patterson function generated using the fast Fourier algorithm (Hubbard, Quicksall & Jacobson, 1971). A Fourier function phased on the Co ion exhibited pseudosymmetry; a false twofold axis containing the Co ion appeared at $\frac{1}{4},y,\frac{1}{4}$, parallel to b. Accordingly, only unique peaks from this function were considered, and this permitted the location of a S atom and a Cl ion both bound to Co^{II}. However, the pseudo-twofold symmetry persisted and became even more pronounced in the subsequent Fourier function generated with phases calculated from these three heavy atoms. At this point, it seemed reasonable to regard such near symmetry as a feature of the structure; thus, all peaks revealed by the function were considered. As a result, the remaining non-hydrogen atoms in the structure were located. Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1976) with isotropic thermal parameters for all nonhydrogen atoms converged at $R_1 = \sum |F_o - |F_c||/\sum F_o = 0·202$, but the values of the thermal parameters for each pair of atoms related by the pseudo-twofold symmetry were unreasonably different. Isotropic refinement was continued by resetting the B values for the atoms of each pair to their average after each cycle of refinement. Three cycles of anisotropic refinement led to convergence with the residual indices $R_1 = 0·100$ and $R_2 =$

$[\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0·137$. A subsequent difference function showed no additional peaks greater than 0·8 e Å^{-3} in height.

Although the residual indices had each reached a minimum, the calculated bond lengths for the refined structure were chemically unrealistic: the C—C bond distances ranged from 1·15 to 1·64 Å, and the two chemically equivalent S—C bond lengths were 1·60 and 1·84 Å.

Of the 1893 observed reflections, those for which $h + k = 2n$ were generally strong while those for which $h + k = 2n + 1$ were weak. An examination of the structure factors indicated that the R values for $h + k = 2n + 1$ were much higher than those for $h + k = 2n$. Evidently, the weak reflections were not phased correctly. These conditions indicate the near presence of C-centering (Fig. 1), twofold symmetry, and the space group $C2/c$ in the structure.

The problem was resolved by destroying the pseudo-twofold symmetry. Since Co was situated nearly at the twofold axis (its position from the last cycle of refinement was 0·248, 0·0556, 0·251), it was logical to experiment with its position alone. Keeping perfect twofold symmetry by properly adjusting the coordinates of the other atoms so that only the Co ion would contribute to the phases of the $h + k = 2n + 1$ reflections, refinement was done using the initial Co positions (*a*) 0·240, 0·0556, 0·240 or (*b*) 0·240, 0·0556, 0·260. After three cycles of refinement, for case (*a*), the Co position had shifted to 0·238, 0·0554, 0·242 with $R_1 = 0·162$ and $R_2 = 0·200$; for case (*b*), the new Co position was 0·247, 0·0554, 0·257 with $R_1 = 0·201$ and $R_2 = 0·254$. Anisotropic refinement of all nonhydrogen atoms using the result of case (*a*) converged at $R_1 = 0·041$.

A difference function clearly showed the positions of all H atoms. Full refinement with anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the H atoms led to the final
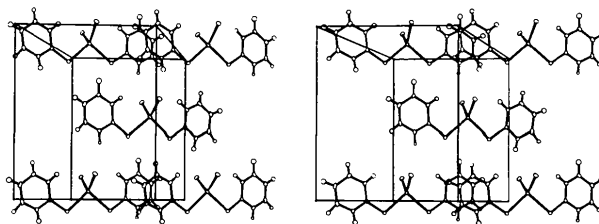

Fig. 1. This stereoview (Johnson, 1965) of the structure shows the near C centering which is found. The view is approximately into the $+c$ direction with $+a$ horizontal to the right and $+b$ extending upward in the plane of the page. One way to see that the C centering is imperfect is to compare the attitudes of those ring bonds which are nearly parallel to b. A comparison of the H thermal spheres shows readily that the central molecule was generated by a 2_1 along b and not by a C-centering operation. Ellipsoids of 10% probability are used.

Table 2. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$)

Numbers in parentheses are estimated standard deviations in the least significant digits. See Fig. 2 for the identities of the atoms.

	x	y	z
Co(1)	2432·8 (6)	557·1 (3)	2457·9 (5)
Cl(2)	3516 (1)	1726 (1)	3847 (1)
Cl(3)	1266 (1)	1598 (1)	1001 (1)
S(4)	4158 (1)	−731 (1)	2158 (1)
C(5)	5278 (4)	77 (3)	1631 (3)
C(6)	5315 (4)	1292 (3)	1551 (3)
C(7)	6279 (4)	1833 (4)	1119 (3)
C(8)	7252 (5)	1181 (4)	765 (3)
C(9)	7226 (4)	6 (5)	840 (3)
N(10)	6248 (3)	−515 (3)	1262 (2)
S(11)	844 (1)	−790 (1)	2847 (1)
C(12)	−335 (4)	−21 (3)	3353 (2)
C(13)	−477 (4)	1186 (4)	3385 (3)
C(14)	−1497 (5)	1668 (4)	3804 (3)
C(15)	−2393 (4)	978 (3)	4196 (3)
C(16)	−2230 (4)	−190 (5)	4180 (3)
N(17)	−1222 (3)	−661 (3)	3764 (2)
H(6)	474 (4)	174 (3)	185 (3)
H(7)	624 (4)	277 (4)	110 (3)
H(8)	794 (4)	154 (3)	49 (3)
H(9)	778 (4)	−51 (3)	62 (3)
H(10)	619 (3)	−123 (3)	127 (2)
H(13)	7 (4)	170 (3)	308 (3)
H(14)	−158 (4)	243 (3)	384 (3)
H(15)	−312 (4)	127 (4)	450 (3)
H(16)	−275 (4)	−79 (3)	445 (3)
H(17)	−104 (4)	−140 (4)	379 (3)

error indices $R_1 = 0.032$ and $R_2 = 0.034$. The 'goodness of fit', $[\sum w(|F_o - |F_c||)^2/(m - s)]^{1/2}$, is 1·74. The number of observations used in least squares is m (1893), and s (194) is the total number of parameters. The overdetermination ratio (m/s) is, therefore, 9·8. In the final cycle of least-squares refinement, the largest shift in a nonhydrogen parameter was less than 17% of its corresponding e.s.d.; for the H atoms, this value was 23%. The final difference function was flat and featureless; the largest peaks observed were 0·3 e Å^{-3} in height with an e.s.d. of 0·07 e Å^{-3}. The positional parameters of the atoms are given in Table 2.*

Discussion

The molecular structure of $C_{10}H_{10}Cl_2CoN_2S_2$ is shown in Fig. 2. The geometry about Co^{II} is distorted tetrahedral with bond angles between adjacent donor atoms ranging from 98·67 (4) to 112·88 (4)°. Co^{II} is coordinated to two Cl ions and to the S atoms (Kennedy &

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* Lists of structure factors and thermal parameters, and Fig. 5, have been deposited with the British Lending Division as Supplementary Publication No. SUP 34632 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Lever, 1972) of two pyridinium-2-thiolate ligands. As can be seen in Figs. 1 and 2 or Tables 2 and 3, the molecule nearly has symmetry $mm2$ (C_{2v}).

The pyridinium-2-thiolate geometry in the complex is quite different from that of the free ligand as reported by Penfold (1953). Fig. 3 shows that although the C—C bond lengths in the free thione range from 1·29 to 1·52

Table 3. *Molecular dimensions*

Numbers in parentheses are estimated standard deviations in the least significant digits.

(*a*) Bond lengths (Å)

Co(1)—Cl(2)	2·266 (1)	C(12)—C(13)	1·392 (5)
Co(1)—Cl(3)	2·264 (1)	C(13)—C(14)	1·377 (6)
Co(1)—S(4)	2·319 (1)	C(14)—C(15)	1·380 (6)
Co(1)—S(11)	2·321 (1)	C(15)—C(16)	1·348 (8)
S(4)—C(5)	1·720 (3)	C(6)—H(6)	0·93 (3)
S(11)—C(12)	1·721 (3)	C(7)—H(7)	1·07 (4)
N(10)—C(5)	1·354 (5)	C(8)—H(8)	0·94 (4)
N(10)—C(9)	1·365 (5)	C(9)—H(9)	0·90 (3)
N(17)—C(12)	1·358 (5)	N(10)—H(10)	0·83 (3)
N(17)—C(16)	1·360 (5)	C(13)—H(13)	0·96 (4)
		C(14)—H(14)	0·88 (4)
C(5)—C(6)	1·399 (5)	C(15)—H(15)	0·97 (4)
C(6)—C(7)	1·374 (5)	C(16)—H(16)	0·98 (3)
C(7)—C(8)	1·380 (6)	N(17)—H(17)	0·87 (4)
C(8)—C(9)	1·352 (7)		

(*b*) Bond angles (°)

Cl(2)—Co(1)—Cl(3)	111·95 (4)	C(5)—C(6)—H(6)	119 (2)
Cl(2)—Co(1)—S(4)	112·07 (4)	C(7)—C(6)—H(6)	119 (2)
Cl(3)—Co(1)—S(4)	110·21 (4)	C(6)—C(7)—H(7)	116 (2)
Cl(2)—Co(1)—S(11)	110·39 (4)	C(8)—C(7)—H(7)	124 (2)
Cl(3)—Co(1)—S(11)	112·88 (4)	C(7)—C(8)—H(8)	121 (2)
S(4)—Co(1)—S(11)	98·67 (4)	C(9)—C(8)—H(8)	120 (2)
		C(8)—C(9)—H(9)	127 (2)
Co(1)—S(4)—C(5)	106·5 (1)	N(10)—C(9)—H(9)	113 (2)
Co(1)—S(11)—C(12)	107·0 (1)	C(9)—N(10)—H(10)	120 (2)
S(4)—C(5)—C(6)	127·1 (3)	C(5)—N(10)—H(10)	116 (2)
S(4)—C(5)—N(10)	117·3 (3)	C(12)—C(13)—H(13)	122 (2)
S(11)—C(12)—C(13)	127·0 (3)	C(14)—C(13)—H(13)	118 (2)
S(11)—C(12)—N(17)	116·4 (2)	C(13)—C(14)—H(14)	121 (2)
		C(15)—C(14)—H(14)	118 (2)
C(6)—C(5)—N(10)	115·6 (3)	C(14)—C(15)—H(15)	125 (2)
C(5)—C(6)—C(7)	121·3 (3)	C(16)—C(15)—H(15)	117 (2)
C(6)—C(7)—C(8)	120·3 (4)	C(15)—C(16)—H(16)	128 (2)
C(7)—C(8)—C(9)	118·9 (4)	N(17)—C(16)—H(16)	112 (2)
C(8)—C(9)—N(10)	119·9 (3)	C(16)—N(17)—H(17)	122 (3)
C(9)—N(10)—C(5)	124·0 (3)	C(12)—N(17)—H(17)	114 (3)
C(13)—C(12)—N(17)	116·6 (3)		
C(12)—C(13)—C(14)	119·9 (3)		
C(13)—C(14)—C(15)	121·4 (4)		
C(14)—C(15)—C(16)	118·4 (4)		
C(15)—C(16)—N(17)	120·0 (4)		
C(12)—N(17)—C(16)	123·8 (4)		

(*c*) Selected torsion angles (°)

Co(1)—S(4)—C(5)—C(6)	−9·3 (4)
Co(1)—S(4)—C(5)—N(10)	171·5 (3)
Co(1)—S(11)—C(12)—N(17)	171·3 (2)
Co(1)—S(11)—C(12)—C(13)	−8·6 (4)
C(5)—S(4)—Co(1)—S(11)	−169·8 (2)
C(12)—S(11)—Co(1)—S(4)	−168·3 (2)

Å, the corresponding values in the complexed 'thione' are all between 1·352 and 1·399 Å. This suggests the existence of much more aromaticity in the pyridine rings of the complexed 'thione' resulting from the contribution of its zwitterionic resonance form [Fig. 4(b)]. This effect can also be seen in the C—S bond length observed in both cases. By calculating the degree of resonance contribution of the thione tautomer [Fig. 4(c)] which gave the best agreement between the observed and calculated bond lengths, Penfold had determined the C—S bond in the 2-pyridinethione molecule to contain ca 65% double-bond character. He had concluded that, analogous to α-pyridone (alternative name: 2-pyridone), 2-pyridinethiol [Fig. 4(a)] exists mainly as the thione or, as he named it, α-thiopyridone. His C—S distance of 1·68 (2) Å also agrees well with the corresponding values of 1·683 (6), 1·671 (8), 1·68 (2), and 1·69 (1) Å, found in a number of compounds where the thione tautomer is predominant (Caira & Nassimbeni, 1975, 1976; Form & Raper, 1976; Hunt & Amma, 1973). Based on a more recent scale (Trinajstić, 1968) relating the C—S bond length to percentage double-bond character, Penfold's C—S distance would have about 60% double-bond character, consistent with his conclusions. However, on the same scale, the C—S bond in the title compound would have only about 40% double-bond character.

Presumably, complexation to the Co[II] ion stabilizes the negative charge on the S atom to some extent, causing the zwitterionic [pyridinium-2-thiolate, Fig. 4(b)] character of the 2-pyridinethiol to be predominant.

It is interesting to note that solution studies of 2-pyridinethiol have shown it to exist mostly as the thione (Jones & Katritzky, 1958; Albert & Barlin, 1958, 1959). The ultraviolet spectrum of the ligand has bands at 271 nm ($\varepsilon = 10\,400$) and 343 nm ($\varepsilon = 7060$) at a pH of 7·2 (Grassetti & Murray, 1967). The positions of these bands are not particularly shifted in aqueous solutions of the Co complex, suggesting that the ligand is not disturbed very much by complexation. However, the intensities of the bands are approximately doubled (the extinction coefficients are 14 300 and 20 400 at 271 and 341 nm, respectively). This is consistent with increased zwitterionic character, leading to increased aromaticity, in the pyridine ring (Albert & Barlin, 1959).

The bond lengths and angles about the Co[II] ion are similar to those found in other Co[II] complexes (Holt, Holt & Watson, 1970; Bruchner, Calligaris, Nardin & Randaccio, 1969; Hall & Horrocks, 1969; Dance & Calabrese, 1975; Bonamico, Dessy, Fares & Scaramuzza, 1973; Antti & Lundberg, 1972; Figgis, 1964). The mean geometry of the pyridine rings is also like that found in other pyridyl groups and in metal complexes of di-2-pyridyl disulfide (Raghavan & Seff, 1977; Warner, Ottersen & Seff, 1974; Warner, Kadooka & Seff, 1975) with the exception of the bond angle about the N atom. For such complexes, the C—N—C bond angles range from 116 to 119° while for this structure they are 123·8 (4) and 124·0 (3)°. This widening of the C—N—C angle is attributed to the presence of the proton on the N atom. Singh (1965), in his studies of six-membered N heterocycles, proposed this empirical rule: for protonated nitrogens, the angle at the N atom will fall within the range 125 ± 3°; for unprotonated nitrogens, this value is 116 ± 3°.
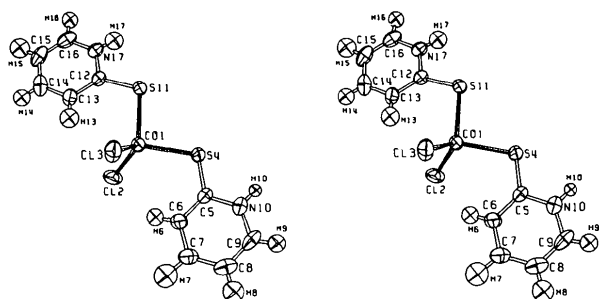

Fig. 2. Stereoview (Johnson, 1965) of dichlorobis(pyridinium-2-thiolate)cobalt(II) showing ellipsoids of 50% probability.
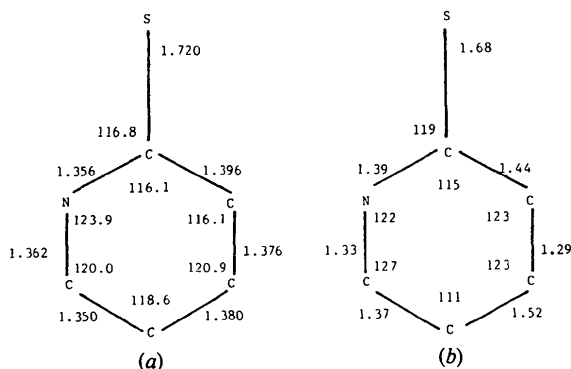

Fig. 3. A comparison of (mean) bond lengths (Å) and angles (°) (a) in complexed 2-pyridinethione with (b) those in the free molecule (Penfold, 1953).
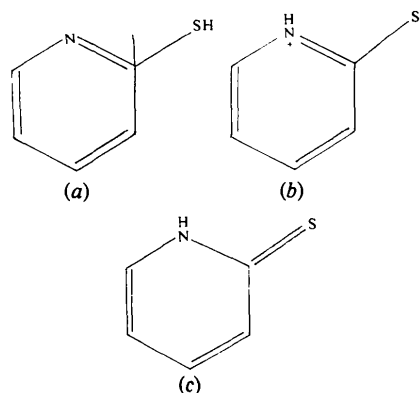

Fig. 4. Structural forms of the ligand: (a) 2-pyridinethiol, (b) zwitterion, pyridinium-2-thiolate, and (c) 2-pyridinethione.

Table 4. *Deviations of atoms from least-squares planes*
($\text{Å} \times 10^3$)

Deviations in boldface indicate the atoms used to define the least-squares plane. A negative deviation from the plane indicates that the atom with coordinates given in Table 2 lies between that plane and the origin. The direction cosines ($\times 10^4$), q, are with respect to the orthogonalized axes. The r.m.s. deviation from the plane ($\text{Å} \times 10^3$) of the atoms used to define the plane is δ. D is the distance (Å) from the plane to the origin. See Fig. 2 to identify the planes.

Plane 1		Plane 2	
C(5)	**1**	C(12)	**−7**
C(6)	**2**	C(13)	**5**
C(7)	**−6**	C(14)	**4**
C(8)	**3**	C(15)	**−10**
C(9)	**3**	C(16)	**4**
N(10)	**−3**	N(17)	**4**
Co(1)	−300	Co(1)	288
S(4)	26	S(11)	−33
q_a	4250		4385
q_b	462		281
q_c·	9040		8983
δ	3		6
D	3·687		3·085

Table 5. *Intermolecular approach distances* (Å)

All intermolecular distances less than $\sum r_{vdw}$ are presented in this table. The van der Waals radii (Å) used are: H 1·2, S 1·85, Cl 1·80, aromatic-ring half thickness for C and N 1·7. The coordinates of the atoms are given in Table 2; those of the second atom of each contact are related to those in the tables by the symmetry operation indicated.

Cl(3)–H(8)	2·96	$-1 + x, y, z$
Cl(2)–H(10)	2·37	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
Cl(3)–H(9)	2·92	$1 - x, -y, -z$
Cl(2)–H(16)	2·84	$-x, -y, 1 - z$
N(17)–Cl(3)	3·16	$-x, -\frac{1}{2} + y, \frac{1}{2} - z$
N(10)–Cl(2)	3·18	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
S(4)–H(7)	3·05	$1 - x, -\frac{1}{2} - y, \frac{1}{2} - z$
H(17)–Cl(3)	2·33	$-x, \frac{1}{2} + y, \frac{1}{2} - z$

Deviations of atoms from the least-squares planes are given in Table 4. Fig. 5 illustrates the packing of the molecules in the unit cell.* Intermolecular hydrogen bonding occurs between N(17) and Cl(3), and N(10) and Cl(2), at distances of 3·159 and 3·177 Å, respectively. Other short intermolecular contacts are listed in Table 5.

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* Fig. 5 has been deposited. See preceding footnote.

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