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4,6-Dichloro-2-[(*E*)-(2-{[(*E*)-3,5-dichloro-2-oxidobenzylidene]azaniumyl}ethyl)-iminiumylmethyl]phenolate

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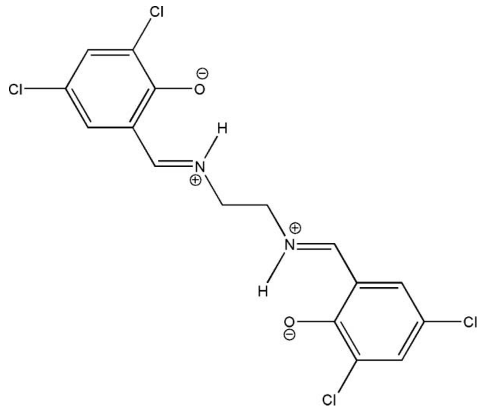
Key indicators: single-crystal X-ray study; *T* = 291 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.042; *wR* factor = 0.097; data-to-parameter ratio = 16.9.

The asymmetric unit of the title compound, $C_{16}H_{12}Cl_4N_2O_2$, comprises half of a potentially tetradentate Schiff base ligand, located about a twofold rotation axis which bisects the central C—C bond of the ethane-1,2-diamine group. In the solid state, the compound exists in the zwitterionic form. There are two intramolecular N—H⋯O hydrogen bonds making *S*(6) ring motifs. In the crystal, molecules are linked by C—H⋯O hydrogen bonds, forming two-dimensional frameworks which lie parallel to (100). There are also short Cl⋯Cl [3.4395 (9) Å] contacts present.

Related literature

For standard bond lengths, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For van der Waals radii, see: Bondi (1964). For related Schiff base ligands, see: Kargar *et al.* (2011); Kia *et al.* (2010).



Experimental

Crystal data

$C_{16}H_{12}Cl_4N_2O_2$
M_r = 406.08
Monoclinic, *C*2/*c*
a = 20.0505 (14) Å
b = 10.1460 (9) Å
c = 9.0579 (6) Å
β = 114.955 (4)°
V = 1670.6 (2) Å^3
Z = 4
Mo *K*α radiation
μ = 0.72 mm^{-1}
T = 291 K
0.21 × 0.14 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.864, T_{max} = 0.932
6453 measured reflections
1838 independent reflections
1146 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.097
S = 0.97
1838 reflections
109 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O1	0.97	1.74	2.585 (3)	143
C8—H8*A*⋯O1^{i}	0.97	2.55	3.436 (3)	152

Symmetry code: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{5}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); 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* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2459).

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Acta Cryst. (2012). E**68**, o2242–o2243 Kargar *et al.* • $C_{16}H_{12}Cl_4N_2O_2$ **o2243**

supplementary materials

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4,6-Dichloro-2-[(*E*)-(2-{[(*E*)-3,5-dichloro-2-oxidobenzylidene]azaniumyl}ethyl)iminiumylmethyl]phenolate

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Comment

In continuation of our work on the crystal structure of Schiff base ligands (Kargar *et al.*, (2011); Kia *et al.*, (2010), we report herein on the crystal structure of the title compound.

The asymmetric unit of the title compound, Fig. 1, comprises half of a potentially tetradentate Schiff base ligand that exists in the keto-amine tautomeric form. The molecule is located about a two-fold rotation axis which bisects the central C8-C8a bond of the ethane-1,2-diamine group. The bond lengths (Allen *et al.*, 1987) and angles are within the normal ranges. The intramolecular N—H···O hydrogen bonds make *S(6)* ring motifs (Table 1; Bernstein *et al.*, 1995).

In the crystal, molecules are linked by C—H···O hydrogen bonds along the *b* and *c* axes directions, forming two dimensional networks which lie parallel to the bc plane [Table 1 and Fig. 2]. There are also short Cl···Cl^{ii} [3.4384 (10)Å; symmetry code: (ii) -x, y, 1/2 - z] contacts present, which are shorter than the sum of the van der waals radius of Cl atoms (Bondi, 1964; Fig. 3).

Experimental

The title compound was synthesized by adding 3,5-dichlorosalicylaldehyde (2 mmol) to a solution of ethylenediamine (1 mmol) in ethanol (30 ml). The mixture was refluxed with stirring for 30 min. The resultant solution was filtered. Yellow single crystals of the title compound, suitable for *X*-ray structure determination, were obtained by recrystallization from ethanol by slow evaporation of the solvents at room temperature over several days.

Refinement

The N-bound H atom was located in a difference Fourier map. It was constrained to ride on the parent N-atom with $U_{iso}(H) = 1.2 U_{eq}(N)$. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93 and 0.97 Å for CH and CH_2 H atoms, respectively, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); 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* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

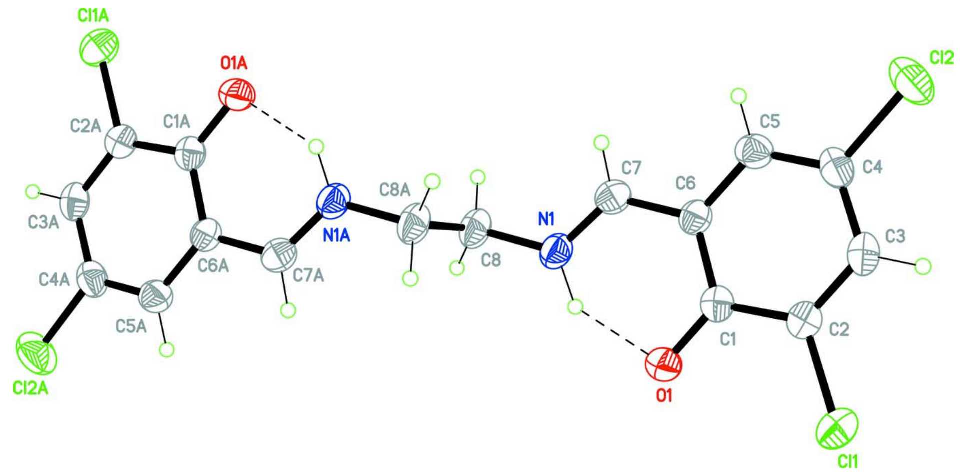

Figure 1

The molecular structure of the title compound, showing 40% probability displacement ellipsoids and the atomic numbering [symmetry code for suffix A = -x + 1/2, -y + 3/2, -z + 2].

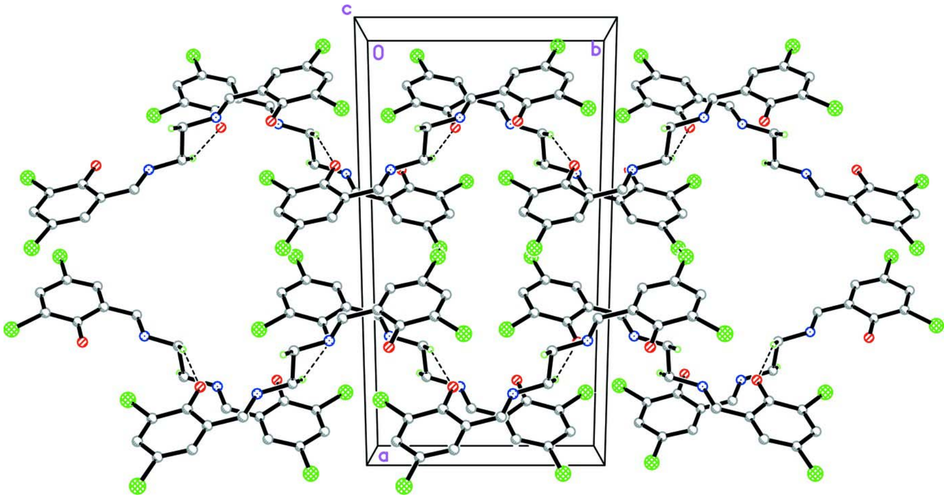

Figure 2

The crystal packing of the title compound viewed down the *c*-axis, showing hoe the molecules are linked via C—H···O interactions (dashed lines), so forming two dimensional networks (see Table 1 for details).

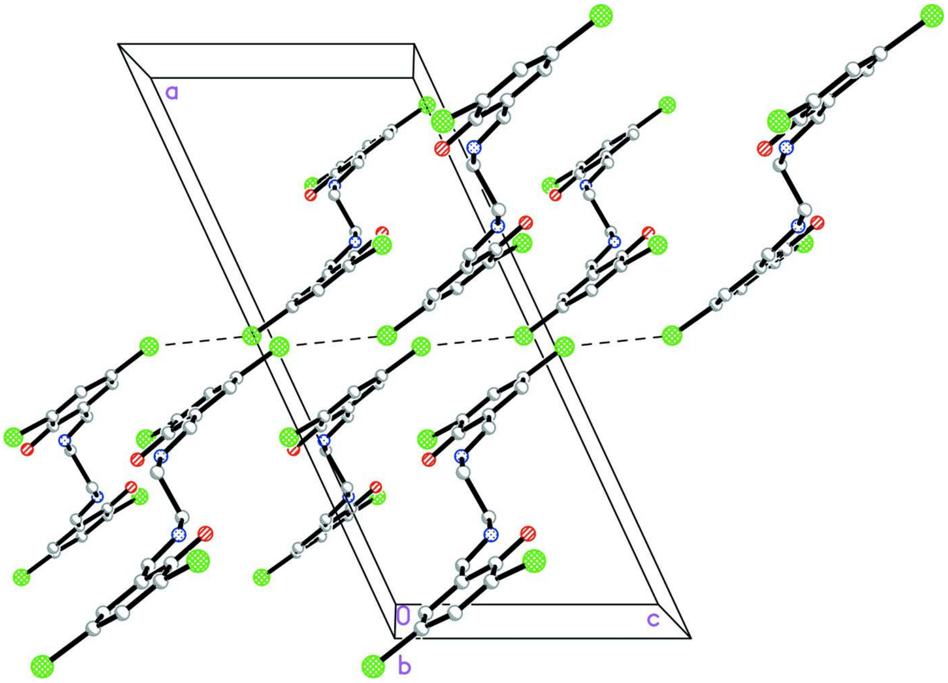

Figure 3

The crystal packing diagram of the title compound viewed down the *b*-axis, showing the short intermolecular Cl···Cl contacts (dashed lines). All H atoms have been omitted for clarity.

4,6-Dichloro-2-[(*E*)-(2-{[(*E*)-3,5-dichloro-2- oxidobenzylidene]azaniumyl}ethyl)iminiumylmethyl]phenolate

Crystal data

$C_{16}H_{12}Cl_4N_2O_2$
$M_r = 406.08$
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
$a = 20.0505 (14)$ Å
$b = 10.1460 (9)$ Å
$c = 9.0579 (6)$ Å
$\beta = 114.955 (4)°$
$V = 1670.6 (2)$ Å^3
$Z = 4$
$F(000) = 824$
$D_x = 1.614$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71073$ Å
Cell parameters from 936 reflections
$\theta = 2.5–27.5°$
$\mu = 0.72$ mm^{-1}
$T = 291$ K
Block, yellow
0.21 × 0.14 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.864$, $T_{max} = 0.932$
6453 measured reflections
1838 independent reflections
1146 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.1°$, $\theta_{min} = 2.2°$
$h = -25\rightarrow25$
$k = -7\rightarrow12$
$l = -9\rightarrow11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.097$
$S = 0.97$
1838 reflections
109 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
$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
C1	0.15792 (12)	0.3326 (2)	0.9612 (3)	0.0382 (6)
C2	0.13797 (12)	0.1976 (3)	0.9247 (3)	0.0402 (6)
C3	0.09283 (12)	0.1562 (3)	0.7713 (3)	0.0451 (6)
H3	0.0814	0.0672	0.7511	0.054*
C4	0.06374 (12)	0.2481 (3)	0.6446 (3)	0.0456 (7)
C5	0.07928 (12)	0.3784 (3)	0.6728 (3)	0.0444 (6)
H5	0.0591	0.4384	0.5877	0.053*
C6	0.12553 (12)	0.4231 (2)	0.8292 (3)	0.0376 (6)
C7	0.14430 (12)	0.5599 (3)	0.8529 (3)	0.0413 (6)
H7	0.1217	0.6175	0.7661	0.050*
Cl1	0.17398 (4)	0.08447 (7)	1.08141 (8)	0.0568 (2)
Cl2	0.00981 (4)	0.19341 (9)	0.44794 (8)	0.0718 (3)
N1	0.19105 (10)	0.6061 (2)	0.9888 (2)	0.0432 (5)
H1	0.2100	0.5376	1.0712	0.052*
C8	0.21355 (13)	0.7436 (3)	1.0075 (3)	0.0479 (6)
H8A	0.2193	0.7756	1.1130	0.057*
H8B	0.1761	0.7963	0.9242	0.057*
O1	0.20257 (9)	0.37045 (17)	1.10541 (17)	0.0482 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0382 (12)	0.0382 (16)	0.0418 (14)	−0.0014 (11)	0.0203 (11)	−0.0028 (12)
C2	0.0407 (12)	0.0379 (16)	0.0450 (13)	0.0008 (11)	0.0210 (11)	0.0003 (12)
C3	0.0474 (14)	0.0370 (16)	0.0545 (16)	−0.0089 (12)	0.0250 (13)	−0.0078 (13)
C4	0.0430 (14)	0.0510 (19)	0.0432 (15)	−0.0101 (12)	0.0185 (12)	−0.0109 (13)

C5	0.0411 (13)	0.0533 (19)	0.0395 (13)	−0.0013 (12)	0.0176 (11)	0.0036 (13)
C6	0.0385 (12)	0.0374 (16)	0.0408 (13)	−0.0017 (11)	0.0206 (11)	0.0008 (12)
C7	0.0443 (14)	0.0415 (17)	0.0424 (13)	0.0029 (11)	0.0224 (12)	0.0030 (12)
Cl1	0.0654 (4)	0.0412 (4)	0.0622 (4)	0.0037 (3)	0.0253 (4)	0.0099 (3)
Cl2	0.0669 (5)	0.0858 (7)	0.0498 (4)	−0.0168 (4)	0.0119 (4)	−0.0205 (4)
N1	0.0539 (12)	0.0323 (14)	0.0452 (12)	−0.0036 (10)	0.0227 (10)	0.0003 (10)
C8	0.0610 (15)	0.0300 (16)	0.0576 (16)	−0.0066 (12)	0.0298 (14)	−0.0038 (12)
O1	0.0571 (10)	0.0443 (12)	0.0361 (9)	−0.0042 (9)	0.0128 (8)	0.0005 (8)

Geometric parameters (Å, º)

C1—O1	1.292 (2)	C5—H5	0.9300
C1—C2	1.426 (3)	C6—C7	1.430 (3)
C1—C6	1.429 (3)	C7—N1	1.281 (3)
C2—C3	1.366 (3)	C7—H7	0.9300
C2—Cl1	1.729 (2)	N1—C8	1.453 (3)
C3—C4	1.401 (3)	N1—H1	0.9724
C3—H3	0.9300	C8—C8^{i}	1.529 (5)
C4—C5	1.358 (4)	C8—H8A	0.9700
C4—Cl2	1.740 (2)	C8—H8B	0.9700
C5—C6	1.401 (3)		
O1—C1—C2	121.8 (2)	C5—C6—C1	120.7 (2)
O1—C1—C6	122.1 (2)	C5—C6—C7	119.1 (2)
C2—C1—C6	116.1 (2)	C1—C6—C7	120.0 (2)
C3—C2—C1	122.2 (2)	N1—C7—C6	122.7 (2)
C3—C2—Cl1	119.9 (2)	N1—C7—H7	118.7
C1—C2—Cl1	117.91 (18)	C6—C7—H7	118.7
C2—C3—C4	119.8 (2)	C7—N1—C8	121.9 (2)
C2—C3—H3	120.1	C7—N1—H1	111.5
C4—C3—H3	120.1	C8—N1—H1	126.5
C5—C4—C3	120.8 (2)	N1—C8—C8^{i}	109.5 (3)
C5—C4—Cl2	119.8 (2)	N1—C8—H8A	109.8
C3—C4—Cl2	119.4 (2)	C8^{i}—C8—H8A	109.8
C4—C5—C6	120.5 (2)	N1—C8—H8B	109.8
C4—C5—H5	119.8	C8^{i}—C8—H8B	109.8
C6—C5—H5	119.8	H8A—C8—H8B	108.2
O1—C1—C2—C3	−177.7 (2)	C4—C5—C6—C1	0.8 (3)
C6—C1—C2—C3	2.4 (3)	C4—C5—C6—C7	176.3 (2)
O1—C1—C2—Cl1	1.4 (3)	O1—C1—C6—C5	177.77 (19)
C6—C1—C2—Cl1	−178.53 (15)	C2—C1—C6—C5	−2.3 (3)
C1—C2—C3—C4	−1.0 (3)	O1—C1—C6—C7	2.3 (3)
Cl1—C2—C3—C4	180.00 (17)	C2—C1—C6—C7	−177.81 (19)
C2—C3—C4—C5	−0.7 (3)	C5—C6—C7—N1	−173.9 (2)
C2—C3—C4—Cl2	177.00 (17)	C1—C6—C7—N1	1.6 (3)
C3—C4—C5—C6	0.8 (3)	C6—C7—N1—C8	175.4 (2)
Cl2—C4—C5—C6	−176.92 (17)	C7—N1—C8—C8^{i}	−97.9 (3)

Symmetry code: (i) $-x+1/2, -y+3/2, -z+2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.97	1.74	2.585 (3)	143
C8—H8*A*···O1^{ii}	0.97	2.55	3.436 (3)	152

Symmetry code: (ii) −*x*+1/2, *y*+1/2, −*z*+5/2.