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X-RAY CRYSTAL STRUCTURE OF AZOXYBENZENE OXOTETRACHLOROTUNGSTEN(VI), $(C_6H_5N)_2OW^{VI}OCl_4$

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Summary

The crystal and molecular structure of azoxybenzene oxotetrachlorotungsten(VI) has been determined from X-ray diffractometer data. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to $R = 0.058$ for 1869 independent reflections.

The crystals are monoclinic, space group $P2_1/c$, with $Z = 4$, in a unit cell of dimensions: $a = 8.314(3)$, $b = 15.100(5)$, $c = 12.901(7)$ Å, $\beta = 95.31(5)°$. The azoxybenzene residue, the structure of which resembles that of free *trans* azobenzene, is linked to the tungsten atom through its oxygen atom. The coordination at the metal (two oxygen atoms and four chlorine atoms) corresponds to a distorted octahedron.

This distortion is very similar to those observed in similar tungsten compounds. There is a intramolecular C···O distance of 2.77 Å between two atoms four bonds apart, of the azoxybenzene residue.

Introduction

In the course of studies on the metathesis of olefinic hydrocarbons, several complexes of tungsten and molybdenum oxychlorides with azoxybenzene have been prepared in our laboratories [1]. The X-ray crystal structure of $(C_6H_5N)_2OW^{VI}OCl_4$ (I) is now reported.

Experimental

Preliminary space group and unit-cell dimensions were obtained from Weissenberg photographs. A crystal, essentially a parallelepiped, having dimensions ca. 0.30 × 0.15 × 0.40 mm was mounted on a Picker FACS 1 four-circle com-

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puter-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser. The orientation matrix and cell dimensions were obtained from a least-squares fit of χ, ϕ, ω and 2θ values from 12 independent reflections.

Crystal data

$WCl_4O_2N_2C_{12}H_{10}$, mol. wt. 539.90. Monoclinic $a = 8.314(3)$, $b = 15.100(5)$, $c = 12.901(7)$ Å, $\beta = 95.31(5)°$, $V = 1612.62$ Å^3, $D_m = 2.19$, $Z = 4$, $D_c = 2.22$. Space group $P2_1/c$ from systematic absences $0k0$ for k odd, $h0l$ for l odd. Mo-K_α radiation, $\lambda = 0.7107$ Å μ(Mo-K_α) = 82.20 cm^{-1}.

Intensity data were collected by use of zirconium-filtered Mo-K_α radiation with $2\theta \leqslant 50°$. The moving crystal/moving counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of 2.0-2.50° in order to allow for the greater separation of the K_{α_1} and K_{α_2} peaks at increasing 2θ values. Background counts of 10 s were measured at each end of every 2θ scan. Three standard reflections, measured after every 50 reflections, showed no fluctuation $> \pm 4\%$ during data collection. 2833 independent reflections were measured of which 1869 were considered observed and had $I \geqslant 3\ \sigma$. An arbitrary intensity equal to 0.5 the observable limit was assigned to the non-significant reflections. All intensities were corrected for Lorentz and polarization effects. The intensities were also corrected for absorption using a general computation program described by Busing and Levy [2].

Determination and refinement of the structure

The structure of I was solved by the heavy atom methods. The coordinates of the W and Cl atoms have been derived from a three-dimensional Patterson map. The Fourier map phased on the W and Cl atoms yielded a clear picture of the whole molecule of I and enabled definite identification of all the non-hydrogen atoms.

The positional and the isotropic thermal parameters of all the non-hydrogen atoms of the molecule, were refined by some cycles of block-diagonal least-squares by use of a program of Immirzi [3]. Atomic scattering factors were calculated from the expression in ref. 4 using values for the parameters given in ref. 5. The weighting scheme of ref. 6 was adopted:

$$\frac{1}{W} = A + B|F_o| + C|F_o|^2$$

where $A = 2\ F_o(\text{min})$, $B = 1.0$ and $C = 2/F_o(\text{max})$.

The conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was at this point 0.11 for the 1869 non-zero reflections.

Four block-diagonal cycles of refinement were run, assuming anisotropic thermal parameters for all the non-hydrogen atoms of the molecule, the hydrogen atoms being introduced into the calculations but not refined, their coordinates being defined on stereochemical grounds and according to a difference Fourier synthesis.

The refinement converged to $R = 0.058$ for the 1869 significant reflections and to 0.099 including all the reflections. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ.

TABLE 1

FINAL FRACTIONAL COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x/a*	*y/b*	*z/c*	*B* (Å^2)
W	0.78233(10)	0.34923(6)	0.61421(7)	—
Cl(1)	0.9309(7)	0.2409(4)	0.5442(5)	—
Cl(2)	0.7099(8)	0.3978(5)	0.4474(5)	—
Cl(3)	0.5822(8)	0.4351(5)	0.6728(6)	—
Cl(4)	0.8056(8)	0.2775(5)	0.7722(5)	—
O(1)	0.5763(18)	0.2506(12)	0.5841(12)	—
O(2)	0.9351(19)	0.4199(13)	0.6404(14)	—
N(1)	0.5207(25)	0.2159(14)	0.4960(17)	—
N(2)	0.5458(29)	0.1445(16)	0.4595(19)	—
C(1)	0.3975(23)	0.2663(16)	0.4230(18)	—
C(2)	0.3156(29)	0.3268(16)	0.4726(21)	—
C(3)	0.1977(27)	0.3726(18)	0.4115(24)	—
C(4)	0.1710(30)	0.3624(21)	0.3020(22)	—
C(5)	0.2595(33)	0.3032(22)	0.2557(26)	—
C(6)	0.3690(30)	0.2504(19)	0.3170(22)	—
C(7)	0.8374(31)	−0.0510(18)	0.6159(21)	—
C(8)	0.7704(32)	0.0065(20)	0.6774(18)	—
C(9)	0.6766(27)	0.0806(16)	0.6380(20)	—
C(10)	0.6552(23)	0.0871(16)	0.5288(20)	—
C(11)	0.7176(31)	0.0259(20)	0.4687(21)	—
C(12)	0.8116(30)	−0.0452(17)	0.5134(25)	—
H(2)	0.3411	0.3395	0.5556	5.0
H(3)	0.1215	0.4192	0.4489	5.0
H(4)	0.0807	0.4026	0.2573	5.0
H(5)	0.2470	0.2955	0.1707	5.0
H(6)	0.4342	0.1970	0.2819	5.0
H(7)	0.9195	−0.1026	0.6501	5.0
H(8)	0.7876	−0.0032	0.7615	5.0
H(9)	0.6247	0.1281	0.6894	5.0
H(11)	0.6961	0.0310	0.3841	5.0
H(12)	0.8599	−0.0953	0.4643	5.0

Table 1 reports the final fractional coordinates and the corresponding estimated standard deviations of the atoms of the molecule I. Table 2 lists the anisotropic thermal parameters of the non-hydrogen atoms. A copy of the table of observed and calculated structure factors can be obtained by application to the authors.

Results and discussion

Views of the molecule I are shown in Figs. 1 and 2. Both figures were obtained by means of the ORTEP computing and drawing programs [7]. The geometrical parameters of the molecule I with their estimated standard deviations are reported in Table 3.

The coordination around the tungsten atom is approximately octahedral. The four W—Cl bond lengths are equivalent within the experimental error (average 2.294(7) Å) and are in good agreement with the values observed in the near-

TABLE 2

ANISOTROPIC THERMAL PARAMETERS[a] FOR THE NON-HYDROGEN ATOMS

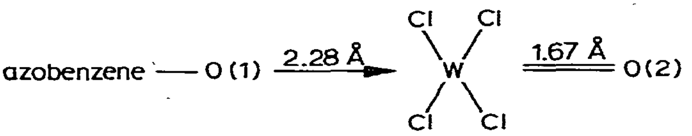
Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	3.17(4)	3.53(4)	3.07(4)	—0.14(3)	—0.20(3)	0.03(3)
Cl(1)	3.56(24)	5.00(29)	4.44(26)	0.59(21)	0.89(20)	0.05(23)
Cl(2)	4.60(28)	5.25(32)	3.90(26)	—0.43(24)	—0.22(21)	1.06(24)
Cl(3)	5.05(29)	4.43(29)	5.39(31)	0.91(24)	0.84(24)	0.23(25)
Cl(4)	5.26(31)	6.13(35)	3.07(23)	0.54(26)	—0.13(21)	0.74(23)
O(1)	3.3(7)	5.2(8)	4.1(7)	—0.3(6)	0.3(5)	—0.9(6)
O(2)	3.6(7)	5.9(10)	5.4(9)	—1.6(7)	—0.6(6)	—0.1(7)
N(1)	4.0(9)	5.2(11)	5.1(10)	—1.1(8)	1.7(8)	—1.2(8)
N(2)	4.9(11)	7.0(13)	5.2(12)	—1.8(10)	0.6(9)	—0.5(10)
C(1)	1.5(7)	5.0(11)	4.5(10)	0.1(7)	—1.2(7)	0.7(9)
C(2)	3.7(10)	3.5(10)	5.5(12)	—0.4(8)	0.3(9)	—0.1(9)
C(3)	2.7(9)	4.7(12)	7.2(15)	—0.6(8)	0.3(9)	1.0(11)
C(4)	2.9(10)	8.5(18)	5.4(13)	0.6(11)	—1.4(9)	—0.1(12)
C(5)	4.3(13)	6.7(16)	6.9(17)	—0.9(12)	—0.9(11)	1.0(13)
C(6)	3.7(11)	5.0(13)	6.5(14)	0.2(10)	0.2(10)	—0.7(11)
C(7)	4.8(11)	4.3(12)	5.1(13)	—0.1(10)	0.5(9)	1.8(10)
C(8)	5.2(13)	7.4(15)	2.6(10)	—2.0(11)	0.4(9)	—0.1(10)
C(9)	3.5(10)	3.3(10)	6.2(13)	0.9(8)	0.9(9)	0.3(9)
C(10)	1.5(7)	4.6(11)	5.9(12)	0.5(7)	—0.1(7)	0.6(9)
C(11)	4.3(11)	6.8(15)	4.1(12)	—0.8(11)	—0.3(9)	—0.1(11)
C(12)	3.9(11)	3.7(12)	9.2(18)	0.7(9)	1.7(10)	—1.4(12)

[a] The temperature factors are in the form

$$T_j = \exp -1/4\ (B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)$$

ly octahedral environments of $WOCl_4$ (2.29 Å) [8], and of $C_4H_{10}Cl_6O_3S_2W_2$ (average 2.32(1) Å) [9].

The O(1) and O(2) atoms are in *trans* position and the W—O(1) and W—O(2) distances found in I (2.28(2) and 1.67(2) Å, respectively) are in line with the values quoted for similar compounds showing a nearly octahedral coordination at the tungsten atom. Tungsten—oxygen distances of 2.2 and 1.8 Å have been found in polymeric $WOCl_4$ [8], of 2.27(2) and 1.71(2) Å in $WSCl_4 \cdot WOSCl_2$-1,2-dimethoxyethane [9], and of 2.09(1) and 1.79(2) Å in Cu_3WO_6 [11]. W—O distances of 1.79 Å have also been found in the tetrahedral $[WO_4]^{2-}$ ions [10]. A substantial multiple bond character is to be attributed to the W—O(2) bond, and the bonding situation around the metal may be represented as follows:



The four chlorine atoms are nearly coplanar (r.m.s. distance 0.006 Å) and the metal is displaced of 0.27 Å out of this plane. Owing to this displacement the O(1)—W—Cl angles are all lower than 90° (av. 83.2°) while the O(2)—W—Cl ones are all greater than 90° (av. 96.9°). As a result the distances of the two oxygen atoms from the least-squares plane of the chlorine atoms are nearly equivalent (—2.000 Å for O(1) and 1.943 Å for O(2)). Very similar distortions of the octahedral environment at the tungsten atom are quoted for $WOCl_4$ [8].

TABLE 3

MOST SIGNIFICANT GEOMETRIC PARAMETERS OF THE MOLECULE I

(a) Bond lengths (Å)	
W—Cl(1)	2.285(6)
W—Cl(2)	2.300(7)
W—Cl(3)	2.292(7)
W—Cl(4)	2.301(7)
W—O(1)	2.276(16)
W—O(2)	1.669(18)
O(1)—N(1)	1.30(3)
N(1)—N(2)	1.20(3)
N(1)—C(1)	1.53(3)
N(2)—C(10)	1.49(4)
C(1)—C(2)	1.34(3)
C(1)—C(6)	1.39(4)
C(2)—C(3)	1.39(4)
C(3)—C(4)	1.42(4)
C(4)—C(5)	1.34(4)
C(5)—C(6)	1.40(4)
C(7)—C(8)	1.33(4)
C(7)—C(12)	1.32(4)
C(8)—C(9)	1.43(4)
C(9)—C(10)	1.41(4)
C(10)—C(11)	1.34(4)
C(11)—C(12)	1.42(4)
Av. C · · · C benzene = 1.38(4)	

(b) Bond angles (deg.)	
W—O(1)—N(1)	128(1)
Cl(1)—W—Cl(2)	87.9(1)
Cl(1)—W—Cl(3)	166.1(7)
Cl(1)—W—Cl(4)	90.5(1)
Cl(1)—W—O(1)	83.7(2)
Cl(1)—W—O(2)	96.2(5)
Cl(2)—W—Cl(3)	89.6(1)
Cl(2)—W—Cl(4)	166.5(7)
Cl(2)—W—O(1)	85.5(2)
Cl(2)—W—O(2)	96.6(4)
Cl(3)—W—Cl(4)	88.8(1)
Cl(3)—W—O(1)	82.5(2)
Cl(3)—W—O(2)	97.7(4)
Cl(4)—W—O(1)	81.0(2)
Cl(4)—W—O(2)	97.0(5)
O(1)—W—O(2)	178(19)
O(1)—N(1)—N(2)	130(1)
O(1)—N(1)C(1)	120(1)
N(1)—C(1)—C(2)	113(1)
N(1)—C(1)—C(6)	124(1)
N(1)—N(2)—C(10)	114(1)
N(2)—N(1)—C(1)	110(1)
N(2)—C(10)—C(9)	131(1)
N(2)—C(10)—C(11)	108(1)
average value of the C—C—C bond angles or the benzene rings 119.9(12) (max. 123.4°, min 115.1°)	

(c) Torsion angles (deg.)	
O(2)—W/O(1)—N(1)	−34
W—O(1)/N(1)—C(1)	83
W—O(1)/N(1)—N(2)	80
O(1)—N(1)/C(1)—C(2)	−23
O(1)—N(1)/C(1)—C(6)	159
O(1)—N(1)/N(2)—C(10)	2
C(1)—N(1)/N(2)—C(10)	184
N(2)—N(1)/C(1)—C(2)	155
N(2)—N(1)/C(1)—C(6)	−24
N(1)—N(2)/C(10)—C(11)	201
N(1)—N(2)/C(10)—C(9)	33

(d) Most relevant intramolecular distances between non-bonded atoms (Å)	
Cl(1) · · · N(2)	3.59
Cl(1) · · · C(9)	3.50
Cl(1) · · · C(10)	3.26
Cl(1) · · · C(11)	3.78
Cl(2) · · · C(1)	3.26
Cl(2) · · · C(2)	3.49
Cl(2) · · · C(6)	3.87
Cl(3) · · · C(2)	3.63
Cl(4) · · · C(9)	3.56
O(1) · · · C(2)	2.74
O(1) · · · C(6)	3.70
O(1) · · · C(9)	2.77
O(1) · · · C(10)	2.67
O(1) · · · C(11)	3.93
N(2) · · · C(6)	2.76
N(2) · · · C(2)	3.37
N(2) · · · C(8)	3.84
N(2) · · · C(12)	3.65
N(1) · · · C(9)	2.96
N(1) · · · C(11)	3.38

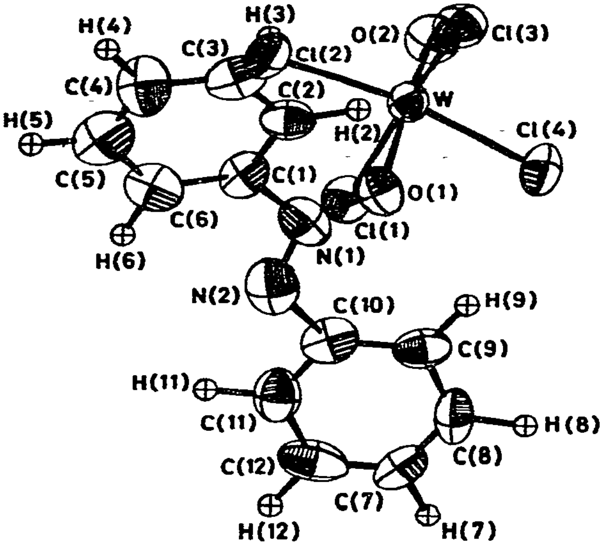


Fig. 1. View of the azoxybenzene oxotetrachlorotungsten(VI) molecule indicating the atom labelling scheme and the 30% probability thermal vibrations ellipsoids.

The azobenzene residue linked to O(1) (O(1)—N(1) bond length 1.30(3) Å) has an overall shape and conformation similar to that found in free *trans*-azobenzene [12].

The mean C—C length and C—C—C angles in the benzene rings of I, (1.38(4) Å and 119.9(12)°) are comparable with the mean values found in numerous other compounds. The N(1)—N(2) bond length of 1.20(3) Å found in I is comparable with the N=N double bond length and is intermediate between the values of 1.243(3) and 1.172(3) Å that have been found for the two different molecules present in the asymmetric unit of *trans*-azobenzene [12]. The two C—N bond lengths (1.53(3) and 1.49(4) Å) found in (I) are a little longer than the values of 1.433(3) and 1.472(3) Å found for the two molecules of free *trans*-azobenzene.

Each benzene ring of I is nearly planar; the r.m.s. distances of the carbon atoms from their least-squares planes are 0.036 Å for the C(1)—C(6) ring and 0.019 Å for the C(7)—C(12) one. The planes of the two benzene rings form a dihedral angle of 13°9′. The O(1), C(1), N(1), N(2) and C(10) atoms are roughly on a plane (r.m.s. distance 0.039 Å) and the torsion angle C(1)—N(1)/N(2)—C(10) is 184°. The corresponding torsion angles are strictly 180° in free *trans*-azobenzene [12] while result highly distorted from 180° in coordinated *trans*-azobenzene [13].

In I there is a dihedral angle of 26°8′ between the plane through C(1), N(1) and N(2) and the plane of the C(1)—C(6) ring and a dihedral angle of 26°2′ between the plane through C(10), N(2) and N(1) and the plane of the C(7)—C(12) ring. The corresponding angles for the two molecules of free *trans*-azobenzene are 17°6′ and 5°57′ [12].

In I the C(10) carbon atom is nearly eclipsed in respect with the O(1) oxygen atom (torsion angle on the N(1)=N(2) bond of 2°) and the N(1)=N(2)/C(10)—

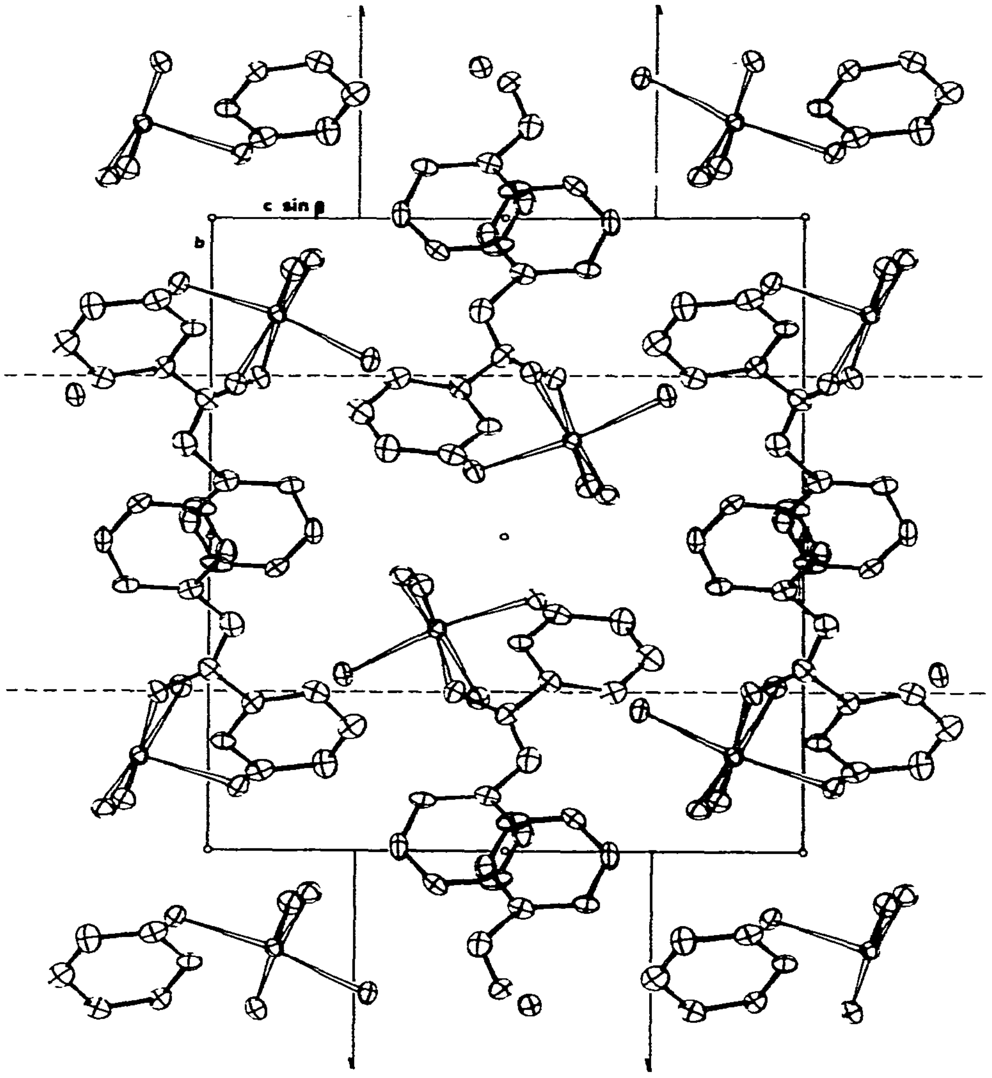


Fig. 2. Packing arrangement of the azoxybenzene oxotetrachlorotungsten(VI) molecules as viewed down the *a* axis of the unit cell.

C(9) torsion angle is 33°. As a result the O(1)···C(9) distance is 2.77 Å. This distance is rather shorter than the Van der Waals O···C distances between atoms four bonds apart found in other compounds. A C···O separation of 3.63 Å was found in 1,3,8,10-tetraoxacyclotetradecane [14] while the value found in 1,3,6,8-tetraoxacyclodecane [15] is 2.951(6) Å. A O(ether)···C(carbonyl) distance of 2.83 Å has been found in 2-oxacyclodecane-1,6-dione by Dunitz and coworkers [16]. These authors postulate that this short O···C=O distance may well correspond to a weak attraction between the intraannular lone pair of the ether-oxygen atom and the partial positive charge on the carbon atom of the carbonyl group. A donor—acceptor interaction between O(1) and C(9) eventually present also in the case of I may tentatively explain the very short distance of

2.77 Å found in this molecule. The other intramolecular Cl···C, Cl···N, O···C, N···C distances reach acceptable values. Distances lower than 3.0 Å between atoms three bonds apart are shown in Table 3 for O(1)···C(2), 2.74 Å, for O(1)···C(10), 2.67 Å and for N(2)···C(6), 2.76 Å. The corresponding N···C distances found for the two independent molecules of free *trans*-azobenzene are 2.73 and 2.75 Å [12]. The intermolecular Van der Waals interactions are also acceptable no Cl···Cl distance being < 3.58 Å while the shortest Cl···C, Cl···N, C···O, C···N and C···C intermolecular distances are 3.65, 3.59, 3.37, 3.38 and 3.47 Å, respectively.

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