

Supporting Information

Dielectric Switching, SHG Response and Pd(II) Adsorption of Multifunctional Phase-transition Complex

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EXPERIMENTAL SECTION

Synthesis of 1. The commercially available chemicals and reagents were of analytical grade, which can be used directly without any further purification. N-(2-Hydroxyethyl)thiomorpholine hydrochloric ($[(C_2H_4OH)C_4H_9NS]Cl$) was synthesized by adding Thiomorpholine (4.014 mL, 40 mmol) and 2-bromoethanol (2.834 mL, 40 mmol) respectively into anhydrous acetonitrile (50 mL) at room temperature. The mixed solution was stirred at 343 K for one day. A pink crystalline solid was gradually separated out by cooling to 273 K and the yield was 59.65%. 1H NMR (DMSO): δ 3.75-3.77 (t, 1.96H), δ 3.41 (s, 8.04H), δ 3.21-3.29 (m, 2.01H), δ 2.85-2.87 (t, 1.00H). Then, the aqueous solution of N-(2-Hydroxyethyl)thiomorpholine hydrobromide (24 mmol, 5.472 g) and Ag_2CO_3 (12 mmol, 3.309 g) were stirred for half an hour in the dark. Filtering and then adding hydrochloric acid (37%, 2.08 mL) to the filtrate. The mixed solution was stirred at room temperature for 30 minutes. The product salt N-(2-Hydroxyethyl)thiomorpholine hydrochloric was obtained as a white solid by adopting rotary evaporation under vacuum and then recrystallized from a mixed solvent (ethanol/ethyl acetate 1/10). The colorless block crystals of $[(C_2H_4OH)C_4H_9NS]CdCl_3$ were gained by slowly evaporating the aqueous solution (50 mL) containing $CdCl_2$ (4 mmol, 0.7332 g) and $[(C_2H_4OH)C_4H_9NS]Cl$ (4 mmol, 0.7340 g) at room temperature over one week.

Synthesis of 1-Pd. The colorless $[(C_2H_4OH)C_4H_9NS]CdCl_3$ (2.00 mmol, 0.734 g) was put into a saturated dichloromethane solution of $[PdCl_2(CH_3CN)_2]$ (0.5188 g, 2 mmol) for a week at room temperature. The crystals become nut-brown after adsorbing most of Pd(II) ions in the solution. Complex **1** demonstrated its adsorption properties by measuring inductively coupled plasma (ICP) and the elemental analysis shows that the molar ratio of Pd/S was 0.236. And the melting point of **1-Pd** is approximately 450 K.

Characterizations.

Phase Purity. The phase purity of $[(C_2H_4OH)C_4H_9NS]^+$ can be confirmed by the mass spectrum with liquid chromatography/time-of-flight mass spectrometry. The powder X-ray diffraction (PXRD) analysis of **1** and **1-Pd** were performed on Rigaku Ultima IV multipurpose X-ray Diffractometer at 293 K. The diffraction pattern is obtained in the range of 2θ ($5 \sim 50^\circ$) with a step size of 0.02° . Infrared (IR) spectroscopy was employed on a Shimadzu model IR-60 spectrometer.

Single-Crystal X-ray Diffraction (SCXRD). The single-crystal X-ray diffraction of **1** at 293 K and 100 K were obtained on Rigaku Saturn 924 diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were processed with the CrystalClear software package. The structures of **1** were solved by direct methods and refined with the SHELXTL software package which used full-matrix least-squares methods based on F^2 data. The anisotropic refinement of all non-H atoms was performed, and the positions of all H atoms were geometrically generated. The crystallographic data and the details of structure refinement are listed in Table S1. CCDC 2082243 (293 K, **1**) and 2082244 (100 K, **1**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis of compound **1** was performed on a Netzsch Model TG 209F1 instrument. The measurements were collected in nitrogen flow from 304 K to 1050 K, and the result shows that the sample begins to decompose at 506 K.

DSC Measurements. Differential scanning calorimetry (DSC) of **1** and **1-Pd** were measured on PerkinElmer Diamond DSC instrument that 20.4 mg (**1**) and 20.0 mg (**1-Pd**) powder samples were placed in aluminum crucibles with heating and cooling rates of 20 K/min under nitrogen atmosphere.

Dielectric Measurements. The dielectric responses of **1** and **1-Pd** were performed on Tonghui Model TH2828A impedance analyzer. The powder-pressed pellets of about 2-3 mm pasted with silver or carbon conducting glue were used in dielectric

measurements. The temperature-dependent dielectric constants were measured on a Tonghui Model TH2828A impedance analyzer at the frequencies of 1 MHz, with an applied ac voltage at 1 V. During the experiment, the heating process is completed by heating furnace, and the cooling is completed by liquid nitrogen.

Second Harmonic Generation (SHG). Second harmonic generation of complex **1** was measured by using a low divergence unexpanded laser beam with low divergence (pulsed Nd:YAG at a wavelength of 1064 nm) on an FLS 920, Edinburgh Instruments.

Elemental Analysis. For the elemental analysis, the regular elemental analysis was determined with Elementar vario EL III instrument. Inductively coupled plasma (ICP) elemental analysis was performed on Spectroblue ICP-OES. Combustion Ion Chromatography elemental analysis was performed on Thermo Scientific Nicolet IS10234

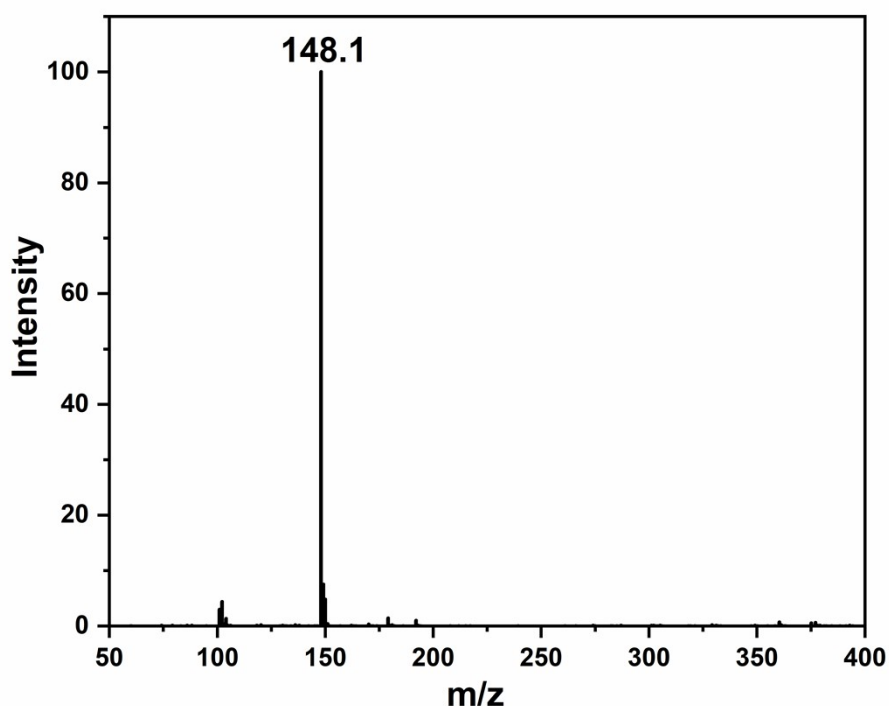


Fig. S1 The mass spectrum of $[(C_2H_4OH)C_4H_9NS]^+$

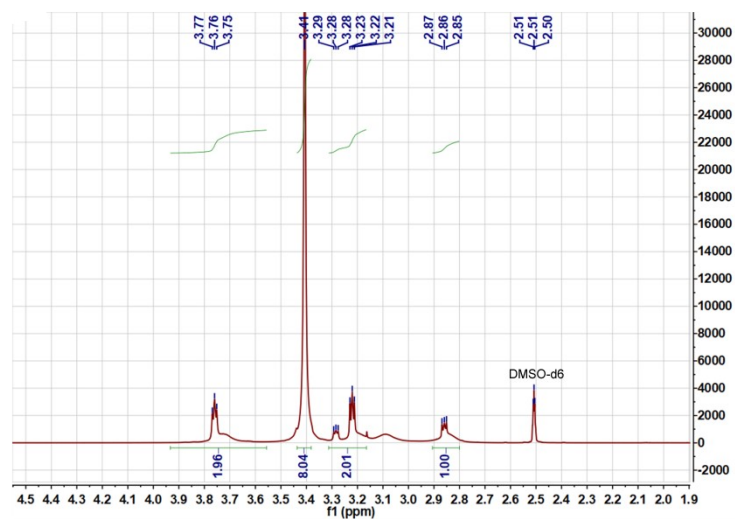


Fig. S2 The ¹H-NMR of [(C₂H₄OH)C₄H₉NS]Br.

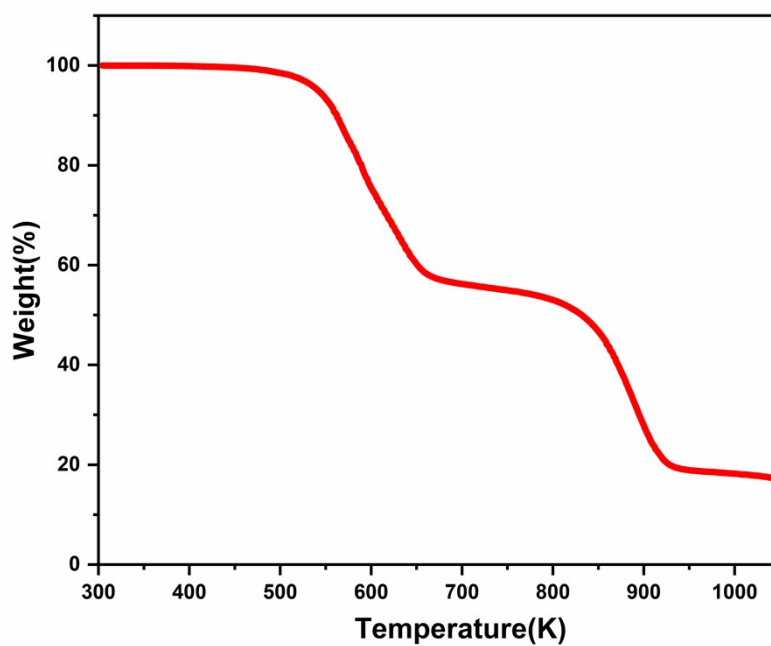


Fig. S3 Thermogravimetric analysis (TGA) curve of compound **1**, showing the stability up to 506 K.

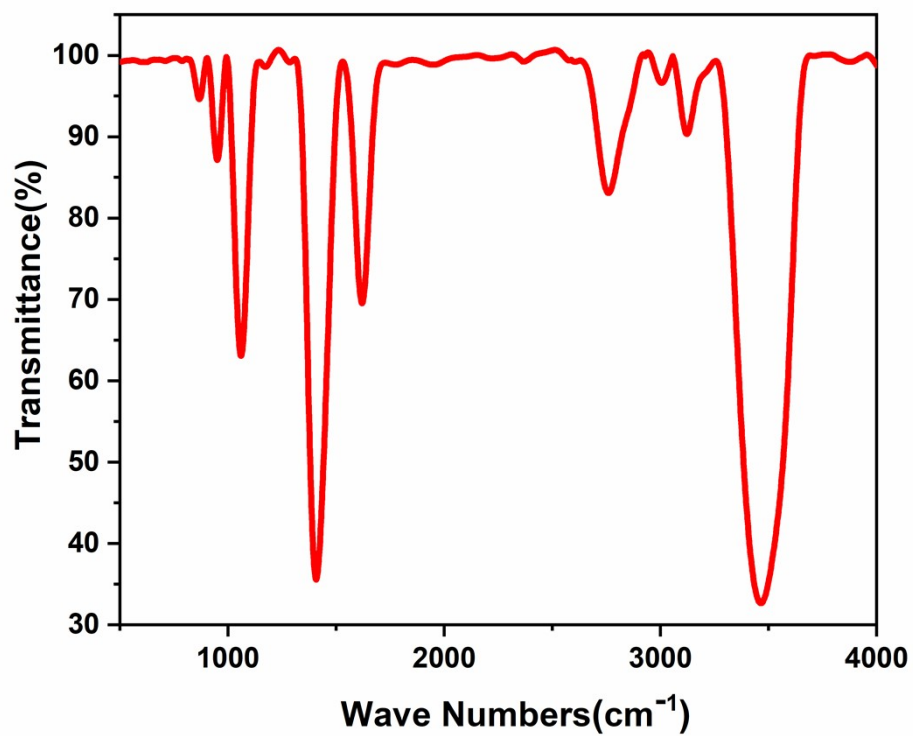


Fig. S4 IR spectrum of **1** measured on a KBr-diluted pellet at room temperature.

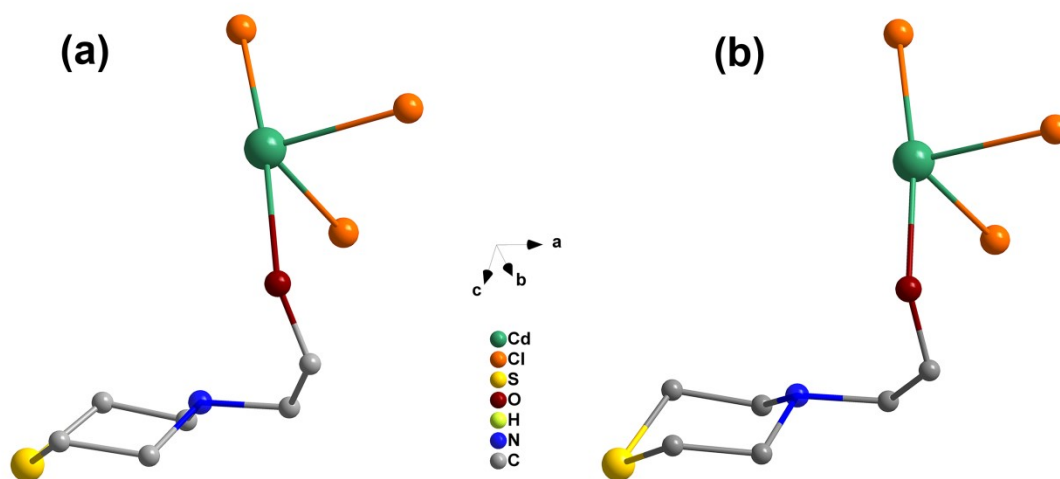


Fig. S5 The minimum asymmetric unit of **1** at RTP (a) and LTP (b).

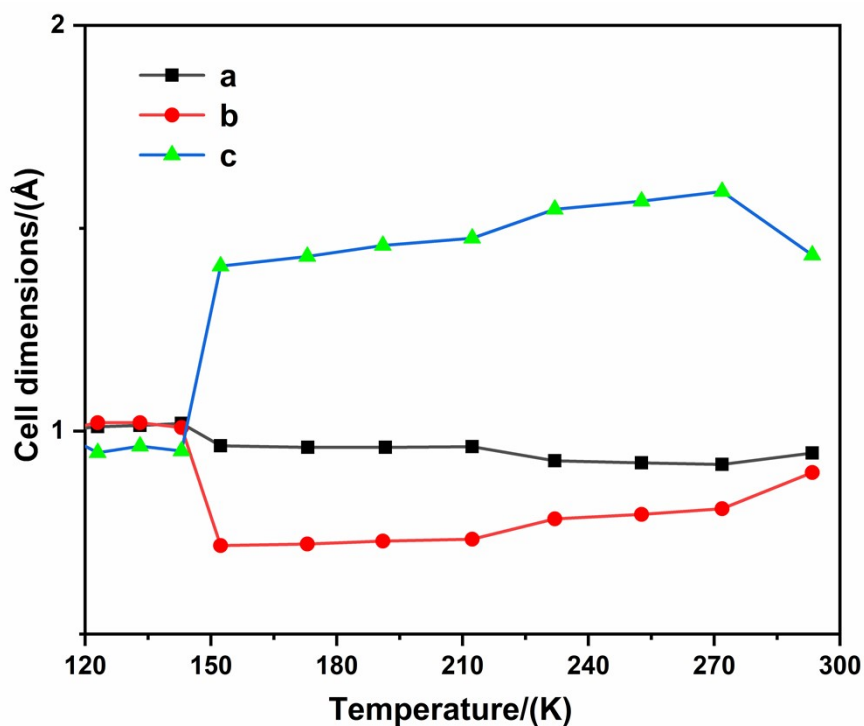


Fig. S6 Temperature-dependent traces of the cell dimensions (a, b and c axes) all under the LT cell settings, and normalized over the dimensions at the lowest temperature points.

Table S1. Crystal data and structure refinement details of complex **1**.

Chemical Formula	[(C ₂ H ₄ OH)C ₄ H ₉ NS]CdCl ₃	
<i>T</i> (K)	293 K	100 K
Formula weight	367.00	367.00
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	7.4184 (4)	7.4609 (5)
<i>b</i> /Å	12.2626 (7)	12.4577 (7)
<i>c</i> /Å	13.5510 (9)	12.9412 (7)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
<i>V</i> /Å ³	1232.72 (13)	1202.83 (12)
<i>Z</i>	4	4

$F(000)$	720.0	720.0
GOF	1.02	1.06
R_1	0.032	0.037
wR_2	0.077	0.093

Table S2. The bond lengths and angles at 293 K.

Bond lengths (Å)		Bond angles (°)	
Cd1—Cl3	2.5389 (14)	Cl3—Cd1—Cl1 ⁱ	95.17 (5)
Cd1—Cl1 ⁱ	2.5802 (13)	Cl3—Cd1—Cl2	93.25 (5)
Cd1—Cl2	2.6016 (13)	Cl1 ⁱ —Cd1—Cl2	95.36 (4)
Cd1—Cl1	2.6111 (13)	Cl3—Cd1—Cl1	99.71 (5)
Cd1—Cl2 ⁱ	2.6122 (13)	Cl1 ⁱ —Cd1—Cl1	164.89 (2)
Cd1—O1	2.641 (4)	Cl2—Cd1—Cl1	86.44 (4)
Cl1—Cd1 ⁱⁱ	2.5802 (13)	Cl3—Cd1—Cl2 ⁱ	101.07 (5)
Cl2—Cd1 ⁱⁱ	2.6121 (13)	Cl1 ⁱ —Cd1—Cl2 ⁱ	86.87 (4)
S1—C5	1.789 (8)	Cl2—Cd1—Cl2 ⁱ	165.261 (16)
S1—C4	1.825 (10)	Cl1—Cd1—Cl2 ⁱ	87.71 (4)
O1—C1	1.422 (7)	Cl3—Cd1—O1	172.29 (9)
N1—C2	1.501 (8)	Cl1 ⁱ —Cd1—O1	78.25 (9)
N1—C6	1.507 (7)	Cl2—Cd1—O1	83.47 (10)
N1—C3	1.509 (8)	Cl1—Cd1—O1	87.08 (9)
C2—C1	1.487 (9)	Cl2 ⁱ —Cd1—O1	82.72 (10)
C6—C5	1.507 (9)	Cd1 ⁱⁱ —Cl1—Cd1	93.09 (4)
C3—C4	1.469 (10)	Cd1—Cl2—Cd1 ⁱⁱ	92.57 (4)
		C5—S1—C4	97.5 (4)
		C1—O1—Cd1	142.8 (4)
		O1—C1—C2	112.0 (5)
		C2—N1—C6	112.3 (4)
		C2—N1—C3	110.7 (5)

C6—N1—C3	112.0 (5)
C3—C4—S1	112.5 (5)
C1—C2—N1	112.7 (5)
N1—C6—C5	111.2 (5)
C6—C5—S1	113.4 (6)
C4—C3—N1	112.6 (6)

Table S3. The bond lengths and angles at 100 K.

Bond lengths (Å)		Bond angles (°)	
C11—Cd1 ⁱ	2.6146 (18)	Cl2—Cd1—Cl3	94.72 (6)
C11—Cd1	2.6636 (19)	O1—Cd1—Cl2 ⁱⁱ	86.46 (13)
Cl3—Cd1	2.5776 (16)	Cl2—Cd1—Cl2 ⁱⁱ	168.93 (3)
Cd1—Cl2	2.5742 (18)	Cl3—Cd1—Cl2 ⁱⁱ	94.64 (6)
Cd1—Cl2 ⁱⁱ	2.5933 (18)	O1—Cd1—Cl1 ⁱⁱ	80.91 (13)
Cd1—Cl1 ⁱⁱ	2.6147 (18)	Cl2—Cd1—Cl1 ⁱⁱ	99.18 (6)
Cl2—Cd1 ⁱ	2.5933 (18)	Cl3—Cd1—Cl1 ⁱⁱ	90.49 (6)
O1—Cd1	2.445 (5)	Cl2 ⁱⁱ —Cd1—Cl1 ⁱⁱ	86.65 (6)
C4—C3	1.508 (11)	O1—Cd1—Cl1	89.31 (13)
C4—S1	1.816 (8)	Cl2—Cd1—Cl1	86.02 (6)
C5—C6	1.489 (10)	Cl3—Cd1—Cl1	99.41 (5)
C5—S1	1.818 (7)	Cl2 ⁱⁱ —Cd1—Cl1	86.62 (6)
C3—N1	1.513 (10)	Cl1 ⁱⁱ —Cd1—Cl1	168.44 (4)
C6—N1	1.501 (9)	Cd1—Cl2—Cd1 ⁱ	93.43 (5)
N1—C2	1.524 (10)	C3—C4—S1	111.5 (5)
C2—C1	1.515 (10)	C6—C5—S1	112.5 (5)
C1—O1	1.427 (8)	C4—S1—C5	95.9 (4)
		C4—C3—N1	111.7 (6)
		C5—C6—N1	113.5 (6)

C6—N1—C3	112.0 (6)
C6—N1—C2	112.6 (6)
C3—N1—C2	109.3 (6)
C1—C2—N1	112.6 (7)
O1—C1—C2	112.6 (6)
C1—O1—Cd1	135.5 (5)
Cd1 ⁱ —Cl1—Cd1	90.90 (5)
O1—Cd1—Cl2	85.19 (13)
O1—Cd1—Cl3	171.26 (12)

Table S4. The selected torsion angles [°] for **1** at 293 K and 100 K.

Bond angles	293 K	100 K
C6—N1—C2—C1	-73.6 (7)	-70.1 (8)
C3—N1—C2—C1	160.4 (5)	164.8 (6)
C2—N1—C6—C5	172.5 (5)	176.2 (6)
C3—N1—C6—C5	-62.3 (7)	-60.2 (8)
N1—C6—C5—S1	61.8 (7)	61.8 (7)
C4—S1—C5—C6	-53.0 (6)	-55.5 (6)
C2—N1—C3—C4	-170.3 (6)	-173.1 (6)
C6—N1—C3—C4	63.6 (7)	61.4 (8)
Cd1—O1—C1—C2	-48.7 (9)	-54.4 (10)
N1—C2—C1—O1	-49.5 (7)	-57.6 (9)
N1—C3—C4—S1	-61.9 (7)	-64.7 (7)
C5—S1—C4—C3	52.9 (6)	57.1 (6)

Table S5. Hydrogen bonds under 293 K for complex **1**.

D—H···A	D—H	H···A	D···A	<DHA
O1—H1A···Cl3 ⁱ	0.93	2.34	3.118 (5)	142
N1—H1···Cl1 ⁱ	0.98	2.36	3.295 (5)	160

C2—H2B···Cl2	0.97	2.78	3.563 (7)	138
C2—H2A···Cl2 ^v	0.97	2.93	3.798 (7)	150
C4—H4B···Cl1 ⁱ	0.97	2.66	3.499 (8)	145
C4—H4A···S1 ⁱⁱⁱ	0.97	2.83	3.619 (9)	139
C4—H4A···Cl3 ^{iv}	0.97	2.86	3.500 (7)	125

Table S6. Hydrogen bonds under 100 K for complex 1.

D—H···A	D—H	H···A	D···A	<DHA
O1—H1E···Cl1 ⁱⁱ	0.96	2.76	3.285 (5)	115
O1—H1E···Cl3 ⁱⁱ	0.96	2.29	3.081 (6)	139
N1—H1···Cl1 ⁱⁱ	0.98	2.34	3.179 (6)	143
C4—H4B···Cl1 ⁱⁱ	0.97	2.86	3.565 (8)	131
C5—H5A···Cl3 ⁱⁱ	0.97	2.88	3.525 (7)	125
C5—H5A···Cl2 ⁱⁱⁱ	0.97	2.98	3.872 (8)	153
C5—H5B···Cl1 ^{iv}	0.97	2.75	3.715 (8)	176
C6—H6A···Cl3 ^v	0.97	2.77	3.692 (8)	159
C6—H6A···Cl2 ^v	0.97	2.80	3.310 (7)	113
C6—H6B···Cl3 ⁱⁱ	0.97	2.85	3.431 (8)	119