Electronic Supplementary Material (ESI) for CrystEngComm.


**Supplementary Information**

# Halogen bonding in chloroiodates(III)

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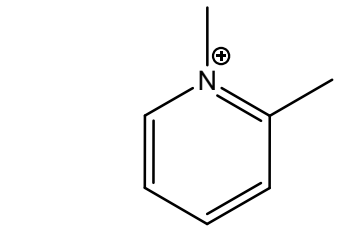
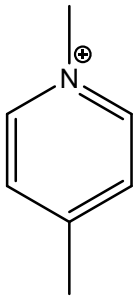
$$CatI(s) + 2Cl_2(g) \xrightarrow{HCl} CatICl_4(s)\ (\mathbf{1\text{-}5}, \mathbf{8}, \mathbf{9})$$

$$CatI_2(s) + 4Cl_2(g) \xrightarrow{HCl} Cat[ICl_4]_2(s)\ (\mathbf{6})$$

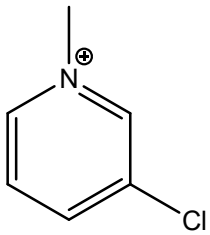
$$Cat(s) + I_2(s) + 4Cl_2(g) \xrightarrow{HCl/CH_3CN} Cat[ICl_4]_2(s)\ (\mathbf{7})$$



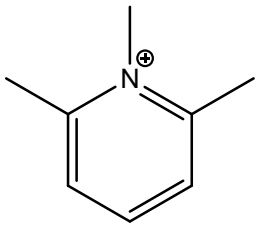
1,2-diMePy$^+$
(1,2-dimethylpyridinium (**1**))



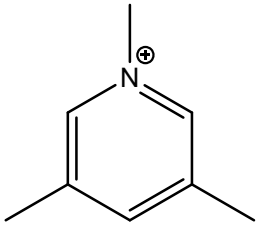
1,4-diMePy$^+$
(1,4-dimethylpyridinium (**2**))



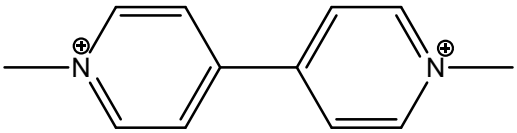
3-Cl-1-MePy$^+$
(3-chloro-1-methylpyridinium (**3**))



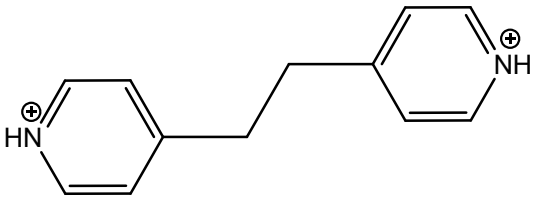
1,2,6-triMePy$^+$
(1,2,6-trimethylpyridinium (**4**))



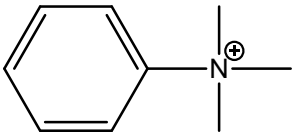
1,3,5-triMePy$^+$
(1,3,5-trimethylpyridinium (**5**))



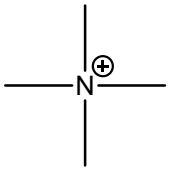
[1,1'-dimethyl-4,4'-dipyridil]$^{2+}$(**6**)



[1,2-bis(4-pyridil)-ethane]$^{2+}$(**7**)



Trimethylphenylammonium (**8**)



Tetramethylammonium (**9**)

**Scheme S1.** Reaction schematics and cations utilized in this work.

**Synthesis of 1–5**

0.20 mmol of corresponding pyridine iodide (47 mg in **1** and **2**, 51 mg in **3**, 50 mg in **4** and **5**) were dissolved in 7 mL of concentrated hydrochloric acid with heating to 60 °C. Then gaseous chlorine was bubbled through the solutions until all reactants were dissolved. Resulting mixtures were slowly cooled to room temperature. Within 24 hours, yellow crystalline precipitates formed in all experiments.

**Synthesis of 6**

44 mg (0.10 mmol) of 1,1'–dimethyl–4,4'–bipyridine diiodide were dissolved in 6 mL of concentrated hydrochloric acid with to 60 °C. Then gaseous chlorine was bubbled through the solution until all reactants were dissolved. Resulting mixture was slowly cooled to room temperature. Within 24 hours, yellow crystals formed.

**Synthesis of 7**

37 mg (0.20 mmol) of 1,2-bis(4–pyridil)ethane were dissolved in 5 mL of concentrated hydrochloric acid upon heating up to 60 °C. Then 51 mg (0.20 mmol) of $I_2$ were added into solution followed by addition of 2 mL of $CH_3CN$. Gaseous chlorine was bubbled through the mixture until all iodine was oxidized. Resulting solution was cooled to room temperature. Upon slow evaporation of solvents ($CH_3CN$ at most) within 24 hours yellow crystals formed.

**Synthesis of 8**

53 mg (0.20 mmol) of trimethylethylammonium iodide were dissolved in 6 mL of concentrated hydrochloric acid upon heating to 60 °C. Then gaseous chlorine was bubbled through the solution until all reactants were dissolved. Mixture was slowly cooled to room temperature. After 6 hours, yellow crystals formed.

**Synthesis of 9**

44 mg (0.22 mmol) of tetramethylammonium iodide were dissolved in 5 mL of concentrated hydrochloric acid upon heating to 60 °C. Then gaseous chlorine was bubbled through the solution until all reactants were dissolved. Mixture was slowly cooled to room temperature. After 6 hours, yellow crystals formed.

**Table S1.** Elemental analysis data and yields for **1**–**9**.

| Compound | C, H, N, calculated/found, % | Yield, % |
|---|---|---|
| **1** | 22.4, 2.7, 3.7/22.1, 2.6, 3.6 | 86 |
| **2** | 22.4, 2.7, 3.7/22.4, 2.5, 3.7 | 82 |
| **3** | 18.2, 1.8, 3.5/18.0, 1.7, 3.5 | - |
| **4** | – | – |
| **5** | – | – |
| **6** | 20.0, 2.0, 3.9/20.1, 2.0, 3.8 | 78 |

| | | |
|---|---|---|
| **7** | – | – |
| **8** | 26.8, 3.5, 3.5/26.9, 3.6, 3.5 | 80 |
| **9** | – | – |

The single crystal X-ray diffraction data for **2**–**7** were collected with a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector and IμS 3.0 source (Mo Kα radiation, λ = 0.71073 Å, ϕ- and ω-scans). Data reduction was performed routinely via Apex3 suite (*Apex3, SADABS 2016/2*; Publisher: Bruker AXS Inc., Madison, WI, USA, 2017.). The data for **1** and **8**–**9** were collected with an Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scans). Data reduction was performed routinely via the CrysAlisPro program package. The crystal structures were solved by SHELXT and refined by the full-matrix least squares technique (SHELXL 2017/1) with Olex2 GUI (2009). Atomic displacements for non-hydrogen atoms were refined in harmonic anisotropic approximation. Hydrogen atoms were were refined in the geometrically calculated positions. The structures of **1**–**9** were deposited to the Cambridge Crystallographic Data Centre (CCDC), No. 2257393-2257401. Details are given in Tables S2-S3.

**Table S2.** Crystal data and structure refinement for compounds **1**-**5**.

| Identification code | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| CCDC number | 2257393 | 2257394 | 2257395 | 2257396 | 2257397 |
| Empirical formula | $C_7H_{10}ICl_4N$ | $C_7H_{10}ICl_4N$ | $C_6H_7ICl_4N$ | $C_8H_{12}ICl_4N$ | $C_8H_{12}ICl_4N$ |
| Formula weight | 376.86 | 376.86 | 397.28 | 390.89 | 390.89 |
| Temperature/K | 140 | 150 | 150 | 150 | 150 |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1$ | C2/c | $P2_1/c$ |
| a/Å | 8.3175(7) | 4.3707(3) | 8.2044(2) | 17.4476(6) | 11.3598(15) |
| b/Å | 9.8500(5) | 11.8303(9) | 9.6553(3) | 9.9715(4) | 8.5116(11) |
| c/Å | 7.6668(5) | 11.8442(10) | 8.2874(2) | 7.8504(3) | 15.140(2) |
| α/° | 90 | 90 | 90 | 90 | 90 |
| β/° | 101.728(7) | 92.985(3) | 105.887(1) | 102.600(1) | 110.486(4) |
| γ/° | 90 | 90 | 90 | 90 | 90 |
| Volume/Å$^3$ | 615.01(8) | 611.59(8) | 631.42 (3) | 1332.91(9) | 1371.3(3) |
| Z | 2 | 2 | 2 | 4 | 4 |
| $D_{calc}$g/cm$^3$ | 2.035 | 2.046 | 2.090 | 1.948 | 1.893 |
| μ/mm$^{-1}$ | 3.43 | 3.45 | 3.55 | 3.17 | 3.08 |
| F(000) | 360 | 360 | 376 | 752 | 752 |
| Tmin, Tmax | 0.726, 1.000 | 0.628, 0.746 | 0.683, 0.746 | 0.679, 0.747 | 0.574, 0.745 |
| 2Θ range for data collection/° | 5.002 to 58.054 | 4.870 to 59.160 | 5.110 to 61.042 | 4.734 to 67.744 | 3.828 to 52.822 |
| Index ranges | -8 ≤ h ≤ 11, -9 ≤ k ≤ 13, -9 ≤ l ≤ 9 | -6 ≤ h ≤ 5, -16 ≤ k ≤ 12, -15 ≤ l ≤ 16 | -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -11 ≤ l ≤ 11 | -26 ≤ h ≤ 26, -15 ≤ k ≤ 15, -11 ≤ l ≤ 10 | -14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -18 ≤ l ≤ 18 |
| $R_{int}$ | 0.049 | 0.0317 | 0.0316 | 0.0305 | 0.0590 |
| No. of measured, independent and observed [I > 2σ(I)] | 2679/1360/1043 | 6479/1712/1479 | 28732/3847/3782 | 13777/2315/2021 | 13909/2811/2334 |

| | | | | | |
|---|---|---|---|---|---|
| reflections | | | | | |
| Data/restraints/parameters | 1360/18/99 | 1712/0/62 | 3847/1/120 | 2315/0/77 | 2811/0/131 |
| Goodness-of-fit on $F^2$ | 1.045 | 1.040 | 1.052 | 1.058 | 1.031 |
| Final R indices [I>=2σ (I)] | $R_1$ = 0.0392, $wR_2$ = 0.0905 | $R_1$ = 0.0191, $wR_2$ = 0.0415 | $R_1$ = 0.0145, $wR_2$ = 0.0336 | $R_1$ = 0.0166, $wR_2$ =0.0351 | $R_1$ = 0.0406, $wR_2$ = 0.0966 |
| R indices [all data] | 0.0557 | 0.0242 | 0.0150 | 0.0220 | 0.0517 |
| $(\sin \theta/\lambda)_{max}$ ($Å^{-1}$) | 0.683 | 0.695 | 0.715 | 0.774 | 0.626 |
| Largest diff. peak/hole/*e*/$Å^3$ | 1.25/−1.40 | 0.35/−0.48 | 0.38/ −0.37 | 0.42/−0.32 | 1.39/−1.21 |

**Table S3.** Crystal data and structure refinement for compounds **6**-**9**.

| Identification code | **6** | **7** | **8** | **9** |
|---|---|---|---|---|
| CCDC number | 2257398 | 2257399 | 2257400 | 2257401 |
| Empirical formula | $C_{12}H_{14}I_2Cl_8N_2$ | $C_{12}H_{14}ICl_5N_2$ | $C_9H_{14}ICl_4N$ | $C_4H_{12}ICl_4N$ |
| Formula weight | 723.65 | 490.40 | 404.91 | 342.85 |
| Temperature/K | 150 | 150 | 140 | 140 |
| Space group | *$P4_2bc$* | *P-1* | *$P2_1/n$* | *$P3_2$* |
| a/Å | 11.5876(8) | 7.4887(5) | 8.4156(4) | 16.4343(5) |
| b/Å | 11.5876(8) | 7.6756(5) | 16.0769(6) | 16.4343(5) |
| c/Å | 16.4371(15) | 8.0494(5) | 10.9381(4) | 11.4451(4) |
| α/° | 90 | 93.199(2) | 90 | 90 |
| β/° | 90 | 110.363(2) | 103.705(4) | 90 |
| γ/° | 90 | 95.058(3) | 90 | 120 |
| Volume/$Å^3$ | 2207.0(4) | 430.22(5) | 1437.75(10) | 2677.02(19) |
| Z | 4 | 1 | 4 | 9 |
| $D_{calc}$g/$cm^3$ | 2.178 | 1.893 | 1.871 | 1.914 |
| μ/$mm^{-1}$ | 3.82 | 2.63 | 2.94 | 3.54 |
| F(000) | 1368 | 238 | 784 | 1476 |
| Tmin, Tmax | 0.616, 0.746 | 0.643, 0.746 | 0.984, 1.000 | 0.966, 1.000 |
| 2Θ range for data collection/° | 4.956 to 63.086 | 5.352 to 59.158 | 4.594 to 57.568 | 3.558 to 57.802 |
| Index ranges | -17 ≤ h ≤ 10, -17 ≤ k ≤ 15, -23 ≤ l ≤ 24 | -9 ≤ h ≤ 10, -10 ≤ k ≤ 10, -11 ≤ l ≤ 10 | -10 ≤ h ≤ 9, -21 ≤ k ≤ 14, -14 ≤ l ≤ 11 | -20 ≤ h ≤ 20, -21 ≤ k ≤ 13, -14 ≤ l ≤ 13 |
| $R_{int}$ | 0.0608 | 0.0258 | 0.0259 | 0.0244 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 23479/3676/3154 | 5544/2276/2207 | 6822/3177/2744 | 8457/6215/5776 |
| Data/restraints/parameters | 3676/1/110 | 2276/0/94 | 3177/0/140 | 6215/5/268 |
| Goodness-of-fit on $F^2$ | 1.027 | 1.079 | 1.042 | 1.017 |
| Final R indices [I>=2σ (I)] | $R_1$ = 0.0300, $wR_2$ = 0.0525 | $R_1$ = 0.0282, $wR_2$ = 0.0619 | $R_1$ = 0.0281, $wR_2$ = 0.0430 | $R_1$ = 0.0351, $wR_2$ = 0.0606 |
| R indices [all data] | 0.0398 | 0.0293 | 0.0366 | 0.0396 |
| $(\sin \theta/\lambda)_{max}$ ($Å^{-1}$) | 0.736 | 0.695 | 0.677 | 0.680 |
| Largest diff. peak/hole/*e*/$Å^3$ | 0.39/−0.53 | 1.40/−0.44 | 0.58/−0.64 | 0.77/−0.60 |

**Powder X-ray diffraction (PXRD)** data for polycrystalline samples of **1**–**9** were collected with Shimadzu XRD-7000 diffractometer in the Bragg—Brentano geometry (Cu$K_\alpha$ radiation, Ni – filter) and Bruker Advance powder diffractometer with an energy discriminating Eyger XE T detector (Cu$K_\alpha$ radiation). The samples were slightly ground with hexane in an agate mortar, and the resulting suspensions were deposited on the polished side of a standard sample holder, and a smooth thin layer being formed after drying. The diffraction patterns of **1**–**2**, **6**, **8** agree well with those simulated from the single crystal XRD data.

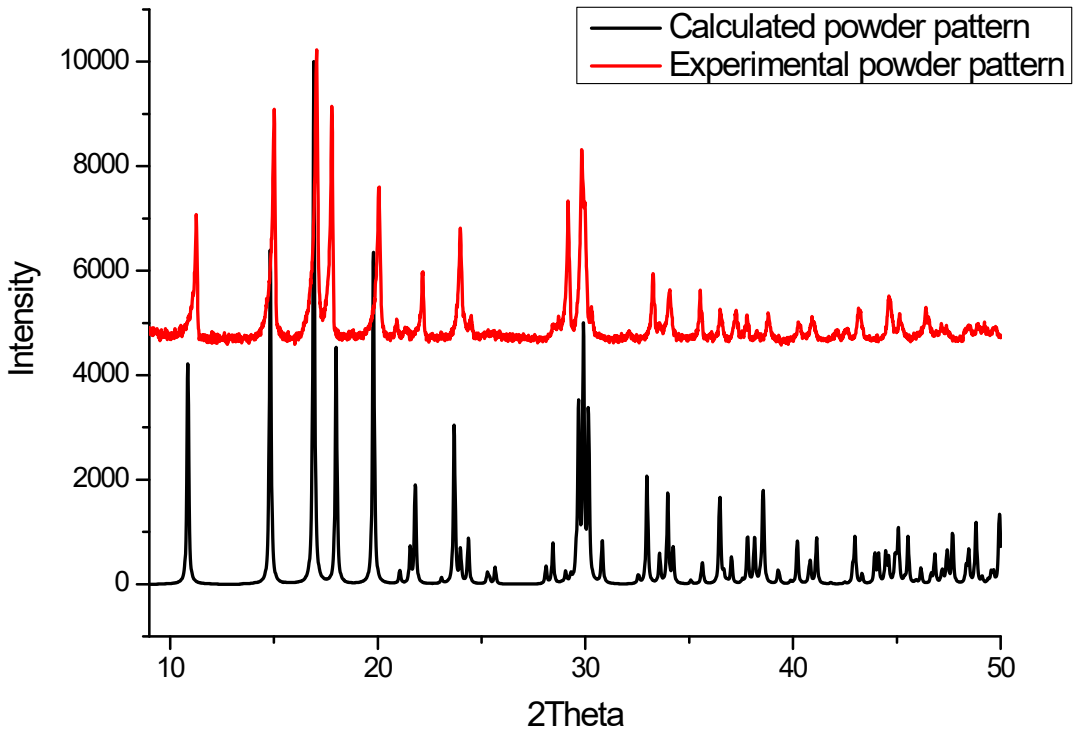



**Figure S1**. Calculated (black) and experimental (red) PXRD patterns of **1.**

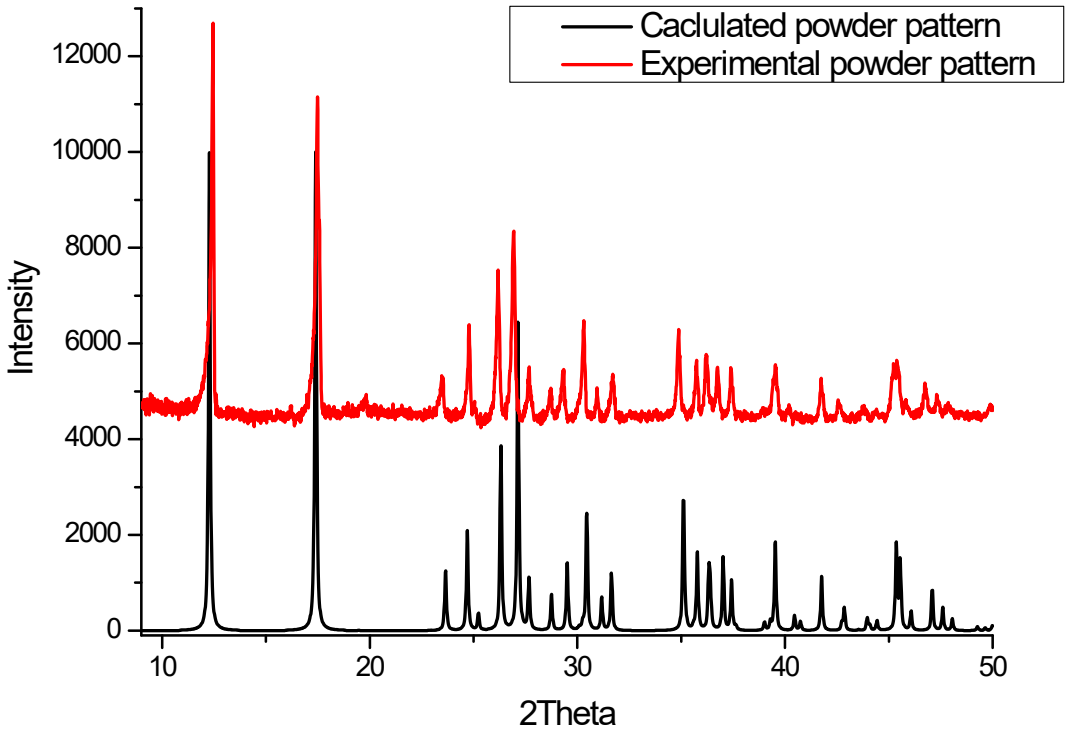



**Figure S2**. Calculated (black) and experimental (red) PXRD patterns of **2.**

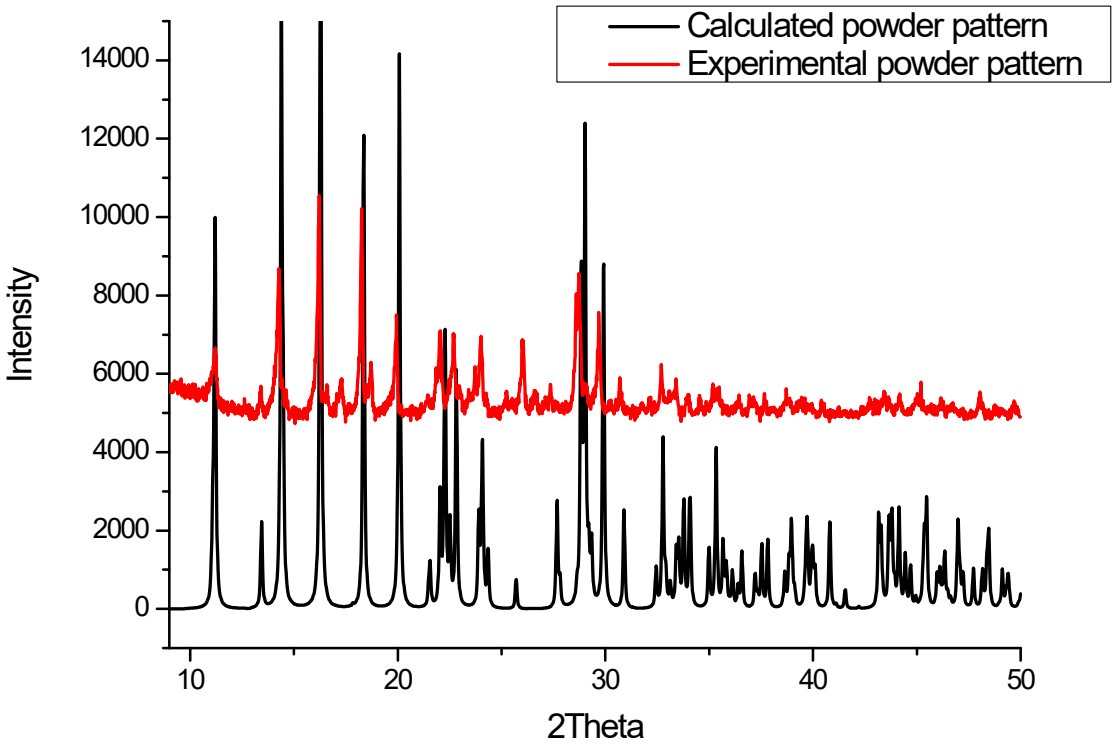


**Figure S3**. Calculated (black) and experimental (red) PXRD patterns of **3.**

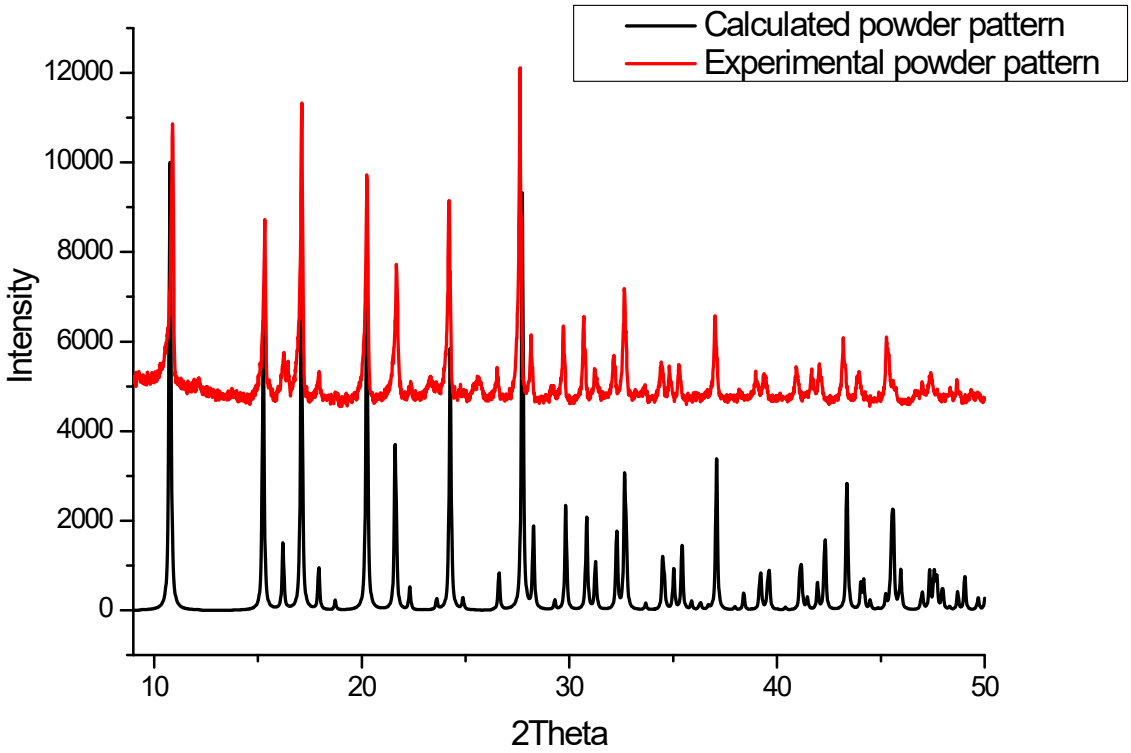



**Figure S4**. Calculated (black) and experimental (red) PXRD patterns of **6.**

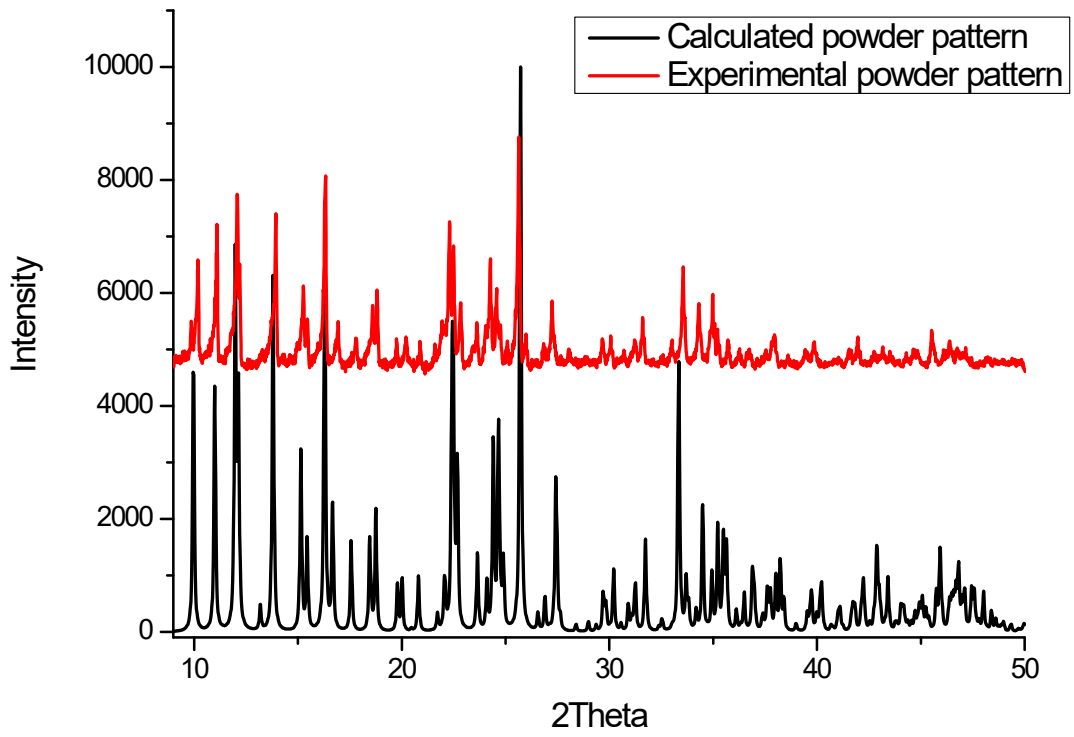



**Figure S5**. Calculated (black) and experimental (red) PXRD patterns of **8.**

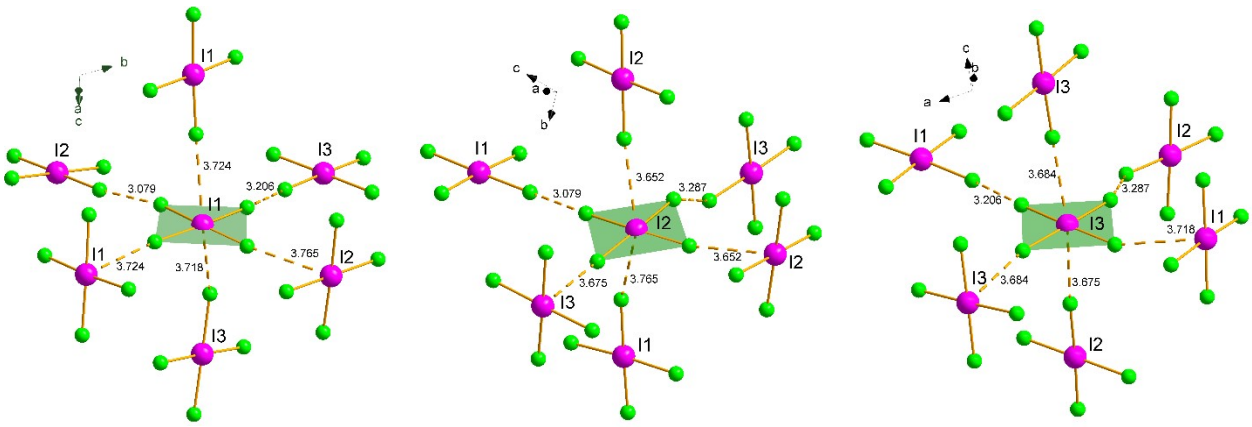



**Figure S6**. Halogen bonding between each of three crystallographically independent $ICl_4^-$ anions in compound **9**.

**Table S4**. Halogen bond angles (deg.) between the anions in compound **9**

| | $I(1)Cl_4$ | $I(2)Cl_4$ | $I(3)Cl_4$ |
|---|---|---|---|
| I–Cl···I | 174.9; 161.2 | 167.2; 177.1 | 169.0; 150.8 |
| I–Cl···Cl | 168.8; 161.5 | 170.9; 146.6 | 169.2; 146.0 |
| I···Cl–I | 174.9; 150.8 | 167.2; 161.2 | 177.1; 169.0 |

**Table S5**. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate $\lambda_2$ eigenvalues, energy density – $H_b$, electron localization function – ELF, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to intermolecular interactions Cl···Cl and Cl···I in the X-ray structures **1**–**9**, and estimated strength for these interactions $E_{int}$ (kcal/mol).

| Model structure* | $\rho(\mathbf{r})$ | $\nabla^2\rho(\mathbf{r})$ | $\lambda_2$ | $H_b$ | ELF | $V(\mathbf{r})$ | $G(\mathbf{r})$ | $E_{int}$** |
|---|---|---|---|---|---|---|---|---|
| **1** | | | | | | | | |
| Cl···Cl 3.563 Å | 0.006 | 0.020 | -0.006 | 0.001 | 0.020 | -0.003 | 0.004 | 0.9 |
| Cl···I 3.755 Å | 0.007 | 0.024 | -0.007 | 0.001 | 0.018 | -0.004 | 0.005 | 1.2 |
| **2** | | | | | | | | |
| Cl···Cl 3.998 Å | 0.003 | 0.008 | -0.003 | 0.001 | 0.009 | -0.001 | 0.002 | 0.3 |
| Cl···Cl 3.973 Å | 0.004 | 0.011 | -0.004 | 0.000 | 0.013 | -0.002 | 0.002 | 0.6 |
| Cl···I 4.119 Å | 0.004 | 0.014 | -0.004 | 0.001 | 0.008 | -0.002 | 0.003 | 0.6 |
| **3** | | | | | | | | |
| Cl···Cl 3.292 Å | 0.010 | 0.035 | -0.010 | 0.002 | 0.031 | -0.005 | 0.007 | 1.5 |
| Cl···Cl 3.652 Å | 0.006 | 0.017 | -0.006 | 0.001 | 0.020 | -0.003 | 0.004 | 0.9 |
| Cl···I 3.679 Å | 0.008 | 0.029 | -0.008 | 0.001 | 0.022 | -0.005 | 0.006 | 1.5 |
| **4** | | | | | | | | |
| Cl···Cl 4.074 Å | 0.003 | 0.009 | -0.003 | 0.001 | 0.008 | -0.001 | 0.002 | 0.3 |
| Cl···I 3.861 Å | 0.005 | 0.020 | -0.005 | 0.001 | 0.014 | -0.003 | 0.004 | 0.9 |
| **5** | | | | | | | | |
| Cl···Cl 3.887 Å | 0.004 | 0.013 | -0.004 | 0.001 | 0.015 | -0.002 | 0.003 | 0.6 |
| Cl···I 3.943 Å | 0.005 | 0.019 | -0.005 | 0.001 | 0.013 | -0.003 | 0.004 | 0.9 |
| Cl···I 4.084 Å | 0.004 | 0.015 | -0.004 | 0.001 | 0.008 | -0.002 | 0.003 | 0.6 |
| **6** | | | | | | | | |
| Cl···Cl 3.330 Å | 0.009 | 0.030 | -0.009 | 0.001 | 0.027 | -0.005 | 0.006 | 1.5 |
| **7** | | | | | | | | |
| Cl···Cl 3.579 Å | 0.006 | 0.020 | -0.006 | 0.001 | 0.021 | -0.003 | 0.004 | 0.9 |
| Cl···I 3.838 Å | 0.007 | 0.024 | -0.007 | 0.001 | 0.023 | -0.004 | 0.005 | 1.2 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **8** | | | | | | | | |
| Cl···Cl 3.491 Å | 0.006 | 0.022 | -0.006 | 0.001 | 0.021 | -0.003 | 0.004 | 0.9 |
| Cl···I 3.963 Å | 0.005 | 0.019 | -0.005 | 0.001 | 0.014 | -0.003 | 0.004 | 0.9 |
| **9** | | | | | | | | |
| Cl12···Cl24 3.802 Å | 0.005 | 0.014 | -0.005 | 0.001 | 0.015 | -0.002 | 0.003 | 0.6 |
| Cl12···I21 3.718 Å | 0.008 | 0.027 | -0.008 | 0.002 | 0.022 | -0.004 | 0.006 | 1.2 |
| Cl15···I16 3.684 Å | 0.008 | 0.028 | -0.008 | 0.002 | 0.022 | -0.004 | 0.006 | 1.2 |
| Cl14···Cl4 3.206 Å | 0.011 | 0.040 | -0.011 | 0.001 | 0.035 | -0.007 | 0.008 | 2.2 |
| Cl18···Cl9 3.287 Å | 0.010 | 0.036 | -0.010 | 0.001 | 0.034 | -0.006 | 0.007 | 1.8 |
| Cl8···Cl3 3.079 Å | 0.014 | 0.050 | -0.014 | 0.002 | 0.042 | -0.009 | 0.011 | 2.8 |
| Cl2···I26 3.766 Å | 0.007 | 0.025 | -0.007 | 0.001 | 0.020 | -0.004 | 0.005 | 1.2 |
| Cl2···Cl28 3.810 Å | 0.005 | 0.014 | -0.005 | 0.001 | 0.015 | -0.002 | 0.003 | 0.6 |
| Cl7···I41 3.652 Å | 0.009 | 0.030 | -0.009 | 0.001 | 0.026 | -0.005 | 0.006 | 1.5 |
| Cl5···I31 3.724 Å | 0.007 | 0.027 | -0.007 | 0.001 | 0.021 | -0.004 | 0.005 | 1.2 |
| Cl10···I36 3.675 Å | 0.008 | 0.029 | -0.008 | 0.001 | 0.024 | -0.005 | 0.006 | 1.5 |

[*] The Bondi's (shortest) van der Waals radii for chlorine and iodine atoms are 1.75 and 1.98 Å, respectively [J. Phys. Chem. 1966, 70, 3006.].

[**] $E_{int} \approx 0.49(-V(\mathbf{r}))$ (this empirical correlation between the interaction energy and the potential energy density of electrons at the bond critical points (3, –1) was specifically developed for noncovalent interactions involving chlorine atoms) [Russ. Chem. Rev. 2014, 83, 1181.].

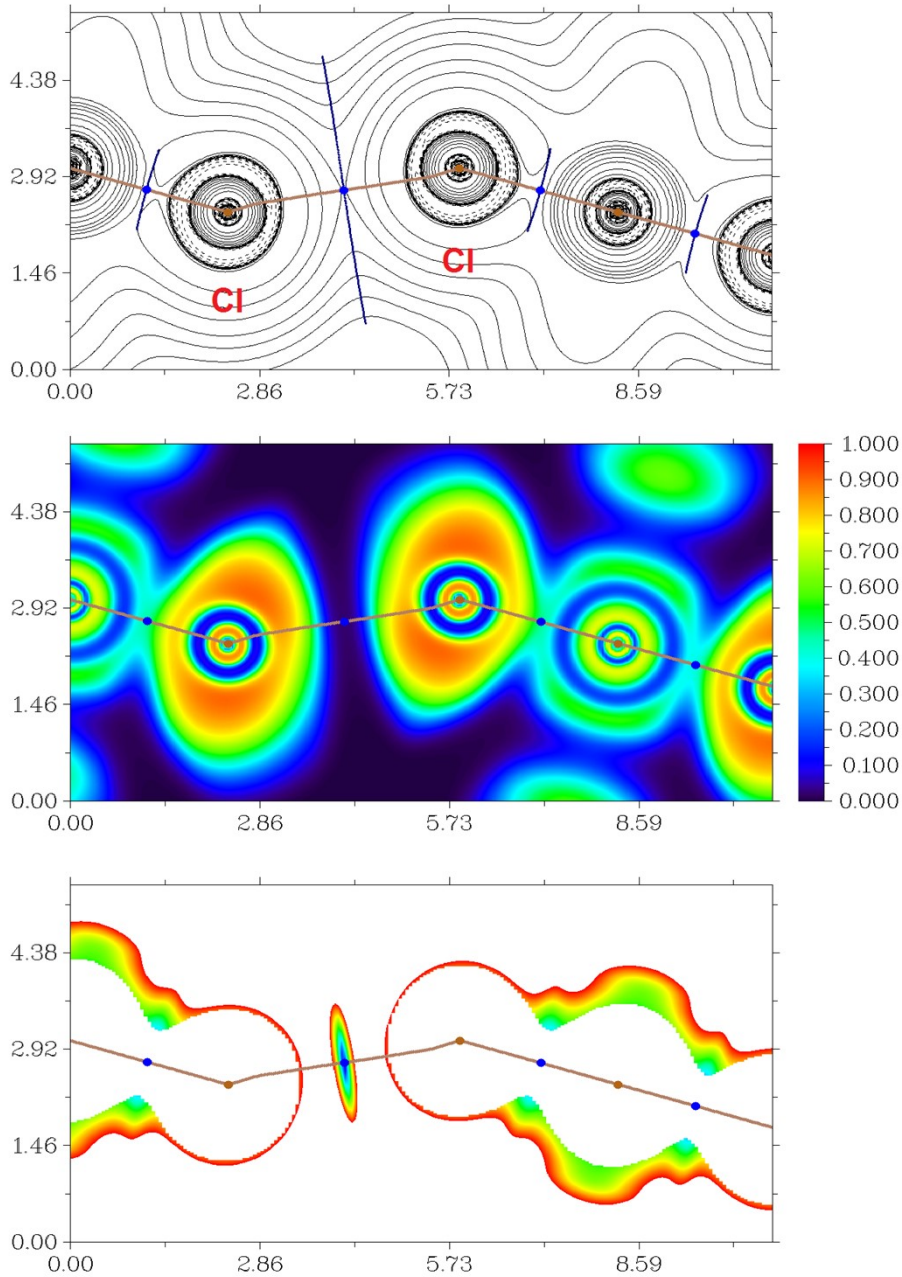



**Figure S7**. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top), visualization of electron localization function (ELF, center) and reduced density gradient (RDG, bottom) analyses for intermolecular interactions Cl···Cl in **1**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

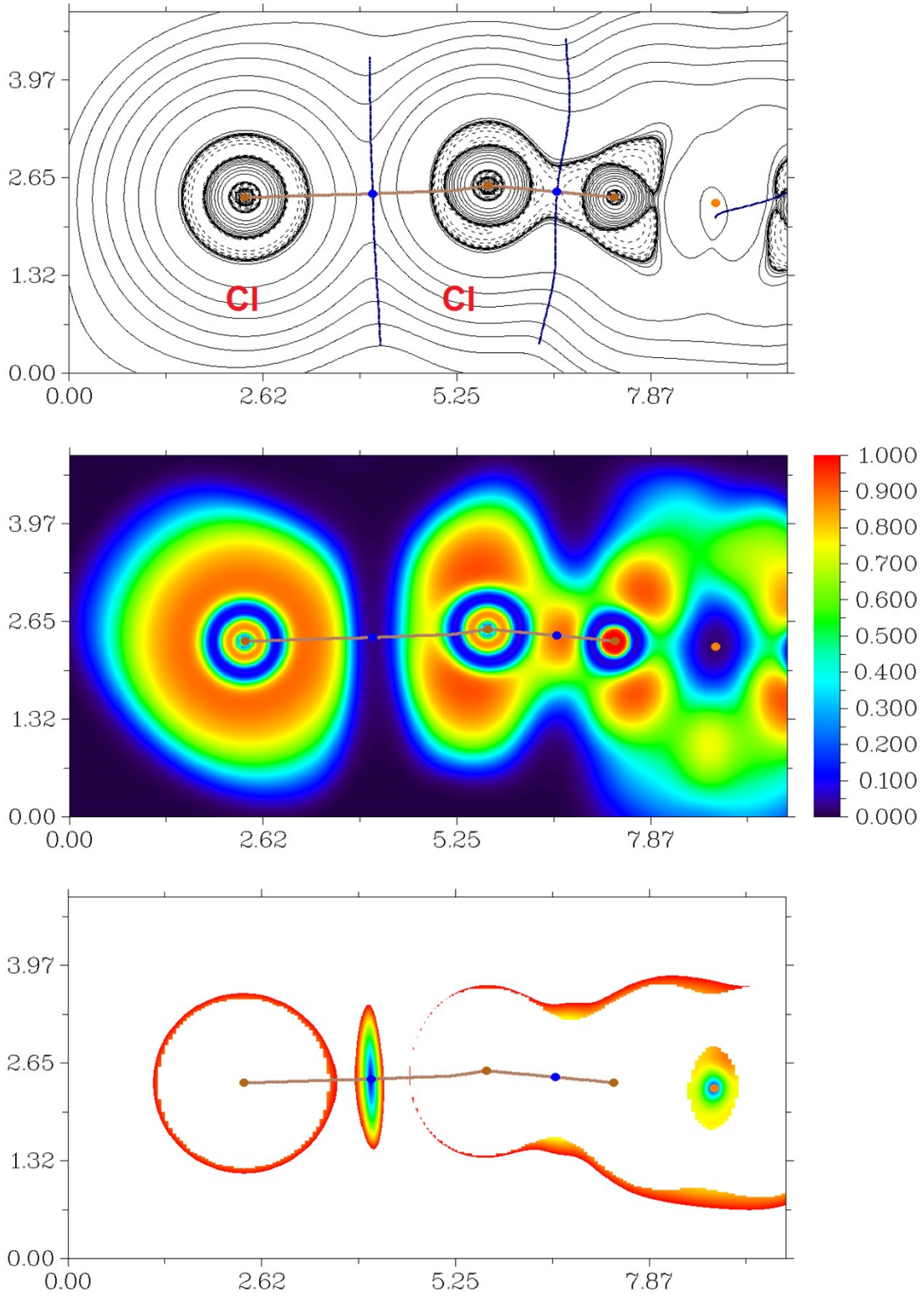



**Figure S8**. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top), visualization of electron localization function (ELF, center) and reduced density gradient (RDG, bottom) analyses for intermolecular interactions Cl···Cl (3.292 Å) in **3**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

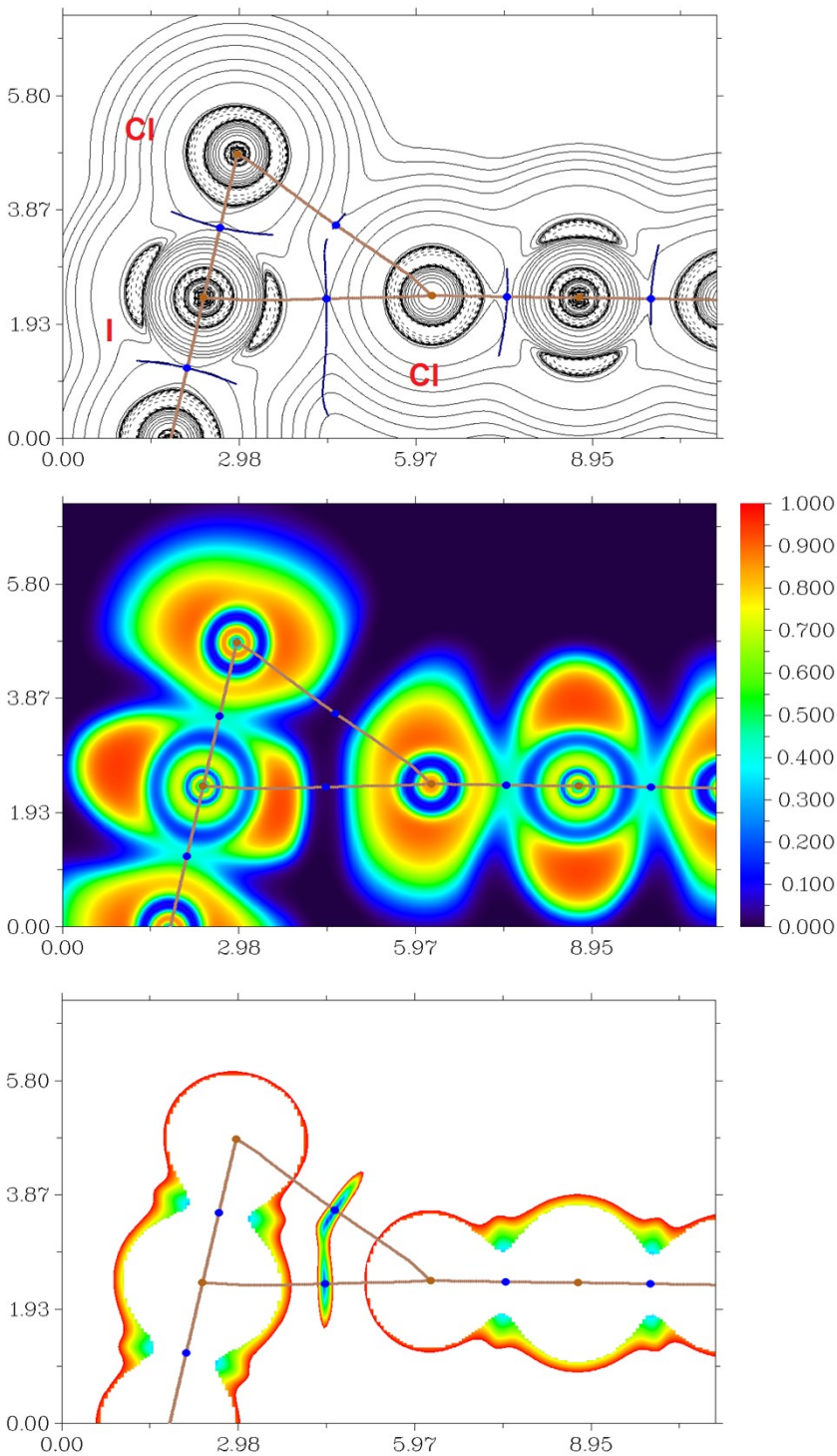



**Figure S9**. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (top), visualization of electron localization function (ELF, center) and reduced density gradient (RDG, bottom) analyses for intermolecular interactions Cl···Cl and Cl···I in **4**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

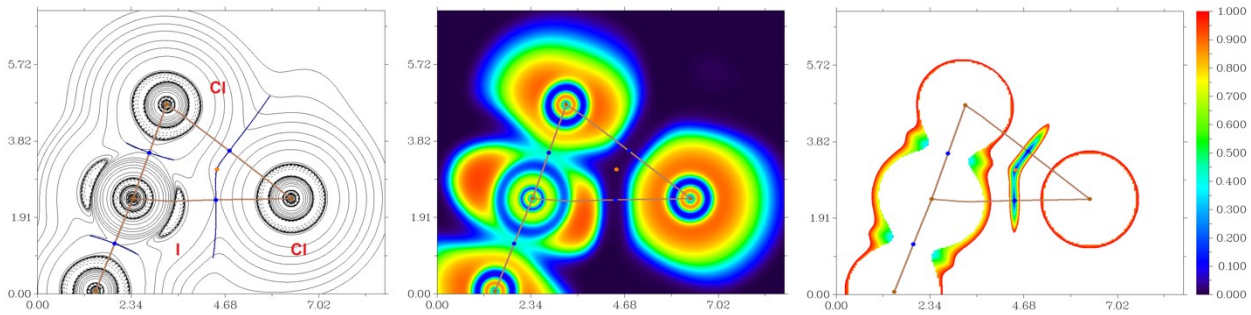



**Figure S10**. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (left), visualization of electron localization function (ELF, center) and reduced density gradient (RDG, right) analyses for intermolecular interactions Cl···Cl and Cl···I (3.887 and 3.943 Å, respectively) in **5**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, ring critical points (3, +1) – in orange, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

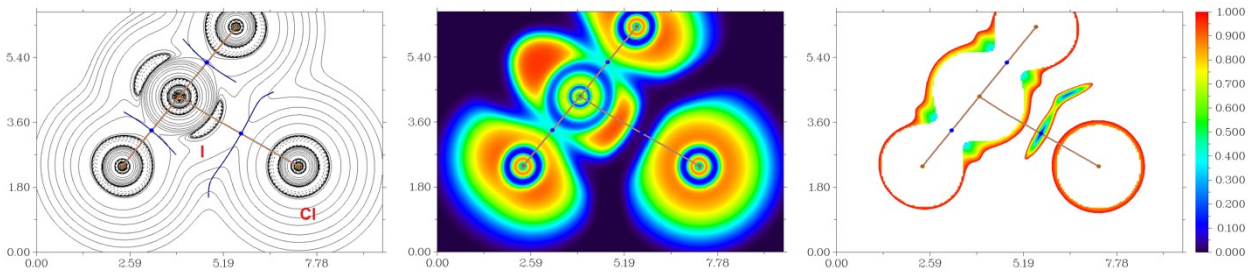



**Figure S11**. Contour line diagram of the Laplacian of electron density distribution $\nabla^2\rho(\mathbf{r})$, bond paths, and selected zero-flux surfaces (left), visualization of electron localization function (ELF, center) and reduced density gradient (RDG, right) analyses for intermolecular interactions Cl···I in **7**. Bond critical points (3, –1) are shown in blue, nuclear critical points (3, –3) – in pale brown, bond paths are shown as pale brown lines, length units – Å, and the color scale for the ELF and RDG maps is presented in a.u.

The balance between the Lagrangian kinetic energy G(**r**) and potential energy density V(**r**) at the bond critical points (3, –1) reveals the nature of these interactions, if the ratio –G(**r**)/V(**r**) > 1 is satisfied, than the nature of appropriate interaction is purely non-covalent, in case the –G(**r**)/V(**r**) < 1 some covalent component takes place [J. Chem. Phys. 2002, 117, 5529.]; based on this criterion one can state that a covalent contribution in intermolecular interactions Cl···Cl and Cl···I in the X-ray structures **1**–**9** is absent (**Table S4**). The Laplacian of electron density is typically decomposed into the sum of contributions along the three principal axes of maximal variation, giving the three eigenvalues of the Hessian matrix ($\lambda_1$, $\lambda_2$ and $\lambda_3$), and the sign of $\lambda_2$ can be utilized to distinguish bonding (attractive, $\lambda_2 < 0$) weak interactions from non-bonding ones (repulsive, $\lambda_2 > 0$).[J. Am. Chem. Soc. 2010, 132, 6498. || J. Chem. Theory Comput. 2011, 7, 625.] Thus, all discussed intermolecular interactions Cl···Cl and Cl···I in the X-ray structures **1**–**9** are attractive.

**Computational details**

The DFT calculations based on the experimental X-ray geometries of **1**–**9** have been carried out using the dispersion-corrected hybrid functional ωB97XD [Phys. Chem. Chem. Phys. 2008, 10, 6615.] with the help of Gaussian-09 [M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. A.;, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, C. J.;, D. J. Fox, in Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010.] program package. The Douglas–Kroll–Hess 2$^{nd}$ order scalar relativistic calculations requested relativistic core Hamiltonian were carried out using the DZP-DKH basis sets [Mol. Phys. 2010, 108, 1965. || J. Chem. Phys. 2009, 130, 064108. || Chem. Phys. Lett. 2013, 582, 158. || J. Mol. Struct. - Theochem 2010, 961, 107.] for all atoms. The topological analysis of the electron density distribution in model supramolecular associates **1**–**9** and calculation of molecular surface electrostatic potential distribution on the optimized equilibrium model structure $[ICl_4]^-$ have been performed by using the Multiwfn program (version 3.7) [J. Comput. Chem. 2012, 33, 580.]. The Chemcraft program [http://www.chemcraftprog.com/] was used for the visualization. The Cartesian atomic coordinates for model supramolecular associates **1**–**9** and optimized equilibrium model structure $[ICl_4]^-$ presented in **Table S5.**

**Table S6**. Cartesian atomic coordinates for model structures.

| Atom | X | Y | Z |
|---|---|---|---|
| | | **1** | |
| I | 6.759102 | 4.925000 | 7.506745 |
| Cl | 4.317899 | 4.787002 | 7.054088 |
| Cl | 7.127966 | 2.969578 | 6.014404 |
| Cl | 9.200304 | 5.062999 | 7.959401 |
| Cl | 6.390238 | 6.880422 | 8.999086 |
| I | -1.558398 | 4.925000 | 7.506745 |
| Cl | -3.999601 | 4.787002 | 7.054088 |
| Cl | -1.189534 | 2.969578 | 6.014404 |
| Cl | 0.882804 | 5.062999 | 7.959401 |
| Cl | -1.927262 | 6.880422 | 8.999086 |
| I | 7.538301 | 9.850000 | 3.753372 |
| Cl | 9.979503 | 9.712001 | 4.206029 |
| Cl | 7.169437 | 7.894578 | 5.245713 |
| Cl | 5.097098 | 9.987998 | 3.300716 |
| Cl | 7.907165 | 11.805422 | 2.261032 |
| | | **2** | |
| I | 1.568569 | 5.915150 | 11.828130 |

| | | | |
|---|---|---|---|
| Cl | 2.419195 | 5.034148 | 9.653055 |
| Cl | 0.605015 | 7.907964 | 10.649457 |
| Cl | 0.717943 | 6.796152 | 14.003205 |
| Cl | 2.532123 | 3.922336 | 13.006803 |
| I | -2.802131 | 5.915150 | 11.828130 |
| Cl | -1.951505 | 5.034148 | 9.653055 |
| Cl | -3.765685 | 7.907964 | 10.649457 |
| Cl | -3.652757 | 6.796152 | 14.003205 |
| Cl | -1.838577 | 3.922336 | 13.006803 |
| I | 1.876960 | 0.000000 | 5.914065 |
| Cl | 1.026334 | -0.881002 | 8.089140 |
| Cl | 2.840514 | 1.992814 | 7.092738 |
| Cl | 2.727585 | 0.881002 | 3.738990 |
| Cl | 0.913405 | -1.992814 | 4.735392 |
| **3** | | | |
| I | 3.060964 | 7.272082 | 2.122558 |
| Cl | 5.437833 | 7.517423 | 2.719654 |
| Cl | 0.629423 | 6.958864 | 1.498759 |
| Cl | 2.780748 | 5.601426 | 3.960954 |
| Cl | 3.359066 | 9.004436 | 0.347290 |
| Cl | 5.434770 | 3.870230 | 3.069415 |
| N | 8.836492 | 2.546103 | 1.633227 |
| C | 7.864518 | 3.369700 | 2.067638 |
| H | 7.998567 | 4.310425 | 2.089901 |
| C | 6.669173 | 2.817417 | 2.479731 |
| C | 6.463466 | 1.471468 | 2.441471 |
| H | 5.633170 | 1.102288 | 2.718881 |
| C | 7.484875 | 0.650767 | 1.991915 |
| H | 7.364383 | -0.291107 | 1.954620 |
| C | 8.677009 | 1.215602 | 1.599750 |
| H | 9.389494 | 0.661446 | 1.303361 |
| C | 10.157376 | 3.139904 | 1.160556 |
| H | 10.849279 | 2.976719 | 1.835671 |
| H | 10.052523 | 4.105240 | 1.027785 |
| H | 10.420575 | 2.720332 | 0.315295 |
| I | 2.874835 | 2.444432 | 5.848292 |
| Cl | 0.497966 | 2.689773 | 5.251196 |
| Cl | 5.306376 | 2.131214 | 6.472091 |
| Cl | 3.155051 | 0.773776 | 4.009895 |
| Cl | 2.576733 | 4.176786 | 7.623560 |
| I | 11.265364 | 7.272082 | 2.122558 |
| Cl | 13.642233 | 7.517423 | 2.719654 |
| Cl | 8.833823 | 6.958864 | 1.498759 |
| Cl | 10.985148 | 5.601426 | 3.960954 |
| Cl | 11.563466 | 9.004436 | 0.347290 |
| **4** | | | |
| Cl | 5.937412 | 7.892343 | 4.243155 |
| I | 3.505644 | 7.478625 | 3.830668 |
| Cl | 2.955179 | 9.425860 | 5.299653 |
| Cl | 1.073876 | 7.064907 | 3.418182 |
| Cl | 4.056109 | 5.531390 | 2.361684 |
| Cl | 1.930132 | 2.906593 | -0.412486 |

| | | | |
|---|---|---|---|
| I | 4.361900 | 2.492875 | 0.000000 |
| Cl | 4.912365 | 4.440110 | -1.468985 |
| Cl | 6.793668 | 2.079157 | 0.412486 |
| Cl | 3.811435 | 0.545640 | 1.468985 |
| **5** | | | |
| Cl | 4.345836 | 11.145515 | 9.465550 |
| Cl | 2.011164 | 8.484193 | 9.433640 |
| I | 4.360513 | 8.782269 | 8.671897 |
| Cl | 4.385629 | 6.397233 | 7.974968 |
| Cl | 6.721591 | 9.067237 | 7.896397 |
| Cl | 1.715289 | 5.877685 | 4.716962 |
| Cl | 4.049961 | 8.539007 | 4.748872 |
| I | 1.700612 | 8.240931 | 5.510615 |
| Cl | 1.675497 | 10.625967 | 6.207544 |
| Cl | -0.660465 | 7.955963 | 6.286115 |
| **6** | | | |
| I | 4.179416 | 10.434518 | 6.822547 |
| Cl | 4.048244 | 10.693037 | 9.305700 |
| Cl | 4.379302 | 10.138339 | 4.363228 |
| Cl | 6.130652 | 8.888037 | 7.168219 |
| Cl | 2.271981 | 12.010432 | 6.457643 |
| I | 4.640718 | 9.973216 | -1.396003 |
| Cl | 4.899237 | 9.842044 | 1.087150 |
| Cl | 4.344539 | 10.173102 | -3.855322 |
| Cl | 3.094237 | 11.924452 | -1.050331 |
| Cl | 6.216632 | 8.065781 | -1.760907 |
| I | 7.408184 | 12.740682 | 6.822547 |
| Cl | 7.539356 | 12.482163 | 9.305700 |
| Cl | 7.208298 | 13.036861 | 4.363228 |
| Cl | 5.456948 | 14.287163 | 7.168219 |
| Cl | 9.315619 | 11.164768 | 6.457643 |
| **7** | | | |
| I | 0.943427 | -0.698852 | 7.513939 |
| Cl | 2.940825 | -0.912247 | 8.996965 |
| Cl | 2.393191 | -0.239379 | 5.542206 |
| Cl | -1.053971 | -0.485456 | 6.030913 |
| Cl | -0.506337 | -1.158324 | 9.485671 |
| Cl | 0.605070 | 3.124004 | 7.513939 |
| I | -1.857496 | -1.397703 | 15.027878 |
| Cl | 0.139902 | -1.611099 | 16.510904 |
| Cl | -0.407733 | -0.938231 | 13.056145 |
| Cl | -3.854894 | -1.184308 | 13.544851 |
| Cl | -3.307260 | -1.857176 | 16.999610 |
| **8** | | | |
| I | -0.333477 | 7.234444 | 7.169818 |
| Cl | 0.606038 | 9.517686 | 7.447280 |
| Cl | 0.866367 | 6.940237 | 4.981467 |
| Cl | -1.273681 | 4.910207 | 7.035284 |
| Cl | -1.541963 | 7.542638 | 9.323207 |
| I | -2.258010 | 8.842456 | 3.456857 |
| Cl | -3.197525 | 6.559214 | 3.179395 |
| Cl | -3.457853 | 9.136663 | 5.645209 |

| | | | |
|---|---|---|---|
| Cl | -1.317806 | 11.166693 | 3.591391 |
| Cl | -1.049524 | 8.534262 | 1.303468 |
| I | -4.849496 | 8.842456 | 14.083533 |
| Cl | -5.789012 | 6.559214 | 13.806070 |
| Cl | -6.049340 | 9.136663 | 16.271884 |
| Cl | -3.909293 | 11.166693 | 14.218067 |
| Cl | -3.641011 | 8.534262 | 11.930143 |
| **9** | | | |
| I | 2.242214 | 11.221631 | 10.557647 |
| Cl | 1.292558 | 12.964404 | 12.090604 |
| Cl | 3.203045 | 9.581333 | 9.015305 |
| Cl | 3.115943 | 12.960134 | 9.026750 |
| Cl | 1.421567 | 9.347920 | 11.993320 |
| I | 5.558409 | 5.530188 | 6.124731 |
| Cl | 6.715055 | 3.851320 | 4.646711 |
| Cl | 4.493138 | 7.187423 | 7.570934 |
| Cl | 6.740528 | 7.371023 | 4.967173 |
| Cl | 4.298391 | 3.733190 | 7.332876 |
| I | 6.063681 | 15.989526 | 5.270354 |
| Cl | 7.185898 | 17.561508 | 3.705923 |
| Cl | 5.249937 | 17.894549 | 6.612979 |
| Cl | 4.946724 | 14.471628 | 6.872783 |
| Cl | 6.831739 | 14.021880 | 3.960005 |
| I | 7.772273 | 11.489060 | 1.455321 |
| Cl | 5.849789 | 11.674937 | -0.109110 |
| Cl | 6.529347 | 9.831826 | 2.797945 |
| Cl | 9.645291 | 11.280696 | 3.057749 |
| Cl | 9.092276 | 13.138040 | 0.144971 |
| I | 8.597111 | 20.912413 | 2.927580 |
| Cl | 10.581224 | 20.863453 | 4.460537 |
| Cl | 6.696156 | 20.900458 | 1.385239 |
| Cl | 9.665834 | 19.286490 | 1.396684 |
| Cl | 7.384753 | 22.559970 | 4.363254 |
| I | 0.648662 | 16.281150 | 13.754797 |
| Cl | 1.524281 | 18.122269 | 12.276777 |
| Cl | -0.253910 | 14.529981 | 15.201000 |
| Cl | -1.536607 | 16.384479 | 12.597240 |
| Cl | 2.834917 | 16.088442 | 14.962942 |
| I | 0.379961 | 6.679892 | 14.372680 |
| Cl | 2.364074 | 6.630932 | 15.905637 |
| Cl | -1.520994 | 6.667936 | 12.830339 |
| Cl | 1.448684 | 5.053968 | 12.841784 |
| Cl | -0.832397 | 8.327448 | 15.808354 |
| I | 2.598345 | 0.986456 | 9.085387 |
| Cl | 3.398613 | -0.771403 | 7.520957 |
| Cl | 4.655015 | 0.738668 | 10.428012 |
| Cl | 1.842285 | 2.712719 | 10.687816 |
| Cl | 0.510285 | 1.305122 | 7.775038 |
| I | 8.865812 | 2.048629 | 2.309697 |
| Cl | 9.741431 | 3.889748 | 0.831677 |
| Cl | 7.963240 | 0.297460 | 3.755900 |
| Cl | 6.680543 | 2.151957 | 1.152140 |

| | | | |
|---|---|---|---|
| Cl | 11.052067 | 1.855921 | 3.517842 |
| $[ICl_4]^-$ | | | |
| I | 1.568569 | 5.915150 | 11.828130 |
| Cl | 2.444626 | 5.010503 | 9.578165 |
| Cl | 0.579753 | 7.962589 | 10.609849 |
| Cl | 0.692513 | 6.819797 | 14.078096 |
| Cl | 2.557385 | 3.867711 | 13.046411 |

The Hirshfeld surfaces analysis was performed in CrystalExplorer program (version 17.5) [M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, P. R. Spackman, D. Jayatilaka and M. A. Spackman, CrystalExplorer17 (2017). University of Western Australia. http://hirshfeldsurface.net || CrystEngComm 2009, 11, 19.]. The normalized contact distances ($d_{norm}$ [Chem. Commun. 2007, 3814.]) based on Bondi's van der Waals radii [J. Phys. Chem. 1966, 70, 3006.] were mapped into the Hirshfeld surfaces.

**Table S7**. Partial contributions of different interatomic contacts to the Hirshfeld surfaces of the $\{ICl_4\}$ moieties in the X-ray structures **1**–**9**.

| X-ray structure | Contributions of different interatomic contacts to the Hirshfeld surfaces |
|---|---|
| **1** | Cl–H 81.3%, I–Cl 5.8%, I–H 4.7%, Cl–C 4.7%, Cl–Cl 2.1%, Cl–N 1.3% |
| **2** | Cl–H 79.4%, I–Cl 7.0%, Cl–Cl 5.8%, I–H 3.2%, Cl–C 3.1%, I–I 1.1%, Cl–N 0.4% |
| **3** | Cl–H 61.7%, Cl–Cl 15.2%, Cl–C 10.5%, I–Cl 7.2%, I–H 3.1%, Cl–N 2.1%, I–C 0.2% |
| **4** | Cl–H 80.6%, I–Cl 5.9%, I–H 4.7%, Cl–C 4.3%, Cl–Cl 2.6%, Cl–N 2.0% |
| **5** | Cl–H 83.0%, I–Cl 4.7%, I–C 3.3%, Cl–Cl 3.2%, Cl–C 2.5%, I–H 1.3%, Cl–N 1.0%, I–I .7%, I–N 0.2% |
| **6** | Cl–H 67.1%, Cl–Cl 14.0%, Cl–C 6.7%, I–Cl 4.8%, I–H 3.2%, I–I 2.2%, Cl–N 2.1% |
| **7** | Cl–H 87.5%, I–H 4.8%, I–Cl 3.4%, Cl–Cl 2.5%, Cl–C 1.8% |
| **8** | Cl–H 82.3%, I–Cl 4.8%, Cl–Cl 3.9%, Cl–C 3.8%, I–C 3.8%, I–H 0.8%, I–I 0.5% |
| **9** | Cl–H 81.2%, Cl–Cl 8.0%, I–Cl 7.0%, I–H 3.8% |