# Impact of halogen···halogen interaction on mechanical motion of a 3D Pb(II) coordination polymer of elusive topology

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## Electronic Supplementary Information

## Experimental Procedures

### Materials and general method

All chemicals purchased were reagent grade and were used without further purification. Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin–Elmer 240C elemental analyzer. Photo irradiation was carried out using Luzchem photoreactor (8 W UVA lamps) at ~350 nm at room temperature.

### Syntheses of compounds

**Synthesis of 1:** A solution of $H_2$DCTP (0.047 g, 0.2 mmol) neutralized with $Et_3N$ (0.021 g, 0.2 mmol) in 2 mL EtOH was slowly and carefully layered onto a solution of $Pb(NO)_3$ (0.066 g, 0.2 mmol), in $H_2O$ (2 mL) using a 2 mL 1 : 1 ( = v/v) buffer solution of MeOH and $H_2O$.The reaction mixture was kept in the dark. The colourless needle shaped crystals of $[Pb(DCTP)]_n$ (**1**), were obtained after six days (0.60 g, yield 67%). Elemental analysis (%) calculated for $C_8H_{3.5}Cl_2O_{4.75}Pb$: C, 21.18; H, 0.78; found: C, 21.3; H, 0.9.

**Synthesis of 2:** The compound **2** was synthesized by UV Irradiation of **1:** colourless needle single crystals of **1** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centred at ~350 nm wavelength for 2 h to obtain photo-irradiated product in almost quantitative yield.

**Synthesis of 3:** The compound **3** was synthesized by UV Irradiation of **1:** colourless needle single crystals of **1** were irradiated using a UV-lamp (LZC-UVA; Luzchem) centred at ~350 nm wavelength for 5 h to obtain photo- irradiated product in almost quantitative yield.

### X-ray crystallography

Single crystals of the all compounds having suitable dimension were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å). The crystal structure was solved using the SHELXT 2018/6 structure solution program.[1] The collected data ($I > 2\sigma(I)$) was integrated by using SAINT[2] program, and the absorption

correction was done by SADABS.[3] Non-hydrogen atoms were refined by the help of anisotropic displacement parameters. All the hydrogen atoms were placed in their geometrically perfect positions and constrained to ride on their parent atoms. Crystallographic data for all compounds are summarized in Table S1, ESI† and selected bond lengths and bond angles are given in Table S2–S3, ESI†.

**Computational methods**

The calculations reported herein were performed using the Turbomole 7.2 program.[4] The crystallographic coordinates were used for the calculations of the supramolecular assemblies. We used the crystallographic coordinates for the assemblies because we are interested in evaluating the interactions as they stand in the solid state. The level of theory used for the calculations was PBE0-D3/def2-TZVP.[5-8] The MEP surface plots were generated using the wavefunction obtained at the same level of theory and the 0.01 a.u. isosurface to simulate the van der Waals envelope. The topological analysis of the electron density was carried out according to the quantum theory of atoms in molecules (QTAIM) and noncovalent interaction plot index (NCIplot) methods proposed by Bader[9] and W. Yang et al.[10], respectively. Both were represented using the VMD program[11] and using the following settings for the NCIplot index representation: s = 0.5 a.u.; cut-off ρ = 0.04 a.u., and color scale $-0.03 \leq \text{sign}(\lambda_2)\rho \leq 0.03$a.u. The electron localization function (ELF)[12] analysis was performed using the MultiWFNprogram[13]at the PBE0-D3/def2-TZVP level of theory. The natural bond orbital (NBO) analysis[14] was used to study charge transfer effects by means of the NBO7 program.[15]

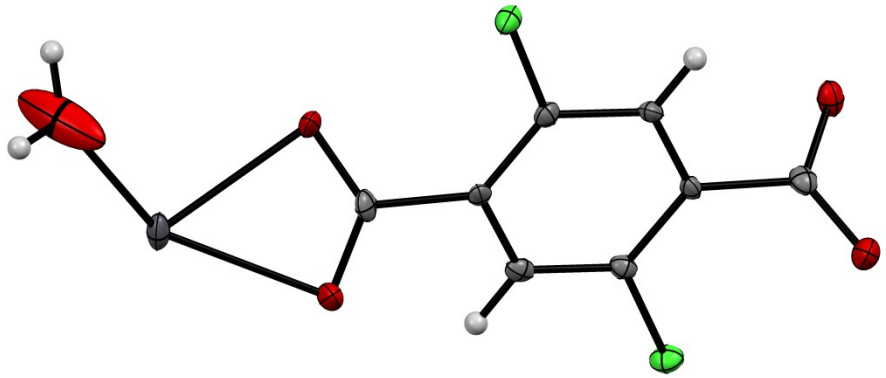

**Fig. S1** Asymmetric unit of **1**with 50% thermal ellipsoid plot.

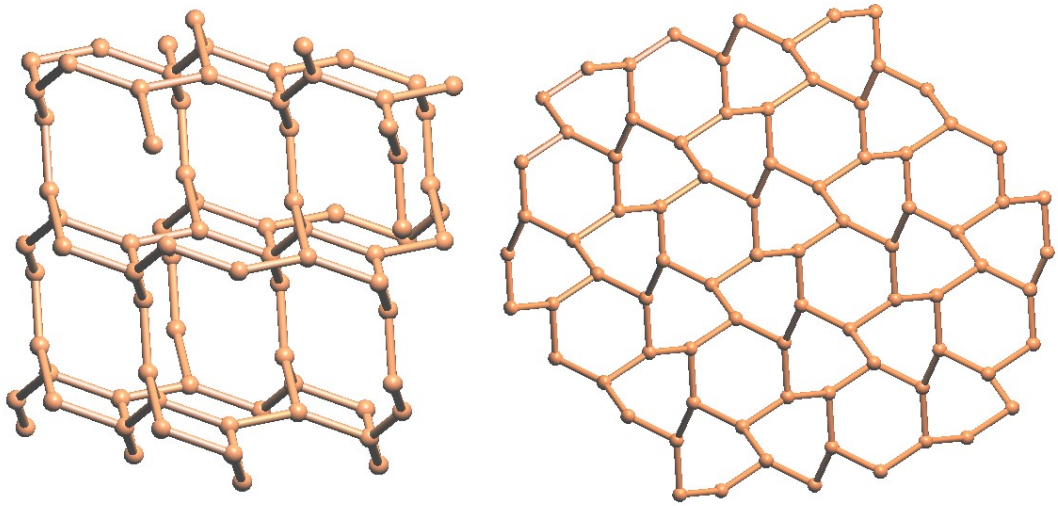

**Fig. S2** The novel 3D-metal SBU of Pb(II) with **pcu-h** topology in **1**.

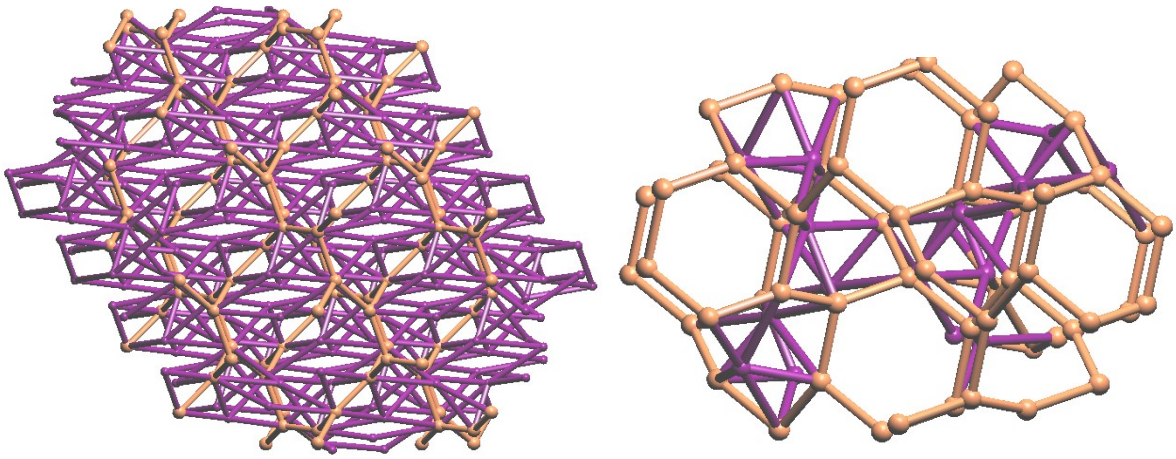

**Fig. S3** 3D network topology of **1** with 3-connected **pcu-h** topology (orange) crossed by the ligand generating two 5-connected new topology of point symbol ($4^6.6^4$).

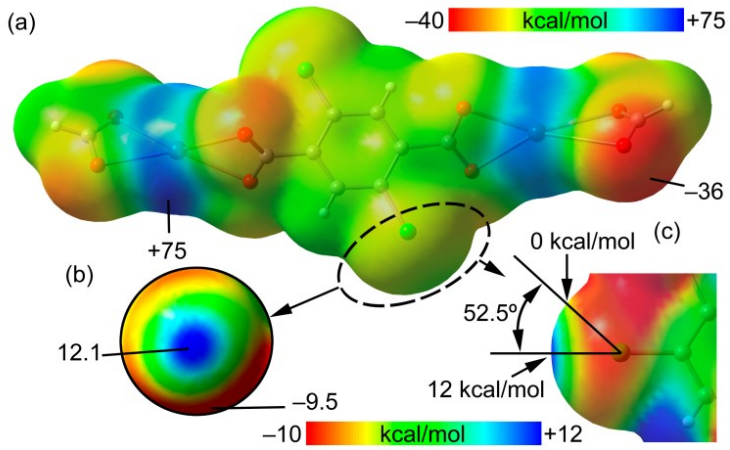


**Fig. S4** (a) MEP surface of the theoretical model (see Fig. 1c for the chemical representation). (b) Detail of the MEP around the Cl-atom. (c) Detail of the MEP (lateral view) around the Cl-atom and the cone angle. The values at selected points are given in kcal/mol.

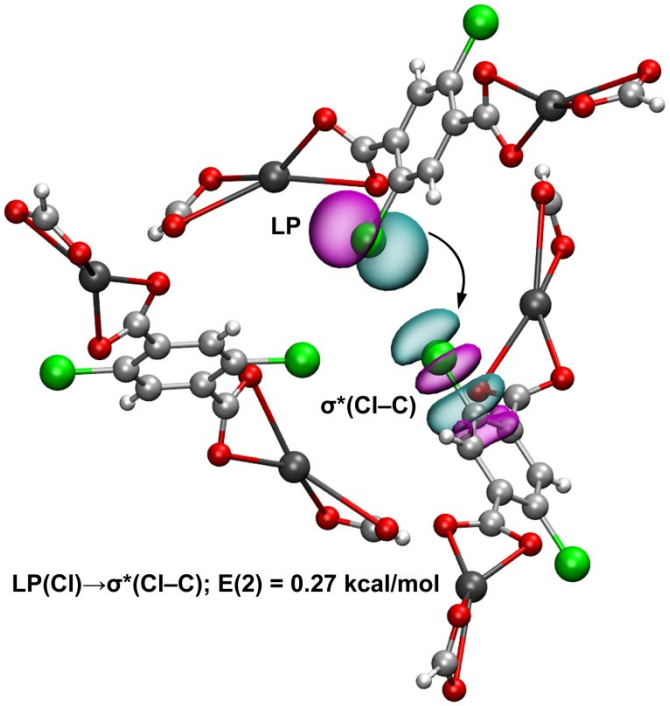


**Fig. S5** NBO representation of the LP(Cl)→σ*(Cl–C) interaction.

**Table S1.** Crystal data and refinement parameters for compound **1-3.**

| Formula | $C_{16}H_7Cl_4O_{9.50}Pb_2$ (**1**) | $C_8H_{3.60}Cl_2O_{4.80}Pb$ (**2**) | $C_8H_{3.814}Cl_2O_{4.907}Pb$ (**3**) |
|---|---|---|---|
| fw | 907.42 | 454.60 | 456.52 |
| crystsyst | Trigonal | Trigonal | Trigonal |
| space group | *R*3 | *R*3 | *R3* |
| *a* (Å) | 19.6265(4) | 19.6501(3) | 19.8059(2) |
| *b* (Å) | 19.6265(4) | 19.6501(3) | 19.8059(2) |
| *c* (Å) | 13.3507(3) | 13.3615(2) | 13.3701(2) |
| $\alpha$(deg) | 90 | 90 | 90 |
| $\beta$(deg) | 90 | 90 | 90 |
| $\gamma$ (deg) | 120 | 120 | 120 |
| *V* (Å$^3$) | 4453.7 | 4468.02 | 4542.07 |
| *Z* | 9 | 18 | 18 |
| Temp(K) | 100 | 100 | 100 |
| $D_{calcd}$(g/cm$^3$) | 3.045 | 3.041 | 3.015 |
| $\mu$(mm$^{-1}$) | 17.583 | 17.527 | 37.458 |
| $\lambda$(Å) | 0.71073 | 0.71073 | 1.54184 |
| GOF on $F^2$ | 1.080 | 1.066 | 1.832 |
| Final *R* indices $[I > 2\sigma(I)]^{a,b}$ | $R1 = 0.0232$ $wR2 = 0.0508$ | $R1 = 0.0222$ $wR2 = 0.0468$ | $R1 = 0.1310$ $wR2 = 0.3836$ |

$^aR1 = \Sigma||F_o| \quad |F_c||/ \Sigma|F_o|$, $^bwR2 = [\Sigma w(F_o^2 \quad F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

**Table S2.** Selected bond lengths and bond angles in **1-2.**

| **Bond length (Å)** | | |
|---|---|---|
| | **1** | **2** |
| Pb(1)-O(1) | 2.495(4) | 2.493(4) |
| Pb(1)-O(2) | 2.461(3) | 2.464(3) |
| Pb(1)-O(3)a | 2.616(3) | 2.619(3) |
| Pb(1)-O(1)b | 2.815(5) | 2.820(5) |
| Pb(1)-O(5)c | 2.902(10) | 2.917(10) |
| Pb(1)-O(3)d | 2.514(5) | 2.522(5) |
| Pb(1)-O(4)d | 2.780(5) | 2.781(5) |
| Pb(1)-O(4)e | 3.023(4) | 3.026(3) |
| **Bond angle (°)** | | |
| O(1)-Pb(1)-O(2) | 52.82(12) | 52.82(12) |
| O(1)-Pb(1)-O(3)a | 113.33(13) | 113.37(13) |
| O(1)-Pb(1)-O(1)b | 140.51(10) | 140.48(10) |
| O(1)-Pb(1)-O(5)c | 108.1(2) | 108.2(2) |
| O(1)-Pb(1)-O(3)d | 82.31(13) | 82.26(13) |
| O(1)-Pb(1)-O(4)d | 72.94(13) | 72.96(11) |
| O(1)-Pb(1)-O(4)e | 75.86(11) | 75.92(11) |
| O(2)-Pb(1)-O(3)a | 80.68(10) | 80.70(10) |
| O(1)b-Pb(1)-O(2) | 107.49(13) | 107.42(12) |
| O(2)-Pb(1)-O(5)c | 141.2(2) | 141.8(2) |
| O(2)-Pb(1)-O(3)d | 102.91(12) | 103.01(11) |
| O(2)-Pb(1)-O(4)d | 123.20(14) | 123.27(13) |
| O(2)-Pb(1)-O(4)e | 72.49(10) | 72.49(10) |
| O(1)b-Pb(1)-O(3)a | 92.91(16) | 92.84(16) |
| O(3)a-Pb(1)-O(5)c | 135.0(2) | 134.6(2) |
| O(3)a-Pb(1)-O(3)d | 62.82(16) | 63.03(16) |
| O(3)a-Pb(1)-O(4)d | 110.44(14) | 110.63(13) |
| O(3)a-Pb(1)-O(4)e | 136.85(13) | 136.76(13) |

| | | |
|---|---|---|
| O(1)b-Pb(1)-O(5)c | 63.8(2) | 64.2(2) |
| O(1)b-Pb(1)-O(3)d | 137.07(12) | 137.16(11) |
| O(1)b-Pb(1)-O(4)d | 126.31(13) | 126.25(13) |
| O(1)b-Pb(1)-O(4)e | 65.00(10) | 64.91(10) |
| O(3)d-Pb(1)-O(5)c | 107.5(2) | 106.7(2) |
| O(4)d-Pb(1)-O(5)c | 65.8(2) | 65.1(2) |
| O(4)e-Pb(1)-O(5)c | 69.8(2) | 70.5(2) |
| O(3)d-Pb(1)-O(4)d | 49.08(12) | 49.08(12) |
| O(3)d-Pb(1)-O(4)e | 155.49(14) | 155.45(14) |
| O(4)d-Pb(1)-O(4)e | 112.47(11) | 112.38(10) |

Symmetric transformation: a =1+x-y, x,1-z; b = 1/3+y, 2/3-x+y, 2/3-z; c = 5/3-y, 1/3+x-y, -2/3+z; d = 2/3-x+y, 4/3-x, -2/3+z; e = 5/3-x, 4/3-y, 4/3-z

**Table S3.** Selected bond lengths and bond angles in **3**

| **Bond length (Å)** | |
|---|---|
| Pb(1)-O(1) | 2.537(19) |
| Pb(1)-O(2) | 2.47(2) |
| Pb(1)-O(3)f | 2.62(2) |
| Pb(1)-O(1)g | 2.86(3) |
| Pb(1)-O(3)h | 2.52(2) |
| Pb(1)-O(4)h | 2.81(2) |
| Pb(1)-O(5)i | 2.86(8) |
| **Bond angle (°)** | |
| O(1)-Pb(1)-O(2) | 53.1(5) |
| O(1)-Pb(1)-O(3)f | 112.1(7) |
| O(1)-Pb(1)-O(1)g | 141.7(6) |
| O(1)-Pb(1)-O(3)h | 82.1(6) |
| O(1)-Pb(1)-O(4)h | 73.1(5) |
| O(1)-Pb(1)-O(5)i | 109.3(10) |

| | |
|---|---|
| O(2)-Pb(1)-O(3)f | 80.1(6) |
| O(1)g-Pb(1)-O(2) | 106.7(6) |
| O(2)-Pb(1)-O(3)h | 103.9(7) |
| O(2)-Pb(1)-O(4)h | 123.9(5) |
| O(2)-Pb(1)-O(5)i | 139.7(12) |
| O(1) g-Pb(1)-O(3)f | 92.3(7) |
| O(3)f-Pb(1)-O(3)h | 63.0(7) |
| O(3)f-Pb(1)-O(4)h | 110.6(6) |
| O(3)f-Pb(1)-O(5)i | 135.8(11) |
| O(1)g-Pb(1)-O(3)h | 136.2(6) |
| O(1)g-Pb(1)-O(4)h | 126.6(6) |
| O(1)g-Pb(1)-O(5)i | 62.7(10) |
| O(3)h-Pb(1)-O(4)h | 48.8(6) |
| O(3)h-Pb(1)-O(5)i | 109.2(11) |
| O(4)h-Pb(1)-O(5)i | 67.8(10) |

Symmetric transformation: f = y, -x+y, 1-z; g = 1/3+x-y, -1/3+x, 2/3-z; h = 2/3-y, 1/3+x-y, -2/3+z; i = 2/3-x+y, 1/3-x, -2/3+z

**References**


(1) G. M. Sheldrick, *Acta Crystallogr. A,* 2015, **71**, 3–8.

(2) *SMART and SAINT*; Bruker AXS Imc.: Madison, WI, 1998.

(3) *SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

(4) R. Ahlrichs, M. Bar, M. Haser, H. Horn and C. Kolmel, *Chem. Phys. Lett.,* 1989, **162**, 165–169.

(5) C. Adamo and V. Barone, *J. Chem. Phys*., 1999, **110**, 6158–6169.

(6) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys*., 2010, **132**, 154104.

(7) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297–3305.

(8) F. Weigend, *Phys. Chem. Chem. Phys*., 2006, **8**, 1057–1065.

(9) R. F.W. Bader, *Chem. Rev.,* 1991, **91**, 893–928.

(10) J. Contreras-García, E.R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.,* 2011, **7**, 625–632.

(11) W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graph.*, 1996, **14**, 33–38.

(12) A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.,* 1990, **92**, 5397.

(13) T. Lu and F. Chen, *J. Comput. Chem.,* 2012, **33**, 580–592.

(14) E. D. Glendening, C.R. Landis and F. Weinhold, *Comput. Mol. Sci*., 2012, **2**, 1–42.

(15) E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis and F. Weinhold, NBO 7.0: New Vistas in Localized and Delocalized Chemical Bonding Theory; Theoretical Chemistry Institute, University of Wisconsin-Madison: Madison, WI, USA, 2018.