SUPPORTING INFORMATION

Experimental and Theoretical Evidences of Anion···Anion Interactions in $[PdCl_4]^{2-}\cdots[PdCl_4]^{2-}$ Dimer

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Compound Preparation

Crystals of complex $[NH_3\text{-}(CH_2)_6\text{-}NH_3]$ $PdCl_4$ were grown by slow evaporation at room temperature of a saturated aqueous solution obtained by dissolving $PdCl_2$ (0.15 g, 0.86 mmol) and $NH_2(CH_2)_6NH_2$ (0.10 g) in an excess of concentrated HCl.

Computational details

The level of theory used in this work is PBE0-D3/def2TZVP. For the models the full optimization was applied while for the geometry of two dianions surrounded by four counterions, the single point calculations were made. These computations were carried out in Gaussian16 set of codes. The QTAIM methodology was engaged to reveal and parametrize bond paths between atoms due to electron density topology protocol embedded in AIMAll software. Molecular electrostatic potentials were indicated by MultiWFN tool while the visualization of them was achieved using VMD program. Noncovalent index (NCI) method was used in order to expose the nonbonded contacts in studied compound thanks to the MultiWFN program. Visualization of interacting orbitals was performed in Chemcraft software. The CSD search was conducted in ConQuest and Mercury programs.

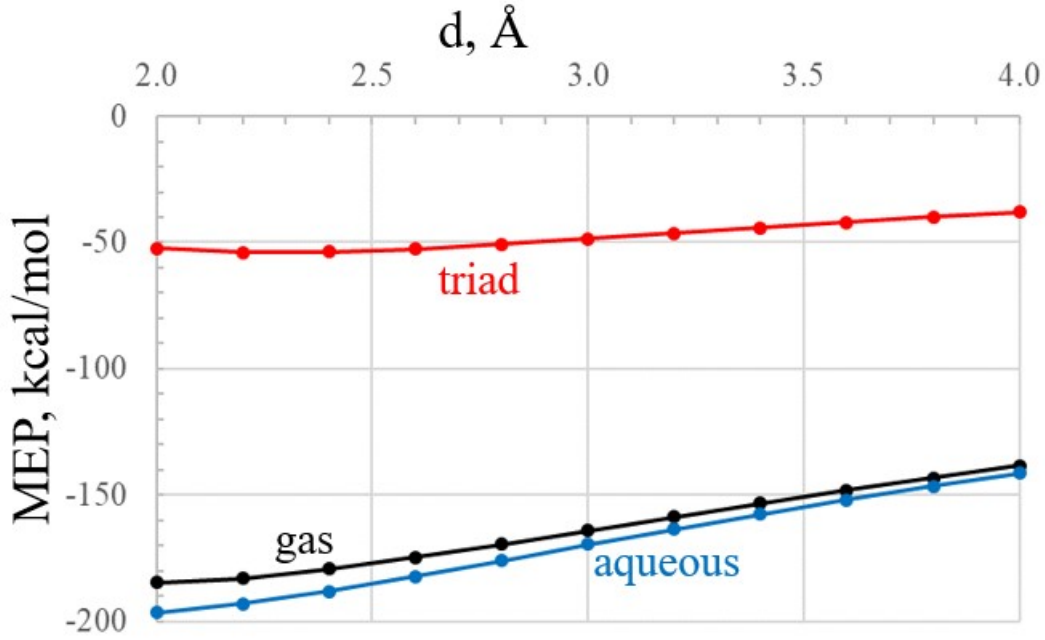


Figure S1. MEP of gas and aqueous phases of $[PdCl_4]^{2-}$ in gas and aqueous phase, and of triad including two $[NH_3(CH_2)_6NH_2]^+$ counterions. d refers to distance above Pd atom along local C_4 rotation axis.

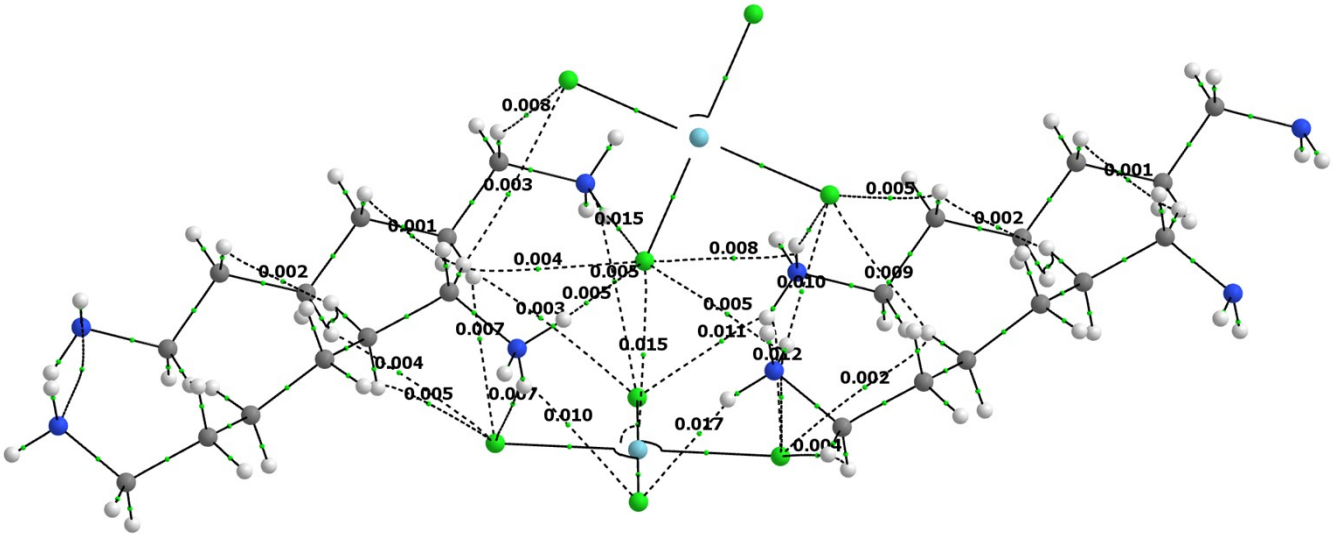
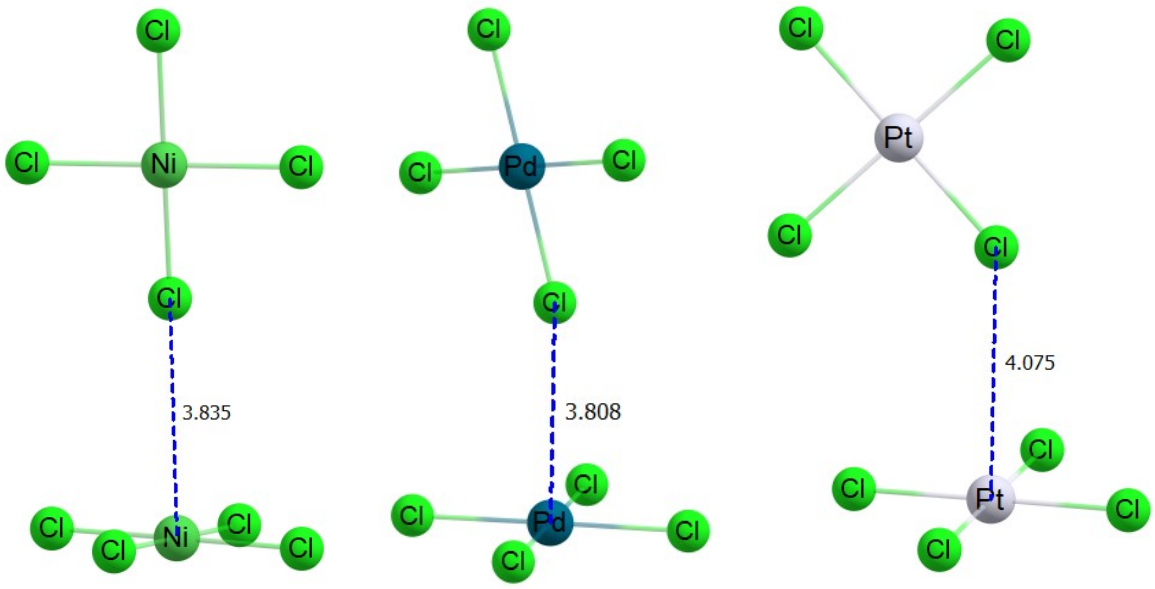
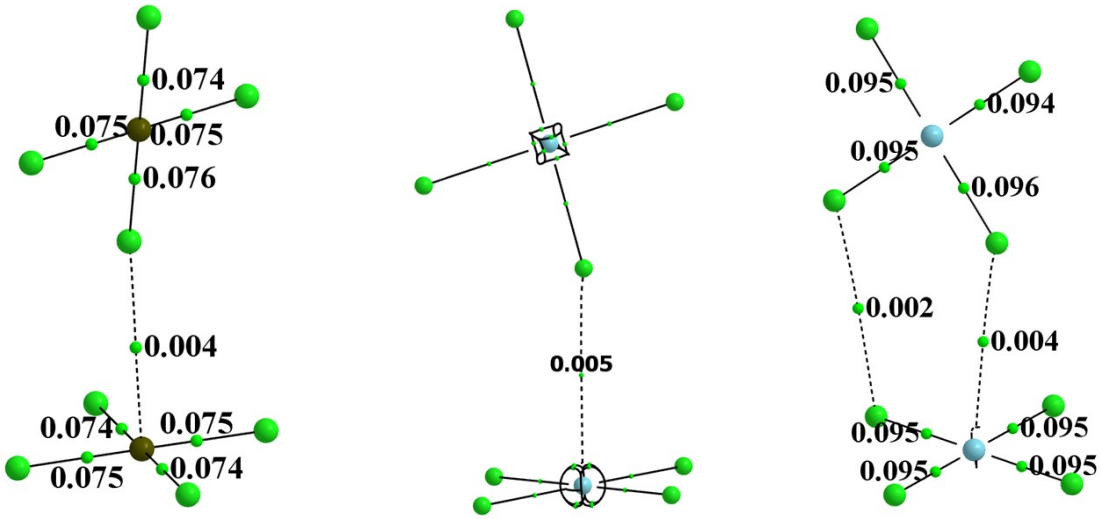


Figure. S2. The distribution of QTAIM bond critical points (green dots) and bond paths (dashed lines) for the $[NH_3\text{-}(CH_2)_6\text{-}NH_2]_4[PdCl_4]_2$ system. ρ at BCP's are given in au.



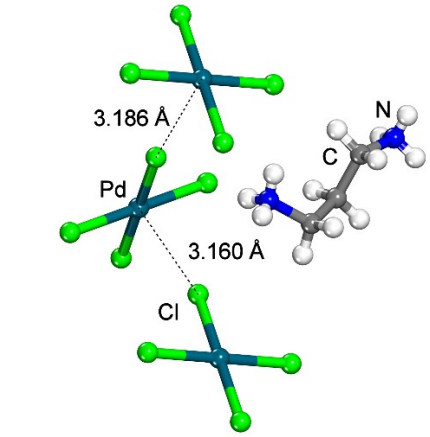
$[NiCl_4]^{2-}\cdots[NiCl_4]^{2-}$ $[PdCl_4]^{2-}\cdots[PdCl_4]^{2-}$ $[PtCl_4]^{2-}\cdots[PtCl_4]^{2-}$

Figure. S3. PBE0 optimized geometries of $[MCl_4^{2-}]_2$ dimers (M= Ni, Pd, Pt). Distances in Å.



$[NiCl_4^{2-}]_2$ $[PdCl_4^{2-}]_2$ $[PtCl_4^{2-}]_2$

Figure. S4. The distribution of QTAIM bond critical points (green dots) and bond paths (dashed lines) for anionic models of $[MCl_4^{2-}]_2$ dimers M= Ni, Pd, Pt optimized in water solvent at PBE0/def2TZVP level of theory. ρ at BCP's are in au.



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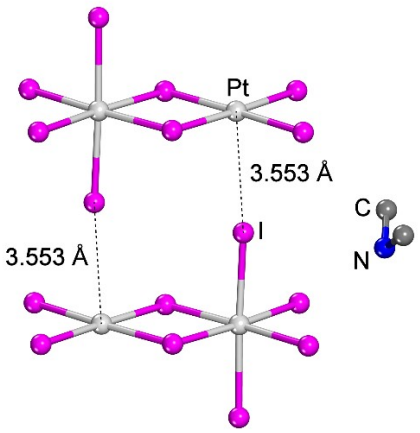
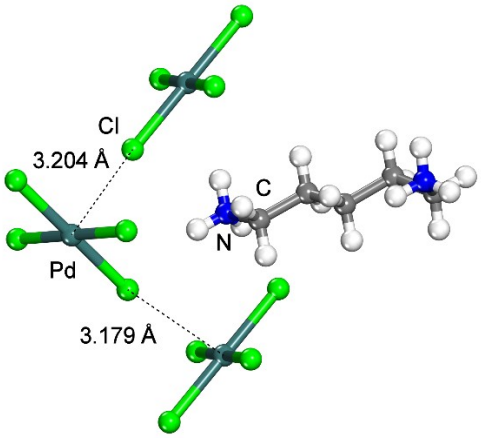


WIDMAX



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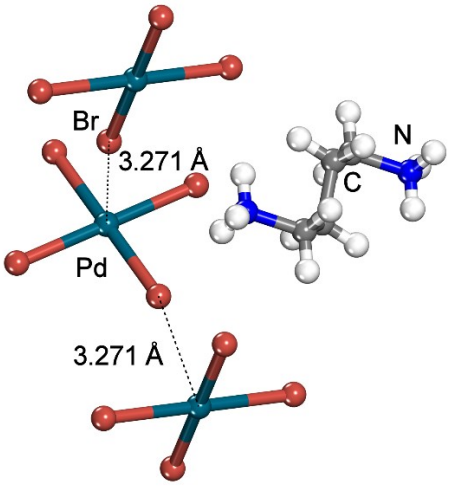

PELMUO

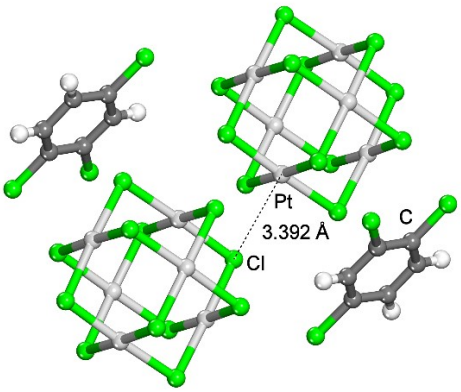

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Figure. S5 Examples of the structures with similar organization as that discussed in current work. Interanionic interactions are indicated by dashed lines with distances given in Å.

Table S1 Interaction energies of $[MCl_4^{2-}]_2$ dimers M= Ni, Pd, Pt optimized in water solvent at PBE0/def2TZVP level of theory. Data given in kcal/mol.

homodimer	Raw values	BSSE corrected
$[NiCl_4]^{2-}\cdots[NiCl_4]^{2-}$	0.90	2.29
$[PdCl_4]^{2-}\cdots[PdCl_4]^{2-}$	0.51	2.88
$[PtCl_4]^{2-}\cdots[PtCl_4]^{2-}$	0.50	2.14

Table S2 Properties of M···Cl contacts BCP's of $[MCl_4^{2-}]_2$ dimers (M= Ni, Pd, Pt) optimized in water solvent at PBE0/def2TZVP level of theory. Data given in atomic units.

homodimer	ρ	$\nabla^2\rho$	H
$[NiCl_4]^{2-}\cdots[NiCl_4]^{2-}$	0.004	0.010	0.000
$[PdCl_4]^{2-}\cdots[PdCl_4]^{2-}$	0.005	0.014	0.001
$[PtCl_4]^{2-}\cdots[PtCl_4]^{2-}$	0.004	0.011	0.000

Table S3. Cartesian Coordinates of the model system of $(PdCl_4^{2-})_2$ with four counterions $[NH_3\text{-}(CH_2)_6\text{-}NH_2]^+$ taken from the crystal structure without optimization.

System: $[NH_3\text{-}(CH_2)_6\text{-}NH_2]_4[PdCl_4]_2$

Pd	3.6778	4.0635	0.0000	H	8.8251	6.8050	7.2154
Cl	2.1693	5.7371	0.4846	H	7.5450	6.1314	7.8241
Cl	3.9905	3.6937	2.2621	C	7.2998	6.6278	5.8343
Cl	5.1863	2.3900	-0.4846	H	7.5728	7.3652	5.2666
Cl	3.3652	4.4334	-2.2621	H	6.3305	6.6209	5.8708
N	4.0566	3.5187	8.9989	N	6.7490	-0.1577	-9.2254
H	3.5296	2.8048	8.9274	H	7.0113	-0.9453	-9.5449
H	4.8834	3.2586	9.2008	H	5.8634	-0.0917	-9.2860
C	4.0762	4.2524	7.7112	C	7.1545	-0.0325	-7.8019
H	4.6526	5.0284	7.7953	H	8.1181	-0.1169	-7.7311
H	3.1804	4.5671	7.5098	H	6.7512	-0.7488	-7.2862
C	4.5711	3.3828	6.5628	C	6.7269	1.2840	-7.2433
H	4.8534	3.9616	5.8376	H	5.7586	1.3221	-7.2154
H	5.3502	2.8895	6.8635	H	7.0387	1.9957	-7.8241
C	3.5673	2.4057	6.0291	C	7.2839	1.4993	-5.8343
H	2.8501	2.8952	5.5953	H	7.0109	0.7619	-5.2666
H	3.1829	1.9118	6.7694	H	8.2533	1.5062	-5.8708
N	3.6735	0.3108	2.0677	N	7.3327	4.4553	-1.8411
H	3.9819	-0.2228	1.4254	H	7.0703	5.2429	-1.5217
H	4.2006	1.0247	2.1392	H	8.2183	4.3893	-1.7806
H	2.8468	0.5709	1.8658	H	6.9534	3.8028	-1.3689
C	3.6540	-0.4229	3.3554	C	6.9271	4.3301	-3.2646
H	3.0775	-1.1988	3.2713	H	5.9636	4.4145	-3.3355
H	4.5497	-0.7376	3.5568	H	7.3305	5.0464	-3.7803
C	3.1591	0.4467	4.5038	C	7.3547	3.0136	-3.8233
H	2.8768	-0.1321	5.2290	H	8.3230	2.9755	-3.8512
H	2.3800	0.9400	4.2031	H	7.0429	2.3019	-3.2425
C	4.1628	1.4238	5.0375	C	6.7978	2.7983	-5.2323
H	4.8801	0.9343	5.4713	H	7.0707	3.5356	-5.8000
H	4.5472	1.9177	4.2972	H	5.8284	2.7914	-5.1958
Pd	7.2281	0.0000	0.0000	N	3.5546	-0.3108	-2.0677
Cl	8.8490	1.6120	-0.3052	H	3.2462	0.2228	-1.4254

Cl	7.2656	0.4327	2.2741
Cl	5.6072	-1.6120	0.3052
Cl	7.1906	-0.4327	-2.2741
N	7.2510	3.6718	1.8411
H	7.5134	2.8842	1.5217
H	6.3654	3.7378	1.7806
H	7.6304	4.3243	1.3689
C	7.6566	3.7970	3.2646
H	8.6202	3.7126	3.3355
H	7.2532	3.0807	3.7803
C	7.2290	5.1135	3.8233
H	6.2607	5.1516	3.8512
H	7.5408	5.8252	3.2425
C	7.7860	5.3288	5.2323
H	7.5130	4.5915	5.8000
H	8.7553	5.3357	5.1958
N	7.8348	8.2848	9.2254
H	8.7204	8.2188	9.2860
H	7.4554	7.6323	9.6976
C	7.4292	8.1596	7.8019
H	6.4656	8.2440	7.7311
H	7.8326	8.8759	7.2862
C	7.8568	6.8431	7.2433
H	3.0275	-1.0247	-2.1392
H	4.3813	-0.5709	-1.8658
C	3.5741	0.4229	-3.3554
H	4.1506	1.1988	-3.2713
H	2.6784	0.7376	-3.5568
C	4.0690	-0.4467	-4.5038
H	4.3513	0.1321	-5.2290
H	4.8481	-0.9400	-4.2031
C	3.0653	-1.4238	-5.0375
H	2.3480	-0.9343	-5.4713
H	2.6809	-1.9177	-4.2972
N	3.1715	-3.5187	-8.9989
H	3.4798	-4.0523	-9.6412
H	2.3447	-3.2586	-9.2008
C	3.1519	-4.2524	-7.7112
H	2.5755	-5.0284	-7.7953
H	4.0477	-4.5671	-7.5098
C	2.6570	-3.3828	-6.5628
H	2.3747	-3.9616	-5.8376
H	1.8779	-2.8895	-6.8635
C	3.6608	-2.4057	-6.0291
H	4.3780	-2.8952	-5.5953
H	4.0452	-1.9118	-6.7694

Table S4. Coordinates of the $(MCl_4^{2-})_2$ M= Ni, Pd, Pt, dimers fully optimized in water as solvent.

System				
$[NiCl_4]^{2-}\cdots[NiCl_4]^{2-}$	Ni	-0.230737	-0.164365	0.046641
	Cl	1.091595	1.621151	-0.046540
	Cl	-0.333504	0.024654	2.263364
	Cl	-1.557399	-1.954514	0.139230
	Cl	-0.128295	-0.353498	-2.170197
	Ni	3.906274	4.226012	-0.046354
	Cl	2.440777	5.863087	0.333340
	Cl	4.249764	4.028050	2.146450
	Cl	5.376277	2.593257	-0.425723
	Cl	3.574348	4.433866	-2.240210
$[PdCl_4]^{2-}\cdots[PdCl_4]^{2-}$	Pd	3.448673	4.313708	-0.005224
	Cl	1.927977	6.029984	0.413086
	Cl	3.328335	3.657448	2.224225
	Cl	4.964778	2.602565	-0.422128
	Cl	3.570972	4.968867	-2.234617
	Pd	7.454271	-0.247762	0.004520
	Cl	9.124040	1.272571	-0.566644
	Cl	7.802621	0.227097	2.256429
	Cl	5.791249	-1.775127	0.578047
	Cl	7.116684	-0.731652	-2.247693
$[PtCl_4]^{2-}\cdots[PtCl_4]^{2-}$	Pt	-0.159279	-0.176010	-0.138549
	Cl	1.170648	1.434358	-1.155804
	Cl	0.232956	0.808942	1.933563
	Cl	-1.490348	-1.790119	0.882687
	Cl	-0.552723	-1.159437	-2.212781
	Pt	3.832514	4.236156	0.136733
	Cl	2.365319	5.961557	0.671971
	Cl	3.693374	3.434740	2.315994

Cl	5.313629	2.521599	-0.394178
Cl	3.983011	5.045914	-2.039635

Table S5. Crystal data and structure refinement for $[NH_3\text{-}(CH_2)_6\text{-}NH_3]\ PdCl_4$

CCDC Number	2109436
Empirical formula	$C_6H_{18}Cl_4N_2Pd$
Formula weight	366.42
Temperature [K]	298(2)
Crystal system	triclinic
Space group (number)	$P\bar{1}$ (2)
a [Å]	7.2281(7)
b [Å]	8.1281(5)
c [Å]	11.7212(12)
α [°]	70.892(4)
β [°]	87.545(5)
γ [°]	89.101(3)
Volume [Å^3]	650.09(10)
Z	2
ρ_{calc} [gcm^{-3}]	1.872
μ [mm^{-1}]	2.212
F(000)	364
Crystal size [mm^3]	0.06×0.09×0.11
Crystal colour	dark red
Crystal shape	block
Radiation	MoK_α (λ=0.71070 Å)
2Θ range [°]	3.68 to 54.90 (0.77 Å)
Index ranges	-9 ≤ h ≤ 9 -9 ≤ k ≤ 10 0 ≤ l ≤ 15
Independent reflections	2982 R_{int} = 0.0233 R_{sigma} = 0.0326
Completeness to θ = 26.50°	100.0 %
Data / Restraints / Parameters	2982 / 0 / 121
Goodness-of-fit on F^2	1.146
Final *R* indexes [*I*≥2σ(*I*)]	R_1 = 0.0370 wR_2 = 0.0882
Final *R* indexes [all data]	R_1 = 0.0410 wR_2 = 0.0894
Largest peak/hole [eÅ^{-3}]	−0.66/0.59

Table S6. Hydrogen bonds data for $[NH_3\text{-}(CH_2)_6\text{-}NH_3]\ PdCl_4$

D–H···A [Å]	**d(D–H) [Å]**	**d(H···A) [Å]**	**d(D···A) [Å]**	**<(DHA) [°]**
N1–H1A···Cl1$^{\#1}$	0.89	2.41	3.2467(16)	155.9
N1–H1B···Cl4$^{\#2}$	0.89	2.68	3.4037(19)	139.1
N1–H1C···Cl1$^{\#2}$	0.89	2.70	3.3968(14)	135.8
N5–H5A···Cl1	0.89	2.60	3.3771(14)	147.0
N5–H5A···Cl2	0.89	2.58	3.2683(17)	135.2
N5–H5B···Cl4$^{\#3}$	0.89	2.42	3.2877(14)	163.7
N5–H5C···Cl3	0.89	2.43	3.2728(14)	158.3

Symmetry transformations used to generate equivalent atoms: #1: +X, +Y, 1+Z; #2: 1-X, -Y, 1-Z; #3: -1+X, +Y, +Z;

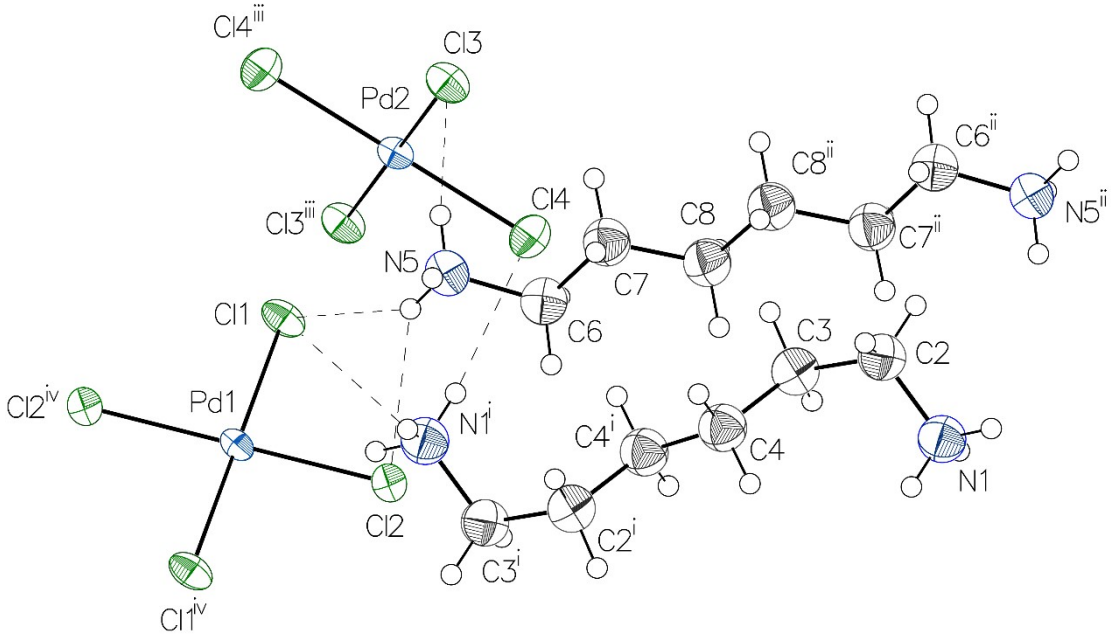

Figure. S6. Thermal displacement ellipsoid plot of the asymmetric unit for the complex $[NH_3\text{-}(CH_2)_6\text{-}NH_3]$ $PdCl_4$. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as sphere of arbitrary size. Selected hydrogen bonds are shown with dashed lines. Symmetry codes: (i): 1-x, -y, 1-z; (ii): -x, 1-y, 1-z; (iii): 1-x, 1-y, -z; (iv): -x, -y, -z.