Electronic Supplementary Material (ESI) for CrystEngComm.

The NX_2 Synthon in Crystals

Fernando Cortés-Guzmán,*[a,b] Pablo Carpio-Matínez[a], Juan de Dios Guzmán-Hernández[b] and Vojtech Jancik[a,b]

Supplementary information.

Hirshfeld atom refinement

High resolution data and initial structure solution used for the Hirshfeld atom refinement (HAR) of $P_3N_3Cl_6$ were published previously by us[1] and were used without any modification. The HAR was performed using olex.refine and NoSperA2[2a] incorporated in Olex2[2b] and Orca 5.0.1.[3] and was initiated by refining one molecule at the cc-VQZ/wB97X[4] level of theory. After achieving convergence Gram-Charlier coefficients up to 4th order were refined for all atoms due to the presence of residual density in the proximity of the atoms congruent with anharmonic motion. Thereafter, the structure was expanded using the space group symmetry to describe the NCl_2 synthon and the obtained wavefunction that was analyzed using AIMALL.[5] This led to an almost featureless residual electron density map (Figure S1) and a gaussian distribution of the residual electron density in the fractal dimension analysis (Figure S2). Table S1 contains the refinement details and the final refinement indices.

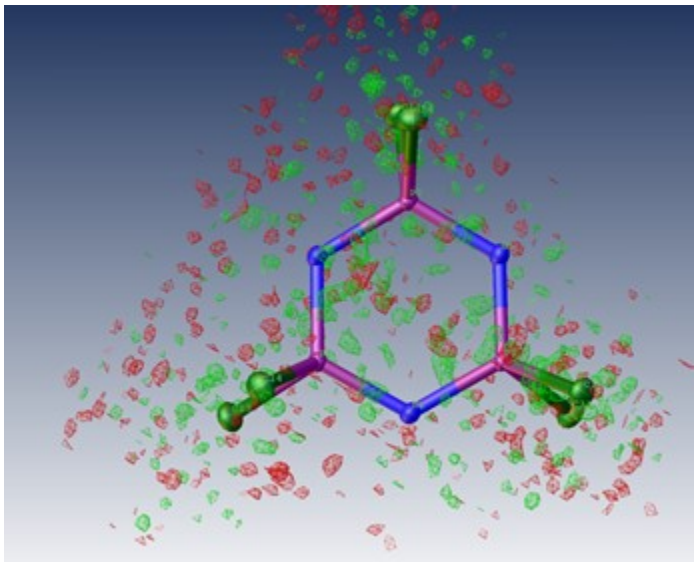

Figure S1. Molecular Structure of **1** obtained from the Hirshfeld Atom Refinement with thermal ellipsoid plots at 50% probability and the residual electron density (green = positive, red = negative) at 0.11 e·Å^{-1}.

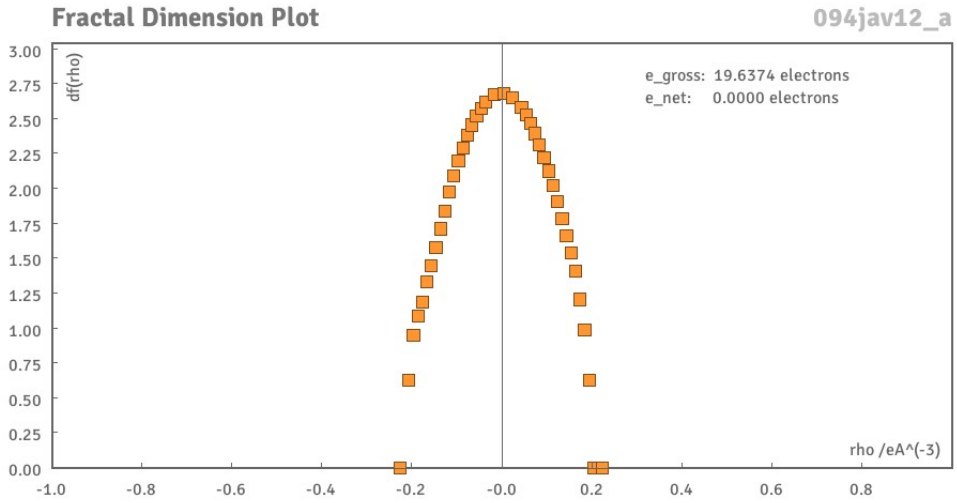

Figure S2. Fractal dimension analysis of the residual electron density after the final cycle of the Hirshfeld atom refinement of $P_3N_3Cl_6$ (**1**).

Table S1: Data collection and Hirshfeld atom refinement details for **1**.

formula	$Cl_6N_3P_3$
fw	347.657
crystal system	orthorhombic
space group	P*nma*
temp, K	100.15
λ, Å	0.71073
a, Å	13.8711(1)
b, Å	12.8328(1)
c, Å	6.0866(1)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1083.45(2)
Z	4
ρ, g·cm^{-3}	2.131
μ, mm^{-1}	1.978
F(000)	676.275
crystal size, mm^3	0.116 x 0.1 x 0.084

θ range for data collection, deg	2.94 to 55.75
index ranges	−32 ≤ h ≤ 32
	−29 ≤ k ≤ 29
	−14 ≤ l ≤ 14
no. of reflns collected	129988
no. of indep. reflns (R_{int})	7300 (0.0197)
no. of data / restraints / parameters	7300 / 0 / 221
GoF on F^2	1.1475
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0085, 0.0132
R_1,[a] wR_2[b] (all data)	0.0115, 0.0137
largest diff. peak / hole, e·Å^{-3}	0.1909 / −0.1917

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(F_o^2)^2]^{1/2}$.

Geometry

Table S2

HAR of the $P_3N_3Cl_6$ trimer			
Name	**X**	**Y**	**Z**
Cl1	10.433483	6.062619	0.913875
Cl2	23.539773	6.062619	16.339135
Cl3	23.539773	6.062619	4.837128
P4	11.512304	6.062619	4.513176
P5	24.618594	6.062619	12.739834
P6	24.618594	6.062619	1.237827
N7	12.924104	3.498586	5.109582
N8	12.924104	8.626653	5.109582
N9	26.030394	3.498586	0.641421
N10	26.030394	3.498586	12.143428
N11	26.030394	8.626653	12.143428
N12	26.030394	8.626653	0.641421
P13	15.602634	8.663107	6.421665
P14	15.602634	3.462132	6.421665
P15	28.708924	8.663107	–0.670661

P16	28.708924	8.663107	10.831346
P17	28.708924	3.462132	10.831346
P18	28.708924	3.462132	–0.670661
Cl19	8.188812	6.062619	6.288112
Cl20	21.295102	6.062619	10.964898
Cl21	21.295102	6.062619	–0.537109
N22	17.012643	6.062619	6.834231
N23	30.118933	6.062619	10.41878
N24	30.118933	6.062619	–1.083227
Cl25	17.890434	10.942353	4.506833
Cl26	17.890434	1.182886	4.506833
Cl27	30.996724	10.942353	1.244171
Cl28	30.996724	10.942353	12.746178
Cl29	30.996724	1.182886	12.746178
Cl30	30.996724	1.182886	1.244171
Cl31	15.338699	10.416767	9.746837
Cl32	15.338699	1.708472	9.746837
Cl33	28.44499	10.416767	–3.995834
Cl34	28.44499	10.416767	7.506173
Cl35	28.44499	1.708472	7.506173
Cl36	28.44499	1.708472	–3.995834

k-means

Table S3

NCl_2			**NBr_2**			**NI_2**	
DESKER	1		YARVOE	0		TUNXIM	0
PICCIN	1		VUZJOQ	0		UXAROD	0
MERVAJ	1		KELGEO03	0		UXARIX	0
ORUHOZ	1		BRMALN	0		OPUPUN	0
XIYVOQ	1		SOMKIO	0		OLOWOE	0
BAWNIW	1		DADRIK	0		DIXXIS	0
ROKCAV	1		QUMSUO	0		IMUQUE	0
MERVAJ	1		YARVOE	1		MOSFOQ	0
TUMJAM	1		YARVOE	1		IHUNUU	0

PICCIN	1		MOTZIE	1		FIWPUZ	0
ETEYIM	1		PONWAR	1		REZQOF02	0
WAPSIS	1		BAQPAL	1		LUKWAS03	0
ETEYIM	1		UXOBUG	1		HOWXAU	0
CMTIPH	1		BAQPAL	1		XUYBAV	0
NAJGEN	1		REMBUI	1		YEXVIJ	0
XIYVOQ	1		LETDIY	1		CACVUA	0
POFFEX	1		YARVOE	1		QAXPAK	0
CMTIPH	1		BRBZNT01	1		IMUREP	0
CAXQUP	1		BELZOK	1		SAJDEP	0
MEBGOR	1		WIBGIA	1		IMUROZ	0
SIXNAQ	1		RADTEW	2		PERLAC	0
CUCGOY	1		LURFIO	2		IMURAL	0
NEFJOZ	1		COPZIS	2		TAXZAW01	0
MEBGUX	1		PEXNIQ07	2		UCEGOC	0
IYEKUV	1		HIJKER	2		LAGGOT	1
DEPVUS	1		OFIZAF	2		VIXXAE	1
ADULEQ	1		VEGGUK	2		ECASAE	1
GINHAP	1		UKIXAO	2		HEZFUP	1
ETEYIM	2		HIZYIB	3		HEZCOH	1
MCPZSI	2		HIQYUE	3		HIRVOV	1
IMIQUT	2		HUYYUV	3		TUWQIO01	1
GAKNEL	2		YEDTIL	3		ANUPOP	2
KUMJEH	2		BARKOX	3		VIHFIC	2
BATBII	2		BEVFOA	3		TOJCEB	2
PADHIL	2		EZIBIA	4		HURNEQ	2
HIDFAB	2		IPOCIB	5		HURNIU	2
IFULUQ02	2		IKABAZ	5		HURNIU	2
RUSCAM	2		HIRWIQ	5		HURNIU	2
FUBXOQ	2		VABBAF	5		UZULOT	2
KOVVOJ	2		LETDIY	5		HURNIU	2
CUGBAK	2		UKIWUH	5		HURNEQ	2
UKIWOB	2		WIWBOV	5		HURNIU	2
KUHGAV	2		INADAE	5		UZUCIE	2
YAVCUT	2		IKABAZ	5		AQECEH	3
RAZCIE	2		IKABAZ	6		LAGHEK	3
LEMREA	2		UKIWUH	6		YIQYOP	3
HEJGAE	2		CONQOL	6		LAZYOD	3
KECRAN	2		UKIWUH	6		LAZYOD	3
DUHRAA	2		XESVUP	6		LAGGOT	3
SIFKOI	2		SERDEB	6		XAFBAL	3

QEKCUE	2		OWURIJ	6		ENIGIR	3
RIHJAV	2		UKIWUH	6		XAFBAL	3
IDELUC	2		WIWBOV	6		XUXMAH	3
HEJGAE	2		VENBEW	6		LILMEA	3
FARQAR	2		YIFDOH	6		HEZGAW	3
SUPFUE	2		NOPWEX	6		XAFBEP	3
FELPIV	2		DBPDZC	7		XUXMAH	3
BEDNFE	2		IKABAZ	7		LOXFOV	3
ETEYIM	2		BTCYME	7		KOVGEH	3
GIPHUI	2		WAWFUY	7		XUXMAH	3
FEGDIF	2		DEGREO	7		LAZYOD	3
TUMJAM	2		OZEBAZ	7		LAZYOD	3
UZETUQ	2		POWBEL	7		XUXMAH	3
BUXMIT	2		KIXZIB	8		UXARIX	3
FEGDIF	2		PEVWOE	8		XAFBEP	3
EGOQOI	3		XAZLOA	8		LAZYOD	3
ECIGAB	3		XAZLOA	8		TIPJUA	4
GASHIU	4		AGATIN01	8		LATFUJ	4
EKAVIV	4		HIZYIB	8		LIQVOY	4
JITXOZ	4		SOKJUZ	8		BUNGEY	4
PUYPUV	4		DADSEH01	8		PERLAC	4
HIDFAB	4		UKIXAO	8		KIVCEA	4
BAWMUH	4		YARVOE	8		YARTAO	4
YIGSIR	4		WOZMUW	9		YANPIP	5
PIJBIT	4		EPUSAM	9		TAWFEF	5
ENAJOU	4		WALYIS	9		TEPKUW	5
KAYRUY	4		HIZYIB	9		HIXVUI	5
VIHHUP	4		HIZYIB	9		GAKGEF	5
IFULUQ02	4		LIZPEQ	9		YANPIP	5
HOXBIH	4		AWIWOV	9		GAKGAB	5
NEWYOF	4		IKABAZ	9		LAGHEK	5
IDITIB	4		NAWYAM	9		EFUGIX	5
IFULUQ02	4		TAJHIZ	9		QINDOI	5
ETEYIM	4		YARVOE	9		SODBET	5
FEDVER	4		DADRUW	9		OJIKEZ	5
ZAMWAL	4		IKEFOV	9		YANPIP	5
GASHIU	4					QINPEK01	5
KEKFAJ	4					YIQYOP	5
AGUVII	4					IOBNIT18	5
PIJBOZ	4					WIBGEW	6
ORUJAN	4					WIBGEW	6

QOBJUM	4					ROYDAM	6
VAHGUH	4					OPUPUN	6
HAZWIQ	4					FAZXAI	6
GASJIW	4					PEPQIN	6
WEDWIM	4					OCIQUN	6
TUMJAM	4					VIXXAE	6
PICCIN	4					PESZOE	6
WARYAQ	4					EFUGET	6
GUZLIX	4					BOWRUC02	6
CUCGOY	4					UNOGEJ	6
TIYDAI	4					HURNIU	7
PESBAT	4					UZULOT	7
MEBGUX	4					GUYLAQ	7
MEBGOR	4					GUYKUJ	7
PALPAV	4					HEZGAW	7
VECWEH	4					HEZFUP	7
UZOPIK	4					TEPKUW	8
HAZWIQ	4					TAWFEF	8
NICXII	5					YANPIP	8
ETEYIM	5					YINYEA	8
KOVVOJ	5					SAJDEP	8
CUCGOY	5					EFUGIX	8
NEBFIJ	5					TAWFEF	8
GOHYOR	5					YANPIP	8
HAYJEW	5					TEPKUW	8
CUCGOY	5					YOGKOX	8
PUYQAC	5					DIXXIS	8
XAKREH	5					YANPIP	8
OXASEN	5					SUZFUR	9
PICCIN	5					ZOBBEZ	9
PUYQIK	5					NEJVIJ	9
XIYVOQ	5					NINSEL	9
ETEYIM	5					XAYLUH	9
IPOJOP	5					LUKWOG	9
DUWKAI	5					OJIHIA	9
ETEYIM	5					HEZCUN	9
TUKZEE	5					OJIGUL	9
CUCGOY	5						
CUCGOY	5						
CUCGOY	5						
BATBAA	5						

RIHLUP	5						
DITJAS	6						
XIZHIX	6						
RIDLOH	6						
GAWBAL	6						
OFIFEQ	6						
WILLUA	6						
WILLEK	6						
HIDFAB	6						
WILLOU	6						
BEXNAV	6						
SARMUX	6						
NEFJOZ	6						
EWIMEC	6						
JALZAB	7						
FOGDAJ	7						
SULCOT	7						
ZIZDOD	7						
YOPTAZ	7						
PUPWII	7						
BEDNFE	7						
SOQKAN	7						
ICUTOT	7						
JIYCAV	7						
JODRAX	7						
JIYCAV	7						
SANGUN	7						
RATMOO	7						
OSEDEX	7						
TULJIT	7						
RATMOO	7						
LEMREA	7						
OSEDIB	7						
PEVPEL	7						
GEHFEF	7						
IQONEK	7						
PUYQAC	7						
JODRAX	7						
LEMREA	7						
CAZCHO	7						
POTCAD	7						

PEVPEL	7						
IJOLEZ	7						
DEYJOG	7						
BALZIZ	7						
RUFXUM	7						
KEKFAJ	7						
OTEHEC	7						
ENAJOU	7						
GAYMIF	7						
TIGWOW	7						
XEFHIA	7						
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UKIWOB	7						
IFULUQ02	7						
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KECRAN	8						
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FOGDAJ	8						
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BUSRAJ	8						
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OFUVAM	9						
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SOPNEQ	9						
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KOVVOJ	9						
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FEDVER	9						
ATOVIQ	9						
PAHCIK	9						
GAYMIF	9						
PUYZIV	9						
JITXOZ	9						
SOPNEQ	9						
POVNOD	9						
LOLSUA	9						
CTHDZO	9						
NIZDIM	9						
POVNOD	9						
TETREQ	9						
NABJIL	9						
HIGMUH	9						
WILLAG	9						
AHOGUB	9						
NOPREP	9						
GIRVEI	9						
UQIBAY	9						
WUDDAD	9						
NOWBOT	9						
BOFVOI	9						
ISUNUH	9						

TRAZSB	9						
AHIWEV	9						
ZUXRER	9						
BARZAY	9						
SIXNAQ	9						
HOGHIX	9						
PATTAG	9						
WILKUZ	9						
OCOXUD	9						
HAFMIL	9						
AXODID	9						
POVKUI	9						
PUYPUV	10						
PIMXUH	10						
IYEKUV	10						
CUCGOY	10						
CUCGOY	10						
GASYIM	10						
GURVIZ	10						

Table S4

k Cluster	Molecules in k-cluster	Prototype structure
NCl_2		
1	28	DESKER
2	37	FUBXOQ
3	2	EGOQOI
4	42	PICCIN
5	24	PUYQIK
6	13	BEXNAV
7	54	RUFXUM
8	19	KECRAN
9	48	NOPREP
10	7	PIMXUH
NBr_2		
1	7	YARVOE
2	13	REMBUI
3	8	VEGGUK
4	6	HIQYUE
5	1	EZIBIA
6	9	WIWBOV

7	12	UKIWUH
8	7	DBPDZC
9	10	UKIXAO
10	13	HIZYIB
NI_2		
1	24	TUNXIM
2	7	VIXXAE
3	12	VIHFIC
4	23	LAZYOD
5	7	BUNGEY
6	16	GAKGAB
7	12	PESZOE
8	6	HEZGAW
9	12	YANPIP
10	9	OJIHIA

Local properties

a. Bond critical points

1 HAR

BCP #	Atoms	Rho	DelSqRho	Ellipticity	G	V	DI(A|B)
11	Cl20 - N22	0.009	0.034	0.016	0.007	–0.005	0.071
17	Cl3 - N22	0.004	0.014	0.007	0.003	–0.002	0.028
19	Cl3 - Cl20	0.007	0.026	0.011	0.005	–0.004	0.063
RCP #	**Atoms**	**Rho**	**DelSqRho**		**G**	**V**	
8	-Cl3 - Cl20 - N22-	0.003	0.011		0.002	–0.001	

1 DFT

BCP #	Atoms	Rho	DelSqRho	Ellipticity	G	V	DI(A|B)
13	Cl7 - N13	0.009	0.031	0.020	0.006	-0.005	0.073
39	Cl7 - Cl32	0.007	0.025	0.031	0.005	-0.003	0.066
40	N13 - Cl32	0.004	0.013	0.045	0.003	-0.002	0.030
RCP #	**Atoms**	**Rho**	**DelSqRho**		**G**	**V**	

11	-Cl7 – Cl32 – N13-	0.003	0.011		0.002	-0.002	

b. Critical points of the Laplacian of the electron density

HAR $P_3N_3Cl_6$ trimer			
CP #	**Rho**	**DelSqRho**	**Distance**
N22			
8	0.502	–1.890	0.749
Cl3			
21	0.268	–0.742	1.180
24	0.215	–0.342	1.218
34	0.068	0.125	1.965
Cl20			
18	0.214	–0.335	1.218
24	0.270	–0.754	1.179
44	0.066	0.150	1.861

DFT $P_3N_3Cl_6$ trimer			
CP #	**Rho**	**DelSqRho**	**Distance**
N13			
112	0.486	-1.721	0.766
121	0.134	0.247	1.381
Cl7			
38	0.069	0.158	1.827
19	0.210	-0.367	1.224
25	0.270	-0.816	1.186
Cl32			
92	0.069	0.155	1.829
74	0.211	-0.373	1.224
72	0.268	-0.793	1.186

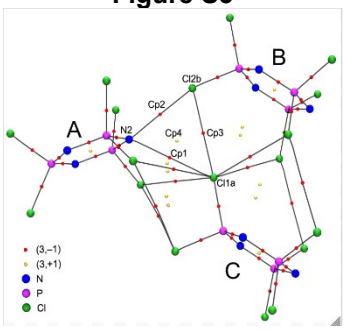
Integrated properties

HAR $P_3N_3Cl_6$ trimer							
Atom	**q(A)**	**N(A)**	**K(A)**	**K_s**	**|Mu(A)|**	**|Q(A)|**	**Vol(A) (0.001)**
Cl3	–0.638	17.638	459.388	459.388	0.983	0.254	218.110
Cl20	–0.634	17.634	459.386	459.386	0.984	0.337	214.536
N22	–2.177	9.177	55.693	55.693	0.873	0.496	127.445

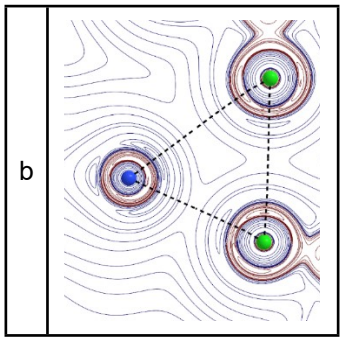
DFT $P_3N_3Cl_6$ trimer							
Atom	**q(A)**	**N(A)**	**K(A)**	**K_s**	**|Mu(A)|**	**|Q(A)|**	**Vol(A) (0.001)**
Cl7	-0.537	17.537	459.563	-460.408	0.567	0.976	219.931
Cl32	-0.532	17.532	459.570	-460.415	1.476	1.226	216.993
N13	-2.050	9.050	55.646	-55.748	0.374	1.296	125.258

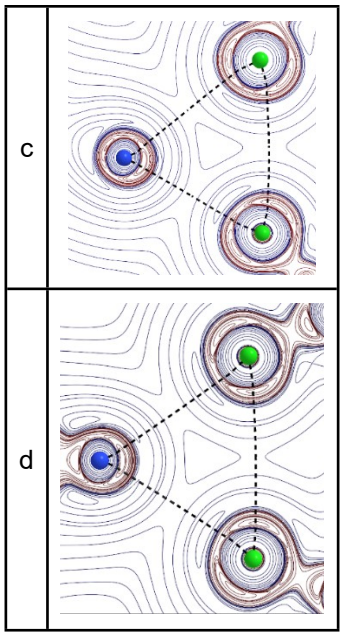
Molecules of **1:** A, B and C

Figure S3



Classification of interactions





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