Supplementary Information

Belonging to the paper "Experimental and Theoretical Characterization of the Hexaazidophosphate(V) ion"

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Content

1. Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters

Table 1. Crystal data and structure refinement for ch1ppx1_0m.

Identification code	ch1ppx1_0m	
Empirical formula	C36 H30 N19 P3	
Formula weight	821.70	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6269(9) Å	α= 92.635(5)°.
	b = 9.8158(9) Å	β= 93.437(5)°.
	c = 10.1414(10) Å	γ = 92.105(4)°.
Volume	954.83(16) $Å^3$	
Z	1	
Density (calculated)	1.429 Mg/m^3	
Absorption coefficient	0.213 mm^{-1}	
F(000)	424	
Crystal size	0.32 x 0.14 x 0.14 mm^3	
Theta range for data collection	2.08 to 28.31°.	
Index ranges	-12<=h<=12, -12<=k<=13, -13<=l<=13	
Reflections collected	16811	
Independent reflections	4674 [R(int) = 0.0277]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9708 and 0.9349	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4674 / 0 / 265	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0385, wR2 = 0.1031	
R indices (all data)	R1 = 0.0452, wR2 = 0.1082	
Largest diff. peak and hole	0.610 and -0.316 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ch1ppx1_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	4034(1)	4071(1)	4033(1)	18(1)
N(1)	5000	5000	5000	23(1)
C(1)	4875(1)	3661(1)	2534(1)	22(1)
C(2)	4674(2)	2390(2)	1857(2)	28(1)
C(3)	5347(2)	2133(2)	698(2)	34(1)
C(4)	6215(2)	3123(2)	216(2)	34(1)
C(5)	6417(2)	4376(2)	884(2)	34(1)
C(6)	5758(2)	4652(2)	2044(2)	27(1)
C(7)	2456(1)	4915(1)	3604(1)	21(1)
C(8)	1744(2)	4707(2)	2368(2)	28(1)
C(9)	514(2)	5373(2)	2109(2)	35(1)
C(10)	1(2)	6238(2)	3063(2)	34(1)
C(11)	712(2)	6456(2)	4287(2)	32(1)
C(12)	1941(2)	5797(2)	4561(2)	26(1)
C(13)	3572(1)	2500(1)	4775(1)	22(1)
C(14)	4491(2)	2007(2)	5739(2)	29(1)
C(15)	4165(2)	789(2)	6317(2)	37(1)
C(16)	2941(2)	57(2)	5931(2)	38(1)
C(17)	2031(2)	540(2)	4971(2)	33(1)
C(18)	2335(2)	1765(2)	4390(2)	27(1)
P(2)	0	10000	10000	21(1)
N(2)	218(1)	8218(1)	9542(1)	25(1)
N(3)	722(1)	7952(1)	8480(1)	25(1)
N(4)	1173(2)	7612(1)	7518(1)	33(1)
N(5)	1811(1)	10345(1)	9728(1)	26(1)
N(6)	2128(1)	11410(1)	9215(1)	27(1)
N(7)	2519(2)	12370(2)	8753(2)	42(1)
N(8)	432(1)	9641(1)	11704(1)	25(1)
N(9)	1548(1)	9118(1)	11969(1)	25(1)
N(10)	2548(2)	8646(2)	12311(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for ch1ppx1_0m.

P(1)-N(1)	1.5503(3)
P(1)-C(7)	1.7971(14)
P(1)-C(13)	1.8003(14)
P(1)-C(1)	1.8006(14)
N(1)-P(1)#1	1.5503(3)
C(1)-C(6)	1.397(2)
C(1)-C(2)	1.3976(19)
C(2)-C(3)	1.393(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.384(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.378(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.390(2)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.3945(19)
C(7)-C(12)	1.396(2)
C(8)-C(9)	1.391(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.384(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.385(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.388(2)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.394(2)
C(13)-C(18)	1.3952(19)
C(14)-C(15)	1.389(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.385(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.381(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.392(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
P(2)-N(5)#2	1.8040(12)
P(2)-N(5)	1.8040(12)
P(2)-N(8)#2	1.8071(12)
P(2)-N(8)	1.8071(12)
P(2)-N(2)#2	1.8121(12)
P(2)-N(2)	1.8121(12)
N(2)-N(3)	1.2290(18)
N(3)-N(4)	1.1325(18)
N(5)-N(6)	1.2254(17)
N(6)-N(7)	1.1341(18)
N(8)-N(9)	1.2282(17)
N(9)-N(10)	1.1266(18)

N(1)-P(1)-C(7)	110.33(5)
N(1)-P(1)-C(13)	110.80(5)
C(7)-P(1)-C(13)	108.06(6)
N(1)-P(1)-C(1)	111.00(5)
C(7)-P(1)-C(1)	108.34(6)
C(13)-P(1)-C(1)	108.22(6)
P(1)#1-N(1)-P(1)	180(2)
C(6)-C(1)-C(2)	119.46(13)
C(6)-C(1)-P(1)	118.36(10)
C(2)-C(1)-P(1)	122.18(11)
C(3)-C(2)-C(1)	119.61(14)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(4)-C(3)-C(2)	120.57(14)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	119.91(15)

C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	120.44(15)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(5)-C(6)-C(1)	120.02(14)
C(5)-C(6)-H(6)	120.0
C(1)-C(6)-H(6)	120.0
C(8)-C(7)-C(12)	119.99(13)
C(8)-C(7)-P(1)	122.28(11)
C(12)-C(7)-P(1)	117.73(10)
C(9)-C(8)-C(7)	119.38(14)
C(9)-C(8)-H(8)	120.3
C(7)-C(8)-H(8)	120.3
C(10)-C(9)-C(8)	120.45(14)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	120.29(14)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	119.91(15)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(7)	119.97(14)
C(11)-C(12)-H(12)	120.0
C(7)-C(12)-H(12)	120.0
C(14)-C(13)-C(18)	119.89(13)
C(14)-C(13)-P(1)	118.66(10)
C(18)-C(13)-P(1)	121.44(11)
C(15)-C(14)-C(13)	119.79(14)
C(15)-C(14)-H(14)	120.1
C(13)-C(14)-H(14)	120.1
C(16)-C(15)-C(14)	120.29(16)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(17)-C(16)-C(15)	120.05(15)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	120.40(14)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(17)-C(18)-C(13)	119.58(14)
C(17)-C(18)-H(18)	120.2
C(13)-C(18)-H(18)	120.2
N(5)#2-P(2)-N(5)	180(1)
N(5)#2-P(2)-N(8)#2	91.04(6)
N(5)-P(2)-N(8)#2	88.96(6)
N(5)#2-P(2)-N(8)	88.96(6)
N(5)-P(2)-N(8)	91.04(6)
N(8)#2-P(2)-N(8)	180(1)
N(5)#2-P(2)-N(2)#2	89.14(6)
N(5)-P(2)-N(2)#2	90.86(6)
N(8)#2-P(2)-N(2)#2	89.08(6)
N(8)-P(2)-N(2)#2	90.92(6)
N(5)#2-P(2)-N(2)	90.86(6)
N(5)-P(2)-N(2)	89.14(6)
N(8)#2-P(2)-N(2)	90.92(6)
N(8)-P(2)-N(2)	89.08(6)
N(2)#2-P(2)-N(2)	180(1)
N(3)-N(2)-P(2)	117.44(9)
N(4)-N(3)-N(2)	175.12(14)
N(6)-N(5)-P(2)	118.03(10)
N(7)-N(6)-N(5)	175.02(15)
N(9)-N(8)-P(2)	117.95(10)
N(10)-N(9)-N(8)	174.65(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+2,-z+2

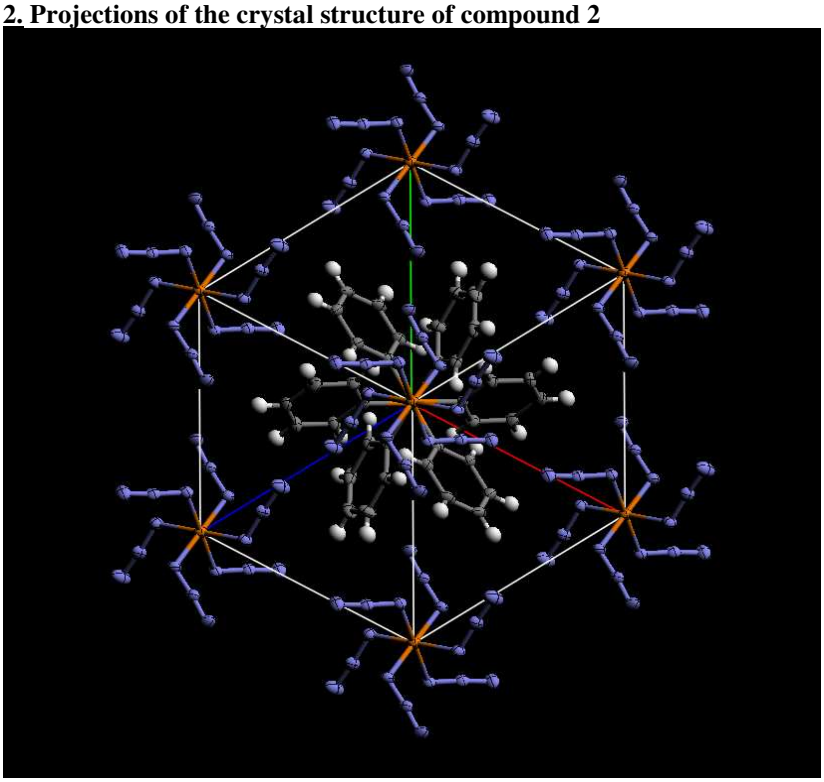
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for ch1ppx1_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	20(1)	15(1)	20(1)	-1(1)	0(1)	0(1)
N(1)	25(1)	21(1)	24(1)	-2(1)	-2(1)	-1(1)
C(1)	22(1)	21(1)	21(1)	-2(1)	0(1)	4(1)
C(2)	33(1)	22(1)	29(1)	-3(1)	1(1)	3(1)
C(3)	42(1)	29(1)	31(1)	-9(1)	1(1)	11(1)
C(4)	35(1)	43(1)	25(1)	-2(1)	6(1)	14(1)
C(5)	34(1)	39(1)	30(1)	2(1)	10(1)	2(1)
C(6)	30(1)	26(1)	26(1)	-1(1)	5(1)	0(1)
C(7)	21(1)	18(1)	25(1)	3(1)	1(1)	0(1)
C(8)	29(1)	29(1)	26(1)	2(1)	-1(1)	0(1)
C(9)	29(1)	43(1)	33(1)	11(1)	-7(1)	1(1)
C(10)	25(1)	34(1)	44(1)	15(1)	0(1)	7(1)
C(11)	29(1)	29(1)	38(1)	4(1)	5(1)	9(1)
C(12)	26(1)	25(1)	28(1)	1(1)	1(1)	4(1)
C(13)	24(1)	16(1)	24(1)	-2(1)	5(1)	1(1)
C(14)	34(1)	23(1)	29(1)	4(1)	0(1)	-1(1)
C(15)	47(1)	28(1)	37(1)	11(1)	2(1)	1(1)
C(16)	49(1)	22(1)	43(1)	5(1)	19(1)	-3(1)
C(17)	31(1)	23(1)	46(1)	-5(1)	17(1)	-6(1)
C(18)	24(1)	23(1)	34(1)	-2(1)	6(1)	-1(1)
P(2)	22(1)	17(1)	24(1)	2(1)	0(1)	1(1)
N(2)	31(1)	18(1)	27(1)	1(1)	3(1)	1(1)
N(3)	26(1)	16(1)	31(1)	1(1)	-1(1)	-1(1)
N(4)	42(1)	23(1)	35(1)	-2(1)	8(1)	0(1)
N(5)	24(1)	22(1)	32(1)	5(1)	2(1)	1(1)
N(6)	22(1)	27(1)	31(1)	5(1)	-3(1)	-2(1)
N(7)	30(1)	40(1)	56(1)	21(1)	-5(1)	-7(1)
N(8)	28(1)	23(1)	25(1)	4(1)	0(1)	4(1)
N(9)	32(1)	21(1)	22(1)	-1(1)	-1(1)	3(1)
N(10)	39(1)	41(1)	27(1)	-3(1)	-5(1)	15(1)

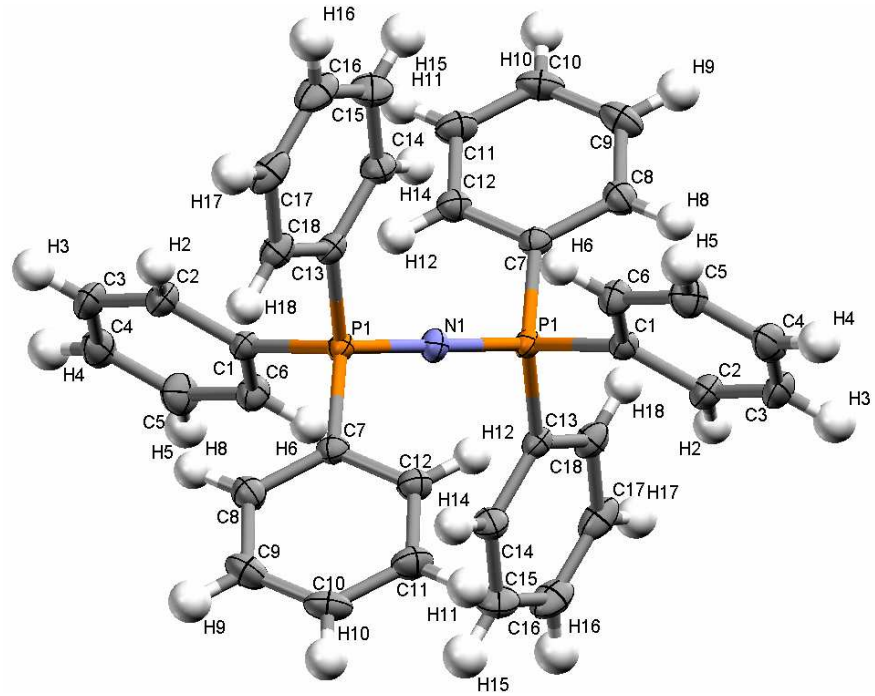
Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ch1ppx1_0m.

	x	y	z	U(eq)
H(2)	4082	1705	2185	34
H(3)	5208	1271	234	41
H(4)	6671	2940	-574	41
H(5)	7012	5055	550	41
H(6)	5908	5515	2504	33
H(8)	2096	4116	1710	33
H(9)	23	5233	1270	42
H(10)	-843	6685	2878	41
H(11)	360	7055	4938	38
H(12)	2431	5947	5400	32
H(14)	5336	2502	6000	34
H(15)	4786	457	6981	45
H(16)	2725	-778	6325	45
H(17)	1193	33	4706	40
H(18)	1705	2097	3735	32

2. Projections of the crystal structure of compound 2



Packing of compound **2** in the crystal, projection (Mercury plot) along the crystallographic S_6 axis. Vibrational ellipsoids set at the 50% probability level, color code: blue, N; grey, C; orange, P; white, H.



Projection (Mercury plot) of the structure of the PPN^+ cation of **2** in the crystal, vibrational ellipsoids set at the 50% probability level, color code as above.

3. Calculated Cartesian Coordinates and energies of the S_6 symmetric minimum structure[1]

	S_6 symmetric minimum structure RHF/6-311G*, E = −1320.643510 a.u., NIMAG = 0			S_6 symmetric minimum structure B3LYP/6-311G*, E = −1326.8986731 a.u., NIMAG = 0			D_3 symmetric minimum structure RHF/6-311G*, E = − 1320.63048985 a.u., NIMAG = 0		
	Coordinates / Å								
Atom	x	y	z	x	y	z	x	y	z
P	0	0	0	0	0	0	0	0	0
N	0.707083	1.300668	1.030555	0.701211	1.327984	1.051951	0.683748	1.324976	1.019645
N	-1.47995	-0.03798	1.030555	-1.50067	-0.05673	1.051951	-1.48934	-0.07035	1.019645
N	-0.70708	-1.30067	-1.03056	-0.70121	-1.32798	-1.05195	-0.80559	-1.25463	-1.01965
N	0.77287	-1.26269	1.030555	0.799462	-1.27126	1.051951	0.805589	-1.25463	1.019645
N	1.479953	0.037983	-1.03056	1.500673	0.056726	-1.05195	1.489336	-0.07035	-1.01965
N	-0.77287	1.262686	-1.03056	-0.79946	1.271258	-1.05195	-0.68375	1.324976	-1.01965
N	0	2.200976	1.415774	0	2.245815	1.43624	1.725971	1.156707	1.607094
N	-1.9061	-1.10049	1.415774	-1.94493	-1.12291	1.43624	-1.86472	0.916381	1.607094
N	0	-2.20098	-1.41577	0	-2.24582	-1.43624	-0.13875	-2.07309	-1.60709
N	1.906101	-1.10049	1.415774	1.944933	-1.12291	1.43624	0.138752	-2.07309	1.607094
N	1.906101	1.100488	-1.41577	1.944933	1.122908	-1.43624	1.864723	0.916381	-1.60709
N	-1.9061	1.100488	-1.41577	-1.94493	1.122908	-1.43624	-1.72597	1.156707	-1.60709
N	-0.58207	3.04873	1.797773	-0.57693	3.13898	1.839794	2.66831	1.093557	2.166581
N	-2.34925	-2.02845	1.797773	-2.42997	-2.06912	1.839794	-2.2812	1.764045	2.166581
N	0.582065	-3.04873	-1.79777	0.576926	-3.13898	-1.83979	0.387107	-2.8576	-2.16658
N	2.93131	-1.02028	1.797773	3.006899	-1.06986	1.839794	-0.38711	-2.8576	2.166581
N	2.349246	2.028448	-1.79777	2.429974	2.069123	-1.83979	2.281203	1.764045	-2.16658
N	-2.93131	1.020283	-1.79777	-3.0069	1.069858	-1.83979	-2.66831	1.093557	-2.16658

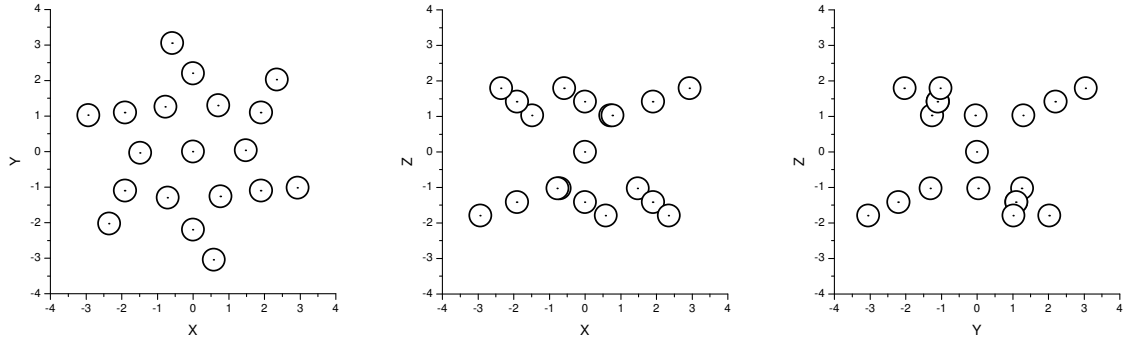
S4. Results of frequency calculations of the S_6 and D_3 minimum energy structures[a]

No	S_6, RHF/6-311G*					S_6, B3LYP/6-311G*				D_3, RHF/6-311G*				
	ν	S	f	IR	Ra	ν	S	f	IR	ν	S	f	IR	Ra
1	53.3	E_u	48.0	0.01	0	37.9	E_u	36.6	0.05	31.0	E	28.0	0.25	4.08
2	53.3	E_u	48.0	0.01	0	37.9	E_u	36.6	0.05	31.0	E	28.0	0.25	4.08
3	54.7	A_g	49.3	0	10.0	41.0	A_g	39.7	0	39.3	A_2	35.4	0.31	0
4	70.1	A_u	63.2	0.30	0	51.4	A_u	49.7	0.17	47.4	E	42.7	0.24	5.86
5	78.1	E_g	70.4	0	17.3	56.8	E_g	54.9	0	47.4	E	42.7	0.24	5.86
6	78.1	E_g	70.4	0	17.3	56.8	E_g	54.9	0	50.8	A_1	45.8	0	16.7
7	101.5	A_u	91.5	0.01	0	85.3	A_u	82.5	0.17	97.4	A_1	87.8	0	0.68
8	120.2	E_u	108.3	1.41	0	100.2	E_u	96.9	1.78	132.1	E	119.1	0.03	5.81
9	120.2	E_u	108.3	1.41	0	100.2	E_u	97.0	1.78	132.1	E	119.1	0.03	5.81
10	162.1	E_g	146.1	0	6.11	132.9	E_g	128.5	0	168.6	E	151.9	2.68	2.85
11	162.1	E_g	146.1	0	6.11	132.9	E_g	128.5	0	168.6	E	151.9	2.68	2.85
12	209.9	A_g	189.1	0	6.69	178.1	A_g	172.3	0	227.7	A_2	205.3	1.79	0
13	288.1	E_u	259.7	1.32	0	249.2	E_u	241.0	1.65	275.8	E	248.6	0.02	9.71
14	288.1	E_u	259.7	1.32	0	249.2	E_u	241.0	1.65	275.8	E	248.6	0.02	9.71
15	310.9	A_u	280.3	4.51	0	265.1	A_u	256.4	4.38	297.8	A_1	268.4	0	6.95
16	343.2	E_g	309.4	0	7.17	300.4	E_g	290.5	0	334.1	E	301.1	1.80	4.66
17	343.2	E_g	309.4	0	7.17	300.4	E_g	290.5	0	334.1	E	301.1	1.80	4.66

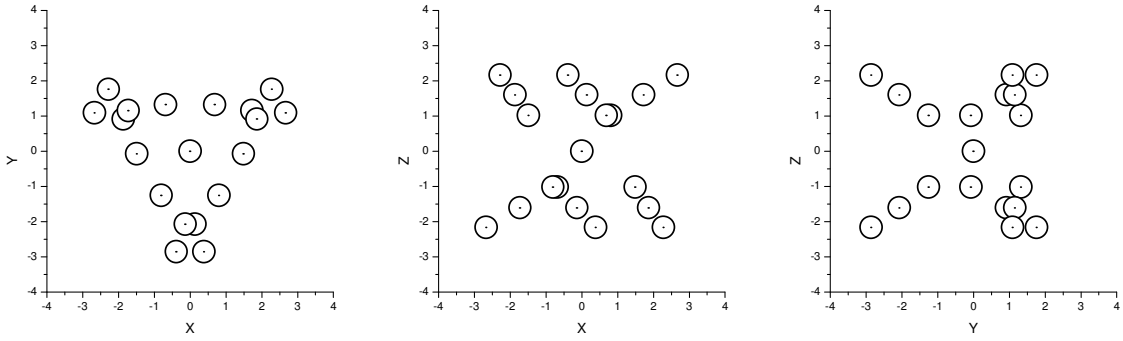
18	413.6	A_g	372.7	0	1.96	358.3	A_g	346.5	0	395.3	E	356.3	23.8	1.26
19	426.9	E_g	384.7	0	8.25	376.5	E_g	364.1	0	395.3	E	356.3	23.8	1.26
20	426.9	E_g	384.7	0	8.25	376.5	E_g	364.1	0	408.4	A_1	368.1	0	4.76
21	454.8	E_u	409.9	10.6	0	394.7	A_u	381.8	5.97	460.7	A_2	415.3	34.9	0
22	454.8	E_u	409.9	10.6	0	395.5	E_u	382.5	5.82	469.7	E	423.3	5.6	1.22
23	460.6	A_u	415.1	30.0	0	395.5	E_u	382.5	5.82	469.7	E	423.3	5.6	1.22
24	509.5	A_g	459.2	0	19.7	432.4	A_g	418.2	0	508.4	A_1	458.2	0	19.4
25	600.2	E_u	541.0	384	0	529.4	E_u	512.0	327	587.9	E	529.9	277	11.7
26	600.2	E_u	541.0	384	0	529.4	E_u	512.0	327	587.9	E	529.9	277	11.7
27	600.8	A_u	541.5	525	0	531.7	A_u	514.3	423	617.7	A_2	556.7	712	0
28	699.8	E_u	630.7	27.1	0	595.0	E_u	575.5	14.8	688.8	E	620.8	0.56	0.01
29	699.8	E_u	630.7	27.1	0	595.0	E_u	575.5	14.8	688.8	E	620.8	0.56	0.01
30	700.0	E_g	630.9	0	0.62	595.0	E_g	575.5	0	697.5	A_2	628.7	198	0
31	700.0	E_g	630.9	0	0.62	595.0	E_g	575.5	0	702.7	E	633.4	45.1	0.41
32	701.5	A_g	632.3	0	0.87	597.5	A_g	577.9	0	702.7	E	633.4	45.1	0.41
33	708.5	A_u	638.5	187	0	600.2	A_u	580.5	110	707.9	A_1	638.0	0	2.34
34	788.0	A_g	710.2	0	14.3	678.7	A_g	656.5	0	788.8	A_2	710.9	122	0
35	809.5	E_g	729.6	0	3.15	697.1	E_g	674.2	0	796.5	A_1	717.9	0	11.8
36	809.5	E_g	729.6	0	3.15	697.1	E_g	674.2	0	803.4	E	724.1	11.4	2.13
37	817.1	A_u	736.4	177	0	698.4	A_u	675.5	90.4	803.4	E	724.1	11.4	2.13
38	844.1	E_u	760.8	399	0	721.9	E_u	698.3	241	832.1	E	750.0	272	3.68
39	844.1	E_u	760.8	399	0	722.0	E_u	698.3	241	832.1	E	750.0	272	3.68
40	1417.1	E_g	1277.2	0	2.67	1353.6	E_g	1309.2	0	1409.6	A_2	1270.5	908	0
41	1414.1	E_g	1274.5	0	2.67	1353.6	E_g	1309.2	0	1413.2	E	1273.7	885	0.31
42	1420.4	A_u	1280.2	521	0	1354.2	A_u	1309.8	202	1413.2	E	1273.7	885	0.31
43	1431.3	E_u	1290.1	1006	0	1358.8	E_u	1314.3	350	1433.4	E	1292.0	52.4	4.95
44	1431.3	E_u	1290.1	1006	0	1358.8	E_u	1314.3	350	1433.4	E	1292.0	52.4	4.95
45	1458.8	A_g	1314.8	0	15.3	1368.2	A_g	1323.3	0	1463.6	A_1	1319.1	0	20.7
46	2461.1	E_g	2218.2	0	190	2236.7	A_u	2163.3	816	2452.6	A_2	2210.5	2209	0
47	2461.1	E_g	2218.2	0	190	2237.1	E_g	2163.7	0	2455.2	E	2212.9	1016	116
48	2467.2	A_u	2223.7	1170	0	2237.1	E_g	2163.7	0	2455.2	E	2212.9	1016	116
49	2472.7	E_u	2228.7	2717	0	2243.2	E_u	2169.6	1732	2464.5	E	2221.3	1458	91.9
50	2472.7	E_u	2228.7	2717	0	2243.2	E_u	2169.6	1731	2464.5	E	2221.3	1458	91.9
51	2505.6	A_g	2258.3	0	297	2262.5	A_g	2188.3	0	2501.7	A_1	2254.8	0	303

a) ν, wavenumber (cm^{-1}); f column shows the wavenumbers obtained using the recommended scaling factors f = 0.9013 (RHF/6-311G*) and 0.9672 (B3LYP/6-311G*) taken from Table 6 in ref. [2]; S denotes the symmetry species of the mode; columns IR and Ra show calculated IR intensities (km mol^{-1}) and Raman scattering activities ($Å^4$ amu^{-1}), respectively.

4A. Projections of the calculated D_3 and S_6 symmetric structures in the x,y and x,z and y,z planes, scale / Å



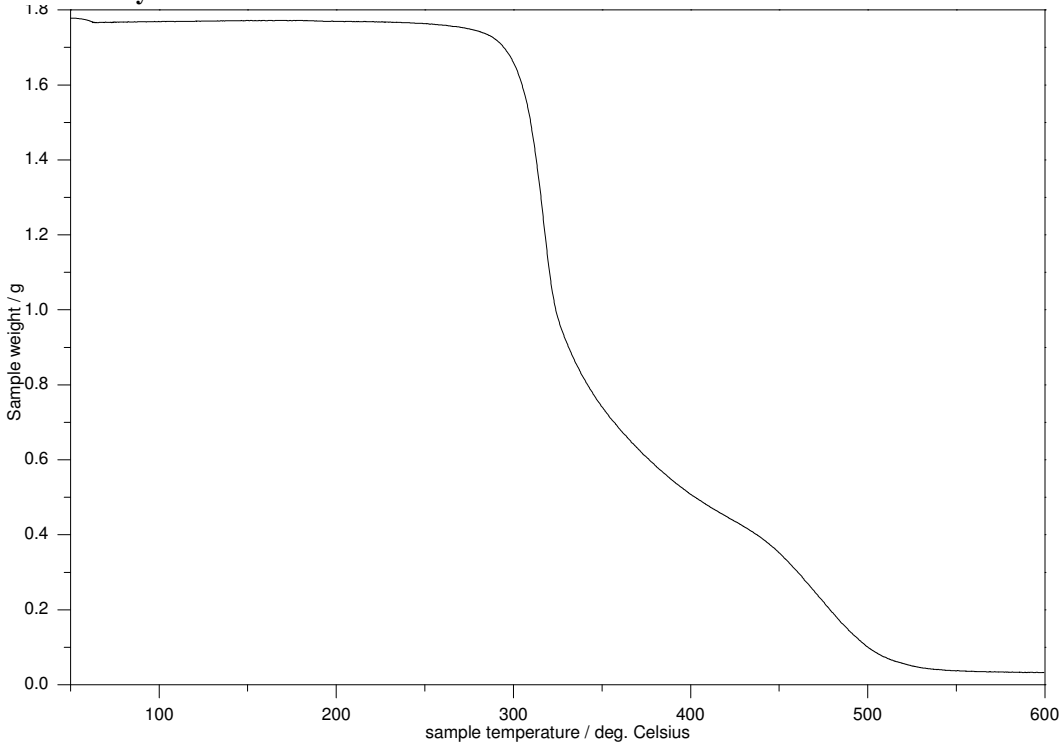
S_6



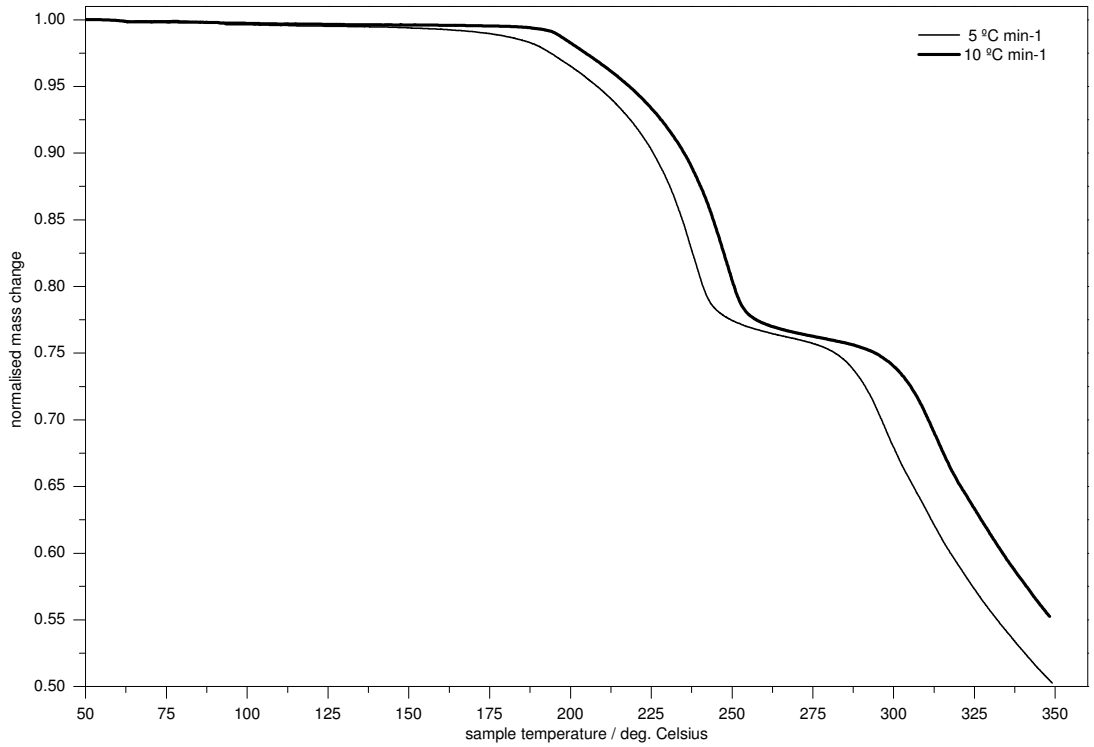
D_3

$D(N_\alpha \cdots N_\beta')$ = 2.7, 2.9; $D(N_\beta \cdots N_\beta')$ = 3.6, 3.2 Å, S_6 vs. D_3. Circles denote the position of N or P atoms.

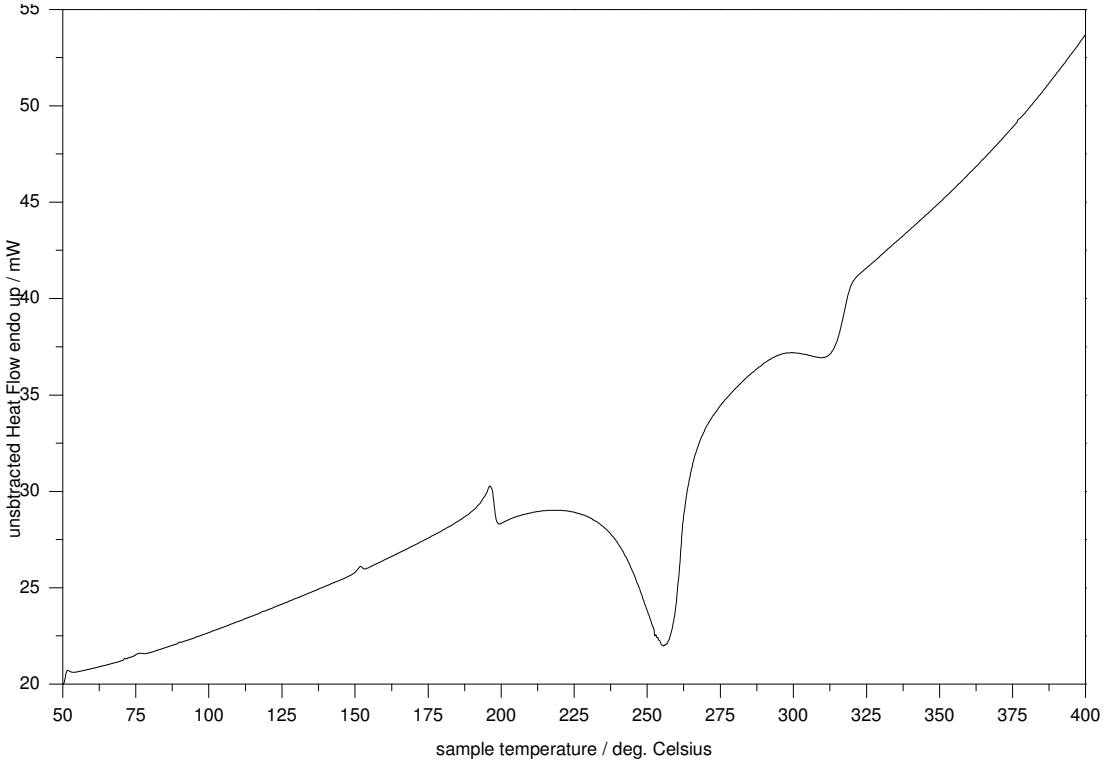
5. Thermal Analyses



TGA curve of $(PPN)N_3$, heating rate 10 ºC / min.



Normalised TGA curves of **2**, heating rate 5 and ºC / min.



DSC curve of **2**, heating rate 10 ºC / min.

6. Spectroscopic data of 2

NMR spectra were recorded in CH_3CN-d_3 or CH_3CN-d_3 / CH_3CN (1 : 4) mixture and are calibrated against residual solvent proton signal (^1H, 1.94 ppm), the natural solvent abundance (^{13}C, 1.32 ppm), or externally (0.0 ppm, 85% H_3PO_4, ^{31}P; neat CH_3NO_2, ^{14}N). Approximate line widths $\Delta\nu_{1/2}$ were determined by Lorentzian curve fitting.

IR (nujol, cm^{-1}) $\tilde{\nu}$ = 3378 vw ($\nu_{asym}(N_3)$ + $\nu_{sym}(N_3)$), 2561 vw $2\times\nu_{sym}(N_3)$, 2113 vs $\nu_{asym}(N_3)$, 1589 vw, 1481(3), 1437(8), 1310(2)sh, 1291(28) $\nu_{sym}(N_3)$, 1182(3), 1163(1), 1117(14), 1105(4)sh, 1026(1), 997(2), 754(3), 724(25), 708(5), 690(13), 573(3), 534(38). IR (CH_3CN, cm^{-1}) $\tilde{\nu}$ = 3379vvw, 2548vvw, 2116vs, 1288w, 1117vw, 999vw, 727w, 696vw, 573vw, 548w, 536w. IR (CH_2Cl_2, cm^{-1}) $\tilde{\nu}$ = 3376 vvw $\nu_{asym}(N_3)$ + $\nu_{sym}(N_3)$, 2559vvw $2\times\nu_{sym}(N_3)$, 2115vs $\nu_{asym}(N_3)$, 1590vw, 1485vw, 1440w, 1288w $\nu_{sym}(N_3)$, 1187vw, 1117m, 1028vw, 999vw, 572vw, 539w. IR (THF, cm^{-1}) $\tilde{\nu}$ = 2112vs $\nu_{asym}(N_3)$, 1291w $\nu_{sym}(N_3)$, 727w, 695vw, 539w.

Raman of **2**: $\tilde{\nu}$ = 2142(3) $\nu_{sym}(N_3)$, 2110(3) $\nu_{sym}(N_3)$, 1590(19), 1577(8), 1440(2), 1303(10) $\nu_{asym}(N_3)$, 1286(5) $\nu_{asym}(N_3)$, 1184(5), 1162(6), 1113(16), 1028(32), 1001(100), 987(5)sh, 724(5), 686(6) δ, 659(30), 616(27), 455(42) δ, 389(10) δ, 313(11) δ; δ indicates lines due to δ vibrations of $[P(N_3)_6]^-$; $(PPN)N_3$: $\tilde{\nu}$= 1591(34), 1577(10), 1140(3), 1321(9)sh $\nu_{asym}(N_3)$, 1316(13) $\nu_{asym}(N_3)$, 1186(9), 1160(7), 1112(24), 1030(33), 1002(100), 726(5), 667(36), 615(31), 489(4) δ N_3, 366(8) δ N_3.

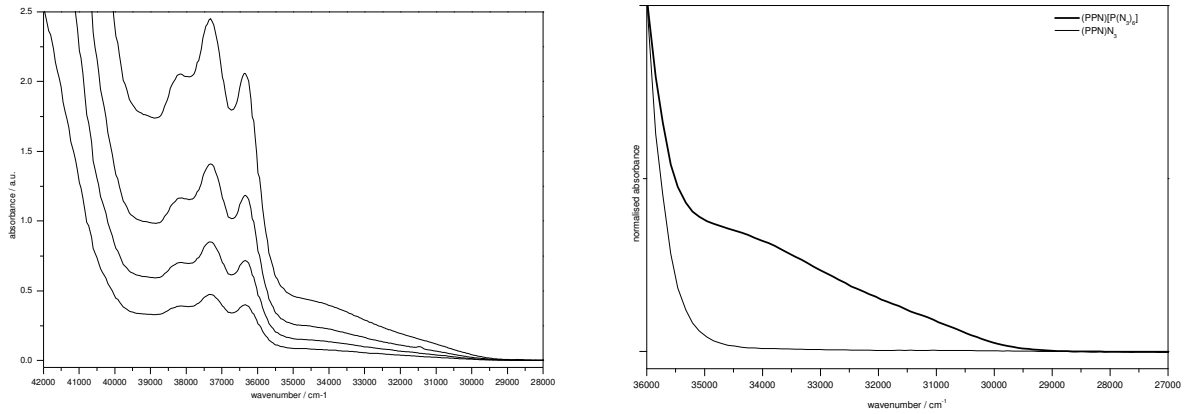
^1H NMR (CD_3CN, ppm) δ = 7.44-7.70 (m).

$^{13}C\{^1H\}$ NMR (CD_3CN, ppm) δ = 128.3 (dd, C_{ipso}, $^1J_{CP}$ = 107.9 Hz, $^3J_{CP}$ = 1.9 Hz), 130.4 (m, C_{meta}), 133.3 (m, C_{ortho}), 134.6 (m, C_{para}).

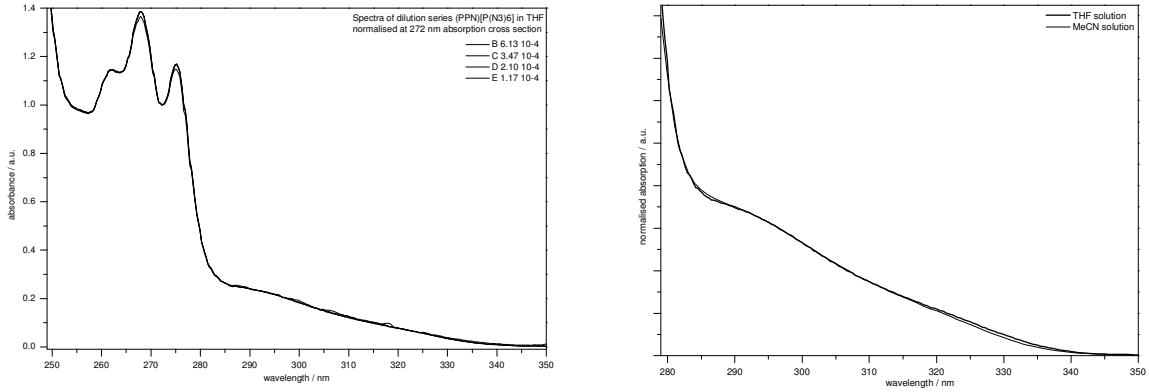
$^{31}P\{^1H\}$ NMR (CD_3CN, ppm) δ = 20.8 (s, $N(P(C_6H_5)_3)_2$, $\Delta\nu_{1/2}$ = 5 Hz), −178.8 (s, $P(N_3)_6$, $\Delta\nu_{1/2}$ = 53 Hz).

$^{14}N\{^1H\}$ NMR (CD_3CN, ppm) δ = −170 ($\Delta\nu_{1/2}$ = 90 Hz), −268 ($\Delta\nu_{1/2}$ = 670 Hz), −141 ($\Delta\nu_{1/2}$ = 30 Hz).

UV absorption spectra of **2** and $(PPN)N_3$ in THF and MeCN



Dilution series of **2** in THF, *c* ca. 6.1, 3.5, 2.1, 1.2 x 10^{-4} mol l^{-1} (left), and layer of normalised spectra of $(PPN)N_3$ (ca. 1.1 x 10^{-3} mol l^{-1}) and $(PPN)[P(N_3)_6]$ (6 x 10^{-4} mol l^{-1}) recorded in MeCN (right).



Dilution series in THF as before, spectra normalized using the absorption cross section at 272 nm, revealing no significant concentration dependence in the investigated range of concentrations of **2** (left); layer of normalized spectra of **2** in THF and MeCN at similar concentrations (right).

7. Details of empirical lattice energy calculations

Lattice potential energies (lattice energies) were calculated using the generalized empirical formula $U_{pot} = |z_+||z_-|\nu(\alpha V^{-1/3}+\beta)$, (i), z_+ = cation charge, z_- = anion charge, α = 138.7 kJ mol^{-1} nm, β = 27.6 kJ mol^{-1}, V = Volume of formula unit obtained from crystal data, ν = number of ions $p + q$ per formula unit M_pX_q, as given in ref. [3].

a) Experimental unit cell volumes of the salts involved in the proposed initial decomposition step

$(PPN)[P(N_3)_6]$	0.95483(16) nm^3, Z = 1
$(PPN)_2[Si(N_3)_6]$	1.6939(7) nm^3, Z = 1 [4]
$(PPN)_2[Ge(N_3)_6]$	1.6946(11) nm^3, Z = 1 [5]
$(PPN)N_3$	4.5775(16) nm^3, Z = 6 [6]

b) Experimental unit cell volumes of reference compounds (diffraction studies)

NaN_3	0.2022 nm^3, Z = 3 [7, 8]
KN_3	0.2620 nm^3, Z = 4 [8-11]
RbN_3	0.2997 nm^3, Z = 4 [8, 11]
CsN_3	0.3631 nm^3, Z = 4 [11]
$(NMe_4)N_3$	1.2787 nm^3, Z = 8 [12]
$(PPN)_2ReCl_6$	6.428(3) nm^3, Z = 4 [13]
$(PPN)UF_6$	1.8256(34) nm^3, Z = 2 [14]
$(PPN)I_3$	1.7793 nm^3, Z = 2 [15]
(PPN)SCN	3.2318 nm^3, Z = 4 [16]
$(PPN)FeCl_4$	3.576056 nm^3, Z = 4 [17]

c) Thermochemical Ion Volumes taken from reference [3]

$ReCl_6^{2-}$	0.224±0.007 nm^3
UF_6^-	0.167±0.041 nm^3
I_3^-	0.171 nm^3
SCN^-	0.071±0.003 nm^3
$FeCl_4^-$	0.155 nm^3
NMe_4^+	0.113±0.013 nm^3

d) Volumes generated using Goldschmidt radii as quoted in reference [3]

Na^+	0.00394 nm^3
K^+	0.00986 nm^3
Rb^+	0.01386 nm^3
Cs^+	0.01882 nm^3

e) Thermochemical volumes derived using the parameters from (a) – (d)

PPN^+	0.726±0.022 nm^3
$P(N_3)_6^-$	0.228±0.022 nm^3
$P(N_3)_4^+$	0.156±0.022 nm^3 (*
$Si(N_3)_6^{2-}$	0.241±0.044 nm^3
$Ge(N_3)_6^{2-}$	0.242±0.044 nm^3
N_3^-	0.060±0.010 nm^3
$Si(N_3)_5^-$	0.203±0.044 nm^3 (**
$Ge(N_3)_5^-$	0.204±0.044 nm^3 (**

*) estimated, $V([P(N_3)_4]^+) \approx 13/19\ V([P(N_3)_6]^-)$

**) estimated, $V([E(N_3)_5]^-) \approx 16/19\ V([E(N_3)_6]^{2-})$

f) Estimated potential lattice energies using formula (i) (*

NaN_3	–749(±36) kJ mol^{-1}
$Na[P(N_3)_6]$	–507(±14) kJ mol^{-1}
$(PPN)[P(N_3)_6]$	–337(±4) kJ mol^{-1}
$[P(N_3)_4]^+[P(N_3)_6]^-$ (**	–447(±15) kJ mol^{-1}
$(PPN)_2[Si(N_3)_6]$	–864(±12) kJ mol^{-1}
$(PPN)_2[Ge(N_3)_6]$	–864(±12) kJ mol^{-1}
$(PPN)[Si(N_3)_5]$ (**	–339(±7) kJ mol^{-1}
$(PPN)[Ge(N_3)_5]$ (**	–339(±7) kJ mol^{-1}
$(PPN)N_3$	–356(±4) kJ mol^{-1}

*) error estimates based on propagation of errors of volumes. Function (i) has a correlation coefficient of R = 0.91 for MX, MX_2 and M_2X salts. Imprecision of the predicted energies as a result of poor correlation have not been included. The experimentally determined lattice energy of NaN_3 is ca. 725 kJ mol^{-1}, which function (i) reproduces within the error margins.

**) Hypothetical compounds.

Estimation of gain or loss of lattice energy:

a)	$Na[P(N_3)_6] \rightarrow NaN_3 + P(N_3)_5$	–242(±50) kJ mol^{-1}
b)	$Na[P(N_3)_6] \rightarrow NaN_3 + ½\ [P(N_3)_4][P(N_3)_6]$	–466(±58) kJ mol^{-1}
c)	$(PPN)[P(N_3)_6] \rightarrow (PPN)N_3 + P(N_3)_5$	–19(±8) kJ mol^{-1}
d)	$(PPN)[P(N_3)_6] \rightarrow (PPN)N_3 + ½\ [P(N_3)_4][P(N_3)_6]$	–243(±16) kJ mol^{-1}
e)	$(PPN)_2[E(N_3)_6] \rightarrow (PPN)N_3 + (PPN)[E(N_3)_5]$	+169(±23) kJ mol^{-1}

Discussion. The nature of phosphorous pentaazide is unknown and there are two obvious structures conceivable at room temperature, $[P(N_3)_4][P(N_3)_6]$ and $P(N_3)_5$. It can be expected that both forms would give rise to a mass spec signal corresponding to $N_{15}P$. The thermochemical measurements of complex **2** show a 130 to 240 kJ mol^{-1} greater enthalpic change than complexes **3** and **4** during step 1 of the decomposition. Depending on the nature of phosphorus pentaazide the difference in the net lattice energy change is ca. 190 kJ mol^{-1} and ca. 410 kJ mol^{-1} (see eq.s c, d and e). The gas phase affinities of N_3^- to $P(N_3)_5$ and $[E(N_3)_5]^-$ are not known. A crude estimate calculated

on the SCF/6-31G* level yielded ca. −200 kJ mol^{-1} for the reaction $P(N_3)_5 + N_3^- \rightarrow [P(N_3)_6]^-$. At this stage it becomes obvious that ΔH for step 1 in the decomposition of (PPN)[$P(N_3)_6$] is much more negative than the sum of azide dissociation energy and net gain in lattice energy, ca. +180 kJ mol^{-1} (eq. c, estimated) vs. −946 kJ mol^{-1} (experimental). Clearly, under the conditions of the thermal analysis the evolved phosphorous pentaazide decomposes itself, releasing dinitrogen. This is supported by the 23% mass loss, which would correspond to ca. 7 equivalents of N_2, leaving behind (PPN)N_3 and 'PN'. Irrespective of the nature of phosphorus azide, it is nevertheless clear that a dissociation of the $E(N_3)_6^{2-}$ salts has a penalty of ca. 170 kJ mol^{-1} of lattice energy to overcome, which contributes to their slightly higher stability. More theoretical and experimental investigations are necessary to fully understand the thermochemical behaviour of these energetic compounds.

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