Supplementary information

Structural and thermodynamic properties of molecular complexes of aluminum and gallium trihalides with bifunctional donor pyrazine: decisive role of Lewis acidity on 1D polymer formation

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Study of the pyrolytic products of Al_2Br_6pyz. In conclusion of the tensimetry experiment 5 the system was kept at 415 ºC for 4 hours, and after the volatile compounds were separated (condensed into the compartment at room temperature upon heating of the system at 280-300 ºC for 36 hours) and analyzed by mass-spectrometry (170 ºC, 70 eV). Ions $AlBr_2pyz^+$ (22%) and $AlBr_3pyz^+$ (15%) indicate that some amount of the $AlBr_3$·pyz complex remained after pyrolysis. However, the most intensive ion signal $AlBr_2NH_3^+$ (100%) indicates the formation of an $AlBr_3NH_3$ adduct. Presumably ammonia is generated via pyrolysis of pyrazine. Moreover, the detection of the ion $AlBr_2C_5H_6N_2^+$ (15%) may be assigned to a fragmentation upon ionization of the $AlBr_3$-methylpyrazine complex. Its occurance suggests that the formation of methylated pyrazine occurs via Friedel-Crafts reactions in the melt, catalyzed by aluminum tribromide. Formation of methylated pyridine complexes was earlier observed via pyrolysis of $GaCl_3$ adduct with piperidine (A. S. Litvinenko, A. Y. Timoshkin and H. F. Schaefer, *Polyhedron*, 2006, **25**, 2465).

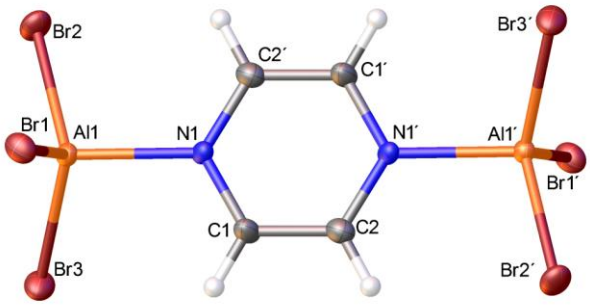


Figure S1. Molecular structure of complex $AlBr_3 \cdot pyz \cdot AlBr_3$ (**1**) in the crystal. Selected interatomic distances (Å): Al1-N1 1.999(6), Al1-Br1 2.2538(18), Al1-Br2 2.267(2), Al1-Br3 2.2465(16). Selected bond angles (deg): Br1-Al1-Br2 113.40(6), Br1-Al1-Br3 116.88(7), Br1-Al1-N1 100.85(18), Br2-Al1-Br3 114.67(9), Br2-Al1-N1 104.43(16), Br3- Al1-N1 104.17(15).

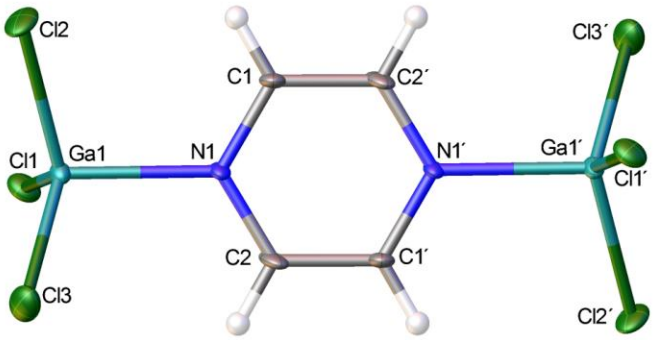


Figure S2. Molecular structure of complex $GaCl_3 \cdot pyz \cdot GaCl_3$ (**2**) in the crystal. Selected interatomic distances (Å): Ga1-N1 2.044(7), Ga1-Cl1 2.135(2), Ga1-Cl2 2.147(2), Ga1-Cl3 2.129(2). Selected bond angles (deg): Cl1- Ga1-Cl2 112.99(8), Cl1-Ga1-Cl3 116.86(8), Cl1-Ga1-N1 101.6(2), Cl2-Ga1-Cl3 116.05(9), Cl2-Ga1-N1 103.10(19), Cl3-Ga1- N1 103.40(19).

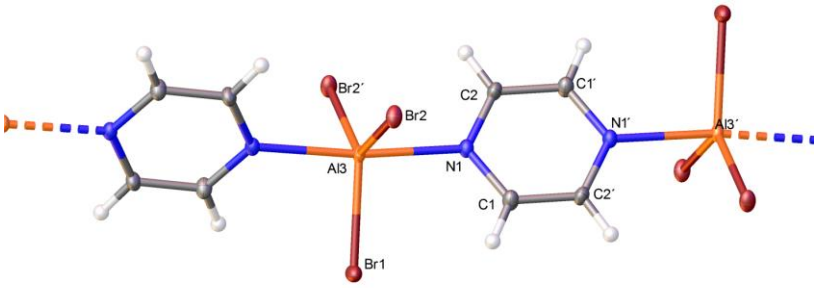


Figure S3. Molecular structure of complex $(AlBr_3 \cdot pyz)_\infty$ (**3**) in the crystal. Selected interatomic distances (Å): Al3-N1 2.133(2), Al3-Br1 2.3099(15), Al3-Br2 2.3257(8). Selected bond angles (deg): Br1-Al3-Br2 115.95(3), Br1-Al3-N1 93.42(8), Br2-Al3-N1 86.38(7), Br2- Al3- Br2' 128.09(6), Br2-Al3-N1 90.63(7), N1-Al3-N1 173.16(13).

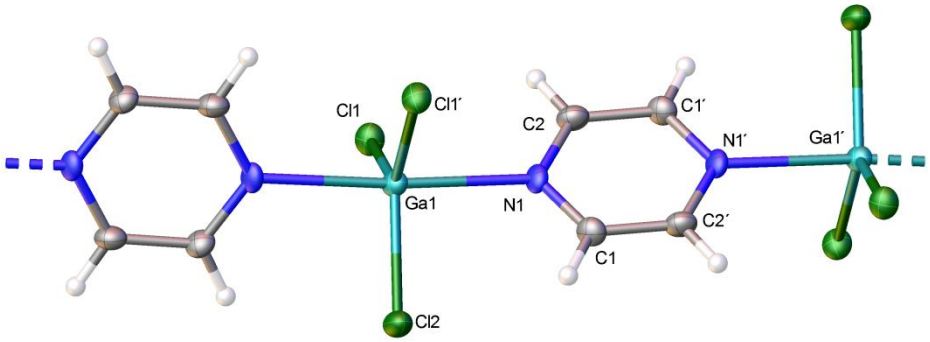


Figure S4. Molecular structure of complex $(GaCl_3 \cdot pyz)_\infty$ (**4**) in the crystal. Selected interatomic distances (Å): Ga1-N1 2.203(5), Ga1-Cl1 2.1855(14), Ga1-Cl2 2.174(2). Selected bond angles (deg): Cl1-Ga1-Cl2 117.32(4), Cl1-Ga1-N1 90.50(12), Cl1-Ga1-Cl1' 125.36(6), Cl1- Ga1-N1 87.51(12), Cl2-Ga1-N1 92.16(12), N1-Ga1-N1' 175.68(17).

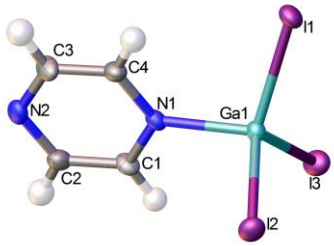


Figure S5. Molecular structure of complex $GaI_3 \cdot pyz$ (**5**) in the crystal. Selected interatomic distances (Å): Ga1-N1 2.037(6), Ga1-I1 2.5137(10), Ga1-I2 2.5094(9), Ga1-I3 2.5081(11). Selected bond angles (deg): I1-Ga1-I2 116.57(4), I1-Ga1-I3 112.09(4), I1-Ga1-N1 102.54(16), I2-Ga1-I3 113.83(3), I2-Ga1-N1 105.09(16), I3-Ga1-N1 105.05(17).

Table S1. Crystal Structure Information for investigated complexes.

empiric formula	$C_4H_4Al_2Br_6N_2$ (**1**)	$C_4H_4Cl_6Ga_2N_2$ (**2**)	$C_4H_4AlBr_3N_2$ (**3**)	$C_4H_4Cl_3GaN_2$ (**4**)	$C_4H_4I_3GaN_2$ (**5**)
	Al_2Br_6·pyz	Ga_2Cl_6·pyz	$(AlBr_3$·pyz$)_\infty$	$(GaCl_3$·pyz$)_\infty$	GaI_3·pyz
M_r	613.45	432.23	346.77	256.16	530.51
crystal size [mm]	0.32 × 0.13 × 0.06	0.49 × 0.32 × 0.23	0.60 × 0.25 × 0.18	0.13 × 0.02 × 0.02	0.43 × 0.20 × 0.20
T [K]	123(1)	123(1)	123(1)	123(1)	123(1)
□ [Å]	1.54178 (Cu)	1.54178 (Cu)	0.71073 (Mo)	1.54178 (Cu)	0.71073 (Mo)
absorption correction type	semi-empirical	analytical	analytical	semi-empirical	analytical
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$	$P\bar{1}$
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
a [Å]	6.9688(3)	6.6265(7)	11.2325(11)	11.1474(7)	7.1493(10)
b [Å]	15.8935(4)	15.4544(10)	6.7023(4)	6.3189(5)	9.3992(17)
c [Å]	7.5060(3)	7.1401(8)	11.8372(19)	11.5922(8)	9.5165(12)
□ [°]	90	90	90	90	60.776(16)
□ [°]	117.596(5)	115.721(13)	104.753(14)	101.953(7)	79.488(12)
□ [°]	90	90	90	90	87.758(13)
V [Å^3]	736.78(6)	658.76(13)	861.77(18)	798.84(10)	547.79(17)
Z	2	2	4	4	2
$□_{calcd}$ [g/cm^3]	2.765	2.179	2.673	2.130	3.216
□ [mm^{-1}]	20.616	15.948	14.072	13.328	10.908
□ range [°]	5.57 – 65.06	5.73 – 66.68	3.56 – 30.51	7.81 – 58.92	3.46 – 26.50
completeness to □	0.990	0.985	0.998	0.989	0.995
index range	$-7 \le h \le 6$	$-6 \le h \le 7$	$-15 \le h \le 16$	$-12 \le h \le 11$	$-9 \le h \le 9$
	$-18 \le k \le 18$	$-17 \le k \le 18$	$-7 \le k \le 9$	$-6 \le k \le 6$	$-12 \le k \le 12$
	$-8 \le l \le 8$	$-8 \le l \le 8$	$-16 \le l \le 16$	$-12 \le l \le 12$	$-12 \le l \le 12$
unique reflections I> 2□ (R_{int})	1056 (0.0713)	1088 (0.1356)	1027 (0.0426)	510 (0.0421)	2125 (0.393)
data/restraints/parameters	1250/0/64	1151/0/64	1316/0/48	565/0/47	2573/0/91
GOF in F^2	1.040	1.099	0.986	1.068	1.025
$R_1/wR_2(I > 2□(I))$	0.0355/0.0841	0.0936/0.2485	0.0322/0.0762	0.0473/0.1127	0.0409/0.0789
R_1/wR_2 (all data)	0.0444/0.0877	0.0957/0.2505	0.0461/0.0795	0.0536/0.1149	0.0550/0.0863
largest diff. [e Å^{-3}]	–1.014/0.910	–2.532/1.566	–0.769/1.265	–0.772/1.212	–1.436/1.358

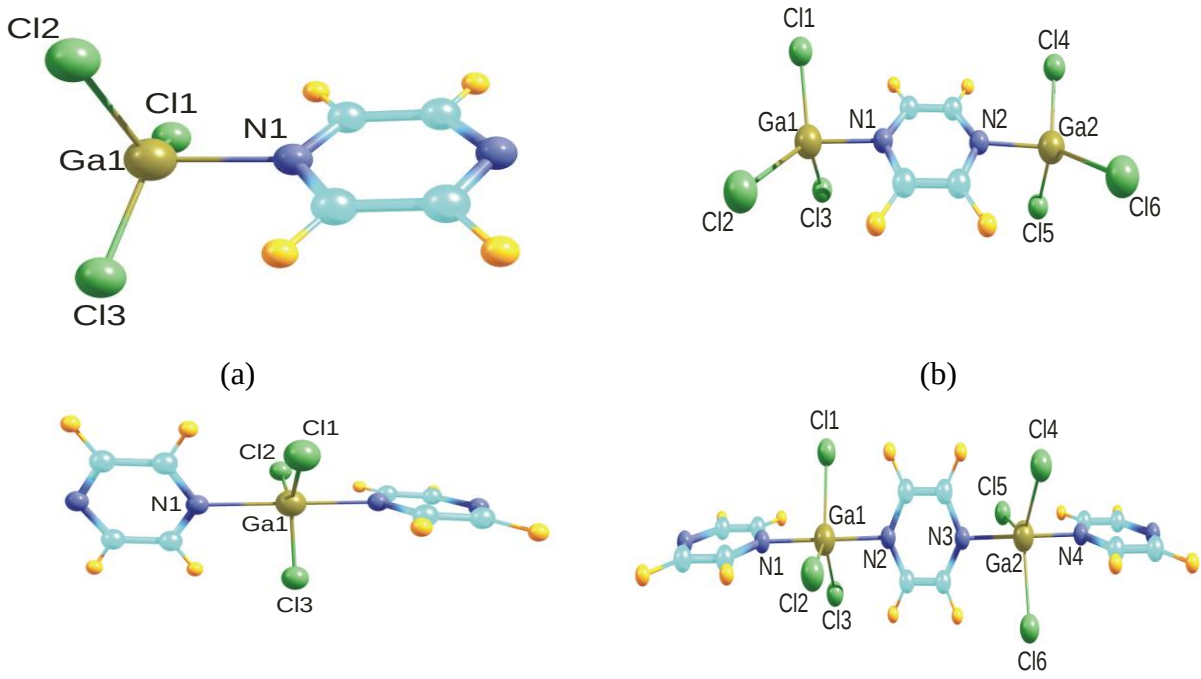


Figure S6. Structures of pyrazine complexes, theoretically considered in the present work, on the example of gallium trihalide complexes. (a) $GaCl_3 \cdot pyz$, (b) $(GaCl_3)_2 \cdot pyz$, (c) $GaCl_3 \cdot 2pyz$, (d) $(GaCl_3)_2 \cdot (pyz)_3$.

Table S2. Comparison of theoretically predicted and experimental bond distances (in angstroms) and bond angles (in degrees).

Compound	Method	rM-N	rM-X	<N-M-X	<X-M-X
$AlCl_3$·pyz	B3LYP	2.028	2.134-2.138	101.9-102.8	115.1-116.2
$AlCl_3$·pyz·$AlCl_3$	B3LYP	2.063	2.1262.131	100.2-101.6	115.9-117.2
pyz·$AlCl_3$·pyz	B3LYP	2.182	2.187	87.8-92.2	119.5-121.0
pyz·$AlCl_3$·pyz·$AlCl_3$·pyz	B3LYP	2.163;2.228	2.181-2.182	88.0-92.9	119.0-120.4
$AlBr_3$·pyz	B3LYP	2.037	2.299-2.303	101.6-103.8	115.0-115.6
$AlBr_3$·pyz·$AlBr_3$	B3LYP	2.074	2.292-2.295	99.9-102.7	115.8-116.6
$AlBr_3$·pyz·$AlBr_3$ (**1**)	X-ray	1.999	2.247-2.267	100.85-104.43	113.4-116.9
pyz·$AlBr_3$·pyz	B3LYP	2.208	2.359-2.361	87.4-93.0	119.7-120.5
pyz·$AlBr_3$·pyz·$AlBr_3$·pyz	B3LYP	2.182; 2.259	2.352-2.355	88.4-89.6	119.8-120.3
$(AlBr_3$·pyz$)_\infty$ (**3**)	X-ray	2.133	2.310-2.326	86.4-93.4	116.0-128.1
AlI_3·pyz	B3LYP	2.053	2.530-2.534	101.1-104.3	114.8-115.2
AlI_3·pyz·AlI_3	B3LYP	2.090	2.522-2.526	99.6-103.5	115.7-116.2
pyz·AlI_3·pyz	B3LYP	2.242; 2.244	2.594-2.603	86.7-94.0	115.0-122.6
pyz·AlI_3·pyz·AlI_3·pyz	B3LYP	2.215; 2.330	2.586-2.591	86.4-95.3	118.4-120.7
$GaCl_3$·pyz	B3LYP	2.096	2.180-2.184	101.6-101.8	115.5-117.1
$GaCl_3$·pyz·$GaCl_3$	B3LYP	2.141	2.173-2.177	100.0-100.4	116.3-118.0
$GaCl_3$·pyz·$GaCl_3$ (**2**)	X-ray	2.044	2.135-2.147	101.6-103.4	113.0-116.9
pyz·$GaCl_3$·pyz	B3LYP	2.276	2.223-2.224	88.1-91.9	119.6-120.8
pyz·$GaCl_3$·pyz·$GaCl_3$·pyz	B3LYP	2.243; 2.336	2.218-2.219	86.7-93.4	119.2-120.3
$(GaCl_3$·pyz$)_\infty$ (**4**)	X-ray	2.203	2.174-2.186	87.5-92.16	117.3-125.4
$GaBr_3$·pyz	B3LYP	2.113	2.334-2.337	101.1-102.6	115.4-116.5
$GaBr_3$·pyz·$GaBr_3$	B3LYP	2.161	2.327-2.330	99.4-101.4	116.2-117.5
pyz·$GaBr_3$·pyz	B3LYP	2.326	2.377-2.378	87.7-92.5	119.7-120.6
pyz·$GaBr_3$·pyz·$GaBr_3$·pyz	B3LYP	2.277; 2.416	2.371-2.373	85.9-94.2	119.3-120.4
GaI_3·pyz	B3LYP	2.143	2.551-2.553	100.4-102.7	115.7-116.1
GaI_3·pyz (**5**)	X-ray	2.027	2.504-2.509	102.6-105.1	112.1-116.7
GaI_3·pyz·GaI_3	B3LYP	2.193	2.542-2.547	99.2-101.3	116.7
pyz·GaI_3·pyz	B3LYP	2.424; 2.425	2.586-2.589	87.6-93.1	120.0

Table S3. Total energies E^{o}_{0}, standard enthalpies H^{o}_{298} (in Hartree) and entropies S^{o}_{298} (in cal mol^{-1} K^{-1}). B3LYP/TZVP level of theory.

Compound	E^{o}_{0}	H^{o}_{298}	S^{o}_{298}
$AlCl_3 \cdot Py$	-1871.7591724	-1871.6513100	108.239
$AlCl_3 \cdot pyz$	-1887.7870231	-1887.6915220	108.056
$AlCl_3 \cdot pyz \cdot AlCl_3$	-3511.1580608	-3511.0489670	148.691
$AlCl_3(pyz)_2$	-2152.2048075	-2152.0251440	136.595
$(AlCl_3)_2(pyz)_3$	-4040.0023628	-4039.7248410	209.795
$AlBr_3 \cdot Py$	-8213.6228039	-8213.5155080	115.781
$AlBr_3 \cdot pyz$	-8229.6506985	-8229.5557760	115.627
$AlBr_3 \cdot pyz \cdot AlBr_3$	-16194.8858137	-16194.7779010	163.708
$AlBr_3(pyz)_2$	-8494.0643503	-8493.8853240	146.622
$(AlBr_3)_2(pyz)_3$	-16723.7224514	-16723.4462290	225.077
$AlI_3 \cdot Py$	-1384.4590963	-1384.352177	121.837
$AlI_3 \cdot pyz$	-1400.4871976	-1400.392624	124.387
$AlI_3 \cdot pyz \cdot AlI_3$	-2536.5599319	-2536.452716	175.051
$AlI_3(pyz)_2$	-1664.8951507	-1664.716600	151.946
$(AlI_3)_2(pyz)_3$	-3065.3841482	-3065.108822	233.288
$GaCl_3 \cdot Py$	-3554.1541594	-3554.046971	111.664
$GaCl_3 \cdot pyz$	-3570.182340	-3570.087489	111.512
$GaCl_3 \cdot pyz \cdot GaCl_3$	-6875.949899	-6875.842102	156.295
$GaCl_3(pyz)_2$	-3834.596631	-3834.417720	141.855
$(GaCl_3)_2(pyz)_3$	-7404.787740	-7404.511645	217.400
$GaBr_3 \cdot Py$	-9896.0303362	-9895.9236330	119.336
$GaBr_3 \cdot pyz$	-9912.0587356	-9911.9643780	119.266
$GaBr_3 \cdot pyz \cdot GaBr_3$	-19559.7035548	-19559.5967440	171.477
$GaBr_3(pyz)_2$	-10176.4685552	-10176.2902200	151.269
$(GaBr_3)_2(pyz)_3$	-20088.5318973	-20088.2569600	235.047
$GaI_3 \cdot Py$	-3066.8807732	-3066.774365	126.040
$GaI_3 \cdot pyz$	-3082.9096463	-3082.815563	126.682
$GaI_3 \cdot pyz \cdot GaI_3$	-5901.4069503	-5901.300666	181.996
$GaI_3(pyz)_2$	-3347.313909	-3347.136003	159.749

Table S4. BSSE energies, kJ mol^{-1}. B3LYP/TZVP level of theory.

Compound	X=Cl	X=Br	X=I
$AlX_3 \cdot py$	7.4	6.2	4.5
$AlX_3 \cdot pyz$	7.4	6.1	3.8
$AlX_3 \cdot pyz \cdot AlX_3$	14.6	12.3	9.9
$AlX_3(pyz)_2$	11.3	9.1	5.7
$(AlX_3)_2(pyz)_3$	22.2	18.3	13.5
$GaX_3 \cdot py$	6.4	5.4	3.9
$GaX_3 \cdot pyz$	6.2	5.2	3.9
$GaX_3 \cdot pyz \cdot GaX_3$	11.9	10.2	7.8
$GaX_3(pyz)_2$	8.9	7.3	5.2
$(GaX_3)_2(pyz)_3$	18.1	15.1	-

Table S5. Structural and energetic parameters of mixed 2:1 complexes. Standard dissociation enthalpies, $\Delta_{diss}H^o_{298}$, kJ mol^{-1} and standard dissociation entropies $\Delta_{diss}S^o_{298}$, J mol^{-1} K^{-1}. B3LYP/TZVP level of theory.

MX_3-pyz-$M'X'_3$	r(N1-M)	r(N2-M')	$\Delta_{diss}H^o_{298}$	$\Delta_{diss}S^o_{298}$
$AlCl_3$-pyz-$GaCl_3$	2.061	2.144	199.5	276.9
$AlCl_3$-pyz-$AlBr_3$	2.062	2.075	213.0	282.1
$AlCl_3$-pyz-$GaBr_3$	2.059	2.167	187.7	278.7
$GaCl_3$-pyz-$AlBr_3$	2.143	2.072	189.7	281.7
$GaCl_3$-pyz-$GaBr_3$	2.138	2.164	164.3	277.8
$AlBr_3$-pyz-$GaBr_3$	2.070	2.166	177.9	282.9

Table S6. Summary of the tensimetry experiments, performed in the $AlBr_3$-pyz system.

Experiment number	Temperature range, K	Number of heating/cooling runs	$AlBr_3$:pyz ratio	Chemical composition (mass of the substance in mg)	Volume, ml
1	291-675	3	1:1	$AlBr_3 \cdot pyz$ (36.2)	27.40
2	293-649	4	1:1	$AlBr_3 \cdot pyz$ (45.5)	33.37
3	291-660	3	1:3.03	$AlBr_3 \cdot pyz$ (45.5), pyz (21.3)	30.60
4		5	2:1	$(AlBr_3)_2$pyz (28.2)	55.50
5		12	2.03:1	$AlBr_3$ (51.4); pyz (7.6)	59.05

Table S7. Melting points, Energies of the M-N bonds, E_{M-N} and melting enthalpies $\Delta_{melt}H$, kJ mol^{-1}.

Compound	E_{M-N}	T_{melt}, K	$\Delta_{melt}H$
$(AlBr_3 \cdot pyz)_\infty$ (**3**)	85	540	64±3[b]
$(GaCl_3 \cdot pyz)_\infty$ (**4**)	77	461-463 [11][a]; 470 [12]	12±7 [12][b]
$(GaBr_3 \cdot pyz)_\infty$	64	361-363 [11][a]	

[a] synthesis in nonaqueous solutions; [b] estimated as difference between sublimation and vaporization enthalpies from tensimetry studies.

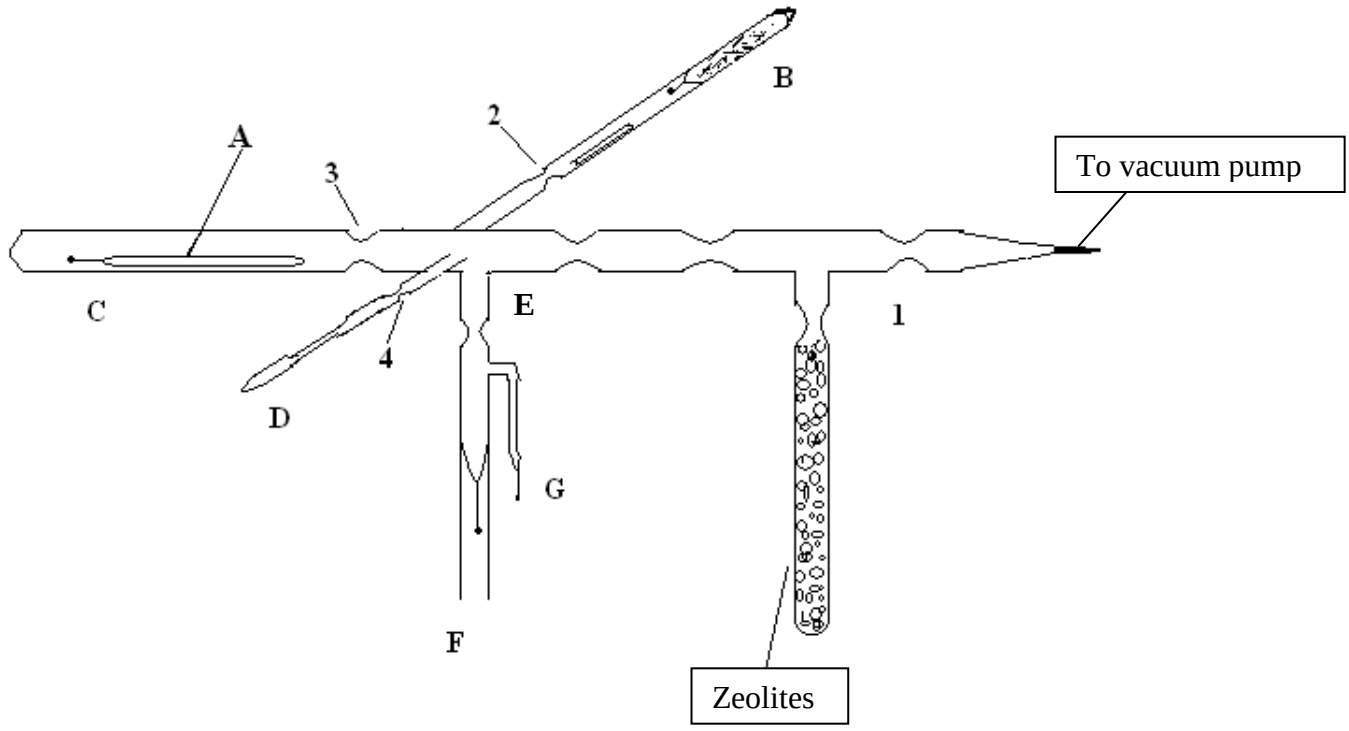
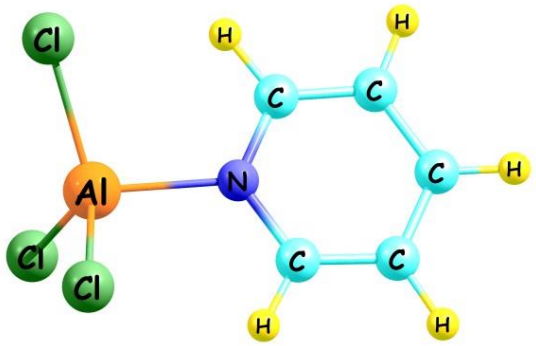


Figure S7. System for synthesis of complexes. 1, 2, 3 and 4 – places for the sealing off; **A** – ampoule with known amount of pyrazine; **B** – ampoule with known amount of $AlBr_3$; **C** – compartment for the introduction of pyz; **D** – ampoule for removal of the excess component; **E** – reaction volume; **F** – ampoule to remove the synthesized complex; **G** – capillary for the mass spectrometry study.

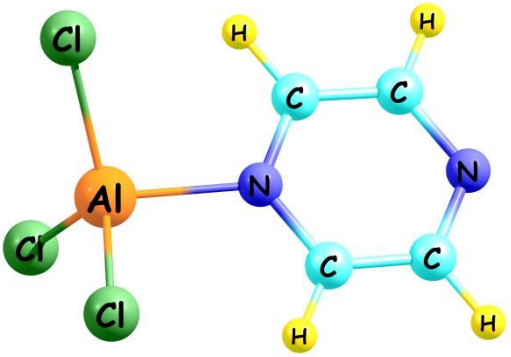
Figure S8. Optimized structures and xyz coordinates for considered aluminum compounds. B3LYP/TZVP level of theory.

a) $AlCl_3$·Py



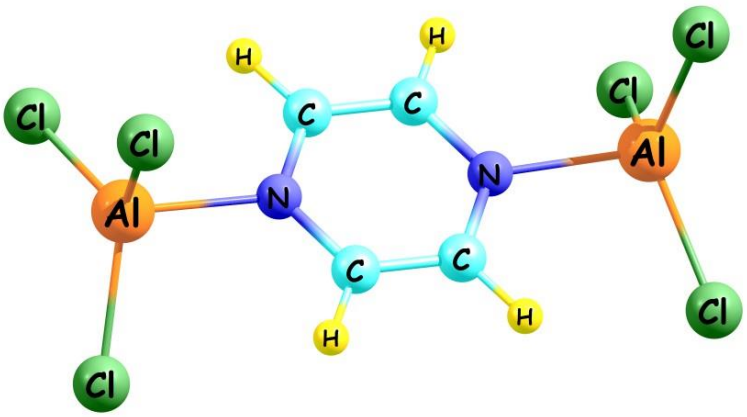
	X	Y	Z
C	-3.663	0.001	0.000
C	-2.962	1.200	-0.018
C	-1.579	1.169	-0.053
N	-0.895	0.010	-0.067
C	-1.572	-1.153	-0.054
C	-2.954	-1.194	-0.019
H	-3.473	2.153	-0.008
H	-0.985	2.072	-0.077
H	-0.973	-2.054	-0.080
H	-3.458	-2.150	-0.010
H	-4.746	-0.003	0.026
Al	1.113	0.001	0.002
Cl	1.517	-0.174	2.095
Cl	1.639	-1.726	-1.149
Cl	1.656	1.886	-0.859

b) $AlCl_3$·pyz



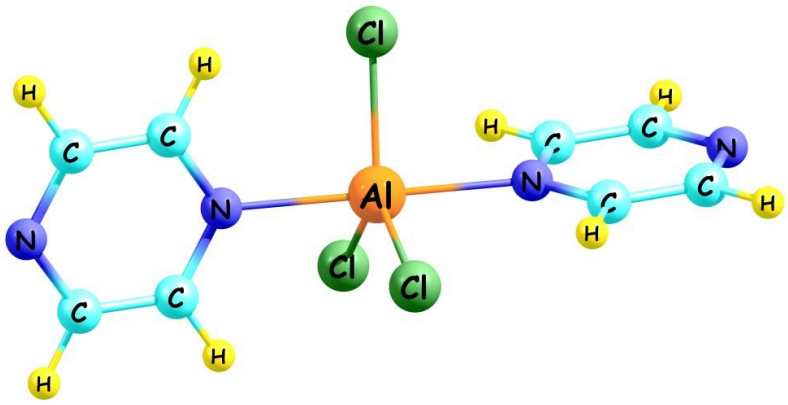
	X	Y	Z
N	3.671	0.002	-0.002
C	2.969	-1.130	-0.018
C	1.582	-1.142	-0.050
N	0.895	0.011	-0.063
C	1.589	1.159	-0.050
C	2.977	1.138	-0.019
H	3.524	-2.061	-0.008
H	1.009	-2.059	-0.075
H	1.020	2.079	-0.074
H	3.537	2.065	-0.009
Al	-1.131	0.001	0.002
Cl	-1.502	-0.192	2.095
Cl	-1.643	1.895	-0.845
Cl	-1.622	-1.719	-1.167

c) $AlCl_3$·pyz·$AlCl_3$



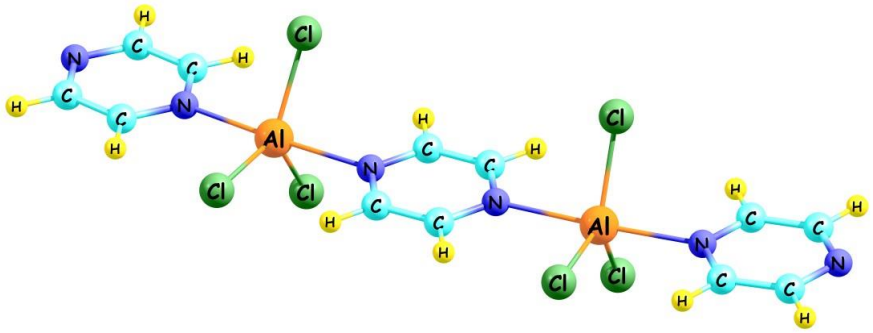
	X	Y	Z
N	-1.377	0.012	-0.093
C	-0.683	1.157	-0.096
C	0.702	1.145	-0.097
N	1.377	-0.011	-0.093
C	0.683	-1.157	-0.096
C	-0.702	-1.145	-0.097
H	-1.248	2.080	-0.108
H	1.279	2.060	-0.113
H	1.248	-2.079	-0.108
H	-1.278	-2.060	-0.112
Al	3.437	-0.001	0.008
Cl	3.710	0.310	2.094
Cl	3.911	-1.943	-0.731
Cl	3.895	1.657	-1.249
Al	-3.438	0.001	0.008
Cl	-3.895	-1.654	-1.252
Cl	-3.710	-0.314	2.093
Cl	-3.911	1.945	-0.727

d) $AlCl_3(pyz)_2$



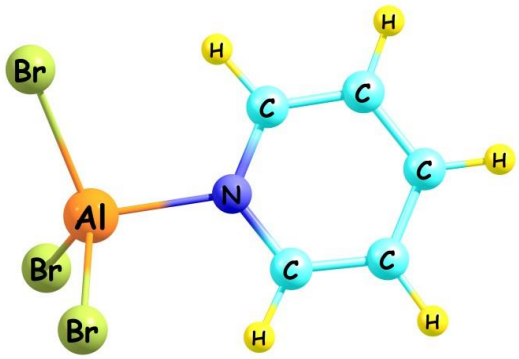
	X	Y	Z
N	-4.969	0.006	-0.030
C	-4.247	0.810	0.750
C	-2.861	0.771	0.775
N	-2.181	-0.091	0.006
C	-2.896	-0.902	-0.781
C	-4.285	-0.844	-0.791
H	-4.786	1.510	1.378
H	-2.284	1.423	1.416
H	-2.345	-1.599	-1.396
H	-4.854	-1.507	-1.432
Al	0.000	0.000	0.006
Cl	0.000	0.000	2.193
Cl	0.164	-1.897	-1.071
Cl	-0.164	1.897	-1.071
N	2.181	0.091	0.007
C	2.896	0.902	-0.781
C	4.285	0.844	-0.791
N	4.969	-0.006	-0.030
C	4.247	-0.810	0.750
C	2.861	-0.771	0.775
H	2.345	1.599	-1.396
H	4.854	1.507	-1.432
H	4.786	-1.511	1.378
H	2.284	-1.423	1.416

e) $(AlCl_3)_2(pyz)_3$



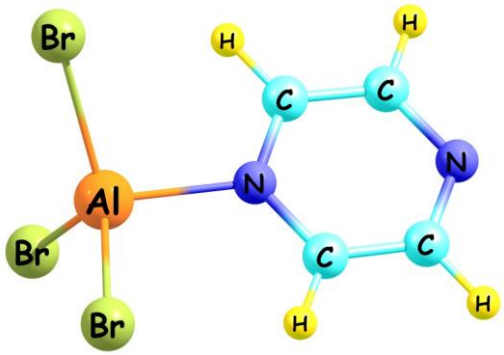
	X	Y	Z
N	0.000	-1.390	0.313
C	0.000	-0.695	1.451
C	0.000	0.695	1.451
N	0.000	1.390	0.313
C	0.000	0.691	-0.830
C	0.000	-0.691	-0.830
H	0.000	-1.258	2.374
H	0.000	1.258	2.374
H	0.000	1.249	-1.755
H	0.000	-1.249	-1.755
Al	0.000	3.614	0.169
Cl	1.880	3.466	-0.928
Cl	-1.880	3.466	-0.928
Cl	0.000	3.798	2.342
Al	0.000	-3.614	0.169
Cl	-1.880	-3.466	-0.928
Cl	1.880	-3.466	-0.928
Cl	0.000	-3.798	2.342
N	0.000	-5.757	-0.124
C	0.000	-6.214	-1.385
C	0.000	-7.574	-1.652
N	0.000	-8.490	-0.683
C	0.000	-8.029	0.564
C	0.000	-6.669	0.855
H	0.000	-5.480	-2.178
H	0.000	-7.932	-2.675
H	0.000	-8.758	1.365
H	0.000	-6.298	1.870
N	0.000	5.757	-0.124
C	0.000	6.669	0.855
C	0.000	8.029	0.564
N	0.000	8.490	-0.683
C	0.000	7.574	-1.652
C	0.000	6.214	-1.385
H	0.000	6.298	1.870
H	0.000	8.758	1.365
H	0.000	7.932	-2.675
H	0.000	5.480	-2.178

f) $AlBr_3 \cdot Py$



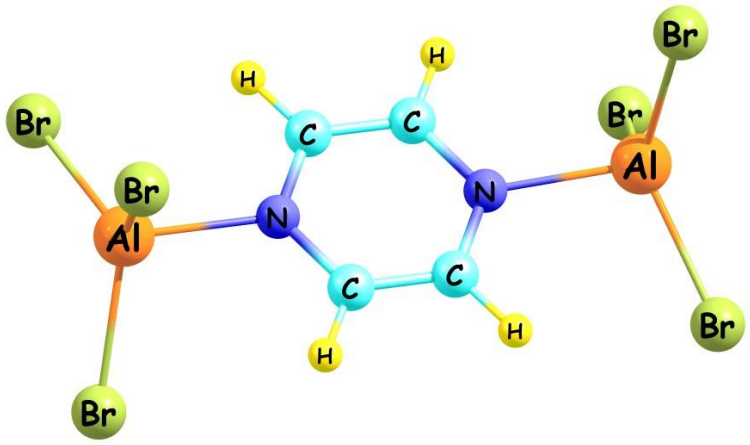
	X	Y	Z
C	-4.242	0.080	-0.114
C	-3.526	1.271	-0.114
C	-2.143	1.223	-0.113
N	-1.471	0.057	-0.111
C	-2.164	-1.098	-0.113
C	-3.546	-1.123	-0.113
H	-4.026	2.230	-0.117
H	-1.539	2.120	-0.119
H	-1.577	-2.007	-0.122
H	-4.062	-2.074	-0.116
H	-5.325	0.089	-0.116
Al	0.541	-0.001	0.004
Br	0.905	-0.462	2.232
Br	1.115	-1.718	-1.426
Br	1.224	2.097	-0.672

g) $AlBr_3 \cdot pyz$



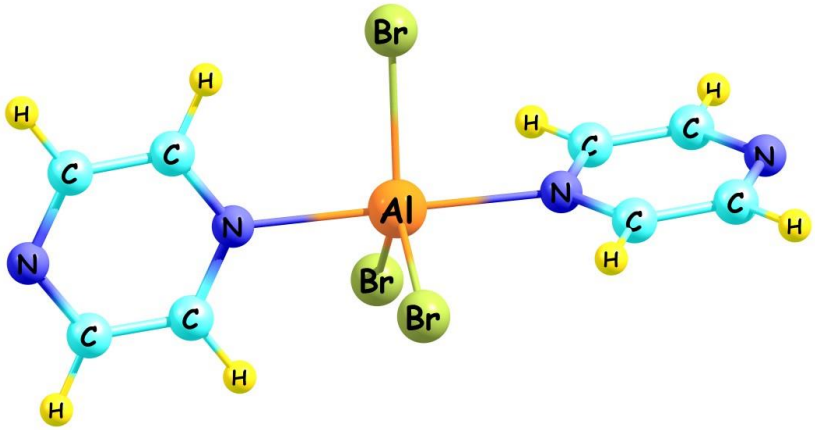
	X	Y	Z
N	4.244	0.081	-0.125
C	3.556	-1.060	-0.119
C	2.169	-1.090	-0.114
N	1.466	0.054	-0.112
C	2.146	1.211	-0.119
C	3.534	1.208	-0.125
H	4.123	-1.983	-0.121
H	1.610	-2.016	-0.119
H	1.565	2.123	-0.126
H	4.082	2.142	-0.132
Al	-0.567	-0.003	0.007
Br	-0.887	-0.431	2.243
Br	-1.216	2.091	-0.699
Br	-1.109	-1.740	-1.402

h) $AlBr_3 \cdot pyz \cdot AlBr_3$



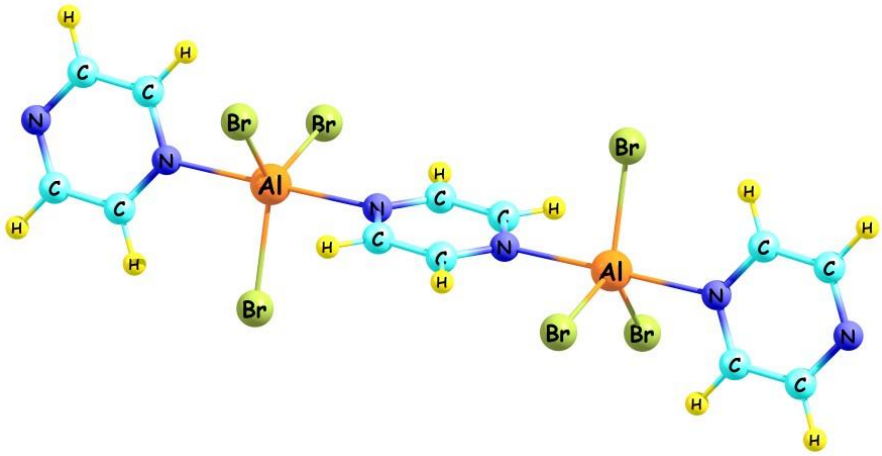
	X	Y	Z
N	-1.379	0.020	-0.102
C	-0.677	1.160	-0.103
C	0.709	1.140	-0.105
N	1.379	-0.020	-0.102
C	0.677	-1.160	-0.103
C	-0.709	-1.140	-0.105
H	-1.235	2.087	-0.110
H	1.287	2.053	-0.119
H	1.235	-2.087	-0.110
H	-1.287	-2.053	-0.119
Al	3.450	0.002	-0.008
Br	3.740	0.589	2.188
Br	4.004	-2.153	-0.570
Br	3.945	1.626	-1.551
Al	-3.450	-0.002	-0.008
Br	-3.945	-1.626	-1.551
Br	-3.740	-0.589	2.188
Br	-4.004	2.154	-0.570

i) $AlBr_3(pyz)_2$



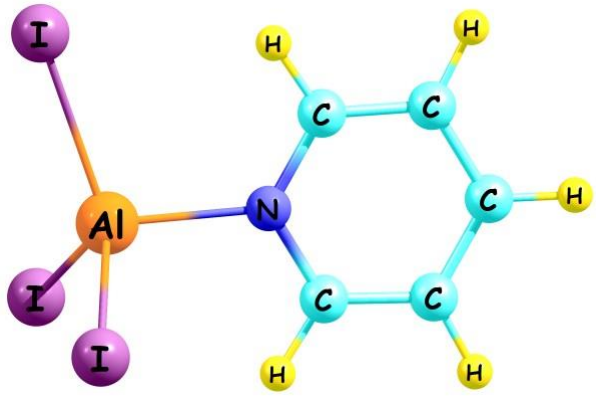
	X	Y	Z
N	-4.996	-0.097	0.013
C	-4.277	0.761	0.737
C	-2.890	0.750	0.739
N	-2.204	-0.137	0.005
C	-2.917	-1.000	-0.728
C	-4.307	-0.970	-0.716
H	-4.819	1.482	1.338
H	-2.320	1.449	1.334
H	-2.364	-1.716	-1.319
H	-4.872	-1.676	-1.314
Al	0.000	0.000	-0.012
Br	0.000	0.000	2.348
Br	0.243	-2.033	-1.182
Br	-0.243	2.033	-1.182
N	2.204	0.137	0.005
C	2.917	1.000	-0.728
C	4.307	0.970	-0.716
N	4.996	0.097	0.013
C	4.277	-0.761	0.737
C	2.890	-0.750	0.739
H	2.364	1.716	-1.319
H	4.872	1.676	-1.314
H	4.819	-1.482	1.338
H	2.320	-1.449	1.334

j) $(AlBr_3)_2(pyz)_3$



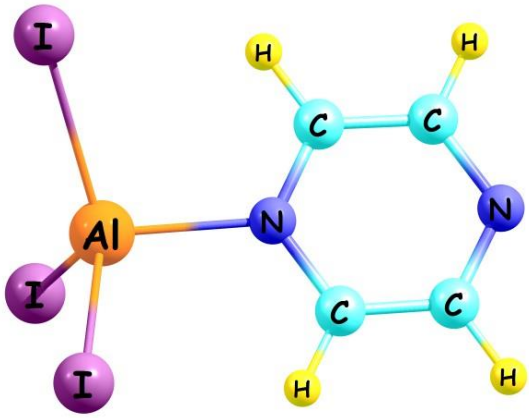
	X	Y	Z
N	-1.391	0.048	-0.040
C	-0.646	0.600	-1.003
C	0.739	0.552	-0.962
N	1.391	-0.048	0.040
C	0.646	-0.600	1.003
C	-0.739	-0.552	0.962
H	-1.169	1.088	-1.813
H	1.332	0.999	-1.747
H	1.169	-1.087	1.813
H	-1.332	-0.999	1.747
Al	3.649	0.031	0.042
Br	3.785	-1.446	1.868
Br	3.615	-0.823	-2.153
Br	3.424	2.342	0.420
Al	-3.649	-0.031	-0.042
Br	-3.424	-2.342	-0.421
Br	-3.615	0.822	2.153
Br	-3.785	1.446	-1.867
N	-5.829	-0.094	0.032
C	-6.572	-1.191	-0.152
C	-7.961	-1.130	-0.096
N	-8.617	0.003	0.138
C	-7.867	1.090	0.320
C	-6.482	1.054	0.269
H	-6.046	-2.115	-0.341
H	-8.551	-2.026	-0.247
H	-8.382	2.024	0.513
H	-5.887	1.943	0.421
N	5.829	0.094	-0.032
C	6.572	1.191	0.151
C	7.961	1.130	0.096
N	8.617	-0.003	-0.138
C	7.867	-1.091	-0.320
C	6.482	-1.054	-0.269
H	6.046	2.115	0.341
H	8.552	2.026	0.247
H	8.382	-2.024	-0.513
H	5.887	-1.943	-0.420

k) AlI_3·Py



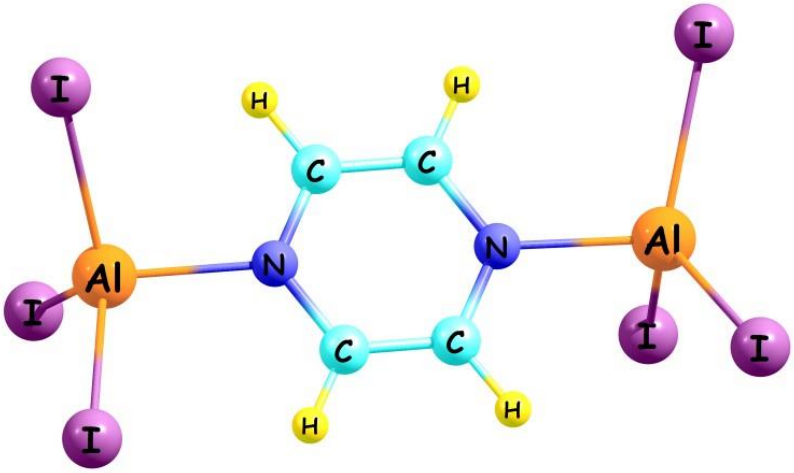
	X	Y	Z
N	-1.808	-0.040	0.000
Al	0.220	0.038	0.000
I	0.828	-1.193	2.134
I	0.828	2.503	0.000
I	0.828	-1.193	-2.134
C	-4.570	-0.274	0.000
C	-2.392	-1.255	0.000
C	-2.585	1.057	0.000
C	-3.967	0.977	0.000
C	-3.765	-1.408	0.000
H	-1.727	-2.108	0.000
H	-2.066	2.007	0.000
H	-4.553	1.886	0.000
H	-4.189	-2.403	0.000
H	-5.649	-0.366	0.000

l) AlI_3·pyz



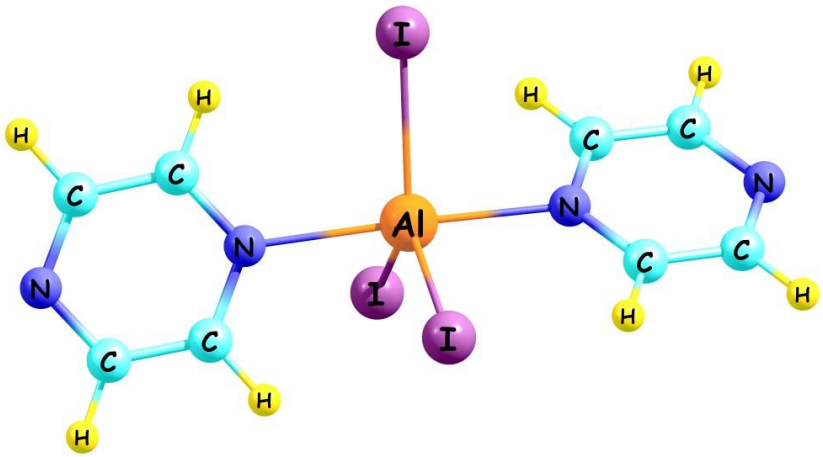
	X	Y	Z
N	-4.439	0.000	-1.124
C	-3.756	1.133	-0.975
C	-2.400	1.149	-0.679
N	-1.722	0.000	-0.532
C	-2.400	-1.149	-0.679
C	-3.756	-1.133	-0.975
H	-4.299	2.063	-1.094
H	-1.843	2.070	-0.567
H	-1.843	-2.070	-0.567
H	-4.299	-2.063	-1.094
Al	0.249	0.000	0.041
I	0.022	0.000	2.561
I	1.178	-2.136	-0.957
I	1.178	2.136	-0.957

m) AlI_3·pyz·AlI_3



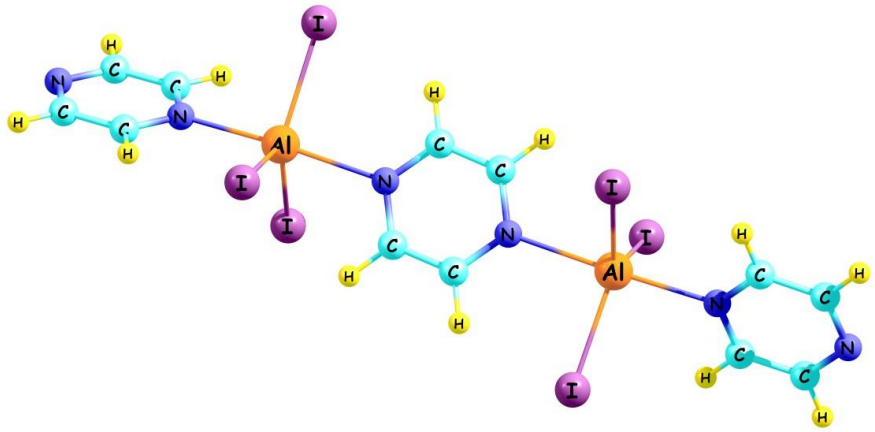
	X	Y	Z
N	1.382	-0.013	-0.121
C	0.682	-1.156	-0.119
C	-0.703	-1.142	-0.120
N	-1.382	0.013	-0.121
C	-0.682	1.156	-0.119
C	0.703	1.142	-0.120
H	1.241	-2.082	-0.128
H	-1.277	-2.059	-0.134
H	-1.241	2.082	-0.128
H	1.277	2.059	-0.134
Al	-3.470	-0.006	-0.020
I	-3.767	-0.416	2.451
I	-4.124	2.286	-0.857
I	-4.054	-1.937	-1.541
Al	3.470	0.006	-0.020
I	4.054	1.937	-1.541
I	3.767	0.416	2.451
I	4.124	-2.286	-0.857

n) $AlI_3(pyz)_2$



	X	Y	Z
N	-5.010	0.212	-0.396
C	-4.286	-0.860	-0.720
C	-2.910	-0.902	-0.560
N	-2.236	0.146	-0.063
C	-2.954	1.226	0.263
C	-4.335	1.248	0.092
H	-4.816	-1.716	-1.121
H	-2.338	-1.779	-0.827
H	-2.416	2.073	0.664
H	-4.902	2.132	0.361
Al	0.000	0.000	0.059
I	0.000	0.000	-2.545
I	0.252	2.176	1.448
I	-0.252	-2.176	1.448
N	2.236	-0.146	-0.063
C	2.954	-1.226	0.263
C	4.335	-1.248	0.092
N	5.010	-0.212	-0.396
C	4.286	0.860	-0.720
C	2.910	0.902	-0.560
H	2.416	-2.073	0.664
H	4.902	-2.132	0.361
H	4.816	1.716	-1.121
H	2.338	1.779	-0.827

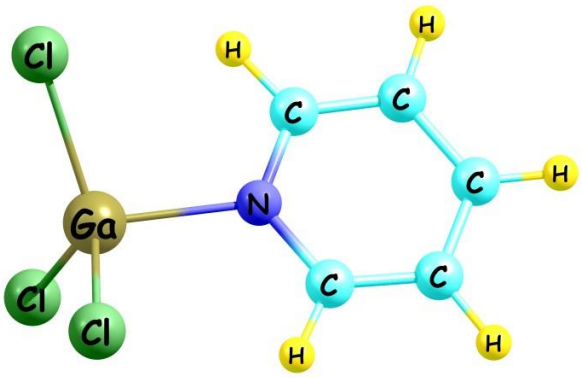
o) $(AlI_3)_2(pyz)_3$



	X	Y	Z
I	-3.903	-0.204	2.588
Al	-3.710	-0.048	0.012
I	-3.578	-2.283	-1.285
I	-3.503	2.245	-1.181
N	-5.911	0.140	-0.143
N	-1.393	-0.075	0.063
N	-8.667	0.571	-0.300
C	-6.698	-0.637	-0.895
C	-6.506	1.137	0.530
C	-7.875	1.342	0.446
C	-8.069	-0.412	-0.967
H	-6.223	-1.441	-1.439
H	-5.877	1.771	1.138
H	-8.341	2.150	0.997
H	-8.694	-1.050	-1.581
N	1.393	-0.075	-0.063
C	-0.643	-0.075	1.169
C	-0.743	-0.073	-1.105
C	0.643	-0.075	-1.169
C	0.743	-0.073	1.105
H	-1.159	-0.078	2.119
H	-1.334	-0.071	-2.009
H	1.159	-0.078	-2.119
H	1.334	-0.071	2.009
I	3.578	-2.283	1.285
Al	3.710	-0.048	-0.012
I	3.903	-0.204	-2.588
I	3.503	2.246	1.181
N	5.911	0.140	0.143
N	8.667	0.571	0.300
C	6.698	-0.637	0.896
C	6.506	1.137	-0.530
C	7.875	1.342	-0.446
C	8.069	-0.412	0.967
H	6.223	-1.441	1.439
H	5.877	1.771	-1.138
H	8.341	2.150	-0.997
H	8.694	-1.050	1.581

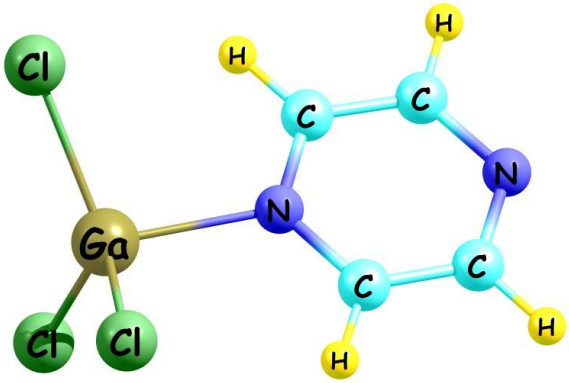
Figure 3S. Optimized structures and xyz coordinates for considered gallium compounds. B3LYP/TZVP level of theory.

a) $GaCl_3 \cdot Py$



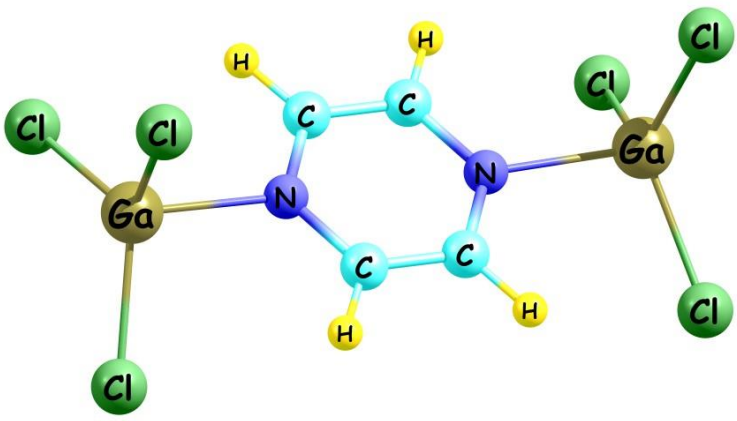
	X	Y	Z
C	-0.090	3.856	0.000
C	-0.091	3.151	-1.198
C	-0.091	1.767	-1.161
N	-0.089	1.093	0.000
C	-0.091	1.767	1.161
C	-0.091	3.151	1.198
H	-0.094	3.660	-2.152
H	-0.103	1.168	-2.062
H	-0.103	1.168	2.062
H	-0.094	3.660	2.152
H	-0.091	4.939	0.000
Ga	0.023	-0.976	0.000
Cl	2.178	-1.337	0.000
Cl	-0.997	-1.513	1.860
Cl	-0.997	-1.513	-1.860

b) $GaCl_3 \cdot pyz$



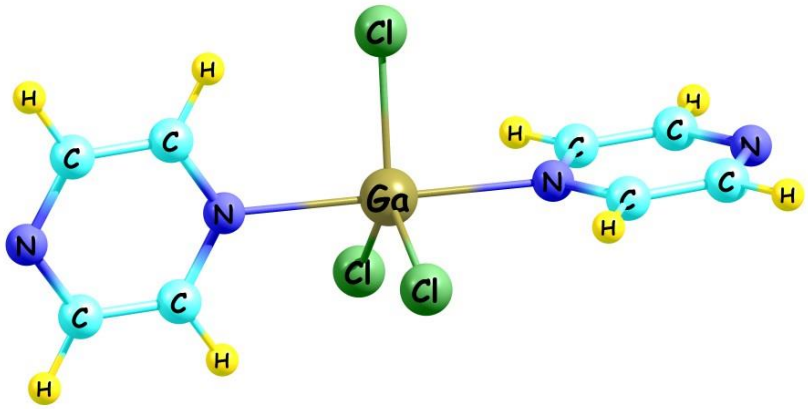
	X	Y	Z
N	0.000	3.870	0.000
C	0.016	3.173	1.135
C	0.046	1.784	1.151
N	0.059	1.100	0.000
C	0.046	1.784	-1.151
C	0.016	3.173	-1.135
H	0.006	3.731	2.063
H	0.071	1.211	2.068
H	0.071	1.211	-2.068
H	0.006	3.731	-2.063
Ga	-0.001	-0.995	0.000
Cl	-2.148	-1.373	0.000
Cl	1.036	-1.470	-1.862
Cl	1.036	-1.470	1.862

c) $GaCl_3 \cdot pyz \cdot GaCl_3$



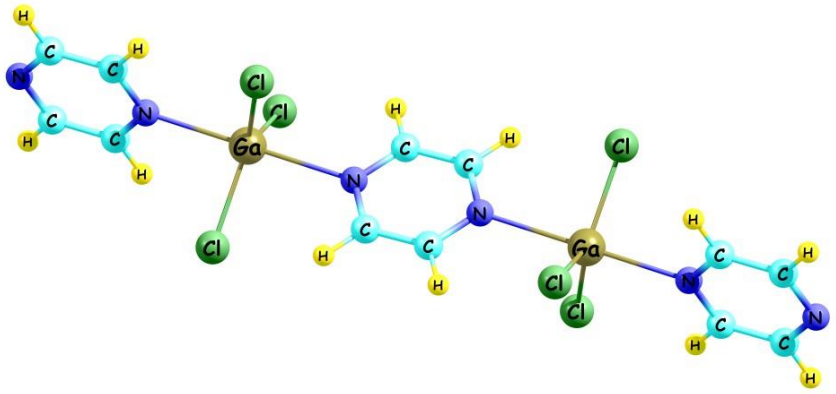
	X	Y	Z
N	1.372	-0.007	-0.090
C	0.688	-1.155	-0.093
C	-0.699	-1.148	-0.094
N	-1.372	0.007	-0.090
C	-0.688	1.155	-0.093
C	0.699	1.148	-0.094
H	1.258	-2.075	-0.107
H	-1.276	-2.063	-0.110
H	-1.258	2.075	-0.107
H	1.276	2.063	-0.110
Ga	-3.511	0.001	0.006
Cl	-3.790	-0.207	2.151
Cl	-3.947	1.955	-0.850
Cl	-3.938	-1.762	-1.197
Ga	3.511	-0.001	0.006
Cl	3.938	1.762	-1.196
Cl	3.790	0.207	2.151
Cl	3.947	-1.955	-0.851

d) $GaCl_3(pyz)_2$



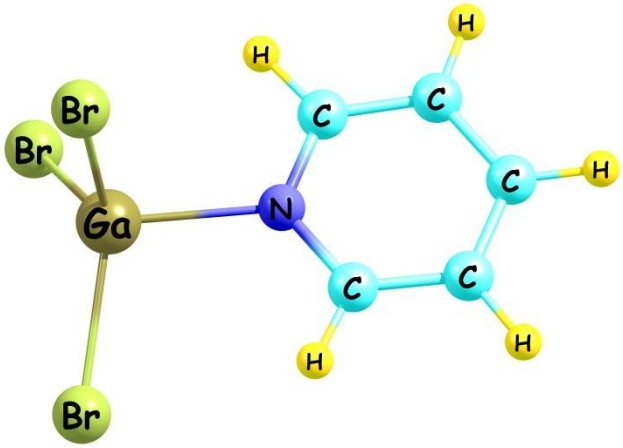
	X	Y	Z
N	5.055	-0.009	-0.045
C	4.342	-0.785	0.770
C	2.954	-0.744	0.805
N	2.274	0.089	0.010
C	2.977	0.872	-0.812
C	4.366	0.815	-0.831
H	4.888	-1.462	1.417
H	2.380	-1.371	1.473
H	2.417	1.546	-1.446
H	4.932	1.454	-1.500
Ga	0.000	0.000	0.011
Cl	0.000	0.000	2.235
Cl	-0.148	1.927	-1.086
Cl	0.148	-1.927	-1.086
N	-2.274	-0.089	0.010
C	-2.977	-0.872	-0.812
C	-4.366	-0.815	-0.831
N	-5.055	0.009	-0.045
C	-4.342	0.785	0.770
C	-2.954	0.744	0.805
H	-2.417	-1.546	-1.446
H	-4.932	-1.454	-1.500
H	-4.888	1.462	1.417
H	-2.380	1.371	1.474

e) $(GaCl_3)_2(pyz)_3$



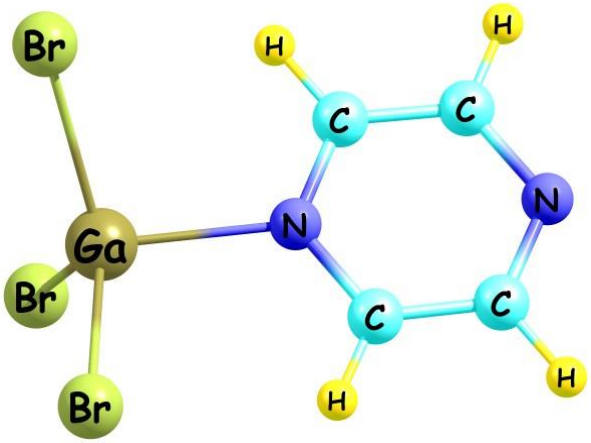
	X	Y	Z
N	1.382	0.085	0.000
C	0.693	0.041	-1.142
C	-0.693	-0.043	-1.142
N	-1.382	-0.085	0.000
C	-0.693	-0.041	1.142
C	0.693	0.043	1.142
H	1.257	0.085	-2.063
H	-1.257	-0.087	-2.063
H	-1.257	-0.085	2.064
H	1.257	0.087	2.064
Ga	-3.717	-0.004	0.000
Cl	-3.752	-1.126	1.914
Cl	-3.513	2.204	-0.001
Cl	-3.752	-1.127	-1.913
Ga	3.717	0.005	0.000
Cl	3.752	1.127	1.914
Cl	3.513	-2.204	0.001
Cl	3.752	1.126	-1.914
N	5.959	-0.072	0.000
C	6.670	-1.203	0.000
C	8.060	-1.164	-0.001
N	8.740	-0.021	-0.001
C	8.018	1.100	-0.001
C	6.630	1.085	0.000
H	6.115	-2.131	0.000
H	8.633	-2.084	-0.001
H	8.558	2.039	-0.001
H	6.050	1.998	0.000
N	-5.959	0.071	0.000
C	-6.630	-1.086	0.000
C	-8.018	-1.100	0.000
N	-8.740	0.020	0.000
C	-8.060	1.164	-0.001
C	-6.670	1.202	-0.001
H	-6.049	-1.998	0.001
H	-8.558	-2.040	0.001
H	-8.634	2.084	-0.001
H	-6.115	2.131	-0.001

f) $GaBr_3$·Py



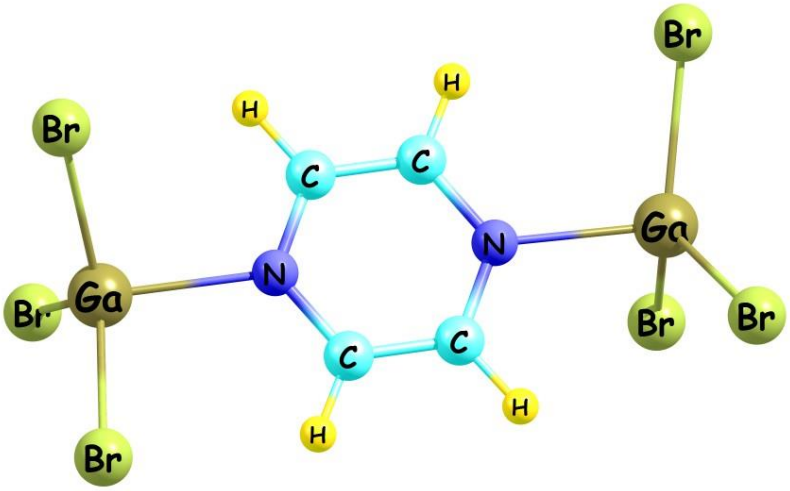
	X	Y	Z
C	-4.333	0.063	-0.094
C	-3.621	1.255	-0.099
C	-2.237	1.210	-0.103
N	-1.568	0.046	-0.104
C	-2.251	-1.111	-0.102
C	-3.635	-1.139	-0.097
H	-4.123	2.213	-0.100
H	-1.631	2.107	-0.115
H	-1.661	-2.017	-0.114
H	-4.149	-2.091	-0.096
H	-5.416	0.069	-0.091
Ga	0.515	0.000	0.002
Br	0.882	-0.422	2.274
Br	1.065	-1.775	-1.423
Br	1.151	2.132	-0.732

g) $GaBr_3$·pyz



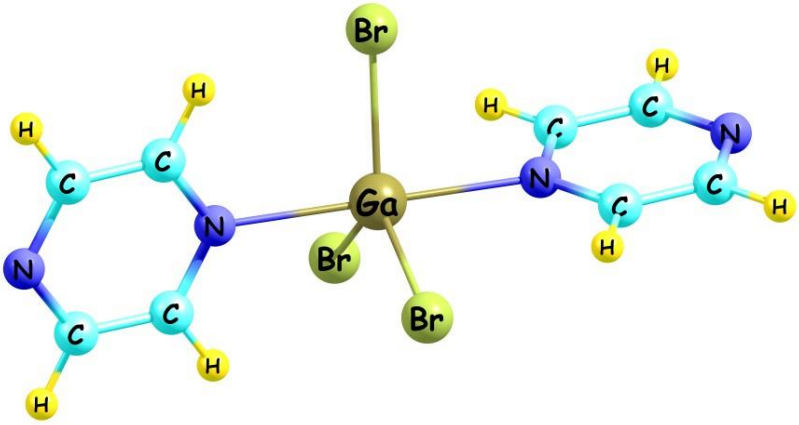
	X	Y	Z
N	4.341	0.063	-0.098
C	3.650	-1.076	-0.097
C	2.262	-1.101	-0.100
N	1.568	0.044	-0.103
C	2.245	1.199	-0.105
C	3.635	1.192	-0.103
H	4.215	-2.001	-0.095
H	1.699	-2.025	-0.110
H	1.665	2.112	-0.117
H	4.186	2.125	-0.106
Ga	-0.542	-0.001	0.004
Br	-0.869	-0.408	2.279
Br	-1.138	2.131	-0.745
Br	-1.053	-1.786	-1.415

h) $GaBr_3$·pyz·$GaBr_3$



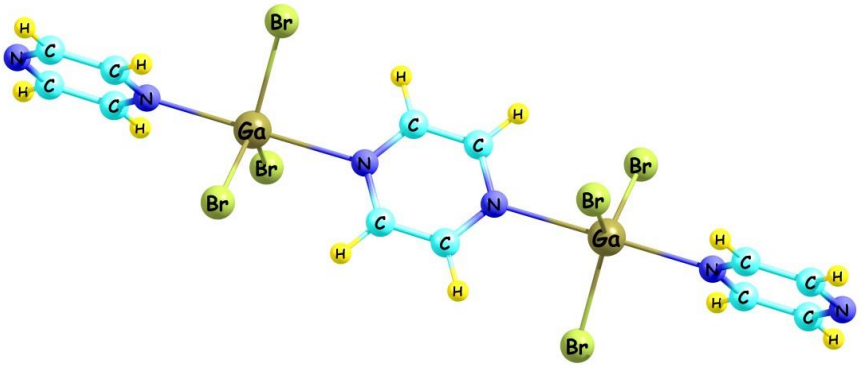
	X	Y	Z
N	1.374	-0.018	-0.110
C	0.679	-1.159	-0.111
C	-0.708	-1.141	-0.113
N	-1.374	0.018	-0.110
C	-0.679	1.159	-0.111
C	0.708	1.141	-0.113
H	1.241	-2.084	-0.119
H	-1.288	-2.054	-0.127
H	-1.241	2.084	-0.119
H	1.288	2.054	-0.127
Ga	-3.533	0.000	-0.006
Br	-3.802	-0.539	2.241
Br	-4.043	2.185	-0.634
Br	-4.003	-1.694	-1.534
Ga	3.533	0.000	-0.006
Br	4.003	1.694	-1.534
Br	3.802	0.539	2.241
Br	4.043	-2.185	-0.634

i) $GaBr_3(pyz)_2$



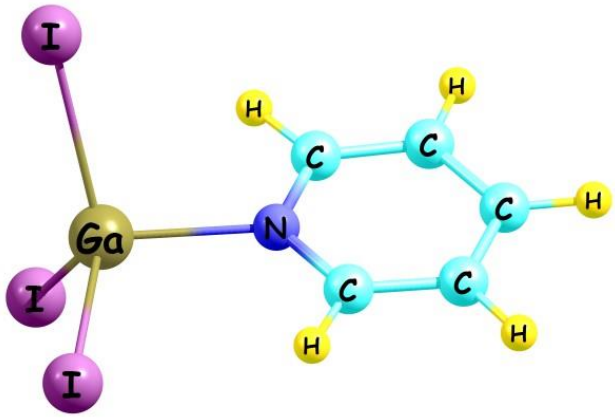
	X	Y	Z
N	5.107	0.077	-0.024
C	4.396	-0.745	0.748
C	3.008	-0.726	0.769
N	2.322	0.132	0.006
C	3.023	0.960	-0.773
C	4.414	0.924	-0.780
H	4.945	-1.442	1.371
H	2.439	-1.393	1.401
H	2.461	1.653	-1.385
H	4.975	1.600	-1.415
Ga	0.000	0.000	-0.001
Br	0.000	0.000	2.377
Br	-0.216	2.054	-1.178
Br	0.216	-2.054	-1.178
N	-2.322	-0.132	0.006
C	-3.023	-0.960	-0.773
C	-4.414	-0.924	-0.780
N	-5.107	-0.077	-0.024
C	-4.396	0.745	0.748
C	-3.008	0.726	0.769
H	-2.461	-1.653	-1.385
H	-4.975	-1.600	-1.415
H	-4.945	1.442	1.371
H	-2.439	1.393	1.401

j) $(GaBr_3)_2(pyz)_3$



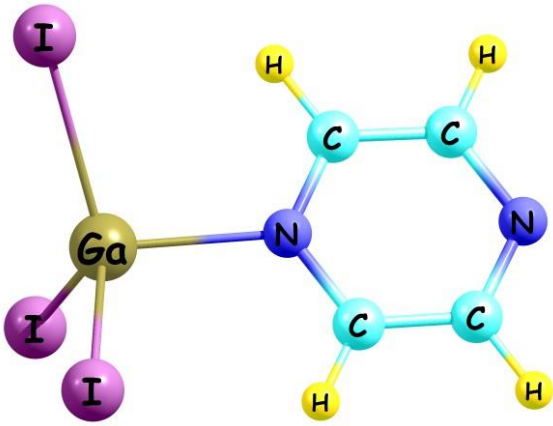
	X	Y	Z
N	-1.385	-0.082	-0.004
C	-0.706	0.124	1.126
C	0.680	0.204	1.130
N	1.385	0.082	0.004
C	0.706	-0.124	-1.126
C	-0.680	-0.204	-1.130
H	-1.276	0.218	2.040
H	1.233	0.376	2.044
H	1.276	-0.218	-2.040
H	-1.233	-0.376	-2.044
Ga	3.800	-0.016	0.004
Br	3.536	-2.369	0.112
Br	3.820	1.086	-2.097
Br	3.859	1.277	1.992
Ga	-3.800	0.016	-0.004
Br	-3.859	-1.277	-1.992
Br	-3.820	-1.086	2.097
Br	-3.536	2.369	-0.112
N	-6.075	0.102	0.007
C	-6.747	-1.051	0.091
C	-8.135	-1.066	0.092
N	-8.858	0.051	0.011
C	-8.178	1.191	-0.072
C	-6.787	1.229	-0.075
H	-6.169	-1.962	0.158
H	-8.674	-2.004	0.161
H	-8.750	2.109	-0.140
H	-6.236	2.157	-0.142
N	6.075	-0.102	-0.007
C	6.747	1.051	-0.091
C	8.135	1.066	-0.092
N	8.858	-0.051	-0.011
C	8.178	-1.191	0.072
C	6.787	-1.229	0.075
H	6.169	1.962	-0.158
H	8.674	2.004	-0.161
H	8.750	-2.109	0.140
H	6.236	-2.157	0.142

k) GaI_3·Py



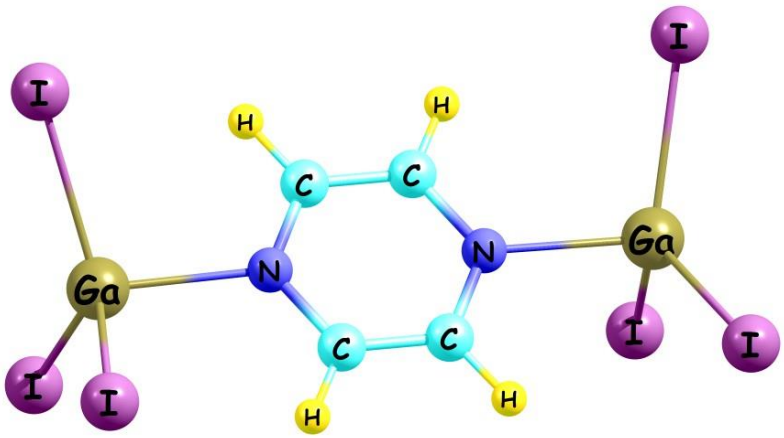
	X	Y	Z
N	-1.868	-0.038	0.000
Ga	0.242	0.034	0.000
I	0.814	-1.216	2.156
I	0.814	2.527	0.000
I	0.814	-1.216	-2.156
C	-4.627	-0.247	0.000
C	-2.457	-1.246	0.000
C	-2.629	1.066	0.000
C	-4.013	0.999	0.000
C	-3.833	-1.388	0.000
H	-1.798	-2.104	0.000
H	-2.100	2.011	0.000
H	-4.591	1.914	0.000
H	-4.267	-2.379	0.000
H	-5.706	-0.329	0.000

l) GaI_3·pyz



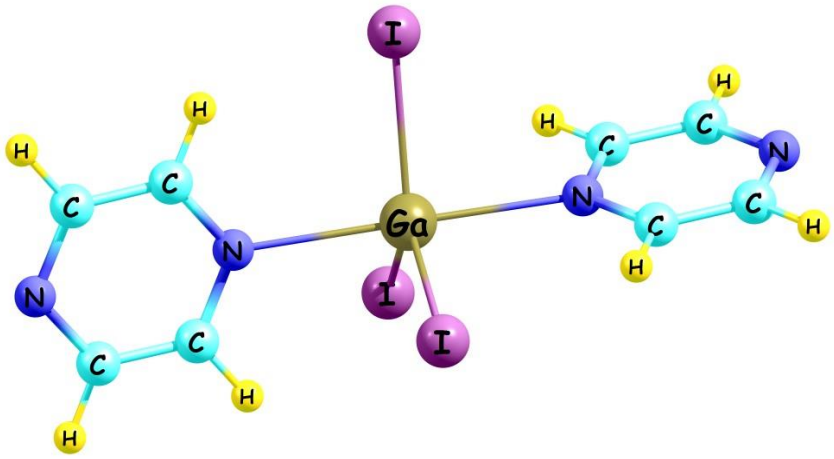
	X	Y	Z
N	-4.529	0.000	-1.004
C	-3.842	1.134	-0.875
C	-2.477	1.148	-0.621
N	-1.801	0.000	-0.495
C	-2.477	-1.148	-0.621
C	-3.842	-1.134	-0.875
H	-4.389	2.063	-0.979
H	-1.914	2.068	-0.525
H	-1.914	-2.068	-0.525
H	-4.389	-2.063	-0.979
Ga	0.274	0.000	0.041
I	0.092	0.000	2.585
I	1.126	-2.166	-1.008
I	1.126	2.166	-1.008

m) GaI_3·pyz·GaI_3



	X	Y	Z
N	1.377	0.000	-0.096
C	0.693	-1.148	-0.090
C	-0.693	-1.148	-0.090
N	-1.377	0.000	-0.096
C	-0.693	1.148	-0.090
C	0.693	1.148	-0.090
H	1.263	-2.069	-0.104
H	-1.263	-2.069	-0.104
H	-1.263	2.069	-0.104
H	1.263	2.069	-0.104
Ga	-3.569	0.000	-0.012
I	-3.879	0.001	2.510
I	-4.113	2.168	-1.234
I	-4.114	-2.168	-1.232
Ga	3.569	0.000	-0.012
I	4.114	2.168	-1.232
I	3.879	-0.001	2.510
I	4.113	-2.168	-1.234

n) $GaI_3(pyz)_2$



	X	Y	Z
N	-5.204	0.257	-0.049
C	-4.505	-0.638	-0.748
C	-3.116	-0.665	-0.736
N	-2.415	0.216	-0.016
C	-3.105	1.115	0.689
C	-4.497	1.128	0.666
H	-5.063	-1.356	-1.336
H	-2.560	-1.395	-1.309
H	-2.537	1.829	1.271
H	-5.047	1.863	1.242
Ga	0.000	0.000	0.015
I	0.000	0.000	-2.574
I	0.325	2.216	1.308
I	-0.325	-2.216	1.308
N	2.415	-0.216	-0.016
C	3.105	-1.115	0.689
C	4.497	-1.128	0.666
N	5.204	-0.257	-0.049
C	4.505	0.638	-0.748
C	3.116	0.665	-0.736
H	2.537	-1.829	1.271
H	5.047	-1.863	1.242
H	5.063	1.356	-1.336
H	2.560	1.394	-1.310