Supplementary information

For the manuscript "Structural Variety of Aluminium and Gallium Coordination Polymers Based on Bis-pyridylethylene: From Molecular Complexes to Ionic Networks" by Nikita Y. Gugin,[a] Alexander Virovets,[b] Eugenia Peresypkina,[b] Elena I. Davydova,[a] Alexey Y. Timoshkin[a]

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Synthetic procedures

General procedures

Due to moisture and air sensitivity of group 13 element trihalides and of the reaction products, syntheses and preparation of samples for physical measurements were carried out in wholeglass apparatuses under vacuum or under an argon atmosphere in a glovebox Inertlab 2GB. The starting materials MX_3 (synthesized from elements, M=Al, X=Br; M=Ga, X=Cl, Br), $AlCl_3$ (99,99%, ABCR) and 1,2-bis(4-pyridyl)ethylene (97%, Sigma-Aldrich) were purified by multiple resublimations in vacuum. Purity control was performed by mass spectrometric measurements (MX_3 and bpe), IR spectroscopy and powder X-ray diffraction (bpe). All complexes were synthesized by direct reaction of group 13 element trihalides with bpe. In general, synthesis was carried out as follows. The self-made wholeglass system with known amounts of reagents in different isolated compartments (Fig. S1a) was evacuated using forvacuum pump with continuous heating of zeolites. After sealing off, compartment with zeolites was placed in a liquid nitrogen bath, providing the residual pressure in the system below 10^{-4} torr as was controlled by disappearance of color of Tesla coil discharge. After that compartment with zeolites was sealed off, thin glass wall was broken with a glass rod, and ligand and metal halide were subsequently sublimed upon heating into the reaction compartment, cooled by liquid nitrogen. The mixture of reagents was sealed (Fig. S1b) and heated in the furnace for several days. The synthesis temperature was chosen in between of melting points of reagents, providing that one of the reagents was in the liquid and another one in the solid state. In several experiments, the excess component after the synthesis was removed by sublimation into special compartment and sealed off.

Synthesis A. $AlCl_3$ (62.0 mg, 0.465 mmol) was sublimed to bpe (149.6 mg, 0.821 mmol). The initial $AlCl_3$ to bpe ratio was 1:1.77 (corresponds to the complex **1**). The system was stored at: ~170ºC (11 days), ~185ºC (5 days). The obtained product was characterized by powder X-ray diffraction analysis (Fig.S24) resulting in a powder pattern of an unidentified phase, mismatching complex **1**.

Synthesis B. $AlBr_3$ (152.7 mg, 0.573 mmol) was sublimed to bpe (209.6 mg, 1.150 mmol). The initial $AlBr_3$ to bpe ratio was 1:2.01. The system was stored at: ~180ºC (11 days), ~200ºC (3 days), ~210ºC (10 days), 220-230ºC (2 days). According to the X–ray analysis single crystals of **4** were grown in this system;

Synthesis C. $AlBr_3$ (98.3 mg, 0.369 mmol) was sublimed to bpe (134.0 mg, 0.735 mmol) with 0.2 ml of toluene. The initial $AlBr_3$ to bpe ratio was 1:2.00. The system was stored at: 135ºC (1 day), ~150ºC (3 days), 160-165ºC (3 days). Then the solvent was condensed into a special compartment and sealed off. The obtained product was characterized by powder X-ray diffraction analysis (Fig.S25) resulting in a powder pattern of poor quality, mismatching $AlBr_3$ complexes **3**, **4**, **8** reported in this work.

Synthesis D. $AlBr_3$ (730.4 mg, 2.739 mmol) was sublimed to bpe (375.8 mg, 2.062 mmol). The initial $AlBr_3$ to bpe ratio was 1.33:1 (corresponds to the complex **3**). The system was stored at 120-125ºC (5 days). After that, an excess of bpe was sublimed (115-130ºC, 6 days) into a special compartment and sealed off. The mass was determined (179.1 mg, 0.983 mmol). The $AlBr_3$ to bpe ratio was 2.54:1, in disagreement with the desired 1.33:1 composition of the complex **3**. The obtained product was characterized by powder X-ray diffraction analysis (Fig.S26) resulting in a powder pattern of **8** (simulated from single crystal data) as well as an unidentified phase. Airtight specimen holder with dome was used.

Synthesis E. $AlBr_3$ (251.3 mg, 0.942 mmol) was sublimed to bpe (265.5 mg, 1.457 mmol). The initial $AlBr_3$ to bpe ratio was 1:1.55 (corresponds to the complex **4**). The system was stored at: ~130ºC (5 days). After that, an excess of bpe was sublimed (~110ºC (4 days), ~120ºC (7 days), ~140ºC (3 days)) into a special compartment, and sealed off. The obtained product was characterized by powder X-ray diffraction analysis (Fig.S27) resulting in a powder pattern of **8** (simulated from single crystal data) as well as an unidentified phase.

Synthesis F. $AlBr_3$ (209.0 mg, 0.784 mmol) and bpe (278.0 mg, 1.526 mmol) were mixed in a glass ampoule and sealed under reduced pressure. The initial $AlBr_3$ to bpe ratio was 1:1.95. The system was stored at: 130ºC (1 day), ~145ºC (4 days), ~160ºC (2 days), ~180ºC (26 days). According to the X–ray analysis single crystals of the protonated ligand $[Hbpe]^+Br^-$ were grown in this system;

Synthesis G. $AlBr_3$ (224.1 mg, 0.840 mmol) and bpe (157.7 mg, 0.865 mmol) were mixed in a glass ampoule and sealed under reduced pressure. The initial $AlBr_3$ to bpe ratio was 1:1.03. The system was stored at ~145ºC (6 days), 163ºC (1 day). The obtained product was characterized by powder X-ray diffraction analysis (Fig.S28) resulting in a powder pattern of **8** (simulated from single crystal data) as well as an unidentified phase.

Synthesis H. $GaCl_3$ (265.7 mg, 1.509 mmol) was sublimed to bpe (274.1 mg, 1.504 mmol). The initial $GaCl_3$ to bpe ratio was 1.00:1 (corresponds to the complex **6**). The system was stored at 120-125ºC for 6 days. After that, an excess of bpe was sublimed (110-125ºC, 5 days) into a special compartment and sealed off. The mass was determined (106.6 mg, 0.585 mmol). The $GaCl_3$ to bpe ratio was 1.64:1, in disagreement with the desired 1:1 composition of the complex **6**. The obtained product was characterized by powder X-ray diffraction analysis resulting in a powder pattern of the mixture of **9** and **6** (simulated from single crystal data) (Fig.S29). Airtight specimen holder with dome was used.

Synthesis I. $GaCl_3$ (163.4 mg, 0.930 mmol) was sublimed to bpe (297.1 mg, 1.630 mmol). The initial $GaCl_3$ to bpe ratio was 1:1.75 (corresponds to the complex **2**). The system was stored at 120-125ºC for 9 days. After that, an excess of bpe was sublimed (110-125ºC, 5 days) into a special compartment and sealed off. The obtained product was characterized by powder X-ray diffraction analysis resulting in a powder pattern that is completely identical to the diffraction pattern of the bulk product of the Synthesis H.

Synthesis J. $GaBr_3$ (254.1 mg, 0.821 mmol) was sublimed to bpe (305.7 mg, 1.678 mmol). The initial $GaBr_3$ to bpe ratio was 1:2.04 (corresponds to the complex **5**). The system was stored at: ~130ºC (8 days), ~145ºC (6 days). After that, an excess of bpe was sublimed (~160ºC, 2 days) into a special compartment and sealed off. The mass was determined (124.0 mg, 0.680 mmol). The $GaBr_3$ to bpe ratio was 1:1.21, in disagreement with the desired 1:2 composition of the complex **5**. The obtained product was characterized by powder X-ray diffraction analysis (Fig.S30) resulting in a powder pattern that matches the desired complex **5** (simulated from single crystal data) in the low-theta region, but differs from **5** in the higher-theta region. Then single crystals suitable for the X-ray analysis were grown from this sample by slow sublimation in a vacuum at 150–160°C during 3 days. This experiment yielded crystals of both complexes **5** and **11**.

Synthesis K. $GaBr_3$ (112.2 mg, 0.363 mmol) was sublimed to bpe (64.0 mg, 0.351 mmol). The initial $GaBr_3$ to bpe ratio was 1.03:1 (corresponds to the complex **11**). The system was stored at 155-165ºC for 8 days. After that, an excess of bpe was sublimed (~120ºC, 2 days) into a special compartment and sealed off. The obtained product was characterized by powder X-ray diffraction analysis (Fig.S31) resulting in a powder pattern that matches the complex **10a**.

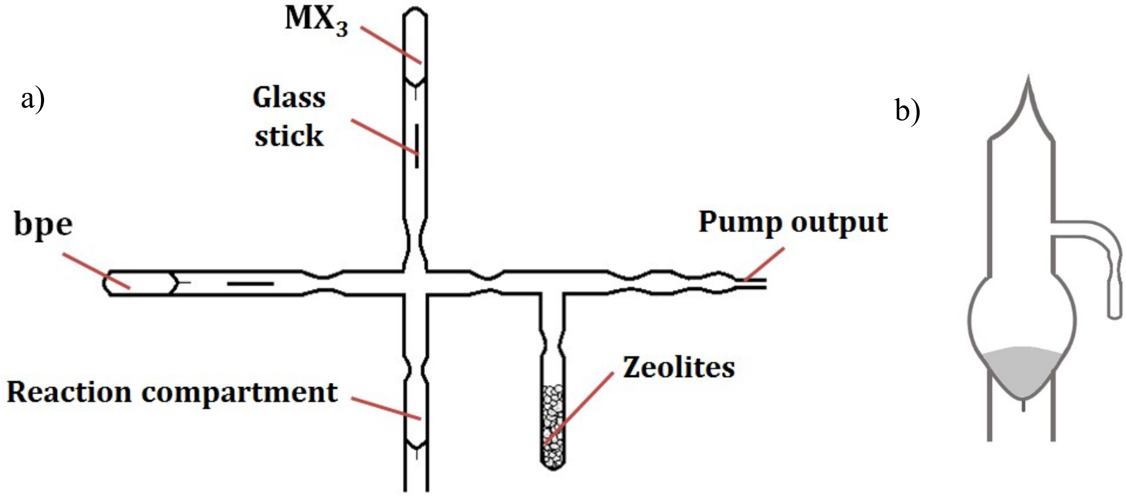


Fig. S1 a) A schematic view of the synthetic system; b) A sealed glass ampoule with the reagent mixture and a compartment for the excess reagent (optional).

Table S1 Crystal data, details of data collection and refinement for $[Hbpe]^+Br^-$.

Compound	$[Hbpe]^+Br^-$
Empirical formula	$C_{12}H_{11}BrN_2$
Formula weight	263.14
Temperature/K	90(2)
Crystal system	orthorhombic
Space group	Pnma
a/Å	23.5470(7)
b/Å	12.0475(3)
c/Å	8.0311(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2278.30(11)
Z	8
ρ_{calc}/ g/cm^3	1.534
μ/mm^{-1}	4.646
F(000)	1056.0
Crystal size/mm^3	0.175 × 0.100 × 0.059
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.508 to 146.978
Index ranges	$-29 \leq h \leq 26$, $-14 \leq k \leq 10$, $-8 \leq l \leq 9$
Reflections collected	5941
Independent reflections	2369 [R_{int} = 0.0326, R_{sigma} = 0.0411]
Data/restraints/parameters	2369/12/157
Goodness-of-fit on F^2	1.006
Final R indexes [I≥2σ (I)]	R_1 = 0.0355, wR_2 = 0.0698
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.0737
Largest diff. peak/hole / e Å^{-3}	0.42/-0.32

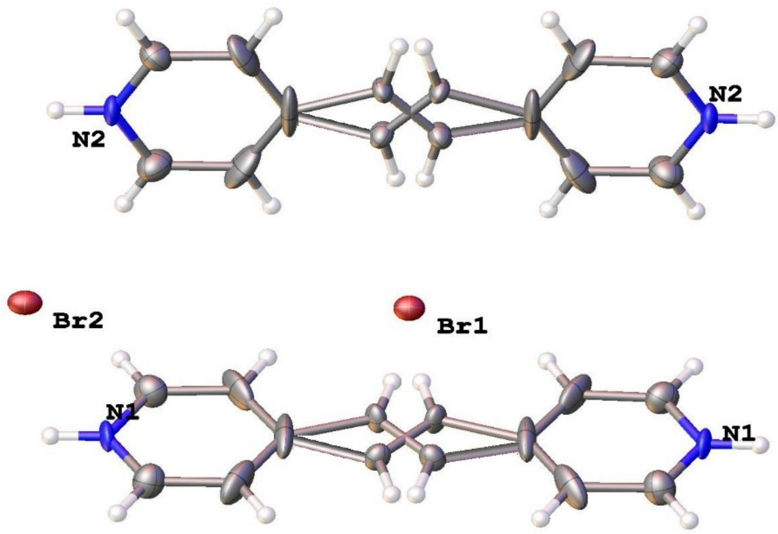


Fig. S2 Molecular structure for $[Hbpe]^+Br^-$.
Structure $[Hbpe]^+Br^-$ was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984541.

Table S2 Selected geometric parameters (Å, º).

C11—C12	1.387 (7)	C21—C22	1.385 (8)
C11—C16	1.391 (7)	C21—C26	1.384 (8)
C11—C17	1.515 (7)	C21—C27	1.534 (7)
C12—C13	1.367 (6)	C22—C23	1.379 (6)
C13—N1	1.338 (5)	C23—N2	1.341 (5)
N1—C15	1.332 (5)	N2—C25	1.344 (5)
C15—C16	1.389 (6)	C25—C26	1.376 (6)
C17—C18	1.315 (8)	C27—C28	1.317 (9)

Crystallographic details on crystal structures **1-11** and $[Hbpe]^+Br^-$

Experimental

The diffraction data were collected by routine technique on Rigaku Oxford Diffraction SuperNova (for **1-7**, **9-11** and $[Hbpe]^+Br^-$) or Gemini R Ultra (for **8**) automatic 4-cycle diffractometers using CuKα radiation focused by mirrors. All measurements were done at 90 K (**1**, **2**, **4**, **6**, **7** and $[Hbpe]^+Br^-$) or 123 K (**3**, **5**, **8**, **9**, **10a**, **10b**) in the stream of cold nitrogen. The absorption corrections were applied taking into account crystal size and shape. The structures were solved using dual-space algorithm realized in SHELXT program and refined by full-matrix least-squares method in anisotropic approximation (except for partly occupied positions of carbon atoms) using various versions of SHELXL program. Hydrogen atoms were positioned geometrically and refined riding on the corresponding pivot atoms with aryl C-H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Some groups of compounds appear to be isostructural with respect to each other, namely, **1** and **2**; **7**, **9** and **10a**; **8** and **10b**.

In the structures of compounds **1**, **3-5** and $[Hbpe]^+Br^-$ a crystallographic disorder was observed (Fig.S3). Thus, in the structure **1** one of the bpe ligands shows conformational disorder that was approximated by splitting of CH=CH fragment over two positions with the relative weights of 60:40%. Our attempt to split the positions of the neighboring C and H atoms (C612-C614 and C618, C619, C622) failed and the disorder here appeared to be better described with the elongated a.d.p. ellipsoids (Fig.S3a). Similar disorder was observed for both crystallographically independent protonated bpe cations in $[Hbpe]^+Br^-$ (Fig.S3b).

In **3** one of the $AlBr_3$ groups is rotationally disordered over two very close positions with the weight of Br31 and Br33 atoms equal to 0.70, and of Br32 and Br34 atoms equal to 0.30 (Fig.S3c).

In **4** $AlBr_4^-$ anion suffers from the positional disorder over two positions with equal weights (Fig.S3d). In addition, free bpe ligand is disordered over the center of symmetry (Fig.S3e). In **5** free bpe ligand is also disordered over two alternative positions with equal weights (Fig.S3f). The refinement of the partly occupied positions of carbon atoms in the structures **4** and **5** was done in isotropic approximation.

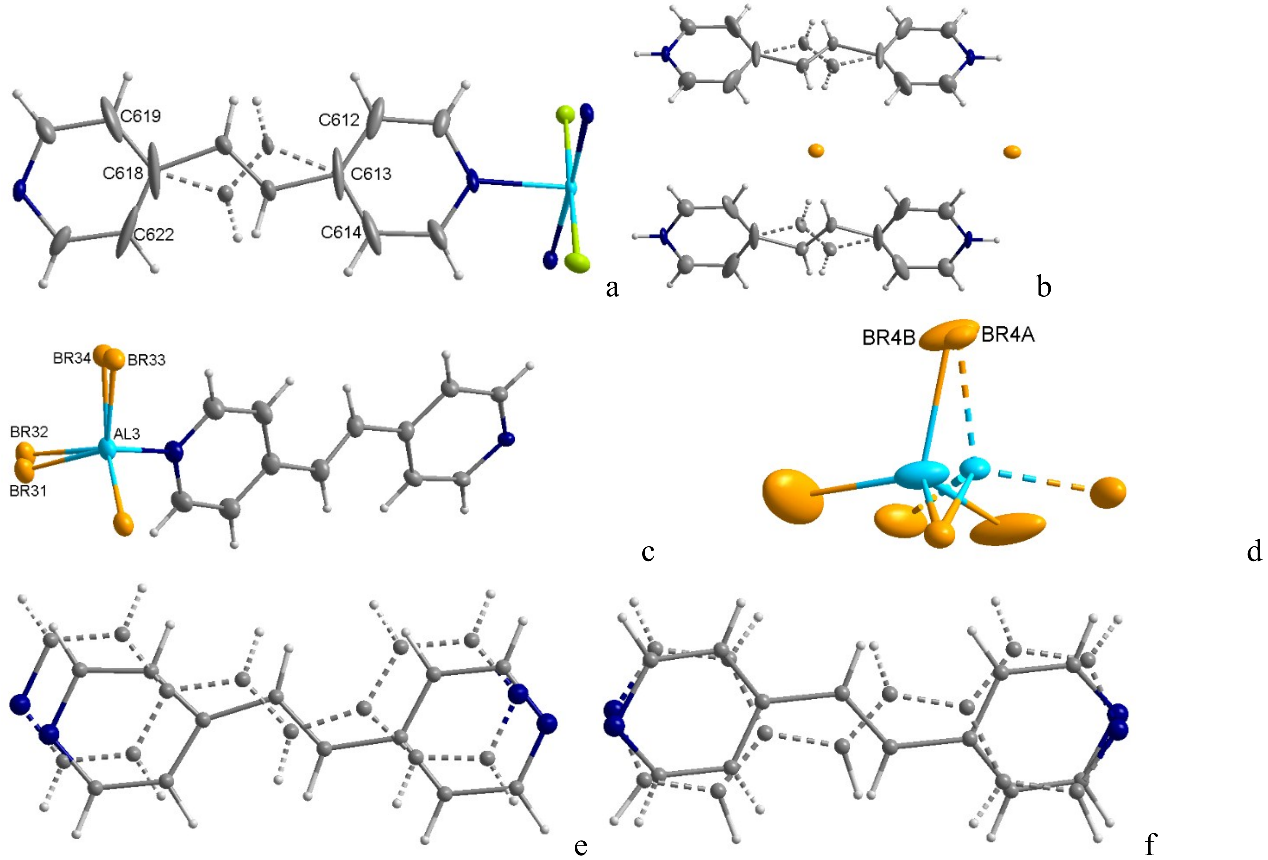
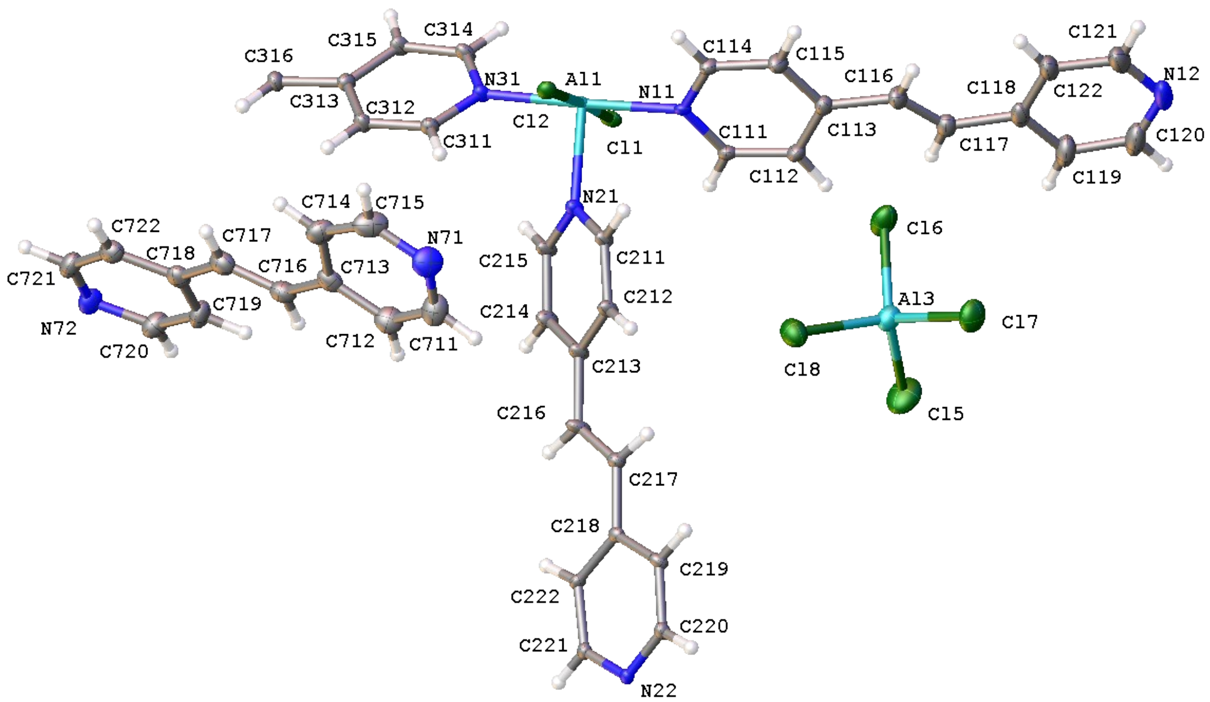


Fig. S3 The crystallographic disorder in **1** (a), $[Hbpe]^{+}Br^{-}$ (b), **3** (c), **4** (d, e), **5** (f).

Crystal structure **1**



a

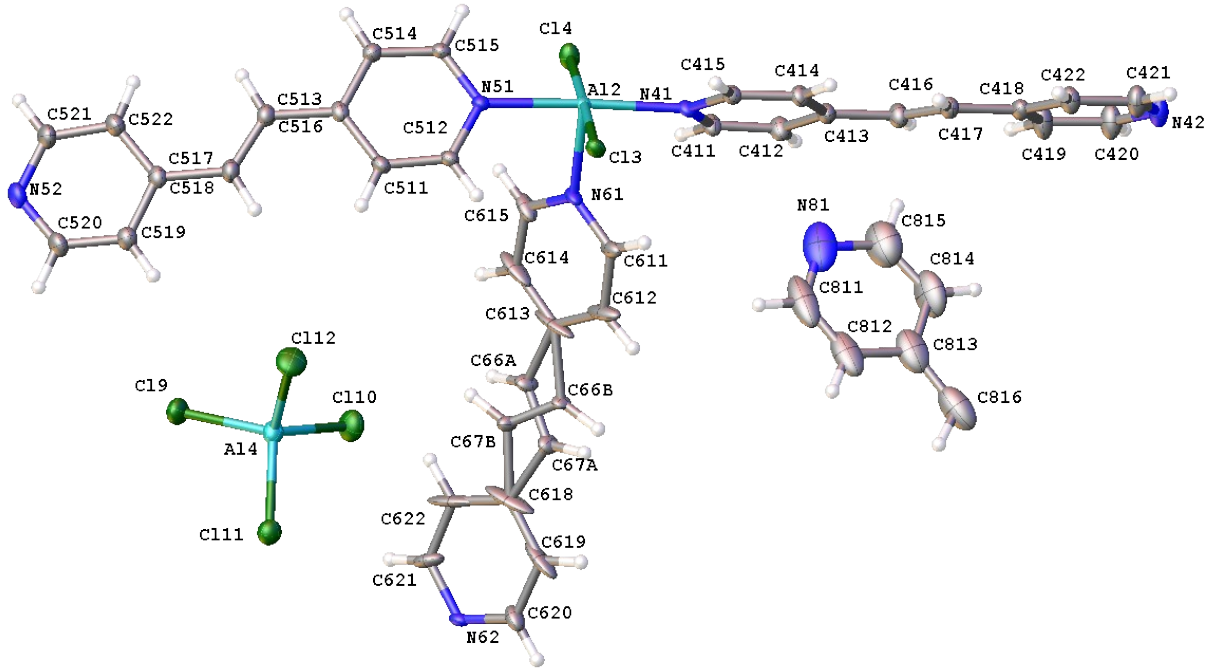


Fig. S4 Asymmetric unit and enumeration scheme in **1** (ellipsoids at 50% probability).
Structure **1** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984540.

Table S3 Selected geometric parameters (Å, º).

Al1—Cl1	2.2607 (7)	N51—C511	1.358 (2)
Al1—Cl2	2.2779 (7)	N51—C515	1.350 (3)
Al1—N11	2.0530 (17)	C511—C512	1.374 (3)
Al1—N21	2.0488 (16)	C512—C513	1.398 (3)
Al1—N22^{i}	2.0508 (16)	C513—C514	1.406 (3)
Al1—N31	2.0526 (17)	C513—C516	1.467 (3)
N11—C111	1.355 (3)	C514—C515	1.380 (3)
N11—C115	1.349 (3)	C516—C517	1.345 (3)
C111—C112	1.367 (3)	C517—C518	1.468 (3)
C112—C113	1.394 (3)	C518—C519	1.396 (3)
C113—C114	1.393 (3)	C518—C522	1.393 (3)
C113—C116	1.462 (3)	C519—C520	1.384 (3)
C114—C115	1.373 (3)	C520—N52	1.337 (3)
C116—C117	1.333 (3)	C521—C522	1.385 (3)
C117—C118	1.460 (3)	C521—N52	1.338 (3)
C118—C119	1.387 (4)	N61—C611	1.348 (3)
C118—C122	1.395 (4)	N61—C615	1.353 (3)
C119—C120	1.385 (4)	C611—C612	1.387 (3)
C120—N12	1.326 (4)	C612—C613	1.387 (5)
C121—C122	1.385 (4)	C613—C614	1.397 (5)
C121—N12	1.338 (4)	C613—C66A	1.488 (4)
N21—C211	1.354 (2)	C613—C66B	1.572 (6)
N21—C215	1.350 (3)	C614—C615	1.368 (3)
C211—C212	1.374 (3)	C66A—C67A	1.316 (5)
C212—C213	1.399 (3)	C67A—C618	1.533 (5)
C213—C214	1.400 (3)	C66B—C67B	1.327 (8)
C213—C216	1.468 (3)	C67B—C618	1.551 (6)
C214—C215	1.376 (3)	C618—C619	1.371 (5)
C216—C217	1.334 (3)	C618—C622	1.379 (6)
C217—C218	1.461 (3)	C619—C620	1.380 (3)
C218—C219	1.398 (3)	C620—N62	1.349 (3)
C218—C222	1.392 (3)	C621—C622	1.390 (4)
C219—C220	1.379 (3)	C621—N62	1.342 (3)
C220—N22	1.353 (2)	N62—Al2^{ii}	2.0359 (16)
C221—C222	1.383 (3)	N71—C711	1.341 (3)
C221—N22	1.352 (2)	N71—C715	1.331 (4)
N22—Al1^{ii}	2.0508 (16)	C711—C712	1.377 (4)
N31—C311	1.348 (3)	C712—C713	1.384 (4)
N31—C315	1.355 (2)	C713—C714	1.397 (3)
C311—C312	1.379 (3)	C713—C716	1.472 (3)
C312—C313	1.395 (3)	C714—C715	1.385 (4)
C313—C314	1.395 (3)	C716—C717	1.324 (3)
C313—C316	1.462 (3)	C717—C718	1.473 (3)
C314—C315	1.372 (3)	C718—C719	1.394 (3)
C316—C316^{iii}	1.333 (4)	C718—C722	1.390 (3)
Al2—Cl3	2.2491 (7)	C719—C720	1.379 (3)
Al2—Cl4	2.2692 (7)	C720—N72	1.343 (3)
Al2—N41	2.0787 (17)	C721—C722	1.382 (3)
Al2—N51	2.0744 (17)	C721—N72	1.329 (3)
Al2—N61	2.0592 (16)	N81—C811	1.338 (6)
Al2—N62^{i}	2.0359 (16)	N81—C815	1.346 (5)
N41—C411	1.343 (3)	C811—C812	1.380 (6)
N41—C415	1.355 (3)	C812—C813	1.391 (5)
C411—C412	1.380 (3)	C813—C814	1.399 (5)
C412—C413	1.397 (3)	C813—C816	1.473 (6)
C413—C414	1.396 (3)	C814—C815	1.373 (6)

C413—C416	1.466 (3)	C816—C816^{iv}	1.328 (7)
C414—C415	1.379 (3)	Al3—Cl5	2.1223 (9)
C416—C417	1.334 (3)	Al3—Cl6	2.1449 (9)
C417—C418	1.470 (3)	Al3—Cl7	2.1275 (9)
C418—C419	1.393 (3)	Al3—Cl8	2.1302 (9)
C418—C422	1.388 (3)	Al4—Cl9	2.1449 (8)
C419—C420	1.384 (3)	Al4—Cl10	2.1249 (9)
C420—N42	1.335 (3)	Al4—Cl11	2.1426 (8)
C421—C422	1.385 (3)	Al4—Cl12	2.1373 (8)
C421—N42	1.333 (3)		
Cl1—Al1—Cl2	176.75 (3)	N61—Al2—Cl3	91.84 (6)
N11—Al1—Cl1	91.41 (5)	N61—Al2—Cl4	88.89 (6)
N11—Al1—Cl2	91.54 (5)	N61—Al2—N41	89.58 (7)
N21—Al1—Cl1	89.05 (5)	N61—Al2—N51	87.82 (7)
N21—Al1—Cl2	89.63 (5)	N62^{i}—Al2—Cl3	89.89 (5)
N21—Al1—N11	88.99 (6)	N62^{i}—Al2—Cl4	89.39 (5)
N21—Al1—N22^{i}	176.96 (7)	N62^{i}—Al2—N41	90.06 (7)
N21—Al1—N31	93.16 (7)	N62^{i}—Al2—N51	92.57 (7)
N22^{i}—Al1—Cl1	91.31 (5)	N62^{i}—Al2—N61	178.24 (8)
N22^{i}—Al1—Cl2	90.16 (5)	Cl5—Al3—Cl6	109.00 (4)
N22^{i}—Al1—N11	87.99 (6)	Cl5—Al3—Cl7	110.51 (4)
N22^{i}—Al1—N31	89.87 (6)	Cl5—Al3—Cl8	110.79 (4)
N31—Al1—Cl1	88.31 (5)	Cl7—Al3—Cl6	108.09 (4)
N31—Al1—Cl2	88.79 (5)	Cl7—Al3—Cl8	110.99 (4)
N31—Al1—N11	177.83 (7)	Cl8—Al3—Cl6	107.35 (4)
Cl3—Al2—Cl4	178.44 (3)	Cl10—Al4—Cl9	110.66 (4)
N41—Al2—Cl3	90.47 (5)	Cl10—Al4—Cl11	109.21 (4)
N41—Al2—Cl4	90.91 (5)	Cl10—Al4—Cl12	109.75 (4)
N51—Al2—Cl3	88.68 (5)	Cl11—Al4—Cl9	107.54 (3)
N51—Al2—Cl4	89.97 (5)	Cl12—Al4—Cl9	109.43 (4)
N51—Al2—N41	177.23 (7)	Cl12—Al4—Cl11	110.22 (4)

Symmetry code(s): (i) *x*-1/2, -*y*+1/2, *z*-1/2; (ii) *x*+1/2, -*y*+1/2, *z*+1/2; (iii) -*x*+1, -*y*, -*z*+1; (iv) -*x*, -*y*+1, -*z*+1.

Crystal structure **2**

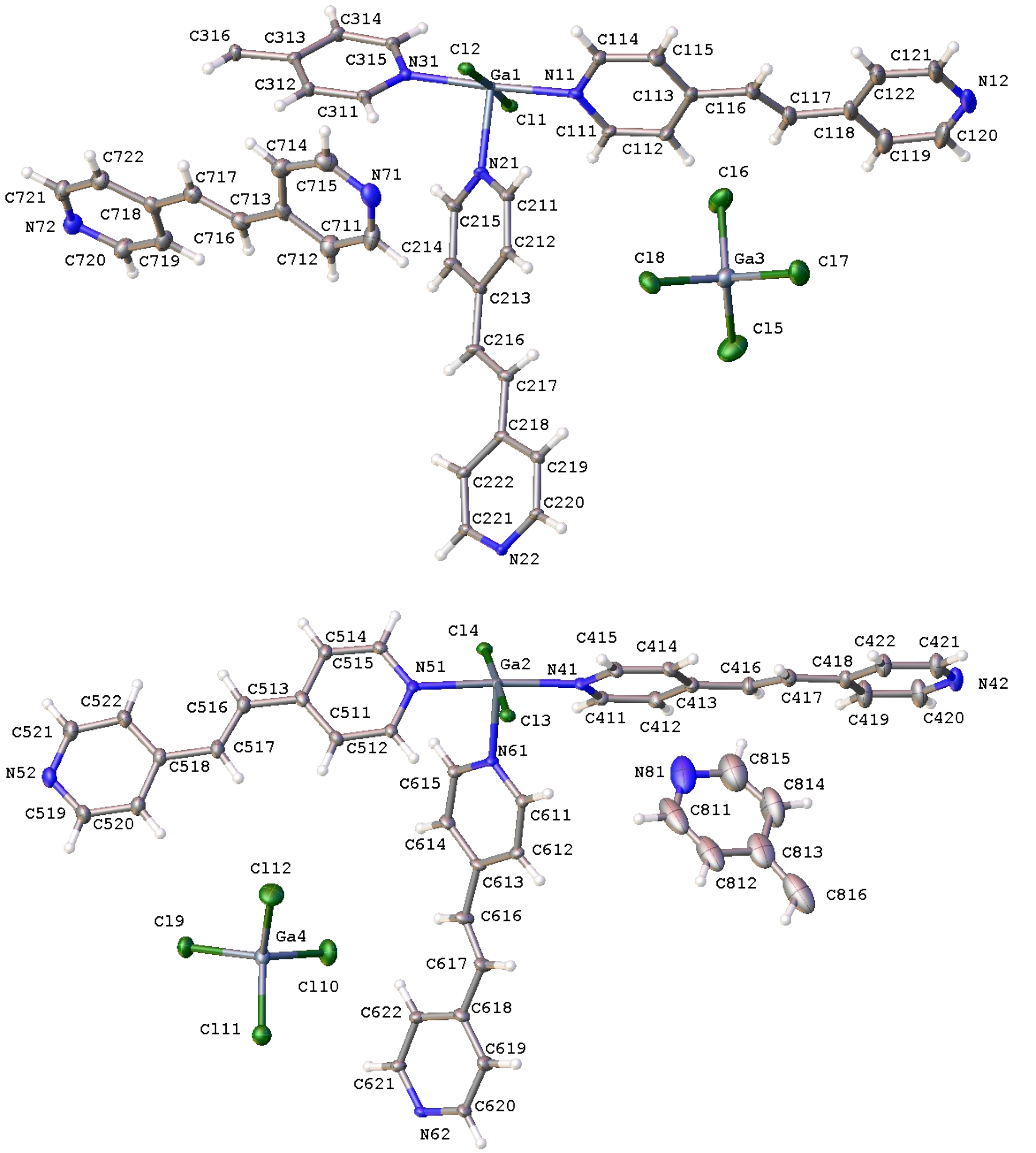


Fig. S5 Asymmetric unit and enumeration scheme in **2** (ellipsoids at 50% probability).

Structure **2** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984532.

Table S4 Selected geometric parameters (Å, º).

Ga1—Cl1	2.2985 (7)	C421—C422	1.386 (4)
Ga1—Cl2	2.3259 (7)	C421—N42	1.331 (4)
Ga1—N11	2.104 (2)	N51—C511	1.346 (3)
Ga1—N21	2.0941 (17)	N51—C515	1.346 (3)
Ga1—N22^{i}	2.1021 (17)	C511—C512	1.382 (3)
Ga1—N31	2.109 (2)	C512—C513	1.400 (4)

N11—C111	1.349 (3)	C513—C514	1.391 (4)
N11—C115	1.349 (3)	C513—C516	1.466 (3)
C111—C112	1.376 (4)	C514—C515	1.384 (4)
C112—C113	1.390 (4)	C516—C517	1.333 (4)
C113—C114	1.390 (4)	C517—C518	1.471 (3)
C113—C116	1.472 (4)	C518—C519	1.391 (4)
C114—C115	1.376 (4)	C518—C522	1.388 (4)
C116—C117	1.321 (4)	C519—C520	1.388 (4)
C117—C118	1.463 (4)	C520—N52	1.334 (4)
C118—C119	1.380 (5)	C521—C522	1.386 (4)
C118—C122	1.392 (5)	C521—N52	1.337 (4)
C119—C120	1.392 (4)	N61—C611	1.333 (3)
C120—N12	1.334 (5)	N61—C615	1.355 (3)
C121—C122	1.385 (4)	C611—C612	1.392 (3)
C121—N12	1.332 (5)	C612—C613	1.387 (4)
N21—C211	1.342 (3)	C613—C614	1.392 (4)
N21—C215	1.341 (3)	C613—C616	1.474 (3)
C211—C212	1.378 (3)	C614—C615	1.372 (3)
C212—C213	1.396 (4)	C616—C617	1.317 (4)
C213—C214	1.394 (4)	C617—C618	1.480 (3)
C213—C216	1.472 (3)	C618—C619	1.386 (4)
C214—C215	1.383 (3)	C618—C622	1.390 (4)
C216—C217	1.324 (4)	C619—C620	1.381 (3)
C217—C218	1.470 (3)	C620—N62	1.348 (3)
C218—C219	1.397 (4)	C621—C622	1.390 (3)
C218—C222	1.395 (3)	C621—N62	1.333 (3)
C219—C220	1.378 (3)	N62—Ga2^{ii}	2.0863 (17)
C220—N22	1.350 (3)	N71—C711	1.332 (4)
C221—C222	1.390 (3)	N71—C715	1.339 (4)
C221—N22	1.337 (3)	C711—C712	1.382 (4)
N22—Ga1^{ii}	2.1021 (17)	C712—C713	1.394 (4)
N31—C311	1.349 (3)	C713—C714	1.391 (4)
N31—C315	1.343 (3)	C713—C716	1.474 (4)
C311—C312	1.382 (3)	C714—C715	1.390 (4)
C312—C313	1.392 (4)	C716—C717	1.323 (4)
C313—C314	1.395 (4)	C717—C718	1.475 (4)
C313—C316	1.464 (3)	C718—C719	1.399 (4)
C314—C315	1.379 (3)	C718—C722	1.388 (4)
C316—C316^{iii}	1.329 (5)	C719—C720	1.373 (4)
Ga2—Cl3	2.2893 (8)	C720—N72	1.345 (4)
Ga2—Cl4	2.3073 (8)	C721—C722	1.384 (4)
Ga2—N41	2.122 (2)	C721—N72	1.334 (4)
Ga2—N51	2.141 (2)	N81—C811	1.353 (6)
Ga2—N61	2.1159 (17)	N81—C815	1.342 (6)
Ga2—N62^{i}	2.0863 (18)	C811—C812	1.360 (7)
N41—C411	1.347 (3)	C812—C813	1.383 (6)
N41—C415	1.346 (3)	C813—C814	1.419 (7)
C411—C412	1.383 (4)	C813—C816	1.491 (7)
C412—C413	1.398 (4)	C814—C815	1.345 (7)
C413—C414	1.401 (4)	C816—C816^{iv}	1.303 (9)
C413—C416	1.472 (4)	Ga3—Cl5	2.1614 (8)
C414—C415	1.378 (4)	Ga3—Cl6	2.1874 (8)
C416—C417	1.331 (4)	Ga3—Cl7	2.1672 (8)
C417—C418	1.478 (4)	Ga3—Cl8	2.1719 (9)
C418—C419	1.388 (4)	Ga4—Cl9	2.1844 (7)
C418—C422	1.385 (4)	Ga4—Cl10	2.1641 (8)
C419—C420	1.390 (4)	Ga4—Cl11	2.1833 (8)
C420—N42	1.334 (4)	Ga4—Cl12	2.1771 (7)

Cl1—Ga1—Cl2	176.44 (2)	N61—Ga2—Cl3	91.27 (6)
N11—Ga1—Cl1	91.96 (6)	N61—Ga2—Cl4	89.25 (6)
N11—Ga1—Cl2	91.34 (6)	N61—Ga2—N41	90.07 (7)
N11—Ga1—N31	177.12 (7)	N61—Ga2—N51	87.04 (7)
N21—Ga1—Cl1	89.15 (6)	N62^{i}—Ga2—Cl3	89.90 (6)
N21—Ga1—Cl2	89.54 (7)	N62^{i}—Ga2—Cl4	89.55 (6)
N21—Ga1—N11	89.10 (7)	N62^{i}—Ga2—N41	90.96 (7)
N21—Ga1—N22^{i}	176.59 (8)	N62^{i}—Ga2—N51	91.95 (7)
N21—Ga1—N31	93.72 (7)	N62^{i}—Ga2—N61	178.43 (9)
N22^{i}—Ga1—Cl1	91.05 (6)	Cl5—Ga3—Cl6	108.72 (4)
N22^{i}—Ga1—Cl2	90.46 (6)	Cl5—Ga3—Cl7	110.56 (4)
N22^{i}—Ga1—N11	87.49 (7)	Cl5—Ga3—Cl8	111.20 (4)
N22^{i}—Ga1—N31	89.69 (7)	Cl7—Ga3—Cl6	108.58 (3)
N31—Ga1—Cl1	88.69 (6)	Cl7—Ga3—Cl8	110.75 (4)
N31—Ga1—Cl2	88.09 (6)	Cl8—Ga3—Cl6	106.91 (3)
Cl3—Ga2—Cl4	178.29 (3)	Cl10—Ga4—Cl9	111.25 (3)
N41—Ga2—Cl3	90.85 (7)	Cl10—Ga4—Cl11	109.46 (3)
N41—Ga2—Cl4	90.77 (6)	Cl10—Ga4—Cl12	109.48 (3)
N41—Ga2—N51	176.99 (7)	Cl11—Ga4—Cl9	107.01 (3)
N51—Ga2—Cl3	88.39 (7)	Cl12—Ga4—Cl9	109.30 (3)
N51—Ga2—Cl4	90.02 (7)	Cl12—Ga4—Cl11	110.31 (3)

Symmetry code(s): (i) *x*-1/2, -*y*+1/2, *z*-1/2; (ii) *x*+1/2, -*y*+1/2, *z*+1/2; (iii) -*x*+1, -*y*, -*z*+1; (iv) -*x*, -*y*+1, -*z*+1.

Crystal structure **3**

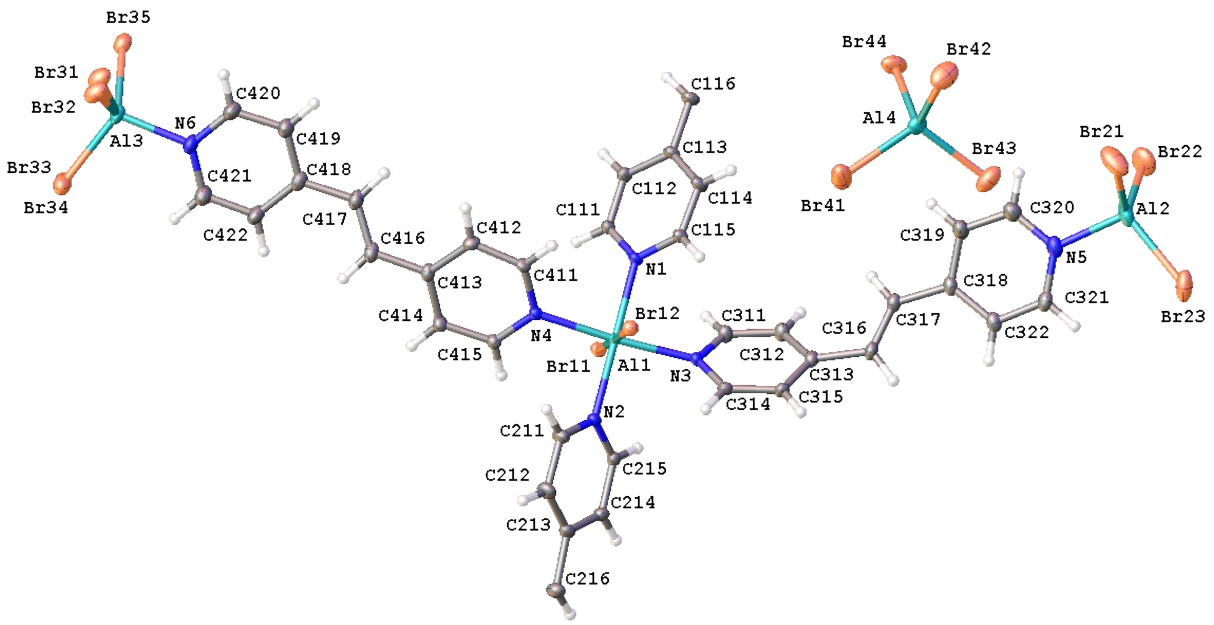


Fig. S6 Asymmetric unit and enumeration scheme in **3** (ellipsoids at 50% probability).
Structure **3** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984537.

Table S5 Selected geometric parameters (Å, º).

Al1—Br11	2.4700 (8)	C112—C113	1.393 (4)
Al1—Br12	2.4621 (8)	C113—C114	1.395 (4)
Al1—N1	2.056 (2)	C113—C116	1.462 (4)
Al1—N2	2.051 (2)	C114—C115	1.376 (4)
Al1—N3	2.068 (2)	C116—C116^{i}	1.328 (6)
Al1—N4	2.049 (2)	C211—C212	1.384 (4)
Al2—Br21	2.2706 (11)	C212—C213	1.395 (4)
Al2—Br22	2.2732 (11)	C213—C214	1.383 (4)
Al2—Br23	2.2649 (12)	C213—C216	1.475 (4)
Al2—N5	1.950 (3)	C214—C215	1.383 (4)
Al3—Br31	2.2860 (19)	C216—C216^{ii}	1.330 (6)
Al3—Br33	2.2934 (17)	C311—C312	1.371 (4)
Al3—Br32	2.254 (5)	C312—C313	1.401 (4)
Al3—Br34	2.246 (4)	C313—C314	1.393 (4)
Al3—Br35	2.2863 (10)	C313—C316	1.471 (4)
Al3—N6	1.936 (3)	C314—C315	1.384 (4)
Al4—Br41	2.2858 (11)	C316—C317	1.331 (4)
Al4—Br42	2.2962 (10)	C317—C318	1.470 (4)
Al4—Br43	2.2871 (10)	C318—C319	1.400 (4)
Al4—Br44	2.2980 (10)	C318—C322	1.397 (4)
N1—C111	1.350 (3)	C319—C320	1.372 (5)
N1—C115	1.352 (3)	C321—C322	1.380 (4)
N2—C211	1.353 (4)	C411—C412	1.372 (4)
N2—C215	1.345 (4)	C412—C413	1.403 (4)
N3—C311	1.353 (4)	C413—C414	1.397 (4)
N3—C315	1.349 (4)	C413—C416	1.465 (4)
N4—C411	1.357 (4)	C414—C415	1.378 (4)
N4—C415	1.349 (4)	C416—C417	1.333 (4)

N5—C320	1.356 (4)	C417—C418	1.467 (4)
N5—C321	1.352 (4)	C418—C419	1.388 (4)
N6—C420	1.348 (4)	C418—C422	1.402 (5)
N6—C421	1.348 (4)	C419—C420	1.379 (5)
C111—C112	1.380 (4)	C421—C422	1.372 (5)
Br12—Al1—Br11	179.23 (4)	N5—Al2—Br22	104.11 (9)
N1—Al1—Br11	88.77 (7)	N5—Al2—Br23	105.58 (10)
N1—Al1—Br12	90.97 (7)	Br31—Al3—Br33	119.69 (6)
N1—Al1—N3	87.98 (9)	Br31—Al3—Br35	108.28 (4)
N2—Al1—Br11	90.41 (7)	Br32—Al3—Br35	116.93 (8)
N2—Al1—Br12	89.85 (7)	Br34—Al3—Br32	103.22 (12)
N2—Al1—N1	179.16 (11)	Br34—Al3—Br35	118.67 (9)
N2—Al1—N3	91.85 (9)	Br35—Al3—Br33	110.02 (4)
N3—Al1—Br11	90.20 (7)	N6—Al3—Br31	107.43 (10)
N3—Al1—Br12	90.52 (7)	N6—Al3—Br33	105.91 (9)
N4—Al1—Br11	90.05 (7)	N6—Al3—Br32	106.45 (14)
N4—Al1—Br12	89.22 (7)	N6—Al3—Br34	106.19 (13)
N4—Al1—N1	87.83 (9)	N6—Al3—Br35	104.41 (9)
N4—Al1—N2	92.35 (9)	Br41—Al4—Br42	110.99 (5)
N4—Al1—N3	175.79 (9)	Br41—Al4—Br43	111.10 (4)
Br21—Al2—Br22	110.79 (5)	Br41—Al4—Br44	107.70 (4)
Br23—Al2—Br21	113.96 (5)	Br42—Al4—Br44	108.60 (4)
Br23—Al2—Br22	115.10 (5)	Br43—Al4—Br42	108.70 (4)
N5—Al2—Br21	106.24 (9)	Br43—Al4—Br44	109.70 (4)

Symmetry code(s): (i) -*x*, -*y*+1, -*z*+1; (ii) -*x*+2, -*y*+2, -*z*+1.

Crystal structure **4**

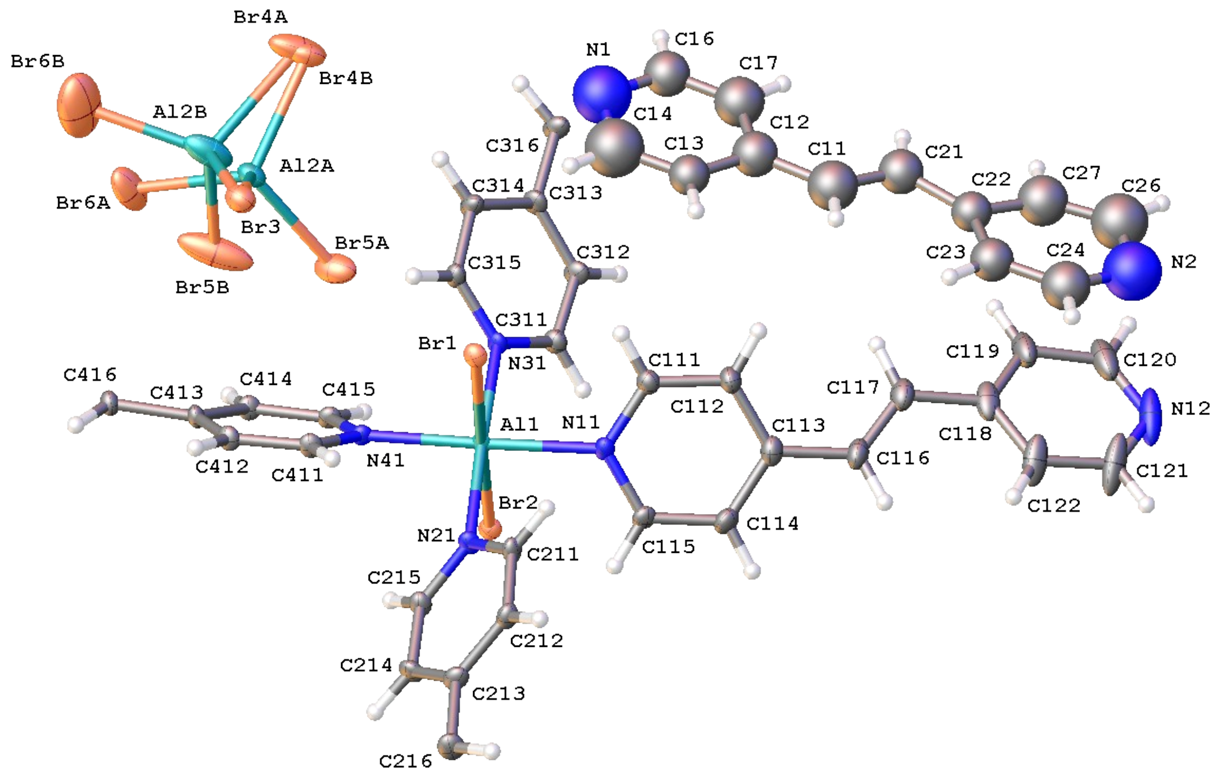


Fig. S7 Asymmetric unit and enumeration scheme in **4** (ellipsoids at 50% probability).

Structure **4** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984538.

Table S6 Selected geometric parameters (Å, º).

Br1—Al1	2.4723 (13)	C312—C313	1.390 (7)
Br2—Al1	2.4784 (13)	C313—C314	1.401 (6)
Al1—N11	2.074 (4)	C313—C316	1.462 (6)
Al1—N21	2.053 (4)	C314—C315	1.381 (6)
Al1—N31	2.065 (4)	C316—C316^{ii}	1.329 (10)
Al1—N41	2.029 (4)	C411—C412	1.381 (6)
N11—C111	1.346 (6)	C412—C413	1.393 (6)
N11—C115	1.347 (6)	C413—C414	1.402 (6)
N12—C120	1.342 (11)	C413—C416	1.470 (6)
N12—C121	1.322 (11)	C414—C415	1.365 (6)
N21—C211	1.354 (6)	C416—C416^{iii}	1.329 (9)
N21—C215	1.351 (6)	Br3—Al2A	2.366 (3)
N31—C311	1.344 (6)	Br3—Al2B	2.212 (4)
N31—C315	1.344 (6)	Al2A—Br4A	2.225 (6)
N41—C411	1.351 (6)	Al2A—Br5A	2.301 (4)
N41—C415	1.357 (6)	Al2A—Br6A	2.294 (4)
C111—C112	1.385 (7)	Al2B—Br4B	2.375 (8)
C112—C113	1.399 (7)	Al2B—Br5B	2.296 (5)
C113—C114	1.400 (7)	Al2B—Br6B	2.296 (7)
C113—C116	1.456 (7)	C11—C21	1.349 (10)
C114—C115	1.382 (7)	C11—C12	1.454 (10)
C116—C117	1.340 (8)	C21—C22	1.453 (9)
C117—C118	1.469 (7)	C12—C13	1.364 (10)
C118—C119	1.383 (9)	C12—C17	1.354 (10)

C118—C122	1.394 (9)	C13—C14	1.360 (10)
C119—C120	1.396 (8)	C14—N1	1.354 (10)
C121—C122	1.383 (8)	N1—C16	1.352 (10)
C211—C212	1.376 (6)	C16—C17	1.327 (10)
C212—C213	1.383 (7)	C22—C23	1.352 (5)
C213—C214	1.401 (7)	C22—C27	1.356 (5)
C213—C216	1.466 (6)	C23—C24	1.350 (5)
C214—C215	1.388 (6)	C24—N2	1.351 (5)
C216—C216^{i}	1.335 (10)	N2—C26	1.350 (5)
C311—C312	1.382 (6)	C26—C27	1.352 (5)
Br1—Al1—Br2	178.31 (6)	N41—Al1—N31	90.02 (15)
N11—Al1—Br1	89.34 (11)	Br4A—Al2A—Br3	107.43 (19)
N11—Al1—Br2	89.72 (11)	Br4A—Al2A—Br5A	108.50 (19)
N21—Al1—Br1	90.86 (11)	Br4A—Al2A—Br6A	114.4 (2)
N21—Al1—Br2	90.54 (11)	Br5A—Al2A—Br3	109.39 (14)
N21—Al1—N11	90.32 (15)	Br6A—Al2A—Br3	109.51 (15)
N21—Al1—N31	178.09 (16)	Br6A—Al2A—Br5A	107.52 (14)
N31—Al1—Br1	88.74 (11)	Br3—Al2B—Br4B	111.1 (3)
N31—Al1—Br2	89.82 (11)	Br3—Al2B—Br5B	109.8 (2)
N31—Al1—N11	87.80 (15)	Br3—Al2B—Br6B	110.1 (2)
N41—Al1—Br1	91.20 (11)	Br5B—Al2B—Br4B	107.6 (3)
N41—Al1—Br2	89.69 (11)	Br6B—Al2B—Br4B	110.6 (3)
N41—Al1—N11	177.74 (15)	Br6B—Al2B—Br5B	107.6 (2)
N41—Al1—N21	91.86 (15)		

Symmetry code(s): (i) -*x*+2, -*y*+1, -*z*+2; (ii) -*x*, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*, -*z*+2.

Crystal structure **5**

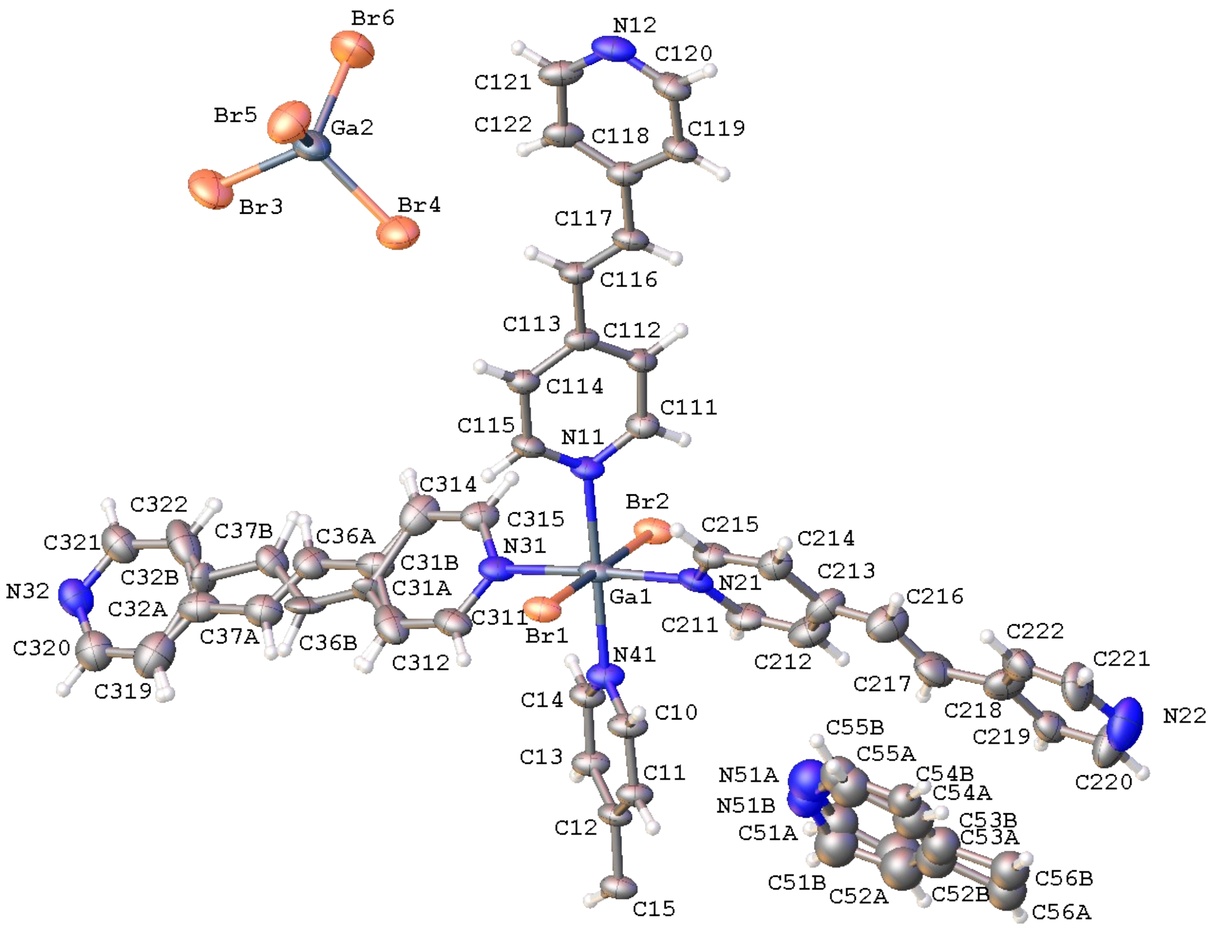


Fig. S8 Asymmetric unit and enumeration scheme in **5** (ellipsoids at 50% probability).
Structure **5** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984539.

Table S7 Selected geometric parameters (Å, º).

Ga1—Br1	2.5192 (9)	C217—C218	1.536 (12)
Ga1—Br2	2.4877 (9)	C218—C219	1.354 (11)
Ga1—N11	2.093 (4)	C218—C222	1.416 (11)
Ga1—N21	2.107 (6)	C219—C220	1.360 (11)
Ga1—N31	2.116 (6)	C221—C222	1.334 (12)
Ga1—N41	2.096 (5)	C311—C312	1.389 (12)
N11—C111	1.346 (8)	C312—C31A	1.481 (15)
N11—C115	1.342 (8)	C312—C31B	1.05 (3)
N12—C120	1.337 (10)	C314—C315	1.377 (11)
N12—C121	1.326 (10)	C314—C31A	1.294 (16)
N21—C211	1.362 (9)	C314—C31B	1.76 (3)
N21—C215	1.353 (8)	C319—C320	1.382 (13)
N22—C220	1.336 (11)	C319—C32A	1.253 (18)
N22—C221	1.327 (13)	C319—C32B	1.76 (4)
N31—C311	1.341 (9)	C321—C322	1.421 (13)
N31—C315	1.343 (8)	C322—C32A	1.528 (17)
N32—C320	1.337 (11)	C322—C32B	1.02 (3)
N32—C321	1.332 (10)	C31A—C36A	1.471 (18)

N41—C10	1.357 (8)	C32A—C37A	1.482 (19)
N41—C14	1.359 (7)	C36A—C37A	1.304 (17)
C10—C11	1.384 (8)	C31B—C36B	1.43 (5)
C11—C12	1.391 (8)	C32B—C37B	1.48 (4)
C12—C13	1.387 (9)	C36B—C37B	1.36 (4)
C12—C15	1.462 (7)	Ga2—Br3	2.3277 (15)
C13—C14	1.372 (8)	Ga2—Br4	2.3590 (14)
C15—C15^{i}	1.332 (13)	Ga2—Br5	2.3083 (14)
C111—C112	1.393 (8)	Ga2—Br6	2.3064 (15)
C112—C113	1.394 (9)	N51A—C51A	1.39 (4)
C113—C114	1.385 (9)	N51A—C55A	1.29 (4)
C113—C116	1.484 (7)	C51A—C52A	1.33 (5)
C114—C115	1.390 (8)	C52A—C53A	1.27 (5)
C116—C117	1.334 (9)	C53A—C54A	1.35 (4)
C117—C118	1.475 (8)	C53A—C56A	1.49 (3)
C118—C119	1.395 (9)	C54A—C55A	1.36 (4)
C118—C122	1.391 (10)	C56A—C56A^{ii}	1.35 (4)
C119—C120	1.409 (8)	N51B—C51B	1.37 (4)
C121—C122	1.392 (9)	N51B—C55B	1.40 (3)
C211—C212	1.374 (12)	C51B—C52B	1.39 (5)
C212—C213	1.380 (10)	C52B—C53B	1.52 (4)
C213—C214	1.403 (10)	C53B—C54B	1.38 (3)
C213—C216	1.408 (12)	C53B—C56B	1.47 (3)
C214—C215	1.366 (10)	C54B—C55B	1.40 (3)
C216—C217	1.318 (13)	C56B—C56B^{ii}	1.30 (4)
Br2—Ga1—Br1	177.75 (4)	N41—Ga1—Br1	89.89 (14)
N11—Ga1—Br1	88.68 (14)	N41—Ga1—Br2	91.49 (15)
N11—Ga1—Br2	89.93 (14)	N41—Ga1—N21	88.0 (2)
N11—Ga1—N21	91.6 (2)	N41—Ga1—N31	88.6 (2)
N11—Ga1—N31	91.8 (2)	Br3—Ga2—Br4	108.23 (5)
N11—Ga1—N41	178.50 (19)	Br5—Ga2—Br3	108.17 (6)
N21—Ga1—Br1	89.61 (14)	Br5—Ga2—Br4	108.32 (6)
N21—Ga1—Br2	88.66 (14)	Br6—Ga2—Br3	111.51 (7)
N21—Ga1—N31	176.61 (18)	Br6—Ga2—Br4	108.12 (6)
N31—Ga1—Br1	90.13 (15)	Br6—Ga2—Br5	112.37 (6)
N31—Ga1—Br2	91.68 (15)		

Symmetry code(s): (i) -*x*+2, -*y*+1, -*z*+2; (ii) -*x*+2, -*y*, -*z*+1.

Crystal structure **6**

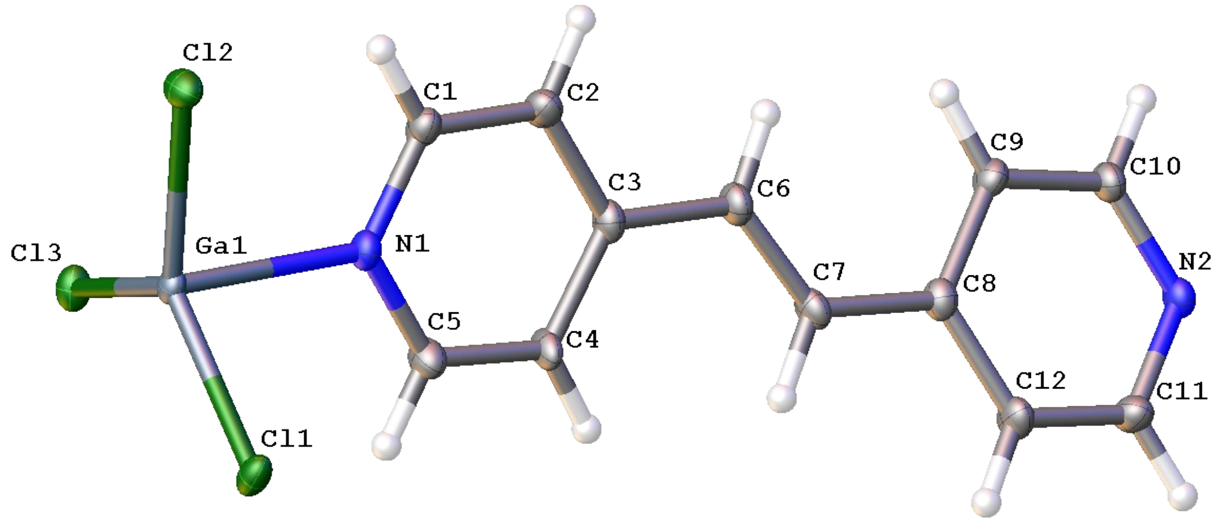


Fig. S9 Asymmetric unit and enumeration scheme in **6** (ellipsoids at 50% probability).
Structure **6** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984529.

Table S8 Selected geometric parameters (Å, º).

Ga1—Cl1	2.1982 (6)	C2—C3	1.399 (4)
Ga1—Cl2	2.2085 (7)	C3—C4	1.402 (4)
Ga1—Cl3	2.2010 (6)	C3—C6	1.464 (3)
Ga1—N1	2.168 (2)	C4—C5	1.376 (3)
Ga1—N2^{i}	2.173 (2)	C6—C7	1.339 (4)
N1—C1	1.340 (3)	C7—C8	1.467 (3)
N1—C5	1.349 (3)	C8—C9	1.400 (4)
N2—Ga1^{ii}	2.173 (2)	C8—C12	1.395 (4)
N2—C10	1.344 (3)	C9—C10	1.386 (3)
N2—C11	1.342 (3)	C11—C12	1.388 (4)
C1—C2	1.389 (3)		
Cl1—Ga1—Cl2	121.87 (3)	N1—Ga1—Cl3	88.55 (6)
Cl1—Ga1—Cl3	120.36 (3)	N1—Ga1—N2^{i}	178.88 (8)
Cl3—Ga1—Cl2	117.77 (3)	N2^{i}—Ga1—Cl1	91.00 (6)
N1—Ga1—Cl1	89.65 (6)	N2^{i}—Ga1—Cl2	88.54 (6)
N1—Ga1—Cl2	91.90 (6)	N2^{i}—Ga1—Cl3	90.33 (6)

Symmetry code(s): (i) *x*-1/2, -*y*+3/2, *z*-1/2; (ii) *x*+1/2, -*y*+3/2, *z*+1/2.

Crystal structure **7**

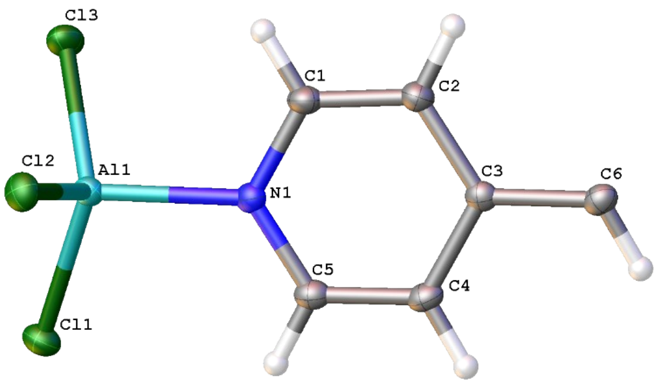


Fig. S10 Asymmetric unit and enumeration scheme in **7** (ellipsoids at 50% probability).
Structure **7** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984530.

Table S9 Selected geometric parameters (Å, º).

Al1—Cl1	2.1187 (7)	C1—C2	1.367 (3)
Al1—Cl2	2.1222 (7)	C2—C3	1.396 (3)
Al1—Cl3	2.1151 (7)	C3—C4	1.408 (2)
Al1—N1	1.9356 (17)	C3—C6	1.456 (3)
N1—C1	1.360 (2)	C4—C5	1.369 (3)
N1—C5	1.354 (2)	C6—C6^{i}	1.352 (4)
Cl1—Al1—Cl2	111.25 (3)	N1—Al1—Cl1	107.23 (5)
Cl3—Al1—Cl1	113.52 (3)	N1—Al1—Cl2	103.52 (5)
Cl3—Al1—Cl2	116.39 (3)	N1—Al1—Cl3	103.68 (5)

Symmetry code(s): (i) -*x*+1, -*y*, -*z*+1.

Crystal structure **8**

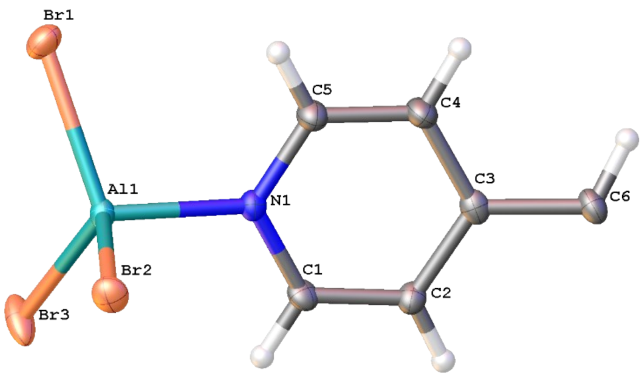


Fig. S11 Asymmetric unit and enumeration scheme in **8** (ellipsoids at 50% probability).
Structure **8** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984533.

Table S10 Selected geometric parameters (Å, º).

Br1—Al1	2.2600 (7)	C2—C1	1.374 (3)
Br2—Al1	2.2950 (7)	C2—C3	1.395 (3)
Br3—Al1	2.2667 (7)	C3—C4	1.402 (3)

Al1—N1	1.9434 (19)	C3—C6	1.469 (3)
N1—C1	1.356 (3)	C4—C5	1.377 (3)
N1—C5	1.346 (3)	C6—C6^{i}	1.330 (5)
Br1—Al1—Br2	111.47 (3)	N1—Al1—Br1	106.14 (7)
Br1—Al1—Br3	116.71 (3)	N1—Al1—Br2	103.20 (6)
Br3—Al1—Br2	111.77 (3)	N1—Al1—Br3	106.33 (6)

Symmetry code(s): (i) -*x*+1, -*y*+1, -*z*.

Crystal structure **9**

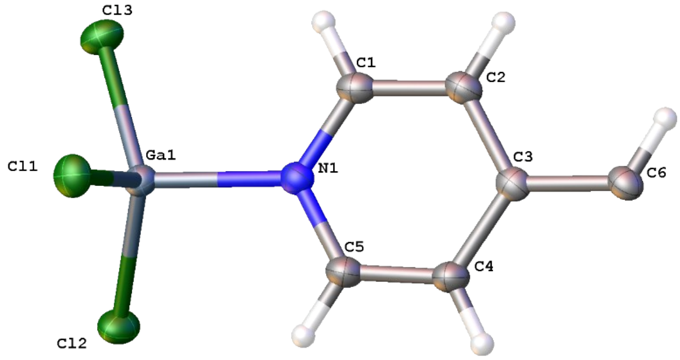


Fig. S12. Asymmetric unit and enumeration scheme in **9** (ellipsoids at 50% probability).
Structure **9** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984534.

Table S11 Selected geometric parameters (Å, º).

Ga1—Cl1	2.1593 (5)	C1—C2	1.379 (3)
Ga1—Cl2	2.1519 (5)	C2—C3	1.398 (3)
Ga1—Cl3	2.1556 (5)	C3—C4	1.399 (3)
Ga1—N1	1.9799 (17)	C3—C6	1.458 (3)
N1—C1	1.349 (3)	C4—C5	1.367 (3)
N1—C5	1.355 (2)	C6—C6^{i}	1.347 (4)
Cl2—Ga1—Cl1	116.71 (2)	N1—Ga1—Cl1	103.30 (5)
Cl2—Ga1—Cl3	113.99 (2)	N1—Ga1—Cl2	102.95 (5)
Cl3—Ga1—Cl1	111.29 (2)	N1—Ga1—Cl3	107.16 (5)

Symmetry code(s): (i) $-x+2$, $-y+1$, $-z+1$.

Crystal structure **10a**

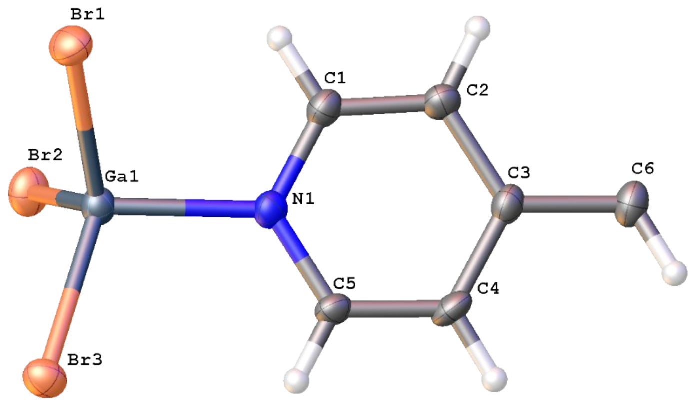


Fig. S13 Asymmetric unit and enumeration scheme in **10a** (ellipsoids at 50% probability).
Structure **10a** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984531.

Table S12 Selected geometric parameters (Å, º).

Br1—Ga1	2.3020 (9)	C1—C2	1.374 (8)
Br2—Ga1	2.3039 (9)	C2—C3	1.401 (8)
Br3—Ga1	2.3020 (9)	C3—C4	1.391 (8)
Ga1—N1	1.997 (5)	C3—C6	1.465 (8)

N1—C1	1.344 (7)	C4—C5	1.386 (8)
N1—C5	1.357 (7)	C6—C6^{i}	1.329 (12)
Br1—Ga1—Br2	116.36 (4)	N1—Ga1—Br1	103.28 (14)
Br3—Ga1—Br1	113.30 (4)	N1—Ga1—Br2	102.91 (14)
Br3—Ga1—Br2	111.94 (3)	N1—Ga1—Br3	107.69 (14)

Symmetry code(s): (i) -*x*+1, -*y*, -*z*+1.

Crystal structure **10b**

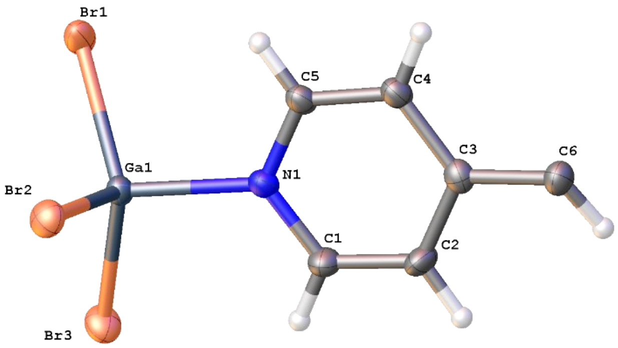


Fig. S14 Asymmetric unit and enumeration scheme in **10b** (ellipsoids at 50% probability). Structure **10b** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984535.

Table S13 Selected geometric parameters (Å, º).

Br1—Ga1	2.2926 (5)	C1—C2	1.371 (5)
Br2—Ga1	2.3235 (5)	C2—C3	1.398 (5)
Br3—Ga1	2.2852 (6)	C3—C4	1.406 (5)
Ga1—N1	1.991 (3)	C3—C6	1.461 (5)
N1—C1	1.345 (5)	C4—C5	1.370 (5)
N1—C5	1.352 (5)	C6—C6^{i}	1.335 (8)
Br1—Ga1—Br2	111.90 (2)	N1—Ga1—Br1	105.59 (8)
Br3—Ga1—Br1	117.90 (2)	N1—Ga1—Br2	102.69 (9)
Br3—Ga1—Br2	111.62 (2)	N1—Ga1—Br3	105.55 (9)

Symmetry code(s): (i) -*x*+1, -*y*, -*z*+1.

Crystal structure **11**

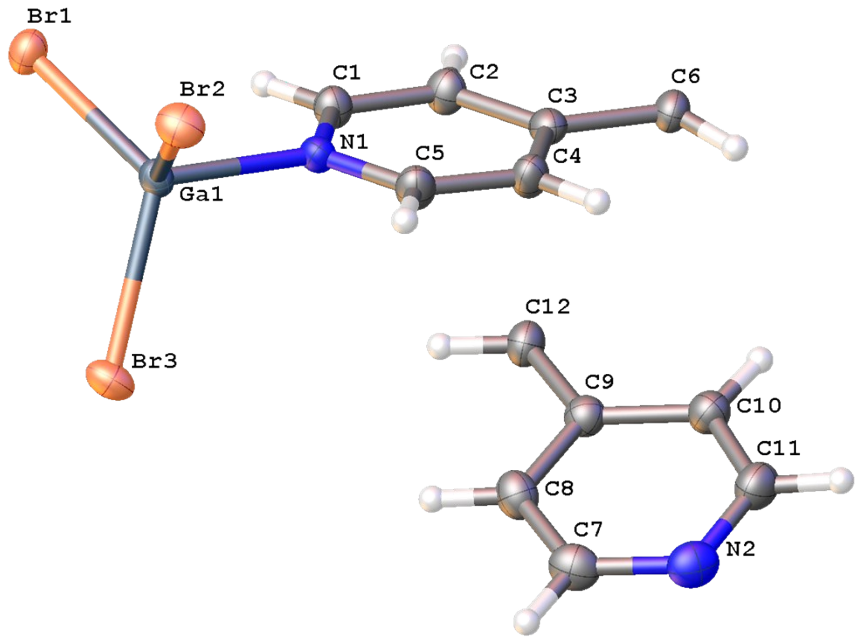


Fig. S15 Asymmetric unit and enumeration scheme in **11** (ellipsoids at 50% probability).
Structure **11** was deposited to the Cambridge Structural Database (CSD), Deposition Number 1984536.

Table S14 Selected geometric parameters (Å, º).

Br1—Ga1	2.3038 (3)	C4—C5	1.370 (3)
Br2—Ga1	2.3024 (3)	C6—C6^{i}	1.328 (5)
Br3—Ga1	2.3015 (3)	N2—C7	1.339 (3)
Ga1—N1	1.9847 (18)	N2—C11	1.340 (4)
N1—C1	1.340 (3)	C7—C8	1.387 (4)
N1—C5	1.351 (3)	C8—C9	1.398 (3)
C1—C2	1.381 (3)	C9—C10	1.401 (3)
C2—C3	1.398 (3)	C9—C12	1.467 (3)
C3—C4	1.395 (3)	C10—C11	1.380 (4)
C3—C6	1.469 (3)	C12—C12^{ii}	1.334 (5)
Br2—Ga1—Br1	113.247 (14)	N1—Ga1—Br1	105.84 (5)
Br3—Ga1—Br1	114.307 (14)	N1—Ga1—Br2	104.96 (5)
Br3—Ga1—Br2	110.431 (14)	N1—Ga1—Br3	107.32 (5)

Symmetry code(s): (i) -*x*+2, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*+1, -*z*+1.

Powder diffraction measurements

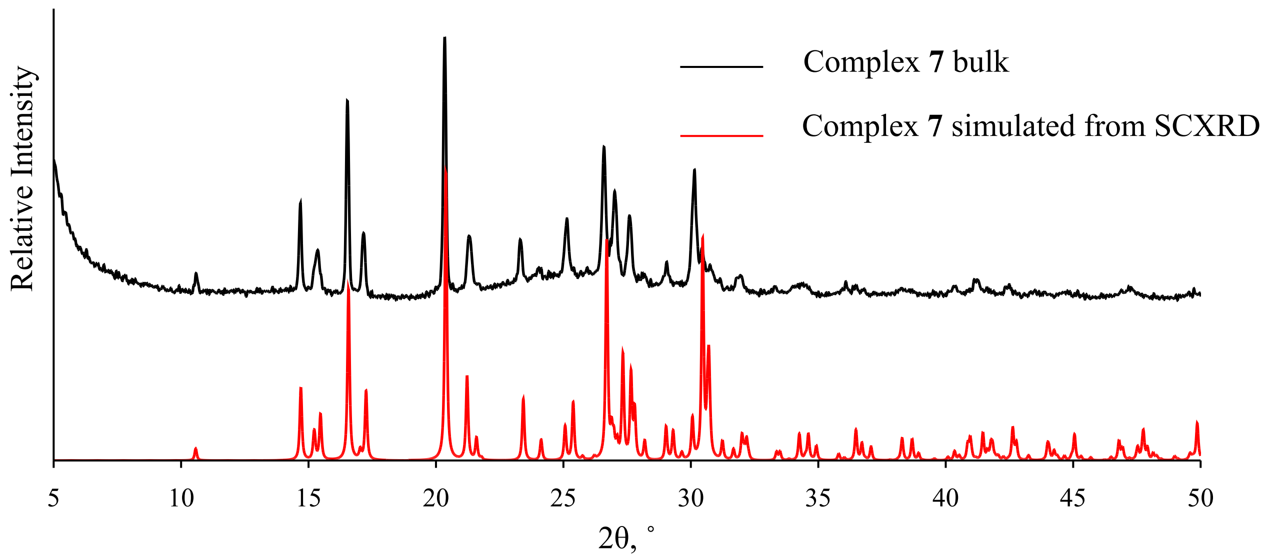


Fig. S16 Comparison of the experimental (black, top) and simulated (red, bottom) diffraction pattern of **7** (Cu-$K_{\alpha1}$ = 154.1 pm).

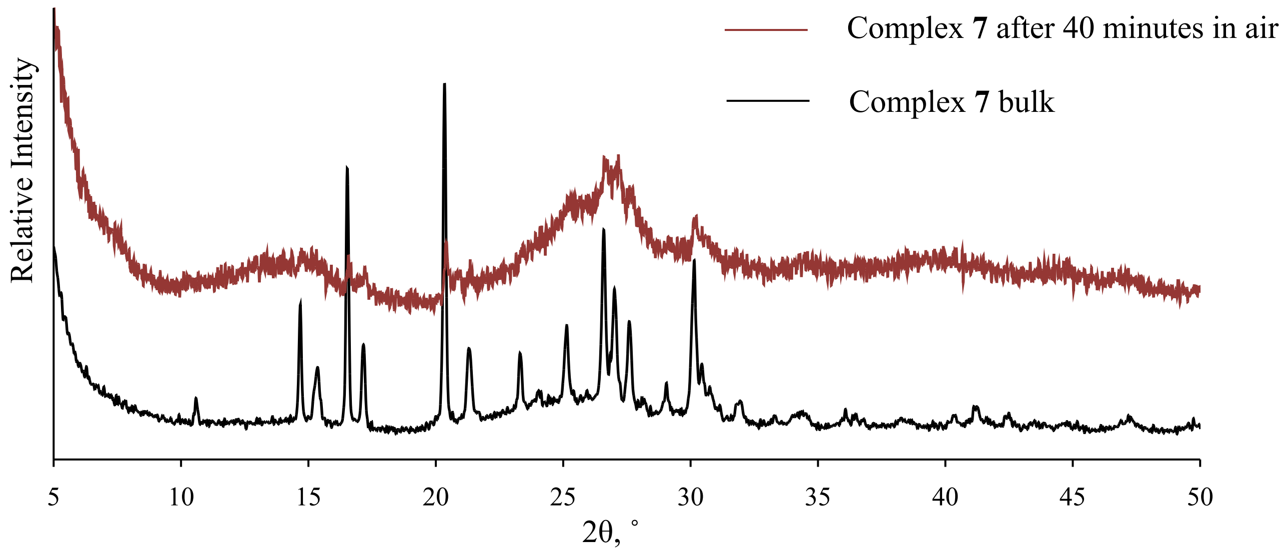


Fig. S17 Comparison of the experimental diffraction pattern of **7** (black, bottom) with the diffraction pattern of **7** after 40 minutes in air (dark red, top) (Cu-$K_{\alpha1}$ = 154.1 pm).

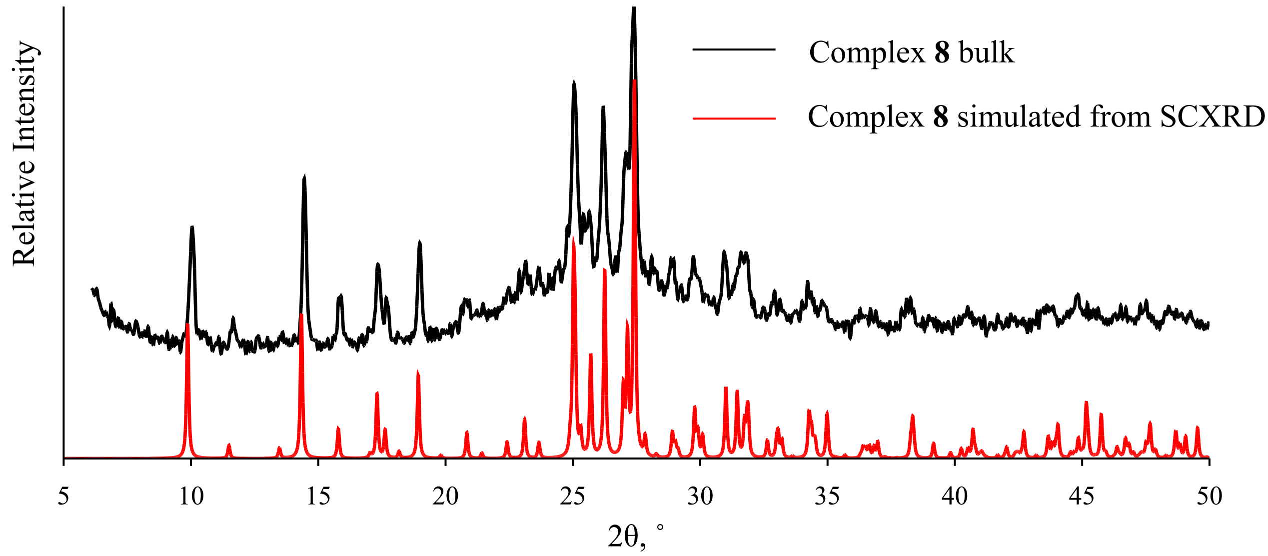


Fig. S18 Comparison of the experimental (black, top) and simulated (red, bottom) diffraction pattern of **8** (Cu-$K_{\alpha1}$ = 154.1 pm).

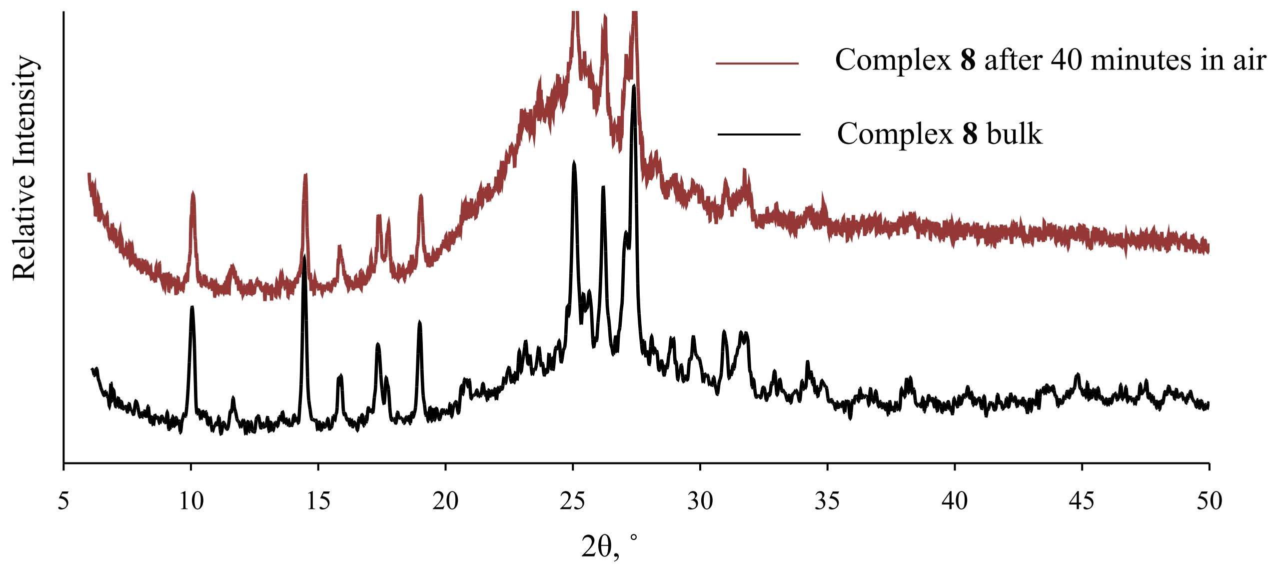


Fig. S19 Comparison of the experimental diffraction pattern of **8** (black, bottom) with the diffraction pattern of **8** after 40 minutes in air (dark red, top) (Cu-$K_{\alpha1}$ = 154.1 pm).

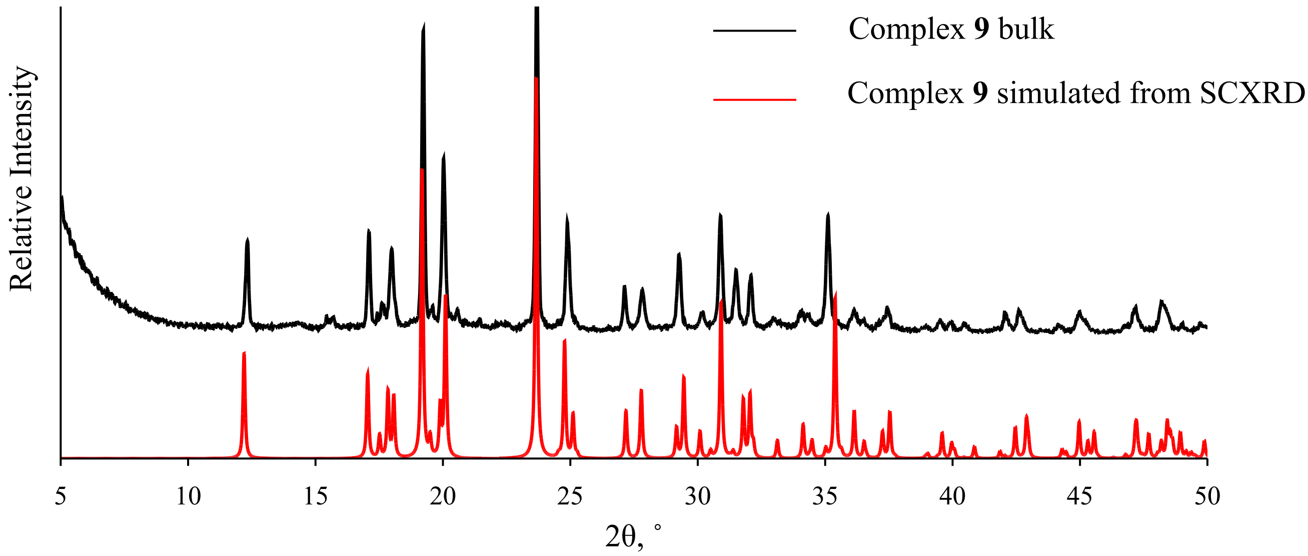


Fig. S20 Comparison of the experimental (black, top) and simulated (red, bottom) diffraction pattern of **9** (Co-$K_{\alpha1}$ = 178.9 pm).

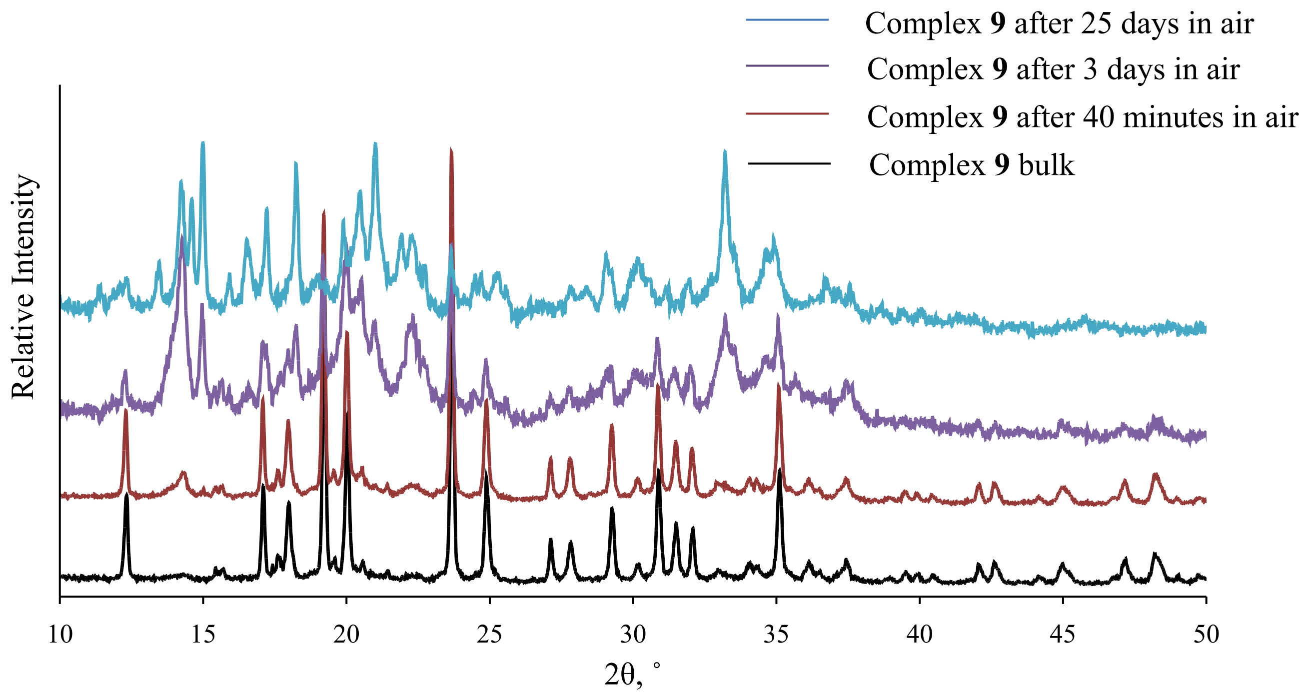


Fig. S21 Comparison of the experimental diffraction pattern of **9** (black) with the diffraction pattern of **9** after 40 minutes (dark red), 3 days (purple) and 25 days (blue) in air (Co-$K_{\alpha1}$ = 178.9 pm).

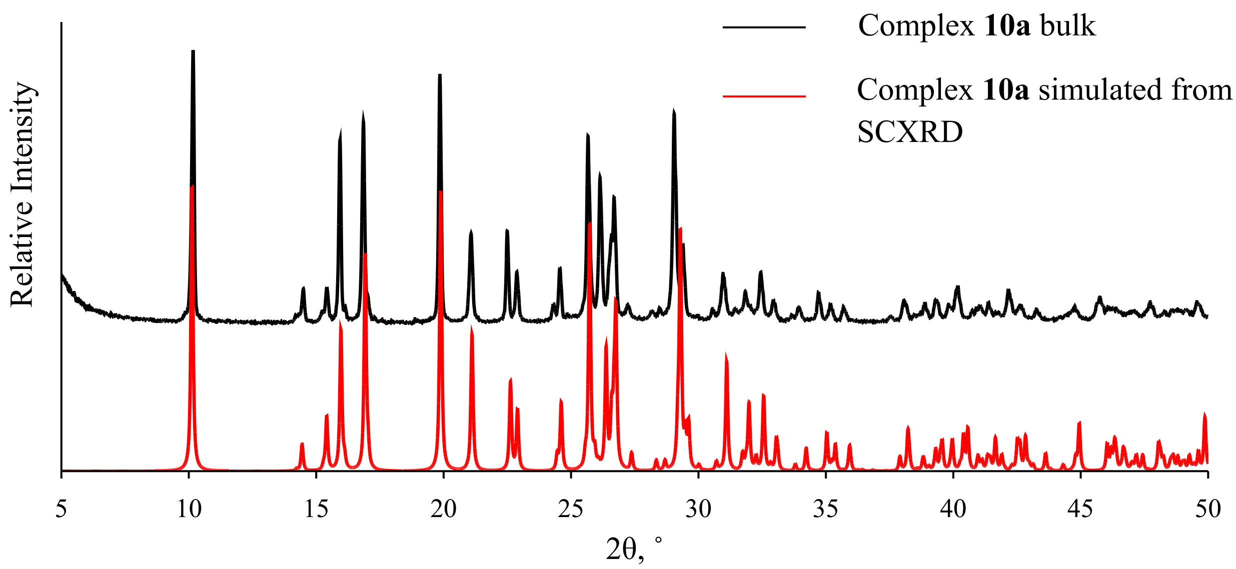


Fig. S22 Comparison of the experimental (black, top) and simulated (red, bottom) diffraction pattern of **10a** (Cu-$K_{\alpha 1}$ = 154.1 pm).

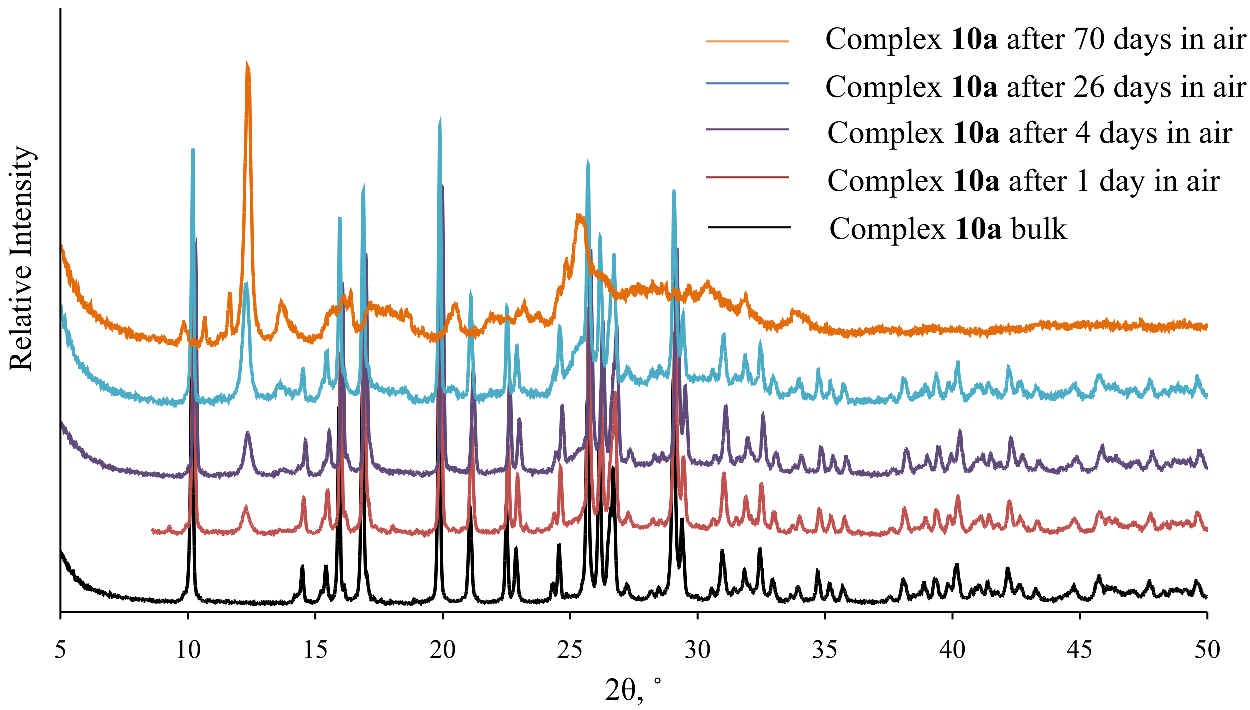


Fig. S23 Comparison of the experimental diffraction pattern of **10a** (black) with the diffraction pattern of **10a** after 1 day (dark red), 4 days (purple), 26 days (blue) and 70 days (orange) in air (Cu-$K_{\alpha 1}$ = 154.1 pm).

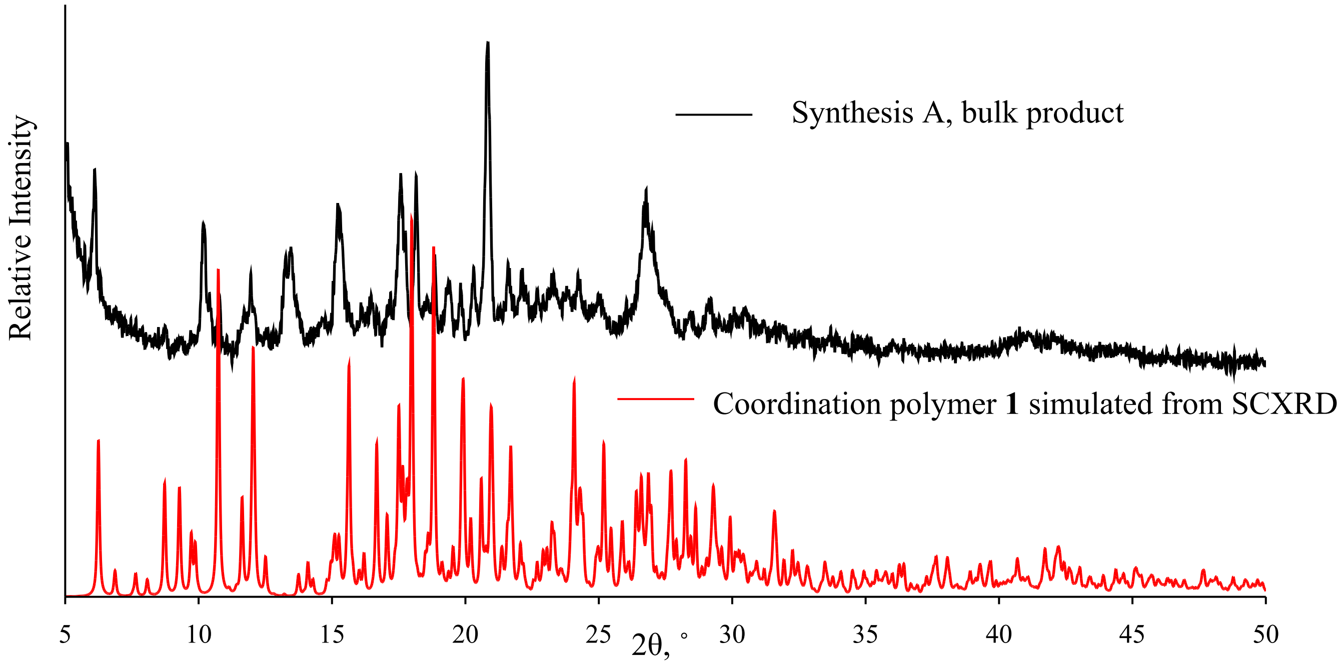


Fig. S24 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis A (black, top) and simulated diffraction patterns of **1** (red, bottom) (Cu-$K_{\alpha1}$ = 154.1 pm).

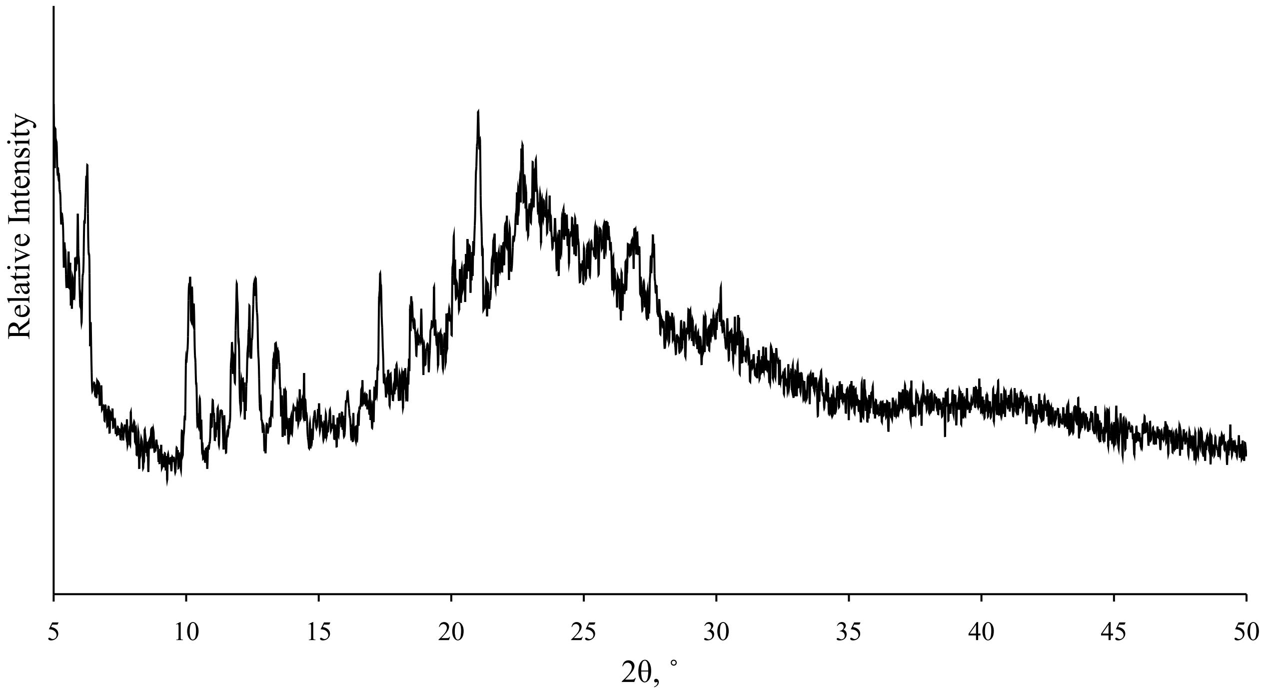


Fig. S25 Experimental diffraction pattern of the bulk product of the Synthesis C (Cu-$K_{\alpha1}$ = 154.1 pm).

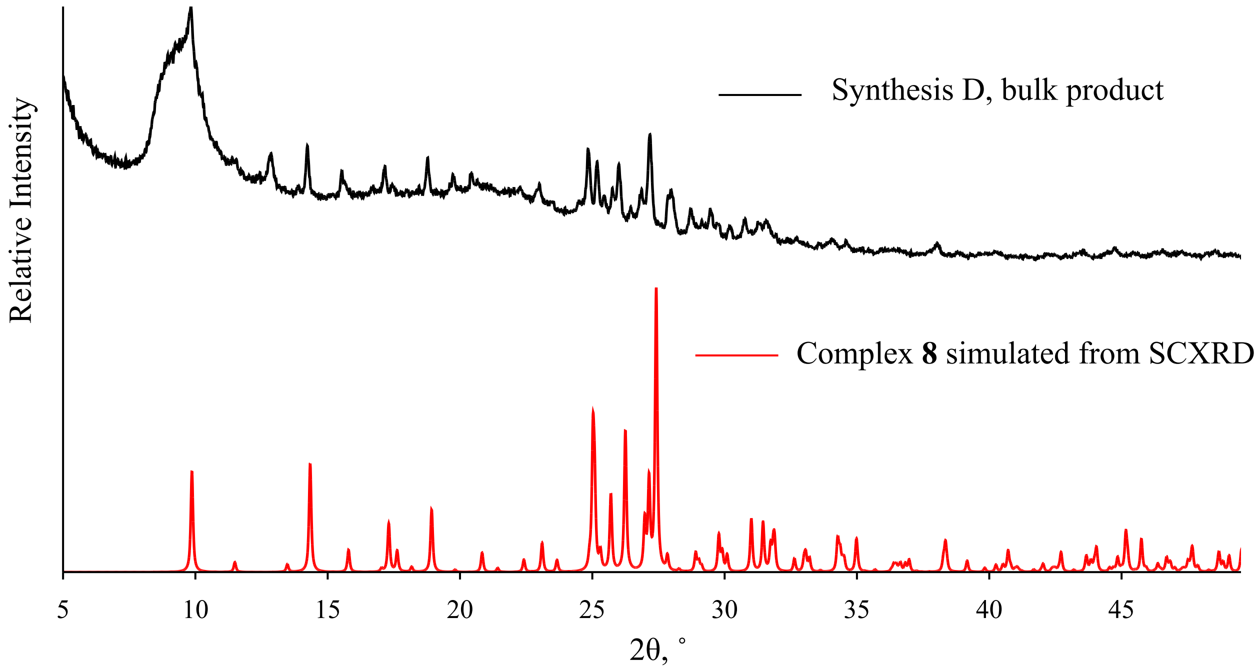


Fig. S26 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis D (black, top) and simulated (red, bottom) diffraction pattern of **8** (Cu-K$_{\alpha1}$ = 154.1 pm). Airtight specimen holder with dome was used.

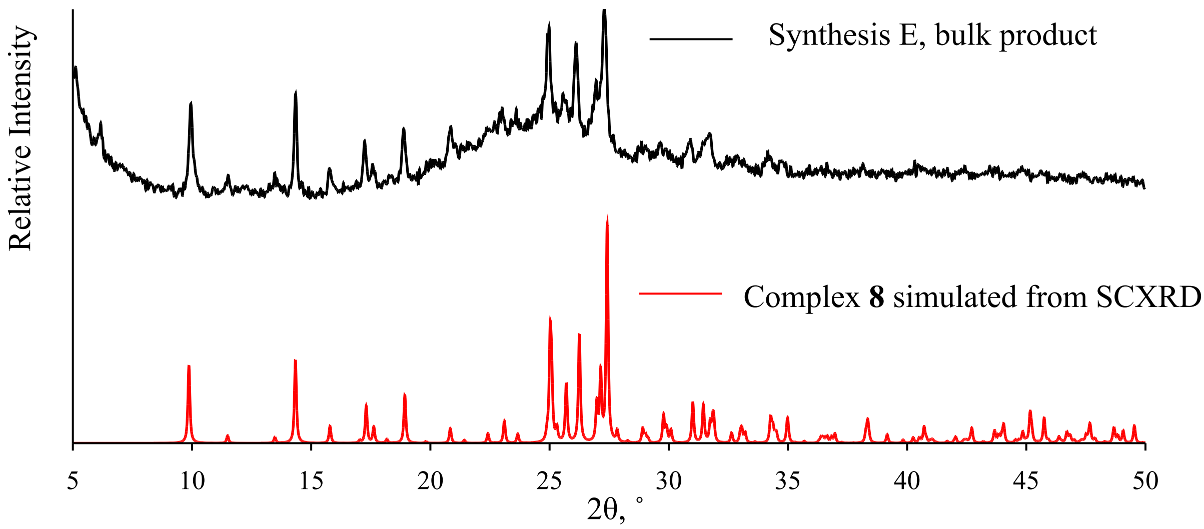


Fig. S27 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis E (black, top) and simulated (red, bottom) diffraction pattern of **8** (Cu-K$_{\alpha1}$ = 154.1 pm).

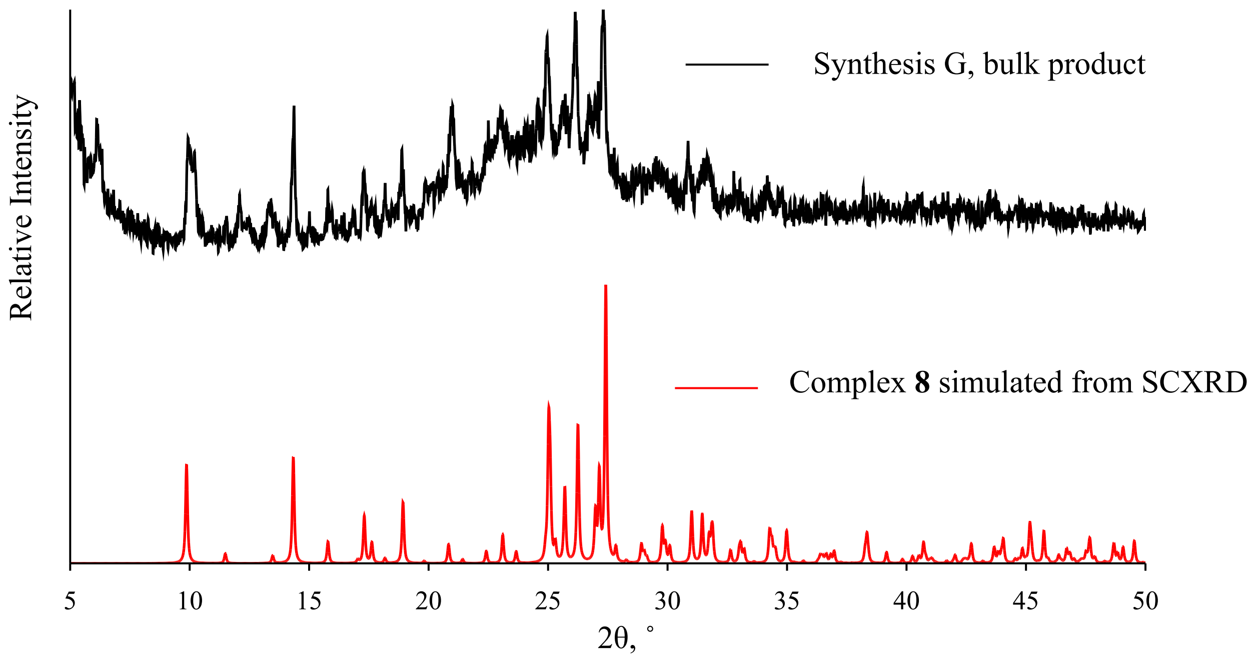


Fig. S28 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis G (black, top) and simulated (red, bottom) diffraction pattern of **8** (Cu-$K_{\alpha1}$ = 154.1 pm).

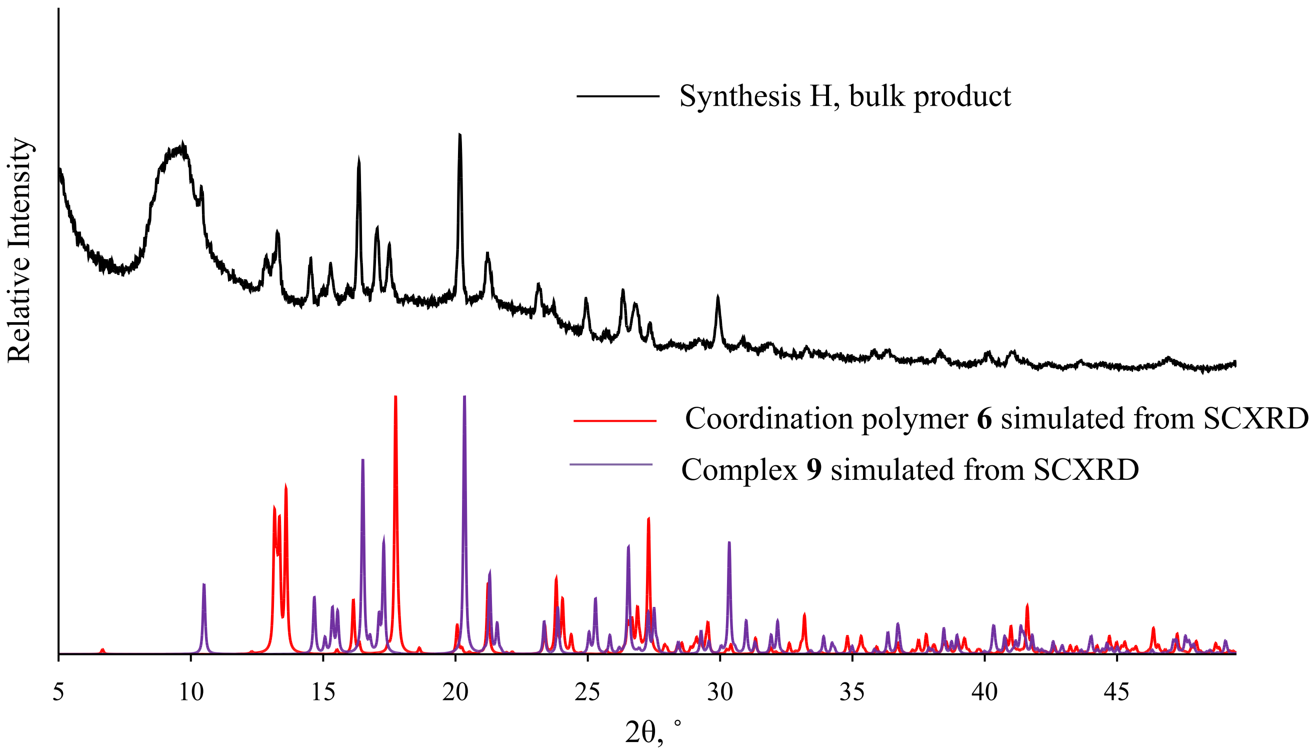


Fig. S29 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis H (black, top) and simulated diffraction patterns of **9** (purple, bottom) and **6** (red, bottom) (Cu-$K_{\alpha1}$ = 154.1 pm). Airtight specimen holder with dome was used.

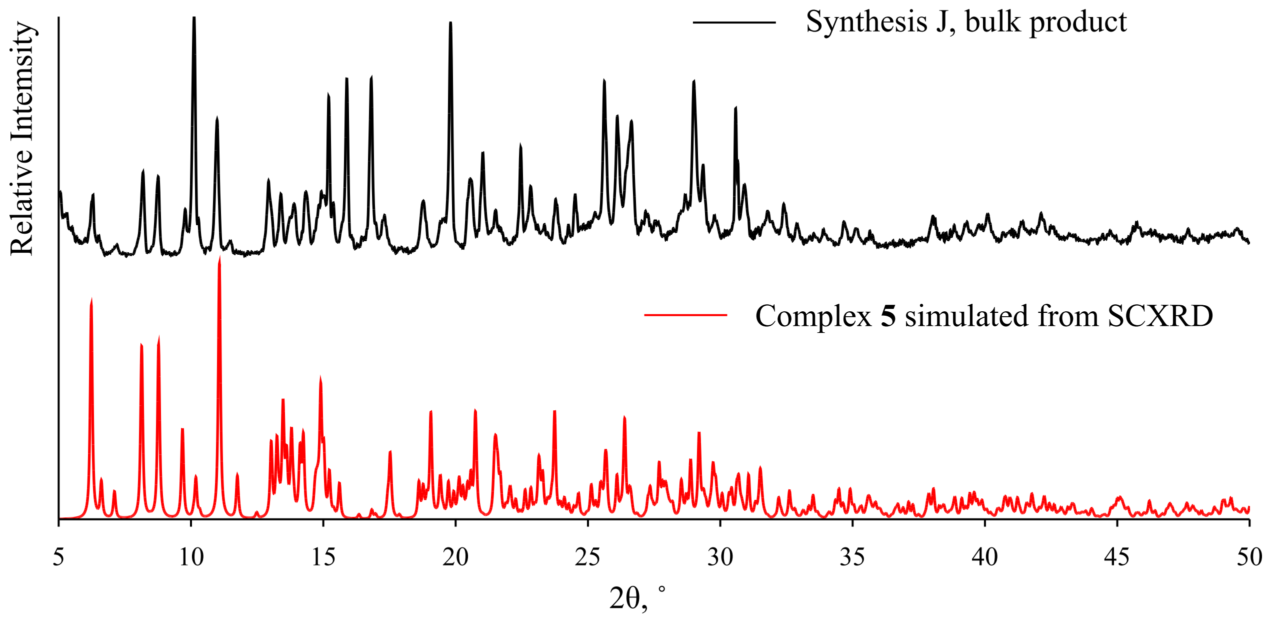


Fig. S30 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis J (black, top) and simulated (red, bottom) diffraction pattern of **5** (Cu-$K_{\alpha 1}$ = 154.1 pm).

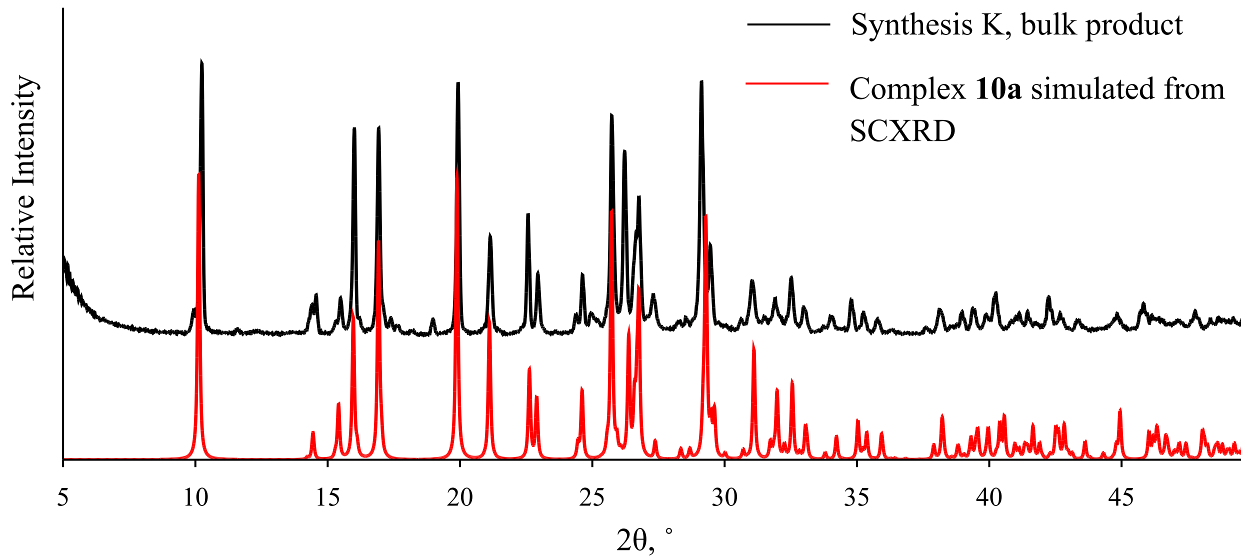


Fig. S31 Comparison of the experimental diffraction pattern of the bulk product of the Synthesis K (black, top) and simulated (red, bottom) diffraction pattern of **10a** (Cu-$K_{\alpha 1}$ = 154.1 pm).

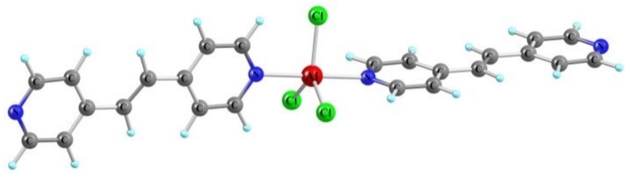
Computational data

Table S15 Total energies E_0, standard enthalpies H^o_{298} (in Hartree) and standard entropies S^o_{298} (in cal mol^{-1} K^{-1}) for studied compounds. B3LYP/def2-SVP level of theory.

Compound (point group)	$\mathbf{E_0}$	$\mathbf{H^o_{298}}$	$\mathbf{S^o_{298}}$
$[AlCl_3(bpe)_2]$ (C_2)	-2767.614035	-2767.190377	208.042
$[AlBr_3(bpe)_2]$ (C_2)	-9109.001831	-9108.578862	217.651
$[GaCl_3(bpe)_2]$ (C_2)	-4449.836106	-4449.413275	213.034
$[GaBr_3(bpe)_2]$ (C_2)	-10791.23586	-10790.81359	221.581
$[AlCl_2(bpe)_4]^+[AlCl_4]^-$ (C_1)	-5535.236277	-5534.386771	370.225
$[AlBr_2(bpe)_4]^+[AlBr_4]^-$ (C_1)	-18218.01156	-18217.16316	388.124
$[GaCl_2(bpe)_4]^+[GaCl_4]^-$ (C_1)	-8899.67966	-8898.831778	381.012
$[GaBr_2(bpe)_4]^+[GaBr_4]^-$ (C_1)	-21582.4757	-21581.62879	399.043

Fig. S32 Optimized structures and xyz coordinates for considered compounds. B3LYP/def2-SVP level of theory.

[$AlCl_3(bpe)_2$] (C_2 point group)

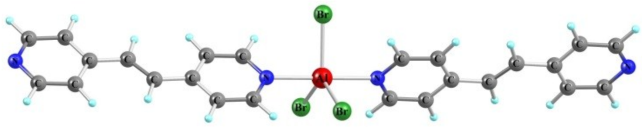


E = -2767.6140352

	X	Y	Z
Cl	0.000000	0.000000	2.077816
Al	0.000000	0.000000	-0.114420
Cl	-1.909157	-0.087865	-1.186586
Cl	1.909157	0.087865	-1.186586
N	0.000000	2.157923	-0.120437
N	0.000000	-2.157923	-0.120437
C	-0.279547	-4.969035	-0.220096
C	-0.881595	-2.800227	0.671918
C	0.747471	-2.896689	-0.955821
C	0.638416	-4.281851	-1.033841
C	-1.050599	-4.176077	0.654616
H	-1.461911	-2.172465	1.349817
H	1.456917	-2.343398	-1.573812
H	1.274675	-4.826415	-1.734926
H	-1.786165	-4.619453	1.326760
C	-0.385936	-6.426599	-0.320344
C	0.279547	4.969035	-0.220096
C	-0.747471	2.896689	-0.955821
C	0.881595	2.800227	0.671918
C	1.050599	4.176077	0.654616
C	-0.638416	4.281851	-1.033841
H	-1.456917	2.343398	-1.573812
H	1.461911	2.172465	1.349817
H	1.786165	4.619453	1.326760
H	-1.274675	4.826415	-1.734926
C	0.385936	6.426599	-0.320344
C	-1.216751	-7.218520	0.391404
H	0.285120	-6.882837	-1.054242
H	-1.886892	-6.759444	1.124979
C	-1.332423	-8.677498	0.291700
H	-0.285120	6.882837	-1.054242
C	1.216751	7.218520	0.391404
C	1.332423	8.677498	0.291700
H	1.886892	6.759444	1.124979
N	-1.640786	-11.490063	0.178747
C	-2.255384	-9.356806	1.107831
C	-0.567878	-9.471164	-0.586085
C	-0.760558	-10.851814	-0.600603
C	-2.368972	-10.746134	1.013321
H	-2.882017	-8.804051	1.812683
H	0.171692	-9.027257	-1.255069
H	-0.169590	-11.476042	-1.281255
H	-3.087245	-11.279755	1.647134
N	1.640786	11.490063	0.178747
C	0.567878	9.471164	-0.586085
C	2.255384	9.356806	1.107831
C	2.368972	10.746134	1.013321
C	0.760558	10.851814	-0.600603

H	-0.171692	9.027257	-1.255069
H	2.882017	8.804051	1.812683
H	3.087245	11.279755	1.647134
H	0.169590	11.476042	-1.281255

[$AlBr_3(bpe)_2$] (C_2 point group)

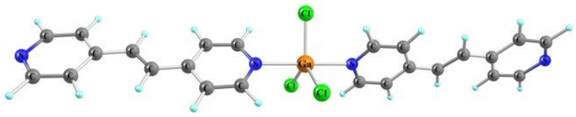


E = -9109.0018314

	X	Y	Z
Br	0.000000	0.000000	2.198755
Al	0.000000	0.000000	-0.167771
Br	-2.059187	-0.123860	-1.326277
Br	2.059187	0.123860	-1.326277
N	0.000000	2.177804	-0.164122
N	0.000000	-2.177804	-0.164122
C	-0.253987	-4.996904	-0.202502
C	-0.919265	-2.809873	0.595692
C	0.790029	-2.934492	-0.942949
C	0.695235	-4.322183	-0.989542
C	-1.075669	-4.186709	0.608180
H	-1.547617	-2.174152	1.221068
H	1.524526	-2.397414	-1.545395
H	1.369220	-4.877659	-1.645275
H	-1.844248	-4.616900	1.251246
C	-0.340221	-6.457502	-0.264904
C	0.253987	4.996904	-0.202502
C	-0.790029	2.934492	-0.942949
C	0.919265	2.809873	0.595692
C	1.075669	4.186709	0.608180
C	-0.695235	4.322183	-0.989542
H	-1.524526	2.397414	-1.545395
H	1.547617	2.174152	1.221068
H	1.844248	4.616900	1.251246
H	-1.369220	4.877659	-1.645275
C	0.340221	6.457502	-0.264904
C	-1.176098	-7.240273	0.451159
H	0.354546	-6.925091	-0.968946
H	-1.865928	-6.770140	1.159056
C	-1.270159	-8.702914	0.390596
H	-0.354546	6.925091	-0.968946
C	1.176098	7.240273	0.451159
C	1.270159	8.702914	0.390596
H	1.865928	6.770140	1.159056
N	-1.536649	-11.521451	0.352726
C	-2.192106	-9.372702	1.215661
C	-0.485131	-9.509032	-0.457264
C	-0.657636	-10.892246	-0.435280
C	-2.284453	-10.765665	1.158786
H	-2.834097	-8.809906	1.898393
H	0.254122	-9.072782	-1.131592
H	-0.050783	-11.526351	-1.092407
H	-3.001558	-11.292160	1.799814
N	1.536649	11.521451	0.352726
C	0.485131	9.509032	-0.457264
C	2.192106	9.372702	1.215661

C	2.284453	10.765665	1.158786
C	0.657636	10.892246	-0.435280
H	-0.254122	9.072782	-1.131592
H	2.834097	8.809906	1.898393
H	3.001558	11.292160	1.799814
H	0.050783	11.526351	-1.092407

$[GaCl_3(bpe)_2]$ (C_2 point group)

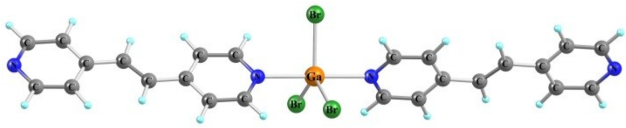


E = -4449.8361057

	X	Y	Z
Cl	0.000000	0.000000	-2.142704
Ga	0.000000	0.000000	0.089750
Cl	1.938415	-0.077184	1.189906
Cl	-1.938415	0.077184	1.189906
N	0.000000	2.241466	0.092974
N	0.000000	-2.241466	0.092974
C	0.278783	-5.043695	0.210035
C	0.853330	-2.884721	-0.723011
C	-0.721560	-2.963933	0.960502
C	-0.612660	-4.349048	1.047972
C	1.022120	-4.261833	-0.698072
H	1.407171	-2.259773	-1.426586
H	-1.409448	-2.399827	1.594456
H	-1.225533	-4.888067	1.773857
H	1.732970	-4.714623	-1.390394
C	0.386937	-6.500858	0.320971
C	-0.278783	5.043695	0.210035
C	0.721560	2.963933	0.960502
C	-0.853330	2.884721	-0.723011
C	-1.022120	4.261833	-0.698072
C	0.612660	4.349048	1.047972
H	1.409448	2.399827	1.594456
H	-1.407171	2.259773	-1.426586
H	-1.732970	4.714623	-1.390394
H	1.225533	4.888067	1.773857
C	-0.386937	6.500858	0.320971
C	1.206233	-7.299464	-0.396435
H	-0.271406	-6.950440	1.070351
H	1.866666	-6.847200	-1.142938
C	1.322447	-8.757691	-0.285869
H	0.271406	6.950440	1.070351
C	-1.206233	7.299464	-0.396435
C	-1.322447	8.757691	-0.285869
H	-1.866666	6.847200	-1.142938
N	1.631506	-11.569500	-0.152744
C	2.239895	-9.443620	-1.102682
C	0.563452	-9.544490	0.602836
C	0.756239	-10.924992	0.627047
C	2.354215	-10.832138	-0.997848
H	2.861907	-8.896529	-1.816003
H	-0.172566	-9.095488	1.272357
H	0.169408	-11.543772	1.316211
H	3.068365	-11.370739	-1.632120
N	-1.631506	11.569500	-0.152744

C	-0.563452	9.544490	0.602836
C	-2.239895	9.443620	-1.102682
C	-2.354215	10.832138	-0.997848
C	-0.756239	10.924992	0.627047
H	0.172566	9.095488	1.272357
H	-2.861907	8.896529	-1.816003
H	-3.068365	11.370739	-1.632120
H	-0.169408	11.543772	1.316211

$[GaBr_3(bpe)_2]$ (C_2 point group)

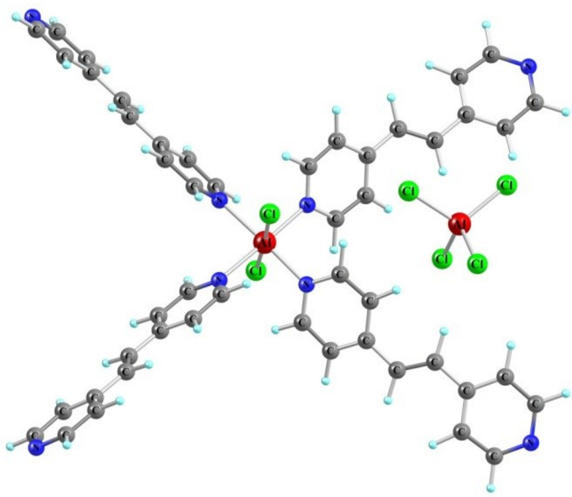


E = -10791.2358619

	X	Y	Z
Br	0.000000	0.000000	2.278022
Ga	0.000000	0.000000	-0.110686
Br	-2.080045	-0.109368	-1.280178
Br	2.080045	0.109368	-1.280178
N	0.000000	2.282223	-0.115742
N	0.000000	-2.282223	-0.115742
C	-0.259565	-5.090871	-0.199932
C	-0.885939	-2.919885	0.670234
C	0.756865	-3.016006	-0.942386
C	0.659117	-4.403176	-1.013129
C	-1.045394	-4.298259	0.661911
H	-1.481934	-2.291231	1.335169
H	1.466550	-2.463131	-1.562041
H	1.303309	-4.948451	-1.706498
H	-1.785026	-4.742986	1.328830
C	-0.351859	-6.550460	-0.288821
C	0.259565	5.090871	-0.199932
C	-0.756865	3.016006	-0.942386
C	0.885939	2.919885	0.670234
C	1.045394	4.298259	0.661911
C	-0.659117	4.403176	-1.013129
H	-1.466550	2.463131	-1.562041
H	1.481934	2.291231	1.335169
H	1.785026	4.742986	1.328830
H	-1.303309	4.948451	-1.706498
C	0.351859	6.550460	-0.288821
C	-1.174583	-7.345563	0.428597
H	0.325016	-7.005737	-1.017971
H	-1.849873	-6.888183	1.158515
C	-1.273763	-8.806578	0.340626
H	-0.325016	7.005737	-1.017971
C	1.174583	7.345563	0.428597
C	1.273763	8.806578	0.340626
H	1.849873	6.888183	1.158515
N	-1.549709	-11.623459	0.250920
C	-2.188153	-9.489863	1.163048
C	-0.500867	-9.598580	-0.531334
C	-0.677576	-10.981433	-0.534404
C	-2.285752	-10.881137	1.080012
H	-2.820521	-8.938671	1.863996
H	0.232979	-9.151735	-1.204660
H	-0.079954	-11.604307	-1.210482

H	-2.997285	-11.417790	1.718850
N	1.549709	11.623459	0.250920
C	0.500867	9.598580	-0.531334
C	2.188153	9.489863	1.163048
C	2.285752	10.881137	1.080012
C	0.677576	10.981433	-0.534404
H	-0.232979	9.151735	-1.204660
H	2.820521	8.938671	1.863996
H	2.997285	11.417790	1.718850
H	0.079954	11.604307	-1.210482

$[AlCl_2(bpe)_4]^+[AlCl_4]^-$ (C_1 point group)



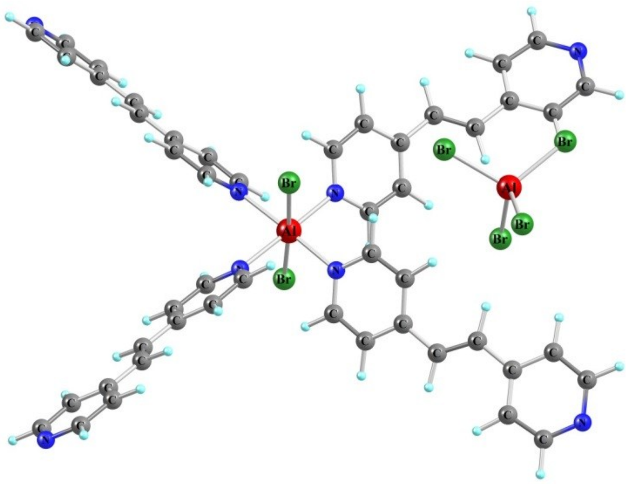
E = -5535.2362773

	X	Y	Z
Al	-1.223998	-0.011747	-0.169925
Cl	-1.184977	-0.153346	2.100266
Cl	-1.386132	0.141471	-2.448643
N	0.183419	-1.531265	-0.349387
C	1.277030	-1.564137	0.448038
H	1.351976	-0.798086	1.220719
C	2.288512	-2.501433	0.305135
H	3.141795	-2.446785	0.982173
C	2.200408	-3.488846	-0.697591
C	1.032779	-3.468099	-1.489375
H	0.888008	-4.204342	-2.282887
C	0.076569	-2.483897	-1.301156
H	-0.796928	-2.421525	-1.950538
C	3.238539	-4.483888	-0.955419
H	2.949371	-5.296598	-1.629342
C	4.500079	-4.423206	-0.471888
H	4.788959	-3.573138	0.153614
C	5.579705	-5.381553	-0.728138
C	6.863171	-5.112164	-0.217126
H	7.043173	-4.202068	0.360676
C	7.898780	-6.018983	-0.459047
H	8.902385	-5.816660	-0.066748
C	6.527146	-7.409824	-1.640182
H	6.417944	-8.341875	-2.207876
C	5.425135	-6.575706	-1.459498
H	4.460139	-6.861810	-1.883095
N	7.746241	-7.148152	-1.154989
N	0.258501	1.445084	-0.142541
C	1.276948	1.409681	-1.029413
H	1.243273	0.614782	-1.774069
C	2.319099	2.321593	-1.020691
H	3.118289	2.207278	-1.751520
C	2.338123	3.359671	-0.070304
C	1.252048	3.405856	0.825985
H	1.202655	4.176302	1.597940
C	0.266768	2.433072	0.777731
H	-0.538702	2.412705	1.512300
C	3.413025	4.346866	0.015850
H	3.159703	5.277893	0.533218
C	4.677249	4.151833	-0.420867

H	4.953762	3.172483	-0.825236
C	5.768679	5.130413	-0.344491
C	7.102857	4.695280	-0.436407
H	7.329986	3.631161	-0.529619
C	8.132535	5.636845	-0.360925
H	9.176320	5.307024	-0.422008
C	6.661497	7.366783	-0.132257
H	6.509809	8.447138	-0.018487
C	5.559326	6.514404	-0.190763
H	4.550764	6.930609	-0.139883
N	7.928909	6.948744	-0.214688
N	-2.737680	1.521706	-0.015704
C	-2.790831	2.536904	-0.90402
H	-2.051526	2.506534	-1.705223
C	-3.733434	3.552648	-0.838525
H	-3.699438	4.34097	-1.591236
C	-4.707304	3.548732	0.181051
C	-4.638981	2.480923	1.096545
H	-5.353732	2.40935	1.919122
C	-3.65275	1.509977	0.972003
H	-3.56068	0.700738	1.697904
C	-5.749492	4.565248	0.33231
H	-6.407502	4.419486	1.193904
C	-5.953564	5.62474	-0.481022
H	-5.295418	5.76435	-1.344424
C	-6.995381	6.647623	-0.342805
C	-7.076193	7.682798	-1.292059
H	-6.368996	7.72751	-2.124453
C	-8.069539	8.657455	-1.165773
H	-8.138429	9.466796	-1.902123
C	-8.896039	7.689262	0.728821
H	-9.640155	7.714887	1.533472
C	-7.946115	6.669136	0.696486
H	-7.954143	5.905563	1.476461
N	-8.966983	8.669124	-0.178884
Al	5.340538	0.069469	1.109178
Cl	6.966848	1.45801	1.367037
Cl	5.857192	-1.899434	1.890844
Cl	4.872481	-0.121744	-1.012091
Cl	3.558842	0.749217	2.157895
N	-2.801098	-1.484829	-0.194939
C	-2.799284	-2.504295	0.68991
H	-1.983825	-2.503143	1.41427
C	-3.775532	-3.489658	0.711642
H	-3.692945	-4.285207	1.452817
C	-4.842776	-3.447741	-0.208763
C	-4.830738	-2.374904	-1.12127
C	-3.807296	-1.435492	-1.087772
H	-3.761907	-0.621785	-1.812929
H	-5.62045	-2.274428	-1.868941
H	-6.651586	-4.266672	-1.064665
C	-5.924695	-4.431988	-0.263998

C	-6.089021	-5.483092	0.568939
H	-5.364481	-5.638868	1.374592
C	-7.167122	-6.476299	0.525001
C	-7.206157	-7.49516	1.494402
H	-6.44105	-7.548256	2.273386
H	-8.269411	-9.238948	2.209728
C	-8.232638	-8.442631	1.457088
N	-9.199932	-8.443006	0.538503
C	-9.169062	-7.478673	-0.387874
C	-8.191844	-6.485606	-0.441657
H	-9.970353	-7.49499	-1.135888
H	-8.234955	-5.734365	-1.232381

$[AlBr_2(bpe)_4]^+[AlBr_4]^-$ (C_1 point group)



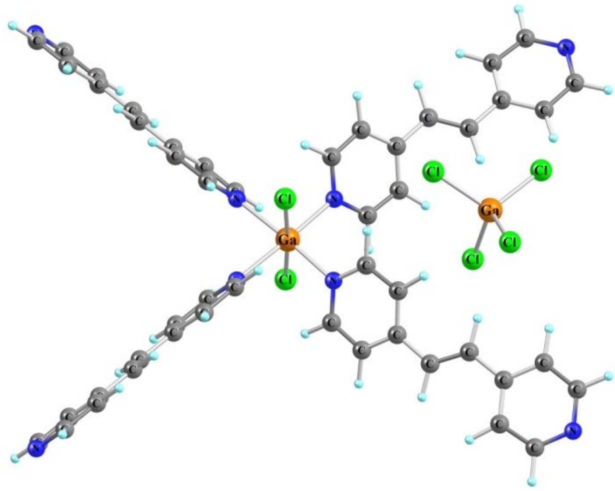
E = -18218.0115606

	X	Y	Z
Al	1.873308	0.006272	0.271246
Br	1.704270	-0.132035	-2.195618
Br	2.187928	0.156014	2.751258
N	0.460770	-1.506925	0.516103
C	-0.684942	-1.526736	-0.208063
H	-0.807685	-0.753743	-0.968525
C	-1.687055	-2.465569	-0.015024
H	-2.581830	-2.397862	-0.635440
C	-1.535270	-3.471873	0.962166
C	-0.318127	-3.462743	1.676210
H	-0.121138	-4.212747	2.445061
C	0.626277	-2.477844	1.441935
H	1.540650	-2.432781	2.033796
C	-2.546331	-4.477952	1.272928
H	-2.218474	-5.265460	1.958620
C	-3.823047	-4.468341	0.825938
H	-4.156545	-3.653015	0.176188
C	-4.862162	-5.450751	1.150898
C	-6.174841	-5.232893	0.692971
H	-6.410685	-4.344410	0.101763
C	-7.170654	-6.162780	1.005026
H	-8.196539	-6.000076	0.654394
C	-5.705076	-7.481321	2.156054
H	-5.541979	-8.394642	2.740906
C	-4.638343	-6.620390	1.904031
H	-3.647099	-6.868128	2.289213
N	-6.952244	-7.268022	1.721211
N	0.399604	1.469348	0.342206
C	-0.595745	1.406229	1.255317
H	-0.543811	0.587614	1.972659
C	-1.634265	2.320140	1.307406
H	-2.411434	2.184973	2.058589
C	-1.675585	3.393620	0.396240
C	-0.610129	3.471208	-0.522920
H	-0.575971	4.270390	-1.265768
C	0.372272	2.494623	-0.537229
H	1.158991	2.504643	-1.292069
C	-2.751515	4.381451	0.365920

H	-2.516543	5.321896	-0.142601
C	-4.001950	4.170466	0.835009
H	-4.257314	3.182318	1.233117
C	-5.106660	5.135208	0.798964
C	-6.429858	4.681869	0.945263
H	-6.641109	3.616436	1.060220
C	-7.475954	5.607552	0.903117
H	-8.511465	5.262700	1.005377
C	-6.039310	7.356785	0.607366
H	-5.908353	8.438328	0.480612
C	-4.923391	6.521044	0.628015
H	-3.924154	6.951576	0.532547
N	-7.296430	6.920763	0.741192
N	3.374146	1.532465	0.056998
C	3.400361	2.600911	0.882948
H	2.645234	2.617326	1.669512
C	4.335377	3.619464	0.775948
H	4.27661	4.451814	1.477973
C	5.332286	3.562889	-0.21968
C	5.292252	2.441085	-1.070076
H	6.025238	2.32568	-1.871198
C	4.311471	1.470589	-0.908438
H	4.247222	0.619262	-1.587553
C	6.369971	4.577157	-0.407996
H	7.038745	4.395597	-1.254302
C	6.560315	5.67271	0.359896
H	5.894395	5.844553	1.211429
C	7.598222	6.694157	0.187683
C	7.676938	7.758676	1.104051
H	6.970734	7.827304	1.935627
C	8.667777	8.731346	0.946508
H	8.735685	9.563259	1.657312
C	9.494283	7.707094	-0.918688
H	10.236963	7.71021	-1.725031
C	8.547116	6.685955	-0.853465
H	8.555371	5.899443	-1.61038
N	9.563858	8.714481	-0.041519
Al	-5.060725	0.089672	-1.032337
Br	-6.875006	1.46908	-1.433986
Br	-5.460022	-2.085805	-1.817081
Br	-4.638083	-0.01341	1.28333
Br	-3.137109	0.8833	-2.109915
N	3.426853	-1.471665	0.206002
C	3.304726	-2.554614	-0.591586
H	2.405578	-2.596994	-1.207336
C	4.261959	-3.555463	-0.661509
H	4.079364	-4.400394	-1.326097
C	5.439636	-3.46295	0.10861
C	5.555374	-2.321507	0.925831
C	4.542018	-1.371663	0.954039
H	4.601789	-0.506143	1.615256
H	6.435998	-2.176758	1.555095

H	7.354194	-4.229503	0.759206
C	6.509228	-4.461337	0.104257
C	6.527095	-5.605053	-0.615181
H	5.676868	-5.834866	-1.265232
C	7.58864	-6.61651	-0.627384
C	7.432327	-7.770693	-1.416447
H	6.529708	-7.914174	-2.016098
H	8.325175	-9.640295	-2.041348
C	8.440729	-8.738011	-1.429465
N	9.569204	-8.63304	-0.72601
C	9.726259	-7.538057	0.025944
C	8.783527	-6.514379	0.111807
H	10.659583	-7.468033	0.596771
H	8.987533	-5.651211	0.748181

$[GaCl_2(bpe)_4]^+[GaCl_4]^-$ (C_1 point group)



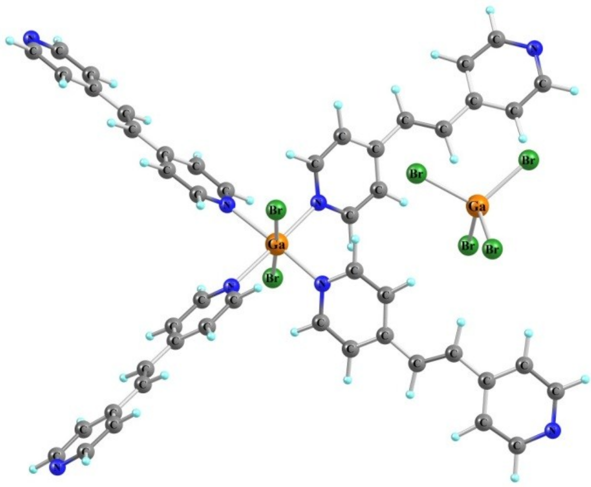
E = -4449.8359946

	X	Y	Z
Ga	1.287745	0.010376	-0.156892
Cl	1.269790	0.151762	2.158775
Cl	1.454464	-0.161330	-2.478613
N	-0.132360	1.580950	-0.343615
C	-1.205284	1.642668	0.474150
H	-1.279926	0.884428	1.255110
C	-2.196833	2.602542	0.334557
H	-3.042829	2.576649	1.022453
C	-2.102435	3.571848	-0.684887
C	-0.950745	3.514275	-1.498023
H	-0.805503	4.235538	-2.305089
C	-0.013708	2.510848	-1.312620
H	0.848790	2.414318	-1.973101
C	-3.123984	4.584951	-0.942110
H	-2.822346	5.392032	-1.617434
C	-4.388018	4.540936	-0.464140
H	-4.692370	3.691510	0.155049
C	-5.453948	5.513004	-0.726972
C	-6.753941	5.239195	-0.262226
H	-6.956894	4.315312	0.285312
C	-7.776904	6.157608	-0.513623
H	-8.793334	5.951468	-0.157982
C	-6.361998	7.569313	-1.616133
H	-6.230083	8.514984	-2.155808
C	-5.270478	6.724229	-1.422532
H	-4.290599	7.015919	-1.806371
N	-7.597012	7.302848	-1.176024
N	-0.219641	-1.491759	-0.115317
C	-1.240607	-1.463798	-0.994245
H	-1.234956	-0.654130	-1.724274
C	-2.256960	-2.406344	-0.990383
H	-3.065016	-2.302306	-1.713374
C	-2.237947	-3.456750	-0.053953
C	-1.149833	-3.480723	0.841564

H	-1.076718	-4.258578	1.604294
C	-0.191089	-2.481101	0.798894
H	0.620394	-2.442205	1.526782
C	-3.278387	-4.482125	0.023168
H	-2.991558	-5.406748	0.534525
C	-4.547749	-4.332742	-0.415388
H	-4.861374	-3.363549	-0.815804
C	-5.603645	-5.350138	-0.343716
C	-6.952035	-4.962895	-0.444942
H	-7.214992	-3.907885	-0.548672
C	-7.948438	-5.939771	-0.371737
H	-9.002836	-5.647290	-0.440856
C	-6.418689	-7.615915	-0.129348
H	-6.229648	-8.689902	-0.011469
C	-5.346790	-6.725528	-0.184799
H	-4.324654	-7.106173	-0.127337
N	-7.699643	-7.243122	-0.219386
N	2.871435	-1.567494	0.000439
C	2.954536	-2.55295	-0.913839
H	2.229961	-2.508485	-1.728731
C	3.912262	-3.556107	-0.853939
H	3.909928	-4.32465	-1.627727
C	4.861721	-3.563395	0.188647
C	4.758084	-2.52143	1.130581
H	5.454364	-2.462146	1.969924
C	3.75984	-1.561284	1.008237
H	3.637687	-0.768543	1.748954
C	5.915871	-4.5686	0.337983
H	6.5583	-4.4291	1.212305
C	6.146731	-5.611965	-0.488637
H	5.502605	-5.747933	-1.363122
C	7.200634	-6.622556	-0.349971
C	7.303141	-7.64882	-1.306736
H	6.603958	-7.695658	-2.145756
C	8.307376	-8.612102	-1.179323
H	8.392772	-9.414552	-1.921491
C	9.105162	-7.648884	0.729832
H	9.842724	-7.671318	1.540615
C	8.142803	-6.640508	0.697159
H	8.135278	-5.882606	1.48268
N	9.196302	-8.620708	-0.184697
Ga	-5.193816	-0.020411	0.911802
Cl	-6.842945	-1.486847	0.962914
Cl	-5.820795	1.940467	1.774652
Cl	-4.547264	0.29622	-1.201215
Cl	-3.448559	-0.74331	2.094878
N	2.93188	1.530105	-0.191406
C	2.973538	2.501238	0.740988
H	2.192133	2.46356	1.502238
C	3.956144	3.481463	0.762122
H	3.917819	4.239802	1.54486
C	4.975028	3.479909	-0.212767

C	4.913424	2.452758	-1.174859
C	3.887643	1.514698	-1.135219
H	3.798199	0.733676	-1.892941
H	5.66508	2.388007	-1.964656
H	6.753162	4.324508	-1.107952
C	6.058089	4.463396	-0.274671
C	6.256158	5.486615	0.584972
H	5.560098	5.62008	1.419168
C	7.335576	6.478238	0.534275
C	7.397666	7.481025	1.519109
H	6.649437	7.522743	2.31501
H	8.478816	9.211649	2.239413
C	8.424713	8.427546	1.475048
N	9.372465	8.4412	0.536384
C	9.320236	7.491539	-0.404096
C	8.34009	6.501109	-0.453122
H	10.1061	7.517881	-1.16804
H	8.366372	5.761183	-1.255171

$[GaBr_2(bpe)_4]^+[GaBr_4]^-$ (C_1 point group)



E = -21582.4757035

	X	Y	Z
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Br	-2.238112	-0.169544	2.783533
N	-0.485433	1.555530	0.535362
C	0.656980	1.576109	-0.187259
H	0.783530	0.801180	-0.946142
C	1.653126	2.521152	0.012009
H	2.551750	2.461855	-0.603846
C	1.490335	3.522607	0.992728
C	0.271647	3.505896	1.704386
H	0.069624	4.253231	2.474587
C	-0.667124	2.516167	1.463759
H	-1.586127	2.459983	2.048456
C	2.495860	4.532721	1.311312
H	2.160774	5.317403	1.996786
C	3.775304	4.528653	0.872898
H	4.115795	3.715938	0.223525
C	4.809415	5.513149	1.207793
C	6.126197	5.299315	0.759864
H	6.368687	4.412558	0.168700
C	7.117596	6.230397	1.082079
H	8.146633	6.070561	0.739399
C	5.640182	7.543091	2.224394
H	5.470447	8.454660	2.810109
C	4.577265	6.680551	1.961794
H	3.582456	6.925304	2.339643
N	6.891273	7.333475	1.799171
N	-0.418960	-1.519445	0.347260
C	0.574220	-1.455759	1.257310
H	0.528234	-0.633541	1.971977
C	1.607010	-2.377726	1.304689

H	2.389024	-2.249242	2.052045
C	1.636838	-3.448779	0.390258
C	0.569449	-3.519343	-0.527589
H	0.529315	-4.317979	-1.270843
C	-0.408237	-2.536793	-0.536327
H	-1.201762	-2.536390	-1.284948
C	2.707102	-4.443748	0.355834
H	2.463022	-5.383972	-0.148850
C	3.961227	-4.241303	0.818133
H	4.226339	-3.254752	1.213706
C	5.057635	-5.215812	0.779654
C	6.385827	-4.774126	0.916097
H	6.607696	-3.710020	1.024038
C	7.423038	-5.709680	0.871905
H	8.462294	-5.374021	0.966915
C	5.968827	-7.446811	0.592494
H	5.827047	-8.527648	0.471456
C	4.860772	-6.600687	0.616349
H	3.857039	-7.022498	0.529582
N	7.230698	-7.021920	0.716714
N	-3.498940	-1.581054	0.063380
C	-3.542595	-2.630568	0.906609
H	-2.794917	-2.639191	1.701581
C	-4.488222	-3.641075	0.802678
H	-4.45056	-4.463758	1.517631
C	-5.469197	-3.587735	-0.209156
C	-5.407274	-2.479408	-1.07608
H	-6.129352	-2.369617	-1.887961
C	-4.417768	-1.516344	-0.91458
H	-4.333804	-0.671924	-1.601394
C	-6.514027	-4.595268	-0.399242
H	-7.173134	-4.414231	-1.253247
C	-6.720278	-5.684996	0.372403
H	-6.063217	-5.858466	1.230468
C	-7.764494	-6.699296	0.194517
C	-7.856724	-7.762716	1.110851
H	-7.156555	-7.835699	1.94714
C	-8.85287	-8.728927	0.947177
H	-8.930892	-9.56	1.657953
C	-9.660169	-7.700248	-0.92371
H	-10.39758	-7.698608	-1.734912
C	-8.706652	-6.685446	-0.852672
H	-8.705165	-5.899096	-1.609833
N	-9.742329	-8.706865	-0.046726
Ga	4.985575	-0.064962	-0.964637
Br	6.837524	-1.480394	-1.314483
Br	5.414285	2.143627	-1.772797
Br	4.499282	0.062089	1.381572
Br	3.049153	-0.874479	-2.101453
N	-3.548391	1.530485	0.224654
C	-3.464587	2.564593	-0.634485
H	-2.596846	2.569175	-1.296804

C	-4.426027	3.562743	-0.705713
H	-4.280323	4.374309	-1.419361
C	-5.558731	3.512634	0.133015
C	-5.627837	2.419482	1.019024
C	-4.614456	1.467698	1.039558
H	-4.631489	0.635784	1.746546
H	-6.472422	2.31297	1.703188
H	-7.414496	4.340896	0.874086
C	-6.629345	4.511048	0.131484
C	-6.719196	5.580387	-0.689385
H	-5.937333	5.739339	-1.438905
C	-7.78294	6.589774	-0.701526
C	-7.746507	7.618652	-1.660356
H	-6.934146	7.667649	-2.390142
H	-8.737314	9.385645	-2.421353
C	-8.75904	8.581627	-1.676367
N	-9.780974	8.588392	-0.819072
C	-9.821864	7.614845	0.097259
C	-8.864986	6.605984	0.200375
H	-10.66716	7.636859	0.795006
H	-8.96786	5.848595	0.979757