Supporting Information

Halometallate and halide ions: nucleophiles in competition for hydrogen bond and halogen bond formation in halopyridinium salts of mixed halide-halometallate anions

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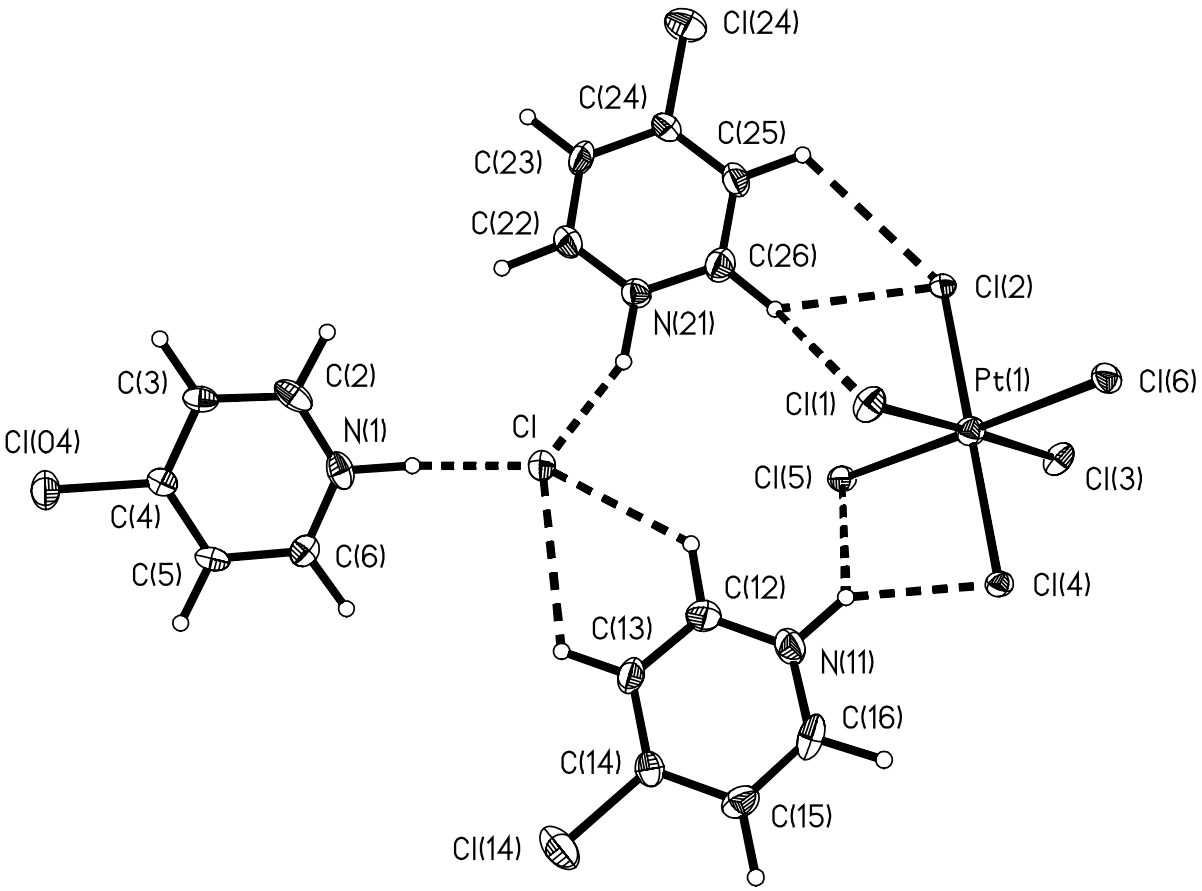
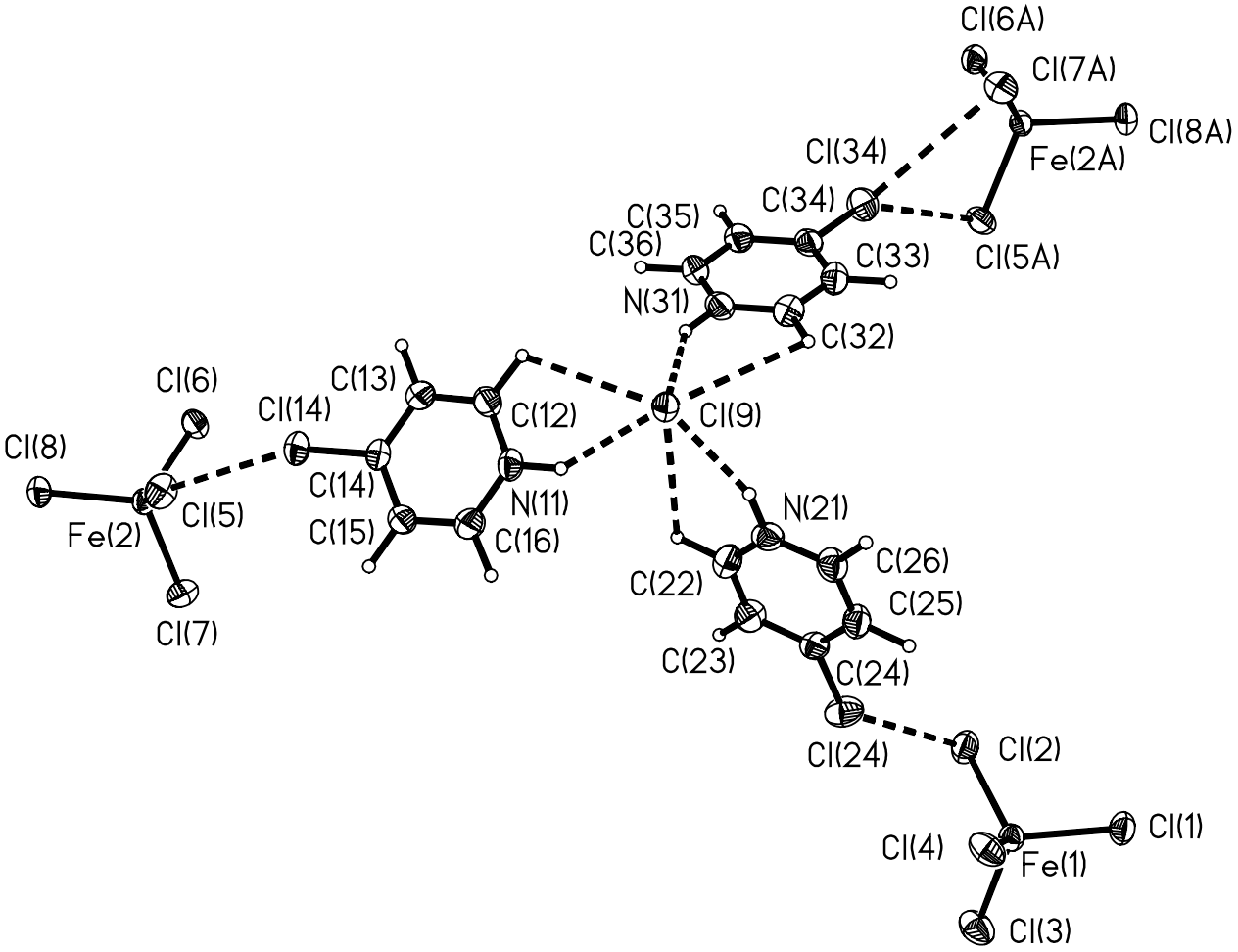
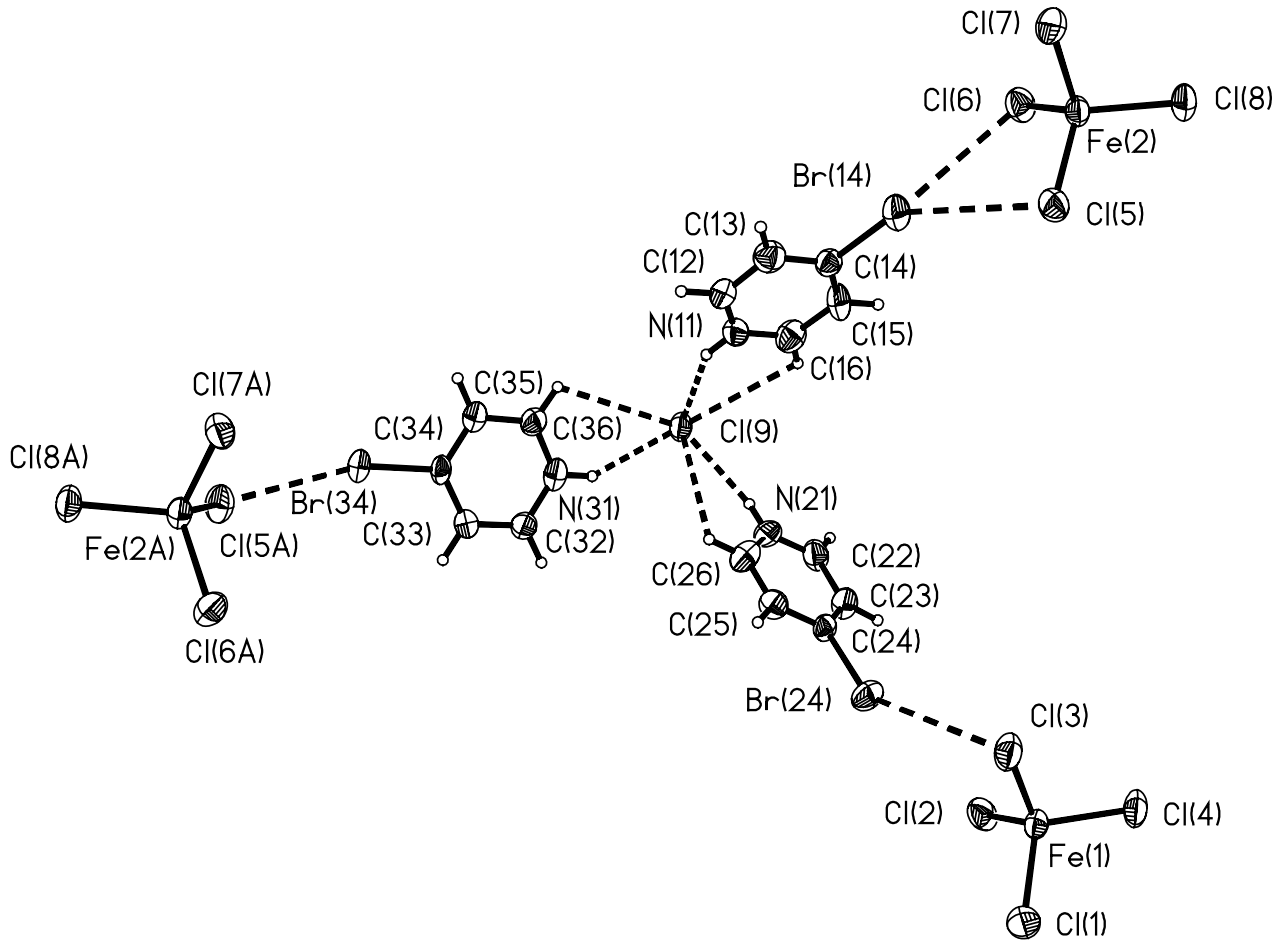
1. Structure of $(4ClpyH)_3[PtCl_6]Cl$ (1) shown with 50% probability ellipsoids



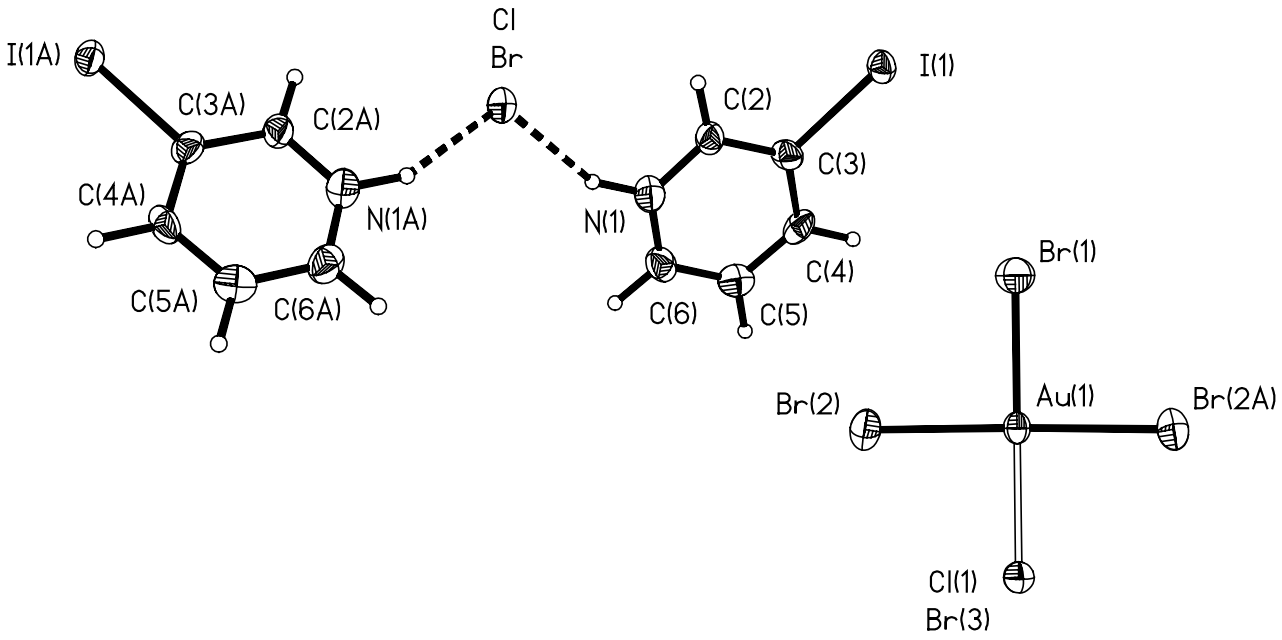
2. Structure of $(4\text{-ClpyH})_3[FeCl_4]_2Cl$ (2) shown with 50% probability ellipsoids



3. Structure of (4-BrpyH)$_3$[FeCl$_4$]$_2$Cl (3) shown with 50% probability ellipsoids



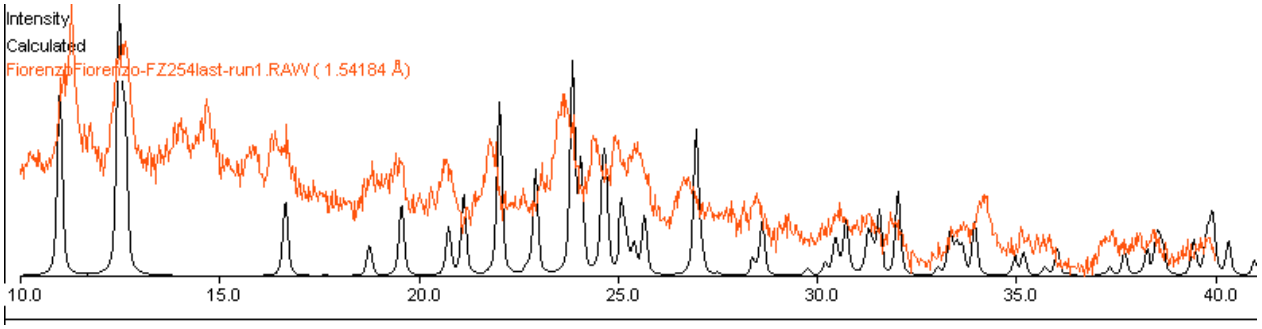
4. Structure of (3-IpyH)$_2$[AuBr$_{3.35}$Cl$_{0.65}$]Br$_{0.30}$Cl$_{0.70}$ (4) (two asymmetric units) shown with 50% probability ellipsoids



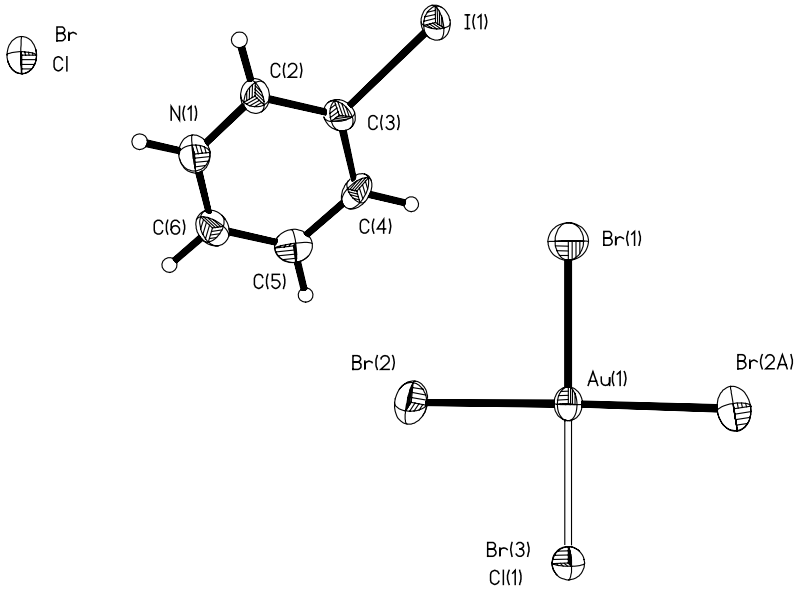
5. X-ray powder pattern for compound (4)

Diffractometer: Bruker D8, equipped with Goebel mirrors and scintillation detector
radiation: Cu-Kα
2θ range: 10 - 40 º
step size: 0.02 º
time/step: 35 s
collected in reflection mode using sample holder rotated at 30 rpm

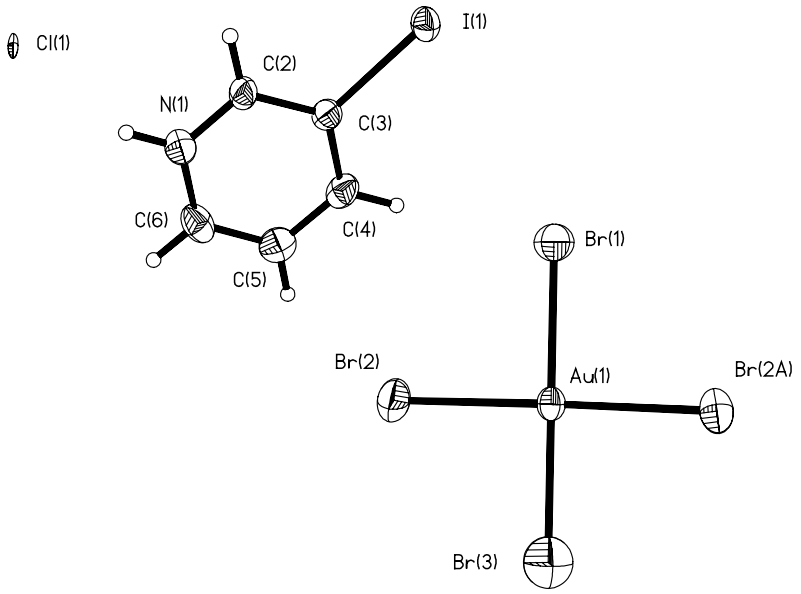
in red: experimental pattern
in black: pattern calculated from single crystal data using Bruker AXS program, XPOW



6. Displacement ellipsoid plots for two refinement models for compound 4 as (3-IpyH)$_2$[AuBr$_4$]Cl and (3-IpyH)$_2$[AuBr$_{3.35}$Cl$_{0.65}$]Br$_{0.30}$Cl$_{0.70}$



Displacement ellipsoid plots with 50% probability ellipsoids based upon refinement model for compound **4** as (3-IpyH)$_2$[AuBr$_{3.35}$Cl$_{0.65}$]Br$_{0.30}$Cl$_{0.70}$



Displacement ellipsoid plots for two refinement models for compound **4** as (3-IpyH)$_2$[AuBr$_4$]Cl

7. Tables of intermolecular interactions for $(4ClpyH)_3[PtCl_6]Cl$ (1)

Hydrogen bonds

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)	M-A···H(°)	
N(1)-H(1)···Cl	1.010	2.041	3.041	170.1	-	
N(21)-H(21)···Cl	1.010	2.064	3.000	153.2	-	
N(11)-H(11)···Cl(4)	1.010	2.280	3.160	144.8	-	
Pt(1)-Cl(4)···H(11)	-	2.280	-	-	88.6	
N(11)-H(11)···Cl(5)	1.010	2.852	3.460	119.6	-	
Pt(1)-Cl(5)···H(11)	-	2.852	-	-	76.4	-

Halogen bonds

C-X···X'-C	(C)-X···X'-(C) (Å)	C-X···X'(°)	C-X'···X(°)	S.O.
C-Cl(04)···Cl(14)-C	3.309	114.2	158.3	(-0.5+x, 0.5-y, 0.5+z)

Weak Hydrogen bonds

Within the 2D sheet (Fig. 1)

(C)H···Cl(Pt) 2.852 Å, C-H···Cl 141.7 °, Pt-Cl···H 81.5 ° and (C)H···Cl(Pt) 2.600 Å, C-H···Cl 128.7 °, Pt-Cl···H 87.3 ° (bifurcated); (C)H···Cl(Pt) 2.412 Å , C-H···Cl 160.6 °, Pt-Cl···H 106.0 °; (C)H···Cl(Pt) 2.944 Å, C-H···Cl 168.5 °, Pt-Cl···H 126.7 °; (C)H···Cl^- 2.568 Å C-H···Cl^- 128.5 °; (C)H···Cl^- 2.843 Å C-H···Cl^- 116.3 °; (C)H···Cl(C) 2.581 Å, C-H···Cl 155.0 °, C-Cl···H 120.1 °.

Between stacking sheets

(C)H···Cl(Pt) 2.635 Å , C-H···Cl 155.2 °, Pt-Cl···H 112.4 °; (C)H···Cl(Pt) 2.607 Å , C-H···Cl 165.7 °, Pt-Cl···H 101.1 °; (C)H···Cl(Pt) 2.861 Å , C-H···Cl 124.6 °, Pt-Cl···H 156.0 °; (C)H···Cl(Pt) 2.900 Å , C-H···Cl 145.0 °, Pt-Cl···H 105.6 °

8. Tables of intermolecular interactions for $(4\text{-ClpyH})_3[FeCl_4]_2Cl$ (2)

Hydrogen bonds

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)	M-A···H(°)	symmetry operation
N(11)-H(11)···Cl(9)	1.010	2.257	3.130	143.9	-	-
N(21)-H(21)···Cl(9)	1.010	2.231	3.121	146.2	-	-
N(31)-H(31)···Cl(9)	1.010	2.169	3.081	149.2	-	-
N(11)-H(11)···Cl(4)	1.010	2.878	3.414	113.9	-	(-0.5+x, -0.5-y, -0.5+z)
Fe(1)-Cl(4)···H(11)	-	2.878	-	-	118.7	(-0.5+x, -0.5-y, 0.5+z)

Halogen bonds

M-X···X'-C	(M)-X···X'-(C) (Å)	M-X···X'(°)	C-X'···X(°)	symmetry operation
Fe(2)-Cl(5)···Cl(14)-C(14)	3.366	137.0	159.4	-
Fe(2a)-Cl(7a)···Cl(34)-C(34)	3.591	94.0	143.8	(1.5-x, 0.5+y, 0.5-z)
Fe(2a)-Cl(5a)···Cl(34)-C(34)	3.684	91.6	148.9	(1.5-x, 0.5+y, 0.5-z)
Fe(1)-Cl(2)···Cl(24)-C(24)	3.673	95.5	142.2	-

Weak Hydrogen bonds

(C)H···Cl(Fe) 2.863 Å, C-H···Cl 111.1 °, Fe-Cl···H 84.3 °; (C)H···Cl(Fe) 2.784 Å, C-H···Cl 143.2 °, Fe-Cl···H 91.8 °; (C)H···Cl(Fe) 2.788 Å, C-H···Cl 122.4 °, Fe-Cl···H 103.2 °; (C)H···Cl(Fe) 2.871 Å, C-H···Cl 119.5 °, Fe-Cl···H 123.3 °; (C)H···Cl(Fe) 2.840 Å, C-H···Cl 128.4 °, Fe-Cl···H 84.9 °; (C)H···Cl(Fe) 2.921 Å, C-H···Cl 138.6 °, Fe-Cl···H 136.3 °; (C)H···Cl(Fe) 2.757 Å, C-H···Cl 153.5 °, Fe-Cl···H 88.8 °; (C)H···Cl(Fe) 2.904 Å, C-H···Cl 127.5 °, Fe-Cl···H 85.1 °; (C)H···Cl(Fe) 2.758 Å, C-H···Cl 135.3 °, Fe-Cl···H 117.7 °; (C)H···Cl(Fe) 2.756 Å, C-H···Cl 121.6 °, Fe-Cl···H 162.0 °; (C)H···Cl(Fe) 2.766 Å, C-H···Cl 114.7 °, Fe-Cl···H 89.2 °; (C)H···Cl(Fe) 2.931 Å, C-H···Cl 110.9 °, Fe-Cl···H 102.6 °; (C)H···Cl(Fe) 2.811 Å, C-H···Cl 114.7 °, Fe-Cl···H 98.6 °; (C)H···Cl^- 2.605 Å, C-H···Cl^- 138.5 °; (C)-H···Cl-C 2.898 Å, C-H···Cl 151.3 °, C-Cl···H 90.8 °.

9. Tables of intermolecular interactions for $(4\text{-BrpyH})_3[FeCl_4]_2Cl$ (3)

Hydrogen bonds

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)	M-A···H(°)
N(11)-H(11)···Cl(9)	1.010	2.191	3.078	145.5	-
N(21)-H(21)···Cl(9)	1.010	2.224	3.114	146.2	-
N(31)-H(31)···Cl(9)	1.010	2.219	3.107	145.9	-

Halogen bonds

M-X···X'-C	(M)-X···X'-(C) (Å)	M-X···X'(°)	C-X'···X(°)	symmetry operation
Fe(2A)-Cl(5A)···Br(34)-C(34)	3.361	135.3	160.8	(0.5-x, -0.5+y, 0.5-z)
Fe(2)-Cl(6)···Br(14)-C(14)	3.509	96.3	149.9	-
Fe(2)-Cl(5)···Br(14)-C(14)	3.773	89.3	145.6	-
Fe(1)-Cl(3)…Br(24)-C(24)	3.635	98.1	146.1	-

Weak Hydrogen bonds

(C)H···Cl(Fe) 2.718 Å, C-H···Cl 126.8 °, Fe-Cl···H 154.6 °; (C)H···Cl(Fe) 2.770 Å, C-H···Cl 116.6 °, Fe-Cl···H 92.0 °; (C)H···Cl(Fe) 2.807 Å, C-H···Cl 116.2 °, Fe-Cl···H 95.2 °; (C)H···Cl(Fe) 2.739 Å, C-H···Cl 139.5 °, Fe-Cl···H 120.6 °; (C)H···Cl(Fe) 2.768 Å, C-H···Cl 156.1 °, Fe-Cl···H 91.2 °; (C)H···Cl(Fe) 2.863 Å, C-H···Cl 156.1 °, Fe-Cl···H 91.2 °; (C)H···Cl(Fe) 2.889 Å, C-H···Cl 113.2 °, Fe-Cl···H 85.6 °; (C)H···Cl(Fe) 2.801 Å, C-H···Cl 143.7 °, Fe-Cl···H 91.9 °; (C)H···Cl(Fe) 2.749 Å, C-H···Cl 125.4 °, Fe-Cl···H 106.1 °; (C)H···Cl^- 2.580 Å, C-H···Cl^- 140.9 °; (C)-H···Br-C 3.032 Å, C-H···Br 151.8 °, C-Br···H 90.1 °.

10. Tables of intermolecular interactions for (3-IpyH)$_2$[AuBr$_{3.35}$Cl$_{0.65}$]Br$_{0.30}$Cl$_{0.70}$ (4)

Hydrogen bonds

D-H···.A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)	M-A···H(°)	symmetry operation
N(1)-H(1)···(Cl, Br)	1.010	2.209	3.137	152	-	-
N(1)-H(1)···(Cl1, Br3)	1.010	2.997	3.550	115.4	-	(-x, +y, 0.5-z)
Au-(Cl1, Br3)···H(1)	-	2.997	-	-	140.9	(-x, +y, 0.5-z)

Halogen bonds

C-X···X'	(C)-X···X' (Å)	C-X'···X(°)	symmetry operation
C(3)-I(1)···(Br, Cl)	3.331	169.5	(-x, -1-y, -z)

M-X···X'	(M)-X···X' (Å)	M-X···X'(°)	symmetry operation
Au(1)-(Cl1, Br3)···(Br, Cl)	3.468	180	(-x, +y, 0.5-z)

M-X···X'-M	(M)-X···X-(C) (Å)	M-X···X'(°)	M-X'···X(°)	symmetry operation
Au(1)-Br(2)···Br(2)-Au(1)	3.520	159.9	159.9	(-x, +y, 0.5-z)

Weak Hydrogen bonds

Between stacking sheets

(C)H···Br(Au) 2.734 Å, C–H···X 159.1 °, Au–Br···H 103.7 °;(C)H···Br(Au) 2.874 Å, C–H···X 151.0 °, Au–Br···H 109.8 °; (C)H···X(Au) 2.563 Å, C-H···X 140.6 °, Au–X···H 97.3.