Supporting information for:

Coordination Chemistry of Platinum and Palladium in the Solid-State: Controlled Synthesis of Imidazole and Pyrazole Complexes.

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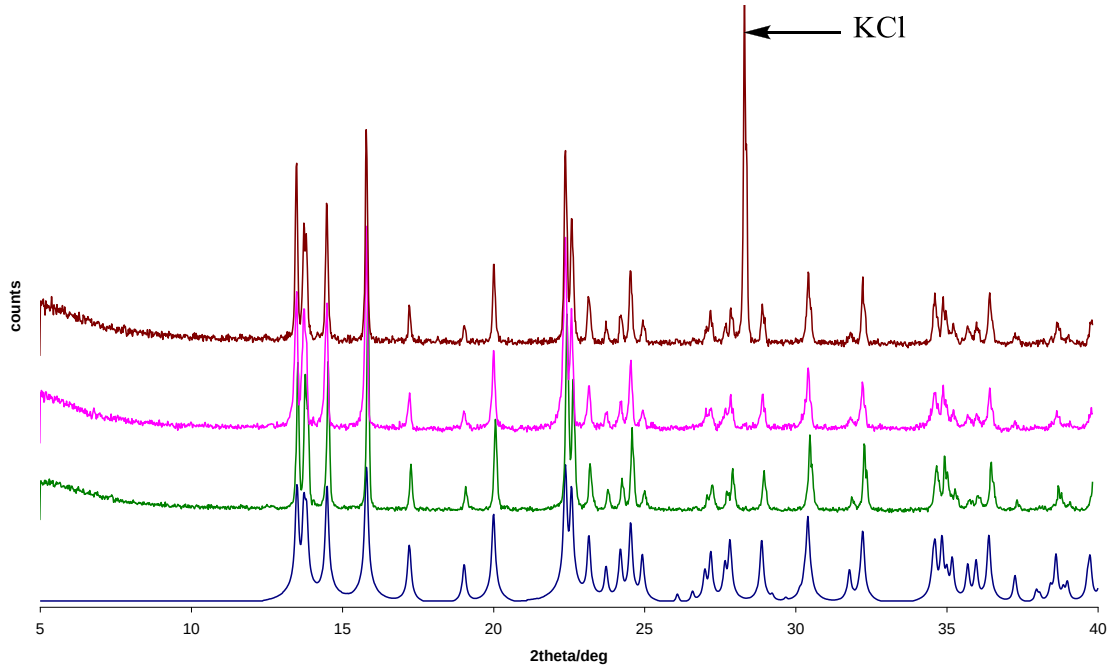
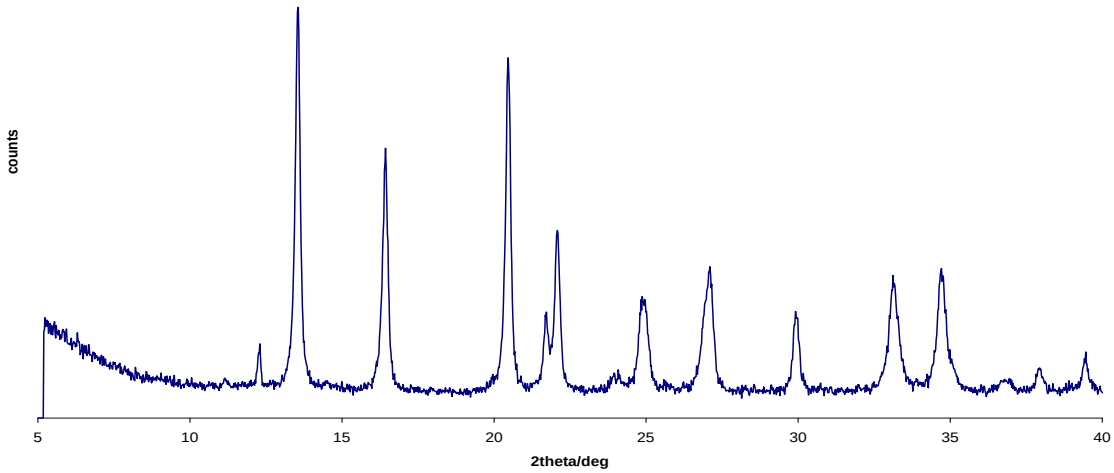
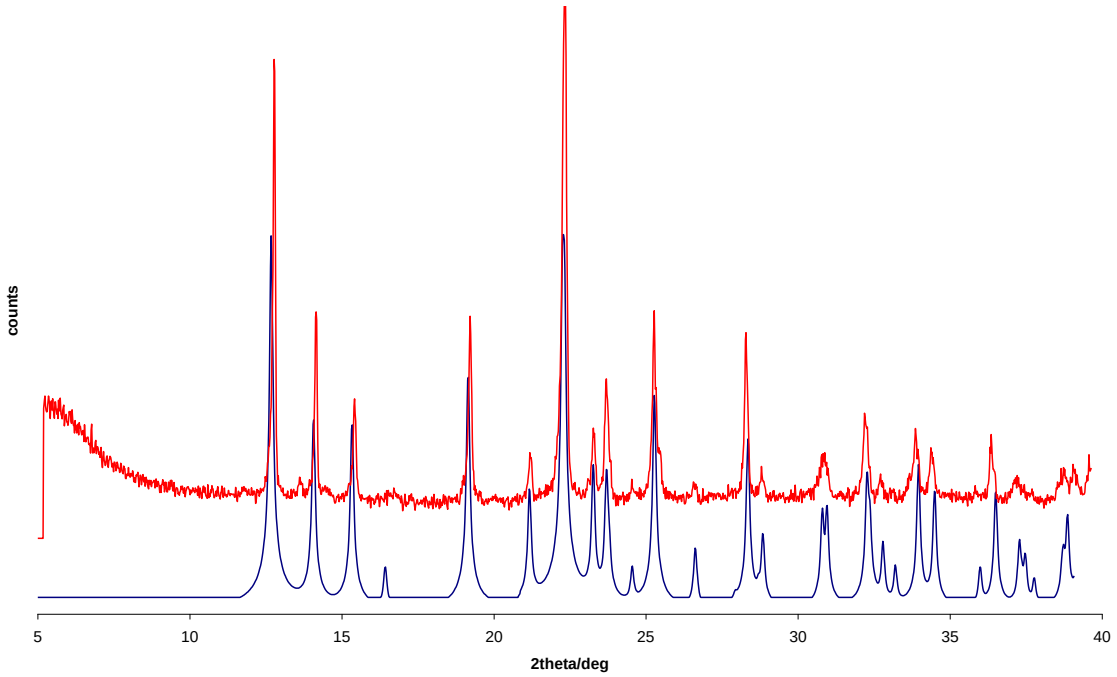
1. XRPD patterns



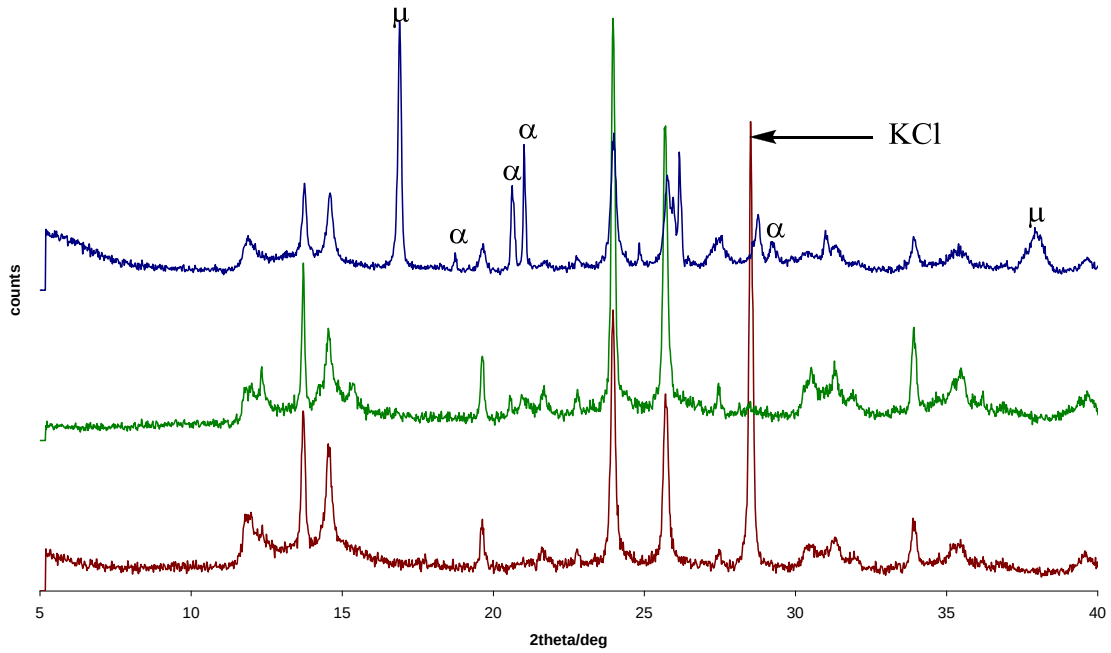
XRPD for $[H_2im]_2[PdCl_4]$ **1**. Dark blue = calculated from RORVOJ;[13] green = mechanochemical using $PdCl_2$; pink = HCl absorption by $[PdCl_2(Him)_2]$; brown = mechanochemical using K_2PdCl_4.



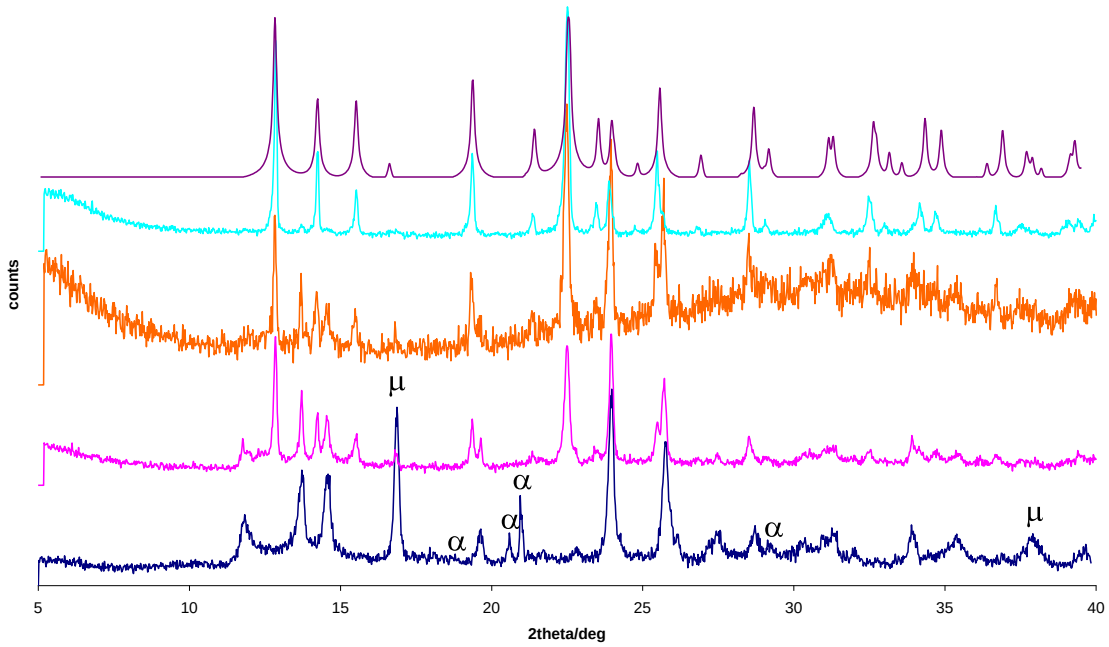
XRPD pattern for *cis*-$[PdCl_2(Him)_2]$ **2**.



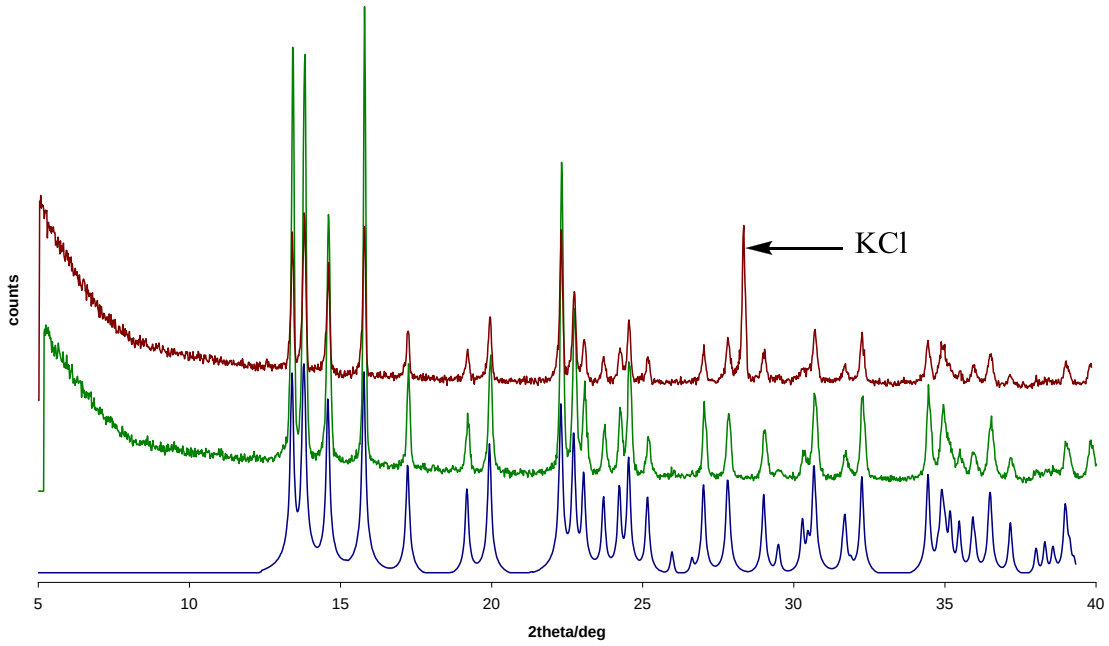
XRPD pattern for *trans*-[$PdCl_2(Him)_2$] **3**. Blue = calculated from the crystal structure; red = sample formed by thermal elimination from **1**.



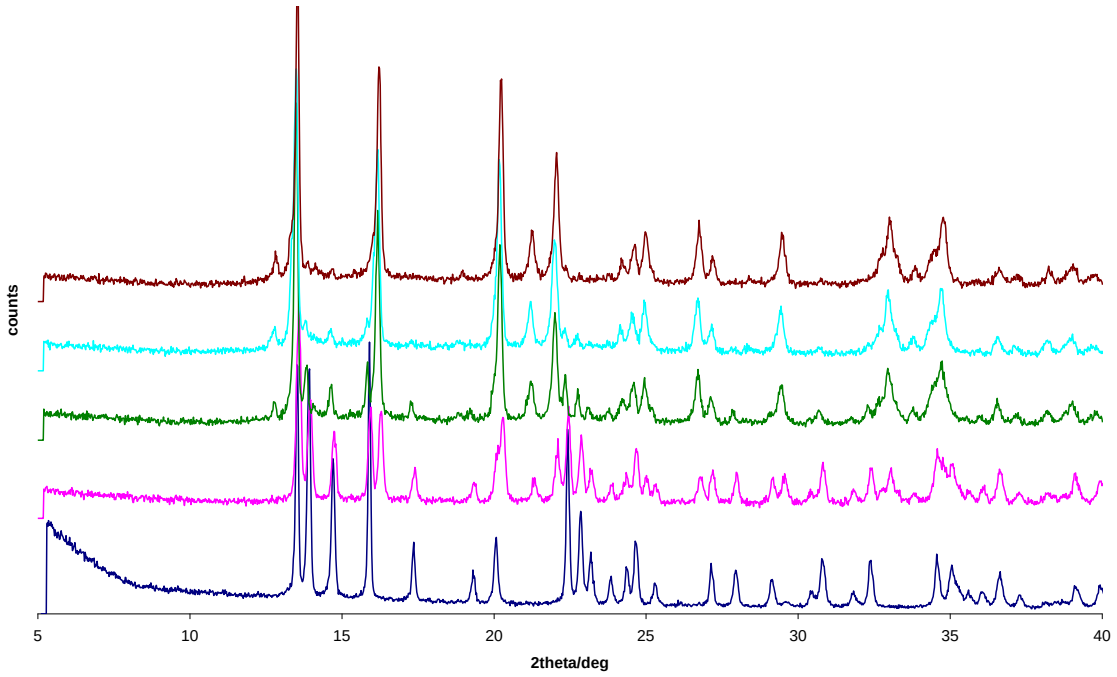
XRPD pattern for $[Pd(Him)_4]Cl_2$ **4**. Brown = K_2PdCl_4 + 4Him; green = $PdCl_2$ + 4Him; blue = $PdCl_2$ + 2Him. Key: μ = $PdCl_2$; α = Him.



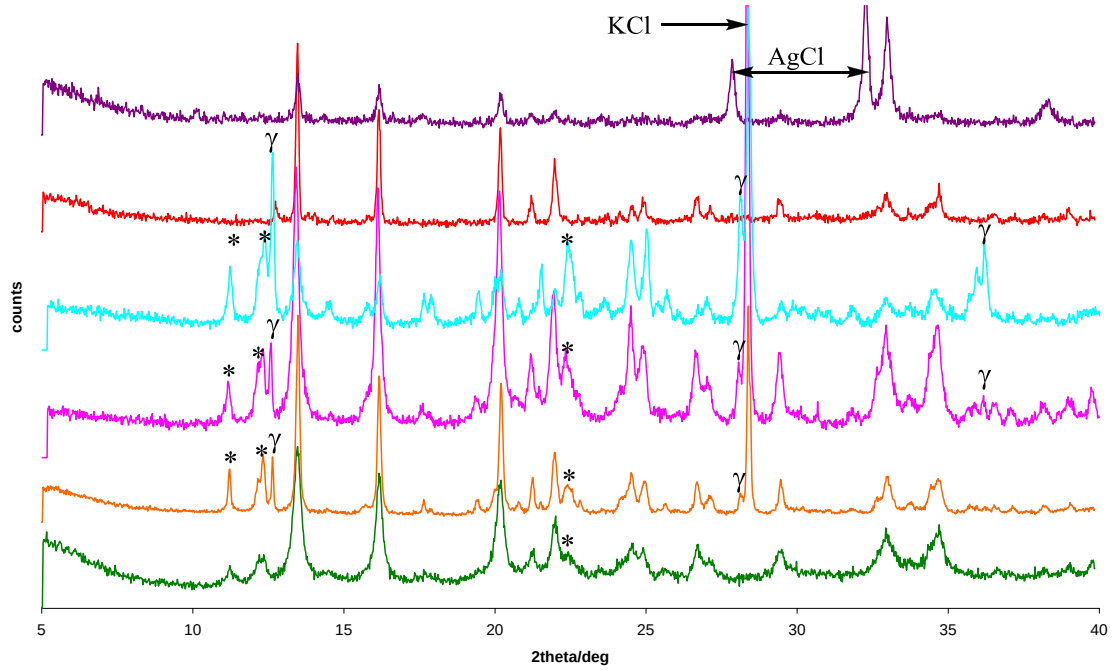
XRPD pattern for $[Pd(Him)_4]Cl_2$ **4**. Blue = $PdCl_2$ + 2Him (0 months); pink = 6 months; orange = 10 months; turquoise = *trans*-$[PdCl_2(Him)_2]$ **3**; violet = calculated from the crystal structure of **3**. Key: μ = $PdCl_2$; α = Him.



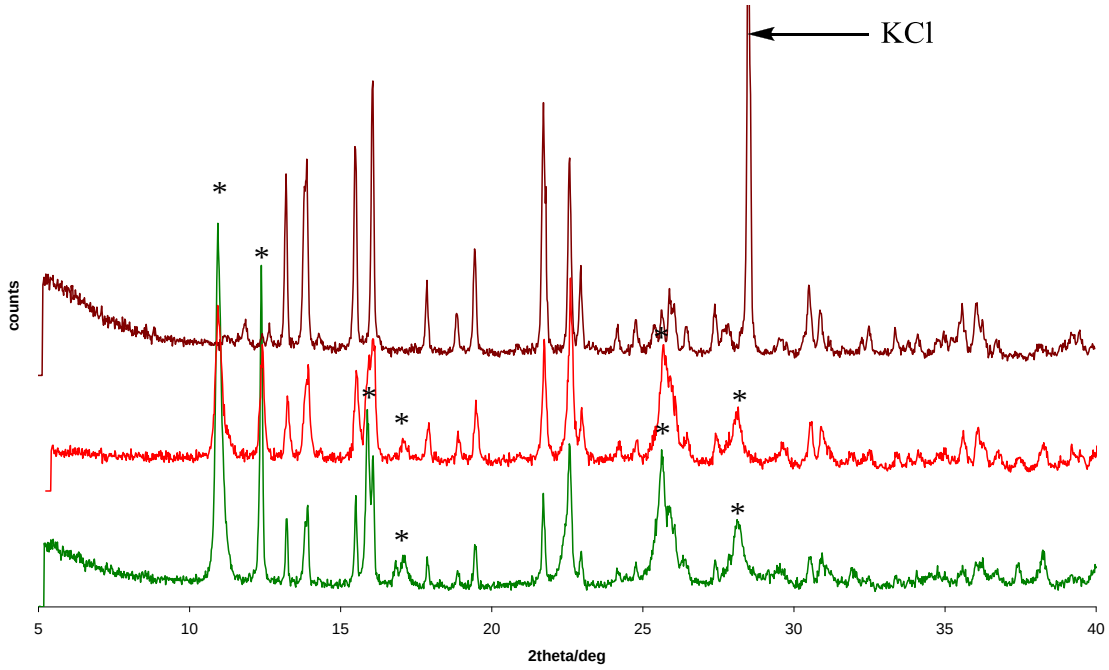
XRPD pattern for $[PtCl_4][H_2im]_2$ **5**. Blue = calculated from the crystal structure; green = mechanochemical using $PtCl_2$; brown = mechanochemical using K_2PtCl_4.



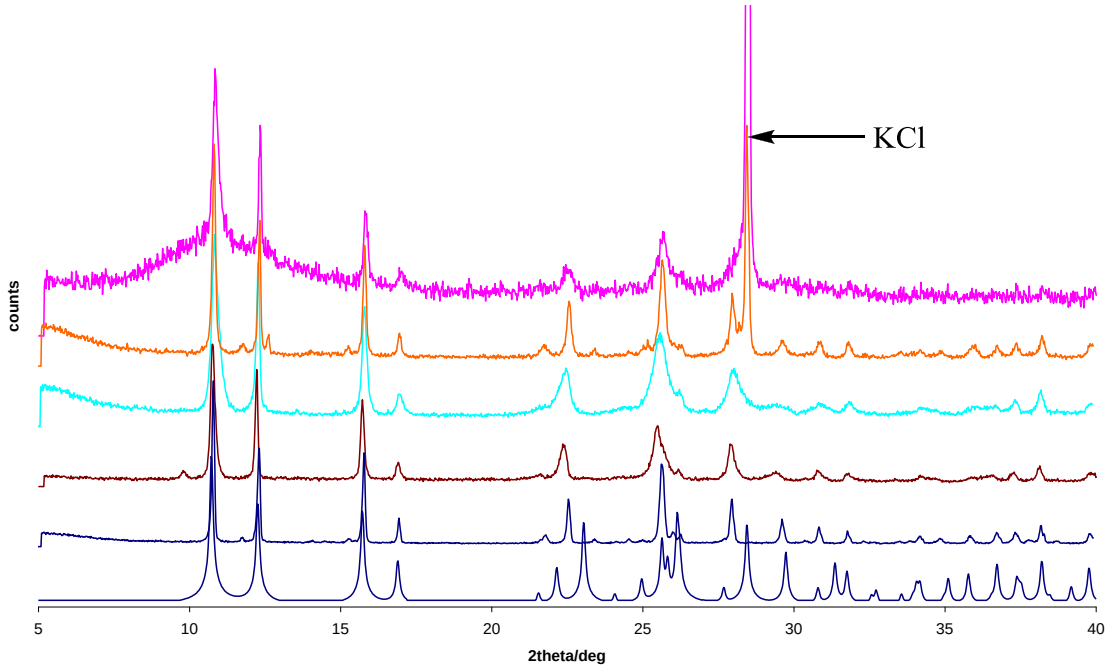
XRPD patterns for thermal conversion of $[H_2im]_2[PtCl_4]$ **5** to *cis*-$[PtCl_2(Him)_2]$ **6**. Blue = 0 hours; pink = 12 hours; green = 40 hours; turquoise = 66 hours; brown = 120 hours.



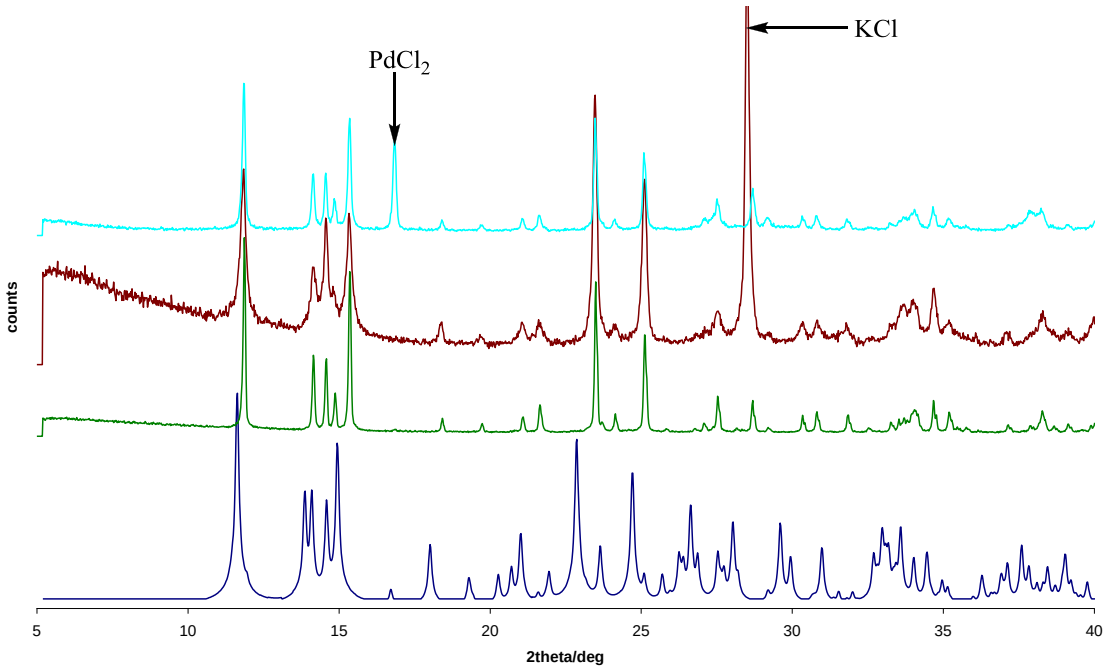
XRPD for *cis*-$[PtCl_2(Him)_2]$ **6**. Green = $PtCl_2$ + 2Him; orange = K_2PtCl_4 + 2Him; pink = **5** + 2KOH; turquoise = **5** + 2t-BuOK; red = thermal elimination; violet = **5** + Ag_2O. Key: γ = peaks from K_2PtCl_4; * = unknown by-product.



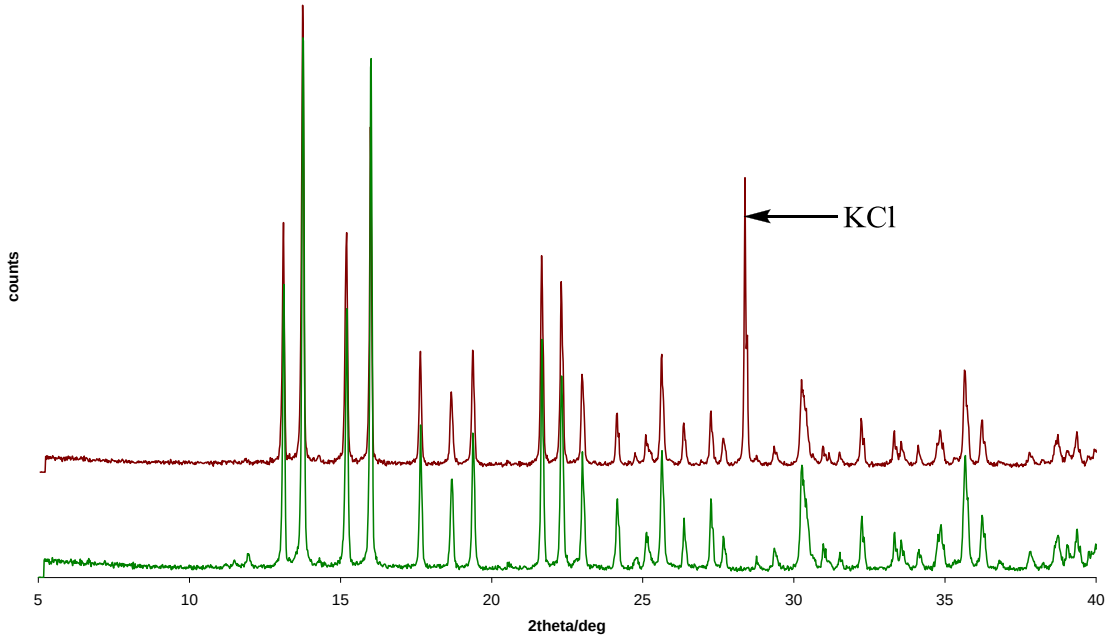
XRPD for $[H_2pz]_2[PdCl_4]$ **7**. Green = mechanochemical syntheses; red = HCl gas absorption by **9**; brown = K_2PdCl_4 + 2$[H_2pz]Cl$. * = peaks from **8**.



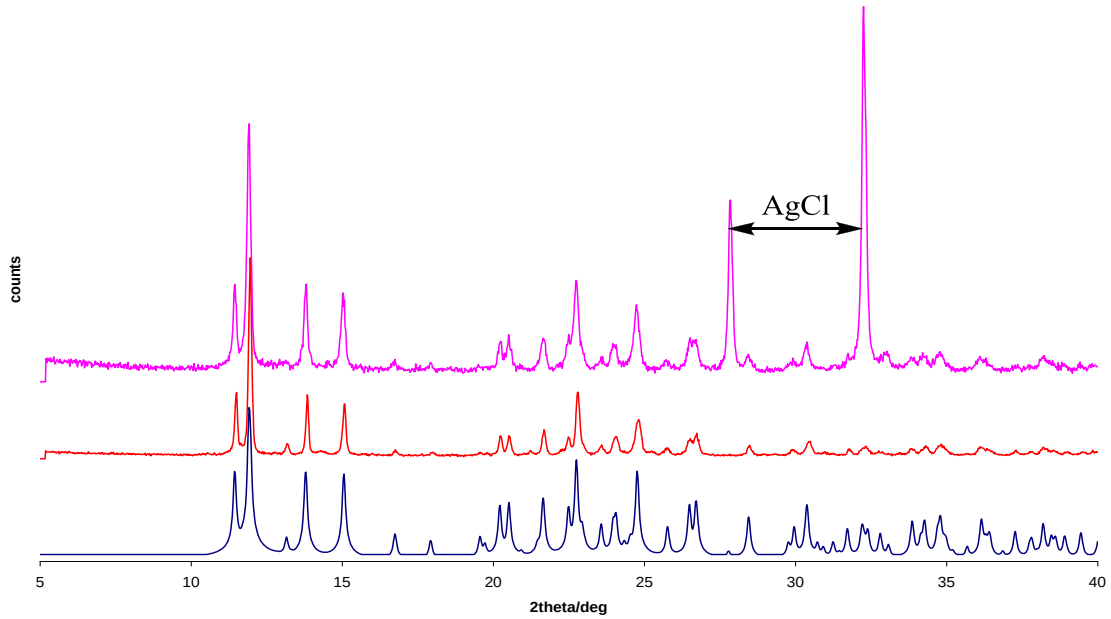
XRPD for *trans*-$[PdCl_2(Hpz)_2]$ **8**. Dark blue = calculated from the structure; blue = solution synthesis; brown = thermal elimination from **7**; turquoise = $Pd(OAc)_2$ + 2$[H_2pz]Cl$; orange = K_2PdCl_4 + 2Hpz (ball milling); pink = **7** + 2*t*-BuOK.



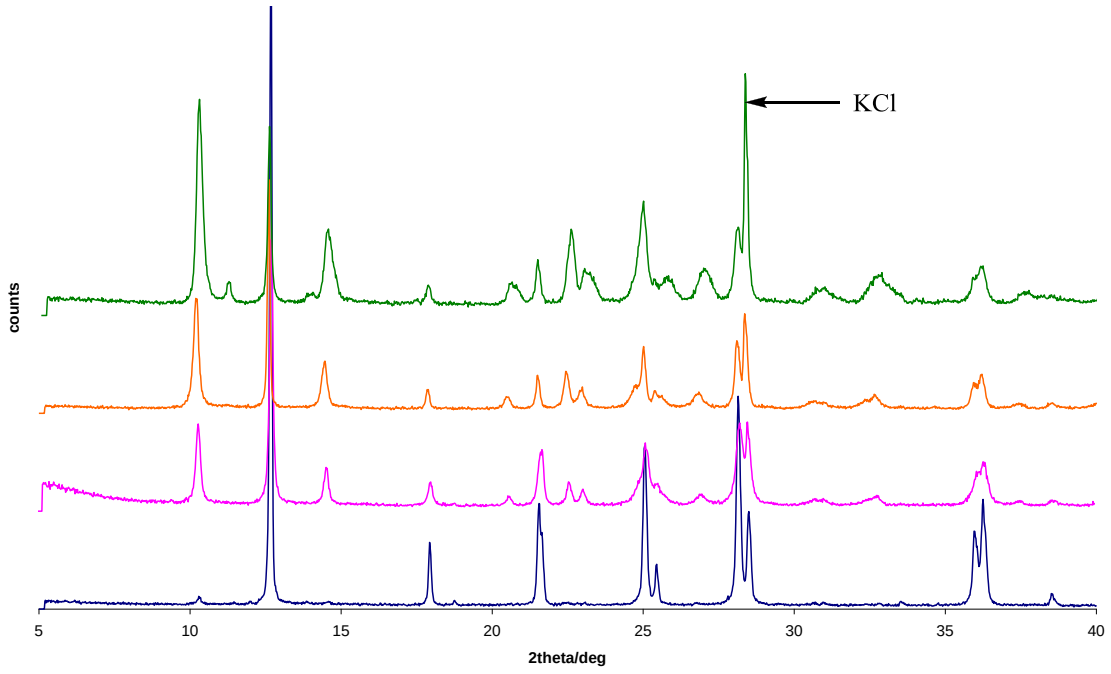
XRPD for $[Pd(Hpz)_4]Cl_2$ **9**. Dark blue = calculated from the crystal structure of a hydrate of **9**; green = $PdCl_2$ + 4Hpz; brown = K_2PdCl_4 + 4Hpz; turquoise = $PdCl_2$ + 2Hpz.



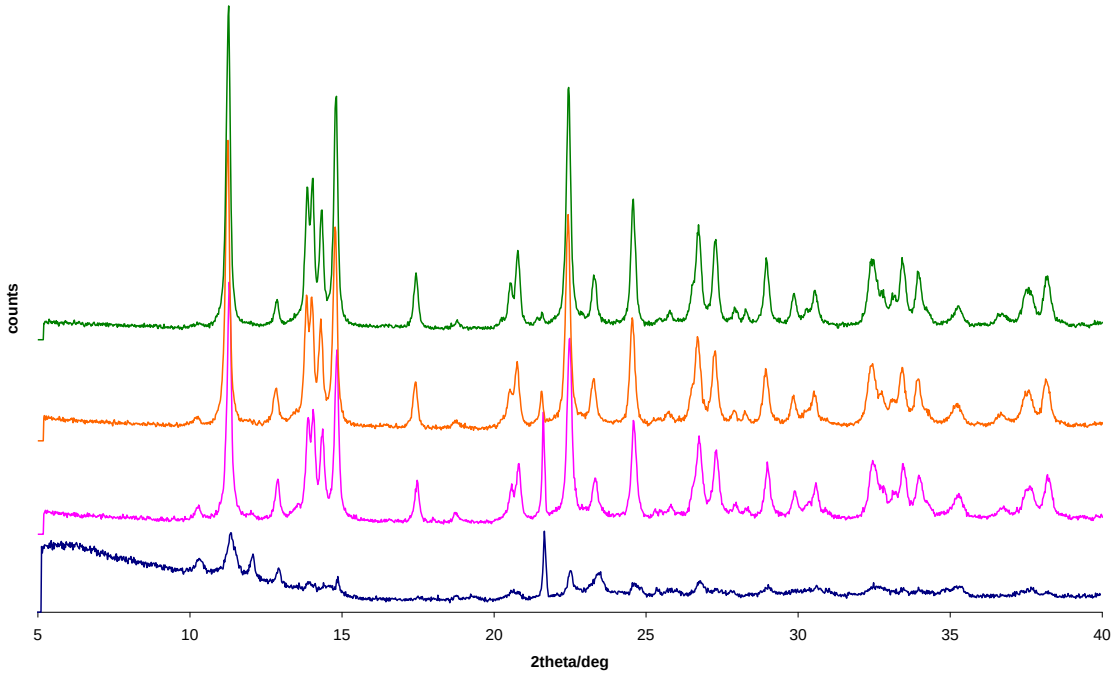
XRPD patterns for mechanochemical syntheses of $[H_2pz]_2[PtCl_4]$ **10**. Green = $PtCl_2$ + 2$[H_2pz]Cl$; brown = K_2PtCl_4 + 2$[H_2pz]Cl$.



XRPD patterns for *cis*-$[PtCl_2(Hpz)_2]$ **11**. Blue = calculated from the crystal structure of VAZWEY01; red = thermal elimination from $[H_2Pz]_2[PtCl_4]$ **10**; pink = **10** + Ag_2O.



XRPD pattern for the grinding reaction of K_2PtCl_4 + 2Hpz. Blue = 0 days; pink = 5days; orange 7 months; green = 12 months.



XRPD patterns for $[Pt(Hpz)_4]Cl_2 \cdot H_2O$ **12**. Blue = $PtCl_2$ + 4Hpz (0 days); pink = 5 days; orange = 6 days; green = 13 days.

2. Hydrogen bonds

Table HB1: Hydrogen-bonding geometry for **5** [Å and º].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1...Cl1[A]	1.06	2.55	3.40	136.4
N1-H1...Cl2[A]	1.06	2.32	3.13	132.6
N2-H2...Cl2[B]	1.07	2.45	3.33	138.0

Symmetry transformations used to generate equivalent atoms: [A] x,y-1,z [B] x,y,z+1.

Table HB2: Hydrogen bond geometry for **8** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H1A...Cl1[A]	0.88	2.46	3.012(3)	120.9
N2-H1A...Cl1[B]	0.88	2.62	3.272(3)	132.1

Symmetry transformations used to generate equivalent atoms: [A] -x+1,-y,-z [B] x,y+1,z.

Table HB3: Hydrogen bond geometry for **$[H_2pz]_2[PtCl_6]\cdot 2H_2O$** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(1)[A]	0.88	1.83	2.684(6)	164.5
N(2)-H(2A)...O(2)[B]	0.88	1.99	2.790(7)	151.1
N(2)-H(2A)...Cl(3)[B]	0.88	2.88	3.420(5)	121.7
N(3)-H(3A)...Cl(5)[C]	0.88	2.47	3.206(5)	141.0
N(3)-H(3A)...Cl(6)[C]	0.88	2.70	3.358(5)	132.2
N(3)-H(3A)...Cl(4)[D]	0.88	2.81	3.440(6)	130.2
N(4)-H(4B)...O(2)[A]	0.88	1.86	2.709(6)	163.0

Symmetry transformations used to generate equivalent atoms: [A] x, y, z [B] x,y+1,z-1 [C] -x,-y+1,-z+2 [D] x,y,z+1

Table HB4: Hydrogen bond geometry for **β-11**[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(12A)...Cl(1) [B]	0.88	2.46	3.241(18)	148.5
N(4)-H(14A)...Cl(6) [A]	0.88	2.53	3.356(16)	156.1
N(4)-H(14A)...Cl(8) [C]	0.88	2.92	3.408(15)	116.7
N(8)-H(8A)...Cl(8) [A]	0.88	2.54	3.294(18)	143.7
N(8)-H(8A)...Cl(6) [D]	0.88	2.91	3.521(16)	128.1
N(10)-H(16B)...Cl(1) [A]	0.88	2.38	3.220(17)	160.0
N(12)-H(10A)...Cl(6) [E]	0.88	2.65	3.36(2)	138.3
N(14)-H(4B)...Cl(3) [A]	0.88	2.74	3.584(19)	160.2
N(16)-H(2A)...Cl(4) [A]	0.88	2.38	3.225(14)	160.7

Symmetry transformations used to generate equivalent atoms: [A] x, y, z [B] -x,-y,-z+1 [C] x,y,z+1 [D] x,y,z-1 [E] -x+1,-y+1,-z+1

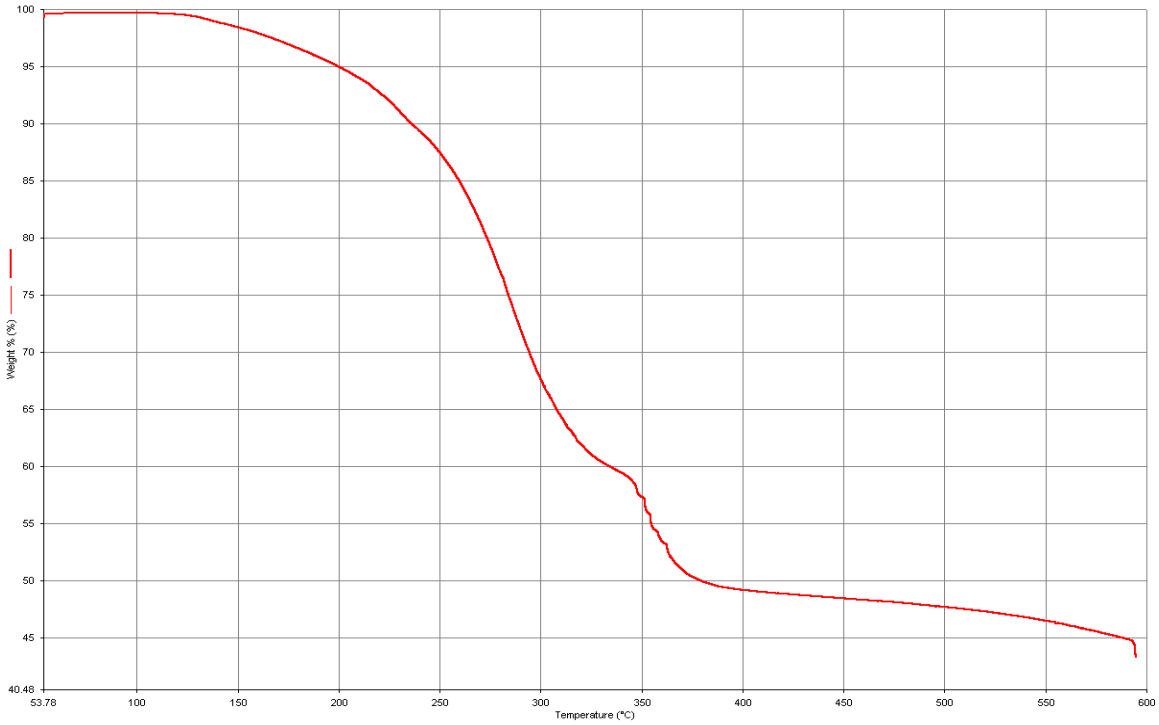
Table HB5: Hydrogen bond geometry for **10** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4B)...Cl(2) [B]	0.86	2.46	3.32	177.6
N(3)-H(3A)...Cl(1) [A]	0.89	2.53	3.40	170.3

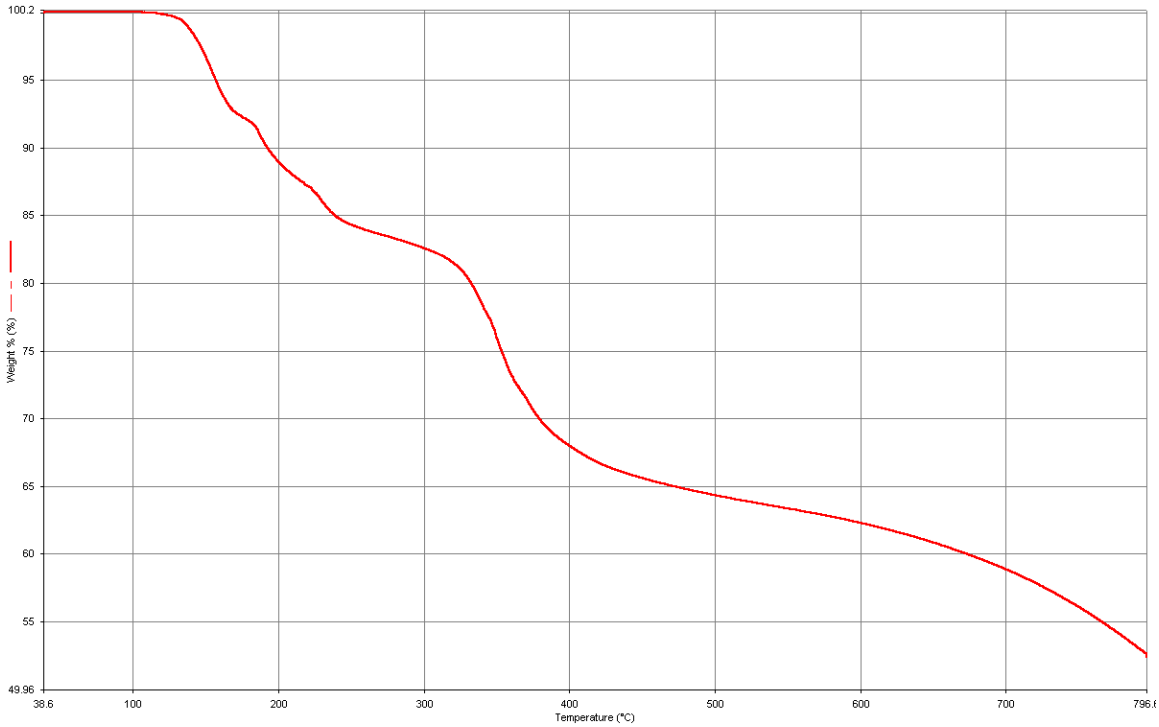
Symmetry transformations used to generate equivalent atoms: [A] x, y, z [B] -x,1-y,-1-z

3 TGA traces

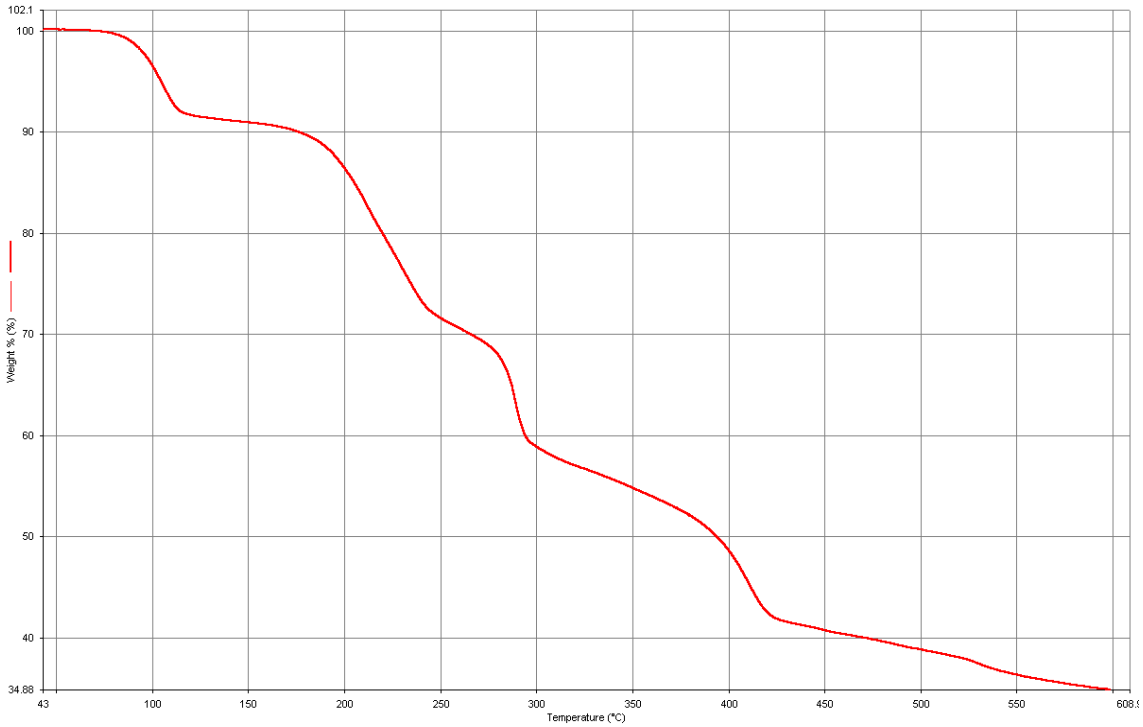
TGA diagram for $[H_2im]_2[PdCl_4]$ **1**.



TGA diagram for $[H_2im]_2[PtCl_4]$ **5**.



TGA diagram for $[H_2pz]_2[PdCl_4]$ **7**.



TGA diagram for $[H_2pz]_2[PdCl_4]$ **10**.