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Electronic Supporting Information

On the many roles of NH_3 ligands in mono- and multinuclear complexes of platinum

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Table S1: ^{1}H NMR chemical shifts (ppm) of 1-MeC$^-$ and NH_3 resonances in **1a**, **1b**, **1c**, and **1e**.[a]

	NH_3	H6[b]	N4H	H5[b]	CH_3	r[c]
1a	4.03; 3.97	6.97	6.18	5.65	3.18	12 (5.2 %)
1b	4.18; 4.07	6.97	6.21	5.65	3.18	24 (10.4 %)
1c	4.10; 4.02	6.97	6.19	5.65	3.18	9 (3.9 %)
1e	4.53; 4.39	6.89	6.14	5.63	3.14	25 (10.8 %)

[a] Concentrations in all cases ca. 6 mM; solvent DMSO-d_6;

[b] Doublet, $^3J \sim 7.5$Hz

[c] r = ratio of dimer **1**: H_2O molecules in sample, as determined by integration; content of water (%) in brackets

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Table S2: Selected details of DFT geometries of trinuclear complex **2** with anions (distances in Å, angles in deg.)

	Anion X(S)[a]				
	without X(S)	Cl^-	Br^-	I^-	SO_4^{2-}
N(am) - X(S)	-	3.220	3.352	3.565	3.238
H6 – X(S)	-	2.547	2.654	2.934	2.720
Pt – X(S)	-	3.997	4.081	4.261	3.971
	Distances to Pt_3 - plane				
Pt_3 – H6	0.0	–0.014	+0.011	–0.012	–0.258
Pt_3 – C9	+0.004	+0.162	+0.127	+0.169	+0.608
Pt_3 – X(S)		+1.827	+1.994	+2.322	+1.801
	Angles between planes				
Pt_3 / PtN_4	89.7	77.5	80.9	85.9	79.1

[a] X = halide anion

S = sulfur atom in sulfate

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Table S3. Select details of DFT geometrics of tetranuclear complex **3** with anions (distances in Å, angles in deg.)

	Anion X(S)[a]				
	without X(S)	Cl^-	Br^-	I^-	SO_4^{2-}
N(am) – X(S)	-	3.681	3.732	4.070	3.989
H6 – X(S)	-	3.388	3.372	3.330	3.091
Pt – X(S)	-	4.824	4.826	4.830	4.690
N(am) – O	-				2.762
	Distances to Pt_4 - plane				
Pt4 – H6	0.0	–0.221	–0.197	–0.143	–0.052
Pt_4 – C9	0.0	+0.571	+0.528	+0.399	+0.206
Pt_4 – X(S)		+1.182	+1.175	+1.098	+0.486
	Angles between planes				
Pt_4 / PtN_4	89.5	59.6	61.2	68.5	60.8

[a] X = halide anion
S = sulfur atom in sulfate

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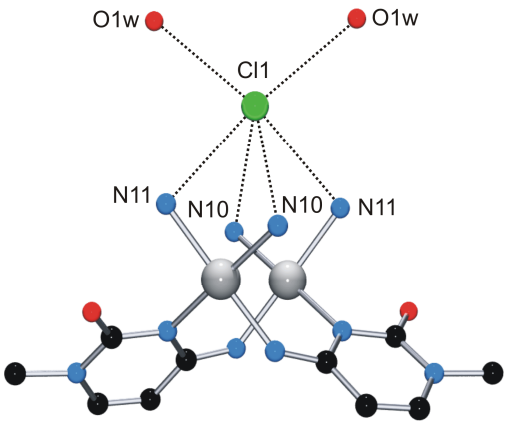

Figure S1: Detail of the chloride anion surrounding the cation of **1b**.

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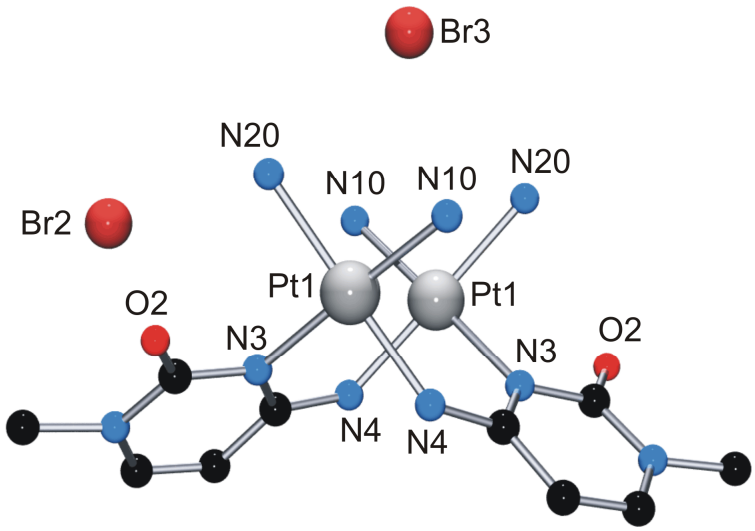

Figure S2: View of **1d** including bromide counter anions.

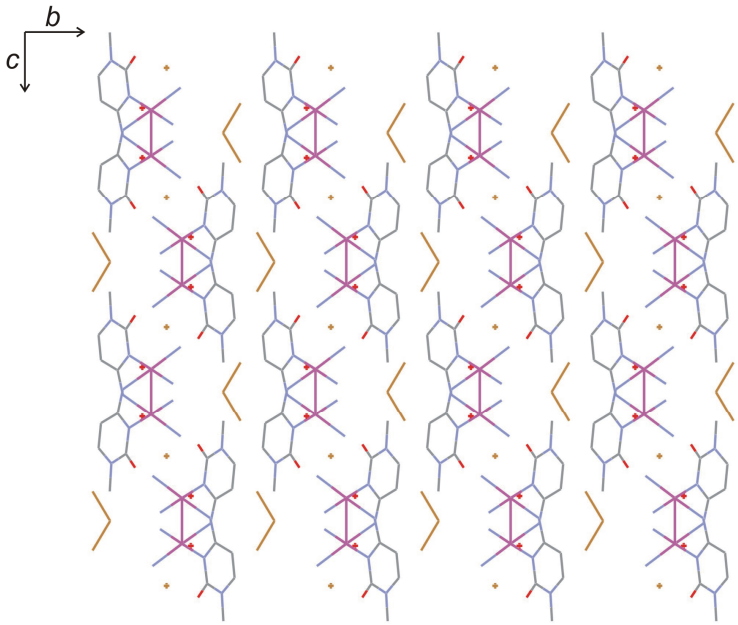

Figure S3: Packing of the molecule **1d** with disordered bromide counter anions.

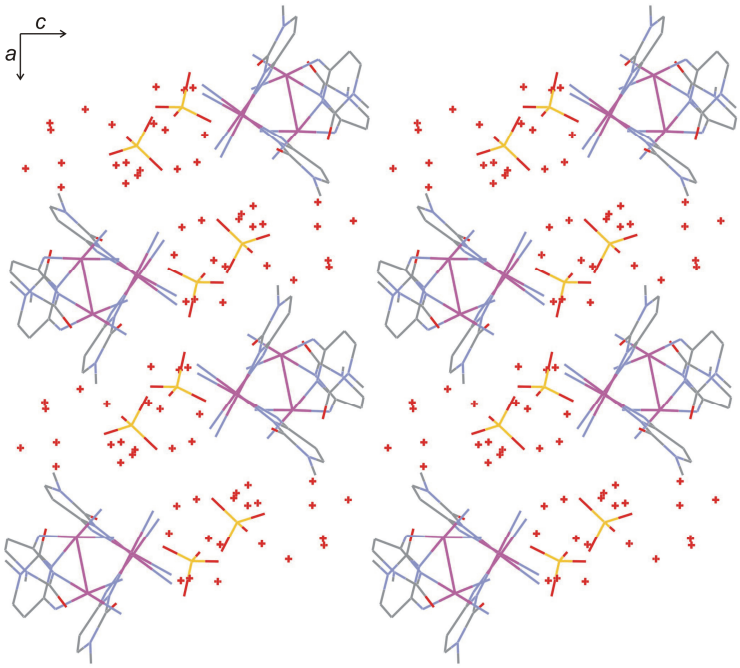

Figure S4: Packing of cations **1e**, including numerous hydrogen bonding interactions of the water molecules of crystallization.

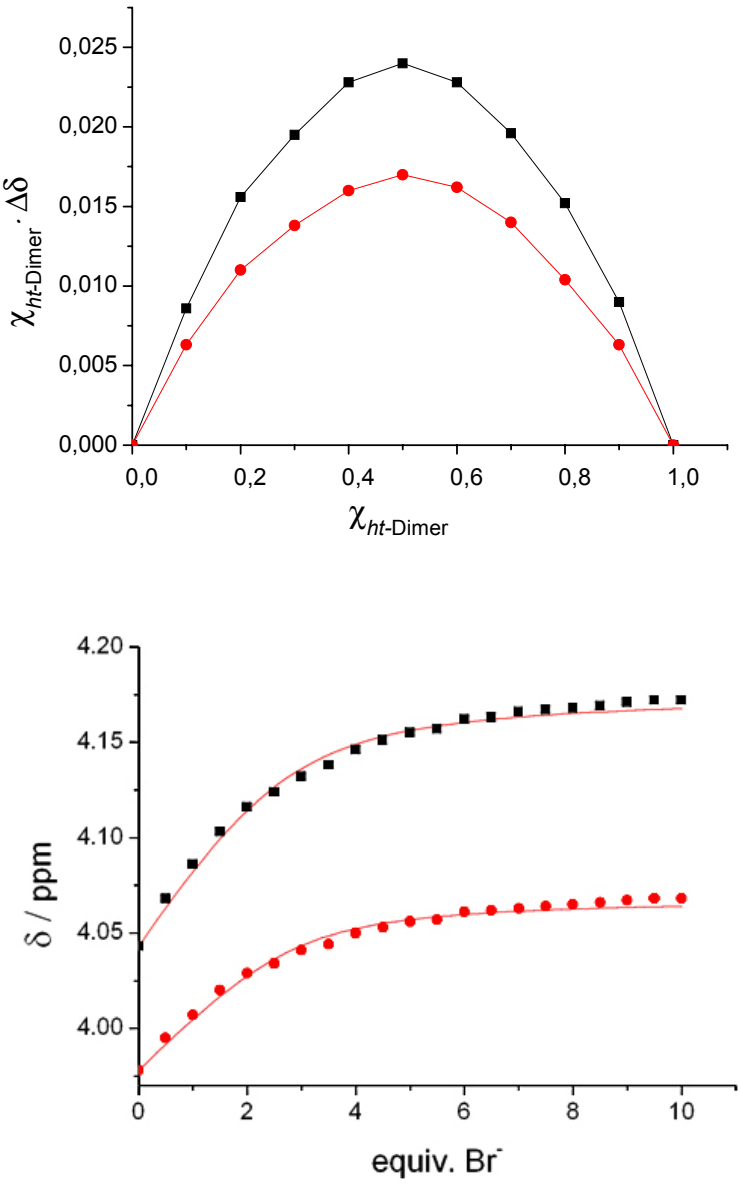

Figure S5: Job plot (top) for system **1a** + KBr (total concentration 0.028 M) and ^{1}H NMR shift changes of the two NH_3 resonances of **1a** (0.01m) in the presence of increasing amounts of KBr.

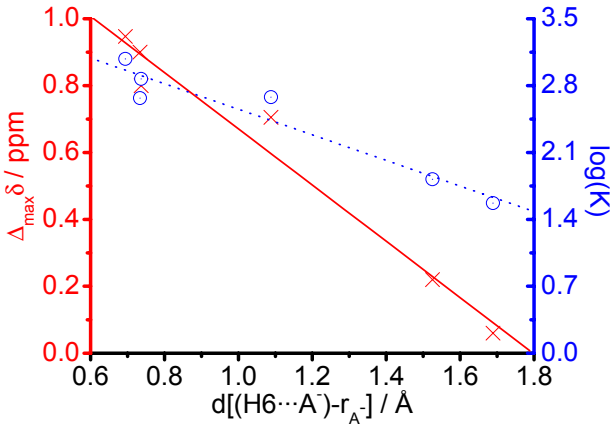

Figure S6: Plot of experimental data from halide anion binding experiments of **2** and **3** versus distance between H6 and anion surface as calculated by DFT. Observed downfield shifting of the H6 resonances caused by anion binding is shown in red, the respective association constants are shown in blue, linear trend lines are indicated.

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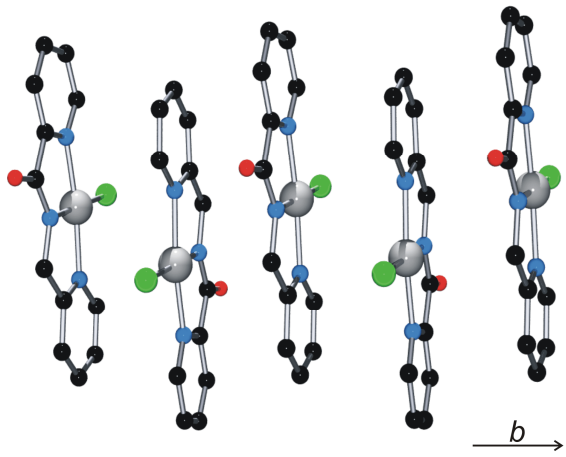

Figure S7: Stacking of molecules **4** along *b* axis

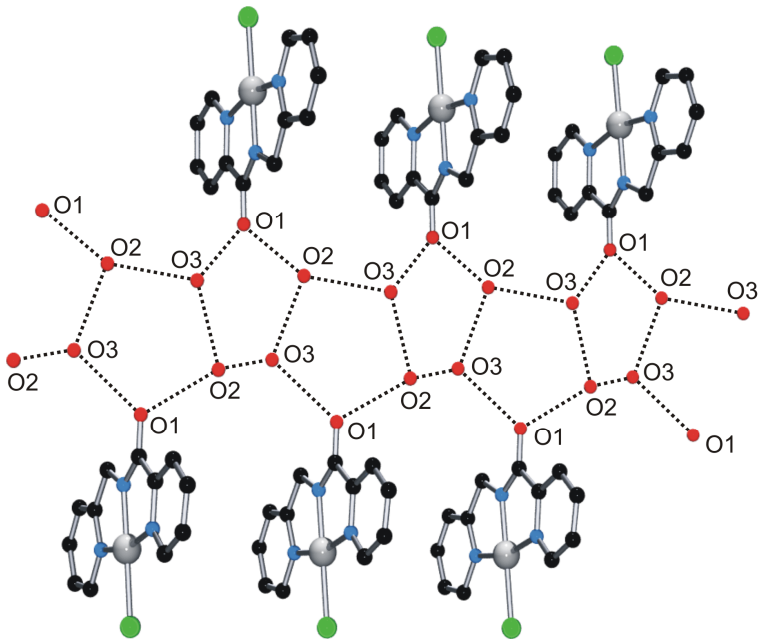

Figure S8: Detail of the packing and formation of a water cluster in **4**.

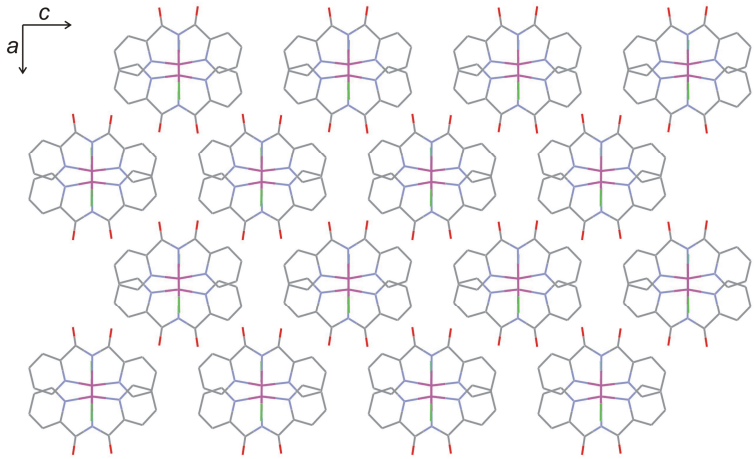

Figure S9: Packing of the molecules of **5**.