Supporting Information for

Acetate-Bridged Platinum(III) Complexes Derived from Cisplatin

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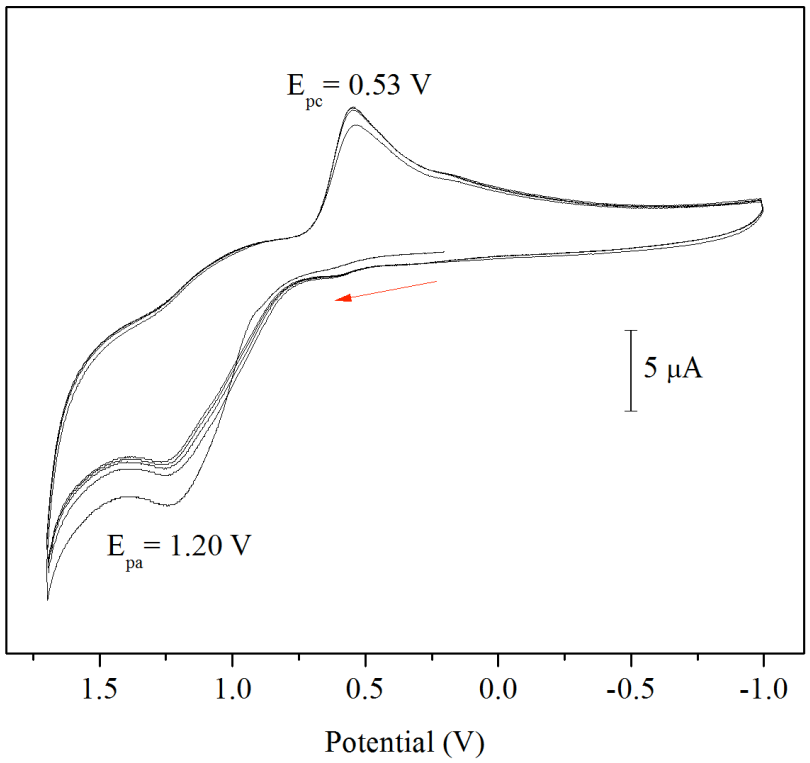

Figure S1. Cyclic voltammogram of [**1**]$(NO_3)_2$ in DMF with 0.1 M $(Bu_4N)(PF_6)$ as supporting electrolyte, obtained at a scan rate of 100 mV/s. The red arrow denotes the initial potential and scan direction. Potentials are referenced to Ag/AgCl.

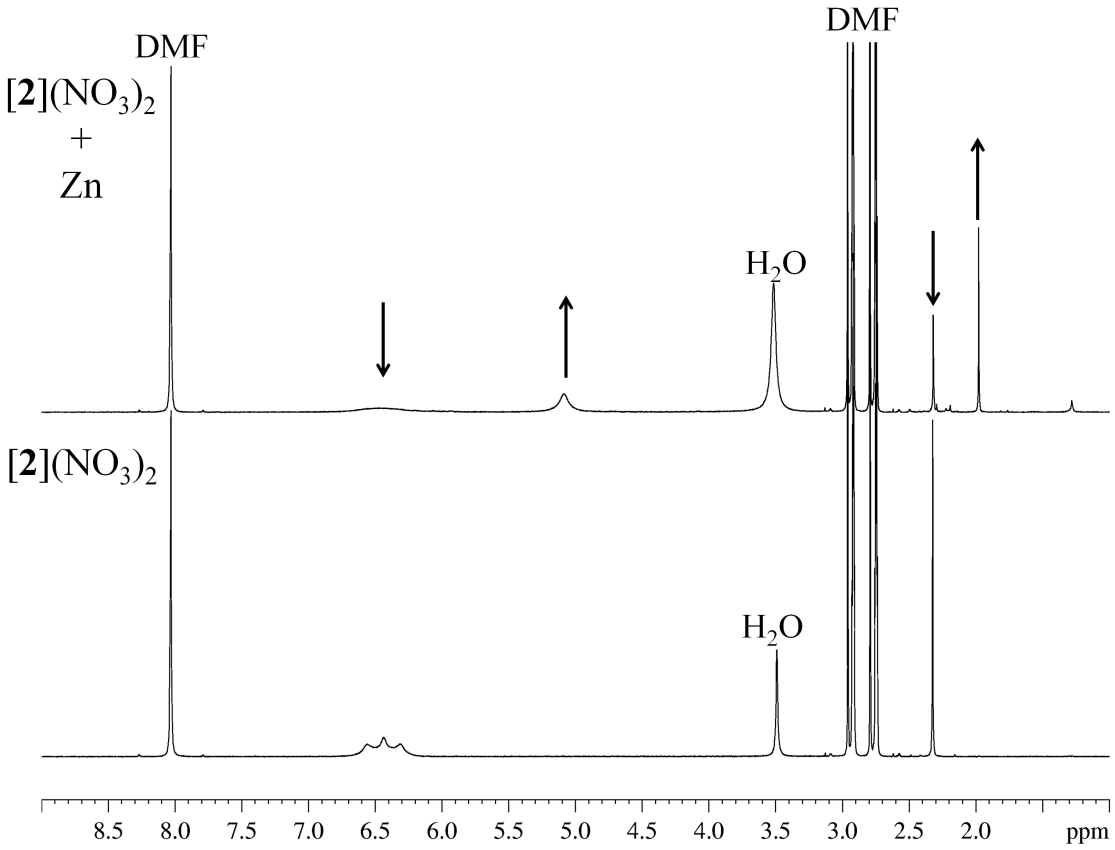

Figure S2. ^{1}H NMR spectra of [**2**](NO$_3$)$_2$ before (bottom) and after (top) stirring with excess Zn dust in DMF-d_7. The downward arrows signify the disappearance of resonances from the platinum(III) starting material, and upward arrows mark the appearance of the resulting reduction product.

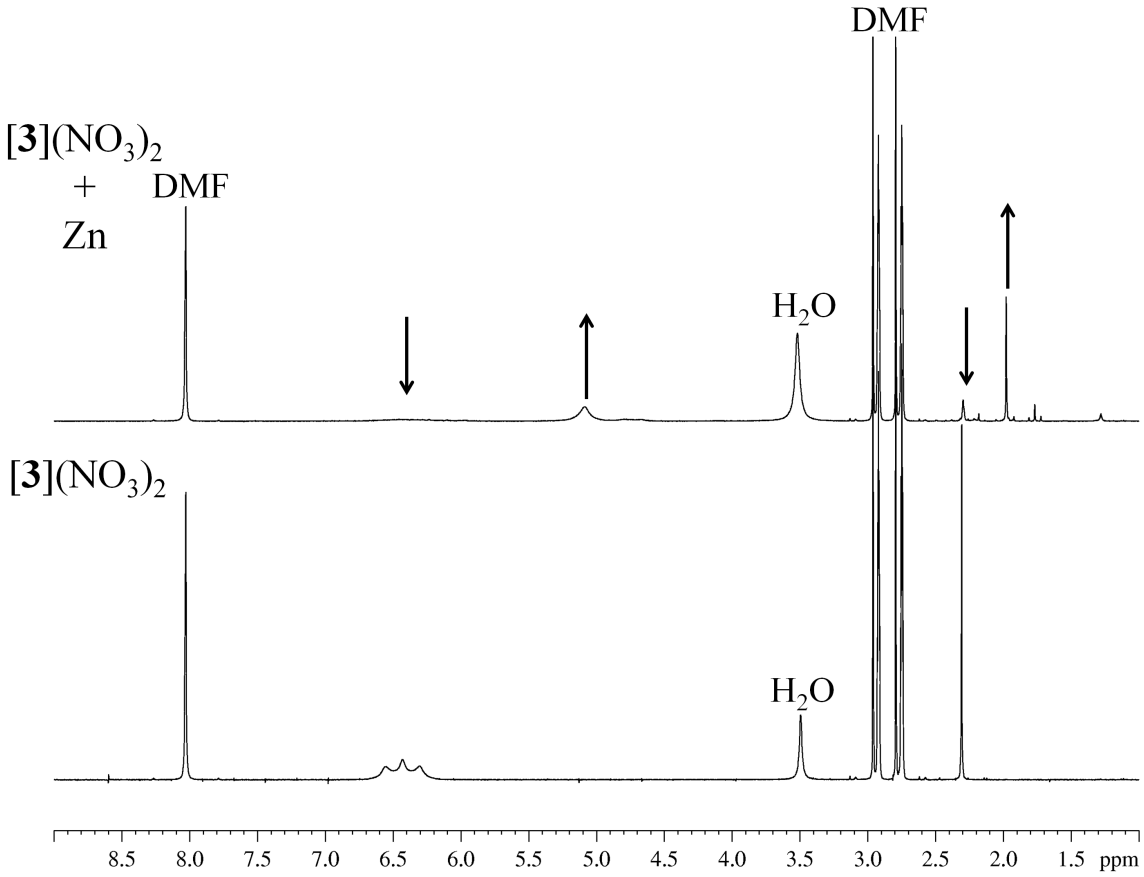

Figure S3. ^{1}H NMR spectra of [**3**](NO$_3$)$_2$ before (bottom) and after (top) stirring with excess Zn dust in DMF-d_7. The downward arrows signify the disappearance of resonances from the platinum(III) starting material, and upward arrows mark the appearance of the resulting reduction product.

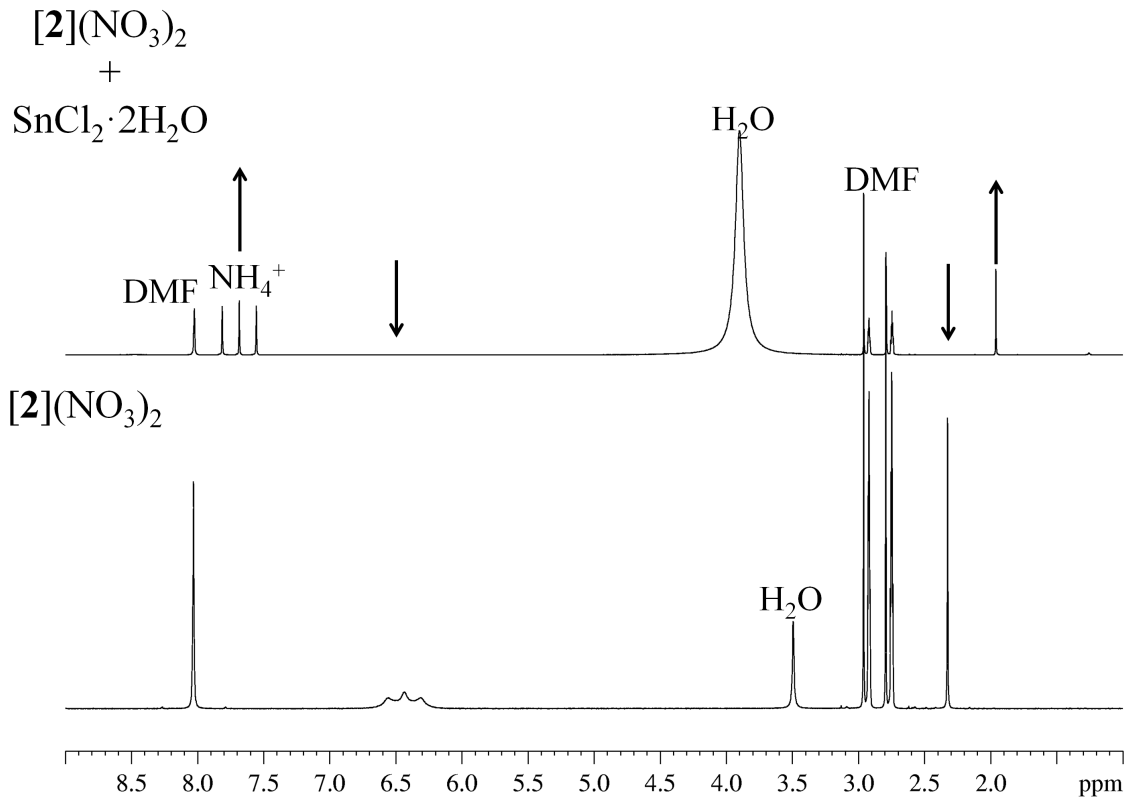

Figure S4. ^{1}H NMR spectra of [**2**](NO$_3$)$_2$ before (bottom) and after (top) stirring with excess $SnCl_2 \cdot 2H_2O$ in DMF-d_7. The downward arrows signify the disappearance of resonances from the platinum(III) starting material, and upward arrows mark the appearance of the resulting reduction product.

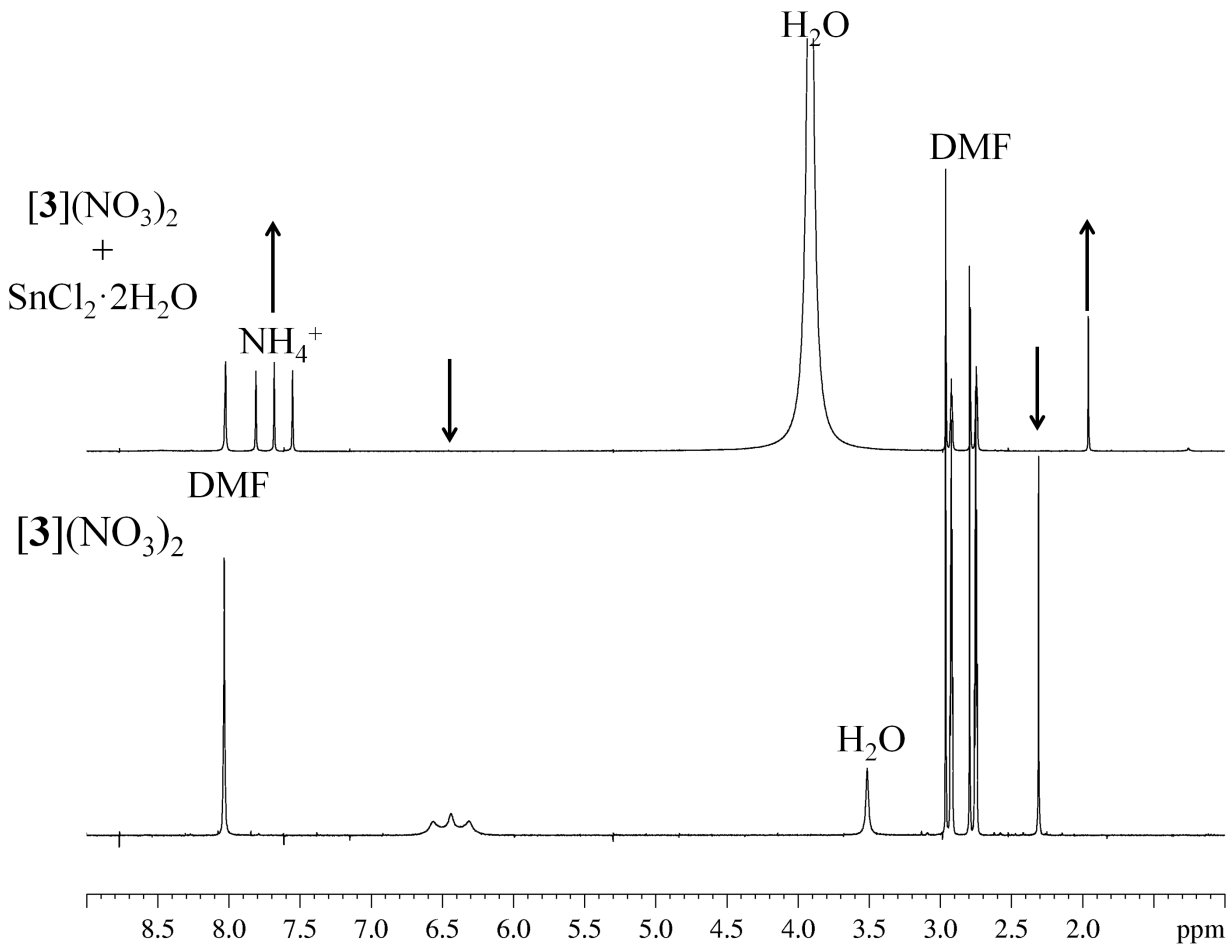

Figure S5. ^{1}H NMR spectra of [**3**]$(NO_3)_2$ before (bottom) and after (top) stirring with excess $SnCl_2 \cdot 2H_2O$ in DMF-d_7. The downward arrows signify the disappearance of resonances from the platinum(III) starting material, and upward arrows mark the appearance of the resulting reduction product.

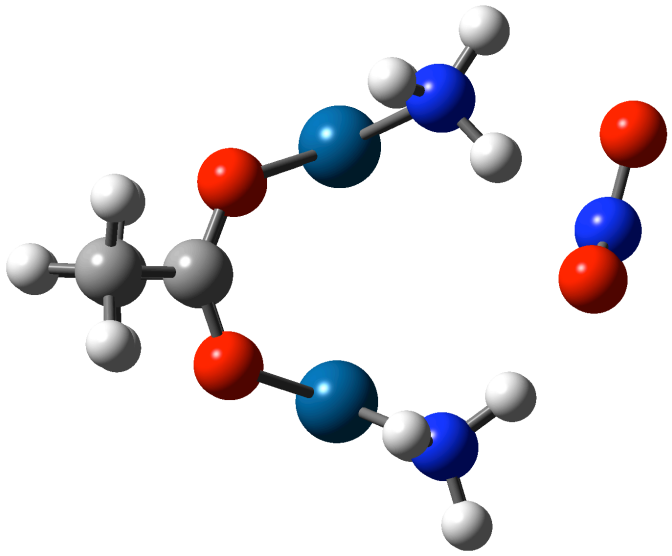

Figure S6. DFT-optimized structure of the ion pair, [**1**]$(NO_3)^+$. Grey, blue, red, white, and teal spheres represent carbon, nitrogen, oxygen, hydrogen, and platinum atoms, respectively.

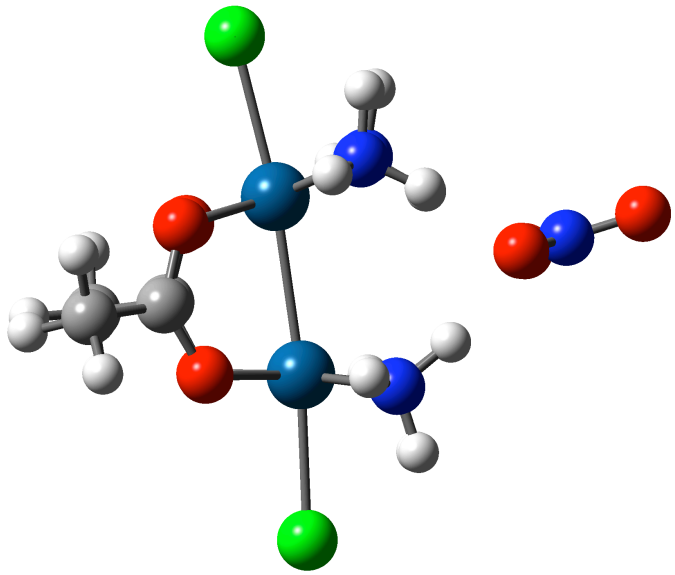

Figure S7. DFT-optimized structure of the ion pair, [**2**]$(NO_3)^+$. Grey, blue, red, white, green, and teal spheres represent carbon, nitrogen, oxygen, hydrogen, chlorine, and platinum atoms, respectively.

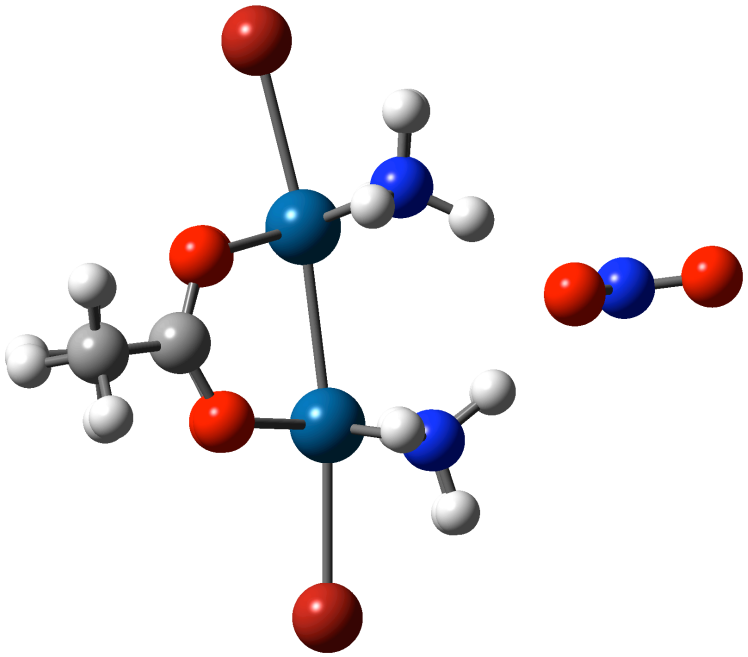

Figure S8. DFT-optimized structure of the ion pair, [**3**](NO$_3$)$^+$. Grey, blue, red, white, maroon, and teal spheres represent carbon, nitrogen, oxygen, hydrogen, bromine, and platinum atoms, respectively.

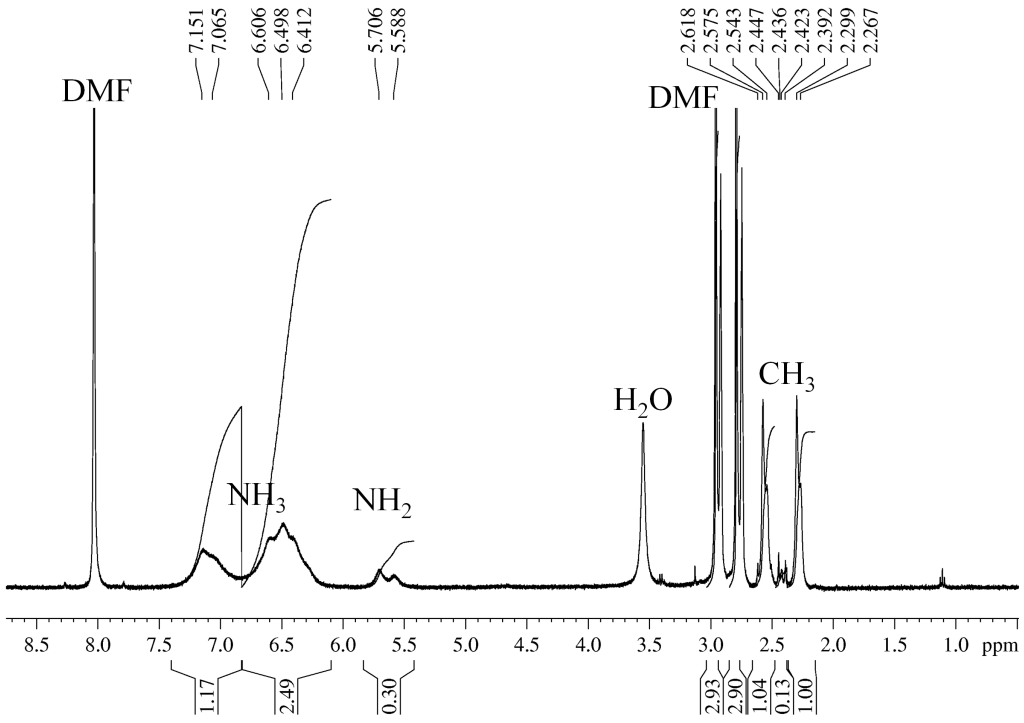

Figure S9. ^{1}H NMR spectrum of [**4**](NO$_3$)$_4$ in DMF-d_7 at room temperature.

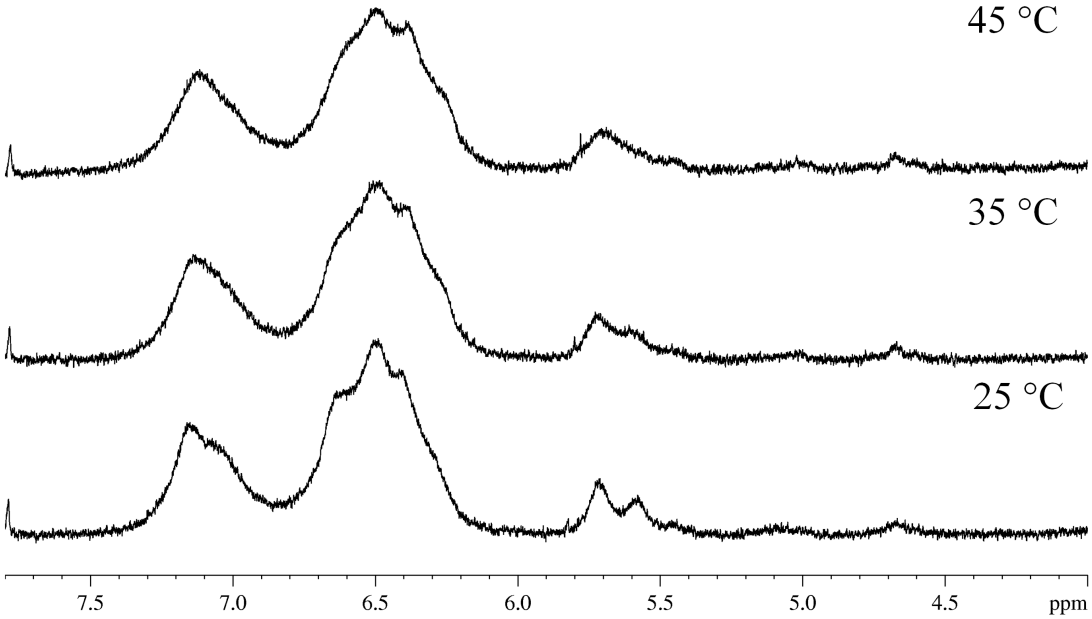

Figure S10. NH-region of the ^{1}H NMR spectrum of [**4**](NO$_3$)$_4$ at different temperatures.

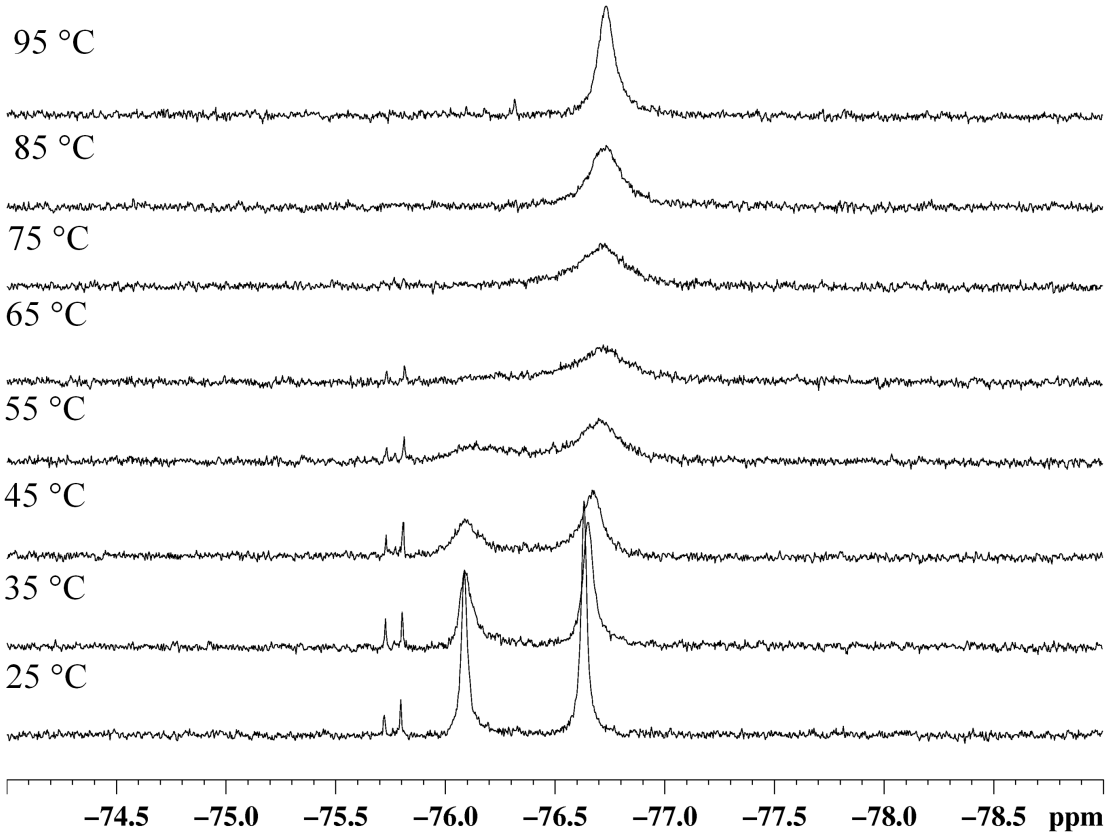

Figure S11. Variable-temperature ^{19}F NMR spectrum of [**4**](NO$_3$)$_4$ in DMF-d_7.

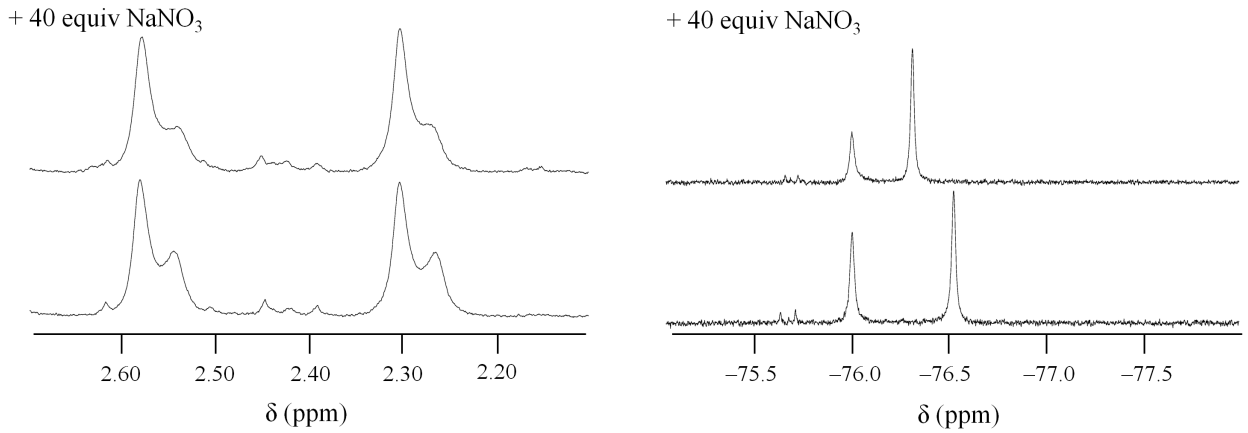

Figure S12. ^{1}H (left) and ^{19}F (right) NMR spectra of [**4**]$^{4+}$ before (bottom) and after (top) the addition of 40 equiv $NaNO_3$ in DMF-d_7.

Table S1. *XYZ*-Cartesian Coordinates (Å) of the DFT-Optimized Structure of [**1**]$^{2+}$

Pt1	-1.7802	0.0001	-0.2392
Pt2	1.7803	-0.0001	-0.2391
O3	-1.1285	1.5253	0.9397
O4	1.1288	-1.5251	0.9401
O5	-1.1286	-1.5237	0.9417
O6	1.1290	1.5235	0.9422
N7	-2.6837	-1.5291	-1.2747
H8	-3.6988	-1.4445	-1.3124
H9	-2.4861	-2.3865	-0.7564
H10	-2.3531	-1.6632	-2.2283
N11	2.6835	1.5292	-1.2749
H12	2.4861	2.3866	-0.7565
H13	2.3526	1.6633	-2.2283
H14	3.6986	1.4444	-1.3129
N15	2.6832	-1.5282	-1.2767
H16	2.3528	-1.6608	-2.2306
H17	2.4850	-2.3863	-0.7598
H18	3.6984	-1.4440	-1.3141
C19	0.0002	1.9391	1.3302
N20	-2.6834	1.5282	-1.2766
H21	-3.6986	1.4441	-1.3136
H22	-2.3533	1.6607	-2.2306
H23	-2.4850	2.3862	-0.7597

C24	0.0001	-1.9391	1.3302
C25	-0.0000	-3.0205	2.3605
H26	0.9016	-3.6269	2.2878
H27	-0.8978	-3.6319	2.2821
H28	-0.0048	-2.5406	3.3453
C29	-0.0004	3.0205	2.3605
H30	-0.0138	2.5407	3.3452
H31	-0.8947	3.6364	2.2769
H32	0.9045	3.6225	2.2931

Table S2. *XYZ*-Cartesian Coordinates (Å) of the DFT-Optimized Structure of [**2**]$^{2+}$

Pt1	-1.3526	0.0050	-0.2804
Pt2	1.3526	-0.0051	-0.2803
Cl3	-3.7596	0.0086	0.1414
O4	-1.0727	1.3094	1.2558
Cl5	3.7596	-0.0087	0.1413
O6	1.0727	-1.3092	1.2560
O7	-1.1223	-1.6005	0.9389
O8	1.1223	1.6006	0.9388
N9	-1.9102	-1.3840	-1.7072
H10	-2.9329	-1.2997	-1.7553
H11	-1.7248	-2.3170	-1.3381
H12	-1.5256	-1.3191	-2.6460
N13	1.9102	1.3837	-1.7074
H14	1.7254	2.3168	-1.3380
H15	1.5251	1.3191	-2.6460
H16	2.9328	1.2991	-1.7560
N17	1.8568	-1.6593	-1.4190
H18	1.5970	-1.6712	-2.4021
H19	1.5215	-2.5189	-0.9865
H20	2.8830	-1.6813	-1.3510
C21	0.0372	1.8454	1.5509
N22	-1.8568	1.6592	-1.4191
H23	-2.8830	1.6816	-1.3505
H24	-1.5976	1.6707	-2.4024
H25	-1.5209	2.5188	-0.9870
C26	-0.0372	-1.8453	1.5511
C27	-0.0745	-2.8125	2.6757
H28	0.9121	-3.2374	2.8548
H29	-0.8207	-3.5849	2.4853
H30	-0.3903	-2.2656	3.5717
C31	0.0744	2.8129	2.6754
H32	0.3906	2.2661	3.5714
H33	-0.9121	3.2375	2.8547

H34	0.8204	3.5854	2.4848

Table S3. *XYZ*-Cartesian Coordinates (Å) of the DFT-Optimized Structure of [**3**]$^{2+}$

Pt1	1.3713	-0.0052	-0.3071
Pt2	-1.3713	0.0052	-0.3071
O3	1.0737	-1.3130	1.2252
O4	-1.0737	1.3130	1.2252
O5	1.1233	1.6023	0.9093
O6	-1.1233	-1.6023	0.9093
N7	1.9226	1.3828	-1.7385
H8	2.9398	1.2829	-1.8357
H9	1.7720	2.3135	-1.3476
H10	1.4942	1.3400	-2.6595
N11	-1.9226	-1.3829	-1.7385
H12	-1.7720	-2.3135	-1.3476
H13	-1.4942	-1.3400	-2.6595
H14	-2.9398	-1.2830	-1.8357
N15	-1.8702	1.6596	-1.4499
H16	-1.5695	1.6854	-2.4210
H17	-1.5594	2.5161	-0.9932
H18	-2.8982	1.6769	-1.4240
C19	-0.0369	-1.8479	1.5183
N20	1.8702	-1.6596	-1.4499
H21	2.8982	-1.6770	-1.4240
H22	1.5695	-1.6854	-2.4210
H23	1.5594	-2.5161	-0.9932
C24	0.0369	1.8479	1.5183
C25	0.0736	2.8193	2.6403
H26	-0.9137	3.2418	2.8204
H27	0.8164	3.5939	2.4457
H28	0.3934	2.2770	3.5376
C29	-0.0736	-2.8192	2.6404
H30	-0.3933	-2.2768	3.5377
H31	0.9137	-3.2418	2.8205
H32	-0.8164	-3.5937	2.4458
Br33	-3.9125	0.0030	0.1749
Br34	3.9125	-0.0030	0.1749

Table S4. *XYZ*-Cartesian Coordinates (Å) of the DFT-Optimized Structure of [**1**]$(NO_3)^+$

Pt1	-0.9128	-1.2040	-0.0000
Pt2	1.2082	1.1083	-0.0000
O3	0.3679	-1.7633	1.5036
O4	1.9087	-0.1148	-1.4907

O5	0.3683	-1.7637	-1.5031
O6	1.9083	-0.1145	1.4911
N7	-2.2369	-0.8195	-1.5162
H8	-3.1981	-1.0799	-1.3104
H9	-1.9380	-1.3396	-2.3390
H10	-2.2597	0.1833	-1.7408
N11	0.5970	2.3998	1.4574
H12	0.8299	2.0164	2.3708
H13	-0.4314	2.4978	1.3825
H14	1.0309	3.3181	1.4039
N15	0.5974	2.3996	-1.4578
H16	-0.4309	2.4983	-1.3831
H17	0.8299	2.0155	-2.3711
H18	1.0320	3.3175	-1.4049
C19	1.4345	-1.2115	1.8985
N20	-2.2373	-0.8193	1.5157
H21	-3.1990	-1.0772	1.3086
H22	-2.2585	0.1831	1.7420
H23	-1.9403	-1.3413	2.3380
C24	1.4349	-1.2120	-1.8980
C25	2.2219	-1.9411	-2.9414
H26	2.8043	-1.2431	-3.5410
H27	1.5658	-2.5479	-3.5640
H28	2.9183	-2.6126	-2.4293
C29	2.2210	-1.9405	2.9424
H30	2.9132	-2.6168	2.4308
H31	1.5639	-2.5426	3.5684
H32	2.8077	-1.2431	3.5384
N33	-2.6919	1.7760	-0.0002
O34	-3.7164	1.1017	0.0001
O35	-2.1531	2.1000	1.0862
O36	-2.1528	2.0985	-1.0870

Table S5. *XYZ*-Cartesian Coordinates (Å) of the DFT-Optimized Structure of [**2**]$(NO_3)^+$

Pt1	1.0971	-0.7529	-0.0047
Pt2	-1.2717	0.4564	-0.0042
Cl3	3.1453	-2.0887	0.0017
O4	0.2427	-1.9504	-1.4303
Cl5	-3.5527	1.3369	-0.0037
O6	-1.7268	-0.8896	1.4713
O7	0.2932	-1.8606	1.5188
O8	-1.7325	-0.8911	-1.4755
N9	2.0792	0.3274	1.4234
H10	3.0772	0.1476	1.2981

H11	1.8378	-0.0536	2.3365
H12	1.8866	1.3480	1.3883
N13	-0.9713	1.8517	-1.4612
H14	-0.9726	1.4095	-2.3776
H15	-0.0912	2.3888	-1.3239
H16	-1.7879	2.4668	-1.4348
N17	-0.9723	1.8593	1.4498
H18	-0.1059	2.4178	1.3188
H19	-0.9616	1.4189	2.3672
H20	-1.8012	2.4588	1.4269
C21	-0.9471	-1.8138	-1.8396
N22	2.0345	0.2548	-1.5155
H23	3.0179	-0.0234	-1.4704
H24	1.9426	1.2868	-1.4525
H25	1.6854	-0.0788	-2.4116
C26	-0.9107	-1.7570	1.8968
C27	-1.4016	-2.7320	2.9099
H28	-2.2174	-2.3012	3.4888
H29	-0.5830	-3.0621	3.5484
H30	-1.7864	-3.6055	2.3732
C31	-1.4635	-2.8152	-2.8137
H32	-1.9730	-3.6010	-2.2464
H33	-0.6428	-3.2678	-3.3681
H34	-2.1942	-2.3547	-3.4779
N35	1.9160	3.5246	-0.0047
O36	2.6188	4.4871	-0.0389
O37	1.5234	2.9454	-1.0734
O38	1.5254	3.0206	1.1005

Table S6. *XYZ*-Cartesian Coordinates (Å) of the DFT-Optimized Structure of [**3**]$(NO_3)^+$

Pt1	-1.3431	-0.1172	-0.0012
Pt2	1.3424	-0.1190	0.0010
O3	-1.1196	-1.5460	1.4521
O4	1.1168	-1.5495	-1.4505
O5	-1.1262	-1.5010	-1.4966
O6	1.1235	-1.5009	1.4978
N7	-1.7184	1.2784	-1.4468
H8	-2.7213	1.4753	-1.4095
H9	-1.5419	0.8714	-2.3628
H10	-1.1655	2.1521	-1.3357
N11	1.7195	1.2777	1.4451
H12	1.5435	0.8713	2.3615
H13	1.1670	2.1517	1.3340
H14	2.7224	1.4740	1.4070

N15	1.7106	1.2439	-1.4784
H16	1.1819	2.1308	-1.3613
H17	1.5019	0.8343	-2.3862
H18	2.7185	1.4186	-1.4665
C19	0.0023	-1.9576	1.8678
N20	-1.7090	1.2485	1.4761
H21	-2.7166	1.4249	1.4641
H22	-1.1786	2.1342	1.3572
H23	-1.5007	0.8402	2.3846
C24	-0.0057	-1.9599	-1.8658
C25	-0.0104	-3.0719	-2.8574
H26	0.9115	-3.0703	-3.4373
H27	-0.8898	-3.0071	-3.4971
H28	-0.0644	-4.0141	-2.3021
C29	0.0057	-3.0684	2.8607
H30	0.0681	-4.0110	2.3070
H31	-0.9196	-3.0702	3.4351
H32	0.8810	-2.9989	3.5056
N33	0.0060	4.0706	-0.0002
O34	0.0126	5.2627	-0.0014
O35	-0.0112	3.4021	1.0879
O36	0.0160	3.3997	-1.0868
Br37	3.9062	-0.4374	-0.0027
Br38	-3.9075	-0.4314	0.0026

Table S7. Comparison of X-Ray Crystallographic Refinement Parameters of [**4**]$^{4+}$ with Isotropically Refined Bridging Amido and Hydroxo Ligands[a]

Atom-Type Assignment	U_{iso}	R1, all data (%)	wR2, all data (%)
N (amido)	0.03029	7.62	14.87
O (hydroxo)	0.04929	7.64	14.86

[a] R1 and wR2 are defined in the footnote of Table 1, main text.

Table S8. Hydrogen-Bonding Metrics Involving the Bridging Amido Ligands of [**4**]$^{4+}$

Donor-Acceptor Pair	Donor-Acceptor Distance (Å)	Hydrogen-Acceptor Distance (Å)	Donor-Hydrogen-Acceptor Angle (deg)
N4···O12 (μ-NH_2···ONO_2^-)	2.845(14)	1.93	170.9
N4···O13 (μ-NH_2···O-DMF)	2.833(12)	1.99	152.2