

Trapping of Ag⁺ into a perfect six-coordinated environment: structural analysis, quantum chemical calculations and electrochemistry

Veronika I. Komlyagina ^{1,2}, Nikolay F. Romashev ¹, Vasily V. Kokovkin ¹, Artem L. Gushchin ^{1,*}, Enrico Benassi ^{2,*}, Maxim N. Sokolov ¹ and Pavel A. Abramov ^{1,3,*}

Supplementary Materials

Table of contents

Table S1. Experimental details.....	2
Table S2. Selected geometric parameters (Å)	3
Figure S1. X-ray powder diffraction patterns comparison.....	4
Table S3. Shape results	4
Table S4. NBO analysis. Ag-involving interactions.....	5
Table S5. Occupancy and composition of Ag NBOs.	6
Table S6. Topological properties computed at the atomic (A), bond (B), ring (R) and cage critical points (C), viz. total electron density (ρ_{tot}), Lagrangian kinetic energy (G), Hamiltonian kinetic energy (K), potential energy (V), energy density (H), Laplacian of the total electron density ($\Delta\rho_{tot}$), Source Function (SF), total Electrostatic Potential (EPStot), ellipticity of electron density (ϵ) and eta index (η)	7
Figure S2. Comparison of CVs of paste electrodes in 0.10 M Bu ₄ NPF ₆ in acetonitrile at a scan rate of 20 mV/s: red curve - complex in paste, blue curve - precursor, green curve - background (blank).....	13
Figure S3. Reproducibility of CV curves (2-4 cycles) for 1 in the paste electrode in aqueous solution of 1.0 M KHCO ₃ at different scan rates (mV/s): blue line – 10, red – 20, green – 50, yellow – 100.	14
Figure S4. The dependences of peak currents on the square root of scan rate for anodic (green circles) and cathodic (blue circles) peak currents. The primary data presented in Figure S3.....	15
Figure S5. IR spectra of 1 (black curve) and (Bu ₄ N) ₄ [β -Mo ₈ O ₂₆] (red curve).....	16
Figure S6. TGA data for 1	10

Table S1. Experimental details

	1
Chemical formula	C ₁₀₄ H ₁₅₂ Ag ₂ Mo ₈ N ₆ O ₂₆
M _r	2885.57
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	150
a, b, c (Å)	38.5675 (16), 12.6898 (6), 26.2540 (11)
β (°)	116.858 (1)
V (Å ³)	11463.0 (9)
Z	4
Radiation type	Mo Ka
μ (mm ⁻¹)	1.25
Crystal size (mm)	0.14 × 0.13 × 0.09
Diffractometer	Bruker D8 Venture diffractometer
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T _{min} , T _{max}	0.643, 0.746
No. of measured, independent and observed [I > 2σ(I)] reflections	71574, 18991, 14894
R _{int}	0.042
θ values (°)	θ _{max} = 31.5, θ _{min} = 2.0
(sin θ/λ) _{max} (Å ⁻¹)	0.736
Range of h, k, l	-56 ≤ h ≤ 56, -18 ≤ k ≤ 14, -36 ≤ l ≤ 38
R[F ² > 2σ(F ²)], wR(F ²), S	0.036, 0.087, 1.09
No. of reflections, parameters, restraints	18991, 744, 18
H-atom treatment	H-atom parameters constrained
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.03129P) ² + 1.7353P] where P = (F _o ² + 2F _c ²)/3
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.78, -0.64

Computer programs: APEX3 (Bruker-AXS, 2016), SAINT (Bruker-AXS, 2016), SHELXT 2014/5 (Sheldrick, 2014), SHELXL2017/1 (Sheldrick, 2017).

Table S2. Selected geometric parameters (\AA)

O2—Ag1	2.5693 (17)	O4—Mo3	2.4739 (15)
O6—Ag1	2.5437 (18)	O4—Mo4	2.3195 (15)
O8—Ag1	2.5398 (19)	O5—Mo2	1.6979 (17)
O10—Ag1	2.4948 (17)	O6—Mo2	1.7114 (17)
N1—Ag1	2.461 (2)	O7—Mo2	1.8932 (16)
N2—Ag1	2.386 (2)	O7—Mo3	1.9154 (16)
O1—Mo1	1.7458 (16)	O8—Mo3	1.7127 (18)
O1—Mo3 ⁱ	2.2973 (17)	O9—Mo3	1.6964 (18)
O2—Mo1	1.7005 (17)	O10—Mo4	1.7074 (17)
O3—Mo1	1.9446 (16)	O11—Mo1	1.9480 (16)
O3—Mo2	2.0061 (16)	O11—Mo2 ⁱ	2.3092 (16)
O3—Mo4 ⁱ	2.3020 (16)	O11—Mo4	2.0028 (16)
O4—Mo1	2.1531 (15)	O12—Mo3	1.9204 (17)
O4—Mo1 ⁱ	2.3343 (15)	O12—Mo4	1.9010 (16)
O4—Mo2	2.3060 (15)	O13—Mo4	1.7000 (17)

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

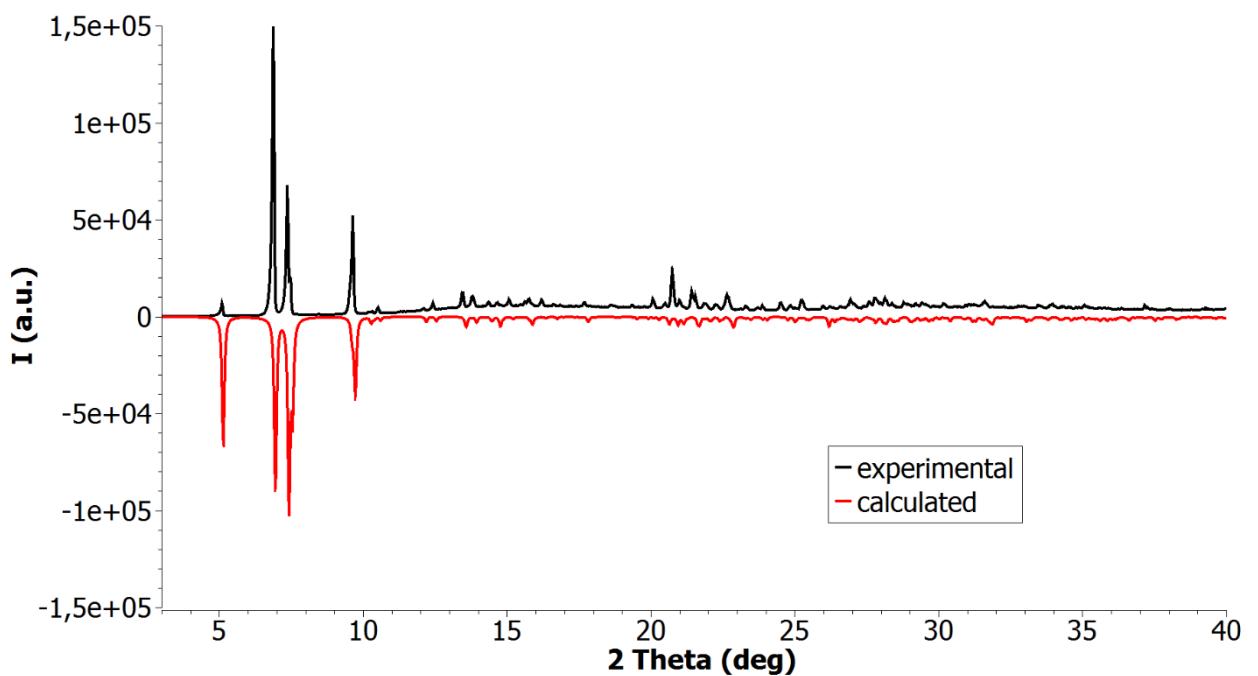


Figure S1. X-ray powder diffraction patterns comparison.

Table S3. Shape results

S H A P E v2.1 Continuous Shape Measures calculation

(c) 2013 Electronic Structure Group, Universitat de Barcelona

Contact: llunell@ub.edu

HP-6 1 D_{6h} Hexagon

PPY-6 2 C_{5v} Pentagonal pyramid

OC-6 3 O_h Octahedron

TPR-6 4 D_{3h} Trigonal prism

JPPY-6 5 C_{5v} Johnson pentagonal pyramid J2

Structure [ML6]	HP-6	PPY-6	OC-6	TPR-6	JPPY-6
struct1 ,	30.590,	7.938,	12.027,	7.827,	11.118

Table S4. NBO analysis. Ag-involving interactions.

		Donor			Acceptor		$E^{(2)} / (\text{kcal}\cdot\text{mol}^{-1})$
301	CR	(Ag)	->	1952 RY*	(C)	283.65
432	LP	(Ag)	->	1814 RY*	(C)	170.37
434	LP	(Ag)	->	1579 RY*	(C)	63.33
434	LP	(Ag)	->	1715 RY*	(C)	101.39
434	LP	(Ag)	->	1718 RY*	(C)	66.67
434	LP	(Ag)	->	1751 RY*	(C)	78.61
434	LP	(Ag)	->	1755 RY*	(C)	58.41
434	LP	(Ag)	->	1964 RY*	(C)	225.68
434	LP	(Ag)	->	1970 RY*	(C)	190.96
436	LP	(Ag)	->	1814 RY*	(C)	63.37
303	CR	(Ag)	->	2133 BD*	(C - C)	71.36
421	LP	(O)	->	1275 RY*	(Ag)	60.77
422	LP	(O)	->	1275 RY*	(Ag)	90.72
463	LP	(O)	->	1275 RY*	(Ag)	80.52
458	LP	(N)	->	1275 RY*	(Ag)	58.55
348	CR	(C)	->	1275 RY*	(Ag)	83.77
348	CR	(C)	->	1276 RY*	(Ag)	58.82
348	CR	(C)	->	1280 RY*	(Ag)	130.10
350	CR	(C)	->	1274 RY*	(Ag)	55.61
353	CR	(C)	->	1276 RY*	(Ag)	50.64
353	CR	(C)	->	1279 RY*	(Ag)	283.48
353	CR	(C)	->	1280 RY*	(Ag)	199.58
355	CR	(C)	->	1275 RY*	(Ag)	183.46
355	CR	(C)	->	1278 RY*	(Ag)	115.75
355	CR	(C)	->	1279 RY*	(Ag)	538.10
355	CR	(C)	->	1280 RY*	(Ag)	389.56
359	CR	(C)	->	1274 RY*	(Ag)	102.35
359	CR	(C)	->	1280 RY*	(Ag)	70.78
366	CR	(C)	->	1274 RY*	(Ag)	59.77
366	CR	(C)	->	1279 RY*	(Ag)	104.30
366	CR	(C)	->	1280 RY*	(Ag)	128.04
367	CR	(C)	->	1275 RY*	(Ag)	151.82
368	CR	(C)	->	1278 RY*	(Ag)	72.95
368	CR	(C)	->	1279 RY*	(Ag)	149.13
368	CR	(C)	->	1280 RY*	(Ag)	69.20
311	CR	(Mo)	->	1280 RY*	(Ag)	275.42
315	CR	(Mo)	->	1280 RY*	(Ag)	60.83
246	CR	(Mo)	->	1280 RY*	(Ag)	60.98
25	BD	(N - C)	->	1275 RY*	(Ag)	110.62
136	BD	(N - C)	->	1275 RY*	(Ag)	118.61
138	BD	(N - C)	->	1279 RY*	(Ag)	59.27
28	BD	(C - C)	->	1275 RY*	(Ag)	144.27
34	BD	(C - C)	->	440 LP*	(Ag)	64.94
50	BD	(C - C)	->	440 LP*	(Ag)	115.07
50	BD	(C - C)	->	1275 RY*	(Ag)	320.45
72	BD	(C - C)	->	1276 RY*	(Ag)	51.11
151	BD	(C - C)	->	1275 RY*	(Ag)	64.25
154	BD	(C - C)	->	1275 RY*	(Ag)	216.24
154	BD	(C - C)	->	1276 RY*	(Ag)	52.20
157	BD	(C - C)	->	1275 RY*	(Ag)	54.47
165	BD	(C - C)	->	1275 RY*	(Ag)	300.69
172	BD	(C - C)	->	439 LP*	(Ag)	61.23
172	BD	(C - C)	->	440 LP*	(Ag)	82.90
172	BD	(C - C)	->	1274 RY*	(Ag)	91.68
172	BD	(C - C)	->	1275 RY*	(Ag)	247.82
172	BD	(C - C)	->	1276 RY*	(Ag)	101.12
173	BD	(C - C)	->	1275 RY*	(Ag)	120.52
177	BD	(C - C)	->	438 LP*	(Ag)	63.45
177	BD	(C - C)	->	440 LP*	(Ag)	75.53
177	BD	(C - C)	->	1275 RY*	(Ag)	115.52
178	BD	(C - C)	->	439 LP*	(Ag)	54.96
178	BD	(C - C)	->	440 LP*	(Ag)	74.31
178	BD	(C - C)	->	1274 RY*	(Ag)	57.11
185	BD	(C - C)	->	1275 RY*	(Ag)	116.60
186	BD	(C - C)	->	439 LP*	(Ag)	71.05
186	BD	(C - C)	->	440 LP*	(Ag)	81.45
186	BD	(C - C)	->	1276 RY*	(Ag)	92.96
190	BD	(C - C)	->	439 LP*	(Ag)	66.61
190	BD	(C - C)	->	440 LP*	(Ag)	72.86
191	BD	(C - C)	->	438 LP*	(Ag)	59.52
191	BD	(C - C)	->	440 LP*	(Ag)	81.15
191	BD	(C - C)	->	1275 RY*	(Ag)	413.77
94	BD	(C - H)	->	440 LP*	(Ag)	51.51
94	BD	(C - H)	->	1275 RY*	(Ag)	135.33
174	BD	(C - H)	->	438 LP*	(Ag)	50.01
179	BD	(C - H)	->	440 LP*	(Ag)	762.85
179	BD	(C - H)	->	1274 RY*	(Ag)	89.45
187	BD	(C - H)	->	438 LP*	(Ag)	50.32
189	BD	(C - H)	->	440 LP*	(Ag)	69.08
192	BD	(C - H)	->	440 LP*	(Ag)	327.47
199	BD	(C - H)	->	439 LP*	(Ag)	70.35
199	BD	(C - H)	->	440 LP*	(Ag)	665.84
199	BD	(C - H)	->	1274 RY*	(Ag)	51.17
200	BD	(C - H)	->	439 LP*	(Ag)	124.55
200	BD	(C - H)	->	440 LP*	(Ag)	243.32
200	BD	(C - H)	->	1274 RY*	(Ag)	86.05
200	BD	(C - H)	->	1275 RY*	(Ag)	1321.85
201	BD	(C - H)	->	439 LP*	(Ag)	82.96
201	BD	(C - H)	->	440 LP*	(Ag)	344.47
205	BD	(C - H)	->	438 LP*	(Ag)	74.22
205	BD	(C - H)	->	440 LP*	(Ag)	145.72
206	BD	(C - H)	->	440 LP*	(Ag)	73.41

207	BD	(C - H)	->	438	LP*	(Ag)	57.13
207	BD	(C - H)	->	440	LP*	(Ag)	154.75
208	BD	(C - H)	->	440	LP*	(Ag)	211.17
209	BD	(C - H)	->	439	LP*	(Ag)	59.85
209	BD	(C - H)	->	440	LP*	(Ag)	135.76
210	BD	(C - H)	->	439	LP*	(Ag)	51.37
210	BD	(C - H)	->	440	LP*	(Ag)	173.22
218	BD	(C - H)	->	439	LP*	(Ag)	87.38
218	BD	(C - H)	->	440	LP*	(Ag)	315.74
219	BD	(C - H)	->	439	LP*	(Ag)	144.68
219	BD	(C - H)	->	440	LP*	(Ag)	243.78
219	BD	(C - H)	->	1274	RY*	(Ag)	57.51
220	BD	(C - H)	->	439	LP*	(Ag)	74.15
220	BD	(C - H)	->	440	LP*	(Ag)	629.71
221	BD	(C - H)	->	440	LP*	(Ag)	212.53
222	BD	(C - H)	->	439	LP*	(Ag)	63.63
222	BD	(C - H)	->	440	LP*	(Ag)	170.00
224	BD	(C - H)	->	438	LP*	(Ag)	81.58
224	BD	(C - H)	->	440	LP*	(Ag)	124.06
225	BD	(C - H)	->	438	LP*	(Ag)	50.78
225	BD	(C - H)	->	440	LP*	(Ag)	197.43
226	BD	(C - H)	->	440	LP*	(Ag)	83.67

Table S5. Occupancy and composition of Ag NBOs.

			occ.	s%	p%	d%
301	CR	(Ag)	1.99822	0.00	100.00	0.00
303	CR	(Ag)	1.99913	0.00	100.00	0.00
432	LP	(Ag)	1.99601	0.00	0.00	100.00
434	LP	(Ag)	1.99323	0.05	0.04	99.92
436	LP	(Ag)	1.99039	0.00	0.01	99.99
437	LP*	(Ag)	0.11626	64.99	34.99	0.02
438	LP*	(Ag)	0.09007	32.91	66.90	0.18
439	LP*	(Ag)	0.07325	0.00	99.97	0.03
440	LP*	(Ag)	0.05996	1.98	98.00	0.03
1274	RY*	(Ag)	0.00118	0.49	25.08	74.43
1275	RY*	(Ag)	0.00096	2.56	75.86	21.58
1276	RY*	(Ag)	0.00069	4.60	30.98	64.42
1278	RY*	(Ag)	0.00041	60.42	7.19	32.39
1279	RY*	(Ag)	0.00032	22.35	27.35	50.30
1280	RY*	(Ag)	0.00010	0.02	0.78	99.20

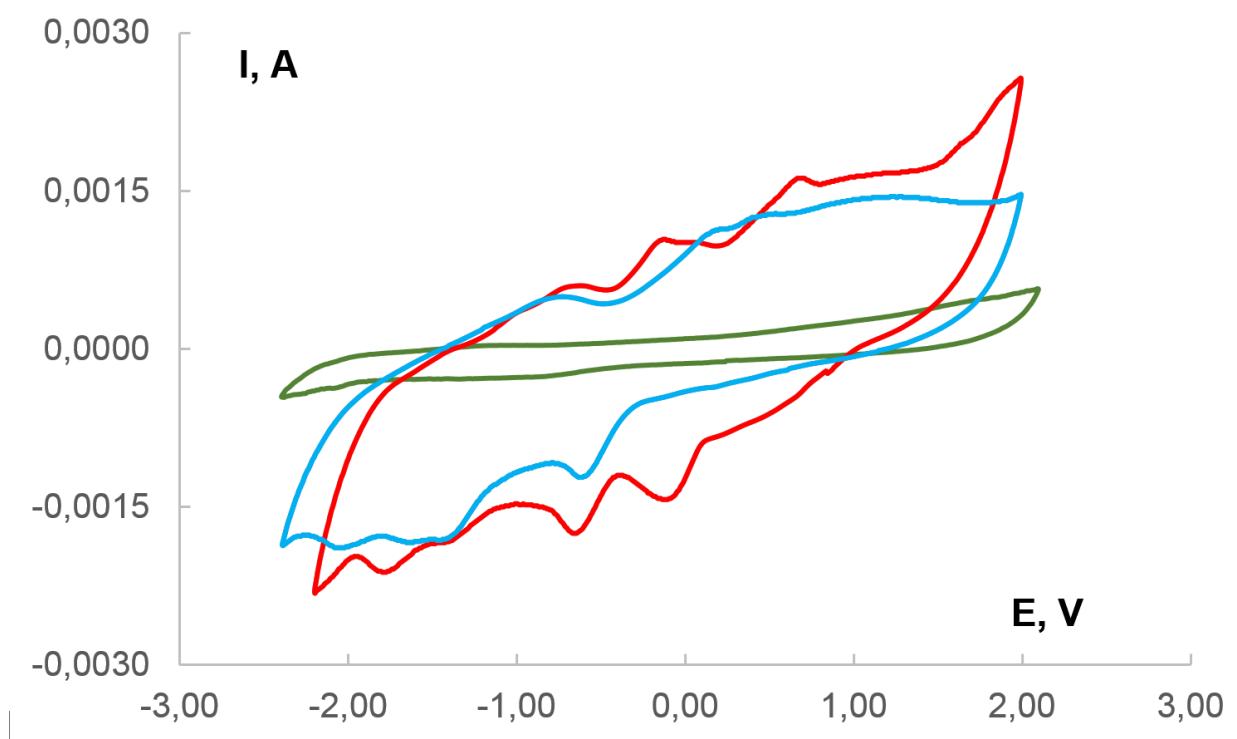


Figure S2. Comparison of CVs of paste electrodes in 0.10 M Bu_4NPF_6 in acetonitrile at a scan rate of 20 mV/s: red curve - complex in paste, blue curve - precursor, green curve - background (blank).

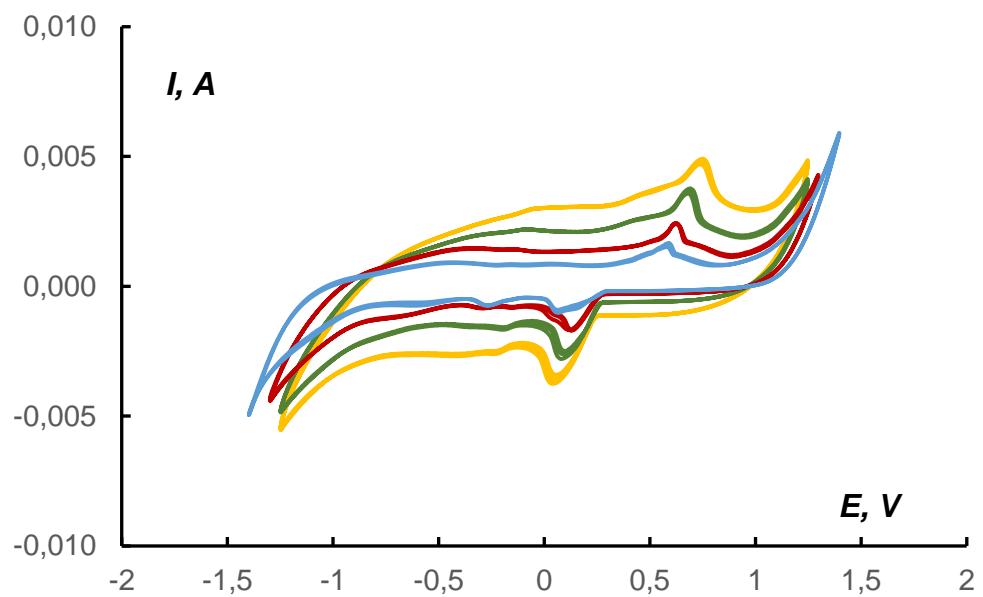


Figure S3. Reproducibility of CV curves (2-4 cycles) for **1** in the paste electrode in aqueous solution of 1.0 M KHCO_3 at different scan rates (mV/s): blue line – 10, red – 20, green – 50, yellow – 100.

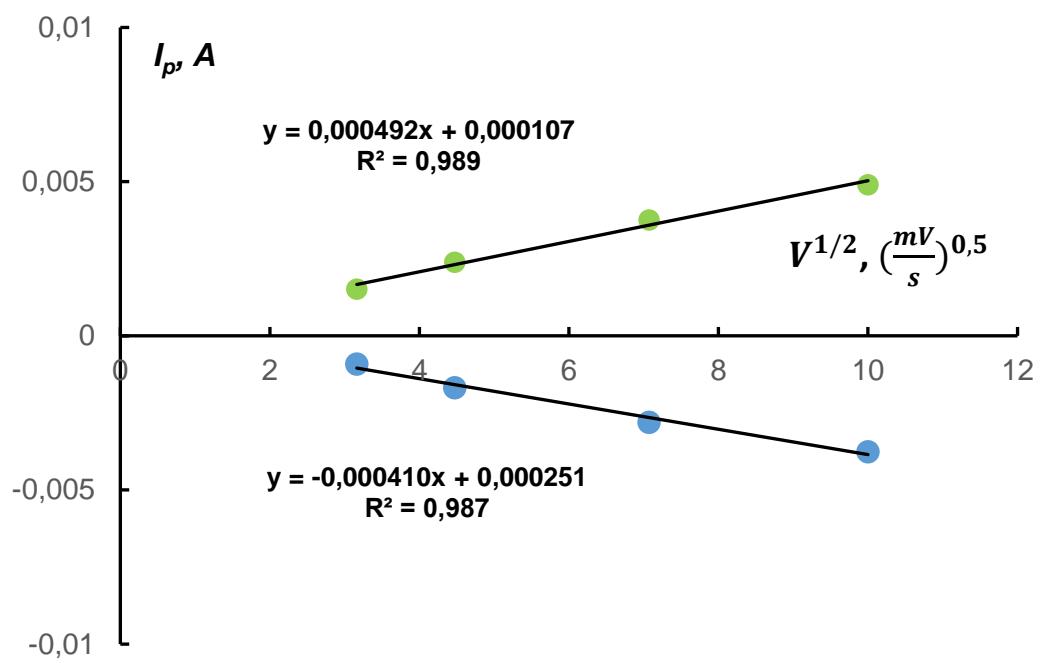


Figure S4. The dependences of peak currents on the square root of scan rate for anodic (green circles) and cathodic (blue circles) peak currents. The primary data presented in Fig. S3.

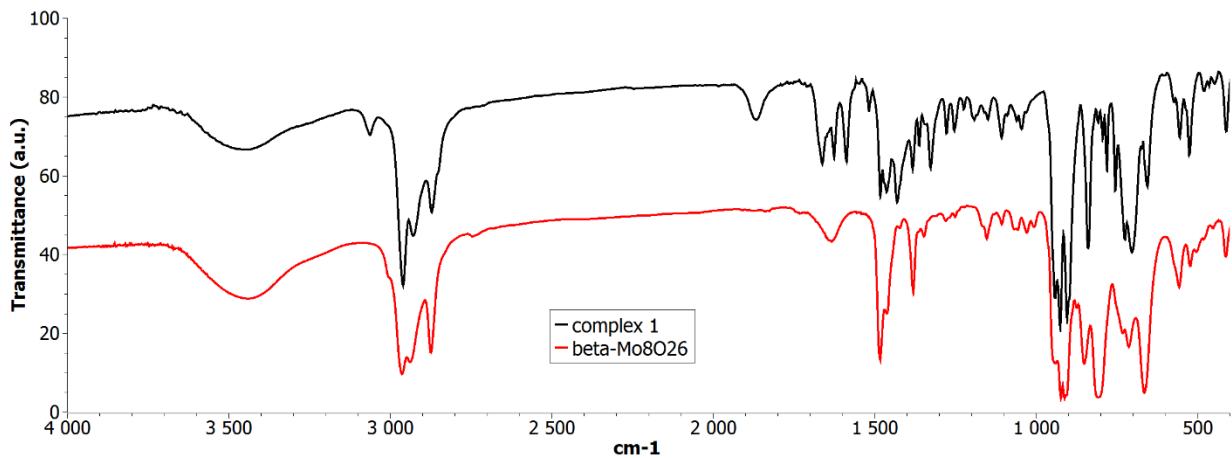


Figure S5. IR spectra of 1 (black curve) and (Bu₄N)₄[β-Mo₈O₂₆] (red curve).

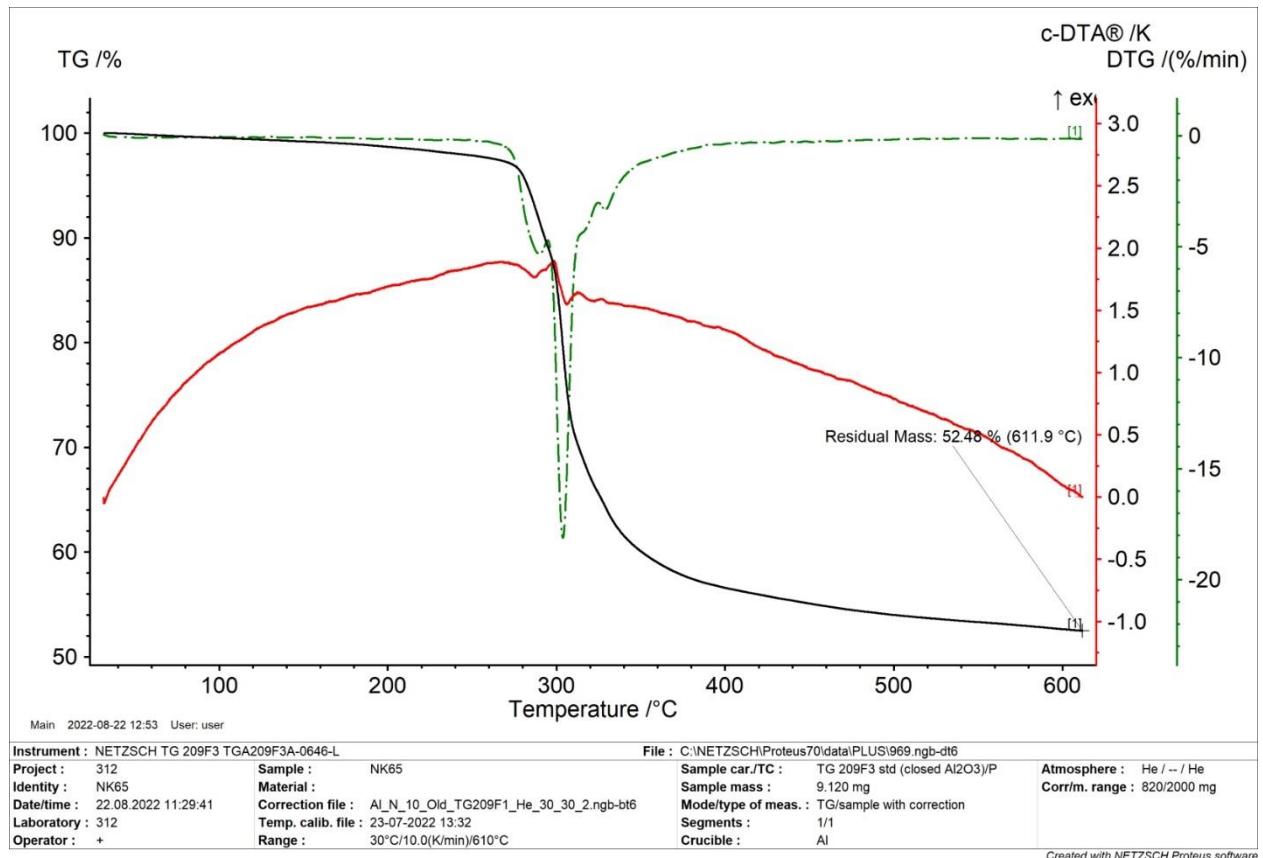


Figure S6. TGA data for 1.