Supporting Materials for "Preparation of rhodium(III) cis-diaquacomplex by a protic acid induced oxalate-releasing from *mer*-[Rh(C_2O_4)Cl(py)$_3$."

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Table 1S. Crystal data and experimental details for **1** and {**3**·(ClO_4)$_2$}·2H_2O

Compound	**1**	{**3**·(ClO_4)$_2$}·2H_2O
Empirical formula	$C_{17}H_{15}ClN_3O_4Rh$	$C_{15}H_{21}Cl_3N_3O_{11}Rh$
Formula weight	463.68	628.61
Temperature, K	296(2) K	150(2) K
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	P-1
***a*, Å**	9.9999(6)	9.930(1)
***b*, Å**	12.0930(7)	11.073(1)
***c*, Å**	14.9368(8)	12.005(1)
α, °	90.00	105.068(4)°
β, °	90.00	103.546(4)°
γ, °	90.00	104.836(4)°
Volume, Å^3	1806.3(2)	1166.4(2)
Z	4	2
ρ_{calc}, g/cm^3	1.705	1.790
μ/mm^{-1}	1.121	1.136
F(000)	928	632
Crystal size, mm^3	0.24 x 0.12 x 0.10	0.14 x 0.08 x 0.07
Radiation	Mo K_α (λ = 0.71073 Å)	Mo K_α (λ = 0.71073 Å)
θ range, °	2.17 to 30.60	2.23 to 29.25
Index ranges	-13 ≤ h ≤ 14, -17 ≤ k ≤ 16, -21≤ l ≤ 21	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	31362	23552
Independent reflections	5538	7207
R_{int}	0.0393	0.0492
Data/restraints/parameters	5538 / 0 / 250	7206 / 3 / 298
Goodness-of-fit on F^2	1.037	1.070
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0284, wR_2 = 0.0654	R_1 = 0.0497, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0365, wR_2 = 0.0683	R_1 = 0.0733, wR_2 = 0.1220
Largest diff. peak/hole, e·Å^{-3}	1.592 / -0.354	2.691 / -1.988

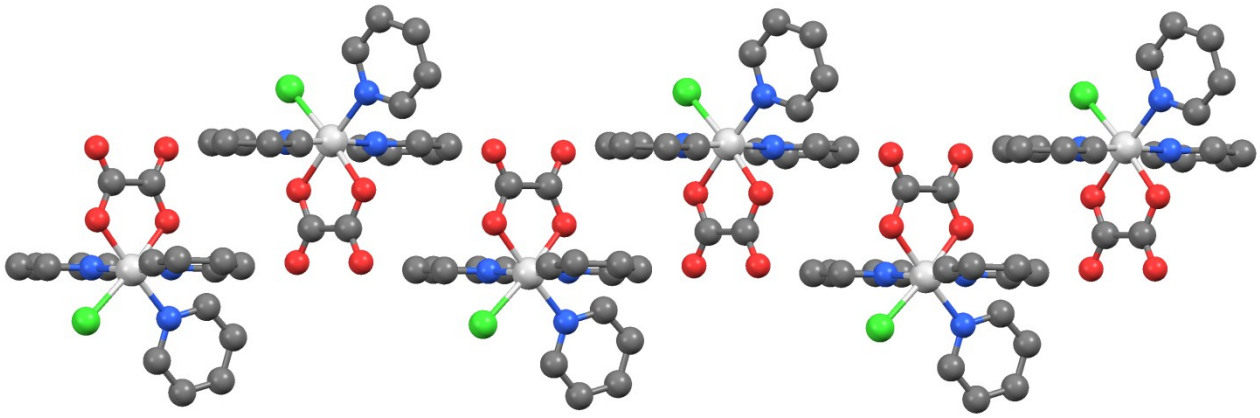


Figure 1S.The column packing of molecules of **1** along *b* axis.

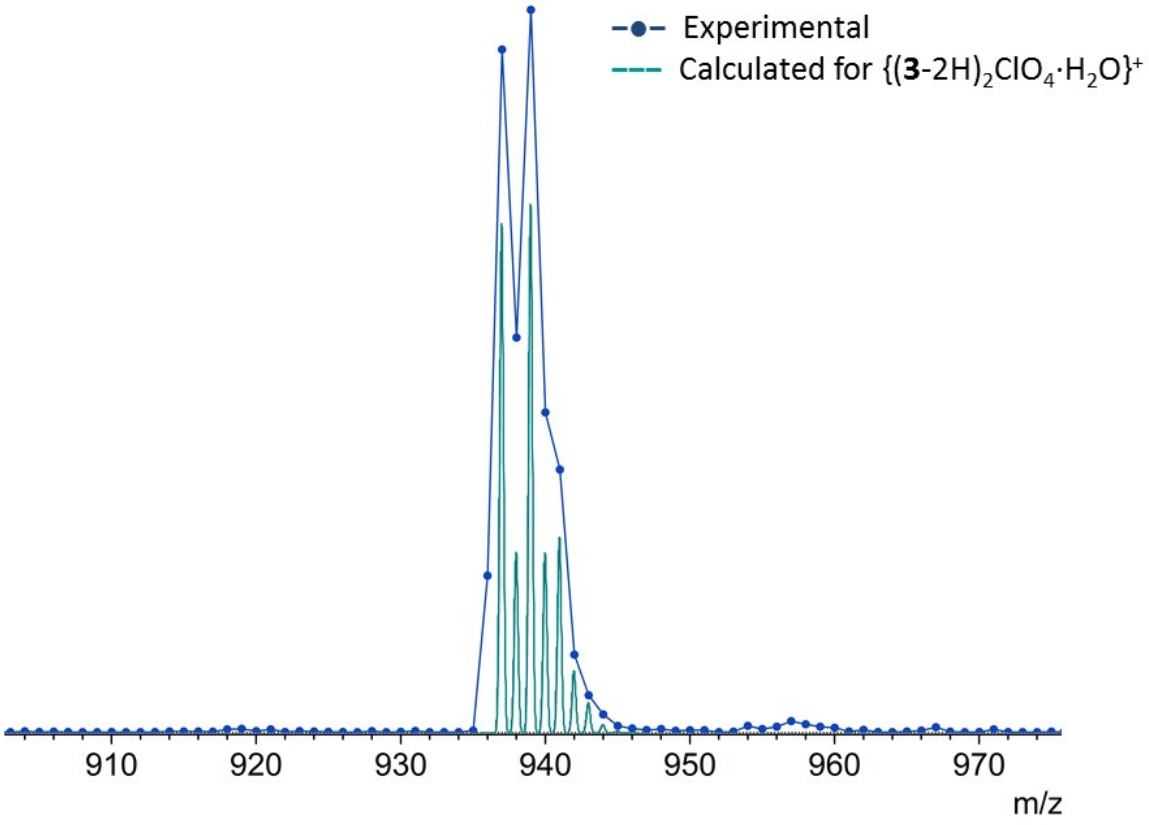
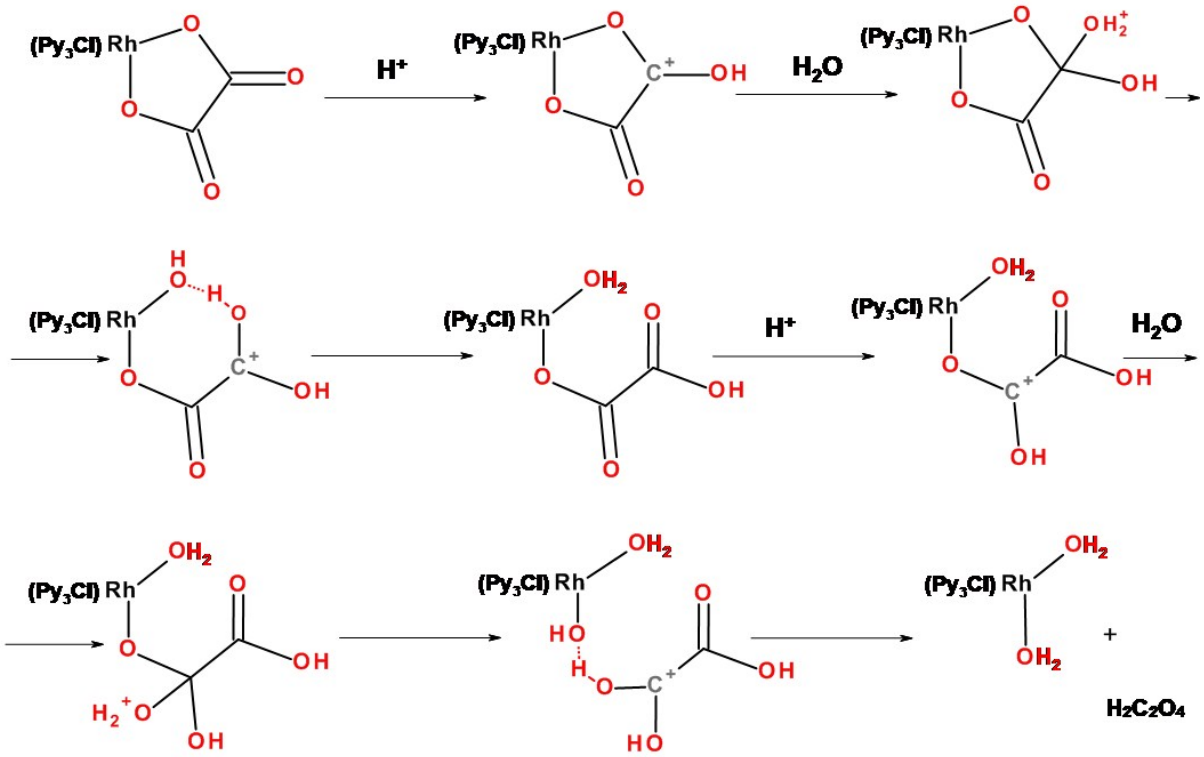


Figure 2S. ESI-MS for {**3**·$(ClO_4)_2$}·$2H_2O$ (positive mode; ACN).



Scheme S1. Proposed mechanism for oxalate detaching from **1** in acidic aqueous solutions.

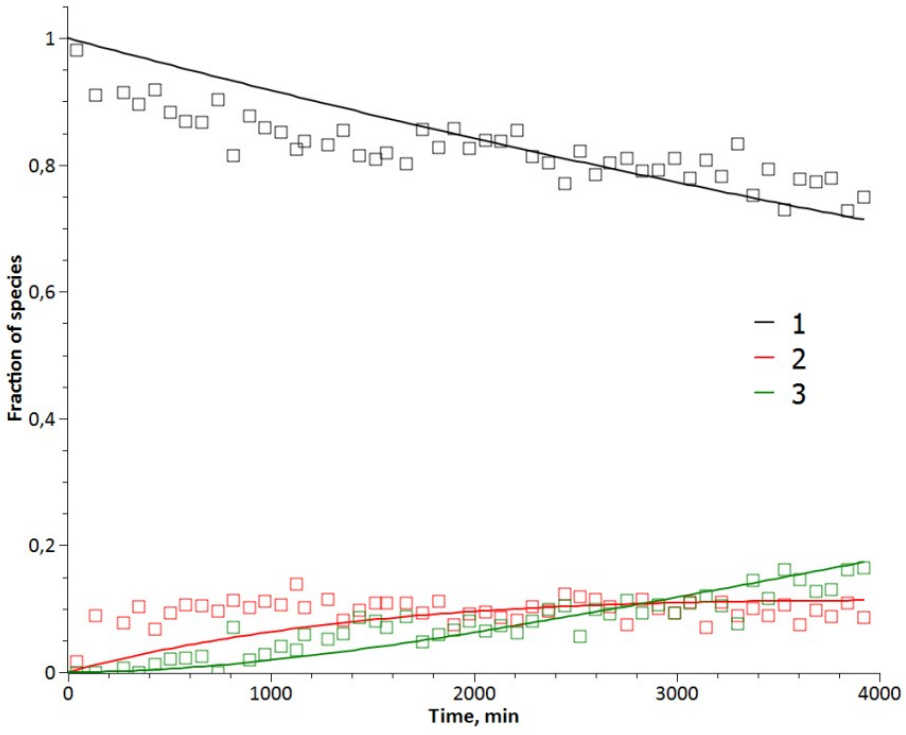


Figure 3S. Kinetic traces depicting the change of species **1**, **2** and **3** fractions during aquation reaction of **1** in 6.00 M TFMSA solution. Temperature is 25°C

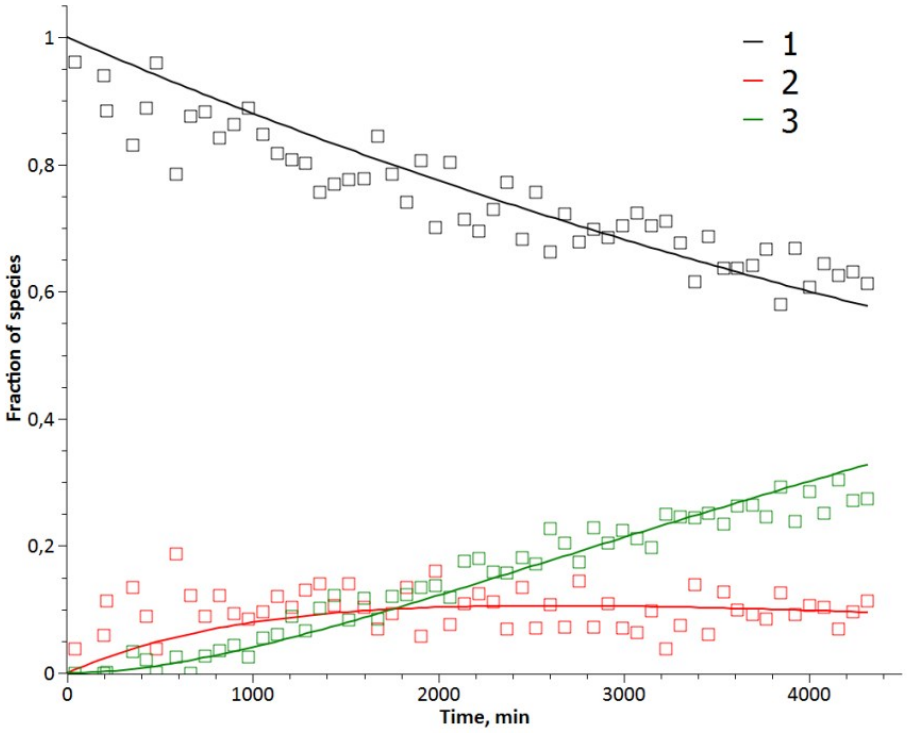


Figure 4S. Kinetic traces depicting the change of species **1**, **2** and **3** fractions during aquation reaction of **1** in 6.37 M TFMSA solution. Temperature is 25°C.

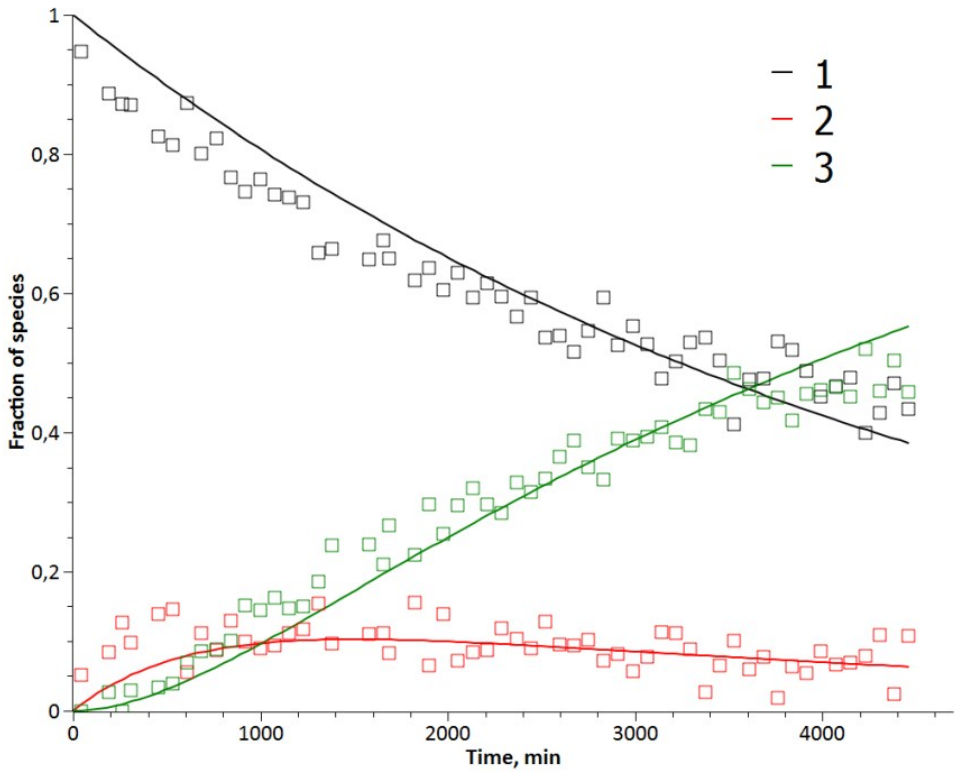


Figure 5S. Kinetic traces depicting the change of species **1**, **2** and **3** fractions during aquation reaction of **1** in 6.75 M TFMSA solution. Temperature is 25°C.

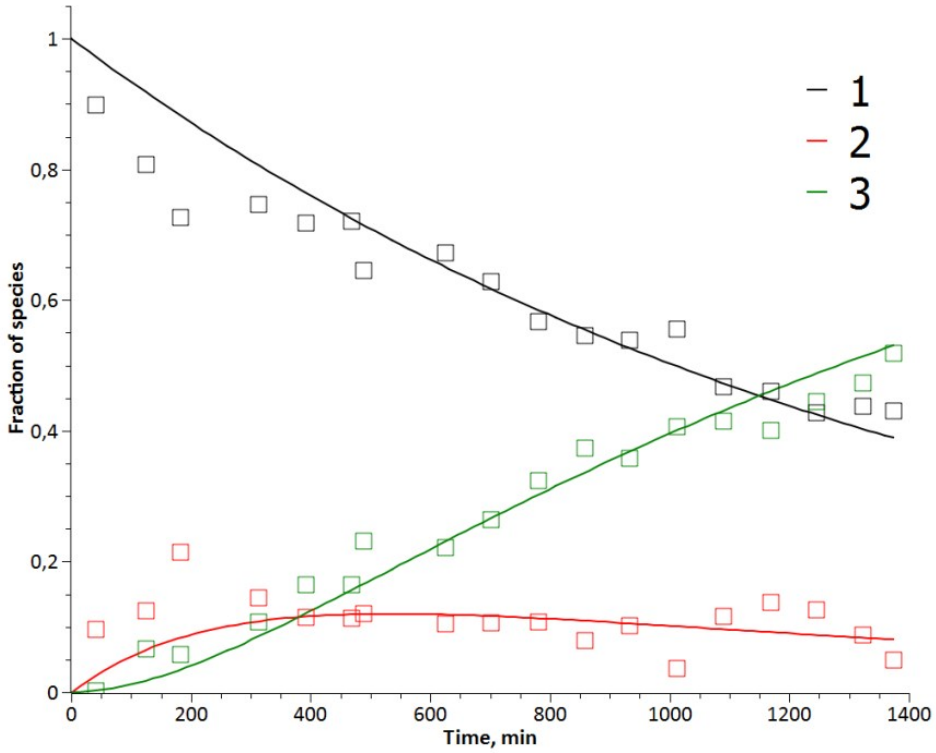


Figure 6S. Kinetic traces depicting the change of species **1**, **2** and **3** fractions during aquation reaction of **1** in 7.12 M TFMSA solution. Temperature is 25°C.

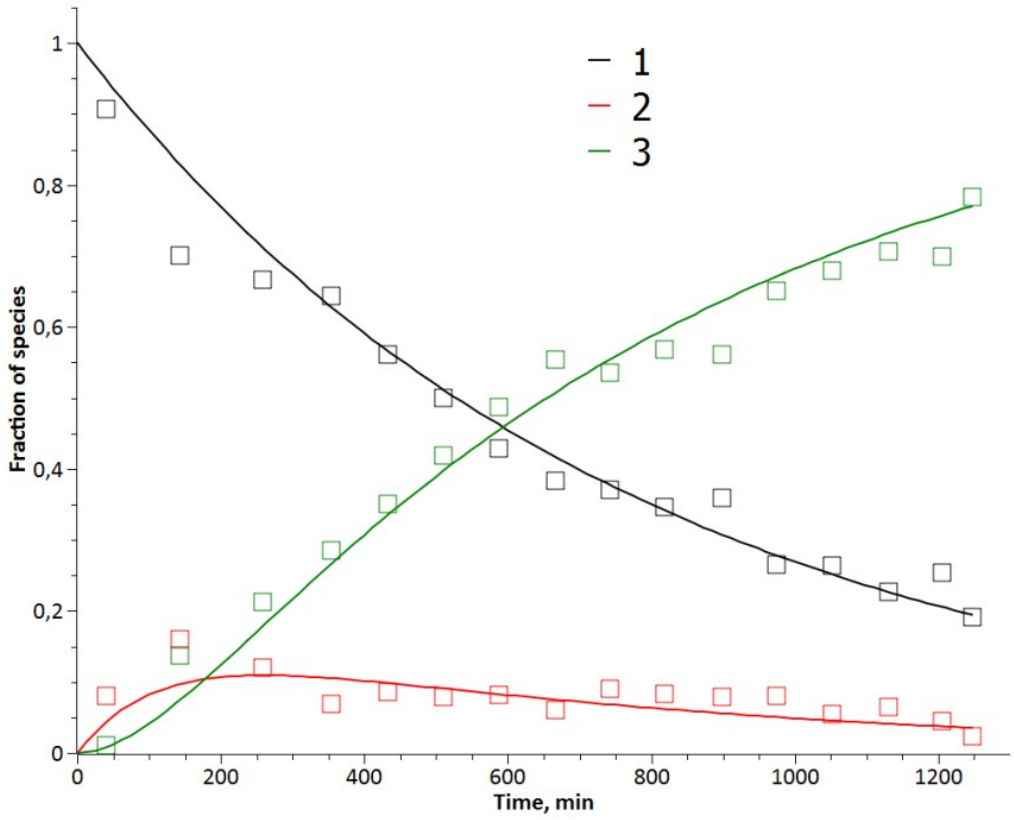


Figure 7S. Kinetic traces depicting the change of species **1**, **2** and **3** fractions during aquation reaction of **1** in 7.50 M TFMSA solution. Temperature is 25°C.

DFT Calculations

Geometry optimization was carried out using the Gaussian 09C software package [1]. The data from crystal structure were used as an initial system state for not protonated complex. The calculations were performed using the B3LYP [2,3,4,5] method and LANL2DZ [6,7,8,9,10] basis set for entire molecules placed in a cavity within the water reaction field (SCRF solvent method [11]). The data obtained were then used for single point calculations performed with ADF-2017 software package [12,13,14]. The basis sets [15] for each atom type summarized in a Table 2S was chosen on the basis of computer efficiency and precision. B3LYP method and COSMO [16] solvation method (solvent – water) with Delley surfaces were used for calculations. The partial atomic charges were found within the Charge Model 5[17].

Table 2S. Basis sets used for or single point calculations performed with ADF-2017

Rh	ZORA*/TZ2P with 3d frozen core
N	ZORA/TZP
Cl	AUG-TZP
O	ET-QZ3P
C	ET-QZ3P
H	ET-QZ3P

*-zero order relativistic approximation

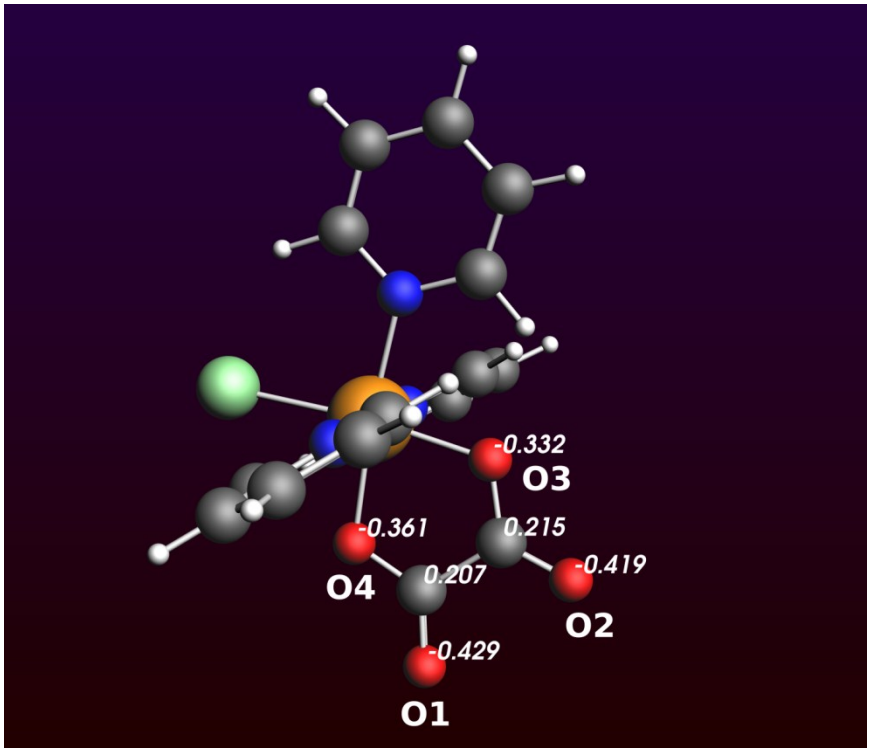


Figure 8S. The DFT-calculated charge distribution on oxalate ligand in **1** complex.

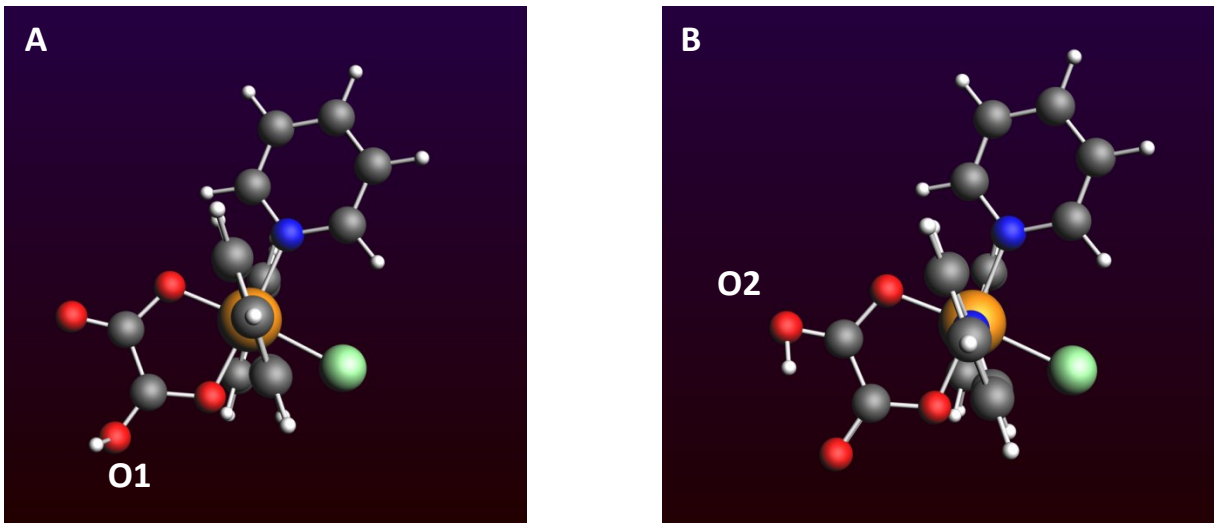


Figure 9S. The DFT-calculated structures of the protonated complexes **1**·H^+.

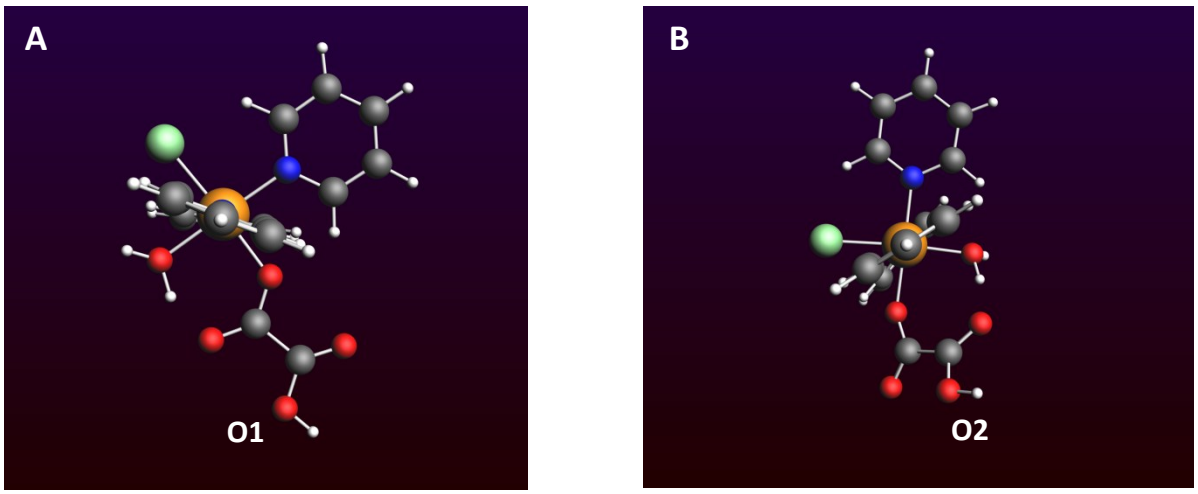


Figure 10S. The DFT-calculated structures of the aquated intermediates **2**

Table 3S. Cartesian coordinates (Angström) for DFT calculated structure of 1.

Atom	x	y	z	Atom	x	y	z
Rh	-0.00003	-0.14591	-0.27810	H	-2.23581	0.79941	1.55856
N	-2.07986	-0.22506	-0.25604	C	-0.00006	2.87146	-0.77497
N	-0.00020	1.89894	0.17844	C	-0.00047	4.60969	0.91674
N	2.07981	-0.22480	-0.25587	C	-0.00059	3.59972	1.89721
Cl	0.00000	0.24150	-2.71353	C	-0.00045	2.25870	1.49729
O	0.00013	-2.19276	-0.52771	C	-0.00019	4.23267	-0.43781
O	-0.00003	-0.68433	1.70344	H	-0.00053	1.44935	2.21761
C	0.00051	-2.87990	0.61361	H	-0.00060	5.65751	1.20025
C	0.00034	-2.00644	1.91264	H	-0.00078	3.83739	2.95518
O	0.00050	-2.52829	3.04992	H	0.00017	2.53806	-1.80389
O	0.00077	-4.13182	0.68497	H	-0.00007	4.97322	-1.23012
C	-2.73221	-0.88677	-1.25242	C	2.79347	0.30939	0.77337
C	-2.79349	0.30856	0.77351	C	4.18988	0.21522	0.82891
C	-4.12704	-1.01904	-1.25434	C	4.87300	-0.45693	-0.20166

C	-4.87300	-0.45784	-0.20150	C	4.12702	-1.01873	-1.25417
C	-4.18987	0.21406	0.82923	C	2.73216	-0.88676	-1.25210
H	-2.11710	-1.29964	-2.03976	H	2.23579	0.80044	1.55829
H	-4.60900	-1.55218	-2.06636	H	4.72025	0.65651	1.66535
H	-5.95478	-0.54597	-0.18151	H	5.95480	-0.54486	-0.18177
H	-4.72020	0.65487	1.66594	H	2.11700	-1.30012	-2.03914
				H	4.60900	-1.55203	-2.06606

Table 4S. Cartesian coordinates (Angström) for DFT calculated structure of 1·**H**$^{+}$ protonated by O1 atom.

Atom	x	y	z	Atom	x	y	z
Rh	0.00003	-0.10645	0.29989	C	-0.00048	2.88628	0.68908
N	2.08603	-0.17616	0.27619	C	0.00023	4.55359	-1.07297
N	-0.00025	1.87909	-0.22865	C	0.00037	3.50598	-2.01260
N	-2.08592	-0.17667	0.27571	C	0.00006	2.18218	-1.56277
Cl	-0.00036	0.34698	2.69170	C	-0.00031	4.23093	0.29508
O	0.00042	-2.22665	0.60382	H	0.00001	1.35004	-2.25510
O	0.00035	-0.75855	-1.68986	H	0.00053	5.58904	-1.39788
C	0.00020	-2.84548	-0.49614	H	0.00072	3.70012	-3.07905
C	0.00005	-2.06797	-1.84081	H	-0.00080	2.59885	1.73055
O	-0.00040	-2.72993	-2.90290	H	-0.00058	5.00106	1.05821
O	-0.00000	-4.17170	-0.55440	C	-2.78069	0.26805	-0.80935
C	2.76035	-0.73041	1.32385	C	-4.17678	0.18743	-0.87250
C	2.78069	0.26831	-0.80901	C	-4.88131	-0.37551	0.20762
C	4.15617	-0.84455	1.31811	C	-4.15603	-0.84453	1.31806
C	4.88137	-0.37557	0.20760	C	-2.76021	-0.73062	1.32357
C	4.17676	0.18749	-0.87240	H	-2.21076	0.67525	-1.63248
H	2.16721	-1.07103	2.16121	H	-4.69021	0.55556	-1.75345
H	4.65429	-1.29223	2.17069	H	-5.96375	-0.45063	0.18213
H	5.96379	-0.45091	0.18191	H	-2.16694	-1.07109	2.16093
H	4.69008	0.55546	-1.75348	H	-4.65411	-1.29195	2.17080
H	2.21067	0.67557	-1.63206	H	-0.00018	-4.50456	-1.48924

Table 5S. Cartesian coordinates (Angström) for DFT calculated structure of 1·**H**$^{+}$ protonated by O2 atom.

Atom	x	y	z	Atom	x	y	z
Rh	0.00263	-0.11797	-0.27703	C	-0.03073	2.89513	-0.74450
N	-2.08078	-0.21077	-0.27768	C	-0.04880	4.60680	0.97429
N	-0.01638	1.90916	0.19509	C	-0.03398	3.58263	1.94021
N	2.08744	-0.18163	-0.27459	C	-0.01813	2.24887	1.52084
Cl	0.00762	0.27519	-2.65305	C	-0.04705	4.25032	-0.38506
O	0.01602	-2.18243	-0.55355	H	-0.00687	1.43825	2.23917
O	0.00596	-0.78249	1.74311	H	-0.06131	5.64988	1.27361
C	0.02005	-2.92100	0.54543	H	-0.03467	3.80358	3.00151
C	0.01512	-2.04837	1.83265	H	-0.02878	2.58278	-1.77919

O	0.02064	-2.69790	2.98595	H	-0.05803	5.00172	-1.16664
O	0.02682	-4.16528	0.61813	C	2.82815	0.46771	0.66645
C	-2.70042	-0.95090	-1.24066	C	4.22579	0.38703	0.68700
C	-2.82790	0.40182	0.68289	C	4.88254	-0.38641	-0.28794
C	-4.09365	-1.08831	-1.27496	C	4.10998	-1.06049	-1.25126
C	-4.87299	-0.45081	-0.29244	C	2.71522	-0.93968	-1.21828
C	-4.22434	0.30300	0.70315	H	2.29816	1.04868	1.40788
H	-2.06380	-1.42587	-1.97391	H	4.77742	0.91961	1.45339
H	-4.54833	-1.68457	-2.05800	H	5.96508	-0.46431	-0.29382
H	-5.95449	-0.54196	-0.29925	H	2.08357	-1.44297	-1.93677
H	-4.78130	0.80654	1.48514	H	4.57110	-1.67239	-2.01828
H	-2.30343	0.96678	1.44065	H	0.01730	-2.13217	3.79680

Table 6S. Cartesian coordinates (Angström) for DFT calculated structure of **2** intermediate complex with oxalato ligand coordinated in *trans*-position to chlorido ligand.

Atom	x	y	z	Atom	x	y	z
Rh	0.00604	-0.32514	-0.55884	C	0.38658	-2.70463	3.69630
N	2.09296	-0.12663	-0.61186	C	0.24109	-1.30591	3.65947
N	0.15339	-1.35022	1.24510	C	0.12689	-0.65839	2.42433
N	-2.07565	-0.41442	-0.52488	C	0.41261	-3.40824	2.47960
Cl	0.09451	-2.33299	-1.94314	H	0.01321	0.41573	2.35764
O	-0.34106	3.47121	2.36459	H	0.47676	-3.22862	4.64247
O	-0.11106	1.44365	0.53475	H	0.21458	-0.71448	4.56770
C	-0.31708	3.72979	1.15399	H	0.31153	-3.21464	0.31941
C	-0.21604	2.65379	0.04796	H	0.52216	-4.48660	2.45141
O	-0.23911	2.98214	-1.17554	C	-2.76871	-0.11187	0.60815
O	-0.37559	4.98647	0.62757	C	-4.16829	-0.12336	0.64028
C	2.81959	-0.55258	-1.68375	C	-4.87872	-0.45010	-0.52952
C	2.73365	0.48281	0.42631	C	-4.15538	-0.75055	-1.69805
C	4.20838	-0.38024	-1.74728	C	-2.75528	-0.72400	-1.66449
C	4.87535	0.24349	-0.67758	H	-2.19641	0.15143	1.48592
C	4.11952	0.67983	0.42589	H	-4.68017	0.12276	1.56376
H	2.27881	-1.04996	-2.47695	H	-5.96404	-0.46550	-0.53114
H	4.74614	-0.73377	-2.61988	H	-2.16171	-0.94561	-2.53924
H	5.95099	0.38609	-0.70327	H	-4.65849	-1.00205	-2.62498
H	4.58581	1.16783	1.27432	H	-0.43819	5.68458	1.32107
H	2.12424	0.82203	1.25168	O	-0.18722	0.73701	-2.35155
C	0.29492	-2.70642	1.27280	H	-0.17322	1.73290	-2.15202
				H	0.25255	0.44434	-3.17005

Table 7S. Cartesian coordinates (Angström) for DFT calculated structure of **2** intermediate complex with oxalato ligand coordinated in *trans*-position to pyridine ligand.

Atom	x	y	z				
Rh	-0.19229	-0.08559	0.10506	C	-2.96195	3.91797	-0.40964
N	1.52659	1.09588	0.27875	C	-2.26647	3.36426	-1.50038
N	-1.38734	1.61048	-0.08475	C	-1.49155	2.21608	-1.30739
N	-1.85355	-1.33845	-0.07131	C	-2.85539	3.28856	0.84242
Cl	-0.43995	-0.15698	2.51835	H	-0.95427	1.75759	-2.12640
O	0.95239	-1.82742	0.32292	H	-3.56928	4.80882	-0.53338
O	2.50294	-0.97983	-2.01078	H	-2.31754	3.80540	-2.48937
C	2.08376	-2.39893	-0.00963	H	-1.95786	1.63278	1.92291
C	2.95335	-1.70582	-1.09441	H	-3.37384	3.67184	1.71416
O	4.26435	-1.99089	-0.97805	C	-2.92240	-1.03062	-0.86072
O	2.50072	-3.48832	0.45730	C	-4.02061	-1.89031	-0.98335
C	2.38872	0.88637	1.31507	C	-4.02601	-3.10215	-0.26841
C	1.81601	2.05408	-0.64594	C	-2.92080	-3.41219	0.54425
C	3.56046	1.64020	1.45904	C	-1.85005	-2.51243	0.62223
C	3.85839	2.63946	0.51447	H	-2.90196	-0.08950	-1.39313
C	2.96862	2.84337	-0.55617	H	-4.84754	-1.60687	-1.62456
H	2.11618	0.11935	2.02659	H	-4.86677	-3.78438	-0.34388
H	4.21795	1.44077	2.29780	H	-0.97402	-2.71349	1.22163
H	4.75913	3.23789	0.60671	H	-2.87935	-4.33429	1.11308
H	3.15705	3.59472	-1.31459	O	0.10143	-0.16860	-1.97970
H	1.12585	2.17556	-1.46819	H	4.82047	-1.57522	-1.67999
C	-2.06395	2.13957	0.97487	H	1.05376	-0.50258	-2.13787
				H	-0.55096	-0.67811	-2.50123

1 Gaussian 09, Revision C, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

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