Remarkable thermal stability of light-induced Ru-ON linkage isomers in mixed salts of ammine ruthenium complex with *trans*-ON-Ru-F coordinate

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Table S1. Experimental and refinement details.

Complex	$(H_3O)[RuNO(NH_3)_4F](NO_3)_{1.5}F_{1.5}\cdot 0.5H_2O$ (**I**)	$[RuNO(NH_3)_4F](ClO_4)Cl$ (**II**)
Empirical formula	$F_{2.5}H_{16}N_{6.5}O_7Ru$	$Cl_2FH_{12}N_5O_5Ru$
Formula weight	367.73	353.12
Temperature/K	150(2)	150(2)
Crystal system	tetragonal	monoclinic
Space group	*I4/m*	$P2_1/n$
a/Å	16.8917(6)	11.4314(17)
b/Å	16.8917(6)	7.4565(11)
c/Å	7.7823(5)	12.5251(17)
α/°	90	90
β/°	90	101.184(4)
γ/°	90	90
Volume/Å^3	2220.5(2)	1047.3(3)
Z	8	4
ρ_{calc}g/cm^3	2.176	2.239
μ/mm^{-1}	1.488	2.030
F(000)	1440.0	696.0
Crystal size/mm^3	0.35 × 0.28 × 0.15	0.200 × 0.130 × 0.090
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.822 to 57.568	4.418 to 61.122
Index ranges	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -10 ≤ l ≤ 10	-15 ≤ h ≤ 16, -9 ≤ k ≤ 10, -14 ≤ l ≤ 17
Reflections collected	16232	9768
Independent reflections	1550 [R_{int} = 0.0287, R_{sigma} = 0.0133]	3206 [R_{int} = 0.0202, R_{sigma} = 0.0196]
Data/restraints/parameters	1550/0/94	3206/0/131
Goodness-of-fit on F^2	1.248	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1130	R_1 = 0.0178, wR_2 = 0.0433
Final R indexes [all data]	R_1 = 0.0466, wR_2 = 0.1134	R_1 = 0.0211, wR_2 = 0.0446
Largest diff. peak/hole / e Å^{-3}	1.08/-1.47	0.33/-0.51

Table S2. Selected bond lengths (Å) and angles (°) in obtained complexes.

Distance/angle	**I**	**II**
N1-O1	1.154(8)	1.137(2)
Ru1-N1	1.721(6)	1.736(2)
Ru1-N2	2.088(4)	2.102(1)
Ru1-N3	2.089(4)	2.113(1)
Ru1-N4	2.088(4)	2.111(1)
Ru1-N5	2.089(4)	2.093(1)
Ru1-F1	1.930(4)	1.944(1)
Ru1-N1-O1	178.9(7)	176.1(1)
F1-Ru1-N1	180.0(2)	177.5(1)
N2-Ru1-F1	85.6(2)	85.5(1)
N3-Ru1-F1	85.3(1)	85.3(1)
N4-Ru1-F1	85.6(2)	85.6(1)
N5-Ru1-F1	85.3(1)	85.2(1)

Table S3. Found hydrogen bond lengths (Å) and angles (°).

Distance (D···A), angle (D-H···A)					
I			**II**		
N2···O2	3.108	148.0	N2···Cl2	3.254	174.8
N2···O3	3.040	167.6	N2···Cl2	3.311	172.5
N2···F1	2.887	118.4	N2···O3	3.154	116.1
N2···F3	3.291	173.5	N2···O4	3.042	163.1
N3···O2	3.089	164.6	N3···Cl2	3.371	165.6
N3···O3	3.006	161.8	N3···Cl2	3.362	173.1
N3···O6	3.209	142.7	N3···O5	3.262	123.7
			N3···O4	3.098	153.6
			N4···Cl2	3.586	159.9
			N4···F1	3.006	160.7
			N4···O5	3.041	111.6
			N4···O2	3.072	153.2
			N5···Cl2	3.451	166.2
			N5···F1	2.955	163.2
			N5···O2	3.018	147.2
			N5···O2	2.926	113.7

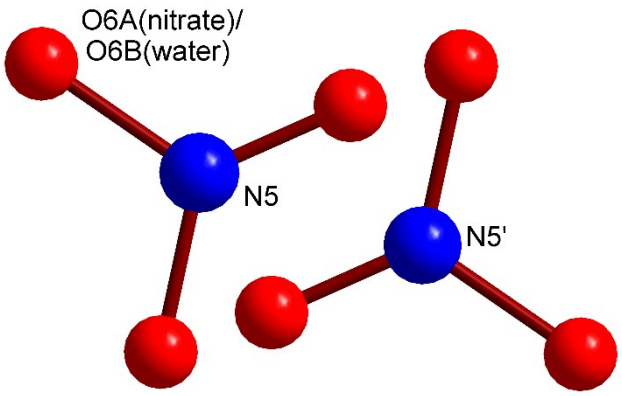


Fig. S1. Disordered nitrate and water molecule in the structure of **I**. Symmetry code for (‘) is -*x*, 1–*y*, *z*.

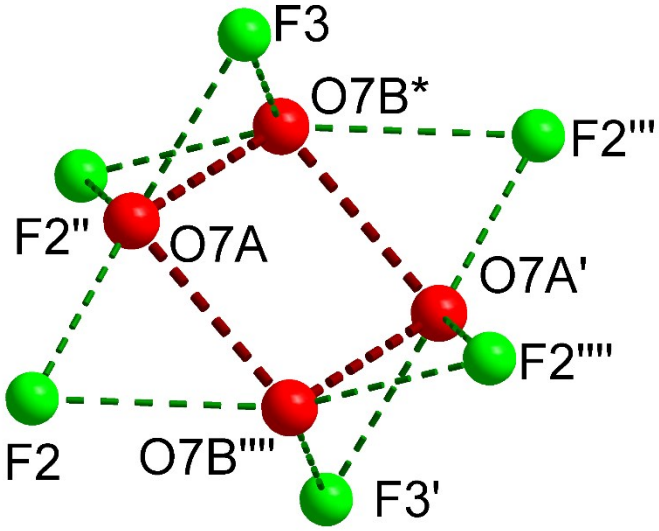
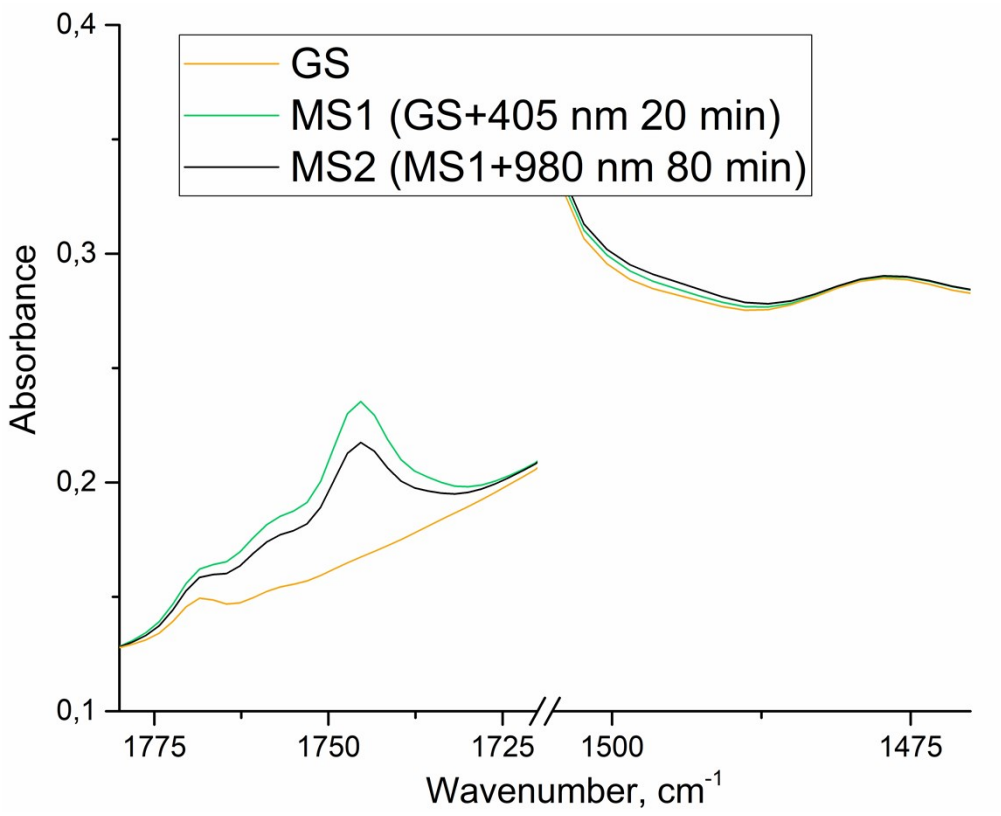


Fig. S2. Variant of the arrangement of the disordered H_3O^+ cations forming hydrogen bond with F^- in the structure of **I**. Symmetry codes: (‘) -*x*, –*y*, 1–*z*; (‘’) *y*, –*x*, *z*; (‘’’) -*x*, –*y*, *z*; (‘’’’) –*y*, *x*, *z*; (*) *y*, –*x*, 1–*z*. Green dashed lines indicate the O-H···F contacts, brown dashed lines indicate the O-H···O contacts. Hydrogen atoms were not localized due to the strong disorder of the H_3O^+ cations.

Table S4. The complexes of $[RuNO(NH_3)_4F]^{2+}$ ion (A) with different anions. The space groups highlighted by the **bold** are non-centrosymmetric. The percentage of the certain intermolecular interaction is calculated using the two-dimensional fingerprints of Hirshfeld surface of the $[RuNO(NH_3)_4F]^{2+}$.

Complex	Space group	N-H···All, %	N-H···Halogen, %	N-H···O, %	Ref.
I	*I4/m*	76	18	52	Present work
II	$P2_1/n$	76	16	35	Present work
$A(ClO_4)_2$	$P\bar{1}$	74	5	67	[1]
$A(SiF_6)$	***Pn***	76	56	6	[2]
$A[PdCl_4]$	$\boldsymbol{Cmc2_1}$	77	52	8	[1]
$A[PtCl_4]$	$\boldsymbol{Cmc2_1}$	76	50	7	[1]
$A[PtCl_6]$	$\boldsymbol{P2_12_12_1}$	76	59	6	[1]



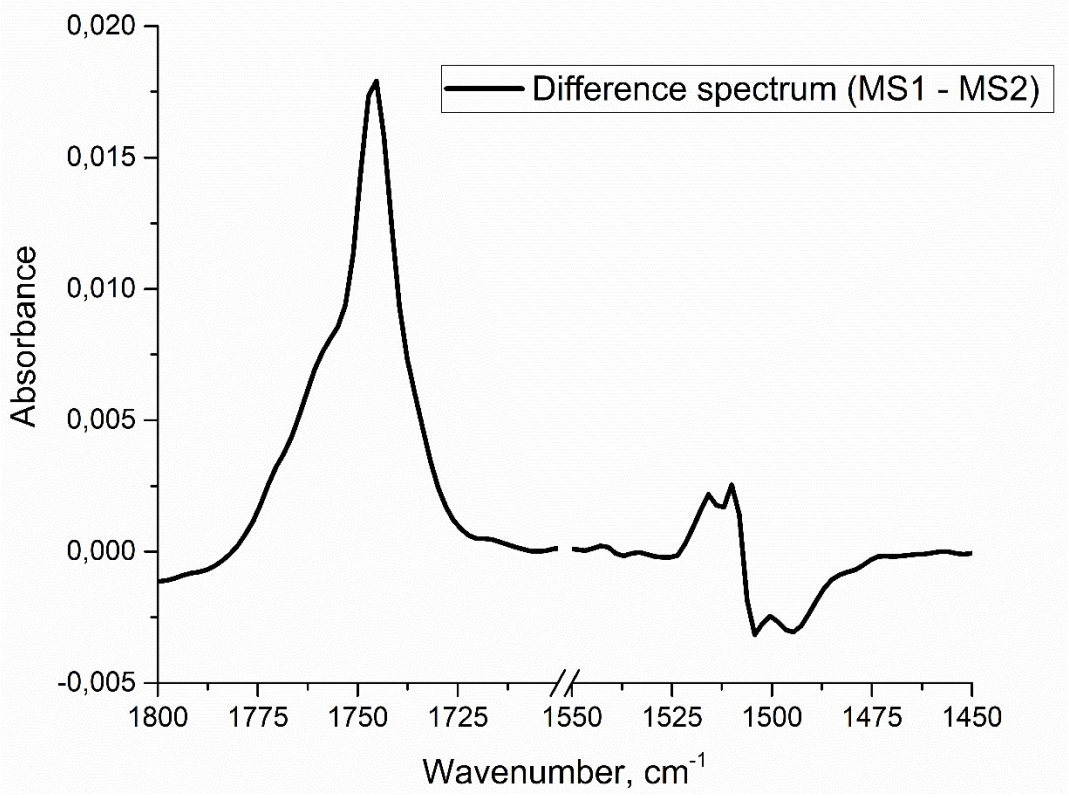


Fig. S3. IR-spectra of the **I** complex before (GS), after light exposure at 405 nm 270 mW (MS1) and after subsequent irradiation at 980 nm 470 mW at 80 K, and the difference spectrum of MS1 and MS2 (MS1 – MS2).

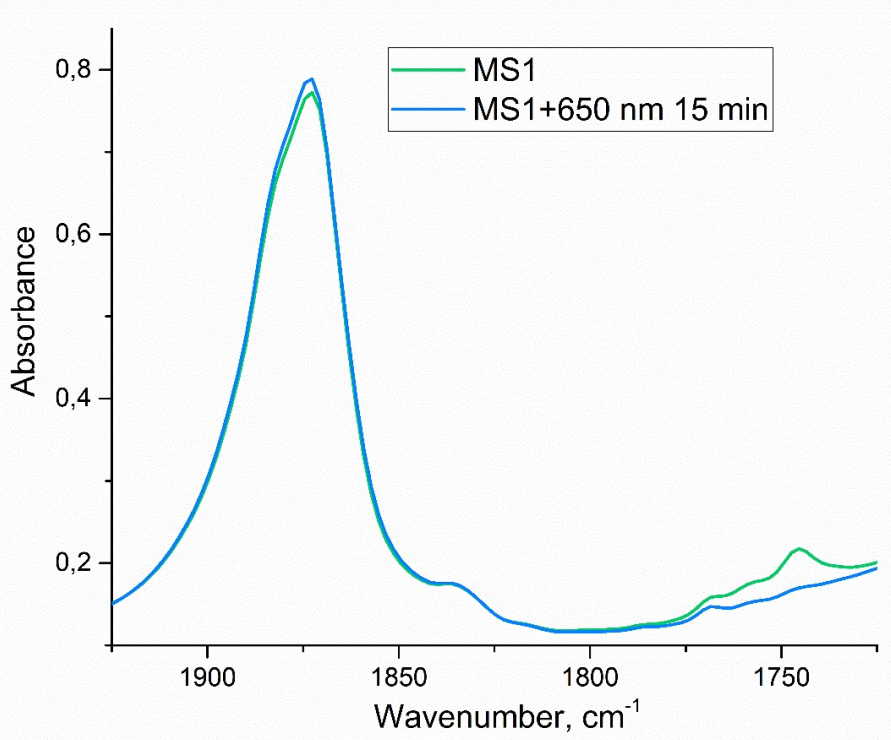


Fig. S4. The IR spectrum of **I** complex with MS1 (green line) and the spectrum after irradiation at 650 nm 60 mW (blue line).

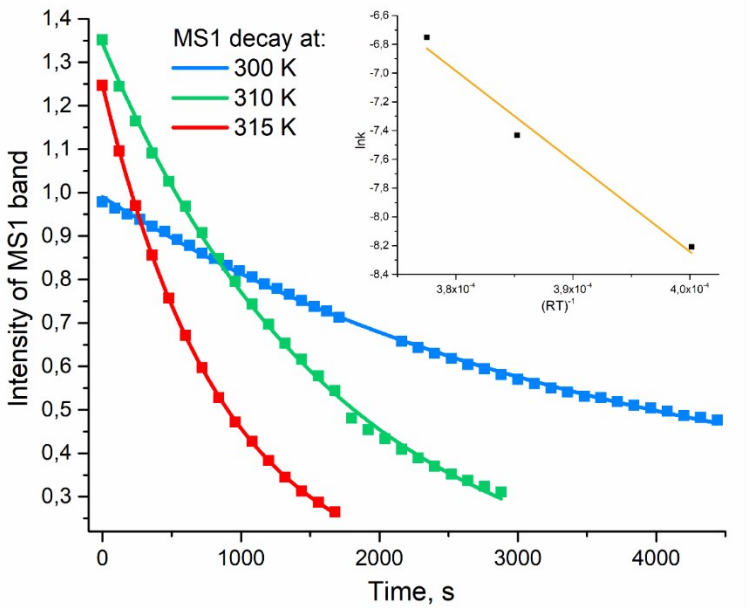


Fig. S5. The decay of the ν(ON) band of MS1 in **II** at 300, 310 and 315 K fitted by the one-exponential function and corresponding Arrhenius plot in the insert.

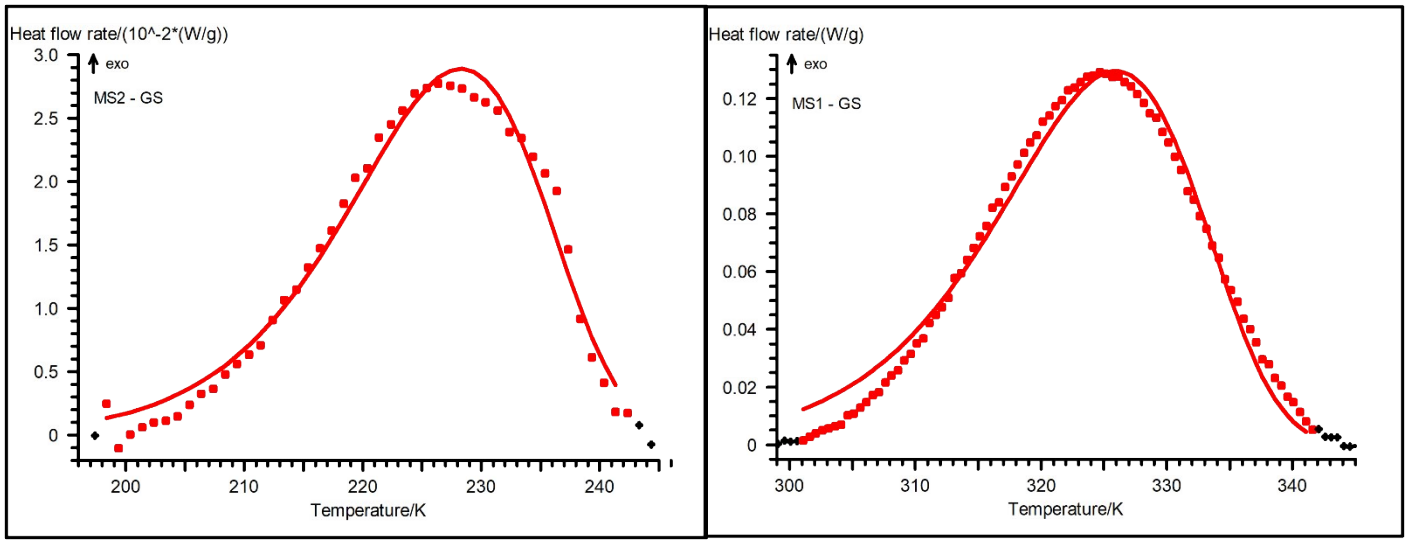


Fig. S6. The DSC curves of the MS2→GS (left panel) and MS1→GS (right panel) reactions of **I** measured by DSC fitted by the kinetic of the first order.

Table S5. The chosen bond distances; positions of ν(NO) bands of GS, MS1 and MS2; populations of MS1 and MS2; decay temperatures (T_d) of MS1 and MS2 and volumes of Hirshfeld surfaces (VHS) of the NO ligand in the complexes of $[RuNO(NH_3)_4F]^{2+}$ ion (A) with different anions.

	Ru-NO, Å	N-O, Å	Ru-F, Å	$\nu(NO)_{GS}$, cm^{-1}	$\nu(NO)_{MS1}$, cm^{-1}	$\nu(NO)_{MS2}$, cm^{-1}	MS1, %	MS2, %	T_d(MS1), K	T_d(MS2), K	VHS, $Å^3$
$A[PtCl_4]$	1.74(2)	1.15(2)	1.96(1)	1895	1762	-	1	-	-	-	22.14
$A[PtCl_6]$	1.728(5)	1.153(7)	1.917(4)	1874	1745	-	2	-	-	-	22.49
$A(SiF_6)$	1.719(2)	1.144(2)	1.938(1)	1902	1769	1545	10	3	292	206	22.31
$A(ClO_4)_2$	1.740(3); 1.736(3)	1.138(4); 1.141(4)	1.927(2); 1.937(2)	1874	1747	1494	7	1	303	-	29.28; 29.18
I	1.721(6)	1.154(8)	1.930(4)	1873	1745	1494	6	2	305	207	23.22
$A[PdCl_4]$	1.728(5)	1.149(5)	1.938(3)	1896	1755	-	1	-	307	-	23.01
II	1.736(2)	1.137(2)	1.944(1)	1873	1745	1494	9	4	313	204	24.35

Table S6. The populations of MS1 and intermolecular contacts shorter than the sum of the van der Waals radii (contacting atoms are underlined) of NO ligand in the complexes of $[RuNO(NH_3)_4F]^{2+}$ ion (A) with different anions.

	MS1, %	Contacts		Ref.
$A(SiF_6)$	10	N<u>O</u>···H	2.66	2
		N<u>O</u>···F	2.66	
		N<u>O</u>···F	2.86	
		<u>N</u>O···F	2.97	
II	9	N<u>O</u>···O	2.90	Present work
		N<u>O</u>···O	2.98	
		<u>N</u>O···O	2.95	
		<u>N</u>O···O	3.06	
$A(ClO_4)_2$	7	N<u>O</u>···O	2.91; 2.92	1
		N<u>O</u>···O	3.04; 3.01	
		<u>N</u>O···O	2.94; 3.01	
		<u>N</u>O···O	2.97; 3.04	
I	6	N<u>O</u>···O*	2.68	Present work
		N<u>O</u>···O	2.83	
		N<u>O</u>···O	2.83	
		N<u>O</u>···N	2.99	
		<u>N</u>O···O*	2.72	
		<u>N</u>O···O	3.00	
		<u>N</u>O···O	3.00	
$A[PtCl_6]$	2	N<u>O</u>···Cl	3.12	1
		N<u>O</u>··· Cl	3.17	
		N<u>O</u>··· Cl	3.17	
		<u>N</u>O··· Cl	3.30	
$A[PtCl_4]$	1	N<u>O</u>···Cl	3.17	1
		N<u>O</u>···Cl	3.17	
		<u>N</u>O···Cl	3.29	
		<u>N</u>O···Cl	3.29	
$A[PdCl_4]$	1	N<u>O</u>···Cl	3.19	1
		N<u>O</u>···Cl	3.19	
*Short distances correspond to the disordered water molecule.				

References

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