Supplementary Information

Reactivity, Photolability, and Computational Studies of the Ruthenium Nitrosyl Complex with a Substituted Cyclam *fac*-[Ru(NO)Cl_2(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]Cl•H_2O.

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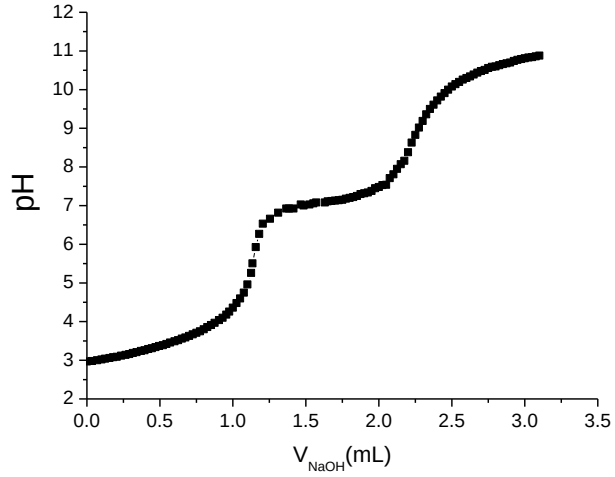

Fig. SI 1 Representative titration curve for **I** ($2.0x10^{-3}$ mol L^{-1}, μ = 0.1 mol L^{-1} NaCl) with 0.025 mol L^{-1} NaOH at room temperature.

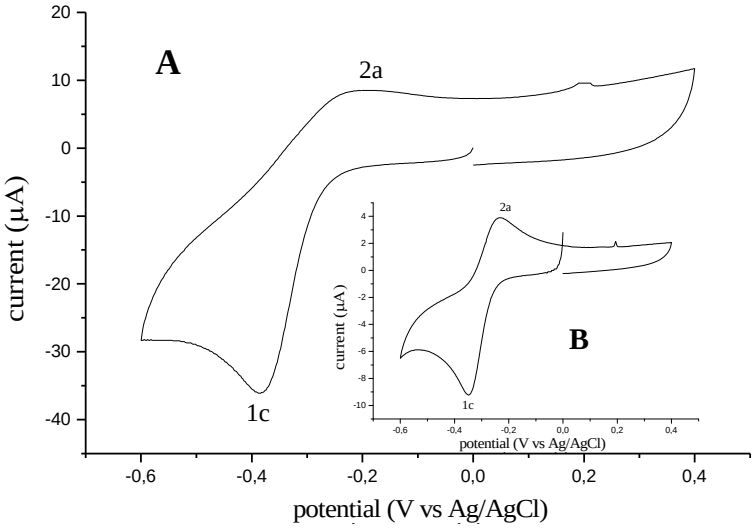

Fig. SI 2 Cyclic voltammogram of **I** in NaCl 0.1 mol L^{-1}, pH 4.7 and T = 25 ^{o}C. (A) scan rate of 200 mV s^{-1} and (B) 20 mV s^{-1}

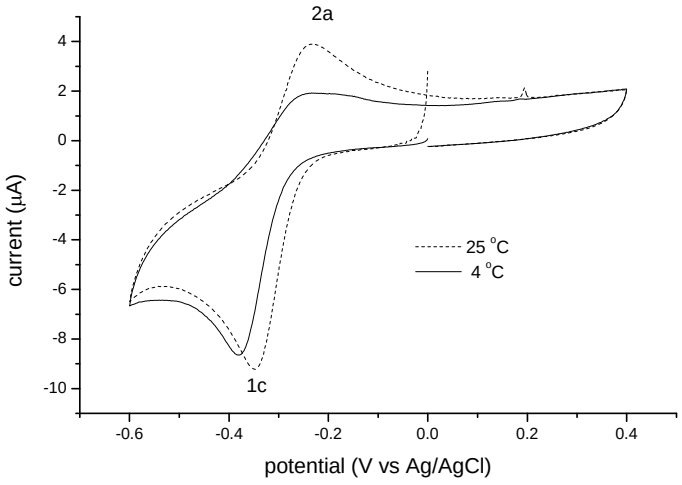

Fig. SI 3 Cyclic voltammogram of **I** in NaCl 0.1 mol L^{-1}, pH 4.7 and scan rate of 20 mV s^{-1} at different temperatures.

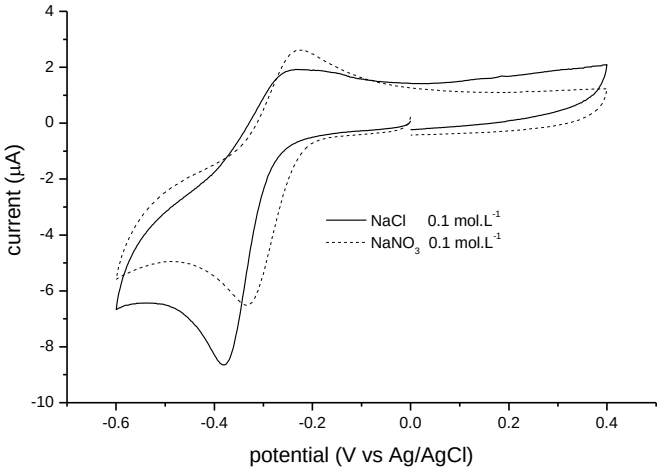

Fig. SI 4 Cyclic voltammogram of **I** at pH 4.7 and T = 4 ^{o}C with scan rate of 20 mV s^{-1}.

Computational models

Initially, the geometry of the complex *fac*-[Ru(NO)Cl_2(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]Cl•H_2O was optimized using some theoretical models (method, basis set for representative atoms, and a pseudopotential (PP) for ruthenium), and compared with the experimental geometry. The model will be indicated by method/PP, basis. The calculations were carried out by BP86[1,2] and B3LYP[3] functionals, 6-31G(d),[4] 6-31+G(d,p),[5] cc-pVDZ,[6,7] and aug-cc-pVDZ[8] basis sets, and ECP28MHF, non relativistic, or ECP28MDF,[9] fully relativistic PPs. The best results were obtained by the B3LYP method, ECP28MDF PP and cc-pVDZ basis set, B3LYP/ECP28MDF,cc-pVDZ.

Table SI 1 Deviations of calculated bond lengths from experimental ones for complex **I**, Å. M1: B3LYP/ECP28MHF,6-31G(d); M2: B3LYP/ECP28MHF,6-31+G(d,p); M3: B3LYP/ECP28MDF, cc-pVDZ; M4: BP86/ECP28MDF,cc-pVDZ.

	M1	M2	M3	M4
all bond lengths				
mean	0.018	0.018	0.014	0.020
std. dev.	0.019	0.018	0.019	0.016
only Ru-X [a]				
mean	0.037	0.037	0.033	0.030
std. dev.	0.026	0.026	0.030	0.026
max. dev.	0.062	0.061	0.065	0.059
excluding Ru-X [a]				
Mean	0.013	0.012	0.009	0.017
std. dev.	0.011	0.010	0.009	0.010
max. dev.	0.040	0.041	0.023	0.041

a: all bond lengths that involve ruthenium.

Table SI 2 Bond angles for **I-VII**, in degrees, calculated in vacuum.

	(I)	**(II)**	**(III)**	**(IV)**	**(V)**	**(VI)**	**(VII)**
N5-Ru-N2	171.73	171.55	171.38	174.23	177.8	172.48	176.54
N5-Ru-N1	103.80	103.50	103.56	103.96	101.69	102.44	100.73
N2-Ru-N1	80.39	80.09	80.55	79.81	79.4	80.1	79.27
N5-Ru-N3	101.93	101.50	104.24	99.46	98.22	103.55	94.67
N2-Ru-N3	85.35	86.22	83.65	85.14	83.72	83.67	81.87
N1-Ru-N3	86.55	87.58	83.27	84.98	87.44	84.9	85.55
N5-Ru-Cl1	89.55	88.83	90.96	91.71	86.94	90.95	89.54
N2-Ru-Cl1	83.36	83.53	81.63	83.80	91.18	82.06	93.92
N1-Ru-Cl1	88.62	88.96	87.00	91.10	88.66	87.4	88.93
N3-Ru-Cl1	168.30	169.61	169.16	168.76	174.07	164.75	173.59
N5-Ru-Cl2	87.32	87.51	87.17	87.37	86.06	87.82	86.55
N2-Ru-Cl2	88.51	88.83	88.16	89.01	92.88	89.45	93.46
N1-Ru-Cl2	168.89	168.93	169.16	168.56	172.23	169.51	172.73
N3-Ru-Cl2	92.05	91.77	95.74	91.70	90.93	94.89	93.74
Cl1-Ru-Cl2	90.66	89.75	91.31	90.10	92.33	90.31	91.33
O5-N5-Ru	170.13	169.50	170.87	170.81	176.73	171.77	122.00

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