Electronic structure alternatives in nitrosylruthenium complexes

Goutam Kumar Lahiri* **and Wolfgang Kaim***

Electronic Supporting Information

Table S1 EPR spectroscopic data[a] of selected nitrosylruthenium complexes; n.o. not observed

Complex	g_1	g_2	g_3	g_{av}	Δ_g	A_1	A_2	A_3	Ref.
$[(py)_4(NH_3)Ru(NO)]^{2+}$ [b]	2.0215	1.9875	1.878	1.963	0.1435	n.o.	3.0	n.o.	18
$[(py)_4(SCN)Ru(NO)]^{+}$ [b]	2.0225	1.9895	1.877	1.963	0.1455	n.o.	2.9	n.o.	18
$[(py)_4ClRu(NO)]^{+}$ [b]	2.025	1.990	1.886	1.967	0.139	n.o.	3.1	n.o.	18
$[(py)_4ClRu(NO)]^{+}$ [c]	2.033	1.989	1.874	1.965	0.159	1.51	3.18	1.07	21
$[(py)_4(OH)Ru(NO)]^{+}$ [b]	2.0235	1.991	1.886	1.967	0.1375	n.o.	3.2	n.o.	18
$[(bpy)_2(CH_3CN)Ru(NO)]^{2+}$ [b]	2.028	1.9925	1.882	1.968	0.146	n.o.	3.3	n.o.	18
$[(bpy)_2ClRu(NO)]^{+}$ [b]	2.029	1.992	1.881	1.968	0.148	n.o.	3.2	n.o.	18
$[(terpy)(bpy)Ru(NO)]^{2+}$ [b]	2.0175	1.998	1.883	1.967	0.1345	n.o.	3.4	n.o.	18
$[(terpy)(bpz)Ru(NO)]^{2+}$ [b]	2.0215	1.999	1.886	1.969	0.1355	n.o.	3.4	n.o.	18
$[(NC)(py)_4Ru(\mu\text{-}CN)(py)_4Ru(NO)]^{2+}$ [c]	2.024	1.990	1.865	1.960	0.159	1.55	3.39	0.97	21
$[(cyclam)ClRu(NO)]^{+}$ [d]	2.035	1.995	1.883	1.971	0.152	1.7	3.21	1.5	46
$[(bpydip)ClRu(NO)]^{+}$ [e]	2.027	1.991	1.889	1.969	0.138	1.69	3.23	1.48	47
$[(dppe)_2ClRu(NO)]^{+}$ [g]	2.011	1.976	1.867	1.951	0.144	1.71	1.85[f]	1.43	46(*b*)
$[(depe)_2ClRu(NO)]^{+}$ [d]	2.010	1.984	1.888	1.961	0.122	1.8	3.5	1.9	46(*b*)
$[(NC)_5Ru(NO)]^{3-}$ [h]	2.004	2.002	1.870	1.959	0.134	n.o.	3.8	n.o.	48
$[(Ph_3P)_2(C_5Me_5)Ru(NO)]^{+}$ [i]	2.0115	1.983	1.900	1.965	0.111	1.63	2.10[f]	2.29	49
	1.995	1.995	1.896	1.962	0.099	n.o.	2.85	n.o.	49[j]

$[(PhMe_2P)_2(C_5Me_5)Ru(NO)]^{+}$ [i]	2.000	1.998	1.915	1.970	0.085	1.06	3.38	1.07	49
	1.996	1.996	1.964[f]	1.985[f]	0.032[f]	n.o.	3.25	n.o.	49[j]
$[(Me_3P)_2(C_5Me_5)Ru(NO)]^{+}$ [i]	2.007	2.002	1.918	1.976	0.089	1.15	3.37	1.20	49
	2.001	1.994	1.912	1.969	0.089	0.6	3.3	1.3	49[j]
$[HCl(OC)(PiPr_3)_2Ru(NO)]$ [k]	2.006	1.993	1.910	1.970	0.096	n.o.	3.45	n.o.	50
$[DCl(OC)(PiPr_3)_2Ru(NO)]$ [k]	2.001	1.994	1.910	1.968	0.091	n.o.	3.45	n.o.	50
$[(bpy)(tpm)Ru(NO)]^{2+}$ [m]	2.031	1.990	1.886	1.969	0.145	n.v.	3.2	n.v.	13
$[(trpy)(L)Ru(NO]^{2+}$ [l]	2.020	1.995	1.884	1.966	0.136	n.o.	3.0	n.o.	7
$[(bpym)(trpy)Ru(NO)]^{2+}$	2.021	1.995	1.885	1.967	0.136	n.o.	3.4	n.o.	45
$[(TPP)(py)Ru(NO)]^{\bullet}$	2.036	1.985	1.880	1.967	0.156	n.o.	3.3	n.o.	8
$[ClRu(py)_4(CN)Ru(py)_4(CN)Ru(py)_4Ru(NO)]^{3+}$	2.028	1.990	1.862	1.960	0.166	n.o.	3.3	n.o.	2

[a] ^{14}N hyperfine coupling A in mT. [b] In CH_3CN/0.1 M Bu_4NPF_6, measured at 110 K. [c] In CH_3CN/0.1 M Bu_4NPF_6, measured at 10 K. [d] In ethylene glycol + 30% H_2O, measured at 77 K; cyclam = 1,4,8,11-tetraazacyclotetradecane; depe = 1,2-bis(diethylphosphanyl)-ethane. [e] In CH_3CN, measured at 110 K; bpydip = N,N′-bis(7-methyl-2-pyridylmethylene)-1,3-diiminopropane. [f] Probably erroneous value. [g] In CH_2Cl_2, measured at 77 K; dppe = 1,2-bis(diphenylphosphanyl)ethane. [h] In CH_3CN/0.1 M Bu_4NPF_6, measured at 3.5 K. [i] In CH_2Cl_2, measured at 113 K. [j] In acetone, measured at 100 K. [k] In toluene, measured at 77 K. Additional ^1H hyperfine coupling observed at about 3.5 mT. [l] L = 2-phenylimidazo[4,5-*f*]-1,10-phenanthroline. [m] tpm = tris(1-pyrazolyl)methane.

Table S2 Selected nitrosyl stretching frequencies ν(NO) of various complexes

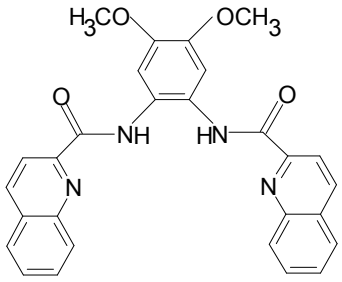
Compound	ν_{NO}^{+} / cm^{-1}	$\nu_{NO}^{\bullet}$ / cm^{-1}	ν_{NO}^{-} / cm^{-1}	Ref.
$[Ru^{II}(NO^{+})(Q^{\bullet-})(trpy)](PF_6)_2$	1900	-	-	1
$[Ru^{II}(NO^{+})(Q^{2-})(trpy)]^{+}$	1830 (CH_3CN)	-	-	
trans-$[ClRu^{II}(py)_4(NC)Ru^{II}(py)_4(CN)Ru^{II}(py)_4(NO^{+})](PF_6)_4$	1919	-	-	2
$[Ru^{II}(trpy)(bik)(NO^{+})](ClO_4)_3$	1951	1630	-	3
$[((OMe)_2bQb)Ru^{II}(NO^{+})(Thnl)]$	1847	-	-	4
$[((OMe)_2bQb)Ru^{II}(NO^{+})(Seln)]$	1847	-	-	
$[(Me_2bpb)Ru^{II}(NO^{+})(OH)]$	1828	-	-	5
$[(Me_2bpb)Ru^{II}(NO^{+})(Resf)]$	1841	-	-	
$[(Me_2bQb)Ru^{II}(NO^{+})(Resf)]$	1847	-	-	
$[(Me_2bQb)Ru^{II}(NO^{+})(OH)]$	1837	-	-	
$[(Me_2bQb)Ru^{II}(NO^{+})Cl]$	1829	-	-	
$[((OMe)_zbQb)Ru^{II}(NO^{+})(OH)]$	1852	-	-	
$[(Me_2bQb)Ru^{II}(NO^{+})(Resf)]$	1848	-	-	
syn-{(μ-bpym-(4-OH)) $[Ru^{II}(NO^{+})(trpy)]_2\}(PF_6)_5$	1946	-	-	6
$[Ru^{II}(trpy)(pip)(NO^{+})](ClO_4)_3$	1948	1634	-	7
$[(TPP^{\bullet-})Ru^{II}(NO^{+})(H_2O)]^{2+}$	1902	-	-	8
$[(TPP^{2-})Ru^{II}(NO^{+})(H_2O]BF_4$	1875	-	-	
$[(TPP^{2-})Ru^{II}(NO^{+})(Py)]BF_a$	1903	-	-	
$[(TPP^{2-})Ru^{II}(NO^{\bullet})(Py)]$	-	1584	-	
$[(OEP^{\bullet-})Ru^{III}(NO^{+})(H_2O)]^{3+}$	1950	-	-	
$[(OEP^{\bullet-})Ru^{II}(NO^{+})(H_2O)]^{2+}$	1895	-	-	
$[(OEP^{2-})Ru^{II}(NO^{+})(H_ZO)]BF_4$	1877	-	-	
$[(OEP^{2-})Ru^{II}(NO^{+})(Py)]BF_4$	1876	-	-	
$[(OEP^{2-})Ru^{ii}(NO^{\bullet})(Py)]$	-	1568		
$[Ru^{II}(trpy)(pdt)(NO^{+})](ClO_4)_3$	1944	1633	-	9
$[(SBPy_3)Ru^{II}(NO^{+})](BF_4)_3$	1920	-	-	10
$[(Py_3P)Ru^{II}(NO^{+})]BF_4$	1877	-	-	
$[(PaPy_3)Ru^{II}(NO^{+})](BF_4)_z$	1899	-	-	
$[(Py_3P)Ru^{II}(NO^{+})Cl]$	1862	-	-	
$[(Papy_2Q)Ru^{II}(NO^{+})](BF_4)_2$	1868	-	-	11
$[Ru^{II}(Me_2bpb)(NO^{+})(4\text{-}vpy)]BF_4$	1872	-	-	12
$[Ru^{II}(bpy)(tpm)NO^{+}](ClO_4)_3$	1959	-	-	13

$[Ru^{II}(trpy)(L^{1-4})(NO^{+})](X)_3$				14
L^1 = 2-(2-pyridyl)benzoxazole L^2 = 2-(2-pyridyl)benzthiazole L^3 = 2-(2-pyridyl)benzimidazole L^4 = 1-methyl-2-(2-pyridyl)-1*H*-benzimidazole X= ClO_4^- for L^1, L^2, L^4; X= NO_3^- for L^3	L^1--1957 L^2--1941 L^3--1940 L^4--1932	- - - -	- - - -	
$[Ru^{II}(trpy)(dpk)(NO^{+})](C10_4)_3$	1949	1666 (CH_3CN)	-	15
$[Ru^{II}(trpy)(L)(NO^{+})](Cl0_4)_3$ L = 2,2'-dipyridylamine	1945	1830 (CH_3CN)	-	16
$K_2[Cl_5Ru^{II}(NO^{+})]$ $[Cl_5Ru^{III}(NO^{+})]^-$	1843 (*n*-PrCN) 1922 (*n*-PrCN)	- -	- -	17
$[(trpy)(bpz)Ru^{II}(NO^{+})](PF_6)_3$ *trans*-$[(py)_4(SCN)Ru^{II}(NO^{+})](PF_6)_2$	1957 1902	- -	- -	18
$[Ru^{II}(NH_3)_5(NO^{+})](PF_6)_3$	1913	-	-	19
$[Ru^{II}(Papy_3)(NO^{+})](BF_4)_2$ *trans*-$[(NC)Ru^{II}(py)_4(CN)Ru^{II}(py)_4(NO)](PF_6)_3$ *trans*-$[(NC)Ru^{III}(py)_4(CN)Ru^{II}(py)_4(NO^{+})]^{4+}$	1899 1917 (CH_3CN) 1952 (CH_3CN)	- 1626 (CH_3CN)	- - -	20 21
$[Ru^{II}(TPP^{2-})(NO^{+})(ONO)]$	1844	-	-	22
$[Ru^{II}(NCS)(NO^{+})(bpy)(py)_2](PF_6)_2$	1925	-	-	23
$[Ru^{II}(trpy)(L)(NO^{+})]$ $[Cl0_4]_3$ L = $NC_5H_4N{=}NC_6H_4(R)$, R = H / *m*-Me / *m*-Cl / *p*-Me / *p*-Cl]	1960 1953 1952 1955 1957	- - - - -	- - - - -	24
$[Ru^{II}(NO^{+})(trpy)Cl_2](PF_6)$ $[Ru^{II}(OH)(NO_2)(NO^{+})(trpy)](PF_6)$ $[Ru^{II}Cl(OCH_3)(NO^{+})(trpy)](PF_6)$ $[Ru^{II}Br_2(NO^{+})(trpy)](PF_6)$	1895 1860 1870 1916	- - - -	- - - -	25
$[(OEP^{2-})Ru^{II}(NO^{+})(p\text{-}C_6H_4F)]$	1759	-	-	26
$[(TTP^{2-})Ru^{II}(NO^{+})(p\text{-}C_6H_4F)]$	1773	-		27
$Ru^{II}(salen)(Cl)(NO^{+})$	1844 (CH_2CI_2)	-	-	28
$K[Ru^{II}(hedta)(NO^{\bullet}]$ $[Ru^{II}(hedta)(NO)]$ $K_z[Ru^{II}(hedta)(NO^{-})]$ $[(OEP^{2-})Ru^{II}(NO^{+})(OH_2)](BF_4)$	- 1846 - 1852	1858 - - -	- - 1383 -	29 30
$[Ru^{II}(FTTP)(NO^{+})(ONO)]$ $[RuII(TTP^{2-})(NO^{+})(ONO)]$ $[(OEP^{2-})Ru^{II}(NO^{+})(Cl)]$	1847 (C_6H_{12}) 1841 1827	- - -	- - -	31
$[(OEP^{2-})Ru^{II}(NO^{+})(OH)]$	1804	-		32

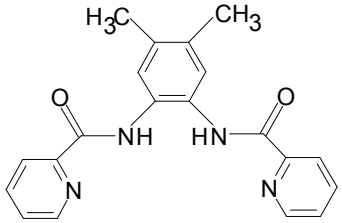
$Na_2[Ru^{II}(CN)_5(NO^+)]$	1926	-	-	33
$[Ru^{II}(Cp)(NO^+)(PPh_3)_2](PF_6)_2$	1860	-	-	34
$[Ru^{II}(trpy)(bpy)(NO^+)]^{3+}$	1952 (CH_3CN)	-	-	35
$Ru^{II}Cl_3(NO^+)(PMePh_2)$	1876	-	-	36
$[Ru^{II}(NH_3)_5(NO^+)]Cl_3$	1913	-	-	
$[Ru^{II}Cl_3(H_2O)_2(NO^+)]$	1895	-		
$NH_4[Ru^{III}(NO^+)Cl_5]$	1900	-	-	37
$[Ru^{I}(NO^+)Cl_2(PPh_3)_2]$	1868	-	-	
$[(bpy)_2Ru^{II}(NO^+)N_3](PF_6)_2$	1923 (CH_3CN)	-	-	38
$[(bpy)_2Ru^{II}(NO^\bullet)Cl]I$	-	1611	-	
$[(bpy)_2Ru^{II}(NO^+)NO_2](PF_6)_2$	1948 (CH_3CN)	-	-	
$[(bpy)_2Ru^{II}(NO^+)NH_3](PF_6)_3$	1950 (CH_3CN)	-		
$[(bpy)_2Ru^{II}(NO^+)py](PF_6)_3$	1953 (CH_3CN)	-	-	
$[(bpy)_2Ru^{II}(NO^+)(CH_3CN)](PF_6)_3$	1956	-	-	
$[(bpy)_2Ru^{II}(NO^\bullet)(CH_3CN)](PF_6)_2$	-	1655	-	
$[Ru^0(\mu\text{-}PPh_2)(NO)(L)]_z$				39
$L=PmePh_2$	1625	-	-	
$L= PPh_3$	1640	-	-	
$[Ru^{II}Cl(bpy)_2(NO^+)](PF_6)_2$	1931 ($(CH_3)_2CO$)	-	-	40
$[Ru^0(NO^+)(H^-)(PPh_3)_3]$	1640	-	-	41
$[Ru^0(NO^+)(diphos)_2]B(C_6H_5)_4$	1673	-	-	
$[Ru^{II}(OH)(NO^+)(NO^\bullet)(PPh_3)_2]BF_4$	1870 (nujol)	1665 (nujol)	-	42
$[Ru^{II}C1(NO^+)(NO^\bullet)(PPh_3)_2]PF_6$	1845	1687	-	43
$Na_2[Ru^{II}(NO^+)(NO_2)_4(OH)]$	1893	-	-	44
$[Ru^{II}(NO^+)(NH_3)_4(OH)]Cl_2$	1834	-		

Table S2

Q = 4,6-di-*tert*-butyl-*N*-phenyl-*o*-iminobenzoquinone
py = pyridine
trpy = 2,2′:6′,2″-terpyridine
bik = 2,2′-bis(1-methylimadazolyl)ketone
$H_2(OMe)_2bQb$ =



Thnl = thionol
Seln = selenophore
H_2Me_2bpb =



Resf = Resorufin
bpym = 2,2′-bipyrimidine
pip = 2-Phenylimidazo[4,5-*f*]1,10-phenanthroline
TPP^{2-} = *meso*-tetraphenylporphyrin dianion
OEP^{2-} = octaethylporphyrin dianion
pdt = 5,6-diphenyl-3-pyridyl-as-triazine
$SBPy_3$ = *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine
Py_3PH_2 = *N,N*-bis(2-(2-pyridyl)ethyl)pyridine-2,6-dicarboxamide
$PaPy_3H$ = *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-carboxamide
$Papy_2QH$ = *N, N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-quinaldine-2-carboxamide
4-vpy = 4-vinylpyridine
bpy = 2,2′-bipyridine
tpm = tris(1-pyrazolyl)methane
dpk = 2,2′-dipyridyl ketone
bpz = 2,2′-bipyrazine
TTP^{2-} = *meso*-tetratolylporphyrinato dianion
Salen = *N*, *N*′-bis-(salicylidene)ethylenediaminate
$hedta^{3-}$ = *N*-(hydroxyethyl)ethylenediaminetriacetate
$FTTP^{2-}$ = [tetra(*m*-trifluoromethylphenyl)porphyrin
Cp = cyclopentadienyl
diphos = 1,2-bis(diphenylphosphino)ethane

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