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Stabilization of $\{RuNO\}^6$ and $\{RuNO\}^7$ States in $[Ru^{II}(trpy)(bik)(NO)]^{n+}$ {trpy = 2,2′:6′,2′′-terpyridine, bik = 2,2′-bis(1-methylimidazolyl) ketone} – Formation, Reactivity, and Photorelease of Metal-Bound Nitrosyl

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Ruthenium nitrosyl complexes have been isolated in the $\{RuNO\}^6$ and $\{RuNO\}^7$ configurations, employing the following reaction pathway for $[Ru(trpy)(bik)(X)]^{n+}$: X = Cl^-, [1](ClO_4) → X = CH_3CN, [2]$(ClO_4)_2$ → X = NO_2^-, [3](ClO_4) → X = NO^+, [4]$(ClO_4)_3$ → X = $NO^\cdot$, [4]$(ClO_4)_2$. The single-crystal X-ray structures of [1](ClO_4)·(C_6H_6)·H_2O, [2]$(ClO_4)_2$·H_2O, and [3](ClO_4)·H_2O have been determined. The successive $NO^+/NO^\cdot$ (reversible) and $NO^\cdot/NO^-$ (irreversible) reduction processes of $[4]^{3+}$ appear at +0.36 and –0.40 V vs. SCE, respectively. While the ν(C=O) frequency of the bik ligand at about 1630 cm^{-1} is largely invariant on complexation and reduction, the ν(NO) frequency for the $\{RuNO\}^6$ state in $[4]^{3+}$ at 1950 cm^{-1} shifts to about 1640 cm^{-1} on one-electron reduction to the $\{RuNO\}^7$ form in $[4]^{2+}$, reflecting the predominant $NO^+ \rightarrow NO^\cdot$ character of this electron transfer. However, a sizeable contribution from ruthenium with its high spin-orbit coupling constant to the singly occupied molecular orbital (SOMO) is apparent from the enhanced g anisotropy in the EPR spectrum $[4]^{2+}$ ($g_1 = 2.015$, $g_2 = 1.995$, $g_3 = 1.881$; $g_{av} = 1.965$; $\Delta g = 0.134$). The $\{RuNO\}^6$ unit in $[4]^{3+}$ reacts with OH^- via an associatively activated process ($\Delta S^\# = -126.5 \pm 2\ J\,K^{-1}\,mol^{-1}$) with a second-order rate constant of $k = 3.3 \times 10^{-2}\ M^{-1}\,s^{-1}$, leading to the corresponding nitro complex $[3]^+$. On exposure to light both $\{RuNO\}^6$ and $\{RuNO\}^7$ in $[4]^{3+}$ and $[4]^{2+}$ undergo Ru–NO photocleavage in CH_3CN via the formation of $[Ru(trpy)(bik)(CH_3CN)]^{2+}$, $[2]^{2+}$. The rate of photocleavage of the $Ru^{II}–NO^+$ bond in $[4]^{3+}$ (k_{NO}, $8.57 \times 10^{-1}\ s^{-1}$, $t_{1/2} = 0.80$ s) is found to be much faster than that of the $Ru^{II}–NO^\cdot$ bond in $[4]^{2+}$, [$k_{NO^\cdot}$, $5.45 \times 10^{-4}\ s^{-1}$, $t_{1/2}$ = 21.2 min (= 1272 s)]. The photoreleased nitrosyl can be trapped as an *Mb*-NO adduct.

Introduction

The nitrosyl ligand can exist as cationic NO^+, as radical $NO^\cdot$, or as anionic NO^-, depending on the electronic properties of the metal and of the co-ligands of a complex.[1] This redox-noninnocent feature of coordinated nitrosyl makes it attractive from the broader perspective of inorganic chemistry.[2] Moreover, the relevance of NO in biological processes such as its role in neuro-signaling,[3] cardiovascular control,[4] or in defense mechanisms against microorganisms and tumor cells[5] prompted an intense renewed research interest towards nitrosyl coordination chemistry. Therefore, research activities on newly designed metal-nitrosyl species (L){M–NO} have grown extensively in recent years with the primary emphasis in the following directions: (a) preferential stabilization of one or more redox states of nitric oxide, NO^+, $NO^\cdot$, or NO^-, in metal complexes and subsequent exploration of the intriguing bonding features of M–NO,[6] (b) mechanistic aspects of the interaction between suitable nucleophiles and the electrophilic $M–NO^+$ center[7] as well as the reaction of dioxygen with $M–NO^\cdot$ in order to probe biological autoxidation processes of free $NO^\cdot$,[8] and (c) designing of (L){M–NO} species that are capable of delivering free NO to biological targets under mild photolytic conditions, e.g. within attempts to improve photodynamic therapy (PDT).[9]

The present work originates from our continuing research interest[10] in exploring the aforesaid features of the coordinated nitrosyl function, using the new ruthenium nitrosyl complex $[Ru(trpy)(bik)(NO)]^{n+}$ ($n = 3$, $[4]^{3+}$ with $\{RuNO\}^6$ and $n = 2$, $[4]^{2+}$ with $\{RuNO\}^7$; trpy = 2,2′:6′,2′′-terpyridine) where bik represents 2,2′-bis(1-methylimidazolyl) ketone, a chelate ligand containing electron-rich N-donor heterocycles as well as an electron-withdrawing carbonyl function. The use of bik as a co-ligand would allow for a monitoring by IR spectroelectrochemistry of the well-defined $\nu_{C=O}$ band as a function of the electron-transfer

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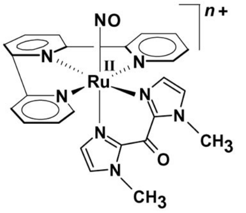
status in addition to the standard observation of ν_{NO} in $[\mathbf{4}]^{3+}$. The present article describes the synthesis of nitrosyl complex ions $[Ru(trpy)(bik)(NO^+)]^{3+}$ $[\mathbf{4}]^{3+}$ and $[Ru(trpy)(bik)(NO^{\cdot})]^{2+}$ $[\mathbf{4}]^{2+}$ along with that of the precursors $[Ru(trpy)(bik)(Cl)]^+$ $[\mathbf{1}]^+$, $[Ru(trpy)(bik)(CH_3CN)]^{2+}$ $[\mathbf{2}]^{2+}$, $[Ru(trpy)(bik)(NO_2)]^+$ $[\mathbf{3}]^+$, including crystal structures of $[\mathbf{1}]ClO_4$, $[\mathbf{2}](ClO_4)_2$, and $[\mathbf{3}]ClO_4$, and spectroscopic as well as electrochemical properties. Moreover, the reactivities of $[\mathbf{4}]^{3+}$ ($\{RuNO\}^6$) towards the nucleophile OH^-, of $[\mathbf{4}]^{3+}$ ($\{RuNO\}^6$)/$[\mathbf{4}]^{2+}$ ($\{RuNO\}^7$) towards O_2, and the photocleavage of the Ru–NO bond in $[\mathbf{4}]^{3+}$ and $[\mathbf{4}]^{2+}$ have been explored.



$\mathbf{4}^{n+}$ ($NO^+ \rightarrow \mathbf{4}^{3+}$; $NO^{\bullet} \rightarrow \mathbf{4}^{2+}$)

Although a large number of reports is available on metal complexes of bik from varying perspectives,[11] only two reports of Ru-bik complexes are available so far, involving $[(\mu\text{-tppz})\{Ru(bik)Cl\}_2]^{n+}$ and $[(tppz)Ru(bik)Cl]^{n+}$ {tppz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine},[12] and $[Ru(PPh_3)_2(CO)(H)(bik)]BF_4$.[13] The bik ligand in the former set of complexes was specifically introduced to monitor IR spectroelectrochemically the change in the $\nu_{C=O}$ frequency of the coordinated bik on ruthenium and tppz-based electron-transfer processes.[12]

Results and Discussion

Synthesis and Characterization

Complexes with NO in the $\{RuNO\}^6$ and $\{RuNO\}^7$ states, $[Ru(trpy)(bik)(NO)](ClO_4)_3$ = $[\mathbf{4}](ClO_4)_3$ and $[Ru(trpy)(bik)(NO)](ClO_4)_2$ = $[\mathbf{4}](ClO_4)_2$, respectively, have been prepared in a stepwise manner starting from $[Ru(trpy)(bik)(Cl)](ClO_4)$ = $[\mathbf{1}](ClO_4)$ → $[Ru(trpy)(bik)(CH_3CN)](ClO_4)_2$ = $[\mathbf{2}](ClO_4)_2$ → $[Ru(trpy)(bik)(NO_2)](ClO_4)$ = $[\mathbf{3}](ClO_4)$ → $[Ru(trpy)(bik)(NO)](ClO_4)_3$ = $[\mathbf{4}](ClO_4)_3$ → $[Ru(trpy)(bik)(NO)](ClO_4)_2$ = $[\mathbf{4}](ClO_4)_2$ (see Exp. Sect.). The direct synthesis of $[Ru(trpy)(bik)(NO)]^{3+}$ either from $[Ru(trpy)(bik)Cl]^+$ or $[Ru(trpy)(bik)(CH_3CN)]^{2+}$ by using either NO gas, $[NO]BF_4$ or $[NO]PF_6$ was not successful. The reduced complex $[Ru(trpy)(bik)(NO)](ClO_4)_2$ = $[\mathbf{4}](ClO_4)_2$ can be prepared from $[\mathbf{4}](ClO_4)_3$ using hydrazine hydrate as a reducing agent or via electrochemical reduction. Electrochemically generated $[\mathbf{4}]^{2+}$ can be quantitatively reoxidized to $[\mathbf{4}]^{3+}$.

The diamagnetic complexes $[\mathbf{1}](ClO_4)$, $[\mathbf{2}](ClO_4)_2$, $[\mathbf{3}](ClO_4)$, $[\mathbf{4}](ClO_4)_3$, and the paramagnetic species $[\mathbf{4}](ClO_4)_2$ exhibit 1:1, 1:2, 1:1, 1:3, and 1:2 conductivities, respectively, and give satisfactory microanalytical data (see Exp. Sect.). The electrospray mass spectra of $[\mathbf{1}](ClO_4)$, $[\mathbf{2}](ClO_4)_2$, $[\mathbf{3}](ClO_4)$, $[\mathbf{4}](ClO_4)_3$, and $[\mathbf{4}](ClO_4)_2$ in CH_3CN show molecular ion peaks centered at m/z = 560.10, 624.19, 571.02, 753.04, and 623.87, respectively, corresponding to $\{[\mathbf{1}](ClO_4)\text{-}ClO_4\}^+$ (calculated molecular mass: 560.05), $\{[\mathbf{2}](ClO_4)_2\text{-}ClO_4\text{-}CH_3CN\}^+$ (calculated molecular mass: 624.03), $\{[\mathbf{3}](ClO_4)\text{-}ClO_4\}^+$ (calculated molecular mass: 571.08), $\{[\mathbf{4}](ClO_4)_3\text{-}ClO_4\}^+$ (calculated molecular mass: 752.98), and $\{[\mathbf{4}](ClO_4)_2\text{-}ClO_4\text{-}NO\}^+$ (calculated molecular mass: 624.03), respectively (Figure S1). The reduced complex $[\mathbf{4}](ClO_4)_2$ shows a magnetic moment of μ = 1.92 B.M. at 298 K in the solid state, corresponding to one unpaired electron (S = 1/2).

The molecular structures of three crystallized precursor compounds $[\mathbf{1}](ClO_4)\cdot H_2O\cdot C_6H_6$, $[\mathbf{2}](ClO_4)_2\cdot H_2O$, and $[\mathbf{3}](ClO_4)\cdot H_2O$ are shown in Figures S2, S3 and Figure 1, respectively. Selected bond lengths and angles are listed in Table 1. The tridentate trpy ligand binds to the ruthenium ion in the meridional mode and the resulting stereochemical constraints are reflected in the small trpy-involving *trans* angles N(5)–Ru–N(7) of about 159.5°. The other two *interligand trans* angles, N(6)–Ru–N(1) and N(3)–Ru–Cl(1)/N(3)–Ru–N(8), are close to 180° for all the three complexes (Table 1). The bik ligand binds with the ruthenium ion through the sp^2-hybridized N(1) and N(3) imine nitrogen donors of the *N*-methylimidazole rings, forming six-membered chelate rings with bite angles of about 87°. The coordinated bik ligand is slightly nonplanar and the dihedral angles between the two *N*-methylimidazole rings of bik are 9.44, 5.99, and 6.66°, in $[\mathbf{1}](ClO_4)$, $[\mathbf{2}](ClO_4)_2$, and $[\mathbf{3}](ClO_4)$, respectively. Ru–N(5,6,7)(trpy), Ru–Cl, and Ru–N(8)(NO_2) distances match well with those of analogous complexes.[14,10a–10f] The Ru–N(6) distance (central trpy nitrogen) of about 1.95 Å is substantially shorter than the corresponding Ru–N(5)/(7) (terminal trpy N) distances of >2.05 Å. Consequently, the Ru–N(1)(bik) distances [*trans* to Ru–N(6), central trpy nitrogen] of 2.084(2), 2.076(6), and

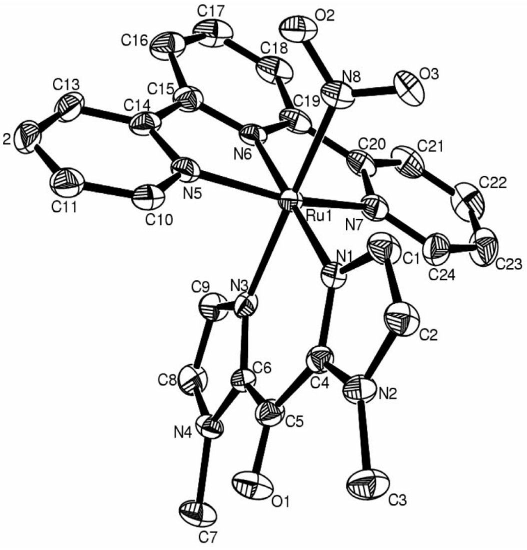


Figure 1. Molecular structure of $[Ru(trpy)(bik)(NO_2)]^+$ in the crystal of $[\mathbf{3}](ClO_4)\cdot H_2O$. Ellipsoids are drawn at 50% probability.

2.100(2) Å in [**1**](ClO_4), [**2**](ClO_4)$_2$, and [**3**](ClO_4), respectively, are longer than the Ru–N(3)(bik) distances of 2.053(2), 2.059(5), and 2.086(2) Å. The intraligand bond parameters of coordinated bik and the bond parameters involving Ru and bik agree with those of [Ru(PPh_3)$_2$(H)(CO)(bik)]BF_4,[13] the only other reported crystal structure of a Ru-bik complex.

Table 1. Selected bond lengths [Å] and bond angles [°].

	[**1**](ClO_4)·C_6H_6·H_2O (X = Cl)	[**2**](ClO_4)$_2$·H_2O (X = N8, CH_3CN)	[**3**](ClO_4)·H_2O (X = N8, NO_2)
Ru–X	2.4058(7)	2.037(6)	2.013(2)
Ru–N(1)	2.084(2)	2.076(6)	2.100(2)
Ru–N(3)	2.053(2)	2.059(5)	2.086(2)
Ru–N(5)	2.059(2)	2.099(5)	2.057(3)
Ru–N(6)	1.943(2)	1.947(5)	1.956(3)
Ru–N(7)	2.059(2)	2.103(5)	2.075(3)
C(5)–O(1)	1.230(4)	1.224(8)	1.222(4)
N(8)–C(25)	–	1.119(9)	–
N(8)–O(2)	–	–	1.254(3)
N(8)–O(3)	–	–	1.256(3)
N(1)–Ru–N(3)	86.92(9)	86.8(2)	87.01(9)
N(1)–Ru–N(5)	100.64(9)	100.8(2)	98.82(10)
N(1)–Ru–N(6)	179.45(10)	178.4(2)	178.70(10)
N(1)–Ru–N(7)	99.86(9)	99.5(2)	101.60(10)
N(3)–Ru–N(5)	92.83(9)	90.43(19)	89.54(10)
N(3)–Ru–N(6)	93.19(9)	94.8(2)	93.78(10)
N(3)–Ru–N(7)	89.70(9)	90.4(2)	90.01(9)
N(5)–Ru–N(6)	79.89(10)	79.1(2)	80.17(10)
N(5)–Ru–N(7)	159.44(10)	159.7(2)	159.53(10)
N(6)–Ru–N(7)	79.60(10)	80.6(2)	79.44(10)
N(1)–Ru–X	92.37(6)	93.3(2)	93.50(10)
N(3)–Ru–X	178.67(7)	179.6(2)	178.67(10)
Ru–N(8)–C(25)	–	172.0(6)	–
Ru–N(8)–O(2)	–	–	120.4(2)
Ru–N(8)–O(3)	–	–	122.0(2)

Spectroscopic Aspects

The ^1H NMR spectra of the diamagnetic complexes in $(CD_3)_2SO$ (Figure S4 and Exp. Sect.) display multiple peaks in the range of 2–9 ppm. Slight variation in chemical shift values is observed on moving from [**1**]$^+$ → [**2**]$^{2+}$ → [**3**]$^+$ → [**4**]$^{3+}$ due to the different electronic nature of the monodentate sixth ligand (Cl^-, CH_3CN, NO_2^-, NO^+). Eleven aromatic signals from the coordinated trpy appear as overlapping doublets or triplets. The four "aromatic" proton resonances of coordinated bik appear well separated due to the different positions of the N-methylimidazole rings; the two N–Me signals appear between 4.3–3.9 ppm. The free bik ligand exhibits ^1H NMR signals at δ = 3.89, 7.51, and 7.12 ppm in $(CD_3)_2SO$, indicating a moderate coordination shift.

The IR vibrational data involving ClO_4^-, CO(bik), and NO vibrations are given in the Experimental Section. The typical Ru–NO_2 frequencies of [**3**](ClO_4) appear at 1331 cm^{-1}(asymmetric) and 1288 cm^{-1}(symmetric).[15] The $\nu_{C=O}$ band of bik and the perchlorate bands remain mostly invariant in the complexes; effects of coordination or reduction are small, in agreement with predominantly NO-centered electron transfer. Notably, the $\nu_{C=O}$ frequency of coordinated bik in [**4**](ClO_4)$_3$ is somewhat shifted to higher energy (1660 cm^{-1}, the value for free bik: 1633 cm^{-1}) in the solid; this shift is not observed in solution or on reduction.

The ν_{NO} stretching frequency of about 1950 cm^{-1} of [**4**](ClO_4)$_3$ ({RuNO}^{6}) suggests an electrophilic character of the coordinated NO^+ group, as observed earlier in an analogous complex with 2,2′-dipyridyl ketone (ν_{NO} frequency at 1949 cm^{-1}).[10d] On reduction of [**4**]$^{3+}$ to [**4**]$^{2+}$ ({RuNO}^{7}), the ν_{NO} band is substantially shifted by about 300 cm^{-1} (Figure 2). Such a large decrease signifies[6] predominantly NO-centered reduction, leading from NO^+ to the $NO^{\cdot}$ state in [**4**]$^{2+}$, which is often but not always[16] associated with a change in the geometry from linear M–NO^+ {MNO}^{6} to bent M–$NO^{\cdot}$ {MNO}^{7}.[6c,10f]

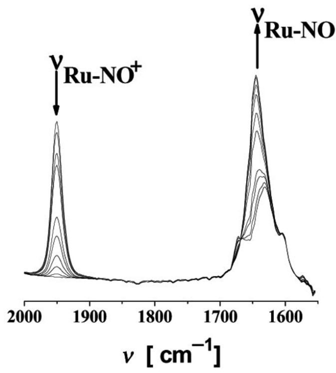


Figure 2. IR spectral changes for the conversion [**4**]$^{3+}$ → [**4**]$^{2+}$ from OTTLE spectroelectrochemistry in CH_3CN/0.1 M Bu_4NPF_6 with stepwise variation of the potential.

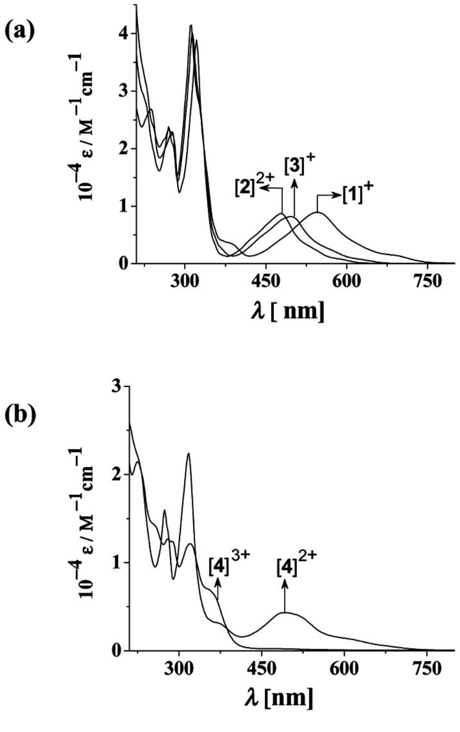


Figure 3. Electronic spectra of (a) [**1**](ClO_4), [**2**](ClO_4)$_2$, and [**3**](ClO_4) and (b) [**4**](ClO_4)$_3$ and [**4**](ClO_4)$_2$ in CH_3CN.

Ruthenium(II)-based MLCT transitions and intraligand absorptions of the complexes appear in the visible and UV regions (Figure 3<yigr3 pos="x22">, Exp. Sect.). The wavelength of the main MLCT transition varies systematically with the change in ligand field strength of the monodentate ligand in $\{Ru^{II}(trpy)(bik)(X)\}$, X = Cl^-, 547 nm > $NO^{\cdot}$, 504 nm > NO_2^-, 492 nm > CH_3CN, 480 nm > NO^+, 364 nm.[17] The increase in MLCT energy on going from the NO_2^- complex ($[\mathbf{3}]^+$, 20325 cm^{-1}) to the NO^+ compound ($[\mathbf{4}]^{3+}$, 27470 cm^{-1}) implies strong $d\pi(Ru^{II}) \rightarrow \pi^*(NO^+)$ back-bonding in $[\mathbf{4}]^{3+}$.

Redox Properties and EPR

The sensitivity of the Ru^{II} state towards oxidation depends on the monodentate ligand $\{Ru(trpy)(bik)X\}$: X = Cl^- ($[\mathbf{1}]^+$) < NO_2^- ($[\mathbf{3}]^+$) < CH_3CN ($[\mathbf{2}]^{2+}$) < NO^+($[\mathbf{4}]^{3+}$), order of increasing Ru^{II} stability (Figure 4, Table 2). This is due to the combined effects from the ligand field strength of X and the electrostatic factor resulting from the overall charge of the complex ions.[18] The mostly irreversible reductions of the bik and trpy acceptor ligands appear in the range of –1.0 to –1.9 V vs. SCE (Table 2).[12,19]

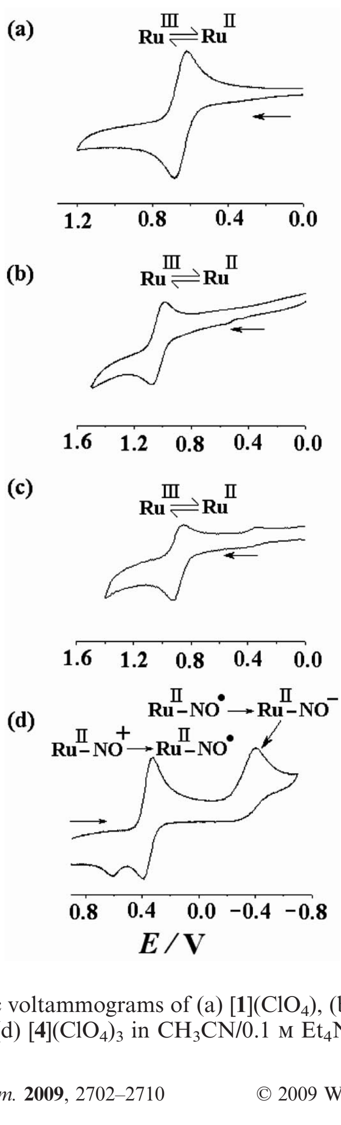


Figure 4. Cyclic voltammograms of (a) $[\mathbf{1}](ClO_4)$, (b) $[\mathbf{2}](ClO_4)_2$, (c) $[\mathbf{3}](ClO_4)$, and (d) $[\mathbf{4}](ClO_4)_3$ in CH_3CN/0.1 M Et_4NClO_4.

Table 2. Redox potentials.[a,b]

Complex	Couple Ru^{III}/Ru^{II}	$NO^+/NO^{\cdot}$	$NO^{\cdot}/NO^-$	bik reduction	trpy reduction
$[\mathbf{1}](ClO_4)$	0.65(60)	–	–	–1.16[c], –1.26[c]	–1.57(90)
$[\mathbf{2}](ClO_4)_2$	1.03(90)	–	–	–1.33[c]	–1.51(200), –1.85(190)
$[\mathbf{3}](ClO_4)$	0.89(80)	–	–	–0.99[c], –1.23(60)	–1.58(170)
$[\mathbf{4}](ClO_4)_3$	>1.9	0.36(65)	–0.40[c]	–1.17[c], –1.26[c]	–1.61(80)

[a] Potentials $E°_{298}$ [V] (ΔE [mV]) vs. SCE. [b] In CH_3CN/0.1 M Et_4NClO_4. Scan rate, 100 mV s^{-1}. [c] Irreversible, cathodic peak potential.

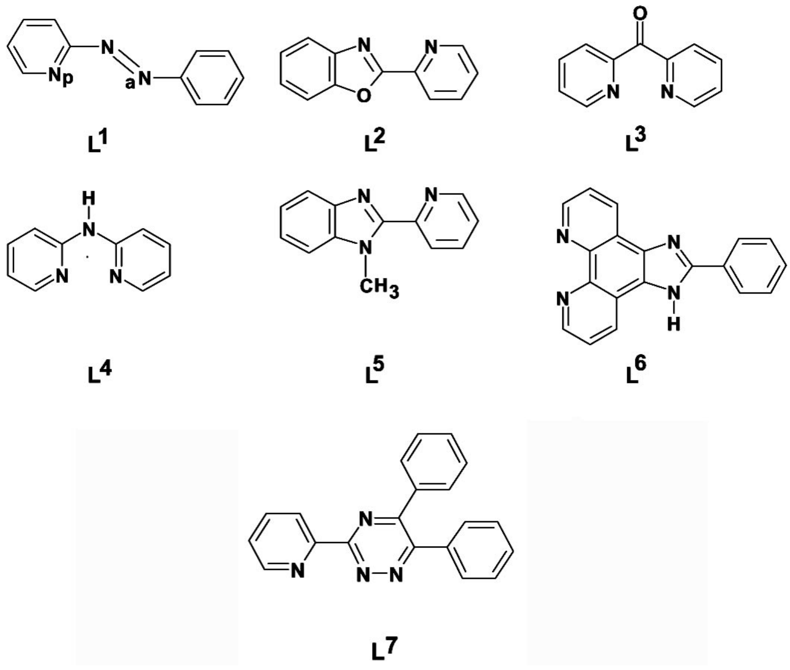
The nitrosyl complex $[\mathbf{4}]^{3+}$ exhibits a reversible NO^+ $\{RuNO\}^6 \rightarrow NO^{\cdot}$ $\{RuNO\}^7$ reduction at 0.36 V, followed by an irreversible reduction corresponding to $NO^{\cdot} \rightarrow NO^-$ at –0.4 V vs. SCE (see part d in Figure 4 and Table 2). The high positive charge associated with $[\mathbf{4}]^{3+}$ and the positive potential have facilitated the isolation of the reduction product $[\mathbf{4}](ClO_4)_2$. The paramagnetic $[\mathbf{4}]^{2+}$ ions exhibit an EPR spectrum typical for $\{RuNO\}^7$ [6h] with g tensor components at g_1 = 2.015, g_2 = 1.995, g_3 = 1.881 ($\langle g \rangle$ = 1.9645; Δg = 0.134[20]) and a nitrogen hyperfine splitting constant $A_2(^{14}N, I = 1)$ of 33 G in CH_3CN at 110 K (Figure S5). As has been similarly discussed for $\{CuNO\}$species,[16] the g anisotropy in the EPR spectrum of $[\mathbf{4}]^{2+}$ arises from the degree of M–N–O bending and from the partial mixing of frontier orbitals from the metal ion with the close lying singly occupied molecular orbital of $NO^{\cdot}$. The data obtained from the simulated EPR spectrum in Figure S5 are compatible with a bend angle of about 150°[6g,16] and with contributions to the SOMO of about 1/3 from the metal ion and 2/3 from the NO group.[6f,6g,10d,10f]

Kinetics of the Reaction Between NO^+ in $[\mathbf{4}]^{3+}$ and OH^-

The nitrosyl complex $[\mathbf{4}]^{3+}$ ($\{RuNO\}^6$) rapidly transforms to the nitro derivative $[\mathbf{3}]^+$ in aqueous solution. Therefore, the reaction of a 10:1 CH_3CN/H_2O mixture with dissolved $[\mathbf{4}]^{3+}$ (0.21×10^{-4} M) with excess aqueous NaOH (0.25×10^{-2} M, pseudo pH ≈ 9.78) was followed spectrophotometrically in the temperature range of 298–318 K under pseudo first-order conditions [Equation (1)] (Figure S6).

$$[Ru^{II}(trpy)(bik)(NO)]^{3+}\ [\mathbf{4}]^{3+} + OH^- \rightarrow [Ru^{II}(trpy)(bik)(NO_2)]^+\ [\mathbf{3}]^+ + H^+ \tag{1}$$

The pseudo first-order rate constant (k [s^{-1}]) values at three different temperatures are determined to be 8.33×10^{-5} (298 K), 1.51×10^{-4} (308 K), and 2.63×10^{-4} (318 K). The plot of pseudo first-order rate constants (k [s^{-1}] in CH_3CN/H_2O (10:1), 298 K) at five different OH^- concentrations shows a linear relation (Figure S6, inset). Therefore, the aforesaid pseudo first-order rate constant values at three different temperatures are divided by the base concentration of 0.25×10^{-2} M to obtain the corre-



Scheme 1.

sponding second-order rate constant values [$k/(\mathrm{M}^{-1}\,\mathrm{s}^{-1})$] of 3.33×10^{-2} (298 K), 6.04×10^{-2} (308 K), and 1.05×10^{-1} (318 K) for the reaction in Equation (1). The computed activation parameters ($\Delta H^{\#}/\Delta S^{\#}$) and equilibrium constant (K at 298 K) values for the reaction in Equation (1) are 43.8 ± 0.6 kJ mol^{-1}/-126.5 ± 2 J K^{-1} mol^{-1}, and 2.9, respectively. The large negative $\Delta S^{\#}$ value of –126.5 J K^{-1} mol^{-1} suggests an associatively activated process.[21]

The second-order rate constant of 3.3×10^{-2} M^{-1} s^{-1} for Equation (1) at 298 K is much lower than those calculated for analogous [Ru(trpy)(L)(NO)]$^{3+}$ complexes in H_2O (Scheme 1, Table 3).[10a–10d] This can be attributed to the effect of the CH_3CN solvent used in the present case instead of using an aqueous medium with OH^- concentrations of ca. 10^{-7} M.[10a–10d] Similar drastic effects of the CH_3CN co-solvent on the second-order rate constant of Equation (1) have been observed earlier in the case of L = L^6 [10f] (Scheme 1, Table 3). The ν(NO) stretching frequencies and the second-order rate constant values of Equation (1) involving the complexes [Ru(trpy)(L)(NO)]$^{3+}$ with different L as set in Table 3 follow an approximately linear relation.

Although an acetonitrile solution of [Ru(trpy)(L^6)(NO)]$^{2+}$ {RuNO}^{7} (L^6 = 2-phenylimidazo[4,5-*f*]1,10-phenanthroline) was susceptible to react with dioxygen in presence of 0.1 M $HClO_4$, leading to the formation of [Ru(trpy)(L^6)(NO)]$^{3+}$ {RuNO}^{6} with a k [s^{-1}] of 5.3×10^{-3} at 298 K,[10f] the present set of nitrosyl complexes with L = bik ([**4**]$^{2+}$ and [**4**]$^{3+}$) was found to be almost inert with respect to the interaction with O_2 even at 333 K, both in H_2O and CH_3CN.

Table 3. Second-order rate constants for the reaction in Equation (1)[a] and the ν(NO$^+$) frequency of the corresponding [Ru(trpy)(L)(NO)]$^{3+}$ complexes.

L	k [M^{-1} s^{-1}]	Solvent	ν(NO$^+$)	Ref.
L^1	6.9×10^5	H_2O	1960	[10a]
L^2	4.7×10^3	H_2O	1957	[10c]
L^3	2.5×10^3	H_2O	1949	[10d]
L^4	1.7×10^3	H_2O	1945	[10b]
L^5	1.1×10^3	H_2O	1932	[10c]
L^6	9.9×10^{-2}	CH_3CN/H_2O (10:1)	1948	[10f]
bik	3.3×10^{-2}	CH_3CN/H_2O (10:1)	1951	this work

[a] As stated in the text.

Photocleavage of the Ru–NO Bond in [4]$^{n+}$ and NO Scavenging by Myoglobin

On exposure to radiation from a 350-W xenon lamp the deoxygenated acetonitrile solution of [Ru^{II}(trpy)(bik)(NO$^{\cdot}$)]$^{2+}$, [**4**]$^{2+}$, undergoes photorelease of NO over a period of ca. 2 h via the selective cleavage of the Ru–NO bond and with concomitant formation of the solvate [Ru(trpy)(bik)(CH_3CN)]$^{2+}$, [**2**]$^{2+}$ (Figure S7). The rate of the first-order photorelease of NO (k_{NO}) has been estimated to be 3.3×10^{-2} min^{-1} (5.45×10^{-4} s^{-1}) with a $t_{1/2}$ of 21.2 min (1272 s) which lies just in between the values reported for the analogous complexes [Ru^{II}(trpy)(L)(NO$^{\cdot}$)]$^{2+}$ with L = L^6 and L^7 (Scheme 1, Table 4).

The feasibility of photolytic Ru–NO cleavage in nonreduced [Ru^{II}(trpy)(L)(NO$^+$)]$^{3+}$ with L = L^6 or L^7 (Scheme 1) was explored earlier, however, both complexes were found to be stable on exposure to light (350-W xenon lamp). However, spontaneous photocleavage of the Ru–NO bond

Table 4. Rates of nitrosyl photorelease and corresponding $t_{1/2}$ values for $[Ru^{II}(trpy)(L)(NO^{\cdot})]^{2+}$ and $[Ru^{II}(trpy)(bik)(NO^+)]^{3+}$ complexes.

$[Ru^{II}(trpy)(L)(NO^{\cdot})]^{2+}$	k_{NO} [min^{-1}]	$t_{1/2}$ [min^{-1}]	Ref.
L = bik	3.3×10^{-2}	21.2	this work
L = L^6	4.4×10^{-3}	157	[10f]
L = L^7	2.0×10^{-1}	3.5	[10e]
$[Ru^{II}(trpy)(bik)(NO^+)]^{3+}$	k_{NO} [s^{-1}]	$t_{1/2}$ [s^{-1}]	Ref.
	8.57×10^{-1}	0.80	this work

takes place on irradiation (350-W xenon lamp) of a degassed acetonitrile solution of $[\mathbf{4}]^{3+}$. This process is accompanied by the formation of the solvate $[\mathbf{2}]^{2+}$. The photocleavage has been monitored spectrophotometrically at 298 K, and the rate of the first-order photorelease (k_{NO}) is estimated at 8.57×10^{-1} s^{-1} with a $t_{1/2}$ of 0.80 s (Figure 5). Therefore, under otherwise identical experimental conditions the photocleavage of the $Ru^{II}–NO^+$ bond in $[\mathbf{4}]^{3+}$ ($\{RuNO\}^6$) is about 1500-times faster as compared to the photocleavage of the Ru–NO$^{\cdot}$ bond in $[\mathbf{4}]^{2+}$ ($\{RuNO\}^7$). Hence, the new molecular framework of $[Ru^{II}(trpy)(bik)(NO)]^{n+}$, $[\mathbf{4}]^{n+}$ extends the feature of photoreleasing NO at quite different rates, depending on the redox state of the coordinated nitrosyl group (NO$^{\cdot}$ or NO$^+$).

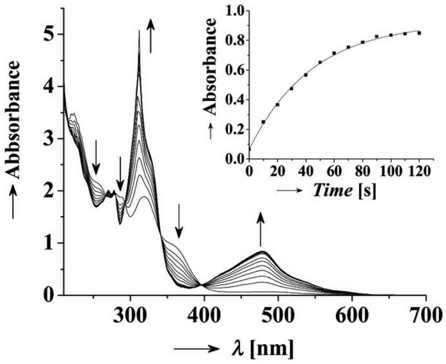


Figure 5. Time evolution of the electronic spectrum (10 s time intervals) of a solution of $[Ru(trpy)(bik)(NO^+)]^{3+}$ $\{[\mathbf{4}](ClO_4)_3$, 0.23×10^{-4} M$\}$ in CH_3CN under the exposure of light (Xe lamp, 350 W). Inset shows the absorbance vs. time plot at 480 nm corresponding to $[\mathbf{2}](ClO_4)_2$.

Liberated NO from photolyzed acetonitrile solutions of $[\mathbf{4}]^{3+}$ or $[\mathbf{4}]^{2+}$ was allowed to pass through an aqueous solution of desoxy-*Mb* which led to spontaneous formation of the *Mb*-NO adduct as evident from the development of a band at λ_{max} = 424 nm, corresponding to the standard absorption of *Mb*-NO (Figure S8).[9,10f,10g]

Conclusions

We have shown in the present work that the "bik" coligand in complex ions $\{(bik)Ru^{II}(trpy)(NO)\}^{n+}$ can easily tolerate both coordinated NO$^+$ $\{RuNO\}^6$ and NO$^{\cdot}$ $\{RuNO\}^7$ redox states. On reduction, the high ν(NO) frequency at about 1950 cm^{-1} shifts by about 300 cm^{-1} to lower frequency while the ν(C=O) frequency does not change much. This implies an electron transfer largely at NO with minor metal contribution, as confirmed by EPR spectroscopic investigation of the Ru^{II}–NO$^{\cdot}$ form. The electrophilic NO$^+$ center in $[\mathbf{4}]^{3+}$ reacts with OH$^-$ to form the structurally characterized Ru–NO_2 derivative $[\mathbf{3}]^+$ through an associatively activated pathway. Interestingly both the Ru–NO$^+$ and Ru–NO$^{\cdot}$ forms in $[\mathbf{4}]^{3+}$ and $[\mathbf{4}]^{2+}$, respectively, undergo photocleavage of the Ru–NO bond on exposure to light, forming the solvate species $[\mathbf{2}]^{2+}$. The photolytic cleavage of the Ru–NO$^+$ bond in the $\{RuNO\}^6$ situation is >1500-times faster than that of the Ru–NO$^{\cdot}$ bond of the$\{RuNO\}^7$ form, a result which requires further investigation of the excited state situations in these redox systems.

Experimental Section

Materials and Instrumentation: The precursor complex Ru(trpy)Cl_3[22] and bik = 2,2′-bis(1-methylimidazolyl) ketone (bik)[23] were prepared as reported. Other chemicals and solvents were reagent grade and used as received. For spectroscopic studies HPLC-grade solvents were used.

Electrical conductivity in solution was checked using a Systronic conductivity bridge 305. Infrared spectra were recorded with a Nicolet spectrophotometer with samples prepared as KBr pellets. ^1H NMR spectra were recorded using a 300-MHz Varian FT spectrometer with $(CD_3)_2SO$ used as solvent. Cyclic voltammetric and coulometric measurements were carried out with a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte and the solution concentration was ca. 10^{-3} M; the scan rate used was 100 mV s^{-1}. A platinum gauze working electrode was used in the coulometric experiments. All electrochemical experiments were carried out under dinitrogen atmosphere. IR spectroelectrochemical studies were performed in CH_3CN/0.1 M Bu_4NPF_6 at 298 K using an optically transparent thin-layer electrode (OTTLE) cell[24] mounted in the sample compartment of a Perkin–Elmer 1760X FTIR instrument. The EPR measurement was made in a two-electrode capillary tube[25] with a X-band Bruker system ESP300. UV/Vis spectral studies were performed with a Perkin–Elmer Lambda 950 spectrophotometer. The elemental analyses were carried out with a Perkin–Elmer 240C elemental analyzer. Electrospray mass spectra were recorded with a Micromass Q-ToF mass spectrometer. Magnetic susceptibility was measured with a CAHN electrobalance 7550.

CAUTION! Perchlorate salts of metal complexes are generally explosive. Care should be taken while handling such complexes.

$[Ru(trpy)(bik)(Cl)](ClO_4)$, $[1](ClO_4)$: A mixture of $[Ru(trpy)Cl_3]$ (100 mg, 0.23 mmol), bik (43 mg, 0.23 mmol), excess LiCl (54 mg, 1.3 mmol) and NEt_3 (0.4 mL) in ethanol (25 mL) was heated at reflux for 5 h under dinitrogen atmosphere. The solvent was removed and the dry residue was redissolved in a minimum volume of acetonitrile followed by addition of excess saturated aqueous solution of $NaClO_4$. The precipitate thus obtained was filtered off and washed several times with ice-cold water. The product was dried in vacuo over P_4O_{10} and purified by using a neutral alumina column. The violet complex $[\mathbf{1}](ClO_4)$ was eluted by 5:1 CH_2Cl_2/CH_3CN. Evaporation of the solvent afforded pure $[\mathbf{1}](ClO_4)$. Yield 102 mg (68 %). $C_{24}H_{21}Cl_2N_7O_5Ru$ (659): calcd. C 43.70, H 3.21, N

14.87; found C 43.51, H 3.18, N 14.76. Molar conductivity [Λ_{M} ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{M}^{-1}$)] in acetonitrile: 120. ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K]: δ = (trpy protons): 8.72 (d, J = 7.8 Hz, 2 H), 8.61 (d, J = 8.1 Hz, 2 H), 8.11 (t, J = 8.1, 7.8 Hz, 1 H), 7.96 (m, 4 H), 7.44 (t, J = 6 Hz, 2 H); (bik protons): 8.53 (s, 1 H), 8.20 (s, 1 H), 7.36 (s, 1 H), 5.86 (s, 1 H), 4.36 (s, 3 H, N-CH_3), 3.92 (s, 3 H, N-CH_3) ppm. IR (KBr disk): ν_{ClO4^-}, 1080, 624 $\nu_{C=O}$, 1626 cm^{-1}. λ [nm] (ε [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$]) ($CH_3CN$): 547 (9145), 388 (3570), 322 (38670), 276 (23000).

[Ru(trpy)(bik)(CH_3CN)](ClO_4)$_2$, [2](ClO_4)$_2$: [**1**](ClO_4) (100 mg, 0.15 mmol) was taken in a 1:1 (v/v) mixture of CH_3CN/H_2O (25 mL) and heated to reflux for 10 min. An excess of $AgNO_3$ (258 mg, 1.52 mmol) was added to the hot solution and the heating was continued for 5 h. It was then cooled to 298 K and the precipitated AgCl separated by filtration through a sintered glass crucible (G-4). The volume of the filtrate was reduced to 10 mL, and an excess saturated aqueous solution of $NaClO_4$ was added. The solid [**2**](ClO_4)$_2$ thus obtained was filtered off and washed thoroughly with ice-cold water. The product was dried in vacuo over P_4O_{10}. Yield 76 mg (66 %). $C_{26}H_{24}Cl_2N_8O_9Ru$ (764.01): calcd. C 40.85, H 3.16, N 14.66; found C 40.74, H 3.20, N 14.52. Molar conductivity [Λ_{M} ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{M}^{-1}$)] in acetonitrile: 210. ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K]: δ = (trpy protons): 8.84 (d, J = 8.1 Hz, 2 H), 8.71 (d, J = 8.1 Hz, 2 H), 8.36 (t, J = 8.1 Hz, 1 H), 8.12 (d, J = 6.9 Hz, 2 H), 7.97 (d, J = 5.1 Hz, 2 H), 7.56 (t, J = 6.3, 6 Hz, 2 H); (bik protons): 8.31 (s, 1 H), 8.11 (s, 1 H), 7.46 (s, 1 H), 5.91 (s, 1 H), 4.34 (s, 3 H, N-CH_3), 3.94 (s, 3 H, N-CH_3) ppm. IR (KBr disk): ν_{ClO4^-}, 1088, 625; $\nu_{C=O}$, 1632 cm^{-1}. λ [nm] (ε [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$]) ($CH_3CN$): 480 (8880), 327 (27140), 312 (41780), 278 (23000), 270 (23380).

[Ru(trpy)(bik)(NO_2)](ClO_4), [3](ClO_4): [**2**](ClO_4)$_2$ (100 mg, 0.13 mmol) was dissolved in hot water (25 mL) and an excess of $NaNO_2$ (206 mg, 2.98 mmol) was added. The mixture was heated to reflux for 6 h. The pure crystalline nitro complex precipitated out on cooling the solution at room temperature. The solid [**3**](ClO_4) thus obtained was filtered off, washed with ice-cold water, and dried in vacuo over P_4O_{10}. Yield 63 mg (72 %). $C_{24}H_{21}ClN_8O_7Ru$ (670.03): calcd. C 42.98, H 3.16, N 16.72; found C 43.01, H 3.15, N 16.95. Molar conductivity [Λ_{M} ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{M}^{-1}$)] in acetonitrile: 105. ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K]: δ = (trpy protons): 8.73 (d, J = 8.1 Hz, 2 H), 8.61 (d, J = 8.1 Hz, 2 H), 8.22 (t, J = 8.1 Hz, 1 H), 8.02 (t, J = 7.8, 8.1 Hz, 2 H), 7.94 (d, J = 5.4 Hz, 2 H), 7.50 (t, J = 6.6, 6.3 Hz, 2 H); (bik protons): 8.18 (s, 1 H), 7.99 (s, 1 H), 7.41 (s, 1 H), 5.89 (s, 1 H), 4.31 (s, 3 H, N-CH_3), 3.92 (s, 3 H, N-CH_3) ppm. IR (KBr disk): ν_{ClO4-}, 1082, 623; $\nu_{C=O}$, 1633 cm^{-1}. λ [nm] (ε [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$]) ($CH_3CN$): 492 (8365), 314 (40220), 279 (20800), 269 (23510).

[Ru(trpy)(bik)(NO)](ClO_4)$_3$, [4](ClO_4)$_3$: Nitric acid (2 mL) was added dropwise to the solid [**3**](ClO_4) (100 mg, 0.15 mmol) whilst stirring at 273 K. The resultant pasty mass was slowly mixed with ice-cold $HClO_4$ (5 mL) whilst stirring. Subsequently, saturated aqueous $NaClO_4$ solution was added which resulted in a yellowish solid product. The precipitate was filtered off immediately, washed with a little ice-cold water, and then dried in vacuo over P_4O_{10}. Yield 99.17 mg (78 %). $C_{24}H_{21}Cl_3N_8O_{14}Ru$ (851.93): calcd. C 33.81, H 2.48, N 13.15; found C 33.91, H 2.55, N 13.05. Molar conductivity [Λ_{M} ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{M}^{-1}$)] in acetonitrile: 320. ^{1}H NMR [300 MHz, $(CD_3)_2SO$, 298 K]: δ = (trpy protons): 9.16 (d, J = 7.5 Hz, 2 H), 9.06 (m, 3 H), 8.59 (t, J = 8.1, 6.9 Hz, 2 H), 8.28 (d, J = 4.8 Hz, 2 H), 7.92 (t, J = 7.2 Hz, 2 H); (bik protons): 8.47 (s, 1 H), 8.32 (s, 1 H), 7.71 (s, 1 H), 6.15 (s, 1 H), 4.30 (s, 3 H, N-CH_3), 3.93 (s, 3 H, N-CH_3) ppm. IR (KBr disk): ν_{ClO4^-}, 1092, 624; $\nu_{C=O}$, 1660; ν_{NO}, 1951 cm^{-1}. IR (CH_3CN/0.1-M Bu_4NPF_6): $\nu_{C=O}$, 1635, 1662sh; ν_{NO}, 1950 cm^{-1}. λ [nm] (ε [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$]) ($CH_3CN$): 364 (6550), 320 (12130), 290 (12510), 278 (12640), 258 (13930).

[Ru(trpy)(bik)(NO)](ClO_4)$_2$, [4](ClO_4)$_2$: Excess hydrazine hydrate was added to an acetonitrile solution (5 mL) of [**4**](ClO_4)$_3$ (100 mg, 0.12 mmol) and the solution was stirred for 0.5 h under a dinitrogen atmosphere. The yellow solution immediately changed to red-brown. On removal of the solvent a dark solid residue was obtained which was washed with a little ice-cold water and then dried in vacuo over P_4O_{10}. Yield 61 mg (69 %). $C_{24}H_{21}Cl_2N_8O_{10}Ru$ (752.98): calcd. C 38.25, H 2.81, N 14.88; found C 38.39, H 2.84, N 14.77. Molar conductivity [Λ_{M} ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{M}^{-1}$)] in acetonitrile: 215. Magnetic moment, μ (B.M.) at 298 K: 1.92. IR (KBr disk): ν_{ClO4^-}, 1086, 625; $\nu_{C=O}$, 1630; ν_{NO}, 1630 cm^{-1} [broad band involving ν_{CO} and ν_{NO} ($\pm$15 cm^{-1})]. IR (CH_3CN/0.1-M Bu_4NPF_6): $\nu_{C=O}$, 1650; ν_{NO}, 1650 cm^{-1} [broad band involving ν_{CO} and ν_{NO} ($\pm$15 cm^{-1})]. λ [nm] (ε [$\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$]) ($CH_3CN$): 504 (4220), 374 (3060), 316 (22470), 280 (13800), 273 (15870).

Kinetic Measurements: In order to determine the rate constant (k) for the conversion process of [Ru^{II}(trpy)(bik)(NO^+)]$^{3+}$ ([**4**]$^{3+}$, 0.21×10^{-4} M) $\rightarrow$ [Ru^{II}(trpy)(bik)(NO_2)]$^+$ ([**3**]$^+$) in acetonitrile/water (10:1) in the presence of aqueous NaOH (0.25×10^{-2} M; pH $\approx$ 9.78), the increase in absorbance (A_t) at 492 nm corresponding to λ_{max} of the nitro complex [**3**]$^+$ was monitored as a function of time (t) at three different temperatures (298, 308, 318 K). A_α was measured when the intensity changes leveled off. The pseudo first-order rate constant (k [s^{-1}]) at each temperature was obtained from the slope of linear least-squares plot of $-\ln(A_\alpha - A_t)$ against t. The same procedures were followed for the determination of k [s^{-1}] at different [OH^{-1}]. The activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ were determined from the Eyring plot.[26]

The first-order rate constant value (k, [s^{-1}]) for the nitrosyl photorelease from [Ru^{II}(trpy)(bik)($NO^{\cdot}$)]$^{2+}$ [**4**]$^{2+}$ or [Ru^{II}(trpy)(bik)(NO^+)]$^{3+}$ [**4**]$^{3+}$ was determined from the single-exponential fitting of the plot of change in absorbance against time under photolysis conditions at λ_{max} = 504 or 480 nm, respectively, in acetonitrile.

Trapping of Photoreleased NO by Myoglobin: Initially an acetonitrile solution (3.0 mL) of [**4**](ClO_4)$_2$ was taken in a quartz cuvette with an optical path length of 1 cm and the cuvette was sealed with a rubber septum. The solution was deoxygenated by purging with nitrogen gas followed by photolysis for 2 h using a 350-W xenon lamp. The photoreleased NO was then passed through the reduced myoglobin solution in water by using a cannula and the UV/Vis spectrum was recorded.

The same operations were also performed with an acetonitrile solution (3.0 mL) of [**4**](ClO_4)$_3$ but the photolysis was continued only for 2 min.

X-ray Crystallography: Single crystals of [**1**](ClO_4)$\cdot H_2O\cdot C_6H_6$, [**2**](ClO_4)$_2\cdot H_2O$, and [**3**](ClO_4)$\cdot H_2O$ were grown by slow evaporation of their respective 1:1 acetonitrile/benzene and acetonitrile solutions. X-ray data were collected with an OXFORD XCALIBUR-S CCD single-crystal X-ray diffractometer. Selected crystallographic parameters are given in Table 5. The structures were solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 program.[27] The absorption corrections were done by the multi-scan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model. Both the hydrogen atoms of the crystallized water molecule in [**2**](ClO_4)$_2\cdot H_2O$ and one hydrogen atom of the water molecule in [**3**](ClO_4)$\cdot H_2O$ could not be located.

Table 5. Crystallographic data.

	[**1**](ClO_4)·C_6H_6·H_2O	[**2**](ClO_4)$_2$·H_2O	[**3**](ClO_4)·H_2O
Formula	$C_{30}H_{29}Cl_2N_7O_6Ru$	$C_{26}H_{26}Cl_2N_8O_{10}Ru$	$C_{24}H_{23}ClN_8O_8Ru$
M_r	755.06	782.02	688.04
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	8.8109(4)	8.9417(7)	14.1422(8)
b [Å]	12.4209(5)	9.129(5)	15.2143(8)
c [Å]	13.3659(5)	18.899(3)	13.6629(8)
α [°]	84.327(3)	81.622(2)	90
β [°]	78.593(3)	83.40(3)	117.222(7)
γ [°]	86.605(3)	88.904(2)	90
V [Å^3]	1425.66(10)	1516.1(8)	2614.2(3)
Z	2	2	4
μ [mm^{-1}]	0.793	0.764	0.769
T [K]	120(2)	150(2)	120(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.669	1.710	1.746
F(000)	726	788	1388
2θ range [°]	5.84 to 50.00	5.98 to 50.00	5.96 to 50.00
Data / restraints / parameters	5010 / 0 / 398	5325 / 0 / 427	4586 / 0 / 385
R_1 [$I > 2\sigma(I)$]	0.0317	0.0626	0.0322
wR_2 [all data]	0.0699	0.1706	0.0845
GOF	0.967	0.979	1.091
Largest difference peak/hole [e Å^{-3}]	0.485/–0.388	1.301/–1.111	0.511/–0.442

CCDC-715776 {for [**1**](ClO_4)·H_2O·C_6H_6}, -715777 {for [**2**](ClO_4)$_2$·H_2O}, and -715778 {for [**3**](ClO_4)·H_2O} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Mass spectra of [**1**](ClO_4), [**2**](ClO_4)$_2$, [**3**](ClO_4), [**4**](ClO_4)$_3$, [**4**](ClO_4)$_2$ in CH_3CN (Figure S1), ORTEP diagrams of [**1**](ClO_4)·C_6H_6·H_2O (Figure S2) and [**2**](ClO_4)$_2$·H_2O (Figure S3), ^{1}H NMR spectra of **1**$^+$, **2**$^{2+}$, **3**$^+$, **4**$^{3+}$ in $(CD_3)_2SO$ (Figure S4), experimental and simulated EPR spectrum of **4**$^{2+}$ (Figure S5), time-monitored plot of electronic spectra of the progression of the reaction of **4**$^{3+}$ with $OH^–$ (Figure S6), time-monitored plot of electronic spectra of the photocleavage reaction of **4**$^{2+}$ (Figure S7) and absorption spectra of met-*Mb*, reduced *Mb*, and *Mb*-NO adduct in water (Figure S8).

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