Structural, Spectroscopic, and Photochemical Investigation of an Octahedral NO-Releasing {RuNO}^{7} Species

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S *Supporting Information*

ABSTRACT: $[Ru(Me_3[9]aneN_3)(bpy)(NO)](BF_4)_2$ ($[1](BF_4)_2$) was explored by single-crystal X-ray diffractometry, leading to the first crystal structure of an octahedral {RuNO}^{7} complex. The metal resides on the center of a distorted octahedron, with d_{N-O} and $\angle Ru-N-O$ at 1.177(3) Å and 141.6(2)°, respectively. $[1](BF_4)_2$ can be stored indefinitely under argon. Solutions of $[1]^{2+}$ show no signs of decomposition when protected from air and light. The electron paramagnetic resonance X-band spectrum at 85 K in vitrified acetonitrile (MeCN) shows signals consistent with an $S = \frac{1}{2}$ spin state, better described as $Ru^{II}NO^\bullet$ ($g = [2.030, 1.993, 1.880]$ and $A = [11.0, 30.4, 3.9]/10^{-4}$ cm^{-1}). In water, the {RuNO}^{7} species reacts with O_2 in a 1:4 stoichiometry. The reaction is first-order in both reactants with $k = (1.9 \pm 0.2)$ M^{-1} s^{-1} at 25 °C ($\Delta H^\ddagger = 11.5 \pm 0.3$ kJ mol^{-1}; $\Delta S^\ddagger = -189 \pm 1$ J K^{-1} mol^{-1}). Solutions of $[1]^{2+}$ evolve NO when irradiated a 365 nm with $\phi_{NO} = 0.024$ and 0.090 mol einstein^{-1} in H$_2$O and MeCN, respectively.

One-electron redox processes of bound nitrosyl species are involved in the reversible conversions of NO$_2^-$ into NH$_3$ in bacteria, in soils, or in the metabolism of NO in mammals.[1] The consecutive 1e$^-$ redox events that turn NO into the nitrosonium cation (NO$^+$) and the nitroxyl anion (NO$^-$) are likely to require a nitrosyl moiety coordinated to a transition metal center, most likely a Fe^{II} in the active site of a metalloprotein. Early work with pentacoordinated (5C) porphyrins[2] showed that the {MNO}^{6,7,8} (Enemark−Feltham formalism)[3] interconversion was plausible in solution. At the beginnings of the 21st century a combined study based on spectroscopic and DFT computations allowed for the first unequivocal oxidation state assignment of the coordinated nitrosyl in an hexacoordinated (6C) system.[4a] [Fe(cyclam-ac)(NO)]$^{3,2,1+}$ stood for several years as the sole example of a nonheme 6C {MNO} complex with no additional change to the coordination environment except for the NO-centered redox process, until similar achievements with the 5C [Fe(TMG$_3$tren)-(NO)]$^{3,2,1+}$ in an organic medium[4b,c] and the 6C [Ru(Me$_3$[9]-aneN$_3$)(bpy)(NO)]$^{3,2,1+}$ ($[1]^{3,2,1+}$; Me$_3$[9]aneN$_3$ = 1,4,7-tri-

methyl-1,4,7-triazacyclononane; bpy = 2,2′-bipyridine) in water and acetonitrile (MeCN)[4d] were reported. In spite of these successful examples in solution, there is not even a single case of structurally characterized 6C {MNO}^{6,7,8} built upon the same metal and coligand platform.[5] Only two out of the three redox states were simultaneously characterized in the very few and always Fe-based examples.[4a,6] Quite recently, a remarkable case of an {FeNO}^{6,7,8} system, which is 6C for $n = 6$ but 5C for $n = 7,8$, has been fully explored by X-ray crystallography.[7] Following the redox and spectroscopic characterization in solution of the $[1]^{3,2,1+}$ family,[4d] we explored the chemical reduction of $[1]^{3+}$ with iodide in acetone to yield the {RuNO}^{7} species $[1]^{2+}$ isolated and crystallized as a BF$_4^-$ salt (see the SI). $[1](BF_4)_2$ can be handled for short periods under air and indefinitely under argon. This ease of manipulation enables reactivity studies that would have been complicated otherwise. We report here two relevant and only partially understood reactions:[8] the reaction with O$_2$ in water and the photodissociation of NO.

Single crystals of $[1](BF_4)_2$ were obtained by slow diffusion of diethyl ether onto a MeCN solution under argon. The X-ray structure[9] reveals four units of $[1]^{2+}$ and eight BF$_4^-$ anions per unit cell (Figure S1). The Ru^{II} center lies in a distorted octahedron comprised of six N-atoms (Figure 1). The reduction of $[1]^{3+}$ to yield $[1]^{2+}$ results in lengthening of the N−O bond from 1.135(5) to 1.177(3) Å and the Ru−N(2) bond from 2.128(4) to 2.169(2) Å, as well as bending of the Ru−N−O angle from almost linear [172.5(4)°] to 141.6(2)° (Table S2). The
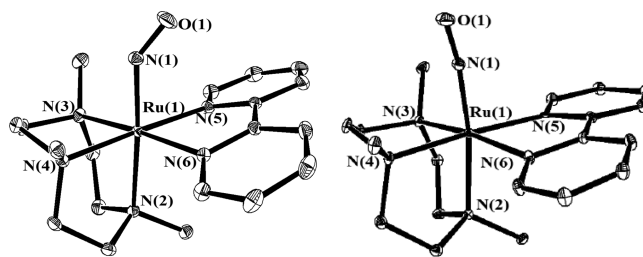

Figure 1. Structure of the cations (30% probability level thermal ellipsoids) in crystals of: left $[1](BF_4)_2$ and (right) $[1](ClO_4)_3$.[4d]

equatorial coligands remain essentially invariable, except for a slight shortening of the Ru−N(5) and Ru−N(6) bondlengths, probably due to the lengthening of the Ru−N(2) bond and a concomitant reduction of the steric interaction between the bpy atoms and the methyl group on the N(2) atom. All these features were nicely predicted by DFT.[4d] The overall changes are compatible with those observed in the very few reported 6C $\{FeNO\}^{6,7}$ systems: $[(PaPy3)Fe(NO)]^{2+/+}$, $[Fe(cyclam-ac)-(NO)]^{3,2,1+}$, and $[Fe(NO)("pyS4")]^{+/0}$ (Table S3).[4a,6] They reflect the simultaneous weakening of the N−O, M−N(O), and M−N(trans) bonds upon reduction. The singly occupied molecular orbital (SOMO) is mostly located in one of the split $\pi^*_{NO\sigma}$ orbitals, partially delocalized over the metal-centered d_{z^2}/d_{xz} orbitals and to a lower degree over the *trans* N atom. The orbital is Ru−NO σ bonding in character and at the same time Ru−N(2) σ antibonding, thus weakening the Ru−L bond trans to the NO. The nature of the SOMO is consistent with the NO stretching frequency variation[10] from $\{MNO\}^6$ to $\{MNO\}^7$ (1898 and 1616 cm^{-1}, respectively; KBr pellets; Figure S2).

In the absence of O_2 and light, solutions of $[\mathbf{1}]^{2+}$ are stable for long periods. The electron paramagnetic resonance (EPR) X-band spectrum at 85 K in frozen MeCN shows signals arising from an $S = {}^1/_2$ spin center with anisotropic g-values and hyperfine coupling with a single ^{14}N nucleus (Figure S3). The spectral profile resembles closely other $\{RuNO\}^7$ systems, described as mostly $Ru^{II}NO^\bullet$ in character.[11] Simulation renders the spin-Hamiltonian parameters $g = [2.030, 1.993, 1.880]$ and $A = [11.0, 30.4, 3.9]/10^{-4}$ cm^{-1}. The rather high value of A_2 indicates that the spin is mostly localized in the vicinity of the N nucleus. The partial delocalization of the spin density on the Ru center ($\zeta_{SO} = 1200$ cm^{-1})[12] induces spin−orbit-mediated mixing with excited states and results in an anisotropic **g** matrix that deviates from the free electron value. The spin-Hamiltonian parameters are within the range reported for other $\{RuNO\}^7$, as expected from their EPR insensitivity.[11]

The autoxidation reaction of NO is relevant not only to environmental chemistry but also to modern aspects of NO-biochemistry.[1c] In the presence of air, solutions of $[\mathbf{1}]^{2+}$ deteriorate within minutes, as revealed by the UV−vis and IR spectral evolution. Studies in the gas phase and nonprotic media reveal that the reaction between free NO and O_2 leads to NO_2 as the main product, while in water, the reaction yields nitrite:[13]

$$4NO^\bullet + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^- \tag{1}$$
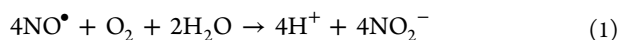
The analogous process involving $\{MNO\}^7$ systems is less explored.[6d,14] The reaction between $[\mathbf{1}]^{2+}$ and an excess of O_2 in water proceeds with well-defined isosbestic points, yielding $[\mathbf{1}]^{3+}$ as the only colored species. The process is first order in $[\mathbf{1}]^{2+}$ (Figure S5). A titration experiment with O_2 is consistent with a consumption ratio of four $[\mathbf{1}]^{2+}$ molecules per O_2 (Figure S6):

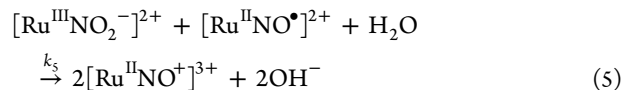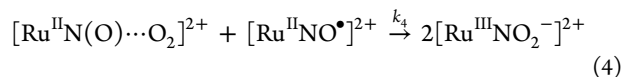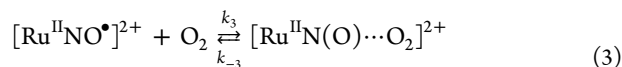$$4[\mathbf{1}]^{2+} + O_2 + 2H_2O \xrightarrow{k_2} 4[\mathbf{1}]^{3+} + 4OH^- \tag{2}$$
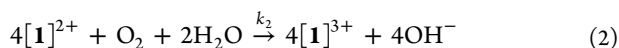
The overall stoichiometry in water differs from the one reported in aprotic media for $\{MNO\}^7$ systems, where the oxidation products were metal(III) nitro complexes.[6d,14c] In our case, the pseudo-first-order rate constant k_{obs} correlates linearly with $[O_2]$, leading to a second-order rate law: $-d[[\mathbf{1}]^{2+}]/dt = 4k_2[[\mathbf{1}]^{2+}][O_2]$, with $k_2 = (1.9 \pm 0.2)$ M^{-1} s^{-1} at 25.0 °C. The activation parameters are $\Delta H^\ddagger = (11.5 \pm 0.3)$ kJ mol^{-1} and $\Delta S^\ddagger = (-189 \pm 1)$ J K^{-1} mol^{-1} (range of 15−40 °C). No evidence of free peroxide, superoxide, nitrate, or other nitrogenated species were found in solution. $[\mathbf{1}]^{2+}$ reacts very slowly with H_2O_2 ($v =$

$(2.8 \pm 0.1) \times 10^{-2}$ M^{-1} s^{-1} $[[\mathbf{1}]^{2+}][H_2O_2]$; $T = 25.0$ °C), precluding peroxide as a possible intermediate. These results agree with our previous kinetic study for the same reaction in $[Fe(CN)_5NO^\bullet]^{3-}$ ($[\mathbf{2}]^{3-}$), $[Ru(NH_3)_5NO^\bullet]^{2+}$ ($[\mathbf{3}]^{2+}$), and $[Ru(bpy)(tpm)NO^\bullet]^{2+}$ ($[\mathbf{4}]^{2+}$; tpm = tris(1-pyrazolyl)-methane).[8a,15] Moreover, a plot of ln k versus $E_{NO^+/NO}$, like the one described in our previous work[8a] for the four above-mentioned complexes (Figure 2a, inset), shows a linear trend
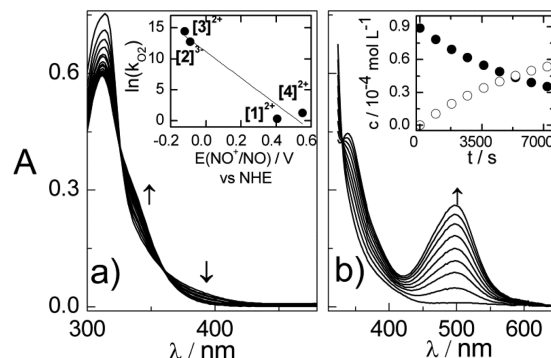
**Figure 2.** (a) Autoxidation of $[\mathbf{1}]^{2+}$ in H_2O, pH = 2.0, I = 1 M (NaCl), T = 25.0 °C. Inset: ln k_{O_2} versus $E_{NO^+/NO}$. (b) Photocleavage of $[\mathbf{1}]^{2+}$ in H_2O, λ_{irr} = 365 nm, pH = 1.9, I = 1 M (CF$_3$SO$_3$Na). Inset: profiles calculated for $[\mathbf{1}]^{2+}$ (●) and $[Ru(solvento)]^{2+}$ (○).

with a negative slope of 21 V^{-1}, in agreement with theoretical predictions based on the Marcus model for outer-sphere electron-transfer reactions, which has been extended to associative processes with inner-sphere character.[16] This correlation suggests that all these complexes should share a common mechanism that requires that the oxidation equivalents remain bound to the reactive species without breaking the metal−N bond. One possibility inspired in the mechanism suggested for the reaction between O_2 and free NO in water,[13] supported by the negative sign of the experimental $\Delta S^\ddagger$ and theory (DFT),[8a] may involve the formation of a NO···O_2 adduct. The mechanism can be resumed in the following equations, where the Enemark−Feltham formalism has been temporarily abandoned for the sake of clarity:

$$[Ru^{II}NO^\bullet]^{2+} + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ru^{II}N(O)\cdots O_2]^{2+} \tag{3}$$

$$[Ru^{II}N(O)\cdots O_2]^{2+} + [Ru^{II}NO^\bullet]^{2+} \xrightarrow{k_4} 2[Ru^{III}NO_2^-]^{2+} \tag{4}$$

$$[Ru^{III}NO_2^-]^{2+} + [Ru^{II}NO^\bullet]^{2+} + H_2O$$
$$\xrightarrow{k_5} 2[Ru^{II}NO^+]^{3+} + 2OH^- \tag{5}$$

Assuming steady state for all of the intermediate species and $k_4[\{MNO\}^7] \gg k_{-3}$, the kinetic rate law reduces to the experimental one when $k_2 = k_3$.

Solutions of $[\mathbf{1}]^{2+}$ (both in H_2O and MeCN) undergo notorious spectral changes when exposed to light (λ_{irr} =365 nm; Figure 2b and S8). The well-defined isosbestic points and the spectral profile of the products indicate a clean conversion of $[\mathbf{1}]^{2+}$ to the metal(II) solvento complex and release of NO with the quantum yield for NO photoliberation $\phi_{NO} = 0.024$ and 0.090 mol einstein^{-1} for H_2O and MeCN, respectively (see the SI). In the absence of O_2, the process can be carried out until virtually 100% conversion without side reactions.

$$[Ru^{II}NO^\bullet]^{2+} \xrightarrow{h\nu} [Ru^{II}(\text{solvento})]^{2+} + NO^\bullet \qquad (6)$$
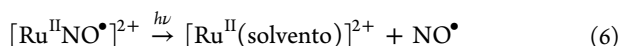
Removal of the light source does not result in regeneration of the $\{RuNO\}^7$ complex, in agreement with the relatively high substitution inertness of the sixth position in the $\{Ru^{II}(Me_3[9]\text{-aneN}_3)(bpy)\}^{2+}$ moiety. The ubiquitous and highly concentration-dependent role of NO in biochemical processes, together with the photochemical reactivity of the $\{MNO\}^6$ species fueled-up the work with nitrosyl transition-metal complexes in medicinal chemistry. The literature is full of examples that show that $\{MNO\}^6$ species photodissociate a neutral NO molecule and form a metal(III) solvento species, as in eq 7.

$$[M^{II}NO^+]^{n+} \xrightarrow{h\nu + H_2O} [M^{III}(OH_2)]^{n+} + NO^\bullet \qquad (7)$$
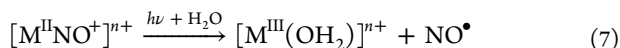
As opposed to the numerous examples with $\{MNO\}^6$ compounds, there seem to be only two reports of photocleavage of NO from $\{MNO\}^7$ species. One investigates the photolysis in water of a $\{RuNO\}^7$ complex generated in situ by electrolysis.[8c] The second reports the photoactivity of a $\{FeNO\}^7$ species in MeCN.[8b,14c] In our system, ϕ_{NO} is comparable to the one reported in the former, cis-$[Ru^{II}(bpy)_2(4\text{-pic})(NO^\bullet)]^{2+}$ [ϕ_{NO} = (0.15 ± 0.03) mol einstein^{-1}].[8c] In this case, photodissociation has been ascribed to a ligand-field state, most probably thermally populated from the lowest-energy $d_\pi(Ru) \rightarrow \pi^*(bpy)$ metal-to-ligand charge-transfer state, as is usually described for other $\{Ru(bpy)_2\}^{2+}$ systems.[17] DFT suggests that the lowest energy quartet excited state in $[\mathbf{1}]^{2+}$ displays weakening and marked elongation of the Ru–N bond from 1.90 to 2.10 Å without charge-transfer to the bpy ligand (Figures S9 and S10). The difference between water and MeCN is probably due to the stabilization of free NO in the less polar medium.

$[\mathbf{1}](BF_4)_2$ might be seen as a novel example of a NO-releasing molecule without the acid–base-related issues displayed by the $\{MNO\}^6$ species, which arise from the well-studied nitrosyl–nitro interconversions.[10] One might envisage its potential as a cage compound for NO photodelivery under biological conditions. Synthetic modifications to red-shift the absorption spectrum and reduce the O$_2$ sensitivity are under development.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00719.

> Complementary experimental details including synthesis, experimental methodology, X-ray crystallographic data collection and refinement, IR and EPR spectra, additional experimental results and DFT computations (PDF)
> X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(9) Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1463223. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (44) 1223 336-033; e-mail deposit@ccdc.cam.ac.uk]. See Table S1 for crystallographic data and the Supporting Information.

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