Redox-Active Ligands

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Discovering More Non-Innocence: Triazenido versus Triazenyl Radical Ligand Function, and a Comment on $[NO_2]^n$ as a "Suspect" Ligand**

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Dedicated to Professor Karl Wieghardt on the occasion of his 70th birthday

There is a striking discrepancy between the redox systems $[NO]^n$ and $[NO_2]^n$ in their interaction with transition metals. In contrast to environmentally and biomedically relevant nitric oxide (NO)[1,2] which was early recognized as the "simplest case of a suspect (=non-innocent[3]) ligand" in coordination chemistry[4] with four established charge forms ($n=+,0,-,2-$[5]) for $[NO]^n$, the textbook nitrogen dioxide[6a] redox system $[NO_2]^n$, $n=+,0,-$, has not attracted the same attention as a potential non-innocently behaving ligand in coordination chemistry. The main focus has rather been on the long recognized (S. M. Jørgensen, A. Werner[6b]) structural alternative, N or O binding, of the nitro/nitrito ligand, NO_2^-.

In the context of $[NO_2]^n$, we now wish to report that the related triazenido redox system $[N(NR)_2]^n$, resulting from the acknowledged relationship $O \hat{=} NR$,[7] can be unambiguously established as a ligand in two forms, $n=-$ and 0, depending on the substituent R. Although triazenido complexes have been studied[8] for example, for stabilizing sensitive metal–organic bonds,[9] their coordination chemistry was described as "less developed" when compared to structurally related analogues containing amidinato or carboxylato ligands.[8b]

Using the $[Ru(bpy)_2]^m$ and $[Ru(Cym)(NCCH_3)]^k$ complex fragments (bpy = 2,2′-bipyridine, Cym = *p*-cymene), we could obtain[10,11] the triazenido ruthenium(II) complexes $[Ru(bpy)_2(RNNNR)]X$, (R = 2-$C_6H_4CF_3$, X = BF_4 (**1**-BF_4), R = 4-C_6H_4OMe, X = BF_4 (**2**-BF_4), R = 4-C_6H_4OMe, X = ClO_4 (**2**-ClO_4), and $[Ru(Cym)(NCCH_3)(RNNNR)]SbF_6$, R = 4-$C_6H_4OMe$ (**3**-SbF_6), and establish their structures, in some cases through X-ray diffraction (Figure 1 and Supporting Information).[12]

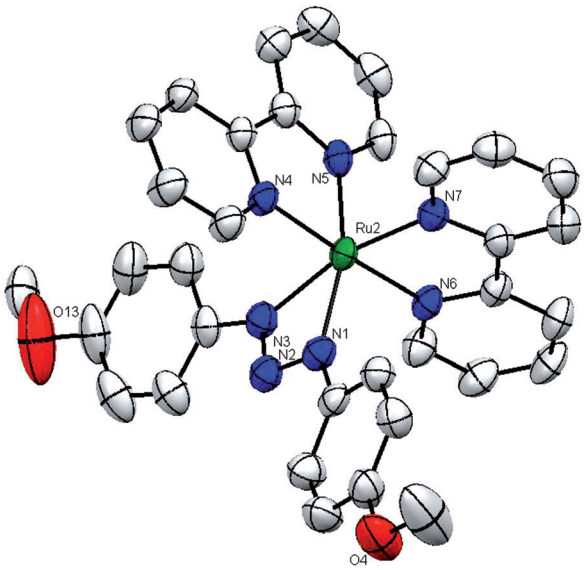

Figure 1. Molecular structure of the cation $[Ru(bpy)_2(RNNNR)]^+$, R = 4-C_6H_4OMe, in **2**-ClO_4. Thermal ellipsoids set at 80% probability. Selected bond lengths [Å] and angles [°]: Ru–N1 2.072(2), Ru–N3 2.078(2), N1–N2 1.312(3), N2–N3 1.316(3); N1-N2-N3 103.9(2), N1-Ru-N3 59.81(9).

triazenido

nitro/nitrito

amidinato

carboxylato

Two alternatives are conceivable for the electrochemically reversible oxidations [Eq. (1) and Table 1] :
Electron loss may lead to a ruthenium(III) complex with the typical EPR signature of a low-spin $4d^5$ configuration[13] for a metal center with a high spin–orbit coupling constant, as

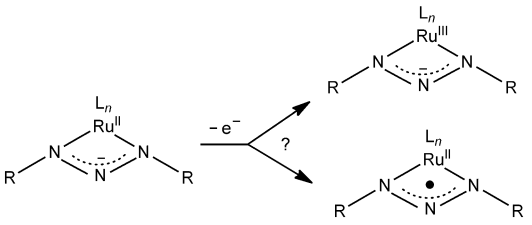

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Table 1: Electrochemical and EPR data of oxidized triazenidoruthenium complexes.[a]

Complex	$E_{1/2}$	g_{iso} (298 K)	g_1, g_2, g_3 (110 K)	g_1-g_3
$\mathbf{1}^{2+}$	0.45	2.194	2.350, 2.273, 1.899	0.451
$\mathbf{2}^{2+}$	−0.10	2.048	2.087, 2.064, 1.987	0.100
$\mathbf{3}^{2+}$	0.39	2.007[b]	[c]	<0.02[c]

[a] Potentials $E_{1/2}$ versus $Fc^{+/o}$ (Fc = [(η-C_5H_5)$_2$Fe]) from cyclic voltammetry in CH_2Cl_2/0.1 M Bu_4NPF_6; EPR data from electrolysis in CH_2Cl_2/0.1 M Bu_4NPF_6; X band results. [b] Hyperfine splitting: 0.199 mT (1×^{14}N), 0.629 mT (2×^{14}N), 0.127 mT (6×^{1}H), 0.109 mT (2×^{1}H), 0.080 mT (2×^{1}H), 0.094 mT (4×^{1}H), 0.272 mT (1×^{99,101}Ru). [c] *g* anisotropy not resolved.

established for $\mathbf{1}^{2+}$ with the accepting substituent R = 2-$C_6H_4CF_3$ and a *g* anisotropy of $g_1-g_3=0.451$ (Figure 2a). In contrast, stronger donors, such as R = 4-C_6H_4OMe, cause

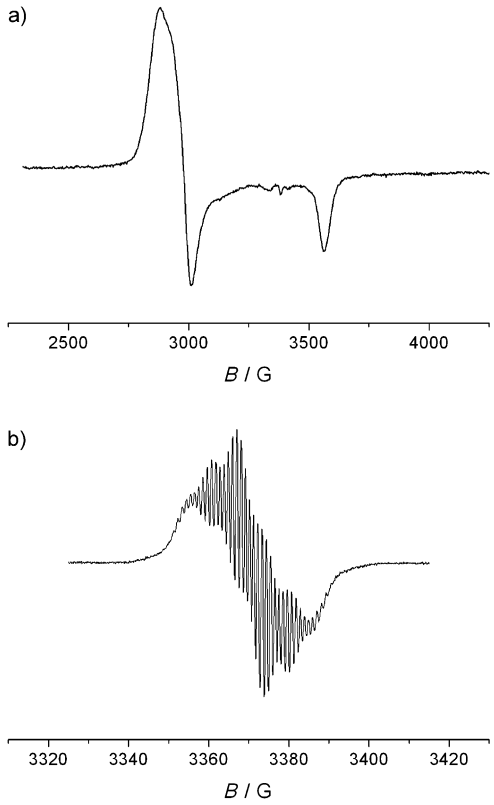

Figure 2. EPR spectra of paramagnetic complexes after one-electron oxidation of a) **1**-BF_4 (110 K) and b) **3**-SbF_6 (298 K) in CH_2Cl_2/0.1 M Bu_4NPF_6.

a distinctly narrower EPR signal near $g=2.0$ (Table 1) with much smaller *g* anisotropy of $g_1-g_3=0.100$, illustrating less spin density on the heavy metal and thus predominantly ligand-based spin.[13] Using the Cym/CH_3CN co-ligand combination with a less-basic but π-accepting arene in $\mathbf{3}^{2+}$, the spin density on ruthenium diminishes further ($g_1-g_3<0.02$), and a hyperfine structure becomes resolved, typical for radical species (Figure 2b). Free triazenyl radicals have been reported only as transient species derived from organic azides, showing spin density concentrated on the peripheral nitrogen centers.[14]

Table 2: DFT (ADF/BP86/COSMO-CH_2Cl_2) calculated spin densities ρ and EPR *g* factors for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$.

	$\mathbf{1}^{2+}$	$\mathbf{2}^{2+}$	$\mathbf{3}^{2+}$
ρ Ru	0.553	0.224	0.023
ρ N1	0.147	0.164	0.161
ρ N2	−0.044	−0.045	−0.045
ρ N3	0.147	0.164	0.161
ρ R1	0.108	0.254	0.349
ρ R2	0.108	0.254	0.349
g_1	2.229	2.056	2.023
g_2	2.160	2.051	2.006
g_3	1.941	1.992	2.004
g_1-g_3	0.288	0.064	0.019
g_{iso}[a]	2.110	2.033	2.011

[a] Calculated from $g_{iso}=((g_1^2+g_2^2+g_3^2)/3)^{1/2}$.

The EPR results (Table 1), demonstrating the triazenyl radical ligand character in $\mathbf{3}^{2+}$ (Figure 2b) and, to a lesser extent, in $\mathbf{2}^{2+}$ are supported by DFT calculations (Table 2).[15a] The spin densities (Figure 3) confirm a significant degree of

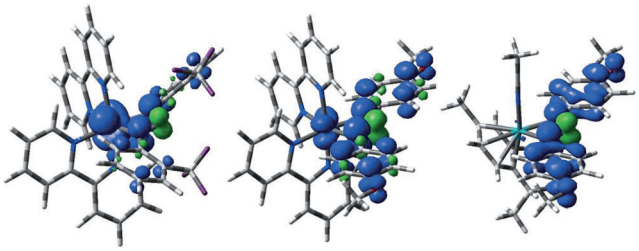

Figure 3. DFT (G09/PBE0/PCM-CH_2Cl_2) calculated spin densities for $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{2+}$from left to right.

metal–ligand spin delocalization in $\mathbf{2}^{2+}$. The calculated N–N bond length variation[15a] between the respective native and oxidized states of $\mathbf{2}^{n+}$ is $\Delta d=0.012$ Å which is remarkably small, and indicates that a significant part of spin density and geometry change involves the N aryl substituents.[15a] For free $NO_2^{\bullet}$, the calculated spin density exhibits a high value at the central atom N (0.528) and lower values at O1,O2 (0.236).[15b]

The above results represent a variation of "hidden non-innocence",[16] in this case of triazenido ligands, which elicits a comment on the apparent absence of the corresponding observations for the $[NO_2]^n$ ligand system. Ruthenium(II) complexes with nitro ligands have been reported to undergo quasi-reversible oxidation,[17] and [(μ-bpym){Ru(NO_2)-(terpy)}$_2$]$^{3+}$ [17b] (bpym = 2,2′-bipyrimidine) showed a distinct, but incomplete decrease of the *g* anisotropy of the nitro complex ($g_1-g_3=0.33$) compared to the chloro analogue ($g_1-g_3=0.75$), indicating some spin shift to the NO_2 ligand. NO_2 radical complexes can be expected for coordination compounds which tolerate this ligand without conversion but which prevent metal→($NO_2^{\bullet}$) electron transfer, for example, by employing lower oxidation-state stabilizing π-acceptor co-ligands at the metal center. The lowest energy coordination mode, κ^2O,O', κN (nitro), or κO (nitrito) is not readily predictable. Even when considering the expected cathodically shifted oxidation potentials of $[NO_2]^n$-containing redox sys-

tems compared to $[N(NR)_2]^n$ analogues as a result of the electronegativity differences between O and N it is thus conceivable that metal complexes of bent $NO_2^{\bullet}$ might be stabilized, as has been postulated for electronic structures of iron(III) nitro porphyrins[18a] and of the oxygen-bound form of nitrite methemoglobin.[18b] The fully oxidized NO_2^+, however, is less suited as a ligand, both for structural reasons (linearity) and because of its less-accepting π^* orbital.[19] It is of note that the $NO_2^{\bullet}$ ligand is isoelectronic to $CO_2^{\bullet-}$ which was shown to be a viable ligand in $[\{(^{Ad}ArO)_3tacn\}U^{IV}(CO_2)]$.[20]

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[10] **1**-BF_4 and **2**-BF_4: $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (200 mg, 0.38 mmol) and $AgBF_4$ (165 mg, 0.85 mmol) were dissolved in acetone and heated under reflux for 2 h. The precipitate of AgCl was removed by filtration through Celite. 2 equivalents (0.76 mmol) of the corresponding triazene and Et_3N (3 equiv, 1.14 mmol) were added to the red solution, and the mixture was stirred at 60 °C for 12 h under argon. After evaporation of the solvent under vacuum, the crude products were purified by column chromatography (aluminum oxide, CH_2Cl_2/MeCN 8:2) to give reddish brown solids. Yield of **1**-BF_4 272 mg (86 %) and of **2**-BF_4 239 mg (83 %).
[11] **3**-SbF_6: **4** ([RuCl(Cym)(RNNNR)]; 150 mg, 0.28 mmol) obtained from $[\{(Ru(p\text{-cymene})_2Cl_2)\}_2]$ and 1,3-bis(4-methoxyphenyl)triazene (see Supporting Information) and $AgSbF_6$ (98 mg; 0.28 mmol) were dissolved in acetonitrile and stirred for 4 h under reflux. The precipitate of AgCl was removed by filtration through Celite. After evaporation of the solvent under vacuum, the crude product was purified by column chromatography (aluminum oxide, CH_2Cl_2/MeCN 9:1) to give a red solid after evaporation. Yield of **3**-SbF_6: 183 mg (85 %). For analytical details see Supporting Information.
[12] CCDC 907942 (**2**-ClO_4) and 907943 (**3**-SbF_6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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