Redoxactive Ligands

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An Odd-Electron Complex $[Ru^k(NO^m)(Q^n)(terpy)]^{2+}$ with Two Prototypical Non-Innocent Ligands**

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Coordination compounds of redox-active transition metals, M, are most suitable for investigating intramolecular electron-transfer phenomena because of the typically well-defined structural framework and the variability of metals and redox-active "non-innocent" ligands, L. Apart from the standard two-component case, M-L, there has been some attention given to symmetrical three-component alternatives, such as M-L-M, involving for example, bridged mixed-valent species,[1] or L-M-L, including for example, metal-bridged chelate ligands of the quinone-type.[2] Less information is available for cases such as L^1-M-L^2, which would involve two different and thus potentially reacting non-innocent ligands in the coordination sphere of a redox-active transition metal.[3]

Combining three prototypical components from electron-transfer research we now show how the "art of establishing oxidation states"[2a] can be applied successfully even to such intricate systems.[4] The components are:

1) $[Ru(terpy)]^k$ ($k = 2+$ or $3+$) with meridionally coordinating and thus configuration-determining tridentate 2,2′:6′,2″-terpyridine (terpy; although potentially non-innocent,[5a] terpy is redox-invariant and thus innocent in the present case owing to its negative reduction potential[5b–d]),
2) the NO^m redox system ($m = 0$, $+$, or $-$) which has received much attention in connection with biochemically relevant Group 8 metal complexes,[6,7]
3) the well-used[2a,8,9a] and most recently reviewed[8d] 4,6-di-*tert*-butyl-*N*-phenyl-*o*-iminobenzoquinone, Q^n, in the structurally distinguishable[2a,8d,9] quinone ($n = 0$), semiquinone ($n = 1-$), and "catecholate" (2-anilidophenolato) forms ($n = 2-$). A metal-free iminosemiquinone derivative has been isolated[8b] and its relevance[8e] for copper-catalyzed oxidative deamination by amine oxidases discussed.

In all instances (1)–(3), the individual redox equilibria involve one paramagnetic ($S = {}^1/_2$) state, namely ruthenium(III) with low-spin $4d^5$ electron configuration, the nitrosyl radical ($NO^\bullet$), or the *o*-iminosemiquinone form ($Q^{\bullet-}$), each of these species is characterized by a typical EPR signature (large *g* factor anisotropy for Ru^{III},[4e,10] intermediate *g* anisotropy with single large ^{14}N hyperfine coupling for $NO^{\bullet-}$,[11] and small *g* anisotropy with small ^{14}N hyperfine splitting for $Q^{\bullet-}$).[8,12]

The combination of the three electron-transfer active components, $Ru^{II/III/IV}$, $Q^{0/\bullet-/2-}$, and $NO^{+/\bullet/-}$, in the system $[Ru^k(NO^m)(Q^n)(terpy)]^{2+}$ allows for several reasonable alternatives (see Figure 2). The combination between ruthenium and quinone-type ligands alone has already received much attention for the following reasons: a) ambiguous oxidation-state assignments,[4,13] b) stability and EPR accessibility of ruthenium(II) semiquinone complexes[8a,12a,14] and their non-trivial spin description,[4a] c) antiferromagnetic coupling between Ru^{III} and semiquinone radicals,[4a,d,e,15] d) the possible stabilization of other coordinated radicals,[16] and e) the established potential of dinuclear systems in water-oxidation catalysis.[17]

In addition, electron transfer within the ruthenium/NO/quinone ligand combination has been discussed in connection with photoinduced release of NO in physiological solution[7c] and also in a very recent study demonstrating the ring nitration of the quinone ligand on exposure to NO.[7d]

2-Anilino-4,6-di-*tert*-butylphenol[2a] and $[Ru(terpy)Cl_3]$ reacted to yield the chloro precursor compound $[RuCl(Q)(terpy)](ClO_4)$ which, through Ag^+/NO_2^- treatment, gave the nitro complex $[Ru(NO_2)(Q)(terpy)](ClO_4)$.[18] Acidification of the nitro compound yields the labile title complex $[Ru(NO)(Q)(terpy)]^{2+}$, isolated and structurally characterized as its bis(hexafluorophosphate)[18] salt in one of two possible positional isomer forms, in this case in the more stable configuration with the NO ligand *trans* to the oxygen donor atom of Q^n (Figure 1). The six conceivable oxidation state alternatives of $[Ru^k(NO^m)(Q^n)(terpy)]^{2+}$ are illustrated

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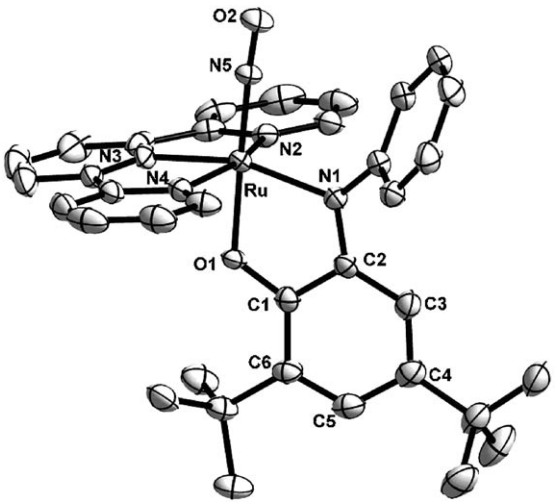

Figure 1. Molecular structure of the dication of [Ru(NO)(Q)(terpy)]-$(PF_6)_2$. Selected bond lengths [Å] [DFT/PBE0 calculated values in square brackets]: Ru–O1 1.965(2) [1.972], Ru–N1 2.078(3) [2.088], N5–O2 1.135(4) [1.142], N1–C2 1.349(4) [1.354], O1–C1 1.324(4) [1.321], C3–C4 1.361(5) [1.384], C4–C5 1.434(6) [1.428], C5–C6 1.378(5) [1.376].

in a three-dimensional representation (Figure 2) and depend on the variable oxidation states of ruthenium, NO, and Q.

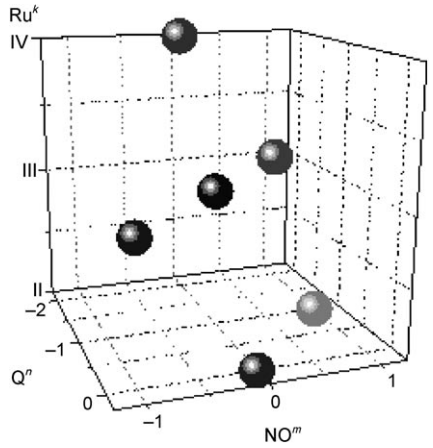

Figure 2. Three-dimensional representation of reasonable oxidation-state combinations in the complex ion $[Ru^k(NO^m)(Q^n)(terpy)]^{2+}$.

Reasonable oxidation-state combinations (Figure 2) include $Ru^{III}(NO^-)(Q^0)$ (an $Fe^{III}(NO^-)$ situation was established[7e] for the "brown ring species") or $Ru^{II}(NO^\bullet)(Q^0)$ which would contain the stabile ruthenium(II)/nitrosyl radical entity $\{RuNO\}^7$.[11b,19]

The Ru-N-O angle of 175.2(3)° and the NO stretching band at 1900 cm^{-1} in the IR vibrational spectrum suggest a $\{RuNO\}^6$ situation[19] although considerable bending may be possible for such an arrangement[4f] and the ν(NO) is very variable even within a given NO^+ oxidation state.[20] The parameters of the quinonoid ligand,[9] especially the C1–O1 distance of 1.324(4) Å, support[4a] an iminobenzosemiquinone complex of the $\{RuNO\}^6$ fragment. This hypothesis appears to be confirmed by DFT calculations[21] (calculated Ru-N-O angle of 176.3° and C1–O1 distance of 1.321 Å, G03/BPW91 calculated ν(NO) at 1877 cm^{-1}). Remenyi and Kaupp[4a] have pointed out, however, that great care has to be exercised in such structure/valence-state correlations;[9] the result can be a "superposition of states" in which two resonance structures contribute "to some extent" to yield an "intermediate" description.[4a] The present case of an isolated odd-electron species is distinguished by offering a clearer picture through application of EPR spectroscopy at high frequency (285 GHz) and at conventional X-band (9.5 GHz, Figure 3).

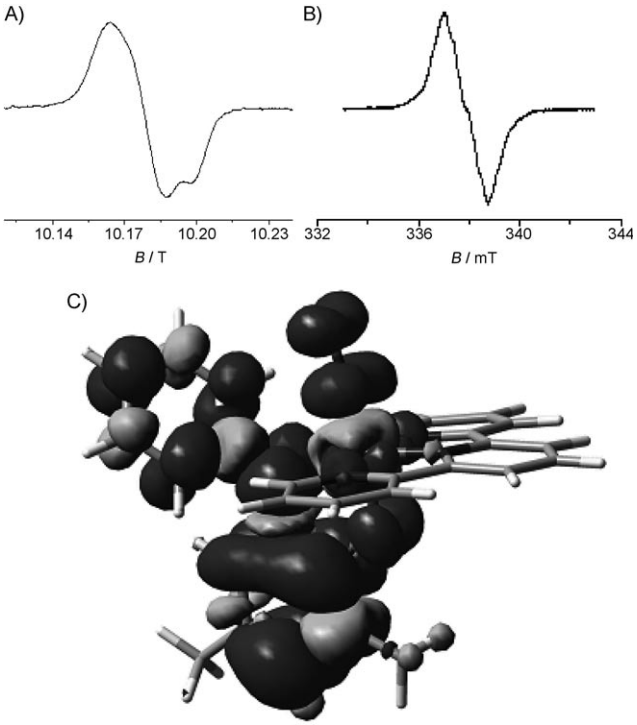

Figure 3. EPR spectra of $[Ru(NO)(Q)(terpy)](PF_6)_2$ A) at 285 GHz in glassy frozen CH_2Cl_2/toluene at 5 K and B) at 9.5 GHz in CH_2Cl_2 at 295 K; C) DFT calculated spin-density.

The very small[22a] resolved *g* anisotropy g_1-$g_3 = 0.0068$ even at 285 GHz[22b] suggests little participation of the metal at the singly occupied molecular orbital (SOMO), in spite of the high spin-orbit coupling constant of ruthenium.[8a,10a] Furthermore, a partially hyperfine-resolved signal observed at 9.5 GHz indicates a small but unresolved contribution from NO to the overall spin distribution and a diminished[12,16] ^{14}N(imine) EPR coupling constant.

DFT calculations reproduce both the structural features (Figure 1) and the nitrosyl stretching frequency and provides a spin-density representation (Figure 3C) with a contribution from the NO group of about 15%. The corresponding ^{14}N coupling constants were calculated as 0.46 mT (imino-N) and 0.09 mT (nitrosyl-N) which would explain the partially resolved X-band EPR spectrum (line distance of about 0.4 mT) measured at ambient temperature. *o*-Iminobenzosemiquinones without additional spin-delocalization sites have

typical ^{14}N hyperfine splittings of about 0.7 mT.[12] The energy minimum for the other positional isomer with NO *trans* to the NPh donor and a slightly more bent nitrosyl ligand (calculated Ru-N-O angle of 169.5°) was calculated to be 2.1 kcal mol^{-1} higher than that of the prepared isomer.

Although a three-spin situation[4a,b] $Ru^{III}(NO^{\bullet})(Q^{\bullet-})$ with the iminosemiquinone ligand and an antiferromagnetically coupled ruthenium(III)/nitrosyl radical pair would also be compatible with Q-centered spin, the nitrosyl stretching frequency at 1900 cm^{-1} clearly favors the NO^{+} formulation $[Ru^{II}(NO^{+})(Q^{\bullet-})(terpy)]^{2+}$.

The characterized radical complex ion $[Ru(NO)(Q)(terpy)]^{2+}$ undergoes facile reversible one-electron reduction at -0.40 V versus $Fc^{+/o}$ ($Fc = [(C_5H_5)_2Fe]$) in CH_2Cl_2/0.1 M Bu_4NPF_6. Based on the EPR silence and the moderate shift of ν(NO) to about 1830 cm^{-1} the reduction of the compound does not yield an $NO^{\bullet}/Q^{\bullet-}$ containing species, in contrast to the postulated[16] but also disputed[17b] radical + semiquinone complexes $[Ru^{II}(L)(Q^{\bullet-})(terpy)]^{n}$ ($L = O^{\bullet-}$ or $RHN^{\bullet}$), and in contrast to clearly nitrosyl-centered reduction observed at $E_{1/2} = +0.17$ V versus $Fc^{+/o}$ for the analogous $[Ru(NO)(bpym)(terpy)]^{3+}$ (bpym = 2,2′-bipyrimidine) complex.[23] Considering the rather negative reduction potential of terpy, for example, in $[Ru(terpy)_2]^{2+}$,[5d] the valence-state combination of the reduced complex can be best described as $[Ru^{II}(NO^{+})(Q^{2-})(terpy)]^{+}$. To shed light on these challenging electronic structures the next investigations will involve studying neighboring charge states and the tuning of the quinonoid component.

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[18] a) See Supporting Information; b) CCDC 718570 contains 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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