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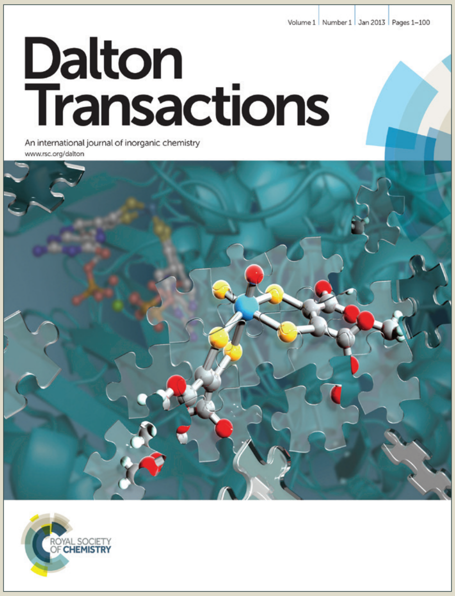

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$\{RuNO\}^6$ vs. Co-Ligand Oxidation: Two Non-Innocent Groups in One Ruthenium Nitrosyl Complex

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th May 2014,
Accepted 00th May 2014

DOI: 10.1039/x0xx00000x

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Recently, a new $\{RuNO\}^6$ complex, $[Ru(L)(NO)(Cl)]^{2+}$ (where L = N'-phenyl-N'(pyridin-2-yl)piclinohydrazide), was reported which exhibits a one-electron quasireversible oxidation. The oxidized product, $[Ru(L)(NO)(Cl)]^{3+}$, was isolated and proposed to be a highly unusual $\{RuNO\}^5$ complex. In this paper, we investigate the electronic structure of both of these ruthenium complexes by DFT calculations and find that the oxidized species is best described as a $\{RuNO\}^6$ complex with a co-ligand radical. $[Ru(L)(NO)(Cl)]^{2+}$ is therefore oxidized to $[Ru(L^{+\bullet})(NO)(Cl)]^{3+}$, i.e. this is an interesting example of a complex with two non-innocent ligands simultaneously bound to a ruthenium center.

Non-innocent ligands (NILs) undergo redox reactions when bound to transition metal ions which causes ambiguity in the electronic structure of the resulting complexes.[1-2] NILs range from small molecules such as dioxygen and nitric oxide (NO) to larger ligand scaffolds such as quinones, porphyrins, dithiolenes, pyrocatechol derivatives, and substituted benzene derivatives.[3] A more specific example are ruthenium(III) nitrosyl complexes, classified as $\{RuNO\}^6$ species in the Enemark-Feltham notation[4] (where the superscript "6" represents the number of ruthenium d–electrons plus the NO $\pi*$ electrons), where one could envision that NO could be bound as NO^+, NO(radical), or NO^- with a concomitant reduction or oxidation of the ruthenium center.[5] Many studies in the literature have shown that in ruthenium(III) nitrosyl complexes the NO ligand is in fact oxidized, which results in a ruthenium(II)-NO^+ type electronic structure.[6-9] Recently, Ghosh and co–workers have characterized a new $\{RuNO\}^6$ complex, $[Ru(L)(NO)(Cl)]^{2+}$ (L = N'-phenyl-N'(pyridin-2-yl)piclinohydrazide).[10] The crystal structure of this species is shown in Figure 1. Interestingly, this $\{RuNO\}^6$ complex exhibits a one-electron quasireversible oxidation at $E_{1/2}$ = –0.18 V (vs. Fc/Fc^+ determined by Cyclic Voltammetry). The oxidation of the $\{RuNO\}^6$ complex with excess ceric ammonium nitrate (CAN) resulted in the isolation of the one-electron oxidized species, $[Ru(L)(NO)(Cl)]^{3+}$, proposed to be a highly unusual $\{RuNO\}^5$ complex. However, the N–O stretching frequency increased by only +20 cm^{-1} in the proposed $\{RuNO\}^5$ species relative to the $\{RuNO\}^6$ starting material. In contrast, the only known $\{RuNO\}^5$ complex was obtained by Kaim and co–workers by the oxidation of the $\{RuNO\}^6$ complex $[Ru(Cl_5)(NO)]^{2-}$ ($E_{1/2}$ = 1.02 V vs. Fc/Fc^+ at –40°C), which is stabilized by five chloride ligands.[11] In this case, the one–electron oxidation of $[Ru(Cl_5)(NO)]^{2-}$ resulted in a large change in the N-O stretching frequency of +79 cm^{-1}. Besides the small shift in the N–O stretching frequency, the co–ligand, "L", used by Ghosh and co–workers as shown in Figure 1 (middle), looks rather suspicious and could potentially be a NIL itself. This suggests that the neutral co–ligand in $[Ru(L)(NO)(Cl)]^{2+}$ could be oxidized to a radical species and not the $\{RuNO\}^6$ unit. To further investigate this interesting case of a ruthenium complex with two NILs and the electronic structure of the two complexes, Density Functional Theory (DFT) calculations were employed.

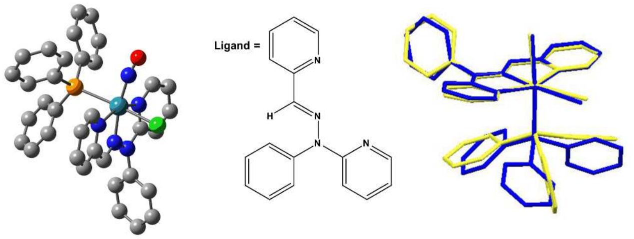

Figure 1. Left: DFT-optimized structure (BP86/TZVP) of the singlet (*S* = 0) ground state of $[Ru(L)(NO)(Cl)]^{2+}$. Middle: Schematic drawing of the co–ligand, "L", of the $[Ru(L)(NO)(Cl)]^{2+/3+}$ complexes.[10] Right: Overlay of the crystal (yellow, PF_6^- counter ions not shown) and calculated (blue, BP86/TZVP) structures of $[Ru(L)(NO)(Cl)]^{2+}$. In both structures the hydrogen atoms are omitted for clarity.

First, the $\{RuNO\}^6$ complex, $[Ru(L)(NO)(Cl)]^{2+}$, was optimized with the BP86 functional and TZVP basis set (see Figure 1 for the optimized structure). The calculated bond lengths in the $\{RuNO\}^6$ complex are relatively long compared to the crystal structure as shown in Table S7 but the overall structure is reproduced well (see Figure 1). The biggest deviation from the crystal structure is found for the Ru–P bond, which is overestimated by 6%. In order to obtain bonds lengths closer to the crystal structure, we optimized the $\{RuNO\}^6$ complex with additional DFT methods, but no further improvement was obtained (see Tables S8 & S9). Also, we employed relativistic corrections by optimizing the $\{RuNO\}^6$ complex with the ZORA approximation, which lead to small improvements in the structure of the $\{RuNO\}^6$ unit, but the Ru–P bond is still overestimated (calc.: 2.507 Å, crystal struct.: 2.406 Å; see Table S9). In order to test whether this deviation could be due to a solid state (crystal packing) effect, we took the BP86/TZVP optimized structure of the $\{RuNO\}^6$ complex, reduced the Ru–P bond length to the experimental value, and calculated the total energy of this structure. This leads to an energy difference of +1.7 kcal/mol compared to the optimized structure, indicating that solid state (crystal packing) effects could be responsible for the shorter Ru–P bond in the crystal structure.

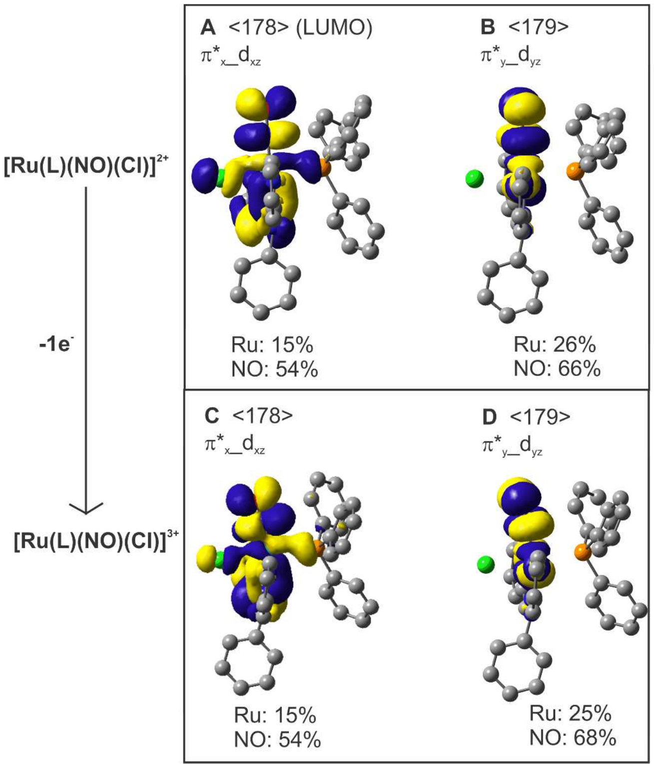

Figure 2. Ru-NO orbital interactions, calculated for $[Ru(L)(NO)(Cl)]^{2+/3+}$ with BP86/TZVP. The Ru–N–O unit lies on the z–axis and hydrogen atoms are omitted for clarity. Top: **(A)** and **(B)** represent the two strong π backbonding interactions in $[Ru(L)(NO)(Cl)]^{2+}$. Bottom: **(C)** and **(D)** represent the corresponding two strong π backbonding interactions in $[Ru(L)(NO)(Cl)]^{3+}$.

On the other hand, the calculated N–O stretching frequency of the $\{RuNO\}^6$ complex is 1889 cm^{-1} (with BP86/TZVP), which is very close to the experimental value of 1890 cm^{-1}.[10] Molecular orbital (MO) analysis of this complex shows the typical Ru(II)–NO^+ electronic structure with two strong π backbonding interactions between the ruthenium d_{xz}/d_{yz} orbitals and the NO π* orbitals (where the Ru–N–O unit lies on the z–axis; see Figure 2, top). In the next step we investigated the electronic structure of the corresponding one-electron oxidation product. Experimentally, Ghosh and co-workers found that the reaction of the $\{RuNO\}^6$ complex with excess CAN results in the oxidized product $[Ru(L)(NO)(Cl)]^{3+}$.[10] This process is completely reversible with the addition of excess sodium dithionite (shown by UV-visible spectroscopy). This oxidation results in a total change in the N–O stretching frequency of +20 cm^{-1}. With this in mind, we optimized the oxidized product $[Ru(L)(NO)(Cl)]^{3+}$ (with BP86/TZVP) and found that the N–O stretching frequency was predicted to be 1911 cm^{-1}, which is in excellent agreement with the experimental value of 1910 cm^{-1}. Analysis of the wavefunction of this complex shows that there is significant spin density on the co–ligand (0.66) and very little on the Ru–N–O unit (0.17) and the Cl^- ligand (0.13), revealing that the co–ligand is in fact oxidized in $[Ru(L)(NO)(Cl)]^{3+}$ rather than the ruthenium center. Hence, the oxidized complex is best described as $[Ru(L^{\bullet+})(NO)(Cl)]^{3+}$. In other words, the complex corresponds to a $\{RuNO\}^6$ species with a bound co–ligand radical. A plot of the spin density shows that the unpaired electron on the co–ligand is delocalized across the entire ligand (see Figure 3). MO analysis of both ruthenium complexes was further performed to identify the exact MO that becomes oxidized, which is shown in Figure 3. The SOMO of the oxidized complex resembles the spin density plot closely, indicating minimal spin polarization and overall similar electronic structures in the two complexes. From the DFT calculations, we obtained the following key findings: (1) there is very little change in the Ru–N–O unit between the $\{RuNO\}^6$ and the oxidized complex (see Figure 2, bottom) and (2) the oxidation is almost entirely ligand centered with very little contribution from the Ru–N–O unit or the Cl^- ligand. In summary, in the complex $[Ru(L)(NO)(Cl)]^{2+}$, "L" acts as a NIL upon oxidation of the

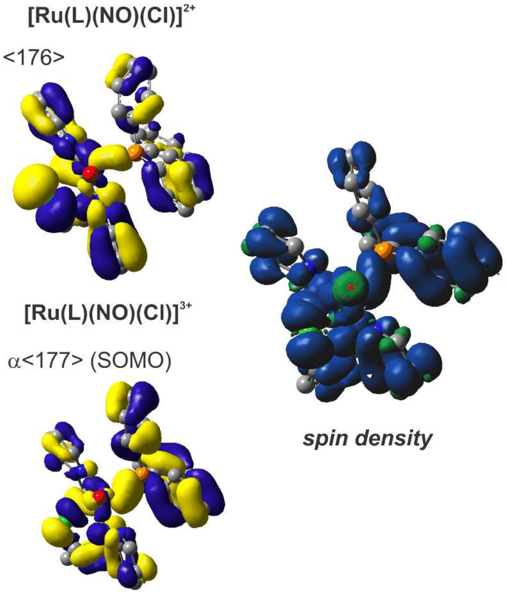

Figure 3. Top left: Contour plot of the donor MO in $[Ru(L)(NO)(Cl)]^{2+}$. Bottom left: the corresponding SOMO in the oxidized complex $[Ru(L)(NO)(Cl)]^{3+}$. Right: Spin density plot for the doublet $S = 1/2$ state of $[Ru(L)(NO)(Cl)]^{3+}$, calculated with BP86/TZVP. Hydrogen atoms are omitted for clarity. Both contour and spin density plots are shown in a top down view looking down the Ru–N–O bond.

complex. The oxidized complex therefore does not correspond to a $\{RuNO\}^5$ complex as initially proposed.

Ghosh and co–workers further characterized the oxidized product by EPR at 77 K. This complex shows a signal indicative of a rhombic $S = 1/2$ system with g values of 2.165, 2.032, and 1.961 ($g_{av} = 2.053$).[10] Interestingly, an axial g anisotropy is observed in the $\{RuNO\}^5$ complex $[Ru(Cl_5)(NO)]^-$ reported by Kaim and co-workers, which exhibits g values of 2.11, 2.11, and 2.058 ($g_{av} = 2.091$).[11] These data have been taken as evidence for a ruthenium–based oxidation in $[Ru(L)(NO)(Cl)]^{3+}$. We used our DFT calculations to further elucidate this point by calculating g values for the oxidized complex. Interestingly, the obtained g values of 2.009, 2.017, and 2.062 ($g_{av} = 2.03$) show some deviations from the experimental values, but emphasize that the ligand–oxidized complex can in fact give rise to a rhombic EPR spectrum with significant g shifts.

In comparison, the only other example of a ruthenium nitrosyl complex with a second NIL was reported by Kaim and co-workers.[12] The crystal structure of $[Ru(NO)(Q^{\bullet -})(terpy)]^{2+}$ is shown in Figure 4. This complex contains a $\{RuNO\}^6$ unit with a quinone–based ligand radical, and the N–O stretching frequency of this complex is located at 1887 cm^{-1}. The one–electron reduction of this complex produces $[Ru(NO)(Q)(terpy)]^+$, along with a decrease in the N–O stretching frequency by 57 cm^{-1}, which is distinctively larger than the change in the N–O stretching frequency observed for $[Ru(L)(NO)(Cl)]^{2+/3+}$. Interestingly, the spin density plot of the oxidized $[Ru(NO)(Q^{\bullet -})(terpy)]^{2+}$ complex in Figure 3 shows a distinctively larger amount of spin density on the Ru–N–O unit compared to $[Ru(L)(NO)(Cl)]^{3+}$. This indicates a somewhat larger degree of $\{RuNO\}^6$ oxidation in Kaim's complex, in agreement with the larger shift in the N–O stretch compared to Ghosh's complex.

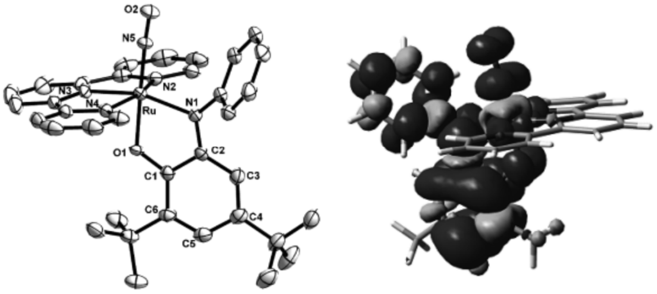

Figure 4. Left: Crystal structure of $[Ru(NO)(Q^{\bullet -})(terpy)]^{2+}$ (the two PF_6^- counter ions and hydrogen atoms are not shown for clarity). Right: The spin density plot of $[Ru(NO)(Q^{\bullet -})(terpy)]^{2+}$ calculated with PBE0/6-31G*. Both images are reprinted with permission from reference 12.

Conclusions

In summary, we have shown through DFT calculations that the one–electron oxidation of the $\{RuNO\}^6$ complex $[Ru(L)(NO)(Cl)]^{2+}$ does not result in the oxidation of the Ru–N–O unit to form a $\{RuNO\}^5$ complex, but, instead, a ligand radical species is formed. This co–ligand applied here is therefore another example of a NIL. For further comparison, we also fully optimized the structure of the analogous $\{RuNO\}^7$ complex, $[Ru(L)(NO)(Cl)]^+$ (with BP86/TZVP). The geometric parameters of this complex are shown in Table S7 and are in good agreement with previously characterized $\{RuNO\}^7$ complexes.[6,9] The N–O stretching frequency of this complex is predicted to be 1705 cm^{-1}, which results in a total calculated change of -184 cm^{-1} in the N–O stretching frequency upon reduction. Additionally, the spin density in this case is localized on the NO ligand (0.65) , while there is very little spin density on the ruthenium center (0.12), Cl^- ligand (0.0), and the co–ligand (0.24) (see spin density plot Figure S1). Hence, the one–electron reduction of the $\{RuNO\}^6$ complex results in a ruthenium(II)–NO(radical) type species and the co–ligand "L" remains innocent. Therefore, in summary, the one–electron oxidation of $[Ru(L)(NO)(Cl)]^{2+}$ is co–ligand centered, whereas the one–electron reduction is predicted to be NO–centered, further emphasizing the non–innocent character of both N'-phenyl-N'(pyridin-2-yl)piclinohydrazide (L) and NO in $[Ru(L)(NO)(Cl)]^{2+}$. NILs are generally important in catalysis as they can be used to control catalytic reactions by accepting/donating electrons or participating in the formation/breaking of the covalent bonds of a substrate.[1,13] For example, as shown by Chirik and co–workers, iron complexes with a bis(imino) pyridine ligand framework utilize the coligand to store electrons that are later used to perform catalytic processes, such as C–C bond formation.[14] Here we present an example for a complex with two non-innocent ligands, where one of them can be used as an electron donor, whereas the other one can function as an electron acceptor, both of them present in the same complex at the same time. This represents a further expansion of the concept of NIL-bound transition metal complexes. These new types of systems provide further versatility to transition metal complexes in terms of their redox chemistry, and might therefore inspire generally new approaches to organometallic catalysis.

Notes and references

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† A.B.M. acknowledges support from the University of Michigan Rackham Graduate School in the form of a Rackham Merit Fellowship.

Electronic Supplementary Information (ESI) available: The cartesian coordinates of $[Ru(L)(NO)(Cl)]^{+/2+/3+}$ and the spin density plot of $[Ru(L)(NO)(Cl)]^+$. See DOI: 10.1039/c000000x/

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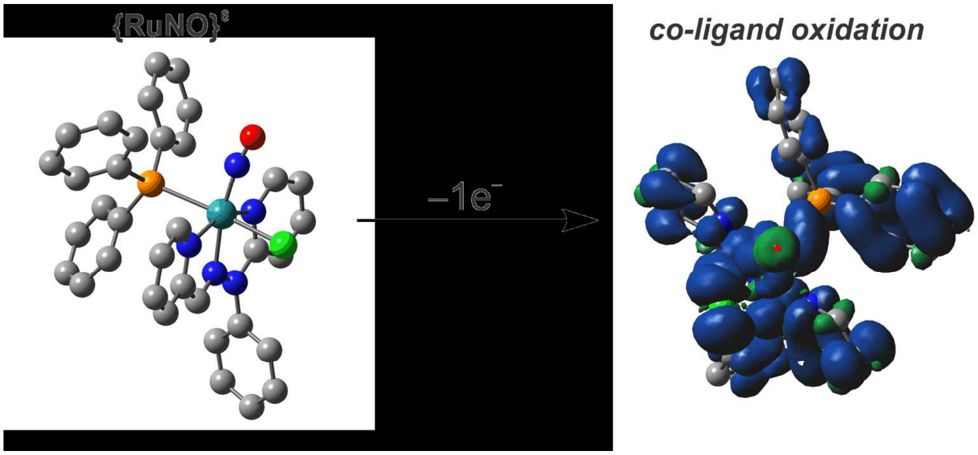

The one-electron oxidation of the {RuNO}6 complex [Ru(L)(NO)(Cl)]2+ (where L = N'-phenyl-N'(pyridin-2-yl)piclinohydrazide) leads to the generation of a coligand radical. This complex therefore represents a rare example of a ruthenium complex with two different non-innocent ligands bound.
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