Communication

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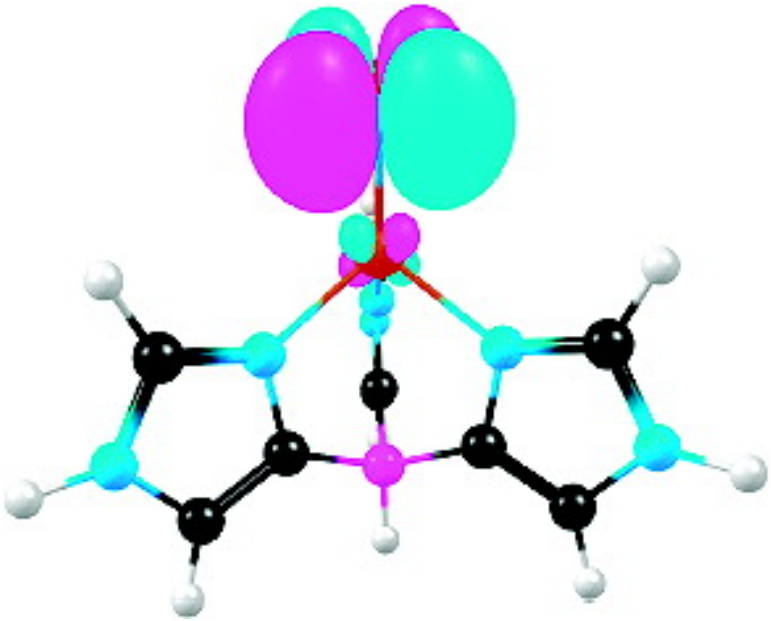

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Modeling Side-On NO Coordination to Type 2 Copper in Nitrite Reductase: Structures, Energetics, and Bonding

Ingar H. Wasbotten and Abhik Ghosh*

Department of Chemistry, University of Tromsø, N-9037 Tromsø, Norway

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Recent crystallographic studies by Murphy[1], Hasnain,[2] and their co-workers have led to major insights into the mechanism of copper nitrite reductase (CuNIR), one of two bacterial enzymes (the other being a heme nitrite reductase) that reduce nitrite to NO.[3−5] The key new result consists of high-resolution CuNIR crystal structures with side-on NO coordination to the catalytically active type 2 copper, which is a unique structural motif in copper coordination chemistry. Though rare, side-on NO coordination has been previously observed, for example, in the photoisomer of a {RuNO}^{6} porphyrin, which has been characterized by low-temperature IR spectroscopy.[6] In the case of the CuNIR, a key unresolved issue concerns the oxidation state—{CuNO}^{10} or {CuNO}^{11}—of this intermediate, where the superscripts refer to the Enemark−Feltham electron counts, namely, the number of metal d plus NO π^* electrons. We present here a DFT (PW91/TZP) study of side-on NO coordination for type 2 Cu model complexes as well as a reexamination[7] of Ru(P)(NO)Cl (P = porphyrin, C_s, $S = 0$.[8,9]

Side-on Ru(P)(NO)Cl, which is about 1.23 eV higher in energy than the end-on isomer,[7] exhibits a quite unsymmetrical RuNO unit, with markedly unequal Ru−N_{NO} (2.0 Å) and RuO (2.4 Å) distances, as shown in Figure 1. Figure 1 also shows the three primarily Ru 4d-based MOs. Note that while the HOMO-4 depicts the main source of bonding between the a′ Ru d_π orbital and the a′ π^* orbital of the side-on NO, the HOMO-2 exhibits π-bonding between the Ru a″ d_π orbital and *the nitrogen end* of the a″ NO π^* orbital. The latter orbital interaction accounts for the unsymmetrical geometry of the side-on RuNO unit.

To model the CuNIR side-on NO intermediate, we have used the following supporting ligands: hydrotris(pyrazolyl)borate ($HBpz_3^-$), hydrotris(4-imidazolyl)borate ($HBim_3^-$), and tris(2-imidazolyl)methane ($HCim_3$). Remarkably, not only do the {CuNO}^{10} species exhibit metastable side-on isomers but so do the {CuNO}^{11} species, which is unprecedented for Enemark−Feltham counts other than 6[5,10] or 10.[11] For these three supporting ligands (in the above order), the energies of the side-on isomer, relative to the end-on isomers, are 0.52, 0.47, and 0.60 eV for {CuNO}^{10} and 0.29, 0.23, and −0.04 eV for {CuNO}^{11}. Thus, compared with side-on Ru(P)(NO)Cl,[7] certain ones of the side-on CuNO isomers have remarkably low energies, and *in one* {*CuNO*}^{11} case, the side-on geometry is actually preferred! On the basis of these results, therefore, the observed CuNIR intermediate may well be a ground state (as opposed to a metastable) species.

Figure 2 depicts the optimized geometries for Cu($HBpz_3$)(η^1-NO) and for [Cu($HBim_3$)(η^2-NO)]$^{0,+}$. Key features of the optimized geometry are in good agreement with a crystal structure of Cu[HB(3-*t*Bu-pz)$_3$](η^1-NO).[12−14] Figure 2 also shows that while the {CuNO}^{10} core is quite unsymmetrical (Cu−N_{NO} 1.9 Å, Cu−O 2.4 Å), the {CuNO}^{11} core is much more symmetrical (Cu−N_{NO} 1.9 Å, Cu−O 2.1 Å). The latter geometry seems to be more in accord with experimental Cu−N/O distances reported for the CuNIR intermediate.[1,2] On a more detailed note, the calculated Cu−N/O distances for the {CuNO}^{11} core are closer to those found in ref 1 (2.0 Å) than in ref 2 (2.2 Å).

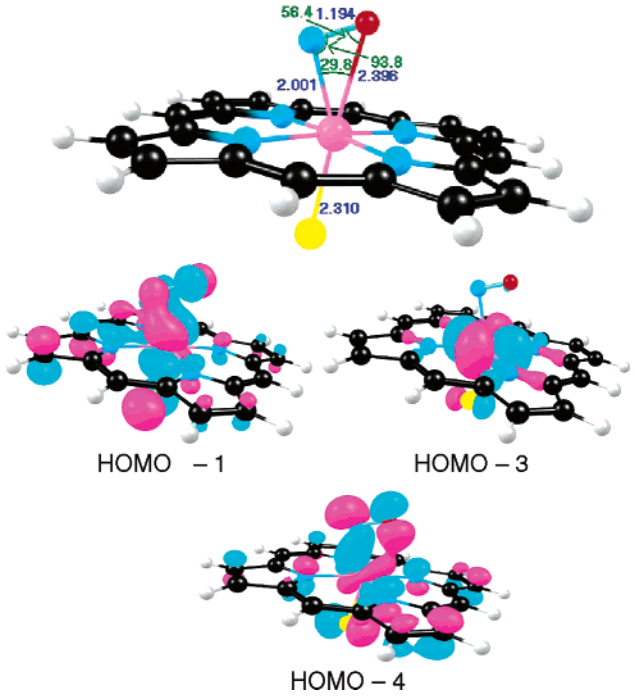

Figure 1. Ru(P)(η^2-NO)Cl geometry (Å, deg) and MOs.

The MOs for analogous {CuNO}^{10} and {CuNO}^{11} complexes are reasonably similar, although the former is $S = 0$ and the latter $S = {}^1/_2$. For simplicity, Figure 3 shows an MO energy level diagram for Cu($HBim_3$)(η^2-NO), using a C_s symmetry-constrained spin-restricted calculation. (The more rigorous but larger spin-unrestricted diagram conveys essentially the same information.) As in the case of side-on Ru(P)(NO)Cl, note from Figure 3 that the bonding between Cu and the side-on NO ligand is mediated by an a′ Cu(d_π)−NO(π^*) orbital interaction. For Cu($HBim_3$)(η^2-NO), note that the Mulliken spin populations, the spin density plot (Figure 2), and a plot of the singly occupied MO (Figure 3) all indicate that the unpaired electron essentially occupies an NO a″ π^* orbital.

For the {Cu(η^2-NO)}^{10} species, a spin-unrestricted (broken symmetry) calculation yields the same solution as a spin-restricted calculation, as opposed to an electronic structure involving metal−NO antiferromagnetic coupling. (However, we are aware that hybrid functionals may result in a somewhat different electronic description, compared with what we have found here.) For the

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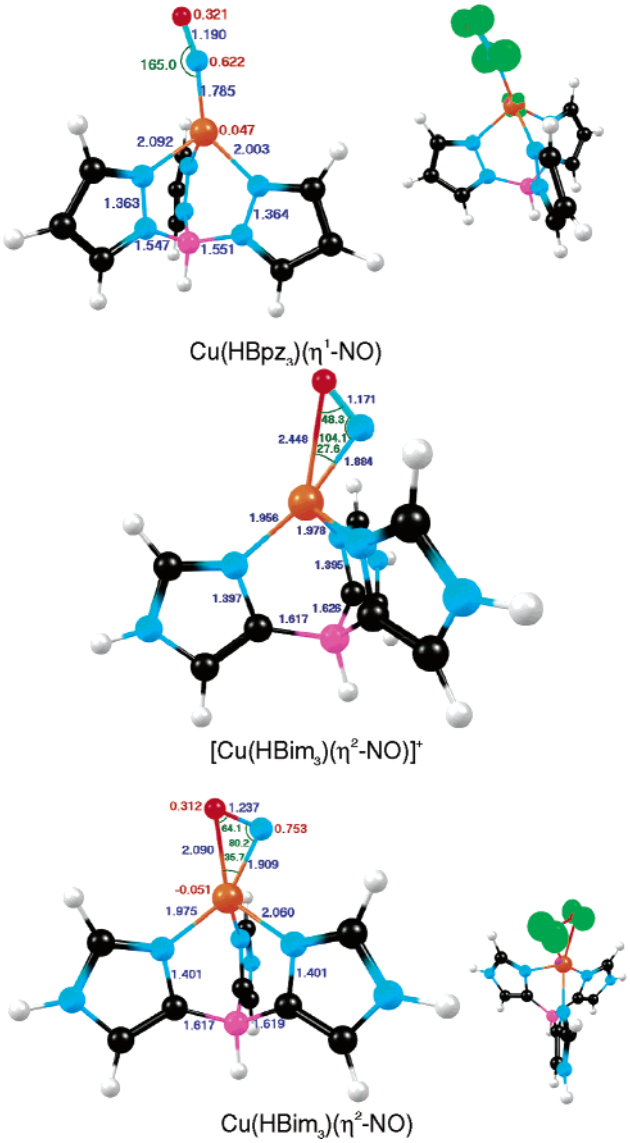

Figure 2. Distances (Å, blue), angles (deg, green), spin populations (red), and spin density plots (green).

$\{Cu(\eta^2\text{-NO})\}^{11}$ species, the spin density profile described above suggests an overall $Cu^{I}-NO^{\bullet}$ electronic description, rather than a tightly antiferromagnetically coupled $Cu^{II}-NO^{-}$ formulation. Moreover, the latter description would have resulted in a large deviation of the calculated expectation value of $\hat{S}^2$ from the theoretically expected value of 0.75, which we do not observe; the calculated value of $<\hat{S}^2>$ is 0.76, in excellent agreement with the expected value.

In summary, PW91/TZP calculations indicate that both $\{CuNO\}^{10}$ and $\{CuNO\}^{11}$ species may exhibit metastable side-on NO linkage isomers. However, the side-on isomers seem to be especially favored for the reduced $S = {}^1/_2$ $\{CuNO\}^{11}$ oxidation level, where in one case, we found the side-on form to be actually more stable than the end-on form (albeit by a small margin). Indeed, it should be a worthwhile goal for synthetic inorganic chemists to attempt the synthesis of side-on $\{CuNO\}^{11}$ species. Moreover, the relatively symmetrical structure of the side-on $\{CuNO\}^{11}$ unit seems to be more consistent with the observed metrical parameters for the CuNIR intermediate.[1,2]

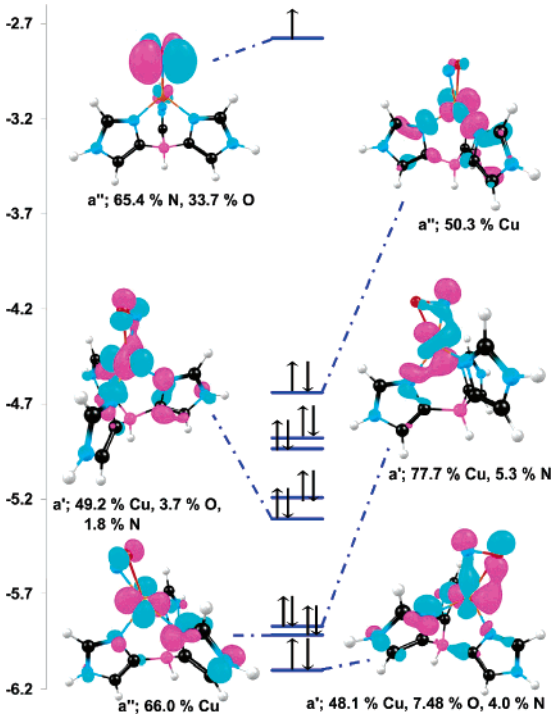

Figure 3. Energy level (eV) diagram for $Cu(HBim_3)(\eta^2\text{-NO})$.

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Supporting Information Available: Optimized Cartesian coordinates are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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