Activation of Nitric Oxide and Organonitroso Complexes (X-NO) at Low-Coordinate Co, Ni, and Cu Centers

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In a remarkably short period of time, nitric oxide has become recognized as a key molecule in biology. In addition, the biochemistry of organic nitroso compounds (X-NO) is in many ways linked to that of nitric oxide (NO). These organic derivatives can serve either as sources of NO \textit{in vivo} or can produce similar biological effects as NO (e.g. vasodilation). Release of NO from many organonitroso compounds, however, requires a reducing equivalent for which redox active metalloenzymes have been implicated.

Employing low-coordinate, monovalent later, first row transition metal β-diketiminates as models, we explore the bonding and reactivity of three-coordinate metal-nitrosyl complexes $[\text{NN}]M(\text{NO})$. Alkyl and aryl C-organonitroso compounds (R-NO) readily add to the Ni-NO bond to give “NONOates” $[\text{NN}]\text{Ni}(\kappa_2^2-\text{O}_2\text{N}_2\text{R})$. Moreover, photoexcitation of $[\text{NN}]\text{Ni}(\text{NO})$ with visible light allows access to $\eta^2$-NO “side-on” states with lowered $\nu$(NO) stretching frequencies.

We also explore the reaction chemistry of these β-diketiminato templates with C-, N-, O-, and S-organonitroso compounds X-N=O connected to the biological reactivity and availability of NO. These organonitroso derivatives exhibit diverse bonding modes and reactivity patterns with the $[\text{NN}]M$ fragments ranging from release of NO to complete cleavage of the N=O bond. Factors that lead to $X$-NO vs. $X$-N=O bond activation will be outlined, and considered in context of the metabolism and formation of these NO-containing substances by non-heme centers.