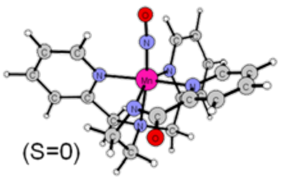
Electronic structure of manganese(II) nitrosyl compounds: a bifocal view.

Kristine Pierloot, Hailiang Zhao

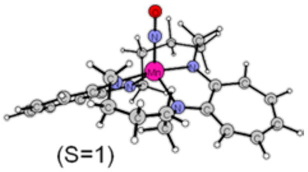
Laboratory of Computational Coordination Chemistry, Department of Chemistry, University of Leuven, Belgium
e-mail:Kristin.Pierloot@chem.kuleuven.be

Manganese nitrosyl systems $\{MnNO\}^6$ are almost invariably diamagnetic (S=0), containing a (close to) linear Mn−N−O unit, although an intermediate (S=1) may be close-lying[1], and in exceptional cases become the ground state. Linear mononitrosyl compounds are traditionally regarded as containing nitrosyl bound to Mn^{I} as NO^{+}, although it is generally recognized that the covalent nature of the M−NO interaction precludes the assignment of a formal oxidation state to the metal and NO in nitrosyl complexes. The Enemark-Feltham notation $\{MnNO\}^6$ in fact stresses the electron delocalization in the MnNO unit, without being committed a certain formal oxidation state on either M or NO. This "noninnocent" character of the NO ligand also complicates the theoretical description of the electronic structure of metal-NO complexes, which is inherently multiconfigurational in nature.

In this work, we present a description of the electronic structure and relative energies of the ground states and the lowest excited states of a number of manganese nitrosyl systems containing an $\{MnNO\}^6$ unit in heme and non-heme environments, making use of multiconfigurational ab initio method C(R)ASPT2. Electron delocalization in the Mn-NO bond is manifested both by the strongly mixed character of the bonding and antibonding $Mn3d_{\pi}{-}NO\pi^{*}$ combinations and by the strong multiconfigurational character of the wave function. Such a wave function may, however, be transformed in a straightforward manner into a valence-bond-style description in terms of contributions from $Mn^{II}{-}NO^{0}$, $Mn^{I}{-}NO^{+}$, $Mn^{III}{-}NO^{-}$, by subjecting the appropriate subset of delocalized molecular orbitals in the CASSCF wave function to a (Cholesky) localization procedure. Quite strikingly, such an analysis indicates that the bonding in manganese nitrosyl systems is built from a resonance hybrid of $Mn^{III}{-}NO^{-}$ and $Mn^{II}{-}NO^{0}$, with the former as the dominant resonance structure. Little or no $Mn^{I}{-}NO^{+}$ character is found in any of the complexes studied.



$Mn(PaPy_3)(NO)^+$



Mn(5,5-TC)(NO)

[1] Kurtikyan, T.S.; Hayrapetyan, V. A., Martirosyan , G. G., Ghazaryan, R. K.; Iretskii, A. V., Zhao. H.; Pierloot, K. Ford, P. C. *Chem. Commun.* 48, 12088, 2012.
[2] Tangen, E.; Conradie, J.; Franz, K.; Friedle, S.; Telser, J.; Lippard, S. J.; Ghosh, A. *Inorg. Chem.* 49, 2701, 2010.