

A new look at the electronic structure of the $\{\text{RuNO}\}^6$ moiety using density-fitting CASSCF calculations and localised orbitals

Leon Freitag¹, Mickaël Delcey², Thomas B. Pedersen^{2,3}, Francesco Aquilante², Roland Lindh² and Leticia González¹

¹ Institute of Theoretical Chemistry, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria

² Department of Chemistry – Ångström, The Theoretical Chemistry Programme, Uppsala University, Box 518, 751 20 Uppsala, Sweden

³ Center for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, 0315 Oslo, Norway

Nitrous oxide (NO) has been found to play a role in neurotransmission, blood pressure control and even control of tumor growth. Therefore, various transition metal nitrosyl complexes have been employed in targeted NO delivery to biological tissues such as photodynamical therapy (PDT)[1]. Understanding the electronic structure of the metal-NO moiety is crucial for the understanding of the mechanisms of the NO liberation and delivery in these complexes.

However, the metal-nitrosyl coordination has been known to be difficult to describe. NO is known as a non-innocent ligand in coordination chemistry, leading to complicated and ambiguous electronic structures of transition metal nitrosyls. Enemark and Feltham [2] have suggested to describe the electronic structure of this moiety as $\{\text{M}(\text{NO})\}^n$, with n being the total number of electrons in the metal d and nitrosyl π^* orbitals. However, within this concept it is neither possible to assign a particular oxidation state to the metal nor to the NO. For example, it is unclear whether $\{\text{RuNO}\}^6$ should be treated as $\text{Ru}^{\text{II}}-\text{NO}^+$ or $\text{Ru}^{\text{III}}-\text{NO}^0$.

In this work we attempt to resolve the ambiguity of the electronic structure of the $\{\text{Ru}(\text{NO})\}^6$ moiety with the help of density-fitting CASSCF (DF-CASSCF) calculations and localised natural orbitals, similarly to the approach of Radoń et al. [3] on $\{\text{Fe}(\text{NO})\}$ complexes. We optimise the S_0 and T_1 structures with the DF-CASSCF method using the newly developed analytical gradients with atomic compact Cholesky Decomposition (acCD) basis sets[4]. Subsequently, we describe the electronic structure of a $\{\text{Ru}(\text{NO})\}^6$ complex with a CASSCF wavefunction expansion in terms of localised orbitals, and conclusions about the electronic structure such as the formal oxidation state of Ru and the charge of NO are drawn from the total contribution of certain classes of electronic configurations to the multiconfigurational wavefunction.

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[3] Radoń, M.; Broclawik, E.; Pierloot, K. *J. Phys. Chem. B* **2010**, *114*, 1518–1528.

[4] Aquilante, F.; Gagliardi, L.; Pedersen, T. B.; Lindh, R. *J. Chem. Phys.* **2009**, *130*, 154107.