

DFT studies of electronic communication in strongly interacting oxo-bridged dimolybdenum nitrosyls

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Examination of the electronic communication in redox-active bimetallic complexes incorporating various bridging ligands is important in the modelling of some key processes in both chemistry and biology. The entirely valence-trapped mixed-valence complexes based on $\{(ON)MoOMo(NO)\}^{3+}$ core stabilised by *tris*(pyrazolyl)borate are the unique examples of symmetrical oxo-bridged bimetallics with doublet ground state [1]. The EPR data suggest that the electron exchange across the Mo-O-Mo array could be thermally activated. The study of such systems could allow greater insight into factors controlling the electron transfer process through short bridges.

The hybrid B3LYP as well as non-hybrid OLYP and BP86 DFT formalism has been applied to calculate the properties of a mixed-valence monoanion and monocation derived from the spectroscopically [1] and structurally [2] characterised $[(HO)(Tp^{Me_2})(NO)MoOMo(NO)(Tp^{Me_2})(OH)]$ complex. The main objective of this study is to characterise the effect of either electronic or geometrical factors, such as the relative orientation of $\{Mo(NO)\}^{2+/3+}$ moieties, on the degree of through-bond electronic coupling between metal-based centres (Fig. 1). The voltammetrically established potentials of formation of both $\{16e:17e\}^-$ and $\{15e:16e\}^+$ complexes as well as IR spectra (especially ν_{NO} and ν_{MoOMo} stretching frequencies) and X-ray crystal data of the precursor complex were successfully related to the computed parameters.

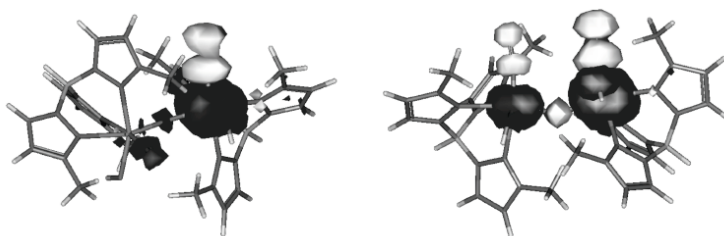


Fig. 1 DFT calculated spin densities for optimised (left) and twisted (right) complex.

[1] Włodarczyk, A.; Coles, S. J.; Hursthouse, M. B.; Abdul, K. M.; Lieberman, H. F. *J. Chem. Soc., Dalton Trans.* **1997**, 2921.

[2] Noga, K.; Romańczyk, P. P.; Włodarczyk A. J.; Nitek, W.; Broclawik, E., manuscript in preparation.