

A NEW LOOK AT MOLECULAR AND ELECTRONIC STRUCTURE OF $[\text{Fe}_2]^{4+}$ AMIDINATES: EXPERIMENTAL AND THEORETICAL STUDIES

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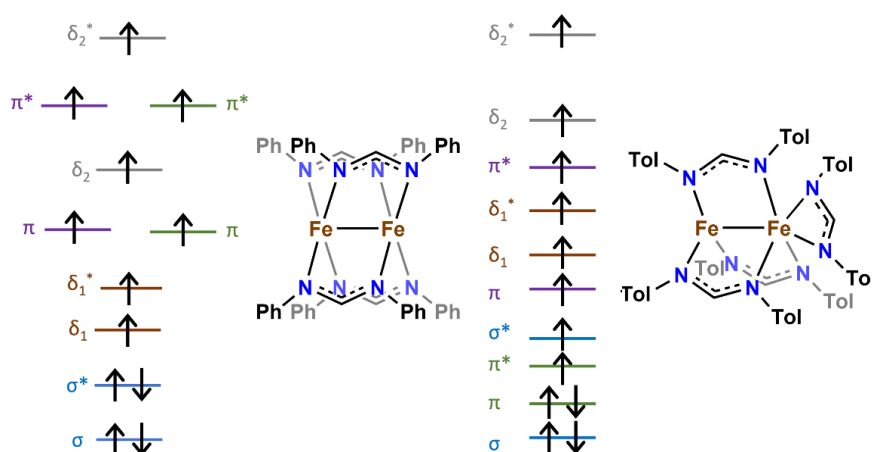
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Transition metal complexes incorporating the metal-metal (M-M) bond are a subject of widespread interest, including fundamental curiosity and potential applications in catalysis and small molecules' activation. The most known M-M bonded compounds are binuclear paddlewheel-type complexes, which generally show strong M-M interactions, leading to a low-spin bimetallic core, often with multiple bonding between metal atoms.[1,2] However, M-M bonded compounds with Fe or Co centres often show a thermally-persistent high-spin ground state, which is interesting from the point of view of molecular magnetism.

Herein, I present our studies about M-M interactions in high-spin $[\text{Fe}_2]^{4+}$ formamidates.[3] Particularly, I show how subtle changes in the ligand backbone can dramatically affect the molecular and electronic structure of $[\text{Fe}_2]^{4+}$ complexes. Thus, switching from phenyl to p-tolyl N-substituted formamidate ligand results in a major structure change – the formation of an unprecedented non-centrosymmetric complex $[\text{Fe}(\mu\text{-DTolF})_3\text{Fe}(\kappa^2\text{-DTolF})]$ incorporating variously coordinated *N,N*-bidentate symmetric ligands. Finally, we also provided a new ground state electronic structure of complexes $[\text{Fe}_2(\mu\text{-DPhF})_4]$ and $[\text{Fe}(\mu\text{-DTolF})_3\text{Fe}(\kappa^2\text{-DTolF})]$, based on high-level *ab-initio* calculations, and supported by magnetic measurements, Mössbauer spectroscopy, and cyclic voltammetry. Moreover, the presented $[\text{Fe}_2]^{4+}$ complexes exhibit field-induced slow magnetic relaxation with the effective magnetisation reversal barrier. Our studies set the stage for further advances in the fundamental chemistry of M-M bonded complexes and their applications in catalysis and molecular magnetism.



[1] Cotton F.A., Murillo C.A., Walton R.A., *Multiple Bonds between Metal Atoms*, Springer, NY, **2005**.

[2] Duncan Lyngdoh R.H., Schaefer H.F., King R.B., *Chem. Rev.* **2018**, *118*, 11626–11706.

[3] Korona K., Terlecki M., Justyniak I., Magott M., Żukrowski J., Kornowicz A., Pinkowicz D., Kubas A., Lewiński J., *Chem. Eur. J.*, **2022**, *28*, DOI: 10.1002/chem.202200620.