

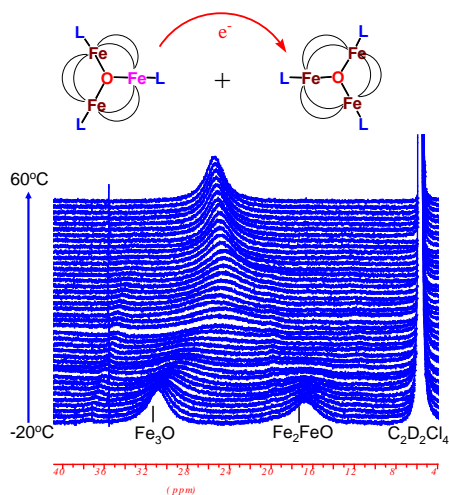
## NMR Study of Ligand Exchange and Electron Self-exchange Between Oxo-centered Trinuclear Clusters

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Ligand substitution and electron transfer reactions are two of the widely investigated processes in coordination chemistry.<sup>1</sup> Most of these investigations are focused on mononuclear compounds and comparatively little work is available for coordination clusters.<sup>2</sup> In this communication the ligand exchange and electron self-exchange reactions for labile paramagnetic carboxylate clusters  $[\text{Fe}^{\text{III}}_2\text{MO}(\text{Ac})_6\text{L}_3]^{0/+}$   $\text{M}=\text{Fe}^{\text{III}}(\mathbf{1})$ ,  $\text{Fe}^{\text{II}}(\mathbf{2})$ ,  $\text{Co}^{\text{II}}(\mathbf{3})$ ,  $\text{Ni}^{\text{II}}(\mathbf{4})$   $\text{L}=\text{Rpy}$  was analysed by dynamic NMR spectroscopy. The variable temperature line-shape NMR analysis of solutions of each cluster showed that these exchange reactions occur with  $D$  limiting dissociative mechanisms.<sup>3</sup> Due to the slow ligand exchanges at the NMR time scale on the homovalent  $\text{Fe}^{\text{III}}_3\text{O}$  cluster, individual signals for the mixed ligand cluster could be observed. The electron self-exchange rate between  $\mathbf{1}$  and  $\mathbf{2}$  has been followed simultaneously with the ligand exchange on  $\mathbf{2}$ . The equilibrium constant for the formation of the precursor to the electron-transfer and the free energy of activation contribution for the solvent reorganisation to reach the electron transfer step have been considered the same for both compounds. The populations of different spin states in  $\text{Fe}^{\text{III}}_3\text{O}$  ( $\mathbf{1}$ ) and  $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}$  ( $\mathbf{2}$ ) are correlated with rate of electron self-exchange reaction.<sup>4</sup>



### References

- [1] F. Basolo, R.G. Pearson, *Mechanisms of Inorganic Reactions*. Wiley, N.Y., (1967). M.L. Tobe, J. Burgess, *Inorganic Reaction Mechanisms*. In Longman: N.Y., (1999). J.D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*. WILEY-VCH: Weinheim, (1997). R. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*. VCH, (1991). R.B. Jordan, *Reaction Mechanism of Inorganic and Organometallic Systems*. Oxford University Press (1991).
- [2] E. Balogh, W.H. Casey, *Progress in Nuclear Magnetic Resonance Spectroscopy* (2008), 53, 193.
- [3] G. Novitchi, F. Riblet, R. Scopelliti, L. Helm, A. Gulea, A.E. Merbach, *Inorg. Chem.* (2008), 47, 10587.
- [4] G. Novitchi, L. Helm, C. Anson, A.K. Powell, A.E. Merbach, *Inorg. Chem.* (2011), 50, 10402.