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Fused ferrocenes come full circle

Chemists have long been fascinated by electron delocalisation from both a fundamental and applied perspective. Macrocyclic oligomers containing fused ferrocenes provide a new structural framework — containing strongly interacting metal centres — that is capable of supporting substantial charge delocalisation.

Rebecca A. Musgrave and Ian Manners

Although the empirical formula of benzene had been known for many years, the cyclic structure of this prototypical aromatic hydrocarbon was not realised until 1865, when Kekulé proposed an alternating arrangement of single and double bonds within a six-carbon ring. Pauling's resonance theory subsequently described the delocalisation of electrons from the three filled π orbitals around the entire ring, satisfying Hückel's aromatic requirement of $(4n+2)\pi$ electrons. The extensive delocalisation of electrons in the benzene molecule gives rise to a number of characteristic and unusual properties: planarity, enhanced stability, aromatic ring currents, and the ability to participate in π - π stacking.

The issue of potential electron delocalisation in linear or cyclic species containing multiple metal centres has been of considerable interest for many decades. Studies of linear mixed-valence metal complexes have been at the forefront of the field¹. With increased mixing of the electronic donor and acceptor wavefunctions, discrete oxidation-state character at each metal decreases and, in extreme cases, a complete averaging of oxidation states is observed (an odd electron is delocalised over two metal sites). The dinuclear pentacationic Creutz-Taube complex **1** (Fig. 1a) is the classic example of a Robin-Day class III complex where the odd electron is completely delocalised: each ruthenium ion exhibits a fractional oxidation state of +2.5 (ref. 2). This electronic coupling of the metal orbitals with those of the bridging pyrazine ligand enabled detailed studies of the rate and activation barrier for inner-sphere electron transfer to be undertaken.

The monocation of linear biferrocene **2** (Fig. 1a) also exhibits rapid intramolecular charge transfer³, which renders it on the borderline between a Robin-Day class II (localisation of distinct valences with a low energy barrier to interconversion) and class III system. The nature of the anion, solvent and ring substitution affects the rate of intramolecular charge

transfer in these types of complex: in some cases they appear to be valence delocalised with electron transfer rates of greater than 10^{12} s^{-1} at room temperature. Significantly, electron delocalisation in linear metal-containing polymers has also been studied and can involve either inner- or outer-sphere mechanisms of electron transfer. This work has led to the development of 'conducting metallopolymers' with a range of applications^{4,5}.

Studies of delocalisation in cyclic species containing multiple metal centres are less common. The fused dinuclear ferrocene species biferrocenylene undergoes one-electron oxidation to monocation **3** (Fig. 1a) that has been shown to be delocalised at room temperature — even on the very short timescale ($\sim 10^{-17} \text{ s}$) associated with X-ray photoelectron spectroscopy — indicating that the iron centres are equivalent (Robin–Day class III)^{6,7}. Studies of larger rings have generally been limited to cases where spacer groups decrease interactions between the metal centres⁸. Now, writing in *Nature Chemistry*, a team led by Tim Albrecht and Nicholas Long report the synthesis of a beautifully simple series of oligoferrocene macrocycles (**cyclo**[*n*], $n = 5–9$, see Fig. 1a) via copper-mediated Ullmann coupling reactions of linear iodinated ferrocene precursors under high-dilution conditions.

Each cyclopentadienyl (Cp) ligand is connected to that of a neighbouring ferrocene unit through direct Cp–Cp linkages. Investigation of the electrochemical properties of **cyclo**[5], **cyclo**[6] and **cyclo**[9] revealed that individual redox events corresponding to successive one-electron oxidations of ferrocene units could be assigned. For example, for **cyclo**[9] a series of six waves was observed within the electrochemical window of the solvent, corresponding to seven different stable redox states. The difference between the potentials of successive redox waves for each species provides a measure of the extent of interaction between the metal sites (which is related to the position of the comproportionation equilibrium between the mixed-valence state and the isoivalent states).

The linear correlation between the Gibbs free energies of interaction (ΔG_{int}) and the number of electrons removed from the **cyclo**[*n*]^{*m+*} rings is indicative of delocalisation of the positive charge between the ferrocene units. This suggests that, on the electrochemical timescale, delocalisation of positive charge exists across the iron centres of the entire macrocycle. This is also reflected in the oxidation potentials: the larger the ring, the more facile oxidation is to a given oxidation state, as the positive charge is accommodated by a larger number of ferrocene units. Albrecht, Long and colleagues conclude that the **cyclo**[*n*]^{*m+*} ($n = 5, 6, 9$)

compounds may belong in the Robin–Day class II regime, as indicated by the nature of the intervalence charge-transfer bands in **cyclo[6]⁺** and **cyclo[6]²⁺** observed by UV-vis/near IR spectroscopy. Further determination of the rate of electron transfer between the metal centres on different timescales — by methods such as Mössbauer, electron spin resonance, IR, and photoelectron spectroscopy — presents a fascinating avenue for future investigation.

One of the ferrocene macrocycles, **cyclo[6]**, which might be considered to be a kind of organometallic analogue of benzene, was also characterised crystallographically (Fig. 1b). Adjacent ferrocene units were found to be twisted with respect to one another in the solid-state structure, with both *anti* and *syn* conformations present (Fe⋯Cp–Cp⋯Fe angles of 164, 138 and 48°, respectively). Such torsion decreases the efficacy of electron transfer between the $d_{x^2-y^2}$ orbitals of neighbouring iron atoms via the antibonding π orbitals of the fulvalene ligand framework, which may suggest why cations of **cyclo[6]** exhibit a lesser degree of delocalisation than that of the monocation of biferrocenylene (**3**), where torsion is negligible^{9,10}.

If the yields (currently < 2%) of Albrecht and Long's **cyclo[n]** compounds can be improved, these macrocycles may have fascinating and important applications in host–guest chemistry. Conformational flexibility (often common in larger rings) is expected in solution as a result of virtual free rotation about the Cp–Fe–Cp axis in each ferrocene unit¹¹, and the introduction of an anionic guest molecule to chemically oxidised **cyclo[n]⁺** may lead to particularly interesting studies. In addition, the design and study of soluble high molar mass polymeric analogues of these oligomers with ferrocene (or other metallocene) repeat units is an extremely appealing prospect¹².

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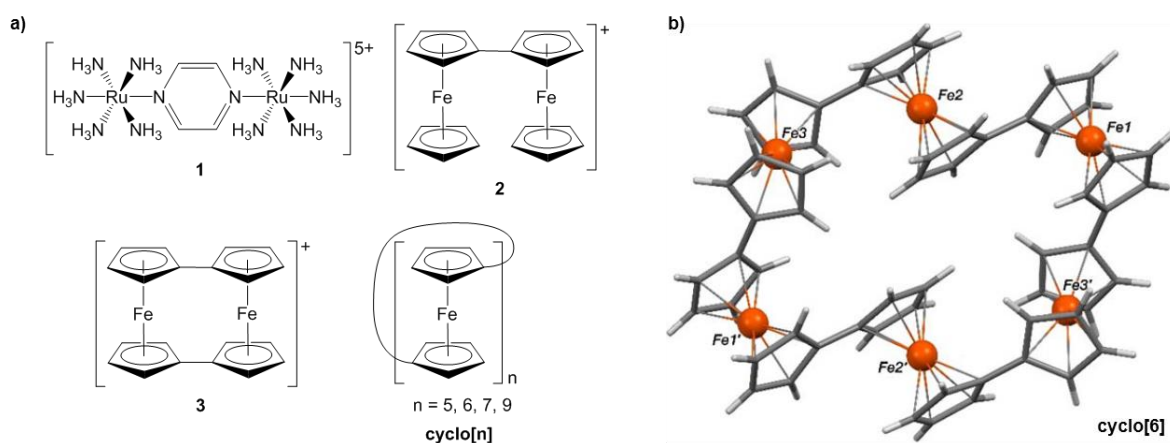


Figure 1 | Electron delocalisation in cyclic and acyclic multinuclear complexes. **a**, The Creutz–Taube complex (**1**) is a Robin–Day class III complex in which electron delocalisation results in each metal centre having a fractional oxidation state of +2.5, whereas the linear biferrocene cation (**2**) sits between a Robin–Day class II (distinct valences are localised but there is a low energy barrier to interconversion) and class III system because of rapid intramolecular charge transfer. The study of electron delocalisation in multinuclear cyclic systems is less well established, but examples include the biferrocenylene cation (**3**) and the oligoferrocene rings (**cyclo[n]**; $n = 5–9$) now reported by Albrecht, Long and co-workers. **b**) The X-ray crystal structure of **cyclo[6]**; electrochemical measurements suggest that in the oxidised form the positive charge is delocalised across all of the iron centres.