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Supplementary material

Direct Synthesis of Heterometallic {$Mn^{II}_3Cr^{III}_4$} Wheel by Decomposition of Reineckes Salt

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Electrochemistry

Cyclic voltammetry and differential pulse voltammetry were carried out by using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). Sample solution (4 cm^3) was prepared from dmf (Fluka, reagent grade) containing 0.1 M tetrabutylammonium (TBA) hexafluorophosphate (Fluka, electrochemical grade) as supporting electrolyte. A cyclic voltammogram was recorded at a scan rate of 100 mVs^{-1}. Differential pulse voltammetry was performed with a scan rate of 20 mVs^{-1}, a pulse height of 75 mV and a duration of 40 ms. The working electrode was a glassy carbon disc (diameter 3 mm). Its surface was routinely polished with a 0.05 mm alumina-water slurry on a felt surface, immediately prior to use. A glassy carbon rod served as counter electrode and the reference electrode was an Ag/Ag^+ electrode (a silver wire immersed into 10 mM $AgNO_3$ in MeCN) with a potential of –0.07 V vs. the ferrocene/ferrocenium (Fc/Fc^+) couple in dry MeCN. The counter and reference electrodes were in compartments separated from the bulk solution by fitted disks. The potentials reported here are given relative to the Fc/Fc^+ couple. Before all measurements, oxygen was removed by bubbling solvent-saturated argon through the stirred solutions. Samples were kept under argon during measurements.

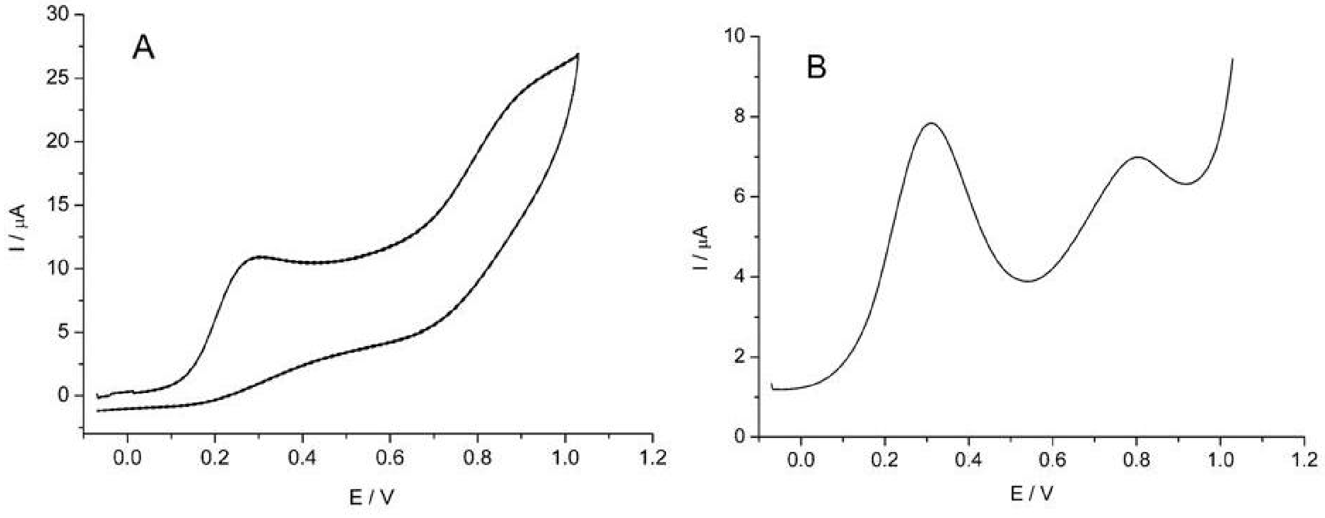

Fig. S1 Cyclic (A) and differential pulse (B) voltammograms of **1.** Potentials are given vs. the $Fc^{+/0}$ couple.

The cyclic voltammogram of **1** (Fig. 2A) displays two irreversible oxidation processes, which are attributed to the subsequent one-electron oxidation of the two Mn(II) ions at the rim to Mn(III). The exact values of $E_{1/2}$, obtained from differential pulse voltammetry (Fig. 2B), were found to be 0.31 and 0.80 V. As expected, the central Mn(II) ion does not undergo oxidation in the given potential range. Similar redox behavior has also been observed for other manganese containing wheels $[\mathrm{NEt_4}]\{\mathrm{Mn^{II}}[\mathrm{Mn^{II}}_3\mathrm{Mn^{III}}_3\mathrm{Cl}_6(\mathrm{L})_6]\}$,[1] $[\mathrm{PPh_4}]\{\mathrm{Mn^{II}}[\mathrm{Mn^{II}}_3\mathrm{In^{III}}_3{}^{\mathrm{Cl}}{}_6(\mathrm{L})_6]\}$ and $\{\mathrm{Mn^{II}}[\mathrm{Mn^{II}}_2\mathrm{In^{III}}_4\mathrm{Cl}_6(\mathrm{L})_6]\}$[2] (L = $\mathrm{RN(CH_2CH_2OH)}$, R = $\mathrm{CH_3}$, Benzyl). The potential displacement of 0.49 V between the individual oxidation reactions of the Mn ions, which are situated in the same coordination environment, indicates intermolecular electronic communication. The electrochemical behavior described above means that the wheel structure of the complex remains intact in solution.

1 R.W. Saalfrank, T. Nakajima, N. Mooren, A. Scheurer, H. Maid, F. Hampel, C. Trieflinger and J. Daub, *Eur. J. Inorg, Chem.,* 2005, 1149.

2 R.W. Saalfrank, R. Prakash, H. Maid, F. Hampel, F.W. Heinemann, A.X. Trautwein and L.H. Bottger, *Chem. Eur. J.*, 2006, **12**, 2428.