A Soluble Tetranuclear Complex Capable of an Eight-electron Change

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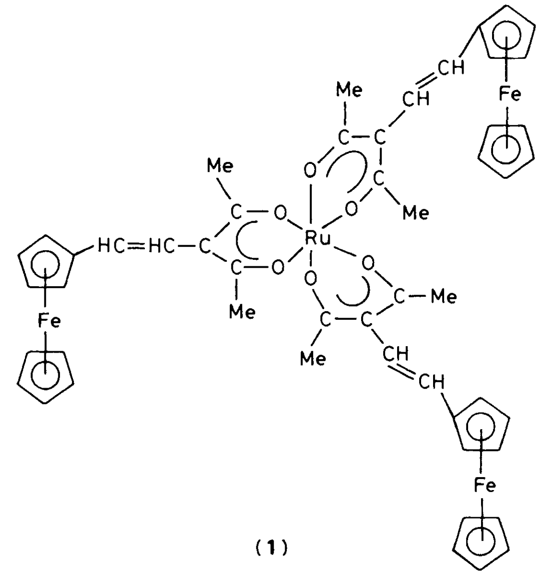
A tetranuclear complex containing one ruthenium ion and three ferrocene moieties has been found to undergo an eight-electron change with four electrons exchanging formally at the central ruthenium atom.

Our attempts to prepare a new class of compounds containing several metal ions in a rigid environment connected by ligands having extensive π-systems have resulted in a remarkable complex which undergoes an $8e^-$ change almost completely reversibly. The compound, (**1**), was prepared by a procedure previously reported[1] using ruthenium in place of the cobalt used in the earlier publication.

The only other systems which come close to duplicating this feat are the cluster complexes, $[Ru_2O(OAc)_6(L)_3]^{n+}$ first described by Spencer and Wilkinson[2] and later studied by Meyer *et al.*[3—5] These molecules may add $6e^-$ per cluster or $2e^-$ per Ru atom. Meyer *et al.*[5] have further described a trimer $[Ru_3O(OAc)_6(pyridine)_2(pyrazine)]_2[Ru_3O(OAc)_6(CO)]^{2+}$ which will undergo a $10e^-$ change *i.e.* slightly more than $1e^-$ per Ru atom. In our molecule, the Ru atom undergoes formally a $4e^-$ change. Each Fe atom additionally undergoes a $1e^-$ transfer, and the final redox transformation, at +0.88 V, is assigned to the organic ligand system.†

The cyclic voltammogram of (**1**) is shown in Figure 1. The three ferrocene iron atoms undergo a redox change at +0.69 V *vs.* NHE. The ruthenium atom, initially in the +3 oxidation state undergoes a series of one-electron reductions at −0.23, −0.41, and −0.56 V, taking it to the zero oxidation



(1)

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† A similar peak corresponding to addition of an electron to the ligand has been observed in the series $[Ru(ptdn)_n(ptdn\text{-}I)_{3-n}]$ $n = 0, 1, 2, 3$, ptdn-I is 3-iodopentane-2,4-dione; N. A. Lewis and B. K. P. Sishta, submitted to *Inorg. Chem.*

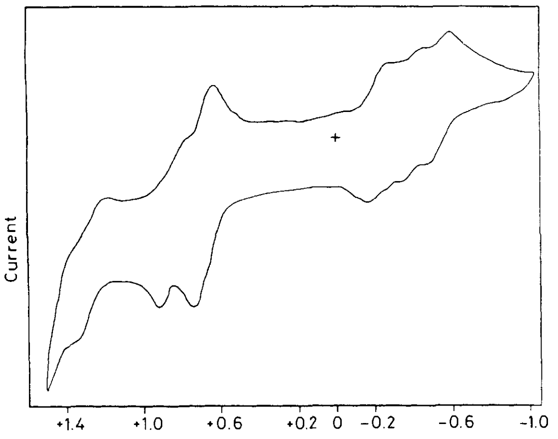

Figure 1. Cyclic voltammogram of 1 × 10^{-3} M tris(3-vinylferrocenylpentane-2,4-dionato)ruthenium(III) in acetonitrile containing 0.10 M $N(C_4H_9)_4PF_6$ as supporting electrolyte. The working and auxiliary electrodes were Pt and the reference was a standard calomel electrode (SCE). The scan rate was 50 mV/s and repeated scans were unchanged. Scans were taken at ambient temperature, and the figure shows the cyclic voltammogram with a normal hydrogen electrode (NHE) as the reference. All $E_{\frac{1}{2}}$ values quoted in the text are also referenced to the NHE.

state, at least in a formal sense (*vide infra*), and it becomes oxidised to the +4 state at a very high positive potential, 1.27 V. The oxidation state of +4 is commonly observed in this region, even for the unsubstituted tris(pentane-2,4-dionato)ruthenium(III) complex, $Ru(ptdn)_3$.[6] The observed peak splittings $\Delta E_p = E_{p,a} - E_{p,c}$ for the waves were in the range 100—140 mV, independent of sweep rate from 50 to 200 mV/s, whereas the peak-to-peak separation for the standard compound, $Ru(ptdn)_3$, was 80 mV. The values are larger than the theoretical value of 58 mV, possibly because of uncompensated solution resistance. The ratio of anodic to cathodic peak heights is essentially unity for all waves except the ligand-centred one which is partially obscured by the ferrocene wave. This indicates that the degree of irreversibility is small.

There is little doubt that the electrons are being delocalised into the π-cloud of the ligands since if only one of the pentane-2,4-dione rings has a ferrocene moiety connected to it, there is only one redox reaction for the ruthenium atom at a fairly negative potential, −0.54 V and when two rings are substituted, two peaks appear, at −0.31 and −0.49 V; it is only when all three rings bear ferrocene substituents that the ruthenium will undergo a three-electron change in the region. Also, the tris(2,2′-bipyrazine)ruthenium(II) shows a similar series of oxidation–reduction processes at similar energies.[7]

The elusive goal of performing multi-electron catalysis, particularly of a small molecule such as dioxygen, using a metal formally capable of undergoing a $4e^-$ change and existing as a seven-co-ordinate species[8] appears to have become a distinct possibility which we are actively pursuing. In addition, these aggregates may easily be linked together to form larger networks which may be useful for theoretical studies as well as electron storehouses in multi-electron catalysis of organic substrates.

We are grateful to the Natural Sciences and Engineering Research Council of Canada for a Co-op grant (1980—81) which initiated this research. Since then, it has been supported by the University of New Brunswick Research Fund and the Department of Employment and Immigration. We thank Dr. P. M. Henry for advice and encouragement.

Received, 22nd May 1984; Com. 718

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