Electronic interactions in multicluster arrays. An electrochemical approach. Part I

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Abstract

An electrochemical study on the electronic interactions occurring between the two '$CCo_3(CO)_9$' redox cores in the dimers $Co_3(CO)_9(C–C)Co_3(CO)_9$ and $Co_3(CO)_9(C–C{\equiv}C–C)Co_3(CO)_9$ is reported. In both derivatives, two well resolved peaks/waves are observed in several solvents by cyclic, square wave voltammetry and d.c. polarography, respectively, for the (0,0)/(0,1 –) and (0,1 –)/(1 –,1 –) reduction processes. The differences in electrode potentials of the two first reductions, $\Delta E^{\circ\prime}$, indicate a moderate electronic interaction between the redox centres in both compounds, which mainly occurs via the carbon chains.

Introduction

There is growing interest in mixed-valence compounds [1] (containing redox centres in more than one oxidation state) because of the opportunity for new conducting, magnetic and optical properties to be developed [2].

Apart from Prussian blue complex, where the deep colour arises from visible light absorption due to electron transfer from Fe^{II} to Fe^{III} (intervalence transition) [1b], the first planned synthesis of mixed-valence afforded the Creutz–Taube complex [1a, 1b]. Mixed-valence compounds can also be electrogenerated from materials having interacting redox centres by controlled change of their oxidation state. This is the case of bis(fulvalene)dimetal complexes [3].

Organometallic clusters may be suitable for producing mixed-valence materials if they (i) adopt a range of valence states, (ii) undergo electrochemically and chemically reversible electron transfer reactions, (iii) have redox potentials tuneable by the electronic properties of ancillary ligands, (iv) are easily linked by polydentate ligands to form dimers or polymers [4]. Robinson and co-workers have studied in great detail a number of such ligand-linked clusters [5].

Electrochemical techniques, especially cyclic voltammetry (CV), are able to reveal the electronic interactions between the redox centres and then to predict the possible formation of mixed-valence compounds [6].

There are two limiting cases for a dimeric compound (A)-L-L-(A') consisting of two identical redox centres (A, A') linked by a polydentate ligand (L-L):

(i) no electronic interaction between the two centres (L-L is an insulator), the $E^{\circ\prime}$ values for the redox processes differ by a small statistic factor ($\Delta E^{\circ\prime} = (RT/F) \ln 4 \cong 36$ mV at 25 °C) and in CV a single peak (having the slope of one-electron transfer process, but the height of two-electron process) is observed (Hush, Robin, Day [1c, 1d] class I, $\alpha \cong 0$ systems);

(ii) complete charge delocalization over the two redox centres (L-L is a conductor): the $E^{\circ\prime}$ values for the two redox processes differ by about 500–600 mV and in CV two well-resolved peaks (each of one electron height) are observed (class III, $\alpha \cong 0.7$ systems).

In between these extremes, there is a large number of compounds having weakly interacting redox centres (class II systems). In this case the quantitative relationship between the separation of formal potentials of the two successive one-electron steps ($\Delta E^{\circ\prime}$) and the electronic delocalization is unclear, since differences in solvation energy, ion pairing effects and structural rearrangements (during or after the electron transfers) play a role [4].

The qualitative differentiation of electronic interactions between the redox centres through space and through the bridging ligand is also possible, since the former is more sensitive to redox centre distance and solvent polarity than the latter [1b].

The methinyltricobalt enneacarbonyl clusters, $[YCCo_3(CO)_9]$, are ready reduced to stable radical

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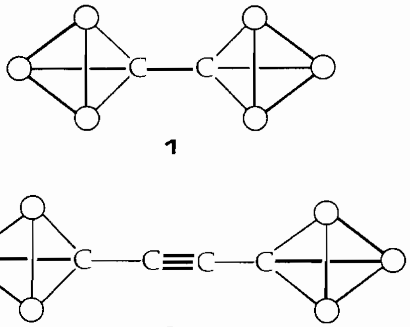
anions and participate to an efficient charge redistribution through the apical carbon atom [7]. Two dimers, namely $Co_3(CO)_9(C{-}C)Co_3(CO)_9$ and $Co_3(CO)_9(C{-}C{\equiv}C{-}C)Co_3(CO)_9$, have been chosen to evaluate the electronic interaction between the '$CCo_3(CO)_9$' redox cores. Some electronic interaction through the carbon chains is expected for both compounds since the structural investigations [8, 9] showed C–C bond distances consistent with partial π delocalization [10].

Results and discussion

The $Co_3(CO)_9(C{-}C)Co_3(CO)_9$ (**1**) and $Co_3(CO)_9(C{-}C{\equiv}C{-}C)Co_3(CO)_9$ (**2**) dimeric derivatives, coupled through C–C bonds, can be obtained as by-products from the reaction of $Co_2(CO)_8$ and CCl_4, which affords mainly $Co_3(CO)_9CCl$ [11]. The yields of **1** and **2** have been improved by further pyrolysis of $Co_3(CO)_9CCl$ in *p*-xylene [9]. Their structures are schematically reported in Fig. 1.

Electrochemical behaviour of 1

Since compound **1** itself and the corresponding electrogenerated anions are quite unstable at room temperature, the relevant electrochemical investigations have been carried out at subambient temperature, mainly −20 °C. Figure 2 shows the cyclic voltammetric response of a tetrahydrofuran (THF) solution of 1 and ferrocene ($FeCp_2$), added as internal standard, at a Hg electrode at −20 °C and at 200 mV s^{-1}. The forward cathodic sweep reveals four reduction processes (peaks A–D), each roughly corresponding to one electron transfer process when compared with the ferrocene/ferrocinium peak system, corrected for different concentrations and different diffusion coefficients (factor = 0.6). The reduction peak potentials are $E_p(A)(0,0/0,1-) = -0.49$, $E_p(B)(0,1-/1-,1-) = -0.95$, $E_p(C)(1-,1-/1-,2-) = -1.58$ and $E_p(D)(1-,2-/2-,2-) = -2.14$ V versus SCE. The lack or the very low height of the associated reoxidation peaks in the reverse scan, as well as the appearance of extra peaks, confirms the instability of the electrogenerated anions. If the cathodic scan is limited to the first couple of reductions (peaks A and B), by inverting the potential at $E_\lambda = -1.30$ V the associated reoxidation peaks (A′ and B′) can be observed (Fig. 3). The i_p^a/i_p^c ratio is 0.70 for the first peak system (A/A′) and 0.73 for the second peak system (B/B′) at a scan rate of 50 mV s^{-1}. Both ratios reach unity at scan rates as high as 1 V s^{-1}. At low scan rates, two other reoxidation peaks E and F are observed at potentials more positive than those of B′ and A′, respectively (Fig. 3). They arise from chemical complications, since they strongly decrease as the scan rate is increased or the temperature is further lowered. The imposition of a holding time (5 s) at the inversion potential ($E_\lambda = -1.30$ V) during the CV scan (Fig. 4) increases the height of peaks E and F with respect to those of peaks B′ and A′, indicating that the chemical complications arise mainly after the electrogeneration of the dianion $[\mathbf{1}]^{2-}$. Indeed, a holding time after the peak A has been traversed is less effective in increasing the height of peak F with respect to that of peak A′ (Fig. 4).



1

2

Fig. 1. Sketch of the structure of $Co_3(CO)_9(C{-}C)Co_3(CO)_9$ (**1**) and $Co_3(CO)_9(C{-}C{\equiv}C{-}C)Co_3(CO)_9$ (**2**). ○ stands for '$Co(CO)_3$' moiety.

Robinson [12] showed by means of spectroelectrochemistry that the electrogenerated anion $[\mathbf{1}]^-$ isomerizes to a form with bridging CO groups. Such bridging groups are able to relieve electronic density in the monoanion and then stabilize it. Therefore, the reoxidation of such isomeric monoanions is expected to occur at less negative potential and we assign peak F to such a process. Peak E could be associated to the reoxidation of the isomeric (bridging form) $[\mathbf{1}]^{2-}$ dianion as well. From these electrochemical data in THF solution we suggest such an isomerization takes place mainly when dianion $[\mathbf{1}]^{2-}$ is generated. A similar switch from terminal to bridging structure is observed in monomeric $MeCCo_3(CO)_{9-x}(PR_3)_x$ ($x = 1, 3$) derivatives, where the increase in electron density on the Co_3 moiety is more effectively dissipated by bridging CO groups [13].

The formal electrode potentials for the two first reductions has been evaluated as $E^{\circ\prime} = (E_p^a + E_p^c)/2$ at a scan rate sufficiently high ($\geqslant 1$ V s^{-1}) to prevent any chemical complication (see Table 1). Also in polarography (Fig. 5) two well resolved waves are observed in the range 0.00 to −1.30 V having half-wave potential, $E_{1/2}$, of −0.47 and −0.96 V, respectively. Both plots of $\log[(i_d - i)/i]$ versus E slope 59 mV, as expected for a Nernstian (fast electron transfer) process. The comparison with the diffusion current of $FeCp_2$, added as internal standard, confirms that each reduction implies a one-electron transfer. The square wave voltammetric (SWV) response of a THF solution of **1**, in the frequency range 30–120 Hz, is reported in Fig. 6. From a qualitative

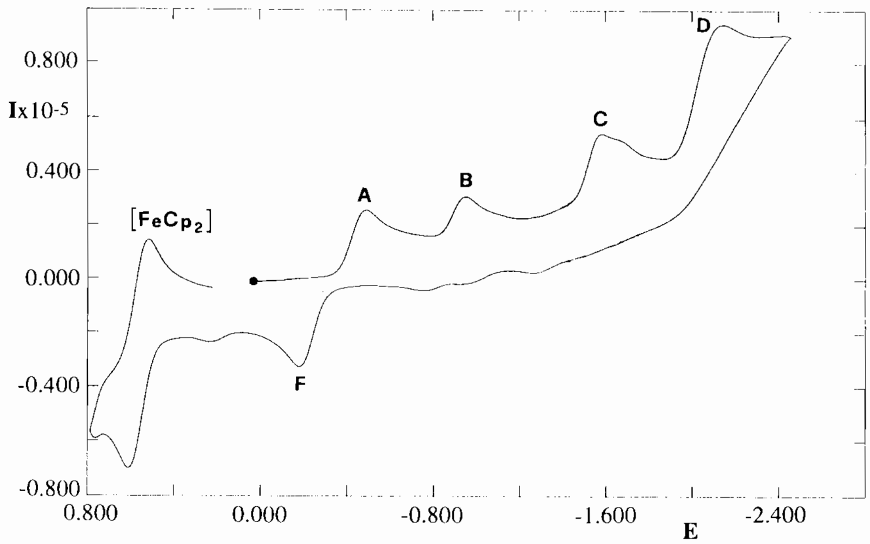


Fig. 2. CV response of a THF solution of **1** and $FeCp_2$ (correction factor = 0.6) at −20 °C, 200 mV s^{-1}. The working electrode is a hanging mercury drop electrode (HMDE).

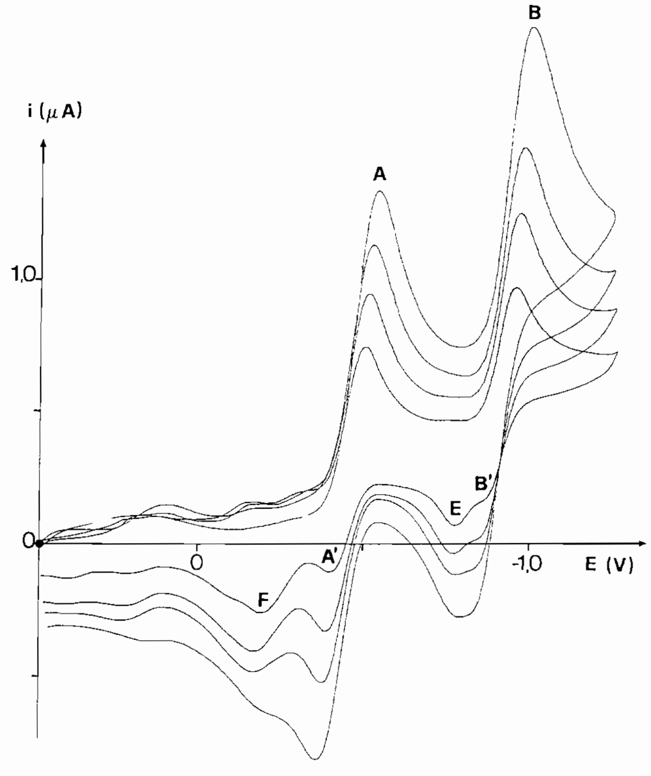


Fig. 3. CV response of a THF solution of **1** within the range 0.00 to −1.30 V, at −20 °C. The working electrode is an HMDE. The scan rate varies from 100 to 400 mV s^{-1}.

point of view [14], the minor summit current* of peak B, $i_{su}(B)$, with respect to that of peak A, $i_{su}(A)$ (at each frequency employed) confirms that chemical complications are mainly associated to the second reduction process. The relevant summit potentials, E_{su}, are reported in Table 1.

The electrochemical behaviour of **1** in different solvents, such as dichloromethane, CH_2Cl_2, and acetone, CH_3COCH_3, is very similar (Table 1).

The overall electrochemical response of **1** is obviously indicative of moderately interacting '$CCo_3(CO)_9$' redox centres.

Electrochemical behaviour of 2

Compound **2** is more stable than **1** in the electrochemical experimental conditions, this is especially true in THF (a solvent able to stabilize metal carbonyl anions [16]), so the electrochemical experiments in such a solvent have been carried out at room temperature. Figure 7 shows the CV response of a THF solution of **2** and $FeCp_2$, added as internal standard, at an Hg electrode and at 200 mV s^{-1}. The cathodic scan reveals four reduction processes (peaks G–L) each roughly corresponding to one electron transfer process, when compared with the ferrocene/ferrocinium peak system, corrected for different concentration and different diffusion coefficient (factor = 0.3). The reduction peak potentials are $E_p(G)(0,0/0,1-) = -0.41$, $E_p(H)(0,1-/1-,1-) = -0.71$, $E_p(I)(1-,1-/1-,2-) = -1.53$ and $E_p(L)(1-,2-/2-,2-) = -1.75$ V versus SCE.

Also in this case there are several oxidation peaks, due to electroactive species generated by chemical reactions following the reductions. If the cathodic scan is limited to the first two reductions ($E_\lambda = -0.80$ V), the two directly associated reoxidation peaks, G' and H', are observed (Fig. 8). The i_p^a/i_p^c ratios for both the peak systems G/G' and H/H' are unity at a scan rate as slow as 200 mV s^{-1}. The comparison of the peak potential differences, $\Delta E_p = E_p^c - E_p^a$, of the two

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*The term summit current has been suggested for SWV by the IUPAC Commission on Electroanalytical Chemistry [15].

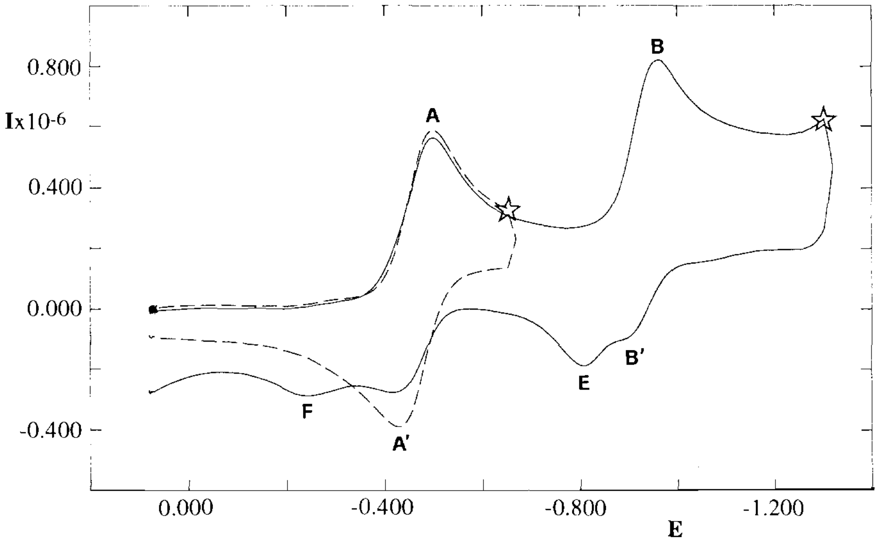

Fig. 4. CV response of a THF solution of **1** within the range 0.00 to −1.30 V, at −20 °C. The working electrode is an HMDE. Holding times of 5 s (indicated with stars) were applied after the first and second reduction processes, respectively.

TABLE 1. Electrochemical data of compounds $Co_3(CO)_9(C–C)Co_3(CO)_9$ (**1**) and $Co_3(CO)_9(C–C{\equiv}C–C)Co_3(CO)_9$ (**2**) in different solvents at an Hg electrode

Compound	Solvent	CV			D.c. polarography		SWV	
		$E°'(0,0/0,1-)$ (V vs. SCE)	$E°'(0,1-/1-,1-)$ (V vs. SCE)	$\Delta E°'$ (mV)	$E_{1/2}(0,0/0,1-)$ (V vs. SCE)	$E_{1/2}(0,1-/1-,1-)$ (V vs. SCE)	$E_{su}(0,0/0,1-)$ (V vs. SCE)	$E_{su}(0,1-/1-,1-)$ (V vs. SCE)
	THF[a]	−0.45	−0.92	470	−0.47	−0.96	−0.46	−0.93
1	CH_2Cl_2[a]	−0.55	−0.89	340	−0.55	−0.90		
	CH_3COCH_3[a]	−0.38	−0.74	360	−0.38	−0.74		
	THF[b]	−0.36	−0.66	300	−0.39	−0.68	−0.38	−0.67
2	CH_2Cl_2[c]	−0.53	−0.73	200	−0.52	−0.73		
	CH_3COCH_3[c]	−0.32	−0.53	210	−0.31	−0.52		

[a] At −20 °C. [b] At room temperature (25 °C). [c] At −10 °C.

reductions with that of the internal standard $FeCp_2$, show that both processes are electrochemically reversible (see 'Experimental'). The formal electrode potentials are $E°'(0,0/0,1-) = -0.36$ and $E°'(0,1-/1-,1-) = -0.66$ V versus SCE. The half-wave potentials from polarography are −0.39 and −0.68 V, respectively. Finally, the SWV response of a THF solution of **2** (Fig. 9) exhibits two reduction peaks of about the same height in the frequency range 30–120 Hz, having E_{su} of −0.38 and −0.67 V, respectively. The plots of i_{su} versus the square root of the frequency are linear through the origin for both reductions; the peak widths, $W_{1/2}$, (*c.* 103 mV for both reductions) are independent of frequency and close to the value expected for a Nernstian one-electron process (99 mV at 25 °C) [14].

The closeness of potentials obtained with different electrochemical techniques, namely CV, polarography and SWV, confirms the electrochemical reversibility of both processes.

Electronic interaction between the '$CCo_3(CO)_9$' redox core in 1 and 2

Table 1 shows that the change of solvents from CH_2Cl_2 to THF and to CH_3COCH_3 makes the reduction potentials of both processes in both dimers less negative. This trend is consistent with the dielectric constants (ϵ) of the solvents. Solvation of the electrogenerated anion and specific cation–anion association are believed to be responsible for these solvent effects in metal clusters [17].

The electronic interaction, roughly evaluated as the difference between the potentials of the two subsequent processes, $\Delta E°' = E°'(0,0/0,1-) - E°'(0,1-/1-,1-)$, does not dramatically change with the polarity of the solvent. Indeed $\Delta E°'$ is 340 mV in CH_2Cl_2 and 360 mV in CH_3COCH_3 for **1**, and 200 mV in CH_2Cl_2 and 210 mV in CH_3COCH_3 for **2**, notwithstanding that the dielectric constant is much higher for CH_3COCH_3 (20.7) than for CH_2Cl_2 (8.9). This suggests that the electronic interaction mainly occurs through the carbon chain; a

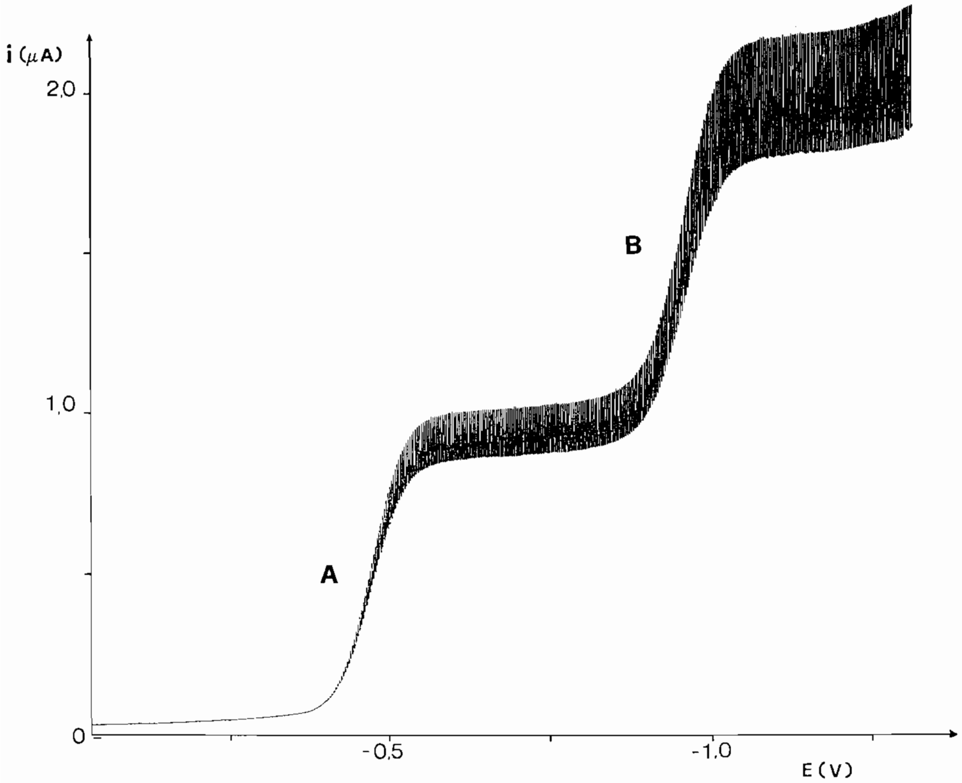

Fig. 5. D.c. polarographic response of a THF solution of **1**, at −20 °C, drop time 2 s, scan rate 1 mV s^{-1}.

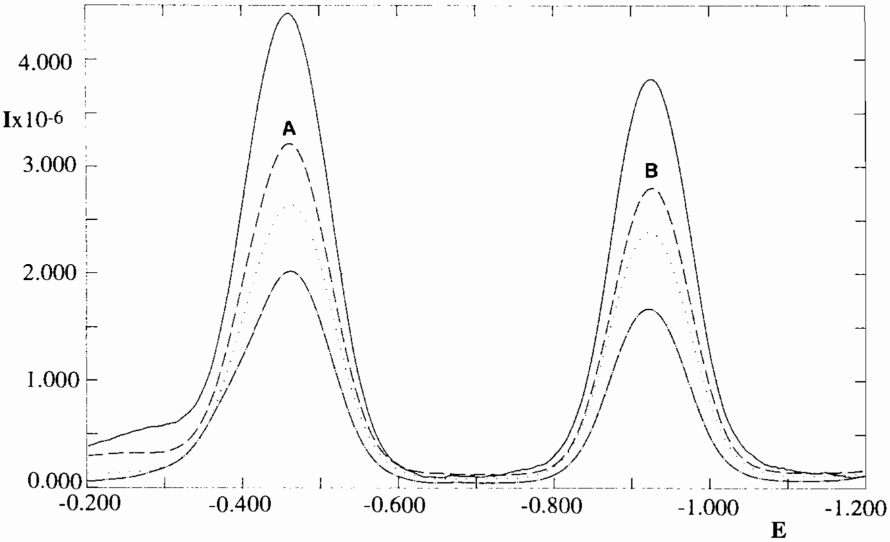

Fig. 6. SWV response of a THF solution of **1**, at −20 °C. Scan increment 0.002 V, pulse height 0.025 V. The frequencies employed were 30 (– · –), 60 (· · ·), 90 (– – –), 120 (——) Hz. The working electrode is an HMDE.

coulombic interaction should be very sensitive to the dielectric properties of the solvents and decrease as ϵ increases. For both derivatives $\Delta E^{\circ\prime}$ in THF is significantly higher with respect to the other solvents employed. THF has excellent donor properties [18] and could stabilize the activated state for the electrogenerated mixed-valence monoanion, thus increasing the interaction between the redox centres. This finding can be expected for class II mixed-valence materials [1b].

Finally $\Delta E^{\circ\prime}$ in **2** is only 170–140 mV (depending on the solvent) smaller than in **1**, while the distance between the redox cores (assumed to be the Co_3 triangle centre), calculated from structural data [8, 9], is almost double in **2** (7.1 Å) than in **1** (4.6 Å). This again

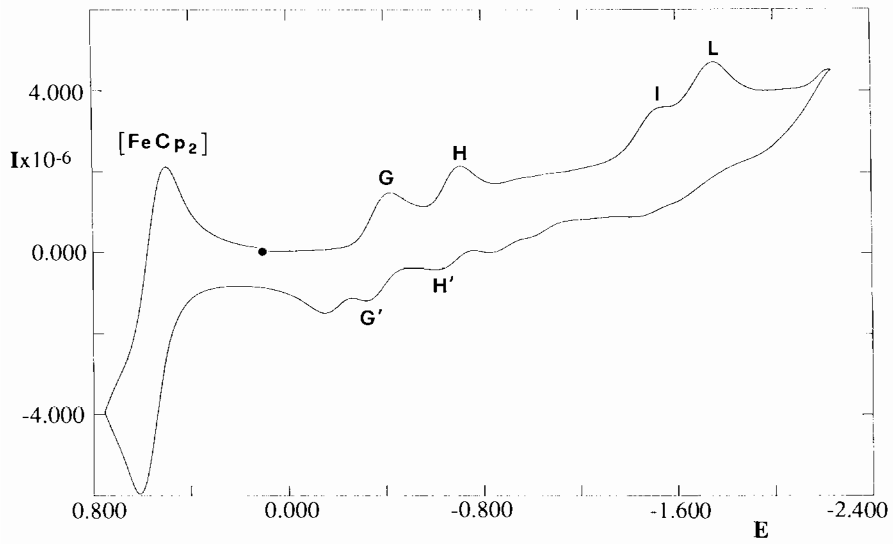

Fig. 7. CV response of a THF solution of **2** and $FeCp_2$ (correction factor = 0.3) at room temperature, 200 mV s^{-1}. The working electrode is an HMDE.

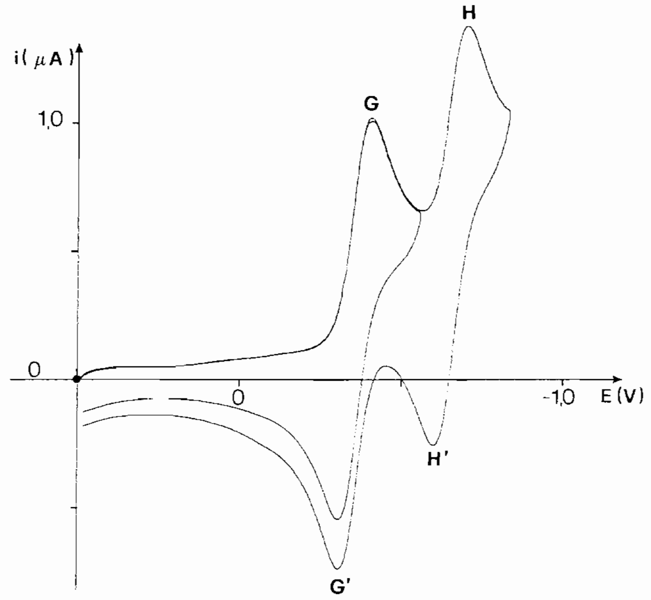

Fig. 8. CV response of a THF solution of **2** within the range 0.00 to −0.80 V, at room temperature, 200 mV s^{-1}. The working electrode is an HMDE.

suggests that the electronic interaction mainly occurs through the carbon chain.

Experimental

The dimeric derivatives **1** and **2** were synthesized according to the literature procedures [9, 11]. Their purity was checked by IR and ^1H NMR spectroscopy.

Electrochemical measurements were performed on a PAR 273 electrochemical analyzer interfaced to an IBM microcomputer. A standard three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. Positive feedback *iR* compensation was applied routinely. Ferrocene was added as internal standard in known concentration. Since some *iR* drop distortion is present in the very high resistance THF medium, the peak-to-peak separations, ΔE_p, as function of the CV scan rates, were corrected by assuming that the $[\text{ferrocene}]^{0/1+}$ couple must have a constant value of 60 mV. Therefore, the statement ‘electrochemically reversible’ indicates a redox process as reversible as the oxidation of ferrocene [19].

All measurements were carried out under Ar in anhydrous deoxygenated solvents; solutions were 1×10^{-3} M with respect to the compounds under study and 1×10^{-1} M with respect to the supporting electrolyte, $[Bu_4N][PF_6]$. The temperature of the solution was kept constant within 1 °C, by circulation of thermostatted water–ethanol mixture through the double wall of the cell. The reference electrode was a AgCl-coated silver wire dipped in a 0.1 M solution of $[Bu_4N][PF_6]$ in the relevant solvent (THF, CH_2Cl_2, CH_3COCH_3), and separated from the cell solution by a Vycor frit. At the end of each experiment, the potential of ferrocene (0/1+) couple was measured versus the pseudo-reference electrode and then versus an aqueous SCE, to which all data are referred. The ferrocene/ferrocenium couple is located at +0.56 in THF, at +0.47 in CH_2Cl_2, and at +0.49 V versus SCE in CH_3COCH_3 [19].

Addendum

Since our initial preparation of this manuscript, we have learned of a seminal electrochemical investigation

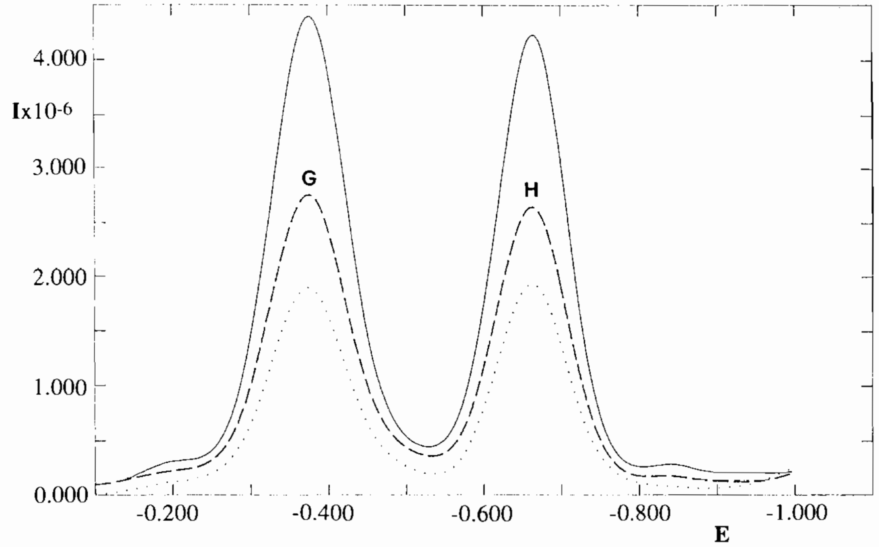

Fig. 9. SWV response of a THF solution of **2** at room temperature. Scan increment 0.002 V, pulse height 0.025 V. The frequencies employed were 30 (· · ·), 60 (– – –), 120 (——) Hz. The working electrode is an HMDE.

on Co_3-alkyne derivatives from Professor B. H. Robinson (University of Otago, New Zealand).

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