On the Reduction of Iron–Sulphur Clusters under Carbon Monoxide

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Multi-electron reduction of $[Fe_4S_4(SPh)_4]^{2-}$ at platinum or mercury cathodes under CO at 1 atm (101 325 Pa) gives $[Fe_2S_2(CO)_6]^{2-}$ *via* the formation of a stable tetranuclear intermediate $[Fe_4S_4(CO)_{12}]^{2-}$. The product, the intermediate, and $[Fe_2S_2(CO)_6]$ are interrelated by a sequence of electrochemically irreversible electron-transfer steps which involve chemically reversible intra- and inter-molecular coupling or cleavage of S–S bonds. Hydrogenases and nitrogenases possessing [4Fe–4S] centres are inhibited by CO but rapid interaction of the synthetic cluster with this substrate only occurs when the highly reduced $[Fe_4S_4(SPh)_4]^{4-}$ state is accessed and this corresponds to a physiologically unusual reduction level.

Carbon monoxide is an inhibitor of the natural function of certain proteins which possess iron–sulphur clusters as prosthetic groups, *e.g.* the iron–molybdenum proteins of the nitrogenases and some of the hydrogenases.[1–3] The understanding of the molecular basis of such biological inhibition is not well developed but it might well be advanced by studies of the chemical interactions of synthetic iron–sulphur clusters with the inhibitor. In this context two earlier studies are relevant.[4,5]

The most detailed of these deals with e.s.r. spectra obtained by reducing $[Fe_4S_4(SPh)_4]^{2-}$ with an excess of the acenaphthylene radical anion under carbon monoxide.[4] Signals arising from more than one paramagnetic species are observed and line-broadening effects seen in the presence of ^{13}CO show that carbon monoxide is bound to iron.

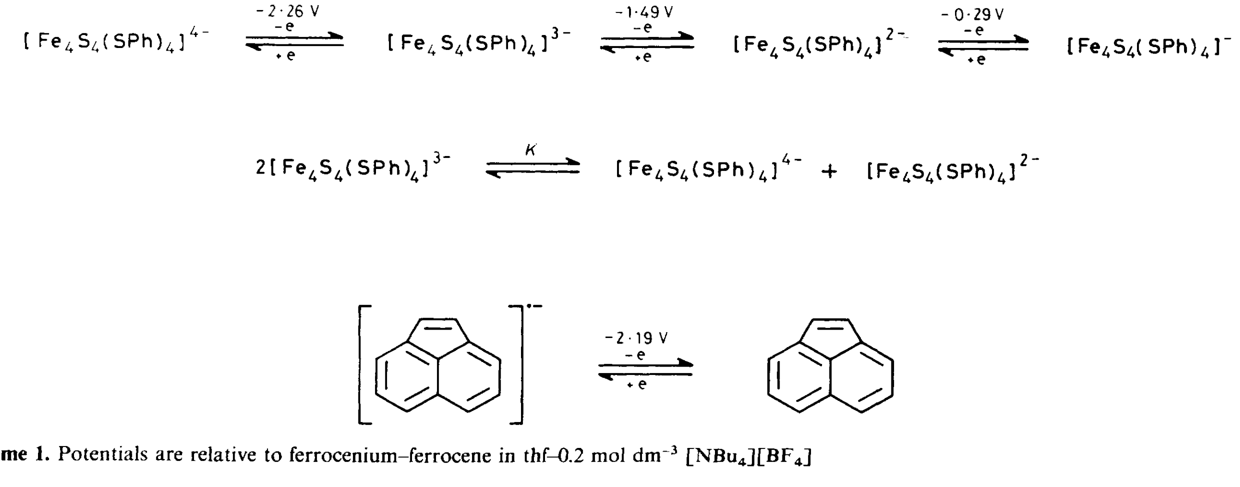
Unfortunately, both the nature of the CO-ligated species and the pathways by which they are formed remain obscure. E.s.r. signal-intensity measurements account for only 5—10% of the Fe present, whilst the supposed precursor which gives rise to these weak signals, the paramagnetic trianion $[Fe_4S_4(SPh)_4]^{3-}$, is formed in only a 30—40% conversion from the dianion. Paramagnetic as well as e.s.r.-silent carbonyls could be formed by reactions involving Fe in a form other than as in the trianion; chemistry involving the excess of reductant cannot be excluded, and the evidence for conservation of a cubane core in the carbonyl products is somewhat equivocal. Thus few firm conclusions as to the nature of the chemistry of carbon monoxide interaction with synthetic clusters can be drawn from this study. Moreover, the correspondence with biological CO inhibition is tenuous because ^{13}CO line-broadening effects differ markedly from those measured for clusters within proteins.

A second less detailed report describes an i.r. study of the interaction of CO with the trianion $[Fe_4S_4(SPh)_4]^{3-}$.[5] Several CO stretches are observed in the region 2 100—1 900 cm^{-1}, indicative of terminally bound CO, but the species present were not identified nor were the conditions specified.

This paper describes the identification of the product and the detection of an intermediate formed by multi-electron reduction of $[Fe_4S_4(SPh)_4]^{2-}$ under carbon monoxide at 1 atm. A brief description of some of this work has been communicated.[6]

Results and Discussion

Effect of Carbon Monoxide on the Primary Electron-transfer Chemistry of $[Fe_4S_4(SPh)_4]^{2-}$.—The primary redox chemistry of $[Fe_4S_4(SPh)_4]^{2-}$ under an inert atmosphere, Ar or N_2, is reasonably well established; under suitable conditions a four-membered electron-transfer series can be observed by cyclic voltammetry[7] of which the parent dianion[8] and the trianion[9] are stable, isolable members, Scheme 1. By using bulky thiolate ligands, O'Sullivan and Millar[10] have been able to isolate a stable monoanion, $[Fe_4S_4(2,4,6\text{-}Pr^i_3C_6H_2S)_4]^-$, a high-potential ferredoxin analogue. A tetra-anion has not been stabilised in an isolable form by thiolate-ligand modification and a physiological role for an intact Fe_4S_4 cluster in this highly reduced ($4Fe^{II}$) state is equivocal.[11]



Scheme 1. Potentials are relative to ferrocenium–ferrocene in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$

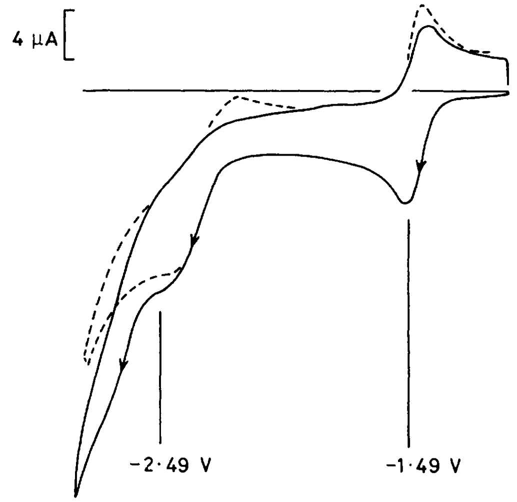
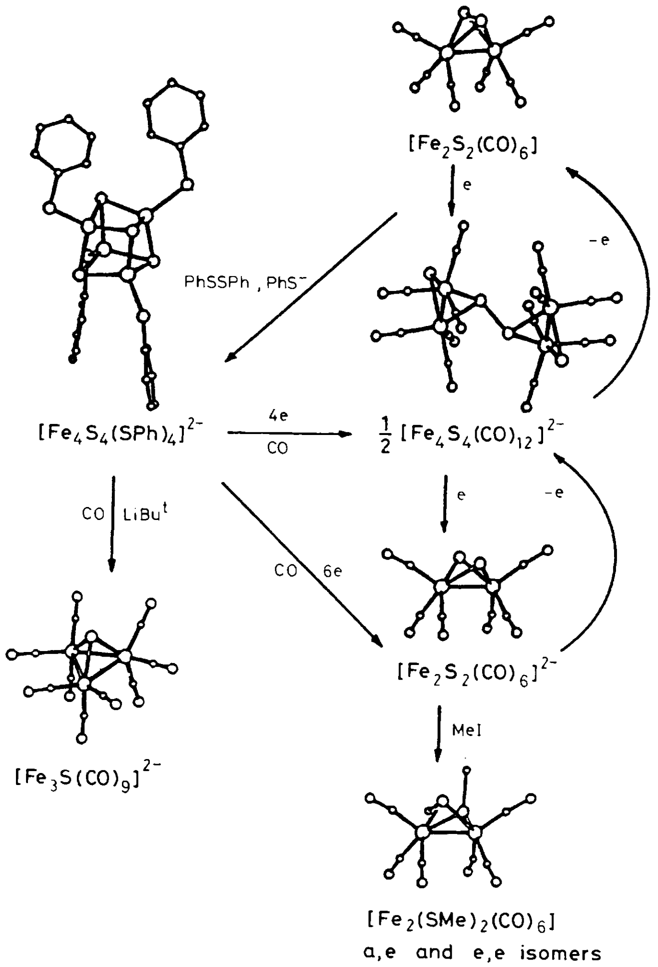


Figure 1. Cyclic voltammetry of $[Fe_4S_4(SPh)_4]^{2-}$ in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ under argon (– – –) and under carbon monoxide (—). The concentration of the cluster was 0.50 mmol dm^{-3} and recordings were made at ambient temperature and pressure using a platinum-wire working electrode and a scan rate of 0.1 V s^{-1}. Scan reversal at -1.80 V (*i.e.* before the secondary reduction) showed that CO had no effect on the reversibility of the primary process. Potentials are relative to the ferrocenium–ferrocene couple



Scheme 2.

Figure 1 shows a typical cyclic voltammogram for $[Fe_4S_4(SPh)_4]^{2-}$ which was recorded under argon (– – –) in a tetrahydrofuran (thf) electrolyte and which encompasses the two successive one-electron steps of the dianion. Saturating the solution with CO (*ca.* 5 mmol dm^{-3}) produces quite a dramatic change in the voltammogram in the region of the $3-/4-$ process, Figure 1(——). The peak current is enhanced and a new peak is detected at a slightly more negative potential. In addition, the reversibility of the $3-/4-$ couple is diminished. Purging the solution with argon restores the voltammetry to that of Figure 1(– – –).

These results show that carbon monoxide reacts rapidly with the tetra-anion and this promotes further electron transfer to the core. Interaction of the trianion with CO is not detectable on the time-scale of the voltammetric experiment thus the lifetime of $[Fe_4S_4(SPh)_4]^{3-}$ under carbon monoxide must be at least several seconds. Bulk electrolysis experiments (described below) confirm this and show that the trianion is unreactive towards CO even when exposed to the gas for 2—3 h.

Multi-electron Reduction of $[Fe_4S_4(SPh)_4]^{2-}$ *under Carbon Monoxide: Identification of Products.*—Controlled-potential electrolysis of $[Fe_4S_4(SPh)_4]^{2-}$ under CO (mercury cathode, thf electrolyte) was performed at a potential *ca.* 100 mV negative of $^2E^{0'}$ for the quasi-reversible secondary reduction (of the trianion) to the unstable tetra-anion, Scheme 1.

After the passage of 6 F per mol of cluster a dark green-brown catholyte was obtained from the initial brown solution. The catholyte was quenched with MeI and this rapidly gave a deep red solution. Removal of the solvent, extraction of the residue with Et_2O, and chromatography on silica gel afforded the axial–equatorial (a,e) and equatorial–equatorial (e,e) isomers of $[Fe_2(SMe)_2(CO)_6]$ in a moderate yield (*ca.* 60%). The compounds were identified by their ^1H n.m.r. spectra, by i.r. spectroscopy, and by comparison of their thin-layer chromatographic (t.l.c.) properties with those of authentic samples of the isomers prepared by an independent route.[12] These results are consistent with the electrochemical generation of the reactive dianion $[Fe_2S_2(CO)_6]^{2-}$ and its subsequent dimethylation, Scheme 2.

The complex $[Fe_2S_2(CO)_6]^{2-}$ has been previously prepared in solution by alkali-metal or 'Superhydride' reduction of $[Fe_2S_2(CO)_6]$.[12] Although it has never been isolated as a crystalline solid, a recent extended *X*-ray absorption fine structure (EXAFS) study[13] suggests it has the structure depicted in Scheme 2 and as originally proposed by Seyferth and co-workers.[12]

We have examined the reduction of the benzenethiolate cluster at potentials 100 mV negative of the primary one-electron reduction step under argon and carbon monoxide but find no evidence for interaction of the trianion with CO. Thus the plots of current *versus* charge passed in Figure 2 show that the one-electron coulometry remains essentially unaffected by the presence of CO. Examination of the catholyte by Fourier-transform i.r. (F.t.i.r.) spectroscopy after one-electron reduction showed no evidence for the formation of carbonyl products; *in situ* cyclic voltammetry on the catholyte after reduction confirmed that the trianion was the product of electrolysis under each gas.

We were concerned that our failure to observe a reaction between the trianionic cubane and CO might be attributed to the reaction medium, thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$. We therefore prepared and isolated $[Fe_4S_4(SPh)_4]^{3-}$ as a crystalline solid by the method of Holm and co-workers[9] and examined its interaction with CO in thf, dimethylformamide, and MeCN.

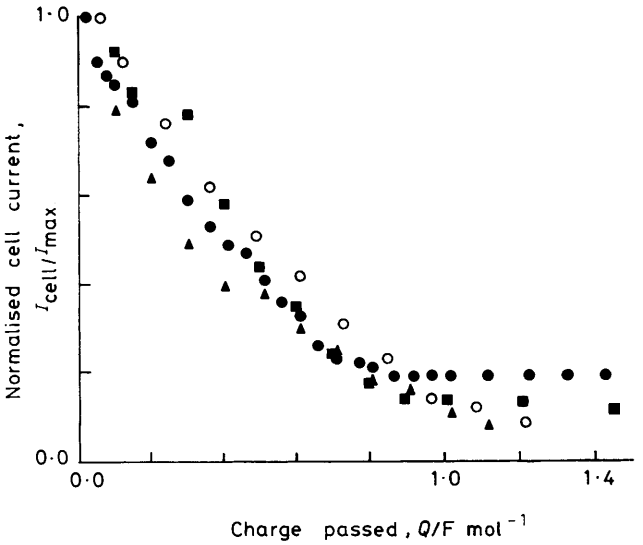


Figure 2. Plots of normalised cell current *versus* charge passed for the reduction of $[Fe_4S_4(SPh)_4]^{2-}$ under carbon monoxide (●, ■) and argon (▲, ○) at mercury (▲, ●) and platinum cathodes (○, ■). Applied potentials are close to that for the primary one-electron reduction step; the electrolyte was thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ and reductions were carried out at room temperature

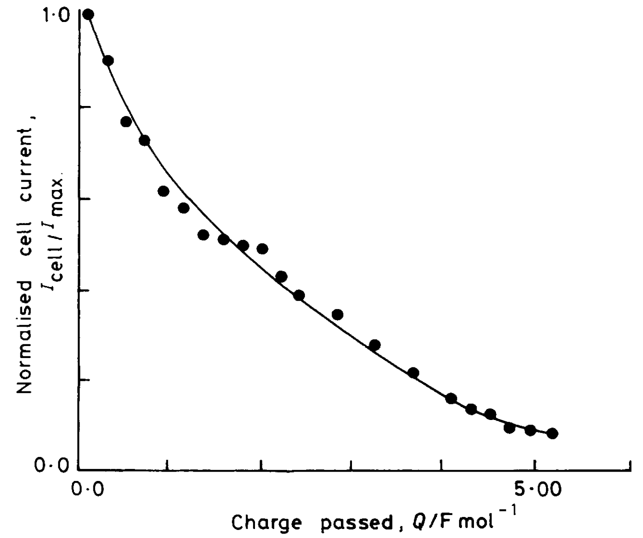


Figure 3. Plots of normalised cell current *versus* charge passed for the controlled-potential reduction of $[Fe_4S_4(SPh)_4]^{3-}$ under CO at a mercury cathode in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$ at room temperature

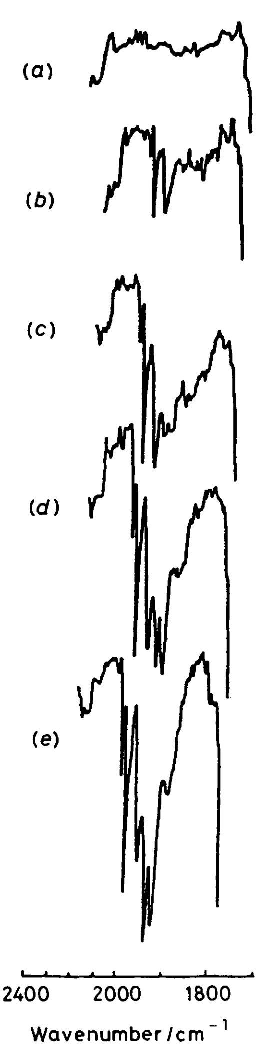


Figure 4. Infrared spectra of the catholyte solution recorded at various stages of reduction of $[Fe_4S_4(SPh)_4]^{2-}$ at -2.5 V *versus* ferrocenium–ferrocene under carbon monoxide at a mercury cathode: (*a*) before electrolysis, (*b*)—(*e*) after the passage of 3, 4, 5, and 6 F mol^{-1} respectively

Solutions of $[Fe_4S_4(SPh)_4]^{3-}$ in these solvents were stirred under CO for several hours but revealed no evidence for the formation of carbonyl species, and this is consistent with our electrolysis experiments. We conclude that if there is an interaction of CO with $[Fe_4S_4(SPh)_4]^{3-}$ it must be exceedingly slow or inextensive.

That $[Fe_4S_4(SPh)_4]^{3-}$ can be reduced under CO to $[Fe_2S_2(CO)_6]^{2-}$ was confirmed by bulk electrolysis, quenching with MeI, and chromatography: coulometry established that the reduction was the expected five-electron process, Figure 3.

Detection of the Intermediate $[Fe_4S_4(CO)_{12}]^{2-}$.—We have monitored the course of electroreduction of $[Fe_4S_4(SPh)_4]^{2-}$ under carbon monoxide by i.r. spectroscopy using an H-type electrochemical cell which was modified to interface with a conventional or F.t.i.r. spectrometer.

The development of the solution i.r. spectra in the ν(CO) region during partial electrolysis at *ca.* 100 mV negative of $^2E^{0\prime}$ is shown by Figure 4. A major intermediate with ν(CO) at 1 960, 2 000, and 2 035 cm^{-1} builds up during the first half of the electrolysis, thereafter its concentration falls off as it is reduced to the product, $[Fe_2S_2(CO)_6]^{2-}$, which has ν(CO) at 1 915, 1 930, 1 970, and 2 000 cm^{-1}, Figure 4. The carbonyl stretching frequencies of the intermediate correspond to those of the complex $[Fe_4S_4(CO)_{12}]^{2-}$ which we have prepared by an independent route.[14]

The involvement of $[Fe_4S_4(CO)_{12}]^{2-}$ as an intermediate requires that it is electroactive at potentials close to or positive of $^2E^{0\prime}$ and that it is reduced to the six-electron product $[Fe_2S_2(CO)_6]^{2-}$. This was confirmed by cyclic voltammetry which showed that the complex is reduced at $E_p = -2.46$ V *versus* the ferrocenium–ferrocene couple and also by controlled-potential electrolysis of the tetranuclear carbonyl and subsequent trapping of $[Fe_2S_2(CO)_6]^{2-}$ with MeI.

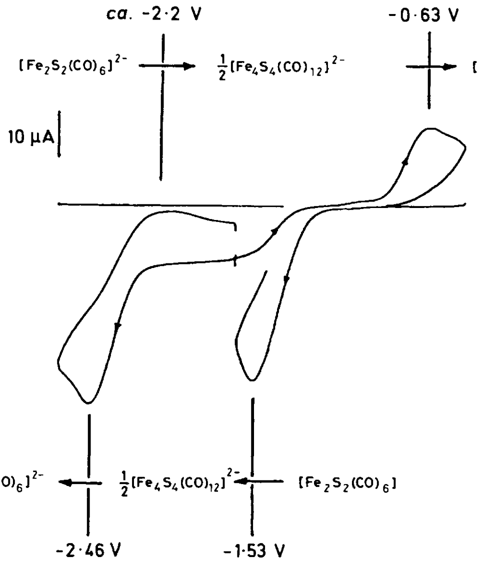


Figure 5. The cyclic voltammogram of $[Fe_2S_2(CO)_6]$ in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$. The scan rate was 0.1 V s^{-1} at a platinum-wire working electrode. The peak potentials are given relative to the ferrocenium–ferrocene couple

Related Electron-transfer Chemistry: Interconversion of $[Fe_2S_2(CO)_6]$, $[Fe_4S_4(CO)_{12}]^{2-}$, *and* $[Fe_2S_2(CO)_6]^{2-}$.—We have examined the electrochemistry of the iron–sulphur carbonyls $[Fe_2S_2(CO)_6]$, $[Fe_4S_4(CO)_{12}]^{2-}$, and $[Fe_2S_2(CO)_6]^{2-}$ as this might be of some relevance to the reduction of the cluster under carbon monoxide.

A cyclic voltammogram of $[Fe_2S_2(CO)_6]$ in a thf electrolyte is shown in Figure 5: two successive irreversible reductions steps are observed. The first of these corresponds to an overall one-electron process that gives $[Fe_4S_4(CO)_{12}]^{2-}$ and the second to the conversion of this product into $[Fe_2S_2(CO)_6]^{2-}$. The evidence for this is as follows. The primary product was identified in the voltammetry by its irreversible reduction near -2.2 and oxidation at -0.63 V relative to the ferrocenium–ferrocene couple which correspond to those found for $[Fe_4S_4(CO)_{12}]^{2-}$. In addition, repetitive cyclic voltammetry with and without oxidation of the product $[Fe_4S_4(CO)_{12}]^{2-}$ (in the diffusion layer) established that the oxidation of the tetranuclear cluster regenerates the parent species $[Fe_2S_2(CO)_6]$. These reactions were also shown to occur in bulk solution by controlled-potential electrolysis and i.r. spectroscopy with reversal coulometry as is now described.

Bulk reduction of $[Fe_2S_2(CO)_6]$ at -1.7 V *versus* ferrocenium–ferrocene is an overall one-electron process as illustrated by the plot of cell current (I_{cell}) *versus* charge passed in Figure 6 (inset). The solution i.r. spectrum obtained before reduction is also shown in Figure 6(*a*), together with that obtained after electrolysis, Figure 6(*b*): this latter spectrum is characteristic of $[Fe_4S_4(CO)_{12}]^{2-}$. Reversal coulometry involving a subsequent oxidation of the catholyte solution at *ca.* 0.0 V *versus* ferrocenium–ferrocene gives the i.r. spectrum in Figure 6(*c*) which shows the regeneration of the starting material. This was confirmed by work-up of a catholyte solution following re-oxidation and identification of $[Fe_2S_2(CO)_6]$ by t.l.c.

Bulk electrolysis performed at a potential just negative of the secondary reduction process involves an overall two-electron reduction and gives an i.r. spectrum corresponding to the formation of $[Fe_2S_2(CO)_6]^{2-}$. The decay of I_{cell} is biphasic: in the first stage of reduction, I tends towards a one-electron process and solution i.r. spectroscopy on the thf catholyte indicates that this corresponds to generation of $[Fe_4S_4(CO)_{12}]^{2-}$ in the bulk solution. In the second phase of electrolysis i.r. spectroscopy shows that reduction of the tetranuclear carbonyl to $[Fe_2S_2(CO)_6]^{2-}$ takes place as I_{cell} decays towards an overall two-electron process.

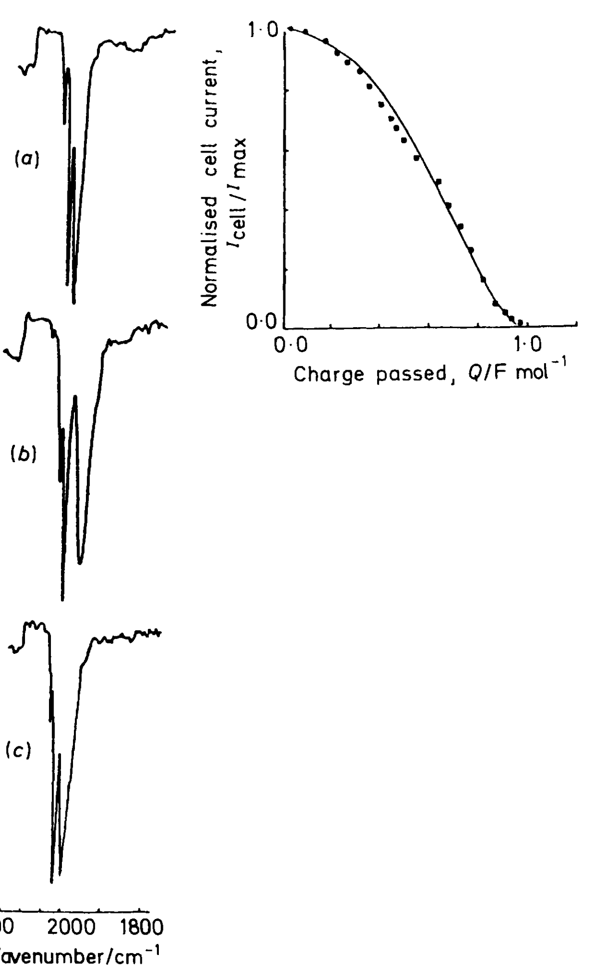


Figure 6. Infrared spectra of catholyte solutions of $[Fe_2S_2(CO)_6]$ in thf–0.2 mol dm^{-3} $[NBu_4][BF_4]$: (*a*) before reduction, the spectrum corresponds to $[Fe_2S_2(CO)_6]$; (*b*) after one-electron reduction, the spectrum corresponds to $[Fe_4S_4(CO)_{12}]^{2-}$; and (*c*) after reversal coulometry in which the one-electron oxidation of the catholyte (*b*) regenerates spectrum (*a*). The inset shows a plot of the normalised cell current (I_{cell}) *versus* the charge passed (Q) for the primary reduction

After the two-electron reduction, we performed reversal coulometry and found that the spectrum obtained after one-electron *oxidation* was virtually identical to that generated by the initial one-electron *reduction* of the starting material, Figure 7(*a*) and (*b*). Thus $[Fe_2S_2(CO)_6]^{2-}$ is reoxidised to $[Fe_4S_4(CO)_{12}]^{2-}$ and this is a chemically reversible process.

We have confirmed the observation that $[Fe_4S_4(CO)_{12}]^{2-}$ reacts with MeI to produce $[Fe_2S_2(CO)_6]$ and the isomers of $[Fe_2(SMe)_2(CO)_6]$.[14] Thus adding MeI to the catholyte containing $[Fe_4S_4(CO)_{12}]^{2-}$ produces the i.r. spectrum in Figure 7(*c*), whilst work-up and t.l.c. of the quenched catholyte shows the formation of the three products.

The redox interconversions of the cluster and the iron–sulphur carbonyls are summarised by Scheme 2 and here we thought it useful to include two chemically driven processes, the fragmentation of the cubane under CO to an Fe_3S carbonyl[6] and the conversion of $[Fe_2S_2(CO)_6]$ into the cubane.[15]

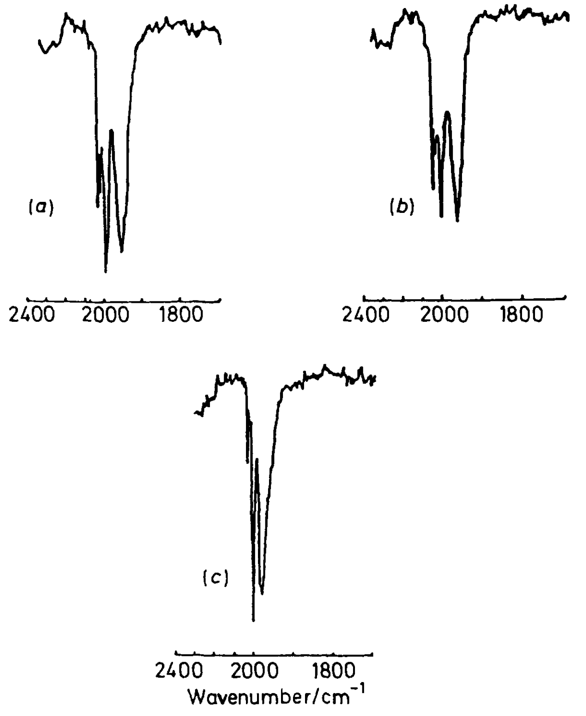


Figure 7. Infrared spectra showing the relationship of the reductive chemistry of $[Fe_2S_2(CO)_6]$ to the oxidative chemistry of $[Fe_2S_2(CO)_6]^{2-}$: (*a*) $[Fe_4S_4(CO)_{12}]^{2-}$ formed by one-electron reduction of $[Fe_2S_2(CO)_6]$; (*b*) further one-electron reduction of the same catholyte to produce $[Fe_2S_2(CO)_6]^{2-}$ followed by one-electron oxidation to regenerate $[Fe_4S_4(CO)_{12}]^{2-}$; and (*c*) after reaction of $[Fe_4S_4(CO)_{12}]^{2-}$ with MeI

Cascade Carbonylation and Electronation of $[Fe_4S_4(SPh)_4]^{2-}$.—The dianion $[Fe_4S_4(CO)_{12}]^{2-}$ is well along the pathway to the product $[Fe_2S_2(CO)_6]^{2-}$ but it is the only intermediate which we detect during the course of bulk electrolysis.

It can be envisaged that the binding of the electron-withdrawing CO ligand to a reduced cubane core promotes a cascade of further electron-transfer and carbonylation reactions. Infrared spectroscopy shows that $[Fe_4S_4(CO)_{12}]^{2-}$ is present in catholyte solutions after the passage of sub-stoicheiometric amounts of charge, *i.e.* <4 F mol^{-1}, Figure 4. We must therefore have facile reduction of the precursors to $[Fe_4S_4(CO)_{12}]^{2-}$ and this accounts for our inability to detect other carbonyl intermediates during the course of electrolysis.

The reduction potentials of the cubane cluster and neutral $[Fe_2S_2(CO)_6]$, Scheme 2, are such that if the latter is generated as an intermediate it would be reduced at a diffusion-controlled rate to $[Fe_4S_4(CO)_{12}]^{2-}$ and thence $[Fe_2S_2(CO)_6]^{2-}$. Here we should also note that $[Fe_2S_2(CO)_6]^{2-}$ formed at the electrode in the early stages of electrolysis might well be oxidised in the solution by $[Fe_4S_4(SPh)_4]^{2-}$ $\{$*i.e.* giving $[Fe_4S_4(CO)_{12}]^{2-}$ and $[Fe_4S_4(SPh)_4]^{3-}\}$.

We have prepared the neutral cubane $[Fe_4S_4(CO)_{12}]$[16] but it has proved to be far too insoluble to examine its electrochemistry: it is not precipitated during the course of electrolysis of the cluster under CO.

Conclusions

(1) Multi-electron reduction of $[Fe_4S_4(SPh)_4]^{2-}$ under CO gives $[Fe_2S_2(CO)_6]^{2-}$ *via* the formation of a stable intermediate $[Fe_4S_4(CO)_{12}]^{2-}$.

(2) The complexes $[Fe_2S_2(CO)_6]^{2-}$, $[Fe_4S_4(CO)_{12}]^{2-}$, and $[Fe_2S_2(CO)_6]$ are interrelated by the sequence of electrochemically irreversible electron-transfer steps which involve the chemically reversible intra- and inter-molecular S–S bond-making and -breaking reactions shown in Scheme 2.

(3) We have no evidence from our work to support the proposal that $[Fe_4S_4(SPh)_4]^{3-}$ reacts with CO.[4,5] We suggest that the previous observations might be explained by the presence of an excess of reductant in the systems. We have measured $E^{0\prime}$ for the acenaphthylene couple in a thf electrolyte.[17] Its value of -2.19 V is sufficiently close to that for the $3-/4-$ couple of the cubane, -2.26 V, for there to be significant levels of the tetra-anion present when the reductant is in excess. Here we also note that a pathway involving the disproportionation reaction of Scheme 1 with CO attacking the tetra-anion is thermodynamically unfavourable since the equilibrium constant K is about 10^{-13}.

(4) Whilst we have shown that Fe–CO bonds are formed by reduction of a simple cubane cluster under CO, rapid interaction is only observed when the highly reduced $[Fe_4S_4(SPh)_4]^{4-}$ state is accessed. This corresponds to a physiologically unusual reduction level for a ferredoxin.

The nature of the leaving group at iron might well be important in determining cluster reactivity, towards CO or other substrates, at less reduced cores and this is being explored.

Experimental

General.—Solvents were freshly distilled under dinitrogen from an appropriate drying agent using standard laboratory methods. Solvent, electrolytes, and complexes were generally handled under an inert atmosphere using Schlenk techniques.

Carbon dioxide, a common impurity in CO, was removed from the gas using a soda-lime trap. The solubility of CO was found to be 5.2 mmol dm^{-3} at 20 °C in the electrolyte 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf.

Preparation of Complexes.—The cubane clusters $[NBu_4]_2[Fe_4S_4(SPh)_4]$[18] and $[NEt_4]_3[Fe_4S_4(SPh)_4]$[17] together with the iron–sulphur carbonyls $[Fe_2S_2(CO)_6]$,[12] $[Fe_4S_4(CO)_{12}]$,[13] $[Fe_4S_4(CO)_{12}]^{2-}$,[14] and the a,e and e,e isomers of $[Fe_2(SMe)_2(CO)_6]^{2-}$[12] were prepared by the literature methods.

Instrumentation.—Electrochemical measurements were made using a DT-101 potentiostat and PP – R1 waveform generator both supplied by Hi-Tek Instruments. Voltammograms were recorded on a Philips PM8043 X-Y recorder and charge was measured using a Chemical Electronics integrator.

Infrared spectra were recorded on either a conventional Pye-Unicam spectrometer type SP2000 or on a Perkin-Elmer 1710 Fourier-transform instrument.

Electrolyses.—Conventional electrolyses to determine current *versus* charge-passed profiles and for preparative work were performed in a four-compartment three-electrode cell using either a platinum gauze or mercury-pool working electrode. The cell and electrolysis procedures have been described elsewhere.[19,20]

In preparative experiments, catholyte solutions (20—30 cm^3) were quenched with MeI (*ca.* 100-fold excess) then removed by syringe under nitrogen from the cell to a Schlenk flask, evaporated to dryness at room temperature *in vacuo*, and extracted with Et_2O (3×50 cm^3). Pooled extracts were concentrated and chromatographed as described elsewhere.[12]

Electrolyses with i.r. monitoring were performed using an H-type cell modified to interface with a solution i.r. cell: a narrow-bore stainless-steel tube (internal diameter 0.5 mm) connected the body of the working-electrode compartment to the chamber of a KBr solution cell of pathlength 0.1 mm. Samples of electrolyte were drawn from or flushed out of the i.r. cell by way of a 0.5-cm^3 gas-tight syringe connected in series. The i.r. cell sat in the cavity of the i.r. or F.t.i.r. spectrometer throughout electrolysis and at appropriate intervals it was flushed and filled with fresh catholyte (or anolyte) samples and spectra recorded. In the conventional i.r. mode a variable-pathlength solution cell placed in the reference beam was used to correct for electrolyte absorption.

Acknowledgements

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