# Paramagnetic Transition-metal Carbonyls and Cyanides. Part 9.† An Electron Spin Resonance Study of the Radiolysis of Some Iron Carbonyls: the Anions $[Fe(CO)_5]^-$ and $[Fe(CO)_4]^-$

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Exposure of dilute solutions of $[Fe(CO)_5]$ in 2-methyltetrahydrofuran to $^{60}Co$ γ-rays at 77 K resulted in electron addition to give species A. On annealing, this rapidly decomposed to give species B, which was stable up to the softening point of the glass. Irradiation of $Na_2[Fe(CO)_4]$ at 77 K gave directly species B, which is therefore identified as $[Fe(CO)_4]^-$. This suggests that A is $[Fe(CO)_5]^-$ or $[Fe(CO)_4]^-$ with a non-equilibrium structure. The form of the *g*-tensor components of both these $3d^9$ complexes requires a $3d_{z^2}{}^1$ assignment for the unpaired electron on iron. When $[Fe(CO)_5]$ enriched in $^{13}CO$ was studied, no well defined splittings were detected in the strongly broadened features of species A and B, but estimates of hyperfine coupling from the enhanced widths could be made. No radical anions were detected in irradiated solutions of $[Fe_2(CO)_9]$, but $[Fe_3(CO)_{12}]$ gave clear features for the anion $[Fe_3(CO)_{12}]^-$, together, probably, with weak features for $[Fe_3(CO)_{11}]^-$. Irradiation of dilute solutions of $[Fe(CO)_5]$ in trichlorofluoromethane gave a species thought to be $[Fe(CO)_5]^+$, despite the fact that its e.s.r. spectrum differs considerably from that assigned to this cation in $[Cr(CO)_6]$.

A range of paramagnetic iron carbonyl species has recently been studied by e.s.r. spectroscopy.[1-5] However, specific assignment of e.s.r. features to particular species has been the subject of considerable debate, in spite of the use of $^{13}C$ and $^{57}Fe$ labelling. In these experiments, $[Fe(CO)_5]$ solutions were electrolysed, or treated with a range of electron donors in fluid solutions, but despite early claims it now seems that none of the species obtained was a simple monomeric anion such as $[Fe(CO)_5]^-$ or $[Fe(CO)_4]^-$. The species identified by Krusic *et al.*[5] in the most recent report were given the structures $[Fe_2(CO)_8]^-$, $[Fe_3(CO)_{11}]^-$, $[Fe_3(CO)_{12}]^-$, and $[Fe_4(CO)_{13}]^-$.

One of us has helped to establish that radiolysis of rigid glassy solutions of substrates in various solvents, including 2-methyltetrahydrofuran (mthf), is an excellent method for adding one electron to these substrates under conditions which often lead to the stabilization of the parent anions, and which prevent the formation of dimer or oligomer species.[6,7] The aim of the present work was to attempt to prepare $[Fe(CO)_5]^-$ or $[Fe(CO)_4]^-$ by this technique. We have also studied the radiolysis of $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ in this solvent, and of $Na_2[Fe(CO)_4]$.

## Experimental

The iron carbonyls $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, and $[Fe_3(CO)_{12}]$ were obtained from Strem Chemicals, and purified as described elsewhere.[3] $[Fe(CO)_5]$ enriched in $^{13}CO$ (*ca.* 80%) was kindly supplied by Dr. M. Poliakoff. $Na_2[Fe(CO)_4]$ was obtained from Lancaster Synthesis and used as a fine powder without purification; mthf (Eastman-Kodak) was dried over molecular sieves and used without further purification.

Degassed solutions (*ca.* $5 \times 10^{-3}$ mol dm$^{-3}$) were irradiated as small glass beads at 77 K in a Vickrad $^{60}Co$ γ-ray source (*ca.* 1.0 Mrad h$^{-1}$) for up to 2 h. E.s.r. spectra were recorded at 77 K on a Varian E-109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardized with a sample of diphenylpicrylhydrazyl. Samples were annealed in the finger Dewar flask until significant spectral changes were observed. They were then recooled to 77 K for careful study.

## Results and Discussion

Exposure of the pure carbonyls $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, and $[Fe_3(CO)_{12}]$ to $^{60}Co$ γ-rays at 77 K after degassing gave no detectable paramagnetic species. However, dilute solutions ($\leqslant 5 \times 10^{-3}$ mol dm$^{-3}$) of $[Fe(CO)_5]$ and $[Fe_3(CO)_{12}]$ in mthf gave well defined features attributable to iron carbonyl derivatives. Unfortunately, $[Fe_2(CO)_9]$, which is sparingly soluble in mthf, gave no signals other than those derived from the solvent, even after careful annealing to remove solvent signals.

*Solutions of* $[Fe(CO)_5]$.—The major species formed at 77 K (A) had a perpendicular feature at $g = 2.071$, and a parallel feature at $g = 2.0015$ [Figure 1(*a*)]. The latter was, initially, partly concealed by solvent features, but could be detected at high power such that the solvent features were strongly saturated. Also, careful annealing removed most of the signal from solvent radicals before species A was completely converted into B. Features for A were replaced by features assigned to species B ($g_x = 2.055$, $g_y = 2.049$, $g_z = 2.008$) (Figure 2) at *ca.* 120 K. Further annealing to the softening point of the glasses resulted in loss of B, but we were unable to detect growth of other features [Figure 2(*a*)]. Satellite lines assigned to $^{13}C$ in natural abundance were detected for the parallel feature of species B.

When samples enriched in $^{13}CO$ were used, all features were greatly broadened [Figures 1(*b*) and 2(*b*)], but no extra resolved features were detected. The form of the broadening rules out the presence of one strongly coupled $^{13}C$, and favours the presence of two equivalent $^{13}C$ nuclei strongly coupled. They have been analysed to give the approximate data listed in the Table.

$Na_2[Fe(CO)_4]$.—Only one well defined species was detected, having features similar to those for species B (Table).

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† Part 8, taken as M. C. R. Symons, J. Wyatt, B. M. Peake, J. Simpson, and B. H. Robinson, *J. Chem. Soc., Dalton Trans.*, 1982, 2037.

*Non-S.I. unit employed:* 1 G = $10^{-4}$ T.

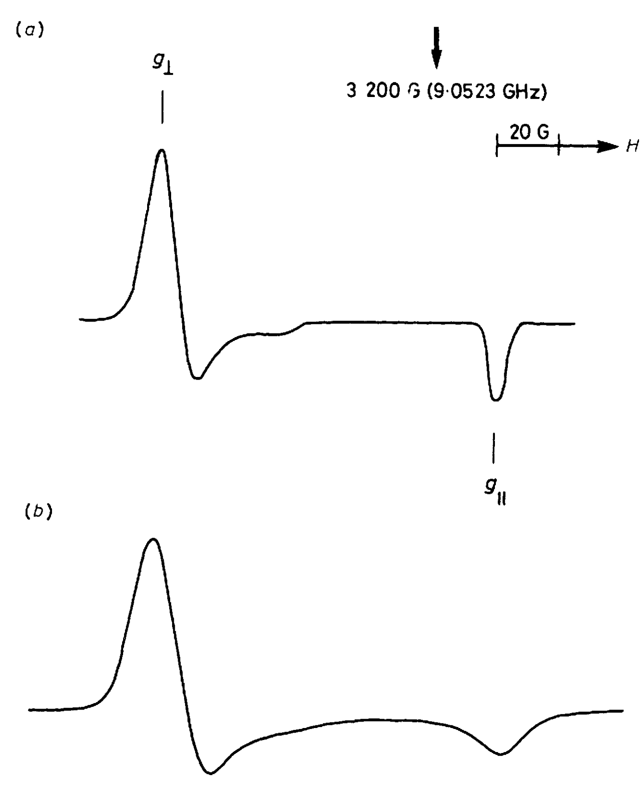


**Figure 1.** First derivative $X$-band e.s.r. spectra for dilute solutions of $[Fe(CO)_5]$ in mthf at 77 K after exposure to $^{60}Co$ γ-rays at 77 K and partial annealing to remove features due to mthf radicals, showing parallel and perpendicular features assigned to $[Fe(CO)_5]^-$ (species A); (*a*) normal $[Fe(CO)_5]$, (*b*) $[Fe(CO)_5]$ enriched in $^{13}CO$ (*ca.* 80%)

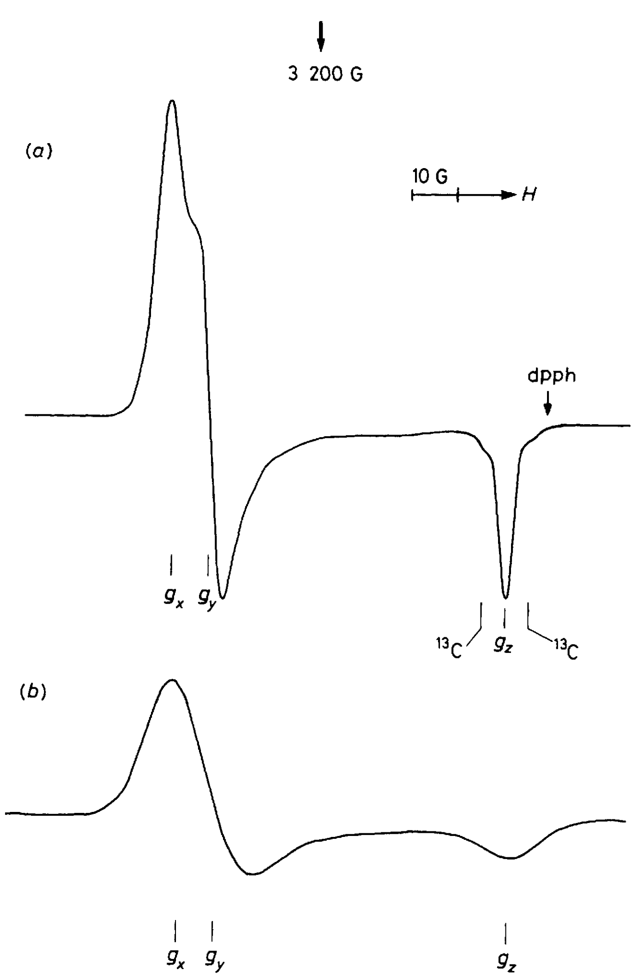


**Figure 2.** First derivative $X$-band e.s.r. spectra for $[Fe(CO)_5]$ in mthf after exposure to $^{60}Co$ γ-rays at 77 K and annealing to *ca.* 120 K showing features assigned to species B, $[Fe(CO)_4]^-$; (*a*) normal $[Fe(CO)_5]$, (*b*) $[Fe(CO)_5]$ enriched in $^{13}CO$ (*ca.* 80%)

**Table.** *g* Values for some paramagnetic iron carbonyls

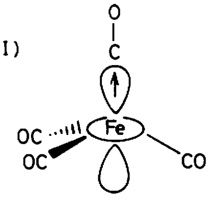
| Species | | *g*-Tensor components | | | | Medium |
|---|---|---|---|---|---|---|
| | | $g_x$ | $g_y$ | $g_z$ | $g_{av}$ | |
| $[Fe(CO)_5]^-$ [a] | | 2.071 | 2.071 | 2.0015 | 2.048 | mthf |
| $[Fe(CO)_4]^-$ [b] | (I) | 2.055 | 2.049 | 2.008 | 2.037 | mthf |
| | (II) | 2.055 | 2.055 | *ca.* 2.008 | | $Na_2[Fe(CO)_4]$ |
| $[Fe(CO)_5]^+$ [c] | | 2.0833 | 2.0797 | 2.0008 | 2.0546 | $[Cr(CO)_6]$ |
| $[Fe(CO)_5]^+$ | | 2.057 | 2.057 | 2.002 | 2.039 | $CFCl_3$ |
| $[Fe_2(CO)_8]^-$ [d] | | 2.054 | 2.054 | 2.0092 | 2.0385 | |
| $[Fe_3(CO)_{11}]^-$ [d] | | 2.0921 | 2.0321 | 2.0243 | 2.0497 | |
| $[Fe_3(CO)_{12}]^-$ [d] | | | | | 2.0016 | |
| $[Fe_3(CO)_{12}]^-$ | | 2.0094 | 2.0045 | 1.990 | 2.0013 | |
| $[Fe_4(CO)_{13}]^-$ [d] | | | | | 2.0134 | |

[a] $^{13}C$ parameters deduced from line-broadening gave $A_\parallel$ (for 1 $^{13}C$) *ca.* 13 G; $A_\perp$ (for 1 $^{13}C$) *ca.* 7 G. [b] $^{13}C$ parameters deduced from line-broadening gave $A_\parallel$ ($^{13}C \geqslant 2$) *ca.* 10 G; $A_\perp$ ($^{13}C \geqslant 2$) $\leqslant$ 10 G. [c] Ref. 16. [d] Ref. 5; Dr. P. J. Krusic has kindly informed us that he has now obtained the solid-state spectrum for $[Fe_3(CO)_{12}]^-$ ions in mthf: his *g* value components are equal to ours within experimental error.

*Identification of Species A and B.*—Since oligomers cannot form in the rigid glasses, and since electron capture certainly occurred, as judged from the suppression of the normal blue colour due to trapped electrons, the species formed are either $[Fe(CO)_5]^-$ or $[Fe(CO)_4]^-$. Since the $[Fe(CO)_4]^{2-}$ ion gave species B, it is most probable that B is $[Fe(CO)_4]^-$, in which case it is tempting to identify species A as $[Fe(CO)_5]^-$. That there should be efficient loss of CO is expected, since $[Fe(CO)_5]^-$ is a 19-electron species and these are normally unstable even at low temperatures. However, it could well be that $[Fe(CO)_5]^-$ decomposes spontaneously at any temperature, in which case both A and B must be $[Fe(CO)_4]^-$.

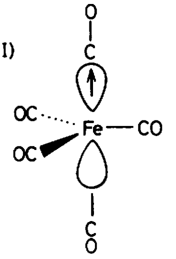
In all cases, the form of the *g*-tensor components for these formally $d^9$ species requires the unpaired electron to be in a $3d_{z^2}$ orbital on iron.[8] Burdett,[9] and Turner and co-workers [10] have prepared a species thought to be $[Fe(CO)_4]^-$ in inert gas matrices at 10 K, by co-condensation of sodium atoms and $[Fe(CO)_5]$ with ultraviolet irradiation, and also by electron bombardment. Their i.r. spectra were not in accord with a five-co-ordinate species having either $D_{3h}$ or $C_{3v}$ symmetry. However, the detailed results were in good accord with expectation for $[Fe(CO)_4]^-$ having a $C_{3v}$ structure (I). The isoelectronic molecule $[Co(CO)_4]$ is also thought to be $C_{3v}$ as judged from its i.r. spectrum.[11] In our e.s.r. study of $[Co(CO)_4]$ [12] we concluded that the electron configuration was $(d\pi)^6,(d_{x^2-y^2})^2,(d_{z^2})^1$, and also suggested a $C_{3v}$ structure. This was confirmed by Hanlan *et al.*[13] for $[Co(CO)_4]$ in a carbon monoxide matrix in the range 6—15 K. The *g* values showed axial symmetry [$g_\parallel = 2.007$, $g_\perp = 2.128$], and were characteristic of a $(d_{z^2})^1$ configuration. This was confirmed by the observation of only one strongly coupled $^{13}C$ nucleus. Their results assigned to $[Co(CO)_4]$ in argon are quite different

(I)



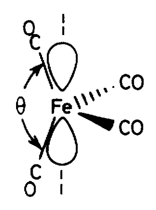
$[Fe(CO)_4]^-(C_{3v})$

(II)



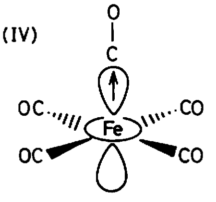
$[Fe(CO)_5]^-$

(III)



$[Fe(CO)_4]^-(D_{2d})$

(IV)



$[Fe(CO)_5]^+(C_{4v})$

and seem to be somewhat contradictory. These will not be considered further here.

The e.s.r. parameters for species B are close to those assigned by Krusic *et al.*[5] to $[Fe_2(CO)_8]^-$, except that their *g* tensor was accurately axial, whereas ours is clearly non-axial. However, we think it most improbable that the reaction (i)

$$[Fe(CO)_4]^- + [Fe(CO)_5] \longrightarrow [Fe_2(CO)_8]^- + CO \quad (i)$$

should occur at *ca.* 120 K in rigid mthf. Our experience with this glass is that such bimolecular processes are completely prevented at this temperature, and we see no reason why $[Fe(CO)_4]^-$ should be an exception. It seems to us that the process is far more likely to be unimolecular. We stress that even extremely dilute solutions, for which conversion into the electron-adducts must have been extensive, still exhibited complete conversion of A into B.

*Structures.*—We consider that there are two reasonable alternatives: (*a*) that species A is $[Fe(CO)_5]^-$ and B is $[Fe(CO)_4]^-$, and (*b*) that both A and B are $[Fe(CO)_4]^-$, A having the $C_{3v}$ structure (I) observed at *ca.* 4 K by Turner and co-workers,[10] and B having the alternative $D_{2d}$ structure (III).

For case (*a*), $[Fe(CO)_5]^-$ probably has the trigonal bipyramidal structure of the parent molecule (II). This accords well with the axial symmetry and the $^{13}C$ evidence, which requires the presence of at least two strongly coupled $^{13}C$ nuclei having their maximum coupling along the major, parallel axis.

Loss of CO on annealing can give the trigonal pyramidal structure (I) formed at low temperatures in inert gas media as judged from the i.r. data,[10] or the $D_{2d}$ structure (III). We consider that the $C_{3v}$ alternative for species B is unlikely. This should still give axial symmetry to the *g* tensor, and we would expect one $^{13}C$ coupling on the *z* axis to be much greater than the other three, partly because these will lie quite close to a nodal surface, and also because the coupling will be closer to the minimum (perpendicular) values than to the maximum (parallel) values.

Case (*b*) accommodates the results less adequately in our view. In this case the axial symmetry for A is accommodated by the $C_{3v}$ structure, but, as stressed above, we would have expected to detect some evidence of doublet splitting from the single axial $^{13}C$ nucleus, and this was not seen [Figure 1(*b*)].

A third, somewhat intermediate, but less well defined possibility would involve some stereochemical control by the ejected carbonyl ligand for structure (A) and possibly some solvent participation in structure B. This would certainly help to bridge the differences between the present work and the low-temperature matrix isolation study.[10]

However, we tend to favour case (*a*), with species A as $[Fe(CO)_5]^-$, having the trigonal bipyramidal structure (II), and species B as $[Fe(CO)_4]^-$ having the $D_{2d}$ structure (III). We suggest that loss of CO at *ca.* 4 K in a rare-gas matrix gives initially the $C_{3v}$ structure (I) but that this rearranges to the $D_{2d}$ structure at temperatures below 120 K. Hence it seems that the $C_{3v}$ structure is kinetically favoured whereas the $D_{2d}$ structure is thermodynamically favoured. The retention of CO in the mthf matrix and not in the rare-gas matrix may reflect the rigidity of the media. These are the conclusions that we feel compelled to take on the basis of the present studies. We stress, however, that the postulate that a 19-electron species could be stable at 77 K is one that many must find unacceptable. Our experience in other areas of chemistry has been that it is quite possible for species that are intrinsically unstable with respect to dissociation to achieve stability at low temperatures *via* distortions that do not lead directly to dissociation. For example, a $PL_4^{\cdot -}$ radical may be unstable with respect to dissociation into $PL_3^{\cdot} + L^-$, but on initial electron capture, $PL_4$ may undergo a bending distortion which confers some stability on $PL_4^{\cdot -}$, the stretching distortion leading to dissociation only setting in at higher temperatures. Nevertheless, such a situation has not been established for transition metal carbonyls, and therefore we must treat case (*a*) with considerable reservation.

It is remarkable that both these $3d^9$ species favour the $\cdots(d_{x^2-y^2})^2,(d_{z^2})^1$ configuration, especially since the $3d^7$ species $[Mn(CO)_5]$ [14,15] and $[Fe(CO)_5]^+$ [16] also clearly favour a $\cdots(d_{z^2})^1$ configuration. In these cases, the $C_{4v}$ structure (IV) is most probable.

$[Fe(CO)_5]$ *in Freon.*—As we have mentioned, Lionel *et al.*[16] have studied a species identified as $[Fe(CO)_5]^+$ formed by radiolysis of solutions in $[Cr(CO)_6]$ and in sulphuric acid. It seemed of interest to check that the same species is formed from $[Fe(CO)_5]$ in freon solvents such as trichlorofluoromethane. Such solvents have proven to be remarkably effective for the formation of radical cations from neutral molecules,[17-19] although they have not been used previously in studies on transition metal complexes. We find that a species is formed having the same form for the *g*-tensor components as those previously published (Table), but with $g_\perp \simeq 2.057$ rather than *ca.* 2.080 as found previously. This is a large difference, for which we have no explanation. We know of no example in which species other than radical cations or their reaction products have been formed in experiments with freon solutions but, at the same time, the evidence in favour of $[Fe(CO)_5]^+$ in $[Cr(CO)_6]$ and sulphuric acid is also very strong.[16] It is possible that loss of a CO ligand occurred in our experiments. It is also possible that there is a significant medium effect, but the close similarity of the $[Cr(CO)_6]$ and $H_2SO_4$ results make this unlikely.

*Solutions of* $[Fe_3(CO)_{12}]$.—The major species obtained from these solutions was also non-axial (Figure 3), with $g_x = 2.0094$, $g_y = 2.0045$, and $g_z = 1.990$, giving $g_{av} = 2.0013$. The species identified as $[Fe_3(CO)_{12}]^-$ by Krusic *et al.*[5] has $g_{av} = 2.0016$, so there can be little doubt that our species is

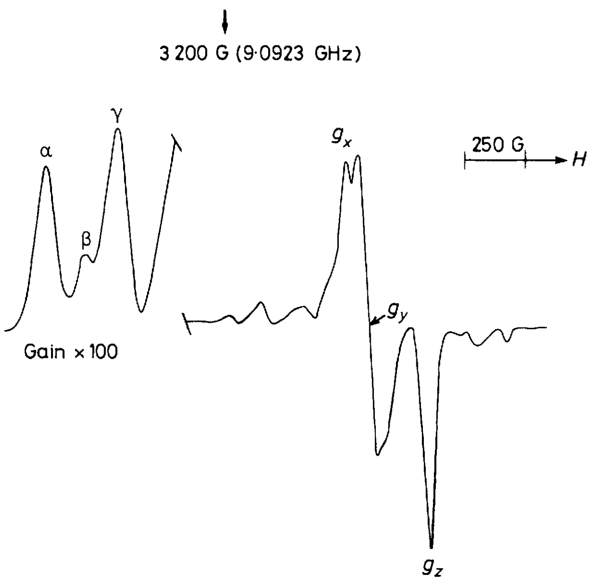


**Figure 3.** First derivative *X*-band e.s.r. spectrum for $[Fe_3(CO)_{12}]$ in mthf after exposure to $^{60}Co$ γ-rays at 77 K, showing features assigned to $[Fe_3(CO)_{12}]^-$ together with features for matrix radicals and weak low-field features discussed in the text

also the parent radical anion (see footnote *d* of Table). This intermediate, together with $[Fe_3(CO)_{11}]^{2-}$, has also been produced electrolytically from $[Fe_3(CO)_{12}]$.[4] The low value for $g_z$ means that there is magnetic coupling with a low-lying empty orbital, which is unusual for complexes derived from monomers having $d^8$ or $d^9$ configurations.

At least two other species were detected in low concentration at 77 K (Figure 3). One had $g_1 = 2.0914$, which is close to the maximum *g* value for a species identified by Krusic *et al.*[5] as $[Fe_3(CO)_{11}]^-$ (see Table). We suggest that loss of CO is a minor pathway on electron addition at 77 K, giving $[Fe_3(CO)_{11}]^-$, but we have not been able to detect the other two *g*-features (3.0321 and 2.0243) [5] because of overlap with features from other species. The third and fourth species, having $g_1 \simeq 2.0785$ (very weak) and $g_1 = 2.071$ (weak) have not been clearly identified. It is probable that the latter species ($g_1 = 2.071$) is species A, $[Fe(CO)_5]^-$, but, if so, this is probably formed from $[Fe(CO)_5]$ impurity rather than from the trimer.

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