Characterisation of a New Solid-state Isomer of the $[Fe_5N(CO)_{14}]^-$ Ion†

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An example of cation-induced solid-state isomerisation in a carbonyl cluster has been found. Whereas the structure of the $[Fe_5N(CO)_{14}]^-$ cluster anion contains five different types of $Fe(CO)_n$ sites when prepared as the $[N(PPh_3)_2]^+$ salt, the $[NMe_4]^+$ salt crystallises with two symmetry-related bridging carbonyls on adjacent iron–iron bonds in the basal plane and contains four different iron sites: monoclinic, space group $P2_1/m$, $a = 9.973(2)$, $b = 11.498(2)$, $c = 12.401(2)$ Å, $\beta = 113.53(1)°$ and $Z = 2$. The structure was refined on the basis of 2441 observed reflections, converging to a final R value of 0.029. The molecule has a plane of symmetry through the apical iron site and both the unbridged and the doubly bridged iron sites in the basal plane. Analysis of the Mössbauer spectra of the $[N(PPh_3)_2]^+$, $[NEt_4]^+$ and $[NMe_4]^+$ salts indicates that the overall arrangement of the carbonyl ligands is different in each case. The electrochemistry of the $[Fe_5N(CO)_{14}]^-$ cluster anion in acetonitrile, tetrahydrofuran and dichloromethane solutions was examined. It is shown that, independent of the cation, the anion undergoes two one-electron reductions. The first cathodic step leads to the relatively stable dianion $[Fe_5N(CO)_{14}]^{2-}$, whereas the second step initiates cluster degradation.

Solid-state isomerisation in clusters which contain carbonyl ligands only is uncommon but not unknown. A well documented example is the neutral species $[Ir_6(CO)_{16}]$.[1] One isomer of this compound is isostructural with $[Rh_6(CO)_{16}]$ with four face-bridging carbonyl ligands while a second isomer has four edge-bridging carbonyl groups each of them asymmetrically bound. An example of isomerisation in an anionic cluster is found with $[Rh_{11}(CO)_{23}]^{3-}$.[2] This anion forms isomers with different carbonyl stereochemistries when the $[NMe_4]^+$ salt is crystallised from different solvent systems, *i.e.* $[NMe_4]_3[Rh_{11}(CO)_{23}]\cdot Me_2CO$ and $[NMe_4]_3[Rh_{11}(CO)_{23}]\cdot C_6H_5Me$. In the case of the anion $[Fe_4(CO)_{13}]^{2-}$, isomers were produced on changing the cation used in the crystallisation process.[3] The Fe_4 anion contained no bridging (or semi-bridging) carbonyl ligands in the $[N(PPh_3)_2]^+$ salt, but there were three semi-bridging carbonyls present in the $[Fe(py)_6]^{2+}$ salt (py = pyridine). We now report the observation of three solid-state carbonyl ligand isomers of the $[Fe_5N(CO)_{14}]^-$ cluster anion. These were formed when the anion was crystallised with $[N(PPh_3)_2]^+$, $[NEt_4]^+$ and $[NMe_4]^+$ cations. Additionally, evidence from electrochemical and infrared spectroscopic studies is presented to show that a single $[Fe_5N(CO)_{14}]^-$ structure (or, alternatively, the same mixture of structures) exists in solutions of these salts irrespective of the cation present.

Results and Discussion

In dichloromethane solution the infrared spectra in the CO region of the compounds $[X][Fe_5N(CO)_{14}]$ ($X^+ = N(PPh_3)_2^+$, NEt_4^+, NMe_4^+ or Cs^+) were identical irrespective of the cation present. However, the Mössbauer spectra of the two compounds which may have been expected to have the most similar structures, *i.e.* $[NMe_4][Fe_5N(CO)_{14}]$ **1** and $[NEt_4][Fe_5N(CO)_{14}]$ **2**,[4] were distinctly different, Fig. 1, and the spectrum of compound **2** was more like that of $[N(PPh_3)_2][Fe_5N(CO)_{14}]$ **3** than of **1**.

It was decided to establish the solid-state structure of $[NMe_4][Fe_5N(CO)_{14}]$ **1** by X-ray crystallographic methods. Slow diffusion of hexane into a concentrated dichloromethane solution of **1** at 0 °C resulted in the production of black crystals suitable for X-ray analysis. The structure of **1** is shown in Fig. 2 together with the atom numbering scheme. Important bond angles and bond lengths are reported in Table 1. The Fe_5 skeleton has a slightly distorted square-based pyramidal geometry. There are twelve terminal carbonyl ligands; three on the apical iron atom, Fe(1), three on the unbridged basal iron atom, Fe(2), and two each on the remaining iron atoms Fe(3), Fe(3*) and Fe(4). The other two carbonyls bridge the Fe(3)–Fe(4) and Fe(3*)–Fe(4) interactions. The cluster possesses a plane of symmetry, passing through Fe(1), Fe(2) and Fe(4), which causes Fe(3) and Fe(3*) to be in symmetry-related mirror-image positions. The carbonyl ligands C(3)–O(3), C(8)–O(8) and C(9)–O(9) are also in the plane of symmetry.

The structure of $[N(PPh_3)_2][Fe_5N(CO)_{14}]$ has been reported previously.[5] It did not contain a plane of symmetry and each iron site had a different arrangement of carbonyl ligands. Since the apical sites in **1** and **3** were both $\{Fe(CO^t)_3\}$ sites (t = terminal), the most significant differences were clearly in the basal sites. These are shown in Scheme 1. Compound **1** contains two symmetry-related bridging carbonyls which are bonded to iron atoms Fe(3) and Fe(4) in an asymmetrical fashion [Fe(3)–C(7) 1.852(3) and Fe(4)–C(7) 2.206(3) Å] whereas compound **3** contains one symmetrically bound bridging carbonyl [Fe(3)–C(43) 2.05(2) and Fe(4)–C(43) 1.96(1) Å] and one terminal carbonyl ligand on Fe(2) which is very weakly interacting with the adjacent iron atom Fe(3) [Fe(2)–C(23) 1.84(2) and Fe(3)–C(23) 2.56(3) Å].

The range of Fe(apical)–Fe(basal) bond lengths in compound **1** is smaller than in **3**, being 2.5635(8)–2.5889(5) Å compared

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

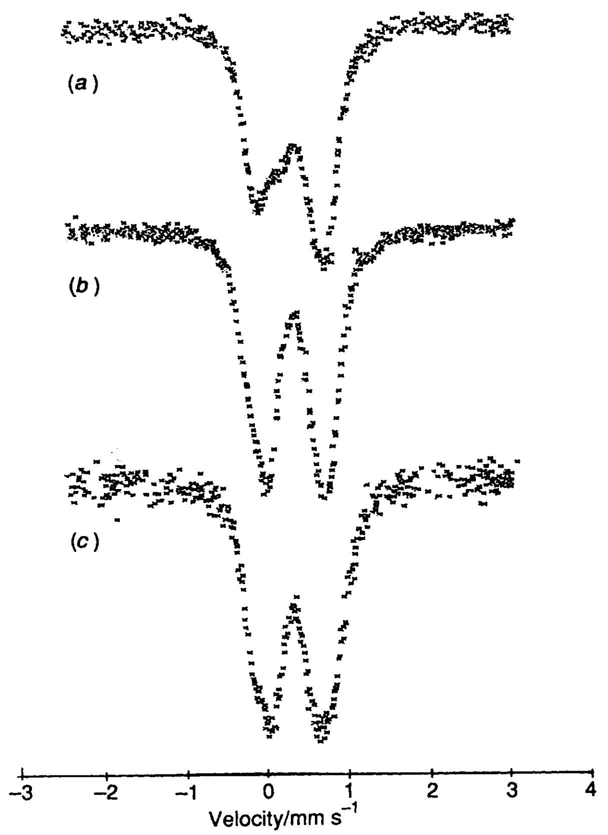


Fig. 1 Mössbauer spectra of the $[Fe_5N(CO)_{14}]^-$ anions of (*a*) $[NMe_4]^+$, (*b*) $[N(PPh_3)_2]^+$ and (*c*) $[NEt_4]^+$ salts

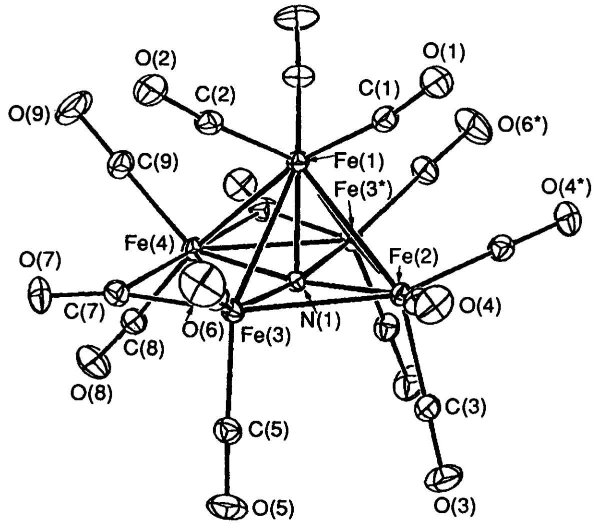


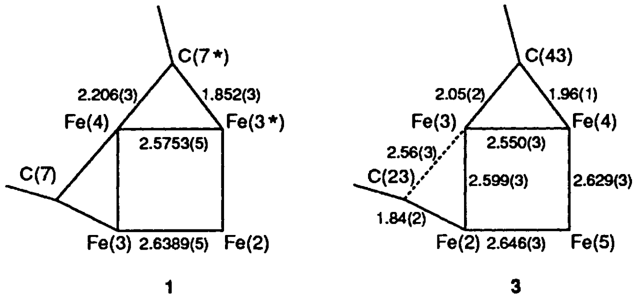
Fig. 2 A perspective view of the $[Fe_5N(CO)_{14}]^-$ anion in **1** showing the atom numbering scheme

with 2.564(3)–2.611(3) Å. The mean values are 2.5789 in **1** and 2.585 Å in **3**. Distances between Fe(basal) atoms depend on the types of $Fe(CO)_n$ sites involved. In **1** the unbridged Fe(2)–Fe(3) distance is 2.6389(5) Å and the bridged Fe(3)–Fe(4) distance is 2.5753(5) Å. Four different Fe–Fe distances are found in **3** (see Scheme 1). These vary from 2.550(3) to 2.646(3) Å.[5] The nitrogen atom in **1** is located at an average distance of 0.128(2) Å below the mean plane containing the four basal iron atoms. The equivalent distance in **3** is 0.11(1) Å. The distance from the apical iron to the interstitial nitrogen atom in **1**, 1.931(3) Å, is longer than that in **3**, 1.916(8) Å. The mean values of the distances from the basal iron atoms to the interstitial nitrogen atom are 1.848 Å in **1** and 1.845 Å in **3**.

Table 1 Interatomic distances (Å) and selected angles (°) in $[NMe_4][Fe_5N(CO)_{14}]$ **1**

Fe(1)–Fe(2)	2.5635(8)	Fe(4)–C(7)	2.206(3)
Fe(1)–Fe(3)	2.5889(5)	Fe(4)–C(8)	1.774(3)
Fe(1)–Fe(4)	2.5743(5)	Fe(4)–C(9)	1.753(5)
Fe(1)–N(1)	1.931(3)	O(1)–C(1)	1.140(4)
Fe(1)–C(1)	1.781(3)	O(2)–C(2)	1.154(4)
Fe(1)–C(2)	1.774(3)	O(3)–C(3)	1.135(6)
Fe(2)–Fe(3)	2.6389(5)	O(4)–C(4)	1.143(4)
Fe(2)–N(1)	1.852(2)	O(5)–C(5)	1.137(4)
Fe(2)–C(3)	1.793(5)	O(6)–C(6)	1.144(4)
Fe(2)–C(4)	1.783(3)	O(7)–C(7)	1.149(4)
Fe(3)–Fe(4)	2.5753(5)	O(8)–C(8)	1.137(4)
Fe(3)–N(1)	1.834(1)	O(9)–C(9)	1.148(6)
Fe(3)–C(5)	1.774(3)	N(2)–C(21)	1.442(8)
Fe(3)–C(6)	1.779(3)	N(2)–C(22)	1.433(12)
Fe(3)–C(7)	1.852(3)	N(2)–C(23)	1.460(5)
Fe(4)–N(1)	1.872(3)		
Fe(2)–Fe(1)–Fe(3)	61.61(1)	Fe(1)–Fe(4)–N(1)	48.37(8)
Fe(2)–Fe(1)–Fe(4)	92.49(2)	Fe(3)–Fe(4)–Fe(3*)	90.59(2)
Fe(2)–Fe(1)–N(1)	46.05(7)	Fe(3)–Fe(4)–C(7)	44.74(7)
Fe(3)–Fe(1)–Fe(3*)	89.99(2)	C(7)–Fe(4)–C(7*)	179.67(9)
Fe(3)–Fe(1)–Fe(4)	59.84(1)	Fe(1)–N(1)–Fe(2)	85.29(8)
Fe(3)–Fe(1)–N(1)	45.02(1)	Fe(1)–N(1)–Fe(3)	86.84(8)
Fe(4)–Fe(1)–N(1)	46.44(7)	Fe(1)–N(1)–Fe(4)	85.2(1)
Fe(1)–Fe(2)–Fe(3)	59.67(1)	Fe(2)–N(1)–Fe(3)	91.44(7)
Fe(1)–Fe(2)–N(1)	48.66(8)	Fe(2)–N(1)–Fe(4)	170.5(2)
Fe(3)–Fe(2)–Fe(3*)	87.83(2)	Fe(3)–N(1)–Fe(3*)	172.8(2)
Fe(1)–Fe(3)–Fe(2)	58.72(2)	Fe(3)–N(1)–Fe(4)	88.03(8)
Fe(1)–Fe(3)–Fe(4)	59.80(1)	Fe(3)–C(7)–Fe(4)	78.3(1)
Fe(1)–Fe(3)–N(1)	48.14(8)	Fe(3)–C(7)–O(7)	151.9(3)
Fe(4)–Fe(3)–C(7)	57.0(1)	Fe(4)–C(7)–O(7)	129.8(2)
Fe(1)–Fe(4)–Fe(3)	60.36(1)		

The asterisk refers to the equivalent position *x*, *y*, $\frac{1}{2} - z$.



Scheme 1 Bond lengths in Å

The Mössbauer spectra of the $[X][Fe_5N(CO)_{14}]$ species with cations $[X]^+$ being $[NMe_4]^+$, $[N(PPh_3)_2]^+$ and $[NEt_4]^+$ are illustrated in Fig. 1(*a*)–(*c*) respectively. There is clear evidence in these spectra for different solid-state structures of the cluster anions with each of the cations used. Without a detailed knowledge of the anion's structure in these compounds assignment of Mössbauer parameters to the $Fe(CO)_n$ sites can only be tentative. In the case of **1**, the established structure and the $Fe(CO)_n$ site-quadrupole splitting parameter correlations from a previous study of *nido*-Fe_5 clusters[6] enable the Mössbauer spectrum to be assigned as follows, see Table 2. Four unique iron sites are expected; these are apical $Fe(CO^t)_3$, $Fe(CO^t)_2(CO^{br})_2$, basal $Fe(CO^t)_3$ and $Fe(CO^t)_2(CO^{br})$ (br = bridging) in the intensity ratio 1 : 1 : 1 : 2 respectively corresponding to iron atoms Fe(1), Fe(4), Fe(2) and Fe(3) and Fe(3*). We assign a quadrupole splitting (q.s.) value of 0.98 mm s^{-1} to the apical $Fe(CO^t)_3$ site by comparison with data for the apical $Fe(CO^t)_3$ sites in $[Fe_5C(CO)_{15}]$ and $[Fe_5H(N)(CO)_{14}]$, both of which had quadrupole splittings of 0.98 mm s^{-1}, and $[Fe_5C(CO)_{14}]^{2-}$ for which a value of 1.03 mm s^{-1} was reported.[4,6] For the last mentioned compound it should be noted, in the light of the

Table 2 Mössbauer parameters (mm s^{-1}) for $[NMe_4][Fe_5N(CO)_{14}]$ **1**

Assignment	Isomer shift (i.s.)	Quadrupole splitting (q.s.)
$Fe(CO^t)_3$ apical	0.31	0.98
$Fe(CO^t)_2(CO^{br})_2$	0.31	1.15
$Fe(CO^t)_3$ basal	0.31	0.65
$Fe(CO^t)_2(CO^{br})$	0.42	0.33

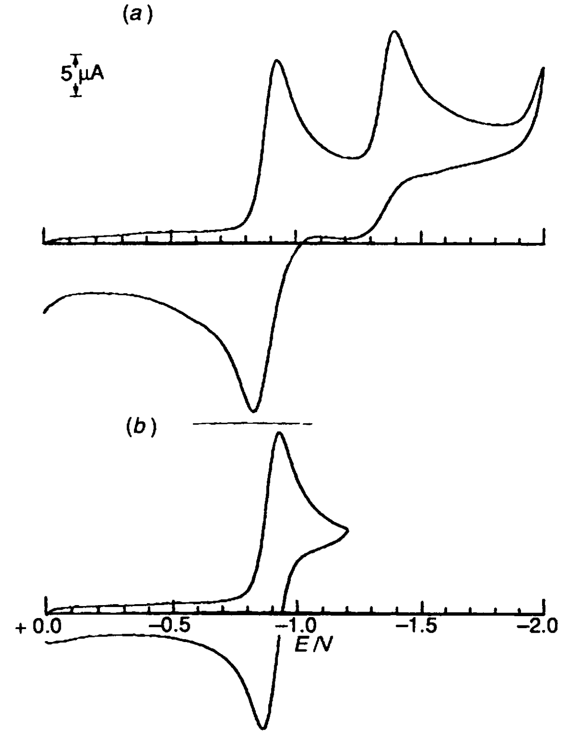


Fig. 3 Cyclic voltammograms recorded at a mercury electrode for a MeCN solution containing $[NEt_4][Fe_5N(CO)_{14}]$ (1.1×10^{-3} mol dm^{-3}) (*a*) and $[NEt_4][ClO_4]$ (0.2 mol dm^{-3}) (*b*). Scan rate 0.2 V s^{-1}

differences in the structures of **1** and **3**, that the solid-state structure was obtained for the $[NBu_4]^+$ salt whereas the sample used for the Mössbauer spectrum was the $[NEt_4]^+$ salt and these may not necessarily have exactly the same anion structures. However, there are no such doubts about the neutral species $[Fe_5C(CO)_{15}]$ and $[Fe_5H(N)(CO)_{14}]$ and our assignments are made on the basis of data from these compounds as well as $[Fe_5C(CO)_{14}]^{2-}$ (see below). In general, the quadrupole splittings for apical $Fe(CO^t)_3$ and $Fe(CO^t)_2(CO^{br})_2$ sites are similar and have values of *ca.* 1.1 ± 0.05 mm s^{-1}. A quadrupole splitting of 1.15 mm s^{-1} is assigned to the $Fe(CO^t)_2(CO^{br})_2$ unit in **1**. This compares with 1.19 and 1.18 mm s^{-1} for similar units in $[Fe_5H(N)(CO)_{14}]$ and $[Fe_5C(CO)_{14}]^{2-}$. The two $Fe(CO^t)_2(CO^{br})$ units in **1** can be assigned a q.s. of 0.33 mm s^{-1}. This is very similar to 0.31 mm s^{-1} assigned to an iron atom in the same environment in $[Fe_5C(CO)_{14}]^{2-}$. Finally, a q.s. value of 0.65 mm s^{-1} is assigned to the basal $Fe(CO^t)_3$ unit. This is somewhat larger than values of 0.43 and 0.45 mm s^{-1} assigned to similar sites in $[Fe_5C(CO)_{14}]^{2-}$ and $[Fe_5C(CO)_{15}]$ respectively.[4,6]

Generally, isomer shifts (i.s.s) are not as useful as quadrupole splittings for identifying iron sites in iron carbonyl clusters because of the similarity of most i.s. data.[4,6] For example, the values for apical $Fe(CO^t)_3$, basal $Fe(CO^t)_3$ and $Fe(CO^t)_2(CO^{br})_2$ sites in $[Fe_5C(CO)_{14}]^{2-}$ are 0.28, 0.32 and 0.25 mm s^{-1} respectively. For a given type of site, anionic cluster carbonyls tend to have isomer shifts which are slightly more positive than those found for the equivalent sites in neutral clusters.[6] In the spectrum of **1** we assign a value of *ca.* 0.31 ± 0.03 mm s^{-1} for the apical $Fe(CO^t)_3$, $Fe(CO^t)_2(CO^{br})_2$ and basal $Fe(CO^t)_3$ sites. The apical and basal $Fe(CO^t)_3$ sites in $[Fe_5C(CO)_{15}]$ had an i.s. of 0.18 and 0.19 mm s^{-1} respectively. An i.s. of 0.42 mm s^{-1} is assigned to the $Fe(CO^t)_2(CO^{br})$ site. This is similar to 0.40 mm s^{-1} reported for an analogous site in $[Fe_5C(CO)_{14}]^{2-}$.

In solution the electrochemical properties of the $[NEt_4]^+$ and $[NMe_4]^+$ salts of the $[Fe_5N(CO)_{14}]^-$ anion are indistinguishable. This supports the evidence from infrared spectroscopy that the form, or forms, of the $[Fe_5N(CO)_{14}]^-$ anion in solution are independent of the cation. Typical electrochemical results for $[NEt_4][Fe_5N(CO)_{14}]$ **2** in acetonitrile solution are shown in Fig. 3. The first reduction process possesses features of chemical reversibility [Fig. 3(*b*)]. This is followed by an irreversible second step.

Controlled-potential coulometric tests in correspondence to the first cathodic process ($E_w = -1.1$ V) show that it involves the consumption of one electron per molecule. The complete chemical reversibility of the $[Fe_5N(CO)_{14}]^-$–$[Fe_5N(CO)_{14}]^{2-}$ redox reaction is demonstrated by the fact that the solution resulting from exhaustive one-electron reduction displays a cyclic voltammogram complementary to that shown in Fig. 3(*b*).

The diagnostic parameters obtained from analysis of the cyclic voltammograms at a mercury electrode (platinum electrodes do not give perfectly reproducible voltammograms) with scan rates varying from 0.02 to 20.48 V s^{-1} show that the chemically reversible one-electron addition is substantially electrochemically reversible too.[7] This may indicate that the addition of one electron to $[Fe_5N(CO)_{14}]^-$ does not cause a significant reorganisation in cluster geometry in solution.[8,9]

In addition to the second reduction step shown in Fig. 3(*a*), $[Fe_5N(CO)_{14}]^-$ also exhibits an irreversible multielectron oxidation step when a platinum electrode is used. The irreversibility of these processes implies cluster decomposition[8,9] and further investigation was terminated.

Table 3 summarises the redox potentials for the redox changes exhibited by $[Fe_5N(CO)_{14}]^-$ in different non-aqueous solutions. It is noteworthy that in dichloromethane solution there are some chemical complications involving the electrogenerated dianion. In macroelectrolysis experiments the current rapidly diminishes after the first one-electron addition but remains somewhat higher than the background current until the slowly completed addition of the second electron per molecule. At this stage the final cyclic voltammetric response no longer shows the characteristic shape of the $[Fe_5N(CO)_{14}]^-$–$[Fe_5N(CO)_{14}]^{2-}$ redox change. The electrochemical–chemical–electrochemical (e.c.e.)-type mechanism involved here might in part be responsible for the previous erroneous suggestion that $[Fe_5N(CO)_{14}]^-$ undergoes a single two-electron reduction step.[5]

Experimental

All syntheses were carried out under an inert atmosphere. Infrared spectra were recorded on Mattson Polaris IR10410 and on Perkin-Elmer 682 spectrometers. Mössbauer spectra were recorded for microcrystalline samples at liquid-nitrogen temperatures using the apparatus previously described.[10] Materials and the apparatus used in the electrochemical study have been described elsewhere.[11]

The cluster compound $[NMe_4][Fe_5N(CO)_{14}]$ was prepared according to a literature method[12] with slight modifications. The literature method was followed to the point where the sodium salt of $[Fe_5N(CO)_{14}]^-$ was precipitated with hexane, but, instead of filtering, the black tarry mixture was added directly to a solution of an excess of $[NMe_4]Cl$ in water. The crude mixture was allowed to stand for 2 h and then filtered. The product was extracted into acetone. Recrystallisation by slow diffusion of hexane into a concentrated dichloromethane

Table 3 Redox potentials (V *vs.* saturated calomel electrode) for the redox changes shown by $[Fe_5N(CO)_{14}]^-$ in different non-aqueous solutions

$[Fe_5N(CO)_{14}]^{-/2-}$ $E^{\circ\prime}$	$[Fe_5N(CO)_{14}]^{2-/3-}$ E_p*	Multielectron oxidation process E_p*	Solvent
−0.90	−1.40	+0.70	MeCN
−0.97	−1.55	+0.60	thf
−1.04	−1.50	+0.64	CH_2Cl_2

* Measured at 0.2 V s^{-1}.

Table 4 Positional parameters and their estimated standard deviations for $[NMe_4][Fe_5N(CO)_{14}]$ **1**

Atom	*x*	*y*	*z*
Fe(1)	0.368 26(5)	0.25	0.332 30(4)
Fe(2)	0.518 03(4)	0.25	0.205 63(4)
Fe(3)	0.314 84(3)	0.090 80(3)	0.172 85(3)
Fe(4)	0.123 94(5)	0.25	0.150 67(4)
O(1)	0.665 7(3)	0.25	0.512 7(3)
O(2)	0.270 2(3)	0.062 5(2)	0.442 9(2)
O(3)	0.535 7(4)	0.25	−0.024 5(3)
O(4)	0.725 1(2)	0.060 2(2)	0.308 6(2)
O(5)	0.305 0(3)	−0.001 3(2)	−0.048 9(2)
O(6)	0.448 5(3)	−0.119 0(2)	0.305 3(3)
O(7)	0.030 8(2)	−0.005 8(2)	0.139 9(2)
O(8)	−0.130 9(3)	0.25	−0.071 6(3)
O(9)	−0.055 6(3)	0.25	0.285 9(3)
N(1)	0.318 0(2)	0.25	0.164 9(2)
C(1)	0.553 1(4)	0.25	0.437 0(3)
C(2)	0.308 7(3)	0.133 0(3)	0.395 5(2)
C(3)	0.530 0(4)	0.25	0.065 1(3)
C(4)	0.640 8(3)	0.132 0(3)	0.267 2(2)
C(5)	0.306 9(3)	0.033 3(3)	0.037 6(2)
C(6)	0.395 1(3)	−0.037 1(3)	0.253 5(3)
C(7)	0.123 6(3)	0.058 2(3)	0.150 1(2)
C(8)	−0.027 9(4)	0.25	0.012 8(3)
C(9)	0.013 9(4)	0.25	0.231 1(4)
N(2)	0.082 7(3)	0.25	0.657 7(3)
C(21)	0.237 0(7)	0.25	0.683(1)
C(22)	0.062 5(12)	0.25	0.765 8(8)
C(23)	0.012 3(5)	0.356 9(4)	0.598 6(6)

solution at 0 °C resulted in black crystals of $[NMe_4][Fe_5N(CO)_{14}]$ **1** (Found: C, 28.65; H, 1.70; N, 3.60. Calc. for $C_{18}H_{12}Fe_5N_2O_{14}$: C, 28.50; H, 1.60; N, 3.70%). IR: (CH_2Cl_2) $\nu(CO^t)$ 2055vw, 2010w, 1985vs, 1979vs, $\nu(CO^{br})$ 1790w(br): (KBr) $\nu(CO^t)$ 2066m, 1991s(br), 1961s(br), 1922s(br), $\nu(CO^{br})$ 1807m(br) cm^{-1}.

Structural Determination of Complex **1**.—*Crystal data.* $C_{18}H_{12}Fe_5N_2O_{14}$, $M_r = 759.5$, monoclinic, space group $P2_1/m$, $a = 9.973(2)$, $b = 11.498(2)$, $c = 12.401(2)$ Å, $\beta = 113.53(1)°$, $U = 1303.7(7)$ Å^3, $Z = 2$, $D_c = 1.94$ g cm^{-3}, $F(000) = 752$, graphite-monochromatised Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 28.0$ cm^{-1}, $T = 21$ °C.

The crystal chosen for the analysis was a black block of approximate dimensions 0.32 × 0.38 × 0.42 mm. Cell dimensions and the orientation matrix were determined from a least-squares refinement of the setting angles of 25 reflections with $12 < \theta < 20°$. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer using the ω–2θ scan technique ($2\theta_{max} = 54°$). 3220 Reflections were measured, of which 2979 were unique (R_{int} 0.027 on I) and 2441 were considered observed with $I > 3\sigma(I)$. Lorentz and polarisation corrections were applied to the data; there was no evidence of decay during the course of the data collection. The systematic absences ($0k0$, $k = 2n + 1$) allow the space group to be either $P2_1/m$ or $P2_1$; the former was indicated by an analysis of E statistics and confirmed the successful refinement. The coordinates of the Fe atoms were obtained from an analysis of the Patterson function and the remaining atoms were located in subsequent Fourier difference syntheses. Refinement (with weights derived from the counting statistics) was by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms; hydrogen atoms were visible at intermediate stages of the analysis and were included in the refinement restrained to ride on the atoms to which they were bound (C–H 0.95 Å). The final cycles of refinement included 200 variable parameters and converged with $R = 0.029$ and $R' = 0.044$. The final difference map had no chemically significant features. Scattering factors and anomalous dispersion terms were from ref. 13. All calculations were performed on a PDP-11 computer using SDP-PLUS.[14] Table 4 lists the atomic coordinates.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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