

Definitive Identification of the Primary Reduction Product of the Nitroprusside Ion, Pentacyanonitrosylferrate(2–), in Aqueous Solution

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The nature of the primary reduction product formed by the nitroprusside ion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ pentacyanonitrosylferrate(2–), in aqueous solution has long been a matter of controversy, and a number of different formulations have been put forward.

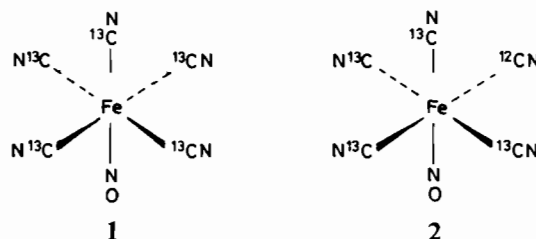
Much of the evidence has been surveyed by Mulvey and Waters [1] who showed that the same product, characterized by $g = 2.024$ and $A(^{14}\text{N}) = 14.9$ G, was formed from $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ by electrochemical reduction, and by chemical reduction using $[\text{BH}_4]^-$, $[\text{S}_2\text{O}_4]^{2-}$, ascorbic acid, and quinol: the same product was formed in reactions between $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ and a number of thiols, including cysteine. Mulvey and Waters also showed [1] that the EPR spectrum of this reduction product was independent of pH in the range 7–13, and they concluded that the nitrosyl group was retained in the reduction product, without addition of either a proton [2] or an oxide ion [3]: the reduction product was formulated [1] as $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$, and two recent kinetic studies [4, 5] of the reaction between $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ and cysteine have accepted this formulation without comment.

On the other hand, reduction of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ with sodium metal in liquid ammonia, yields a solution from which, after acidification, salts of $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ can be crystallized: this tetracyano anion was characterized by X-ray crystallography and shown to have an approximately square pyramidal C_{4v} geometry [6]. However the existence of $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ in a crystal provides no evidence for the nature of the reduction product in aqueous solution.

The work of Mulvey and Waters [1] did not provide a definite demonstration that the pentacyano structure for the reduction product, *viz.* $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ is retained in solution, and the mere existence of $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ [6] shows that alternative formulations must be considered. The simplest way to establish the number of cyanide ligands present in the reduction product in solution is the use of ^{13}C , and its effect upon the observed EPR spectrum.

Early studies using ^{13}C disagreed upon the magnitude of $A(^{13}\text{C})$ and values of 4.6 G [7] and 10.0 G [8] were reported. In a subsequent study [9] using $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ which had been synthesized from KCN enriched in ^{13}C to between 20% and 30%, it was reported that reduction gave a species characterized by an EPR spectrum having $A(^{14}\text{N}) = 15$ G and $A(^{13}\text{C}) = 10$ G in which the unpaired electron was coupled equally to five ^{13}C nuclei; this was cited as evidence for the formulation $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$. However with a statistical distribution of the available ^{13}C label [10], even with 30% ^{13}C overall, fewer than 1% of the $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ ions contain five ^{13}C -labelled ligands. Throughout the possible range of ^{13}C labelling cited [9], 20%–30%, easily the most abundant isotopic species is $[\text{Fe}(^{12}\text{CN})_4(^{13}\text{CN})\text{NO}]^{2-}$, containing only one ^{13}C labelled ligand. Whatever the origin of the reported EPR spectrum [9], it is unlikely to have been any product derived from $[\text{Fe}(^{13}\text{CN})_5\text{NO}]^{2-}$. For effective counting, by use of EPR spectroscopy, of the number of cyanide ligands in the reduction product a high level of ^{13}C enrichment is required.

We have now solved this problem using a sample of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ enriched to 90% in ^{13}C . The spectroscopic properties [10, 11] of this material are dominated by two isotopic species 1 and 2:



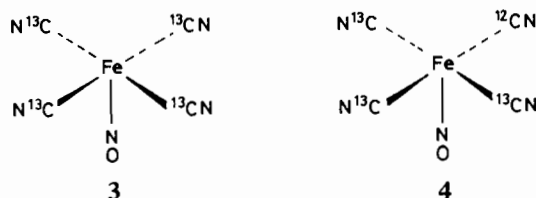
These two forms represent 59.1% and 26.2% respectively of the total numbers of nitroprusside ions.

We first confirmed, using nitroprusside of normal isotopic composition, that the reduction product reported by Mulvey and Waters [1] is readily produced using either $[\text{S}_2\text{O}_4]^{2-}$ or cysteine. The EPR spectra resulting from these reductions were characterized by $g = 2.024$, $A(^{14}\text{N}) = 15.2$ G. Reduction of 90% ^{13}C -labelled $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ by $[\text{S}_2\text{O}_4]^{2-}$ under identical conditions yielded an EPR spectrum, readily interpreted in terms of coupling to a single ^{14}N nucleus, $A(^{14}\text{N}) = 15.2$ G, and to four ^{13}C nuclei, $A(^{13}\text{C}) = 9.2$ G. In addition, minor features, having the same A values, but derived from the isotopic species containing a single ^{12}C nucleus, were also observed. The spectral assignment was satisfactorily confirmed using spectral simulation.

The major spectrum, with coupling to four ^{13}C nuclei is assigned to the species $[\text{Fe}(^{13}\text{CN})_4\text{NO}]^{2-}$

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(3) and the minor spectrum is $[\text{Fe}(\text{}^{13}\text{CN})_3(\text{}^{12}\text{CN})\text{NO}]^{2-}$ (4):



If no isotope scrambling occurs upon loss of the axial cyano ligand, complex 3 represents 65.7% and complex 4 represents 28.9% of the total $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ population.

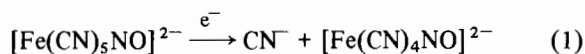
There remains just the possibility that although coupling to four ^{13}C nuclei is observed, a fifth cyanide ligand is still present in the reduction product but having a negligibly small A value. EHMO calculations dispose of this possibility.

The $A(^{14}\text{N})$ value of 15 G observed here in solution is very similar to that observed [12] in solution for the square pyramidal $\text{Fe}(\text{NO})(\text{S}_2\text{CNMe}_2)_2$ [13] and $[\text{Fe}(\text{NO})(\text{S}_2\text{MoS}_2)_2]^{2-}$, and for matrix-isolated [14] square pyramidal $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ [6]. EHMO calculations show that for each of these square pyramidal species, having linear Fe–N–O fragments and $A(^{14}\text{N}) \sim 15$ G, the SOMO is a σ orbital concentrated along the FeNO direction. However, paramagnetic iron nitrosyls in which the SOMO is a π orbital with respect to the Fe–NO direction are all found to have $A(^{14}\text{N})$ values in the range 2–6 G [12, 15].

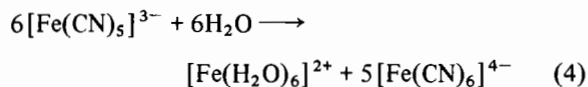
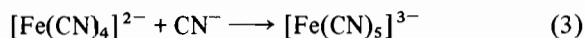
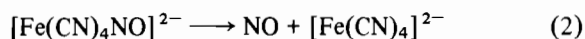
The pentacyano complex $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ is calculated to have a SOMO of π type with respect to the Fe–NO direction, regardless of the angle Fe–N–O: this angle is 180° in $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ [16] but is expected to be rather less in $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$. On the other hand the SOMO for $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ is calculated to be of σ type, along the Fe–N–O axis.

Removal of the axial cyanide from $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ to give $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ causes the iron d_{z^2} orbital to shift from being an almost pure metal orbital at the top of the d-manifold (binding energy 1.02 eV) to 10.99 eV where it is admixed with the iron $4p_z$ and with σ (NO) to give a σ orbital bonding over the whole Fe–N–O fragment. The difference in the SOMO between $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ and $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ is therefore dominated by the σ donor capacity of the ligand *trans* to the nitrosyl, and even for non π -bonding ligands X such as X = H_2O it is expected that *trans*- $[\text{XFe}(\text{CN})_4\text{NO}]^{2-}$ will have a SOMO of π type. Our EHMO calculations confirm this both for the non π -bonding ligands X = H_2O and CH_3^- , and for the weakly [17] π -bonding isocyanide *cf.* ref. 18, and thus make it certain that no *trans* axial ligand can be present.

Thus the ^{13}C hyperfine coupling shows coupling to only four cyano ligands in the reduction product, and the ^{14}N hyperfine coupling demonstrates that this product has square pyramidal geometry in solution. Hence, by use of a high level of ^{13}C labelling, we have provided for the first time definitive evidence that the primary reduction product of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ in aqueous solution at ambient temperature is $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ rather than $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$, eqn. (1)



At ambient temperature, the EPR spectrum of $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ decays slowly with time, yielding eventually an EPR silent solution. Examination of such a solution by ^{13}C NMR spectroscopy shows the presence of $[\text{Fe}(\text{CN})_6]^{4-}$ as the ultimate product, formed according to eqns. such as (2)–(4):



Subsequent reaction of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ with NO, giving $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$ would remove any free Fe(II) from the solution.

Support for eqns. (2)–(4) came from the observation that the conversion of $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ is markedly accelerated by addition of excess cyanide: in the presence of an equimolar aliquot of $[\text{}^{13}\text{CN}]^-$, the conversion to $[\text{Fe}(\text{CN})_6]^{4-}$ was much faster than any ligand exchange of $[\text{}^{13}\text{CN}]^-$ with $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$.

The reassignment here as $[\text{Fe}(\text{CN})_4\text{NO}]^{2-}$ of the species originally assigned [1] by Mulvey and Waters as $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ may require that their assignment of the two-electron reduction product as $[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$ also be revised. Likewise kinetic schemes which have attempted to interpret, for example, the cyanide dependence of the reaction between $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ and cysteine [4, 5] (and other thiols also) may also now need revision.

Experimental

$\text{Na}_2[\text{Fe}(\text{}^{13}\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ was prepared as previously described [10]: EPR spectra were measured, at ambient temperature, in 1 mm quartz capillaries using a Bruker ER200D spectrometer; di-*t*-butyl nitroxide was used as the standard for the measurement of line positions.

Acknowledgement

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