# Oxidation of Copper(II)-coordinated Diethylenetriamine by Hexacyanoferrate(III) Ion. A Kinetic Investigation

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## Abstract

The stoichiometry and kinetics of the reaction between $[Cu(dien)(OH)]^+$ and $[Fe(CN)_6]^{3-}$ in aqueous alkaline medium are described. The rate equation

$$-(d[Fe(III)]/dt) = \{k_1[OH^-]^2[[Cu(dien)(OH)]^+] + k_2[OH^-] \times [[Cu(dien)(OH)]^+]^2\}([Fe(III)]/[Fe(II)])$$

($Fe(III) = [Fe(CN)_6]^{3-}$; $Fe(II) = [Fe(CN)_6]^{4-}$), the 4:4:1 $OH^-/Fe(III)/[Cu(dien)(OH)]^+$ stoichiometric ratio and the nature of the ultimate products identified in the reaction solution suggest the fast formation of a doubly deprotonated Cu(III)–diamido complex which slowly undergoes an internal redox process where the ligand is oxidised to the Schiff base $H_2NCH_2CH_2N{=}CHCH{=}NH$.

The $[[Cu(dien)(OH)]^+]^2$ term in the rate equation is explained with the formation of a transient $\mu$-hydroxo mixed-valence Cu dimer. A two-electron internal reduction of the Cu(III) complex yielding a Cu(I) intermediate is suggested to account for the presence of monovalent copper in a precipitate which forms at relatively high reactant concentrations and in the absence of dioxygen.

## Introduction

The oxidation of the amines in the presence of transition metal ions is a widely investigated field. The reactions refer to either metal-bound monodentate [1–3] or polydentate [4–15] amines. In all cases the oxidation product is a metal complex of increased insaturation and, as a rule, an imine complex is formed. Thus, the reaction may be often described as a dehydrogenation of a coordinated nitrogen and of its α-carbon.

The metals involved are Ru [1, 2, 8], Cu [3, 4, 6, 7, 11–15], Ni [5, 6, 11, 13], Co [6], and Fe [9–11]. The oxidant may be the metal ion itself, as in $[Fe(en)(CN)_4]^-$ [9] (en = ethylenediamine) and $[Ni(\text{tetra-aza macrocycle})]^{3+}$, or, more often, an external oxidand such as $O_2$ [3, 7, 11], peroxides [2, 10], NaClO [8], $[Fe(CN)_6]^{3-}$ [9], Ce(IV) [1] or an electrode [1, 4, 12–15].

In most cases an intermediate complex in a higher oxidation state is postulated [1, 8, 12–14, 16–19], which is eventually reduced by the coordinated ligand. However, there is a substantial lack of systematic information on the mechanistic course of this reaction with specific reference to the role of the metal and to the structure of the coordinated amine.

During our studies on the preparation and the structure of the adducts between $[Cu(dien)]^{2+}$ (dien = diethylenetriamine) and hexacyanoferrate(III) [20, 21] it was observed that the latter was reduced to hexacyanoferrate(II), very likely by the copper complex, and it was considered of interest to study this reaction in detail.

In this paper we discuss the mechanism of this reaction and the products obtained, and also show that an intermediate Cu(III) species is indeed formed as expected [20].

## Experimental

### *Materials*

Diethylenetriamine was a Merck 'for synthesis' reagent, potassium hexacyanoferrate(III) and hexacyanoferrate(II) were C. Erba pure grade chemicals and were used as purchased. Sodium perchlorate was a Backer reagent and was recrystallised before use. Lithium perchlorate was prepared by reacting C. Erba reagent grade lithium carbonate with 70% perchloric acid (Merck). All other reagents used in this work were pure grade chemicals.

Diethylenetriaminecopper(II) perchlorate was prepared as previously described [22].

### *Instruments*

UV and visible spectra were run on either a Perkin-Elmer 555 or a Beckman DU 8 recording spectrophotometer, using cells of appropriate path length. IR spectra were recorded on a Perkin-Elmer 577 apparatus on Nujol or fluorocarbon mulls of the

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solid compounds. $^1H$ and $^{13}C$ NMR spectra were run on a Varian XL 300 instrument. ESCA experiments were carried out on a VG ESCA-3 MKI spectrometer employing $AlK_{1,2}$ X rays ($h\nu = 1486.6$ eV). Samples were deposited on gold plates, the Au $4f_{7/2}$ signal of which at 84.0 eV was used as the reference. GC-MS analyses were performed on a Hewlett Packard 5970 apparatus.

### *Kinetics*

The reaction progress was monitored by the decrease of the 416 nm $[Fe(CN)_6]^{3-}$ band ($\epsilon_{416} = 1.02 \times 10^3$ $M^{-1}$ $cm^{-1}$ [23]). The measurements were carried out with a Beckman DU 8 instrument which, in addition to the instantaneous absorbance, also gives the 'instantaneous rate' in terms of $\Delta D/\Delta t$ ($\Delta D$ = change in absorbance between two consecutive readings separated by a time interval $\Delta t$).

The general procedure for the kinetic experiments was as follows. Two distinct solutions were prepared by dilution of stock aqueous solutions of $K_3[Fe(CN)_6]$, $NaClO_4$, $[Cu(dien)](ClO_4)_2$ and NaOH. Solution A contained $K_3[Fe(CN)_6]$ and $NaClO_4$ (for the ionic strength control, $I = 0.15$ M); solution B contained the copper complex and NaOH. Equal volumes of solutions A and B were separated in a two-compartment quartz cell, allowed to equilibrate for 5 min at 20.0 ± 0.1 °C and then mixed. The absorbance variations at $\lambda = 416$ nm with time were recorded. The first absorbance could be read after no more than 3–5 s from mixing and the time interval between two consecutive readings was set at a value between 3 and 10 s according to the reaction rate. These time intervals were sufficiently narrow to allow a good measure of the instantaneous rate $\Delta D/\Delta t$.

In each kinetic run the starting concentration of the Cu complex after mixing the solutions A and B was in the range 2–20 mM while the free hydroxide ion concentration* was set equal to 10, 20, 30, 40 mM. In all cases the hexacyanoferrate(III) ion concentration was lower than a half of that of Cu(II) and less than $[OH^-]/10$ to ensure pseudo-zero order conditions with respect to these latter reagents.

## Results

### *Reaction Stoichiometry*

Since the equilibrium constant for the reaction

$$[Cu(dien)]^{2+} + OH^- \rightleftharpoons [Cu(dien)(OH)]^+$$

is $1.5 \times 10^5$ $M^{-1}$ [24], $[Cu(dien)]^{2+}$ is virtually 100% converted to $[Cu(dien)(OH)]^+$ at present pH conditions.

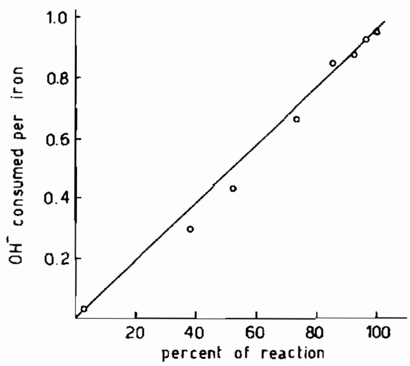

Fig. 1. Hydroxide ions consumed per iron(III) as a function of the reaction percent.

When $[Fe(CN)_6]^{3-}$ (hereafter Fe(III)) is allowed to react with $[Cu(dien)(OH)]^+$ in the presence of excess NaOH, it is reduced to $[Fe(CN)_6]^{4-}$, as demonstrated by the disappearance of the 416 nm band and the growth of the bands characteristic of $[Fe(CN)_6]^{4-}$ [23] (hereafter Fe(II)). An aliquot of a solution containing Fe(III) (3.76 mM), $[Cu(dien)(OH)]^+$ (4.04 mM) and $OH^-$ (40 mM) was allowed to react until the 416 nm absorption band reached its minimum. The solution was then exchanged on a cationic Amberlite IR 120 resin ($Na^+$ form), which eliminated any copper species, and suitably diluted. The spectrum of this solution was that expected for an essentially quantitative conversion to $[Fe(CN)_6]^{4-}$ ($\epsilon_{216} = 2.31 \times 10^4$ $cm^{-1}$ $M^{-1}$, lit. [23]: $\epsilon_{216} = 2.24 \times 10^4$ $cm^{-1}$ $M^{-1}$).

The disappearance of Fe(III) is accompanied by a decrease in concentration of $OH^-$ ions. In an especially designed experiment, a solution (250 ml) containing Fe(III) (3.12 mM), $[Cu(dien)(OH)]^+$ (2.04 mM) and $OH^-$ (10.0 mM) was thermostatted at 20.0 °C. A sample of this solution was kept at the same temperature in the spectrophotometer so as to monitor ($\lambda = 416$ nm) the reaction progress. At proper time intervals 20-ml aliquots of the solution were titrated with standard $H_2SO_4$**. Figure 1 shows the plot of the $OH^-$ consumed per Fe(III) *versus* the percent of reaction, the latter calculated as the ratio $(D_t - D_0)/(D_f - D_0)$, $D_0$, $D_t$, and $D_f$ being the 416 nm absorption measured at zero time, at time $t$ and at the end of the reaction, respectively. The trend is linear and indicates a 1:1 stoichometry between Fe(III) and $OH^-$ ions.

When the reaction is carried out with a $[Cu(dien)(OH)]^+$/Fe(III) ratio lower than *ca.* 0.25 the reduction of Fe(III) is no longer complete as shown in

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*Since $[Cu(dien)]^{2+}$ converts to $[Cu(dien)(OH)]^+$ in alkaline medium [24], the amount of NaOH was calculated so as to leave the reported concentration of free $OH^-$ ion after quantitative formation of the hydroxo complex.

**At pH 6.5 precipitation of both $Cu_2[Fe(CN)_6]$ and $Cu_3[Fe(CN)_6]_2$ occurs and the pH remains virtually constant upon addition of acid. Above this value the potentiometric titration profile shows no irregularities and the equivalence was assumed to correspond to pH = 7,

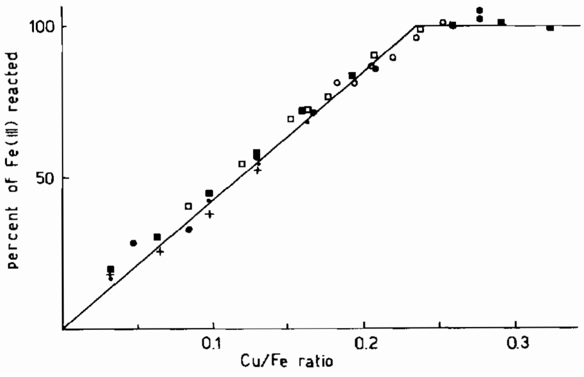


Fig. 2. Percent of Fe(III) reacted as a function of the mole ratio Cu/Fe. Different symbols correspond to different experiments and conditions: ○, □, ●, $[OH^-] = 37.5$ mM, $[[Cu(dien)(OH)]^+] = 0.194$ mM; ■, ·, +, $[OH^-] = 50$ mM, $[Fe(III)] = 2$ mM (■), 1 mM (+, ·).

Fig. 2. This indicates that Fe(III) and $[Cu(dien)(OH)]^+$ react in a 4:1 stoichiometry, the slight excess of Fe(III) consumed over this ratio being possibly due to side reactions (see footnote on p. 143).

### *Reaction Products*

When the reagents concentrations are progressively raised above those used in the kinetic experiments, conditions are reached where the reaction is accompanied by the formation of a precipitate, the more abundant the higher the concentrations of the reagents and the lower the concentration of dioxygen. Solids were obtained by reacting anaerobically $[Cu(dien)(OH)]^+$ in the range 10–20 mM in 0.1 M NaOH and Fe(III) ranging from 0.5 to 4 times the copper content. The solids obtained after the completion of the reaction were separated by centrifugation, washed with water and dried in a desiccator over $CaSO_4$. Their colour depends on the Fe/Cu solution ratio being gray with a blue shade for low Fe(III) contents and gray with a pink shade for high Fe/Cu ratios.

The compounds obtained with about four $[Fe(CN)_6]^{3-}$ ions per $[Cu(dien)(OH)]^+$ contain three copper atoms per iron. Magnetic susceptibiliy measurements indicate only one unpaired electron per iron. IR spectra show the presence of prevailing Cu(II)-coordinate ethylenediamine [25], and of CN-bridged hexacyanoferrate(III) [26]. ESCA signals were recorded at 932.6 and 934.6 eV (Cu(I) and Cu(II) 2p electrons, respectively, in approximately a 2:1 ratio) [27], at 708.5 eV (Fe $2p_{3/2}$) [28] and at 401.7 and 403.0 eV (N1s of –CN and of $>$CH–$NH_2$, approximately in a 3:2 ratio) [29].

A sample (1 g) of this product was treated with 37% HCl (3 ml) and $H_2O$ (7 ml) under rapid stirring for 30 min. After centrifugation, a pale green solution was obtained which turned blue after neutralisation with $NaHCO_3$. The solid residue that was left when the solvent was evaporated *in vacuo* over $H_2SO_4$, was extracted with EtOH (15 ml), the solution filtered and treated with $LiClO_4$. A crystalline product formed which, after recrystallisation from MeOH, was found to correspond to $[Cu(en)_2](ClO_4)_2$ ($\lambda_{max} = 655$ nm. *Anal.* Found (calc.): C, 13.6 (12.6); H, 4.3 (4.2); N, 14.7 (14.6)%). The above observations indicate for the gray solid the formula $Cu(I)_2Cu(II)(en)_2Fe(CN)_6$. When a lower Fe(III)/Cu(II) ratio was used the IR spectrum of the solid indicated that en was replaced to a variable extent by another amine more closely resembling the starting dien but containing some insaturation, as indicated by a broad shoulder at 1660 $cm^{-1}$ assignable to –CH=N– (and possibly to –CH=CH–) groups [7]. Accordingly, the elemental analysis gave a Cu:N:C ratio close to 3:9:10 and definitely different from 3:14:14 expected for the en- containing precipitate.

An aliquot of the clear solution obtained after separation of the precipitate was extracted with $CH_2Cl_2$ and the extract analysed on a GC-MS analyser. Molecular ion peaks were measured at $m/z =$ 80.1, 73.1, 71.0 and 57.1 assignable to pyrazine (**1**) iminoacetic acid (**2**) oxalic acid mononitrile (**3**) and iminoethanol (**4**) in the order. The assignment of **1** was confirmed by extracting the same solution with $CHCl_3$ and diluting the extract with cyclohexane. The spectrum of the resulting solution showed the characteristic absorbancies of pyrazine (two structured bands centred at 260 and 320 nm) [30].

If the oxidation of $[Cu(dien)(OH)]^+$ was carried out in the presence of 1 atm of dioxygen no gray solid formed and only a little $Cu(OH)_2$ precipitated. The filtered solution was exchanged on an anionic resin (Amberlite IR 400, $Cl^-$ form), brought to pH 8 by careful addition of 37% HCl and then evaporated to dryness in a rotary evaporator. The solid was extracted with the minimum amount of ethanol. The solution was evaporated to dryness and the residue extracted with a small volume of isopropanol. Evaporation of the organic solvent under vacuum gave a blue, sticky oil which resisted any attempt to crystallise. Addition of 37% (or gaseous) HCl to an ethanol solution of this material caused the precipitation of a yellow, crystalline tetrachlorocuprate(II) which could be recrystallised from water–ethanol. The $^1H$ and $^{13}C$ NMR spectra of this solid dissolved in $D_2O$ were identical with those of an acidic ($D_2SO_4$) solution of ethylenediamine.

Any attempt to detect the presence of glycine in the reaction mixture was unsuccessful.

### *Kinetics*

The analysis of the optical data shows that under conditions where copper complex and $OH^-$ concentrations may be considered constant, the instantaneous rate $\Delta D/\Delta t$ is a linear function of the ratio

$[\mathrm{Fe(III)}]/[\mathrm{Fe(II)}] = (D_t - D_f)/(D_0 - D_t)$. This is shown in Fig. 3 where a typical experiment is reported. In no cases was the correlation coefficient of the straight line lower than 0.9997. Thus the instantaneous rate obeys the linear equation

$$-(\mathrm{d}D/\mathrm{d}t) = a[\mathrm{Fe(III)}]/[\mathrm{Fe(II)}] \qquad (1)$$

Figure 4 shows the dependence of $a$ on the concentration of $[\mathrm{Cu(dien)(OH)}]^+$ and of $\mathrm{OH^-}$. It is immediately evident that the dependence of the rate coefficient $a$ on copper complex concentration at constant $[\mathrm{OH^-}]$ is greater than first order. Indeed, as is shown in Fig. 5 for $[\mathrm{OH^-}] = 10$ mM, the $a/[[\mathrm{Cu(dien)(OH)}]^+]$ *versus* $[[\mathrm{Cu(dien)(OH)}]^+]$ plot is linear with a positive slope up to the highest Cu(II) concentration used. Hence, the following equation was assumed to hold at any hydroxide ion concentration

$$a = a_1[[\mathrm{Cu(dien)(OH)}]^+] + a_2[[\mathrm{Cu(dien)(OH)}]^+]^2 \qquad (2)$$

with $a_1$ and $a_2$ being functions of $[\mathrm{OH^-}]$.

When the experimental data reported in Fig. 4 were analysed according to eqn. (2), at each hydroxide ion concentration, the values of $a_1$ and $a_2$ reported in Table I were obtained. The Table also shows that the ratios $a_1/[\mathrm{OH^-}]^2$ and $a_2/[\mathrm{OH^-}]$ are essentially constant. Considering that $\mathrm{d}D/\mathrm{d}t = \epsilon_{416} \times (\mathrm{d}[\mathrm{Fe(III)}]/\mathrm{d}t)$ and using eqn. (2), eqn. (1) may be rewritten as

$$\begin{aligned} &-(\mathrm{d}[\mathrm{Fe(III)}]/\mathrm{d}t) \\ &\quad = \{k_1[\mathrm{OH^-}]^2[[\mathrm{Cu(dien)(OH)}]^+] \\ &\quad + k_2[\mathrm{OH^-}][[\mathrm{Cu(dien)(OH)}]^+]^2\} \\ &\quad \times ([\mathrm{Fe(III)}]/[\mathrm{Fe(II)}]) \qquad (3) \end{aligned}$$

with $k_1 = a_1/\epsilon_{416} \times [\mathrm{OH^-}]^2$ and $k_2 = a_2/\epsilon_{416} \times [\mathrm{OH^-}]$. Use of the proper values for $a_1$, $a_2$, and $\epsilon_{416}$ gives $k_1 = (1.5 \pm 0.2) \times 10^2$ $\mathrm{M^{-3}}$ $\mathrm{min^{-1}}$ and $k_2 = (4.4 \pm 1.1) \times 10^2$ $\mathrm{M^{-3}}$ $\mathrm{min^{-1}}$.

## Discussion and Conclusions

All literature reports concerning the oxidation of amines coordinated to a metal ion agree on the fact that for each pair of electrons lost by the ligand two protons are also lost and a $>$C=N– double bond forms [1–15]. Hence, the 4:1 stoichiometry between Fe(III) and $\mathrm{OH^-}$, on one hand, and $[\mathrm{Cu(dien)(OH)}]^+$, on the other, suggests that the primary oxidation product of dien should contain two double bonds. Furthermore, the presence of large amounts of ethylenediamine among the ultimate products indicates that the unsaturated species should be the Schiff base $\mathrm{NH_2CH_2CH_2N{=}CHCH{=}NH}$ (5a) the hydrolysis of which at the tertiary nitrogen–carbon

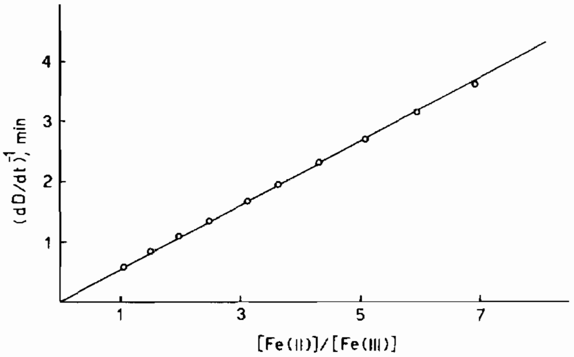


Fig. 3. Reciprocal rate *vs.* the ratio [Fe(II)]/[Fe(III)]. Reaction conditions: initial Fe(III) concentration: 1.00 mM, $[\mathrm{Cu(dien)(OH)}]^+ = 5.0$ mM, $[\mathrm{OH^-}] = 40$ mM.

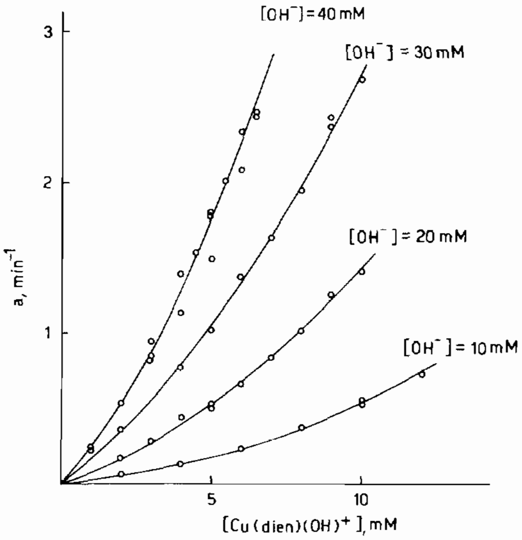


Fig. 4. Dependence of the slope $a$ of eqn. (1) on $[\mathrm{Cu(dien)(OH)}]^+$ and $\mathrm{OH^-}$ concentrations. The lines are calculated according to eqn. (2) and using the parameters listed in Table I.

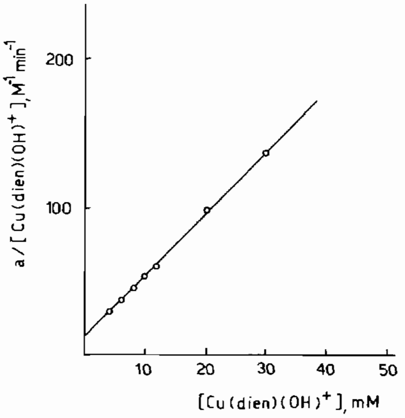
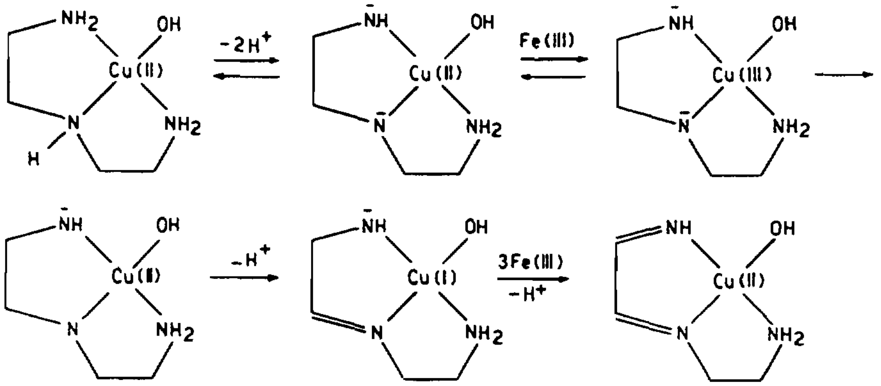


Fig. 5. $a/[[\mathrm{Cu(dien)(OH)}]^+]$ ratio as a function of $[\mathrm{Cu(dien)(OH)}]^+$ concentration. $[\mathrm{OH^-}] = 10$ mM.

TABLE I. $a_1$ and $a_2$ Parameters of Eqn. (2) at Different $OH^-$ Concentrations

| $OH^-$ (mM) | $a_1$ ($M^{-1}$ $min^{-1}$) | $a_1/[OH^-]^2$ ($M^{-3}$ $min^{-1}$) | $a_2$ ($M^{-2}$ $min^{-1}$) | $a_2/[OH^-]$ ($M^{-3}$ $min^{-1}$) |
|---|---|---|---|---|
| 10 | 12.7 | $1.27 \times 10^5$ | $4.14 \times 10^3$ | $4.14 \times 10^5$ |
| 20 | 68.4 | $1.71 \times 10^5$ | $7.45 \times 10^3$ | $3.72 \times 10^5$ |
| 30 | 146 | $1.62 \times 10^5$ | $12.7 \times 10^3$ | $4.25 \times 10^5$ |
| 40 | 220 | $1.31 \times 10^5$ | $24 \times 10^3$ | $6.0 \times 10^5$ |



Scheme 1.

double bond would, in fact, generate en and iminoethanal (4). Amounts of the latter have been found in the reaction mixture.

Although 5a seems to be the main oxidation product, its isomer $NH{=}CHCH_2N{=}CHCH_2NH_2$ (5b) is also formed as suggested by the presence of pyrazine (1). Indeed, hydrolysis of 5b, at the tertiary nitrogen–carbon double bond yields aminoethanal (6) and iminoethylamine (7) or, directly, 6 and $NH_3$*. Cyclisation of two molecules of 6, reacting as the hydrated form, followed by elimination of water and mild oxidation readily gives pyrazine [31]. Compounds 2 and 3 are due to further oxidation of 4 [32]** (see Scheme 1).

At this stage, we were unable to carry out a quantitative analysis of the reaction products so as to establish a stoichiometric relationship among them. Nevertheless, in our opinion, the compounds identified lend sufficient support to the scheme proposed.

The kinetic results summarised in eqn. (4) have brought into light the following aspects of the oxidation mechanism. (i) The instantaneous rate is only proportional to the ratio [Fe(III)]/[Fe(II)] at constant concentration of $[\mathrm{Cu(dien)(OH)}]^+$ and $OH^-$, irrespective of the time elapsed. (ii) Hydroxide ions are involved before or during the rate determining step. (iii) There are at least two reaction pathways leading to the oxidation of the amine, one of which involving two copper atoms in the slow step. All the observations are consistent with the reactions set (4)–(9)

$$[\mathrm{Cu(II)(dien)(OH)}]^+ + 2\mathrm{OH}^- \overset{K_A}{\rightleftharpoons} [\mathrm{Cu(II)(dien{-}2H)(OH)}]^- + 2\mathrm{H_2O} \qquad (4)$$

$$[\mathrm{Cu(II)(dien{-}2H)(OH)}]^- + [\mathrm{Cu(II)(dien)(OH)}]^+ \overset{K_D}{\rightleftharpoons} [\mathrm{Cu(II)(dien){-}OH{-}Cu(II)(dien{-}2H)}]^+ + \mathrm{OH}^- \qquad (5)$$

$$[\mathrm{Cu(II)(dien{-}2H)(OH)}]^- + \mathrm{Fe(III)} \overset{K'_{ox}}{\rightleftharpoons} [\mathrm{Cu(III)(dien{-}2H)(OH)}] + \mathrm{Fe(II)} \qquad (6)$$

$$[\mathrm{Cu(II)(dien){-}OH{-}Cu(II)(dien{-}2H)}]^+ + \mathrm{Fe(III)} \overset{K''_{ox}}{\rightleftharpoons} [\mathrm{Cu(II)(dien){-}OH{-}Cu(III)(dien{-}2H)}]^{2+} + \mathrm{Fe(II)} \qquad (7)$$

$$[\mathrm{Cu(III)(dien{-}2H)(OH)}] \xrightarrow[+\ 3\mathrm{Fe(III)} + 2\mathrm{OH}^-]{k'} [\mathrm{Cu(III)(diimine\ 5)(OH)}]^+ \qquad (8)$$

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*Indeed, ammonia was detected in one experiment where the reaction solution, brought to pH 8 after removal of the gray precipitate, was dried in a rotary evaporator. Significant amounts of $NH_3$ were found in the liquid nitrogen trap used to protect the oil pump of the apparatus.

**The small difference of the Fe(III)/Cu(II) ratio (4.2) from the nearest integer, shown in Fig. 2, might be due to this effect.

$$[\mathrm{Cu(II)(dien){-}OH{-}Cu(III)(dien{-}2H)}]^{2+} \xrightarrow[\substack{+3\mathrm{Fe(III)}\\ +2\mathrm{OH}^-}]{k''}$$

$$[\mathrm{Cu(II)(dien){-}OH{-}Cu(II)(diimine\ 5)(OH)}]^{3+} \tag{9}$$

In fact, if $x$ and $y$ represent the concentrations of $[\mathrm{Cu(III)(dien{-}2H)(OH)}]$ and $[\mathrm{Cu(II)(dien){-}OH{-}Cu(III)(dien{-}2H)}]^{2+}$, respectively, and all the equilibria (4)–(7) are shifted far to the left

$$x = K_\mathrm{A}K'_\mathrm{ox}[[\mathrm{Cu(dien)(OH)}]^+][\mathrm{OH}^-]^2 \times ([\mathrm{Fe(III)}]/[\mathrm{Fe(II)}]) \tag{10}$$

$$y = K_\mathrm{A}K_\mathrm{D}K''_\mathrm{ox}[[\mathrm{Cu(dien)(OH)}]^+]^2[\mathrm{OH}^-] \times ([\mathrm{Fe(III)}]/[\mathrm{Fe(II)}]) \tag{11}$$

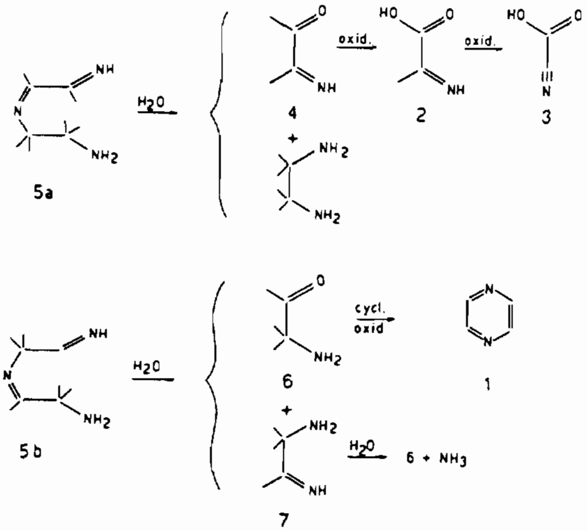
and the rate of the overall Fe(III) consumption is

$$\begin{aligned} -(\mathrm{d}[\mathrm{Fe(III)}]/\mathrm{d}t) &= k'x + k''y \\ &= 4\{k'K_\mathrm{A}K'_\mathrm{ox}[[\mathrm{Cu(dien)(OH)}]^+][\mathrm{OH}^-]^2 \\ &\quad + k''K_\mathrm{A}K_\mathrm{D}K''_\mathrm{ox}[[\mathrm{Cu(dien)(OH)}]^+]^2[\mathrm{OH}^-]\} \\ &\quad \times ([\mathrm{Fe(III)}]/[\mathrm{Fe(II)}]) \end{aligned} \tag{12}$$

Equation (13) is identical with eqn. (4) if $k_1 = 4k'K_\mathrm{A}K'_\mathrm{ox}$ and $k_2 = 4k''K_\mathrm{A}K_\mathrm{D}K''_\mathrm{ox}$.

Here reaction (4) is written as a deprotonation reaction involving the NH protons of the coordinated dien. These protons are likely to be the secondary nitrogen proton and a chain terminal $\mathrm{NH_2}$ proton [9, 33]. Reaction (5) is a fast equilibrium generating a $\mu$-hydroxo dimer*. Reactions (6) and (7) each represents a redox equilibrium where the deprotonated monomer and dimer, respectively, undergo a one-electron oxidation by Fe(III). This mechanism requires that the oxidised species is relatively inert and all the above considerations point towards a Cu(III) species. It is stressed here that the conditions in which this reactive species forms also provide the copper with those strong $\sigma$-donor imido ligands which are thought to stabilise this oxidation state [13, 35]. Besides the well known polypeptide complexes [36], Cu(III)–imido compounds [35] have been obtained by electrochemical oxidation of Cu(II)–polyamine complexes. These Cu(III) species are unstable, with a variable degree of lability, towards an internal ligand-to-metal electron transfer followed by a further fast multielectron oxidation. In spite of its complexity, the overall process conforms to a simple first order kinetics [12, 15]. An analogous sequence of events is implied in eqns. (8) and (9) with the difference that a chemical, instead of an electrochemical, oxidation is operating here.

There are no direct evidences on the nature of the chemical processes which follow the first, rate determining ligand-to-copper electron transfer. However, the presence of Cu(I) in the gray precipitate (see above) suggests the idea that the intramolecular electron transfer does not stop at Cu(II) but rather involves the formation of Cu(I), the whole process being represented by the sequence (for the monomer) (Scheme 2) where the secondary nitrogen is depicted as reacting first according to the greater ease of oxidation of secondary *versus* primary amines [37]. The two-electron reaction is also consistent with the spin conservation rule, both Cu(III) and Cu(I) being spin paired species [38]. Fabbrizzi *et al.* have also shown that insaturation [39] and flexibility [14] of the amine ligand act as stabilising factors towards the formation of Cu(I) complexes, by making possible metal-to-ligand $\pi$-bonding and by allowing an easier matching to the tetrahedral geometry of Cu(I). It is then conceivable that after the first one-electron transfer, the radical formed may not survive enough to be oxidised by Fe(III) but undergoes a second internal electron transfer to Cu(I). The latter species could then be trapped into the gray precipitate when the conditions for its formation are matched. The effect of dioxygen in preventing the formation of this precipitate could be due to a fast reoxidation of the Cu(I) formed. Of course, other alternative routes to Cu(I) are conceivable in the present system as Cu(II) ions are likely to be a strong enough oxidant towards some of the reaction products so that the actual origin of the monovalent copper deserves further investigation.



Scheme 2.

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*A dimeric copper(II) species with a single bridging $\mathrm{OH^-}$ group has been postulated by Margerum *et al.* [34] as a precursor of a dimeric Cu(III) hydroxide complex. In keeping with the more common doubly bridged $\mathrm{OH^-}$ species, eqn. (6) can also be represented as a reaction between $[\mathrm{Cu(dien)(OH)}]^+$ and the monodeprotonated bis-hydroxide $[\mathrm{Cu(dien{-}H)(OH)_2}]^-$.

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## References

1 F. R. Keene, D. J. Salmon and T. J. Meyer, *J. Am. Chem. Soc., 98*, 1884 (1976).
2 S. I. Murahashi, T. Naota and H. Taki, *J. Chem. Soc., Chem. Commun.*, 613 (1985).
3 M. M. Al-Arab and G. A. Hamilton, *J. Am. Chem. Soc., 108*, 5972 (1986).
4 D. C. Olson and J. Vasilevskis, *Inorg. Chem., 10*, 463 (1971).
5 E. K. Barefield and M. T. Mocella, *J. Am. Chem. Soc., 97*, 4238 (1975).
6 S. C. Tang and R. H. Holm, *J. Am. Chem. Soc., 97*, 3359 (1975).
7 M. G. Burnett, V. McKee, S. Martin Nelson and M. G. B. Drew, *J. Chem. Soc., Chem. Commun.*, 829 (1980).
8 D. F. Mahoney and J. K. Beattie, *Inorg. Chem., 12*, 2561 (1973).
9 M. Goto, M. Takeshita, N. Kauda, T. Sakai and V. L. Goedken, *Inorg. Chem., 24*, 582 (1985).
10 M. Goto, M. Takeshita and T. Sakai, *Bull. Chem. Soc. Jpn., 54*, 2491 (1981).
11 V. L. Goedken and D. H. Bush, *J. Am. Chem. Soc., 94*, 7355 (1972).
12 P. Zanello, R. Seeber, A. Cinquantini, G. A. Mazzocchin and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 893 (1982).
13 L. Fabbrizzi, A. Perotti and A. Poggi, *Inorg. Chem., 22*, 1411 (1983).
14 L. Fabbrizzi, A. Poggi and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 2191 (1983).
15 L. Fabbrizzi, A. Poggi and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1495 (1984).
16 G. A. Hamilton, R. Daniell Libby and C. R. Hartzel, *Biochem. Biophys. Res. Commun., 55*, 333 (1973).
17 G. R. Dyrkacz, R. Daniell Libby and G. A. Hamilton, *J. Am. Chem. Soc., 98*, 626 (1976).
18 G. A. Hamilton, P. K. Adolf, J. de Jersey, G. C. Du Bois, G. R. Dyrkacz and R. Daniell Libby, *J. Am. Chem. Soc., 100*, 1899 (1978), and refs. therein.
19 C. J. Hipp and D. H. Bush, 'Coordination Chemistry', Vol. 2, American Chemical Society, Washington D. C., 1978, p. 435.
20 G. O. Morpurgo, V. Mosini, P. Porta, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 111 (1981).
21 G. O. Morpurgo, P. Porta, A. Desideri and S. Morante, *Inorg. Chim. Acta, 107*, 111 (1985).
22 M. J. Bew, B. J. Hathaway and R. Fereday, *J. Chem. Soc., Dalton Trans.*, 1229 (1972).
23 O. Benali Baitich, M. Meklati and M. Achour, *Rev. Roum. Chim., 15*, 15 (1970).
24 J. W. Allison and R. J. Angelici, *Inorg. Chem., 10*, 2233 (1971).
25 D. B. Powell and N. Sheppard, *Spectrochim. Acta, 17*, 68 (1961).
26 D. A. Dows, A. Haim and W. K. Wilmarth, *J. Inorg. Nucl. Chem., 21*, 33 (1961); G. O. Morpurgo, V. Mosini, P. Porta, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1272 (1980).
27 M. Bressan, C. Furlani and G. Polzonetti, *Polyhedron, 2*, 523 (1983).
28 D. Brigys and M. P. Seah (eds.), 'Practical Surface Analysis', Wiley, New York, 1983.
29 V. I. Nefelov, 'Rentgeno-elektron Naya Spektroscopiya Khimiceskih Soedinenniy', Khimiya, Moscow, 1984.
30 S. F. Mason, *J. Chem. Soc.*, 1247 (1959).
31 S. Hauptmann, 'Organische Chemie', Veb Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1985.
32 A. Bruylants and E. Feytmants-De Medicins, in S. Patai (ed.), 'The Chemistry of the Carbon–Nitrogen Double Bond', Interscience, New York, 1970, p. 465.
33 J. Clark and D. D. Perrin, *Q. Rev., 18*, 2941 (1964).
34 E. T. Gray, Jr., R. W. Taylor and D. W. Margerum, *Inorg. Chem., 16*, 3047 (1977).
35 W. Levason and M. D. Spicer, *Coord. Chem. Rev., 76*, 45 (1987), and refs. therein.
36 A. W. Hamburg and D. W. Margerum, *Inorg. Chem., 22*, 3884 (1983).
37 C. E. Castro, M. Jasmin, N. Yokoyama and R. Wade, *J. Am. Chem. Soc., 108*, 4179 (1986).
38 G. A. Hamilton, in O. Hayaishi (ed.), 'Molecular Mechanism of Oxygen Activation', Academic Press, New York, 1974, p. 405.
39 L. Fabbrizzi, A. Lari, A. Poggi and B. Seghi, *Inorg. Chem., 21*, 2083 (1982).