Dependence of Dehydrogenation of Amines towards Coordination Geometry: Oxidation Products of Tricyano[di(2-pyridylmethyl)amine]ferrate(II) from mer and fac Isomers

Masafumi Goto,*[a] Nobuhiro Koga,[a] Yasuhiko Ohse,[a] Hiromasa Kurosaki,[a] Takayuki Komatsu[b] and Yoshitaka Kuroda[b]

[a] Faculty of Pharmaceutical Sciences, Kumamoto University, Oe-honmachi, Kumamoto 862, Japan
[b] Faculty of Pharmaceutical Sciences, Nagoya City University, Mizuho-Ku, Nagoya 467, Japan

Two geometrical isomers, mer- and fac-tricyano[di(2-pyridylmethyl)amine]ferrate(II) give the iron(II) complex with dehydrogenated ligand and iron(III) complex with intact ligand, respectively, upon oxidation with $(NH_4)_2SO_4$ or H_2O_2 at neutral pH, which is confirmed by electrochemical measurements.

The dehydrogenation of amines coordinated to Fe^{II}, Ru^{II} and Os^{II} has been the subject of extensive studies for the last two decades.[1] The oxidative degradation of proteins, one of the possible causes of ageing, has been reported to involve MCO(metal catalysed oxidation), where Fe^{II}/Fe^{III} and H_2O_2 participate, and an Fe-bound dehydrogenated amine side chain is postulated to form as an intermediate.[2] Thus the determination of factors which govern the ease of the reaction is crucial. Alkylation of the primary amine enhances oxidation by a factor of several thousand.[1c] Polyamines have not been studied so far, except for tri- and tetra-amine macrocycles[1a,1f] and a hexadentate cage polyamine.[1h] We have isolated the fac and mer isomers of the title compounds, $[Fe(CN)_3(2\text{-}DPA)]^-$ salts, and found that the mer-isomer is exclusively subject to the dehydrogenation. [(2-DPA) = di(2-pyridylmethyl)amine].

Successive addition of 2 equiv. of 2-DPA and 3 equiv. of NaCN to a methanolic solution of $Fe(ClO_4)_2\cdot 6H_2O$ under inert gas yielded a mixture of fac and mer isomers of $Na[Fe(CN)_3(2\text{-}DPA)]$. After concentration under reduced pressure, the remaining residue was triturated with propanol. Thorough washing of the separated crystals with propanol left mer-$Na[Fe(CN)_3(2\text{-}DPA)]\cdot 1.5H_2O\cdot PrOH\cdot NaClO_4$, 1, as the sparingly soluble product. An oxygen-free aqueous solution of 1 isomerized to the fac isomer by heating at 50 °C for 18 h.† After concentration under reduced pressure, the residue was crystallized from methanol–ether, yielding fac-$Na[Fe(CN)_3(2\text{-}DPA)]\cdot 0.75NaClO_4$, 2. Oxidation of 1 with H_2O_2 yielded a deep red dehydrogenated product, and gel filtration afforded mer-$Na[Fe(CN)_3(2\text{-}DPA - 2H)]\cdot 2H_2O$, 3. The spectroscopic data of complexes 1–3 are listed in Table 1.

The assignments of the isomers are based on their ^1H NMR spectra. Both isomers belong to the C_s point group, and the two pyridylmethyl halves are equivalent. The isomer showing the larger difference in chemical shifts for the two methylene protons (AB pattern) is assigned as the fac-isomer. For 3, the two pyridyl groups are not equivalent; a new singlet (azomethine) appeared at δ 9.24, and the remaining pyridylmethyl reduced to a sharp singlet at δ 5.93.

Oxidation of 1 and 2 with $(NH_4)_2S_2O_8$ yielded products belonging to different types. The visible spectral differences between them are shown in Fig. 1. 1 changed to 3 with isosbestic points at 461, 383, 325, and 305 nm, while 2 changed to the corresponding iron(III) complex, 4, with a decrease in
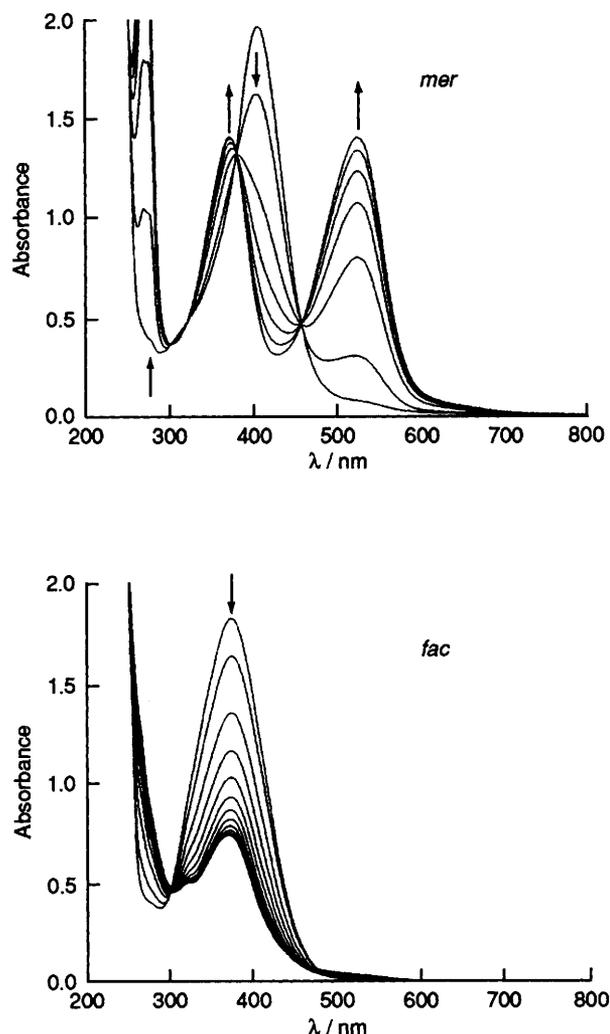

Fig. 1 UV–VIS spectral change of mer- and fac-$[Fe^{II}(CN)_3(2\text{-}DPA)]^-$ with $(NH_4)_2S_2O_8$ in phosphate buffer (pH 6.5) at 25 °C mer: $[Fe^{II}]_0 = 0.28$ mmol dm^{-3}, $[(NH_4)_2S_2O_8] = 0.5$ mmol dm^{-3}, repetition period = 3 min. fac: $[Fe^{II}]_0 = 0.30$ mmol dm^{-3}, $[(NH_4)_2S_2O_8] = 0.6$ mmol dm^{-3}, repetition period = 3 min

Table 1 Spectroscopic data for $[Fe(CN)_3(2\text{-}DPA)]^-$ and its dehydrogenated complexes

	$\nu_{C\equiv N}/cm^{-1}$ [a]	Electronic spectra[b] λ_{max}/nm [log(ε/dm³ mol^{-1} cm^{-1})]	^1H NMR[c] δ(multiplicity, J/Hz, assignment)
1	2054	413(3.903), 251(4.146)	4.53, 4.60(AB, 15.4, H_m), 7.03(t, 4.4, H_5), 7.55(t, 7.5, H_4), 8.30(d, 4.4, H_6)
2	2065, 2044	385(3.733), 251(3.956)	4.15, 4.68(AB, 17.2, H_m), 7.16(t, 6.1, H_5), 7.24(d, 8.1, H_3), 7.57(t, 7.5, H_4), 9.17(d, 5.1, H_6)
3	2073	529(3.754), 380(3.720) 283(5.045), 279(4.037) 242(4.117)	5.93(s, H_m), 7.12(t, 6.4, $H_{5'}$), 7.33(t, 7.7, H_3), 7.68(t, 7.7, H_4), 7.81(t, 7.5, $H_{4'}$) 7.85(d, 7.3, H_3), 8.40(d, 5.5, H_6), 8.55(d, 5.5, $H_{6'}$), 9.24(s, $H_{m'}$)

[a] KBr pellets. [b] Aqueous solution. [c] D_2O solution, internal standard NaTSP.

Scheme 1
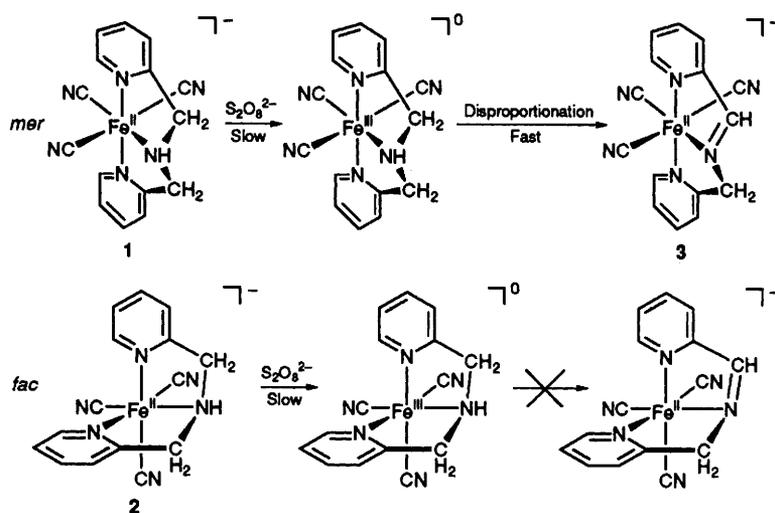
absorbance at 375 nm. The initial rate, v_i, of the oxidation was determined by following the absorbance change at 530 and 375 nm for **1** and **2** respectively. The rate was expressed by $v_i = k[\text{Fe}^{II} \text{ complex}]_0 [(\text{NH}_4)_2\text{S}_2\text{O}_8]_0$ in the pH region 6.51–9.05 for both the isomers. The magnitudes of k are similar: 4.8 and 2.9 dm^3 mol^{-1} s^{-1} for **1** and **2** at 25 °C, respectively.

One quasi-reversible anodic and cathodic peak was observed for both **2** and **3**, and their redox potentials were 0.50 and 0.66 V, respectively, vs. NHE with peak separations of 70 and 60 mV, respectively, under conditions of pH 4 acetate buffer (0.1 mol dm^{-3} NaCl) with a scan rate of 200 mV s^{-1}. Under the same conditions, **1** showed two anodic peaks at 0.50 and 0.68 V, and two cathodic peaks at 0.61 and 0.43 V, but the intensity of the second cathode peak was very weak. The pair at the higher potential is due to the formation of **3**. Thus an ECE (electrochemical–chemical–electrochemical) mechanism operates, and the iron(III) species generated from **1** near the electrode surface undergo a rapid disproportionation to yield **1** and **3** under these conditions.

These observations are consistent with Scheme 1. The dehydrogenation of coordinated amines consists of (i) oxidation of the central metal ion, and (ii) a disproportionation of the deprotonated species of the metal-oxidized species yielding iron(II) species, iron(III) aminyl species and/or iron(IV) species; the latter undergo deprotonation to yield the ligand-dehydrogenated iron(II) complex.[1c,1i] The present study shows that process (i) is the rate determining step for the oxidation of **1** and **2** with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. Process (ii) is rapid for **1** but very slow for **2**. This difference is accounted for by the steric effect of producing the deprotonated species or the planar intermediate on the way to the coordinated imine. The

slow ligand oxidation of bis(1,4,7-triazacyclononane)iron(II)[1a] and rapid ligand oxidation of low-spin dicyano(cyclam)-iron(II)[1f] is due to their differences in coordination geometry.

Footnote

† This isomerization followed a rate expression of $-d[1]/dt = k[1]$, where $k = 1.2 \times 10^{-5}$ s^{-1} at 50 °C. The crystal structure of $[\text{Fe}(2\text{-DPA})_2](\text{PF}_4)_2$ has been reported, and two 2-DPA are bound in a cis-cofacial fashion.[3]

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