Redox in a Ferroverdin Analogue: Recognition of Isomeric Co-ordination Spheres by Fe^{II} and Fe^{III}

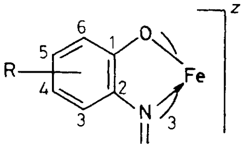
Partha Basu, Samudranil Pal, and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

The N_3O_3 co-ordination sphere of (**1b**) and (**1c**) selectively stabilises low-spin Fe^{II} and Fe^{III} in *fac* (**2a**) and *mer* (**2b**) geometries, respectively; mismatched combinations generated by rapid chemical/electrochemical electron transfer at low temperatures undergo spontaneous isomerisation at measurable rates to achieve equilibrium populations.

Ferroverdin [(**1a**), cc = counter-cation], a green biological pigment,[1] includes the low-spin[2] (S = 0) *fac*-$Fe^{II}(N_3O_3)$ co-ordination sphere[3] provided by a nitrosophenol having substantial quinone–oxime character.[4] While exploring the redox chemistry of ferroverdin analogues we have observed that the Fe^{II} and Fe^{III} states can recognise and differentiate the isomeric *fac* (**2a**) and *mer* (**2b**) N_3O_3 octahedra, the matched combinations being *fac*-Fe^{II} and *mer*-Fe^{III}. Metastable populations of *mer*-Fe^{II} and *fac*-Fe^{III} can be generated but in each case the mismatch is spontaneously corrected by isomerisation. This phenomenon is illustrated with the help of (**1b**) and (**1c**), which have been known for a long time[5] but without isomeric characterisation. The experiments reported below were performed in dimethylformamide (dmf).

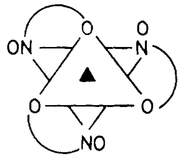
Green solutions of diamagnetic (**1b**) give rise to the same ^1H n.m.r. signals for the three chelate rings corresponding to the axially symmetric *fac* geometry as in ferroverdin.[3]† Rapid and quantitative oxidation of (**1b**) to brown (**1c**) occurs when 1 mole of Fe^{3+} $(ClO_4^-)_3$ or $Ag^+ClO_4^-$ is added. The e.s.r. spectrum [Figure 1(a)(i); frozen glass, 77 K] of solutions freshly oxidised at 253 K or below is due to axial species ($g_{\parallel}$ = 1.940, $g_{\perp}$ = 2.317). Oxidation at higher temperatures [Figure 1(a)(ii)] affords additional resonances (g_1 = 1.957, g_2 = 2.224, g_3 = 2.350) due to a rhombic species which grows in concentration with time at the expense of the axial species. At equilibrium the latter is a minor constituent and the g resonance is observable only at high gain [not shown in Figure 1(a)(iii)]. From the solution low-spin (S = 1/2) (**1c**) can be isolated in the solid state and the e.s.r. spectrum of its solution is identical with the equilibrium spectrum.†



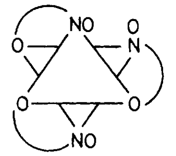
(**1a**) R = 4-[p-$(CH_2{=}CH)C_6H_4OC({=}O)$-], z = −1, cc = Na^+

(**1b**) R = 3,4-benzo, z = −1, cc = Na^+

(**1c**) R = 3,4-benzo, z = 0



(**2a**) (*fac*)



(**2b**) (*mer*)

Stereoretentive oxidation, equation (1), and subsequent isomerisation, equation (2), provide the rationale. The axial and rhombic spectra correspond to *fac*- and *mer*-(**1c**) respectively. The observed rate of the isomerisation reaction is first order in (**1c**) but is independent of oxidant concentration.

$$fac\text{-}(\mathbf{1b}) + Fe^{3+}(Ag^+) \xrightarrow{\text{fast}} fac\text{-}(\mathbf{1c}) + Fe^{2+}(Ag) \qquad (1)$$

$$fac\text{-}(\mathbf{1c}) \underset{k'_{III}}{\overset{k_{III}}{\rightleftharpoons}} mer\text{-}(\mathbf{1c}) \qquad (2)$$

Equilibrium solutions (298—253 K) of (**1c**) display the couples of equations (3) and (4), the former being dominant [Figure 1(b)]. In contrast, solutions of (**1b**) show little of the *mer* couple. Thus, upon redox the isomeric structures of the parent solutions are conserved on the voltammetric time scale. Solutions having *mer*-(**1b**) and *fac*-(**1c**) as major constituents can be electrogenerated by constant potential coulometry on equilibrated solutions of (**1c**) (0.0 V *vs.* standard calomel electrode, s.c.e.) and (**1b**) (0.70 V *vs.* s.c.e.), respectively, at 253 K. Upon warming the *mer*-(**1b**) solution undergoes first order isomerisation, equation (5).

$$mer\text{-}(\mathbf{1c}) + e \overset{E^\circ_{mer}}{\rightleftharpoons} mer\text{-}(\mathbf{1b}) \qquad (3)$$

$$fac\text{-}(\mathbf{1c}) + e \overset{E^\circ_{fac}}{\rightleftharpoons} fac\text{-}(\mathbf{1b}) \qquad (4)$$

$$mer\text{-}(\mathbf{1b}) \underset{k'_{II}}{\overset{k_{II}}{\rightleftharpoons}} fac\text{-}(\mathbf{1b}) \qquad (5)$$

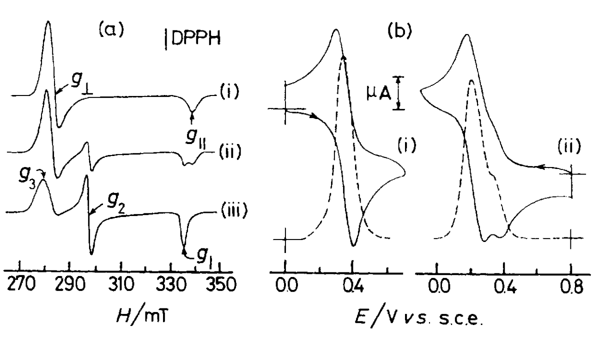


Figure 1. (a) E.s.r. spectra (77 K) of (**1c**) generated by oxidising (**1b**) with Ag^+ in 1 : 1 dmf–toluene. (i) Oxidation at 253 K, solution frozen after 25 s; (ii) oxidation at 298 K, solution frozen after 25 s; and (iii) same as (ii) but frozen after 5 min (DPPH = diphenylpicrylhydrazyl). (b) Cyclic (c.v.) (———) and differential pulse (d.p.v.) (– – –) voltammograms of (i) (**1b**) and (ii) (**1c**). The marked current range is 10 μA (c.v.) or 5 μA (d.p.v.).

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† Satisfactory elemental analyses were obtained. (**1b**) was prepared as reported;[5] δ_H (270 MHz; J in Hz) at 298 K: 5-H, 7.91 (9.6, d); 6-H, 7.12 (9.1, d); 7-H, 8.86 (8.6, d); 8-H, 7.51 (7.5, t); 9-H, 7.31 (7.2, t); 10-H, 7.76 (7.4, d). The benzo ring is numbered 7—10 starting at C-3. (**1c**): $\mu_{eff.}$ = 1.99 μ_B at 298 K.

Table 1. Equilibrium and rate constants at 298 K.

k_{III}/s^{-1}	k'_{III}/s^{-1}	K_{III}	k_{II}/s^{-1}	k'_{II}/s^{-1}	K_{II}	K_{cr}	E°_{fac}/V	E°_{mer}/V
13.40×10^{-3}[a]	2.44×10^{-3}[b]	5.50[c]	0.39×10^{-3}[d]	0.02×10^{-3}[e]	19.41[f]	106.76[g]	0.39[h]	0.27[h]

[a] Spectrophotometry at 1040 nm. [b] From K_{III} and k_{III}. [c] Differential pulse voltammetry. [d] Spectrophotometry at 700 nm. [e] From K_{II} and k_{II}. [f] From K_{cr} and K_{III}. [g] From E° values and equation (7). [h] Cyclic voltammetry at Pt electrode *vs.* s.c.e., supporting electrolyte $[NEt_4][ClO_4]$, scan rate 50 mV s^{-1}.

The superior thermodynamic stabilities of *mer*-(**1c**) and *fac*-(**1b**) as well as the stronger oxidising power of *fac*-(**1c**) compared to *mer*-(**1c**) can be expressed[6] in terms of K_{cr}, the equilibrium constant of the cross-reaction (6). In equation (7), $K_{III} = k_{III}/k'_{III}$ and $K_{II} = k_{II}/k'_{II}$. All kinetic and thermodynamic parameters at 298 K are listed in Table 1. A few examples of redox-regulated isomerisation reactions have been documented in literature but these mostly deal with carbonyl species[6] and none pertains to iron chemistry.

$$fac\text{-}(\mathbf{1c}) + mer\text{-}(\mathbf{1b}) \overset{K_{cr}}{\rightleftharpoons} fac\text{-}(\mathbf{1b}) + mer\text{-}(\mathbf{1c}) \qquad (6)$$

$$K_{cr} = K_{III}K_{II} = \exp[(F/RT)(E^\circ_{fac} - E^\circ_{mer})] \qquad (7)$$

The *mer* geometry is expected to be sterically more favourable than the *fac* geometry since the pendant oxygen atoms have greater separation in the former. For statistical ligand distribution, $K_{III} = 3$. The observed K_{III} value is larger and the steric factor may be partly or wholly responsible for this. The steric factor would tend to make $K_{II} < 3$. The large observed value signifies electronic control, the nature of which is under scrutiny. The basis of recognition appears to be quite different for the two oxidation states.

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