Oxidative Dehydrogenation of Diamine Ligands Co-ordinated to Low-spin Iron(II)

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Summary The reaction of tetracyanodiamineiron(II) species with oxidizing agents yields transient iron(III) species which undergo metal-ion-assisted oxidative dehydrogenation of the amine ligand.

METAL ions are important in the activation of co-ordinated ligands and also in their ability to stabilize normally reactive species (*e.g.* Schiff bases). This communication reports the isolation and characterization of new low-spin (tetracyano)diamine-iron(II) complexes, $Na_2[Fe(CN)_4(aa)]$ (aa = 1,2-diamine ligand) and the reactions of these complexes with oxidizing agents. The products of the metal-assisted ligand oxidation are new complexes containing α-di-imine linkages.

There are a number of reports where a high, unstable oxidation state of copper or nickel promotes unusual ligand-oxidation reactions.[1-3] However, iron appears to be a more ideal metal ion to study metal assisted ligand oxidations for the following reasons. First, the Fe^{III} state of the Fe^{II}–Fe^{III} couple is readily accessible with a number of mild oxidizing agents. Secondly, when forced into a low-spin state, Fe^{II} is expected to be more stable than Fe^{III} (thermodynamically and kinetically) from ligand-field considerations. Thirdly, when ligand oxidation occurs and iron returns to the bivalent state, the low-spin d^6 configuration will lead to substitutionally inert complexes and allow isolation and characterization of normally reactive ligand species, but which are stabilized by complex formation.

To study the type of reactions expected with low-spin iron(II) diamine complexes, spin pairing of the iron(II) diamine d^6 systems was first induced with cyanide ion as the strong field ligand since most aliphatic diamine ligands are not of sufficient field strength to produce low-spin iron(II). Thus the previously unreported low-spin tetracyanodiamineiron(II) complexes were prepared by the addition of cyanide (4 equiv.) to high-spin trisdiamineiron(II) complex species. Ligand substitution by cyanide ion generally proceeded until a low-spin complex $Na_2[Fe(CN)_4(aa)]$ was obtained (see Table). All complexes are diamagnetic and were characterized by their n.m.r., vibrational, and electronic spectra as well as solution conductivities and analytical data.

These complexes are reactive towards oxidizing agents to yield products containing α-di-imine ligands. The sequence of complex preparation and metal-assisted ligand oxidation is shown in the Scheme.

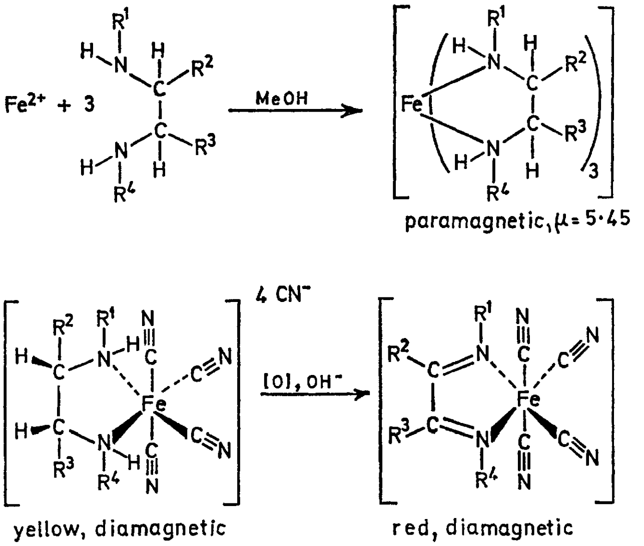
TABLE

Properties of the new complexes

Compound[a]	Conductivity[b]	δ (p.p.m.)	Electronic spectra[c]
$Na_2[Fe(en)(CN)_4],4H_2O$	193	2·53	25·6(342), 29·8(362), 42·4(4554)
$Na_2[Fe(oen)(CN)_4,4H_2O$	200	8·50	19·2(3600), 46·3(6300)
$Na_2[Fe(Me_2en)(CN)_4],4H_2O$	210	2·51, 2·82—2·33	25·6(590), 31·9(490), 43·1
$Na_2[Fe(oMe_2en)(CN)_4],4H_2O$	205	3·92, 8·16	19·3(3900), 45·24(12,000)
$Na_2[Fe(pica)(CN)_4],3H_2O$	215	4·20, 7·0—7·30, 7·65, 7·53, 8·83, 8·95	21·3(3998)
$Na_2[Fe(opica)(CN)_4],3H_2O$	208	5·95, 6·9, 7·88, 7·95 8·72, 9·27, 9·19	19·3(3600), 30·7(2800) 35·8(8432), 36·9(844)
$Me_2dab[Fe(obqd)(CN)_4],2H_2O$	199	7·4—6·8	17·4(12,355), 39·2(10,820)

[a] en = ethylenediamine; oen = ethylenedi-imine; Me_2en = *NN'*-dimethylethylenediamine; oMe_2en = *NN'*-dimethylethylenedi-imine; pica = picolylamine; opica = picolylimine; obqd = *o*-benzoquinonedi-imine; Me_2dab = *NN'*-dimethyl-1,4-diazabicyclo-[2,2,2]octanium cation. [b] For aqueous solutions; concentrations *ca.* 10^{-3} M. [c] Molar extinction coefficients in parentheses.

Under the action of the oxidizing agent, the introduction of the α-di-imine linkage is accompanied by a change in colour from yellow to red (or blue) characteristic of the charge-transfer absorptions normally observed with low-spin iron(II) complexes containing α-di-imine type ligands.[4] The colour change occurs with the formation of the second imine linkage.



SCHEME. [O] = O_2, H_2O_2, Cl_2, OCl^-, $[Fe(CN)_6]^{3-}$, quinone diamines = ethylenediamine, *NN'*-dimethylethylenediamine, *o*-phenylenediamine.

The general reaction of oxidative dehydrogenation of co-ordinated diamines to yield α-di-imine structures is best exemplified with the *NN'*-dimethylethylenediamine complexes. The i.r. spectrum has a single ν(N–H) at 3230 cm^{-1}; n.m.r. spectrum: δ (D_2O) 2·33–2·82 (A_2B_2, $CH_2{\cdot}CH_2$) and (s, Me); u.v.: 25,600 and 31,900 cm^{-1} assignable to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions expected in O_h symmetry for the cation, $[Fe(CN)_4(Me_2en)]^{2-}$. On oxidation of the material, the new intensely red diamagnetic product contains no ν(N–H) absorption, and new absorptions at 1520 and 1620 cm^{-1} (coupled C=N); n.m.r. spectrum δ 8·3 (2H, s, CH) and 3·92 (6H, s, Me); visible spectrum: single intense absorption at 19,300 cm^{-1} (ϵ_{max} 3700) (metal–ligand charge transfer absorption[4]). This absorption was very close in energy to that for other iron(II) complexes containing α-di-imine ligands and has approximately one-third the intensity of that in tris-α-di-imine complexes.

If the diamine ligands already contain double bonds (*e.g.* *o*-phenylenediamine and 2-aminomethylpyridine) an α-di-imine structure can be obtained by the introduction of a single double bond. The product obtained by the oxidation of the *o*-phenylenediamine complex anion, $[Fe(C_6H_8N_2)(CN)_4]^{2-}$ contains co-ordinated *o*-benzoquinone-di-imine, the two-electron-oxidation product of the diamine. An *X*-ray investigation has confirmed the alternating double bond structure expected for the *o*-benzoquinonedi-imine structure (final $R = 3{\cdot}30\%$).[5]

The formation of an iron(III) intermediate in these ligand oxidations is demonstrated by the isolation of $Na_2[Fe^{III}(CN)_4(en)]$ under acidic conditions with Cl_2 or $Fe(CN)_6^{3-}$ as oxidants. When base is added to this iron(III) complex, all the Fe^{III} is reduced immediately to Fe^{II}; some of the ethylenediamine is oxidised to yield a mixture of co-ordinated mono- and di-imine linkages. Spectrophotometric titrations of basic solutions $[Fe(CN)_4(en)]^{2-}$ with $[Fe(CN)_6]^{3-}$ require 4 equiv. of oxidant per α-di-imine group formed. Similar diamine complexes with iso-electronic Co^{III} fail to yield di-imine ligands under similar conditions thus supporting the necessity of achieving a higher unstable metal oxidation for ligand oxidation to proceed.

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