Redox Reactions of Some Iron(II), Iron(III), and Cobalt(III) Picolinate Complexes

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The kinetics of reduction of iron(III) in pyridine-2-carboxylate, picolinate (pic^-), solutions by ascorbate ion show a complex dependence upon pH, ligand concentration, and reductant concentration. The data analysis reveals a single redox-active species, $[Fe(pic)_2(OH)]$, which is reduced by ascorbate ion with a second-order rate constant of 6.4×10^3 dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.10$ mol dm^{-3}. This species is in rapid equilibrium with $[Fe(pic)_3]$, and the equilibrium constant between the two species is evaluated. Oxidations of iron(II) in picolinate solutions by $[Co(pic)_3]$ and $[Co(ox)_3]^{3-}$ [ox = oxalate(2−)] reveal a dominant pathway involving $[Fe(pic)_2]$ and a minor pathway involving $[Fe(pic)_3]^-$. It is suggested that these are outer-sphere processes and Marcus theory is used to estimate self-exchange rates for the complexes.

Reductive dissolution of metal oxides, particularly those of iron(III), is readily accomplished using low oxidation-state metal ion complexes.[1-3] Tris(picolinato)vanadate(II), $[V(pic)_3]^-$ (Hpic = picolinic acid, pyridine-2-carboxylic acid) has been shown [1] to be particularly effective in this role and is a powerful outer-sphere reductant.[4,5] The ultimate products of the dissolution of iron-containing oxides are iron(II) picolinate complexes. Generally, other metal ions such as cobalt(II) are present also,[2] and the redox interactions between the various complexes are of potential importance.

Potentiometric and kinetic studies have established the composition of a number of iron(III)[6-8] and iron(II)[9] picolinate species in aqueous media, Table 1. Considerable work has been reported for iron(III) complexes. The kinetics and mechanism of mono-complex formation have been investigated[10] in acidic solution. At higher pH values, the chemistry is dominated by the hydroxy species $[Fe(pic)_2(OH)]$ in equilibrium with the dimeric form and the dimerization kinetics have been examined.[11] Mössbauer,[12] magnetic,[13] and *X*-ray crystallographic[14] work has also been carried out indicating that the complexes are high-spin, octahedral species, but there are few reports of redox properties.[15]

The complex $[Fe(pic)_3]^-$ appears to dominate[9,16] in iron(II) solutions though dimeric species have been reported.[17] In contrast to the wealth of data on the iron species, studies on the cobalt complexes in aqueous solutions are less well reported.[9,18]

The studies in this paper are aimed at elucidating the redox properties of iron and cobalt picolinate complexes. The kinetics and mechanisms of reduction of iron(III) picolinate complexes have been probed by ascorbate ion, a useful organic reductant with well characterized interactions with $[Fe(H_2O)_6]^{3+}$[19,20] and other iron(III) complexes.[21,22] The oxidations of iron(II) picolinate complexes by $[Co(ox)_3]^{3-}$ [ox = oxalate(2−)][23,24] and $[Co(pic)_3]$ have been examined as have reductions of the latter reagent by $[Fe(edta)]^{2-}$ [edta = 1,2-diaminoethane-*N,N,N',N'*-tetra-acetate(4−)][25,26] and $[V(pic)_3]^-$.[4]

Experimental

(*a*) *Materials.*—Stock solutions of iron(III) were prepared from $Fe(NO_3)_3 \cdot 9H_2O$ (Hopkin and Williams, or Fisher) and were standardized iodometrically. Iron(III) picolinate solutions (*ca.* 2×10^{-5} mol dm^{-3}) are colourless and were prepared by diluting the stock iron(III) with solutions containing the appropriate amounts of buffer and picolinic acid in the range $(3—600) \times 10^{-4}$ mol dm^{-3}. The ionic strength was adjusted to 0.10 mol dm^{-3} using $NaClO_4$ (B.D.H., AnalaR or Fluka, purum). Although the total iron(III) content was kept low to minimize complications from dimer formation, problems of oligomer formation and subsequent precipitation were experienced, especially at higher pH and lower $[pic^-]$. The precipitates were removed by Millipore filtration.

Table 1. Stability constants for iron(III), iron(II), cobalt(II), and cobalt(III) picolinate complexes at 25 °C and $I = 0.10$ mol dm^{-3}

Reaction	log *K*	Ref.
$Hpic \rightleftharpoons pic^- + H^+$	5.21	*a*
Iron(III)		
$Fe^{3+} + pic^- \rightleftharpoons [Fe(pic)]^{2+}$	6.02	*a*
$[Fe(pic)]^{2+} + pic^- \rightleftharpoons [Fe(pic)_2]^+$	6.86	6—8
$[Fe(pic)_2]^+ + pic^- \rightleftharpoons [Fe(pic)_3]$	4.37	*b*
$[Fe(pic)_2]^+ \rightleftharpoons [Fe(pic)_2(OH)] + H^+$	2.96[c]	7, 8
$2[Fe(pic)_2(OH)] \rightleftharpoons [Fe_2(pic)_4(OH)_2]$	3.06[c]	7
Iron(II)		
$Fe^{2+} + pic^- \rightleftharpoons [Fe(pic)]^+$	4.90	9
$[Fe(pic)]^+ + pic^- \rightleftharpoons [Fe(pic)_2]$	4.10[c]	9
$[Fe(pic)_2] + pic^- \rightleftharpoons [Fe(pic)_3]^-$	3.30[c]	9
Cobalt(II)		
$Co^{2+} + pic^- \rightleftharpoons [Co(pic)]^+$	5 74[c]	9
$[Co(pic)]^+ + pic^- \rightleftharpoons [Co(pic)_2]$	4.70[c]	9
$[Co(pic)_2] + pic^- \rightleftharpoons [Co(pic)_3]^-$	3.65[c]	9
Cobalt(III)		
$Co^{3+} + 3pic^- \rightleftharpoons [Co(pic)_3]$	34.17[d]	18

[a] J. E. Powell and J. W. Ingemanson, *Inorg. Chem.*, 1968, **7**, 2459. [b] This work. [c] Measured at 20 °C. [d] $I = 0.5$ mol dm^{-3}.

L-Ascorbic acid (B.D.H. or Baker Analysed) was added to solutions, previously bubbled with chromium(II)-scrubbed nitrogen gas and containing the same amounts of buffer, picolinic acid, and sodium perchlorate as in the iron-containing solutions. Solutions were prepared immediately prior to use, used within 4 h, and then discarded.

The complex $Na_3[Co(ox)_3] \cdot 3H_2O$[27] was prepared by literature methods. $[Co(pic)_3]$ was obtained by the addition of picolinic acid to $Na_3[Co(CO_3)_3] \cdot 3H_2O$[28] followed by recrystallization from water to yield pink crystals. The complex

Table 2. Pseudo-first-order rate constants for the reduction of iron(III) by ascorbate ion (HA^-) in picolinate media, 25.0 °C, I = 0.10 mol dm^{-3} [a]

$-\log[H^+]$	$10^3[HA^-]$/ mol dm^{-3}	$10^3[pic^-]$/ mol dm^{-3}	$k_{obs.}$/ s^{-1}
4.48	0.45	1.07	1.69
4.48	1.88	1.07	7.1
4.96	0.55	2.66	2.28
4.98	0.23	2.75	0.84
5.48	0.59	5.46	2.9
5.50	2.47	5.57	11.6
5.99	2.52	7.96	15.6
6.04	0.61	8.14	3.0
6.62	0.61	9.43	3.4
6.78	2.55	9.60	17.6
6.96	2.55	9.73	15.9
7.06	0.61	9.79	3.73
4.99	0.23	1.40	1.07
5.00	0.23	5.69	0.54
4.99	0.23	8.54	0.44
5.00	0.23	11.40	0.40
5.02	0.23	14.70	0.37
7.93 [b]	1.00	2.49	6.0
7.48 [b]	1.00	2.48	8.2
6.80	0.26	3.85	1.67
6.99	0.26	7.80	1.76
7.01	0.26	23.40	1.41
7.01	0.26	39.00	1.37
5.01	0.37	1.16	1.55
4.96	0.37	2.13	1.41
4.98	0.23	2.75	0.97
4.98	2.29	2.75	9.2
4.02	1.26	0.40	5.6
4.00	0.30	0.38	1.41
4.98	0.37	5.51	1.05
4.98	0.37	11.00	0.82
5.00	0.45	14.20	0.82
7.18	11.80	4.92	90
7.10	4.92	4.90	48
7.10	1.97	4.90	19.2
7.20	0.98	4.92	8.6
6.96	0.49	4.87	4.1
3.92	21.9	1.63	50
4.01	24.9	1.96	53
4.52	37.8	5.94	60
4.54	39.0	6.06	61
5.01	45.8	14.8	80
5.52	48.4	29.0	130
4.98	0.49	14.7	0.82
4.98	0.99	14.7	1.37
4.98	2.97	14.7	3.29

[a] All reactions done under conditions of $[Fe^{3+}]_T$ = (2.0—2.5) × 10^{-5} mol dm^{-3} and $[O_2CMe^-]_T$ = 0.01 mol dm^{-3} except where indicated otherwise. Observed rate constants are averages of 3—5 runs. [b] [2-Amino-2-(hydroxymethyl)propan-1,3-diol]$_T$ = 0.01 mol dm^{-3}.

has absorption maxima at 516 (ε = 105) and 380 nm (ε = 216 dm^3 mol^{-1} cm^{-1}). Procedures for the preparation of solutions of $[Fe(edta)]^{2-}$[29] and $[V(pic)_3]^-$[4] have been described previously.

Solutions of $[Fe(pic)_3]^-$ were prepared by the addition of $[NH_4]_2[SO_4]\cdot FeSO_4\cdot 6H_2O$ to solutions containing appropriate amounts of picolinic acid, buffer and either NaCl or $NaClO_4$ as supporting electrolyte. The complex has an absorption maximum at 440 nm (ε = 1 080 dm^3 mol^{-1} cm^{-1}).

(*b*) *Methods.*—The stoicheiometries of the reactions under investigation were determined spectrophotometrically. Kinetic experiments were run under pseudo-first-order conditions using an Applied Photophysics or Durrum D-110 stopped-flow spectrophotometer. Absorbance changes were recorded and analysed as described previously.[4] The pH of the reaction solutions was determined immediately after reaction using an E.I.L. 7055 or a Beckmann Select Ion 2000 pH meter equipped with a modified (NaCl) Corning combination glass electrode. Hydrogen ion concentrations were evaluated using the relationship $-\log[H^+]$ = pH − 0.02, correcting for activity coefficients and the liquid-junction potentials.

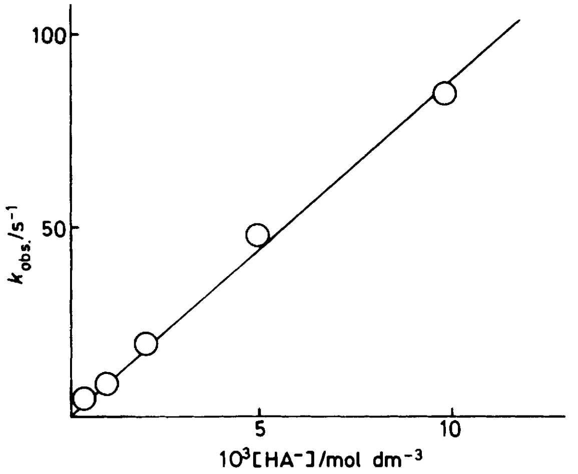

Figure 1. Plot of $k_{obs.}$ against ascorbate ion concentration for the reduction of iron(III) in picolinate solutions at pH 7.0, 25 °C, and I = 0.10 mol dm^{-3}

Since iron(III), iron(II), and vanadium(II) picolinate complexes are substitution labile, reactions were run in solutions containing excess pic^-. Reduction of iron(III) with ascorbate and oxidations of iron(II) with $[Co(pic)_3]$ and $[Co(ox)_3]^{3-}$ were monitored by the change in $[Fe(pic)_3^-]$ at 440 or 500 nm in the latter case. The reactions of $[V(pic)_3]^-$ and $[Fe(edta)]^{2-}$ were followed with $[Co(pic)_3]$ in excess at 680 and 360 nm respectively.

Results and Discussion

(*a*) *Reduction of Iron*(III) *by Ascorbate in Picolinate Solution.*—The stoicheiometry of the reduction of iron(III) in picolinate solution by ascorbate was found to be (2.08 ± 0.04) : 1 in accord with equation (1), where A′ is dehydroascorbate. This

$$2Fe^{III} + HA^- \longrightarrow 2[Fe(pic)_3]^- + A' + H^+ \qquad (1)$$

stoicheiometry is found in the anaerobic oxidation of ascorbic acid by a number of iron(III) complexes[19,21,22,30,31] and is in agreement with the result expected on thermodynamic grounds.

The rate of production of $[Fe(pic)_3]^-$ is a complex function of $[H_2A]_T$, $[Hpic]_T$ (T denotes total concentration), and pH, even at low iron(III) concentrations where any contribution from the dimer $[Fe_2(pic)_4(OH)_2]$ is small, Table 2.[7] According to potentiometric measurements,[7,8] the dominant species in solution, at pH 5—7, is $[Fe(pic)_2(OH)]$. However, at high $[pic^-]$, a contribution from $[Fe(pic)_3]$ might be expected. A value of $10^{26.2}$ mol^3 dm^{-9} quoted[15] for β_3, the cumulative stability constant for $[Fe(pic)_3]$ is in error as it is the product $\beta_1\beta_2\beta_3$ for the iron(II) species.[32]

At pH 7.0 under pseudo-first-order conditions with an excess of ascorbate ion and constant $[pic^-]$ (4.9 × 10^{-3} mol dm^{-3}) sufficient to form quantitatively the bis(picolinate) complex, $[Fe(pic)_2(OH)]$, a first-order dependence of the reaction rate on $[HA^-]$ was found [Figure 1, equation (2)]. The second-order

$$\text{Rate} = k'_{so}[Fe(pic)_2(OH)][HA^-] \qquad (2)$$

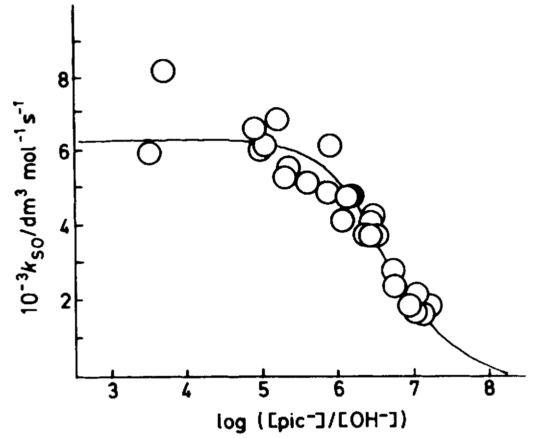

Figure 2. Plot of the ascorbate-corrected second-order rate constant, k_{so}, as a function of [pic$^-$]/[OH$^-$] for the reduction of iron(III) in picolinate solutions at 25 °C, and I = 0.10 mol dm^{-3}

constant k'_{so} is inhibited by increased [pic$^-$] and by decreased pH. The pH dependence might be ascribed to a number of sources.

Protonation of ascorbate to give the generally less reactive ascorbic acid with pK_a 4.03[33] provides a partial explanation. Studies at pH 3 suggest that the ascorbate ion, HA$^-$, is the major reductant, behaviour which has been noted with other iron(III) complexes.[22,30,31] Accordingly, and to simplify the analysis, all second-order rate constants were corrected for ascorbate ion concentrations, equation (3).

$$k_{so} = k'_{so}([\mathrm{H}^+] + K_a)/K_a \qquad (3)$$

The ascorbate-corrected second-order rate constants, k_{so}, also show a decrease with decreasing pH. Protonation of the complex [Fe(pic)$_2$(OH)], equation (4), with a pK_a of 2.96[7,8]

$$[\mathrm{Fe(pic)_2(OH_2)}]^+ \rightleftharpoons [\mathrm{Fe(pic)_2(OH)}] + \mathrm{H}^+ \qquad (4)$$

is unlikely to account for the observed behaviour. An explanation of both [pic$^-$] and pH dependencies could be the result of conversion of [Fe(pic)$_2$(OH)] to [Fe(pic)$_3$], equation (5). A plot

$$[\mathrm{Fe(pic)_2(OH)}] + \mathrm{pic}^- \overset{K}{\rightleftharpoons} [\mathrm{Fe(pic)_3}] + \mathrm{OH}^- \qquad (5)$$

of k_{so} as a function of [pic$^-$]/[OH$^-$] is shown in Figure 2. The data cover the concentration ranges pH 4—8 and [pic$^-$] = (4—450) × 10^{-4} mol dm^{-3}, though most of the data below pH 6 refer to low [HA$^-$], and may be described by the function in equation (6), where k_1 = 6.38 × 10^3 dm^3 mol^{-1} s^{-1} and K = 2.13 × 10^{-7}. The curve shown is calculated from these data. The expression (6) is consistent with a single redox process, equation (7), as the rate-determining step. At low [pic$^-$]/[OH$^-$] values, [Fe(pic)$_2$(OH)] is the dominant species but the data at very high pH lose reliability as much of the iron(III) is precipitated as [Fe(OH)$_3$] or the dimer [Fe$_2$(pic)$_4$(OH)$_2$]. At lower pH and high [pic$^-$], [Fe(pic)$_2$(OH)] is converted to [Fe(pic)$_3$] which is much less reactive with ascorbate ion than [Fe(pic)$_2$(OH)] and both species are in rapid equilibrium with respect to the redox process.

$$k_{so} = k_1 \Big/ \left\{1 + K\left(\frac{[\mathrm{pic}^-]}{[\mathrm{OH}^-]}\right)\right\} \qquad (6)$$

$$[\mathrm{Fe(pic)_2(OH)}] + \mathrm{HA}^- \xrightarrow{k_1} \text{products} \qquad (7)$$

Table 3. Pseudo-first-order rate constants for the slow phase of reduction of iron(III) in picolinate solutions by ascorbate ion

$-\log$ [H$^+$]	10^2[HA$^-$]/ mol dm^{-3}	10^3[pic$^-$]/ mol dm^{-3}	$k_{obs.}$/ s^{-1}
3.92	2.19	1.63	2.1
4.01	2.49	1.96	2.3
4.52	3.78	5.94	3.6
4.54	3.90	6.06	3.8
4.98	0.99	14.7	7.2
4.98	1.19	14.7	7.2
4.98	4.63	14.7	7.9
5.01	4.58	14.8	8.0
5.52	4.84	29.0	8.9

Under conditions where [Fe(pic)$_3$] is the dominant species, the dependence of the rate on ascorbate ion concentration is complex. At low [HA$^-$] the reaction is first order in both [Fe$^{\mathrm{III}}$] and [HA$^-$] consistent with equation (6). At higher ascorbate ion concentrations the rates show deviations from a first-order dependence on [Fe$^{\mathrm{III}}$] and at very high [HA$^-$], the reaction is biphasic, consisting of a dominant fast and a minor (< 10%) slow absorbance change, Table 3. Both reactions are first order and sufficiently different in rate to be treated as independent processes.

The faster, dominant reaction is also first order in [HA$^-$] and the second-order rate constant is in agreement with equation (6). The slow reaction is independent of [HA$^-$] at high [HA$^-$] and this limiting rate is dependent on pH, increasing from *ca.* 2 s^{-1} at pH 4 to *ca.* 12 s^{-1} at pH 5. Since the fast reaction rate corresponds with equation (6), the slow reaction must arise from a minor solution component which is not in rapid equilibrium with [Fe(pic)$_3$] and [Fe(pic)$_2$(OH)] at high [HA$^-$]. However, for reactions much slower than the limiting rate, the minor component appears to be in rapid equilibrium indicating that the limiting rate is the interconversion process.

It is likely that the minor component is the dimer [Fe$_2$(pic)$_4$(OH)$_2$] which has been shown[11] to dissociate to give [Fe(pic)$_2$(OH)] with a first-order rate constant of 1.6 s^{-1} at low pH (< 1.5), 25 °C, and I = 0.2 mol dm^{-3}, equation (8). A plot of

$$[\mathrm{Fe_2(pic)_4(OH)_2}] \rightleftharpoons 2[\mathrm{Fe(pic)_2(OH)}] \qquad (8)$$

the limiting rate for this dissociation against [OH$^-$] gives an intercept of 2 s^{-1}, in good agreement with the literature value,[11] and a slope of *ca.* 10^{10} dm^3 mol^{-1} s^{-1}. This latter rate constant might correspond to a base-catalysed dissociation process, equation (9), and as such is uncommon. A number of

$$[\mathrm{Fe_2(pic)_4(OH)_2}] + \mathrm{OH}^- \rightleftharpoons 2[\mathrm{Fe(pic)_2(OH)}] + \mathrm{OH}^- \qquad (9)$$

dissociation reactions of iron(III) dimeric complexes have been examined.[11,34—36] Most dimers are negatively charged and dissociations are dominated by acid catalysis. The present dimer is neutral and may allow attack by OH$^-$. However, it should be pointed out that the fraction of the absorbance change due to this slow phase, though small, is larger than the absorbance expected on the basis of the reported[7] equilibrium constants. It may be that at higher pH, more complex oligomers exist and that the base dependence of the rate reflects the changing composition of these species.

The sole redox pathway involves the interaction of [Fe(pic)$_2$(OH)] with HA$^-$ with a second-order rate constant of

Table 4. Pseudo-first-order rate constants for reactions of iron(II) and cobalt(III) picolinate complexes at 25 °C and $I = 0.10$ mol dm$^{-3\,a}$

$-\log [H^+]$	$10^2[pic^-]$/ mol dm^{-3}	10^3[oxidant]/ mol dm^{-3}	$10^3 k_{obs.}$/ s^{-1}
(*a*) $[Co(ox)_3]^{3-} + [Fe(pic)_3]^-$			
5.19	1.91	26.8	260
5.34	2.33	11.9	96
5.34	2.33	8.00	73
5.37	2.41	5.70	49
5.37	2.41	3.34	28
5.45	0.26	2.68	23
4.23	0.32	1.97	48
4.58	0.66	2.02	28
5.02	1.47	1.99	17
5.28	2.16	2.00	13
5.77	3.51	2.00	11.4
6.38	4.53	1.69	8.9
6.99	4.87	1.69	8.2
7.48	4.96	1.49	8.3
4.49	2.08	1.30	10.8
4.98	5.23	1.30	6.3
(*b*) $[Co(pic)_3] + [Fe(pic)_3]^-$			
5.00	1.42	0.400	4.7
5.00	1.42	0.320	4.0
5.03	1.49	0.298	3.9
5.00	1.42	0.240	2.9
4.00	0.19	0.402	18.6
4.43	0.48	0.402	8.8
5.43	2.59	0.402	2.95
6.00[b]	4.00	0.482	2.53
6.47[b]	4.61	0.482	2.62
6.95[b]	4.86	0.482	2.88
$-\log [H^+]$		10^3[oxidant]/ mol dm^{-3}	$k_{obs.}$/ s^{-1}
(*c*) $[Co(pic)_3] + [Fe(edta)]^{2-}$			
5.51		0.397	0.70
5.53		0.238	0.42
5.56		0.159	0.29
5.55		0.079	0.14
4.74[c]		0.362	0.63
5.16[c]		0.362	0.60
5.90[c]		0.362	0.59
6.09[c]		0.362	0.61
6.92		4.0[d]	6.3
7.24		12.0[d]	1.96
7.24		16.0[d]	28.8
(*d*) $[Co(pic)_3] + [V(pic)_3]^-$			
6.12[e]		0.017	91
6.09[e]		0.052	400

[a] All reactions in 10^{-2} mol dm^{-3} acetate buffer except where stated otherwise. Observed rate constants are averages of 3—5 runs. [b] 10^{-2} mol dm^{-3} phosphate buffer. [c] 5×10^{-3} mol dm^{-3} acetate buffer. [d] Reductant in excess. [e] $I = 0.5$ mol dm^{-3}.

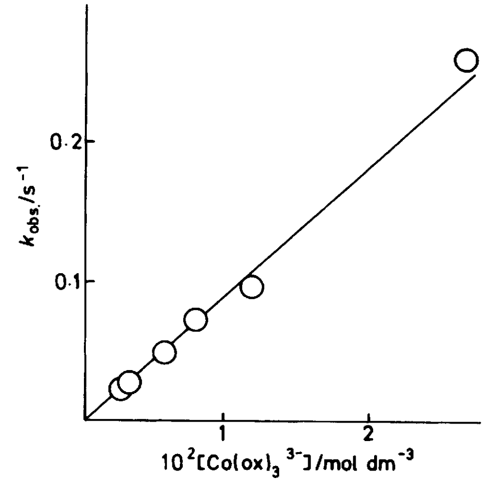

Figure 3. Plot of $k_{obs.}$ against $[Co(ox)_3{}^{3-}]$ for the oxidation of iron(II) in picolinate solution at pH 5.3—5.4, 25 °C, and $I = 0.10$ mol dm^{-3}

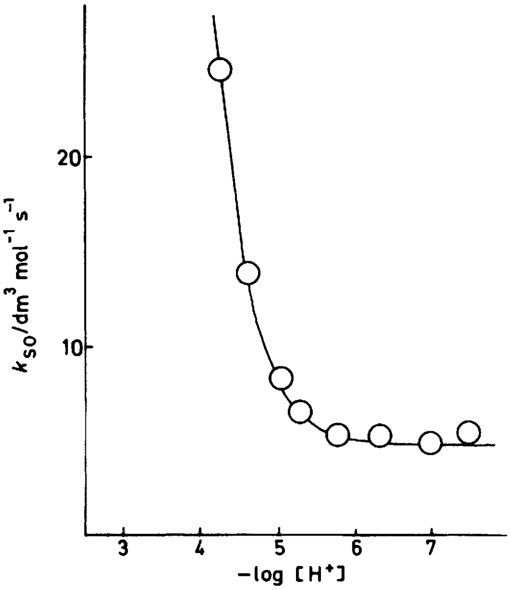

Figure 4. Plot of second-order rate constant, k_{so}, as a function of pH, at 25 °C, $I = 0.10$ mol dm^{-3}, and $[pic^-]_T = 5.0 \times 10^{-2}$ mol dm^{-3}

Table 5. Second-order rate constants (dm^3 mol^{-1} s^{-1}) for redox reactions of various metal picolinate complexes at 25 °C, $I = 0.1$ mol dm^{-3}

Reaction	k_{so}
$[Co(pic)_3] + [V(pic)_3]^-$	7.4×10^6 *
$[Co(pic)_3] + [Fe(edta)]^{2-}$	1.8×10^3
$[Co(pic)_3] + [Fe(pic)_2]$	2.0×10^2
$[Co(pic)_3] + [Fe(pic)_3]^-$	3.5
$[Co(ox)_3]^{3-} + [Fe(pic)_2]$	1.6×10^2
$[Co(ox)_3]^{3-} + [Fe(pic)_3]^-$	3.4

* $I = 0.5$ mol dm^{-3} (NaCl).

6.38×10^3 dm^3 mol^{-1} s^{-1}. This second-order rate constant is comparable with the corresponding reaction rate for $[Fe(dipic)_2]^-$ (H_2dipic = pyridine-2,6-dicarboxylic acid) for which an outer-sphere mechanism was assumed.[22] No conclusion as to the nature of the reaction with ascorbate can be made in this case since, clearly, the complexes are labile on the time-scale of the redox process. However the fact that no reaction of $[Fe(pic)_3]$ was detected suggests that an accessible co-ordination position on the metal centre is a prerequisite for electron transfer and favours an inner-sphere mechanism. No evidence for an iron(III)–ascorbate complex[19,20] was found in this instance.

The value of K for equation (5) allows calculation of K_3 for formation of $[Fe(pic)_3]$ from the bis-complex as 2.3×10^4 dm^3 mol^{-1}. The calculated reduction potential of $[Fe(pic)_3]^{0/-}$ is 0.48 ± 0.02 V.

Table 6. Parameters used in and self-exchange rates obtained from application of Marcus theory to the redox reactions of iron(II) and cobalt(III) picolinate complexes

Reagents						
1		2	E°_1/V	E°_2/V	k_{11}/dm^3 mol^{-1} s^{-1}	k_{22}/dm^3 mol^{-1} s^{-1}
$[Co(pic)_3]$	+	$[V(pic)_3]^-$	0.41	−0.41[a]	6.6×10^{-5}	3.1×10^{6}[a]
$[Co(pic)_3]$	+	$[Fe(edta)]^{2-}$	0.41	0.12[b]	1.3×10^{-3}	3.0×10^{4}[c]
$[Co(pic)_3]$	+	$[Fe(pic)_2]$	0.41	0.54[d]	6.8×10^{-4}	8.4×10^{9}
$[Co(pic)_3]$	+	$[Fe(pic)_3]^-$	0.41	0.48[d]	6.8×10^{-4}	3.8×10^{4}
$[Co(ox)_3]^{3-}$	+	$[Fe(pic)_2]$	0.54[e]	0.54	2.8×10^{-7}[f]	1.2×10^{8}
$[Co(ox)_3]^{3-}$	+	$[Fe(pic)_3]^-$	0.54	0.48	2.8×10^{-7}	5.0×10^{5}

[a] Ref. 4. [b] Ref. 25. [c] Ref. 26. [d] Redox potential based on stability constants. [e] Ref. 24. [f] Ref. 23.

(*b*) *Oxidation of Iron*(II) *by Metal Complexes in Picolinate Solution.*—Stability constants for the formation of iron(II) picolinate complexes have been reported.[9] Conditions for this study were chosen such that the dominant species in solution is $[Fe(pic)_3]^-$. The value of K'_3 is 2×10^3 dm^3 mol^{-1} and in general $[pic^-]$ was $\geqslant 5 \times 10^{-3}$ mol dm^{-3}, sufficient to form $\geqslant 90\%$ of the tris-complex. The complex $[Fe(pic)_3]^-$ has an absorption maximum at 440 nm (ε = 1 080 dm^3 mol^{-1} cm^{-1}).

Oxidations of $[Fe(pic)_3]^-$ by two complexes, $[Co(ox)_3]^{3-}$ and $[Co(pic)_3]$, have been examined. In both cases the reactions were studied under pseudo-first-order conditions ($[Fe^{II}] \approx 10^{-5}$ mol dm^{-3}, $[Co^{III}] = (0.08-27) \times 10^{-3}$ mol dm^{-3}) and good first-order traces were obtained.

For the two cobalt(III) complexes studied with Co^{III} in excess, the reaction is first-order in $[Co^{III}]$, Figure 3, and the second-order rate constant has a complex dependence on $[Hpic]_T$ and pH [Figure 4 and Table 4]. The behaviour can be explained by a single inhibition process due to $[pic^-]$ suggesting that the tris-complex $[Fe(pic)_3]^-$ is less reactive than the bis-complex $[Fe(pic)_2]$. The proposed mechanism, equations (10)—(12), yields the second-order rate constant, equation (13), where

$$[Fe(pic)_2] + pic^- \xrightleftharpoons{K'_3} [Fe(pic)_3]^- \qquad (10)$$

$$[Fe(pic)_2] + Co^{III} \xrightarrow{k'_1} \text{product} \qquad (11)$$

$$[Fe(pic)_3]^- + Co^{III} \xrightarrow{k'_2} \text{product} \qquad (12)$$

$$k_{so} = \frac{k'_1 K'_3[pic^-] + k'_2}{K'_3[pic^-] + 1} \qquad (13)$$

$K'_3 = 2 \times 10^3$ dm^{3}mol^{-1}.[9] Least-squares analysis leads to $k'_1 = (1.61 \pm 0.23) \times 10^3$ dm^3 mol^{-1} s^{-1} and $k'_2 = 3.40 \pm 0.32$ dm^3 mol^{-1} s^{-1} for $[Co(ox)_3]^{3-}$ and $k'_1 = (2.02 \pm 0.27) \times 10^3$ dm^3 mol^{-1} s^{-1} and $k'_2 = 3.45 \pm 0.41$ dm^3 mol^{-1} s^{-1} for $[Co(pic)_3]$.

Oxidations of $[Fe(pic)_3]^-$ and $[Fe(pic)_2]$ by $[Co(pic)_3]$ are driven thermodynamically by the subsequent formation of $[Fe(pic)_2(OH)]$. This causes no kinetic complication because the rate of ligand exchange (>80 s^{-1}) exceeds that of the electron-transfer processes under the conditions of the study.

(*c*) *Reduction of* $[Co(pic)_3]$ *by* $[V(pic)_3]^-$ *and* $[Fe(edta)]^{2-}$.—The reduction of $[Co(pic)_3]$ by $[Fe(edta)]^{2-}$ was studied under pseudo-first-order conditions with an excess of Co^{III} and an excess of Fe^{II}. Pseudo-first-order rate constants are first order in the reagent in excess and the second-order rate constants are independent of pH, Table 4, with a value of $(1.76 \pm 0.08) \times 10^3$ dm^3 mol^{-1} s^{-1}. A limited study of the reduction by $[V(pic)_3]^-$ was also carried out and a second-order rate constant of $(7 \pm 1) \times 10^6$ dm^3 mol^{-1} s^{-1} evaluated.

(*d*) *General Remarks.*—Second-order rate constants for the various reactions of metal picolinate complexes are presented in Table 5. The simplest behaviour is shown by the cobalt(III) species, $[Co(pic)_3]$, where the magnitude of the second-order rate constant is consistent with an outer-sphere mechanism since the chelated picolinate ligands afford no 'lead-in' groups to form an inner-sphere bridge to the more labile reductants.

Both iron oxidation states show complex reactivity patterns because the picolinate ligands are substitution labile on the time-scale of the electron-transfer processes. It is interesting to note that bis(picolinate) species for both oxidation states are more reactive than the tris(picolinate) complexes since oxidation of $[Fe(pic)_3]^-$ is thermodynamically more favourable than oxidation of $[Fe(pic)_2]$. The bis-complex has labile co-ordination sites where solvent is bound and which could accommodate a bridging ligand in an inner-sphere mechanism. Such a mechanism is possible in the reaction with $[Co(ox)_3]^{3-}$ where the oxidant has potential 'lead in' carboxylate groups but is unlikely with $[Co(pic)_3]$. However, the similarity in rate parameters for both oxidants suggests a common mechanism, most likely outer-sphere.

To support this suggestion, Marcus theory* was applied to the rate data as indicated in Table 6. An estimate of the $[Co(pic)_3]^{0/-}$ self-exchange rate of 7×10^{-4} dm^3 mol^{-1} s^{-1} can be obtained from the literature potentials and self-exchange rate for $[V(pic)_3]^{0/-}$ (ref. 4) and $[Fe(edta)]^{-/2-}$ (ref. 25) with reasonable consistency. This value and the literature values for $[Co(ox)_3]^{3-/4-}$ (refs. 23, 24) yield self-exchange rates of 8×10^9 dm^3 mol^{-1} s^{-1} and 1×10^8 dm^3 mol^{-1} s^{-1} respectively for $[Fe(pic)_2]^{+/0}$ and 4×10^4 dm^3 mol^{-1} s^{-1} and 5×10^5 dm^3 mol^{-1} s^{-1} respectively for $[Fe(pic)_3]^{0/-}$. Again, agreement is reasonable and, though limited, the general consistency of these Marcus calculations is supportive of outer-sphere mechanisms.

The geometric mean value of the self-exchange rate for the $[Fe(pic)_2]^{+/0}$ complex is 9×10^8 dm^3 mol^{-1} s^{-1}, very fast, and comparable with the value for $[Fe(phen)_3]^{3+/2+}$ (phen = 1,10-phenanthroline).[37] In contrast the tris-complex, $[Fe(pic)_3]^{0/-}$ has a much slower rate of 1×10^5 dm^3 mol^{-1} s^{-1} explaining the more sluggish reactivity.

The self-exchange rate for $[Co(pic)_3]^{0/-}$ is higher than values noted[4] for a number of the cobalt(III) complexes and despite differences between the bis- and tris-species, self-exchange rates for the iron complexes are also rather fast. The overriding impression arising from this and a previous study[4] is that picolinate ligands appear to play an important role in electron-transfer reactions. The nature of the role is yet unclear but may

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* For electrostatics-corrected Marcus treatment see G. M. Brown and N. Sutin, *J. Am. Chem. Soc.*, 1979, **101**, 883. Radii of complexes used in Marcus calculations: $[Fe(pic)_2]$, 5.5; $[Fe(pic)_3]^-$, 6.0; $[Co(pic)_3]$, 6.0; $[Co(ox)_3]^{3-}$, $[Fe(edta)]^{2-}$, 4.0; $[V(pic)_3]^-$, 6.0 Å.

be related to the lowering of inner-sphere and outer-sphere reorganization energies in a manner similar to that observed with phenanthroline and bipyridyl ligands.

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