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Pentacyano(pyridine)ferrates(II) and (III) and Related Compounds

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Many pentacyano(ligand)ferrates of general formula $Fe(CN)_5L$ have been examined [1], but there has been no exhaustive study when L refers to a given family of ligands. In this paper, we are concerned with 42 pyridine derivatives as ligands, in order to underline the effects of substituents by comparison with the parent molecule. The relevant complexes will be denoted by f•Py and the aquopentacyanoferrate ion by f•w.

The complexes of 2-, 3- and 4-substituted pyridine have been examined electrochemically in order to complete the literature data [2–7]. We report also on the spectral data of the reduced and oxidized complexes which have been occasionally given [2–12].

Experimental

The complexes $f{\cdot}L^{3-}$ were prepared *in situ* by mixing $f{\cdot}(NH_3)^{3-}$ obtained according to [13] with the appropriate ligand. Numerous 3- and 4-substituted pyridine complexes were also prepared as solids for structural studies following published procedures [7, 12]; they analyzed satisfactorily.

The voltammetric study was performed with a classical 3-electrode set including a platinum rotating electrode and a SCE as the working and the reference electrode respectively. For some experiments a 'Tacussel Controvit EDI' device was used and fitted with either Pt or Carbon tip and provided similar results to those obtained with the conventional device. The concentration of complex in the test solutions was about 10^{-3} *M*, with an excess of ligand (5 to 10 times) to favour complex formation. The ionic strength was fixed at 0.5 by addition of KCl or $NaClO_4$. Two alternative methods were used to vary the acidity of the medium: the use of buffers or the addition of small quantities of strong acid or base. In each case, the pH was measured immediately after recording the i–E curves.

The determination of the various ligands was performed by potentiometric titrations in 0.5 *M* KCl media. This provided apparent values of pK_as, differing slightly from the thermodynamic values [14], but corresponding to the acidity constants under the polarographic conditions.

The oxidized complexes $Fe(CN)_5(Py)^{2-}$ were prepared *in situ* by electrochemical oxidation of the corresponding ferrates(II), and their spectra were recorded.

Spectrophotometric measurements were performed on a Beckman Acta 3 spectrophotometer fitted with 1 cm quartz cells and thermostatted at 20 °C.

Results and Discussion

The oxidation voltammograms consist of a single oxidation wave for a given complex. Analysis of the curves showed that the classical criteria for reversibility were satisfied: *i*) the difference $E_{1/4} - E_{3/4}$ was found to be 0.06 V for any voltamperometric curve; *ii*) the plots $\log (i_{lim} - i)/i = f(E)$ were linear and the slope indicated that one electron was involved in the redox process, which is otherwise diffusion controlled; *iii*) experiments performed with $f{\cdot}(NH_3)^{2-}$ and Py (in excess) as starting material gave reduction waves with the same $E_{1/2}$ values as those obtained for the oxidation of the corresponding ferrate(II); *iv*) cyclic voltammetry studies confirmed the rapidity of the electrochemical process.

Furthermore, the oxidation wave was not modified by increasing concentrations of L, and the limiting current depended upon both the iron concentration, provided an excess of L was present in solution, and the speed of rotation of the electrode according to Levich's law.

These results can be interpreted by attributing the voltammetric curves to the redox reaction:

$$Fe(CN)_5L^{3-} = Fe(CN)_5L^{2-} + e^- \qquad (1)$$

The corresponding i–E equation is

$$E = E'^{\circ}_{fL} + RT/F{\cdot}\ln(fL^{2-}/fL^{3-}) \qquad (2)$$

where E'°_{fL} refers to the apparent standard potential of the system fL^{3-}/fL^{2-}. Under the usual conditions of polarography (*i.e.* considering that the diffusion coefficients are equal for the oxidized and reduced species), the half-wave potential is close to E'°. Equilibrium (1) is pH-independent, and consequently the graph $E_{1/2}$ *vs.* pH must be represented by a straight horizontal line. This is effectively verified for all the complexes in the range of pH: $3 < pH <$

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TABLE I.

No	X-substituted Pyridine	$E^*_{1/2}$ (plateau) mV, *vs.* SCE	pK_a apparent	pK_a thermo	λ^{II}_{max}, nm	λ^{III}_{max}, nm
1	H	237	5.45	5.16	362 (2)	368, 414 (4)
2	4-CH_3	208	6.27	6.02	356 (2)	362, 418 (4)
3	4-C_2H_5	207	6.27	6.02	360 (7)	
4	4-C_6H_5	235	5.50	5.55	405 (7)	
5	4-vinyl	200	6.44	5.62		
6	4-CHO	270	4.58	4.77[a]	385 (4), 504(2) (4)	366, 416 (4)
7	4-CO·CH_3	285	3.86		475 (11), 480 (9)	
8	4-CO·NH_2	269	3.71	3.61	435 (2, 11)	364, 418 (4)
9	4-CO·C_6H_5	287			257, 487 (28)	
10	4-COO^-	265	4.61	4.86	413 (8)	
11	4-CH_2OH	229	5.39		376	355 (sh), 418
12	4-OH	285	3.59	3.27		
13	4-CN	315		1.90	405/476 (12)	
14	4-NH_2	138	9.20	9.17	320 (6), 550 (11)	560 (6)
15	4-$N(CH_3)_2$	112	9.65		330 (sh), 655	345, 665
16	4-Cl	348			383 (2)	
17	4-Br	308				
18	3-CH_3	233	6.02	5.68	360 (11)	367, 412
19	3-C_2H_5	232	5.92	5.70	364	370, 412
20	3-CHO	258	4.02	3.80[a]	372	370, 412 (sh)
21	3-CO·CH_3	283	3.70	3.18	368	367, 412
22	3-CO·NH_2	280	3.59	3.35	392 (8)	370, 414
23	3-CO·C_6H_5	280	3.52			
24	3-COO–	267	4.06	4.90	382 (8)	370, 412
25	3-$COOC_2H_5$	275		3.13[a]	388	
26	3-CH_2OH	250	5.10		372	369, 413
27	3-OH	250	5.07	4.86[a]	365 (11)	367(sh), 412
28	3-CN	325		1.45	370/414 (12)	383/392
29	3-NH_2	210	6.41	5.98[a]	360 (11)	
30	3-Cl	275		2.84	382	
31	3-Br	266	3.93	2.84		
32	2-CH_3	230	6.05	5.94	362	380
33	2-CO·CH_3	307			395	394
34	2-COO^-	305		1.01[a]		
35	2-$COOC_2H_5$	305				
36	2-CH_2OH	133				
37	2-OCH_3	272	3.60	3.28[a]	395	
38	2-CN	439		−0.26	385	395
39	2-NH_2	204	6.84	6.86	387/470 (12)	
40	2-Cl	307		(0.72)	345(sh), 705(11)	450, 678
41	2-Br	335		(0.90)		
42	2-F	480		(−0.44)		

[a] 20 °C.

12. Consequently, each complex can be characterized by the value of the plateau potential $E^*_{1/2}$ (Table I).

In highly alkaline media, only spot tests were achieved, and the criteria of reversibility were not fully satisfied. This suggests that another equilibrium may occur concurrently with eqn. 1 (*e.g.*: $fL^{3-} + OH^- = f{\cdot}OH^{4-} + L$). An alternative explanation consists in the attack of OH^- ion at the ligand

L in a way similar to that observed for the pyrazole ferrates [15].

In highly acidic media, the i *vs.* E curves recorded for freshly acidified solutions showed a noticeable increase of $E_{1/2}$ compared to $E^*_{1/2}$, which can be attributed to the protonation of a CN^- group. With time, the solutions turned bluish and gave only reduction waves, the $E_{1/2}$ of which continuously decreased to a limiting value which was independent of L. This suggests that the great excess of protons in solution reacts with the pyridine to give LH^+, while either a water molecule replaces L as the 6th ligand or, more likely, that two $Fe(CN)_5$ moieties react to form a dimer. At this juncture, oxidation by impurities or by dissolved O_2 (even after a long bubbling of N_2) could take place, with a speed depending on the proton concentration. The L-independent limit value of the reduction potential, and the colour of the solution suggest the formation of a dimer III–III, $Fe_2(CN)_{10}^{4-}$ or $Fe_2(CN)_{11}^{5-}$, discovered by Emschwiller [16].

The $E^*_{1/2}$ values (Table I) make easy the comparison with the literature data. Some discrepancy with the results reported by Malin [2, 6] can be found, especially for the complexes involving the 4-chloropyridine (10 mV) or the 4-NH_2·pyridine (35 mV), but the methods used for the determination of E'° and the ionic strength were different. On the contrary, it is worthwile to point out fair agreement for pyridine (14 mV) and isonicotinamide (16 mV) ferrates, and excellent agreement for 4-methylpyridine ferrate (5 mV). Other authors [3] have also determined the standard potential of $f{\cdot}Py^{3-}/f{\cdot}Py^{2-}$, but the difference of ionic strength (0.1) and temperature (0 °C) can easily explain the small discrepancy (24 mV).

The $E^*_{1/2}$ values cover a large range of potential, from 0.1 V to 0.5 V *vs.* SCE. The acidity constants of the substituted pyridines involved are also very different, as evident from the selected data of thermodynamic pK_as listed in [14]. Among these values, only reliable data are considered (*i.e.*, the pK_as of the 2-halogenopyridines are omitted) and are corrected when necessary to refer to the same temperature. The pK_a values relevant to various substituted pyridines have also been examined with respect to the nature and the position of the substituted group [17, 18] and it has been shown that the stability constants of complexes of the type $M{\cdot}Py^{n+}$ (with M:Zn, Cd, Ag) were affected by the substituent group in the same manner as the pK_as [19–21].

In recent papers [22, 23], a correlation was found between the half-wave potentials of complexes and Hammett's $\Sigma\sigma_p$ relative to the substituted ligands. Since σ_p depends linearly on the protonation constants in the pyridine series [24], a linear correlation between $E_{1/2}$ and pK_a can be expected, and was suggested by a preliminary study dealing with the 4-substituted pyridine ferrates(II) [7]. It was of interest to show if it was a more general character and reliable for the three families of substituted pyridines.

The data (Table I) allow us to calculate the parameters of the relevant relationship

$$E^*_{1/2}\ (\text{mV}, vs.\ \text{SCE}) = -25.32\ pK_a + 365.77 \qquad (3)$$

(correlation coefficient: 0.91) where pK_a refers to the thermodynamic values. However, we found it better to determine when possible the *apparent* values of the pK_as (referred as pK'_a) under the polarographic conditions: these values (Table I) differ slightly from the thermodynamic values as expected. The linear correlation between $E^*_{1/2}$ and pK'_a then becomes:

$$E^*_{1/2}\ (\text{mV}, vs.\ \text{SCE}) = -26.00\ pK'_a + 376.14 \qquad (4)$$

(correlation coefficient: 0.96). Among the consequences of this experimental correlation, it can be pointed out that eqn. 4 is verified for the *ortho*-substituted pyridines as well as for the *m*- and *p*-substituted molecules. This appears as a very particular feature compared to the various Hammett relations which have been proposed.

Table I reports also original results together with literature data on the absorption peaks of the complexes (II) and of some oxidized ferrates. Examination of the values indicates some discrepancies between authors: the 4-CHO·Py and 4-NH_2·Py ferrates(II) (Nos. 6, 14) appear as the most striking examples and will be discussed later.

The energy of the electron-transfer band in the UV–visible region is proportional to λ^{-1}_{max}. Many attempts have been made to correlate this parameter with other characteristics of the compounds. For a series of pentaammine(L)ruthenium complexes, λ^{-1}_{max} was found to be proportional to the half-wave oxidation potential of the free ligand [25] and to be also in linear relationship with λ^{-1}_{max} of the corresponding ferrate [2]. More recently, Toma [26], following other authors [27] who worked on copper complexes, found that the charge-transfer energies and the redox potentials of some pentacyano(L)-ferrates(II) were linearly correlated; Malin *et al.* [6] found a correlation between the optical energy and Hammett's σ_p for the (4-substituted pyridine)-pentacyanoferrates.

The data listed in Table I allow us to plot λ^{-1}_{max} *vs.* $E^*_{1/2}$ for 31 pyridine ferrates: the graph is linear and verifies the equation

$$\lambda^{-1}_{max,nm} = -2.69\ 10^{-6}\ E^*_{1/2,mV} + 3.30\ 10^{-3} \qquad (5)$$

(correlation coefficient: 0.50) which is a new illustration of the correlations reviewed by Vlček [28].

Equation 5 indicates that some spectral data reported in the literature are erroneous if they refer to the same electron transfer band. Two λ_{max} values were published [6, 11] for No 14 complex, namely: 550 and 320 nm. Equation 5 requires that the absorption peak at 550 nm has to be discarded. Similarly, we select 345 nm and 330 nm for the absorption peaks of No 39 and No 15 complexes respectively. Among the two λ_{max} values given by Toma [4] for the (4-formyl·Py) ferrate and for the corresponding hydrated ligand, the latter fits much better with the suggested correlation. Furthermore, when the data for 6 complexes among the 31 ferrates (*i.e.* Nos: 4, 7, 8, 13, 16, 36) are discarded, the correlation becomes much improved

$$\lambda_{nm}^{-1} = -3.06\ 10^{-6}\ E^{*}_{1/2,mV} + 3{,}44\ 10^{-3} \qquad (6)$$

($r^2 = 0.9$). Structural considerations can be suggested as possible explanations for some of the 6 complexes being aberrant. The ligand can be bounded to the Fe atom either through the pyridine N atom, or through some other atom from a substituent group (*e.g.* O atom from the carboxy group in No 10, N atom from the amido group in No 8, or from a nitrile group as suggested by [12]). A possible hydration or enolisation of the 4-acetylpyridine might also be considered for No 7. The correlation coefficient of eqn. 6 can be considered satisfactorily, since the shape of the absorption peaks does not allow a very good accuracy on λ_{max}.

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