σ -Bonded Organotransition-metal lons. Part VI.† Kinetics and Mechanism of Insertion of Hydrogen Isocyanide in Organopentacyano-cobaltate(III) lons

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The 2- and 3-pyridiomethylpentacyanocobaltate(III) ions have been prepared as their potassium salts. In aqueous acidic solution (pH < 0) their conjugate acids and that of the 4-pyridiomethylpentacyanocobaltate(III) ion undergo insertion of the hydrogen isocyanide ligand between the pyridiomethyl group and the cobalt atom. The insertion product is hydrolysed further, in acid solution, to the corresponding pyridioacetic acid, but in basic solution to the corresponding pyridylacetonitrile. Analogous reactions of the methylpentacyanocobaltate(III) ion are also described. The mechanism of the insertion reactions are discussed with special reference to the relative rates of reaction of the various isomers.

WE have reported ¹ the preparation, acid-base equilibria, and kinetics of decomposition of the air-stable 4-pyridiomethylpentacyanocobaltate(III) ion (I). In alkaline solution the stable conjugate base (II) is formed as in equation (1) but in acid solution decomposition occurs by two routes; at low acidities, irreversible de-

† Part V, D. Dodd and M. D. Johnson, J. Chem. Soc. (A), 1968, 34.

composition occurs following the reversible loss of one of the cyanide ligands as in equation (2) and, at high acidities, the reversibly formed conjugate acid of the 4-pyridiomethylpentacyanocobaltate(III) ion decomposes unimolecularly as in equation (3).

¹ M. D. Johnson, M. L. Tobe, and Lai Yoong Wong, J. Chem., Soc. (A), 1967, 491.





The only product that could be isolated on basification of the final solution from the latter reaction was the nitrile (XIII) and an insertion reaction similar to that originally suggested by Kwiatek and Seyler² was suggested.

As a comparison of the rates and products of reaction of the 2-, 3-, and 4-pyridiomethylmetal ions has been shown in several cases to be diagnostic of the mechanism of reaction at the (methylene) carbon-metal bond,³⁻⁵ it was of interest to study also the 2- and 3pyridiomethylpentacyanocobaltate(III) ions ((IV) and (V)]. This paper describes the preparation of these two ions as their potassium salts, their acid-base equilibria, the kinetics of their decomposition in acidic solution, and, by comparison with the behaviour of the 4-ion, makes further deductions about the mechanism of the insertion reaction.

RESULTS

Preparation, Physical Properties, and Acid-Base Equilibria. -The potassium salts of the 2- and 3-pyridiomethylpentacyanocobaltate(III) ions (IV) and (V) were prepared by fractional crystallisation of the products from the reaction of cobaltous bromide and potassium cyanide with 2- and 3-bromomethylpyridine respectively in absence of air, in aqueous solution. Both salts are stable to air in solution, but decompose in sunlight. All reactions were therefore carried out in darkened vessels.

The characteristic features of the ultraviolet spectra of the two ions are shown in Table 1, together with those of the 4-ion and those of the corresponding penta-aquopyridio-

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methylchromium(III) ions with which they show a distinct similarity.⁵ The infrared spectra of the potassium salts of the 2- and 3-ions show strong multiple CN stretching bands at 2080w, 2115s, and 2135m cm.⁻¹ and at 2105s, 2130m, and 2060sh cm.⁻¹, respectively. The ¹H n.m.r. spectra of the 2-ion in D₂O shows the heteroaromatic proton resonances

TABLE 1

Ultraviolet spectra of organometal complexes

Ion	Position	Formula	λ_{\max} (log ε)
Pyridiomethylpenta-	2-	(IV)	326.5 (4.30), 268 (4.00)
cyanocobaltate(III)	3-	(V)	292.5 (4.20)
	4-	(1)	326 (4.30)
Pyridylmethylpenta-	2-	(VI)	305 (4·30), 272sh (4·11)
cyanocobaltate(111)	3-	(VII)	293 (4.21)
	4-	(II)	299 (4.29)
Protonated pyridio-	2-	(VIII)	316·5, 4 315 b
methylpentacyano-	3-	(IX)	285 "
cobaltate(III)	4-	(III)	305,ª 293 °
Penta-aquopyridio-	2-		550 (1.86), 318 (4.02),
methylchromium(III)	5		262 (3.79)
	3-		534 (1.69), 320 (3.98),
			285 (4.17)
	4-	—	550 (1·96), 308 (4·19)
a 7m-Acid	. в 8м-А	Acid. °	12м-Acid.

in the region τ 1.49–2.68 and the singlet methylene resonance at τ 6.99. The corresponding resonances for the 3-ion are τ 1.8—2.6 (principally a doublet τ 1.87 and 2.0) and τ 7.03. No exchange of the methylene protons with the solvent was observed during several days.

The pyridiomethylpentacyanocobaltate(III) ions show spectral shifts in moderately alkaline solution owing to the loss of the proton from the pyridine ring (equation 1), and likewise in concentrated perchloric acid solutions $(\geq 2.5M)$ owing to protonation of the cyanide ligands (equation 3). The spectra of the conjugate bases (II, VI, and VII) and the conjugate acids (III), (VIII), and (IX) of the pyridiomethylpentacyanocobaltate(III) ions are shown in Table 1. Application of standard spectrophotometric and potentiometric methods shows that the pK_a 's are 10.4 ± 0.1 , 8.3 ± 0.1 , and 9.2 ± 0.1^{-1} for the 2-, 3-, and 4-pyridiomethylpentacyanocobaltate(III) ions respectively. Similar methods were not used accurately to determine the pK_a 's of the conjugate acids of the pyridiomethylpentacyanocobaltate(III) ions, because of the accompanying solvent spectral shifts and the high acidities required. However, approximate values in the region -2 ± 1 (on the H₋ scale ⁶) were estimated; *i.e.*, in the region 3.5— 6M-perchloric acid, for both 2- and 3-ions. This protonation is also reflected in a shift of the methylene ¹H n.m.r. singlet from τ 6.99 to 6.67 and from τ 7.03 to 6.85 on going from D₂O solvent to 50% sulphuric acid, for the 2- and 3-ions respectively.

Kinetics .-- The rates of decomposition of the 2- and 3pyridiomethylpentacyanocobaltate(III) ions in from 0.1 to 9M-perchloric acid were measured from the changes in optical density of the principal band (ca. 310 m μ) as a function of time. In no case was a reaction followed over less than two half-lives and the majority were followed for more than three half-lives. Good first-order kinetics

² J. Kwiatek and J. K. Seyler, J. Organometallic Chem., 1965,

 <sup>8, 421, 433.
 &</sup>lt;sup>3</sup> R. G. Coombes and M. D. Johnson, J. Chem. Soc. (A), 1966, ⁴ J. R. Coad and M. D. Johnson, J. Chem. Soc. (B), 1967,

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⁵ R. G. Coombes and M. D. Johnson, J. Chem. Soc. (A), 1966,

<sup>177.
&</sup>lt;sup>6</sup> M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, 57, 1 (H⁻ values used in this work are taken from M. W. Fuller, Thesis, London, 1961).

were obtained in all cases except with the 3-ion in solutions of pH >0. The first-order rate coefficients for the 2- and 3-ions at 40° are assembled in Tables 2 and 3, respectively, and those for the 2-, 3-, and 4-ions at 25·1° are shown in Table 4. A combined plot of log k against H_{-} for the three ions is shown in the Figure. The activation parameters for the first-order reaction of the three protonated pyridiomethylpentacyanocobaltate(III) ions, in that region of acidity where the rate is independent of acidity, are also shown in Table 4.

TABLE 2

Kinetics of reaction of 2-pyridiomethylpentacyanocobaltate(III) ion $(6-9.5 \times 10^{-5}M)$ at 40° in perchloric acid

· · · · ·		
$[HClO_4]$ (M)	$-H_{-}$	k (hr1) \pm 5%
8.20	3.87	0.582
8.00	3.73	0.498
7.20	3.19	0.489
7.00	3.06	0.520
6.10	2.52	0.469
5.00	1.93	0.370
4·00 a	1.44	0.235
4.00	1.44	0.312
3.10	1.01	0.196
3.08 a	0.99	0.135
3.08	0.99	0.202
2.46	0.70	0.154
2·46 ª	0.70	0.100
1.78 a	0.39	0.057
a	0.05м-HCN р	resent.

TABLE 3

Kinetics of reaction of 3-pyridiomethylpentacyanocobaltate(III) ion (8.4—20 \times 10⁻⁵M) in perchloric acid at 40°

[HClO,] (M)	$-H_{-}$	$k (hr.^{-1}) + 5\%$
7.00	3.06	19.9
6.00	2.45	20.3
5.00	1.93	17.9
4 ·00	1.45	12.3
3.10	1.00	9.47
2.48	0.71	6.84
1.24	0.14	3.02
1·24 ª	0.14	3.21
0.60	$-0.22 {}^{b}$	4·18 °
0.57 4	-0·24 ^b	1.44
0.123	-0·91 ^b	0.752 *
0·123 ª	-0.91 %	0.374

^а 0.05м-HCN present. ^b −pH. ^c From initial rate.

TABLE 4

Kinetics of reaction at 25·1° and activation parameters for the reaction of pyridiomethylpentacyanocobaltate(III) ions in perchloric acid

	-			$\Delta H^{\ddagger}_{\text{(kcal,/mole)}}$	$\Delta S^{\ddagger}_{(e.u.)}$
Jon	$[HClO_4]$ (M)	$-H_{-}$	$k (hr.^{-1}) \pm 5\%$	$1 \cdot 2$	$\mathbf{\hat{\pm}4}$
2-	8.0	3.73	0.099	20.5	-11
2-	8.6	4.14	5.103		
3-	6.0	2.45	3.65	20.6	-3
3-	7.0	3.06	3.64		
4-	8.0	3.73	0.868	21.1	-4
4-	8.6	4.14	0.855		

¹H N.m.r. Spectra.—Addition of the potassium pyridiomethylpentacyanocobaltate(III) salts to sulphuric acid (25—50%) caused immediate precipitation of the corresponding light yellow organocobalt acids. In the case of the 4-acid in 50% sulphuric acid this precipitation was such that insufficient remained in solution for measurement of the ¹H n.m.r. spectrum. In all three cases, however, in contact with the aqueous acid, the organocobalt acid redissolved to give a green solution (and green precipitate in the case of the 2- and 4-ions) which later changed to a light yellow solution. The changes in ¹H n.m.r. spectra of the three ions in 25% sulphuric acid are shown in Table 5 in terms of (i) initial spectrum, (ii) spectrum of green intermediate, (iii) spectrum of final yellow solution, and (iv) spectrum obtained when the solution of the green intermediate is basified and reacidified. Similar results (not shown) were obtained in 50% sulphuric acid.

TABLE 5

¹ H N.m.r. spectral changes of pyridiomethylpenta-
cyanocobaltate(111) ions in <i>ca</i> . 25% H ₂ SO ₄

Droton

				110001	
				τ	
Ion	Period	aromatic	-CH2-	NH_4^+	other
2-	Initial Intermediate " Final	0.90 - 1.55 0.90 - 1.55 0.90 - 1.55	7.00br 4.90br 5.55 ^b	None None 2.05, 2.97, 3.87	None None 1·34 °
3-	Initial Intermediate " Final Final f	$\begin{array}{c} 0.92 - 1.7 \\ 0.92 - 1.7 \\ 0.92 - 1.7 \\ 0.92 - 1.7 \\ 0.92 - 1.7 \end{array}$	6·90br 5·1br 5·75 ^d 5·51 9	None None 1.98, 3.80 ° 1.92, 2.83, 3.75	None None 1·38 °
4-	Initial Intermediate ^a Final Final ^f	0.88, 1.70 0.88, 1.70 0.88, 1.70 0.88, 1.70 0.88, 1.70	6·95br 5·1br 5·70 ^k 5·45 ⁱ	None None 2·16, 3·86 ° 2·47, 4·17 °	None None
P e re P	^a Maximum $_{\rm yCH_2CO_2H.}$ ^c Central $\rm NH_4^+$ acidification. yCH_2CN.	concentration Unknown, peak obscu 9 3-pyCH ₂	1 of in see te nred. f CN. f	nsertion produce ext. ^d 3-pyCH After basificatio ^h 4-pyCH ₂ CO ₂ H.	t. ^b 2- I ₂ CO ₂ H. on and ⁱ 4-

DISCUSSION

One of the principal characteristics of many pyridiomethyl compounds is that the 2- and 4-compounds have a much greater tendency to heterolytic dissociation, with formation of the pyridiomethyl carbanion,⁴ than the corresponding 3-ion. This is due to the effect, in the transition state, of the high stability of the incipient, partly quinonoid, 2- and 4-pyridiomethyl carbanions [e.g. (X)]. However, though this effect is usually only apparent in chemical reactions of pyridiomethyl compounds, there is evidence here that it is also present in the ground states of the pyridiomethylpentacyanocobaltate(III) ions. Thus the pK_a of the 2-pyridiomethylpentacyanocobaltate(III) ion (10.3) is, as expected, considerably higher than that of the 4-ion (9.24), owing largely to the distance of the negatively charged inorganic group from the ring nitrogen atom. However, the p K_a of the 3-ion, which one would expect to be intermediate between these two values, or at least larger than that of the 4-ion, if normal inductive effects only are operating, is in fact considerably less (8.3) than either of the others. The effect of the negative charge on the inorganic group of the 2- and 4-ions is therefore relatively enhanced by some special interaction, almost certainly a result of the strong conjugative interaction between the 2- and 4-methylene groups and the ring nitrogen atom. We write this interaction provisionally as in the bond-no-bond resonance structure (XI). It is important to note that this effect is apparent in the pK_a values because similar interactions in the conjugate bases would be very much less favourable.



An observation that may be connected with these ground-stage interactions is that the ultraviolet spectra of the 2- and 4-ions undergo marked shifts on deprotonation whereas the spectra of the 3-ion and its conjugate base almost coincide with, and are very similar to, those of the conjugate bases of the 2- and 4-ions (Table 1).

Mechanism of Decomposition.—As with the 4-ion,¹ the rate of disappearance of the 2- and 3-pyridiomethylpentacyanocobaltate(III) ions were found to be influenced by added HCN in the less acidic solutions. This is due to the effect of HCN on the concentration of, and hence the extent of reaction through, the corresponding aquotetracyanocobaltate(III) ions (equation 2). That the effect of HCN is as marked for the 3- as for the 2- and 4-ions suggests that the decomposition of the methylene-cobalt bond in aquotetracyanocobaltate(III) ions is homolytic and this is confirmed by the product (aldehyde) spectra. However, in this paper, as we are primarily interested in the acid-catalysed reactions, we henceforth consider only those rate coefficients that are uninfluenced by added HCN or which were measured in the presence of an excess of HCN; *i.e.*, where only the acid-catalysed decomposition is operative.

The rate coefficients for the decomposition of the 2and 3-pyridiomethylpentacyanocobaltate(III) ions, like those for the 4-ion, rise with increasing acidity to an upper limit. The character of the approach to the upper limit (Figure) is consistent with the mechanism described in equation (3), *i.e.*, a rate-determining decomposition of the conjugate acid of the appropriate pyridiomethylpentacyanocobaltate(III) ion. The differences between the acid-independent rate coefficients for the three ions are small, but the primary decomposition product from the 2-ion (λ_{max} . 262·5-263 mµ) decomposes further at a rate comparable with that at which it is formed, whereas those from the 3-(λ_{max} . 262-262·5 mµ) and 4-(λ_{max} . 256 mµ) ions are stable for many hours, in acidic solution

This behaviour initially suggested to us that the initial products from the 3- and 4-ions were the stable nitriles [(XII) and (XIII)] which were isolated on basification, whereas the initial product from the 2-ion was too unstable to be the nitrile (XIV) and might be a transient insertion product corresponding to that described by Kwiatek and Seyler² for the benzylpentacyano-

cobaltate(III) ion. However, as the discussion below shows, the initial product in all three reactions is the insertion product [(XV), (XVI), and (XVII)], formed as shown in equation (4).

Thus the ¹H n.m.r. spectra of each of the fresh solutions show the rather broad singlet of the methylene group of the pyridiomethylpentacyanocobaltate(III) ion (or its time-averaged spectrum with that of its conjugate acid). This spectrum changes, at a rate consistent with the kinetics measured on more dilute solutions, to the broad methylene singlet of the insertion



Kinetics of reaction of 2-, 3-, and 4-pyridiomethylpentacyanocobaltate(III) ions in perchloric acid

• Reaction in the absence of hydrogen cyanide. O Reaction in the presence of an excess of hydrogen cyanide

product. After several hours at 60° in the case of the 4- and 3-ions and about 1 hr. in the case of the 2-ion, the spectrum changes to that of the ammonium ion and other products described below.



The evidence for the structure of the insertion products is as follows: (i) the methylene singlets ($\tau 4.9$, 5·1, and 5·1 for the 2-, 3-, and 4-ions respectively) are different from, but in the same region as, those of the corresponding nitriles ($\tau 5.34$, 5·51, and 5·50 respectively) and acids [(XVIII), (XIX), and (XX)] ($\tau 5.53$, 5·80, and 5·72). They are also inconsistent with those of the alcohols, methylpyridines, or dipyridylethanes which have been observed in the decomposition of other pyridiomethylmetal ions.⁵ Similarly, the ultraviolet spectra of the insertion products (λ_{max} 262·5—263, 262—262·5, and 256 m μ , respectively) are also very close to, but not the same as, those of the nitriles (λ_{max} 260·5, 259·5—260, and 254·5 m μ).

(ii) On cooling of the solution of the 2-insertion product in 25% sulphuric acid, it precipitates as a green gelatinous solid which changes to a dark green powder on drying. These solids gave variable analyses, but all showed a carbon : nitrogen : cobalt ratio consistent with the presence of pyridiomethyl, cyanide, and cobalt. (A similar green product was obtained previously from the reaction of acid with benzylpentacyanocobaltate(III) ion and claimed to be an insertion product.²)

(iii) Three products were observed in the decomposition of each insertion product in sulphuric acid; these were the ammonium ion, the corresponding pyridioacetic acid [(XVIII), (XIX), and (XX)], and an unknown product having a singlet proton resonance in the region τ 1·34—1·40. The pyridioacetic acid could not have been formed from the pyridioacetonitrile for we have shown that the latter are not significantly hydrolysed under these conditions. They must therefore have been formed by the hydrolysis of some other species, in which the carbonyl carbon is already present, *i.e.*, by nucleophilic attack (of water or hydrogen sulphate ion) on the iminyl carbon atom of the insertion product, with subsequent loss of ammonium ion by one of the paths shown in equation (5). The much faster hydrolysis of the 2- than of the 3- and of the 4-insertion product (the 2-product would be expected normally to behave in an analogous manner to the 4-product) is likely to be due to hydrogen bonding of the imine nitrogen to the pyridine



nitrogen, which assists the nucleophilic attack on the iminyl carbon atom. The fate of the cobalt remains obscure, but the process d^6 cobalt(III) to d^8 cobalt(I) suggested in equation (5) is not unreasonable.

(iv) Basification of the acidic solutions of the insertion products gave the corresponding pyridioacetonitriles which were detected from the ¹H n.m.r. spectrum of the reacidified solution and by isolation. No attempt was made to maximise the yields of the 3- and 4-insertion products, but that from the 2-insertion product was 60% overall or *ca.* quantitative when allowance was made for unchanged starting material present at the time of basification. The mechanism of the base-catalysed decomposition of the insertion products is unlikely to involve nucleophilic attack on the iminyl carbon, since this would lead (as above) to the pyridio-acetic acid. It must therefore involve the removal of the iminyl proton with the subsequent or synchronous loss of the d^8 cobalt(I) cyanide as in equation (6).

(v) In deuterated acid, the methylene protons of the insertion products exchange at a similar rate to those of the corresponding nitriles but faster than those of the methylpyridines, indicating that they are relatively acidic.



The 'insertion' reaction described in equation (4) shows similarities to the corresponding carbonyl 'insertion' reaction of methylmanganese carbonyl,7 and effectively involves a migration of the pyridiomethyl group from cobalt to iminyl carbon. Further evidence as to the nature of this process comes from the relative rates of insertion of the protonated 2-, 3-, and 4-pyridiomethylpentacyanocobaltate(III) ions. The observed order, 3 > 4 > 2, with a 38-fold difference overall, is completely inconsistent with carbanion character of the pyridiomethyl group in the transition state,⁴ but is similar to that observed in the homolytic dissociation of pyridiomethylmetal ions.⁵ However, since the reactions were carried out in the presence of an excess of oxygen and the products were not those formed from reaction of pyridiomethyl radicals with oxygen, complete homolysis of the methylene-cobalt bond cannot have occurred. In view of the apparent ground-state differences between the 3-ion and the 2- and 4-ions, as manifested in the pK_{a} of the pyridine nitrogen, it seems most probable that the reactivity order is merely a reflection of these and that the reaction involves concerted methylene-cobalt bond breaking and methyleneiminyl carbon bond formation. The distinction, between migration of the organic group from cobalt to protonated or to unprotonated cyanide ligand, cannot yet be made. Nor can any decision yet be made about the function of the solvent water as a ligand in, and subsequent to, the migration process.

⁷ R. J. Mawby, F. Basolo, and R. G. Pearson, J. Amer. Chem. Soc., 1964, 86, 5043.

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Methylpentacyanocobaltate(III) Ion.—Methylpentacyanocobaltate(III) salts have not been prepared pure and, as they do not have as strong and accessible an absorption band in the region 250-350 mµ as the pyridiomethylpentacyanocobaltate(III) ions, accurate kinetic and product studies are much more difficult to carry out. However, the following limited studies on the methylpentacyanocobaltate(III) ions show that the reactions are essentially though not entirely analogous.

Thus, in acidic solution (pH 2–0) the methyl pentacyanocobaltate(III) ion (XXI; λ_{max} 318 mµ, log ε 2·46)⁸ is rapidly monoprotonated and the conjugate acid (XXII; λ_{max} 370 mµ, log ε 2·39; pK_a 2·7 ± 0·1) reacts further at a rate comparable with that of the protonated 3-pyridiomethylpentacyanocobaltate(III) ion (IX). The reaction almost certainly involves an analogous insertion to give (XXIII) (λ_{max} 356 mµ, log ε 2·37) since it is accompanied by a shift of the methylene proton resonance downfield by τ 2·67 p.p.m. from 9·42 to 6·75 and the rate ($k = 3 \pm 1$ hr.⁻¹ at 25°) is independent of acid concentration over the range studied.

However, the insertion reaction is followed by a somewhat slower first-order process $(k = ca. 7 \times 10^{-2} \text{ hr.}^{-1}$ in 0·1M-H₂SO₄) to a further organocobalt ion $(\lambda_{\text{max}}. 343 \text{ m}\mu, \log \varepsilon 2.44)$ with a methylene singlet only 0·1 p.p.m. lower than that of the insertion product.

We believe this to be the corresponding acetyltetracyanocobaltate(III) ion (XXIV) because its formation is accompanied by the formation of the ammonium ion and it is apparently unchanged after several days in acid solution and after basification with sodium carbonate and reacidification. No acetonitrile could be detected in these products.

$$\begin{array}{c} \operatorname{CH}_{3} \cdot \operatorname{Co}(\operatorname{CN})_{5}^{3^{-}} &\longrightarrow \operatorname{CH}_{3} \cdot \operatorname{Co}(\operatorname{CN})_{4}(\operatorname{CNH})^{2^{-}} \longrightarrow \\ (XXI) & (XXII) \\ & (XXII) \\ & CH_{3} \cdot \operatorname{C} \cdot \operatorname{Co}(\operatorname{CN})_{4}^{2^{-}} \longrightarrow CH_{3} \cdot \operatorname{C} \cdot \operatorname{Co}(\operatorname{CN})_{4}^{2^{-}} \\ & || \\ & || \\ & \operatorname{NH} & O + \operatorname{NH}_{4}^{+} \\ (XXIII) & (XXIV) \end{array}$$

EXPERIMENTAL

Materials.-Perchloric acid and 2- and 3-bromomethylpyridinium bromide were prepared as described earlier. 2- and 3-Pyridylacetonitrile were prepared by the method of Schulze ⁹ (2-nitrile; b.p. 128—129°/16 mm. $n_{\rm D}^{24}$ 1.5215, λ_{max} 260.5 mµ (log ϵ 3.82) in 0.1M-HClO₄. 3-Nitrile; b.p. 146–147°/15 mm., $n_{\rm p}^{24}$ 1.5268, $\lambda_{\rm max}$ 259.5 mµ (log ε 3.73) in 0.8M-HClO₄; v_{CN} 2260 cm.⁻¹.) 2-, 3-, and 4-Pyridylacetic acid were prepared by hydrolysis of the corresponding nitrile (1.2 g., 0.01 mole) in sulphuric acid (40-50%), 7 ml.) at 60° for 5 days. The $^1\!\mathrm{H}$ n.m.r. spectra showed the gradual replacement of the methylene singlets of the nitriles $(\tau 5.34, 5.60, \text{ and } 5.50)$ by those of the acids $(\tau 5.53, 5.80,$ and 5.71, respectively), accompanied by the triplet resonance of the ammonium ion (τ 2.27, 3.18, and 4.09). The excess of acid was removed by addition of sodium hydroxide and the precipitated sodium sulphate was filtered off. The solution was acidified to ca. pH 5 with hydrochloric acid and the pyridylacetic acid (or its hydrochloride) allowed to crystallise. Yields 0.67, 0.52 (as hydrochloride), and 0.45 g. (as hydrochloride) (49, 30, and 26%) respectively (λ_{max} 266, 263.5, and 255 m μ , respectively, in water; λ_{max} 261.5, 260.5, and 255 m μ , respectively, in perchloric acid).

Organopentacyanocobaltate (III) Salts.—2-Bromomethylpyridinium bromide was treated with potassium cyanide and cobaltous bromide in deaerated water as described for the 4-compound. The solution was worked up as described previously to give potassium 2-pyridylmethylpentacyanocobaltate (III) monohydrate in 27% yield (Found: C, 31.6; H, 2.2; Co, 13.5; K, 28.3; N, 19.7. $C_{11}H_8COK_3N_6O$ requires C, 31.7; H, 1.9; Co, 14.2; K, 28.2; N, 20.2%). Similar reaction of 3-bromomethylpyridinium bromide gave slightly impure potassium 3-pyridylmethylpentacyanocobalt ate(III) (Found: C, 26.9; H, 2.7; Co, 12.9; K, 28.4; N 16.7%). Impure potassium methylpentacyanocobaltate(III) was prepared by the method of Halpern and Maher.⁸

Dissociation Constants.—(a) The acid-dissociation constant of the 2-pyridiomethylpentacyanocobaltate(III) ion was determined from the changes in its ultraviolet spectrum as a function of pH (carbonate buffers), as described for the 4-ion. (b) The pK_a of the 3-pyridiomethylpentacyanocobaltate(III) ion (2.43 g.) in carbonate-free water (50 ml.) was determined potentiometrically by titration against 1M-hydrochloric acid at 22°.

Kinetics.—The kinetics of decomposition of the 2- and 3-pyridiomethylpentacyanocobaltate(III) ion were measured spectrophotometrically, using the principal absorption band (ca. 300 m μ) as described for the 4-ion.¹

¹H N.m.r. Studies.—The changes in ¹H n.m.r. spectrum of each of the 2-, 3-, and 4-pyridiomethylpentacyanocobaltate(III) ion (ca. 0·1M) in 25% and in 50% sulphuric acid were measured at 10 min. intervals for 1 hr. and then at longer intervals first at 33°, later at 60°. When the methylene proton resonance at ca. τ 7 had disappeared a portion of the solution was basified and reacidified before measuring the spectrum again. The other portion was kept at 60° and its spectrum was measured at intervals during several days until there was no further change. The spectra are described in Table 5.

Products.—Potassium 2-pyridylpentacyanocobaltate(III) (0.61 g., 1.5 mmoles) in water (5 ml.) was made up to 15 ml. with 12M-perchloric acid and kept at 40° for 6 hr. The dark green insertion product (Found: C, 40.3; H, 3.6; Co. 21.2; N, 24.2%) was filtered off, leaving a green solution, and dissolved in an excess of potassium carbonate. The orange solution formed was extracted with ether to give 2-pyridylacetonitrile (0.12 g., 66%) identical with an authentic sample as shown by its i.r., u.v., and ¹H n.m.r. spectra. Similar reaction of potassium 3-pyridylmethylpentacyanocobaltate(III) gave 3-pyridylacetonitrile (0.033 g., 26%).

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