1297. *σ-Bonded Organotransition-metal Ions. Part I. The Formation of Air-stable Penta-aquopyridiomethylchromium*(III) *Ions*

By R. G. Coombes, M. D. Johnson, and N. Winterton

The air-stable penta-aquo-2-, -3-, and -4-pyridiomethylchromium(III) ions having carbon–chromium σ-bonds have been prepared in aqueous solution by the reaction of chromous sulphate with aqueous solutions of the corresponding 2-, 3-, or 4-bromomethylpyridinium bromide. The products of decomposition of these ions depend upon the conditions. In perchloric acid the main products include the corresponding 1,2-dipyridylethane, but in slightly alkaline solution the only organic product is the corresponding methylpyridine, indicating a change in mechanism as the pH is changed. Similarly, penta-aquo-2-(1-methylpyridio)methylchromium(III) ion has been prepared in aqueous solution and characterised. All four pyridiomethylchromium ions undergo rapid and reversible dissociation, at pH *ca.* 3 in acetate buffers, involving the loss of a proton from one of the co-ordinated water molecules.

Many organic halides react with oxidisable transition-metal ions. Free radicals have frequently been postulated as intermediates in these reactions [1] and in some cases such free radicals are themselves understood to react with the transition-metal ion to form organometallic compounds of different stability. One reaction, whose mechanism and products have been studied in some detail is that between chromous ion and benzyl halides.[2] The postulated mechanism involves[1] the formation of benzyl radicals as shown in equation (1) followed by reaction of the benzyl radicals with more chromous ion as shown in equation (2) to form the benzylchromium(III) ion (I). So far neither benzyl- nor substituted benzylchromium(III) salts have been isolated, but there can be little doubt about their structure. However, these ions are all fairly rapidly decomposed by oxygen, and all quantitative studies of their solvolytic behaviour have been hampered by the necessity to work in an

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[1] J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 5264.

[2] F. A. L. Anet and E. LeBlanc, *J. Amer. Chem. Soc.*, 1957, **79**, 2649.

inert atmosphere.[3,4] As will be seen, in this and subsequent Papers, a number of fundamental characteristics of these compounds are likely to be obscured under these conditions.

This Paper describes the preparation and characterisation in solution of four ions which are related to the benzylchromium(III) ions, but which are stable towards oxygen. Subsequent Papers will describe further examples and some of their reactions.

$$\mathrm{ArCH_2Br + Cr^{2+} \longrightarrow ArCH_2\cdot + CrBr^{2+}} \qquad (1)$$

$$\mathrm{ArCH_2\cdot + Cr^{2+} \longrightarrow ArCH_2Cr^{2+}} \qquad (2)$$

$$\mathrm{CrBr^{2+} \longrightarrow Cr^{3+} + Br^-} \qquad (3)$$

The addition of an excess of chromous sulphate to a solution of 4-bromomethylpyridinium bromide (II) in water immediately produces a red solution. In the presence of an excess of chromous ion the red colour changes slowly to green, but if the excess of chromous ion is destroyed by the addition of air the red colour is stable for long periods. On evaporation of the solution, even at low temperatures, decomposition occurs before solid material can be obtained.

The red solution was separated into its component cations by elution from a cation-exchange resin with various concentrations of perchloric acid. The principal fraction eluted with 1M-perchloric acid was a red solution ($\lambda_{max.}$ 550, 308, 225 mμ; Table) believed to contain only a single cationic species (other than H^+). This view is supported by the following facts. (i) On addition of alkali to the red solution the only organic product is 4-methylpyridine, though experiments showed that methylpyridines are eluted from the ion-exchange resin well before the red solution. (ii) The only inorganic product obtained on warming the red solution with 5M-perchloric acid is the hexa-aquochromium(III) ion. This ion, together with other chromium(III) species present in the crude solution is also eluted from the resin before the red solution. No halide or sulphate ions were present in the acid decomposition product. (iii) The rates of change of the visible (550 mμ) and the ultraviolet (308 mμ) peaks of the red solution are identical, indicating that they belong to a single ion. (iv) The variation of ultraviolet and visible spectra of the fractions eluted from the resin was consistent with a single absorbing species in the red solution. (v) The ion has a magnetic susceptibility of 3·8 ± 0·4 B.M. (vi) Analysis by decomposition in alkali followed by separate determinations of 4-methylpyridine and chromium indicated a methylpyridine : chromium ratio of 1·00 ± 0·06. In view of the proposed mechanism for

Spectra of penta-aquo-(X-pyridiomethyl)chromium(III) ions

X	pH	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	$\lambda_{max.}$ (ε)	Isosbestic points
4	1	225 (6750)	308 (15,600)	550 (92)	
4	5[g]	[b]	324	[a]	313
3[d]	1	285 (15,000)	*320* (*9600*)	534 (49)	
3	5[g]	289	*325*	[a]	275
2	1	262 (6200)	318 (10,400)	550 (73)	
2	5[g]	266	333		270 283 320
1-CH_3-2	1	266 (8700)	322 (15,900)	548 (127)	
1-CH_3-2	5	271	335	[a]	271 288 320
Benzyl chromium ion			358 (high)	540 (low)	
		274 (8380), 299 (7920)	360 (2470)	[c]	

[a] Too weak to measure under the conditions of the experiment. [b] No corresponding maximum. [c] Existence disputed.[1] [d] Least accurate values of extinction coefficient due to some decomposition of stock solutions. [e] From ref. 2; pH *ca.* 1. [f] From ref. 1; pH not specified. [g] In acetate buffer; extinction coefficients are within 20% of those at pH 1.

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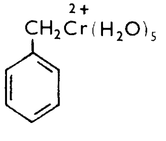
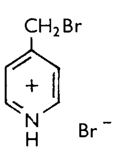
[3] L. H. Slaugh and J. H. Raley, *Tetrahedron*, 1964, **20**, 1005.

[4] J. K. Kochi and D. Buchanan, *J. Amer. Chem. Soc.*, 1965, **87**, 853.

the formation of the benzylchromium ion,[1] two possible structures can be drawn for a complex with this ratio of components. These are the *C*-bonded penta-aquopyridiomethylchromium(III) ion (III) and the *N*-bonded 4-methylpyridinopenta-aquochromium(III) ion (IV), which have the same molecular formulæ and charge.* The former ion would be expected from the normal reaction similar to that described in equations (1)—(3); the latter might be expected if the attack of chromous ion on the 4-pyridylmethyl radical (V) took place on nitrogen as shown in equation (4) rather than on carbon.


(I)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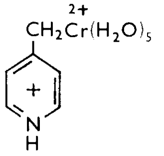
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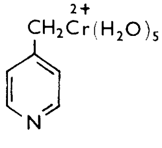
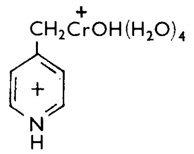
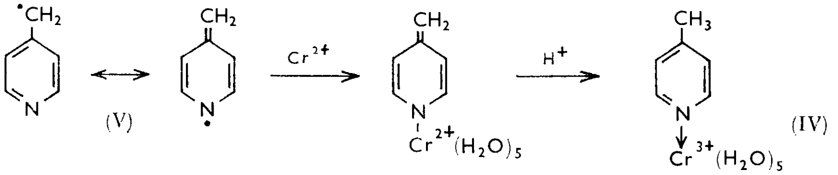

(IIIa)


(IIIb)



(4)

A choice between the *N*- and *C*-bonded ions was made by consideration of three factors: (*a*) the products of decomposition of the ions in alkaline deuterated media; (*b*) comparison of the ultraviolet spectrum with that of the benzylchromium compound; (*c*) the products of decomposition of the ion in acidic media.

(*a*) A sample of penta-aquo-4-pyridiomethylchromium(III) ion was prepared in aqueous medium and decomposed by addition of sodium carbonate after having largely replaced the water by D_2O. The main products were 4-methylpyridine (*ca.* 50%) and 4-[α-${}^{2}\mathrm{H}_{1}$]-methylpyridine (*ca.* 50%). This favours the presence of a carbon–chromium bond in the ion, because, had random hydrogen–deuterium exchange taken place in the methyl group of free picoline or the *N*-bonded ion, some 4-[α-${}^{2}\mathrm{H}_{2}$]methylpyridine and 4-[α-${}^{2}\mathrm{H}_{3}$]methylpyridine would also have been present in the product. The mass spectrum of the product clearly shows that these are absent. Moreover, no deuterium exchange occurs with 2-methylpyridine under the same conditions.

(*b*) The ultraviolet spectrum of the red solution is similar to that recorded[2] for the benzylpenta-aquochromium(III) ion, as shown in the Table. However, the connection of the longest-wavelength band with this ion has been disputed.[1] Our observations, though dealing with ions other than the benzylchromium ion, show that the rate of change of the corresponding visible and ultraviolet bands of the red solution are identical and certainly belong to the same species.

(*c*) On addition of perchloric acid to the red solution at 55°, decomposition occurs and an organic product is 1,2-di-(4-pyridyl)ethane, which is likely to have been formed from the *C*-bonded rather than the *N*-bonded ion.

The solutions therefore contain pure penta-aquo-4-pyridiomethylchromium(III) ion (III). An alternative formulation would be the corresponding conjugate bases (IIIa) or (IIIb), but these are only likely to be present in small amounts in acidic solution.

The corresponding penta-aquo-3-pyridiomethylchromium(III) (VI) and penta-aquo-2-pyridiomethylchromium(III) (VII) ions have similarly been prepared by the reaction of

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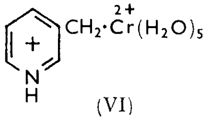
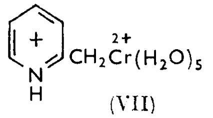
* It is possible that the failure to distinguish between these two types of complex has led to wrong assignments of structure in the past. For example, the supposed *C*-bonded 2-pyridylmethyltriethyltin [5] is more likely to be *N*-bonded 2-pyridinotriethyltin on the basis of its chemical reactions.

[5] H. Zimmer and G. Gold, *Chem. Ber.*, 1956, **89**, 712.

chromous ion with 3- and 2-bromomethylpyridinium hydrobromide, respectively. The chromatographic separation of the ions and their characterisation as *C*-bonded ions correspond in all respects to those described above for the penta-aquo-4-pyridiomethylchromium-(III) ion. The ultraviolet spectra of these ions in acidic solution are described in the Table.

Further evidence for the *C*-bonded structure of the penta-aquo-2-pyridiomethylchromium(III) ion comes from the preparation of the corresponding *N*-methylated ion, penta-aquo-2-(1-methylpyridio)methylchromium(III) ion (VIII). The intermediate 2-(1-methylpyridyl)methyl radical (IX) cannot react with chromous ion at other than the methylene group, and the characteristics of the *N*-methylated complex ion are similar in almost all respects to those of the 2-pyridiomethylchromium ion.


(VI)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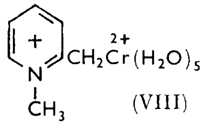
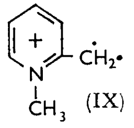
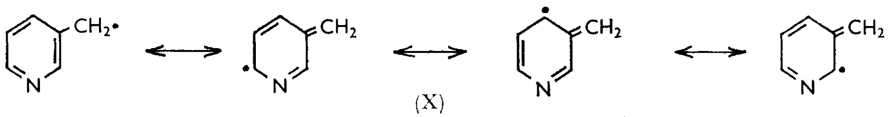

(VIII)


(IX)

The fact that the 3-pyridiomethylchromium ion has similar characteristics and is formed in the same manner as the 2- and 4-pyridiomethylchromium is also evidence in favour of the *C*-bonded structure of these ions. Only the intermediate radicals derived from the 2- and 4-bromomethylpyridinium ions are likely to react with chromous ion at both


(X)

nitrogen and methylene-carbon atoms. The intermediate radical (X) derived from the 3-bromomethylpyridinium ion cannot be expected to react at nitrogen because of the much higher (probable) free-radical localisation energy at that position. This can be seen on consideration of the valence-bond structures of the radical (X).

Properties.—The stability of these complexes towards air over long periods at room temperature is in marked contrast to the behaviour of the closely related benzylchromium complexes. The reason for this difference is not immediately apparent, but other quite marked differences in stability of the carbon–chromium bond will be described in more detail in Part II of this Series. However, the extent of the stability is of immense value for the future study of the properties of carbon–chromium bonds.

The decomposition in acidic solution shows similarities to the corresponding decomposition of the benzylchromium ion,[4] but the decomposition in alkaline solution to give the corresponding methylpyridines in quantitative yield is a reaction that has not so far been described. It points to a change of mechanism as the pH is raised, but the range of pH at which such a change occurs with these ions, and probably with the benzylchromium ion, is not yet known. Previous work on the decomposition in the range above pH 3, which probably includes the borderline region, must therefore be regarded with caution until more detailed studies have been carried out.

However, one further property of the pyridiomethylchromium ions is of importance and is probably related to the change of mechanism. The pyridiomethylchromium ions all undergo rapid and reversible acid–base dissociation in sodium acetate–perchloric acid buffers at about pH 3. The spectra of the conjugate bases of the pyridiomethylchromium ions are all shifted to longer wavelengths, as shown in the Table. The dissociation is unlikely to involve loss of a methylene proton, but could involve loss of either the proton from the ring nitrogen atom, to (IIIa), or a proton from one of the water molecules co-ordinated to the metal atom, to (IIIb), since the pK_a of the methylpyridines[6] is *ca.* 6 and the first

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[6] H. C. Brown and X. R. Mihm, *J. Amer. Chem. Soc.*, 1955, **77**, 1723.

pK_a of the hexa-aquochromium(III) ion [7] is *ca.* 4 at 25°. The choice between these two possibilities was made by reference to the corresponding penta-aquo-2-(1-methylpyridio)-methylchromium(III) ion which was found to have a very similar acid–base dissociation in the same pH range. The dissociation must therefore involve one of the water molecules co-ordinated to the metal atom, and this must be expected to have some influence on the rate and mechanism of decomposition of the ions in the region around and above pH 3.

EXPERIMENTAL

Preparation of Materials.—2- and 4-Bromomethylpyridinium bromide, prepared by the method of Bixler and Niemann,[8] had m. p. 143—146 and 187—188°, respectively (lit.,[9] 145—146, 185—187°). 3-*Bromomethylpyridinium bromide*, prepared by a similar method, had m. p. 148—149° (from ethanol) (75%) (Found: C, 28·6; H, 2·9; Br, 63·2; N, 5·7. $C_6H_7Br_2N$ requires C, 28·5; H, 2·7; Br, 63·2; N, 5·5%). 2-*Hydroxymethyl*-1-*methylpyridinium bromide* was prepared by anion-exchange chromatography from a solution of the corresponding iodide obtained from 2-pyridylmethanol and methyl iodide. 2-*Bromomethyl*-1-*methylpyridinium bromide*, prepared by the method described above for 2-bromomethylpyridinium bromide, had m. p. 186° (Found: C, 31·9; H, 3·7; Br, 58·9; N, 5·3. $C_7H_9Br_2N$ requires C, 31·5; H, 3·4; Br, 59·9; N, 5·2%).

Penta-aquo-4-*pyridiomethylchromium*(III) *ion.* On addition of 0·5M-aqueous chromous sulphate (20 ml.), in the absence of air, to a degassed solution of 4-bromomethylpyridinium bromide (0·79 g., 0·0031 mole) in water, a red-brown solution was formed. In the presence of an excess of chromous sulphate the colour slowly changed to green, but on removal of the excess of chromous sulphate, by shaking in air for several minutes, the solution was stable. The red-brown solution was separated into its component cations by chromatography on a 14 × 1·5 cm. column of ZeoKarb 225 SRC 10 ion-exchange resin previously washed with 5M-perchloric acid (250 ml.) and distilled water (500 ml.). The solution was eluted at a rate of 200 ml. per hour and the main fractions were as follows (solvent added, appearance of eluant, principal spectral peaks, conclusion): (a) water (100 ml.) with the red-brown solutions, deep green, 590 mμ, $CrSO_4^+$; (b) 0·1N-perchloric acid (100 ml.), light green, 420 and 590 mμ, $CrSO_4^+$; (c) 0·1N-perchloric acid (1 l.), light green becoming colourless, 252·5 mμ, methylpyridinium ion; (d) 1M-perchloric acid (150 ml.), violet becoming colourless, 409 and 574 mμ, $Cr(H_2O)_6^{3+}$; (e) 1N-perchloric acid (800 ml.), red brown, 225, 308, and 550 mμ, *penta-aquo*-4-*pyridiomethylchromium*(III) *ion*; (f) 5N-perchloric acid, red-brown becoming colourless, 225, 308, and 550 mμ, remainder of penta-aquo-4-pyridiomethylchromium(III) ion (total yield 0·0022 mole, 70%). Similar preparations and chromatographic separations gave solutions of pure *penta-aquo*-2- and *penta-aquo*-3-*pyridiomethylchromium*(III) *ions* and of *penta-aquo*-2-(1-*methylpyridio*)*methylchromium*(III) *ion.*

As a check on the chromatographic behaviour of the methylpyridinium ions on the resin, a similar quantity of 3-methylpyridine was subjected to the same treatment and found to be completely eluted by 1100 ml. of 0·1M-perchloric acid and 150 ml. of 1N-perchloric acid. When the preparations were carried out in more dilute solution, *e.g.*, 2 × 10^{-3}M, the yields of penta-aquopyridiomethylchromium(III) ions were essentially quantitative, as indicated by the ultraviolet spectrum of the product. More concentrated solutions of the pure penta-aquopyridiomethylchromium(III) ions could be obtained by using more concentrated acid in the final stages of the elution.

Decomposition of Penta-aquopyridiomethylchromium(III) *Ions.*—(a) *In basic solution.* A solution of the crude penta-aquo-4-pyridiomethylchromium(III) ion (from 0·51 g. of 4-bromomethylpyridinium bromide) was treated with an excess of sodium carbonate and then extracted with ether. The ethereal extract was dried ($MgSO_4$) and the ether was removed by distillation to give 4-methylpyridine (0·09 g., 50%). No 1,2-di-(4-pyridyl)ethane could be detected in the product. Since only a part of the 4-methylpyridine can be extracted from the aqueous solution in this way, a similar experiment was carried out on a pure solution of penta-aquo-4-pyridiomethylchromium(III) ion, and the yield of 4-methylpyridine, determined by ultraviolet spectroscopy, was essentially quantitative. Similar yields of 2- and 3-methylpyridine were obtained from penta-aquo-2- and -3-picolylmethylchromium(III) ions, respectively.

[7] "Stability Constants," *Chem. Soc. Special Publ.*, No. 17, 1964, p. 48.

[8] R. L. Bixler and C. Niemann, *J. Org. Chem.*, 1958, **23**, 575.

[9] K. Winterfield and K. Flick, *Arch. Pharm.*, 1956, **26**, 448.

(b) *In acidic solution.* (i) On warming a purified solution of penta-aquo-4-pyridiomethylchromium(III) ion in an excess of 5M-perchloric acid with access to air for 4 days at 64°, the only inorganic species that could be identified was $Cr(H_2O)_6^{3+}$ ($\lambda_{max.}$ 408 and 575 mμ). No bromide or sulphate ion was presented in these solutions. (ii) The crude ion (from 0·6 g. of 4-bromomethylpyridinium bromide) was decomposed in 2M-perchloric acid for a similar period and then made alkaline with sodium carbonate. The product was worked up as described for 4-methylpyridine in (a), above, and found to contain 1,2-di-(4-pyridyl)ethane (30%) and 4-methylpyridine (70%). The 1,2-di-(4-pyridyl)ethane had m. p. 106—109° (lit.,[10] 110—111°) and was identified by its mass spectrum and proton magnetic resonance spectrum. 1,2-Di-(3-pyridyl)ethane with 3-methylpyridine and 1,2-di-(2-pyridyl)ethane with 2-methylpyridine were the principal products from solutions of penta-aquo-3- and -2-pyridiomethylchromium(III) ions, respectively.

The rate of decomposition of penta-aquo-4-pyridiomethylchromium perchlorate (3×10^{-5}M) in 1M-perchloric acid was measured at 55° from observations of the rate of change of the spectrum at 308 mμ. Standard methods for first-order reactions gave $k = 18{\cdot}6 \times 10^{-2}$ hr.$^{-1}$. Similar observations of the rate of change of the visible absorption maximum (550 mμ) of 10^{-3}M-solutions in 1M-perchloric acid gave $k = 18{\cdot}6 \pm 0{\cdot}2 \times 10^{-2}$ hr.$^{-1}$.

(c) *In alkaline deuterated medium.* Penta-aquo-4-pyridiomethylchromium(III) ion (from 0·65 g. of 4-bromomethylpyridinium bromide) was stirred in air for 10 min. and then evaporated *in vacuo* at 25° to approximately 10 ml. Deuterium oxide (10 ml.) was added and the solution was again evaporated to *ca.* 10 ml. The addition of deuterium oxide and the evaporation were repeated, and after addition of a further 10 ml. of deuterium oxide an excess of sodium carbonate (*ca.* 2 g.) was added. The product (0·11 g.) was extracted as described in (a), above, and found, by proton magnetic resonance and mass spectroscopy, to contain 4-methylpyridine (*ca.* 50%) and 4-[α-$^2H_1$]methylpyridine (*ca.* 50%). Similar experiments with penta-aquo-2- and -3-pyriodiomethylchromium(III) ions gave 2-methylpyridine with 2-[α-$^2H_1$]methylpyridine and 3-methylpyridine with 3-[α-$^2H_1$]methylpyridine, respectively.

As a check on the possible exchange of methylpyridines with deuterium oxide, 2-methylpyridine (0·238 g.) was subjected to the same evaporation procedure and worked up as described above. It contained no 2-[α-$^2H_1$]methylpyridine.

Analysis of Penta-aquopyridiomethylchromium(III) *Salts.*—A solution of purified penta-aquo-4-pyridiomethylchromium(III) perchlorate (10·0 ml.) was mixed with 0·5M-sodium hydroxide (25 ml.). After stirring the mixture, 1M-sulphuric acid (10 ml.) was added and the solution was made up to 250 ml. The ultraviolet spectrum of this solution showed the presence of 4-methylpyridine equivalent to $2{\cdot}90 \pm 0{\cdot}1 \times 10^{-5}$ moles in the original solution ($\lambda_{max.}$ 252·5 mμ, ε 4500).

An identical sample of penta-aquo-4-pyridiomethylchromium(III) perchlorate (10·0 ml.) was neutralised to pH 8 with sodium carbonate, and 1M-sulphuric acid (12 ml.) was added. 0·1M-Silver nitrate (2 ml.) and 5% potassium persulphate solution (5 ml.) were added and the solution was boiled for 20 min. After cooling, 0·01M-ferrous ammonium sulphate (25 ml.) and 1N-sulphuric acid (40 ml.) were added, and the excess of ferrous ion was titrated against 0·01M-potassium dichromate using *N*-phenylanthanilic acid as indicator. The amount of chromium in the original sample, calculated by the method of Vogel,[11] was $2{\cdot}88 \pm 0{\cdot}06 \times 10^{-5}$ mole. Similar analyses of penta-aquo-2- and -3-pyridiomethylchromium(III) perchlorate gave chromium : methylpyridine ratios of 1·00 ± 0·06.

Dissociation Constants.—Aliquots of a solution of penta-aquo-2-pyridiomethylchromium(III) perchlorate in 1M-perchloric acid were added to a series of sodium acetate–perchloric acid buffers so that the final pH of the solutions varied between 1 and 5·2. The pK_a of the complex ion (3·0 ± 0·25) was calculated by standard methods from the variation of the concentration of the complex ion and its conjugate base as measured by the change in optical density at 340 and 350 mμ. The existence of similar dissociation constants for penta-aquo-3- and -4-pyridiomethylchromium(III) and penta-aquo-2-(1-methylpyridio)methylchromium(III) ions was demonstrated by measurement of the spectra of these ions in a buffer of pH 5·2 and observation of the changes in spectra as the pH was progressively lowered to unity. In all cases isosbestic points were observed between the spectra of the ions and their conjugate bases (Table).

Magnetic Susceptibility.—The magnetic susceptibility of the 4-pyridiomethylchromium

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[10] H. I. Corson and B. B. Thayer, *J. Amer. Chem. Soc.*, 1948, **70**, 2330.

[11] A. I. Vogel, " Textbook of Quantitative Inorganic Analysis," 2nd edn., Longmans, London, 1955, p. 297.

ion in 2·5M-perchloric acid was measured by the method of Evans[12] using a Perkin-Elmer 60 Mc. spectrometer. t-Butyl alcohol and acetone were used as references, but in view of the uncertainties introduced by partial dissociation of the solution, and the bulk susceptibility of 2·5M-perchloric acid, the value obtained is only accurate to ±10%.

We thank the D.S.I.R. for the nuclear magnetic resonance and mass spectrometers, the University of London for a Postgraduate Studentship (R. G. C.), and Dr. M. L. Tobe for stimulating discussions.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET, LONDON W.C.1.

[*Received, June* 21*st*, 1965.]

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[12] D. F. Evans, *J.*, 1959, 2003.