pyrophosphate complex with a twofold increase in the total magnesium ion concentration and from $10^{6.10}$ to $10^{6.97}$ for the triphosphate complex with a tenfold increase in the total magnesium ion concentration. These variations which are much greater than the experimental deviation of $10^{\pm 0.06}$ can only be accounted for by the presence of a Mg_2L complex. Including this species in eq. (2) and solving pairs of equations simultaneously for both complexity constants yielded constant values for both complexity constants. The presence of a complex Mg_2L under these experimental conditions is not surprising since the experiments are performed with an excess of magnesium ion present. These experiments do not deny the existence of a species MgL_2 which might be obtained in the presence of a large excess of ligand. Martell and Schwarzenbach[10] mentioned $Mg_2P_3O_{10}^-$ as a possible complex species under these experimental conditions.

Our agreement with Martell and Schwarzenbach for the complexity constants of $MgP_3O_{10}^{3-}$ and $MgHP_3O_{10}^{2-}$ is fortuitous. Their supporting electrolyte was 0.1 *M* KCl with sodium ion added during the titration at 20° while our supporting electrolyte was close to 1.0 *M* $(CH_3)_3HCl$ at 25° with no alkali metal ion present since previous studies in this Laboratory have shown that alkali metals form stable complexes with pyro- and triphosphate ion. The effect of their larger acidity constants is cancelled by their finding no $Mg_2P_3O_{10}^-$ complex. This may have been the result of their varying the metal ion concentration over a smaller range of concentrations or the effect may have been masked as a result of the formation of mixed complexes containing both magnesium and alkali metal ions.

$$\beta_{MgP_2O_7} = \frac{(MgP_2O_7^{2-})}{(Mg^{2+})(P_2O_7^{4-})} = 10^{5.41 \pm 0.06}$$

$$\beta_{Mg_2P_2O_7} = \frac{(Mg_2P_2O_7)}{(Mg^{2+})^2(P_2O_7^{4-})} = 10^{7.75 \pm 0.09}$$

$$\beta_{MgP_3O_{10}} = \frac{(MgP_3O_{10}^{3-})}{(Mg^{2+})(P_3O_{10}^{5-})} = 10^{5.83 \pm 0.06}$$

$$\beta_{Mg_2P_3O_{10}} = \frac{(Mg_2P_3O_{10}^{-})}{(Mg^{2+})^2(P_3O_{10}^{5-})} = 10^{7.96 \pm 0.09}$$

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COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MALAYA]

Chelate Compounds of Nickel(II) with Picolinic Acid

BY R. W. GREEN

RECEIVED MAY 29, 1957

A spectrophotometric method has been used to demonstrate the existence of a tris-picolinato chelate of nickel(II) and to determine the three stability constants in aqueous solutions of ionic strength not exceeding 10^{-3}. The values found were log K_1, 6.68; log K_2, 5.98; log K_3, 5.12. Reasons are discussed for preferring these values to the slightly smaller figures given by the *p*H titration method.

A stable chelate compound of picolinic acid and nickel, having the formula $Ni(C_6H_4NO_2)_2 \cdot 2H_2O$, was prepared by Cox, Wardlaw and Webster[1]; and stability constants of the mono- and bis-picolinato derivatives recently have been determined by Holmes and Crimmin[2] and by Suzuki, Yasuda and Yamasaki.[3] In spite of the well-known hexacovalency of nickel(II), there appears to be no record of a tris-picolinato chelate. The system has been investigated here by a spectrophotometric method to which the high molar extinction of picolinic acid[4] is particularly favorable. The results are compared with those obtained by the *p*H titration method.

Experimental

Materials.—Picolinic acid, supplied by Hopkin and Williams, Ltd., was resublimed at 100° *in vacuo*. Its equivalent weight was checked by *p*H titration with standard alkali. A filtered solution of Analar nickel(II) chloride in boiled-out water was analyzed for nickel by electrodeposition and gravimetrically for chloride, the two values agreeing within 0.1%. The *p*H of the 0.1 *M* solution was 5.8.

Spectrophotometric Method.—Appropriate volumes of 0.1 *M* picolinic acid and 0.1 *M* nickel(II) chloride were mixed and diluted with boiled distilled water so that the total picolinic acid concentration was 2.5×10^{-3} *M*. The spectrophotometric solution was then prepared by further dilution to 10^{-4} *M* with respect to picolinic acid, with the addition of sufficient sodium hydroxide or hydrochloric acid to produce the required *p*H. Absorption spectra were measured at 25° in 1 cm. cells with a Beckman Model DU spectrophotometer, using a water-jacketed cell compartment. At 2650 Å. the molar extinction of the hydrated Ni^{++} ion is negligible compared with that of picolinic acid. Nevertheless, when high concentrations of nickel were present in the test solution, they were matched by equal nickel concentrations in the blank cell.

***p*H Method.**—Solutions for titration were 0.0025 *M* with respect to nickel and contained 2, 3 or 4 moles picolinic acid per mole nickel. They were titrated with carbonate-free 0.1 *M* NaOH while being stirred continuously with a current of purified nitrogen in a closed vessel. Measurements were made at 25° with the Beckman Model G *p*H meter and a glass electrode standardized at *p*H 4.00 with *M*/20 potassium hydrogen phthalate. Because of the uncertainties associated with calculations at low *p*H,[2] titrations with a strong acid were not attempted.

Results and Discussion

The addition of small amounts of nickel ion to aqueous picolinic acid causes changes in the absorption spectrum of the acid between 2400 and 2800 Å. However, the wave length of the absorption maximum remains unchanged at 2650 Å. and

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[1] E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 775 (1936).

[2] F. Holmes and W. R. Crimmin, *ibid.*, 1175 (1955).

[3] K. Suzuki, M. Yasuda and K. Yamasaki, *J. Phys. Chem.*, **61**, 229 (1957).

[4] R. W. Green and H. K. Tong, THIS JOURNAL, **78**, 4896 (1956).

at high nickel concentrations the molar extinction coefficient of the total acid attains a constant value, independent of nickel concentration and of *p*H between 2.5 and 8.0. The absorption curve in the presence of 0.1 *M* Ni^{++} is compared in Fig. 1 with curves for the three ionic species of free picolinic acid.

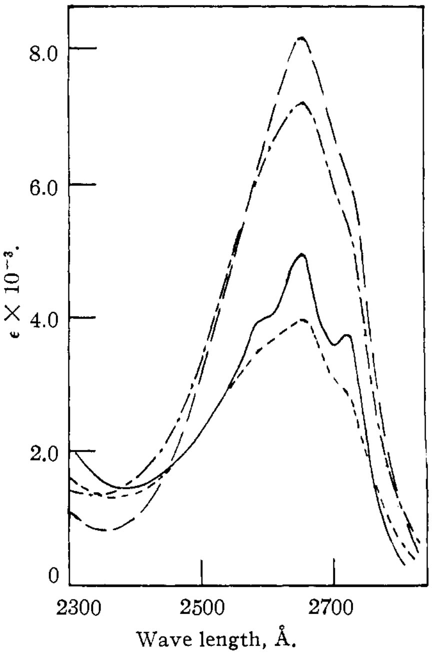

Fig. 1.—Absorption spectra: ——, picolinic acid in the presence of excess Ni^{++}; — —, cationic form of picolinic acid; — — — —, isoelectric form of picolinic acid; - - - -, anionic form of picolinic acid.

The very high values of the molar extinction coefficients of free and chelated picolinic acid at 2650 Å., and the fact that they differ widely at most *p*H values suggests their application to the study of the stability constants of nickel picolinates in dilute solution. In Fig. 2 the molar extinction coefficient, ϵ, of the total picolinic acid is plotted against *r*, the molar ratio of nickel to picolinic acid, at several *p*H values. The ionic strength of the test solutions varied with the amount of acid or alkali required to adjust the *p*H. At the lowest *p*H investigated (3.0), the ionic strength was 10^{-3}, but in other solutions it was much less.

While the curves in Fig. 2 differ markedly in slope when *r* is small, all were found to be asymptotic to $\epsilon = 4970$, which must be the molar extinction for the species NiA^+. Curve D, for *p*H 4.5, falls rapidly to $\epsilon = 4860$, when *r* is slightly greater than 0.5, but finally increases again to the common asymptote. The shape of the later part of this curve is most simply explained by the assumption that bis-picolinato nickel(II), NiA_2, is readily formed at this *p*H and that its molar extinction is 2×4860. However, if NiA_2 were the highest complex formed, curve D should lie throughout its course to the right of the straight line F, drawn through the points ($r = 0$, $\epsilon = 7040$) and ($r = 0.5$, $\epsilon = 4860$). Line F would be tangential to D when *r* is small and the degree of divergence of the two lines would be a measure of the dissociation of NiA_2. In fact, all the early part of D lies to the left of F, which can be explained only by postulating the existence of a third complex, presumably NiA_3^-.

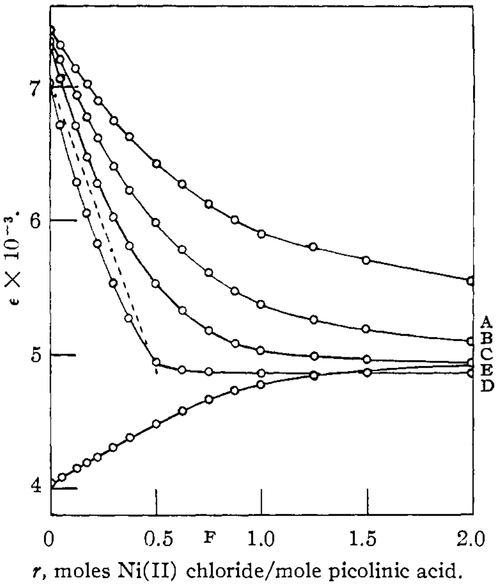

Fig. 2.—Effect of nickel(II) chloride on molar extinction of picolinic acid at 2650 Å.: A, *p*H 3.0; B, *p*H 3.5; C, *p*H 4.0; D, *p*H 4.5; E, *p*H 7.0; F, dotted line.

Above *p*H 4.5, the molar extinction of free picolinic acid decreases rapidly with increasing *p*H, approaching and then falling below that of the chelated acid. At *p*H 7.0 the acid exists almost entirely in the anionic form and the molar extinction coefficient has become almost constant at 4000, so that chelate formation now causes an increase, as shown in curve E. When $r = 0.33$ at *p*H 7.0, the greater part of the total acid should be present as NiA_3^-. Successive approximations based on the calculations to be described below lead to the conclusion that at this point $\bar{n}$ is near 2.6 and that ϵ for NiA_3^- is 3×4180. The course of curve E is then explained as initial almost quantitative formation of the tris-chelate, which is subsequently converted to the lower chelates as the mole ratio of nickel is increased. This causes a slow increase in ϵ until the asymptotic value is closely approached.

The observed optical density of a nickel–picolinic acid solution is now represented by the expression

$$D = [Ni^{++}]\epsilon_{Ni} + [NiA^+]\epsilon_{NiA} + [NiA_2]\epsilon_{NiA_2} + [NiA_3^-]\epsilon_{NiA_3} + [A_F]\epsilon_A \quad (1)$$

where $[A_F]$ represents the total free picolinic acid and ϵ_A is the molar extinction of the free acid at the *p*H of the solution being considered. The first term of the above expression is negligible and, depending on the *p*H, it is usually possible to neglect either the second or the fourth without serious error. The values of ϵ_{NiA} and ϵ_{NiA_2} are accurately known and that of ϵ_{NiA_3} can be estimated and then refined by successive approximation. It is now possible to calculate $[A_F]$ and hence $\bar{n}$ from the observed optical density.

In order to plot the formation curve of $\bar{n}$ against log $[A^-]$, values of $[A^-]$ are derived from the expression

$$[A^-]/[A_F] = k_1k_2/(a_H^2 + \gamma k_1 a_H + k_1k_2) \quad (2)$$

where $pk_1 = 1.01$, $pk_2 = 5.32$,[4] $\log a_H = -pH$, and, at the low ionic strengths used here, $\gamma = 1.0$. The points shown in Fig. 3 have been calculated in this way, omitting those where $[A_F]$ is less than 10% or greater than 90% of the total picolinic acid present. They support the conclusion already drawn concerning the existence of a third chelate. Stability constants for the complexes can now be calculated by the method of Irving and Rossotti[5] extended to the case for three constants

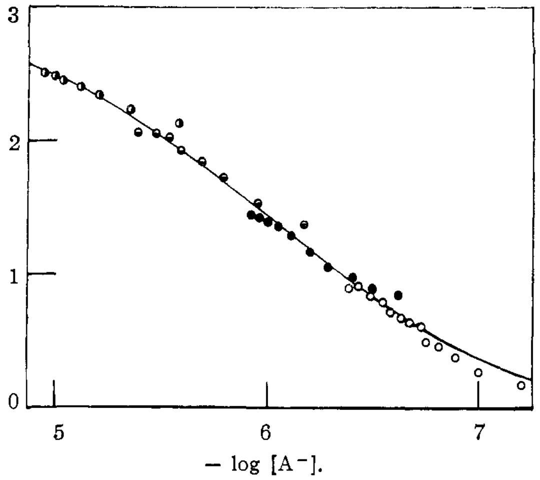

Fig. 3.—Formation curve for nickel(II) chelates of picolinic acid from spectrophotometric measurements: ○, *p*H 3.0; ●, *p*H 3.5; ◒, *p*H 4.0; ◑, *p*H 4.5.

$$\frac{\bar{n}}{(\bar{n}-1)[A^-]} = \frac{3-\bar{n}}{\bar{n}-1}[A^-]^2K_1K_2K_3 + \frac{2-\bar{n}}{\bar{n}-1}[A^-]K_1K_2 - K_1 \qquad (3)$$

The experimental data, transformed for substitution in eq. 3, were subjected to a multiple regression analysis, leading to the stability constants shown in the second column of Table I.

TABLE I

STABILITY CONSTANTS FOR NICKEL CHELATES OF PICOLINIC ACID

	This paper	Holmes and Crimmin[a]	Suzuki, *et al.*[b]
$\log K_1$	6.68	5.9	6.4
$\log K_2$	5.98	5.4	5.5
$\log K_3$	5.12		

[a] Ref. 2. [b] Ref. 3.

The continuous line in Fig. 3 is the theoretical formation curve calculated by substituting these values for K_1, K_2 and K_3 in eq. 3.

Table I shows that our stability constants differ appreciably from those found by other workers by *p*H titration. Moreover, values of $\bar{n}$ greater than 2 have not previously been recorded for this system. We therefore carried out *p*H titrations with alkali on three solutions in which the total nickel concentration was 2.5×10^{-3} *M*, in the presence of 2, 3 and 4 molar proportions of picolinic acid, respectively. The difference in shape between curves B and C in Fig. 4 provides qualitative support for the existence of the tris-chelate. The inflection in curve C near *p*H 5, characteristic of the second dissociation of picolinic acid, is absent from curve B. It is only in solutions containing more than three moles picolinic acid per nickel atom that the titration curve of the free acid makes its appearance. Values of $\bar{n}$, calculated from each titration curve in the usual way, are plotted in Fig. 5 together with the points reported by Holmes and Crimmin[2] and by Suzuki, *et al.*[3] The formation curve of Fig. 3 has also been reproduced here for comparison.

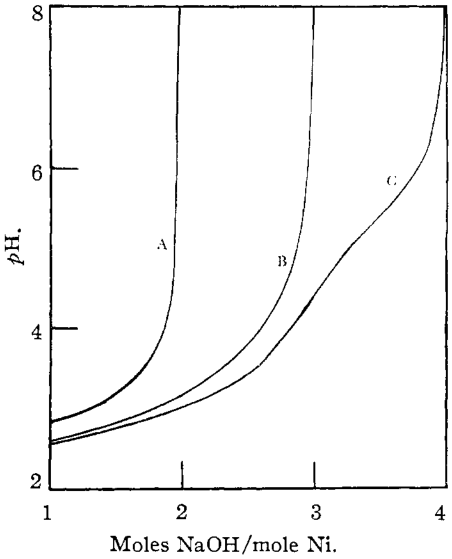

Fig. 4.—*p*H titration of solutions of nickel(II) chloride in the presence of 2, 3 and 4 moles picolinic acid (curves A, B, C, respectively).

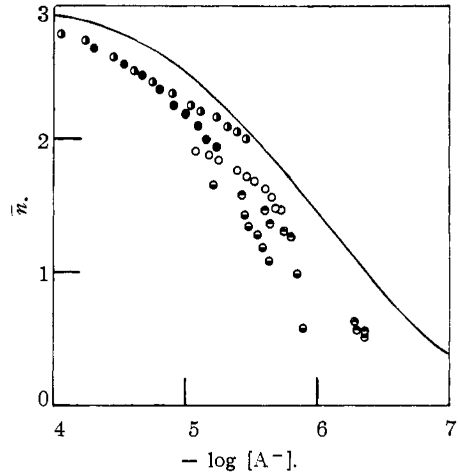

Fig. 5.—Formation function of nickel(II) chelates of picolinic acid. Continuous curve from spectrophotometric measurements. Experimental points from *p*H titrations: ○, curve A, Fig. 4; ◑, curve B; ●, curve C; ◒, ref. 2; ◓, ref. 3.

It will be seen at once that if a sufficient proportion of picolinic acid is available, values of $\bar{n}$ greater than 2 are readily obtained, but the points by this method all lie below the spectrophotometric formation curve. Part of the apparent disagreement between the results of the two methods may originate in the large random errors in $\bar{n}$ and $[A^-]$ which are

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(5) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 3397 (1953).

inherent in the titration method at low pH. The limitations of this method have been clearly indicated by Schwarzenbach and Freitag[6] and have been referred to by Holmes and Crimmin[2] in connection with chelates of pyridine carboxylic acids. This source of error, which is greatest in K_1, is augmented at appreciable ionic strengths by uncertainty about the activity coefficient, particularly of the divalent metal ion. The latter difficulty is absent from the present spectrophotometric measurements, where the ionic strength is so low that the activity coefficient can be safely taken as unity. Moreover, the points taken from the work of Suzuki, *et al.*, can be reconciled with our own by using our value of 1.01 for pk_1. Picolinic acid is a fairly strong acid in its first dissociation, so that the term $\gamma k_1 a_H$ is the principal one in the denominator of (2), which is thus fairly sensitive to errors in k_1. If the experimental points of Suzuki, *et al.*, are recalculated using our value of $pk_1 = 1.01$ instead of the earlier spectroscopic value, $pk_1 = 1.60$, then they are moved to the right and do not differ significantly from our pH titration figures.

Although the rather large random error appears as a marked degree of scattering in Fig. 5, nevertheless, even after reasonable assumptions have been made about the activity coefficients, the pH method still seems to lead to a formation curve significantly lower than that from spectrophotometric measurements, and it becomes necessary to inquire whether some fundamental error in the method of calculation may be responsible for the discrepancy. In the computation of $\bar{n}$ and $[A^-]$ it is assumed that the picolinic acid is either chelated or entirely free from the metal, and, while this is reasonable enough for ligands like ethylenediamine or oxalic acid, it is not quite so obvious for unsymmetrical ligands like the amino acids or picolinic acid. The isoelectric point of picolinic acid is about 3.16, and picolinic acid between pH 2 and pH 4 is present almost entirely as dipolar ions.[4] While some of these will undergo the normal chelation reaction with metals and contribute normally to the value of $\bar{n}$, others may possibly coördinate with the metal at the carboxylate ion only leaving the pyridinium ion unchanged. An effect of this kind already has been demonstrated[7] for compounds of chromium(III) with alanine, where both chelation and simple carboxylate coördination occur together in the same complex.

In the present case simple coördination would be undetected both in the pH method, which is concerned with displacement of the proton of the NH^+ group by a metal ion, and in the spectrophotometric method, since changes in the spectrum depend almost entirely on the state of combination of the nitrogen atom. If such an effect does occur, it will result in the true value of $[A^-]$ being less than the calculated value, so that the calculated experimental points in Fig. 5 will be too far to the left. It is shown easily by an approximate calculation that in this case the error in log $[A^-]$ will be roughly proportional to $m(3 - \bar{n})$, where m is the total nickel concentration. This provides a possible explanation of the results shown in Fig. 5. In the spectrophotometric method, m lay between 5×10^{-6} M and 1×10^{-4} M, while in our pH titrations m was 2.5×10^{-3} M throughout. If the effect we have described does occur, its magnitude in our pH titrations would be at least 25 times greater than in the spectrophotometric method and might cause the observed displacement of the potentiometric points to the left. The error would be most serious for low values of $\bar{n}$, causing differences particularly in K_1 found by the two methods.

We have therefore not calculated stability constants from the pH titrations, since we consider the spectrophotometric method to be superior in this instance, not only because of its lower random error but also because the use of dilute solutions tends to minimize possible systematic errors of the kind we have described.

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(6) G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1942 (1951).

(7) R. W. Green and K. P. Ang, THIS JOURNAL, **77**, 5482 (1955).

SINGAPORE 10, MALAYA

[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY OPERATED BY UNION CARBIDE NUCLEAR COMPANY]

The Estimation of Bisulfate Ion Dissociation in Sulfuric Acid–Sodium Sulfate Solutions

BY C. F. BAES, JR.

RECEIVED MAY 6, 1957

From available dissociation and activity coefficient data for pure sulfuric acid solutions, it is pointed out that the product of the ionic activity coefficients $(g^2_{H^+}g_{SO_4^-})$ varies with ionic strength in much the same way as does $(\gamma\pm)_{Na_2SO_4}^3$ for pure sodium sulfate solutions. The assumption that $(g^2_{H^+}g_{SO_4^-})$ shows a similar dependence on ionic strength in sulfuric acid–sodium sulfate solutions is then used to calculate bisulfate ion dissociation in such mixtures. The results are compared with published dissociation measurements in acidic sulfate solutions and with published isopiestic results for sodium bisulfate solutions.

In dealing with the chemistry of acidic sulfate solutions it is often desirable to assign values to the bisulfate ion dissociation quotient

$$Q = [H^+][SO_4^=]/[HSO_4^-] \qquad (1)$$

Necessary information concerning the variation of Q as a function of ionic strength and as a function of solution composition, however, is limited. The most reliable and extensive values of Q, primarily for solutions containing sulfuric acid alone, are provided by the Raman measurements of Young and co-workers.[1] In addition, less direct determinations of Q are available as a result of the conduc-

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(1) T. F. Young, *Rec. Chem. Progr.*, **12**, 81 (1951). Private communication from Prof. T. F. Young, L. F. Maranville and H. M. Smith, March, 1956.