[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Complexes of Nickel(II) Ion in Aqueous Solutions Containing Oxalate Ion and Ethylenediamine[1]

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The composition and complexity constants of the nickel(II) complexes in solutions containing mixtures of ethylenediamine and oxalate ion have been determined. Two new saturated mixed complex species, $Ni(C_2O_4)_2en^{-2}$ and $Ni(C_2O_4)(en)_2^0$, have been identified in aqueous solutions containing an excess of oxalate and the corresponding stoichiometric proportions of nickel(II) ion and ethylenediamine. With less oxalate present, the mixed complex $NiC_2O_4en^0$ also was obtained. The stepwise equilibria of nickel(II) with one to three oxalate ions have been established and the previously unreported formation constants have been solved on the basis of *p*H titrations. The stepwise formation constants of $Ni(C_2O_4)_3^{-4}$ are $K_1 = 10^{4.10}$, $K_2 = 10^{3.05}$ and $K_3 = 10^{1.36}$. The over-all complexity constants of the mixed complexes in terms of equilibria with the aquo nickel(II) ion and the free ligands are: $NiC_2O_4en^0$, $\beta_{11} = 10^{11.29}$; $Ni(C_2O_4)_2en^{-2}$, $\beta_{21} = 10^{13.02}$; $NiC_2O_4(en)_2^0$, $\beta_{12} = 10^{16.15}$. These constants were obtained in 1 *M* KNO_3 at 25°.

Introduction

The equilibria of tetracoördinate copper(II) ion with mixtures of oxalate ion and ethylenediamine have been discussed in previous papers.[3,4] Since nickel forms hexacoördinate complexes with ethylenediamine and other ligands, the possibility of forming at least three mixed complexes with two bidentate ligands was recognized. The system nickel(II) ion, oxalate ion and ethylenediamine, was investigated with the purpose of gaining more insight on the factors influencing the stability and the absorption spectra of complexes, especially those containing different kinds of ligands.

The stepwise addition of three ethylenediamine ligands (hereafter indicated by the symbol, en) to nickel(II) ion has been extensively investigated.[5,6] Poulsen and Bjerrum[7] recently obtained the values $10^{7.51}$, $10^{6.35}$ and $10^{4.42}$ for the successive formation constants and $10^{18.28}$ for the over-all complexity constant of $Ni(en)_3^{+2}$ in the presence of 1 *M* KNO_3 at 25°, in close agreement with the values obtained in this Laboratory.

The oxalate complex has been investigated at very low ionic strengths by means of conductivity[8] and solubility[9] measurements, but no previous systematic study of the stepwise equilibria has been reported. In the latter study it was found that two oxalate ions are bound even in millimolar oxalate concentrations. The total complexity constant for bis-(oxalato)-nickelate(II) was found to be $10^{6.51}$ at 25°. In the present investigation it will be shown that a third oxalate ion can also be bound to nickel(II) in solutions containing larger oxalate ion concentrations. Sartori[10] found that the polarographic electrode reaction of nickel(II) in oxalate solution was irreversible, so the shift in half wave potential is not a reliable criterion for complex stability.

Theoretical

The general equation for the various complex equilibria, assuming the absence of polynuclear species is

$$M + aA + bB \rightleftarrows MA_aB_b;\ \beta_{ab} = \frac{(MA_aB_b)}{(M)(A)^a(B)^b} \quad (1)$$

Throughout this paper the numerical subscripts after the complexity constant, β, or the stepwise constant, K, indicate the numbers of A and B ligands, respectively, in the higher complex involved in the equilibria. In the present study M indicates Ni^{+2}, A indicates $C_2O_4^{-2}$ and B indicates en. The coefficients, a and b, may vary from zero to three, but their sum does not exceed three. Parentheses indicate concentrations and brackets indicate activities. N' indicates the maximum number of bound ligands.

One may write for the mean number of bound A and B ligands

$$\bar{n}_a = \frac{\sum_{a=0}^{3}\sum_{b=0}^{3} a(MA_aB_b)}{\sum_{a=0}^{3}\sum_{b=0}^{3} (MA_aB_b)} = \frac{\sum_{a=0}^{3}\sum_{b=0}^{3} a\beta_{ab}(A)^a(B)^b}{\sum_{a=0}^{3}\sum_{b=0}^{3} \beta_{ab}(A)^a(B)^b} \quad (2)$$

$$\bar{n}_b = \frac{\sum_{a=1}^{3}\sum_{b=1}^{3} b(MA_aB_b)}{\sum_{a=0}^{3}\sum_{b=0}^{3} (MA_aB_b)} = \frac{\sum_{a=1}^{3}\sum_{b=1}^{3} b\beta_{ab}(A)^a(B)^b}{\sum_{a=0}^{3}\sum_{b=0}^{3} \beta_{ab}(A)^a(B)^b} \quad (3)$$

The coördination by hexacoördinate nickel (II) of three bidentate ligands, instead of two as is usual for copper (II), makes the mathematical treatment more involved than that in the previous paper in which the calculations were explained.[4] Just as in the former case, the formation functions can be solved for the cases in which $\bar{n}_b$ is equal to or close to a half integer while $\bar{n}_a$ is equal to or close to an integer.

The calculations are further complicated by the simultaneous existence of several complex species in practically all of the solutions. In this study, the complex species which must be considered are MA, MA_2, MA_3, MB, MB_2, MB_3, MAB, MA_2B and MAB_2. Since there is an unknown complexity constant for each of these nine complex species, at least nine, or, in general, $(N'+3)N'/2$ equations

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[2] Based in part on a thesis submitted by Robert DeWitt in partial fulfillment of the requirements for the M.S. degree, June, 1956.

[3] R. DeWitt and J. I. Watters, THIS JOURNAL, **76**, 3810 (1954).

[4] J. I. Watters, *ibid.*, **81**, 1560 (1959).

[5] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability" Constants," Part I, Organic Ligands, Special Publication No. 6, The Chemical Society, Burlington House, W. 1, London, 1957.

[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[7] J. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407, 1955.

[8] R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

[9] J. E. Barney, W. J. Argersinger, Jr., and C. A. Reynolds, THIS JOURNAL, **73**, 3785 (1951).

[10] G. Sartori, *Gazz. chim. ital.*, **64**, 3 (1934).

are required. In general, three additional equations are required since the oxalate ion concentrations are unknown in the ligand deficient solutions. The following $\bar{n}_b$ equations fulfill the requirements for solving the complexity constants, while $(C_2O_4^{-2})$ can be solved by means of the $\bar{n}_a$ equations.

In the present study the $\bar{n}_a$ function can be written

where the subscript r after K indicates that K is a replacement constant, and the numerical subscript indicates the number of B ligands present in the complex after the replacement of an A ligand. A combination of equations 1 and 17 yields the relations (18–20) between complexity and replacement constants. Temporary values for this constant can be obtained from the known

$$\bar{n}_a = \frac{3(MA_3) + 2(MA_2) + (MA) + 2(MA_2B) + (MAB_2) + (MAB)}{(MA_3) + (MA_2) + (MA) + (MA_2B) + (MAB_2) + (MAB) + (MB_3) + (MB_2) + (MB) + (M)} \quad (4)$$

Substituting complexity constants for complex concentrations yields

$$\bar{n}_a = \frac{3\beta_{30}(A)^3 + 2\beta_{20}(A)^2 + \beta_{10}(A) + 2\beta_{21}(A)^2(B) + \beta_{12}(A)(B)^2 + \beta_{11}(A)(B)}{\beta_{30}(A)^3 + \beta_{20}(A)^2 + \beta_{10}(A) + \beta_{21}(A)^2(B) + \beta_{12}(A)(B)^2 + \beta_{11}(A\ (B) + \beta_{03}(B)^3 + \beta_{02}(B)^2 + \beta_{01}(B) + 1} \quad (5)$$

The latter equation can be rearranged as follows to collect terms

$$(3 - \bar{n}_a)\beta_{30}(A)^3 + (2 - \bar{n}_a)\beta_{20}(A)^2 + (1 - \bar{n}_a)\beta_{10}(A) + (2 - \bar{n}_a)\beta_{21}(A)^2\,B + (1 - n_a)\beta_{12}(A)(B)^2 + (1 - \bar{n}_a)\beta_{11}(A)(B) = \bar{n}_a\beta_{03}(B)^3 + \bar{n}_a\beta_{02}(B)^2 + \bar{n}_a\beta_{01}(B) + \bar{n}_a \quad (6)$$

For the particular case in which $\bar{n}_a$ has the values 1 or 2 the later equation takes the following forms

For $\bar{n}_a = 1$ it becomes

$$2\beta_{30}(A)^3 + \beta_{20}(A)^2 + \beta_{21}(A)^2(B) = \beta_{03}(B)^3 + \beta_{02}(B)^2 + \beta_{01}(B) + 1 \quad (7)$$

For $\bar{n}_a = 2$ it becomes

$$\beta_{30}(A)^3 - \beta_{10}(A) - \beta_{12}(A)(B)^2 - \beta_{11}(A)(B) = 2\beta_{03}(B)^3 + 2\beta_{02}(B)^2 + 2\beta_{01}(B) + 2 \quad (8)$$

Equations 9 and 10 for $\bar{n}_b$ correspond to equations 4 and 5 for $\bar{n}^a$

$$\bar{n}_b = \frac{3(MB_3) + 2(MB_2) + (MB) + 2(MAB_2) + (MA_2B) + (MAB)}{(MB_3) + (MB_2) + (MB) + (MAB_2) + (MA_2B) + (MAB) + (MA_3) + (MA_2) + (MA) + (M)} \quad (9)$$

$$\bar{n}_b = \frac{3\beta_{03}(B)^3 + 2\beta_{02}(B)^2 + \beta_{01}(B) + 2\beta_{12}(A)(B)^2 + \beta_{21}(A)^2(B) + \beta_{11}(A)(B)}{\beta_{03}(B)^3 + \beta_{02}(B)^2 + \beta_{01}(B) + \beta_{12}(A)(B)^2 + \beta_{21}(A)^2(B) + \beta_{11}(A)(B) + \beta_{30}(A)^3 + \beta_{20}(A)^2 + \beta_{10}(A) + 1} \quad (10)$$

$$(3 - \bar{n}_b) - \beta_{03}(B)^3 + (2 - \bar{n}_b)\beta_{02}(B)^2 + (1 - \bar{n}_b)\beta_{01}(B) + (2 - \bar{n}_b)\beta_{12}(A)(B)^2 + (1 - \bar{n}_b)\beta_{21}(A)^2(B) + (1 - \bar{n}_b)\beta_{11}(A)(B) = \bar{n}_b\beta_{30}(A)^3 + \bar{n}_b\beta_{20}(A)^2 + \bar{n}_b\beta_{10}(A) + \bar{n}_t \quad (11)$$

For $\bar{n}_b = 1/2$ it becomes

$$5\beta_{03}(B)^3 + 3\beta_{02}(B)^2 + \beta_{01}(B) + 3\beta_{12}(A)(B)^2 + \beta_{21}(A)^2(B) + \beta_{11}(A)(B) = \beta_{30}(A)^3 + \beta_{20}(A)^2 + \beta_{10}(A) + 1 \quad (12)$$

For $\bar{n}_b = 3/2$ it becomes

$$3\beta_{03}(B)^3 + \beta_{02}(B)^2 - \beta_{01}(B) + \beta_{12}(A)(B)^2 - \beta_{21}(A)^2(B) - \beta_{11}(A)(B) = 3\beta_{30}(A)^3 + 3\beta_{20}(A)^2 + 3\beta_{10}(A) + 3 \quad (13)$$

For $\bar{n}_b = 5/2$ it becomes

$$\beta_{03}(B)^3 - \beta_{02}(B)^2 - 3\beta_{01}(B) - \beta_{12}(A)(B)^2 - 3\beta_{21}(A)^2(B) - 3\beta_{11}(A)(B) = 5\beta_{30}(A)^3 + 5\beta_{20}(A)^2 + 5\beta_{10}(A) + 5 \quad (14)$$

One set of conditions which often can be used to solve the complexity constants of the saturated species is that in which the excess concentration of ligand A is large enough so that most of the coördination positions are occupied. Under these conditions certain unsaturated species can be omitted from equations 9 to 13. Equations of the form $\bar{n}_a = N' - \bar{n}_b$ are equivalent to the corresponding $\bar{n}_b$ equations.

The stepwise addition of B to unsaturated species can be used to correlate and consequently to solve complexity constants from data obtained in ligand deficient solutions, thus

$$MA_aB_{b-1} + B \rightleftarrows MA_aB_b;\ K_{ab} = \frac{(MA_aB_b)}{(MA_aB_{b-1})(B)} \quad (15)$$

$$K_{ab} = \frac{\beta_{ab}}{\beta_{a(b-1)}} \quad (16)$$

where the subscripts after the K indicate the formula of the product after the stepwise addition of one molecule of B. It is possible to use these temporary constants obtained for mixed complexes at half integer values of $\bar{n}_b$ to solve mixed complexity constants by successive approximations.[6] For example, the complexity constant β_{12} of MA_1B_2 can be expressed as $\beta_{10}\cdot K_{11}\cdot K_{12}$.

Replacement equilibria prove very useful in evaluating complexity constants in solutions containing sufficient excess of ligand A so that most of the coördination positions of M are occupied by A or B ligands.

The general expression for these equilibria is

$$MA_{a+1}B_{b-1} + B \rightleftarrows MA_aB_b + A;\ K_{rb} = \frac{(MA_aB_b)(A)}{(MA_{a+1}B_{b-1})(B)} \quad (17)$$

A and B concentrations by assuming that (MA_aB_b) and $(MA_{a+1}B_{b-1})$ are equal at $\bar{n}_b = b - 1/2$.

$$K_{rb} = \frac{\beta_{ab}}{\beta_{(a+1)(b-1)}} \quad (18)$$

$$K_{r_1}\cdot K_{r_2}\cdot\cdots\cdot K_{rn} = \beta_{on}/\beta_{no} \quad (19)$$

$$K_{r_1}\cdot K_{r_2}\cdot K_{r_3} = \beta_{03}/\beta_{30} \quad (20)$$

The exact procedure for solving the formation functions for the various complexity constants depends somewhat on the relative stabilities of the various complexes. If the bonding of oxalate ion by nickel(II) had been essentially quantitative when present in (1:1) or (2:1) ratios, the calculations of complexity constants on the basis of temporary stepwise constants, K_{rb} or K_{ab}, would have been relatively easy. That such was not the case was discovered when $(C_2O_4^{-2})$ was calculated by substituting the temporary constants and the known (en) into the $\bar{n}_{ox} = 1$ or $\bar{n}_{ox} = 2$ equations, particularly in the later case, where the subscript ox indicates oxalate. When this situation became evident, the complexity constants of the saturated species and of bis-(oxalato)-nickelate(II), as well, were calculated first by successive substitutions of data for solutions containing an excess of oxalate into the appropriate $\bar{n}_{en}$ equations containing only the terms for these species, with alternate corrections of the free oxalate ion concentration for loss through complex formation.

The complexity constants of the unsaturated species, $Ni(C_2O_4)_2^{-2}$, $NiC_2O_4^0$ and $NiC_2O_4en^0$ were then solved simultaneously in determinant form by substituting data for solutions which were deficient or low in ligand concentration into the appropriate $\bar{n}_{en}$ equations. The oxalate concentrations were solved alternately by substituting the improving temporary constants and the known en concentration into the appropriate $\bar{n}_{ox}$ equation. The values of $\bar{n}_{ox}$ were successively corrected for free ion concentration. Details of the calculation will be discussed in the next section.

Spectrophotometric calculations are based on the expression

$$A = \log I_0/I = \sum_{a=0}^{3} \sum_{b=0}^{3} \epsilon_{ab} C_{ab} l \qquad (21)$$

where A is the absorbance and ϵ_{ab} and C_{ab} are the molar absorbance coefficient and the molar concentration, respectively, of the complex species MA_aB_b. The cell's light path length in cm. is indicated by l.

After solving pB from the known $\bar{n}_b$ value or pH with a known excess concentration of A, it is possible to solve the concentration of each species by the equation

$$(MA_aB_b) = \beta_{ab}(A)^a(B)^b \times C_M \div \sum_{a=0}^{N'} \sum_{b=0}^{N'} \beta_{ab}(A)^b(B)^a \qquad (22)$$

In solutions containing so large an excess of ligands that only saturated species are present, the two absorbance curves obtained with pure ligands A and B and two obtained in the presence of known pB or $\bar{n}_b$ are sufficient for the calculation of the molar absorbance coefficients and the absorbance curves of the two saturated mixed complex species.

Experimental

The apparatus, spectrophotometric techniques and preparation of the ethylenediamine are described in a previous paper.[11] In addition, stock solutions of 0.500 M nickel (II) nitrate were prepared and standardized by the conventional electrolytic and gravimetric[12] dimethylglyoxime methods. Separate portions of potassium oxalate were weighed to prepare concentrated 1 M oxalate solutions. A stock solution of 1 M $K_2C_2O_4$ was used in preparing the more dilute oxalate solutions for the pH titrations. The pH titrations at $\mu = 1$ were performed by adding 2.372 N HNO_3 from a microburet to 50 ml. of the solution containing 0.02 M Ni^{+2}, 0.06 M en, and varied concentrations of $C_2O_4^{-2}$. The ionic strength was adjusted to 1 M with KNO_3. The solutions were stirred by bubbling purified nitrogen through them until the pH readings became constant. Most of the spectrophotometric experiments were made in 1 M $K_2C_2O_4$. All experiments were performed at 25°.

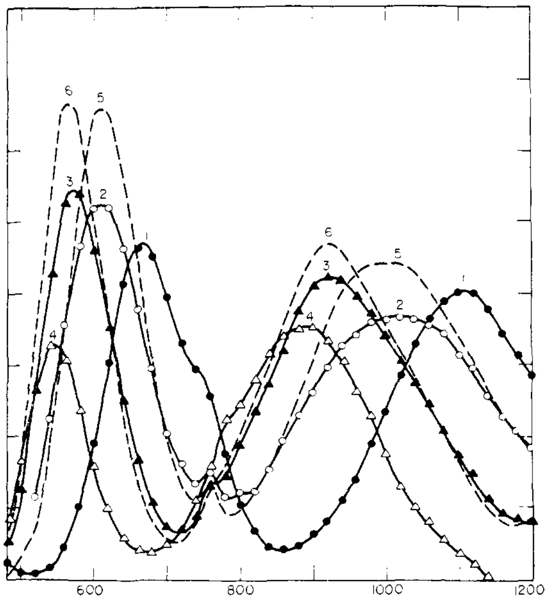

Fig. 1.—Absorbance curves of nickel(II) complexes with ethylenediamine, oxalate and their mixtures. Effect of varying the ratio (Ni^{+2}):$(C_2O_4^{-2})$:(en) by varying the amount of ethylenediamine added. All solutions contained 0.05 M $NiSO_4$ and 1.0 M $K_2C_2O_4$. Absorbance = $\log I_0/I$: 1 cm. cells were used: (1) no en; (2) 0.05 M en; (3) 0.10 M en; (4) 0.3 M en; (5) calculated for $Ni(C_2O_4)_2en^{-2}$; (6) calculated for $NiC_2O_4(en)^0_2$.

Results and Discussion

The first phase of the research[2] consisted of spectrophotometric experiments in which the concentrations and ratios of oxalate ion to ethylenediamine were varied stoichiometrically or by the addition of acid. It was observed that with en absent the absorption of 0.025 M nickel(II) increased greatly as the concentration of potassium oxalate increased from 0.1 M to 1 M. On the basis of published complexity constants, the conversion to bis-(oxalato)-nickelate(II) should have been essentially quantitative at the lower oxalate concentration. That a third oxalate ion is bound by the nickel (II) ion in high oxalate ion concentrations was confirmed in pH titration experiments discussed later. Most of the spectrophotometric studies were performed on solutions containing 1 M $K_2C_2O_4$ in order to shift the equilibrium between $Ni(C_2O_4)_2^{-2}$ and $Ni(C_2O_4)_3^{-4}$ nearly quantitatively toward the latter. Absorbance curves of solutions containing 0.05 M Ni^{+2}, 1.0 M $K_2C_2O_4$, and with concentrations of en increased by 0.01 M increments, were obtained in the wave length range of 500 to 1300 mμ. A third absorbance band in the ultraviolet was not investigated because of its proximity to the oxalate band. For clarity only the absorbances of solutions containing nickel ion and en in integral concentration ratios of 1:0, 1:1, 1:2 and 1:6 are included in Fig. 1. The theoretical absorbance curves 5 and 6 for the pure species $Ni(C_2O_4)_2en^{-2}$ and $NiC_2O_4en_2^0$ can be compared to curves 2 and 3, respectively, for the actual equilibrium mixture containing the same ratios of (Ni^{+2}) : (en).

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[11] J. I. Watters and E. Dan Loughran, THIS JOURNAL, **75**, 4819 (1953).

[12] W. F. Hildebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 408.

Curve 4, Fig. 1, for Ni $(en)_3^{+2}$ contains a maximum in the visible region at 540 mμ and one in the photoelectric infrared region at 890 mμ. Curve 1 for $Ni(C_2O_4)_3^{-4}$ contains two corresponding maxima at 668 and 1105 mμ. The absorbances of all the intermediate solutions exceeded those of the simple complexes in the region between 540 and 665 mμ, proving the presence of other complex species. The absorbance was much greater than was obtained by a similar change in en concentration in the absence of oxalate ion, indicating the presence of oxalate ions in addition to the en in the intermediate complexes. The first few curves of solutions having (Ni^{+2}):(en) ratios of 1:0 to 1:1 had isosbestics close to 485, 660, 800, 1090 and 1240 mμ. The last curves in the (Ni^{+2}):(en) ratios of 1:2 to 1:6 had a different set of isosbestics close to 470, 710 and 840 mμ. These effects can be accounted for by the presence of at least two new species. The failure of the isosbestics to persist in the region of (Ni^{+2}):(en) ratios of 1:1 and 1:2 indicated the simultaneous presence of more than two complex species in these solutions, with stepwise replacement constants differing by less than 100 fold.

By analogy with the observed behavior of copper (II) in similar solutions, the presence of saturated mixed complexes having formulas $Ni(C_2O_4)(en)_2^0$ and $Ni(C_2O_4)_2en^{-2}$ was postulated. Precipitates formed quickly in the solutions having compositions corresponding to $Ni(C_2O_4)en^{-2}$ and $NiC_2O_4en_2^0$. Consequently, Job's method was now applied to the absorbance in a somewhat different way to indicate the existence of complexes containing Ni^{+2} and en in 1:1 and 1:2 ratios. In this study the role of the oxalate ligand became analogous to that of water in the usual Job's method, since its concentration was kept large and constant. Furthermore, any of nickel's six coördination positions not occupied by en were assumed to be occupied by bidentate oxalate ions. The solutions containing (Ni^{+2}):(en) ratios of 1:0 and 1:3, respectively, corresponded to the solutions to be mixed, while the solutions containing intermediate ratios of (Ni^{+2}):(en) corresponded to their mixtures in various ratios. The presence of species containing Ni^{+2} and en in ratios of 1:1 and 1:2 was indicated by maxima at $x = 0.33$ at 640 mμ and at $x = 0.67$ at 540 mμ.

As a consequence of the simultaneous presence of several complex species in most of the solutions, the *p*H method based on formation functions proved to be less cumbersome and more accurate than spectrophotometric methods for calculating the various equilibrium constants. The procedure for the calculations differed somewhat from that in the previous publication[4] because the oxalate was not always quantitatively bound in the ligand deficient solutions, or even in the presence of a moderate excess of oxalate. In Table I are summarized the pertinent data from the *p*H titrations of 0.06 *M* ethylenediamine solutions in the presence of 0.02 *M* nickel(II) ion and concentrations of oxalate equal to zero or integral multiples of the nickel(II) concentration. Just as in the corresponding copper system, the presence of nickel (II) resulted in the lowering of the *p*H titration curve by about 3 *p*H units and the elimination of the first, but not the second, inflection. Increasing concentrations of oxalate caused the lowering in *p*H to decrease without changing the shapes of the titration curves.

The titration data are given in Table I. The total added concentrations of $C_2O_4^{-2}$ and H^+ are listed under the columns indicated by C_{ox} and C_H, respectively. The values of *p*en and $\bar{n}_{en}$ were calculated in the usual way[6] from the *p*H and C_H, using the values $K_1 = 10^{-7.56}$ and $K_2 = 10^{-10.22}$ for the acidic dissociation constants of H_2en^{+2} in 1 *M* KNO_3 at 25°. These values decreased to $10^{-7.66}$ and $10^{-10.30}$, respectively, when the ionic strength was maintained at unity with 0.25 *M* $K_2C_2O_4$ and 0.25 *M* KNO_3 at 25°. The *p*en values at half integral values of $\bar{n}_{en}$ were obtained by interpolation. Duplicate series of titrations using 0.05 *M* Ni^{+2} and 0.15 *M* en are not included since they yielded nearly identical results.

The stepwise formation constants of the simple $Ni(en)_3^{+2}$ complex were calculated by Bjerrum's method[6] of successive approximations in which the temporary formation constants were substituted into the formation functions. The calculated stepwise formation constants for $Ni(en)_3^{+2}$ were $10^{7.61}$, $10^{6.39}$ and $10^{4.35}$, all with a maximum deviation of $10^{\pm 0.04}$. These values agree well with the corresponding values $10^{7.51}$, $10^{6.35}$ and $10^{4.42}$ reported by Poulsen and Bjerrum[7] based on the values $K_1 = 10^{-7.49}$ and $K_2 = 10^{-10.17}$ for the acid dissociation constants of H_2en^{+2} under identical conditions.

At this point six equilibrium constants remained to be determined. Furthermore, the oxalate ion concentrations were unknown in the ligand deficient solutions but could be estimated quite accurately in the presence of excess ligand. Attention first was directed to those solutions containing a relatively large excess of both ligands, so that the only species besides $Nien_3^{+2}$ present in significant concentrations were $NiC_2O_4(en)_2^0$, $Ni(C_2O_4)_2en^{-2}$, $Ni(C_2O_4)_3^{-4}$ and $Ni(C_2O_4)_2^{-2}$.

Temporary constants were obtained for $NiC_2O_4(en)_2^0$, $Ni(C_2O_4)_2en^{-2}$ and $Ni(C_2O_4)_3^{-4}$ on the basis of the following considerations. When $\bar{n}_{en}$ changes from 3 to 2.5, in the presence of excess oxalate, stoichiometry considerations indicate the presence of approximately equal concentrations of $Nien_3^{+2}$ and $NiC_2O_4en_2^0$. At $\bar{n}_{en} = 1.5$, approximately equal concentrations of $NiC_2O_4(en)_2^0$ and $Ni(C_2O_4)_2en^{-2}$ are indicated. At $\bar{n}_{en} = 0.5$, approximately equal concentrations of $Ni(C_2O_4)_2en^{-2}$ and a mixture of $Ni(C_2O_4)_3^{-4}$ and $Ni(C_2O_4)_2^{-2}$ should be obtained. These temporary constants, indicated by primes, were obtained from the titration in the presence of 0.25*M* oxalate as indicated: at $\bar{n}_{en} = 2.5$, neglecting the trace of $Ni(C_2O_4)_2^{-2}$, the free oxalate ion is calculated to be 0.24 *M*, so $p_{ox} = 0.62$. Substitution of the data into equations 17 and 18 yielded $K'_{r3} = 10^{2.13}$, so $\beta'_{12} = 10^{16.25}$. At $\bar{n}_{en} = 1.5$, neglecting $Ni(C_2O_4)_2^{-2}$, $(C_2O_4^{-2}) = 0.22$ *M*, so $p_{ox} = 0.66$. Substitution of these data into equations 14 and 15 yielded $K'_{r2} = 10^{3.36}$ and $\beta'_{21} = 10^{12.89}$. At $\bar{n}_{en} = 0.5$, no significant error was introduced in $(C_2O_4^{-2})$ by neglecting $Ni(C_2O_4)_2^{-2}$, so $(C_2O_4^{-2}) = 0.20$ *M* and $p_{ox} = 0.70$. Substitution

TABLE I

TITRATION DATA AND CALCULATIONS WITH VARIED OXALATE CONCENTRATION

Fifty ml. of the solution titrated contained 0.06 *M* ethylenediamine, 0.02 *M* Ni^{+2} and varied concentrations of $C_2O_4^{-2}$ ion, with KNO_3 added to produce an ionic strength of unity at 25°. Nitric acid, 2.372 *N*, was added from a 10 ml. microburet. The total concentration of nitric acid in 50 ml. of solution is indicated under the heading C_H, while *pen* and *pox* indicate −log (en) and −log ($C_2O_4^{-2}$).

C_{ox}	C_H	*p*H	*pen*	$\bar{n}_{en}$	*pen* at half integer	*pox* at half integer	Equil. const.	Log temporary *K*
0.0	0.010	8.15	4.25	2.585	4.37	0.0	K_{03}	4.37
	.015	7.88	4.46	2.433				
	.055	6.54	6.28	1.56	6.38	.0	K_{02}	6.38
	.060	6.43	6.46	1.447				
	.095	5.79	7.53	0.645	7.67	.0	K_{01}	7.67
	.100	5.70	7.68	0.485				
.02	.010	8.53	3.77	2.544	3.85	2.00	K_{r3}	1.83
	.015	8.16	4.06	2.375				
	.055	7.06	5.33	1.579	5.42	2.42 ($\bar{n}_{ox}$ = 0.81)	K_{12}	5.42
	.060	6.97	5.45	1.469				
	.095	6.08	6.95	0.581	7.11	3.19 ($\bar{n}_{ox}$ = 0.97)	K_{11}	7.11
	.100	5.96	7.17	0.470				
.04	.010	8.80	3.47	2.526	3.43	1.52	K_{r3}	1.91
	.015	8.37	3.79	2.338				
	.050	7.42	5.00	1.508	5.01	..	K_{r2}	3.01
	.055	7.15	5.12	1.401				
	.095	6.38	6.36	0.549	6.46	1.86	K_{21}	6.46
	.100	6.26	6.57	0.439				
.06	0.010	8.99	3.26	2.517	3.29	1.30	K_{r3}	1.99
	.015	8.57	3.55	2.311				
	.050	7.50	4.58	1.535	4.62	1.52	K_{r2}	3.10
	.055	7.40	4.71	1.427				
	.095	6.54	6.04	0.516	6.06	1.84	K_{r1}	4.22
	.100	6.44	6.17	0.400				
.08	.010	9.10	3.14	2.513	3.16	1.15	K_{r3}	2.01
	.015	8.66	3.45	2.301				
	.040	7.69	4.32	1.597	4.41	1.30	K_{r2}	3.11
	.045	7.58	4.45	1.463				
	.085	6.80	5.56	0.570	5.84	1.46	K_{r1}	4.38
	.090	6.70	5.87	0.492				
.15	.010	9.36	2.92	2.508	2.93	0.85	K_{r3}	2.08
	.015	8.94	3.18	2.228				
	.040	7.84	4.15	1.540	4.21	.92	K_{r2}	3.29
	.045	7.72	4.29	1.444				
	.085	6.90	5.46	0.505	5.47	.99	K_{r1}	4.48
	.090	6.70	5.76	0.354				
.25	.01	9.57	2.74	2.506	2.75	.62	K_{r3}	2.13
	.015	9.16	3.02	2.396				
	.040	8.01	3.97	1.585	4.02	.66	K_{r2}	3.36
	.045	7.90	4.10	1.352				
	.080	7.24	4.95	0.680	5.08	.70	K_{r1}	4.38
	.085	7.15	5.11	0.465				

of these data in equations 17 and 18 yielded $K'_{r1} = 10^{4.38}$ and $\beta_{30} = 10^{8.51}$. More accurate values of β_{12}, β_{21} and β_{30} were obtained by means of successive approximations in the appropriate equation 12, 13 or 14, with successive corrections of ($C_2O_4^{-2}$) for bound oxalate in saturated complexes and finally in $Ni(C_2O_4)_2^{-2}$ as well. Temporary values of $10^{7.22}$ and $10^{8.51}$ were obtained for the complexity constants of the bis- and tris-(oxalato)-complexes by simultaneously solving equations of the form of equation 13 containing the data obtained for the titration in the presence of 0.15 *M* and 0.25 *M* oxalate at $\bar{n}_{en} = 0.5$. Then, values of $10^{16.19}$ and $10^{13.04}$ for β_{12} and β_{21}, respectively, were recalculated by means of equations 13 and 14, from the data of the titration in the presence of 0.08 *M* oxalate at $\bar{n}_{en} = 2.5$ and 1.5.

At this stage, the constants β_{11} and β_{10} for unsaturated species, $NiC_2O_4en^0$ and $NiC_2O_4^0$, were unknown and β_{20} for $Ni(C_2O_4)_2^{-2}$ needed confirmation. Equation 7 for $\bar{n}_{ox} = 1$ contains no β_{11} or β_{10} terms, so this expression was first solved for ($C_2O_4^{-2}$) using the p_{en} values of the titration in the presence of 0.02 *M* oxalate at $\bar{n}_{en} = 0.5$ and 1.5. These results indicated that $C_2O_4^{-2}$ was essentially quantitatively bound only at $\bar{n}_{en} = 0.5$ in the titration in the presence of 0.02 *M* oxalate, and not even approximately in the presence of 0.04 *M* oxalate. Consequently ($C_2O_4^{-2}$) was solved by successive approximations in general equation 6, with alternate corrections of $\bar{n}_{ox}$ for free oxalate ion concentration. The small contribution of $NiC_2O_4en^0$ was solved by the use of a temporary constant calculated from the 0.02 M oxalate titration data at $\bar{n}_{en} = 3/2$. Substitution of these data into equations 18 and 19 yielded $K_{12} = 10^{5.42}$ and $\beta'_{11} = 10^{10.77}$. These improved data were substituted into equation 11 to obtain $\beta'_{11} = 10^{11.29}$.

Finally, values of β_{10}, β_{20} and β_{11} for the unsaturated complexes were solved simultaneously by means of determinants. The data of the 0.02 M oxalate titration at $\bar{n}_{en}$ = 0.5 and 1.5, and the titration in the presence of 0.06 M oxalate at $\bar{n}_{en}$ = 0.5 were substituted into equations 12 and 13 along with ($C_2O_4^{-2}$) previously solved according to equation 6 by means of successive approximations. All of the constants converged quickly.

The complexity constants values obtained for the mixed complexes are

$$\beta_{12} = \frac{(NiC_2O_4en_2{}^0)}{(Ni^{+2})(C_2O_4{}^{-2})(en)^2} = 10^{16.15 \pm 0.06}$$

$$\beta_{21} = \frac{(Ni(C_2O_4)_2en^{-2})}{(Ni^{+2})(C_2O_4{}^{-2})^2(en)} = 10^{13.02 \pm 0.08}$$

$$\beta_{11} = \frac{(NiC_2O_4en^0)}{(Ni^{+2})(C_2O_4{}^{-2})(en)} = 10^{11.29 \pm 0.10}$$

The values obtained for stepwise formation constants of the oxalate complexes are

$$K_{10} = \frac{(NiC_2O_4{}^0)}{(Ni^{+2})(C_2O_4{}^{-2})} = 10^{4.10 \pm 0.10}$$

$$K_{20} = \frac{(Ni(C_2O_4)_2{}^{-2})}{(NiC_2O_4{}^0)(C_2O_4{}^{-2})} = 10^{3.05 \pm 0.10}$$

$$K_{30} = \frac{(Ni(C_2O_4)_3{}^{-4})}{(Ni(C_2O_4)_2{}^{-2})(C_2O_4{}^{-2})} = 10^{1.36 \pm 0.10}$$

The latter correspond to a value of $10^{8.51 \pm 0.10}$ for the over-all complexity constant β_{30} of tris-(oxalato)-nickelate (II), a value of $10^{7.15 \pm 0.10}$ for the complexity constant β_{20} of bis-(oxalato)-nickelate(II) and $10^{4.10 \pm 0.10}$ for mono-(oxalato)-nickel(II).

It is of interest to compare the mixed complexity constants with the values which one might predict from those of the simple complexes. The free energy change, ΔF^0, due to the replacement of the bound water in the aquo complex by N' ligands in the simple saturated complex, is equal to $- RT \ln \beta_{N'}$. If all of the bonds are equivalent the free energy change for each bound ligand must be $-(RT/N') \ln \beta_{N'}$. Accordingly, the logarithm of the N'th root of $\beta_{N'}$ for a simple complex, $\log \beta_{N'}^{1/N'}$ may be taken as a measure of this free energy change per bound ligand. Bjerrum[13] has used this value as a measure of the complex formation tendency of a ligand.

The gross statistical effect is absent in the complexity constant of the saturated complex, since there are N' ligands in the complex and N' positions available in the aquo ion. However, there is a statistical factor in the complexity constant of mixed complexes which can be arrived at thus: with equal concentrations of A and B ligands the probability that the first bonded ligand will be A is $^1/_2$. The probability that three successive A's will bond with M to form MA_3 is $^1/_2 \cdot {}^1/_2 \cdot {}^1/_2$, or one in eight. The same probabilities hold for MB_3. The remaining six of eight probabilities are equally divided between MA_2B and MAB_2. The statistical probability of forming either of the latter is three times that of either simple complex. On the basis of these considerations one would predict a complexity constant for $Ni(C_2O_4)_2en^{-2}$ of $3 \times \beta_{20}{}^{2/3} \times \beta_{03}{}^{1/3}$, or $10^{12.29}$, compared to $10^{13.02}$ observed. The enhancement is $10^{+0.73}$. Similar calculations for $NiC_2O_4(en)_2{}^0$ lead to a calculated complexity constant of $10^{15.58}$, corresponding to an enhancement of $10^{+0.57}$.

In the calculation of the complexity constant, β_{11}, for $NiC_2O_4en^0$, the statistical factor favoring mixed complex formation is two. In this case, however, the term $\beta_{N'}^{1/N'}$ also contains a gross statistical factor of 3/2, since there are only two ligands in the complex whereas the aquo ion has a capacity for three ligands. Thus, the ligand factor becomes $(2/3\beta)^{1/N'}$. The observed value, $10^{11.29}$, is larger than the calculated value, $10^{10.70}$, by $10^{0.59}$. Similar calculations for the copper(II) complexes, $CuP_2O_7(NH_3)_2{}^{-2}$ and $CuC_2O_4en^0$, indicate enhancements of about $10^{0.50}$. The enhancement may be due to some weak bonding between unlike bound ligands, possibly through hydrogen bonding between the oxygen atoms and the hydrogen of the amine. In any event these calculations indicate an interesting and fairly accurate method for estimating mixed complexity constants. Studies of this enhancement of the bonding in mixed complexes for various types of ligands are being continued.

The calculations of the molar absorbance coefficients and the absorbance curves for $NiC_2O_4(en)_2{}^0$ and $Ni(C_2O_4)_2en^{-2}$ require the molar concentrations of the various species. Accordingly the titration procedure was used to calculate the complexity constants of the saturated species in the 1 M $K_2C_2O_4$ solutions in which the spectrophotometric measurements were made.

The formation constants of $Ni(en)_3{}^{+2}$ at $\mu = 3$ were obtained in a solution containing 3 M KNO_3 with oxalate absent. In 3 M KNO_3 at 25°, pK_1 and pK_2 of H_2en^{+2} were found to be 7.80 and 10.40, while in 1 M $K_2C_2O_4$ the values were 8.17 and 10.63. From the mean p_{en} values of 7.70, 6.59 and 4.64 at $\bar{n}_{en}$ = 0.5, 1.5 and 2.5, respectively, were calculated for the stepwise formation constants of $Ni(en)_3{}^{+2}$ in 3 M KNO_3 at 25°: $K_0 = 10^{76.1}$, $K_{02} = 10^{6.67}$ and $K_{03} = 10^{4.65}$, which correspond to an over-all value of $10^{18.93}$ for β_{03}.

In 1 M $K_2C_2O_4$ the p_{en} values were 4.60, 3.58 and 2.42 at $\bar{n}_{en}$ = 0.5, 1.5 and 2.5, respectively. From these data, these values were calculated for the replacement constants in 1 M $K_2C_2O_4$ at 25: $K_{r1} = 10^{4.49}$, $K_{r2} = 10^{3.59}$ and $K_{r3} = 10^{2.49}$. The β values obtained were $NiC_2O_4(en)_2{}^0$, $\beta_{12} = 10^{16.44}$; $Ni(C_2O_4)_2en^{-2}$, $\beta_{21} = 10^{12.85}$; $Ni(C_2O_4)_3{}^{-4}$, $\beta_{30} = 10^{8.36}$.

The absorbance calculations were made on the basis of the spectrophotometric data for solutions containing 0.05 M $Ni(NO_3)_2$, 1.0 M $K_2C_2O_4$ and these various (Ni^{+2}):(en) ratios; 1:0, 1:1, 1:2 and 1:10. Values of 4.07 and 3.03 were calculated for p_{en} in the (1:1) and (1:2) solutions, respectively, by means of the $\bar{n}_{en}$ formation functions assigned values of 1 and 2, respectively, proving that the en was essentially quantitatively bound. The con-

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[13] J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

TABLE II

ABSORBANCE DATA

	Visible band			Near infrared band			
Species	Wave length, mμ	Absorb, M^{-1} cm.$^{-1}$	Half band width, cm.$^{-1}$	Wave length, mμ	Absorb., M^{-1} cm.$^{-1}$	Half band width, cm.$^{-1}$	Freq. ratio
$Nien_3^{+2}$	540	6.56	3220	890	7.12	3050[a]	1.648
$NiC_2O_4(en)_2^0$	562	13.44	3000	924	9.46	2820	1.644
$Ni(C_2O_4)_2en^{-2}$	612	13.30	2910	1010	8.88	2790	1.650
$Ni(C_2O_4)_3^{-4}$	668	9.44	3340[a]	1105	8.08	2220	1.654

[a] These bands have a shoulder in the 700–800 mμ range.

centrations of the four saturated species in equilibrium then were solved by means of equation 22. These values in turn were substituted into equation 21 to obtain the absorbance data of Table II for the two absorbance peaks in the 400 to 1300 mμ region.

No detailed study has been made as yet in this Laboratory of the theoretical significance of the absorbance curves. In a series of papers on the application of ligand field theory to complex ions, Jorgensen[14] has included calculations on $Ni(en)_3^{+2}$ which agree well with the experimental values for the absorbance maxima. There are indications that a similar treatment of the mixed complexes may not be too involved. First, the frequency of either absorbance maximum was found to be essentially a linear function of the logarithm of the complexity constant of the corresponding complex. As expected, other ligands having a different number of coördination positions, for example, ammonia and ethylenediaminetetraacetic acid, did not fit this relation. This is reasonable, since the statistical and other entropy factors, which also contribute to the equilibrium constant, must be different for ligands having a different number of coordination positions. This linear relation indicates that, at least to a first approximation, the energy level is a linear function of the ligand field strength. This follows if one may assume that for a particular type of complex the logarithms of the complexity constants are proportional to the bond strength[13] and, in turn, to the field strength.

Although both maxima shifted to higher frequencies with increasing log K, the frequency ratio of the two maxima for a particular complex retained the constant value of 1.65. This effect, which depends on the fact that the various d-orbitals are subjected to the same ligand fields, indicates that the bond type and electron distribution are not changed in this series of complexes.

A third characteristic is the enhanced molar absorbance of the mixed complexes compared to that of the simple complexes. This effect may be associated with a greater multiplicity of the d-orbital energy levels associated with the unsymmetrical electric field of the mixed octahedral complex. In this connection, the polyethylenediamine[15] complexes with nickel(II) also exhibit exceptionally high absorbances. Since there is evidence of some strain in these complexes, these fields may also be quite unsymmetrical. In this connection, it should be mentioned that during the stepwise addition of ammonia to nickel(II) to form $Ni(NH_3)_6^{+2}$, the molar absorbance coefficient[6] increases regularly to a maximum for $Ni(NH_3)_4^{+2}$, after which it decreases. $Ni(NH_3)_3^{+2}$ and $Ni(NH_3)_5^{+2}$, as well as one of the geometric isomers of $Ni(NH_3)_4^{+2}$, are unsymmetrical. Statistically, the probability of forming the latter unsymmetrical isomer is two out of three. This enhancement does not necessarily occur in complexes having different geometric configurations. For example, the corresponding copper(II) complex, $CuC_2O_4en^0$, which has a square configuration, has a molar absorbance coefficient[3] which is intermediate between those of the simple species, $Cu(C_2O_4)_2^{-2}$ and $Cu(en)_2^{+2}$.

In all of the curves there is either a small peak or a shoulder in the wave in the 700–800 mμ range. This is believed to correspond to a relatively improbable additional electronic transition in all of the species, rather than to other species such as a hydroxy complex, because this characteristic persists independently of *p*H variations. Jorgensen[16] has discussed some low intensity bands of transition metal complexes. All curves having the same maxima have the same shoulders even though the composition and *p*H are varied.

The half band widths given in Table II do not yield any unique information. Except for the shoulders and the exceptionally narrow near infrared band of $Ni(C_2O_4)_3^{-4}$, the widths are 3000 ± 200 cm.$^{-1}$.

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[14] C. K. Jorgensen, *Acta Chem. Scand.*, **8**, 1495 (1954); **9**, 1362 (1955); **10**, 887 (1956); **11**, 1223 (1957); **12**, 903 (1958).

[15] T. A. Youness, Ph.D. Thesis, The Ohio State University, 1959.

[16] C. K. Jorgensen, *Acta Chem. Scand.*, **8**, 1502 (1954).