cyclohexane, these are termed axial and equatorial. With *meso*-stilbenediamine as ligand, one of the phenyl groups is axial to the ring and the other equatorial, while, in the case of the active isomers, both groups are equatorial. The relative disposition of the two phenyl groups is clearly seen in the diagrams of the two crystal structures. To this difference in stereochemistry, between the complexes containing the *meso* isomer on the one hand and the active isomer on the other, can thus be attributed the much greater tendency of the former to give planar, tetracoordinate complexes,[21] as in these the axial positions are sterically hindered to a large degree, preventing the close approach of bulky anions or large solvent molecules, and the absence of tris-complexes with the *meso* isomer. In contrast, the active bases readily form hexacoordinated complexes containing either two or three molecules of diamine, which are very similar to the nickel ethylenediamine complexes.

In conclusion, then, it can be seen that the mechanism put forward by Ballhausen and Liehr[22] to explain the changes in magnetic and spectroscopic properties which occur on dissolution, solvation, etc., is confirmed, although some of their detailed predictions regarding the structures of these complexes and their probable similarity to the Cu(II) acetate bridged systems are incorrect. It is clear that in all the compounds described by Lifschitz,[21] the planar coordination of diamine molecules is retained throughout and the changes are brought about by variation in the axial ligand field. In the yellow diamagnetic complexes, the effective axial ligand field is zero and the strong in-plane ligand field, due to the diamine molecules, causes the singlet ${}^1A_{1g}$ state to be the ground state, whereas in the blue octahedral complexes, the axial ligand field stabilizes the triplet ${}^3A_{2g}$ state (assuming a ligand field of O_h symmetry) and the complexes are paramagnetic. It is interesting to note that the in-plane field in these is weaker than that in the yellow complex according to the observed bond length differences in the two molecules.

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Complexes of Nickel with N,N,N′,N′-Tetrakis(2-hydroxyethyl)ethylenediamine and Sodium Hydroxide[1]

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Complex ions formed by the nickel(II) ion with N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine, TKED, have been investigated in dilute aqueous solution. Spectrophotometric data and potentiometric titrations give evidence of the formation of the complex ion containing one molecule of TKED per nickel(II) ion (NiTKED^{+2}). This complex ion behaves as a dibasic acid by reacting with hydroxyl ions to form complexes of the type Ni(TKED-H$^+$)$^+$ and Ni(TKED-2H$^+$)^0. However, only the first dissociation constant could be calculated: $pK_{A_1} = 9.07$. The acid dissociation constants for the protonated TKED molecule, TKEDH$_2^{+2}$, were determined and the average values are $K_{AH_2} = 3.54 \times 10^{-5}$ and $K_{AH} = 3.54 \times 10^{-9}$. The formation constant for the formation of NiTKED^{+2} was found to be 3.17×10^6.

Introduction

This paper reports a study of the complexes of nickel(II) ion with N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (TKED) in the presence and absence of a strong base. On chelation, the four nitrogen-to-oxygen chains are in favorable position for the formation of stable five-membered chelate rings as well as the nitrogen chain. The hydroxyl radicals of TKED are found to have nearly negligible acidic properties in water solution. Their acidity increases appreciably, however, when the hydroxyl radical becomes a part of the chelate ring.[2] The ions formed by the successive additions of protons to the first and second nitrogen atoms of TKED will be designated TKEDH$^+$ and TKEDH$_2^{+2}$, respectively. The complex ion formed from the nickel(II) ion and TKED will be designated NiTKED^{+2}, the ion formed by the removal of a single proton from a coordinated hydroxyl group of the NiTKED^{+2} complex ion will be written as Ni(TKED-H$^+$), while the corresponding neutral molecule formed by the removal of two such protons will be written as Ni(TKED-2H$^+$)^0.

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[1] Presented before the Division of Inorganic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962.

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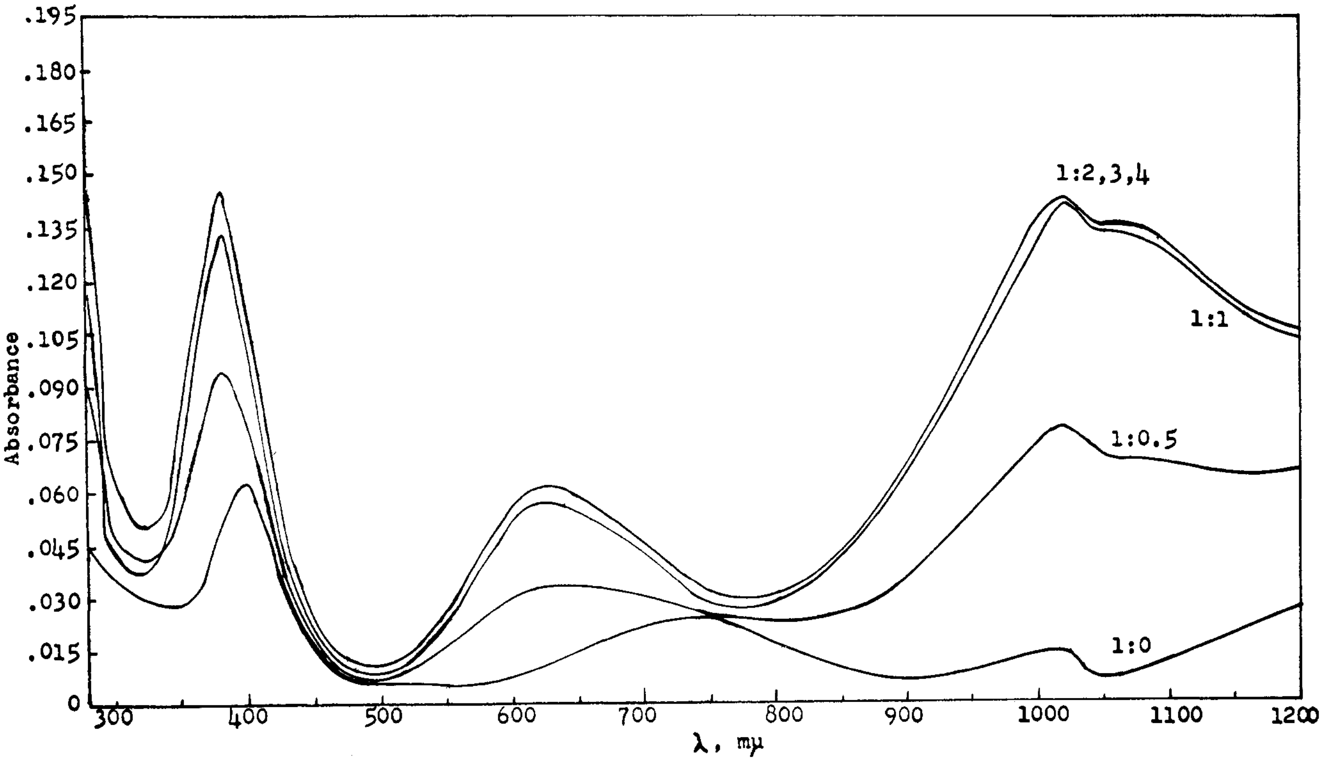

Fig. 1.—Absorption spectra of solutions 0.010 *M* in $Ni(ClO_4)_2$ with varying amounts of TKED.

Experimental

The TKED was a gift of Arnold, Hoffman and Company and was designated as being 98% pure, the only significant impurity being water; therefore, the purity was determined by Fritz's method.[3] Standard solutions of disodium dihydrogen ethylenediamine tetraacetate were prepared according to the procedure of Blaedel and Knight[4] and tested for purity according to the procedure of Fritz, Lane, and Bystroff.[5] Carbonate-free sodium hydroxide and nitric acid solutions were prepared from reagent grade stock and were standardized by the usual methods. Solutions of potassium nitrate, sodium perchlorate, and nickel(II) perchlorate were prepared from reagent grade stock. The nickel(II) perchlorate solutions were standardized by titration with standard EDTA solution using Murexide as the indicator.[6]

A Beckman DU quartz spectrophotometer using matched 1-cm. silica cells was used in all the absorbance measurements. The cells had only negligible differences in light path and thus no calibration factors were employed. The solutions for spectrophotometric studies were made up to a constant ionic strength of 0.5 by addition of $NaClO_4$. Potentiometric titrations and pH measurements were performed with a Beckman Model G pH meter using appropriate calomel and 1190-72 or 290-E high-pH glass electrodes. All pH titrations were performed under nitrogen with a Koch buret at a constant temperature of 25 ± 0.1°. The solutions for potentiometric titrations were made 0.5 *M* in KNO_3.

Results

Spectrophotometric Work.—As TKED is added to a solution of nickel(II) perchlorate, the color changes from a very pale green to a light blue. The nickel(II) ion–TKED system is completely soluble in all proportions in dilute solutions; therefore, a spectrophotometric study should yield information about the complex ions that are stable and formed in these solutions. Figure 1 shows the absorbance from 280 to 1200 mμ for solutions 0.010 *M* in nickel(II) perchlorate with varying amounts of TKED. The curves for the 1:2, 1:3, and 1:4 ratios of nickel to TKED are so close as not to permit separate plots to be made on the same graph. Throughout the whole graph the curves of the 1:2, 1:3, and 1:4 ratios lie slightly above the 1:1 curve, except the 1:4 which has slightly lower absorbance between 900 and 1000 mμ. The intermediate position of the 1:0.5 (Ni^{+2}:TKED) curve, midway between the Ni^{+2} ion curve (1:0) and the 1:1 curve, indicates that no complex forms of ratio less than 1:1, and the near-coincidence of the succeeding curves with the 1:1 curve indicates most strongly that the complex or complexes formed in this system have a ratio of nickel(II) ion to TKED of 1:1.

This 1:1 ratio was further verified by studies of a second set of solutions made up with various ratios of nickel(II) ion to TKED at a constant total concentration of 0.010 *M*. The absorbances for these solutions were determined and analyzed by Vosburgh and Cooper's extended method of continuous variation at a number of wave lengths.[7] Figure 2 shows the results of these analyses for 380, 610, and 1020 mμ. In each case, the Y curve shows only a single maximum at a ratio of 1:1 with no indication of any other complex.

Potentiometric Titrations.—Figure 3 shows the results of titrating solutions initially 0.5 *M* in KNO_3, 0.030 *M* in HNO_3, and 0.010 *M* in TKED with 1.0000 *M* sodium hydroxide. Solution A contained no nickel ion,

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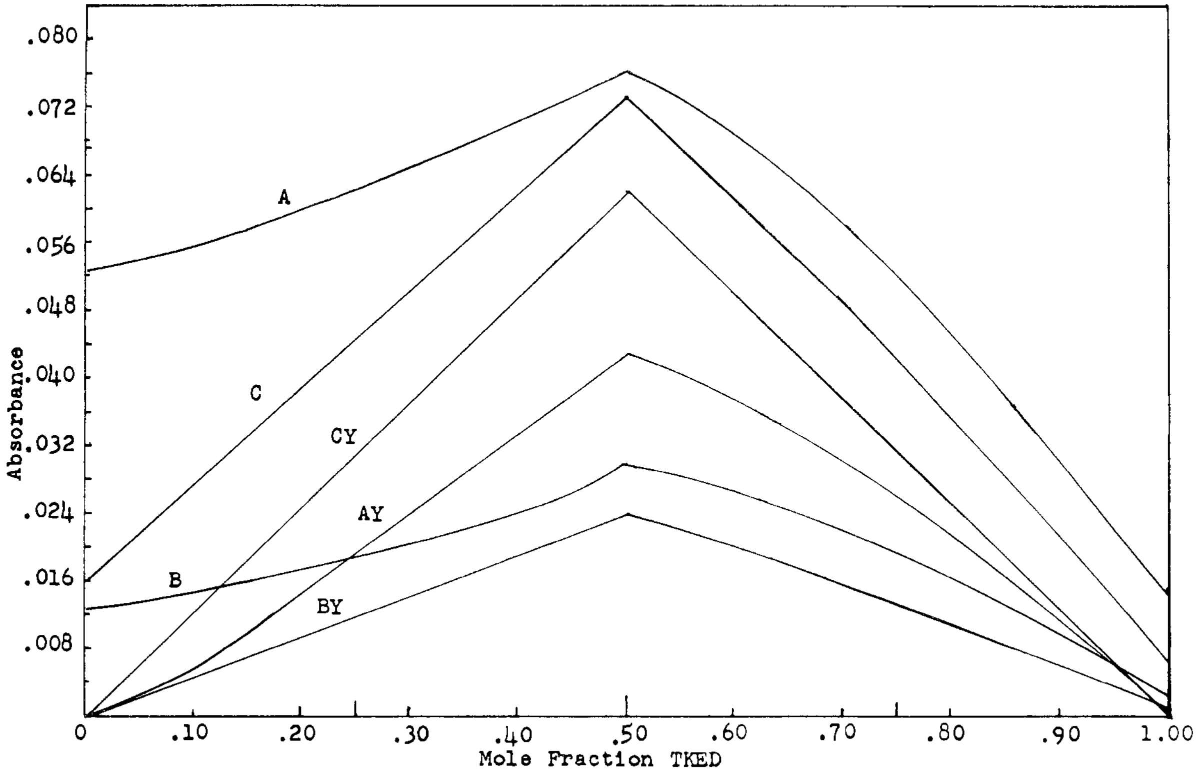

Fig. 2.—Continuous variation at: A, 380 mμ; B, 610 mμ; and C, 1020 mμ of 0.010 constant molar solutions with various amounts of $Ni(ClO_4)_2$ and TKED.

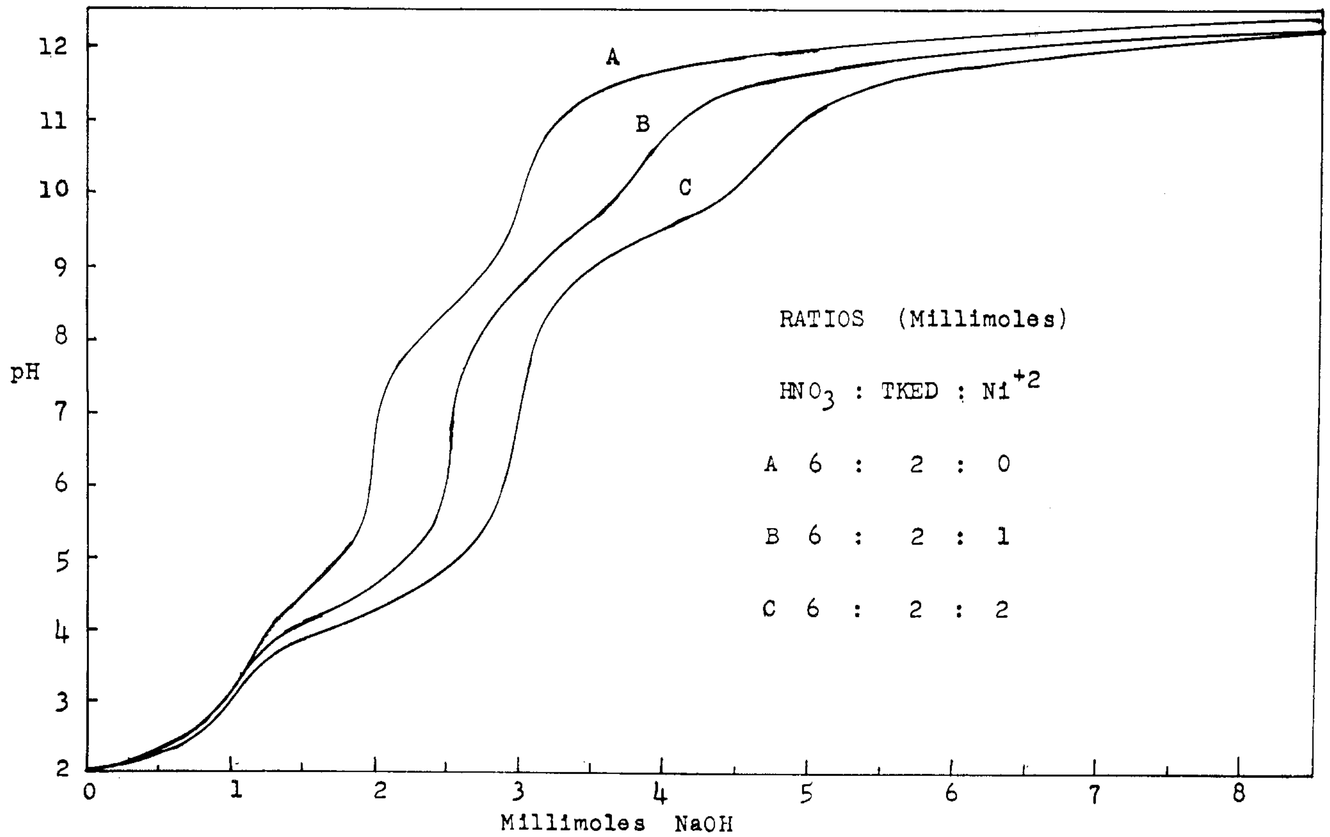

Fig. 3.—Potentiometric titrations of Acid–TKED and acid–TKED–$Ni(ClO_4)_2$ mixtures with 1.0000 M NaOH.

solution B was 0.005 M in $Ni(ClO_4)_2$, and solution C was 0.010 M in $Ni(ClO_4)_2$. Solution B had a Ni^{+2}:TKED ratio of 0.5:1 and solution C had a Ni^{+2}:TKED ratio of 1:1. At corresponding pH values, curve B is very nearly halfway between curves A and C, indicating that solution B was simply a mixture of nickel(II) TKED complex with a ratio of 1:1 and an equal amount of TKED not complexed with nickel. This is very strong evidence that the nickel(II) ion and TKED do not form a 1:2 complex.

The titration of TKED shown in curve A, Fig. 3, has three very distinct end points. The initial solution contained an excess of nitric acid so that at the beginning of the titration the TKED is all in the form of the $TKEDH_2^{+2}$ ion. The first end point for this titration is for the neutralization of the excess nitric acid, the second is for the formation of $TKEDH^+$, and the third is for the formation of free TKED.

Curve C, Fig. 3, is for a solution which initially contained Ni^{+2} and TKED in the ratio of 1:1. The first step in curve C, corresponding to the neutralization of the excess nitric acid, is distinct. The second end point corresponds to the formation of the $NiTKED^{+2}$ complex which corresponds to a pH of 6.9. The further addition of sodium hydroxide to the $NiTKED^{+2}$ complex does not produce very distinct end points and the reaction is at a very high pH. The amine salt is thus seen to be a very weak dibasic acid.

Discussion

Spectrophotometric and potentiometric studies of the Ni(II) ion–TKED system prove that the complexes formed have a ratio of ligand to metal of 1:1. Excess TKED serves only as a base to partially neutralize one of the four coordinated hydroxyl radicals of the first TKED molecule, whereas sodium hydroxide will neutralize two of the acidic hydrogen atoms of the complex.

Since the potentiometric titration data shown in Fig. 3 for mixtures of $Ni(ClO_4)_2$, TKED, and HNO_3 do not indicate distinct end points corresponding to the formation of $Ni(TKED\text{-}H^+)^+$ and $Ni(TKED\text{-}2H^+)^0$, and since at pH 9.3–9.4 a precipitate began to appear, it was only possible to obtain an approximate value for the first acid dissociation constant for $NiTKED^{+2}$. The second acid dissociation constant cannot be evaluated because of the competition of the hydroxyl ion for the Ni^{+2} ion to form $Ni(OH)_2$ according to the equations

$$Ni^{+2} + TKED \longrightarrow NiTKED^{+2}$$

$$NiTKED^{+2} + OH^- \longrightarrow Ni(TKED\text{-}H^+)^+ + H_2O$$

$$Ni^{+2} + 2OH^- \longrightarrow \underline{Ni(OH)_2}$$

The first acid dissociation constant was estimated by assuming that at 3.50 mmoles of sodium hydroxide added (curve C), the concentration of $NiTKED^{+2}$ equals that of $Ni(TKED\text{-}H^+)^+$. Thus, $K_{A_1} = 8.51 \times 10^{-10}$ or $pK_{A_1} = 9.07$.

The acid dissociation constants K_{AH_2} and K_{AH} were calculated from the pH values from a series of points from curve A of Fig. 3 using the method of Bjerrum.[8] The value $K_{AH_2} = 3.54 \times 10^{-5}$ is the average of the K_{AH_2} values in the pH range 4.08–5.40. The value $K_{AH} = 3.54 \times 10^{-9}$ is the average of the K_{AH} values in the pH range 8.27–9.05.

The very distinct pH rise after the addition of 1 mmole of hydroxyl ion to the Ni^{+2} and $TKEDH_2^{+2}$ mixture (Fig. 3, curve C) indicates that the formation of $NiTKED^{+2}$ is essentially complete before the neutralization of the hydrogen atoms of the bound hydroxyl radicals of the complex is begun. Therefore, calculation of the formation constant of $NiTKED^{+2}$ from the Ni^{+2} and TKED concentrations by the method of Bjerrum is applicable.[8] The equations used were those of Bjerrum modified by Carlson, McReynolds, and Verhoek.[9] The value of log $k_1 = 6.48$ was obtained graphically from the equation

$$K_1 = \frac{1}{[A]}\frac{\bar{n}}{(1 - \bar{n})}$$

To obtain algebraically the value of the formation constant, values of pA and $\bar{n}$ were calculated for the pH range 3.97–5.49 along with the corresponding values of k_1. The average value of k_1 for the $\bar{n}$ interval 0.207 to 0.816 was found to be 3.17×10^6 or log $k_1 = 6.50$. Thus both graphically and algebraically the value of the formation constant of $NiTKED^{+2}$ was found to be approximately 3×10^6.

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