

THE BEHAVIOR OF NICKEL (II) SALTS IN GLACIAL ACETIC ACID

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY Joseph T. Lundquist, Jr. 1965



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ABSTRACT

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The preparation of stoichiometric complexes of nickel(II) have been investigated. These complexes were $NiCl_2 \cdot 2H_2O$ and $NiBr_2 \cdot 2H_2O$. A complex from NiI_2 of this stoichiometry could not be prepared. The complexes were prepared by diluting an aqueous solution of the salt with acetic acid until a precipitate formed which was isolated.

Complexes of Ni(ClO₄)₂ and Ni(C₂H₃O₂)₂ solvated with acetic acid were isolated and studied.

Nickel <u>p</u>-toluenesulfonate was prepared in aqueous medium by reaction of nickel carbonate with a saturated solution of <u>p</u>-toluenesulfonic acid. Drying the hexahydrate at 130° C. gave the anhydrous yellow salt.

Near infrared and visible spectra and magnetic data suggested octahedral coordination for all complexes studied.

Solubilities were determined for NiCl₂, NiBr₂, Ni $(ClO_4)_2$ and Ni $(OTs)_2$ in glacial acetic acid. The solubility of the salt increases with decreasing basicity of the anion except for perchlorate whose solubility fell between NiCl₂ and Ni $(OTs)_2$.

THE BEHAVIOR OF NICKEL(II) SALTS IN GLACIAL ACETIC ACID

By

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A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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INTRODUCTION

There is very little research reported on nickel(II) salts in glacial acetic acid. Before any work can be done with nickel(II) salts in acetic acid one must know something about the physical properties of these salts and the reactions these salts undergo in this solvent.

There have been conflicting reports as to the stability of nickel acetate solutions in anhydrous glacial acetic acid. Campbell and Davidson (4) reported a solubility for nickel acetate of 12.37 mole percent and that above these concentrations a green white solid separated out which was 54-66 mole percent nickel acetate. The color of the solution was reported as green. Hardt and Eckle (12) reported that nickel acetate forms no stable solutions in acetic acid and that their solution was yellowish green which indicated the presence of acetonickolate. Tappmeyer and Davidson (32) found that the solubility of nickel acetate at 23°C. in glacial acetic acid was 0.557 mole percent. Above this concentration a green white solid precipitated out which appeared to be the hemi-solvate $2Ni(C_2H_3O_2)_2 \cdot HC_2H_3O_2$.

Hardt and Eckle (12) found that the precipitation of nickel(II) ions with acetylchloride which yielded anhydrous NiCl₂ was nearly quantitative. However, about three percent $[NiCl_4]^{2-}$ was formed.

It was also found qualitatively by Davidson (8) that nickel(II) sulfate was insoluble in acetic acid. This anhydrous sulfate was yellow and could be formed from the addition of concentrated sulfuric acid to hydrated nickel(II) nitrate, small amounts of water did not

seem to interfere.

Various solvated nickel(II) salts have been isolated from different solvents. Hexasolvated nickel(II) perchlorates have been made with tetramethylene sulfoxide, dimethyl sulfoxide, and pyridine Noxide by Meek, Drago, and Piper (23). Buffagni and Dunn (3) have isolated the nickel(II) hexadimethylformamide perchlorate and also nickel(II) chloride di-dimethylformamide. Wickandin and Krause (34) have isolated nicke1(II) perchlorate complexes with acetonitrile containing 6, 4, and 2 acetonitrile molecules per nickel ion. These complexes were all octahedral with the perchlorate being monodentate in Ni(CH₃CN)₄(C10₄)₂ and bidentate in Ni(CH₃CN)₂(C10₄)₂. Other references for the existence of bidentate perchlorate groups are given in this article (13,14,25). Monnier (24) isolated complexes of nickel(II) perchlorate with dioxane. The di- and monohydrates of nickel(II) chloride have been isolated by the stepwise azeotropic dehydration of the hexahydrate using ethanol as a solvent (19). Thermogravimetric data have also indicated the formation of these two complexes (5).

Kolling (15) determined the dissociation constant for nickel(II) acetate in acetic acid. This was done by comparing the concentration and potential of a known base, sodium acetate, to the concentration and potential of nickel(II) acetate. Potentiometric measurements were made with a glass calomel electrode pair. He obtained a value of pK_b for nickel acetate of 7.63.

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EXPERIMENTAL

Chemica1s

The chemicals used in this investigation were generally reagent or A.C.S. specification grades. Their names, commercial source and labeled purity are as follows:

Acetic acid, Baker, A.C.S. Acetic anhydride, Matheson, Coleman, and Bell, A.C.S. Ammonium acetate, Baker Reagent Ammonium hydroxide, Mallinckrodt, 58% NH₄OH, Reagent Cobalt(II) perchlorate, G.F. Smith, Reagent Crystal Violet, Eastman, Reagent Cupric perchlorate, G.F. Smith, Reagent Disodium ethylenediaminetetraacetate, Baker, Reagent Eriochrome Black T, Baker, Reagent Ferric perchlorate, G.F. Smith, Reagent Ferrous ammonium sulfate, Fisher, Reagent Ferrous perchlorate, G.F. Smith, Reagent Hydrochloric acid (37.3%) Baker, Reagent Hydriodic acid (47%), Mallinckrodt, Reagent Nickel (ous) acetate, Baker, Reagent Nickel bromide, Amend, c.p. Nickel (ous) carbonate, Baker, Reagent Nickel (ous) chloride, Fisher, Reagent Nickel (ous) oxide, Baker, Reagent

Nickel (ous) perchlorate, G.F. Smith, Reagent

1-<u>n</u>-octy1-4-benzy1-5-imino-tetrazolinium ditartrate monohydrate (15) <u>p</u>-Toluenesulfonic acid, Matheson, Coleman, and Be11, Practica1 Perchloric acid (70-72 percent), Baker, Reagent Phenolphthalein, Mallinckrodt, U.S.P. XII Phenosafranin, Eastman, C.P. Potassium acetate, Baker, Reagent Sodium acetate, Baker, Reagent Tetraphenylarsonium chloride, G.F. Smith, Reagent Zinc perchlorate, G.F. Smith, Reagent Zinc sulfate, Allied, A.C.S. specification.

Standard Solutions

Standard perchloric acid in acetic acid was prepare by diluting 8.5 ml. of 72 percent perchloric acid to about 1 liter with acetic acid and then adding 20 ml. of acetic anhydride with constant swirling. This solution was standardized after 24 hours by titration of weighed amounts of dried potassium acid phthalate. Crystal violet indicator was used to the blue-green endpoint, (three drops 0.1 percent solution in acetic acid) (30).

Standard potassium acetate in acetic acid was prepared by dissolving 0.1 mole of dried potassium acetate in 900 ml. of acetic acid. The amount of water present in this solution was determined by Karl Fischer titration. It was removed by reaction with a stoichiometric amount of acetic anhydride. About four days were required for this reaction to proceed to completion. Again it was analyzed for water to make sure the reaction between acetic anhydride and water was complete. The solution was then diluted to exactly one liter. It

was standardized with the standard perchloric acid in acetic acid utilizing crystal violet indicator (31).

Standard sodium acetate was prepared by dissolving 0.1 mole of sodium acetate trihydrate in 900 ml. of acetic acid. The procedure for the preparation of standard potassium acetate solution was followed from this point.

Standard 0.01M disodium salt of ethylenediaminetetraacetic acid (EDTA) solution was prepared by dissolving 0.02 mole of the disodium salt in distilled water and diluting to exactly two liters.

Standard 0.01M zinc sulfate solution was prepared by dissolving approximately 0.02 mole of zinc sulfate in 1500 ml. of distilled water. An aliquot of this solution was titrated with standard 0.01M EDTA using Eriochrom black T indicator. The concentration of the zinc sulfate solution was determined and it was diluted with water until the concentration was exactly 0.01M.

Solubility Measurements

Solubilities were determined by equilibrating an excess of salt with one hundred milliliters of glacial acetic acid. In certain cases acetic anhydride was added to remove water. Equilibrium was attained by heating the mixture for twenty-four hours at 70°C. and then cooling at 25° C. for one week. The excess solid was removed by filtration.

An aliquot of the filtrate was analyzed for water by Karl Fischer titration. Another aliquot was evaporated to dryness. The solid residue was dissolved in water and the nickel was determined complexometrically with standard O.OIM EDTA solution, the excess being back

titrated with standard 0.01M zinc sulfate solution utilizing Eriochrom black T indicator (28). A solubility was then calculated from the amount of nickel present in the aliquot.

Magnetic Moment Measurements

Magnetic moments were determined using the Gouy method utilizing an Alpha Scientific Laboratories Incorporated electromagnet. Ferrous ammonium sulfate, magnetic moment 5.25 Bohr magnetons, was used as a standard to calibrate the magnet and tube. All moments are at 296°K.

Spectral Measurements

Electronic spectral data were obtained with a Cary (model 14) recording spectrophotometer.

Infrared spectra of potassium bromide pellets and mulls of solid compounds were run with a Beckman IR5 recording spectrophotometer with sodium chloride optics.

Potentiometric Measurements

A Beckman Zeromatic pH meter equipped with a grounded solution shield, a calomel reference electrode and a glass electrode were used to make potentiometric measurements. The electrodes were stored in distilled water. Prior to use they were dried and rinsed several times with glacial acetic acid. No drift was noted upon standing in solution so it was assumed the liquid junction potential remained constant.

RESULTS AND DISCUSSION

Nicke1(II) Chloride Dihydrate

The preparation of NiCl₂·2H₂O from NiCl₂·6H₂O has been accomplished by the addition of glacial acetic acid to an aqueous solution of nickel(II) chloride hexahydrate. The precipitation was carried out at room imperature with stirring and a slow rate of addition of acetic acid. The most suitable concentration of nickel(II) chloride hexahydrate in the aqueous solution was found to be 1.0 gram per ml. of water. The amount of acetic acid required for a good yield of nickel(II) chloride dihydrate was 30.0 ml. per ml. of aqueous solution. The precipitate was removed by filtration under atmospheric conditions and then dried at 105° C. for two hours to remove adsorbed acetic acid.

This compound can also be prepared directly from the action of excess hydrochloric acid on nickel oxide in the presence of acetic acid and water mixture, followed by the addition of acetic anhydride. The reaction mixture contained: 5.0 grams of nickel oxide, 100 ml. of concentrated hydrochloric acid, 100 ml. of glacial acetic acid, and 50 ml. of water. The reaction was allowed to proceed with stirring until all the nickel oxide was converted to soluble nickel chloride.

Acetic anhydride was added to this solution dropwise keeping the temperature less than 50° C. Upon the addition of 100 ml. of acetic anhydride a precipitate forms and by 200 ml. most of the nickel was precipitated as NiCl₂.2H₂O. The water is added to the above reaction mixture to accelerate the reaction of hydrochloric acid and nickel

oxide since the reaction in glacial acetic acid proceeds very slowly if at all.

Each component of $NiCl_2 \cdot 2H_2O$ was determined analytically. Nickel was determined by a complexometric titration with standard EDTA solution using Eriochrom black T indicator. The excess EDTA was back titrated with standard zinc sulfate solution.

Chloride was determined volumetrically using standard silver nitrate solution with phenosafranine indicator. Water was determined by Karl Fischer titration. The sample of $NiCl_2 \cdot 2H_2O$, however, was not soluble in the Karl Fischer reagent, but on standing for a few minutes all the water was apparently extracted and could be determined. The results are tabulated in Table I.

| Samp1e | % Ni | % C1 | %Н ₂ О |
|-------------|-------|-------|-------------------|
| 1 | 35.41 | 42.71 | 21.9 |
| 2 | 35.32 | 42.81 | 21.7 |
| 3 | 35.32 | 42.81 | 21.8 |
| 4 | 35.43 | 42.91 | 21.6 |
| 5 | 35.43 | 42.82 | |
| 6 | 35.40 | 42.78 | |
| 7 | 35.58 | 42.50 | |
| Average | 35.43 | 42.77 | 21.7 |
| Theoretica1 | 35.40 | 42.84 | 21.76 |
| | | | |

Table I. Analytical Data for NiCl₂·H₂O

The near infrared and visible spectra of nickel(II) complexes are quite indicative of the structure of these complexes.

Jørgenson (17,18) has determined the spectra for a large number of octahedral nickel(II) complexes. There are generally four bands for these complexes in the ranges 8,000-11,000; 12,000-13,000; 15,000-19,000; 25,000-29,000 cm⁻¹. The band at 8,000-11,000 cm⁻¹ was assigned as v_1 and represents the transition from ${}^{3}A_{2g}(F) \longrightarrow {}^{3}T_{2g}(F)$. This band therefore gives the value of 10Dq (27) which is indicative of the strength of the ligands surrounding the nickel(II) ion. Weaker ligands will split the 3d orbitals less than will stronger ligands which results in lower Dq values for weaker ligands.

 v_2 represents the transition ${}^{3}A_{2g}(F) \longrightarrow {}^{3}T_{1g}(F)$. v_3 is represented by ${}^{3}A_{2g}(F) \longrightarrow {}^{1}E_{g}$ and v_4 by ${}^{3}A_{2g}(F) \longrightarrow {}^{3}T_{1g}(P)$. This assignment was given by Brown (1) and Dunn (9) (Figure 1).

A series of solutions with fixed nicke1(II) chloride concentration (0.0314M) and varying concentrations of water and acetic acid were prepared to examine spectroscopically the effects of acetic acid on the spectrum of nicke1(II) chloride. The solutions were run against reference solutions which were exactly the same minus the nicke1(II) chloride. The data obtained are reported in Table II.

Generally as the symmetry of a complex decreases the molar absorbtivity, \in , increases (6) and as the base strength of the ligands decreases the molar absorbtivity decreases.

The data in Table II indicate that as the mole fraction of acetic acid increases the value of **Dq** decreases and the molar absorbtivity increases up to a mole fraction of 0.82. At this concentration, however, NiCl₂·2H₂O began to precipitate from solution.





| Mole Fraction Acetic Acid | ν ₁ cm ⁻¹ | ∨2 cm ⁻¹ | ∨3 cm ⁻¹ | ∨ 4 cm ⁻¹ | € v 4 | D q cm ⁻¹ |
|--|------------------------------------|------------------------|------------------------|--------------------------------|-----------------|--------------------------------|
| 0.0000 | 8550 | 13800 | 15400 | 25250 | 5.20 | 855 |
| 0.23 | 8550 | 13800 | 15400 | 25250 | 5 .3 0 | 855 |
| 0.56 | 8340 | 13600 | 15150 | 25000 | 5.65 | 8 3 4 |
| 0.77 | 8070 | 13150 | 14700 | 24200 | 7.00 | 807 |
| 0.82 | 7910 | 13000 | 14500 | 24000 | 7.50 | 79 1 |
| 0.9940 | 7510 | 12500 | 13900 | 23200 | 1.44 | 751 |
| 1.0000 | 7510 | 12500 | 13900 | 23200 | 1.41 | 751 |
| NiCl ₂ ·2H ₂ O in a KBr pellet | | 12200 | 13300 | 22500 | | |

Table II. Nickel(II) Chloride Spectra (in acetic acid water solutions)

As the waters of hydration are replaced by acetic acid or by bridged chloride the symmetry of the complex is decreased. The symmetry is also decreased by distortion since these ligands are much weaker ligands than water. Therefore, they will be at a longer distance from the nickel ion than will water. Since acetic acid is a weaker base than water one would expect that the molar absorbtivity would be decreased but the symmetry effects apparently over compensate this effect.

At a mole fraction acetic acid of 0.9940 the molar absorptivity decreases to 1.44. The spectrum is still representative of an octahedral complex but shifted to lower energy. The spectrum at a mole fraction acetic acid of 1.0000 is the same as that for mole fraction 0.9940. It can be assumed that the species in solution for these two solutions is identical. If one assumes the species in solution to be $NiCl_2 \cdot 4HC_2H_3O_2$, the symmetry of this complex would be only slightly less than that for hexaquonickel(II) ion, but the basicity of chloride and acetic acid ligands are much less than that for water ligands. Therefore, a lower molar absorptivity would result than that for the hexaquonickel(II) complex.

A near infrared and visible spectrum of $NiCl_2 \cdot 2H_2O$ was obtained by preparing a potassium bromide pellet of the solid $NiCl_2 \cdot 2H_2O$. Only the wave length of absorption maxima could be determined from the spectrum. These are listed in Table II. The spectrum appeared to be like the characteristic octahedral spectrum for nickel(II) complexes.

Solubility measurements of NiCl₂ versus water concentration in glacial acetic acid were made. Table III contains these results. These data are plotted in Figure 2. Apparently the solubility of NiCl₂ is directly proportional to water concentration in glacial acetic acid.

| Solubility M/1 | H ₂ O M/1 |
|-------------------|-------------------------|
| 0.0214 | 0.0000 |
| 0.0298 | 0.0392 |
| 0.0444 | 0.1050 |
| | |

Table III. Solubility of Nickel Chloride in Acetic Acid



A thermogravimetric analysis of NiCl₂·2H₂O was determined by the Dow Chemical Company analytical laboratories (Figure 3). The analysis was carried out in vacuum and the heating rate was approximately 2.5° C. per minute. The volatilization began quite slowly at approximately 96°C. The rate of volatilization increased until a rapid rate was attained. At about twelve percent weight loss the rate of volatilization decreased slightly indicating possibly a stable monohydrate. At 255°C. the weight loss was 22.3 percent which is larger than 21.76 percent water of hydration. This can be explained if one considers the volatilization of a small amount of hydrochloric acid leaving behind a basic nickel oxide. Also one cannot neglect the possibility of a small amount of adsorbed moisture.

The infrared spectrum of NiCl \cdot 2H₂O shows considerable hydrogen bonding, the hydroxyl peak at approximately 3.0 microns is split into two maxima, the lesser at 2.85 microns and the larger at 2.95 microns. The maxima at 2.85 corresponds to nonhydrogen bonded hydroxyl and the other at 2.95 corresponds to hydrogen bonded hydroxyl (Figure 4).

A 3.5 gram sample of NiCl $\cdot 2H_2O$ was exposed to atmospheric moisture for seventy hours. A gain in weight of only 0.0040 grams was noted. However, when the humidity was very high the salt became hydroscopic. It was concluded that it was difficult for water to enter into the coordination sphere of this complex.

The magnetic moment for nickel(II) in an octahedral field based on electron spin, angular momentum alone is given by the formula

Magnetic moment = $\sqrt{n(n+2)}$ Bohr magnetons where n is the number of unpaired electrons. This formula gives a





value of 2.83 Bohr magnetons for nickel(II). However, due to spin orbit coupling slightly larger values are obtained which apparently depends on the ligands surrounding the nickel(II) ion. A range of moments is therefore expected for octahedral nickel(II) complexes. This range is generally defined by the following limits, 2.9 to 3.3 Bohr magnetons (10). The magnetic moment for NiCl₂·2H₂O was found to be 2.98 Bohr magnetons, which is in agreement with the above range. This magnetic moment suggests that NiCl₂·2H₂O is an octahedral complex.

The structure of $NiC1_2 \cdot 2H_2O$ was determined by x-ray techniques (33) and is shown in Figure 5.

The above spectral and magnetic data are in agreement with an octahedral structure.



Figure 5. The Structure of NiCl2.2H20.

Nicke1(II) Bromide Dihydrate

Preparation of NiBr₂·2H₂O from NiBr₂·XH₂O was done in a manner similar to that of the preparation of NiCl₂·2H₂O. One ml. of a saturated solution of NiBr₂ in water was diluted slowly with stirring with glacial acetic acid until thirty ml. of acetic acid had been added. During this procedure a light brown precipitate formed which was removed by filtration under atmospheric conditions. The precipitate was dried at 100°C. for three hours. This temperature should be held within five degrees for the volatilization of water begins at approximately 105-110°C. Analysis before drying showed less than seven percent acetic acid.

Analytical data for $NiBr_2 \cdot 2H_2O$ are presented in Table IV. Analytical methods parallel to those used for $NiCl_2 \cdot 2H_2O$ were used to determine the various components in $NiBr_2 \cdot 2H_2O$.

| Samp1e | % Ni | % Br | % Н ₂ О |
|-------------|----------------|-------|--------------------|
| 1 | 23.30 | 62.72 | 14.2 |
| 2 | 23.37 | 62.58 | 14.1 |
| 3 | 2 3.3 7 | 62.60 | 14.1 |
| Average | 2 3.3 5 | 62.63 | 14.1 |
| Theoretica1 | 23.10 | 62.65 | 14.17 |

Table IV. Analytical Data for NiBr₂·2H₂O

The near infrared and visible spectrum of $NiBr_2$ in glacial acetic acid was similar to that of $NiCl_2$ (Table V). The absorption maxima

are shifted to still lower energies. This would be expected since bromide is a weaker ligand than chloride (26).

| Mole Fraction Acetic Acid | cm ¹ | cm ² 1 | ∨3 cm ⁻¹ | ν 4 cm ⁻¹ | E _V 4 | Dq cm ⁻¹ |
|------------------------------|-----------------|-------------------|------------------------|--------------------------------|------------------|------------------------|
| 0.9940 | 7 3 50 | 12250 | 13300 | 22500 | 2.7 | 735 |

Table V. Nickel Bromide Spectrum.

The infrared spectrum was also very similar to that of $NiCl_2 \cdot 2H_2O$. Slightly weaker hydrogen bonding was noted in this compound.

A thermogravimetric analysis was run on NiBr₂·2H₂O by the Dow Chemical Company analytical laboratories. The rate of heating was approximately 2.5°C. per minute and it was carried out under vacuum (Figure 3). The volatilization of NiBr₂·2H₂O began quite slowly at 70°C. This rate increased, held steady and then decreased until volatilization ceased. This occurred at 210°C. where the percent weight loss was 14.4 percent. This indicates either adsorbed moisture or volatilization of small amounts of HBr or both. This compound is less stable than NiCl₂·2H₂O as indicated by the different decomposition temperatures.

 $NiBr_2 \cdot 2H_2O$ apparently does not have a stable monohydrate because no change in the rate of volatilization curve is noted.

The solubility of $\operatorname{NiBr}_2 \cdot 2\operatorname{H}_2O$ was measured as a function of water \cdot concentration in glacial acetic acid (Table VI). These values when plotted as in the case for NiCl_2 practically paralleled the curve obtained for NiCl_2 (Figure 2). Kolling (20) reported in the case of

 $CdCl_2$ and $CdBr_2$ and also in the case of $PbCl_2$, $PbBr_2$ and PbI_2 that the solubility decreased with increasing base strength of the halides which is Cl - > Br - > I- in glacial acetic acid.

Table VI. Solubility of NiBr₂ in Acetic Acid.

| NiBr ₂ M./L. | H ₂ 0 M./L. |
|-------------------------|------------------------|
| 0.036 | 0.0000 |
| 0.0416 | 0.0420 |
| 0.0508 | 0.1050 |

The polarity of the nickel halogen bond decreases with electronegativity of the halide. This makes displacement of the halide by acetic acid easier with increasing atomic number of the halide.

The magnetic moment for $NiBr_2 \cdot 2H_2O$ was 3.24 Bohr Magnetons. This is in agreement with the expected range of moments for nickel(II) complexes in an octahedral field (16).

The above data suggest that $NiBr_2 \cdot 2H_2O$ has a structure very similar to that of $NiC1_2 \cdot 2H_2O$.

Nicke1(II) Iodide

The preparation of NiI₂ from nickel carbonate and hydriodic acid (47 percent) was accomplished by adding the acid to the carbonate which was in slight excess. Isolation was difficult because iodide is readily oxidized to iodine leaving behind a basic salt.

A saturated solution of NiI₂ in water was diluted with acetic acid which had previously had prepurified nitrogen passed through it to remove dissolved oxygen. No precipitate formed as in the case of NiCl₂ and NiBr₂. But upon the addition of acetic anhydride a black precipitate formed which fits the description of anhydrous NiI₂ (29).

Two methods were used to dry the material, oven drying at 90° C. and vacuum drying at room temperature. Both methods resulted in a product which was not pure NiI₂. The percent nickel was approximately 22.0 while the calculated value was 18.82 percent. It is felt that either nickel oxide or nickel acetate are present in substantial amounts.

Nickel(II) Acetate

In an attempt to prepare a standard solution of Ni($C_2H_3O_2$)₂ in glacial acetic acid 0.1 moles of Ni($C_2H_3O_2$)· $4H_2O$ was dissolved in one liter of glacial acetic acid. The solution that resulted was dark green. The visible and near infrared spectrum of this solution gave the characteristic spectrum for nickel(II) in an octahedral field as shown in Table VII. The position of v_1 indicated that nickel was probably solvated to a greater extent by water rather than by acetic acid. The water concentration was 0.43 molar.

| Tab1e | VII. | Spectra | of | Ni | (C ₂ H ₃ O ₂) |)2. |
|-------|------|---------|----|----|---|-----|
|-------|------|---------|----|----|---|-----|

| Mole Fraction Acetic Acid | $v_1 \text{ cm}^{-1}$ | $v_2 \text{ cm}^{-1}$ | v3 cm ⁻¹ | ν 4 cm ⁻¹ | Dq cm ⁻¹ |
|------------------------------|-----------------------|-----------------------|---------------------|-----------------------------|---------------------|
| 0.975 | 8370 | 13600 | 15200 | 25000 | 837 |
| 1.000 | 8120 | 13150 | 14600 | 24400 | 812 |
| 0.0000 | 850 | 13800 | 15400 | 25250 | 855 |

To prepare anhydrous nickel acetate acetate solution, a stoiciometric amount of acetic anhydride was added to the above solution to react with the water. After three days the water concentration was observed to be nill by Karl Fischer titration. The color of the solution was a green yellow. The visible and near infrared spectrum of this solution still indicated octahedral coordination for nickel(II) but the absorption maxima in the spectrum were shifted to lower energies as shown in Table VII. This would be expected if nickel were solvated by acetic acid rather than water since acetic acid is a weaker base than water.

It was observed that when the anhydrous solution stood for a few days a light green fluffy precipitate formed. This precipitate approximated the composition of nickel acetate monoacetic acid. Similar results were obtained by Chappel and Davidson (4).

Two methods were attempted to obtain a stoichiometric material, vacuum drying at room temperature, and oven drying at 110°C. Both drying methods gave a product which had slightly less than one acetic acid per each nickel. The analysis of each component was done by direct determination and the results are shown in Table VIII. Nickel was determined as before by complexometric titration. Acetate was determined potentiometrically by titration in acetic acid as a solvent with standard 0.1M perchloric acid. Small amounts of water present in the acetic acid solvent did not interfere. Acetic acid was determined by dissolving the sample in water and titrating with 0.05 molar sodium hydroxide utilizing phenolphthalein indicator.

| | % Ni | % C ₂ H ₃ O ₂ | % HC ₂ H ₃ O ₂ |
|--------------|--------------|--|---|
| Calculated | 24.81 | 49.85 | 25.34 |
| Undried | 24.52 | 49.35 | 26.2 |
| Vacuum dried | 25.80 | 51.86 | 22.2 |
| Oven dried | 26.40 | 52.97 | 20.5 |
| All values | are the aver | age of three. | |

Table VIII. Analytical Data for Ni(C₂ H₃O₂)₂·HC₂H₃O₂

The magnetic moment for this compound was 2.80 Bohr magnetons.

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It is believed that this compound is a dimer similar in structure to that of the cupric acetate monohydrate (7,11) illustrated in Figure 6 because the magnetic moment is slightly less than the value of 3.20 Bohr magnetons for nickel(II) acetate tetrahydrate. This low value is probably the result of partial 3d orbital overlap.

A method for determining the dissociation constants for bases in glacial acetic acid (22) involved the use of a glass calomel electrode pair which have been shown to respond to the hydrogen ion activity in this solvent (16). A plot of potential versus the logarithm of concentration of the base gave for most divalent transition metal acetates including nickel acetate a slope of 0.5 which corresponded to $\frac{59}{2}$ millivolts per ten fold change in concentration (2). This slope suggests that the overall mechanism for dissociation of these bases is:

 $M(C_2H_3O_2)_2 \longrightarrow M(C_2H_3O_2)^+ + C_2H_3O_2^-$

Therefore one can use the following equation (2) to describe this mechanism:

$$[H^+] = \sqrt{\frac{K_s}{K_b - C_b}}$$

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 K_s = autoprotolysis constant of solvent K_b = basic dissociation constant

Now if one uses a reference base and divides $[H^+]$ reference by $[H^+]$ unknown the following equation results:

 $C_{\rm b}$ = total analytical concentration of base.

$$\frac{[H^+]_{reference}}{[H^+]_{unknown}} = \begin{bmatrix} \frac{K_b unknown (C_b)_{unknown}}{K_b reference (C_b)_{reference}} \end{bmatrix}^{1/2}$$



Figure 6. The Structure of $Cu(C_2H_3O_2)_2 \cdot 2H_2O$.

It follows that

$$\Delta pH = \frac{pK_{b} \text{ unknown}}{2} - \frac{pK_{b} \text{ reference}}{2} - \frac{1}{2} \log C_{b} \text{ unknown} + \frac{1}{2} \log C_{b} \text{ reference}$$
or

 pK_{b} unknown = $2\Delta pH + pK_{b}$ reference + $\log C_{b}$ unknown - $\log C_{b}$ reference. This assumes the liquid junction potentials are equal. If one uses reference bases of known concentration one can determine a pH scale in acetic acid.

For this work standard 0.001 molar solutions of sodium acetate, pK_b 6.58 and potassium acetate pK_b 6.11 were used (22). They were prepared by diluting aliquots of the standard 0.1 molar solutions of these bases 100 fold with glacial acetic acid.

A small amount of water had to be present in the nickel acetate solution because the anhydrous solution is unstable. Apparently small amounts of water do not effect potentiometric measurement in glacial acetic acid but it may tend to drive the equilibrium.

$$Ni(C_2H_3O_2)_2 \longrightarrow Ni(C_2H_3O_2)^+ + C_2H_3O_2^-$$

to the right making pK_b appear smaller than it actually is. A value for pK_b of 7.63 has been reported and this work gave a value of 7.54 ± 0.07. These values seem to be in good agreement.

Nicke1(II) Perchlorate

A 0.01 mole portion of Ni(ClO₄)₂.6H₂O was dissolved in 100 ml. of glacial acetic acid. The water concentration was 0.7 molar. To this solution 0.07 mole of acetic anhydride was added. The solution was mixed and it became quite warm (approximately fifty °C.) almost immediately because perchlorate ions accelerate the exothermic reaction between water and acetic anhydride. Within thirty minutes the reaction was complete and upon standing for about one hour a yellow green precipitate had formed. The color of the precipitate indicated solvation by acetic acid. The solution was allowed to stand for one week before filtration. Both the precipitate and filtrate were anhydrous as determined by Karl Fischer titration. The filtrate was also analyzed for nickel. The solubility of nickel perchlorate in anhydrous acetic acid was found to be 0.00185 ± 0.00050 mole per liter at 23°C.

Each component of the precipitate was determined analytically. Nickel and acetic acid were determined as before. Perchlorate ion was determined gravimetrically by precipitation with tetraphenylarsonium chloride. The data are presented in Table IX.

Because a precipitate formed with nickel the above method was tried with cupric, cobaltous, zinc, ferrous and ferric perchlorates. With the above mentioned 0.1M divalent transition metal perchlorate solutions a precipitate formed, with the empirical formula $M(C10_4)_2 \cdot 6-8 HC_2H_3O_2 \cdot A O.1M$ ferric perchlorate solution on the other hand gave no precipitate. It is believed that these complexes would

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| % Ni | % C10 ₄ | % HC ₂ H ₃ O ₂ |
|----------------|------------------------|--|
| 7.51 | 25.62 | 67.0 |
| 7.58 | 25.80 | 66.5 |
| 7.70 | 26.25 | 66.0 |
| The above data | suggested an empirical | formula of Ni(C10 ₄) ₂ (8-9)HC ₂ H ₃ O ₂ |

Table IX. Analysis of Ni(C10₄)₂·XHC₂H₃O₂

probably be good intermediates for the preparation of other complexes since acetic acid is a very weak ligand which should be easily replaced. Solubilities of these transition metal perchlorates are listed in Table X.

Table X. Solubility of Transition Metal Perchlorates in Acetic Acid

| Compound | Solubility M/L. |
|--|-----------------|
| Co(C10 ₄) ₂ XHO ₂ H ₃ O ₂ | 0.007 |
| Zn(C10 ₄) ₂ XHC ₂ H ₃ O ₂ | 0.008 |
| Cu(C10 ₄) ₂ XHC ₂ H ₃ O ₂ | 0.009 |
| Fe(C10 ₄) ₂ XHC ₂ H ₃ O ₂ | 0.010 |
| Fe (C10 ₄) ₃ XHC ₂ H ₃ O ₂ | > 0.1. |

Only two measurements were made for each perchlorate therefore, only rough averages are reported. It would appear from the above data that ferrous perchlorate could be separated from ferric perchlorate by this method.

For Ni $(C10_4)_2 \cdot 8.5 \text{HC}_2\text{H}_3\text{O}_2$ desolvation rate studies at 125°C. were made as shown in Table XI. The sample was placed in an oven at 125°C. and as time proceeded the percents nickel and acetic acid were measured as above and finally at the conclusion of the experiment each component was determined directly to see if decomposition had occurred.

| $\frac{HC_2H_3O_2}{Ni}$ | Time Hour s |
|-------------------------|--------------------|
| 8.5 | 0 |
| 5.1 | 2.5 |
| 3.7 | 15.0 |
| 2.0 | 72.0 |
| 1.25 | 120.0 |
| 1.12 | 180.0 |

Table XI. Desolvation Rate Data of Ni(C104)2.8.5HC2H302 at 125°C.

These data are plotted in Figure 7 and one can see that the final ratio of acetic acid to nickel approaches unity. The analysis of the final product indicates that no decomposition occurred. The percents of each component were; % Ni = 17.90, % ClO₄ = 61.10 and % HOAc = 20.58 which results in an empirical formula Ni(ClO₄)₂·1.12HC₂H₃O₂.

The material was liquid at 125°C. over the whole range of solvation. Only an increase in viscosity of the liquid was noted. It went from a light syrup initially to a thick paste finally.



In some recent work it has been shown that perchlorate was bidentate in some other low solvated complexes with organic solvents (34). If this were the case for nickel perchlorate solvated with acetic acid, which is likely since no shift in color is noted on desolvation, an increase in viscosity could be explained by bridging of the perchlorate group forming polymeric species along with the fact that the "solution" is becoming more concentrated.

Nickel(II) p-Toluenesulfonate

To prepare nickel(II) <u>p</u>-toluenesulfonate a slurry of nickel carbonate in water was prepared. To this slurry, a saturated solution of <u>p</u>-toluenesulfonic acid in water was added slowly with stirring. For simplicity HOTs represents <u>p</u>-toluenesulfonic acid and OTs represents <u>p</u>-toluenesulfonate. Excess nickel carbonate was used since it could be removed by filtration leaving only soluble Ni(OTs)₂ in solution and a small amount of soluble carbonate. To minimize the amount of soluble carbonate as carbonic acid a vacuum was applied for thirty minutes. The dark green solution was then evaporated to dryness.

An attempt was made to isolate a dihydrate of this salt by dissolving it in water forming a saturated solution and diluting with glacial acetic acid as was done with the other salts. Five m1. of the saturated aqueous solution gave a precipitate which was light green upon the addition of 50 m1. of acetic acid. The composition of this precipitate approximated the empirical formula $Ni(OTs)_2 \cdot 2H_2O$. However, the water composition varied as the drying temperatures varied from 85 to $100^{\circ}C$. from more than two to less than two waters per nickel respectively.

Drying at 130° C. gave a yellow compound which corresponded to anhydrous Ni(OTs)₂. The nickel was determined as before and the OTs⁻ was determined gravimetrically by precipitation with 1-<u>n</u>-octy1-4-benzy1-5-imino-tetrazolinium ditartrate monohydrate (15). These data are presented in Table XII.

| % Ni | % OTs | |
|-------------|-------|--|
| 14.85 | 85.32 | |
| 14.77 | 85.49 | |
| 14.68 | 85.60 | |
| 14.72 | 85.40 | |
| Average | | |
| 14.76 | 85.45 | |
| Theoretica1 | | |
| 14.65 | 85.35 | |

Table XII. Ni(OTs)₂ Analytical Data

Ni(OTs)₂ was hydroscopic upon standing open to the atmosphere. After one week the empirical formula for the compound was Ni(OTs)₂. 6.60 H₂O which was approaching Ni(OTs)₂.7H₂O.

The color of the $Ni(OTs)_2$ $^{\circ}GH_2O$ was a light blue but shifted over to a light green upon the addition of one more water.

Ni(OTs)₂ seems to be very similar to NiSO₄ (28). Anhydrous nickel sulphate is green yellow while the hexahydrate exists in two forms, α which is a blue form and β which is a green form. The \cdot heptahydrate is green.

Solubility measurements indicate that $Ni(OTs)_2$ is quite insoluble in glacial acetic acid. Its solubility is 0.0016 ± 0.0003 moles per liter at 25°C. with the water concentration of 0.0280 moles per liter.

The magnetic moment was 3.20 Bohr magnetons. This indicated an octahedral structure.

SUMMARY AND CONCLUSIONS

Several compounds containing nickel(II) were isolated from aqueous solution by dilution with glacial acetic acid. They were $NiCl_2 \cdot 2H_2O$, $NiBr_2 \cdot 2H_2O$ and $Ni(OTs)_2 \cdot XH_2O$ where X is approximately two. $NiCl_2 \cdot 2H_2O$ and $NiBr_2 \cdot 2H_2O$ were formed with the exact empirical formula stated.

These halide complexes were found to have octahedral coordination by spectroscopic and magnetic techniques. The infrared spectrum showed some hydrogen bonding in the solid state.

Drying Ni(OTs)₂·XH₂O at 130°C. gave the anhydrous salt. The physical properties of this compound were very similar to those of NiSO₄.

It was found with NiCl₂ in solutions of acetic acid and water mixtures spectroscopically that as the acetic acid concentration increased the band positions shifted to lower energies and the molar absorbtivity increased. These effects were explained through basicity of ligands and symmetry effects. Generally the weaker the base strength of the ligand the lower the molar absorbtivity will be. Also the band positions will be shifted to lower energy. The higher the symmetry is, the lower the molar absorbtivity will be. After a mole fraction of acetic acid of 0.82 (NiCl₂·2H₂O begins to precipitate out) the molar absorbtivity decreases with increasing acetic acid concentration but the band positions still continue to shift to lower energies. The above effects can again be employed to explain this effect but now they oppose one another in explaining the low molar absorbtivity.

Apparently the base strength of the ligand is most important here.

From anhydrous acetic acid $Ni(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ and $Ni(C1O_4)_2 \cdot 8HC_2H_3O_2$ were isolated but the solvated acetic acids did not appear to exactly fit these empirical formulas.

Ni $(C_2H_3O_2)_2$ ·HC₂H₃O₂ probably has a structure similar to Cu $(C_2H_3O_2)$ ·H₂O which is a dimer because the magnetic moment is slightly less than what is expected for octahedral nickel(II).

The pK_b 7.54 determined for nickel acetate in acetic acid was found to be in good agreement with another experimental value.

Desolvation rate studies on Ni(ClO₄)₂·8HC₂H₃O₂ showed that at 125° C. the non-solvated salt could not be obtained but that the empirical formula Ni(ClO₄)₂·HC₂H₃O₂ was approached. This complex was probably octahedral and apparently contained bidentate perchlorate.

Complexes similar to Ni(C10₄) $_{2}^{\prime} \cdot 8HC_{2}H_{3}O_{2}$ were prepared from the hydrated perchlorates of cobalt(II) cupric, ferrous and zinc. These compounds were quite insoluble in glacial acetic acid.

A possible separation of ferrous and ferric perchlorates could be made in this manner since the solubility of ferric perchlorate was greater than 0.1 molar and the ferrous perchlorate solubility was less than 0.01 molar.

The solubilities of the nickel(II) salts investigated here generally decrease with increasing basicity of the anion. It was found that the solubility increased in the order $Ni(OTs)_2 < NiCl_2 < NiBr_2$. Per-chlorate ion should be the weakest base of all anions investigated therefore, it should have the largest solubility but its solubility fell between $Ni(OTs)_2$ and $NiCl_2$. No solubility for nickel acetate

could be determined because no stable solutions could be prepared. This would probably be expected since acetate ion should be a strong base in this solvent. One would, therefore, expect a low solubility for nickel acetate.

 NiI_2 and $Ni(OTs)_2$ were prepared from the reaction of the corresponding acid on a slurry of nickel carbonate in water. Excess carbonate was used because it can be removed by filtration leaving behind a stoichiometric product.

Pure nickel iodide could not be isolated but a product which contained some nickel oxide was isolated. Ni(OTs), was isolated.

Acetic acid would appear to be a good medium for preparing complexes since it is a weak ligand and could easily be displaced by slightly stronger ligands. The low solubilities of various salts should also aid in isolation of these complexes. Also anhydrous salts could probably be prepared by the reaction of the hydrated waters with acetic anhydride. These questions are unanswered and further work could be done in these areas.

LITERATURE CITED

- 1. Brown, R. D., Quart. Revs., 6, 63 (1952).
- Bruckenstein, S., and Kolthoff, I. M., J. Am. Chem. Soc., <u>78</u>, 2975 (1956).
- 3. Buffagni, S. and Dunn, T. M., Nature, <u>188</u>, 937 (1960).
- 4. Chappell, W. and Davidson, A. W., J. Am. Chem. Soc., <u>55</u>, 3531 (1933).
- Chia Shu Shen and Ming Hsiao Chang, Hua Hsuch Hsuch Pao, <u>26</u>, No. 3, 124-130 (1960); Chem. Abstracts (1963) <u>3523b</u>.
- 6. Cotton, F. A., <u>Chemical Applications of Group Theory</u>, Interscience Publishers, Inc., New York and London (1964) p. 231.
- 7. Cotton, F. A. and Wilkinson, G., <u>Advanced Inorganic Chemistry</u>, Interscience Publishers, Inc., (1962) pp. 755-756.
- 8. Davidson, A. W., J. Am. Chem. Soc., 50, 1890 (1928).
- 9. Dunn, T. M., in Lewis J., and Wilkins, R. G., <u>Modern Coordination</u> <u>Chemistry</u>, Interscience Publishers, Inc., New York (1960).
- 10. Figgis, B. N., Nature, <u>182</u>, 1568 (1958).
- 11. Figgis, B. N., and Martin, R. L., J. Am. Chem. Soc., 3837 (1956).
- 12. Hardt, H. D., and Eckle, M., Z. Anal. Chem., 197(2), 160-81 (1963).
- Harris, C. M., and McKenzie, E. D., J. Inorg. Nucl. Chem., <u>19</u>, 372 (1961).
- 14. Hathaway, B. J. Holah, D. G. and Hudson, M., J. Chem. Soc., 4586 (1963).
- 15. Herbst, R. M., and Stone, K. G., J. Organic Chem., 22, 1139 (1957).
- Higuchi, T., Danguilan, M. L. and Cooper, A. D., J. Phys. Chem. 58, 1167 (1954).
- 17. Jorgenson, C. K., Acta. Chem. Scand., 9, 1362 (1955).
- 18. Jorgenson, C. K., Ibid., 10, 887 (1956).

- Khristov, D., Karaivanov St., and Nenov, N., Godishnik, Sofuskiya Univ. Fiz-Mat. Fak. Khim, <u>55</u>, 33-48 (1960-1961) Chem. Abstracts (1963) 3522h.
- 20. Kolling, O. W., Inorganic Chem., 1, 561 (1962).
- 21. Kolling, O. W., Inorganic Chem., 3, 202 (1964).
- 22. Lambert, J. L., and Kolling, O. W., Inorganic Chem., 3, 202(1964).
- Meek, D. W., Drago, R. S. and Piper, T. S., Inorganic Chem., <u>1</u>, 285 (1962).
- 24. Monnier, G., Ann. Chim., 13, 2, 14-57 (1957).
- Moore, L. E., Gayhart, R. B. and Bull, W. E., J. Inorg. Nucl. Chem., <u>26</u>, 896 (1964).
- 26. Orgel, L. E., <u>An Introduction to Transition-Metal Chemistry-Ligand</u> Field Theory, Butler and Tanner Ltd. (1960), p. 46.
- 27. Orgel, L. E., J. Chem. Phys., 23, 1004 (1955).
- Schwarzenbach, G., <u>Complexometric Titrations</u>, Interscience Publishers, Inc., New York (1957) pp. 81-82.
- 29. Sidgwick, N. V., The Chemical Elements and Their Compounds, 2, Oxford University Press, (1950) pp. 1436-1437.
- 30. Stone, K. G., <u>Determination of Organic Compounds</u>, McGraw Hill, New York, (1956) p. 92.
- 31. Stone, K. G., <u>Ibid.</u>, p. 172.
- 32. Tappmeyer, W. P. and Davidson, A. W., Inorg. Chem., <u>2(4)</u>, 823-5 (1963).
- 33. Vainstein, B. K., J. Fiz Khim., <u>26</u>, 1774, (1952) in Wells, A. F., <u>Structural Inorganic Chemistry</u>, <u>3rd Edition</u>, Oxford University Press, (1962) p. 875.
- 34. Wickenden, A. E., and Krause, R. A., Inorganic Chem., <u>4</u>, 404 (1965).