

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. IX. Magnetic Susceptibilities of Nickel and Cobalt Complex Ions from 0 to 80^oBY FRANK H. FIELD² AND W. C. VOSBURGH

The decrease in the effective magnetic moment of nickel and copper ions when complex ions are formed in solution has been ascribed by Russell, Cooper and Vosburgh³ to an increased quenching of the orbital contribution. In accord with this explanation Werbel, Dibeler and Vosburgh⁴ found no change in the moment of iron(III) ion on complex formation, iron(III) ion having no orbital moment. These conclusions were based on measurements at one temperature only and an alternative explanation for the change in the nickel and copper effective moments based on the neglect of a changing Weiss constant is not excluded. This investigation was undertaken to explore that possibility for nickel ion and to investigate the behavior of cobalt(II) ion under similar circumstances. It has been found that while the Weiss constant of nickel ion seems to change a little on complex formation, the change is in the wrong direction to account for the decreasing moment calculated on the assumption of the Curie equation. For cobalt ion, on the other hand, a small increase in the effective moment on formation of the ethylenediamine complex in solution might be accounted for on the basis of a changing Weiss constant.

Materials.—Nickel nitrate and nickel sulfate of reagent grade were recrystallized twice from water and found by the cobaltinitrite test to be free from cobalt. Stock solutions were prepared and analyzed by the dimethylglyoxime method.

Cobalt nitrate of reagent grade, and low nickel content, was recrystallized twice and a stock solution prepared and analyzed by the electrolytic method as described by Hillebrand and Lundell.⁵

Ethylenediamine, Eastman Kodak Co., 95–100%, was twice distilled and a fraction boiling between 116.2 and 116.5° collected. Its composition was determined by titration with hydrochloric acid.

Potassium oxalate of reagent grade was recrystallized.

Phenanthroline was obtained from the G. Frederick Smith Chemical Company and was free from iron, as evidenced by absence of color.

Apparatus.—The apparatus described by Russell, Cooper and Vosburgh³ was altered to make possible measurements at several temperatures. A heater and thermoregulator were introduced into the water-bath, and the top of the bath was covered to reduce evaporation and heat losses at high temperatures. The glass jacket within which the sample tube was hung in the earlier work was replaced by one of copper of one-eighth inch wall thickness. The water was stirred by an air stream and its temperature was measured by means of a calibrated three-junction

thermoelement and potentiometer. Without the magnetic field the temperature could be held constant within 0.1°. The field interfered with the operation of the regulator, and manual regulation of the heating current was necessary during the relatively brief periods when the field was on. The most convenient procedure was to allow the temperature to drift downward in measurements at 50 and 60° and upward in measurements at the higher temperatures while the field was on. The temperature was measured frequently and the drift during measurements seldom amounted to more than 0.2°. It is believed that errors resulting from temperature drifts are not appreciable.

For measurements at 28° the temperature was regulated as described by Russell, Cooper and Vosburgh and at room temperature the water was stirred, but was not heated or cooled. At 0° the tank was packed full of crushed ice, after sweeping moisture from within the copper jacket by a stream of dry air.

By means of a thermoelement the difference in temperature between the air in the copper jacket and the bath-water was found to be less than 0.1° when equilibrium was established. Water in a glass tube suspended in the copper jacket attained in a short time a temperature within 0.1° of the bath-water when the latter was at 90°.

With the bath packed with ice it was found that the temperature of a sample would pass slowly through a minimum of about 0.5 ± 0.2° between approximately thirty and fifty minutes after packing the ice. The procedure was arranged accordingly and the temperature taken as 0.5°.

Sample tubes of Pyrex glass, 9 mm. inside diameter, similar to those of Russell, Cooper and Vosburgh and Freed and Casper⁶ were used, except that the lower chamber was left empty instead of being filled with water. The tube used in most of the measurements was calibrated at four different times and at six temperatures. The apparent increase in weight of the water on application of the field, $\Delta W_{\text{water-air}}$, varied with temperature from -34.46 to -32.83 mg. with an average deviation from the mean values of ±0.04 mg.

Nickel, tris-(Ethylenediamine)-nickel, and tris-(o-Phenanthroline)-nickel Ions.—To test the apparatus and method, some measurements were made on solutions of nickel nitrate. Then, since the effect of complex formation in solution on the effective moment has been studied at only one temperature, some measurements were made on the ethylenediamine and phenanthroline complex ions.

While dissolved air would not make serious errors in these measurements, it was desired to develop a procedure for its elimination for use with cobalt complexes. Accordingly, considerable care to exclude air was taken. The procedure was later found inadequate when very small amounts of oxygen were objectionable.

Solutions were prepared by dilution of the stock solution with or without inclusion of ethylenediamine or phenanthroline in excess. Dissolved air was removed by alternate evacuation and bubbling of purified nitrogen through the solution. A correction was made for the water lost in the process by weighing before and after. A portion of the solution was then transferred to the sample tube with a minimum of exposure to air. The value of $\Delta W_{\text{solution-air}}$ was then determined at various temperatures.

The mass susceptibilities of ethylenediamine and phenanthroline in water solution at concentrations of 0.0349 and 0.0320 g. per ml., respectively, were determined at 28° and found to be 0.75 and 0.63 × 10⁻⁶. These values were used in the calculation of diamagnetic corrections.

The densities of the solutions were determined in a pyc-

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(3) Russell, Cooper and Vosburgh, *THIS JOURNAL*, **65**, 1301 (1943).

(4) Werbel, Dibeler and Vosburgh, *ibid.*, **65**, 2329 (1943).

(5) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 323.

(6) Freed and Casper, *Phys. Rev.*, **36**, 1002 (1930).

nometer made from a 25-ml. flask by sealing a 7-cm. length of 8-mm. tubing to its neck. Ten equally spaced marks were made on the neck and the volume between them determined. The pycnometer was filled by a hypodermic syringe. It was calibrated by water at 0, 26 and 90°, and then used for measuring the solutions at 0, 28, 50 and 90°. The densities were plotted against temperature and from the graph densities were read at the exact temperatures at which $\Delta W_{\text{solution-air}}$ values had been determined.

The molal paramagnetic susceptibility, χ_m , was calculated by means of the equation

$$\chi_m = \frac{1000(\kappa_w - \kappa_a) \Delta W_{\text{para}}}{(\Delta W_{\text{water-air}}) C} \quad (1)$$

in which κ_w and κ_a are the volume susceptibilities of water and air, C is the concentration in moles per liter, and ΔW_{para} is given by

$$\Delta W_{\text{para}} = (\Delta W_{\text{solution-air}}) - (\Delta W_{\text{solvent-air}}) \quad (2)$$

The value of $\Delta W_{\text{solvent-air}}$ was calculated by the equation

$$\Delta W_{\text{solvent-air}} = \frac{\kappa_{\text{solvent}} - \kappa_a}{\kappa_w - \kappa_a} (\Delta W_{\text{water-air}}) \quad (3)$$

in which

$$\kappa_{\text{solvent}} = C_w X_w + C_a X_a + C_b X_b + \dots \quad (4)$$

C_w , C_a , and C_b are the concentrations of water and the various components of the solution other than the paramagnetic component in grams per milliliter, and X_w , X_a , and X_b are the corresponding mass susceptibilities. Values of κ_w were calculated from the mass susceptibility data of Cabrera and Fahlenbrach⁷ and values of κ_a from the equation of Klemm.⁸

An empirical equation of the form $1/\chi_m = aT + b$ was fitted to the experimental data for each solution by the method of least squares. From the equation were calculated susceptibilities at 0, 28 and 80°. The effective moments, μ_{eff} , were calculated from these susceptibility values by means of the equation

$$\mu_{\text{eff}} = 2.828 \sqrt{X_m T} \quad (5)$$

The results are given in Table I in the form of the least-squares equations, the interpolated susceptibilities at 0, 28 and 80° and the corresponding moments.

The moment for nickel ion in solution is in agreement with 3.25 at 23.3° calculated from the data of Nicolau⁹ by Equation 5, and 3.25 at 28° by Russell, Cooper and Vosburgh,³ the latter corrected for a change in the value of the Bohr magneton. It is in fair agreement with 3.20 calculated from the molar susceptibility 0.00436 of Fahlenbrach.¹⁰ The agreement of the values of Δ in Table I with each other and with -21.2° K. of Nicolau⁹ and zero of Foex¹¹ is as good as can be expected in view of the long extrapolation involved. The data for nickel ion can be considered a check on the apparatus and method.

(7) Cabrera and Fahlenbrach, *Z. Physik*, **82**, 759 (1933).

(8) Klemm, "Magnetochemie," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1936, p. 45.

(9) Nicolau, *Compt. rend.*, **205**, 557 (1937).

(10) Fahlenbrach, *Ann. Physik*, [5] **13**, 270 (1932).

(11) Foex, *Ann. phys.*, [9] **16**, 224 (1921).

TABLE I

MAGNETIC MOMENTS OF NICKEL ION AND NICKEL COMPLEX IONS

| Temp., °C. | $X_m \times 10^6$ c. g. s. u. | μ_{eff} | $X_m \times 10^6$ c. g. s. u. | μ_{eff} |
|--|----------------------------------|--------------------|----------------------------------|--------------------|
| Ni(NO ₃) ₂ , 0.1016 M at 23.7° | | | | |
| $1/X_m = 0.7527 T + 2.5;$ $\Delta = -3^\circ\text{K}.$ | | | | |
| 0 | 4805 | 3.240 | 4805 | 3.240 |
| 28 | 4363 | 3.241 | 4382 | 3.248 |
| 80 | 3727 | 3.244 | 3765 | 3.261 |
| Ni(en) ₃ (NO ₃) ₂ , 0.1017 M at 23.7° | | | | |
| $1/X_m = 0.7189 T + 11.7;$ $\Delta = -16^\circ\text{K}.$ | | | | |
| Ni(en) ₃ (NO ₃) ₂ , 0.1018 M at 23.6° | | | | |
| $1/X_m = 0.8402 T + 3.0;$ $\Delta = 4^\circ\text{K}.$ | | | | |
| 0 | 4414 | 3.105 | 4417 | 3.107 |
| 28 | 4000 | 3.104 | 4003 | 3.105 |
| 80 | 3405 | 3.102 | 3413 | 3.104 |
| Ni(phen) ₃ (NO ₃) ₂ ; 0.05054 M at 22.5° | | | | |
| $1/X_m = 0.8496 T - 4.3;$ $\Delta = 5^\circ\text{K}.$ | | | | |
| 0 | 4390 | 3.096 | 4409 | 3.104 |
| 28 | 3975 | 3.094 | 3971 | 3.093 |
| 80 | 3381 | 3.090 | 3355 | 3.078 |
| Ni(phen) ₃ (NO ₃) ₂ , 0.05065 M at 21.3° | | | | |
| $1/X_m = 0.8915 T - 16.8;$ $\Delta = 19^\circ\text{K}.$ | | | | |

The complex ions of nickel seem to have been measured in solution previously at only single temperatures. From the measurements of Cambi, Cagnasso and Tremolada¹² moments can be calculated for solid tris-(ethylenediamine)-nickel and tris-(phenanthroline)-nickel chlorides of 3.02 and 3.14 at 21°. Somewhat different values for these complexes were obtained with other anions. Russell, Cooper and Vosburgh³ found for the two complex ions in solution at 28° effective moments (corrected) of 3.11 and 3.09, respectively, with which the results of this investigation are in good agreement. From Table I it is apparent that the effective moments change very little with temperature. These complex ions are unlike basic iron(III) acetate for which in the solid state Cambi and Szegö¹³ found a very large Weiss constant.

The use of the Weiss equation for the calculation of nickel ion moments does not seem to be justified theoretically according to Gorter¹⁴ and it is impractical because of the uncertainty of the Weiss constants. However, if the Weiss constants of Table I are considered to have some significance relative to each other, because of having been determined with the same apparatus and technique, a general trend can be noticed. The constants increase in the positive direction with the stability of the complex. This change is in the wrong direction to account for the decrease in

(12) Cambi, Cagnasso and Tremolada, *Gazz. chim. ital.*, **64**, 767 (1934).

(13) Cambi and Szegö, *Ber.*, **66**, 657 (1933).

(14) Gorter, *Physica*, **11**, 17 (1931); *Physik. Z.*, **33**, 546 (1932); **34**, 462 (1933).

the effective moment if the Weiss equation

$$\mu = 2.828 \sqrt{\chi(T - \Delta)} \quad (6)$$

should be used instead of Equation 5.

Cobalt and Oxalatocobaltate(II) Ions.—Since cobalt nitrate and potassium oxalatocobaltate (II) are not oxidized by air, rigid exclusion of oxygen was not needed in the preparation of these solutions for measurement. The procedure was the same as for the nickel compounds, both solutions being made from the same stock cobalt nitrate solution. For the oxalato compound

TABLE II

MAGNETIC MOMENTS OF COBALT(II) AND OXALATOCOBALTATE(II) IONS

| Co(NO ₃) ₂ , 0.1172 M at 28.6° | | K ₂ Co(C ₂ O ₄) ₂ , 0.1175 M at 21.9° | | |
|---|-------------------------------------|--|-------------------------------------|--------------------|
| Temp., °C. | $\chi_m \times 10^6$ c. g. s. u. | μ_{eff} | $\chi_m \times 10^6$ c. g. s. u. | μ_{eff} |
| 0 | 11,200 | 4.947 | 11,260 | 4.960 |
| 28 | 10,180 | 4.952 | 10,240 | 4.967 |
| 80 | 8,710 | 4.960 | 8,750 | 4.972 |

enough potassium oxalate was included in the solution to form the compound and leave an excess of about 0.7 mole per liter. The stock cobalt nitrate solution was diluted in both cases to give a 0.1173 M solution. This was found to be too large a concentration for the oxalate compound

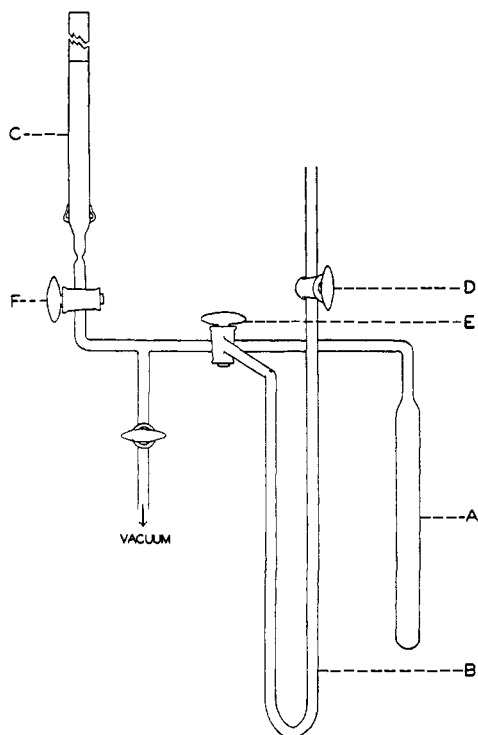


Fig. 1.—Apparatus used for rigid exclusion of air during preparation of the sample and its introduction into the (inverted) sample tube, C.

at 0.5° since crystallization occurred, and at this temperature another solution half as concentrated was used. Table II gives a summary of the results for the two solutions.

tris-(Ethylenediamine)-cobalt(II) Ion.—A new technique was perfected in experiments on tris-(ethylenediamine)-cobalt(II) ion. The sample tube, which could be sealed at the top during measurements, was at the beginning of the procedure made part C of the apparatus shown in Fig. 1. Some cobalt chloride solution was placed in compartment A which was then sealed in place as shown. Some ethylenediamine was introduced into B through stopcock D. Both liquids were frozen by immersion in a bath of acetone and Dry Ice, and the apparatus was evacuated as they melted. The freezing and evacuation were repeated four times, and the cobalt nitrate solution was transferred to the sample tube without contact with air. The excess solution between stopcocks E and F was cleaned out, and then the ethylenediamine in B was transferred to the sample tube under vacuum. By means of calibration marks on the sample tube the volume of the solution before and after the addition of the ethylenediamine could be measured. As a check on the procedure, a cobalt nitrate solution was carried through it and measured without the addition of ethylenediamine. The results, shown in Table III, were in agreement with the previous measurement.

Attempts to use some of the cobalt nitrate stock solution in the preparation of the ethylenediamine complex failed because of continuous variation in ΔW . This was ascribed to slow oxidation of the complex ion by the nitrate ion. With the nitrate ion replaced by chloride ion (by careful evaporation of a portion of the stock solution with an excess of hydrochloric acid) no evidence of oxidation was observed when an excess of ethylenediamine and a small amount of hydrochloric acid was added, in absence of oxygen. Measurements at 28° made before and after those at the other temperatures agreed, indicating absence of slow oxidation. A summary of the results is given in Table III.

TABLE III

MAGNETIC MOMENTS OF COBALT(II) AND TRIS-ETHYLENEDIAMINECOBALT(II) IONS

| Co(NO ₃) ₂ , 0.1172 M at 28.6° | | [Co(en) ₃]Cl ₂ 0.1106 M at 28.6° | | |
|---|-------------------------------------|---|-------------------------------------|--------------------|
| Temp., °C. | $\chi_m \times 10^6$ c. g. s. u. | μ_{eff} | $\chi_m \times 10^6$ c. g. s. u. | μ_{eff} |
| 0 | 11,140 | 4.934 | 11,360 | 4.982 |
| 28 | 10,180 | 4.952 | 10,350 | 4.992 |
| 80 | 8,780 | 4.980 | 8,870 | 5.006 |

It will be observed that the Weiss constant for cobalt nitrate given in Table III differs from that in Table II. This is ascribed to the fact that

different sample tubes were used in obtaining the two values, and it was found in this work that it was often impossible to reproduce Weiss constant values if any changes were made in apparatus or procedure. Because of the long extrapolation involved even minor changes in the experimental conditions were found to affect the value obtained considerably. However, while some doubt exists as to the absolute values of the Weiss constants, it is believed that the Weiss constants of different substances determined in a given sample tube with a given technique are roughly comparable.

For cobalt(II) ion the most reliable measurements seem to be those of Chatillon,¹⁵ who found a Weiss constant of -12° K, and a moment of 4.94 calculated by Equation 5. The effective moments for cobalt ion given in Tables II and III are in close agreement with those of Chatillon, and the Weiss constants agree as well as can be expected. The effective moment of the oxalato-cobalt ion is practically the same as that of cobalt ion. This behavior is different from that of nickel and recalls the constancy of the moment of iron(III) ion on formation of certain complexes.⁴

The formation of the ethylenediamine complex causes an increase in the effective moment, according to Table III. The use of Equation 6 for the calculation of moments may be justifiable theoretically for cobalt.¹⁴ If calculated in this way using the Weiss constants of Table III the moment for the complex is less than that for cobalt ion, namely, 5.09 as compared with 5.15 c. g. s. u. If the use of Equation 6 can be justified, and if the Weiss constants of Table III are not too much in error, the effect of complex formation on the moment is in the same direction as for nickel ion. While the Weiss constants are of questionable accuracy it is to be noted that the trend in them is the same as for nickel: toward less negative values as the stability of the complex increases.

Iron(II) Complexes.—Attempts to measure iron(II) complexes in alkaline solution were only partially successful even by the technique developed for the cobalt(II) complexes. Measurements on acidified iron ammonium sulfate solutions which had been treated with hydrogen sulfide to ensure absence of appreciable iron(III)

gave for the average of two solutions $1/X_m = 0.2761 T + 1.2$ and effective moments of 5.340, 5.345, and 5.349 c. g. s. u. at 0, 28, and 80° , respectively, and a Δ value of -4° K. Nicolau⁹ found a Δ value of -20.6° K., and from his susceptibility the moment at 22° calculated by Equation 5 is 5.36. From the data of Foex¹¹ at 18° the moment 5.34 can be calculated.

Solutions to which an excess of ethylenediamine was added were never entirely free from a small amount of precipitate. With the most rigid exclusion of oxygen the amount was very small. It appeared as a finely divided, light colored precipitate not long after the solution was prepared, and under the influence of the magnetic field some collected on the glass in the regions of intense field. In time this precipitate turned dark in color and settled readily as a small black precipitate. This suggests conversion to magnetic iron oxide.

If it can be assumed that the first precipitate was not ferromagnetic, the error caused by its presence could not have been large compared with the effect of the ethylenediamine, since the effective moment for the ethylenediamine complex was 5.54 c. g. s. u. at 0.5° and 28.6° , an increase of 0.2 c. g. s. u. attributable to the formation of the complex. After formation of the black precipitate the apparent moment increased to 5.7 c. g. s. u. Because of this change it was not possible to make reliable measurements at more than one or two temperatures.

Summary

The magnetic susceptibility of nickel ion and its ethylenediamine and phenanthroline complexes and of cobalt(II) ion and its oxalate and ethylenediamine complexes have been measured from 0° to 80° . The decrease in effective magnetic moment of nickel ion on complex formation cannot be explained as the result of the use of the Curie equation instead of the Weiss equation in the calculation of the moments. There was no significant change in the effective moment of cobalt(II) ion on formation of the oxalate complex, but a small increase on formation of the ethylenediamine complex.

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(15) Chatillon, *Ann. phys.*, [10] **11**, 187 (1928).