

slightly to loosen the mass, and then stirred until the taffy-like material has changed to a granular white precipitate. The mixture is allowed to stand at room temperature for one hour. The precipitate is collected on a Büchner funnel and washed with 50 cc. of absolute alcohol. If the red alcoholic filtrate is allowed to evaporate slowly, more of the carbazide will precipitate out. The yield of crude diphenylthiocarbazide is 100–125 g. (60–75%, based on the phenylhydrazine).

Diphenylthiocarbazono (III).—The crude carbazide is added to a solution of 60 g. of potassium hydroxide in 600 cc. of methanol in a 1-liter round-bottomed flask. The flask is heated in a water-bath until refluxing takes place. The mixture is refluxed for exactly five minutes, after boiling begins. (If it is boiled for a longer time, the yield is decreased.) The red solution is cooled with ice water and filtered by gravity. The carbazono is precipitated by adding ice-cold 1 *N* sulfuric acid with stirring, until the solution just tests acid to congo red paper. About 900–1100 cc. is necessary. When the end-point is reached, the liquid is no longer red but colorless. The blue-black precipitate is filtered by suction and washed with 50 cc. of cold water. The crude carbazono is recrystallized by dissolving it in 500 cc. of 5% sodium hydroxide solution, filtering by suction and acidifying immediately with 1 *N* sulfuric acid (about 650 cc.) until just acid to congo red paper. The precipitate is filtered by suction and then washed thoroughly with water by transferring it to a 2-

liter beaker, adding 1600–1800 cc. of cold water, stirring thoroughly and re-filtering. This process is repeated until there is no trace of sulfate in the washings. Four or five washings are usually necessary. Air is drawn through the precipitate on the Büchner funnel for twenty to thirty minutes. It is then dried in an oven at 40°. The yield of this crude diphenylthiocarbazono is 63–85 g. (75–102% based on phenylhydrazine). The decomposition range is anywhere from 120–140°. The carbazono is purified by putting a 5–10 g. portion of it in a Soxhlet extractor, covering with ether, allowing it to stand one hour, and then extracting one and one-half hours. The product is transferred immediately to a beaker, washed again with 50 cc. of ether, filtered by suction just long enough to remove most of the liquid, and then further dried by pressing between filter paper. The recovery is 60–87%. The purer the crude dithizono, the higher the percentage recovery. The pure compound is completely soluble in chloroform and decomposes sharply at a temperature between 165–169°.

The over-all yield of pure diphenylthiocarbazono based on the phenylhydrazine is 43–54.8 g. (52–66%).

Summary

An improved method for the preparation of dithizono has been developed.

BLOOMINGTON, INDIANA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. V. The Magnetic Moments of Some Complex Ions of Nickel and Copper¹

BY CHARLES D. RUSSELL,² GERALD R. COOPER AND W. C. VOSBURGH

Shaffer and Taylor³ have shown that the paramagnetic susceptibilities of nickel and copper (II) ions in solution decrease on addition of substances that form complex ions with them. They concluded, in agreement with Pascal,⁴ that the formation of a chemical bond lowers the susceptibility of a paramagnetic ion and that this lowering is proportional to the firmness of the bond.

The magnetic moments of the iron group ions are not much larger than the calculated spin moments of the unpaired 3*d* electrons and the relatively small differences between calculated and observed values are considered to be contributions of the orbital moments. These contributions are small because the orbital moments are largely

“quenched” by the perturbing action of the electrostatic fields of neighboring atomic groups.⁵ Nickel is typical of the latter half of the iron group, the ion having a calculated spin moment of 2.83 Bohr magnetons and an observed moment of about 3.2 or 3.3 Bohr magnetons.

The theory of Pauling^{5b} and Van Vleck^{5a} suggests that when the formation of a bond with a paramagnetic ion is accompanied by a small reduction of the magnetic moment, it is the orbital contribution to the moment that is reduced. Some additional measurements of the changes in the moments of nickel and copper (II) ions on formation of paramagnetic complex ions have given results in agreement with this.⁶

(1) Thesis submitted by Charles D. Russell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, June, 1941.

(2) Now at The Texas Company, Research Laboratories, Beacon, N. Y.

(3) Shaffer and Taylor, *THIS JOURNAL*, **48**, 843 (1926). A number of references to older work are given by Shaffer and Taylor.

(4) Pascal, *Ann. chim. phys.*, [8] **16**, 571 (1909).

(5) (a) Van Vleck, “The Theory of Electric and Magnetic Susceptibilities,” The Clarendon Press, Oxford, 1932, pp. 283–301. (b) Pauling, “The Nature of the Chemical Bond,” Cornell University Press, Ithaca, N. Y., 1939, p. 108.

(6) The magnetic moments of ferric and manganous ions are purely spin moments according to Van Vleck (ref. 5a, p. 301) and have no orbital contribution. If the formation of a bond affects only the orbital moment of an ion, the moments of iron (III) and manganese

Reagents.—Nickel sulfate and copper sulfate of analytical reagent grade were twice recrystallized. The nickel sulfate so obtained gave no test for cobalt. Stock solutions were prepared and analyzed by the dimethylglyoxime and iodometric methods, respectively.

A solution of nickel chloride in methanol was prepared. Commercial absolute methanol (99.5%) was refluxed for several hours with magnesium turnings, with a little iodine as catalyst, and then distilled in an all-glass still with air excluded. The middle fraction, boiling within the range 64.56–64.58° at 760 mm. pressure, was used. Hydrated nickel chloride was dehydrated by heating in the presence of gaseous hydrogen chloride. The anhydrous methanol was then introduced and the mixture allowed to stand for about a month, since the dehydrated nickel chloride was very slow to dissolve. The solution which was yellowish-green in color was analyzed by the dimethylglyoxime method.

A potassium oxalate solution was made by weighing from material of analytical reagent grade.

Pyridine and ethylenediamine, both of the best commercial grade, were diluted with water and the solutions standardized by titration with standard hydrochloric acid solution, with methyl orange as the indicator.

An ammonia solution was standardized by titration with standard hydrochloric acid and protected from carbon dioxide during storage.

A sodium aminoacetate solution was prepared by neutralization of a weighed quantity of aminoacetic acid with a standard sodium hydroxide solution and dilution to known volume.

Apparatus and Measuring Technique.—Measurements of magnetic susceptibility were made by the Gouy method. A Pyrex sample tube of the type described by Freed and Kasper⁷ was suspended from one pan of an Ainsworth semi-micro balance so as to hang between the poles of a large electromagnet, with the glass partition in a region of homogeneous field. The lower part of the sample tube was filled with water and the upper part with the solution to be measured. The lengths of the two parts of the tube were such that the columns of liquid extended above and below the poles of the magnet to regions of negligible field.

(II) ions should not decrease on complex ion formation unless pairing of electrons takes place. More recent measurements in this Laboratory by Mr. V. H. Dibeler and Mr. Burton Werbel have confirmed this for iron (III) ion. Iron (II) ion is also an exception, since its moment sometimes increases on complex formation.

(7) Freed and Kasper, *Phys. Rev.*, **86**, 1002 (1930).

The sample tube was enclosed within a glass jacket so as to hang freely and the jacket immersed in a water-bath situated between the coils of the magnet. An oiled silk cord by which the tube was suspended passed through a small tube at the top of the jacket to the balance above. When the sample tube was to be introduced into the jacket or removed from it, the water level was lowered and the jacket taken apart at a ground glass junction. The temperature of the water bath was maintained constant by a continuous flow of water from a much larger bath maintained at $28 \pm 0.1^\circ$. This larger bath furnished water for cooling the magnet coils also. Experience showed that careful control of temperature was necessary if the sample tube was to be weighed with the desired accuracy of a few hundredths of a milligram. The use of a magnetic damper on the balance seemed to improve the precision.

The pole-pieces of the magnet were in the form of truncated cones with ends 5 cm. in diameter. The distance between the poles was about 2.5 cm. The current through the magnet coils was furnished by a 150-volt storage battery and was measured by means of a Weston ammeter calibrated in fifths of an ampere. With 0.1 *M* nickel sulfate solution at 28° in the upper part of a sample tube of 11 mm. outside diameter and water in the lower part, the apparent increase in weight, ΔW , on passing 15 amperes through the magnet coils was 18.53 mg. This was reproducible to well within 0.05 mg.

The molal paramagnetic susceptibility, $\chi_{m,p}$, was calculated from ΔW solution–water (solution in the upper compartment and water in the lower), ΔW solvent–water, and ΔW air–water, each of these being corrected for the deformities of the measuring tube. The apparent increase in weight for solvent *versus* water (ΔW solvent–water) can be considered to be an empirical diamagnetic correction. It is the sum of the measured corrections for the various diamagnetic substances in solution and the calculated diamagnetic correction for the paramagnetic salt furnishing the central atom of the complex ion.

The method of calculation is given by the equation

$$\chi_{m,p} = \frac{\Delta W \text{ solution-water} - \Delta W \text{ solvent-water}}{C} \times (23.54 \times 10^{-6}) \text{ c. g. s. u.}$$

where ΔW values are expressed in milligrams and *C* is the concentration of the nickel or copper ion

in moles per liter. The factor, 23.54×10^{-6} , is

$$\frac{(\kappa_{\text{air}} - \kappa_{\text{water}})(1000)}{\Delta W_{\text{air-water}}}$$

where κ_{air} and κ_{water} represent the volume magnetic susceptibilities of air and water, respectively. The value of $(\kappa_{\text{air}} - \kappa_{\text{water}})$ was calculated to be 0.749×10^{-6} c. g. s. u. from data in the "International Critical Tables," and $\Delta W_{\text{air-water}}$ was found experimentally to be 31.82 mg.

The moment, μ , or effective Bohr magneton number was obtained by the equation

$$\mu = 2.828(\chi_{m,p}T)^{1/2}$$

where $T = 301.1^\circ\text{K}$.

For the spectrophotometric measurements a Coleman D. M. photoelectric spectrophotometer, model 10-S, was used.

Magnetic Data.—In the investigation of both nickel and copper complexes, a series of several solutions containing a constant concentration of nickel or copper (II) ion and progressively increasing concentrations of a coordinating reagent were made and measured with the Gouy apparatus. In some of the solutions, it was necessary to include an additional diamagnetic salt to prevent precipitation of nickel or copper hydroxide. Proper empirical diamagnetic corrections for these compounds were made. In a few cases the solutions were supersaturated and it was necessary to measure the ΔW rapidly before actual precipitation occurred.

The molal paramagnetic susceptibility values, $\chi_{m,p}$, and the magnetic moments, μ , were calculated on the basis of the total nickel or copper concentration.

Most of the results are shown in Figs. 1 and 2 in which the moment is plotted against the total number of equivalents of the coordinating compound per mole of nickel or copper ion. By an equivalent of the coordinating reagent is meant either a mole or a half mole, depending on whether a molecule of the reagent occupies one or two coordination positions, respectively, in the complex ion.

Figures 1 and 2 show that the magnetic moment decreases at first when a coordinating reagent is added and then becomes constant. For nickel ion the decrease continues until approximately six equivalents of the reagent have been added. For copper, constancy is attained after about four equivalents have been added. When the reagent was pyridine, a further decrease took

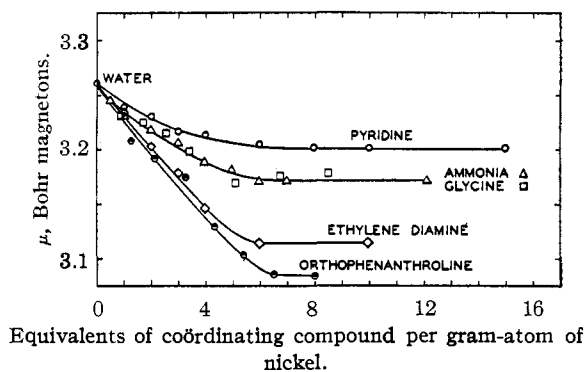


Fig. 1.—Magnetic moments of complex ions of nickel in solution.

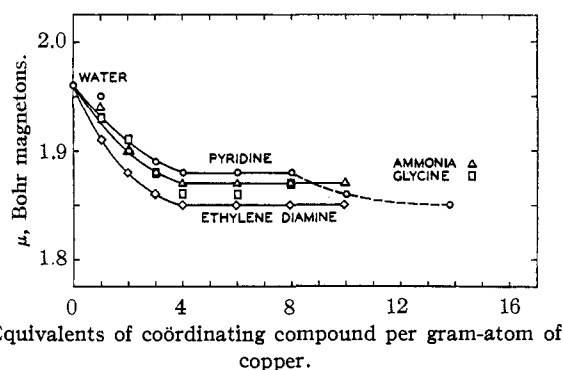


Fig. 2.—Magnetic moments of complex ions of copper (II) in solution.

place after a region of constancy. This is shown as the dotted portion of the copper-pyridine curve in Fig. 2. This may have been the result of the formation of higher complexes following a range of concentrations in which most of the copper was in the form of the tetrapyridine ion. Bjerrum⁸ has evidence of the formation of a pentammine cupric ion in sufficiently concentrated ammonia solutions following a range in which the tetrammine is stable. According to his data, little of the pentammine would have been formed at the highest ammonia concentration of this investigation. However, it is possible that a pentapyridine complex can be formed which is more stable than the pentammine.

Table I contains the experimental data for the systems in which enough of the coordinating reagent was present to give a constant magnetic moment, and also data for nickel sulfate in water and nickel chloride in methanol.

A few measurements were made on methanol solutions containing small amounts of water.

(8) Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 290.

TABLE I
 MAGNETIC SUSCEPTIBILITIES OF NICKEL AND COPPER COMPLEX IONS

Reagent (or solvent)	Ni or Cu, M	Reagent per g.-at., equivalents	$\Delta W_{\text{solution-water}}$, mg.	$\Delta W_{\text{solvent-water}}$, mg.	μ
A. Nickel sulfate (or chloride) with various reagents					
(Methanol)	0.2470	..	54.36	7.27	3.288
(Methanol)	.1787	..	42.63 ^a	7.45 ^a	3.300
(Water)	.08908	..	16.51 ^b	-0.21	3.262
(Water)	.09352	..	17.32	-.21	3.260
(Water)	.09484	..	17.94 ^a	-.21	3.254
Oxalate	.08908	12.7	15.34	-1.00	3.225
Oxalate	.08908	19.0	15.20	-1.22	3.232
Oxalate	.08908	24.1	14.82	-1.66	3.238
Pyridine	.08908	6.0	15.92	-0.22	3.205
Pyridine	.08908	8.0	15.96	-.15	3.202
Pyridine	.08908	10.0	16.01	-.09	3.201
Pyridine	.08908	15.0	16.37	+.27	3.201
Aminoacetate	.08908	5.1	15.39	-.40	3.170
Aminoacetate	.08908	6.8	15.38	-.47	3.176
Aminoacetate	.08908	8.5	15.33	-.55	3.179
Ammonia	.08908	6.0	15.65	-.15	3.171
Ammonia	.08908	7.0	15.67	-.14	3.172
Ammonia	.08908	12.1	15.71	-.10	3.172
Ethylenediamine	.08908	4.0	15.35	-.21	3.147
Ethylenediamine	.08908	6.0	15.04	-.21	3.115
Ethylenediamine	.08908	10.0	15.04	-.21	3.115
<i>o</i> -Phenanthroline	.09352	6.5	15.37	-.34	3.086
<i>o</i> -Phenanthroline	.09352	8.0	15.28	-.41	3.084
B. Copper sulfate with various reagents					
(Water)	.0967	..	6.33 ^c	-.21	1.96
(Water)	.0967	..	5.23	-1.35	1.96
Pyridine	.0967	4.0	5.88	-.14	1.88
Pyridine	.0967	6.0	5.99	-.07	1.88
Pyridine	.0967	8.0	6.05	.00	1.88
Pyridine	.0967	10.0	5.97	+.07	1.86
Pyridine	.0967	13.8	6.02	+.21	1.85
Ammonia	.0967	4.0	4.65	-1.32	1.87
Ammonia	.0967	6.0	4.67	-1.30	1.87
Ammonia	.0967	8.0	4.66	-1.29	1.87
Ammonia	.0967	10.0	4.70	-1.27	1.87
Aminoacetate	.0967	4.0	5.54	-0.37	1.86
Aminoacetate	.0967	6.0	5.44	-.46	1.86
Aminoacetate	.0967	8.0	5.44	-.53	1.87
Ethylenediamine	.0967	4.0	5.62	-.21	1.85
Ethylenediamine	.0967	6.0	5.61	-.21	1.85
Ethylenediamine	.0967	7.9	5.60	-.21	1.85
Ethylenediamine	.0967	9.9	5.60	-.21	1.85

^a Different sample tube; $\Delta W_{\text{air-water}} = 32.60$ mg. ^b Average of five closely agreeing results. ^c Average of three closely agreeing results.

The data are omitted because the diamagnetic corrections were somewhat uncertain. It was clear, however, that water caused a decrease in the moment, but the lowest moment in aqueous methanol was larger than the moment for nickel sulfate in water.

Spectrophotometric Measurements.—Quantitative data on the stabilities of most of the nickel and copper complex ions in solution were not

available. Hence it seemed desirable to make some qualitative comparisons of their relative stabilities by means of a spectrophotometer. The absorption spectra of the various complex ions were measured in solutions containing large excesses of the coordinating reagents, usually 10 equivalents per gram-atom of nickel or copper. The total concentration of nickel or copper was about 0.1 gram-atom per liter. The wave length

range covered was from 500 to 600 or 700 $m\mu$ for many of the solutions, but for some it was from 500 to 800 or 900 $m\mu$. The measurements were then repeated on solutions in which two reagents were present, both at the same relatively large concentration. When the transmittance curve for a solution containing two reagents was identical with the curve for the solution containing only one of the reagents and the same central atom, it could be concluded definitely that one complex ion was much more stable than the other. This was true in all but one of the comparisons. A possible alternative hypothesis that the less stable complex ion was formed first and was not changed to the more stable on addition of the second reagent was eliminated by some simple observations. When the complex found to be the less stable was formed first and the other reagent added, a change in color indicating a change to the more stable ion was always observed.

In this way the order of increasing stability of the nickel complex ions was found to be as follows: aquo < pyridine < ammine < ethylenediamine < *o*-phenanthroline. The oxalatonickelate ion was placed between the aquo and pyridine ions by a qualitative observation of color changes. Precipitation occurred soon after addition of pyridine to a solution containing potassium oxalatonickelate and excess potassium oxalate, but before precipitation a change in color from green to blue could be observed. The complex compound formed from nickel and aminoacetate ions gave indeterminate results in the relative stability test, but it was indicated that the stability of the compound was comparable to that of the ammine nickel ion.

Comparison of the order of stability with the magnetic data of Table I shows that the decrease in magnetic moment follows the same order; the most stable complex ion is the one in the formation of which the greatest decrease in moment has occurred.

The same was observed to be true of the copper complex ions. Here the order of stability was found to be aquo < pyridine < ammine < aminoacetate < ethylenediamine. The differences in magnetic moment for the copper complex ions are less than for nickel, but the moments decrease in the order of increasing stability of the ions, as for the nickel complexes. It is assumed here that the pyridine-copper ion for which the relative stability was determined was the tetrammine ion

rather than the ion of lowest magnetic moment.

Discussion.—For every complex ion system studied the magnetic moment decreases on addition of the coordinating reagent, as illustrated in Figs. 1 and 2. This is in accord with the postulate of Shaffer and Taylor,³ that the formation of a complex ion in solution lowers the paramagnetism of the ion forming the complex.⁶

The magnetic moment decreases with progressively increasing amounts of added reagents until a definite limit is reached. The copper-pyridine system is probably only an apparent exception. Complete quenching of the orbital moment or anything approaching it was not observed in any of the systems.

The formation of a complex ion from a cation in the water solution probably involves replacement of water molecules in the coordination sphere by molecules of the coordinating reagent. Nickel ion in water solution has a magnetic moment with an orbital contribution presumably dependent on the magnitude and symmetry of the electrostatic field in the coordination sphere.^{5a} When for example, pyridine is added to the solution, it gradually replaces the water molecules in this coordination sphere. The electrostatic field of the surrounding pyridine molecules has a greater quenching effect than the field of the displaced water, and the magnetic moment decreases steadily until all positions are filled. Then the moment remains constant on further addition of pyridine.

It was found on examination of the absorption spectra of the various complex ions that in passing from the less stable to the more stable complexes (and from higher to lower magnetic moments) the absorption band in the visible spectrum was displaced toward the violet. The displacement can be correlated quantitatively with the change in moment. In Table II the magnetic moments and frequencies of maximum absorption of the various

TABLE II

MAGNETIC MOMENTS AND MAXIMUM ABSORPTION FREQUENCIES OF SOME NICKEL AND COPPER COMPLEX IONS

Reagent (or solvent)	Nickel ions		Copper ions	
	μ	$\nu, \text{cm.}^{-1} \times 10^{-3}$	μ	$\nu, \text{cm.}^{-1} \times 10^{-3}$
(Methanol)	3.29	13.1
(Water)	3.26	14.1	1.96	12.3
Oxalate	3.23	14.9
Pyridine	3.20	15.9	1.88	14.9
Aminoacetate	3.18	16.5	1.86	15.8
Ammonia	3.17	16.9	1.87	16.5
Ethylenediamine	3.12	18.3	1.85	18.2
<i>o</i> -Phenanthroline	3.09	19.2

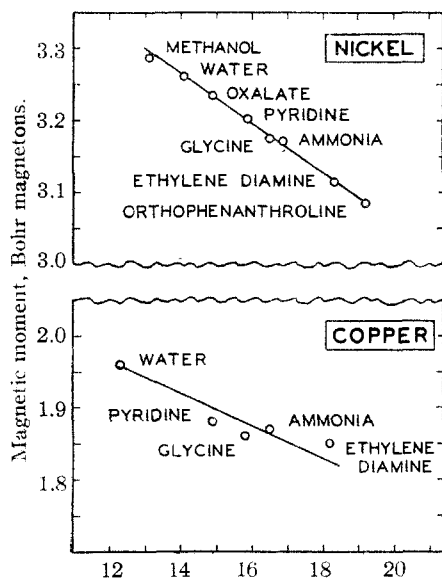


Fig. 3.—Magnetic moments of nickel and copper (II) complex ions plotted against frequency of maximum in absorption spectrum in visible region.

complexes are given. The values are plotted in Fig. 3. It is evident that for the nickel complexes there is a linear relationship between the moment and the frequency of maximum absorption. Even the value for the methanol solution falls practically on the line. For the copper complexes the relationship appears to hold only roughly, but the deviations are not much larger than the experimental error.

Van Vleck⁹ has developed a theory of the effect of coordinated groups on the magnetic behavior of a central atom. This theory is applicable to complex ions with a coordination number of six, and some of the nickel complex ions of this investigation offered a chance for a further test of the theory. Combination of Van Vleck's Equations 32, 33 and 34 gives

$$Dq = (15.18 \times 10^{-42})E/R^6$$

in which numerical values have been inserted for the constants, including a value of 4.8 for the effective ionic charge of the nickel ion, and E is the

(9) Van Vleck, *J. Chem. Phys.*, **7**, 81 (1939).

electrical dipole moment and R is the distance from the center of the nickel ion to the dipole of the coordinating group. Schlapp and Penney¹⁰ give an equation for Dq in terms of the magnetic susceptibility, from which the following can be derived

$$Dq = 4(3kT - 8\lambda)/5(\mu^2 - 8)$$

In this, λ is the constant of spin-orbit coupling with a value of -335 cm.^{-1} and μ is the magnetic moment. Combination of these two equations gives

$$R = [29E(\mu^2 - 8)]^{1/6}$$

Substitution of the measured values of μ for several of the nickel complex ions together with measured or estimated values of E gives values of R varying between 2.0 and 2.3 Å. This is a reasonable value.

If in the hydrated nickel ion the middle points of the water dipoles are located near the centers of the oxygen atoms, it can be estimated from the value 2.3 Å. for R that the ion has a radius of about 3 Å. or a diameter of 6 Å. This is the value assigned by Kielland¹¹ to the hydrated nickel ion.

The authors wish to express their thanks to the Department of Physics for the loan of the magnet, to Professors Paul M. Gross and F. W. Constanant for their help in the construction of the apparatus and to Dr. Malcolm Hebb for valuable discussion.

Summary

The magnetic moments of several complex ions of nickel and copper have been measured in aqueous solution. The relative stabilities have been qualitatively determined by a spectrophotometric method. For both series of complex ions, the orbital magnetic moment decreases as complex ions are formed in solution, and this decrease is greater the more stable the complex. A linear relationship between magnetic moment and maximum absorption frequency has been observed.

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(10) Schlapp and Penney, *Phys. Rev.*, **42**, 666 (1932).

(11) Kielland, *THIS JOURNAL*, **59**, 1676 (1937).