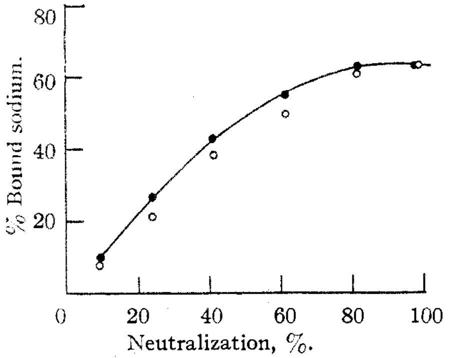


Fig. 3.—Sodium ion association as a function of neutralization for 0.0151 N polyacrylic acid: open circles, diffusion measurements; solid circles, transference measurements.[3]

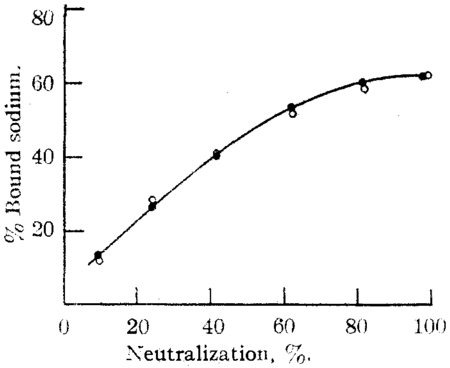


Fig. 4.—Sodium ion association as a function of neutralization for 0.0378 N polyacrylic acid: open circles, diffusion measurements; solid circles, transference measurements.[3]

able values of ω_{Na} can be chosen which will bring the two sets of results into even better agreement.

It was mentioned above that the values of f obtained from diffusion measurements do not depend on how the bound sodium is distributed among the different polymer species. The same is not true, however, for the transference calculation. If the polymer exhibits heterogeneity of mobilities, as might be expected, then the transference–conductance results will give rise to a different kind of average for f. Judging from the present results, the assumption of a narrow distribution of polymeric mobilities appears warranted.

At 61.7% neutralization the fraction of sodium ions associated with polymer is significantly lower at c = 0.00378 N than at 0.0151 N or 0.0378 N. Transference results show this quantity to be virtually constant over the higher concentration range 0.0151 N to 0.1189 N.

VI. Summary

1. The steady state diffusion of radioactive sodium ion in mixtures of polyacrylic acid and sodium hydroxide has been determined at 25°. Measurements have been made on the following solutions: stoichiometric polyacrylic acid concentration equal to 0.0151 and 0.0378 N, at 9.6, 24.0, 41.3, 61.7, 81.6, and 97.9% neutralization, and for an acid concentration equal to 0.00378 N at 61.7% neutralization.

2. Similar measurements were also made on four sodium chloride solutions in the range of concentration: 2×10^{-3} to 2×10^{-2} N. The results of these experiments were used to calibrate the diffusion cells.

3. For polyacrylic acid–sodium hydroxide solutions, extrapolation of the results to zero neutralization yields values of the mobility of sodium ion that are in good agreement with the known limiting mobility of sodium ion in pure water.

4. The fraction of sodium ions associated with polymer has been computed on the basis of the diffusion measurements. These results are in satisfactory agreement with those reported earlier based on transference measurements.

Urbana, Illinois Received February 20, 1950

[Contribution from the Department of Chemistry of the University of Texas]

The Absorption Spectra of Certain Nickel(II) and Cobalt(II) Complex Ions[1]

By Grady L. Roberts and Frank H. Field

In some recent work, Field and Vosburgh[2] found that certain magnetic properties of nickel(II) and cobalt(II) ions in the form of complex salts in aqueous solution were unexpectedly different. When the magnetic moments were calculated from the Curie equation, the formation of more stable complex ions resulted in a decrease in the nickel moment, but a small increase in the cobalt moment. The cobalt moments calculated from the Curie–Weiss equation decreased. It is of interest, therefore, to investigate more directly what changes occur in the energy levels of these ions as the stability of the complex ions changes.

We have measured the aqueous solution spectra of the cobalt(II) complex ions formed from water, oxalate ion, ammonia, ethylenediamine, and o-phenanthroline. In addition we have checked and extended previous work on the nickel(II) complex ions formed from these coördinating reagents.

All of these complex salts are known[2,3] to be para-

---

(1) Taken from the M.A. thesis of G. L. Roberts, January, 1950.

(2) Field and Vosburgh, This Journal, **71**, 2398 (1949).

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

magnetic except that formed from cobalt(II) ion and *o*-phenanthroline, which, however, by analogy might be expected to be paramagnetic also.

Experimental

All materials used in the work were of reagent grade and were further purified as necessary by standard techniques. The metal ions were introduced in the form of nickel nitrate and perchlorate and cobalt nitrate.

The solutions of the complex salts used for the measurements were prepared by quantitative dilutions of standardized stock solutions, followed by the addition of seven or eight g.-equivalents of coördinating reagent per g.-ion of metal and, when necessary, sufficient acid and additional coördinating reagent to prevent the precipitation of metal hydroxide. The cobalt ammine complex was prepared by adding a very large excess of ammonium hydroxide to diluted stock solution. Under these conditions, it is considered that the hexa-coördinated complex ions were formed, with the possible exception of the oxalate complexes.

The preparation and spectral measurements of the cobalt complexes were performed in a vacuum apparatus, and no evidence of oxidation of the solutions used for the measurements was ever observed. Oxidation could be easily detected because of the resulting darkening of the solution.

The order of stability of the cobalt complex ions was determined by the method of Russell, Cooper and Vosburgh.[3] The spectrum of a solution prepared by adding equivalent excess amounts of two coördinating reagents to a solution containing cobalt ion was determined. This spectrum was compared with those of the complex ions formed from the two coördinating reagents taken individually. The complex ion having the spectrum which corresponded more closely to that of the mixture was taken to be the more stable. Coincidence of the curves involved in these comparisons was not attained, but the agreement was sufficiently satisfactory to determine the following order of complex ion stability: aquo < ammine < ethylenediamine < *o*-phenanthroline. The same order was found by Russell, Cooper and Vosburgh with nickel ion.

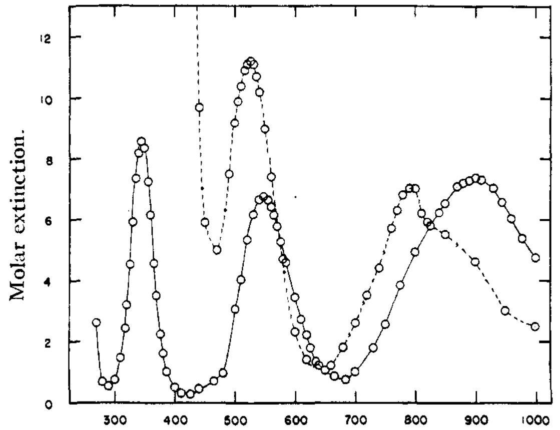
The absorption spectra were measured with a Beckman model DU quartz photoelectric spectrophotometer. In making the optical measurements, the slit width of the instrument was adjusted so far as possible to give a constant band width. Band widths of 1, 2 and 3 mμ were used in the spectral regions *ca.* 350–600, 600–800 and 800–1000 mμ, respectively. Below *ca.* 350 mμ it was usually necessary progressively to increase the slit width in order to balance the instrument.

As a measure of the reproducibility of the absorption spectra, a measurement was made on two different solutions of the nickel ethylenediamine complex ion. Identical curves were obtained.

In the spectral measurements, the comparison cell was filled with a solution identical with the complex salt solution except that the metal ion was absent. It was hoped that in this way the absorption of all of the components except that of the metal ion would be cancelled, but unfortunately, this did not appear to be true in the critical cases of the *o*-phenanthroline and oxalate complexes. However, anion absorption was cancelled. With most of the complex ions this practice imposed a wave length limit below which the measurements could not be made because of inability to balance the spectrophotometer.

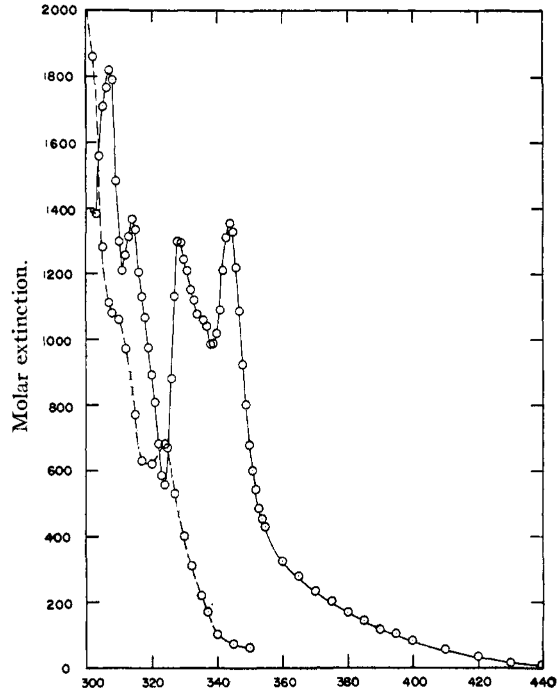
Results and Discussion

The results of the measurements are given in Figs. 1–5 and in Table I. In the figures, the molecular extinction coefficient is calculated from the equation $\epsilon = (\log_{10}I_0/I)/cd$. The spectrum of the nickel ethylenediamine complex (Fig. 1) is given as being typical of the nickel absorption. The spectra of the aquo, oxalate and ammine complexes lack the longest wave length band, but its existence beyond the limits of our measurements is shown in the case of the aquo and ammine complexes by the near infrared measurements of Dreisch and Trommer.[4] The aquo and oxalate peaks at about 700 mμ are broad and show a doublet structure.



Wave length, mμ.

Fig. 1.—Absorption spectra of Ni(II) complex ions: O—O, Ni(en)_3^{++}; O- - - -O, $\text{Ni}(o\text{-phen})_3^{++}$.



Wave length, mμ.

Fig. 2.—Absorption spectra of Ni(II) complex ions: O—O, $\text{Ni}(o\text{-phen})_3^{++}$; O- - - - -O, *o*-phenanthroline.

The strong, complicated absorption found in the *o*-phenanthroline complexes below about 350 mμ probably does not arise from electronic transitions within the metal ions. No similar absorption is

---

[4] Dreisch and Trommer, *Z. physik. Chem.*, B37, 37 (1937).

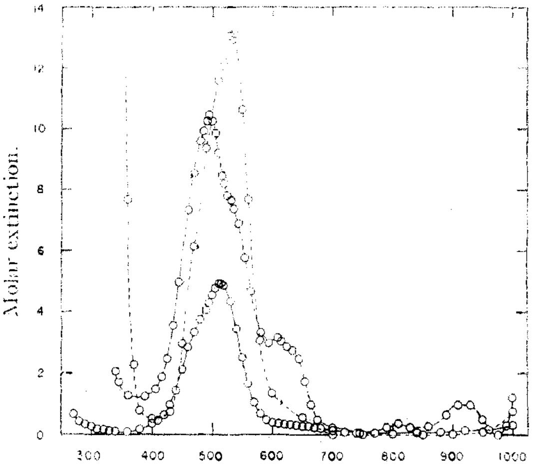


Fig. 3.—Absorption spectra of Co(II) complex ions: O—O, $Co(H_2O)_6^{++}$; O- - -O, $Co(C_2O_4)_2^{=}$; O— - —O, $Co(NH_3)_6^{++}$.

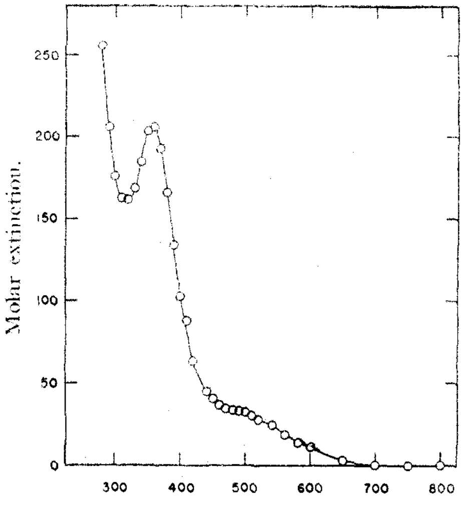


Fig. 4.—Absorption spectrum of $Co(en)_3^{++}$ complex ion.

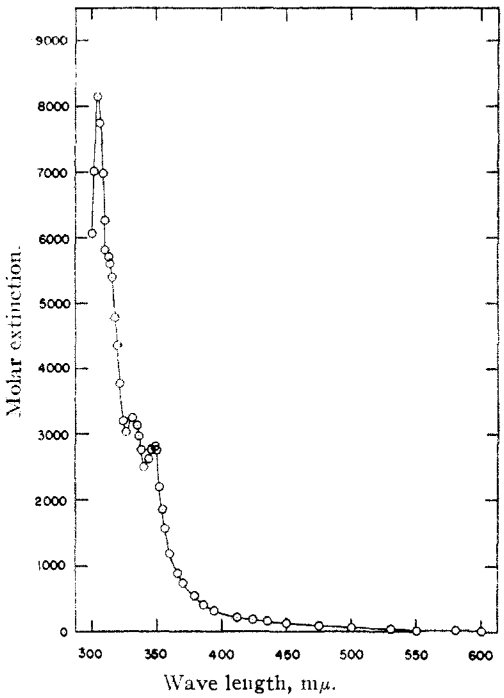


Fig. 5.—Absorption spectrum of Co(*o*-phen)$_3^{++}$ complex ion.

found in the other nickel and cobalt complex ions, but recent work in this Laboratory shows that the zinc *o*-phenanthroline complex does have a similar absorption. The absorption of *o*-phenanthroline itself is of a different form (Fig. 2). It seems reasonable to attribute most of the absorption to the coördinated molecules which are polarized by the electric field of the metal ion. The nickel oxalate complex also shows a relatively strong absorption band (ϵ = 370 at λ = 250 mμ) which can be interpreted in the same way.

Russell, Cooper and Vosburgh[3] have measured the visible absorption of the nickel complex ions used in this work; Babaeva and Mosyagina[5] have measured the short wave length absorption of the nickel oxalate complex, and Tréhin[6] has measured the short wave length absorption of the nickel aquo complex. Our results agree with those reported.

TABLE I

SUMMARY OF THE POSITIONS OF THE ABSORPTION MAXIMA

Complex ion	$\lambda_{max.}$ for Ni complex, mμ	$\lambda_{max.}$ for Co complex, mμ	$\lambda^{-1}_{max.} \times 10^{-3}$ for Ni complex, cm.$^{-1}$	$\lambda^{-1}_{max.} \times 10^{-3}$ for Co complex, cm.$^{-1}$
Hydrate	395	513	25.3	19.5
	662		15.1	
	725		13.8	
Oxalate	252		39.8	
	391	534	25.6	18.8
	670		14.9	
	730		13.7	
Ammine	365	496	27.4	20.2
	597	609	16.7	16.4
Ethylenediamine	345	356	29.0	28.1
	546	480	18.3	20.8
	895		11.2	
o-Phenanthroline	307	304	32.6	32.9
	314	313	31.8	32.0
	328	331	30.5	30.2
	335	348	29.8	28.8
	344		29.1	
	525		19.1	
	790		12.7	

The wave lengths of maximum absorption of hydrated cobalt(II) ion given by Bose and Mukherji[7] in a review article are 770 and 515 mμ. Our peak at 513 mμ is in good agreement, but we find

---

[5] Babaeva and Mosyagina, *Doklady Akad. Nauk. S. S. S. R.*, **64**, 823 (1949).

[6] Tréhin, *Compt. rend.*, **216**, 558 (1943).

[7] Bose and Mukherji, *Phil. Mag.*, **26**, 757 (1938).

no evidence whatsoever for the existence of the longer wave length peak. However, our spectrum is in satisfactory agreement with that reported by v. Kiss and Gerendàs.[8] The only previous work on the other cobalt(II) complex ions seems to be that of Samuel,[9] who found the maximum absorption of the cobalt(II) ammine complex to lie at 519 mμ, which does not agree very well with our peak at 496 mμ.

It may be seen from Table I that excepting the oxalate complexes the wave lengths of maximum absorption of both the nickel and cobalt complex ions decrease as the stability of the complex ions increases. This behavior has been previously reported for the visible bands of the nickel complexes.[3]

The displacements of the absorption show that for both types of ions the separation of the energy levels responsible for the absorption increases as the stability of the complex ions increases. This is of interest in view of the previously mentioned difference in the magnetic behavior of cobalt and nickel ions, for if it be assumed, as seems reasonable, that the magnetic and optical properties involve the same energy levels, only the cobalt ion moments calculated from the Curie–Weiss equation are in accord with the view that the orbital moment and the energy level separation are connected by an inverse type of relationship. Such a view is justified theoretically[10] for nickel ion, and seems to be a good preliminary assumption for cobalt ion. Within the limits of these assumptions, it would appear that the magnetic moments of cobalt ion should be calculated from the Curie–Weiss equation.

It is possible further to compare the spectral and magnetic data of nickel ion by means of the Schlapp and Penney[10] theory. Schlapp and Penney relate the magnetic susceptibility with the splitting of the ground energy level by a crystalline electric field of cubic symmetry. Using the magnetic data of Russell, Cooper and Vosburgh[3] and of Field and Vosburgh,[2] we have calculated that the over-all splittings of the ground level of nickel ion in the aquo, oxalate, ammine, ethylenediamine and *o*-phenanthroline complexes are 18.7, 19.9, 23.1, 29.0 and 30.1 $\times 10^3$ cm.$^{-1}$, respectively. Assuming that the shortest wave length optical band results from transitions between the highest and lowest of the decomposed levels (except for the oxalate band at 252 mμ), the corresponding spectral values are 25.3, 25.5, 27.4 and 29.0 $\times 10^3$ cm.$^{-1}$, no value being obtainable from our data for the *o*-phenanthroline complex. The agreement is such as to indicate that the Schlapp and Penney theory gives the order of magnitude of the splitting of the ground level in nickel ion. However, attempts to interpret other aspects of the absorption by means of this theory do not meet with much success.

Summary

The absorption spectra of several complex ions of nickel(II) and cobalt(II) in aqueous solution have been measured. In both nickel and cobalt the wave lengths of maximum absorption shift to smaller values as the stability of the complex ions increases. The results were discussed briefly in connection with the magnetic properties of the complex ions.

AUSTIN, TEXAS RECEIVED FEBRUARY 13, 1950

---

[8] v. Kiss and Gerendàs, *Z. physik. Chem.*, **180A**, 117 (1937).

[9] Samuel, *Z. Physik*, **70**, 43 (1931).

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

[CONTRIBUTION FROM PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Alkylthio-(trifluoromethyl)-benzenes[1,2]

BY EARL T. MCBEE AND PETER J. GRAHAM

As a part of an extensive investigation of the properties of trifluoromethyl-substituted benzenes and their derivatives, alkylthio-(trifluoromethyl)-benzenes were synthesized. The preparation and properties of the thio compounds were correlated with alkoxy-(trifluoromethyl)-benzenes.[3]

Müller, Scherer and Schumacher[4] reported the preparation of (trifluoromethylthio)-3-(trifluoromethyl)-benzene from (trichloromethylthio)-3-(trifluoromethyl)-benzene by an adaptation of reactions performed by Zincke,[5] who prepared (trichloromethylthio)-4-methylbenzene.

Alkylthio-(trifluoromethyl)-benzenes were prepared by treating a bromo- or chloro-(trifluoromethyl)-benzene with a sodium alkyl sulfide in an alcoholic solvent. The conditions for the reaction depend upon the reactivity[3] of the bromo- or chloro-(trifluoromethyl)-benzene which is directly comparable to the corresponding bromo- or chloronitrobenzene. It is well known that the chlorine in 3-chloronitrobenzene is of about the same order of activity as chlorobenzene but that the activity of the chlorine increases with the number of nitro groups ortho and para to it. For example, 1-chloro-2,4,6-trinitrobenzene is the most active of the chloronitrobenzenes. Simi-

---

[1] From the doctoral thesis of Peter J. Graham.

[2] Presented before Division of Organic Chemistry at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April, 1947.

[3] E. T. McBee, R. O. Bolt, P. J. Graham and R. F. Tebbe, THIS JOURNAL, **69**, 947 (1947).

[4] F. Müller, O. Scherer and W. Schumacher, to Gen. Aniline Works Inc., U. S. Patent 2,108,606, February 15, 1938.

[5] T. Zincke and W. Frohneberg, *Ber.*, **43**, 845 (1910).