[CONTRIBUTION NO. 177 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

# Spectrophotometric Investigations of Some Complexes of Ruthenium. I. The Ruthenium–Thiocyanate System

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The ruthenium (IV)–thiocyanate system has been studied spectrophotometrically. It was found that both Ru(III) and Ru(IV) form the same deep-blue complex, with a formula $Ru(CNS)_1^{+2}$, and a stability constant of 60 ± 1, at unit ionic strength. A method of interpretation of spectrophotometric data, applicable to one complex of low stability, was developed.

The reaction of ruthenium(III) and ruthenium (IV) with thiocyanate to form a pink to violet color has been reported by several investigators.[2,3a,b] Aside from noting the production of a color, no investigation of the nature of the reaction between ruthenium and thiocyanate has ever been made. This research was undertaken to obtain information about the formulas and stability constants of the thiocyanate complexes of ruthenium. These should be of interest in comparison with its homolog iron. It has adequately been shown that the complex, $FeCNS^{+2}$, is formed with higher complexes also being suspected.[4-9]

Preliminary investigation of the reaction of ruthenium(IV) perchlorate with thiocyanate suggested that before any complex formation occurred the ruthenium(IV) was being reduced to ruthenium(III) at the expense of the ligand. These experiments also revealed that no very stable complex was formed. The fact that ruthenium was being reduced by the ligand meant, first, that the extinction coefficient of the uncomplexed ruthenium was unknown and, second, that at low concentration of ligand, its concentration was unknown. In order to keep the relative loss of thiocyanate insignificant, it was necessary to work only with solutions in which its concentration was high.

## Method

Although numerous methods have been developed for interpreting spectrophotometric data[4-6,10-15] as they are presented in various cases none is applicable to this particular system.

Consequently a method was developed which is a modified combination of those of Kingery and Hume[15] and of Edmonds and Birnbaum.[5] In the present paper the case of a single complex will be presented. In a subsequent paper the modifications necessary for more than one complex will be discussed. For the reaction

$$A + nB \rightleftarrows AB_n \qquad (1)$$

the non-thermodynamic stability constant equals

$$K = [AB_n]/[A][B]^n \qquad (2)$$

If the total concentration of A is $c$, and its equilibrium concentration is $x$, the equilibrium concentration of $[AB_n]$ will equal $c - x$. If a large excess of B is present, the equilibrium concentration of B will essentially equal the total concentration of B. The equilibrium constant may then be written

$$K = (c - x)/x[B]^n \qquad (3)$$

If the extinction coefficient of A is $e_0$, of $AB_n$ is $e_1$, and if B is colorless, the optical density of the solution, $D$, at any wave length may be written

$$D = lxe_0 + l(c - x)e_1 \qquad (4)$$

where $l$ is the cell length. By use of the Beer–Lambert law, $d = lce$, to eliminate the extinction coefficients

$$D = \frac{xd_0}{c} + \frac{(c - x)d_1}{c} \qquad (5)$$

Solving for $x$ and $c - x$ in equation (3) and substituting these into equation (5) yields

$$D = d_0 + K[B]^n(d_1 - D) \qquad (6)$$

This equation can be used if $d_1$, the optical density of the complex, can be determined experimentally. Values of the optical density, $D$, at various concentrations, B, are plotted against $[B]^n(d_1 - D)$. This should give a straight line with slope $K$ and intercept $d_0$. The constant $n$ is evaluated by trial and error, since only the correct choice of $n$ will yield a straight line of positive slope. As $K$ is not a function of wave length, the determination of $K$ at numerous wave lengths permits averaging and improved precision. From the intercepts, or better from equation (6) after $K$ and $n$ have been evaluated, $d_0$ can be calculated at all the wave lengths involved, giving the absorption spectrum of the uncomplexed substance A.

## Experimental

**Absorption Measurements.**—A Cary automatic recording photoelectric spectrophotometer was used for all of the optical density measurements. Matched silica cells of 5.00-cm. optical length were used. The results are expressed in terms of optical density, $D$, defined by the relationship $D = \log_{10}(I_0/I)$, where $I_0$ and $I$ are the incident and transmitted light intensities, respectively.

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**Materials.**—Ruthenium metal powder, from Eimer and Amend, analyzed spectrographically, showed only a faint trace of rhodium, with all other platinum and iron group elements being absent. Potassium ruthenate, obtained from an alkali fusion of the metal[3b,16,17] was oxidized by potassium permanganate in sulfuric acid to ruthenium tetroxide.[18] The tetroxide was reduced to ruthenium(IV) perchlorate by absorption in an ice-cold solution containing 1 *M* $HClO_4$ and a 200% excess of $H_2O_2$.[19,20] This stock solution of ruthenium(IV) perchlorate was standardized by distilling the tetroxide from 70% $HClO_4$,[21] absorbing the tetroxide, precipitating the dioxide, reducing, and weighing the metal by the standard Gilchrist and Wichers procedure.[22] The concentration of acid in the solution was determined by titration. The ruthenium(IV) perchlorate stock solution was found to be $5.585 \times 10^{-3}$ *M*, in 1.27 *M* $HClO_4$. The absorption spectrum of this stock solution of ruthenium(IV) perchlorate agreed with the published spectrum.[23,24,25]

Using a controlled cathode electrodeposition apparatus, generously loaned by Dr. Harvey Diehl, of the analytical chemistry department of Iowa State College, ruthenium(III) perchlorate was prepared by controlled cathode reduction at −10° of ruthenium(IV) perchlorate. The absorption spectrum of the ruthenium(III) perchlorate solution agreed with that given by Wehner and Hindman.[24,25]

The sodium thiocyanate was Mallinckrodt reagent grade chemical. To maintain the ionic strength constant, G. Frederick Smith reagent grade lithium perchlorate was used. The perchloric acid was G. Frederick Smith doubly vacuum distilled. These reagents were purified, recrystallized and standardized as necessary by standard procedures. Particular care was taken to prevent iron contamination.

**Technique.**—A study of the ruthenium–thiocyanate system revealed that heating was necessary to attain equilibrium within a reasonable length of time. A minimum period of heating of 12 min. in a 70 ± 1° water-bath was required to produce equilibrium. With heating periods longer than 27 min. in the 70° bath, decomposition of the complex occurred. In this study all solutions were heated exactly 15.0 min. in the 70° bath, and then cooled in an ice-bath to 25 ± 1°. Immediately after preparation each solution was scanned as quickly as possible on the spectrophotometer. It was determined on the Cary that the colored solution, after preparation, was stable for one-half hour at room temperature, after which a slow fading occurred, less than 0.01 o.d. unit in three hours. In this investigation all spectrophotometric measurements were performed within 10 minutes after attainment of equilibrium.

In the determination of the formulas and stability constants, in all solutions the ruthenium concentration was maintained constant at $5.585 \times 10^{-5}$ *M*, with the perchloric acid concentration constant at 0.127 *M*, and the ionic strength constant at 1.0. Solutions were prepared by mixing necessary quantities of a solution of ruthenium(IV) perchlorate, and a freshly prepared solution of sodium thiocyanate to give the final concentration. Equilibrium was attained by the previously described heating and cooling procedure. More than fifty solutions, which contained ratios of $CNS^-/Ru$ from 13,500 to 10, were so prepared and scanned.

## Discussion

A typical plot at constant wave length of the optical density as a function of the $CNS^-/Ru$ ratio is given in Fig. 1. This shows clearly that the optical density of the solution does not change for ratios of $CNS^-/Ru$ greater than 8000 (the line labeled $d_1$ in Fig. 1). Hence the absorption spectrum of the last complex is known from experimental data. The absorption spectrum of this complex is given in Fig. 2, from which it may be seen that the complex obeys Beer's law.

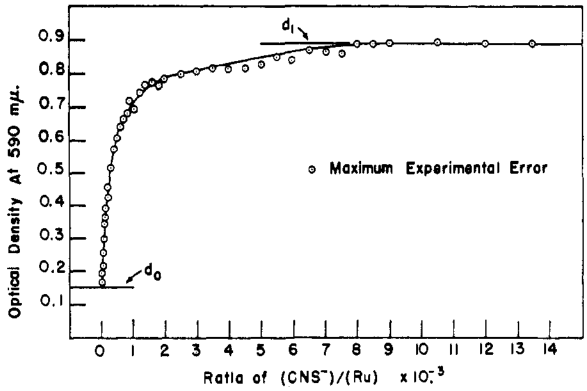

Fig. 1.—Optical densities at 590 mμ of various solutions with excess thiocyanate present: [Ru] = $5.585 \times 10^{-5}$ *M*; [$H^+$] = 0.127 *M*; cell length = 5.00 cm.; $\mu$ = 1.0; circles, experimental points; curve, calculated on basis of $Ru(CNS)_1^{+2}$.

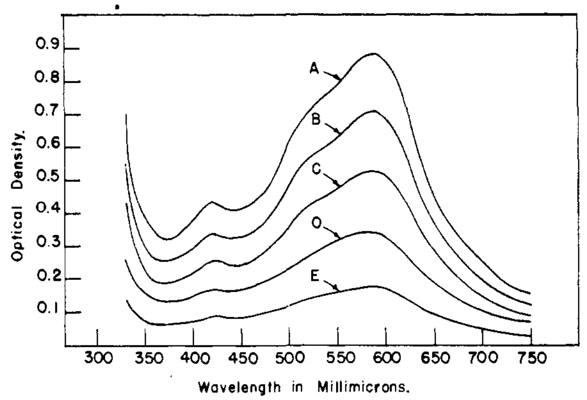

Fig. 2.—Absorption spectra of $Ru(CNS)_1^{+2}$: [$H^+$] = 0.127 *M*; $\mu$ = 1.0; cell length = 5.00 cm.; A, [Ru] = $5.585 \times 10^{-5}$*M*, B, [Ru] = $4.468 \times 10^{-5}$ *M*, C, [Ru] = $3.351 \times 10^{-5}$ *M*, D, [Ru] = $2.234 \times 10^{-5}$ *M*, E, [Ru] = $1.117 \times 10^{-5}$ *M*.

Assuming only one complex to be present, and using the method presented, it was necessary to select a value *n*, for the complex $Ru(CNS)_n^{3-n}$. Knowing that iron forms a complex $Fe(CNS)_1^{+2}$ it seemed reasonable to assume that ruthenium did also, and so the value *n* equal to one was chosen. The experimentally determined optical density, *D*, at any wave length was plotted against $[CNS^-] \cdot (d_1 - D)$, [see equation (6)]. This gave a straight line, the slope of which was interpreted to be *K*, and the intercept, $d_0$. Values of *n* equal to one-half, two, three, three-halves, and four were tried, but none gave as good results as was obtained from the choice of *n* equal to one. The entire system was also analyzed using the assumption that two complexes were formed,[26] but the data could not

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be fit as well as could be done with the assumption of a single complex.

It is seen from Fig. 1 that the curve of optical density asymptotically approaches the optical density $d_1$ of the last complex. Points near $d_1$ were not useful in the calculation since small differences $(d_1 - D)$ could not be expected to be accurate.

The graph of the calculation at 590 mμ, showing the plot of $D$ against $[CNS^-]$ $(d_1 - D)$ is given in Fig. 3. From the graph it is found that the slope, and hence the equilibrium constant equals 59.0, while the intercept, $d_0$, equals 0.155.

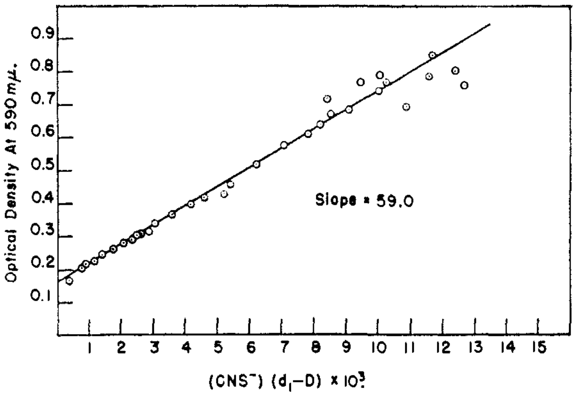

Fig. 3.—Plot of $D$ *vs.* $[CNS^-](d_1 - D)$ for calculation of $K$ at 590 mμ: $[Ru] = 5.585 \times 10^{-5}$ $M$, $[H^+] = 0.127$ $M$, $\mu = 1.0$; cell length = 5.00 cm.

This procedure was carried out at 13 different wave lengths, at 10 mμ intervals from 510 to 630 mμ, and the data are given, in Table I. The equilibrium constants so obtained were averaged to give a value of $K = 60 \pm 1$.

Using this equilibrium constant, the absorption spectrum of the uncomplexed ruthenium was calculated from equation (6). This absorption spectrum was essentially that of ruthenium(III) perchlorate,[24,25] and differed from ruthenium(IV) perchlorate sufficiently to justify the conclusion that the ruthenium is in the III oxidation state in the complex.

Using the calculated equilibrium constant, and the calculated value of $d_0$, together with the experimental value of $d_1$, the optical density curve as a function of the $CNS^-$/Ru ratio was calculated at 590 mμ. This is the curve drawn through the experimental points in Fig. 1.

To test the acid dependence of the system, the above procedure was repeated at a perchloric acid concentration of 0.254 $M$ instead of 0.127 $M$. It was found that the ruthenium–thiocyanate system is essentially independent of the acid concentration present. The conclusion was anticipated on the basis of the fact that thiocyanic acid is a strong acid.[27,28]

TABLE I

AVERAGE OF $Ru(CNS)_1^{+2}$ STABILITY CONSTANT[a]

| Wave length | $K$ | $d$ | $d^2$ |
|---|---|---|---|
| 510 | 60.0 | 0.2 | 0.04 |
| 520 | 61.8 | 1.6 | 2.56 |
| 530 | 60.0 | 0.2 | 0.04 |
| 540 | 60.9 | .9 | .81 |
| 550 | 60.0 | .2 | .04 |
| 560 | 60.0 | .2 | .04 |
| 570 | 60.0 | .2 | .04 |
| 580 | 58.2 | 2.0 | 4.00 |
| 590 | 59.0 | 1.2 | 1.44 |
| 600 | 60.0 | 0.2 | 0.04 |
| 610 | 59.0 | 1.2 | 1.44 |
| 620 | 61.2 | 1.0 | 1.00 |
| 630 | 62.7 | 1.5 | 2.25 |
| | 13/782.8 | | 13/13.74 |
| | 60.2 | | 1.06 |

Average: $K = 60 \pm 1$

[a] $[H^+] = 0.127$ $M$, $\mu = 1.0$.  $\sqrt{1.06} = 1.0 +$

Since ruthenium(III) perchlorate is not stable at room temperature,[24,25] no extensive work was carried out using it. It was found, however, that the absorption spectrum of the $Ru(CNS)_1^{+2}$ complex was identical regardless of whether Ru(III) or Ru(IV) was used to prepare it.

## Conclusion

Ruthenium(III) and ruthenium(IV) perchlorate react with thiocyanate to form a deep-blue complex, with a formula, $Ru(CNS)_1^{+2}$. In the case of Ru(IV) reduction to Ru(III) occurs at the expense of the thiocyanate. At unit ionic strength, the complex has a stability constant of 60 ± 1, which is essentially independent of the acid concentration present. No evidence was found for higher complexes; if such are present, they exist at concentrations too small to be detected by this spectrophotometric method.

AMES, IOWA RECEIVED DECEMBER 6, 1951

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