[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Metal–Amine Coördination Compounds. V. The Ruthenium–2,2′-Bipyridine System[1,2,3]

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Mono- and bis-2,2′-bipyridine–ruthenium(III) complexes have been identified as intermediates in the stepwise formation of the tris-2,2′-bipyridine-ruthenium(II) complex ion. Spectrophotometric curves are shown for these complexes as well as the oxidized and reduced forms of the bis-tervalent complex and the oxidized and tris-bivalent complex. Evidence is presented for a chloro-series of ruthenium–2,2′-bipyridine complexes. Comparisons to the corresponding iron system are made.

The accumulation of considerable information on the Fe(II) complexes with 2,2′-bipyridine made the investigation of the corresponding ruthenium system seem desirable, especially in view of the similarity of the coördination chemistry of the two metals.[4] Since the common spectrophotometric techniques for studying complexes involve their formation under a variety of conditions in solution, an attempt was made to find suitable means of preparing the well-established complex[5-8] $[Ru(bipy)_3]^{++}$, by solution techniques. The standard procedure for its preparation involves heating $RuCl_3$ and 2,2′-bipyridine at 250° for three hours and subsequently isolating the complex as a salt such as $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$.[5] In the process of finding a suitable preparative scheme, new complexes of Ru(III) and 2,2′-bipyridine were obtained.

When commercial ruthenium chloride (about 40% $RuCl_3$ and 60% $RuCl_4$) and 2,2′-bipyridine are refluxed together in dilute H_2SO_4 (*p*H 2), the first species noted is $[Ru(bipy)]^{+++}$.[9] This first complex is converted quite rapidly to a green $[Ru(bipy)_2(H_2O)_2]^{+++}$ which is slowly converted on continued heating to $[Ru(bipy)_3]^{++}$, the final product. The reactions are given by the equations

$$\begin{matrix} Ru^{+++} \\ Ru^{++++} \end{matrix} \rightleftharpoons [Ru(bipy)]^{+++} \rightleftharpoons [Ru(bipy)_2(H_2O)_2]^{+++} \rightleftharpoons [Ru(bipy)_2]^{++} \rightleftharpoons [Ru(bipy)_3]^{++}$$ [9]

The green complex, $[Ru(bipy)_2(H_2O)_2]^{+++}$, may be oxidized by Ce(IV) to a purple product and reduced by $NaHSO_3$ or H_2SnCl_4 to a rose species.

If commercial ruthenium chloride is refluxed in dilute HCl until the characteristic yellow chloro complexes[10,11] are obtained, and then is refluxed with 2,2′-bipyridine, the observed sequence of reactions is

$$\begin{matrix} Ru^{+++} \\ Ru^{++++} \end{matrix} \begin{matrix} \text{(chloro} \\ \text{complexes)} \end{matrix} \rightleftharpoons [Ru(bipy)_2Cl_2]^{+} \rightleftharpoons [Ru(bipy)_2Cl_2]^{++} \rightleftharpoons [Ru(bipy)_3]^{++}$$

This investigation was concerned with the characterization of $[Ru(bipy)]^{+++}$, $[Ru(bipy)_2(H_2O)_2]^{+++}$ and $[Ru(bipy)_2Cl_2]^{+}$ and the elucidation of the reactions outlined.

Experimental

Standardization of Ruthenium Solutions.—The Ru(IV) content was obtained by using Crowell and Yost's titrimetric method.[12] The procedure was altered by extracting the iodine into chloroform and titrating to the disappearance of the red color in a nitrogen atmosphere. The total ruthenium concentration was determined colorimetrically with thiourea.[13]

Spectrophotometric Study.—When solutions of pure Ru(III) or Ru(IV) chloride are heated with excess 2,2′-bipyridine, the only detectable product is the tris-2,2′-bipyridine-ruthenium(II) ion. However, when commercial ruthenium chloride (about 40% $RuCl_3$ and 60% $RuCl_4$) is used, a green species which exhibits maximum absorbance at 630 mμ is noted. On continued heating, this green complex, $[Ru(bipy)_2(H_2O)_2]^{+++}$, is slowly converted to $[Ru(bipy)_3]^{++}$. Since Ru(IV) reduces very slowly to Ru(III),[14] it was assumed the Ru(III) was reacting preferentially—an assumption that was borne out by the results obtained. In all of the studies conducted, therefore, the concentration was calculated for Ru(III) only.

The course of the reaction between 2,2′-bipyridine and commercial ruthenium chloride in H_2SO_4 (*p*H 2) at reflux was followed spectrophotometrically. At zero time the spectrum is that of the commercial ruthenium chloride. As the refluxing continues the spectrum of $[Ru(bipy)]^{+++}$ increases in intensity for a short period and then begins to decrease. As this decline occurs the characteristic absorption due to $[Ru(bipy)_2(H_2O)_2]^{+++}$ rises slowly to a maximum and then decreases. Following the decline of the $[Ru(bipy)_2(H_2O)_2]^{+++}$ spectrum, the absorption due to $[Ru(bipy)_3]^{++}$ slowly increases until complete formation is reached. Figure 1 shows the spectrophotometric curve for each of the three species at its maximum value.

Identification of $[Ru(bipy)]^{+++}$.—A continuous variation study of the first species formed upon heating commercial ruthenium chloride and 2,2′-bipyridine (curve A, Fig. 1) was conducted at 70°. The maximum absorbance obtained at 705 mμ for solutions containing 15.4×10^{-6} total moles of reactants in 100 ml. at *p*H 2.0 was plotted against the mole fraction of Ru(III). The fact that the plot attains a maximum at 0.50 indicates the presence of a 1:1 complex. It is assumed to be a complex of Ru(III) since both the initial reactant and the subsequent 2:1 complex formed were tervalent. The molar absorptivity was determined to be

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[1] For previous paper in this series see R. T. Pflaum and W. W. Brandt, THIS JOURNAL, **77**, 2019 (1955).

[2] Presented at the 126th A.C.S. Meeting, New York City, New York, September, 1954.

[3] Abstracted from theses submitted by Ronald R. Miller and Sister Marina Puke, O.S.F., to the Graduate School of Purdue University in partial fulfillment of the requirements of the degrees of Doctor of Philosophy, 1954, and Master of Science, 1952, respectively.

[4] W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, **54**, 959 (1954).

[5] F. Burstall, *J. Chem. Soc.*, 173 (1936).

[6] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 170 (1950).

[7] W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

[8] J. Steigman, N. Birnbaum and S. Edmonds, *Ind. Eng. Chem., Anal. Ed.*, **14**, 30 (1942).

[9] In all complexes in which the remaining coördination groups (OH^-, H_2O, Cl^- or HSO_4^-) are not known with certainty, only the coördinated bipyridine molecules will be indicated.

[10] R. Charronnat, *Compt. rend.*, **181**, 866 (1925).

[11] P. Wehner and J. Hindman, *J. Phys. Chem.*, **56**, 10 (1952).

[12] W. Crowell and D. Yost, THIS JOURNAL, **50**, 374 (1928).

[13] G. Ayers and F. Young, *Anal. Chem.*, **22**, 1277 (1950).

[14] D. DeFord, Ph.D. Thesis, University of Kansas, 1948.

11,500 by measuring a series of solutions containing increasing excesses of 2,2′-bipyridine.

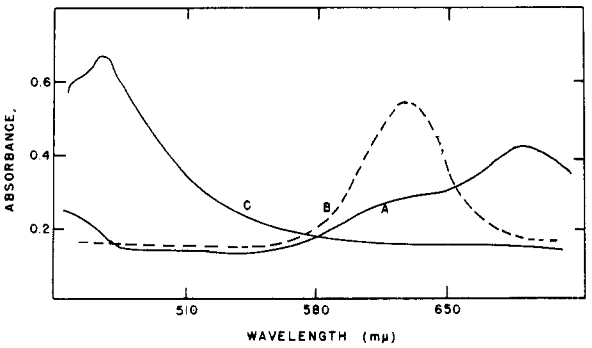

Fig. 1.—Transitions of the absorption spectrum upon heating ruthenium(III) with 2,2′-bipyridine: A, first product $[Ru(bipy)]^{+++}$; B, second product $[Ru(bipy)_2(H_2O)_2]^{+++}$; C, final product $[Ru(bipy)_3]^{++}$. $[Ru]^{+++} = 5.0 \times 10^{-5}$ *M;* [Bipy] $= 1.5 \times 10^{-4}$ *M;* General Electric Recording Spectrophotometer; 10 mμ band width; 1.00-cm. cells; 25°.

It is known that interpretation of continuous variation data can be misleading, particularly in systems where more than one species may be present. However, in this case, the stepwise formation is quite definite and little interference of the various spectra is encountered.

Identification of $[Ru(bipy)_2(H_2O)_2]^{+++}$.—Although $[Ru(bipy)_3]^{+++}$ is green[7] or blue[6] (Fig. 2), it is shown by the absorption spectrum to be different from the green $[Ru(bipy)_2(H_2O)_2]^{+++}$ (Fig. 1).

Job's method of continuous variations[15] was used to study the green intermediate, $[Ru(bipy)_2(H_2O)_2]^{++}$, at *p*H 2 at 70 and 100°. Stock solutions of the commercial ruthenium chloride and 2,2′-bipyridine were mixed in varying ratios, always keeping a total of 15.4×10^{-6} mole of reactants in 100 ml. The maximum absorbance at 630 mμ attained by each mixture was plotted against the mole fraction of Ru(III). The fact that each plot (70 and 100°) reaches a maximum at 0.33 demonstrates that the complex absorbing at 630 mμ is $[Ru(bipy)_2]^{n+}$. The molar absorptivity was determined to be 14,300.

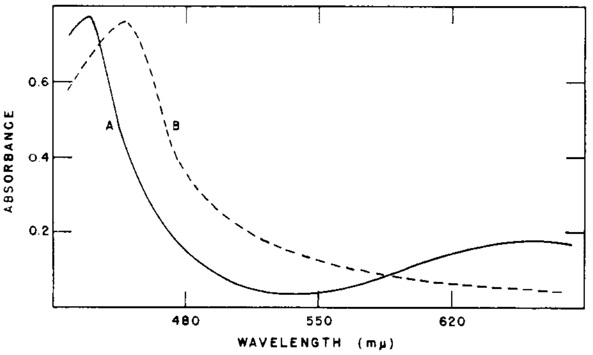

Fig. 2.—Absorption spectrum of ruthenium-bipyridine complexes: A, $[Ru(bipy)_3]^{+++}$ 9.5×10^{-5} *M;* B, $[Ru(bipy)_3]^{++}$ 5.2×10^{-5} *M;* General Electric Recording Spectrophotometer; 10 mμ band width; 1.00-cm. cells; 25°.

The green $[Ru(bipy)_2]^{n+}$ was precipitated with perchlorate ion. Analysis shows the empirical composition to be $[Ru(bipy)_2](ClO_4)_3 \cdot 3H_2O$. Found: C, 29.77; H, 3.12; N, 6.95; Calcd.: C, 29.44; H, 3.43; N, 6.85. Assuming a coördination number of six for Ru(III) permits the formulation $[Ru(bipy)_2(H_2O)_2](ClO_4)_3 \cdot H_2O$.

Oxidation of $[Ru(bipy)_2(H_2O)_2]^{++}$ with Ce(IV) yields a purple product (Fig. 3), and reduction with $NaHSO_3$ or H_2SnCl_4 yields a rose species (Fig. 3). The demonstration that both products yield the starting material when the reactions are reversed, indicates the existence of the bis-2,2′-bipyridine complexes of Ru(IV) and Ru(II).

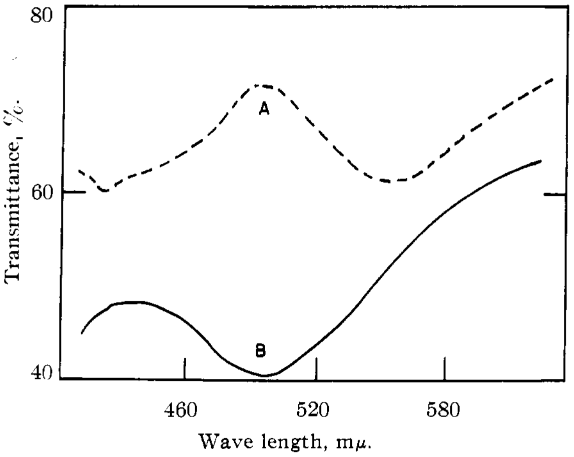

Fig. 3.—Absorption spectra for the oxidized and reduced products of $[Ru(bipy)_2(H_2O)_2]^{+++}$ (2.5×10^{-4} *M*): A, oxidized; B, reduced. General Electric Recording Spectrophotometer; 10 mμ band width; 1.00-cm. cells, 25°.

Effect of a Reducing Agent upon Complex Formation.—A solution of 2.54×10^{-4} *M* Ru(III) containing an excess of 2,2′-bipyridine at *p*H 1.9 was analyzed spectrophotometrically during refluxing. In the presence of Na_2SO_3 the time required for $[Ru(bipy)_3]^{++}$ to begin to form is reduced from 10 hours to immediately, and no intermediate $[Ru(bipy)_2(H_2O)_2]^{+++}$ is observed. The increase in rate, which is much greater than can be explained by the excess bipyridine, indicates that the reduction of $[Ru(bipy)_2(H_2O)_2]^{+++}$ is slow compared to the successive addition of a 2,2′-bipyridine molecule to the $[Ru(bipy)_2]^{++}$.

Effect of Chloride Ion.—Refluxing commercial ruthenium chloride in 1 *M* HCl causes the formation of a purple solution which rapidly changes to yellow. Both colors are due to chloro complexes of Ru(III) and/or Ru(IV).[10,11] Refluxing the yellow solution of the chloro complexes with an equimolar amount of 2,2′-bipyridine at *p*H 2 results in the formation of a red complex, $[Ru(bipy)_2Cl_2]^{+}$, while excess 2,2′-bipyridine causes the formation of $[Ru(bipy)_3]^{++}$. These data demonstrate the difference in the path of the formation of $[Ru(bipy)_3]^{++}$ caused by having chloro complexes of the Ru(III) present initially. This difference explains the lack of intermediates when solutions of pure Ru(III) and Ru(IV) are refluxed with 2,2′-bipyridine, since their preparation requires heating in the presence of Cl^-. The absence of any red $[Ru(bipy)_2Cl_2]^{+}$ in the presence of excess 2,2′-bipyridine is readily explained by the observation that refluxing $[Ru(bipy)_2Cl_2]^{+}$ with excess 2,2′-bipyridine causes its rapid conversion to $[Ru(bipy)_3]^{++}$. The composition of $[Ru(bipy)_2Cl_2]^{+}$ is inferred from its rapid formation when $[Ru(bipy)_2(H_2O)_2]^{+++}$ is warmed with dilute HCl.

Discussion

In the proposed mechanism the reduction step is indicated as taking place with the 2:1 complex since the rate of formation of $[Ru(bipy)_3]^{++}$ from $[Ru(bipy)_2(H_2O)_2]^{+++}$ was greatly accelerated by the addition of a reducing agent. In addition, at no stage in the reaction was there any sign of the presence of $[Ru(bipy)_3]^{+++}$ which is known to have absorption maxima at 418 and 680 mμ.

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(15) P. Job, *Ann. chim.*, **9**, 113 (1928).

The possibility that Ru(IV) is reacting in appreciable concentrations to form $[Ru(bipy)_2H_2O)_2]^{+++}$ seems unlikely due to its known slow rate of reduction and the lack of any evidence for additional complexes which might be expected. In addition, test calculations of the molar ratio and continuous variation studies assuming that Ru(IV) is reacting alone or in combination with Ru(III) give meaningless results. However, it would be expected that quantitative studies of the formation of $[Ru(bipy)_3]^{++}$ could not be justified in the same manner due to the reduction step involved and the much longer periods of heating required.

Comparison to the Iron System.—The reaction between Fe(III) and 2,2′-bipyridine to give $(Fe(bipy)_3]^{++}$ differs from the analogous reaction with Ru(III) in that the Fe(III) reaction gives no indication of the formation of intermediates. Simon and Haufe[16] state that there is no reaction between Fe(III) and 2,2′-bipyridine in aqueous media, but rather that the reaction is

$$Fe^{+++} \rightleftharpoons Fe^{++} \rightleftharpoons [Fe(bipy)_3]^{++}$$

However, there is the possibility that the Fe(III) complexes do form, but that successive complexes form at a rate such that their presence has not been detected.

Considering the complexes individually, each metal, when in the bivalent state, forms a complex of great stability. The tervalent 3:1 complexes of both have been prepared by oxidation of the bivalent forms and are strong oxidizing agents. Although Ru(II), Ru(III) and Ru(IV) all apparently form bis complexes with 2,2′-bipyridine, there is no reliable evidence for the existence of analogous iron complexes in solution. Mono-2,2′-bipyridine complexes of Fe(II)[17] and Fe(III)[18] have been characterized. The present investigation is the first presentation of evidence for the $[Ru(bipy)]^{+++}$ complex. The ruthenium complexes demonstrate the necessity of considering elevated temperatures when seeking evidence of complex formation.

Dwyer[19] has recently prepared solid $[Fe(bipy)_2Cl_2]$, $[Fe(bipy)Cl_2]$ and $[Fe(phen)_2Cl_2]$ by removal of the organic base from the corresponding tris complexes at elevated temperatures *in vacuo*. Dissolution of these solids gave only the tris complexes, however.

The rates of reaction of Ru(II) and Fe(II) differ quite markedly from those of the corresponding tervalent ions. The Fe(II) reaction is essentially instantaneous. Qualitative data indicate that the Ru(II) reaction is considerably faster than the corresponding Ru(III) reaction, but still much slower than that of Fe(II).

In summary, it can be said that these two Group VIII metals are quite different in their reactions with 2,2′-bipyridine. A study of the osmium system would be of interest since osmium would be expected to be qualitatively more similar to ruthenium than to iron.

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(17) J. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Stability of Complexes of Uranium(IV) with Chloride, Sulfate and Thiocyanate

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Values of stability constants of complexes of uranium(IV) with chloride, sulfate and thiocyanate have been determined at ionic strength 2.0 at 10, 25 and 40°. The solvent extraction method, using 2-thenoyltrifluoroacetone as a chelating agent, was employed. Values for the changes in free energy, heat content and entropy at 25° are reported.

A quantitative study of the extraction of tetravalent uranium into benzene by the action of the organic chelating agent 2-thenoyltrifluoroacetone (TTA) has been reported by Betts and Leigh.[1] It was found that uranium (IV) was extracted into benzene as a neutral molecule containing four chelate groups per metal atom. Betts and Leigh also studied the extraction from aqueous solutions of sulfuric acid and found the existence of at least two complex species, $U(SO_4)^{++}$ and $U(SO_4)_2$. They reported values of the stability constants of these complexes but their method of calculation was questioned by Sullivan and Hindman[2] who recalculated their results by several methods. Ahrland and Larsson[3] reported stability constants of uranium(IV) with chloride and thiocyanate at 20° and ionic strength 1.00. They employed a potentiometric method for their measurements.

The purpose of the present work was to study the stability of some uranium(IV) complexes at dif-

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(1) R. H. Betts and R. M. Leigh, *Can. J. Research*, **B28**, 514 (1950).

(2) J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 609 (1952).

(3) S. Ahrland and R. Larsson, *Acta Chem. Scand.*, **8**, 137 (1954).