

Table III. Unfortunately this pattern for the magnitudes of the radial parameters in these trigonal complexes is not readily

Table III. Correlation of Sign of Trigonal Field Splitting Parameter,  $K$ , with the Polar Angle,  $\alpha$ , for Ruthenium(III)

	$K^k$	$\alpha$
LuGaG <sup>a</sup>	+387	49° 48'
YGaG <sup>b</sup>	+371	50° 36'
LuAlG <sup>a</sup>	+280	51° 36'
YAlG <sup>b</sup>	+273	52° 24'
Ru(acac) <sub>3</sub> <sup>c</sup>	+233	53° 36' <sup>h</sup>
Al <sub>2</sub> O <sub>3</sub> <sup>d</sup>	-250	55° 24'
Ru(en) <sub>3</sub> <sup>3+</sup> <sup>e</sup>	-418	57° 19'
Ru(ox) <sub>3</sub> <sup>3-</sup> <sup>f</sup>	-440	57° 30' <sup>i</sup>
Ru(phen) <sub>3</sub> <sup>3+</sup> <sup>g</sup>	-605	57° 45' <sup>j</sup>
Ru(bipy) <sub>3</sub> <sup>3+</sup> <sup>g</sup>	-670	?

<sup>a</sup> Reference 15. <sup>b</sup> Reference 14. <sup>c</sup> Reference 10 and B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. A*, 422 (1966). <sup>d</sup> Reference 11. <sup>e</sup> This work and ref 20. <sup>f</sup> R. W. Olliff and A. L. Odell, *J. Chem. Soc.*, 2467 (1964). <sup>g</sup> Reference 17. <sup>h</sup> Polar angle estimate from the crystal structure of the rhodium analog, Rh(acac)<sub>3</sub>: E. B. Parker, *Diss. Abstr.*, 24, 3654 (1966); J. C. Morrow, University of North Carolina, personal communication. <sup>i</sup> Polar angle estimate from the crystal structure of the rhodium analog, Rh(ox)<sub>3</sub><sup>3-</sup>: B. Dalzell and K. Ericks, *J. Amer. Chem. Soc.*, 93, 4298 (1971). <sup>j</sup> Polar angle estimate from the crystal structure of the iron analog, Fe(phen)<sub>3</sub><sup>2+</sup>: D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Crystallogr., Sect. A*, 21, 154 (1966). <sup>k</sup> Where only values of  $3K/\zeta$  were cited, a value for  $\zeta$  of 1050 cm<sup>-1</sup> was used to compute  $K$ .

ly explicable but should have predictive utility in the future. It would appear, as has been suggested previously, that the ultimate origin of the trigonal splitting must be sought in the molecular orbital theory.<sup>38-40</sup>

In this regard Schaffer<sup>41</sup> has treated trigonal complexes using his angular overlap model, which is founded on the molecular orbital approach, and has predicted from it a negative  $K$  value for the Co(en)<sub>3</sub><sup>3+</sup> complex based only on the known angular distortions of the coordinated nitrogens from octahedral positions. Similarly, O'Reilly and Offenbacher,<sup>42</sup> performing a more in-depth molecular orbital calculation, were able to account successfully for the positive  $K$  values observed for the Ru<sup>3+</sup> ion in the axially elongated RuO<sub>6</sub> units in garnets.

**Registry No.** [Ru(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub>·xH<sub>2</sub>O ( $x \cong 2$ ), 37668-71-6; [Ru(en)<sub>3</sub>]Cl<sub>3</sub>·xH<sub>2</sub>O ( $x \cong 4$ ), 37668-72-7.

**Acknowledgment.** This work was supported in part by a research grant from the National Science Foundation.

- (38) L. E. Orgel, *J. Chem. Soc.*, 3683 (1961).  
 (39) R. Englman, *J. Chem. Phys.*, 45, 3862 (1966).  
 (40) R. Dingle, *Acta Chem. Scand.*, 20, 1435 (1966).  
 (41) C. E. Schaffer, *Proc. Roy. Soc., Ser. A*, 297, 96 (1967).  
 (42) T. J. O'Reilly and E. L. Offenbacher, *J. Chem. Phys.*, 54, 3065 (1971).

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## Reduction of Oxygen by Hexaammineruthenium(II) and by Tris(ethylenediamine)ruthenium(II)

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The reaction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> with oxygen takes place quantitatively according to the stoichiometry: 2Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> + 2H<sup>+</sup> + O<sub>2</sub> = 2Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> + H<sub>2</sub>O<sub>2</sub>. The rate law over a wide range of Ru(II), O<sub>2</sub>, and H<sup>+</sup> concentrations (1.00 M H<sup>+</sup> to pH 6.05) has the form  $-d[O_2]/dt = k[Ru(II)][O_2]$ . At 25° and  $\mu = 1.00$  maintained with LiOAc,  $k = 1.26 \times 10^2 M^{-1} \text{sec}^{-1}$ . With Ru(en)<sub>3</sub><sup>2+</sup> as the reducing agent, the first stage involving oxidation to Ru(en)<sub>3</sub><sup>3+</sup> takes place rapidly enough so that this stage can be studied with initially no complication caused by oxidation of the ligand. If published values of  $E^\circ$  for the Ru(III)-Ru(II) and O<sub>2</sub>-O<sub>2</sub><sup>-</sup> couples are correct, we conclude that the reaction does not involve O<sub>2</sub><sup>-</sup> as an intermediate. The oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> by H<sub>2</sub>O<sub>2</sub> is a very slow reaction, and under the optimum conditions we were able to realize, we were dealing not with the intrinsic reaction but with a path involving catalysis by iron salts. The specific rate for the oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> by O<sub>2</sub> is at least 10<sup>4</sup> times greater than for the oxidation by H<sub>2</sub>O<sub>2</sub>.

A particular point of interest in the reactions with oxygen to be described is that the metal ion reducing agents retain their primary coordination spheres intact. To our knowledge, no other system of this type has been subjected to a detailed kinetic analysis. A second point of interest is that the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> is much more facile than that of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O. In this respect, the system is by no means unique, H<sub>2</sub>O<sub>2</sub> having been identified as an intermediate stage in the reduction of O<sub>2</sub> by Eu(II)<sup>1</sup> and Pu(III).<sup>2</sup> However, with Eu(II) and Pu(III) as reducing agents there is no ready means of establishing whether, when oxygen acts upon them, the oxidant makes use of a normal coordination position on the metal. For our system, it can be concluded with certainty

that O<sub>2</sub> does not occupy a normal coordination position in oxidizing Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, and this places an important limitation on the mechanisms which are possible for the reaction. Another point of interest has been emphasized by recent work<sup>3-5</sup> on the reaction of molecular oxygen with tris(ethylenediamine), hexakis(methylamine), and other substituted amine complexes of ruthenium(II) which describe evidence for oxidation of the ligands. We have established the first step in the reaction of molecular oxygen with tris(ethylenediamine)ruthenium(II) as being oxidation to tris(ethylenediamine)ruthenium(III). By continued action of oxygen or of other oxidizing agents tris(ethylenediamine)-

(1) T. W. Newton, private communication.  
 (2) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 60, 1417 (1956).

(3) W. R. McWhinnie, J. D. Miller, and J. B. Watts, *Chem. Commun.*, 629 (1971).  
 (4) B. C. Lane, J. E. Lester, and F. Basolo, *Chem. Commun.*, 1618 (1971).  
 (5) H. Elsbernd and J. K. Beattie, *J. Chem. Soc. A*, 2598 (1970).

ruthenium(III) is converted to the diimine-bis(ethylene-diamine) complex,  $\text{Ru}(\text{en})_2(\text{C}_2\text{H}_2\text{N}_2\text{H}_2)^{2+}$ .<sup>4</sup>

### Experimental Section

We have made repeated attempts over a period of several years to study the rate of the reaction between  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{O}_2$  by spectrophotometric means. Until the work described here was done, our efforts were plagued by irreproducible absorbance changes which could not be accounted for in terms of reactants or of reasonably expected products. In addition, attempted kinetic studies were frustrated by irreproducible rate data. These effects have been eliminated thanks to rigorous purification of the ruthenium complex as its hexaammineruthenium(III) trichloride salt and to using rapid and efficient techniques for reduction and subsequent reaction of the ruthenium(II) complex.

**Materials.** Distilled water was prepared by redistillation of laboratory distilled water from alkaline permanganate.

Lithium acetate and lithium chloride, Baker Reagent grade, were recrystallized twice from distilled water. Acetic acid and hydrochloric acid, Baker Reagent grade, were diluted and used without further purification.

Europium(III) solutions were prepared by dissolving weighed amounts of  $\text{Eu}_2\text{O}_3$  (99.99% purity purchased from Grace Chemical) in acid solution.

Hexaammineruthenium(III) trichloride was purchased from Matthey Bishop and purified<sup>6</sup> as follows. Twelve grams of  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  was dissolved in 150 ml of water and filtered. Acetone (250 ml) was then added to the filtrate to reprecipitate the ruthenium complex. The complex was redissolved in 80 ml of water and reprecipitated with 300 ml of acetone. The complex was redissolved in 80 ml of water and reprecipitated by adding 200 ml of concentrated HCl. The solution was cooled and the complex collected by filtration. The solid was then recrystallized three times from warm ( $<40^\circ$ ) 1 M HCl by dissolving the solid in a minimum of warm 1 M HCl and cooling the solution slowly over a period of several hours. The crystals were collected by filtration, washed with cold 1 M HCl followed by acetone and then ether, and dried under vacuum.

Hexaammineruthenium(II) solutions were prepared by weighing an amount of hexaammineruthenium(III) trichloride and dissolving it in a known volume of LiOAc-HOAc buffer under argon. This solution was then reduced with a deficient amount of a stock Eu(II) solution prepared by reducing a Eu(III) solution under argon with Zn-Hg for 30 min. This method is preferable to Zn-Hg reduction of the  $\text{Ru}(\text{NH}_3)_6^{3+}$  directly since it shortens by 30 min the time that  $\text{Ru}(\text{NH}_3)_6^{2+}$  is kept before use. All solutions were prepared, stored, and transferred under argon using glass syringes and platinum needles. Hexaammineruthenium(II) solutions prepared in this manner were used immediately.

Tris(ethylenediamine)ruthenium(III) tribromide was prepared, purified, and analyzed as described by Meyers.<sup>7</sup>

Tris(ethylenediamine)ruthenium(II) solutions were prepared in a manner analogous to that used for the hexaammineruthenium(II) solutions already described.

Oxygen (Liquid Carbonic) of 99.5% purity was used without further purification. However, in saturating reaction solutions with oxygen, prebubblers of the same composition as the desired solution were used to prevent depletion of acetic acid or hydrochloric acid in the reaction solutions.

**Analysis.** The initial concentrations of hexaammineruthenium(II) and tris(ethylenediamine)ruthenium(II) were determined by sampling the reaction vessel prior to reaction and injecting the sample into an excess of iron(III) solution buffered at pH 5.4 which had been purged with argon. An excess of *o*-phenanthroline was then added and the iron(II) produced by the Fe(III)-Ru(II) reaction<sup>7</sup> was determined spectrophotometrically as the tris(*o*-phenanthroline) complex ( $\lambda_{\text{max}}$  508 nm,  $\epsilon$   $1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). The hexaammineruthenium(III) in the reaction was taken to be the difference between Ru(II) found by analysis and the amount of Ru(III) salt weighed out.

The analysis for oxygen in solution was carried out as follows. A sample of an oxygen-saturated solution, taken by syringe, was slowly injected under the surface of an argon-purged Cr(II) solution with reducing agent in excess (the concentration of Cr(II) in an identical solution with no oxygen added was determined by adding excess iron(III) solution and analyzing the iron(II) produced as described in the  $\text{Ru}(\text{NH}_3)_6^{2+}$  analysis). The Cr(II) that remained after reaction was then determined by adding iron(III) and deter-

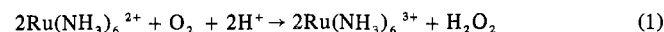
mining the iron(II) produced as above. Blanks were done on water saturated solutions at  $25^\circ$ . Comparing our values of oxygen content to handbook values, we found the method to be accurate to only 3%. Oxygen-saturated buffer solutions analyzed in like manner were then diluted with argon-purged solutions to give the desired oxygen concentrations.

**Methods.** All uv and visible spectral and kinetic measurements were made on either a Cary Model 14 or 15 recording spectrophotometer. In the kinetic experiments, to magnify the small absorbance changes accompanying the reactions, the reactions were run in 5- and 10-cm cells and a 0.0-0.1 absorbance unit slide-wire was used. Typical absorbance changes in a 10-cm path length were between 0.06 and 0.15 absorbance unit. Two types of experiments were carried out; in one type, the ruthenium(II) complex concentration was in at least a 10-fold stoichiometric excess of the oxygen concentration and in the second type the oxygen concentration was in 10-fold stoichiometric excess of the ruthenium(II) complex. Experiments with ruthenium(II) in excess were performed by preparing a ruthenium(II) solution in a spectrophotometric cell, analyzing the solution for Ru(II), and after temperature equilibration injecting a small volume of oxygen-saturated buffer to initiate the reaction. Experiments with oxygen in excess were done by diluting a saturated standardized oxygen solution in a spectrophotometric cell with an argon-purged solution. Time was then allowed for temperature equilibration and the reaction was initiated by injecting a small volume of Ru(II). All experiments were done under pseudo-first-order conditions and all first-order plots were linear to greater than 90% completion of reaction.

For the reaction of  $\text{Ru}(\text{NH}_3)_6^{2+}$  with  $\text{O}_2$ , the stoichiometry was determined by two methods. In both methods the Ru(II) complex was injected into an oxygen-saturated solution containing a tenfold excess of oxygen. The  $\text{H}_2\text{O}_2$  formed was then determined in one method by addition of excess Ce(IV). The excess Ce(IV) was then determined by reduction with excess iron(II) followed by analysis of the iron(II) remaining as its *o*-phenanthroline complexes as described earlier. The  $\text{H}_2\text{O}_2$  present is obtained by difference from the amount of Ce(IV) initially added and that consumed by the iron(II). In the second method excess iron(II) was injected into the reaction product solution containing the  $\text{H}_2\text{O}_2$ . The iron(II) is oxidized by the  $\text{H}_2\text{O}_2$  to iron(III).<sup>8</sup> The iron(II) remaining was again obtained by the *o*-phenanthroline analysis. The stoichiometry studies were carried out at pH 5.44 for  $\text{Ru}(\text{NH}_3)_6^{2+}$  and pH 2.0 for  $\text{Ru}(\text{en})_3^{2+}$ ,  $\mu = 1.00$  (LiOAc-HOAc) and  $\mu = 1.00$  (HCl-LiCl), respectively. In the case of the  $\text{Ru}(\text{en})_3^{2+}$  reaction only the Ce(IV) oxidation method was used to determine  $\text{H}_2\text{O}_2$  produced. Since  $\text{Ru}(\text{en})_3^{3+}$  could be further oxidized by Ce(IV), the  $\text{Ru}(\text{en})_3^{3+}$  was removed by rapid ion exchange prior to adding Ce(IV). All solutions were acidified to pH 1 before Ce(IV) or Fe(II) was added and were then brought to pH 5.4 before *o*-phenanthroline addition.

### Results

**Stoichiometry.** The stoichiometry of the reaction of hexaammineruthenium(II) with oxygen is given by eq 1.



The evidence for this stoichiometry is multiple. First we note that  $\text{Ru}(\text{NH}_3)_6^{2+}$ , when oxidized by  $\text{O}_2$ , has a uv-visible spectrum that is identical (within 5% and making proper allowance for  $\text{H}_2\text{O}_2$  and other ingredients) with that of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . Second, the presence of  $\text{H}_2\text{O}_2$  in the reaction products is detected by removing the oxidized ruthenium complex by passing the solution through a cation-exchange column and then treating the product solution with  $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ . The development of the deep blue color of "perchromic" acid represents a positive test for  $\text{H}_2\text{O}_2$ . Third, we have analyses for  $\text{H}_2\text{O}_2$  produced in reaction 1 by both oxidizing it with Ce(IV) or reducing it with Fe(II). Results of Ce(IV) oxidation and Fe(II) reduction of a reaction solution immediately after  $\text{O}_2$  oxidation are given in Table I. It should be pointed out that during the time of these titrations  $\text{Ru}(\text{NH}_3)_6^{3+}$  does not react with either Fe(II) or Ce(IV). Hence the quantitative production of

(6) J. N. Armor, Ph.D. Thesis, Stanford University, 1970.

(7) T. J. Meyers, Ph.D. Thesis, Stanford University, 1966.

(8) W. G. Barb, J. M. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

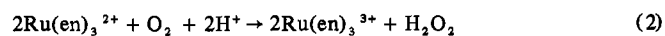
**Table I.** Stoichiometry Data for Molecular Oxygen Oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>

Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>2+</sup> oxidized	Amt, mmol		% of expected amt
	Ce(IV) consumed by H <sub>2</sub> O <sub>2</sub> produced	Fe(II) consumed by H <sub>2</sub> O <sub>2</sub> produced	
2.89	2.80		97
2.62	2.72		104
2.62	2.62		100
2.60	2.70		103
2.78		2.66	96
2.93		2.52	86
2.54		2.39	94
2.54		2.21	87

H<sub>2</sub>O<sub>2</sub> has been established both in an oxidative and a reductive test.

Fourth, to ensure that the coordination sphere of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> remains intact throughout the oxidation and to show that Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> was the only ruthenium product of this reaction, it was necessary to prove that no Ru(NH<sub>3</sub>)<sub>5</sub>-OH<sub>2</sub><sup>3+</sup> or more highly aquated forms of ruthenium(III) were produced in significant amounts. It is well known<sup>9</sup> that isonicotinamide (INA) reacts with Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub><sup>2+</sup> to give the intensely colored Ru(NH<sub>3</sub>)<sub>5</sub>-(INA)<sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>4</sub>(INA)<sub>2</sub><sup>2+</sup> complexes. These complexes have extinction coefficients of approximately (1-2) × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> at 480 nm. Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> are transparent in this spectral region. To search for aquated species, a solution of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> was oxidized with oxygen and subsequently rereduced with Eu(II). After this reduction isonicotinamide was added to convert any Ru(NH<sub>3</sub>)<sub>5</sub>-OH<sub>2</sub><sup>2+</sup> that had been produced to the readily detectable Ru(NH<sub>3</sub>)<sub>5</sub>(INA)<sup>2+</sup> complex. Within an experimental error of 1%, no aquoruthenium(II) complexes were detected in this way.

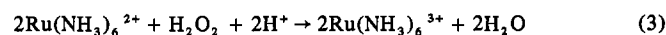
The stoichiometry of the reaction of tris(ethylenediamine)-ruthenium(II) and oxygen is given by



The stoichiometry of this reaction was established in a similar manner to that already described for the oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. The reaction of O<sub>2</sub> with Ru(en)<sub>3</sub><sup>2+</sup> suffers from the additional complication that the Ru(en)<sub>3</sub><sup>3+</sup> produced can undergo subsequent oxidation of the ligand accompanied by metal reduction.<sup>4</sup> This subsequent oxidation by additional oxygen is slow compared to the step shown in eq 2 under all conditions studied here, as is any subsequent reaction with H<sub>2</sub>O<sub>2</sub>.

Oxygen oxidation by O<sub>2</sub> of a buffered solution of Ru(en)<sub>3</sub><sup>2+</sup> produced by Eu(II) reduction yields the spectrum of the original Ru(en)<sub>3</sub><sup>3+</sup> solution. In addition, the H<sub>2</sub>O<sub>2</sub> produced by this oxidation, can be titrated with Ce(IV) after the Ru(en)<sub>3</sub><sup>3+</sup> is removed by ion exchange. The results of Ce(IV) titrations are given in Table II.

H<sub>2</sub>O<sub>2</sub> + Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. In the reaction of oxygen with Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, eq 1, the formation of H<sub>2</sub>O<sub>2</sub> leads to the possibility of subsequent reaction of unreacted Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> with H<sub>2</sub>O<sub>2</sub> as in eq 3. Since this represents a kinetic com-

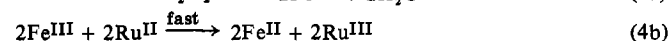
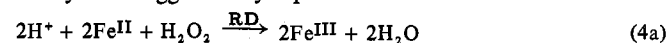


plication to the study of the first step and because we are interested in the relative rates of oxygen reduction to hydrogen peroxide reduction by metal ion complexes, attempts

**Table II.** Stoichiometry Data for Molecular Oxygen Oxidation of Ru(en)<sub>3</sub><sup>2+</sup>

Ru(en) <sub>3</sub> <sup>2+</sup> oxidized	Amt, mmol		% of expected amt
	Ce(IV) consumed by H <sub>2</sub> O <sub>2</sub> produced		
2.79	2.68		96
2.64	2.51		95
2.64	2.51		95

were made to measure the kinetics of reaction 3 independently. Experiments with Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> in 20-fold excess over H<sub>2</sub>O<sub>2</sub> established a first-order dependence of the reaction rate on H<sub>2</sub>O<sub>2</sub>. However, the observed rate constants were irreproducible. In addition, experiments with either H<sub>2</sub>O<sub>2</sub> or Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> in excess were found to be cleanly zero order in [Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>]. These observations suggest that a catalytic impurity was controlling the reaction. A drastic reduction in the rate was observed on replacing stainless steel syringe needles with platinum needles. The rates, while slower, were still irreproducible. Copper(II) and iron(III) were tested for catalytic activity in the reaction and only Fe(III) was found to be effective. The mode of catalysis is suggested by eq 4a and 4b. The rates of both



reactions are known.<sup>7,8</sup> Under all conditions used in our study, step 4a would be rate determining. This would explain the first-order dependence on (H<sub>2</sub>O<sub>2</sub>), the zero-order dependence on [Ru(II)], the irreproducible rates, and the catalytic effects of small (1 × 10<sup>-7</sup>–1 × 10<sup>-5</sup> M) amounts of either iron(II) or iron(III).

Efforts to diminish the amount of iron present by purifying the solvent and reactants decreased the rates slightly but did not eliminate the irreproducibility. Attempts to analyze the iron present as its iron(II) *o*-phenanthroline complex indicated that the residual iron concentration in these experiments was less than 4 × 10<sup>-7</sup> M. Even at these levels the rate was independent of [Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>] and hence the reaction is likely being carried completely by the iron-catalyzed path.

Addition of 8 × 10<sup>-6</sup> M iron(III) to the reaction mixture enhanced the rate greatly and also rendered the reaction reproducible. This is as would be expected since the iron concentration is now being controlled.

EDTA was added to the reaction mixture in an attempt to complex the residual iron. Experiments with EDTA added had slightly accelerated rates. This is not surprising in view of other comparisons of rates of reduction by Fe(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> and Fe(EDTA).<sup>2-10</sup>

While we have not been able to establish the intrinsic reaction rate between Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>, our results do show that if iron impurities are kept below 4 × 10<sup>-7</sup> M, the H<sub>2</sub>O<sub>2</sub>-Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> reaction will not interfere with kinetic studies of the O<sub>2</sub> oxidation of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. Furthermore, by using the slowest observed reaction rates (presumably those with the least amount of iron impurity) an upper limit can be obtained for the H<sub>2</sub>O<sub>2</sub>-Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> reaction. Under reaction conditions of [Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>]<sub>0</sub> = 3.8 × 10<sup>-3</sup> M, [H<sub>2</sub>O<sub>2</sub>] = 2 × 10<sup>-4</sup> M, pH 5.44, and μ = 1.00 in LiOAc-HOAc at 25° the lowest pseudo-first-order observed rate constant was 4.5 × 10<sup>-4</sup> sec<sup>-1</sup>. Even if all of the reaction is being carried by the intrinsic H<sub>2</sub>O<sub>2</sub>-Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> reaction

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under these conditions one would derive an upper limit for the second-order rate constant of  $0.12 M^{-1} \text{ sec}^{-1}$  for the  $\text{H}_2\text{O}_2\text{-Ru}(\text{NH}_3)_6^{2+}$  reaction. Furthermore, several facts (zero-order dependence on  $[\text{Ru}(\text{II})]$ , estimates of trace amounts of iron present in these reactions, and extrapolation of rate data from experiments with added iron(III)) indicate that much, if not all, of the observed rate for the experiment in question is a result of the iron-catalyzed path and not the intrinsic  $\text{H}_2\text{O}_2\text{-Ru}(\text{NH}_3)_6^{2+}$  reaction. Hence, we feel that no more than one-tenth of the observed reaction could have resulted from the intrinsic  $\text{H}_2\text{O}_2\text{-Ru}(\text{NH}_3)_6^{2+}$  reaction and that a more reasonable upper limit for this rate constant is  $0.012 M^{-1} \text{ sec}^{-1}$ .

**Rate Laws and Kinetic Data.**  $\text{Ru}(\text{NH}_3)_6^{2+} + \text{O}_2$ . The oxidation of  $\text{Ru}(\text{NH}_3)_6^{2+}$  by molecular oxygen, eq 1, was found to obey the rate law

$$-1/2 d[\text{Ru}(\text{NH}_3)_6^{2+}]/dt = -d[\text{O}_2]/dt = k[\text{Ru}(\text{NH}_3)_6^{2+}] \times [\text{O}_2] \quad (5)$$

The data used to establish this rate law and to determine  $k$  are given in Table III. The second-order rate constant,  $k$ , was found to be independent of hydrogen ion concentration from pH 6.05 to 1.00  $M$  HCl. All kinetic measurements were made by following the decrease in absorbance at 250 nm where  $\text{Ru}(\text{NH}_3)_6^{2+}$  ( $\epsilon_{250} 540 M^{-1} \text{ cm}^{-1}$ ) is oxidized to  $\text{Ru}(\text{NH}_3)_6^{3+}$  ( $\epsilon_{250} 300 M^{-1} \text{ cm}^{-1}$ ). Experiments with each  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{O}_2$  in large excess were done. In experiments with oxygen in excess the observed rate constant,  $k_{\text{obsd}}$ , is given by eq 6, where  $A_t$  and  $A_\infty$  refer to absorbance

$$k_{\text{obsd}} = -d \ln (A_t - A_\infty) / dt \cong 2k[\text{O}_2]_{\text{av}} \quad (6)$$

at time  $t$  and infinity, respectively. The subscript "av" refers to the average of initial and final reactant concentration in an experiment. For experiments with  $\text{Ru}(\text{NH}_3)_6^{2+}$  in excess the observed rate constant is given by eq 7. In these

$$k_{\text{obsd}} = -d \ln (A_t - A_\infty) / dt \cong k[\text{Ru}(\text{NH}_3)_6^{2+}]_{\text{av}} \quad (7)$$

experiments, the large absorbance background accompanying the excess  $\text{Ru}(\text{NH}_3)_6^{2+}$  increases the signal to noise ratio slightly and is reflected in a somewhat greater uncertainty in observed rate constants. All pseudo-first-order rate plots from which  $k_{\text{obsd}}$  was obtained were linear to greater than 90% reaction completion.

From the data at 6.8, 16.3, and 25.5°  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are calculated as  $11.5 \pm 0.3 \text{ kcal/mol}$  and  $-10.4 \pm 1.0 \text{ eu}$ , respectively. At 6.8° only the data at pH 5.44 are used in the activation energy computations since most of the data were obtained at that pH and since changing  $[\text{H}^+]$  causes unavoidable changes in reaction medium.

**$\text{Ru}(\text{en})_3^{2+} + \text{O}_2$ .** The oxidation of tris(ethylenediamine)-ruthenium(II), eq 2, was found to obey the same rate law as that found for  $\text{Ru}(\text{NH}_3)_6^{2+}$ , eq 5, including the observation that the rate is independent of hydrogen ion concentration. The data for this reaction were obtained by monitoring the decrease in absorbance at  $\lambda 304 \text{ nm}$  where  $\text{Ru}(\text{en})_3^{2+}$  ( $\epsilon_{304} 1000 M^{-1} \text{ cm}^{-1}$ ) is oxidized to  $\text{Ru}(\text{en})_3^{3+}$  ( $\epsilon_{304} 345 M^{-1} \text{ cm}^{-1}$ ).<sup>7</sup> The results of the rate experiments are given in Table IV. Again all pseudo-first-order rate plots were linear to greater than 90% reaction completion. From the data at 8.5 and 25.3°  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  of  $12.1 \pm 0.4 \text{ kcal/mol}$  and  $-9.5 \pm 1.4 \text{ eu}$ , respectively, were computed. All experiments were recorded with  $\mu = 1.00$  maintained with LiCl-HCl.

## Discussion

Oxidation of various transition metals ions  $[\text{Fe}(\text{OH}_2)_6^{2+}]$ ,<sup>4</sup>

**Table III.** Kinetic Data for  $\text{O}_2$  Oxidation of  $\text{Ru}(\text{NH}_3)_6^{2+}$  <sup>a</sup>

pH	$10^4 [\text{Ru}(\text{NH}_3)_6^{2+}]_0, M$	$10^4 [\text{O}_2]_0, M$	$k, M^{-1} \text{ sec}^{-1}$
			6.8°
5.44	$2.87 \pm 0.06$	0.15	$32.1 \pm 0.9$ (5) <sup>b</sup>
5.44	3.92	0.15	31.3
5.44	$5.98 \pm 0.17$	0.30	$31.5 \pm 2.5$ (2)
5.44	$9.67 \pm 0.02$	0.40	$34.2 \pm 0.4$ (2)
5.44	0.40	$2.05 \pm 0.05$	$33.9 \pm 1.9$ (2)
5.44	0.80	$4.28 \pm 0.05$	$29.6 \pm 0.3$ (2)
5.44	0.40	2.04	31.5 <sup>c</sup>
5.44	0.40	2.00	30.8 <sup>d</sup>
			Av $32.0 \pm 1.7$ (16)
6.05	$3.07 \pm 0.16$	0.15	$26.0 \pm 0.3$ (2)
6.05	0.30	2.06	32.4
4.44	$2.81 \pm 0.11$	0.15	$33.0 \pm 1.7$ (2)
4.44	5.05	0.30	34.3
4.44	0.30	2.05	33.2
1.00	$3.03 \pm 0.02$	0.15	$28.6 \pm 2.0$ (2)
0.0	0.30	1.64	24.8
			16.3°
5.44	3.00	0.15	$66.2 \pm 1.2$ (2)
5.44	0.40	2.03	$61.5 \pm 2.9$ (2)
			Av $63.8 \pm 2.7$ (4)
			25.5°
5.44	$2.87 \pm .09$	0.15	$126 \pm 3$ (3)

<sup>a</sup> All data at  $\mu = 1.00$  maintained with HOAc-LiOAc (pH 5.44, 6.05, 4.44) and HCl-LiCl (pH 1.00, 0.00). <sup>b</sup> The numbers given in parentheses indicate that this row represents the average of the given number of similar experiments. <sup>c</sup>  $\text{Ru}(\text{NH}_3)_6^{3+}$  was added in this experiment such that  $[\text{Ru}(\text{NH}_3)_6^{3+}]_0 = 2.8 \times 10^{-4} M$ . <sup>d</sup>  $\text{Ru}(\text{NH}_3)_6^{3+}$  was added in this experiment such that  $[\text{Ru}(\text{NH}_3)_6^{3+}] = 4.13 \times 10^{-4} M$ .

**Table IV.** Kinetic Data for the  $\text{O}_2$  Oxidation of  $\text{Ru}(\text{en})_3^{2+}$  <sup>a</sup>

$[\text{H}^+], M$	$10^4 [\text{Ru}(\text{en})_3^{2+}]_0, M$	$10^4 [\text{O}_2]_0, M$	$k_2, M^{-1} \text{ sec}^{-1}$
			8.5°
0.010	2.75	0.15	20.8
0.010	3.07	0.15	22.6
0.010	3.60	0.15	19.8
0.010	8.20	0.40	19.9
0.010	0.40	1.78	19.2
0.010	0.40	1.78	17.5
0.010	0.20	2.18	21.6
0.010	0.20	2.18	22.2
0.010	0.40	2.04	19.8
0.100	3.01	0.15	20.3
			Av $20.4 \pm 1.1$
			25.3°
0.010	3.47	0.15	71.3
0.010	3.21	0.15	75.4
0.010	1.85	0.07	69.0
0.010	1.87	0.07	73.4
			Av $72.3 \pm 2.4$

<sup>a</sup> All data at  $\mu = 1.00$  maintained with HCl-LiCl.

$\text{Cr}(\text{OH}_2)_6^{2+}$ ,<sup>11</sup>  $\text{V}(\text{OH}_2)_6^{2+}$ ,<sup>12</sup>  $\text{Co}(\text{CN})_5^{3-}$ ,<sup>13</sup>  $\text{Cr}(\text{NH}_3)_5\text{OH}_2^{2+}$ <sup>14</sup>] by molecular oxygen occur with involvement of  $\text{O}_2$  in the primary coordination sphere as a possibility. Only one previously studied reaction, the oxidation of  $\text{Cr}(\text{II})$  in  $\text{CN}^-$  medium,<sup>13</sup> which yields  $\text{Cr}(\text{CN})_6^{3-}$  as a product, seems certain not to have such an inner-sphere involvement. The oxidations of  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Ru}(\text{en})_3^{2+}$  in this study are examples of reactions that must occur without involvement of  $\text{O}_2$  in normal coordination positions, and they clearly

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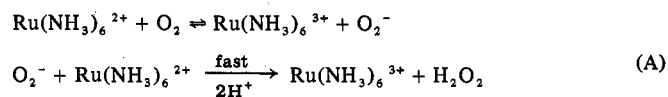
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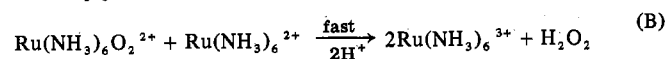
establish that reduction of molecular oxygen with transition metal ions can occur while the primary coordination sphere remains intact. They also show that such reduction can occur without the aid of an electron "conducting" ligand such as cyanide.

While the production of H<sub>2</sub>O<sub>2</sub> as the immediate product for these reactions is not surprising, the very large difference in reactivities toward Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> of O<sub>2</sub> (126 M<sup>-1</sup> sec<sup>-1</sup>) and H<sub>2</sub>O<sub>2</sub> (≤0.012 M<sup>-1</sup> sec<sup>-1</sup>), a factor of ≥10<sup>4</sup>, is remarkable. While specific rate studies on the H<sub>2</sub>O<sub>2</sub>-Ru(en)<sub>3</sub><sup>2+</sup> reaction were not carried out, indications from the O<sub>2</sub>-Ru(en)<sub>3</sub><sup>2+</sup> kinetic and stoichiometric studies are that Ru(en)<sub>3</sub><sup>2+</sup> too reacts slowly with H<sub>2</sub>O<sub>2</sub> as compared to its reaction rate with O<sub>2</sub>. It is possible that for these complexes part of this vast disparity in rates will only be observed when substitution in a normal coordination position is excluded. For this reason studies of reaction of H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> with Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> or Ru(OH<sub>2</sub>)<sub>6</sub><sup>2+</sup> would be of interest.

With regard to mechanism, the rate law implies a rate-determining step involving one molecule of Ru(II) and one molecule of O<sub>2</sub>, and not involving additional protons. It does not, however, distinguish between a one-electron step to give Ru(III) and superoxide ion, mechanism A, or a two-



electron step to give a Ru<sup>IV</sup>-O<sub>2</sub><sup>2-</sup> intermediate, mechanism B



(energetically it is unlikely that free O<sub>2</sub><sup>2-</sup> could be generated). Using an E° value of 0.10 V for the Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>-Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> potential and a calculated<sup>15</sup> value of -0.38 V for the O<sub>2</sub>-O<sub>2</sub><sup>-</sup> potential, an equilibrium constant for the first step of mechanism A of 10<sup>-8</sup> is calculated. This value combined with the measured rate constant of 126 M<sup>-1</sup> sec<sup>-1</sup> at 25.5° would yield a reverse rate for that step of ca. 10<sup>10</sup> M<sup>-1</sup> sec<sup>-1</sup> or a value very close to the diffusion-controlled limit. Considering the large driving force and the nature of the reactants for the second step of mechanism A, it is likely that this step is also diffusion controlled. Hence, in experiments with oxygen in excess of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and with added Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> in initial tenfold excess of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>

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concentration, deviation from first-order kinetics should be observed as the reverse of step 1 in mechanism A becomes important. The deviation should be most dramatic near the end of reaction where the Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> concentration approaches zero and the ratio of the concentration of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> to Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> becomes very large. In fact, this deviation was not observed and experiments under these conditions were linear to greater than 95% completion of reaction.

It should be noted that the acid dissociation constant of HO<sub>2</sub> has been reported as 2 × 10<sup>-5</sup>.<sup>16</sup> The experiments with Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> added initially were done at pH 5.44, and the argument advanced is therefore not vitiated by possible association of O<sub>2</sub><sup>-</sup> with H<sup>+</sup>.

It is possible of course that the E° value for the O<sub>2</sub>-O<sub>2</sub><sup>-</sup> couple which has been estimated is in error and consequently that the reverse of step 1 in mechanism A is not diffusion controlled. If this is the case, then there is no experimental conflict with mechanism A.

Mechanism B suggests that the intermediate formed is a complex of Ru(IV) with O<sub>2</sub><sup>2-</sup>, in which Ru(IV) is assumed to have a coordination number of 7. Similar species can reasonably be inferred to figure in the release of NH<sub>3</sub> from Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> under the influence of H<sup>+</sup><sup>17</sup> and in the reaction of Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> with HONO.<sup>6</sup>

In a recent communication<sup>4</sup> it has been reported that the oxidations with O<sub>2</sub> of Ru(en)<sub>3</sub><sup>2+</sup> and Ru(en)<sub>3</sub><sup>3+</sup> yield Ru(en)<sub>2</sub>(C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>H<sub>2</sub>)<sup>2+</sup>. The results of oxidation of Ru(en)<sub>3</sub><sup>2+</sup> in our study show that O<sub>2</sub> oxidation, under the conditions employed here, results first in Ru(en)<sub>3</sub><sup>3+</sup>. This indicates that ligand oxidation must occur subsequent to metal oxidation by O<sub>2</sub> of Ru(en)<sub>3</sub><sup>2+</sup>. Whether or not this is a general feature that applies to other ruthenium complexes with oxidizable ligands and/or other oxidizing agents is not yet known.

**Registry No.** Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, 19052-44-9; Ru(en)<sub>3</sub><sup>2+</sup>, 21393-86-2; O<sub>2</sub>, 7782-44-7; H<sub>2</sub>O<sub>2</sub>, 7722-84-1; iron, 7439-89-6.

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