**Table III.** Mutual Atom Polarizabilities,[a] $\pi_{r,1} = \partial q_r/\partial\alpha_1$

| | Atom (r) | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| $\rho = 1$ | +0.273 | −0.096 | −0.023 | −0.006 | −0.023 |
| $\rho = 2$ | +0.166 | −0.068 | −0.010 | −0.003 | −0.004 |

[a] HMO calculations; $\alpha_N = \alpha_P + \rho\beta$; homomorphic.

by an addition reaction, which can be understood similarly, and a preliminary account of this work has appeared.[19] Conjugative,[20] solvent, and reagent effects are also important and will be considered later.

**Registry No.** MeLi, 917-54-4; $N_4P_4F_8$, 14700-00-6; $MeN_4P_4F_7$, 37110-97-7; 1,1-$Me_2N_4P_4F_6$, 29021-59-8; *trans*-1,5-$Me_2N_4P_4F_6$, 37110-98-8; $Me_2N_4P_4F_6$, 37164-25-3; 1,1,3-$Me_3N_4P_4F_5$, 37110-93-3; 1,1,5-$Me_3N_4P_4F_5$, 37110-94-4; 1,1,5,5-$Me_4N_4P_4F_4$, 29144-50-1; $Me_8N_4P_4$, 4299-49-4.

**Acknowledgments.** We thank the National Research Council of Canada for financial support, the University of British Columbia for a University Graduate Fellowship (to T. N. R.), and Dr. L. D. Hall and Mr. R. Burton for the heteronuclear decoupling experiments.

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# Hydroxide Ion as a Reducing Agent for Cations Containing Three Ruthenium Atoms in Nonintegral Oxidation States

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Hydroxide ion is oxidized by $Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5^{7+}$ in a second-order reaction for which $k$ is $1.9 \times 10^4$ $sec^{-1}$ $M^{-1}$ (at 25° in buffered media of ionic strength 0.25 $M$) and $\Delta H^{\ddagger}$ is 19 kcal/mol. An isosbestic point exists throughout the reaction but chemical evidence shows than an intermediate is involved. The corresponding oxidant which has two ethylenediamine ligands replacing the four ammonias on the central ruthenium atom is reduced faster but with a similar $\Delta H^{\ddagger}$. The spectra of the four ruthenium trimers involved in these reactions are consistent with a molecular orbital scheme. All the data are consistent with a mechanism involving rate-determining attack of $OH^-$ on the central ruthenium atom.

There have been reports[1,2] of a curious reaction by which $OH^-$ is rapidly oxidized by $(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5{}^{7+}$ ("ruthenium brown," hereafter I) with the production of the corresponding 6+ cation ("ruthenium red," hereafter II). Previous workers[1] suggested that the OH radical was the oxidation product of $OH^-$, but this seems unlikely since the I → II potential is only 0.75 V *vs.* the normal hydrogen electrode, which appears insufficient[3] to produce OH. Strong oxidants such as $MnO_4^-$ normally react with $OH^-$ only quite slowly,[4] but the ruthenium trimer I reacts rapidly with $OH^-$. We have investigated this system to determine why such a mild oxidant oxidizes $OH^-$ so readily.

We recently described[5] the synthesis of an analog of the 6+ ion with two ethylenediamine (en) groups replacing the $NH_3$ groups on the central ruthenium atom and also an X-ray structure determination of this ion. We now report spectra of four interrelated compounds (en and $NH_3$, 6+ and 7+). The remarkable reactivity of I with $OH^-$ can be rationalized on the basis of a molecular orbital scheme based on these spectra.

## Experimental Section

$LiClO_4$ was prepared from $Li_2CO_3$ and $HClO_4$, digested in solution overnight at 40–50° to remove $SiO_2$, and recrystallized three times from triply distilled water.

The chloride salt of "ruthenium red" (II) was prepared as follows. $RuCl_3 \cdot 3H_2O$ (5 g) was dissolved in 25 ml of 0.25 $M$ HCl. Absolute alcohol (5 ml) and ascorbic acid (0.1 g) were added and the brown solution was refluxed at 85° for 3 hr and then concentrated to 5 ml under reduced pressure. Concentrated $NH_3$ (20 ml) was added a few milliliters at a time and the mixture was held at 85–90° for 1 hr while streams of air and ammonia gas were passed through the solution. Concentrated ammonia solution was added as necessary to maintain the volume of the reacting solution at approximately 20 ml. The reaction mixture was centrifuged while hot, and the supernatant liquid was then cooled in an ice bath. A brown powder was collected by filtration, recrystallized from 0.1 $M$ ammonia, and washed with ethanol and ether (yield 2 g). *Anal.* Calcd for $Ru_3O_2(NH_3)_4Cl_6 \cdot 3H_2O$: Ru, 36.10; N, 23.33; Cl, 25.31. Found:[6] Ru, 36.12; N, 23.10; Cl, 27.58.

In order to prepare the chloride salt of ruthenium brown (I), the chloride of II (1.0 g) was dissolved in water at 40° and 2 $M$ HCl was added until the pH of a cooled aliquot was 1.0. A stream of air was then passed through the warm solution for several hours. The mixture was cooled and a brown powder was collected by filtration and washed with 0.1 $M$ HCl and ether (yield 0.8 g). *Anal.* Calcd for $Ru_3O_2(NH_3)_{14}Cl_7 \cdot 2H_2O \cdot HCl$: Ru, 33.82; N, 21.90; Cl, 31.69. Found: Ru, 33.48; N, 21.90; Cl, 31.18. Needle-shaped crystals were grown by rapid evaporation of solutions of the chloride of I.

The ethylenediamine (en) analog of II, namely, $Ru_3O_2(NH_3)_{10}(en)_2Cl_6 \cdot H_2O$ (hereafter II′), was prepared as previously described.[5] In order to prepare the oxidized analog (hereafter I′), 50 mg of II′ chloride was dissolved in a minimum quantity of water. The solution was acidified and 2 drops of chlorine water (~10 m$M$) were added. The color of the solution rapidly changed from red to brown. A few drops of a saturated solution of NaCl in 0.01 $M$ HCl

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(6) P. M. Smith, Thesis, Georgetown University, 1971.

**Table I.** Kinetic Data[a] for Reaction 1 in Buffered $LiClO_4$ Media ($\mu = 0.25\ M$, $T = 25.0°$)

| pH | $10^2 k_{obsd}$, $sec^{-1}$ | $10^{-4}k$,[b] $M^{-1}\ sec^{-1}$ | pH | $10^2 k_{obsd}$, $sec^{-1}$ | $10^4 k$,[b] $M^{-1}\ sec^{-1}$ |
|---|---|---|---|---|---|
| 6.60 | | | | | |
| 6.60[c] | 0.06 | 1.6 | 8.17 | 3.10 | $2.0_5$ |
| 6.85[c] | 0.11 | $1.4_5$ | 8.35[e,f] | 5.36 | 2.2 |
| 7.30[d] | 0.41 | 2.0 | 8.65[e] | 11.3 | 2.5 |
| 7.36 | 0.48 | 2.1 | 8.70[c,b] | 11.1 | 2.2 |
| 7.42 | 0.65 | 2.5 | 8.85[e] | 14.4 | $2.0_5$ |
| 7.80 | 0.99 | $1.6_5$ | 9.14[f] | 23.0 | $1.6_5$ |
| 7.95 | 1.28 | $1.5_5$ | | Av | 1.9 ± 0.3[g] |
| 8.10 | 1.68 | 1.4 | | | |

[a] Duplicates in Trisma base buffer (0.5 *M*) unless otherwise noted. $[I] = 2.25 \times 10^{-5}\ M$. [b] $k = k_{obsd}/[OH^-]$. [c] Imidazole buffer 0.05 *M*. [d] Single run. [e] Triplicate. [f] Borate buffer 0.05 *M*. [g] Weighted average and weighted average deviation.

**Table II.** Variation of *k* with Substrate and $Ru^{3+}$ Concentrations[a]

| X | $10^6[X]$, *M* | *k*, $M^{-1}\ sec^{-1}$ |
|---|---|---|
| I | 4.0 | $2.6_4$ |
| | 2.0 | $1.8_6$ |
| | 0.4 | $1.6_4$ |
| | (0) | (1.4) |
| I[b] | 3.1 | $2.6_8$ |
| | $1.5_4$ | $2.0_6$ |
| | $0.7_4$ | 1.8 |
| | (0) | (1.7) |
| $Ru^{3+}$ | 0.5[c] | 2.4 |
| | 1.0[c] | 4.3 |

[a] Conditions as in Table I. [b] Purified by chromatography. [c] $[I] = 2 \times 10^{-5}\ M$.

was added and caused a brown microcrystalline precipitate to form. The solid was collected by filtration and washed with 0.01 *M* HCl and ether and air-dried. The solid was recrystallized from 0.01 *M* HCl. *Anal.* Calcd for $Ru_3O_2(en)_2(NH_3)_{10}Cl_7 \cdot 5H_2O$: Ru, 31.79; N, 20.55; Cl, 26.05; C, 5.03; H, 5.87. Found: Ru, 32.9; N, 19.69; Cl, 25.86; C, 5.41; H, 5.84.

Imidazole was twice recrystallized from benzene (with charcoal) and dried under vacuum for 2 days. Tris(hydroxymethyl)aminomethane (hereafter Trisma base) and boric acid were reagent grade and used without further purification. Buffer concentrations are expressed as the sum of concentrations of acidic and basic components.

Rate measurements were made using Gilford and Durrum-Gibson kinetic spectrophotometers with temperature control to 0.05 and 0.2°, respectively. Kinetic runs were initiated by syringe addition of buffer to an equal volume of acidic substrate solution. Both solutions had previously been deaerated by bubbling with argon. The pH of the reaction was measured after reaction was complete. Potentials were measured *vs.* the saturated calomel (NaCl) electrode (sce) or saturated mercuric sulfate electrode and are reported *vs.* the sce.

During the I-$OH^-$ reaction, the spectrum characteristic of I disappeared and was replaced by that characteristic of II. A single, well-defined isosbestic point at 492 nm was observed. Reactions were followed at 532 nm, the wavelength of maximum absorption of II. The reaction followed first-order kinetics (within 3%) for 3 or more half-times when the initial concentration of I was greater than $10^{-6}$ *M*. Rate plots for those runs involving [I] less than $10^{-6}$ *M* showed upward deviations after 1 half-time suggesting some tendency toward a higher order dependence on substrate concentration at extremely low initial concentration of I.

For some experiments the substrate (I) solution was purified by chromatography. A 20 × 2.5 cm column of Bio Rex 70 (a weak carboxylic acid resin) in the $H^+$ form was loaded with I in 1 m*M* $HClO_4$. The column was then washed with 5 l. of m*M* $HClO_4$ and then with a solution 4 m*M* in $HClO_4$ and 4 m*M* in $LiClO_4$, which eluted some II but did not elute I. I was eluted from the column using a solution ~9 m*M* in $HClO_4$ and 4 m*M* in $LiClO_4$. The concentration of I in the eluted solution was determined spectrophotometrically on the basis of known extinction coefficients.

Quantitative formation of I was brought about by adding chlorine water to a solution of II which had been formed by adding base to a solution of I and then, after argon deaeration, reacidifying. This cyclical procedure could be repeated up to ten times (under argon) with the same solution and resulted in only minor decomposition of the trimeric ions.

## Results

Both at the dme and at the rotating platinum electrode, waves corresponding to the I → II and II → I changes appeared at +0.49 ± 0.03 V *vs.* the sce. An additional cathodic wave for II appeared in the neighborhood of −0.6 V. This wave is assigned to further reduction of II. The I → II redox potential was independent of pH between 2 and 10.

## Stoichiometry

At the dme, $O_2$ is reduced to $H_2O_2$ near 0 V and the latter is further reduced to $H_2O$ near −1.0 V. Polarographic experiments designed to detect $H_2O_2$ (at −1.0 V) were inconclusive, due, in part at least, to high background currents at that potential. Addition of $OH^-$ to solutions of I causes an increase in polarographic current near −0.1 V, and this increase can be destroyed by deaeration with nitrogen, suggesting that the increase in current is caused by $O_2$. In one series of nine experiments involving a suspension of total composition 0.3 m*M* in I, an initial current enhancement at −0.1 V corresponding to 60 ± 20% of the $O_2$ to be expected on the basis of eq 1 was observed. The product solution is

$$I + OH^- \rightarrow II + {}^1/_4O_2 + {}^1/_2H_2O \qquad (1)$$

identical with a solution prepared from recrystallized II in all properties examined except one: if the product solution is reacidified within a few minutes after its formation, part (~20%) of II is reconverted to I in a reaction which proceeds at a rapid but measurable rate.[7] II is oxidized by $O_2$ or $H_2O_2$ at rates that are several orders of magnitude less. This difference indicates that there is an intermediate of some stability formed in this reaction, but the existence of the isosbestic point shows that this intermediate has the same chromophore as II.

## Kinetics

As shown in Table I, observed first-order rate constants depend on $[OH^-]$. The second-order rate constant ($k = k_{obsd}/[OH^-]$) was constant within the precision of the measurements. Experiments in which $Cl^-$ or $Br^-$ (up to 0.1 *M*) were substituted for some of the $ClO_4^-$ (15 experiments) or in which buffer concentrations were varied in the range 0.01-0.70 *M* (10 experiments) all gave values of $k'$ within the range shown in Table I. Values of *k* in the same range were obtained in the presence of $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, $AgBF_4$, or $C_6H_5NH_3Cl$ at concentrations of the order of 0.02 m*M*, but $Ru(H_2O)_6(BF_4)_3$ showed a catalytic effect, approximately doubling the rate when present in 0.001 m*M* concentration. As shown in Table II, the observed rate has a small dependence on the initial concentration of substrate and this dependence is reduced, but not entirely eliminated, by chromatographic treatment of the substrate. This behavior and the analytical data are consistent with the presence of a trace (<1%) of a catalytically active impurity such as $Ru^{3+}$ in the several preparations of I used. Since [I] was constant at $2.2 \times 10^{-5}$ *M* for all experiments reported in Table I, the catalytic path accounts for a constant and minor fraction of the reaction. Further experiments on the origin of this catalysis will be reported separately.

Hydroxide reduction of I′ (the en analog of I) was faster than the corresponding reaction of I but followed the same

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[7] J. E. Earley and H. Razavi, *Inorg. Nucl. Chem. Lett.*, in press.

**Table III.** Variation of $k$ with Temperature[a]

| Substrate | $T$, °C | $10^{-3}k$ $M^{-1}$ sec$^{-1}$ | $\Delta S^\ddagger$, eu | $\Delta H^\ddagger$, kcal/mol |
|---|---|---|---|---|
| I | 7.25[b] | $1.5_3$ | | |
| | 16.28 | $4.5_1$ | 25 | 19 |
| | 25.0 | 19 | | |
| | 31.90 | 24.0 | | |
| I′ | 11.15 | 35.2 | | |
| | 25.0 | 198 | 35 | 22 |
| | 34.40 | 595 | | |

[a] Ionic strength 0.25 $M$ ($LiClO_4$): Trisma buffer 0.05 $M$; averages of duplicate runs, measured at pH 7. [b] Triplicate

rate law. Table III contains data on the temperature variation of the rate constant for both reactions. The reaction of the en analog has a higher activation enthalpy but a more favorable entropy of activation. The observed activation enthalpies are twice as large as those normally observed for electron-transfer reactions and are in the range of those to be expected for ligand substitution reactions.

## Spectra

Table IV gives ir spectral data for the amine trimers and for $Ru(NH_3)_6Cl_3 \cdot nH_2O$. The ethylenediamine compounds show quite similar bands plus others which can be ascribed to the organic ligand. The band near 810 cm$^{-1}$ ($\nu_{as}$) is assigned to an asymmetric M-O-M stretch. For linear dimers, $\nu_{as}$ generally occurs close to 850 cm$^{-1}$, but for bent dimers the same vibration occurs below 750 cm$^{-1}$. For linear dimers, the symmetric M-O-M stretch, $\nu_s$ normally occurs below 240 cm$^{-1}$, but for bent dimers it occurs above 270 cm$^{-1}$.[8] The hexaammine shows N-M-N bands in this region.

The reduced ethylenediamine trimer has been shown to be linear in the solid state[5] and preliminary X-ray work strongly indicates a linear structure for the oxidized form as well.[6] The ir data are consistent with that structure and with the suggestion that[8] $\nu_{as}$ for trimers is close to the corresponding frequency for dimers.

Absorption spectra of pulverized crystalline samples of the chloride of the amine trimers (in KBr pellets) showed peaks at 375, 535, and 755 nm for the reduced form and 380, 480, 900, and 1400 nm for the oxidized form. The similarity of these solid-phase spectra with the solution spectra shown in Table V indicates that the linear trimeric chromophore is also present in solution.

The proton resonance of the methylene group in II′, the reduced en trimer (nearly saturated, ~2% solution in $D_2O$, 90-Mc Brucker instrument) showed a downfield shift 19 Hz relative to that in free en; the oxidized form (in $D_2O$-DCl) showed no corresponding resonance.

## Bonding

A molecular orbital scheme for II has been proposed by Orgel and Jorgensen.[9] The cation of the ethylenediamine analog of ruthenium red has $D_{4h}$ symmetry and the similarities of spectra just mentioned lead us to consider that all four cations have closely related structures. We choose the $C_4$ axis as the $z$ axis and erect $x$ and $y$ axes through the inversion center in the planes of the Ru-N bonds of the (eclipsed) terminal ruthenium atoms. The linearity of the molecule requires that the two $\mu$ oxygen atoms be in sp hybridization. The two unshared pairs of electrons on each oxygen atom occupy a set of e orbitals.

**Table IV.** Infrared Spectra of Some Ruthenium Ammine Salts[a]

| $SCl_6$[b] | $SCl_7$[b] | $Ru(NH_3)_6Cl_3$ | Assignment |
|---|---|---|---|
| 3250 s, b | 3215 s, b | | Coordinated N-H str |
| 3160 sh | 3160 sh | | |
| 1620 s, b | 1615 s, b | 1610 s, b | N-H def |
| 1300 sh | 1305 sh | 1335 sh | N-H degen str |
| 1285 ss | 1295 ss | 1314 ss | |
| 1035 vw | 1025 w | | |
| 805 s, b | 820 s, b | | Metal-oxygen str |
| 760 sh | 750 sh | 775 m, b | $NH_3$ rock |
| 445 ss | 475 sh | 460 ms | Metal-ligand str |
| | 465 s, sh | | |
| | 455 sh | | |
| 310 ms | 305 sh | | Ligand-metal-ligand |
| 270 ms | 270 ms | 265 ms | |

[a] Key: s, strong; b, broad; m, medium; sh, shoulder; w, weak; ss, strong and sharp; vw, very weak. KBr disks are Perkin-Elmer 225; all salts are hydrates; OH bands are not listed. [b] S refers to $Ru_3O_2(NH_3)_{14}$.

**Table V.** Spectral[a] Data for $(NH_3)_5RuORu\,L_4ORu(NH_3)_5{}^{n+}$

| L = $NH_3$ | | | | L = en/2 | | | | |
|---|---|---|---|---|---|---|---|---|
| $n = 6$[b] | | $n = 7$[c] | | $n = 6$[b] | | $n = 7$[c] | | Assignment[e] |
| $10^{-3}$ $\Delta E$, cm$^{-1}$ | $10^{-3}\epsilon$ | $10^{-3}$ $\Delta E$, cm$^{-1}$ | $10^{-3}\epsilon$ | $10^{-3}$ $\Delta E$, cm$^{-1}$ | $10^{-3}\epsilon$ | $10^{-3}$ $\Delta E$, cm$^{-1}$ | $10^{-3}\epsilon$ | $D_{4h}$ |
| | | 7.46[d] | 1.5[d] | | | 7.3[d] | 1.7[d] | $n \rightarrow n'$ |
| 13.2 | 1.0 | 11.3 | 1.8 | 12.5 | 0.7 | 11.1 | 1.8 | $n' \rightarrow \pi^*$ |
| 18.8 | 69.9 | 21.5 | 43.8 | 18.5 | 81.8 | 21.4 | 46.1 | $\pi^n \rightarrow \pi^*$ |
| 26.7 | 6.3 | 28.6 | 14.1 | 26.3 | 6.4 | 27.0 | 14.0 | $\pi' \rightarrow \pi^*$ |
| 40.8 | 6.0 | 39.2 | 6 | 41.6 | 3.4 | 40.0 | 2.8 | $\pi \rightarrow \pi^*$ |

[a] Temperature 25°; absorption spectra in dilute ($\mu$ = 0.1–0.2 $M$) aqueous solutions; Cary 14 instrument. [b] pH 8–10 $NH_4Cl$-$NH_3$ buffers. [c] pH 2–5 NaAc–HAc buffers. [d] In $D_2O$-DCl solutions. [e] $\pi$, $\pi'$, $\pi^n$, n, n′, and $\pi^*$ refer to $e_u{}^\circ$, $e_g$, $e_u$, $b_{1g}$, $b_{1u}$, and $e_g{}^*$ molecular orbitals, respectively.

In $D_{4h}$, the five orbitals of the central metal atom Ru(2) split into $a_{1g}(d_{z^2})$, $b_{1g}(d_{xy})$, $b_{2g}(d_{x^2-y^2})$, and $e_g(d_{xz}, d_{yz})$ sets. The terminal ruthenium atoms have $C_{4v}$ local symmetry and the five d orbitals split into $a_1(d_{z^2})$, $b_2(d_{x^2-y^2})$, $b_1(d_{xy})$, and $e(d_{xz}, d_{yz})$ sets.

The $\sigma$ bonding system of the molecule makes use of the sp orbitals of both oxygens, the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals of both terminal ruthenium atoms, and the $d_{z^2}$ and $d_{xy}$ orbitals of Ru(2), as well as ligand $\sigma$ orbitals from each of the 14 nitrogen atoms and s and p orbitals of all three ruthenium atoms.

Overlap is possible between the oxygen e orbitals and the $e(d_{xz}, d_{xy})$ orbitals of the terminal ruthenium atoms. This gives rise to two orbitals on each side of the molecule

$$\epsilon' = e(Ru) + e(O)$$

$$\epsilon = e(Ru) - e(O)$$

of which $\epsilon$ corresponds to a bonding Ru-O interaction and $\epsilon'$ to an antibonding interaction. The $\epsilon$ orbitals on each end of the molecule may combine either through the $e(d_{xy}, d_{xz})$ orbitals on the center Ru or by mixing with some of the $\sigma$-bonding p orbitals of that atom. Since the $\epsilon$ orbitals of the central Ru are g with respect to the center of inversion, only g combinations involving this set of orbitals are possible.

There are three possible g combinations

$$e_g{}^* = \epsilon' - e - \epsilon' \text{ (antibonding)}$$

$$e_g = \begin{cases} \epsilon' + e - \epsilon' \\ \epsilon + e - \epsilon \end{cases}$$

$$e_g{}^\circ = \epsilon - e - \epsilon \text{ (bonding)}$$

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(8) G. W. Watt and W. C. McMordie, *J. Inorg. Nucl. Chem.*, 27, 2013 (1965).

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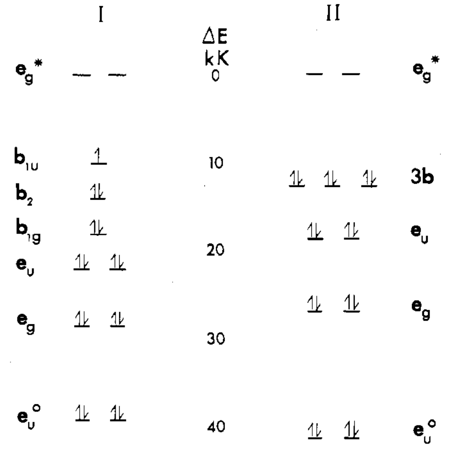

**Figure 1.** Molecular orbital scheme for ruthenium trimeric cations I and II. The filled and low-lying $e_g^\circ$ orbitals have been omitted. Energy spacings are consistent with spectra and assignments shown in Table V.

Formation of molecular orbitals u with respect to the inversion center of the cation requires use of the p-orbital system of Ru(2); these p orbitals are also involved in the Ru(2)-N σ-bond system which lies halfway between the $x$ and $y$ axes. The ε orbitals will therefore be located similarly and will combine to give rise to the molecular orbitals $\mathbf{e}_u = \epsilon' + \epsilon'$ and $\mathbf{e}_u^\circ = \epsilon + \epsilon$ (bonding). The $b_1$ orbitals of the terminal Ru atoms are in the same planes as the Ru(2)-N σ-bond system ($xy$, $z$) and combine to form $\mathbf{b}_{1g} = b_1 + b_1$ and $\mathbf{b}_{1u} = b_1 - b_1$. The $b_2$ orbital of Ru(2) lies along the $x$ and $y$ axes and does not overlap with the $\mathbf{b}_1$ set so that it forms a $\mathbf{b}_2$ molecular orbital. Figure 1 represents this scheme.

The main peak in the visible region is assigned as the $\mathbf{e}_g^* \leftarrow \mathbf{e}_u$ transition; the peak in the far-uv region present only in the oxidized form is assigned $\mathbf{b}_{1u} \leftarrow \mathbf{b}_{1g}$ (Table V).

An almost equivalent but simpler result can be obtained by ignoring (after the manner of Orgel and Jorgensen[9]) the bridging oxygen atoms in constructing the molecular orbital scheme. Using 1 and 3 for the terminal Ru atoms and 2 for the central one, molecular orbitals are (in order of decreasing energy) $\mathbf{e}_g^* = e_1 + e_2 + e_3$, $\mathbf{b}_u = b_1 - b_3$, $\mathbf{b}_{g'} = b_2$, $\mathbf{b}_g = b_1 + b_3$, $\mathbf{e}_u = e_1 - e_3$, and $\mathbf{e}_g = e_1 - e_2 + e_3$. The transition near 40 kK is then assigned to ligand (O)-to-metal charge transfer.

Using ψ for wave functions of e sets, this abridged scheme requires

$$\psi(\mathrm{e_g}^*) = a\psi_1 + b\psi_2 + a\psi_3$$

$$\psi(\mathrm{e_u}) = c\psi_1 + c\psi_3$$

$$\psi(\mathrm{e_g}) = d\psi_1 + f\psi_2 + d\psi_3$$

From the normalizing conditions, $c = 1/\sqrt{2}$ and $a^2 + d^2 = {}^1/_2$.

If $a$ should equal $d$, the terminal ruthenium atoms of the 6+ ions would have a population of five d electrons and the central ruthenium atom would have a population of four d electrons. This is in precise agreement with the integral oxidation state assignment (III, IV, III) which is most consistent with the Mossbauer spectrum.[10] However, the isomer shift of Ru(2) is closer to that to be expected for Ru(VI) than that to be expected for Ru(IV)[11] which suggests that $d$ is somewhat larger than $a$. In the case of the 7+ ion, the electron is considered to be removed from a $\mathbf{b}_{1u}$ orbital located mainly on the terminal atoms and arguments similar to those above lead to a population of 4.5 d electrons on the terminal Ru atoms and 4 on the central one. The differences between the spectra (both Mossbauer and electronic) of the 6+ and 7+ cations are consistent with a somewhat larger concentration of charge on the central atom than this rough reckoning predicts.

The previously reported diamagnetism of the 6+ ion and the low paramagnetism of the 7+ ion are consistent with the bonding scheme and with the proton nmr results reported here. The downfield shift of the methylene proton of the 6+ ion is consistent with the positive nature of Ru(2).

The interesting fact that treatment of ruthenium red with en replaces only the $NH_3$ groups on Ru(2), not those on the terminal ruthenium atoms, is rationalized by the more complete bonding scheme. Involvement of the p orbitals of Ru(2) with the $\mathbf{e}_u$ orbitals weakens the Ru(2)-N σ-bond system and labilizes the $NH_3$ groups on that metal atom. The spectra indicate that this involvement is greater in I (red) than in II (brown). The involvement of these p orbitals with the $\mathbf{b}_1$ orbitals constrains the σ-bonding system of the terminal rutheniums to lie at 45° from that of the central ruthenium and implies that the staggered configuration of the cation is not solely due to packing, but involves a fundamentally electronic effect.

## Discussion

Graff and Wilmarth[12] reported that $OH^-$ functions as a reducing agent for μ-amido-μ-superoxo-bis[bis(ethylenediamine)cobalt(III)] ion and Zia[13] studied the stoichiometry and kinetics of this process. This reaction involves[14] the coordinated ligands and leads to formation of hydroxylamine ligands. In the reaction system we studied, $Cl_2$ oxidation appears to regenerate the original substrate, even though substitution on II is slow. This suggests that reduction of the ruthenium trimer I (unlike the dicobalt system) does not entail a major and permanent change in the Ru-N bonding system.

Ruthenium(III) readily forms amido complexes[15,16] and it is conceivable that the rate-determining step for reduction of I involves formation of an amido complex. Hydrogen-transfer reactions are important in reduction of the Ce(IV) aquo ion.[17] Ruthenium(III) also forms seven-coordinate species as kinetic intermediates.[18,19] The magnitude of the activation thermodynamic quantities indicates a substitution on either central or terminal rutheniums rather than atom or electron transfer.

The more favorable entropy of activation for the ethylenediamine analog, I′, as compared to the ammine substrate I can be understood on the basis of rate-determining attack of $OH^-$ on the central ruthenium atom. The organic ligand tends to open up (96° *vs.* 90°)[5] two of the N-Ru-N angles

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on that atom and should facilitate attack. There is little spectral or electrochemical difference between I and I$'$. The hydrogen-transfer mechanism does not seem to explain the rate difference between I and I$'$; we conclude that the activation process for this reaction is attack of OH$^-$ on the central Ru atom.

Rapid internal rearrangement could lead to interaction of ligand OH$^-$ with either the bridging oxygen ligand (to form a $\mu$-peroxy-species)[20] or with an amine ligand removing a proton (to form an amido complex). The species first formed after OH$^-$ attack, whatever its detailed structure, will be designated III. Any strictly intramolecular rearrangement, following OH$^-$ attack, should lead to a paramagnetic species with a chromophore more similar to that of I than to that of II. The chemical evidence for the existence of the intermediate and the isosbestic point at 492 nm require that III participate in an intermolecular reaction to yield a species with a chromophore like that of II, that is, a diamagnetic species with linear RuORuORu grouping. A trimeric ion (hereafter IV) containing either a bridging dioxygen ligand or a ligand hydroxylamine (as suggested for the dicobalt system) could fit this description. The simplest reaction leading to the intermediate IV would be

$$2\text{III} \rightarrow \text{II} + \text{IV} \qquad (2)$$

The polarographic results suggest formation of dioxygen ligands and eventual formation of oxygen,[21] but these results are relatively imprecise and are subject to error, so that other mechanisms can not be ruled out. Investigations[7] involving membrane-protected oxygen-sensitive electrodes are in progress.

It is now possible to address the question, "Why is I unusually effective as an oxidant for OH$^-$?" Strong oxidants are often anions (*e.g.*, $CrO_4^{2-}$, $MnO_4^-$) or cations subject to hydrolysis ($Ce^{4+}$, etc.). Both negative charge and hydrolysis might be expected to complicate reaction with OH$^-$. The oxidants (I and I$'$) studied here are cations which are protected from hydrolysis by nonlabile ligands. A recent report[22] gives kinetic data for the reduction (by OH$^-$) of Fe(III) complexes which are similarly protected by nonlabile ligands, but in spite of greater oxidizing strength, this reaction is much more sluggish than the one reported here.

Much of the oxidizing strength of oxidants like $MnO_4^-$ is associated with oxidizing equivalents beyond the first redox change. With respect to the first equivalent, $MnO_4^-$ is a slightly poorer oxidant ($E = +0.5$ V *vs.* nhe) than is I: however, the rate of the one-electron reduction of $MnO_4^-$ by OH$^-$ is much smaller[4] than would be expected even taking this fact into account. A significant part of this activation barrier may be due to symmetry restrictions.[23,24] Molecular chlorine is a powerful oxidant. Hydration of $Cl_2$ precedes its reduction and has been found to be rapid.[25] Low-lying antibonding orbitals facilitate attack by oxygen on the end of the molecule and no symmetry restriction is to be anticipated. It is of some interest to examine whether symmetry restrictions should be expected in the I → II reduction.

Attack of a hydroxide ion on the central ruthenium atom of I would be expected to be most probable along that direction which is least blocked by ligand nitrogen atoms. This is the direction of one of the $C_2$ axes which is perpendicular to the $C_4$ axis of the molecular ion. The pseudomolecular activated complex for this sort of attack would have $C_{2v}$ symmetry. The highest occupied molecular orbital of I would transform as the $\mathbf{b}_1$ representation of $C_{2v}$. The lowest unoccupied molecular orbital (which followed $\mathbf{e}_g$ in $D_{4h}$) would split into two orbitals each of which transforms according to the $\mathbf{b}_1$ representation of $C_{2v}$. Frontier orbitals would have the same symmetry and would have a smaller difference in energy than that between the $\mathbf{b}_{1u}$ and $\mathbf{e}_g$ orbitals (in $D_{4h}$) for I, namely, 33 kcal/mol. A fairly low activation enthalpy for the reaction would be expected; the observed value of 18.7 kcal/mol is consistent with this mechanism. Any other perturbation which would destroy the $C_4$ axis (such as OH$^-$ attack on a terminal Ru) would also mix frontier orbitals and facilitate reaction.

Several factors contribute to the rapid rate of OH$^-$ oxidation by I. The oxidizing center is protected from hydrolysis by nonlabile ligands. The positive centers have some tendency to increase coordination number, and mixing of frontier orbitals is opposed by a modest activation barrier.

Manganese is a necessary component of photosynthetic "photosystem II"[26] through which green plants release $O_2$ from $H_2O$. It seems likely that this photosystem involves metal cluster compounds (perhaps oxo bridged) which have features of molecular and electronic structure related to those of I.[27]

**Registry No.** $[Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5]Cl_6$, 36965-92-1; $[Ru(NH_3)_5ORu(NH_3)_4ORu(NH_3)_5]Cl_7$, 36926-69-9; $[Ru(NH_3)_5ORu(en)_2ORu(NH_3)_5]Cl_6$, 36965-93-2; $[Ru(NH_3)_5ORu(en)_2ORu(NH_3)_5]Cl_7$, 36994-45-3; $Ru(NH_3)_6Cl_3$, 14282-91-8; hydroxide, 14280-30-9.

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