stability constants were calculated by using a published program.[53]

**Stopped-Flow Determinations.** A Durrum D 110 stopped-flow apparatus was used for all the kinetic measurements. In a typical experiment 50 mL of a buffer solution ([triethanolammonium nitrate] = 0.02 M, $[KNO_3] = 0.1$ M) was added to 1 mL of ligand solution (0.1 M) and 0.95 mL of cobalt nitrate solution (0.1 M). All the solutions were carefully degassed under vacuum. This constitutes the cobaltous complex solution ($[LCo^{II}] = 0.002$ M). A 50-mL sample of the same buffer solution degassed and saturated with dioxygen constitutes the second one. The concentration of dioxygen was measured with an Orion electrode, Model 97.08 ($[O_2] = 2.7\ 10^{-4}$ M). After the solution was mixed the rate of appearance of the complex was observed at 400 nm which corresponds to the tail of the charge-transfer band.

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# Solar Energy Storage Reactions. Thermal and Photochemical Redox Reactions of Polynuclear Rhodium Isocyanide Complexes

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**Abstract:** The binuclear $Rh^I$ complex $Rh_2(bridge)_4^{2+}$ (or $Rh_2^{2+}$) (bridge = 1,3-diisocyanopropane) reacts with 12 M HCl to form $H_2$ and $(Rh_2(bridge)_4)_2Cl_2^{4+}$ (or $Rh_4Cl_2^{4+}$). Air oxidation of 1 N $H_2SO_4$ solutions of $Rh_2^{2+}$ produces $(Rh_2(bridge)_4)_2^{6+}$ (or $Rh_4^{6+}$). Irradiation ($\lambda > 520$ nm) of this tetranuclear species in 12 M HCl solutions at 25 °C produces $H_2$ and $Rh_2(bridge)_4Cl_2^{2+}$ (or $Rh_2Cl_2^{2+}$). Product analyses and redox titrations ($Rh_2Cl_2^{2+}$ with $Cr^{2+}$; $Rh_4^{6+}$ with $Ce^{4+}$) have confirmed the following reaction scheme: $Rh_2^{2+} + HCl \xrightarrow{\Delta} {}^1/_2Rh_4Cl_2^{4+} + {}^1/_2H_2$; ${}^1/_2Rh_4Cl_2^{4+} + HCl \xrightarrow[550\ nm]{h\nu} Rh_2Cl_2^{2+} + {}^1/_2H_2$. $Rh_4^{6+}$ reacts photochemically (500–600 nm irradiation) with $Fe^{3+}$ to give $Rh_2^{4+} + Fe^{2+}$ ($Rh_4^{6+} + 2Fe^{3+} \xrightarrow{h\nu} 2Rh_2^{4+} + 2Fe^{2+}$). Controlled reduction of $Rh_4^{6+}$ in 10 M $H_2SO_4$ produces a hexanuclear cation, $(Rh_2(bridge)_4)_3^{8+}$ (or $Rh_6^{8+}$) ($\lambda_{max} = 780$ nm), and an octanuclear cation, $(Rh_2(bridge)_4)_4^{10+}$ (or $Rh_8^{10+}$) ($\lambda_{max}$ : 960 nm); $Rh_6^{8+}$ reacts with $Ce^{4+}$ to form $Rh_4^{6+}$ ($Rh_6^{8+} + Ce^{4+} \rightarrow {}^3/_2Rh_4^{6+} + Ce^{3+}$). Dimerization of $Rh_6^{8+}$ occurs to give $Rh_{12}^{16+}$ ($\lambda_{max} > 1300$ nm). The following interpretation of the photoreactions of $Rh_4Cl_2^{4+}$ in HCl solutions is proposed. In 12 M HCl, $Rh_2^{2+}$ produced by irradiation reacts with HCl to give $H_2$. In 6 M HCl, however, photogenerated $Rh_2^{2+}$ is trapped by $Rh_4^{6+}$ to give $Rh_6^{8+}$.

An attractive means of solar energy storage involves the photocatalytic conversion of water to hydrogen and oxygen.[1-10] Much progress has been made recently in running the reductive half of this cycle, that is, the step in which protons from water are reduced to hydrogen.[5-10] Particularly promising from a mechanistic point of view are the systems in which $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) is utilized as the photoreceptor and hydrogen production is facilitated by homogeneous[9a] or heterogeneous[5-8,9b] catalysts.

Our interest in this area began in 1977, when we discovered that $Rh_2(bridge)_4^{2+}$ (bridge = 1,3-diisocyanopropane)[11] (or $Rh_2^{2+}$) dissolved in 12 M HCl produces $H_2$ and $Rh_2(bridge)_4Cl_2^{2+}$ (or $Rh_2Cl_2^{2+}$) upon irradiation at 550 nm.[10] This system is very attractive for mechanistic study in the sense that additional catalysts are not necessary for $H_2$ evolution. From early observations it was known that the photoactive species ($\epsilon_{572} = 56\,500$ $M^{-1}\ cm^{-1}$) most likely was produced in a thermal reaction of $Rh_2^{2+}$ with 12 M HCl.[10,12,13] Subsequently, flash photolysis experiments strongly suggested that the photoactive species was $(Rh_2(bridge)_4Cl)_2^{4+}$ (or $Rh_4Cl_2^{4+}$).[14,15] The tetranuclear nature of this species has recently been confirmed by a crystal structure determination.[16] Although the measured bond lengths (2.93 Å for the two outer Rh–Rh bonds and 2.78 Å for the inner one) are consistent with a $Rh^IRh^{II}Rh^{II}Rh^I$ unit, the presence of hydronium

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ions within the crystal structure precluded an unambiguous assignment of charge to the tetranuclear cation.

In this paper we present the results of our studies of the thermal and photoredox reactions of $Rh_2(bridge)_4^{2+}$ and its oligomers. We have confirmed the oxidation level of the tetranuclear photoactive species by redox titrations, and we have discovered that hexanuclear, octanuclear, and dodecanuclear rhodium–isocyanide oligomers are formed by incomplete reduction of $Rh_4^{6+}$. Selected aspects of the photochemistry of $Rh_4Cl_2^{4+}$ in HCl solutions are discussed in terms of these findings.

## Experimental Section

**Materials.** Spectral grade acetonitrile was obtained from Burdick and Jackson. The tetrabutylammonium salts of $BF_4^-$ and $CF_3SO_3^-$ (triflate, or $TfO^-$) were prepared by neutralizing aqueous solutions of the acids with a methanol solution of tetrabutylammonium hydroxide.

**Rhodium Compounds.** $Rh_2(bridge)_4(BPh_4)_2{\cdot}2CH_3CN$[17] and $Rh_2(bridge)_4Cl_4{\cdot}8H_2O$[18] were prepared as described previously. $Rh_2(bridge)_4(BPh_4)_2{\cdot}2CH_3CN$ was recrystallized from acetonitrile prior to use.

**$Rh_2(bridge)_4(BPh_4)(BF_4)$.** $Rh_2(bridge)_4(BPh_4)_2{\cdot}2CH_3CN$ (0.84 g) was dissolved in 250 mL of hot acetonitrile. Tetrabutylammonium tetrafluoroborate (1.35 g) was added in 10 mL of acetonitrile. The solution was allowed to cool to room temperature. After 5 h the solution was further cooled to 4 °C for 12 h. The resulting black prismatic needles were filtered by suction to give 0.49 g of product. Anal. Calcd for $Rh_2C_{44}H_{44}N_8B_2F_4$: C, 53.47; H, 4.49; N, 11.34. Found: C, 53.41; H, 4.91; N, 11.99. IR: $\nu$(CN) = 2180 $cm^{-1}$; $\nu$(Ph) = 1578 $cm^{-1}$ (KBr disk).

**$Rh_2(bridge)_4(CF_3SO_3)_2$.** $Rh_2(bridge)_4(BPh_4)_2{\cdot}2CH_3CN$ (0.2 g) was dissolved in 200 mL of acetonitrile. Tetrabutylammonium triflate (3.0 g) was added to the hot solution. After the mixture was allowed to stand for 12 h at room temperature, 85 mg of product (long fibrous needles) was filtered out. A second crop of 15 mg was collected after 1 day. The product was not analytically pure, although its visible spectrum in acetonitrile solution was identical with that of $Rh_2(bridge)_4(BPh_4)_2{\cdot}2CH_3CN$.

**$(Rh_2(bridge)_4)_2(BF_4)_6$.** In the dark a suspension of $Rh_2(bridge)_4(CF_3SO_3)_2$ (approximately 10 mg) in 5 mL of 1 M $H_2SO_4$ was stirred overnight in the presence of air. A small amount of residue was separated by suction filtration. Aqueous $HBF_4$ (48%) was added dropwise to the solution until the blue color faded. After the mixture was allowed to stand for 10 min, the precipitate (6 mg) was collected by suction filtration and washed with ethanol. The black powder was dried in vacuo over $P_2O_5$ for 2 days. Anal. Calcd for $Rh_2C_{20}H_{24}N_8B_3F_{12}$: C, 28.50; H, 2.87; N, 13.30. Found: C, 28.93; H, 3.04; N, 13.62. IR: $\nu$(CN) = 2218 $cm^{-1}$ (KBr disk).

**General Methods.** Electronic absorption spectra were measured on solutions at 25 ± 1 °C using a Cary 17 spectrophotometer. Samples were maintained at 25 ± 1 °C in all photochemical experiments. Infrared spectra were measured with a Beckman IR 4240 spectrophotometer.

**Titrations. General Methods.** All transfers were conducted by using glass syringes and platinum needles. Argon was purified by passing through two 7-in. bubblers (1 M $Cr^{2+}$). Titrations were performed in either ultraviolet–visible cells (1-cm path length) sealed with serum caps or in cells (1-cm path length) fitted with glass stopcocks. For titrations for which a 1-mm path length was necessary a reaction vessel was used that consisted of a 5-mL tube to which a stopcock and a quartz cuvette (1-mm path length) were connected. Prior to the addition of either oxidant or reductant the solutions (2.0 mL) were thoroughly purged with argon by using platinum needles. Solutions of oxidant or reductant were added in 0.05-mL aliquots. The titrations were followed spectrophotometrically by scanning with the Cary 17. Each titration involved at least three aliquots.

**Reductant.** A stock chromous solution (0.02 M) in 1 N $H_2SO_4$ was prepared by reacting chromium dust (Ventron) with 1 N $H_2SO_4$ while the system was purged with argon. Chromous solutions of desired concentrations were then prepared by dilution. The activities of the solutions were assayed as follows. A solution (2.0 mL) prepared from 1.6 mL of AcOH (0.3 M)–NaOAc (0.7 M) buffer, 0.2 mL of 0.25% aqueous 1,10-phenanthroline, and 0.2 mL of aqueous $Fe(NH_4)(SO_4)_2$ (2 mM in 0.1 M $H_2SO_4$) was purged with argon. An aliquot (0.05–0.1 mL) of the chromous solution (~0.4 mM) was added, and the $[Fe^{2+}]$ formed was calculated from the observed $\Delta A_{508}$ ($\epsilon(Fe(phen)_3^{2+})$ = 1.1 × $10^4$ $M^{-1}$ $cm^{-1}$).

**Oxidant.** Ceric sulfate solutions were prepared in 1 N $H_2SO_4$ by dilution of a 0.05 M stock solution (G. Frederick Smith). The $Ce^{4+}$ titrant was determined as follows. To a solution (1.8 mL) prepared from 1.6 mL of AcOH (0.3 M)–NaOAc (0.7 M) buffer and 0.2–0.4 mL of aqueous $Fe(NH_4)_2(SO_4)_2$ (0.2 mM in 0.1 M $H_2SO_4$) was added 0.05–0.1 mL of the ceric solution (0.2–1.0 mM). After the addition of 0.2 mL of a 0.25% aqueous solution of 1,10-phenanthroline, the $[Fe^{2+}]$ was measured as described above. The amount of ceric ion added was determined by the difference in $[Fe^{2+}]$ before and after the addition of the oxidant.

**Extinction Coefficients.** In 6 M HCl, $\epsilon_{572}(Rh_4Cl_2^{4+})$ = 1.07 × $10^5$ $M^{-1}$ $cm^{-1}$ and $\epsilon_{340}(Rh_2Cl_2^{2+})$ = 5.65 × $10^4$ $M^{-1}$ $cm^{-1}$. In 1 N $H_2SO_4$, $\epsilon_{558}(Rh_4^{6+})$ = 8.8 × $10^4$ $M^{-1}$ $cm^{-1}$, and in 10 M $H_2SO_4$, $\epsilon_{572}(Rh_4^{6+})$ = 7.4 × $10^4$ $M^{-1}$ $cm^{-1}$.

**Measurement of Hydrogen Evolution from HCl Solvents.** Hydrogen evolution measurements utilized reaction vessels consisting of a quartz cuvette (1.0-cm path length) connected to a Pyrex tube which in turn was connected to a Teflon valve and a 10-mL Pyrex bulb. The rhodium compounds (~0.02 mmol) were stored in the cuvette while the 12 M HCl (5 mL) was degassed in the bulb with seven freeze–evacuate–thaw cycles. The vessel was then sealed under a vacuum by means of the Teflon valve and the solution allowed to reach room temperature. The acid was added to the rhodium samples in the dark. After complete dissolution, the solution was frozen and the $H_2$ was transferred by means of a Toepler pump through three liquid-$N_2$ traps into a 11.7-mL volume. The pressure was manometrically measured. So that only $H_2$ was measured, the collected gas was passed over hot copper oxide (300 °C) and the water was collected in a trap immersed in liquid $N_2$. A negligible amount of gas remained after this step. Measurements of $H_2$ were reproducible to ±5–10%. The vessel could be opened at this stage and the amount of compound present determined spectrophotometrically after dilution. Most importantly, no $Rh_2Cl_2^{2+}$ formed in this dark reaction.

For the determination of the yield of $H_2$ in the light reaction, the vessel was resealed after removal of the $H_2$ formed in the dark reaction. The solutions were then irradiated with a 1000-W Hg–Xe arc lamp using a filter with a cutoff at 520 nm. For quantitative conversion to the $Rh_2Cl_2^{2+}$ species it was necessary to remove the $H_2$ formed (one intermediate Toepler pumping was sufficient). The amount of $H_2$ formed was determined as described above. Spectrophotometric determination of $[Rh_2Cl_2^{2+}]$ was made upon dilution of the final yellow solution.

**Photochemical Oxidation of $Rh_4^{6+}$ by $Fe^{3+}$.** $(Rh_2(bridge)_4)_2(BF_4)_6$ was dissolved in 0.1 M $H_2SO_4$ to give a 1.0 mM solution of $Rh_4^{6+}$. With careful exclusion of light a 0.2-mL aliquot of the above solution was added to 2 mL of 0.1 M $H_2SO_4$ containing 2 mM $Fe^{3+}$ ion. Immediately, 0.1 mL of this solution was diluted with 1 N $H_2SO_4$ (2.0 mL) and the $[Rh_4^{6+}]$ measured spectrophotometrically. The remaining solution was purged with argon and then irradiated (>520 nm) until completely bleached. A 0.1-mL aliquot of the bleached solution was added to a solution prepared from 1.6 mL of AcOH (0.3 M)–NaOAc (0.7 M) buffer and 0.2 mL of a 0.25% 1,10-phenanthroline solution. The $[Fe^{2+}]$ formed was measured spectrophotometrically ($\epsilon_{508}(Fe(phen)_3^{2+})$ = 1.1 × $10^4$ $M^{-1}$ $cm^{-1}$).

**Titration of $Rh_6^{8+}$.** Titrations of $Rh_6^{8+}$ utilized a reaction vessel consisting of a 40-mL tear-shaped flask fitted at the top with a three-way stopcock. At the neck at right angles to the bulb a quartz cuvette (1-cm path length) was attached. $H_2SO_4$ (10.0 mL, 10 M) was placed in the flask and deoxygenated by means of an argon purge. $(Rh_2(bridge)_4)_2(BF_4)_6$ (0.23 mg, 1.4 × $10^{-4}$ mmol) was added and the solution maintained under an argon atmosphere. Chromous ion as a 3.0 mM solution in 1 N $H_2SO_4$ was added (0.025 mL, 0.75 × $10^{-4}$ mmol) and the solution shaken. The amount of $Rh_6^{8+}$ formed was measured spectrophotometrically. Once formed, $Rh_6^{8+}$ was stable for at least 1 h. Ceric ion was added in 0.05-mL aliquots as a 0.5–1.0 mM solution in 1 N $H_2SO_4$ (deoxygenated by means of an argon purge). The oxidation of $Rh_6^{8+}$ to $Rh_4^{6+}$ was monitored by scanning from 1100 to 300 nm. In the final part of the titration the oxidation was biphasic for each aliquot, the initial phase being complete immediately upon mixing. The latter phase took approximately 20 min and was due to the slow reaction of $Rh_6^{8+}$ with $Rh_2^{4+}$, the latter being formed by $Ce^{4+}$ oxidation of $Rh_4^{6+}$. The intermediacy of $Rh_2^{4+}$ in the oxidation of $Rh_6^{8+}$ was evident from the rise and fall in the absorption at 320 nm. The amount of oxidation that occurred as a result of adventitious $O_2$ was determined by substituting a 1 N $H_2SO_4$ solution for the ceric solutions and repeating the procedure described above. Intervention by adventitious oxidants required a 6% correction to be made in the observed amount of reaction.

## Results

**Thermal and Photochemical Reactions in 12 M HCl.** When $Rh_2^{2+}$ is dissolved in 12 M HCl and irradiated with visible light (550 nm), $H_2$ and $Rh_2Cl_2^{2+}$ are produced. Evidence presented

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Table I. Hydrogen Yields

| amt of sample, mmol | amt of 12 M HCl, mL | $H_2$ yield, mmol |  |
|---|---|---|---|
|  |  | thermal | photochemical |
|  | $Rh_2(bridge)_4(BPh_4)(BF_4)$ |  |  |
| 0.015 | 5.0 | 0.005 (0.3)[a] |  |
| 0.015 | 5.2 | 0.005 (0.3) |  |
| 0.012 | 5.3 | 0.004 (0.3) | 0.006 (0.5) |
| 0.012 | 4.3 | 0.005 (0.4) | 0.006 (0.5) |
|  | $Rh_2(bridge)_4(TfO)_2$ |  |  |
| 0.016 | 4.6 | 0.005 (0.3) | 0.008 (0.5) |
| 0.016 | 5.1 | 0.003 (0.2) | 0.007 (0.4) |
|  | $(Rh_2(bridge)_4)_2(BF_4)_6$ |  |  |
| 0.01 | 4.9 | 0.00 | 0.005 (0.5) |

[a] Numbers in parentheses represent yields with respect to initial equivalents of $Rh_2^{2+}$.

below demonstrates that the reaction occurs in two distinct steps, a thermal reaction of $Rh_2^{2+}$ with $H^+$ to form $H_2$ and $Rh_4Cl_2^{4+}$ and a photochemical reaction ($\lambda > 520$ nm) of $Rh_4Cl_2^{2+}$ with $H^+$ to form $H_2$ and $Rh_2Cl_2^{2+}$, according to eq 1 and 2.

$$Rh_2^{2+} + HCl \xrightarrow{\Delta} {}^1/_2Rh_2Cl_2^{4+} + {}^1/_2H_2 \qquad (1)$$

$$ {}^1/_2Rh_4Cl_2^{4+} + HCl \xrightarrow[550\ \mathrm{nm}]{h\nu} Rh_2Cl_2^{2+} + {}^1/_2H_2 \qquad (2)$$

The mixed salt $Rh_2(bridge)_4(BPh_4)(BF_4)$ is a convenient source of $Rh_2^{2+}$ for experiments in aqueous media. Reaction of this salt with 12 M HCl in the dark yielded 0.3–0.4 equiv of $H_2$ and $Rh_4Cl_2^{4+}$ ($\epsilon_{572} = 1.07 \times 10^5$ M$^{-1}$ cm$^{-1}$). After removal of the $H_2$ formed in the thermal reaction, irradiation of the solution with visible light ($\lambda > 520$ nm) produced an additional 0.5 equiv of $H_2$. The spectrum of the final solution was identical with that of a solution of authentic $Rh_2Cl_2^{2+}$ ($\epsilon_{340} = 5.65 \times 10^4$ M$^{-1}$ cm$^{-1}$).[10] The yield of $Rh_2Cl_2^{2+}$ was quantitative. Similar behavior was observed when $Rh_2(bridge)_4(TfO)_2$ was used in place of $Rh_2(bridge)_4(BPh_4)(BF_4)$.

The photochemical $H_2$ yield was checked independently by irradiation ($\lambda > 520$ nm) of solutions (12 M HCl) of $Rh_4Cl_2^{4+}$ prepared from $(Rh_2(bridge)_4)_2(BF_4)_6$; the latter experiment produced 0.5 equiv of $H_2$ and a quantitative yield of $Rh_2Cl_2^{2+}$. The $H_2$ yields obtained in the three series of experiments are set out in Table I.

**Titration of $Rh_2Cl_2^{2+}$.** The assignment of the redox state for $Rh_4Cl_2^{4+}$ is supported by the stoichiometry established from spectroscopic measurements of the $Cr^{2+}$ reduction of an authentic sample of $Rh_2Cl_2^{2+}$ in 6 M HCl. The only reduction product observed upon addition of aliquots of $Cr^{2+}$ solution was $Rh_4Cl_2^{4+}$, and the experimental ratio $Rh_2Cl_2^{2+}/Cr^{2+}$ was found to be 1.0 ± 0.1:

$$Rh_2Cl_2^{2+} + Cr^{2+} \rightarrow {}^1/_2Rh_4Cl_2^{4+} + Cl^- + Cr^{3+} \qquad (3)$$

**Formation of $Rh_4^{6+}$.** In 1 M $H_2SO_4$ in the presence of air $Rh_2(bridge)_4(TfO)_2$ slowly reacts to give solutions of $Rh_4^{6+}$ ($\epsilon_{558} = 8.8 \times 10^4$ M$^{-1}$ cm$^{-1}$), according to eq 4. Upon addition of

$$Rh_2^{2+} + H^+ + {}^1/_2O_2 \rightarrow {}^1/_2H_2O_2 + {}^1/_2Rh_4^{6+} \qquad (4)$$

aqueous $HBF_4$ (48%), $Rh_4^{6+}$ was isolated as an analytically pure $(Rh_2(bridge)_4)_2(BF_4)_6$ salt. Solutions (1 M $H_2SO_4$) of $Rh_4^{6+}$ prepared from the tetrafluoroborate salt were titrated with $Ce^{4+}$ (Figure 1). The observed ratio $Ce^{4+}/Rh_4^{6+}$ was found to be 2.0 ± 0.2:

$$ {}^1/_2Rh_4^{6+} + Ce^{4+} \rightarrow Rh_2^{4+} + Ce^{3+} \qquad (5)$$

The product ($Rh_2^{4+}$) of the ceric oxidation was identified by adding chloride ion and analyzing the $Rh_2Cl_2^{2+}$ formed.[14]

In experiments in which the initial solution resulting from air oxidation of $Rh_2^{2+}$ to $Rh_4^{6+}$ was titrated immediately with $Ce^{4+}$, the first aliquots of $Ce^{4+}$ were consumed but oxidation of $Rh_4^{6+}$ did not occur. However, if the initial solution was allowed to stand for 24 h, the titration proceeded straightforwardly (eq 5).

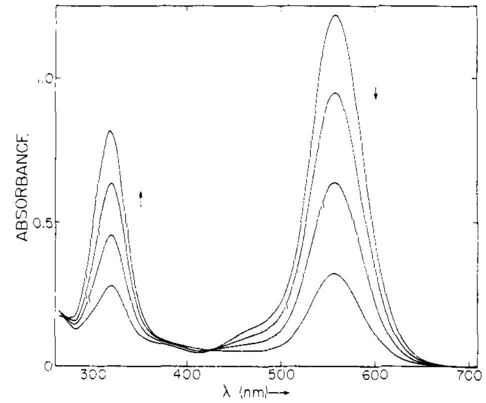

**Figure 1.** Electronic absorption spectral changes (1-cm path length; 25 °C) during the titration of $Rh_4^{6+}$ ($\lambda_{max} = 558$ nm) with $Ce^{4+}$ in 1 N $H_2SO_4$, yielding $Rh_2^{4+}$ ($\lambda_{max} = 315$ nm). $[Rh_4^{6+}]_0 = 1.4 \times 10^{-5}$ M. Each $[Ce^{4+}]$ aliquot = $0.7 \times 10^{-5}$ M (initial).

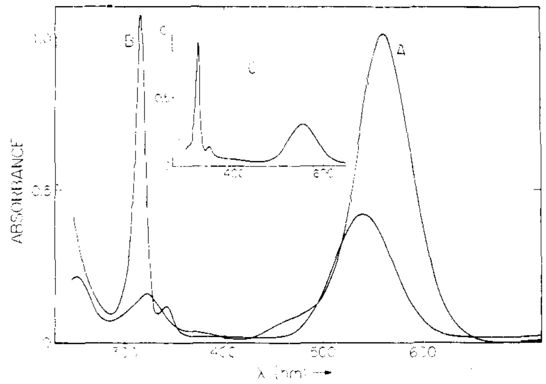

**Figure 2.** Electronic absorption spectra (1-cm path length; 25 °C): (a) $Rh_4^{6+}$ ($1.2 \times 10^{-5}$ M) in 1 M $CH_3SO_3H$ solution; (B) $Rh_4^{6+}$ ($1.2 \times 10^{-5}$ M) in 1 M $CH_3SO_3H$ solution with $[Cr^{2+}] = 1.5$ mM; (C) $Rh_2(bridge)_4(BPh_4)(BF_4)$ ($2 \times 10^{-5}$ M) in acetonitrile solution.

The above behavior was completely reproduced by a solution prepared by the addition of $H_2O_2$ to a 1 M $H_2SO_4$ solution of $Rh_4^{6+}$ prepared from the tetrafluoroborate salt. Apparently, $H_2O_2$ competes with $Rh_4^{6+}$ in reducing $Ce^{4+}$, but it disproportionates upon standing in the presence of $Rh_4^{6+}$.

**Photochemical Oxidation of $Rh_4^{6+}$.** In the dark, $H_2SO_4$ (0.1 M) solutions of $Rh_4^{6+}$ ($10^{-5}$ M) do not react with $Fe^{3+}$. However, upon irradiation (500–600 nm) the tetranuclear cation splits into $Rh_2(bridge)_4^{3+}$ ($\epsilon_{440} = 3 \times 10^4$ M$^{-1}$ cm$^{-1}$), which is oxidized by $Fe^{3+}$ to $Rh_2^{4+}$.[14] The observed ratio $Fe^{2+}/Rh_4^{6+}$ was found to be 2.0 ± 0.2:

$$Rh_4^{6+} + 2Fe^{3+} \xrightarrow{h\nu} 2Rh_2^{4+} + 2Fe^{2+} \qquad (6)$$

**Reduction of $Rh_4^{6+}$.** When excess (~100-fold) $Cr^{2+}$ is added to aqueous 1 M $CH_3SO_3H$ solutions of $Rh_4^{6+}$ ($10^{-5}$ M), the visible absorption at 558 nm immediately disappears and the spectrum of $Rh_2^{2+}$ is observed (Figure 2). The spectrum of an aqueous solution of $Rh_2^{2+}$ differs very little from that of an acetonitrile solution.[17,19] The two prominent electronic absorption bands ($\lambda = 318$ nm, $\epsilon = 4.54 \times 10^4$ M$^{-1}$ cm$^{-1}$; $\lambda = 553$ nm, $\epsilon = 1.45 \times 10^4$ M$^{-1}$ cm$^{-1}$ in acetonitrile solution) occur in aqueous solution at 318 ($\epsilon = 4.3 \times 10^4$ M$^{-1}$ cm$^{-1}$) and 540 nm ($\epsilon = 1.7 \times 10^4$ M$^{-1}$ cm$^{-1}$). When excess $Cr^{2+}$ is added to 1 N $H_2SO_4$ solutions of $Rh_4^{6+}$, reduction to $Rh_2^{2+}$ occurs. However, some insoluble material is also present; the proportion of this material is minimized at low initial concentrations of $Rh_4^{6+}$ and high concentrations of $Cr^{2+}$.

Whereas exhaustive reduction of $Rh_4^{6+}$ leads to $Rh_2^{2+}$, partial reduction in aqueous acid produces a large number of species. If

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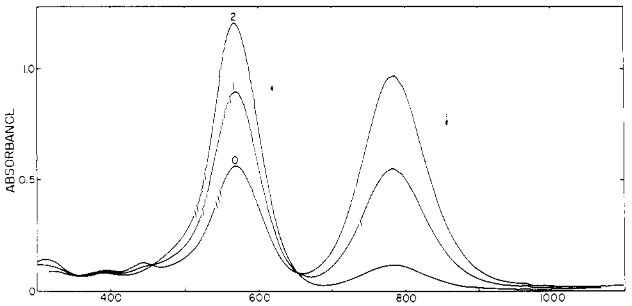

**Figure 3.** Electronic absorption spectral changes (1-cm path length; 25 °C) during the titration of $Rh_6^{8+}$ ($\lambda_{max}$ = 780 nm) with $Ce^{4+}$ in 10 M $H_2SO_4$, yielding $Rh_4^{6+}$ ($\lambda_{max}$ = 572 nm). $[Rh_4^{6+}]_0 = 0.75 \times 10^{-5}$ M; $[Rh_6^{8+}]_0 = 1 \times 10^{-5}$ M. Each $[Ce^{4+}]$ aliquot = $2.5 \times 10^{-6}$ M (initial).

$Cr^{2+}$ is not in excess to $Rh_4^{6+}$ ($10^{-5}$ M) in 1 M $CH_3SO_3H$, immediate bleaching of the absorption signal for $Rh_4^{6+}$ occurs, but the initial product is not $Rh_2^{2+}$. As $Cr^{2+}$ is added, a progression of species is formed, distinguished by unique absorptions in the visible and near-IR spectra; the dominant absorptions are at 770, 960, 1100, and 670 nm (this order is that of their appearance with respect to the addition of reductant). These changes are completely reversed upon oxidation with air, $Fe^{3+}$, or $Ce^{4+}$. The simultaneous occurrence of more than two species throughout the reduction prevents the quantitation of the titration. Upon the addition of 2 equiv of $Cr^{2+}$ per $[Rh_4^{6+}]_0$, detectable amounts of $Rh_2^{2+}$ are formed with reaction times on the order of hours. Hence, the reduction of $Rh_4^{6+}$ by even a powerful reductant such as $Cr^{2+}$ is kinetically difficult.

When chromous solutions are added to 10 M $H_2SO_4$ solutions of $Rh_4^{6+}$ ($10^{-5}$ M), bleaching of the $Rh_4^{6+}$ absorbance ($\epsilon_{572} = 7.2 \times 10^4$ $M^{-1}$ $cm^{-1}$) occurs and absorbances at 780, 960, and 670 nm appear. The small differences in absorption from those observed in aqueous 1 M $CH_3SO_3H$ are undoubtedly due to solvent effects. $Rh_2^{2+}$ is not detected in 10 M $H_2SO_4$ in the presence of excess $Cr^{2+}$; the predominant product under these conditions absorbs at 670 nm. Most importantly, in 10 M $H_2SO_4$ the reduction of $Rh_4^{6+}$ to the species that absorbs at 780 nm and the subsequent oxidation of this species to $Rh_4^{6+}$ is not accompanied by the appearance of the other absorbances (Figure 3). Only after more than 80% of the $[Rh_4^{6+}]_0$ is reduced are increases in $A_{960}$ aand $A_{670}$ observed. Consequently, 10 M $H_2SO_4$ solutions of $Rh_4^{6+}$ ($10^{-5}$ M) were reduced with $Cr^{2+}$ to produce solutions whose spectra revealed only the presence of the species that absorbs at 780 nm and unreacted $Rh_4^{6+}$ ion. Back-titrations of these solutions with ceric solutions allowed the determination of the stoichiometry presented in eq 7. The redox state of the species

$$Rh_6^{8+} + Ce^{4+} \rightarrow {}^3/{}_2Rh_4^{6+} + Ce^{3+} \qquad (7)$$

responsible for the 780-nm absorption is consistent with its formulation as the hexanuclear $(Rh_2(bridge)_4)_3^{8+}$ (or $Rh_6^{8+}$) cation ($\epsilon_{780} = 14.4 \times 10^4$ $M^{-1}$ $cm^{-1}$). The experimental ratio of the equivalents of $Rh_4^{6+}$ formed per equivalents of $Ce^{4+}$ added was found to be 1.5 ± 0.1. In more concentrated solutions of $Rh_4^{6+}$ ($10^{-4}$ M), the reduction to $Rh_6^{8+}$ is not quantitative. When 80% of the initial amount of $Rh_4^{6+}$ is reduced, the yield of $Rh_6^{8+}$ is 60%. The remaining $Rh_4^{6+}$ is reduced to a species or group of species that can be detected by the increase in $A_{1300}$. Although absorption by the medium did not allow a determination of $\lambda_{max}$, it is apparent from the shape of the absorption band that it falls above 1300 nm.

## Discussion

The stoichiometries observed for reactions 1, 2, 3, and 5 together with the crystal structure data[16] confirm the oxidation level and the tetranuclear nature of $Rh_4^{6+}$ and $Rh_4Cl_2^{4+}$. Formally, the oxidation states for the individual Rh atoms of $Rh_4^{6+}$ or $Rh_4Cl_2^{4+}$ can be represented as $Rh^IRh^{II}Rh^{II}Rh^I$. Whereas the two outer Rh atoms are attached to the inner two Rh atoms by the diisocyanopropane ligands, a direct, single metal–metal bond exists between the two inner Rh atoms (which are formally $d^7$). As has been discussed previously, the intense electronic absorption band at 572 nm in the spectrum of $Rh_4Cl_2^{4+}$ in 6 M HCl ($\epsilon_{572} = 1.07 \times 10^5$ $M^{-1}$ $cm^{-1}$) is attributable to a $\sigma \rightarrow \sigma^*$ transition in the $Rh_4^{6+}$ unit.[15]

Three cations in the $(Rh_2(bridge)_4)_m^{n+}$ family have now been structurally and chemically characterized. These cations are (in order of increasing oxidation state per Rh atom) $Rh_2^{2+}$,[11,19] $Rh_4^{6+}$,[14-16] and $Rh_2^{4+}$.[11,18] It is clear that many additional species are formed as $Rh_4^{6+}$ is progressively reduced to $Rh_2^{2+}$. The present data taken together with the results of a study[20] of the binding of $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) to $Rh_4^{6+}$ have allowed us to identify several of these new species. The hexanuclear cation, $Rh_2(TMB)_4Rh_4^{8+}$, and the octanuclear cation, $Rh_2(TMB)_4Rh_4Rh_2(TMB)_4^{10+}$, have been characterized by reacting $Rh_4^{6+}$ with $Rh_2(TMB)_4^{2+}$.[20] In 1 N $H_2SO_4$, $Rh_2(TMB)_4Rh_4^{8+}$ absorbs at 785 nm ($\epsilon = 13.2 \times 10^4$ $M^{-1}$ $cm^{-1}$) and $Rh_2(TMB)_4Rh_4Rh_2(TMB)_4^{10+}$ absorbs at 980 nm ($\epsilon = 23.2 \times 10^4$ $M^{-1}$ $cm^{-1}$).[20] Species with nearly identical spectral properties are observed in the partial reductions of $Rh_4^{6+}$ in 10 M $H_2SO_4$. These species (in order of decreasing average oxidation state of Rh) absorb at 780 ($\epsilon = 14.4 \times 10^4$ $M^-$ $cm^{-1}$) and 960 nm and are therefore proposed to be $(Rh_2(bridge)_4)_3^{8+}$) and $(Rh_2(bridge)_4)_4^{10+}$ (or $Rh_8^{10+}$), respectively. The redox titration of $Rh_6^{8+}$ with $Ce^{4+}$ (eq 7) confirms the assigned redox state of the hexanuclear cation. Although we have not obtained a similar proof for the redox state of $Rh_8^{10+}$, the fact that the electronic absorption spectrum of this species is so closely analogous to that of $Rh_2(TMB)_4Rh_4Rh_2(TMB)_4^{10+}$ gives us confidence that the proposed formulation is correct.

The concentration dependence observed in the reduction of $Rh_4^{6+}$ (in which the $Rh_6^{8+}$ fraction of the reduced products decreased as the concentration of $Rh_6^{8+}$ increased) is consistent with the known dimerization of the analogous $Rh_2(TMB)_4Rh_4^{8+}$ ion.[20] The additional species that forms in the reduction of concentrated $Rh_4^{6+}$ solutions exhibits a near-IR spectrum ($\lambda_{max}$ > 1300 nm) that is similar to that of the dimer of $Rh_2(TMB)_4Rh_4^{8+}$.[20] Thus it is reasonable to assign the absorption in the 1300-nm region to a dodecanuclear species, $Rh_{12}^{16+}$.

In summary, three of the species that are formed as $Rh_4^{6+}$ is reduced to $Rh_2^{2+}$ are identified as $Rh_6^{8+}$, its dimer ($Rh_{12}^{16+}$), and $Rh_8^{10+}$. These species probably represent a minor fraction of all of the oligomers that can be formed from the partial reduction of $Rh_4^{6+}$. At least two other absorptions (670 and 1100 nm) are observed at the lowest rhodium concentrations ($10^{-5}$M) studied. From the trend in structures observed thus far, the investigation of more concentrated solutions likely will reveal additional oligomers.[21]

The new redox chemistry described above allows a reasonably detailed interpretation to be put forward in regard to the observed photochemistry of $Rh_4Cl_2^{4+}$.[10,12,13] It has previously been noted[13] that $Rh_4Cl_2^{4+}$ in a 6 M HCl glass (240 K) disproportionates upon irradiation (550 nm) to $Rh_2Cl_2^{2+}$ and a more reduced species that absorbs at 780 nm. This same 780-nm species is the product of the reaction of $H_2$ with $Rh_4Cl_2^{4+}$ in 6 M HCl[13] and on the basis of the results detailed above can reasonably be identified as $Rh_6^{8+}$ or its chloride adduct. Although lack of knowledge of the temperature dependences of the extinction coefficients of the species involved has as yet precluded an accurate material balance, the disproportionation can by means of the known redox levels be written as

$$2Rh_4Cl_2^{4+} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} Rh_2Cl_2^{2+} + Rh_6^{8+} + 2Cl^- \qquad (8)$$

It is likely that the differences in the oligomeric nature of the species involved in the photochemistry of $Rh_4Cl_2^{4+}$ influence

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[20] Sigal, I. S.; Gray, H. B., to be submitted for publication.

[21] Certain of the Rh oligomers are related in an electronic structural sense to the mixed-valence platinum blues studied by Lippard and co-workers (Barton, J. K.; Szalda, D. J.; Rabinowitz, H. N.; Waszczak, J. V.; Lippard, S. J. *J. Am. Chem. Soc.* **1979**, *101*, 1434. Barton, J. K.; Caravana, C.; Lippard, S. J. *Ibid.* **1979**, *101*, 7269).

significantly the kinetics of the thermal reactions that follow the primary photochemical event.

The discovery that the $Rh_2^{2+}$ ion reacts spontaneously with 12 M HCl to form $H_2$ suggests a possible mechanism for photoreaction (2):

$$Rh_4Cl_2^{4+} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} Rh_2^{2+} + Rh_2Cl_2^{2+} \tag{9}$$

$$Rh_2^{2+} + HCl \xrightarrow{\Delta} {}^1/_2Rh_4Cl_2^{4+} + {}^1/_2H_2 \tag{10}$$

At low concentrations of HCl, where net formation of $H_2$ does not occur upon irradiation of $Rh_4Cl_2^{4+}$,[15] presumably both the thermal back-reaction (eq 9) and reaction of $Rh_2^{2+}$ with $Rh_4^{6+}$ (from ($Rh_4Cl_2^{4+}$) to give $Rh_6^{8+}$ compete effectively with the $H_2$-producing step (eq 10). We are currently examining the temperature dependences of the photoreactions of $Rh_4Cl_2^{4+}$ in HCl solutions,[22] in the hope that under suitable conditions we can observe the photoproduction of $Rh_2^{2+}$ directly.

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# Electronic Relaxation in Azurin: Picosecond Reverse Charge Transfer

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**Abstract:** Ultrafast relaxation of the 625-nm charge-transfer absorption band of a blue copper protein, azurin, is studied by the use of subpicosecond light pulses. The blue protein solution is transiently bleached, but the absorption reversibly reappears with a time constant of 1.6 ± 0.2 ps, due to reverse charge transfer. A fast transient (<0.5 ps) interpreted as excited-state vibrational relaxation/internal conversion is also observed. The results suggest that ligand rearrangement is not rate determining in the biochemical reactivity of azurin.

Azurin is a small (mol wt 14 000) deep blue protein found in a number of bacteria, in particular *Pseudomonas*. The blue color is due to a single copper(II) ion which is related to the apparent role of the protein as an electron carrier. This blue copper center[2] is ubiquitous, occurring in such proteins as plastocyanins, an essential component in plant photosynthesis, in numerous oxidases, and even in the human blood as ceruloplasmin.

The intense absorption band (orders of magnitude stronger than that of $Cu^{2+}$(aq) in the red) peaks at 625 nm. Spectroscopic evidence has been put forth[3,4] to show that this band is due to a charge-transfer transition of a $\sigma$ electron from a cysteine sulfur atom to the singly occupied Cu 3d orbital. Preliminary X-ray structures of oxidized azurin[5] and plastocyanin[6] have shown that the $Cu^{2+}$ is coordinated to the nitrogen atoms of two imidazole side chains, the sulfur atom of a methionine, and the negatively charged sulfur of a cysteine ion. The charge-transfer model for the optical transition is thus well supported.

Until now little has been known about the electronic relaxation rate associated with this blue color. Inasmuch as no fluorescence is observed, the lifetime of the upper state must be in the subnanosecond range. Accordingly, an experiment was done by using subpicosecond light pulses at 615 nm to measure this lifetime.

## Experimental Section

The picosecond dynamic studies are performed by using a pump-probe technique in which one pulse excites the sample and a second pulse monitors the induced, transient absorption change.[7] Subpicosecond pulses from a cavity-dumped, passively mode-locked, CW dye laser[8,9] are divided into two beams. The more intense beam, the pump, traverses a variable length optical delay, and the weaker beam, the probe, traverses a fixed optical path. Both beams are focused to a common 10-$\mu$m diameter spot at the sample. The pump beam is chopped, and the modulation of transmission induced on the probe beam is observed by using a diode detector and a lock-in amplifier. The variable length delay is controlled by a digital stepping motor which also indexes a multichannel analyzer. As the path delay is repetitively scanned, the time profile of the induced transmission is displayed and averaged. The pulses used in the present experiments have a wavelength centered at 615 nm, duration of 0.5 ps, and 5-kW peak power. Seventy-five percent of the pulse energy is contained in the pump beam. The pulse repetition rate is $10^5$ Hz for most experiments, but the results are not changed when a pulse repetition rate of $10^4$ Hz is used.

The sample is contained in a 0.1-mm path length cell which is translated continuously during the experiments, at a rate of 0.3 cm/s. At the 100-kHz pulse rate, the exposed sample volume is thus changed every 300 pulses, in order to avoid excessive heating and possible damage. The sample shows no spectral changes or other evidence of damage, even after several hours of irradiation. The optical density at 630 nm of the azurin solution in the 0.1-mm cell is 0.2, which corresponds to a concentration of $5 \times 10^{-3}$ M.[3] The preparation of the azurin from the bacteria *Psuedomonas aeruginosa* has been previously described.[10]

## Results

A typical experiment utilized about 2 h of signal averaging and resulted in a curve such as A in Figure 1. The sample response is a transient bleaching which fully recovers on a picosecond time scale. Curve A was obtained for the case of parallel pump and probe pulse polarization and corresponds to a maximum modulation (at $t = 0$) of 0.7% in the probe pulse transmission. For such small modulations, transmission changes are linearly proportional

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