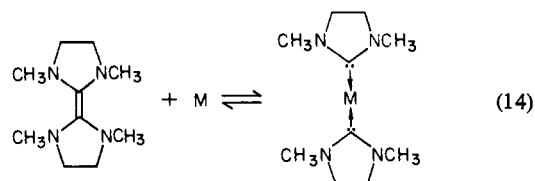


It was anticipated at the outset of the present work that the additional steric bulk provided by dialkylamide substituents ($R = NR_2$) as well as possible electronic stabilization accruing from π -donative interaction with the nitrogen lone pair might well stabilize a bis(η^2 -carbamoyl) complex sufficiently to allow isolation or at least observation. The syntheses and characterization of compounds **10a**, **10b**, and **11a** show unambiguously that this approach is possible and that organoactinide species with two proximate η^2 -carbonyl functionalities exist. From the structural data it would appear that such a molecular configuration is ideally poised for ring closure and enediolate formation but that the process is inhibited by the steric bulk of the *N*-alkyl functionalities and the necessity of twisting the ligands about C-N bonds with appreciable multiple bond character (as judged by bond distance and the barrier to rotation). Closely related is evidence from the spectroscopic data suggesting a reduction in the carbenoid character of the C-O functionalities in the actinide carbamoyls (relative to the acyls). There are, however, two other factors, of as yet unquantified importance, which may further hinder ring closure. First, the open bis(carbamoyl), bis(carbenoid) complex may actually be thermodynamically more stable than the closed di-aminoenediolate. Reactions are known where metal ions insert into the C=C double bonds of electron-rich olefins to form bis(carbene) complexes⁶⁵ (e.g., eq 14). Such considerations are

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undoubtedly less important for a bis(η^2 -acyl). The second factor is kinetic in nature, is applicable to both acyls and carbamoyls, and reflects the fact that orbital symmetry conservation places constraints upon the mutual orientations from which free carbenes can couple thermally to form olefins.⁶⁶ The immobilization in the bis(carbamoyl) introduced by the η^2 ligation, the C-N multiple bond character, and the prodigious intramolecular steric congestion as well as the compensatory effects which may be imparted by the metal ion d and f orbitals are difficult to assess with the data presently at hand. Further investigations of this problem are in progress.

Acknowledgment. We thank the National Science Foundation (T.J.M., Grants CHE76-84494 A01 and CHE8009060) and the University of Nebraska Computing Center (V.W.D.) for generous support of this work.

Supplementary Material Available: Anisotropic thermal parameters for nonhydrogen atoms (Tables IV and IX), detailed experimental descriptions of the X-ray crystallographic studies, and structure factor tables (40 pages). Ordering information is given on any current masthead page.

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Characterization of Cationic Rhodium Isocyanide Oligomers in Aqueous Solutions

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Abstract: The tetranuclear complex $(Rh_2(\text{bridge})_4)_2^{6+}$ (or Rh_4^{6+}) (bridge = 1,3-diisocyanopropane) forms 1:1 and 1:2 complexes with $Rh_2(\text{TMB})_4^{2+}$ (TMB = 2,5-dimethyl-2,5-diisocyanohexane) in aqueous 1 N H_2SO_4 solution at 25 °C. The formation constant of $Rh_2(\text{TMB})_4Rh_4^{8+}$ is $1.5 \times 10^7 M^{-1}$ ($\lambda_{\text{max}} = 785 \text{ nm}$), and that of $Rh_2(\text{TMB})_4Rh_4Rh_2(\text{TMB})_4^{10+}$ is $4.5 \times 10^{13} M^{-2}$ ($\lambda_{\text{max}} = 980 \text{ nm}$). The hexanuclear complex dimerizes, the formation constant of the dodecanuclear cation ($\lambda_{\text{max}} \sim 1350 \text{ nm}$) being $1.8 \times 10^4 M^{-1}$. Air oxidation of $Rh_2(\text{TMB})_4Rh_4Rh_2(\text{TMB})_4^{10+}$ gives the "mixed" tetranuclear complex, $Rh_2(\text{TMB})_4Rh_2^{6+}$. The intense band ($\epsilon(\text{Rh})$ in the range $(2-3) \times 10^4 M^{-1} \text{ cm}^{-1}$) observed in the electronic absorption spectrum of each of the oligomers is attributable to a $\sigma \rightarrow \sigma^*$ transition; the transition energy decreases systematically with increasing rhodium chain length. Electronic structural relationships of certain of the rhodium oligomers to *cis*-diammineplatinum α -pyridone blue are discussed briefly.

It is well established that certain planar isocyanide complexes of Rh(I) and Ir(I) form dimers, trimers, and even higher oligomers in concentrated solutions.¹⁻³ Elucidation of the nature of the

metal-metal interactions in these oligomers has been facilitated by our work⁴⁻¹⁰ on discrete binuclear complexes containing the

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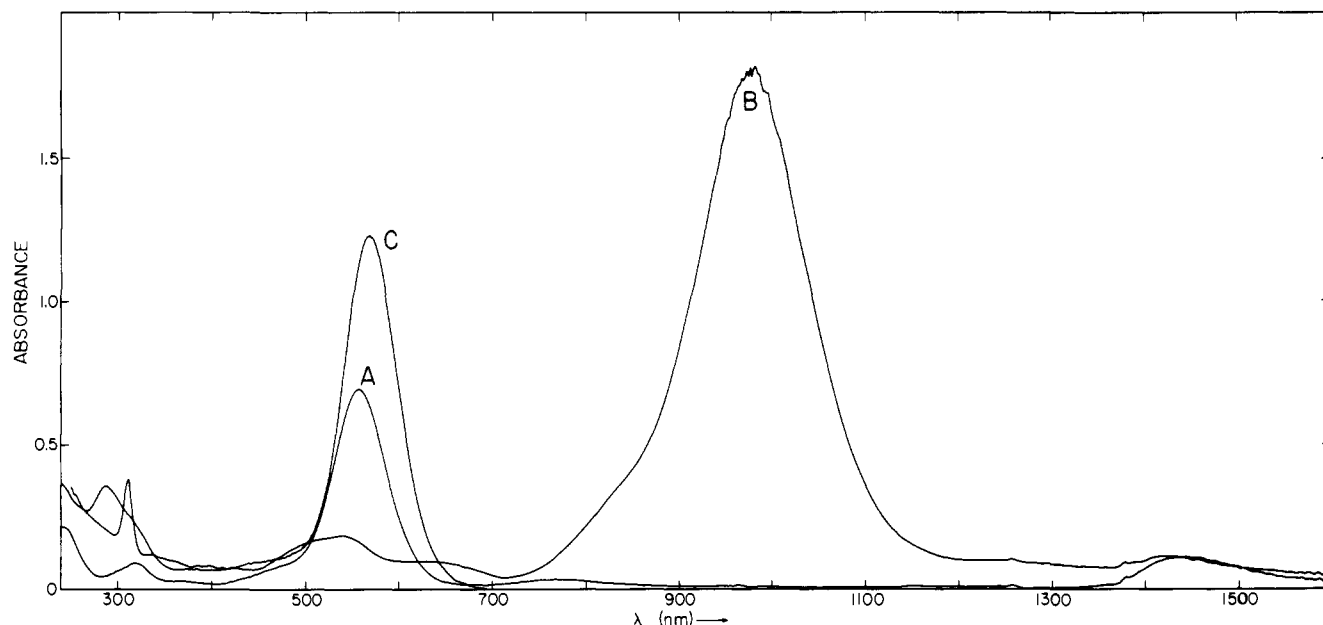
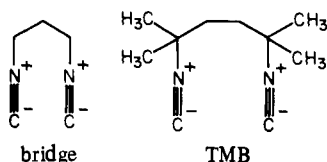


Figure 1. Formation of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ in 1 N H_2SO_4 (25 °C). Absorption spectra (1-mm path length): (A) $[\text{Rh}_4^{6+}] = 0.8 \times 10^{-4}$ M; (B) solution A + initial $[\text{Rh}_2(\text{TMB})_4^{2+}] = 2.4 \times 10^{-4}$ M (the final $[\text{Rh}_2(\text{TMB})_4^{2+}] = 0.7 \times 10^{-4}$ M (4% CH_3CN in 1 N H_2SO_4); the absorptions for unreacted $\text{Rh}_2(\text{TMB})_4^{2+}$ occur at 313 and 505 nm); (C) after air oxidation of solution B (4% CH_3CN in 1 N H_2SO_4). Absorption above 1400 nm is attributable to the aqueous medium.

binucleating ligands 1,3-diisocyanopropane (bridge) and 2,5-dimethyl-2,5-diisocyanohexane (TMB).



Oxidation of $\text{Rh}_2(\text{bridge})_4^{2+}$, abbreviated Rh_2^{2+} , in aqueous acidic solutions yields¹¹⁻¹⁴ a linear tetranuclear complex, Rh_4^{6+} . Reduction of Rh_4^{6+} by Cr^{2+} in aqueous sulfuric acid solution produces¹² a rich array of Rh_m^{n+} oligomers with n/m ratios between 1.5 for the parent Rh_4^{6+} and 1 for the final reduction product, Rh_2^{2+} . For example, species with the formulas Rh_6^{8+} , Rh_8^{10+} , and Rh_{12}^{16+} have been observed.¹²

The metal-metal bonding in the Rh_m^{n+} chains must include some mixture of d^8d^8 , d^8d^7 , and d^7d^7 interactions. Certain of these interactions are important in the extensively studied platinum chain compounds,¹⁵ e.g., the partially oxidized cyanoplatinates and the platinum blues. An important step toward understanding such interactions has been taken by Lippard and co-workers, who have characterized^{16,17} a discrete tetranuclear platinum blue. With a similar goal we have studied the rhodium oligomers formed in reactions between $\text{Rh}_2(\text{TMB})_4^{2+}$ and Rh_4^{6+} . Addition of the sterically congested $\text{Rh}_2(\text{TMB})_4^{2+}$ complex to Rh_4^{6+} has allowed

us to characterize species containing linear chains of six, eight, and twelve rhodium atoms.

Experimental Section

Materials. Spectral grade acetonitrile was purchased from Burdick and Jackson. H_2SO_4 (1 N) was purchased from J. T. Baker and was "Baker Analyzed" reagent grade.

Rhodium Compounds. The preparation of $\text{Rh}_2(\text{bridge})_4(\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$ has been reported.^{5,6} This salt was recrystallized from hot acetonitrile prior to use.

$\text{Rh}_2(\text{bridge})_4(\text{BPh}_4)(\text{BF}_4)$. $\text{Rh}_2(\text{bridge})_4(\text{BPh}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (0.84 g) was dissolved in 250 mL of hot acetonitrile. Tetrabutylammonium tetrafluoroborate (1.35 g) in 10 mL of acetonitrile was added, and 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: IR $\nu(\text{CN})$ 2180, $\nu(\text{Ph})$ 1578 cm^{-1} (KBr disk). Anal. Calcd for $(\text{Rh}_2\text{C}_{44}\text{H}_{44}\text{N}_8\text{B}_2\text{F}_4)$: C, 53.47; H, 4.49; N, 11.34. Found: C, 53.41; H, 4.91; N, 11.99.

$(\text{Rh}_2(\text{bridge})_4)_2(\text{BF}_4)_6$. In the dark a suspension of $\text{Rh}_2(\text{bridge})_4(\text{BF}_4)(\text{BPh}_4)$ (approximately 12 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 solution was left standing 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 $(\text{Rh}_2\text{C}_{20}\text{H}_{24}\text{N}_8\text{B}_3\text{F}_{12})$: C, 28.50; H, 2.87; N, 13.30. Found: C, 28.93; H, 3.04; N, 13.62. IR $\nu(\text{CN})$ 2218 cm^{-1} (KBr disk).

$\text{Rh}_2(2,5\text{-dimethyl-2,5-diisocyanohexane})_4(\text{CF}_3\text{SO}_3)_2$. The synthesis of the triflate salt paralleled that of the hexafluorophosphate salt.⁸ AgTfO (0.1 g, 0.19 mmol) in 2 mL of acetonitrile was added to a warm solution (6 mL) of $(\text{Rh}(\text{C}_6\text{H}_5)\text{Cl})_2$ ¹⁸ (0.1 g, 0.2 mmol) in acetonitrile. After the AgCl precipitate was removed by suction filtration, 2,5-dimethyl-2,5-diisocyanohexane⁸ (0.13 g, 0.2 mmol) was added in 1 mL of acetonitrile. An equal volume of diethyl ether was then added to the dark red solution. The resulting precipitate was filtered and dried in vacuo. The product could be recrystallized from hot acetonitrile: Anal. Calcd for $(\text{Rh}_2\text{C}_{42}\text{H}_{64}\text{N}_8\text{F}_6\text{S}_2\text{O}_6)$: C, 43.45; H, 5.56; N, 9.65. Found: C, 43.52; H, 5.47; N, 9.74. IR $\nu(\text{CN})$ 2160 cm^{-1} (KBr disk).

General Methods. Electronic absorption spectra were measured at room temperature by using a Cary 17 spectrophotometer. Infrared spectra were measured with a Beckman IR 4240 spectrophotometer. Acetonitrile solutions of $\text{Rh}_2(\text{TMB})_4(\text{TfO})_2$ were deoxygenated by three freeze-evacuate-thaw cycles. The final vacuum was broken with oxygen-free argon. Aliquots were transferred by means of argon-purged glass syringes with platinum needles through stopcocks fitted with serum caps.

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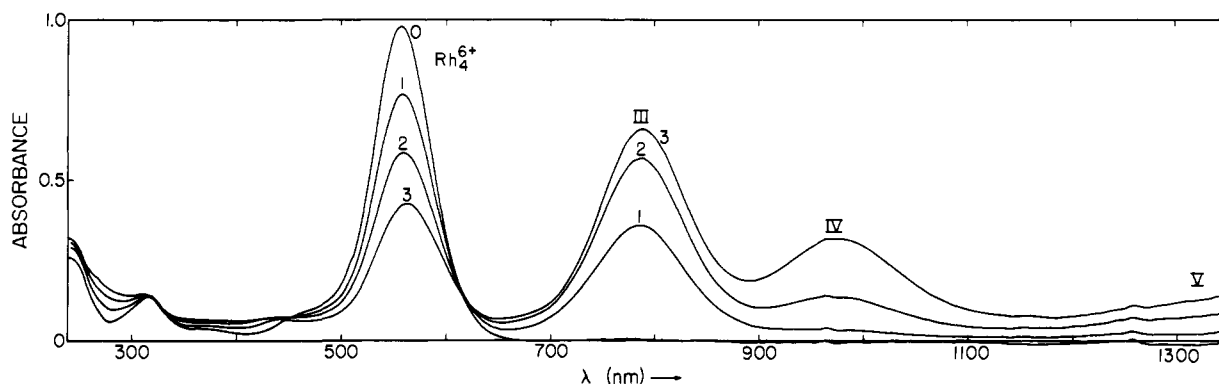


Figure 2. Absorption spectral changes (1-cm path length) during the titration of Rh_4^{6+} (1.1×10^{-5} M) in 1 N H_2SO_4 (25 °C) with $\text{Rh}_2(\text{TMB})_4^{2+}$. Each aliquot would give an initial $[\text{Rh}_2(\text{TMB})_4^{2+}] = 3.2 \times 10^{-6}$ M (III, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$; IV, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$; V, $(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)^{16+}$).

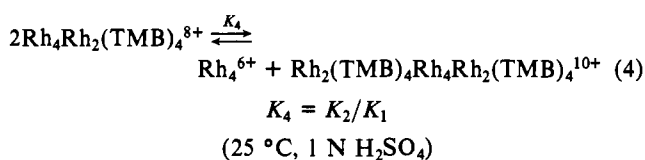
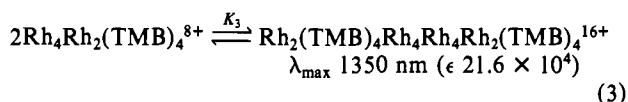
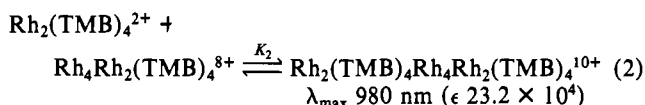
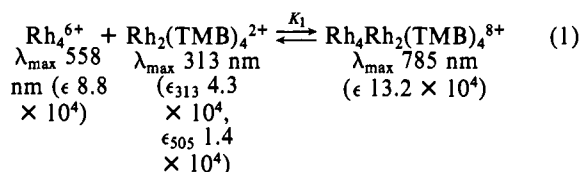
$\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ Solutions. Solutions of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ were prepared in tubes (5 mL) to which a stopcock and a quartz cuvette (1-mm path length) were connected. Solutions (2 mL of 1 N H_2SO_4) of $(\text{Rh}_2(\text{bridge})_4)_2(\text{BF}_4)_6$ (10^{-4} M) were deoxygenated with oxygen-free argon through a Teflon needle inserted through the stopcock. Aliquots (0.025–0.1 mL) of an acetonitrile solution of $\text{Rh}_2(\text{TMB})_4(\text{TfO})_2$ (5×10^{-3} M) were added as described above.

Titration of Rh_4^{6+} with $\text{Rh}_2(\text{TMB})_4^{2+}$. Titrations utilized a reaction vessel consisting of a 40-mL tear-shaped flask that was connected to a three-way stopcock. At the neck of the flask a quartz cuvette (1-cm pathlength) was fused at a right angle. Solutions (10 mL) of 1 N H_2SO_4 containing $(\text{Rh}_2(\text{bridge})_4)_2(\text{BF}_4)_6$ (5×10^{-6} to 5×10^{-5} M) were deoxygenated by four freeze–evacuate–thaw cycles. The final vacuum was broken with oxygen-free argon. Alternatively, 1 N H_2SO_4 was degassed in the bulb and then added to the $(\text{Rh}_2(\text{bridge})_4)_2(\text{BF}_4)_6$ present in the cuvette. Aliquots (0.025–0.05 mL) of an acetonitrile solution of $\text{Rh}_2(\text{TMB})_4(\text{TfO})_2$ (6×10^{-4} M) were added as described above.

Results and Discussion

The axially hindered $\text{Rh}_2(\text{TMB})_4^{2+}$ ion reacts cleanly with Rh_4^{6+} to form $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ (Figure 1). Both ends of this octanuclear complex ion are capped by $\text{Rh}_2(\text{TMB})_4^{2+}$ groups, thereby disfavoring further oligomerization. The chemistry is more complex when the mole ratio of $\text{Rh}_2(\text{TMB})_4^{2+}$ to Rh_4^{6+} is less than 2:1, as outlined in Scheme I and documented in the following sections.¹⁹

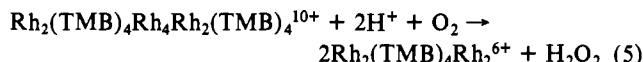
Scheme I



(19) Redox titrations show that species with similar spectral properties and oxidation states identical with those of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ and $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ are formed by reduction of Rh_4^{6+} in aqueous acidic solutions.¹² Methanol solutions of $\text{Rh}_2(\text{bridge})_4\text{Cl}_2$ also exhibit absorption bands in the near-infrared region whose intensities vary nonlinearly with $[\text{Rh}(\text{total})]$. It is likely that these absorptions, which were attributed⁵ previously to pure Rh_2^{2+} oligomers, are due to partially oxidized species that are analogous to those set out in Scheme I.

Preparation of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$. Separate, stable solutions of Rh_4^{6+} ($\epsilon_{558} = 8.8 \times 10^4$ M⁻¹ cm⁻¹) and $\text{Rh}_2(\text{TMB})_4^{2+}$ ($\epsilon_{313} = 4.3 \times 10^4$ M⁻¹ cm⁻¹) can be prepared in deoxygenated 1 N H_2SO_4 from $(\text{Rh}_2(\text{bridge})_4)_2(\text{BF}_4)_6$ and $\text{Rh}_2(\text{TMB})_4(\text{TfO})_2$, respectively. However, upon mixing a 2:1 mole ratio of $\text{Rh}_2(\text{TMB})_4^{2+}$ in acetonitrile to Rh_4^{6+} in 1 N H_2SO_4 immediate bleaching of the absorbances of both species occurs. The visible and near-infrared spectrum of the resulting solution (Figure 1) is dominated by an intense band at 980 nm. Spectra of solutions for which the ratio of added $\text{Rh}_2(\text{TMB})_4^{2+}$ to Rh_4^{6+} is less than 1.8 show no increase in A_{318} . The stoichiometry of the oligomerization was determined at relatively high $[\text{Rh}_4^{6+}]$ (1×10^{-4} M) in order to minimize the effect of adventitious oxidants. In a typical experiment, 4.6×10^{-4} mmol of $\text{Rh}_2(\text{TMB})_4(\text{TfO})_2$ in 0.075 mL of acetonitrile was added to 2 mL of 1 N H_2SO_4 containing 1.6×10^{-4} mmol of Rh_4^{6+} . The spectrum of the resulting solution revealed the absence of Rh_4^{6+} , the presence of 1.4×10^{-4} mmol of unreacted $\text{Rh}_2(\text{TMB})_4^{2+}$ ($\Delta A_{313} = 0.3$), and an absorption signal at 980 nm due to $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ ($\epsilon_{980} = 23.2 \times 10^4$ M⁻¹ cm⁻¹).

Oxidation of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$. Air oxidation of solutions of the octanuclear ion results in the replacement of the absorption signal at 980 nm with one at 572 nm. Except for a red shift, this signal is in appearance identical with the spectrum of Rh_4^{6+} ($\lambda_{\text{max}} = 558$ nm). (Addition of $\text{Rh}_2(\text{TMB})_4^{2+}$ to a solution of Rh_4^{6+} ($A_{558} = a$) in 2:1 mole ratio gives $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$; air oxidation yields a species whose sole absorption in the visible–near-IR region is at 572 nm ($A_{572} = 2a$); Figure 1.) Absorption at 300 nm from $\text{Rh}_2(\text{TMB})_4^{2+}$ is also observed.²⁰ The similarity of the position and intensity of the 572-nm absorption band to the obviously analogous spectroscopic properties of Rh_4^{6+} suggests the species in question is the “mixed” tetranuclear $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ ion (eq 5). From the



magnitude of A_{980} observed after addition of $\text{Rh}_2(\text{TMB})_4^{2+}$ to the air-oxidized solution described above, we determined that approximately 10% of the $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ ions converted to Rh_4^{6+} . Attempts to separate $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ from the solution by addition of triflate and tetrafluoroborate salts resulted in the formation of powders that upon redissolution in 1 N H_2SO_4 yield a spectral band with $\lambda_{\text{max}} = 568$ nm, indicating approximately 70% $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ and 30% Rh_4^{6+} .

Titration of Rh_4^{6+} with $\text{Rh}_2(\text{TMB})_4^{2+}$. The spectral changes that accompany the titration of Rh_4^{6+} (5×10^{-6} to 5×10^{-5} M) in 1 N H_2SO_4 with $\text{Rh}_2(\text{TMB})_4^{2+}$ are the decrease in A_{558} and the increase in absorptions at 785, 980, and 1350 nm (Figure 2). With less than 1.8 equiv of $\text{Rh}_2(\text{TMB})_4^{2+}$ added to initial Rh_4^{6+}

(20) Solutions of $\text{Rh}_2(\text{TMB})_4^{4+}$ in 1 N H_2SO_4 were prepared by oxidation of $\text{Rh}_2(\text{TMB})_4^{2+}$ with Ce^{4+} . Spectra of these solutions were similar to those of solutions of authentic $\text{Rh}_2(\text{bridge})_4^{4+}$ (see ref 11). The λ_{max} for $\text{Rh}_2(\text{TMB})_4^{4+}$ is very solvent dependent, varying from 311 to 290 nm as the concentration of CH_3CN in 1 N H_2SO_4 solutions is increased from 0 to 4%.

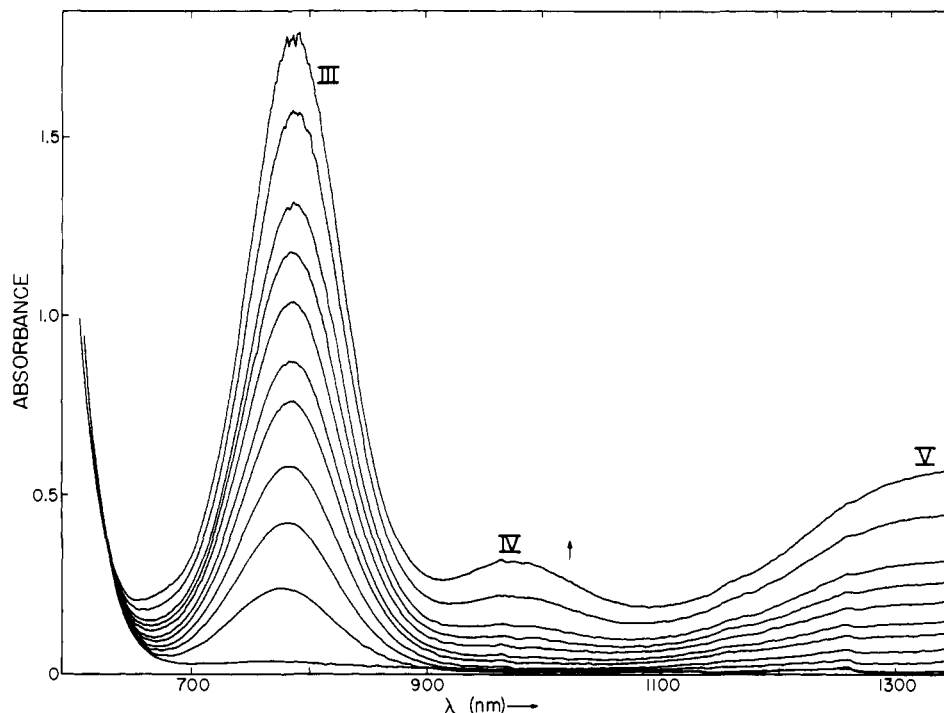


Figure 3. Absorption spectral changes (1-cm path length) during the titration of Rh_4^{6+} (5.2×10^{-5} M) with $\text{Rh}_2(\text{TMB})_4^{2+}$ in 1 N H_2SO_4 (25 °C). The final two aliquots would give an initial $[\text{Rh}_2(\text{TMB})_4^{2+}] = 3.6 \times 10^{-6}$ M. The remaining aliquots would give an initial $[\text{Rh}_2(\text{TMB})_4^{2+}] = 1.8 \times 10^{-6}$ M (III, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$; IV, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$; V, $(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}$).

an isobestic point is maintained at 318 nm and very little increase in A_{1313} occurs, all the added $\text{Rh}_2(\text{TMB})_4^{2+}$ having reacted. Furthermore, as neither $\text{Rh}_2(\text{TMB})_4^{4+}$ ($\epsilon_{313} = 3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)²⁰ nor $(\text{Rh}_2(\text{TMB})_4)_2^{6+}$ ²¹ was detected by absorption spectroscopy, electron transfer between $\text{Rh}_2(\text{TMB})_4^{2+}$ and Rh_4^{6+} is precluded. The appearance of signals at 785 and 1350 nm precedes that at 980 nm. However, as the amount of added $\text{Rh}_2(\text{TMB})_4^{2+}$ exceeds 1 equiv, the former absorbances decrease and finally only signals for $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ ($\lambda_{\text{max}} = 980 \text{ nm}$) and $\text{Rh}_2(\text{TMB})_4^{2+}$ ($\lambda_{\text{max}} = 313, 505 \text{ nm}$) remain. For solutions with $[\text{Rh}^{\text{total}}] < 10^{-4}$ M, the equilibria presented in Scheme I are necessary and sufficient to describe the spectral changes mentioned above. Two constraints apply (eq 6 and 7).

$$[\text{Rh}_2(\text{TMB})_4^{2+}]_{\text{added}} = [\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}] + 2[\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}] + 2[(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}] \quad (6)$$

$$-\Delta[\text{Rh}_4^{6+}] = [\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}] + [\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}] + 2[(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}] \quad (7)$$

$\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ and $(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}$. When low initial concentrations (10^{-6} M) of $\text{Rh}_2(\text{TMB})_4^{2+}$ are allowed to react with a large excess of Rh_4^{6+} in 1 N H_2SO_4 , we have found that greater than 90% of the increase in absorption in the near-infrared spectrum of the solution occurs at 785 nm. From the increase in A_{785} , $[\text{Rh}_2(\text{TMB})_4^{2+}]_0$, and the decrease in A_{558} , the ratio of Rh_4^{6+} to $\text{Rh}_2(\text{TMB})_4^{2+}$ for the formation of the 785 nm absorbing species was measured as 1 and $\epsilon_{785} = 13.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. With a large ratio $[\text{Rh}_4^{6+}]_0/[\text{Rh}_2(\text{TMB})_4^{2+}]_0$, the concentration of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ was minimized and oligomerization of $\text{Rh}_2(\text{TMB})_4^{2+}$ with Rh_4^{6+} was confined to the formation of the hexanuclear ion ($\lambda_{\text{max}} = 785 \text{ nm}$) and its dimer ($\lambda_{\text{max}} = 1350 \text{ nm}$) (Figure 3). Applying eq 6, we determined the stoichiometry $\text{Rh}_4^{6+}/\text{Rh}_2(\text{TMB})_4^{2+} = 1$ and $\epsilon_{1350} = 21.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the 1350-nm absorbing species. Finally, since the stoichiometries and ϵ 's of all the species had been determined, eq 6 and 7 were used to calculate the amount of $\text{Rh}_2(\text{TMB})_4^{2+}$ and Rh_4^{6+} incor-

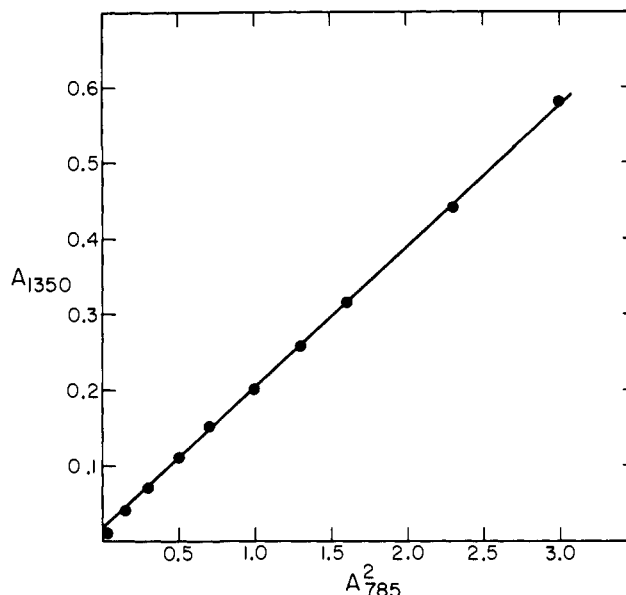


Figure 4. Dimerization of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ (K_3) (1 N H_2SO_4 , 25 °C; $[\text{Rh}_4^{6+}] \approx 5 \times 10^{-5}$ M).

porated in the oligomers for a series of solutions. These calculated values agreed with the experimental values to within 10%.

K_3 : Dimerization of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$. The evidence that $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ dimerizes is the fact that a plot of A_{1350} vs. A_{785}^2 is a straight line (Figure 4). From the slope (0.22), we obtain $K_3 = 1.8 \times 10^4 \text{ M}^{-1}$. The variation in K_3 of 10% that occurred as $[\text{Rh}_4^{6+}]$ was varied between 5×10^{-5} and 5×10^{-6} M was within experimental error. The constant K_3 measured for 1 M $\text{CH}_3\text{SO}_3\text{H}$ solutions was found to be approximately $1/3$ to $1/2$ that for 1 N H_2SO_4 .

K_4 : Disproportionation of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$. The constant K_4 was found to be 0.2. Representative data for the determination of K_4 are collected in Table I. Measurement of K_4 for a wide variation of ratios $[\text{Rh}_4^{6+}]/[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]$ and $[\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}]/[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]$ is made difficult in that the quantitation from A_{558} of small $[\text{Rh}_4^{6+}]$'s is susceptible

(21) The tetranuclear $(\text{Rh}_2(\text{TMB})_4)_2^{6+}$ has not been isolated. A species with the spectrum expected for $(\text{Rh}_2(\text{TMB})_4)_2^{6+}$ ($\lambda_{\text{max}} = 595 \text{ nm}$) was obtained by adding Ti^{3+} to 1 N H_2SO_4 solutions (10^{-2} M) to $\text{Rh}_2(\text{TMB})_4^{2+}$.

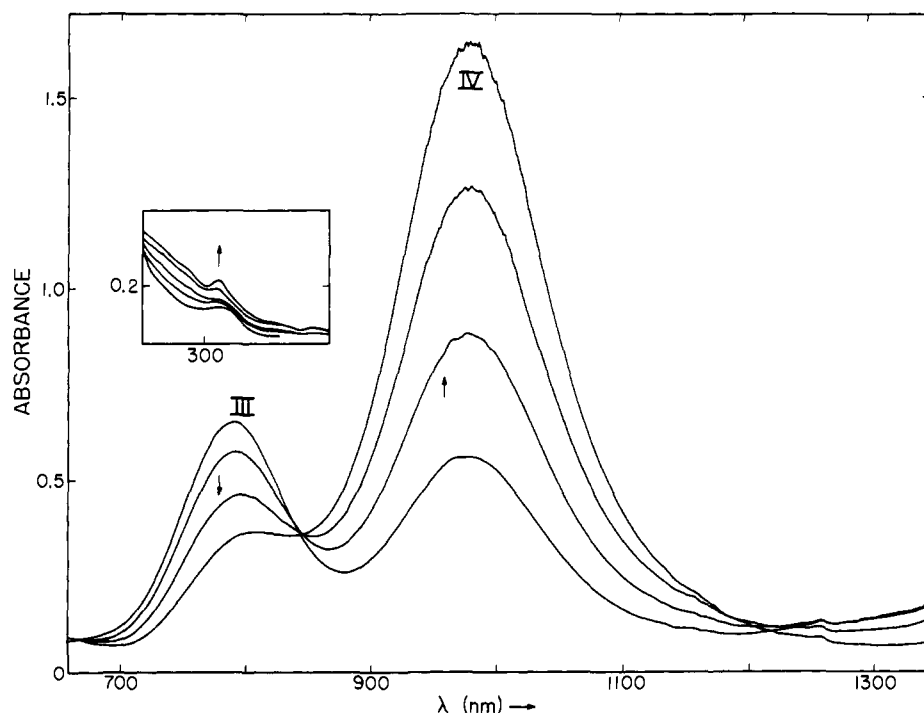


Figure 5. Determination of K_2 by absorption spectral measurements (1-cm path length). The inset shows the absorption for unreacted $\text{Rh}_2(\text{TMB})_4^{2+}$ (1 N H_2SO_4 , 25 °C): III, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$; IV, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$.

Table I. Determination of K_4

$[\text{Rh}_4^{6+}]^a$	$[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]$	$\{\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}\}$	$\{(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}\}$	K_4
3.3 ^b	1.34	0.11	0.27	0.2
1.65 ^c	0.87	0.09		0.19
0.8 ^b	0.27	0.017	0.014	0.19
0.54 ^b	0.43	0.06	0.042	0.18
0.33 ^b	0.5	0.14	0.07	0.19
0.21 ^b	0.5	0.24	0.08	0.2

^a Concentrations are in units of 10^{-5} M. ^b $[\text{Rh}_4^{6+}]$ is calculated as $[\text{Rh}_4^{6+}]_0 - [\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}] - [\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}] - 2[(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}]$. ^c $[\text{Rh}_4^{6+}]$ is calculated from A_{558} .

to error from the absorption of other species at 558 nm. In particular, the $\epsilon_{558}(\text{Rh}_2)$ for the "mixed" $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ ion arising from the oxidation of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ is twice that of Rh_4^{6+} . Consequently, the amount of Rh_4^{6+} consumed in the formation of the higher oligomers was calculated and subtracted from the initial $[\text{Rh}_4^{6+}]$. The error from ignoring the amount of Rh_4^{6+} incorporated as $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ as a result of oxidation is half that from calculating $[\text{Rh}_4^{6+}]$ from A_{558} . Furthermore, no error is incurred from the absorption of $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$, $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$, and $(\text{Rh}_2(\text{TMB})_4\text{Rh}_4)_2^{16+}$ at 558 nm. Because $[\text{Rh}_4^{6+}]$ was calculated from the measured concentrations of the higher oligomers, the constancy of the calculated K_4 's, though consistent with the assumed stoichiometries and ϵ 's for these ions, does not prove that the values are correct.

K_1 and K_2 . In the initial part of the titration of Rh_4^{6+} with $\text{Rh}_2(\text{TMB})_4^{2+}$ an isosbestic point occurs at 318 nm. Just prior to the increase in A_{318} , the ratio $[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]/[\text{Rh}_4^{6+}]$ is observed to be 1.4. From these observations and with the assumption that $\Delta A_{318} \sim 0.005$ can be detected, an upper limit can be set for $[\text{Rh}_2(\text{TMB})_4^{2+}]$ of 2×10^{-7} M (for $\text{Rh}_2(\text{TMB})_4^{2+}$, $\epsilon_{318} \approx 0.6 \epsilon_{313}$) and a lower limit placed on K_1 of $7 \times 10^6 \text{ M}^{-1}$. In the latter part of the titration Rh_4^{6+} has all reacted and the oligomerization involves $\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ and its dimer with $\text{Rh}_2(\text{TMB})_4^{2+}$ to form $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ (Figure 5). During this time A_{318} increases and the absorption characteristic of $\text{Rh}_2(\text{TMB})_4^{2+}$ appears. From ΔA_{313} , A_{785} , and A_{980} , the concentrations $[\text{Rh}_2(\text{TMB})_4^{2+}]$, $[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]$, and $[\text{Rh}_2-$

Table II. Determination of K_2

$[\text{Rh}_2(\text{TMB})_4^{2+}]^a$	$[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]$	$\{\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}\}$	$10^6 K_2, \text{ M}^{-1}$
1.7	1.25	7.1	3.3
1.1	2.1	5.4	2.3
0.35	3.2	3.8	3.4
3.5	0.83	6.7	2.3
1.6	1.25	6.0	3.0
0.81	2.3	4.4	2.4
0.5	3.2	2.8	1.8

^a Concentrations are in units of 10^{-6} M.

$(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$) and, therefore, the constant K_2 are known. In practice the magnitude of K_2 ($3 \times 10^6 \text{ M}^{-1}$) restricts accurate measurements to a narrow range of ratios $[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]/[\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}]$. Deviation from this ratio allows more accurate quantitation of either $[\text{Rh}_2(\text{TMB})_4^{2+}]$ or $[\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}]$ at the expense of the other. Representative data used in the determination of K_2 are collected in Table II. With both K_2 and K_4 determined, K_1 is calculated to be $1.5 \times 10^7 \text{ M}^{-1}$. This latter value is above the lower limit imposed on it above.

The Oxidation Problem. All the rhodium isocyanide complexes discussed here whose formal oxidation states per Rh atom are less than that of Rh_4^{6+} (1.5) are air sensitive. Oxidation of the oligomers formed from both $\text{Rh}_2(\text{TMB})_4^{2+}$ and Rh_4^{6+} units invariably leads to the "mixed" $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ ion ($\lambda_{\text{max}} = 572 \text{ nm}$). In more concentrated solutions ($[\text{Rh}]^{\text{total}} = 3 \times 10^{-4} \text{ M}$), the oxidation was insignificant. However, formation of the "mixed" tetranuclear ion was detected in the dilute solutions (10^{-6} – 10^{-5} M) necessary for the measurement of $[\text{Rh}_4^{6+}]$ and K_2 . From control experiments it is known that for the concentrations of $\text{Rh}_2(\text{TMB})_4^{2+}$ ion present in the titrations, oligomerization reactions involving $\text{Rh}_2(\text{TMB})_4^{2+}$ and the "mixed" cation do not occur. The amount of oxidation can then be ascertained by measuring the quantity of $\text{Rh}_2(\text{TMB})_4\text{Rh}_2^{6+}$ remaining after complete reaction of Rh_4^{6+} . For a solution with $[\text{Rh}_4^{6+}]_0 = 1 \times 10^{-5} \text{ M}$, the amount of Rh_4^{6+} lost through oxidation of the more reduced oligomers was approximately 7%. To check the effect of the oxidation on the measurements reported here, the equilibrium constants K_2 and K_4 were determined for a series of

solutions varying in the amount of oxidation and were found to be constant.

Electronic Spectroscopic Comparisons. The intense ($\epsilon(\text{Rh}) = (2-3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) absorption band observed for each oligomer containing at least two Rh(II) centers (in a formal sense) can be assigned to a $\sigma \rightarrow \sigma^*$ transition that is delocalized over the polynuclear rhodium framework. The $\sigma \rightarrow \sigma^*$ transition in the parent complex, Rh_2^{4+} , falls at 311 nm in aqueous sulfuric acid solution.¹¹ Adding two Rh(I) centers to give Rh_4^{6+} shifts the $\sigma \rightarrow \sigma^*$ transition to 558 nm, and further rhodium chain length increases lead to still lower $\sigma \rightarrow \sigma^*$ transition energies [$\text{Rh}_2(\text{TMB})_4\text{Rh}_4^{8+}$ (787 nm) > $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$ (980 nm) > $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{16+}$ (1350 nm)], as would be expected from simple theoretical considerations.

The electronic structures of the rhodium oligomers are related in a rough sense to those of the platinum blues.^{16,17} The Rh_4^{6+} species may be compared, for example, with Lippard's *cis*-diammineplatinum α -pyridone blue (PPB), where the bulkiness of the α -pyridone ligand restricted the chain length to four platinum atoms with an average formal oxidation state of 2.25.^{16,17} For-

mally, the Pt_4^{9+} unit is $d^8d^7d^8d^8$, whereas Rh_4^{6+} is $d^8d^7d^7d^8$ (the electronic analogue of Pt_4^{9+} is Rh_4^{5+} , which has not been observed as a separate entity, but rather as a higher oligomer, Rh_8^{10+} or $\text{Rh}_2(\text{TMB})_4\text{Rh}_4\text{Rh}_2(\text{TMB})_4^{10+}$). Lippard's ESR studies suggest^{16,17} that the unpaired electron in Pt_4^{9+} is located in a molecular orbital derived from d_{z^2} interactions along the platinum chain. Presumably, this molecular orbital is analogous to the σ^* orbital involved in the allowed $\sigma \rightarrow \sigma^*$ transition in Rh_4^{6+} . However, the characteristic absorption band in the platinum blues in the 550-730-nm region (680 nm in PPB)¹⁷ is much less intense than the 558-nm system in the Rh_4^{6+} spectrum, and it is entirely possible that this particular transition in Pt_4^{9+} is not $\sigma \rightarrow \sigma^*$. Much more extensive spectroscopic studies will be required to elucidate the nature of the lowest electronic excited states in the platinum blues as well as in the rhodium isocyanide oligomers.

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Hydrogen Isotope Effects on the Excited-State Decay Properties of Polynuclear Metal Carbonyl Hydrides. Emission Properties of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$

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Abstract: The two pairs of complexes $\text{H}_4\text{Re}_4(\text{CO})_{12}$, $\text{D}_4\text{Re}_4(\text{CO})_{12}$ and $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$, $[\text{n-Bu}_4\text{N}]_2[\text{D}_6\text{Re}_4(\text{CO})_{12}]$ have been compared with respect to excited-state decay properties. The $\text{H}_4\text{Re}_4(\text{CO})_{12}$ complex exhibits emission from the lowest excited state at 298 K in hydrocarbon solution or as a solid and also at 77 K in glassy hydrocarbon solution or as a pure solid. The emission maximum is between 13 700 and 14 600 cm^{-1} depending on solvent conditions, and the lifetimes range from <0.02 μs at 298 K in 3-methylpentane solution ($\Phi \approx 0.003$) to 16 μs at 77 K in 3-methylpentane glass ($\Phi = 0.25$). The effect of replacing ^1H by ^2H is to lengthen emission lifetime by 20-30% with an equal percent increase in emission quantum yield. The lowest (emissive) excited state can be rapidly quenched by anthracene (triplet energy ≈ 42 kcal/mol) but not by *trans*-stilbene (triplet energy ≈ 50 kcal/mol), consistent with the high-energy onset (~ 46 kcal/mol) of the structureless emission spectrum of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ attributable to a lowest-lying triplet excited state associated with a Re_4 localized electronic transition. $[\text{n-Bu}_4\text{N}]_2[\text{H}_6\text{Re}_4(\text{CO})_{12}]$ does not detectably emit in solution or as the solid at 298 K, but emission is detectable at 77 K from the solid or glassy solutions of the salt. The emission is at $\sim 18 000 \text{ cm}^{-1}$ with a lifetime of $\sim 2 \mu\text{s}$ and a quantum yield of ~ 0.01 . The effect of ^1H replacement by ^2H is to increase lifetime and quantum yield by $\sim 50\%$ depending on the medium. Under a given set of conditions for either $\text{H}_4\text{Re}_4(\text{CO})_{12}$ or $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^{2-}$, the effect of replacing ^1H by ^2H is to lower the rate constant for nonradiative decay; there is no effect on the radiative decay constant.

While studying the photocatalytic activity of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ as a comparison to that for $\text{H}_4\text{Ru}_4(\text{CO})_{12}$,¹ we discovered that $\text{H}_4\text{Re}_4(\text{CO})_{12}$ exhibits visible emission when excited by ultraviolet or high-energy visible light. This discovery afforded us an opportunity to examine the effect of replacing ^1H with ^2H on the excited-state decay properties of the cluster. There are earlier studies of hydrogen isotope effects on excited-state decay of organic molecules and of inorganic complexes where the ligands bear hydrogen atoms.²⁻⁵ The importance of these studies rests in the

fact that the replacement of ^1H by ^2H results in little change in the essential electronic structure or geometry of the molecule while the vibrational energies are altered significantly. Thus, replacing ^1H by ^2H provides a probe of the importance of high-energy vibrations on the rates of nonradiative excited-state decay.

Of particular interest is the fact that the ^1H in $\text{H}_4\text{Re}_4(\text{CO})_{12}$ is directly bonded to the metal.⁶ Often, the highest energy

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