X-ray powder data for $Co(NH_3)_6MCl_6$ would allow for only about a 0.05 Å variation in the bond length in these lattices.

The axial zero-field splitting parameter D for $[Cr(NH_3)_6]^{3+}$ increases from 490 G in the In host to 1014 G in the Sb host and to 1160 G in the Bi host, in accord with the above model of the lattice interactions. At the anion site, D for $[FeCl_6]^{3-}$ is the same (276 ± 4 G) in all three lattices at room temperature which suggests that the iron complex is large enough to suffer some trigonal distortion by the host lattice but not so large that it feels small variations in the lattice. The 15% increase in the magnitude of D for $[FeCl_6]^{3-}$ in the indium host which occurs when the temperature is lowered to liquid nitrogen temperature suggests that the iron complex may be experiencing a further distortion by compression in this the smallest of the three hosts used, but other effects may also be involved at low temperatures.

The absence of any zero-field splitting for $[CrCl_6]^{3-}$ in the indium host suggests that this ion is somewhat smaller than the iron complex and is thus able to occupy the anion site without suffering any distortion from the lattice. This size effect could also account for our failure to obtain $[CrCl_6]^{3-}$ substitution in the antimony and bismuth hosts.

Acknowledgments. The authors gratefully recognize the assistance of Professor R. S. McEwen in obtaining the X-ray data and their interpretation and thank Professor H. H. Dearman for making available his data on $[CrCl_5]^{2-}$ prior to publication.

Registry No. $[FeCl_6]^{3-}$, 19639-41-9; $[Cr(NH_3)_6]^{3+}$, 14695-96-6; $Co(NH_3)_6InCl_6$, 17499-93-3; $Co(NH_3)_6SbCl_6$, 17805-63-9; $Co(NH_3)_6$-$BiCl_6$, 16591-55-2; $[CrCl_6]^{3-}$, 15276-03-6.

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Characterization of the Products Resulting from Electrochemical Reduction of $Rh(en)_2Cl_2{}^+$ at Mercury Electrodes

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An intermediate product resulting from the reduction of *trans*-$Rh(en)_2Cl_2{}^+$ at mercury electrodes that had been identified as "a rhodium(II) dimer" is shown, instead, to be a mercury(II)-bridged complex of rhodium(I), $[(en)_2Rh]_2Hg^{4+}$. The experimental conditions under which the formation of this complex is favored during electrochemical reductions of $Rh(en)_2Cl_2{}^+$ are delineated. Nonelectrochemical production of the same complex *via* homogeneous reactions between Hg(II) and $Rh(en_2)H(OH_2)^{2+}$ is also described.

As part of an investigation of the electrochemical behavior of rhodium(III) complexes, we have been examining the reduction of the *trans*-$Rh(en)_2Cl_2{}^+$ cation (en = ethylenediamine) at mercury pool electrodes maintained at constant potential. Gillard and coworkers[1] have reported recently on similar studies in which they believed to have produced a relatively stable, binuclear rhodium(II) complex by one-electron reduction of $Rh(en)_2Cl_2{}^+$. In initial attempts to reproduce the results of Gillard, *et al.*,[1] we found that the apparent number of electrons required to reduce solutions of $Rh(en)_2Cl_2{}^+$ at mercury electrodes was a very sensitive function of electrode potential and pH as were the final reduction products obtained. When conditions were optimized for producing the species whose wavelength of maximum absorption matched that reported by Gillard, *et al.*,[1] the solution was found (by atomic absorption analysis) to contain a high concentration of mercury. In addition, a species having the same spectrum could be produced by mixing solutions of mercury(II) salts with solutions of the hydridorhodium(III) complex, $Rh(en)_2H(OH_2)^{2+}$, obtained from the two-electron reduction of $Rh(en)_2Cl_2{}^+$. The same species could also be prepared by oxidizing solutions of $Rh(en)_2H(OH_2)^{2+}$ at mercury electrodes. These observations, coupled with recent reports of other transition-metal complexes that yield mercury adducts when exposed to mercury electrodes at appropriate potentials,[2] led us to try to characterize more carefully the species produced when *trans*-$Rh(en)_2Cl_2{}^+$ is reduced at mercury electrodes.

Experimental Section

Apparatus. Electrolyses were carried out in a conventional two-compartment cell wrapped in aluminum foil to avoid photodecomposition of reaction products. A Wenking potentiostat (Model TR) was employed and electrolysis currents were integrated using operational amplifiers. The coulomb-time behavior was obtained with a pen and ink recorder.

A Varian Model AA5 atomic absorption apparatus was used for rapid measurements of the total rhodium and mercury in solutions of the complexes. The estimated accuracy of these analyses was ±5–10%.

Electronic spectra were recorded with a Cary 11M spectrophotometer. Standard serum cap-syringe techniques were used to exclude oxygen during transferring of solutions between the electrolysis or reaction vessels and spectrophotometer cells.

Reagents. Reagent grade chemicals were used throughout without further purification. Solutions of sodium methanesulfonate were prepared by neutralizing the commercially available acid, CH_3SO_3H (Eastman Kodak) with solid NaOH, filtering, and diluting with triply distilled water. All solutions were deaerated using prepurified N_2 which was passed over hot copper turnings and through a distilled water washing tower before use.

trans-$[Rh(en)_2Cl_2]ClO_4$ was prepared by standard procedures[3] and its purity was determined by comparison with previously measured extinction coefficients.[4]

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(1) R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc. A*, 734 (1971).

(2) D. N. Hendrickson, Y. S. Sohn, W. H. Morrison, Jr., and H. B. Gray, *Inorg. Chem.*, 11, 808 (1972).

(3) S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1, 925 (1962).

(4) L. P. Gendernalik, Ph.D. Thesis, University of Detroit, 1970.

Solutions of $Rh(en)_2H(OH_2)^{2+}$ were prepared by a procedure similar to that used by Gillard, *et al.*[5] Dilute (0.1-1 m*M*) solutions of *trans*-$Rh(en)_2Cl_2^+$ were reduced at −1200 mV (all potentials are reported *vs.* a sodium chloride saturated calomel electrode whose potential was 5 mV more negative than the standard sce) at a stirred Hg pool cathode in 0.1 *M* CH_3SO_3Na supporting electrolyte. Coulometric analysis, after correcting for the significant background currents from rhodium-catalyzed hydrogen evolution in initially acidic or neutral solutions,[6] showed that 2 faradays of charge per mole of complex had been consumed, and the uv spectrum of the resultant solution agreed with the two values of λ_{max} and ϵ given by Gillard, *et al.*[5]

Rhodium(I)-Mercury(II) Complexes. A moderately pure sample of a complex containing both mercury and rhodium was isolated by the following procedure. A 25-ml aliquot of 0.1 *M* CH_3SO_3Na-0.1 *M* NaOH electrolyte was used to dissolve 99 mg of *trans*-$[Rh(en)_2Cl_2]ClO_4$. The resulting solution was thoroughly deaerated and then reduced at −1200 mV at a Hg pool electrode (2 faradays per Rh were consumed). On completion of the reduction, the solution was protected from light, the electrode potential was changed to −100 mV, and the resulting anodic current was integrated. The oxidation was terminated when 1 faraday per rhodium had been consumed and the resultant yellow-brown solution was transferred (under a nitrogen atmosphere in a glove bag) to a flask containing 25 ml of a deaerated 8 *M* $NaClO_4$-0.1 *M* NaOH solution. The fine, dark red precipitate which formed immediately was collected and filtered under nitrogen. The precipitate was stored in a vacuum desiccator and protected from light. A *p*-toluenesulfonate salt of the complex resulted when this anion was substituted for perchlorate in the precipitation step. Samples of both salts were dissolved in deaerated 0.1 *M* CH_3SO_3Na and the resulting solution analyzed for total mercury and total rhodium by atomic absorption with the results shown in Table I.

An analogous procedure was used to prepare a second mercurated complex, the only difference being that the oxidation step was carried out at −60 mV rather than −100 mV and the electrolysis was allowed to proceed until 2 faradays per rhodium had been consumed, at which point the electrolysis current had decreased to background levels. The resulting complex failed to precipitate when perchlorate or tosylate anions were added, but a pale yellow precipitate resulted when sodium tetraphenylborate was added. Samples of this solid were dissolved in dimethyl sulfoxide and the resulting solution was analyzed for rhodium and mercury by atomic absorption. The weight percentages of the two metals did not correspond closely to any reasonable stoichiometry for the solid but the rhodium to mercury mole ratios for three samples (0.9, 0.7, 0.7) indicated that the primary component present contained approximately equal molar quantities of mercury and rhodium.

Procedure for Kinetic Measurements. The rates of reaction between $Rh(en)_2H(OH_2)^{2+}$ and Hg(II) were followed spectrophotometrically at room temperature (25 ± 1°). Buffer solutions, containing 0.05 *F* sodium borate and 1.0 *M* NaCl, were adjusted to the desired pH values with HCl or NaOH and deaerated with nitrogen. An aliquot of $Rh(en)_2H(OH_2)^{2+}$ [prepared by the reduction of *trans*-$Rh(en)_2Cl_2^+$] was added under nitrogen by means of a syringe and the mixture was stirred briefly with nitrogen. The reaction was initiated by adding an aliquot of a deaerated $HgCl_2$ solution and the resulting reactant mixture was transferred without exposure to air to a spectrophotometer cell. The increase in absorbance at 290 nm was monitored using the appropriate borate buffer-1.0 *M* NaCl as the blank.

Results

Controlled Potential Electrolysis of *trans*-$Rh(en)_2Cl_2^+$. A crucial feature that has not been emphasized in the previous studies on controlled potential electrolytic reduction of solutions of *trans*-$Rh(en)_2Cl_2^+$ is the importance of the solution pH. The ultimate reduction product is $Rh(en)_2H(OH_2)^+$ at pH values between 3 and 13 but this complex engages in a pH-dependent reaction which yields $Rh(en)_2^+$.[5]

$$Rh(en)_2H(OH_2)^{2+} + OH^- \rightleftarrows Rh(en)_2^+ + 2H_2O \qquad (1)$$

At pH values of *ca.* 10 or greater the following catalytic decomposition of the initial reactant ensues.[6]

Table I. Atomic Absorption Analysis of Precipitated Salts of the Mercury-Rhodium Complex[a]

Perchlorate salts		Tosylate salts			
Sample wt, mg	Molar ratio, Rh/Hg	Sample wt, mg	Molar ratio, Rh/Hg	Wt % Rh	Wt % Hg
4.5	1.82	2.3	1.85	17.4	18.2
8.2	2.06	4.6	2.08	16.8	15.2
15	2.23	7.4	2.05	16.3	15.4
16.1	1.92		Av 2.0 ± 0.1	16.8	16.3
29.2	2.02				

[a] Calculated Rh/Hg molar ratio, weight per cent Rh, and weight per cent Hg: $[(en)_2Rh]_2Hg(C_6H_5SO_3)_4$, 2.0, 15.5, 15.0; $[(en)_2Rh]_2Hg(OH)_2(C_6H_5SO_3)_2$, 2.0, 20.1, 19.5.

$$Rh(en)_2Cl_2^+ + Rh(en)_2^+ + OH^- \rightarrow Rh(en)_2Cl(OH)^+ + Rh(en)_2^+ + Cl^- \qquad (2)$$

The catalysis of reaction 2 by Rh(I) is analogous to previously reported cases in which the Rh(I) acts by engaging in rapid inner-sphere electron-transfer reactions with Rh(III) complexes.[7-9] Only one of the two chloride ions initially present in *trans*-$Rh(en)_2Cl_2^+$ is lost because the remaining chloride is continually transferred from the Rh(III) to the Rh(I) as the latter delivers two electrons to the Rh(III) in the subsequent inner-sphere reactions resulting in no net chemical change.

The sensitivity of the rate of reaction 2 to pH results from the effect of pH on equilibrium 1 which generates the presumed catalyst, $Rh(en)_2^+$. Sufficiently alkaline solutions of *trans*-$Rh(en)_2Cl_2^+$ are rapidly converted into solutions of $Rh(en)_2Cl(OH)^+$ by electrolytic generation of small amounts of $Rh(en)_2H(OH_2)^{2+}$. The potential at which $Rh(en)_2Cl(OH)^+$ begins to be reduced [to $Rh(en)_2H(OH_2)^{2+}$] is pH dependent, and at pH 11 it is *ca.* 300 mV more negative than that at which *trans*-$Rh(en)_2Cl_2^+$ is reduced (−700 mV);[6] thus, the reduction current falls to zero after only *ca.* 0.05 faraday of charge per rhodium(III) has been passed if reduction of *trans*-$Rh(en)_2Cl_2^+$ is carried out at −700 mV. The spectrum of the resulting solution shows that the *trans*-$Rh(en)_2Cl_2^+$ initially present has been converted to $Rh(en)_2Cl(OH)^+$.[10] This solution can be readily electrolyzed to yield $Rh(en)_2H(OH_2)^{2+}$ but only at more negative potentials ($\geqslant -1100$ mV) and under these conditions there is no evidence of the intensely colored intermediate described by Gillard, *et al.*, as a "rhodium(II) dimer."

These workers prepared their "rhodium(II) dimer" by reducing a solution of *trans*-$Rh(en)_2Cl_2^+$ at −1000 mV (a later, review paper[11] lists −600 mV) in an unbuffered, initially neutral, nitrate-supporting electrolyte. They observed the highest concentration of the colored intermediate after *ca.* 1 faraday of charge per rhodium(III) had been passed. In an attempt to duplicate these results we obtained a colored intermediate with a maximum absorbance at 325 nm (*vs.* 338 nm reported by Gillard,[1] Figure 2C), but the maximum absorption from this species occurred well before 1 faraday of charge per rhodium had been passed at −1000 mV. We found that a much higher concentration of the intermediate could be generated if the reduction were carried out at −700 mV rather than −1000 mV, Figure 1. The maximum absorb-

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(5) R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc. A*, 3126 (1970).

(6) J. Gulens, D. Konrad, and F. C. Anson, unpublished results.

(7) J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 658 (1964).

(8) J. V. Rund, *Inorg. Chem.*, **7**, 24 (1968).

(9) R. D. Gillard, B. T. Heaton, and D. H. Vaughan, *J. Chem. Soc. A*, 1840 (1971).

(10) H. L. Bott and A. J. Poe, *J. Chem. Soc. A*, 205 (1967).

(11) R. D. Gillard, *Rec. Chem. Progr.*, **32**, 17 (1971).

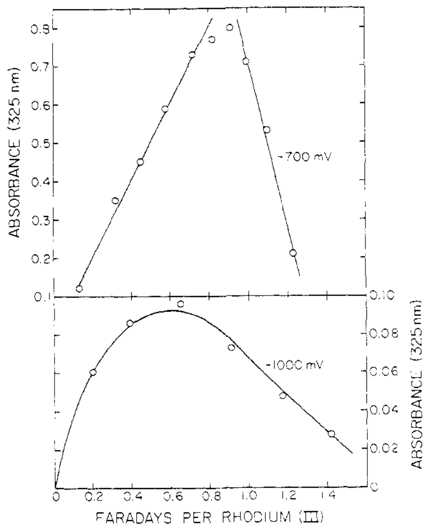

Figure 1. Dependence of the absorbance due to the intermediate generated by reduction of *trans*-Rh(en)$_2$Cl$_2^+$ upon the extent of electrolysis. Initial conditions: [Rh(en)$_2$Cl$_2^+$] = 1.1 m*M*, [NaNO$_3$] = 0.1 *M*, pH 7. The stirred mercury pool was maintained at −700 mV (upper graph) or −1000 mV (lower graph). The absorbance measurements were made with 1-mm (upper graph) and 1-cm (lower graph) cells but the plotted values correspond to 1-mm optical path lengths for both cases. That is, the maximum concentration of intermediate obtained is *ca.* nine times greater at −700 mV than at −1000 mV.

ance at 325 nm resulting from reduction at −700 mV occurred when anywhere from 0.6 to 1.3 faradays of charge per rhodium had been passed, the exact value depending on the initial pH of the solution.

Electrooxidation at −100 mV of a fully reduced solution of *trans*-Rh(en)$_2$Cl$_2^+$ at pH 13 [*i.e.*, a solution of Rh(en)$_2$H(OH$_2$)$^{2+}$] also generates the strongly absorbing species, Figure 2A. At pH 13, λ_{max} is at 345 nm but it shifts back to 325 nm upon acidification of the solution (Figure 2B). Even at potentials as negative as −700 mV a slow oxidation proceeds at a mercury electrode in solutions of Rh(en)$_2$H(OH$_2$)$^+$ (pH 13) and the same intense absorption band develops in the spectrum at 345 nm.

Analysis of solutions containing the species which gave the spectra shown in curves B and C of Figure 2 demonstrated the presence of dissolved mercury in quantities comparable to the amount of rhodium present. A rhodium(I)-mercury(II) complex thus seemed implicated as the source of the spectra obtained in partially reduced solutions of *trans*-Rh(en)$_2$Cl$_2^+$. This possibility was tested by exploring the reactions that occur when reduced solutions of *trans*-Rh(en)$_2$Cl$_2^+$ are mixed with salts of mercury(II).

Chemical Formation of the Colored Intermediate by Reaction with Hg(II). During the electrolytic reduction at −1200 mV of a 1.0 m*M* solution of *trans*-Rh(en)$_2$Cl$_2^+$ adjusted to pH 13, no highly colored intermediates are formed and the resulting solution contains a mixture of Rh(en)$_2$H(OH$_2$)$^{2+}$ and Rh(en)$_2^+$. The relative amounts of each ion are determined by reaction 1 whose equilibrium quotient, Q_1 = [Rh(en)$_2^+$]/[Rh(en)$_2$H(OH$_2$)$^{2+}$][OH$^-$], had not been measured. However, qualitative observations[5] indicate that it is certainly no greater than unity and could be much smaller.[12]

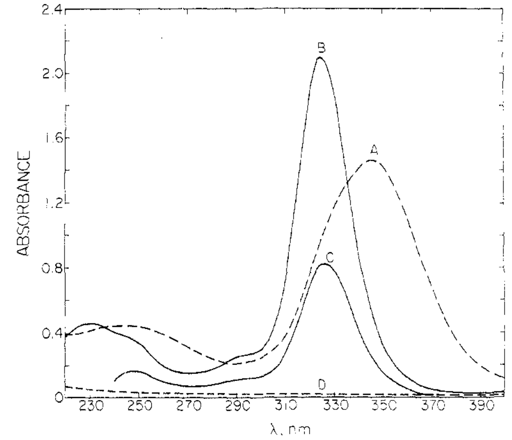

Figure 2. Spectra of the intermediate species generated electrochemically at mercury electrodes: (A) 1.1 m*M* solution of Rh(en)$_2$H(OH$_2$)$^{2+}$ in 0.1 *M* CH$_3$SO$_3$Na-0.1 *M* NaOH oxidized at −100 mV until 0.9 faraday per Rh(III) had been consumed; (B) solution A acidified with CH$_3$SO$_3$H to pH 1.9; (C) 1.1 m*M* solution of *trans*-Rh(en)$_2$Cl$_2^+$ in pH 7, 0.1 *M* NaNO$_3$ reduced at −700 mV until 0.9 faraday per Rh(III) had been consumed; (D) base line. The spectrophotometer cells employed provided an optical path length of 1 mm.

Addition of small aliquots of an oxygen-free solution of HgCl$_2$ to a solution of Rh(en)$_2$H(OH$_2$)$^{2+}$ at pH 13 produces an immediate color change. An intense absorption band develops at 345 nm which is stable for hours if oxygen and light are excluded. Figure 3 shows the development of the absorbance at 345 nm as a function of the mercury(II) to rhodium ratio. This figure also shows the increase in absorbance for a second band at 277 nm when the mercury to rhodium ratio exceeds 0.5. The band at 345 nm reaches maximum intensity at a mercury to rhodium ratio near 1:2 and the band at 277 nm becomes most intense at a ratio of 1:1 at which point its intensity is unaffected by further additions of mercury(II) (Figure 3).

Identical spectral changes and Job's plots result if a pH 13 solution of Rh(en)$_2$H(OH$_2$)$^{2+}$ is oxidized at a Hg anode at −60 mV with the Hg to Rh ratio calculated from Faraday's law and the number of anodic coulombs passed.

Figure 4 shows how the bands at 345 and 277 nm change on addition of further deaerated aliquots of HgCl$_2$ to a solution where the initial ratio of Hg to Rh is 0.5. Isosbestic points are observed at *ca.* 232, 257, and 302 nm.

The sequence of events may be reversed by adding aliquots of a reduced rhodium solution to an excess of HgCl$_2$. The band at 277 nm now appears first and grows with an increasing Rh to Hg ratio to a maximum intensity when Rh/Hg = 1.0, at which point the band at 345 nm begins to develop at the expense of the band at 277. Isosbestic points are again observed at 232, 257, and 302 nm. In a 0.1 *M* CH$_3$SO$_3$Na-0.1 *M* NaOH solution the molar absorbance of the band at 345 nm is *ca.* 35,000 M^{-1} cm^{-1} and at 277 nm it is *ca.* 25,000 M^{-1} cm^{-1}. These high absorbances are similar to those reported for similar mercury-transition metal adducts.[2,13]

These observations are consistent with the following overall reactions

$$\mathrm{Rh(en)_2H(OH_2)^{2+} + OH^- = Rh(en)_2^+ + 2H_2O} \qquad (1)$$

$$\mathrm{2Rh(en)_2^+ + Hg(II) \rightarrow (en)_2RhHgRh(en)_2^{4+}} \qquad (3)$$

$$\mathrm{(en)_2RhHgRh(en)_2^{4+} + Hg(II) + 2X^- \rightarrow 2(en)_2RhHgX^{2+}} \qquad (4)$$

where X$^-$ is most likely OH$^-$ in solutions at pH 13. The

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[12] An approximate value for Q_1 of *ca.* 1.0 was suggested[5] on the basis of the disappearance of the hydridic peak in the nmr spectrum of solutions of Rh(en)$_2$H(OH$_2$)$^{2+}$ at pH values above 13. However, this behavior could have resulted from base-catalyzed exchange of hydridic protons with those of the solvent so that a much smaller value of Q_1 is not incompatible with the presently available data.

[13] H. S. Lim and F. C. Anson, *Inorg. Chem.*, **10**, 103 (1971).

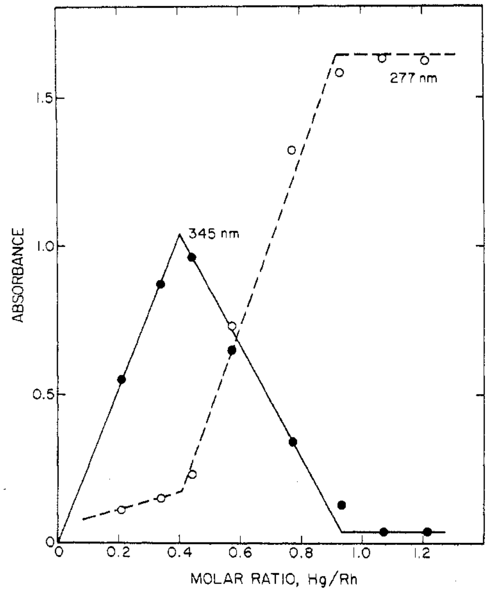

Figure 3. Variation in the absorbances at 345 (●) and 277 nm (○) as successive aliquots of $HgCl_2$ are added to $Rh(en_2)H(OH_2)^{2+}$. Initial conditions: $[Rh(en_2)H(OH_2)^{2+}] = 1.1$ m*M*, in 0.1 *M* CH_3SO_3Na-0.1 *M* NaOH. The spectrophotometric cells employed provided an optical path length of 1 mm.

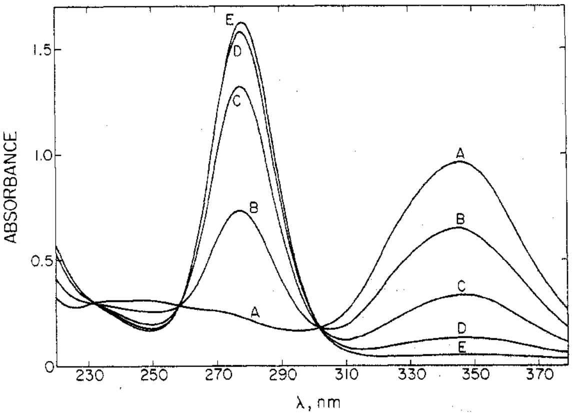

Figure 4. Spectra of mixtures of $Rh(en)_2H(OH_2)^{2+}$ with $HgCl_2$ as a function of the Hg to Rh ratio. The Hg/Rh ratios are: (A) 0.44; (B) 0.57; (C) 0.77; (D) 0.93; (E) 1.07. Initial conditions: $[Rh(en)_2H(OH_2)^{2+}] = 0.72$ m*M* in 0.1 *M* CH_3SO_3Na-0.1 *M* NaOH. The spectrophotometer cells employed provided an optical path length of 1 mm.

bands at 345 and 277 nm would then correspond to the ions $(en)_2RhHgRh(en)_2^{4+}$ and $(en)_2RhHg(OH)^{2+}$, respectively.

The stoichiometry proposed in reactions 3 and 4 was also examined by atomic absorption analysis of the Rh to Hg ratio in precipitates obtained by adding excesses of perchlorate, *p*-toluenesulfonate, or tetraphenylborate anions to solutions containing Rh to Hg ratios of 2.0 and 1.0. Solutions of the filtered (but unwashed) precipitates gave Rh to Hg ratios of 2.0 ± 0.1 and 0.8 ± 0.1 (see Experimental Section).

Anion Effects on Spectra and Complex Stability. The chemical experiments just described leave little doubt that the intensely absorbing species formed during the reduction of *trans*-$Rh(en)_2Cl_2^+$ at mercury electrodes at -700 to -1000 mV is a mercury-rhodium adduct containing two rhodium atoms per mercury atom. However, the wavelength of maximum absorption (345 nm) obtained by oxidizing a solution of $Rh(en)_2H(OH_2)^{2+}$ at -100 mV or by reacting it with mercury(II) in 0.1 *M* NaOH differs somewhat from that obtained when the complex is generated by electrochemical reduction of *trans*-$Rh(en)_2Cl_2^+$ in neutral 0.1 *M* $NaNO_3$ (325 nm in our hands; 338 nm according to ref 1). A more detailed evaluation of the effects of electrolyte composition on the observed spectra, summarized in Table II, reveals that both λ_{max} and ϵ are affected by the nature of the anion present, a result also noted by Gillard, *et al.*[1] The size of the shifts in λ_{max} appears to correlate with the complexing ability of the anions, but whether true complex formation or ion pairing is responsible for the shifts was not investigated. The primary point to note is that both the chemically and electrochemically generated mercury adducts give identical spectra when they are compared in the same background electrolyte.

The importance of coordinating anions, X^-, in stabilizing the binuclear complex, $(en)_2RhHgX^{2+}$, became apparent in experiments where we sought to form this complex in solutions having pH values below 12 with 0.1 *M* methanesulfonate as the only anion present (at concentrations above millimolar). A rapid reaction occurred when equivalent quantities of $Rh(en)_2H(OH_2)^{2+}$ and Hg(II) were mixed to produce the band at 277 nm thought to be associated with $(en)_2RhHgOH^{2+}$. However, the intensity of this band subsequently underwent a first-order decay with a rate that increased as the pH decreased. Addition of further Hg(II) to the resulting solution produced no enhancement of the absorbance at 277 nm indicating that the decomposition of $(en)_2RhHgOH^{2+}$ did not yield $Rh(en)_2H(OH_2)^{2+}$. The spectrum of the decomposed solution indicated that the rhodium was present as $Rh(en)_2(OH)_2^{+}$ [4,14] so that it seems likely that the decomposition results from an irreversible internal redox reaction.

$$(en)_2RhHgOH^{2+} + H_2O \rightarrow (en)_2Rh(OH)_2^{+} + Hg + H^+ \qquad (5)$$

The rate of this reaction is strongly affected by the nature and bulk concentration of the anion bound to the mercury(II). For example, addition of 0.1 *M* chloride to a solution of $(en)_2RhHgOH^{2+}$ buffered at pH 9 (0.05 *M* borax) which would otherwise decompose in *ca.* 45 min decreases the decomposition rate by a factor of 5. The much greater stability of this complex in pH 13 solutions reflects the ability of hydroxide to serve as the stabilizing anion. Nitrate is less effective as a stabilizer than chloride or hydroxide but more effective than methanesulfonate. The correlation seems to match the trend in mercury(II)-anion complex stabilities, the more stable complexes presumably being those in which the strength of Hg(II) as an oxidant is decreased because of the complex formation.

Kinetics of the Reaction between Hg(II) and $Rh(en)_2H(OH_2)^{2+}$. The ability of chloride ion to stabilize what we presume to be $(en)_2RhHgCl^{2+}$ toward (probably redox) decomposition was exploited in order to observe the kinetics of formation of this complex from $Rh(en)_2H(OH_2)^{2+}$ and Hg(II) at lower pH values (8.5-9.5) where the rate was slow enough to measure. In the absence of chloride the subsequent decomposition of $(en)_2RhHgOH^{2+}$ was too rapid to permit reliable values of its formation rate to be obtained. However, in the presence of 1 *M* chloride ion the decomposition proceeded to a negligible extent during the 4-10 min required for kinetic runs at pH values between 8.5 and 10. Reasonable second-order kinetic plots were obtained in solutions buffered (0.05 *F* sodium borate) at pH values in this range (Figure 5). The logarithm of the slopes of these linear plots as a function of pH, shown in Figure 6, indicates a first-order dependence of the rate on hydroxide ion. These results

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(14) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 85, 1741 (1963).

Table II. Anion and pH Effects on the Intense Absorption Band of $[(en)_2Rh]_2Hg^{4+}$ and $(en)_2RhHgX^{2+}$ Complexes

	$[(en)_2RhHg\text{-}Rh(en)_2]^{4+}$		$[(en)_2Rh\text{-}HgX]^{2+}$	
Supporting electrolyte	λ_{max}, nm	$\epsilon \times 10^{-4}$ [a] M^{-1} cm^{-1}	λ_{max}, nm	$\epsilon \times 10^{-4}$ [b] M^{-1} cm^{-1}
0.1 M CH_3SO_3Na	325[c]	5.0		
1 M CH_3SO_3H	325	5.0	267	~2.4
1 M CH_3SO_3H + 1 M NaCl			290	~2.7
0.1 M CH_3SO_3Na + 1.0 M NaCl	347	5.5	290	~3.6
0.1 M CH_3SO_3Na + 0.1 M NaOH	345	3.5	277	~2.5
0.1 M CH_3SO_3Na + 2 M NaOH	347	3.6	277	~3.5
0.1 M CH_3SO_3Na + 2 M NaOH + 1 M NaCl	347	5.5	280	~3.6

[a] Molar extinction coefficients for $[(en)_2Rh]_2Hg^{4+}$ are based on the mercury analysis (atomic absorption) of a solution of the ion in 0.1 M CH_3SO_3Na from which the other solutions were prepared. The estimated accuracy of the ϵ values is *ca.* ±20%. [b] The solutions of $(en)_2RhHgX^{2+}$ were prepared by air oxidation of the corresponding $[(en)_2Rh]_2Hg^{4+}$ solutions. The extinction coefficients given involve the assumption that this oxidation proceeds according to reaction 11 and are only approximate values. [c] Other absorption maxima in this medium: λ_{max} = 233, 250 (sh), 290 (sh), 440 nm. Respective approximate ϵ values: 10^4, 8.5×10^3, 5×10^3, 900.

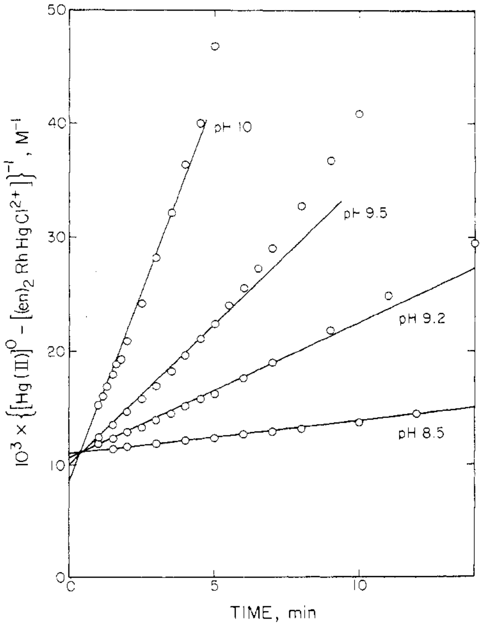

Figure 5. Second-order kinetic plots for the reaction between $Rh(en_2)H(OH_2)^{2+}$ and Hg(II) in 1 M NaCl. The value of the parameter plotted as ordinate was obtained from the known initial concentration of Hg(II), the measured absorbance at 290 nm, and an extinction coefficient for the presumed product based on the measured absorbance after the reaction had gone to completion. Other reaction conditions are given in the Experimental Section.

suggest the following mechanism for the complex formation reaction.

$$Rh(en)_2H(OH_2)^{2+} + OH^- \underset{\text{equilibrium}}{\overset{Q_1}{\rightleftharpoons}} Rh(en)_2^+ + 2H_2O \qquad (1)$$

$$Rh(en)_2^+ + Hg(II) \xrightarrow{k} (en)_2RhHg^{3+} \qquad (6)$$

$$(en)_2RhHg^{3+} + Cl^- \xrightarrow[\text{fast}]{} (en)_2RhHgCl^{2+} \qquad (7)$$

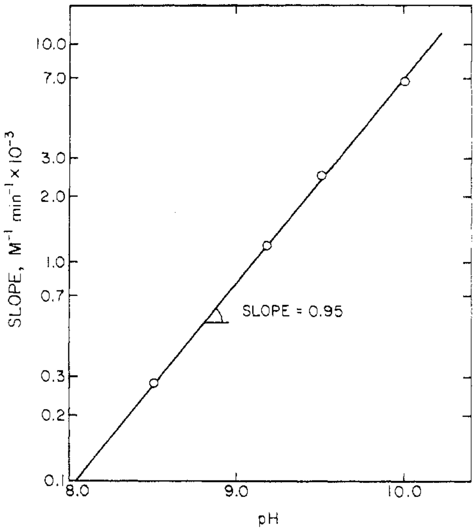

Figure 6. pH dependence of the logarithm of the slopes of the lines in Figure 5.

The rate law corresponding to this mechanism at pH values where virtually all of the rhodium is in the form of $Rh(en)_2H(OH_2)^{2+}$ and equilibrium 1 is rapidly established is

$$d[(en)_2RhHgCl^{2+}]/dt = kQ_1[OH][Rh(en)_2H(OH_2)^{2+}] \times [Hg(II)] \qquad (8)$$

The slopes of the second-order kinetic plots correspond to an average value of kQ_1 of 1.2 M^{-2} sec^{-1}.

The rate of formation of the trinuclear ions $[(en)_2Rh]_2Hg^{4+}$ from $(en)_2RhHgCl^{2+}$ and excess $Rh(en)_2H(OH_2)^{2+}$ according to

$$(en)_2RhHgCl^{2+} + Rh(en)_2H(OH_2)^{2+} + OH^- \rightarrow [(en)_2Rh]_2Hg^{4+} + Cl^- + 2H_2O \qquad (9)$$

was also measured under pseudo-first-order conditions by monitoring the decrease in absorbance at 290 nm. At pH 9.5 with $[(en)_2RhHgCl^{2+}]$ = 0.05 mM and $[(en)_2RhH(OH_2)^{2+}]$ = 1.0 mM, the pseudo-first-order rate constant obtained was *ca.* 1×10^{-4} sec^{-1}. Assuming a rate law of the form

$$-d[(en)_2RhHgCl^{2+}]/dt = k'Q_1[OH^-][Rh(en)_2H(OH_2)^{2+}] \times [(en)_2RhHgCl^{2+}] \qquad (10)$$

it follows that $k'/k = 2500$.

The concentration of Hg^{2+} in equilibrium with a mercury electrode at −1000 mV can be calculated to be *ca.* 10^{-54} M. The total concentration of Hg(II) (*i.e.*, $[Hg^{2+}] + [HgOH^+] + [Hg(OH)_2]$) in a solution at pH 8 will be *ca.* 10^6 times greater than $[Hg^{2+}]$[15] so the concentration of Hg(II) at the electrode surface is *ca.* 10^{-48} M and essentially constant. Thus, during the electrolysis of a 10^{-3} M solution of *trans*-$Rh(en)_2Cl_2^+$ at −1000 mV in a solution at pH 8, the rate at which $(en)_2RhHgCl^{2+}$ would be formed according to eq 1, 6, and 7 is only *ca.* 1.2×10^{-57} mol liter^{-1} sec^{-1}.[16] The resulting $(en)_2RhHgCl^{2+}$ would then be converted to the trinuclear complex, $[(en)_2Rh]_2Hg^{4+}$, about 2500 times as fast, so that the rate-determining step is the formation of $(en)_2RhHgCl^{2+}$. In fact, the trinuclear complex, $[(en)_2Rh]_2Hg^{4+}$, is actually

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(15) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17, 64 (1964).

(16) For the purposes of this rough calculation we have neglected the fact that the Hg(II) will be present chiefly as hydroxide complexes in the absence of excess chloride ion but as chloro or hydroxychloro complexes in 1 M NaCl at the pH values where the kinetic measurements were made.

obtained during such an electrolysis at a rate many orders of magnitude greater than the value calculated above. Thus, the generation of the mercury-rhodium adducts during electrolyses cannot proceed homogeneously according to the scheme of reactions 1, 6, and 7. The fact that $Rh(en)_2^+$ appears to be strongly adsorbed on mercury electrodes[6] suggests that the electrolytic preparation of the mercury-rhodium complexes may proceed by a series of heterogeneous reactions that are much more rapid than their homogeneous analogs.

Reactions with Oxygen. Gillard, *et al.*,[1,5] reported that the electrogenerated species they believed to be a rhodium(II) dimer (*i.e.*, the species we believe to be $[(en)_2Rh]_2Hg^{4+}$) reacts with oxygen to produce a new species with λ_{max} at 280 nm. When a solution of $[(en)_2Rh]_2Hg^{4+}$ prepared chemically from $Rh(en)_2H(OH_2)^{2+}$ and Hg(II) in the ratio of 2 to 1 is exposed to oxygen at pH 13 a rapid reaction occurs; the absorption band at 345 nm disappears and a new band appears at 277 nm which matches that obtained when the binuclear mercury-rhodium complex is prepared chemically using a 1 to 1 ratio of rhodium to mercury. Similar spectral changes also occur in acidic solutions of the trinuclear complex as indicated in Table II. This behavior is understandable on the basis of the following reaction.

$$[(en)_2Rh]_2Hg^{4+} + O_2 + X^- \rightarrow (en)_2RhHgX^{2+} + (en)_2Rh(OOH)X^+ \qquad (11)$$

Oxidation by oxygen of the rhodium(I) in the complex has the effect of shifting the rhodium(I) to mercury(II) ratio below 2.0 which has been shown to lead to the dissociation of the trinuclear adduct into the binuclear complex for which $\lambda_{max} = 277$ nm (Figure 4). The rhodium-hydroperoxide species, described by Gillard, *et al.*,[5] does not absorb significantly at this wavelength. Continued exposure of the resulting solution to oxygen leads to the slow diminishment of the band at 277 nm, as well. This decrease presumably reflects the eventual total oxidation of all of the rhodium(I) and eliminates the remaining rhodium-mercury bond that is responsible for the high absorbance at 277 nm.

Thus, the chemically prepared complex, $[(en)_2Rh]_2Hg^{4+}$, displays the same spectral behavior toward oxygen and the anions present in the electrolyte as does the electrochemically prepared species described in ref 1, adding further support to our contention that they are the same species.

Reaction with Acid. The value of λ_{max} changes from 345 to 325 nm when an alkaline solution of $[(en)_2Rh]_2Hg^{4+}$ is acidified with methanesulfonic acid. This spectral shift is rapidly reversible and does not involve the breaking of a rhodium-mercury bond because acidification of an alkaline solution of the binuclear complex, $(en)_2Rh\text{-}HgOH^{2+}$, produces a different spectrum ($\lambda_{max} = 267$ nm, $\epsilon \sim 24{,}000$). However, if chloride (or nitrate) anions are added to the acidic solution of $[(en)_2Rh]_2Hg^{4+}$, the spectrum rapidly changes to that characteristic of the binuclear complexes, $(en)_2RhHgX^{2+}$, Table II. The overall reaction occurring is evidently

$$[(en)_2Rh]_2Hg^{4+} + H_3O^+ + X^- \rightleftarrows (en)_2RhHgX^{2+} + Rh(en)_2H(H_2O)^{2+} \qquad (12)$$

In acidic media the sensitivity of equilibrium 12 to the nature of the anion present (Table II) reflects the stability of the resulting mercury(II)-anion bond. In sufficiently alkaline solutions the equilibrium favors the reactants over products so completely that the nature of the other anions present becomes unimportant.

Discussion

The formation of mercurated products when certain transition-metal complexes are *oxidized* at mercury electrode is well established.[2,17] That electrode reaction products containing mercury can also be formed during reductions at mercury electrodes is also well known,[17-19] although the present case appears to be the first example involving a simple amine complex in aqueous solution. One of the most surprising features of the behavior of *trans*-$Rh(en)_2Cl_2^+$ is the fact that its reduction leads to concomitant oxidation of the mercury electrode at potentials as negative as -1000 mV. This observation imposes a minimum value on the equilibrium quotient for the reaction

$$2Rh(en)_2^+ + Hg^{2+} \rightleftarrows [(en)_2Rh]_2Hg^{4+} \qquad (13)$$

$$Q_{13} = \frac{[((en)_2Rh)_2Hg^{4+}]}{[Rh(en)_2^+]^2[Hg^{2+}]} > 10^{54}$$

This lower limit on Q_{13} is calculated from the standard potential of the Hg/Hg^{2+} couple and the assumption that the mercury oxidation reaction proceeds reversibly at -1000 mV. (If the reaction were irreversible the lower limit on Q_{13} would be even larger.) This large value of Q_{13} points out the intrinsic stability of the rhodium-mercury bonds in this complex and is consistent with its persistence, once formed, even in acidic solutions where the equilibrium concentration of $Rh(en)_2^+$ is extremely low.

Although the charge distribution in the ions $[(en)_2Rh]_2Hg^{4+}$ and $(en)_2RhHgX^{2+}$ is not known, the fact that they can be produced by homogeneous reactions between Hg(II) and a source of Rh(I), as well as by electrolysis at a mercury *anode* in a solution of $Rh(en)_2H(OH_2)^{2+}$ at suitable pH values, makes it natural to regard the ions as compounds of Rh(I) and Hg(II). Nevertheless, the available data are insufficient to rule out other equivalent assignments of the relative valences of the two metals in these complexes. Possibilities such as $(en)_2Rh^{III}Hg^0Rh^I(en)_2^{4+}$ or $(en)_2Rh^{III}Hg^0X^{2+}$ seem unlikely because we were never able to prepare the ions by exposing an unelectrolyzed mercury pool to salts of Rh(III) or a mixture of Rh(III) and Rh(I) [in the form of $Rh(en)_2H(OH_2)^{2+}$ at high pH]. However, the possibility could not be conclusively eliminated that the trinuclear ion might be $(en)_2Rh^{II}Hg^0Rh^{II}(en)_2^{4+}$, formed by a redox reaction between Hg(II) and Rh(I) in the homogeneous synthesis or by abstraction of Hg(0) from the electrode by Rh(II) produced from electrochemical reduction of Rh(III) in the heterogeneous synthesis. The strongest evidence arguing against this possibility is the fact that the electrochemical preparation of the trinuclear species is facilitated when the mercury electrode is held at the most positive potentials at which the reduction of *trans*-$Rh(en)_2Cl_2^+$ still proceeds. This potential dependence has no evident explanation if Rh(II) and Hg(0) are the precursors to the trinuclear complex but it is nicely accommodated by the need to produce Rh(I) and Hg(II).

The primary factor that led to the previous erroneous identification of $[(en)_2Rh]_2Hg^{4+}$ as $[(en)_2Rh\text{-}Rh(en)_2]^{4+}$ was the observation that about one electron is required to convert *trans*-$Rh(en)_2Cl_2^+$ to the product complex.[1] This feature of the electrochemical behavior is explained according to the

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[17] R. E. Dessy, F. E. Stary, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, **88**, 471 (1966).

[18] N. S. Hush and K. B. Oldham, *J. Electroanal. Chem.*, 6, 34 (1963).

[19] R. E. Dessy and L. A. Bares, *Accounts Chem. Res.*, **5**, 415 (1972).

present interpretation by the following pair of cathodic and anodic electrode reactions proceeding simultaneously.

$$\mathrm{Rh(en)_2Cl_2^+ + 2e^- \rightarrow Rh(en)_2^+ + 2Cl^-} \qquad (14)$$

$$\mathrm{2Rh(en)_2^+ + Hg \rightarrow [(en)_2Rh]_2Hg^{4+} + 2e^-} \qquad (15)$$

The resulting overall electrode reaction consumes only one electron per rhodium despite the fact that the initial rhodium(III) complex is reduced to a complex containing rhodium(I).

$$\mathrm{2Rh(en)_2Cl_2^+ + 2e^- + Hg \rightarrow [(en)_2Rh]_2Hg^{4+} + 4Cl^-} \qquad (16)$$

If the reduction of *trans*-$\mathrm{Rh(en)_2Cl_2^+}$ at mercury electrodes proceeded exclusively as indicated by reactions 14 and 16, the concentration of $\mathrm{[(en)_2Rh]_2Hg^{4+}}$ would reach its maximum value when precisely 1 faraday of charge per Rh(III) had been consumed by the electrolysis. In fact, the maximum concentration of this ion appears at charge values that range from *ca.* 0.7 to 1.3 faradays per Rh(III) depending on the initial pH of the solution and the potential at which the reduction is conducted. Furthermore, the maximum concentration obtained never corresponds to more than *ca.* half of the initial rhodium(III) being converted to $\mathrm{[(en)_2Rh]_2Hg^{4+}}$. The remainder of the rhodium is presumably present as a mixture of unreduced *trans*-$\mathrm{Rh(en)_2Cl_2^+}$, $\mathrm{Rh(en)_2H(OH_2)^{2+}}$, and $\mathrm{Rh(en)_2(OH)Cl^+}$ (formed *via* reaction 2). These observations suggest that the $\mathrm{Rh(en)_2^+}$ produced in reaction 14 is partitioned between subsequent reaction with the electrode according to reaction 15, which yields $\mathrm{[(en)_2Rh]_2Hg^{4+}}$, and reaction 17, which yields $\mathrm{Rh(en)_2H(OH_2)^{2+}}$.

$$\mathrm{Rh(en)_2^+ + 2H_2O \rightarrow Rh(en)_2H(OH_2) + OH^-} \qquad (17)$$

The fact that the maximum concentration of $\mathrm{[(en)_2Rh]_2Hg^{4+}}$ appears near the point at which 1 faraday of charge has passed in initially neutral solutions[1] is thus a fortuitous result. Indeed, charge values differing considerably from 1.0 faraday per Rh(III) are obtained when lower pH values or more negative reduction potentials are employed because these factors affect the partitioning of $\mathrm{Rh(en)_2^+}$ between reactions 15 and 17. The strong potential dependence of the products of the electrolysis is also readily rationalized in terms of reactions 12, 13, and 15. Reaction 12 is diffusion controlled at electrode potentials more negative than *ca.* −600 mV. Reaction 15 is favored by less negative potentials because oxidation of the mercury electrode is involved. Thus, as the potential is made more negative the rhodium(I) product of reaction 14 is increasingly diverted from reaction 15 by reaction 17 which is not potential dependent. At sufficiently negative potentials ($\geqslant -1100$ mV) all of the $\mathrm{Rh(en)_2^+}$ produced in reaction 14 is consumed by reaction 17 so that no spectral evidence of mercury-rhodium complexes appears and a clean two-electron reduction is observed.

A remaining question is why the concentration of $\mathrm{[(en)_2Rh]_2Hg^{4+}}$ ion generated by reduction of *trans*-$\mathrm{Rh(en)_2Cl_2^+}$ at −700 to −1000 mV decreases from its maximum value upon continued electrolysis at the same potential (Figure 1). The decrease is definitely associated with the continued passage of current because it ceases if the electrolysis is terminated. Separate studies of the electrochemical behavior of chemically prepared solutions of $\mathrm{[(en)_2Rh]_2Hg^{4+}}$ containing no other rhodium complexes have shown that this complex is electrochemically reduced [to produce $\mathrm{Rh(en)_2H(OH_2)^{2+}}$ and $\mathrm{Hg^0}$] in the same potential range where it can be generated *via* reaction 15 during the reduction of *trans*-$\mathrm{Rh(en)_2Cl_2^+}$.[6] Thus, it appears that both the amount and the persistence of the $\mathrm{[(en)_2Rh]_2Hg^{4+}}$ ion formed during controlled potential reduction of $\mathrm{Rh(en)_2Cl_2^+}$ at mercury electrodes are the result of a delicate balance between opposing reactions whose relative rates depend upon the varying concentrations of the products and reactant as well as the potential and pH at the surface of the electrode.

A more detailed account of this aspect of the electrochemistry, particularly the evidence for very strong adsorption of $\mathrm{Rh(en)_2^+}$ on the surface of mercury electrodes, will be given in a forthcoming report.[6]

Conclusions

The previously described intermediate[1] that can be electrochemically generated by reduction of *trans*-$\mathrm{Rh(en)_2Cl_2^+}$ at mercury electrodes has been shown to be a mercury(II)-bridged trinuclear complex of rhodium(I), rather than a "rhodium(II) dimer." The observation that the mercury electrode is oxidizable at potentials as negative as those required to reduce *trans*-$\mathrm{Rh(en)_2Cl_2^+}$ reveals the great stability of the mercury-rhodium bonds in $\mathrm{[(en)_2Rh]_2Hg^{4+}}$. It seems reasonable to regard the formation of this complex as the result of a Lewis acid-base reaction in which the extreme basicity of the $\mathrm{(en)_2Rh^+}$ ion is expressed.

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Registry No. *trans*-$\mathrm{[Rh(en)_2Cl_2]ClO_4}$, 41367-59-3; $\mathrm{Rh(en)_2H(OH_2)^{2+}}$, 41367-60-6; Hg(II), 14302-87-5; $\mathrm{[(en)_2Rh]_2Hg(C_6H_5SO_3)_4}$, 41367-61-7; $\mathrm{[(en)_2Rh]_2Hg(OH)_2(C_6H_5SO_3)_2}$, 41429-83-8.