variation of the anionic ligand. The additional binding modes of the chloro complex reflect the relative weakness of the Au–Cl bond compared to the Au–SR bond. Thus, Cl^- is displaced by cys-34 ($AlbSAuPEt_3$ formation) and also by other ligands on albumin which cannot displace $ATgS^-$.

Under physiological conditions during chrysotherapy, albumin concentrations in serum far exceed the levels of gold obtained with auranofin. Thus $AlbSAuPEt_3$ will be the dominant circulating form of gold until the oxidation of the phosphine to Et_3PO is completed over approximately 24 h. Et_3PAuCl has antiarthritic activity but causes severe gastrointestinal irritation.[28] Reaction at additional binding sites not available to auranofin may in part explain this difference in biological activities, if the Et_3PAuCl concentration exceeds the availability of membrane sulfhydryl sites in the stomach or gut.

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Kinetics and Mechanism of the Reduction of Rhodium(III) Complexes $Rh(H_2O)_5X^{2+}$ by Cr^{2+}

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Reduction of the yellow rhodium(III) ions $[Rh(H_2O)_6]^{3+}$, $[Rh(H_2O)_5Cl]^{2+}$, and $[Rh(H_2O)_5Br]^{2+}$ by Cr^{2+} in aqueous $HClO_4$ solution to give the green rhodium(II) aqua dimer Rh_2^{4+} has been studied by the stopped-flow method at 25 °C, $I = 2.0$ M ($LiClO_4$). An $[H^+]^{-1}$ term is dominant in the reduction of $[Rh(H_2O)_6]^{3+}$ ($pK_a = 3.4$), and rate constants ($M^{-1}\ s^{-1}$) for the different oxidants are $[Rh(H_2O)_5OH]^{2+}$ (2.3×10^5), $[Rh(H_2O)_5Cl]^{2+}$ (2.2×10^3), $[Rh(H_2O)_5Br]^{2+}$ ($>8 \times 10^3$). The products $[Cr(H_2O)_5Cl]^{2+}$ and $[Cr(H_2O)_5Br]^{2+}$ have been identified, and reactions are of the inner-sphere type. Addition of Cr^{3+} (0.03 M) and Co^{2+} (0.03 M) as possible reactants with monomeric Rh^{2+} had no effect on the rate of formation of Rh_2^{4+}. Free halide ions react with Rh_2^{4+} and induce Rh metal formation. Reduction of $[Rh(H_2O)_6]^{3+}$ with V^{2+} also gives Rh metal, probably as a result of outer-sphere generation of monomeric Rh^{2+}.

Introduction

The aquarhodium(II) ion was first prepared by Maspero and Taube.[1] Its chromatographic behavior compared to that of the 3+ Rh(III) and Cr(III) aqua ions has indicated a dimeric 4+ structure, which has only slight paramagnetism from proton NMR measurements. The dimer has a single metal–metal bond and is believed to have the structure $[Rh_2(H_2O)_{10}]^{4+}$. Other studies have enlarged on these properties,[2-4] but on the whole the ion has not been extensively studied. In addition to investigating the manner of its formation we intended studying substitution reactions with simple monodentate 1– anions. These attempts lead to formation of Rh metal, which in the case of the halide ions is believed to be of some relevance to the Rh(III) to Rh(II) redox interconversions described.

Experimental Section

Hexaaquarhodium(III) was prepared by the method of Ayres and Forrester[5] with some modifications. The reaction of $RhCl_3 \cdot xH_2O$ (Johnson Matthey Chemicals) and concentrated (72%) perchloric acid (BDH, AnalaR) was carried out in a three-necked round-bottomed flask complete with thermometer and condenser, which was connected to a water pump to reduce the pressure and hence help concentrate the solution. The reaction mixture obtained was diluted and loaded onto a Dowex 50W-X8 column (1.6 cm in diameter, 10 cm long) washed with 0.5 M and then 1.0 M $HClO_4$, which resulted in the removal of chloro complexes of charge <2.0. The major fraction of $[Rh(H_2O)_6]^{3+}$ was eluted as a bright yellow band with 2 M $HClO_4$. Solutions were standardized spectrophotometrically by using the known spectrum of $[Rh(H_2O)_6]^{3+}$, with peaks at 311 ($\epsilon = 67.4\ M^{-1}\ cm^{-1}$) and 396 nm ($\epsilon = 62\ M^{-1}\ cm^{-1}$).[6] The two absorbance peaks are well-defined and are of nearly equivalent intensity, not as indicated in ref 7.

Solutions of the green aqua Rh(II) dimer were prepared according to the method of Ziolkowski and Taube,[2] which involved the addition of stoichiometric amounts of Cr^{2+} to a 0.03 M solution of $[Rh(H_2O)_6]^{3+}$ in 2 M $HClO_4$. After separation of the different bands on a Dowex 50W-X2 column, the Rh_2^{4+} ion was eluted with 3 M $HClO_4$ and gave the literature spectrum with peaks at 402 ($\epsilon = 63\ M^{-1}\ cm^{-1}$ per Rh) and 648 nm ($\epsilon = 46.5\ M^{-1}\ cm^{-1}$).[4] Solutions stored under N_2 at 0 °C were stable for ~3 weeks. Subsequently some disproportionation to Rh metal and Rh(III) was noted.

To prepare solutions of $[Rh(H_2O)_5Cl]^{2+}$ and $[Rh(H_2O)_5Br]^{2+}$ a freshly generated (unpurified) solution of Rh_2^{4+} was treated with an excess of Cl_2 (gas) or Br_2 in solution (eq 1). The 2+ ions were purified

$$Rh_2^{4+} + X_2 \rightarrow [Rh(H_2O)_5X]^{2+} \tag{1}$$

chromatographically by elution from a Dowex 50W-X8 resin with 0.5 M $HClO_4$ and concentrated by reloading onto a short column and eluting with 2 M $HClO_4$ to give >0.1 M solutions. Peak positions (and ratios) were consistent with literature spectra: for $[Rh(H_2O)_5Cl]^{2+}$, 335 ($\epsilon = 50\ M^{-1}\ cm^{-1}$) and 426 nm ($\epsilon = 50.4\ M^{-1}\ cm^{-1}$);[6] for $[Rh(H_2O)_5Br]^{2+}$, 342 ($\epsilon = 70.6\ M^{-1}\ cm^{-1}$) and 441 nm ($\epsilon = 70.6\ M^{-1}\ cm^{-1}$).[2] Essential features of the latter were confirmed in a quantitative experiment in

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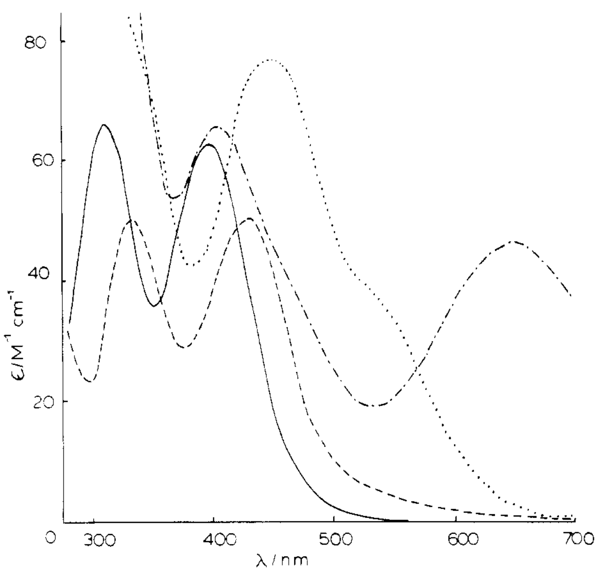

Figure 1. UV-vis spectra for $[Rh(H_2O)_6]^{3+}$ (—), $[Rh(H_2O)_5Cl]^{2+}$ (- -), $[Rh(H_2O)_5Br]^{2+}$ (···), and $[Rh_2(H_2O)_{10}]^{4+}$ (–·–) (ε's per Rh) in 1–3 M $HClO_4$ solutions.

which Br_2 was added to Rh_2^{4+} to give a spectrum with peaks at 340 (sh) ($\epsilon = 71.4$ M^{-1} cm^{-1}), 446 ($\epsilon = 74.8$ M^{-1} cm^{-1}), and 530 nm (sh) ($\epsilon = 36$ M^{-1} cm^{-1}). These values were used subsequently. Reference 8 gives an ϵ value of 81 M^{-1} cm^{-1} for the main peak at 450 nm. All relevant spectra are shown in Figure 1.

Solutions of hexaaquachromium(II) and -vanadium(II) were obtained by electrolytic reduction of $[Cr(H_2O)_6]^{3+}$ and the V(IV) vanadyl ion $[VO(H_2O)_5]^{2+}$, respectively, at a Hg-pool cathode by procedures previously described.[9] These were standardized by using known absorption coefficients.

Experiments involving Cr^{2+}, V^{2+}, and Rh_2^{4+} were carried out under rigorous air-free conditions (N_2). All transfers were using Teflon needles. The $[H^+]$ of the solutions was determined by titrating the total $[H^+]$ after removal of the metal ions on an Amberlite IR120(H) ion-exchange resin. Lithium perchlorate (Aldrich) was recrystallized twice prior to use. A sample of hydrated cobalt(II) perchlorate (G. F. Smith) was used without further purification.

Absorbance changes for the Cr^{2+} reductions were consistent with the stoichiometric equation (2). All kinetic measurements (25 °C) were on

$$2Cr^{2+} + 2Rh(III) \rightarrow 2Cr(III) + Rh_2^{4+} \tag{2}$$

a Dionex D-110 stopped-flow spectrophotometer. The ionic strength of run solutions was adjusted to 2.0 M ($LiClO_4$), and the Rh(III) was in >8-fold excess of the Cr^{2+} reductant, thus avoiding reduction of Rh_2^{4+} to Rh metal. Formation of Rh_2^{4+} was monitored at the 640-nm peak. First-order plots of absorbance changes $\ln(A_\infty - A_t)$ against time were linear to 3 half-lives; the slope gave first-order rate constants k_{obsd}.

Experiments in which the reactions of Rh_2^{4+} with anions were examined used the following AnalaR grade reagents: NaCl, NaBr, NaI, Na_2SO_4. Sodium thiocyanate (Reagent grade) was recrystallized from ethanol.

Errors in rate constants were obtained by using an unweighted least-squares treatment.

Results

Cr^{2+} Reduction of $[Rh(H_2O)_6]^{3+}$. At $[H^+] = 1.5$ M a first-order dependence of k_{obsd} (Table I) on $[Rh(H_2O)_6]^{3+}$, 0.010–0.035 M, was observed. This plot gives a second-order rate constant (k) of 57 ± 6 M^{-1} s^{-1}. Figure 2 illustrates the dependence of second-order rate constants on $[H^+]^{-1}$, which conforms to (3), where

$$k = a[H^+]^{-1} \tag{3}$$

$a = 93 \pm 3$ s^{-1}. From the least-squares fit a small negative intercept is obtained (which is meaningless), and contributions from an $[H^+]$-independent path are therefore small and negligible. Addition of $[Cr(H_2O)_6]^{3+}$ (0.03 M) and $[Co(H_2O)_6]^{2+}$ (0.03 M) had no measurable effect on rate constants outside experimental error.

Table I. Rate Constants k_{obsd}(25 °C) for the Cr^{2+} Reduction of $[Rh(H_2O)_6]^{3+}$, $I = 2.0$ M ($LiClO_4$)

$[H^+]$/M	$10^3[Cr^{2+}]$/M	10^2[Rh(III)]/M	k_{obsd}/s^{-1}
0.76	2.0	2.1	2.57
1.0	2.0	2.1	1.94
1.25	1.0	2.1	1.59
1.25	2.0	2.1	1.59
1.37	1.0	2.1	1.48
1.5	2.0	1.0	0.63
	2.0	2.0	1.21
	2.0	2.1	1.34
	2.0	2.1	1.30
	2.0	2.5	1.43
	3.0	3.0	1.70
	2.0	3.5	2.10
	2.0	2.1	1.34[a]
	2.0	2.1	1.18[b]
	2.0	2.1	1.14[c]

[a] 0.030 M $[Cr(H_2O)_6]^{3+}$ added. [b] 0.020 M $[Co(H_2O)_6]^{2+}$ added. [c] 0.030 M $[Co(H_2O)_6]^{2+}$ added.

Table II. Rate Constants k_{obsd}(25 °C) for the Cr^{2+} Reduction of $[Rh(H_2O)_5Cl]^{2+}$, $I = 2.0$ M ($LiClO_4$)

$[H^+]$/M	$10^3[Cr^{2+}]$/M	$10^2[RhCl^{2+}]$/M	k_{obsd}/s^{-1}
1.0	1.5	1.25	26
1.5	1.5	1.25	27
0.93	1.5	1.25	36
0.85	2.0	2.0	43
1.0	2.0	2.5	55
1.0	3.5	3.0	66

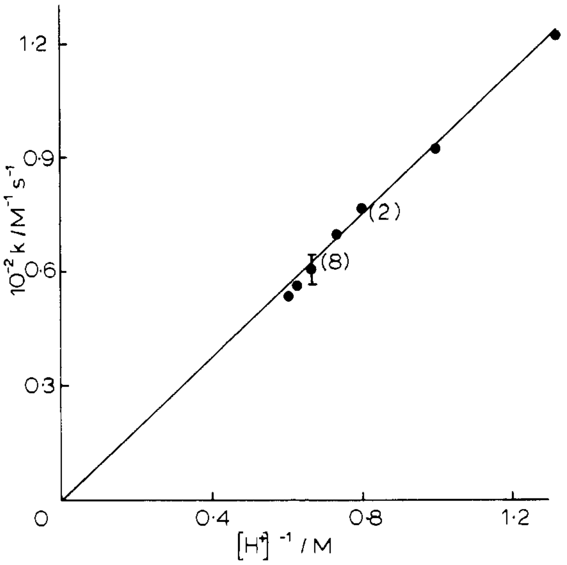

Figure 2. Dependence of second-order rate constants, k(25 °C), for the Cr^{2+} reduction of $[Rh(H_2O)_6]^{3+}$ on $[H^+]$, $I = 2.0$M ($LiClO_4$).

Cr^{2+} Reduction of $[Rh(H_2O)_5Cl]^{2+}$. First-order rate constants k_{obsd} are listed in Table II. From the slope of a plot of k_{obsd} against $[Rh(H_2O)_5Cl^{2+}]$ the second-order rate constant $k = (2.20 \pm 0.24) \times 10^3$ M^{-1} s^{-1} was obtained.

Cr^{2+} Reduction of $[Rh(H_2O)_5Br]^{2+}$. At 25 °C (and 5 °C) the reaction was complete within mixing time (~5 ms). With $[Cr^{2+}] = 3.5 \times 10^{-3}$ M and $[Rh(H_2O)_5Br^{2+}] = 3.5 \times 10^{-2}$ M the first-order rate constant at 25 °C is estimated to be >300 s^{-1}, indicative of a second-order rate constant $>8 \times 10^3$ M^{-1} s^{-1}.

V^{2+} Reduction of $[Rh(H_2O)_6]^{3+}$. Under all conditions investigated with V^{2+} or Rh(III) in excess, Rh metal was formed. Reactant concentrations were $[V^{2+}] = (1.9–4.5) \times 10^{-3}$ M, $[Rh(H_2O)_6^{3+}] = (4.5–19) \times 10^{-3}$ M, and $[H^+] = 1.5–2.0$ M. In an experiment with 1:1 reactants substantial amounts of Rh-

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$(H_2O)_6^{3+}$ remained, and disproportionation of the Rh(II) generated is possible. As an alternative, evolution of O_2 was tested for by passing N_2 gas through the reactant mixture and then into Cr^{2+} or a solution of the sepulchrate cage complex $[Co(sep)]^{2+}$.[12] No O_2 was detected by this procedure.

Reactions of Anions with Rh_2^{4+}. With Cl^-, Br^-, I^- and sulfate at concentrations in the range $(2-5) \times 10^{-4}$ M, and $[Rh_2^{4+}] = (0.5-2.0) \times 10^{-3}$ M, $[H^+] = 0.5-1.0$ M, and $I = 1.0$ M ($LiClO_4$), Rh metal formation was observed. A yellow precipitate was obtained with thiocyanate, which is probably a μ-thiocyanato polymer. No substitution reactions could be monitored.

Discussion

Figure 2 for the Cr^{2+} reduction of $[Rh(H_2O)_6^{3+}]$ clearly implicates $RhOH^{2+}$ as reactant with little or no contribution from the path involving the hexaaqua ion. From an acid-dissociation pK_a of 3.4 for $[Rh(H_2O)_6]^{3+}$,[10,13] a true rate constant for the path involving Cr^{2+} reduction of $RhOH^{2+}$ is 2.3×10^5 M^{-1} s^{-1}. The Cr^{2+} reductions of RhX^{2+} ions ($X^- = OH^-, Cl^-, Br^-$) can be formulated as involving outer-sphere electron transfer (4) followed by (5), or inner-sphere electron transfer (6) followed by (7). In

$$Cr^{2+} + RhX^{2+} \rightarrow Cr(III) + Rh^{2+} + X^- \qquad (4)$$

$$2Rh^{2+} \rightarrow Rh_2^{4+} \qquad (5)$$

$$Cr^{2+} + RhX^{2+} \rightarrow (CrXRh)^{4+} \qquad (6)$$

$$2(CrXRh)^{4+} \rightarrow 2CrX^{2+} + Rh_2^{4+} \qquad (7)$$

the case of the Cr^{2+} reduction of $[Rh(H_2O)_6]^{3+}$ no effect of $[Cr(H_2O)_6]^{3+}$ (0.03 M) in supressing formation of Rh^{2+} in (4) by the back-reaction was noted (Table I). Moreover with $RhCl^{2+}$ and $RhBr^{2+}$ it has been demonstrated that $CrCl^{2+}$ and $CrBr^{2+}$ are products.[2,4] Had Cl^- and Br^- been released as free anions, then reaction with the Rh_2^{4+} product would have resulted in formation of Rh metal. Also, the pronounced $[H^+]^{-1}$ dependence for the Cr^{2+} reduction of $[Rh(H_2O)_6]^{3+}$ carries the implication of an inner-sphere reaction involving $RhOH^{2+}$. Outer-sphere reactions would not discriminate as markedly between the aqua and hydroxo forms.[14]

Different behavior is observed with V^{2+} as reductant, when Rh metal is formed.[1] Previous work has demonstrated a clear preference of V^{2+} for outer-sphere electron-transfer pathways.[15] The fact that a $(CrXRh)^{4+}$ binuclear intermediate is generated in (6) presumably stabilizes the Rh^{2+} until dimerization to Rh_2^{4+} can occur. The formation of Rh metal in the V^{2+} reaction is consistent with an outer-sphere reaction as in (4), which generates monomeric Rh^{2+}. Since O_2 formation was not detected, disproportionation of Rh^{2+} to Rh metal and Rh(III) is likely as the dominant process. We have not been able to quantity any of these processes, and although Rh(III) is formed, this may not be a clean reaction with formation of only $[Rh(H_2O)_6]^{3+}$. It is possible that addition of coordinating anions to Rh_2^{4+} results in the formation of increasing amounts of monomeric Rh^{2+} due to a weakening of the Rh–Rh bond, and hence Rh metal is formed. Addition of another d^7 ion, Co^{2+} (up to 0.03 M), has no influence on either the Cr^{2+} or V^{2+} reductions of $[Rh(H_2O)_6]^{3+}$. Here the stabilization of Rh^{2+} by formation of a $(RhCo)^{4+}$ dimer was considered possible. That no such effect is observed suggests that the 2+ ions do not have a sufficient affinity for each other (in accordance with the observation that Co^{2+} does not itself dimerize).

Finally the order of effectiveness of the bridging halide ions $Br^- > Cl^-$ in the Cr^{2+} reduction of RhX^{2+} is consistent with the normal order of effectiveness $I^- > Br^- > Cl^-$ of halide ions, which has been observed previously in other metal ion redox processes.[16]

Acknowledgment. We are grateful to the SERC for a studentship (to E.F.H.), to the British Council for financial support, and to Wroclaw University in Poland for leave of absence (to M.M.). We also wish to acknowledge the helpful collaboration of Professor J. J. Ziolkowski and the loan of rhodium compounds from Johnson Matthey Chemicals.

Registry No. $[Rh(H_2O)_6]^{3+}$, 16920-31-3; $[Rh(H_2O)_5Cl]^{2+}$, 15696-62-5; $[Rh(H_2O)_5Br]^{2+}$, 48019-52-9; Cr^{2+}, 22541-79-3; V^{2+}, 15121-26-3; Rh_2^{4+}, 55569-94-3; Cl^-, 16887-00-6; Br^-, 24959-67-9; I^-, 20461-54-5; SO_4^{2-}, 14808-79-8.

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Mechanism of Electron Transfer to Pentaammine(pyridine)cobalt(III) Complexes by Aliphatic Radicals, Hexaaquovanadium(II), and Hexaammineruthenium(II) Ions

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The rates of electron transfer to a series of pentaammine(pyridine)cobalt(III) complexes, $Co(NH_3)_5(NC_5H_4X)^{3+}$ (X = 3-CN, 3-Cl, H, 4-CH_3, 4-$C(CH_3)_3$, and 4-$N(CH_3)_2$), have been determined. A kinetic competition method based on the homolytic scission of the chromium–carbon bond in $(H_2O)_5CrC(CH_3)_2OH^{2+}$ was used to evaluate rate constants for the reducing agent $\cdot C(CH_3)_2OH$, whereas direct measurements were carried out for the reductions by $V(H_2O)_6^{2+}$ and $Ru(NH_3)_6^{2+}$. In all three cases the rate constants show mild and similar sensitivity to the substituent on the pyridine ring. The variations are well correlated by the Hammett equation, the reaction constants being 1.1, 1.3, and 1.5, respectively. Arguments are advanced that in each case the reactions proceed by direct outer-sphere electron transfer to the cobalt(III) and not by a "chemical mechanism" entailing prior electron transfer to the pyridine ring.

Introduction

The mechanism by which an electron donor (reducing agent) reacts with a suitable acceptor has been widely explored in the case where both are transition-metal complexes. More specifically, outer-sphere electron-transfer constitutes one large, well-recognized, and extensively studied group of reactions.[2-6]

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