$RhCl_5(H_2O)^{2-}$ to $Rh(H_2O)_6^{3+}$ because the increase must cease and be reversed for the entry of chloride into $Rh(H_2O)_6^{3+}$, a very slow process occurring *via* an ion-pair intermediate. The aquation of $Rh(H_2O)_5Cl^{2+}$ must necessarily be very slow indeed to give a formation constant greater than 10^3 M^{-1}, as reported in the literature.[9] This point of view is confirmed by the fact that prolonged boiling of $RhCl_3(H_2O)_3$ with concentrated $HClO_4$ is required to expel all coordinated chloride in the preparation[15] of $Rh(H_2O)_6^{3+}$.

The ever-present question of *cis–trans* isomers of $RhCl_4(H_2O)_2^-$ deserves a comment. Kleinberg, *et al.*,[9] found no evidence for the existence of *cis* and *trans* isomers in their chromatographic studies nor did Garner, *et al.*,[5] in the chloroiridium(III) system. Figure 2 also gives the spectrum of pure $K_2RhCl_5(H_2O)$ in aqueous acid medium of ionic strength 4. There are three distinct isosbestic points at 398, 443, and 493 mμ, respectively. The full spectral change occurring upon aquation of the aquopentachlororhodium(III) exhibited three isosbestic points at 399, 445, and 494 mμ, respectively, for more than 60% of the equilibrium hydrolysis reaction. It is clear that the aquopentachlororhodium(III) anion hydrolyzes to a single product which may be one isomer only or an equilibrium mixture of *cis*- and *trans*-diaquotetrachlororhodium(III). Considering the experimental conditions used by Kleinberg, *et al.*,[9] it is more likely that, in fact, they obtained the equilibrium mixture whose spectrum is given here in Figure 2.

[15] G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

Notes

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The *cis-trans* Isomers of Tetrachlorodiaquorhodate(III) Anion[1a]

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Although Wolsey, Reynolds, and Kleinberg[2] had isolated a series of chloroaquorhodium(III) complexes by ion-exchange chromatography, they reported only one tetrachloro species. Robb and Harris[3] studied the aquation of hexachlororhodate(III) anion but did not isolate any tetrachloro complex produced by the secondary aquation. Since Fine[4] had found the *cis–trans* isomers of tetrachlorodiaquoruthenate(III) anion and Garner and co-workers[5] recently isolated the *cis–trans* isomers of tetrachlorodiaquoiridate(III) anion, both by ion-exchange chromatography, we decided that it should also be possible to obtain the *cis–trans* isomers of tetrachlorodiaquorhodate(III) anion by ion-exchange chromatography. Furthermore, the aquation of pentachloroaquorhodate(III) anion cannot be studied until the product of this aquation is identified.

Procedure and Results

The tetrachlorodiaquorhodate(III) anion was produced by two methods: the aquation of hexachlororhodate(III) anion and the chloride anation of hexaaquorhodium(III) cation. In the aquation method, 5 ml of a 50 m*F* solution of $Na_3RhCl_6 \cdot 12H_2O$ in 1 *F* $HClO_4$ was heated at about 100° for 1.5 min, and the resulting solution, after cooling in ice–water, was chromatographed on a 15-cm NO_3^- Dowex AG 1-X8 (100–200 mesh) column at 2°, using a jacketed condenser-type column with ice water circulated through the jacket. After eluting the cationic and neutral species completely with 0.001 *F* $HClO_4$, a pink band was eluted next by 0.3 *F* HNO_3. Only one pink band was eluted by 0.3 *F* HNO_3, and all fractions of this effluent gave similar visible absorption spectra. The Cl:Rh atom ratio of this complex, designated as complex X, was found to be essentially 4 (3.93–4.12 for seven different samples). Rh was determined spectrophotometrically by the method of Ayres, *et al.*,[6] and ligand chloride was determined by the method of Clarke[7] after decomposing the complex with excess NaOH.[8] Chromatography of the aquation solution on an HSO_4^- Dowex AG 1-X8 column at 2° gave the same result: one pink complex, which has essentially the same Cl:Rh atom ratio (4.01–4.10 for three different samples) and the same visible absorption spectrum as complex X, was eluted by 0.3 *F* H_2SO_4. The visible absorption spectrum of this complex was the same, within experimental error, both in the original effluent and in a solution made 6 *F* in HCl: λ_{max} 492 ± 2 and 392 ± 2 mμ (ϵ 101 and 113 M^{-1} cm^{-1}, $\epsilon_{392}/\epsilon_{492} = 1.12$) and λ_{min} 440 ± 2 mμ (ϵ 48.3 M^{-1} cm^{-1}).

In the chloride-anation method, about 0.3 g of hexaaquorhodium(III) perchlorate, prepared by the method of Ayres and Forrester,[9] was boiled in 2 *F* HCl until the color of the solution was changed from yellow to red.

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[1] (a) Abstracted in part from the M.A. thesis of K. L. Bridges, State College of Iowa, Cedar Falls, Iowa, July 1966; (b) NSF-AYI participant, 1965–1966.

[2] W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963).

[3] W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965).

[4] D. A. Fine, U. S. Atomic Energy Commission Report UCRL-9050, 1960.

[5] C. S. Garner, private communications.

[6] G. H. Ayres, B. L. Tuffly, and J. S. Forrester, *Anal. Chem.*, **27**, 1742 (1955).

[7] F. E. Clarke, *ibid.*, **22**, 553 (1950).

[8] J. C. Chang and C. S. Garner, *Inorg. Chem.*, **4**, 209 (1965).

[9] G. H. Ayres and J. S. Forrester, *J. Inorg. Nucl. Chem.*, **3**, 365 (1957).

Five ml of the resulting solution was then chromatographed on a 20-cm Cl^- Dowex AG 1-X8 column at 2°, after first swirling the solution with *ca.* 15 g of H^+ Dowex AG 50W-X8 (100–200 mesh) to remove excess cationic species. The elution was again made first with 0.001 *F* $HClO_4$ to remove the residual cationic and neutral species and then with 0.3 *F* HNO_3. The 0.3 *F* HNO_3 eluted two overlapping pink bands, the lower being of lighter color. The lower band (designated as complex Y) gave a visible absorption spectrum similar to that reported by Wolsey, *et al.*,[2] for their tetrachloro species but with higher molar absorptivities: λ_{max} 484 ± 2 and 384 ± 2 mμ (ϵ 99.6 and 78.2 M^{-1} cm^{-1}, $\epsilon_{384}/\epsilon_{484} = 0.78$) and λ_{min} 429 ± 2 mμ (ϵ 38.5 M^{-1} cm^{-1}).[10] The upper band (designated as complex Z) gave the same visible absorption spectrum, within experimental error, as complex X. The determination of Cl:Rh atom ratio of complexes Y and Z was not possible because excess chloride was present in the solutions; Fine[4] and Wolsey, *et al.*,[2] encountered the same difficulties in their work. Attempts to chromatograph the chloride-anation solution on a NO_3^- Dowex AG 1-X8 column were unsuccessful.

Since the chloroaquorhodate(III) anions aquate quite rapidly at room temperature, all solutions being eluted were kept in ice; and all visible absorption spectra were measured at about 5°, using a Beckman DB spectrophotometer.

Discussion

The procedure of Wolsey, *et al.*,[2] for the production of tetrachlorodiaquorhodate(III) anion was tried but without success. One wide, red band was eluted by 2 *F* HCl, as reported by Wolsey, but the visible absorption spectra of the different fractions of the effluent were not consistent. On the other hand, if the elution was made with more dilute acids, three overlapping bands of yellow and orange colors were eluted by 0.001 *F* $HClO_4$ and two overlapping pink bands were eluted by 0.3 *F* HNO_3. The yellow and orange bands must be neutral and cationic species, and the identification of these species will be reported in a later communication. The two pink bands appeared to be the two isomers of tetrachlorodiaquorhodate(III) anion because of their elution behavior.

It is quite obvious that, from the Cl:Rh atom ratio, complex X is a tetrachlorodiaquorhodate(III) anion. Since its visible absorption spectrum is different from that reported by Wolsey, *et al.*, for their tetrachloro species, complex X and their complex must be the two isomers of tetrachlorodiaquorhodate(III) anion. Furthermore, two complexes were eluted by 0.3 *F* HNO_3 in the chromatography of chloride-anation solution, and the visible absorption spectrum of one corresponds to the tetrachloro species reported by Wolsey while that of the other corresponds to complex X. The fact that these two complexes were both eluted by 0.3 *F* HNO_3 further suggests that they have the same charge and similar structure. This elution behavior is similar to the corresponding iridium(III) complexes.[8] From these considerations, it was concluded that complexes X and Z are the same and are the *cis* isomer, and complex Y is the *trans* isomer of tetrachlorodiaquorhodate(III) anion, the assignment of configuration being made based upon the order of elution from the ion-exchange column.

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(10) Wolsey, *et al.*, reported λ_{max} 488 and 385 mμ (ϵ 72.0 and 54.1 M^{-1} cm^{-1}, $\epsilon_{385}/\epsilon_{488} = 0.75$) and λ_{min} 430 mμ (ϵ 25.0 M^{-1} cm^{-1}) as interpolated from the spectrum in ref 2.

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High-Resolution Nuclear Magnetic Resonance Spectroscopy of Some Beryllium-Containing Compounds. Beryllium-9 and Fluorine-19 Spectra[1a]

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Although the literature contains reports on the ^{9}Be wide-line spectra of the solids beryl,[2a] chrysoberyl,[2b] and beryllium oxide,[3] the nmr signal of the ^{9}Be nucleus in solution apparently has not been reported. Therefore, owing to the recent interest in beryllium chemistry and the variety of structural problems encountered,[4] we have undertaken an investigation of high-resolution ^{9}Be nmr spectroscopy in order to determine its suitability for structural studies. This investigation has led also to a brief study of the ^{19}F spectra of ammonium tetrafluoroberyllate, $(NH_4)_2BeF_4$, solutions.

Results

^{9}Be Spectra.—Spectra of the following compounds were observed: $BeCl_2 \cdot 2[O(C_2H_5)_2]$ in diethyl ether; beryllium acetylacetonate in chloroform; beryllium(8-hydroxy)quinaldinate in chloroform; ammonium tetrafluoroberyllate, 1 *M*, in water; beryllium sulfate, 0.1 *M*, pH 2.8; beryllium sulfate, 1.1 *M*, pH 1.8; beryllium sulfate, 1.9 *M*, pH 1. All of the compounds showed a single resonance line; the width at half-height of the band was generally 5–10 cps. Within the limits of experimental error (*ca.* 6 cps) no chemical shifts from the basic beryllium acetate standard were observed, except for ammonium tetrafluoroberyllate

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(3) J. F. Hon, *ibid.*, **124**, 1368 (1961).

(4) D. A. Everest, "The Chemistry of Beryllium," Elsevier Publishing Co., New York, N. Y., 1964.