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Rhodium(III) Complexes of the *trans*-Tetraammine Series. Synthesis and Purification

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The synthesis and purification of a number of salts of the rhodium(III) complexes *trans*-$[Rh(NH_3)_4X_2]^+$ (X=Cl, Br, or I) has been critically re-examined and detailed procedures are given. A new and reliable method for the preparation of *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ is also described.

During the course of studies on the photochemical reactions of *trans*-dihalo tetraammine complexes of rhodium(III) [1–3] we encountered problems in reproducing the published syntheses of the complexes [4] and we were unable to obtain satisfactory agreement with the reported absorption spectra.[4–5] We have therefore made a thorough re-examination of the synthesis and purification of these complexes, the results of which are reported here together with an improved procedure for the preparation of the *trans*-diaquatetraamminerhodium(III) ion (as the perchlorate salt). The latter has previously been prepared by the oxidation of pentaamminehydridorhodium(III) with hydrogen peroxide in perchloric acid medium,[6,7] but the yield obtained by this method has proved to be very variable.

EXPERIMENTAL

Materials. Pentaamminechlororhodium(III) chloride was prepared as described previously.[8,9] All other chemicals were of analytical or reagent grade.

Instruments and Spectra. Electronic absorption spectra were recorded on a Cary 219 or a Zeiss DMR 21 spectrophotometer. Solutions were prepared in the dark at room temperature and the spectrum recorded immediately after complete dissolution of the sample, Table 1.

Analyses. All analyses were carried out by the Microanalytical Laboratory of the H. C. Ørsted Institute, University of Copenhagen. In the case of the complexes *trans*-$[Rh(NH_3)_4Br_2]ClO_4.\frac{1}{2}H_2O$ and *trans*-$[Rh(NH_3)_4I_2]ClO_4.\frac{1}{2}H_2O$, containing two different halogens, it was not possible to determine accurately the percentages of the individual halogens. However, the total molar percentages of halogen could be determined with great precision, and we have therefore used these results in assessing the purity of the latter two complexes.

Purity of products. Unless otherwise stated, all the complexes were reprecipitated to constant spectrum.

SYNTHESES

1. trans-*tetraamminedichlororhodium(III)-chloride hydrate,* *trans*-$[Rh(NH_3)_4Cl_2]Cl\cdot H_2O$. The following procedure is a slight modification of that given by Poë and Twigg.[4]

A mixture of $[Rh(NH_3)_5Cl]Cl_2$ (4.00 g) and zinc dust (3.50 g) is heated in a solution containing 12 M ammonia (10 ml) and water (13 ml) at 50 °C for 5 min with constant agitation. The mixture is filtered through a fine-porosity sintered glass funnel and the filter is washed with 2–3 ml of water. The pale-yellow filtrate is cooled in an ice-bath and the pH is adjusted to 6–7 by the cautious, dropwise addition of 12 M hydrochloric acid. The solution is then warmed quickly to *ca.* 35 °C and then again cooled in ice. Potassium chloride (4.0 g) is added, followed by 12 M hydrochloric acid (5 ml) and finally a 30 % (v/v) solution of hydrogen peroxide (3.5 ml).

The mixture is then heated rapidly to boiling and boiled gently under reflux for 30 min. The cloudy orange solution is quickly filtered through

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Table 1. Ligand-field absorption spectra of *trans*-tetraamminerhodium(III) complexes.

Complex salt	$\lambda_{max}(\varepsilon_{max})$	$\lambda_{min}(\varepsilon_{min})$	Medium	Ref.
trans-$[Rh(NH_3)_4Cl_2]Cl \cdot H_2O$	414 (86.1), 292 (95.0)	359 (10.9), 272 (71)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4Cl_2]ClO_4 \cdot H_2O$	414 (86.6), 292 (95.4)	359 (11.3), 272 (76)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4Cl_2]NO_3 \cdot H_2O$[a]	414 (86.7), 292 (95.9)	359 (11.0), 272 (78)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4Cl_2]Cl$	415 (74), 294 (85)		[b]	4
trans-$[Rh(NH_3)_4Cl_2]NO_3 \cdot H_2O$	412 (66),		[b]	5
trans-$[Rh(NH_3)_4Br_2]Br \cdot H_2O$	437 (140.1)	375 (11.2)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4Br_2]ClO_4 \cdot \frac{1}{2}H_2O$	437 (139.6)	375 (10.8)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4Br_2]Br$	441 (111)		[b]	4
trans-$[Rh(NH_3)_4I_2]I$[c]	470 (319)	420 (97)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4I_2]ClO_4 \cdot \frac{1}{2}H_2O$	470 (323)	420 (99)	10^{-3} M $HClO_4$	This work
trans-$[Rh(NH_3)_4I_2]I$	471 (288)		[b]	4
trans-$[Rh(NH_3)_4I_2]ClO_4$	470 (333)		[b]	10
trans-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$	354 (52), 273 (95)	332 (47), 228 (10)	1.0 M $HClO_4$	This work
trans-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$	353 (52), 273 (94)		1.0 M $HClO_4$	6
trans-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$	353 (52), 273 (96)		0.10 M $HClO_4$	7

[a] Corrected for the absorbance of NO_3^-. [b] Not specified. [c] Product mentioned in footnote to synthesis 6.

a fine-porosity sintered glass funnel (*ca.* 5 cm diameter) and the flask and funnel are washed with a total of 70 ml of boiling 0.1 M hydrochloric acid. The mixture is then kept in a refrigerator (*ca.* 5 °C) overnight. The orange-yellow crystals are isolated by filtration and reprecipitated twice as follows:The crude product is dissolved on the filter in portions in warm (50 °C) 0.1 M hydrochloric acid (total dissolution volume *ca.* 200 ml) and each portion of solution is filtered immediately into a single flask containing 6 M hydrochloric acid (50 ml). After cooling the mixture in an ice-bath for 2 h the product is isolated by filtration, washed with a small amount of ice-cold 4 M hydrochloric acid, then 96 % ethanol and finally ether. Drying in air gives 2.9 g (70 %). Anal. H, N, Cl.

2. trans-*tetraamminedichlororhodium(III) perchlorate hydrate,* *trans*-$[Rh(NH_3)_4Cl_2]ClO_4\cdot H_2O$. *trans*-$[Rh(NH_3)_4Cl_2]Cl\cdot H_2O$ (0.50 g) is dissolved in portions on a fine-porosity sintered glass funnel in warm (50 °C) 0.1 M hydrochloric acid (total dissolution volume *ca.* 50 ml). Each successive portion of solution is immediately filtered into a single flask containing 6 M perchloric acid (10 ml), whereupon rapid precipitation of the perchlorate salt occurs. After cooling the mixture in an ice-bath for 2 h the product is isolated by filtration on a fine-porosity sintered glass funnel, washed thoroughly with 96 % ethanol and dried in air. Yield 0.60 g. This product is of sufficient purity for synthetic purposes. It is reprecipitated by dissolving it on the filter in portions in warm (50 °C) 0.1 M hydrochloric acid (total volume *ca.* 35 ml) and filtering the solution into 6 M perchloric acid (10 ml). After cooling in ice for 2 h the product is isolated as before, washed with 96 % ethanol and ether, and dried in air. Yield 0.56 g, 90 %. Anal. H, N, Cl (ionic), Cl (total).

3. trans-*tetraamminedichlororhodium(III) nitrate hydrate,* *trans*-$[Rh(NH_3)_4Cl_2]NO_3\cdot H_2O$. This salt was prepared from *trans*-$[Rh(NH_3)_4Cl_2]Cl\cdot H_2O$ (0.50 g) in exactly the same way as the perchlorate, replacing 6 M perchloric acid with 7 M nitric acid. Initial yield 0.50 g. The product was likewise reprecipitated once analogously from warm 0.1 M HCl. Yield 0.46 g (85 %). Anal. H, N, Cl.

4. trans-*tetraamminedibromorhodium(III) bromide hydrate,* *trans*-$[Rh(NH_3)_4Br_2]Br\cdot H_2O$. *trans*-$[Rh(NH_3)_4Cl_2]Cl\cdot H_2O$ (0.74 g) is dissolved in water (25 ml) with heating. A boiling solution of sodium bromide (10 g) in 0.1 M hydrobromic acid (100 ml) is added and the solution is heated under reflux for 2 h. The solution is allowed to cool to room temperature and is then kept in a refrigerator (*ca.* 5 °C) overnight. The crystals are filtered off, washed with a little ice-cold water and then 96 % ethanol and ether, and air-dried. The dissolution, reflux and isolation are then repeated twice more as before, giving 0.78 g of an almost pure product. Further purification is achieved as follows: The latter product is dissolved with stirring in the minimum volume of warm (50 °C) water (ca. 15 ml). The solution is filtered, and warm (50 °C) filtered 0.1 M hydrobromic acid (15 ml) is added. The mixture is allowed to cool to room temperature and is then kept in a refrigerator (*ca.* 5 °C) overnight. The crystals are isolated by filtration, washed with a small amount of ice-cold water and then ethanol and ether, and dried in air. Yield 0.67 g. One further similar reprecipitation gives 0.57 g (55 %). Anal. H, N, Br.

5. trans-*tetraamminedibromorhodium(III) perchlorate hemihydrate,* *trans*-$[Rh(NH_3)_4Br_2]ClO_44\cdot\frac{1}{2}H_2O$. This preparation is exactly analogous to that for the perchlorate of the dichloro complex, starting from *trans*-$[Rh(NH_3)_4Br_2]Br\cdot H_2O$ (0.25 g) and using warm (50 °C) 0.1 M hydrobromic acid (*ca.* 30 ml) and 6 M perchloric acid (5 ml). The initial product (yield 0.24 g) is reprecipitated likewise, using warm (50 °C) 0.1 M hydrobromic acid (*ca.* 20 ml) and 6 M perchloric acid (5 ml). Yield 0.20 g (80 %). Anal. H, N, total halogen.

6. trans-*tetraamminediiodorhodium(III) perchlorate hemihydrate,* *trans*-$[Rh(NH_3)_4I_2]ClO_4\cdot\frac{1}{2}H_2O$. Preparation of crude *trans*-$[Rh(NH_3)_4I_2]$ I: *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ (*vide infra*) (0.60 g) and sodium iodide (2.7 g) are dissolved together in 0.01 M perchloric acid (100 ml). The solution is protected against light and maintained at 80 °C for 5 h with the passage of a stream of nitrogen gas to exclude oxygen. During this time a brick-red precipitate forms. A solution of sodium iodide (20 g) in water (20 ml) is added and the mixture is kept in a refrigerator (*ca.* 5 °C) overnight. The microcrystalline product is isolated by filtration, washed with a little ice-cold water, then 96 % ethanol and ether, and dried in air. Yield 0.47 g (70 %).

The yield and the visible absorption spectrum of the crude product vary from one synthesis to another, and the purity of the product is very sensitive to even minor modifications in the experimental conditions.[*] One such crude pro-

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[*] One experiment was performed using *trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$ (0.20 g), sodium iodide (0.60 g), and 0.01 M perchloric acid (20 ml) at room temperature with nitrogen flushing for 1 ½ h in the dark, and the solution was then sealed in an ampoule and kept at room temperature for 2 ½ years in the dark. Yield 0.20 g (90 %) of very beautiful red crystals. The electronic absorption spectrum of this product was identical to that of the pure perchlorate hemihydrate.

duct was analyzed: Anal: Found: H 2.18; N 10.06; I 68.25; Calc.: H 2.19; N 10.16; I 69.01. Electronic absorption spectrum of this crude product: $(\lambda,\varepsilon)_{max}$ 470 nm, 327; $(\lambda,\varepsilon)_{min}$ 422 nm, 104.

Purification of the complex was achieved by conversion to the perchlorate as follows: Crude *trans*-$[Rh(NH_3)_4I_2]I$ (0.40 g) is dissolved in water (20 ml) by rapid heating to 80 °C with rigorous protection against light. The solution is filtered into an ice-cooled flask containing 12 M perchloric acid (20 ml). A glittering, finely crystalline precipitate is formed immediately, and after cooling in ice for a further 10 min the precipitate is filtered off, washed with a small amount of absolute ethanol (CAUTION) and ether, and air-dried. Yield 0.33 g. This crude product is dissolved in water (50 ml) by heating to 60 °C in the dark. The solution is filtered through a fine-porosity sintered glass funnel, allowed to cool slowly to room temperature and then kept in a refrigerator (*ca.* 5 °C) overnight. The resulting ruby-red elongated prisms are collected on a filter, washed with absolute ethanol and ether, and air-dried. Yield 0.10 g (25 %). Anal. H, N, total halogen.

7. trans-*tetraamminediaquarhodium(III) perchlorate, trans*-$[Rh(NH_3)_4(H_2O)_2](ClO_4)_3$. Mercury(II) oxide (2.50 g) is dissolved in 0.4 M perchloric acid (200 ml) and to the solution is added *trans*-$[Rh(NH_3)_4Cl_2]Cl\cdot H_2O$ (1.0 g). The mixture is heated under reflux in the dark for 2 h and the volume of the solution is then reduced to *ca.* 25 ml by gentle boiling. 12 M perchloric acid (25 ml) is added, whereupon immediate precipitation of the product occurs. After keeping the mixture in an ice-bath for 1 h the product is isolated by filtration, washed with a very small amount of ice-cold 2 M perchloric acid, then absolute ethanol and finally ether, and air-dried. Yield 1.55 g. The crude complex is reprecipitated by dissolving it in water (10 ml per g of product) and adding an equal volume of 12 M perchloric acid to the filtered solution. After cooling in ice for 1 h the product is isolated as before. The product is reprecipitated once more in this manner. Yield 0.80 g (45 %).

The solid *trans*-diaqua perchlorate is rather unstable to prolonged storage and can, if desired, readily be converted to the more stable *trans*-aquahydroxotetraamminerhodium(III) dithionate as described previously.[6]

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