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The Dipole Moments of *cis*- and *trans*-Trichlorotriaquoruthenium(III)[1]

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Received May 21, 1965

The dipole moments of *cis*- and *trans*-trichlorotriaquoruthenium(III) have been found to be 7.5 and 4.4 D., respectively. The measurements were made at −78.5°, using ethyl acetate as a solvent. On the basis of the dipole moments, the assignment of the *trans* configuration to the isomer which elutes first from an anion-exchange column was confirmed.

Dilute aqueous solutions of the two neutral monomeric isomers of trichlorotriaquoruthenium(III) were first separated and characterized by Connick and Fine.[2] Those authors reported the ultraviolet spectrum of each of the pure complexes and designated them A and B. On the basis of the order of elution from an anion-exchange column and incomplete data on the hydrolysis of the entire series of the chloro complexes of ruthenium(III), they tentatively assigned the *trans* configuration to the A isomer and the *cis* configuration to isomer B. In order to establish the configuration of these two isomers unequivocally, we have measured the dipole moments of both isomers in ethyl acetate solution. Dipole moments have been used only infrequently in structural studies of coordination compounds, because only relative structural information can be obtained by this method and because of the difficulty in finding suitable solvents.

Results

The solid trichlorotriaquoruthenium(III) complexes were prepared by first separating these neutral species in aqueous solution by elution from an anion-exchange column and freeze drying the resulting solution, while keeping the sample cold. The product was an orange crystalline material, which was very hygroscopic and had a melting point of about 0°. The solid complexes could be stored below their melting points for several weeks with no decomposition. At room temperature, however, they decomposed to give a green, uncharacterized liquid. When the orange solids were dissolved in water, the spectrum was the same as that given by Connick and Fine[2] for the pure isomers. The mole ratio of chloride to ruthenium was within 2% of the expected 3.00 on all samples analyzed.

The ethyl acetate solutions of the complexes were less stable than the aqueous solutions and were kept at Dry Ice temperature until after the measurements were completed. The locations of the absorption maxima in the ultraviolet–visible spectra are shifted about 50 mμ toward longer wave lengths from those observed in aqueous solution, but the intensity and shapes of the curves remained approximately the same (Figure 1). The complexes were completely extracted from the ethyl acetate by water, and the spectra of the water phase, recorded immediately after extraction, were also identical with those obtained on the pure isomers. These experiments indicate that no isomerization or ligand exchange had taken place in the ethyl acetate solutions.

The capacitance of the ethyl acetate solutions was measured in a cell with nickel electrodes at a temperature of −78.5°, maintained by immersing the cell in a Dry Ice–acetone bath. The dielectric constant of each solution was calculated from the capacitance and was plotted as a function of the molar concentration of the complex. The data are summarized in Table I. Linear relationships were found to fit the experimental points for each isomer. Onsager's equation,[3] in the form given by Gilkerson and Srivastava,[4] was used to calculate the dipole moments of the complexes. In the very dilute solutions used here, this equation reduces to

$$\mu^2 = a(d\epsilon/dc) + b$$

where μ is the dipole moment of the solute and a and b are constants, involving the infinite frequency dielectric constants of the solvent and solute and other known physical properties of the solvent. The infinite frequency dielectric constant of ethyl acetate was set equal to the square of the refractive index, and that of the complexes was calculated from ionic and group refractions given by Smyth.[5] The values of a and b were evaluated as 3.06 and 2.36, respectively, when μ has the units of Debyes. The dipole moments calculated using these values are μ_A = 4.4 D. and μ_B = 7.5 D. The ratio $\mu_A/\mu_B = 1.7_0$ is in excellent agreement with the value of 1.73, calculated for the *cis*/

TABLE I

THE CHANGE IN DIELECTRIC CONSTANT WITH CONCENTRATION OF THE COMPLEXES

Complex	Molar concn.	($\epsilon_{soln} - \epsilon_{solv}$)
$RuCl_3$(A)	0.0136	0.163
	0.0192	0.202
	0.0228	0.228
	0.0323	0.279
$RuCl_3$(B)	0.0090	0.253
	0.0098	0.266
	0.0151	0.378
	0.0164	0.403

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[1] Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

[2] R. E. Connick and D. A. Fine, *J. Am. Chem. Soc.*, **83**, 3414 (1961).

[3] L. Onsager, *ibid.*, **58**, 1486 (1936).

[4] W. R. Gilkerson and K. K. Srivastava, *J. Phys. Chem.*, **64**, 1485 (1960).

[5] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, Chapter XIV.

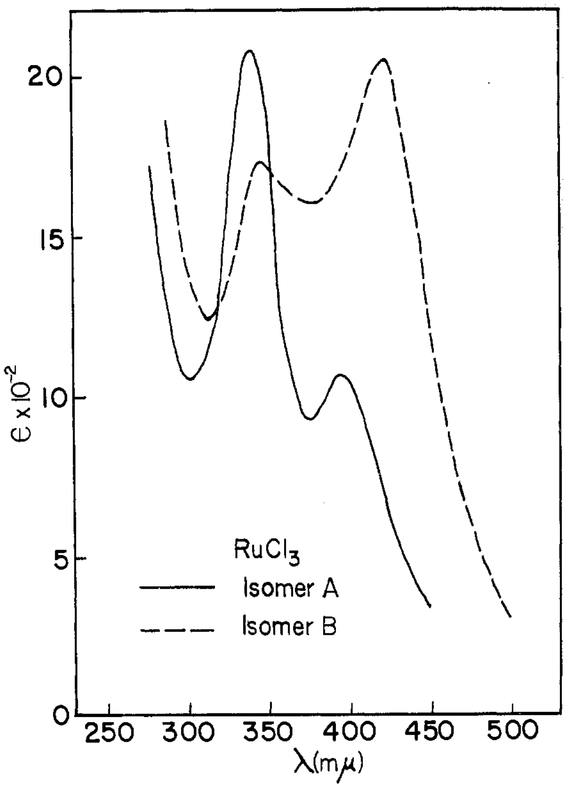

Figure 1.—The spectra of the $RuCl_3(H_2O)_3$ isomers in ethyl acetate at 0°. The molar extinction coefficients were determined on solutions ranging in concentration from 5×10^{-3} to 2×10^{-2} *M*.

trans ratio, based on the assumption of an octahedral geometry of the complexes.

Discussion

The use of dipole moments as a structural tool has been largely ignored by the coordination chemist in the past, mainly because of the slight solubility of most complexes in nonpolar solvents. The use of polar solvents, as has been used in this work, eliminates the problem of insolubility in many cases, thus permitting a much wider range of applicability. When polar solvents are used, it is necessary to use a bridge method for determining the capacitance of the solutions, because the phase shift due to conductivity decreases the sensitivity of the null detection, unless a resistance balance is also made. The method can be applied only to complexes which are inert to substitution.

The confirmation of the assignment of the *trans* configuration to the neutral isomer which is eluted first from an anion-exchange column indicates that these complexes are retained on the resin by ion–dipole interactions. The order of elution is the same as that observed in elutions of cationic complexes, where the less polar *trans* isomer has been shown to be less tightly held by cation resins.[6]

While the ratio of moments found in this work is in very good agreement with that expected from purely geometric considerations, the values themselves seem quite low, based on known bond moments. Estimating the bond moment of Ru–Cl as 2.5 D., and the contribution of the moment of the coordinated water to the dipole of the *trans* complex at approximately 0.8 D., then the O–Ru bond moment would be only 1.1 D. According to Smyth,[7] such bonds are normally expected to have moments of about 3 D. A small amount of this discrepancy may possibly be attributed to atomic polarization, for which no satisfactory means of estimation was available.

Experimental

(A) **Preparation of the Complexes.**—Solutions of potassium pentachloroaquoruthenate(III) in 0.05 *M* hydrochloric acid were aged at room temperature for 12–15 hr. The resulting solution was washed through a column of Dowex 50X8 cation-exchange resin in the hydrogen ion form with water, to remove potassium ion and any cationic ruthenium complexes which were present. The effluent from this column was absorbed on a 2.5 × 20 cm. column of Dowex 1X8 anion resin in the chloride form, which was held at approximately 0° by circulating a coolant through an outer jacket. The two neutral complexes were separated from anionic species and from each other by elution with 0.01 *M* hydrochloric acid. The purity of each fraction was determined from the ratio of absorbances at 320 and 360 mμ, using the extinction coefficients previously reported.[2] Those fractions which contained only one of the isomers were combined in a 200-ml. round-bottom flask, from which the solvent and hydrochloric acid were removed by freeze drying. It was necessary to maintain the temperature of the sample at approximately −20° to prevent decomposition of the product into a green, uncharacterized material. The product was a deep orange powder. If this solid was dissolved in water and the solvent was removed by freeze drying a second time, the resulting material was crystalline in appearance.

(B) **Capacitance Measurements.**—The flask containing the solid complex was cooled in a Dry Ice–acetone bath and approximately 25 ml. of ethyl acetate was added slowly and the flask was swirled to dissolve the solid. Twenty ml. of the solution was transferred to the capacitance cell, which was in a large dewar flask containing a Dry Ice–acetone mixture. The cell was designed to permit the addition of 15 ml. of the solvent, so that the capacitance of solutions of two concentrations could be measured without opening the cell. All measurements were made at Dry Ice temperature, using a frequency of 100 kc. on a Leeds and Northrup capacitance bridge (No. 1554-A2-S), a General Radio oscillator (Type 1302-A), and a General Radio tuned amplifier and null detector (Type 1232-A). The capacitance cell was a dipping type, with cylindrical nickel electrodes (Type 2TN25, Balsbaugh Laboratories).

(C) **Analysis.**—The chloride to ruthenium ratio was determined by dissolving a sample of the complex in 1 *M* sodium hydroxide and heating for 1 hr. The hydrated ruthenium dioxide was removed by filtration and dried to a constant weight at 140°. The filtrate was made slightly acidic with nitric acid, and the chloride was determined gravimetrically as silver chloride. In calculating the ratio, the weighed form of the ruthenium was assumed to be $RuO_2 \cdot 2H_2O$, as reported by Connick and Hurley.[8] The ruthenium was also determined spectrophotometrically on a separate aliquot of solution, using the isosbestic point at 415 mμ of ruthenate and perruthenate, after oxidation of the metal in basic solution.[9] Both methods of analysis gave essentially the same results.

(D) **Reagents.**—Ruthenium was obtained as ruthenium chloride (38.4% Ru) from Engelhard Industries. This was converted to the sulfate by fuming with sulfuric acid. Ruthenium tetroxide was distilled from an acid solution of potassium per-

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(6) E. L. King, Sr. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

(7) See ref. 5, p. 390.

(8) R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, **74**, 5012 (1952).

(9) J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).

manganate and was collected in 6 *M* hydrochloric acid. The potassium pentachloroaquoruthenate(III) was prepared from this solution by the method of Charronat.[10] The ethyl acetate used was Baker and Adamson Analyzed Reagent Grade. All other chemicals used were reagent grade.

(E) **Equipment.**—All spectra were recorded on a Cary Model 14 recording spectrophotometer. The freeze drying was done on a VirTis micro freeze dryer.

Acknowledgments.—The authors wish to thank Professor W. R. Gilkerson for his advice on dipole moment measurements and the National Science Foundation for financial support on grant GP-1584. W. A. McA. is an N.D.E.A. Fellow for the years 1963–1966.

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(10) R. Charronat, *Ann. Chim.* (Paris), **16**, 52 (1931).

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Kinetics of Aquation of *cis*-Dibromobis(ethylenediamine)cobalt(III) Cation

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Received May 20, 1965

The kinetics of aquation of *cis*-$[Co(en)_2Br_2]^+$ has been studied in 0.1 *F* HNO_3 at 15.0, 20.0, and 25.0°. The pseudo-first-order rate constant for the loss of one bromide at 25.0 ± 0.03° was found to be $(10.4 \pm 0.4) \times 10^{-4}$ sec.$^{-1}$. The rate is independent of initial concentration of the complex over the range 2.0–8.0 m*F*, of pH from 1.0 to 3.0, and of ionic strength 0.014 to 0.304. Added sulfate ion accelerates the aquation. The Arrhenius activation energy is 23.8 ± 0.9 kcal./mole and ΔS^* is +5.0 ± 3 cal./deg.

In the present study, we have investigated the first-step aquation of *cis*-dibromobis(ethylenediamine)-cobalt(III) cation under various conditions of added electrolytes. A considerable amount of kinetic data has been reported for the aquation of *cis*- and *trans*-dihalobis(ethylenediamine)cobalt(III) cations of the type $[Co(en)_2X_2]^+$ where X = F or Cl.[2] The only cobalt(III) dibromo analog whose aquation has been studied kinetically is *trans*-$[Co(en)_2Br_2]^+$ ion.[3,4] Therefore, this study completes the *cis*- and *trans*-dihalocobalt(III) series and permits comparisons to be made within the series. It is also of interest to compare these results with those of the corresponding chromium(III) analogs insofar as data are available.

Experimental

***cis*-Dibromobis(ethylenediamine)cobalt(III) Bromide.**—Carbonatobis(ethylenediamine)cobalt(III) bromide was prepared according to the method of Pfeiffer.[5] This compound was treated with alcoholic hydrogen bromide according to the method of Werner[6] to produce *cis*-$[Co(en)_2Br_2]Br \cdot H_2O$. Purification was effected by quickly dissolving 4 g. of the crude material in 1 l. of ice-cold H_2O and suction filtering the solution onto 110 g. of NaBr. The resulting precipitate was washed with three 20-ml. portions of cold H_2O, then with four bed volumes of absolute alcohol, and dried over H_2SO_4. *Anal.* Calcd. for *cis*-$[Co(en)_2Br_2]Br \cdot H_2O$: C, 11.00; H, 4.15; Br, 54.87; N, 12.83; Co, 13.49. Found: C, 10.91; H, 4.08; Br, 54.70; N, 12.82; Co, 13.04. It was found that this monohydrate could be stored over H_2SO_4 up to 7 weeks without dehydration. The anhydrous salt was obtained by heating the monohydrate at 125° for 12 hr. and then at 130° for an additional 3.5 hr. *Anal.* Calcd. for *cis*-$[Co(en)_2Br_2]Br$: C, 11.47; H, 3.85; Br, 57.23; N, 13.38; Co, 14.07. Found: C, 11.43; H, 4.07; Br, 57.30; N, 13.47; Co, 13.86.

***cis*-Dibromobis(ethylenediamine)cobalt(III) Nitrate.**—This compound was prepared according to the method of Werner[6] by recrystallizing the crude bromide with $NaNO_3$ in place of NaBr in the salting-out step. *Anal.* Calcd. for *cis*-$[Co(en)_2Br_2]NO_3$: C, 11.98; H, 4.02; Br, 39.86; N, 17.47; Co, 14.70. Found: C, 12.12; H, 4.18; Br, 40.07; N, 17.18; Co, 14.20. All other reagents used in this study were commercially available materials of reagent grade and were used without further purification.

Analytical Methods.—Nitrogen was determined in this laboratory by Kjeldahl microanalysis. Bromide analyses were performed by dissolving the sample in excess 1 *F* NaOH and digesting on a steam bath for 30 min. The resulting solution was then allowed to cool, acidified with a twofold excess of 1 *F* HNO_3, diluted by a factor of ten, and titrated to a potentiometric end point with standard $AgNO_3$ in the presence of a nonionic detergent. The remaining elements were determined by microanalysis.[7]

Kinetic Measurements.—Titrimetric runs were begun by placing a sample of the complex sufficient to give the desired concentration in a glass-stoppered actinic glass flask. This flask and a separate container of reaction solvent were placed in a thermostatic bath whose temperature was controlled to ±0.03°. After the establishment of thermal equilibrium, 100 ml. of the solvent was withdrawn from the solvent container and discharged into the sample flask by means of a volumetric pipet. As soon as the pipet was drained the flask was removed from the bath, wiped dry (to prevent evaporative cooling), shaken vigorously for 30 sec., and returned to the bath. As soon as was convenient, an aliquot (ordinarily 10 ml.) was withdrawn and discharged into a quenching solution which consisted of an acidified acetone solution of a nonionic detergent at about −20° and titrated to a potentiometric end point with standard $AgNO_3$. The temperature at the end of the titration was −2 to −5°. Further ali-

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(1) Taken from the M.S. thesis submitted by William F. Cain to the University of Detroit, 1965.

(2) For a review see D. R. Stranks in J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers Inc., New York, N. Y., 1960, p. 78.

(3) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

(4) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

(5) P. Pfeiffer, S. Golther, and O. Angern, *Chem. Ber.*, **60**, 308 (1927).

(6) A. Werner, *Ann.*, **386**, 114 (1912).

(7) Microanalysis by Weiler and Strauss; Microanalytical Laboratory, Oxford, England.