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Preparation of *cis*- and *trans*-Dichlorobis(ethylenediamine)-Iridium(III) Chlorides

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Potassium tetrachloro(ethylenediamine)iridate(III) and *cis*-dichlorobis(ethylenediamine) iridium(III) chloride were obtained by the reaction of iridium(III) chloride and ethylenediamine in a weakly acid aqueous solution. The condition for the formation of each compound depends on the mole ratio of iridium to ethylenediamine and pH of the solution. Trans-dichlorobis(ethylenediamine)iridium(III) chloride was prepared from potassium tetrachloro(ethylenediamine)iridate(III) and ethylenediamine.

The geometrical configurations of the two isomers were determined by infrared spectra, and checked by ultraviolet spectra.

In the study of electronic spectra of d^6 complexes, it was desired to discuss the spectra of a series of complexes, *cis*- and *trans*-$[M\ Cl_2en_2]^{n+}$ ($M=$ Co(III),1) Rh(III),2) Ir(III) and Pt(IV),3) where preparation of all compounds, except iridium(III) complexes, have been reported. Therefore, it has been attempted to prepare *cis*- and *trans*- dichlorobis(ethylenediamine)iridium(III) complexes.

Anderson and Basolo2) have prepared *cis*- and *trans*-dichlorobis(ethylenediamine)rhodium(III) complexes from an aqueous solution of rhodium(III) chloride, ethylenediaminedihydrochloride and potassium hydroxide (with the mole ratio of 1 : 2 : 4). However, iridium(III) analogues have not been obtained by the similar methods so far attempted, because iridium (III) chloride readily hydrolyzes in an alkaline or even neutral solution to form amorphous precipitate, and therefore, boiling this mixture with ethylenediamine leads to formation of tris(ethylenediamine)iridium(III) complex irrespective of the ratio of ethylenediamine to iridium.

In the present study, iridium(III) chloride was tried to react with ethylenediamine in a weakly acid medium, with various ratios of ethylenediamine to iridium. In this way, potassium tetrachloro(ethylenediamine)iridate(III), $K[IrCl_4en]$, was obtained, and then *cis*-dichlorobis(ethylenediamine) iridium(III) chloride, *cis*-$[IrCl_2en_2]Cl$. The trans isomer was prepared from $K[IrCl_4en]$ and ethylenediamine.

Experimental

Preparation of a Solution of Iridium(III) Chloride from Iridium Metal.—Five grams of iridium powder was heated at 300—400°C with 15 g. of sodium hydroxide and 10 g. of sodium peroxide in a nickel crucible for one hour, ($Ir+3\ Na_2O_2 \rightarrow IrO_3+3\ Na_2O$). The resulting black mixture was dissolved in 150 ml. of water forming a colloidal solution. This was neutralized with hydrochloric acid, and added another 20 ml. of concentrated hydrochloric acid. When this solution was boiled for 30 min., iridium(VI) oxide was reduced to iridium(IV) chloride evolving chlorine gas to form dark brown solution, ($IrO_3+6\ HCl \rightarrow IrCl_4+Cl_2+3\ H_2O$). Iridium(IV) chloride was further reduced to iridium(III) chloride by adding hydrogen sulfide, ($6\ IrCl_4+H_2S+2\ H_2O \rightarrow 6\ IrCl_3+SO_2+6\ HCl$). The red-brown solution thus prepared contained iridium(III) chloride and much excess of sodium chloride and hydrochloric acid.

***cis* - Dichlorobis (ethylenediamine) iridium (III) Chloride.**—The iridium(III) chloride solution, prepared by the method described above, was neutralized with potassium hydroxide and adjusted at pH 3 with acetic acid. This solution, containing 533 mg. of iridium, was diluted with water to 300 ml., and boiled in a 500 ml. round-bottom flask. To the boiling solution 25 ml. of 2% aqueous ethylenediamine($Ir/en=1/3$) was slowly added. It was boiled for 3 hr., being frequently supplied with water to keep the volume constant. Then, this solution was evaporated to form crystals of sodium chloride and potassium chloride, cooled, and filtered. This procedure was repeated twice until the solution was concentrated to 15 ml. After one night yellow prisms were formed in the solution. These crystals were separated by filtration, washed with ethanol, and recrystallized from 6 N hydrochloric acid solution; yield, 276 mg.. The well-formed bright light-yellow prisms were obtained. This compound is fairly soluble in water, (soluble more than 1.1 g. in 100 ml. of water at 10°C).

Found: C, 11.42; H, 4.26; N, 12.93. Calcd. for $[IrCl_2en_2]Cl$: C, 11.47; H, 3.85; N, 13.38%.

Potassium Tetrachloro(ethylenediamine)Iridate (III).—The iridium(III) chloride solution prepared by the method described before, was neutralized with

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1) "Inorganic Syntheses," Vol. 2, McGraw-Hill, New York (1946), p. 222.

2) S. Anderson and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4423 (1960).

3) F. Basolo, J. C. Bailar Jr. and B. R. Tarr, ibid., **72**, 2433 (1950).

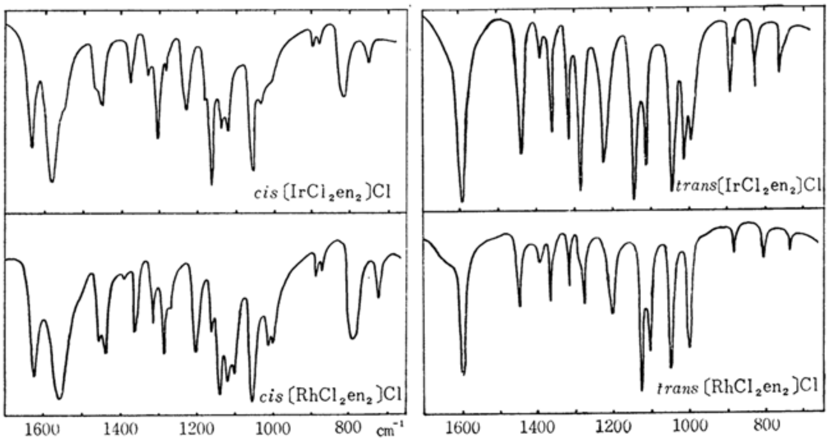

Fig. 1. Infrared spectra of *cis*- and *trans*- [IrCl$_2$en$_2$]Cl, with comparison of the Rh(III) analogues whose geometrical configurations were alreacly known.

potassium hydroxide, and was again acidified by adding 1.2 g. of acetic acid. The solution containing 1 g. of iridium was diluted to 200 ml. with water, and boiled. To the boiling solution, 0.6 g. of ethylenediamine in 30 ml. of water was slowly added (Ir/en=1/2). The solution was boiled for 3 hr., being kept the volume constant by frequent addition of water, and then evaporated to about 60 ml. When cooled, the solution was quickly filtered to separate off the resulting crystals of sodium chloride and potassium chloride. The filtrate was strongly acidified with conc. hydrochloric acid, and again evaporated to 30 ml., cooled, and quickly filtered. After standing one night at room temperature, the filtrate yielded orange-red crystals, which were separated by filtration, washed with water and ethanol. Upon further evaporation of the filtrate, more crystals may be obtained. All these crystals were recrystallized from 6 N hydrochloric acid; yield, 768 mg.. The orange-red crystals thus obtained contain 2 molecules of water for one atom of iridium, and readily lose crystal water when heated at 100°C. This compound is sparingly soluble in cold water and fairly soluble in hot water.

Found: C, 5.57; H, 2.17; N, 6.25. Calcd. for K[IrCl$_4$en]: C; 5.55; H, 1.86; N, 6.47%.

***trans*-Dichlorobis(ethylenediamine)Iridium(III) Chloride.**—One half gram of K[IrCl$_4$en]·2H$_2$O, was dissolved in 30 ml. of hot water. Three milliliters of 1% aqueous ethylenediamine was slowly added to this solution which was stirred and heated on a steam bath. After the addition of ethylenediamine, the solution was kept at 95—100°C for one hour, and its color gradually changed from red to orange. Then another 3 ml. of 1% aqueous ethylenediamine was slowly added to the hot solution, and the solution was heated at 95—100°C for one hour as before. Throughout the above processes, the volume of the solution had been kept at 30 ml. by frequent supply of water. The solution was evaporated on a steambath to a small volume—ca. 3 ml., and left at room temperature for one night. The resulting orange-red crystals, the unreacted starting material, was filtered off. The filtrate was acidified with conc. hydrochloric acid, and concentrated to a very small volume—less than 1 ml. Upon ice cooling, light yellow flakes were formed in the solution. These crystals were filtered, and recrystallized with 6 N hydrochloric acid; yield, 96 mg. This compound is very soluble in water, (much more soluble than the cis isomer), and fairly soluble in 99% ethanol.

Found: C, 11.27; H, 4.33; N, 13.02. Calcd. for [IrCl$_2$en$_2$]Cl: C, 11.47; H, 3.85; N, 13.38.

Discussion

The *cis*- and *trans*-isomers were identified by infrared spectra. Morris and Busch[4] pointed out that in diacidobis(ethylenediamine)cobalt(III) complexes trans isomer has one strong absorption near 1600 cm^{-1}, while the corresponding band of a *cis* isomer always splits into two bands. Examining the spectra, which are shown in Fig. 1, one could easily determine the geometrical configuration of the two isomers which has been obtained in this study.

The UV spectrum of aqueous solution of each new compound was measured, and the first spin-allowed bands of the cobalt(III), rhodium(III) and iridium(III) complexes were listed in Table I. It is seen in Table I that the first spin-allowed

TABLE I. ABSORPTION MAXIMA OF THE FIRST SPIN-ALLOWED BANDS OF DICHLOROBIS(ETHYLENEDIAMINE) COMPLEXES OF Co(III), Rh(III) AND Ir(III)

M	Co(III)*		Rh(III)		Ir(III)	
	$\bar{\nu}$(kK.)	log ε	$\bar{\nu}$(kK.)	log ε	$\bar{\nu}$(kK.)	log ε
cis[MCl$_2$en]$^+$	18.64	1.95	28.5	2.27	34.2	2.15
trans[MCl$_2$en]$^+$	16.12	1.61	24.4	1.92	28.9	1.66

* M. Linhard and M. Weigel, *Z. anorg. u. allgem. Chem.*, **271**, 101 (1952).

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[4] M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 1521 (1960).

band of *cis*-isomer is located in the shorter wavelength region and has higher intensity than that of the trans isomer in the case of the iridium(III) complexes, as in the cases of the cobalt(III) and the rhodium(III) complexes whose geometrical configurations were already determined. This fact implies that the investigation of ultraviolet spectra supports the conclusion on the geometrical configuration deduced from IR spectra. The detailed discussion of electronic spectra will be reported separately.

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