[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereoisomerism of Complex Inorganic Compounds. XVI. The Stereoisomers of Dichlorobis-(ethylenediamine)-platinum(IV) Salts[1]

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A synthesis for *cis*-dichlorobis-(ethylenediamine)-platinum(IV) nitrate was developed. The product was isolated and its structure proven. The proof of structure included partial resolution into the optically active components and comparison of the X-ray diffraction patterns of the *cis* and *trans* isomers.

The preparation of dichlorobis-(ethylenediamine)-platinum(IV) chloride has been reported by several investigators. In each case the compound was obtained by oxidation of the bis-(ethylenediamine)-platinum(II) ion. This work was summarized in a previous paper[3] in which the authors described three procedures by which they were able to prepare [Pt en_2Cl_2]Cl_2: (1) chlorination of [Pt en_2]Cl_2, (2) reaction of [Pt $en_2(CO_3)_2$] with hydrochloric acid and (3) reaction of [Pt $en_2(OH)_2$]Cl_2 with hydrochloric acid. The fact that samples of the [Pt en_2Cl_2]Cl_2 prepared by different methods all had the same structure was established by their identical absorption spectra. Evidence was cited to show that the cation had a *trans* configuration.

Basolo, Bailar and Tarr attempted to prepare *cis*-[Pt en_2Cl_2]Cl_2 by several different methods, but unsuccessfully.

The present work was undertaken in an attempt to prepare *cis*-[Pt en_2Cl_2]Cl_2. If a synthesis for the *cis* isomer could be developed, the way would be open for stereochemical investigations, not only with this compound, but with similar complexes of platinum containing other negative groups or other diamines.

Since earlier workers have been unsuccessful in their attempts to rearrange the *trans* isomer to the *cis*, it was concluded that the *cis* isomer could best be prepared from a compound containing chloro groups already in the *cis* positions. Such a synthesis was achieved as follows: Potassium chloroplatinate(II), K_2PtCl_4, was treated with ethylenediamine under controlled conditions to give [Pt en Cl_2], in which the chloro groups must occupy *cis* positions. This compound was then oxidized with hydrogen peroxide to yield the insoluble [Pt en $(OH)_2Cl_2$]. From the method of synthesis, it was expected that the two hydroxo groups in this compound would occupy *trans* positions; *i.e.*, one above and one below the plane containing the ethylenediamine and chloro groups. Rearrangement would not take place under the conditions employed.

The [Pt en $(OH)_2Cl_2$] was treated with just enough nitric acid to neutralize the two hydroxo groups. It has previously been shown, however,[3] that only one hydroxo group is readily neutralized, so the product was [Pt en (H_2O) $(OH)Cl_2$]NO_3. The resulting solution was then treated with an equivalent amount of ethylenediamine. Since the chloro groups are so firmly held by the central platinum ion, they will not be replaced by the incoming ethylenediamine molecule as readily as will the coördinated water molecule. The water molecule is easily replaceable, and is in a position *trans* to the next most readily replaceable group, the hydroxo group. Since the ethylenediamine cannot span the *trans* positions, it can replace the water and hydroxo groups only if a rearrangement takes place. Since the nitrogen atoms of the original ethylenediamine molecule occupy positions *trans* to the very negative chloro groups, such a rearrangement might be expected to involve the ethylenediamine rather than the chloro groups. This would be favored by the "*trans* effect"[4] according to which ligands *trans* to negative groups are more labile than those *trans* to neutral groups.

A conclusive proof that the compound prepared in this way has the *cis* configuration would lie in the resolution of the product into its optically active components. Resolution was effected through fractional crystallization of the *d*-α-bromocamphor-π-sulfonate. A solution of the platinum complex and ammonium *d*-α-bromocamphor-π-sulfonate was concentrated at room temperature, yielding three successive fractions of crystals. The first two fractions did not exhibit observable optical activity, but the third showed a specific rotation of +16.4°. The mother liquor was then allowed to evaporate to dryness at room temperature. A solution of the residue showed a specific rotation of +65.5°. This value did not change upon heating the solution at 82–85° for six hours. However, racemization was accomplished by boiling for 87 hours (Table I).

TABLE I

Total boiling time, hr.	Observed rotation	Temp., °C.	Specific rotation, $[\alpha]_D$
0	+1.400°	23	+65.5°
1	1.355	23	63.5
3	1.335	22	62.5
7	1.315	21	61.5
23	1.280	21	59.8
44.5	1.250	22	58.5
68	1.200	22	56.2
87	1.185	22	55.5

Boiling for an additional 44 hours did not produce any further change in the optical rotation. It was found that the rotation of an aqueous solution of the pure resolving agent was not changed by similar treatment.

It was calculated that if the complex were in-

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[1] Taken from part of a thesis submitted by Leo F. Heneghan to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1950.

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[3] For a summary of this work, see F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, THIS JOURNAL, **72**, 2433 (1950).

[4] I. I. Cherynaev, *Ann. inst. platine*, **4**, 243 (1926).

active and the observed rotation were due to the presence of the resolving agent alone, the specific rotation would be +55.8°—almost exactly the value obtained after racemization of the active fraction. Comparison of this value with those of the individual fractions and especially with the data from the racemization study indicates that at least a partial resolution has been attained and that the complex must therefore have the *cis* configuration.

X-Ray diffraction studies were carried out on the *cis* and *trans* salts; the powder patterns obtained clearly indicate that the two samples possess markedly different crystal dimensions. Care was taken to crystallize the two samples chosen for X-ray analysis under identical conditions, so the difference in crystal dimensions must be due to differences in internal molecular arrangement.

Experimental

X-Ray Diffraction Study.—The X-ray diffraction patterns were taken using a Machlett Diffraction Tube with CuK$_\alpha$ radiation (nickel filtered), at 40 kv. and 15 ma. The same circular camera (radius 6.95 cm.), was used for each sample with an exposure time of 11 hours.

Potassium Chloroplatinate(II), K_2PtCl_4, was prepared by the method of Keller.[5]

Dichloroethylenediamineplatinum(II), [Pt en Cl$_2$], was prepared by a modification of the method of Jorgensen.[6] Three and six-tenths grams (0.0087 mole) of K_2PtCl_4 was dissolved in 25 ml. of water and the solution was cooled in an ice-bath. One milliliter of 64% ethylenediamine solution (0.0104 mole), diluted with an equal volume of water, was added in 5-drop portions over a period of approximately 8 hr. The insoluble, yellow, crystalline [Pt en Cl$_2$] separated slowly and was removed on a filter every 15–20 min. to prevent contamination with the possible by-products, [Pt en$_2$]Cl$_2$ and [Pt en$_2$][Pt Cl$_4$]. The crude material was recrystallized from water acidified with hydrochloric acid. The product, washed with water and ethanol and air-dried, weighed 1.99 g. (70% yield).

Dihydroxydichloroethylenediamineplatinum(IV), [Pt en (OH)$_2$Cl$_2$].—A suspension of 1.62 g. of [Pt en Cl$_2$] (0.00497 mole) in 20 ml. of 10% hydrogen peroxide solution was heated on a steam-cone with frequent shaking. Within 30–45 minutes the bright yellow [Pt en Cl$_2$] was converted to the pale yellow [Pt en (OH)$_2$Cl$_2$]. The product was filtered on sintered glass, washed with water and ethanol and air-dried. The yield was 1.58 g. (88%).

Anal. Calcd. for [Pt en (OH)$_2$Cl$_2$]: Pt, 54.1; C, 6.66; H, 2.79. Found: Pt, 54.1; C, 6.62; H, 2.84.

***cis*-Dichlorobis-(ethylenediamine)-platinum(IV) Nitrate,** [Pt en$_2$ Cl$_2$](NO$_3$)$_2$.—One and forty-five hundredths grams of [Pt en (OH)$_2$Cl$_2$] (0.00402 mole) was treated with 0.00804 mole (42.1 ml. of 0.1920 *M*) of nitric acid. To the resulting yellow solution was added 0.00402 mole (53.6 ml. of 0.0691 *M*) of ethylenediamine. Addition of the ethylenediamine caused some of the starting material to separate from solution. The resulting suspension was evaporated to dryness on steam-cone, treated with 50 ml. of hot water and again evaporated to dryness. The residue was extracted with 30 ml. of hot water and 0.52 g. of unchanged [Pt en (OH)$_2$Cl$_2$] (0.00145 mole) was removed by filtration. The filtrate was evaporated to crystallization on a steam-cone and cooled to room temperature. The crystals were removed on sintered glass and the filtrate was evaporated to give a second crop of crystals. The cream-colored crystalline product was recrystallized from water and dried in a vacuum desiccator over phosphorus pentoxide. The yield of purified product was 0.221 g. (16.8%).

Anal. Calcd. for [Pt en$_2$ Cl$_2$](NO$_3$)$_2$: Pt, 38.20; C, 9.41; H, 3.14; N, 16.45. Found: Pt, 38.32; C, 9.55; H, 3.17; N, 16.25.

Resolution of *cis*-Dichlorobis-(ethylenediamine)-platinum (IV) Nitrate.—A solution of 0.113 g. of *cis*-[Pt en$_2$ Cl$_2$](NO$_3$)$_2$ (0.00022 mole) dissolved in 5 ml. of water, was added to 0.1452 g. of ammonium-*d*-*α*-bromocamphor-*π*-sulfonate (0.0044 mole) ($[\alpha]^{31}\mathrm{D}$ +85.5°) dissolved in 3 ml. of water. The clear, colorless solution was concentrated on a steam-cone to a volume of approximately 3 ml. Upon standing at room temperature overnight, the solution deposited white crystals. These were removed on a sintered glass filter and washed with a small amount of water followed by acetone and ether. A solution of the 0.0569 g. of this material in 5 ml. of water showed no optical rotation at the D line of sodium.

The filtrate was evaporated at room temperature to a volume of approximately 2 ml. whereupon more crystals separated. A solution of this second fraction (0.0034 g.) in 5 ml. of water showed no optical activity. When the mother liquor was concentrated to a volume of one milliliter a third fraction of white crystals separated from solution. These were removed by filtration and washed with ice-water followed by acetone. The 0.0122 g. of material, dissolved in 5 ml. of water, showed a rotation was +0.040° in a one decimeter tube; $[\alpha]^{23}\mathrm{D}$ +16.4°. This value did not change upon standing at room temperature for 43 hours, nor did it change upon heating for 4 hours at 85°.

The mother liquor was evaporated to dryness at room temperature. The 0.1069 g. of solid residue, dissolved in 5 ml. of water, showed a rotation of +1.400° in a one decimeter tube; $[\alpha]^{23}\mathrm{D}$ +65.5°. This value did not change upon heating the solution at 82° for 6 hours; however, racemization was accomplished by boiling the aqueous solution (Table I).

Preparation of *trans*-Dichlorobis-(ethylenediamine)-platinum(IV) Nitrate, [Pt en$_2$ Cl$_2$](NO$_3$)$_2$.—A solution of *trans*-[Pt en$_2$ Cl$_2$]Cl$_2$ prepared by the method of Basolo, Bailar and Tarr[3] was treated with a solution of the calculated amount of silver nitrate. After digestion on a steam-cone, the silver chloride was removed by filtration, and the filtrate was concentrated to crystallization and cooled to room temperature. The pale yellow crystals were collected on sintered glass. The product was recrystallized from water, washed with small portions of water and dried in a vacuum desiccator over phosphorus pentoxide.

Anal. Calcd. for [Pt en$_2$ Cl$_2$](NO$_3$)$_2$: Pt, 38.20; C, 9.41; H, 3.14; N, 16.45. Found: Pt, 38.30; C, 9.54; H, 3.36; N, 16.25.

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[5] R. N. Keller, *Inorg. Syntheses*, **2**, 250 (1946).

[6] S. M. Jorgensen, *J. prakt. Chem.*, **39**, 1 (1889).