of the pK's. Calculations of pK_1 are independent of pK_2, pK_3 and pK_4 because pK_1 differs from pK_2 by over three pK units. Only in the solutions in which $\bar{n}$ is less than 2.5 is the calculation of pK_2 affected very slightly by the value of pK_3, because pK_2 differs from pK_3 by approximately 2.4 units. Since pK_3 and pK_4 differ by only 0.6 pK unit, equations used to calculate either one must involve the value of the other.

Tri en decomposes in very acid solutions. The solutions turn brown and the pH varies. Measurements of pK_1, therefore, were made in solutions 0.01 molar in nitric acid instead of 0.1 molar. Determinations of pK_2, pK_3, and pK_4 were obtained from solutions 0.1 molar in nitric acid.

TABLE III

DISSOCIATION CONSTANTS AT 40° AND HEATS OF NEUTRALIZATION OF DI EN AND TRI EN

	pK	ΔH, kcal.
	Di en	
pK_1	4.59	− 8.2
pK_2	8.94	−12.6
pK_3	9.68	−11.7
	Tri en	
pK_1	3.76	− 5.6
pK_2	6.79	− 9.6
pK_3	9.14	− 9.6
pK_4	9.76	−10.0

Table III gives the values for the pK's of di en and tri en at 40°, and heats of neutralization calculated from the equation

$$d \ln K/dT = \Delta H/RT^2$$

Undoubtedly, the values for the heats of neutralization are no better than the accuracy to which the change in pK with temperature is known.

The above values, however, are of the right order of magnitude, which indicates that the pK values are correct within the limits of the accuracy of the pH determination.

Work is being continued in this Laboratory on the purification of tetraethylenepentamine and the determination of its acid-base constants.

Summary

1. A method of purification of diethylenetriamine and triethylenetetramine is described.

2. Acid-base dissociation constants of diethylenetriamine and triethylenetetramine have been determined at 30 and 40°.

3. Approximate heats of neutralization of these bases have been calculated from the acid-base constants at 30 and 40°.

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[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of Complex Inorganic Compounds. X. The Stereoisomers of Dichlorobis-(ethylenediamine)-platinum(IV) Chloride[1]

BY FRED BASOLO, JOHN C. BAILAR, JR., AND BETTY RAPP TARR[2]

Dichlorobis-(ethylenediamine)-platinum (IV) chloride has been reported by several investigators, all of whom obtained it by oxidation of bis-(ethylenediamine)-platinum(II) ion. Tschugajeff and Chlopin[3] used ozone and hydrochloric acid, while Grinberg and Ptitsuin[4] employed potassium permanganate. The latter work is open to question, as the product was not analyzed. Kurnakow[5] reported that $[\text{Pt en}_2\text{Cl}_2]$ Cl_2[6] is formed as an orange-yellow, insoluble crystalline material when $[\text{Pt en}_2]\text{Cl}_2$ is treated with chlorine. However, he did not analyze the product. Schleicher, Henkel and Spies[7] got no orange salt when they chlorinated $[\text{Pt en}_2]\text{Cl}_2$, but obtained several pale yellow hydrates of $[\text{Pt en}_2\text{Cl}_2]\text{Cl}_2$. We have been able to repeat Kurnakow's experiment without difficulty, and to show that the orange product is $[\text{Pt enCl}_4]$. If care is taken to avoid prolonged action of an excess of chlorine, the bis-ethylenediamine compound described by Schleicher is obtained.

Schleicher and his co-workers believed that the $[\text{Pt en}_2\text{Cl}_2]\text{Cl}_2$ obtained in their chlorination experiments had the *trans* configuration. They based this conclusion upon the similarity of the material with $[\text{Pt en py}_2\text{Cl}_2]\text{Cl}_2$, the configuration of which they deduced from its reactions with ethylenediamine. This conclusion has been attacked by Chernyaev and Rubinshtein.[8] They argue that the compound which Schleicher used in his proof of structure was not $[\text{Pt en py}_2\text{Cl}_2]\text{Cl}_2$ but was instead $[\text{Pt enCl}_4]\cdot 2\text{py}$.

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[1] Presented before the Physical and Inorganic Division at the 116th meeting of the American Chemical Society, Atlantic City, N. J., September 18-23, 1949.

[2] Most of the work reported in this article was taken from the doctorate theses of Betty Rapp (1941) and Fred Basolo (1943). The remainder was done by Mr. Basolo at Northwestern University.

[3] Tschugajeff and Chlopin, *Z. anorg. allgem. Chem.*, **151**, 264 (1926).

[4] Grinberg and Ptitsuin, *Ann. inst. platine*, **11**, 77 (1933).

[5] Kurnakow, *Z. anorg. Chem.*, **17**, 226 (1898).

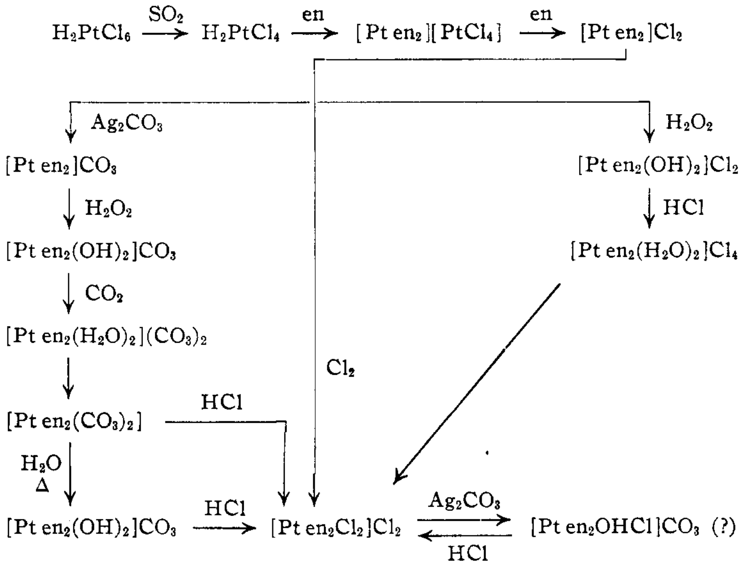
[6] The following symbols are used: en = ethylenediamine and py = pyridine.

[7] Schleicher, Henkel and Spies, *J. prakt. Chem.*, **105B**, 31 (1922).

[8] Chernyaev and Rubinshtein, *Ann. inst. platine*, **11**, 63 (1933).

The present work was undertaken in an attempt to determine the configuration of the known $[Pt\,en_2Cl_2]Cl_2$ and to prepare the geometrical isomer of this compound. If the isolation of both isomers were possible, an unequivocable proof that one salt is the *cis* isomer would consist of its resolution into optically active forms. The possibility of isolating optically active $[Pt\,en_2Cl_2]Cl_2$ is likewise of extreme interest since it could be used in studies of substitution reactions similar to those made with the corresponding cobalt(III) complex.[9]

The procedure employed was that of preparing dichlorobis-(ethylenediamine)-platinum(IV) chloride by various methods and then determining whether these products had the same or different structures. The series of reactions studied that yielded this compound may be conveniently outlined as



That geometric isomers of certain metallic complexes exhibit distinctly different colors (*cis* and *trans* $[Co\,en_2Cl_2]Cl_2$ are purple and green, respectively) has long been known.[10] Shibata[11] suggests that *cis–trans* isomers have different absorption spectra, although this difference may not manifest itself in the visible range. More recent studies of Babaeva[12] show that the ultraviolet absorption spectra of the two forms of $[Pt(NH_3)_2Cl_2]$ are different. This technique was applied to determine the relative configurations of the five samples of $[Pt\,en_2Cl_2]Cl_2$ obtained by the various paths outlined above. All of these substances showed identical absorption spectra (Fig. 1) and it must therefore be concluded that they have the same structure.

The reaction between $[Pt\,en_2Cl_2]Cl_2$ and silver carbonate appeared to be a logical method of attack because it has been widely used to convert the analogous *trans*-dichlorocobalt(III) compound into the carbonato complex which in turn reacts with alcoholic hydrogen chloride to yield the *cis*-dichloro-isomer.[13] Our experiments, however, have made it clear that no such analogy exists between these complexes of platinum(IV) and cobalt(III). The coördinately bound chloride atoms were only partially removed from the complex by means of silver carbonate. The solution extracted from the reaction mixture gave no qualitative test for chloride ion by the conventional treatment with nitric acid and silver nitrate, which at first suggested that the dichloro chloride had been transformed into $[Pt\,en_2CO_3]CO_3$, but the carbon analysis of this compound was always low. Subsequent conductivity measurements[14] on a solution of $[Pt\,en_2Cl_2]Cl_2$ showed that it was hydrolyzed to an extent of less than a half of a per cent. even after standing several days. This lack of hydrolysis clearly establishes the fact that the chloro groups are firmly held in the complex in contrast to those in the corresponding cobalt(III) compound.[15] Additional evidence for this was obtained by treating a solution of $[Pt\,en_2Cl_2]Cl_2$ with an excess of silver nitrate and removing the silver chloride on a filter; the filtrate from this precipitate showed no sign of further precipitation even after standing for several days. The coordinated chloride was detected only after the complex had been digested in a mixture of caustic and silver oxide followed by the acidification of the mixture with nitric acid. The fact that the chloro groups are more covalently bonded in the platinum(IV) than they are in the analogous cobalt(III) complex cation may be attributed to the greater positive charge on platinum or to its higher electronegativity.[16]

Werner[17] determined the relative basic strength of ten complex cations and placed $[Pt(NH_3)_4(OH)_2]^{+2}$ at the bottom of the list. Although he states that this cation is so weak a base that it does not absorb carbon dioxide, we were able to show that the corresponding $[Pt\,en_2(OH)_2]^{+2}$ slowly takes up carbon dioxide to yield an insoluble product. The fact that this substance is not soluble in water while most car-

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[9] Bailar and Auten, THIS JOURNAL, **56**, 774 (1934); Jonassen, Bailar and Huffman, *ibid.*, **70**, 756 (1948).

[10] Jörgensen, *J. prakt. Chem.*, **39**, 16 (1889).

[11] Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, **37**, 1 (1915).

[12] Babaeva, *Compt. rend. acad. sci. U. R. S. S.*, **20**, 365 (1938).

[13] Bailar and Peppard, THIS JOURNAL, **62**, 105 (1940).

[14] The conductivity measurements were made with a Jones bridge by Professor R. G. Pearson.

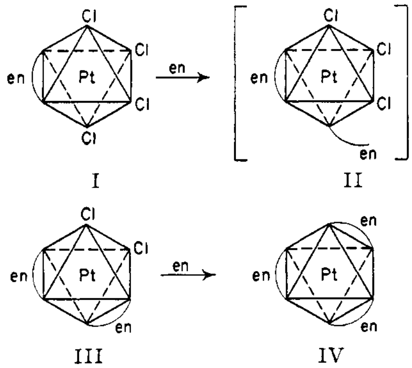
[15] Mathieu, *Bull. soc. chim.*, **3**, 2152 (1936).

[16] Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 257.

[17] Werner, "New Ideas on Inorganic Chemistry," Longmans, Green and Co., London, 1911, p. 201.

bonato complexes are extremely soluble suggests that it is a non-ionic complex and analysis shows that it is $[\mathrm{Pt\,en_2(CO_3)_2}]$. The carbonato groups in this complex must therefore be monodentate. This certainly indicates that they occupy *trans* positions for the chelation effect of the carbonato group is strong enough that if the two hydroxo groups were in *cis* positions, one carbonate group would replace them both. Since the dichloro chloride obtained from this complex has the same structure as that produced by the oxidation of $[\mathrm{Pt\,en_2}]\mathrm{Cl_2}$ with chlorine, the latter complex must likewise have a *trans* configuration. It has also been shown that the supposed $[\mathrm{Pt\,en_2(CO_3)_2}]$ does not rearrange to $[\mathrm{Pt\,en_2CO_3}]\mathrm{CO_3}$ when heated; instead carbon dioxide is liberated and $[\mathrm{Pt\,en_2(OH)_2}]\mathrm{CO_3}$ is formed. This finding is not surprising since the dihydroxy cation is a weak base and its carbonate may be expected to lose carbon dioxide at elevated temperatures. In addition it is known that coördination compounds of platinum generally resist such changes in configuration.[18]

That an excess of $[\mathrm{Pt\,enCl_4}]$ and ethylenediamine react to yield $[\mathrm{Pt\,en_3}]\mathrm{Cl_4}$ was confirmed,[7] while with exactly the same conditions no such product can be isolated from a reaction mixture containing $[\mathrm{Pt\,en_2Cl_2}]\mathrm{Cl_2}$ and ethylenediamine. These observations indicate that the $[\mathrm{Pt\,en_2Cl_2}]\mathrm{Cl_2}$ has a *trans* configuration and that the reaction of ethylenediamine with $[\mathrm{Pt\ enCl_4}]$ may proceed as shown.



This mechanism is suggested because it has been demonstrated[19] that ligands *trans* to a negative group are more labile so that one of the chloro groups in I should be more easily displaced than the other three as illustrated by II. Since ethylenediamine can span only adjacent positions, compound III, which can undergo further reaction with ethylenediamine to yield IV, is to be expected. Conclusive proof of this mechanism of reaction would necessitate the isolation of III. This has not been realized chiefly because I is insoluble in water and reacts very slowly with ethylenediamine while II, which is being formed gradually, is extremely soluble and readily converted to IV. Unfortunately I is likewise insoluble in non-aqueous solvents.

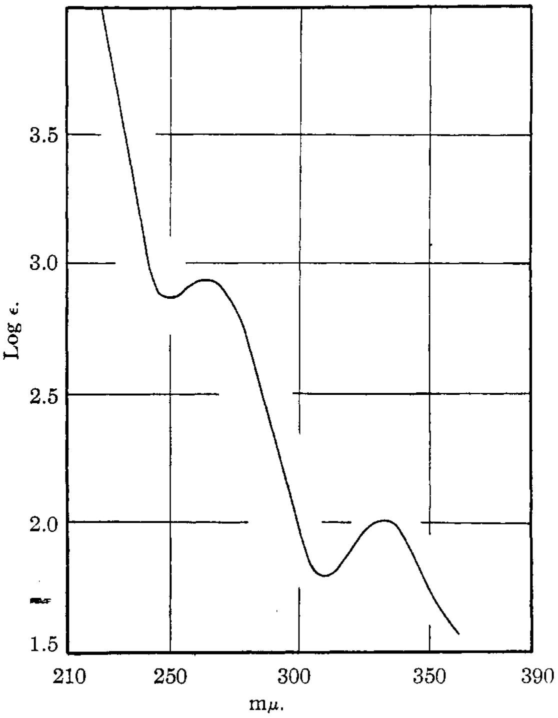


Fig. 1.—Absorption spectrum of dichlorobis-(ethylenediamine)-platinum(IV) chloride.

An analogous compound $[\mathrm{Pt\,en\,(OH)_2Cl_2}]$ in which two hydroxo groups take the place of two chloro groups was prepared. This non-ionic complex is likewise insoluble but reacts with nitric acid to yield the water soluble salt $[\mathrm{Pt\ enH_2O(OH)Cl_2}]\mathrm{NO_3}$. Treatment of this solution with an excess of ethylenediamine at room temperature regenerates the insoluble $[\mathrm{Pt\ en\,(OH)_2Cl_2}]$ and at elevated temperatures $[\mathrm{Pt\ en\,(OH)_4}]$ is formed.

Still another approach to the synthesis of *cis*-$[\mathrm{Pt\,en_2Cl_2}]\mathrm{Cl_2}$ is suggested by the elimination reaction[20] which converts $[\mathrm{Pt\ (NH_3)_4}]\mathrm{Cl_2}$ to *trans* $[\mathrm{Pt(NH_3)_2Cl_2}]$. It is likewise known that a molecule of ethylenediamine is displaced when tris-(ethylenediamine)-chromium(III) chloride is heated.[21] Although it seems plausible that platinum(IV) would have a greater attraction for negative chloro groups than does chromium(III), it was found that $[\mathrm{Pt\,en_3}]\mathrm{Cl_4}$ is largely decomposed when heated yielding only small amounts of the reduced salt $[\mathrm{Pt\ en_2}]\mathrm{Cl_2}$.

Experimental[22]

Spectral Measurements.—Ultraviolet absorption spectra were measured with the Beckman quartz spectrophotometer, using 1-cm. silica

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[18] Mathieu, *Bull. soc. chim.*, **5**, 776 (1938).

[19] Chernyaev, *Ann. inst. platine*, **4**, 243 (1926).

[20] Reiset, *Compt. rend.*, **18**, 1103 (1844).

[21] Pfeiffer, *Z. anorg. Chem.*, **24**, 294 (1900); **29**, 113 (1901); Rollinson and Bailar, THIS JOURNAL, **66**, 641 (1944).

[22] Platinum, carbon and hydrogen analyses by Miss Margaret Hines.

cells. Extinction coefficients were calculated from the familiar equation

$$\epsilon = \frac{1}{cd}\log_{10}(I_0/I)$$

Aqueous solutions of the complex salt were used at concentrations of 5.5×10^{-3}, 5.5×10^{-4} and 5.5×10^{-5} molar in order that the complete absorption spectrum could be obtained from 400 mμ to 220 mμ. The measurements were made at room temperature; a total operation time of approximately one hour was required.

Tetrachloroplatinic(II) Acid.—A solution of 10 g. of hexachloroplatinic(IV) acid, $H_2PtCl_6 \cdot 6H_2O$, in 60 cc. of water and 2 cc. of concentrated hydrochloric acid was reduced with a freshly prepared solution of sulfur dioxide by the method described by Keller,[23] except that the solution of sulfur dioxide was added by means of a dropping funnel. The tetrachloroplatinic(II) acid was not isolated but, instead, this reaction mixture was employed in the subsequent synthesis of $[Pt\,en_2]Cl_2$.

Bis-(ethylenediamine)-platinum(II) Chloride.—The procedure used by Keller[23] for the preparation of $[Pt(NH_3)_4]Cl_2$ was followed with slight modifications to yield the analogous $[Pt\,en_2]Cl_2$. The above reaction mixture, which contains chiefly tetrachloroplatinic(II), hydrochloric and sulfuric acids was diluted to exactly 100 cc. This solution was divided into equal portions and one portion was diluted to 100 cc. and heated to boiling. A slight excess of ethylenediamine (4 g. of 95–100% base) was cautiously added to the boiling mixture. The precipitate which immediately separated was gradually dissolved during vigorous mechanical stirring at this elevated temperature. After cooling the clear reaction mixture to room temperature dilute hydrochloric acid was added until a *p*H of 7 was reached. This solution was then added to the second 50-cc. portion of the original tetrachloroplatinic(II) acid and the pink salt, $[Pt\,en_2][PtCl_4]$, which precipitated was collected on a Buchner filter and washed with distilled water. The washed press cake was suspended in 100 cc. of water and an excess (10 g. of 95–100% base) of ethylenediamine was added. This mixture was boiled over an open burner and stirred vigorously until the precipitate had completely dissolved. The resulting solution was then concentrated until crystals began to separate, at which time the volume was increased fivefold by the addition of ethanol. The product which was collected on a filter, washed with ethanol followed by ether and dried at 75°, weighed 6.5 g. (88% yield).

Anal. Calcd. for $[Pt\,en_2]Cl_2$: Pt, 50.53; C, 12.43; H, 4.17. Found: Pt, 50.53; C, 12.60; H, 4.14.

***trans*-Dichlorobis-(ethylenediamine)-platinum(IV) Chloride.**—Five grams of $[Pt\,en_2]Cl_2$ was dissolved in 100 cc. of water and chlorine was slowly bubbled through this solution until a faint cloudiness appeared, at which time the original yellow color of the solution began to deepen to orange. The chlorination was allowed to continue for three minutes after the cloudiness first appeared and then air was bubbled through the solution to remove the excess chlorine. The trace of insoluble material was removed on a filter and the filtrate was concentrated to crystallization. This concentrate was diluted to five times its volume with ethanol and the crystalline product was collected on a filter, washed with alcohol followed by ether and dried at 75°. A quantitative yield of the *trans*-dichloro salt was obtained.

Anal. Calcd. for $[Pt\,en_2Cl_2]Cl_2$: Pt, 42.69; C, 10.51; H, 3.53. Found: Pt, 42.01; C, 10.69; H, 3.67.

Reaction of Dichlorobis-(ethylenediamine)-platinum(IV) Chloride with Silver Carbonate.—Five grams (0.009 mole) of this dichloro complex was ground in a mortar with 7.5 g. (0.027 mole) of freshly precipitated silver carbonate and 5 cc. of water for three hours. The residue was then extracted with 25 cc. of water; the extract contained carbonate ion and a trace of silver ion but no ionizable chloride. However, when the solution was digested for 15 min. with potassium hydroxide and silver oxide and the mixture acidified with nitric acid, a precipitate of silver chloride was obtained. The solution was concentrated to approximately 5 cc. and an excess of alcohol and ether was added; the yellow viscous oil which separated became solid after several extractions with absolute alcohol. The solid was so soluble that it could not be purified by recrystallization, so it was dissolved in a small amount of water and reprecipitated with alcohol and ether. The yellow product was dried *in vacuo* at 65° for two days during which time it gradually changed to a dark gray color suggesting the presence of silver impurity. Analysis of this material indicated that it was a mixture, but showed clearly that it could not be the carbonato complex.

Anal. Calcd. for $[Pt\,en_2OHCl]CO_3$: Pt, 45.60; C, 14.03; H, 4.06; Cl, 8.29. Found: Pt, 43.92; C, 14.84; H, 4.13; Cl, 7.8.

When this material was ground in a mortar with an alcoholic solution of hydrogen chloride immediate reaction occurred with the liberation of carbon dioxide and the formation of a yellow solid. The yellow solid was collected on a filter and washed with ethanol to remove the excess hydrogen chloride. For purification, chiefly from silver chloride, the yellow salt was dissolved in a small amount of water and reprecipitated as pale yellow crystals by addition of absolute ethanol.

Anal. Calcd. for $[Pt\,en_2Cl_2]Cl_2$: Pt, 42.69; C, 10.51; H, 3.53. Found: Pt, 42.82; C, 10.71; H, 3.59.

Reaction of Dichlorobis-(ethylenediamine)-platinum Chloride with Ethylenediamine.—A reaction mixture which contained 1.5 g. (0.0033 mole) $[Pt\,en_2Cl_2]Cl_2$, 8 cc. of a 5% solution (0.0066 mole) of ethylenediamine and 15 cc. of water was stirred for twenty-four hours at room temperature. The solution was concentrated to dryness at room temperature by means of a slow current of air. This residue was dissolved in a small amount of water and an excess of ethanol and ether were added to precipitate the resulting salt. The product was collected on a filter, washed with alcohol and ether, then dried at 65° to give 1.2 g. (90% yield) of $[Pt\,en_2(OH)_2]Cl_2$.

Anal. Calcd. for $[Pt\,en_2(OH)_2]Cl_2$: Pt, 46.44; C, 11.43; H, 4.32. Found: Pt, 46.53; C, 11.82; H, 4.47.

The same salt was prepared essentially by the method of Tschugajeff and Chlopin[3] for the synthesis of $[Pt(NH_3)_4(OH)_2]Cl_2$. A reaction mixture containing 0.5 g. (0.0013 mole) of $[Pt\,en_2]Cl_2$ and 5 cc. of a 10% solution of hydrogen peroxide was heated on a water-bath at 80° for one hour. An excess of ethanol and ether were added to the resulting solution and the theoretical yield of the desired salt was isolated.

Anal. Found: Pt, 46.74; C, 11.63; H, 4.62.

Reaction of Dihydroxybis-(ethylenediamine)-platinum(IV) Chloride with Hydrogen Chloride.—One half a gram (0.0013 mole) of $[Pt\,en_2]Cl_2$ was oxidized with hydrogen peroxide as described above. The reaction mixture which contained $[Pt\,en_2(OH)_2]Cl_2$ was made acid with 1 cc. of concentrated hydrochloride acid and the solution was placed on a steam-bath for five minutes. An excess of ethanol and ether was added to the acid solution and 0.5 g. (85% yield) of $[Pt\,en_2Cl_2]Cl_2$ was obtained.

Anal. Found: Pt, 42.47; C, 10.47; H, 3.72.

Dihydroxybis-(ethylenediamine)-platinum(IV) Carbonate.—Two grams (0.0052 mole) of $[Pt\,en_2]Cl_2$ was ground in a mortar with 4.3 g. (0.01 mole) of freshly precipitated silver carbonate. After approximately one hour the slurry was extracted with three 5-cc. portions of water; the solution contained silver ions but no chloride. Ten cubic centimeters of 10% hydrogen peroxide was added to the extract and a vigorous reaction occurred with the formation of a small amount of black silver resi-

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[23] Keller, *Inorg. Syntheses*, **2**, 250 (1946).

due. This mixture was then heated on a water-bath for fifteen minutes at 80° and the silver residue was removed on a filter. An additional 5 cc. of hydrogen peroxide was added to the filtrate and the mixture was concentrated on a water-bath to a volume of approximately 10 cc. A small portion of the concentrate was diluted with an excess of ethanol and ether to yield the dihydroxy carbonate.

Anal. Calcd. for $[\text{Pt en}_2(\text{OH})_2]\text{CO}_3\cdot 2\text{H}_2\text{O}$: Pt, 43.82; C, 13.48; H, 4.98. Found: Pt, 43.99; C, 13.48; H, 4.99.

Dicarbonatobis-(ethylenediamine)-platinum(IV).—The concentrated solution of $[\text{Pt en}_2(\text{OH})_2]\text{CO}_3$ described above had a *p*H of 11. This solution was surrounded by an ice-bath and previously washed carbon dioxide was slowly bubbled through the solution by means of a glass sintered filter stick. After a short time the reaction mixture became cloudy and finally a thick slurry was formed. After one day the silky white insoluble product was washed with cold water, dried at 75° and weighed 1.2 g. (53% yield).

Anal. Calcd. for $[\text{Pt en}_2(\text{CO}_3)_2]$: Pt, 44.83; C, 16.65; H, 3.70. Found: Pt, 44.69; C, 16.61; H, 3.78.

Reaction of Dicarbonatobis-(ethylenediamine)-platinum(IV) with Hydrogen Chloride.—Two-tenths of a gram (0.0005 mole) of $[\text{Pt en}_2(\text{CO}_3)_2]$ was ground in a mortar with an excess of alcoholic hydrogen chloride. When the liberation of carbon dioxide was no longer apparent, the residue was collected on a filter and washed with ethanol followed by ether. This salt was recrystallized from a mixture of ethanol and water and $[\text{Pt en}_2(\text{OH})_2]\text{Cl}_2$ was isolated.

Anal. Found: Pt, 46.45; C, 11.47; H, 4.39.

However, treatment of 0.5 g. (0.0011 mole) of $[\text{Pt en}_2(\text{CO}_3)_2]$ with 2 cc. of concentrated hydrochloric acid did yield the dichloro salt. The acid solution was heated on a steam-bath for five minutes and then the salt was precipitated by the addition of ethanol and ether.

Anal. Found: Pt, 42.73; C, 10.62; H, 3.60.

Hydrolysis of Dicarbonatobis-(ethylenediamine)-platinum(IV).—A suspension of 0.2 g. (0.0005 mole) of $[\text{Pt en}_2(\text{CO}_3)_2]$ in 25 cc. of water was boiled for a period of approximately one hour. During this time the insoluble complex was dissolved and water was added on three occasions to prevent evaporation to dryness. The water soluble dihydroxy carbonate was then isolated from this cold concentrate by precipitation with ethanol and ether.

Anal. Found: Pt, 43.82; C, 13.48; H, 4.98.

This salt was allowed to react with an excess of hydrochloric acid and the dichloro chloride was isolated by the usual procedure.

Anal. Found: Pt, 42.53; C, 10.58; H, 3.57.

Potassium Tetrachloroplatinate(II).—This was prepared essentially by the method of Keller[23] and the pink salt was used as the starting material in the synthesis of $[\text{Pt enCl}_2]$.

Dichloroethylenediamineplatinum(II).—The method described by Drew[24] for the preparation of this salt was slightly modified. Ten cubic centimeters of 5% ethylenediamine (0.008 mole) was added to 90 cc. of solution containing 6.4 g. (0.015 mole) of K_2PtCl_4 (it should be pointed out that this suggests the solubility of this salt as reported by Keller[23] is perhaps in error). The reaction mixture was stirred occasionally at room temperature and yellow crystals which separated were collected at rather short intervals to prevent any further reaction with ethylenediamine. Whenever the yellow product ceased to separate from this mother liquor, 8 cc. (0.007 mole) of the amine was again added and the procedure was continued. After approximately two hours and ten filtrations the pink salt $[\text{Pt en}_2][\text{PtCl}_4]$ began to separate along with the desired product. After this had started it became impossible to isolate any more of the desired product. The total amount of yellow crystals which had been repeatedly collected on the same filter were washed with water, ethanol and ether, then dried at 75°. Four grams (78% yield) of $[\text{Pt enCl}_2]$ was obtained.

Tetrachloroethylenediamineplatinum(IV).—This compound was prepared by the oxidation of $[\text{Pt enCl}_2]$ with chlorine.[6] A gentle stream of chlorine was bubbled through a suspension of 3.9 g. (0.012 mole) in 225 cc. of water which was surrounded by a boiling water-bath. During this treatment the yellow crystals became reddish brown and then gradually changed back to a yellow color. After forty-five minutes the chlorine treatment was discontinued and the excess chlorine was swept out of the solution by a stream of air. The yellow product was collected on a filter and washed with water, then the filtrate was concentrated on a steam-bath to 20 cc. to yield additional material. A total of 4.4 g. (82% yield) of $[\text{Pt enCl}_4]$ was obtained.

Reaction of Tetrachloroethylenediamineplatinum(IV) with Ethylenediamine.—One gram (0.0025 mole) of $[\text{Pt enCl}_4]$ was suspended in 20 cc. of water and 3 cc. of 5% (0.0025 mole) ethylenediamine was added. This mixture was kept at room temperature and agitated for twenty-four hours and then the unchanged $[\text{Pt enCl}_4]$ was removed on a filter. The filtrate was evaporated to dryness at room temperature by a stream of air and the residue was redissolved in a minimum amount of water. The tris-(ethylenediamine) salt was precipitated from this solution by the addition of ethanol and ether and purified by recrystallization from an ethanol-water mixture.

Anal. Calcd. for $[\text{Pt en}_3]\text{Cl}_4$: Pt, 37.74; C, 13.93; H, 4.68. Found: Pt, 37.78; C, 13.61; H, 4.99.

Dihydroxydichloroethylenediamineplatinum(IV).—Dichloroethylenediamineplatinum(II) was oxidized with hydrogen peroxide by the same procedure described for the preparation of $[\text{Pt en}_2(\text{OH})_2]\text{Cl}_2$. The reaction mixture consisted of 1.5 g. (0.0046 mole) $[\text{Pt enCl}_2]$, 15 cc. of water and 10 cc. of 30% hydrogen peroxide. The insoluble product was collected on a filter, washed with water, alcohol and ether and dried at 75°. One and a half grams of $[\text{Pt en}(\text{OH})_2\text{Cl}_2]$ was obtained (90% yield).

Anal. Calcd. for $[\text{Pt en}(\text{OH})_2\text{Cl}_2]$: Pt, 54.2. Found: Pt, 54.5.

One-half a gram (0.0014 mole) of the $[\text{Pt en }(\text{OH})_2\text{Cl}_2]$ was suspended in 10 cc. of water and 0.1 cc. (0.0016 mole) of 95% ethylenediamine was added. The mixture was shaken at room temperature for twenty-four hours but no reaction occurred, as was indicated by theoretical recovery of unchanged complex and the absence of any platinum in the filtrate.

This insoluble complex does dissolve, however, when heated with an excess of ethylenediamine. One and a half grams (0.0042 mole) of $[\text{Pt en}(\text{OH})_2\text{Cl}_2]$ was suspended in 20 cc. of water and 5 cc. (0.84 mole) of 95% ethylenediamine was added. This reaction mixture was heated to boiling over an open flame during vigorous agitation. After approximately five minutes the complex was completely dissolved and ethanol and ether were added to the cold solution. The hygroscopic oily residue which separated on the bottom of the beaker was washed by decantation with alcohol and ether but could not be conviently collected. Instead, it was dissolved in a small amount of water and the solution was made acid with an excess of concentrated hydrochloric acid. After a few minutes, yellow insoluble crystals of $[\text{Pt enCl}_4]$ separated from solution.

Anal. Calcd. for $[\text{Pt enCl}_4]$: Pt, 49.2. Found: Pt, 49.0.

Dichlorohydroxyaquoethylenediamineplatinum(IV) Nitrate.—One gram (0.0028 mole) of $[\text{Pt en}(\text{OH})_2\text{Cl}_2]$ was dissolved in 10 cc. of 1:1 nitric acid solution. This solution was concentrated on a steam-bath to approximately half its volume and the concentrate was then cooled in an ice-salt mixture. Well defined crystals separated and at this point an excess of ethanol and ether were added. The crystalline product was collected on a filter and washed with alcohol and ether and dried at 75° to give 0.75 g. (65% yield) of $[\text{Pt enH}_2\text{O}(\text{OH})\text{Cl}_2]\text{NO}_3$.

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[24] Drew, *J. Chem. Soc.*, 2328 (1932).

Anal. Calcd. for [Pt en$H_2O(OH)Cl_2$]NO_3: Pt, 46.2. Found: Pt, 45.8.

An aqueous solution of [Pt en$H_2O(OH)Cl_2$]NO_3 at room temperature reacts with an excess of ethylenediamine to give an immediate precipitate of [Pt en$(OH)_2Cl_2$].

Anal. Found: Pt, 54.3.

Tris-(ethylenediamine)-platinum(IV) Chloride.—The method used by Smirnoff[25] to produce [Pt en_3]Cl_4 was applied in the preparation of this salt. Three grams (0.0058 mole) of $H_2PtCl_6.6H_2O$ was dissolved in 65 cc. of absolute ethanol and 2.2 cc. of 95% (0.035 mole) ethylenediamine was added. This mixture was placed in a water bath at 80° and stirred constantly for one-half hour. During this time the original yellow precipitate of en H_2PtCl_6 gradually changed to the pale yellow [Pt en_3]Cl_4. This salt was collected on a filter and washed with absolute ethanol followed by ether. After drying at 75° the complex weighed 3 g. (theoretical yield) and a portion of this material was purified for analysis by recrystallization from a mixture of ethanol and water.

Anal. Found: Pt, 37.80; C, 13.61; H, 4.75.

Decomposition of Tris-(ethylenediamine)-platinum(IV) Chloride.—One half a gram of solid [Pt en_3]Cl_4 which contained a trace of ethylenediamine hydrochloride was placed in a large test-tube which was surrounded by an oil-bath and attached to a vacuum pump. At a pressure of 3 mm. there was no apparent change until a temperature of 175° had been reached at which time the salt became gray. The solid was then kept at 165° at this reduced pressure for ten hours during which time the ethylenediamine hydrochloride sublimed to the cooler portions of the test-tube. The gray residue which weighed 0.4 g. was then transferred to a beaker and 10 cc. of water was added. An appreciable amount of insoluble brown residue was removed on a filter and the tan filtrate was decolorized with a small amount of charcoal. This clear solution yielded 0.2 g. of [Pt en_2]Cl_2 when treated with a mixture of ethanol and ether.

Anal. Found: Pt, 50.58; C, 12.60; H, 4.18.

Summary

Dichlorobis-(ethylenediamine)-platinum(IV) chloride has been prepared by (1) the chlorination of [Pt en_2]Cl_2, (2) the reaction of [Pt $en_2(OH)_2$]Cl_2 with hydrochloric acid and (3) the reaction of [Pt $en_2(CO_3)_2$] with hydrochloric acid.

The fact that in every case the [Pt en_2Cl_2]Cl_2 isolated had the same structure was established by their identical absorption spectrum. Evidence has likewise been cited which indicates that this cation has a *trans*-configuration.

It has been demonstrated that the coördinated chloro groups in this compound are extremely covalent compared to those of the corresponding cobalt(III) complex.

Attempts to prepare *cis*-[Pt en_2Cl_2]Cl_2 were not successful.

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[25] Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Carbon Dichloride as an Intermediate in the Basic Hydrolysis of Chloroform. A Mechanism for Substitution Reactions at a Saturated Carbon Atom[1]

BY JACK HINE[2]

In a literature survey on the effect of halogen atoms on the reactivity of other halogen atoms attached to the same carbon atom it was found that chloroform is much more reactive toward basic hydrolysis than methylene chloride or carbon tetrachloride (see Tables I and II). No clear explanation of this behavior was found by consideration of the two mechanisms (S_N1 and S_N2)[3] commonly accepted for substitution reactions at a saturated carbon atom. However, it seemed that mechanism I

$$\text{(I)}\qquad CHCl_3 + OH^- \overset{\text{fast}}{\rightleftharpoons} CCl_3^- + H_2O$$

$$CCl_3^- \xrightarrow{\text{slow}} Cl^- + CCl_2$$

$$CCl_2 \xrightarrow[H_2O]{OH^-,\ \text{fast}} CO + HCO_2^-$$

offered an adequate explanation of the behavior of chloroform.

The idea that carbon dichloride is an intermediate in the basic hydrolysis of chloroform is not new. Upon learning that chloroform and alkali yield carbon monoxide as well as formate, Geuther,[4] in 1862, suggested that chloroform is actually $CCl_2{\cdot}HCl$ and that the hydrogen chloride may be removed by alkali to give carbon dichloride, which is further hydrolyzed to carbon monoxide. A number of other workers have expressed similar views.[5] Most of them seem to utilize the fact that carbon monoxide is formed in the reaction as the sole evidence for the intermediacy of carbon dichloride, but Mossler also cites the reaction of chloroform vapor and air with solid potassium hydroxide to give phosgene. Since it was believed that neither of these facts is sufficient evidence to indicate that carbon dichloride is an intermediate in the basic hydrolysis of chloroform, a study of the subject was initiated.

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[3] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[4] A. Geuther, *Ann.*, **123**, 121 (1862).

[5] J. U. Nef, *ibid.*, **298**, 367 (1897); J. Thiele and F. Dent, *ibid.*, **302**, 273 (1898); G. Mossler, *Monatsh.*, **29**, 573 (1903); G. Urbain, *Bull. soc. chim.*, [4] **51**, 853 (1932); **53**, 647 (1933); A. Tchakerian, *ibid.*, [4] **51**, 846 (1932); P. B. Sarkar, *Proc. Natl. Inst. Sci. India*, **2**, 63 (1936); *C. A.*, **32**, 2083^2 (1938); E. N. Allott, "Richter's Organic Chemistry," 3rd ed., Nordeman Publ. Co., New York, N. Y., 1934, Vol. I, p. 291.