(II) analog results in the inner complex.[1,3] In addition, *cis–trans* isomerism is observed for the inner complex of platinum(II).[3] Due to the stable nature of the platinum(II) and palladium(II) complexes, heteropolynuclear chelates can be prepared. The silver(I) heteropolynuclear chelates with platinum(II) and palladium(II) have the same structure as the copper(II) compound (structure II), as indicated by their virtually identical infrared spectra. The action of excess cupric chloride on either *trans*-bis(pyridine-2-aldoxime)palladium(II) or *cis*-bis(pyridine-2-aldoxime)platinum(II) yields a compound with a structure completely analogous to the structure of the copper(II) compound (structure IV). Again the virtually identical infrared spectra of these compounds indicate that such is the case. Coordination of two bis(pyridine-2-aldoxime)platinum(II) molecules to each copper(II) ion yields the heteropolynuclear chelate whose structure is analogous to that of the homopolynuclear chelate of copper(II) (structure III). The infrared spectrum of bis[bis(pyridine-2-aldoxime)platinum(II)]copper(II) perchlorate and that of the corresponding homopolynuclear copper(II) compound are essentially identical.

The method used to prepare the tris[bis(pyridine-2-aldoxime)platinum(II)]rhodium(III) ion is similar to the one used by Dwyer and Sargeson[5] to prepare the trisacetylacetone rhodium(III) complex. The formation of the heteropolynuclear chelate is considerably slower than the formation of the acetylacetone complex. The structure of this interesting heteropolynuclear chelate is probably that of a regular octahedral complex.

(5) F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **75**, 984 (1953)

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Complexes of Ethylenediamine-N,N′-diacetic Acid and Platinum. *cis*-Oxidation

BY CHUI FAN LIU

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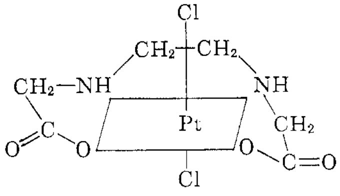
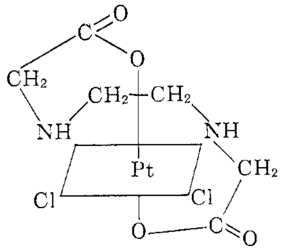
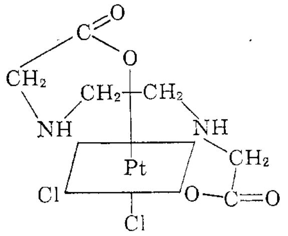
The complexes of ethylenediamine-N,N′-diacetic acid and platinum were studied. The ligand formed bidentate and tetradentate complexes with platinum(II). With platinum(IV) tridentate and tetradentate complexes were obtained. Oxidations of the platinum(II) complexes to form the dichloro(ethylenediamine-N,N′-diacetato)platinum(IV) were carried out. It was found that the regular type of addition reaction could be performed to yield the *trans*-dichloro isomer. It is of interest that the *cis*-dichloro isomer could also be obtained either by a ring closure reaction or by direct oxidation with the hexachloroplatinate(IV) ion.

The chelating ability of ethylenediamine-N,N′-diacetic acid was first investigated by Chaberek and Martell,[1] who measured the stability constants of several divalent metal ion complexes of this ligand. The complexes investigated, however, were of the labile type. No products were isolated and the structural aspects of the complexes were not examined. The present investigation is concerned with the nonlabile complexes between ethylenediamine-N,N′-diacetic acid and platinum(II), and the oxidation of the platinum(II) complexes to platinum(IV) compounds. The stereochemistry of this oxidation is of particular interest. Dichloro(ethylenediamine-N,N′-diacetato)platinum(IV) can exist in three possible isomers. One isomer has the two coordinated chloride groups *trans* to each other. The second isomer has one chloride group *cis* to the other but the two carboxyl groups *trans* to each other. In the third isomer the chloride groups are *cis* to each other as are the carboxyl groups.







When a square-planar platinum(II) compound is oxidized to an octahedral platinum(IV), it has been found in the past that the two incoming groups always go *trans* to each other,[2,3] which fact would make the two *cis*-dichloro isomers difficult to obtain through oxidation. The stereochemistry of the oxidation of platinum(II) complexes of ethylenediamine-N,N′-diacetic acid has been examined and it has been found that oxidation can give a *cis*-dichloro isomer. It has also been found

(1) S. Chaberek and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 6228 (1952).

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

(3) A. Werner, "Lehrbuch der Stereochemie," 1904.

that ethylenediamine-N,N′-diacetic acid in forming complexes with platinum can act as a bidentate, a tridentate, or a tetradentate ligand, a fact quite analogous to the case of EDTA reported by Busch and Bailar.[4]

Experimental

Starting Materials.—Potassium tetrachloroplatinate(II) was prepared by a modification of the method of Cooley and Busch.[5,6] Ethylenediamine-N,N′-diacetic acid was obtained from K and K Laboratories, Inc. *Anal.* Calcd. for $C_6H_{12}N_2O_4$: C, 40.91; H, 6.82; N, 15.91. Found: C, 40.59; H, 6.51; N, 16.43.

Analyses.—Platinum analyses were carried out by ignition. The microanalyses of carbon, hydrogen, nitrogen, and chlorine were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Infrared Spectra.—All spectra were obtained on a Perkin-Elmer Model 21 double beam instrument. Nujol mulls were employed in all cases.

Dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II).—Six grams of potassium tetrachloroplatinate(II) and 2.54 g. of ethylenediamine-N,N′-diacetic acid were dissolved in 400 ml. of water and heated on a steam bath for 3 hr., and 72 ml. of 0.1 *N* NaOH was added. The mixture was heated for 3 hr. more and filtered. The filtrate was evaporated on a steam bath to about 30 ml. and about 10 ml. of concentrated hydrochloric acid was added. Light yellow needles immediately crystallized which were filtered, washed with a small amount of distilled water, and dried. The yield was 58% of the theoretical. *Anal.* Calcd. for $[Pt(C_6H_{12}N_2O_4)Cl_2]$: C, 16.29; H, 2.71; N, 6.33; Pt, 44.12. Found: C, 16.30; H, 2.74; N, 6.45; Pt, 44.70. Titration of this compound with a Beckman Model G pH meter gave a titration curve which showed a single break and gave the equivalent weight of the compound as 221, which corresponds to the theoretical value. The pK_a value was determined to be 2.88. The infrared spectrum of the compound showed a sharp single COO band at 1730 cm.$^{-1}$.

Diammine(ethylenediamine-N,N′-diacetic acid)platinum(II) Chloride.—Dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) (0.375 g.) was dissolved in about 10 ml. of concentrated aqueous ammonia. On heating for about 15 min. on a steam bath the solution changed from a yellow color to virtually colorless. Heating was discontinued and 15 ml. of concentrated hydrochloric acid was added. Upon standing overnight, colorless crystals formed which were filtered, washed with a small amount of distilled water, and air dried. *Anal.* Calcd. for $[Pt(C_6H_{12}N_2O_4)(NH_3)_2]Cl_2$: C, 15.13; H, 3.78; N, 11.76; Pt, 40.9. Found: C, 15.28; H, 3.92; N, 11.12; Pt, 39.7. Again the infrared spectrum showed a single sharp COO stretching band at 1735 cm.$^{-1}$. When this compound was heated with concentrated hydrochloric acid on a steam bath a yellow crystalline product resulted which was identified by its infrared spectrum to be *cis*-dichlorodiammineplatinum(II). Attempts to prepare ethylenediamine(ethylenediamine-N,N′-diacetic acid)platinum(II) chloride by the same procedure yielded only the yellow insoluble dichloroethylenediamineplatinum(II).

(Ethylenediamine-N,N′-diacetato)platinum(II) Monohydrate.—A method similar to that of Busch and Bailar[4] was used. A solution of 2.000 g. of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) was treated with a hot solution of 1.412 g. of silver sulfate. After heating on a steam bath to coagulate the silver chloride precipitate, the mixture was filtered and the filtrate heated with a solution of 1.430 g. of barium hydroxide 8-hydrate. The precipitated barium sulfate was filtered off. Evaporation of the filtrate yielded a white crystalline precipitate which was filtered, washed thoroughly with distilled water, and air dried. *Anal.* Calcd. for $[Pt(C_6H_{10}N_2O_4)]H_2O$: C, 18.60; H, 3.10; N, 7.24; Pt, 50.4. Found: C, 19.12; H, 3.14; N, 7.28; Pt, 50.7. The infrared spectrum of the compound indicated the presence of water and also showed a single somewhat broader COO stretching band at 1650 cm.$^{-1}$.

Oxidation of (Ethylenediamine-N,N′-diacetato)platinum(II) with Chlorine.—The oxidation was carried out by suspending 0.250 g. of (ethylenediamine-N,N′-diacetato)platinum(II) in about 20 ml. of water in a glass-stoppered flask. A small amount of chlorine gas was admitted into the flask (but not bubbled through the suspension), and the mixture was shaken vigorously. The process was repeated two times and the mixture was left standing for 2 hr. At the end of this time the original white precipitate turned to a light yellow solid and the solution was also yellow in color. The mixture was filtered and the precipitate washed with distilled water and air dried. *Anal.* Calcd. for $[Pt(C_6H_{10}N_2O_4)Cl_2]\cdot 2H_2O$: C, 15.13; H, 2.94; N, 5.88; Cl, 14.92; Pt, 41.0: Found: C, 15.16; H, 2.73; N, 5.92; Cl, 15.45; Pt, 42.0.

Evaporating the filtrate on a steam bath to a small volume and cooling to room temperature yielded a crop of light yellow crystals. These proved to be the same as the yellow solid by their identical infrared spectra. *Anal.* Found: C, 15.24; H, 2.85; N, 5.89; Pt, 41.2. The infrared spectrum of this compound showed the presence of water and also a single COO stretching band at 1680 cm.$^{-1}$.

Trichloro(ethylenediamine-N,N′-diacetic acid)platinum(IV) Monohydrate.—In the chlorination of (ethylenediamine-N,N′-diacetato)platinum(II), when chlorine was bubbled through the mixture and the resulting yellow solution was left standing for several days a light yellow product crystallized which proved to be trichloro(ethylenediamine-N,N′-diacetic acid)platinum(IV) monohydrate. *Anal.* Calcd. for $[Pt(C_6H_{11}N_2O_4)Cl_3]\cdot H_2O$: C, 14.57; H, 2.63; N, 5.67; Cl, 21.43; Pt, 39.5. Found: C, 14.10; H, 2.32; N, 5.76; Cl, 20.41; Pt, 40.0. In the 1600–1800 cm.$^{-1}$ region the infrared spectrum of this compound showed three bands. Two bands of approximately equal intensity are situated at 1735 and 1675 cm.$^{-1}$ and a much weaker band at 1620 cm.$^{-1}$. The same compound was synthesized from a different route: A small sample of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) was dissolved in 50 ml. of 0.1 *N* hydrochloric acid with warming on a steam bath. Chlorine was then bubbled through the solution for 1 min. The solution was evaporated on a steam bath until crystallization occurred. After cooling to room temperature the crystals were filtered off, washed with small amounts of distilled water, and air dried. The infrared spectrum of this product proved to be identical with that of the compound prepared from vigorous chlorination of (ethylenediamine-N,N′-diacetato)platinum(II). *Anal.* Found: C, 14.58; H, 2.91; N, 5.68; Pt, 39.9.

Reaction between Ethylenediamine-N,N′-diacetic Acid and the Hexachloroplatinate(IV) Ion.—Potassium hexachloroplatinate(IV) (3.24 g.) and ethylenediamine-N,N′-diacetic acid (1.17 g.) were dissolved in 400 ml. of water and heated on a steam bath for 12 hr. during which period 127 ml. of 0.105 *N* LiOH solution was added in small portions. The solution was then filtered and evaporated on a steam bath until crystallization. After cooling, the crystals were filtered off, washed thoroughly with water, and air dried. The compound can be recrystallized from water without change. *Anal.* Calcd. for $[Pt(C_6H_{10}N_2O_4)Cl_2]$: C, 16.36; H, 2.28; N, 6.36; Cl, 16.13; Pt, 44.3. Found: C, 16.17, 16.21; H, 2.45, 2.39; N, 6.24, 6.20; Cl, 16.40; Pt, 44.3, 44.6. The infrared spectrum showed a single COO band at 1730 cm.$^{-1}$.

Oxidation of Dichloro(ethylenediamine-N,N′-diacetic acid) platinum(II) with Hydrogen Peroxide.—Dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) (0.254 g.) was placed in 10 ml. of water, and 10 ml. of 30% H_2O_2 was added. The mixture was heated on a steam bath for 6 hr. The resulting yellow solution was evaporated until crystallization began. After cooling to room temperature, the crystals were filtered, washed with water, and air dried. *Anal.* Calcd. for $[Pt(C_6H_{10}N_2O_4)Cl_2]$: C, 16.36; H, 2.28; N, 6.36; Pt, 44.3. Found: C, 16.36; H, 2.41; N, 6.56; Pt, 44.6. The infrared spectrum of

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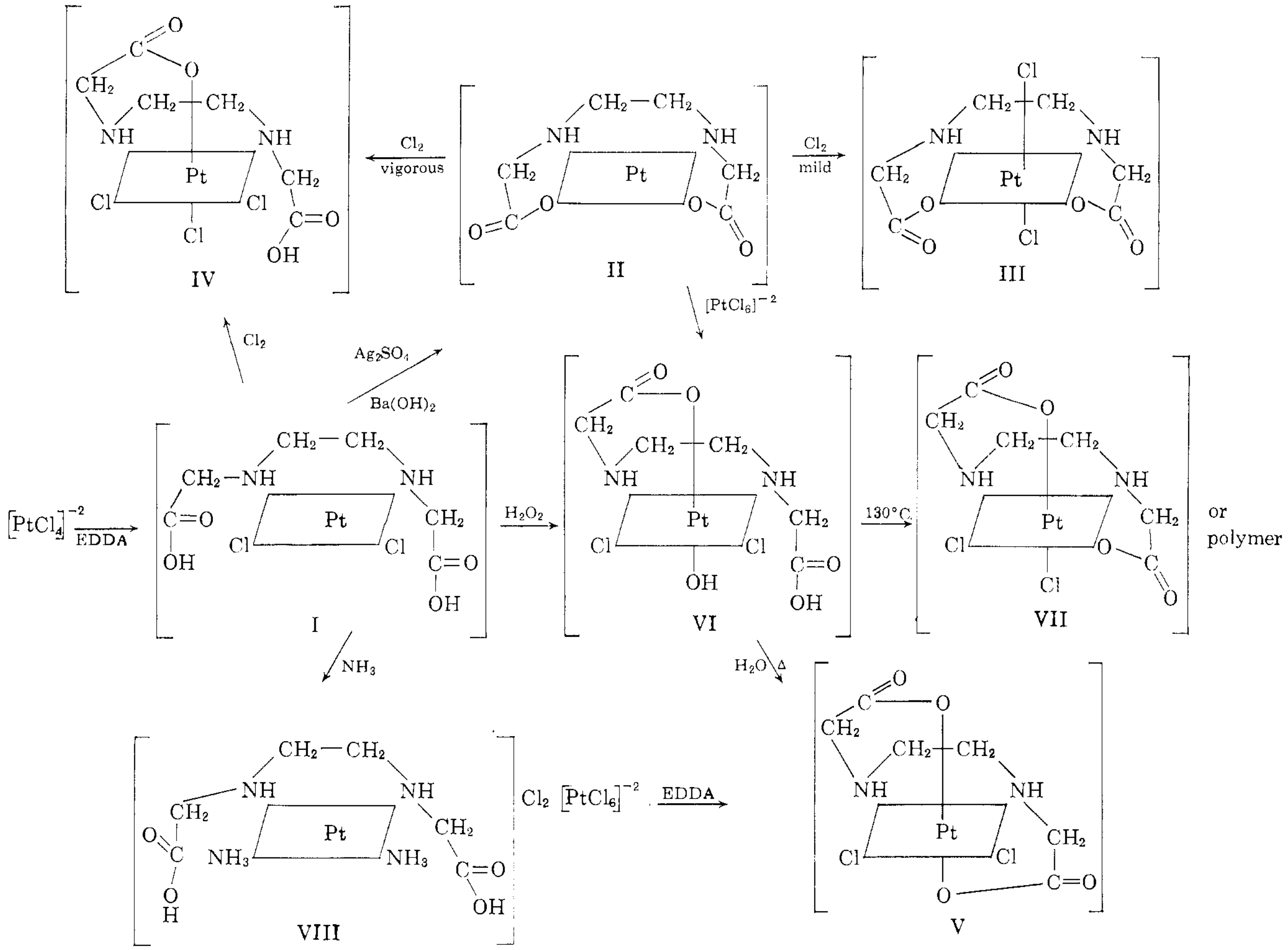
[4] D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **78**, 716 (1956).

[5] C. F. Liu and C. H. Liu, *ibid.*, **83**, 2615 (1961).

[6] W. E. Cooley and D. H. Busch, *Inorg. Syn.*, **5**, 208 (1957).

Scheme I



the product proved to be identical with that of the product obtained from the reaction between ethylenediamine-N,N′-diacetic acid and the hexachloroplatinate(IV) ion.

Under milder reaction conditions dichlorohydroxo(ethylenediamine-N,N′-diacetic acid)platinum(IV) was obtained: (Dichloroethylenediamine-N,N′-diacetic acid)platinum(II) (0.5 g.) was placed in about 20 ml. of water, and 5 ml. of 30% H_2O_2 was added. The mixture was heated on a steam bath until all the solid dissolved, then for 5 min. longer. The mixture was filtered; the filtrate yielded light yellow crystals on cooling. These were filtered off, washed with water, and air dried. The infrared spectrum of this product showed a sharp O–H stretching band at 3410 cm.$^{-1}$. There were also two COO stretching bands, one occurring at 1710 cm.$^{-1}$ and the other at 1650 cm.$^{-1}$. *Anal.* Calcd. for $\mathrm{Pt(C_6H_{11}N_2O_4)(OH)Cl_2}$: C, 15.72; H, 2.62; N, 6.11; Cl, 15.50; Pt, 42.6. Found: C, 16.00; H, 2.36; N, 6.06; Cl, 15.81; Pt, 43.0. When this complex was placed in water and heated on a steam bath for 5 hr. the product isolated gave an infrared spectrum identical with that of *cis*-dichloro(ethylenediamine-N,N′-diacetato)platinum(IV) prepared by either the direct action of the ligand on the hexachloroplatinate(IV) ion or by prolonged H_2O_2 oxidation of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II).

A sample of *cis*-dichlorohydroxo(ethylenediamine-N,N′-diacetic acid)platinum(IV) was heated in an oven at 130° overnight. The infrared spectrum of the resulting light yellow product showed that the sharp O–H stretching band at 3410 cm.$^{-1}$ disappeared. A single COO stretching band remained at 1650 cm.$^{-1}$. The rest of the spectrum was very similar to that of the starting material. *Anal.* Calcd. for $\mathrm{[Pt(C_6H_{10}N_2O_4)Cl_2]}$: C, 16.36; H, 2.28; N, 6.36; Cl, 16.13; Pt, 44.3. Found: C, 16.36; H, 1.81; N, 6.39; Cl, 16.19; Pt, 44.4. When this product was recrystallized from water the solid obtained proved to be identical with the dichloro(ethylenediamine-N,N′-diacetic acid)platinum(IV) formed by prolonged H_2O_2 oxidation of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II).

Oxidation of (Ethylenediamine-N,N′-diacetato)platinum(II) with the Hexachloroplatinate(IV) Ion.—To 24 ml. of a 0.0386 *M* solution of lithium hexachloroplatinate(IV) was added 0.375 g. of (ethylenediamine-N,N′-diacetato)platinum(II). The mixture was heated on a steam bath until all the solid dissolved, then for 5 min. more. On cooling yellow crystals formed. These were filtered, washed thoroughly with water, and air dried. The infrared spectrum of this compound was identical with that of the *cis*-dichlorohydroxo(ethylenediamine-N,N′-diacetic acid)platinum(IV) prepared by H_2O_2 oxidation of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II). *Anal.* Calcd. for $\mathrm{[Pt(C_6H_{11}N_2O_4)(OH)Cl_2]}$: C, 15.72; H, 2.62; N, 6.11; Cl, 15.50; Pt, 42.6. Found: C, 15.78; H, 2.44; N, 6.24; Cl, 16.30; Pt, 42.9.

Prolonged heating of the reaction mixture yielded *cis*-dichloro(ethylenediamine-N,N′-diacetato)platinum(IV) identical with that prepared by the other methods.

Discussion

The reactions studied are summarized in Scheme I. The formation of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) is straightforward. The COO band at 1730 cm.$^{-1}$ is very similar to the uncoordinated carboxyl band reported by Busch and Bailar[4] in their investigation of complexes of EDTA and platinum(II) and palladium(II). The experimental results indicate that the compound has structure I in

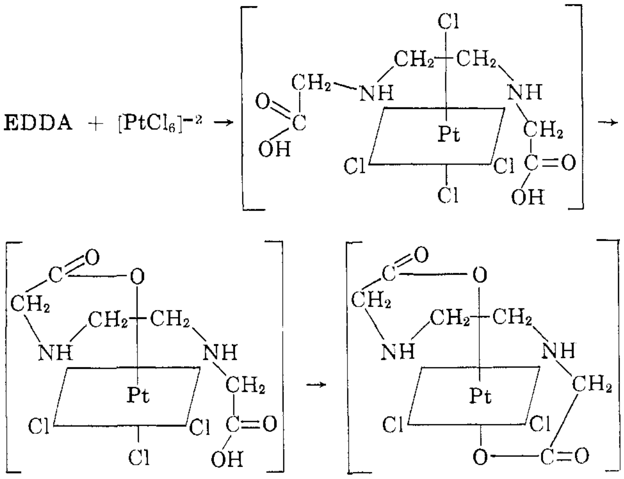
Scheme I. The reaction of I with aqueous ammonia gives a compound which undoubtedly has the structure indicated by VIII. It is interesting to note that this compound loses ethylenediamine-N,N′-diacetic acid in concentrated hydrochloric acid.

The inner complex II was obtained from I by neutralizing the carboxyl groups with the simultaneous removal of the chloride ions. Simple neutralization did not yield the inner complex. The complex II has one water of crystallization. The question of whether the water molecule is coordinated or just lattice water can be resolved by observing the COO stretching band in the infrared spectrum. If the water were coordinated there should be present either an un-ionized COOH group or a free COO$^-$ group, which should give rise to absorption bands at above 1700 cm.$^{-1}$ or in the 1600 cm.$^{-1}$ region, respectively. The spectrum, however, shows a single band at 1650 cm.$^{-1}$, which is consistent with the coordinated COO stretching bands reported by Busch and co-workers.[4,7] On the basis of this and the fact that the compound is insoluble in either aqueous acid or base, it is concluded that the compound is the inner complex.

The mild chlorination of II yields III. The assignment of this configuration to the product is based on the fact that the chlorine oxidation of platinum(II) complexes has been shown previously[2] to yield exclusively the *trans*-dichloroplatinum(IV) compounds. Even though there are two molecules of water present in the compound, it is concluded that the inner complex is obtained as, again, the infrared spectrum shows one single COO stretching band at 1680 cm.$^{-1}$, and the compound is insoluble in water and aqueous acid.

In the case of the more vigorous chlorination a product is obtained which is assigned structure V. The infrared absorption bands at 1735 and 1675 cm.$^{-1}$ are interpreted as the un-ionized and coordinated COO stretching, respectively. The weaker band at 1620 cm.$^{-1}$ is most likely the bending band of lattice water discussed by Lucchesi and Glasson.[8] The chlorination reaction is somewhat similar to the chlorination of bis(ethylenediamine)platinum(II), where the use of a large excess of chlorine results in the displacement of one ethylenediamine molecule and yields tetrachloroethylenediamineplatinum(IV). It is most likely that in the more vigorous chlorination of II the chelate rings open at the carboxyl groups, yielding the tetrachloro(ethylenediamine-N,N′-diacetic acid)platinum(IV) as an intermediate. Subsequently, one of the chelate rings recloses to give structure IV. This hypothesis is supported by the fact that the same compound is obtained by chlorination of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(II) in hydrochloric acid solution.

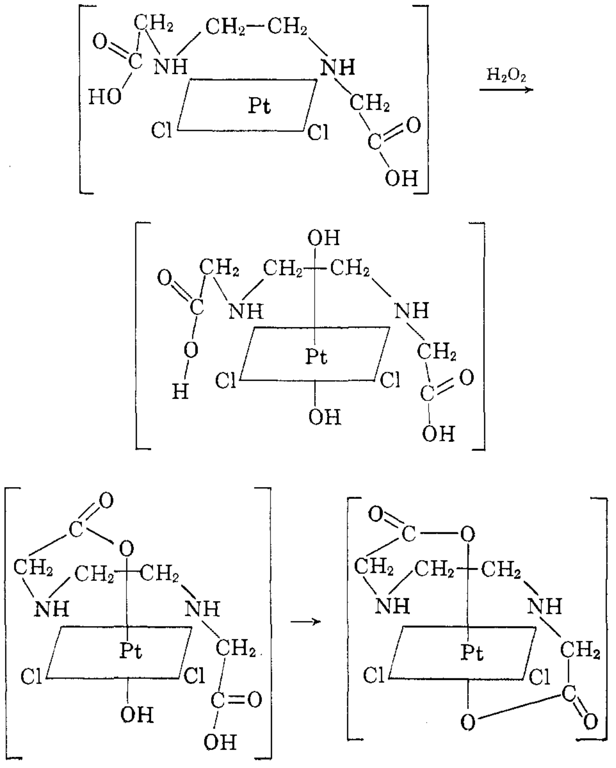
Quite analogous to the above is the reaction between ethylenediamine-N,N′-diacetic acid and the hexachloroplatinate(IV) ion. From experimental evidence it seems logical to assume that the amine groups on the ligand coordinate first, in which case the intermediate would again be tetrachloro(ethylenediamine-N,N′-diacetic acid)platinum(IV). Since both carboxyl groups are neutralized with base the chelate rings close. The *trans* effect should direct the carboxyl groups to be situated *trans* to each other and results in structure V.



The COO stretching frequency of 1730 cm.$^{-1}$ is considerably higher than that of the other coordinated COO stretching bands. However, from the method of preparation, elemental analyses, and the identity of the product to that prepared by other synthetic methods there is little doubt that the carboxyl groups are coordinated.

Oxidation of I by hydrogen peroxide seems to follow the usual path. In all known cases hydrogen per-

SCHEME II



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(7) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956); K. Swaminathem and D. H. Busch, *J. Inorg. Nucl. Chem.*, **20**, 159 (1961).

(8) P. J. Lucchesi and W. A. Glasson, *J. Am. Chem. Soc.*, **78**, 1347 (1956).

oxide oxidizes platinum(II) complexes to platinum(IV) compounds with the added OH groups occupying *trans* positions. Assuming this is the case with the above oxidation the reaction should proceed through the following route to form the product with the indicated structure (Scheme II).

The infrared spectrum of the compound shows that the assignment of the structure (V) is correct. It is interesting to note that by shortening the reaction time the ring closure reaction shown above may be stopped at a point where only one carboxyl group has reacted to close the ring. The infrared spectrum of the product shows a sharp band at 3410 cm.$^{-1}$ which is interpreted as O–H stretching of a coordinated hydroxyl group. The two bands at 1710 and 1650 cm.$^{-1}$ are assumed to be un-ionized and coordinated COO stretching bands, respectively. On the basis of these data the assignment of structure VI to the compound is quite obvious.

Of particular interest is the oxidation of II by $[PtCl_6]^{-2}$. Since the products obtained are shown to have structures V and VI, the incoming chloride groups are situated *cis* to each other. This is quite unlike other oxidations involving Pt(II) complexes where the incoming groups generally occupy *trans* positions in the resulting Pt(IV) compounds. It is quite possible that a different mechanism is operative in the present case.

When VI is heated at 130° a product is obtained in which all the carboxyl groups are coordinated and there are no coordinated OH groups. The elemental analyses confirm the simple formula of $Pt(C_6H_{10}N_2O_4)Cl_2$. It is likely the third isomer of dichloro(ethylenediamine-N,N′-diacetic acid)platinum(IV), the structure of which is depicted by VII in Scheme I. It is also possible that a polymer is formed in the heating process.

Acknowledgment.—The investigator wishes to thank the National Science Foundation for the support of this study.

Contribution from the Central Research Division,
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Biscyclopentadienyl Titanoxane Polymers

By S. A. GIDDINGS

Received October 30, 1963

A novel sequential reduction–oxidation process was used to prepare the biscyclopentadienyl titanoxane polymers from bis(cyclopentadienyl)titanium dichloride (I). The formation of the polymers was accompanied by a loss of one cyclopentadienyl ring for each metal atom, leading to materials of lower solubility and thermal stability than expected. The dimeric intermediate $TiCp_2Cl–O–TiCp_2Cl$ was isolated by reduction of I with zinc followed by air oxidation.

Introduction

Titanoxane polymers obtained by the controlled hydrolysis of tetraalkoxytitanium compounds have been studied extensively by Bradley and co-workers.[1,2] In other studies, Rust and co-workers[3] utilized monomers containing two univalent bidentate chelate groups (8-hydroxyquinoline and acetylacetonates) and two labile groups in an effort to prepare linear polymers. Consideration was then given to converting the known soluble and stable dichloride, bis(cyclopentadienyl)titanium dichloride (I), to the polymer $(–TiCp_2–O–)_n$ (II). Dipole moment measurements[4] were recently used to deduce the tetrahedral nature of I. The tetrahedral arrangement does not preclude polymer formation as evidenced by the existence of silicone and carbon resins. Furthermore, the expected Ti–O–Ti bond angle of 180°, which has been shown for $CpCl_2Ti–O–TiCl_2Cp$,[5] should promote chain growth with respect to cyclization.

An obvious route to the proposed polymer II, similar to the preparation of siloxane linear polymers, would be reaction with hydroxide ion, but treatment with aqueous base cleaves metal–cyclopentadienyl bonds.[6] The bis(cyclopentadienyl)titanium dialkoxides might also be effective precursors for titanoxane polymers but obvious attempts at their synthesis were not successful.[7]

The reduction of I by metallic zinc has been reported[8] in oxygen-containing solvents such as acetone and tetrahydrofuran. It was considered that oxidation of the reduced species should afford a dimer with an oxo bridge as demonstrated by Nöth and Hartwimmer

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(1) D. C. Bradley, R. Gaze, and W. Wardlaw, *J. Chem. Soc.*, 469 (1957).

(2) D. C. Bradley, R. Gaze, and W. Wardlaw, *ibid.*, 3977 (1955).

(3) J. B. Rust, U. S. Dept. of Commerce, AD262707 (1961).

(4) S. A. Giddings and R. J. Best, *J. Am. Chem. Soc.*, **83**, 2393 (1961).

(5) G. Allegro, P. Ganis, L. Porri, and P. Corradini, *Atti Accad. Naz. Lincei*, **30**, 44 (1961).

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