Conceivably, this is due to some special coordinate geometry; thus Jonas and Wilke[21] found no Ni–H absorptions in the usual region for hydrido-bridged binuclear nickel complexes, and an unusual example of an Ir–H stretch at 1634 cm^{-1} has been reported.[24]

A nondissociative mechanism involving formation of $Ni(P(OCH_3)_3)_4$ and its subsequent reaction with hydrogen chloride can be ruled out, since we find that these compounds react to form hydrogen gas (*cf.* ref 23, 25).

A summation of the methanolysis and oxidation–reduction processes is represented by the equations

$$Ni(PCl_3)_4 + 17CH_3OH \longrightarrow [Ni(CH_3OH)_6]Cl_2 + 3HP(O)(OCH_3)_2 + \{H_2P(O)(OCH_3)\} + 6HCl + 4CH_3Cl \quad (6)$$

$$\{H_2P(O)(OCH_3)\} \longrightarrow xPH_3 + \text{other products} \quad (7)$$

Accompanying these steps is the known process[26] of cleavage of the organophosphorus esters by hydrogen chloride, *e.g.*

$$HP(O)(OCH_3)_2 + HCl \longrightarrow HP(O)(OH)(OCH_3) + CH_3Cl \quad (8)$$

$$HP(O)(OH)(OCH_3) + HCl \longrightarrow HP(O)(OH)_2 + CH_3Cl \quad (9)$$

Thus, the analytical result in one experiment that 30.1% of the original phosphorus appeared in the form of $HP(O)(OCH_3)_2$ is fortuitous, depending on the particular extent of ester cleavage. Similarly, the hydrogen chloride and methyl chloride balance of eq 6 is greatly changed by eq 8 and 9. It is also apparent why, after evaporation of the reaction mixture to dryness, the nonvolatile residue is a mixture of nickel(II) salts, chloride and phosphite with a small organic content.

In conclusion, when the donor atom changes from phosphorus to oxygen during methanolysis in this system, spontaneous oxidation of nickel(0) occurs, with reduction of part of the organophosphorus ester. This is in interesting contrast to the nickel(II)–trialkyl phosphite system studied by Vinal and Reynolds.[14] There, with phosphorus as the donor atom, spontaneous reduction of nickel(II) occurs, with oxidation of part of the organophosphorus ester.

Acknowledgments.—This work was supported by National Science Foundation Grant GP-4185, which is acknowledged with thanks. We also thank the Oregon State University Research Council and General Research Fund for equipment funds.

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Complexes with Six-Membered Chelate Rings. IV. Preparation of Some Complexes of 1,3-Diaminopropan-2-ol and 2-Chloropropane-1,3-diamine with Platinum and Palladium

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Preparations are reported for the complexes $M(tnOH)Cl_2$, $M(tnCl)X_2$, $Pt(diamine)(NH_3)_2^{2+}$, $M(diamine)_2^{2+}$, *trans*′-$Pt(diamine)Cl_2(OH')_2$, $Pt(diamine)Cl_4$, *trans*′-$[Pt(tnOH)(NH_3)_2Cl'_2]Cl_2$, and *trans*-$[Pt(tnOH)_2Cl_2]Cl_2$, where M = Pt or Pd, X = Cl or Br, and diamine = 1,3-diaminopropan-2-ol (tnOH) or 2-chloropropane-1,3-diamine (tnCl). Some complexes, $M(tnCl)X_2$, show an unusual polymorphism.

Introduction

In previous papers we have described the preparation[2] and pmr spectra[3,4a] of some complexes of platinum and palladium with trimethylenediamine (propane-1,3-diamine, tn) and some methyl-substituted derivatives. This work has now been extended to the hydroxy- and chloro-substituted trimethylenediamines 1,3-diaminopropan-2-ol ($NH_2CH_2CHOHCH_2NH_2$, tnOH) and 2-chloropropane-1,3-diamine ($NH_2CH_2CHClCH_2NH_2$, tnCl), respectively. This paper describes the preparation of some complexes of these ligands and the following paper[4b] describes their pmr and infrared spectra. A few complexes of the ligand 2-bromopropane-1,3-diamine (tnBr) have also been prepared for comparison.

Experimental Section

Ligands. 1,3-Diaminopropan-2-ol.—This was obtained as a highly deliquescent, pale yellow solid from Koch-Light. Its dihydrochloride, a white solid, was prepared in the usual way[2] (some tar was always formed when the diamine was neutralized, but this could be removed by boiling aqueous solutions with charcoal). *Anal.* Calcd for $(tnOH)(HCl)_2$, $C_3H_{12}Cl_2N_2O$: C, 22.1; H, 7.4; N, 17.2; Cl, 43.5. Found: C, 22.1; H, 7.7; N, 17.2; Cl, 43.5.

2-Chloropropane-1,3-diamine.—Approximately 13.6 g of tnOH was mixed in a flask with 44.8 g of phthalic anhydride (molar ratio 1:2). The flask was fitted with an air condenser and heated in a fume hood, at first gently and then more strongly, as the whole mass melted and became brown. The solid obtained on cooling was extracted from the flask with hot chloroform and the solution was evaporated to dryness. After two recrystallizations from glacial acetic acid, followed by recrystallization from a large volume of 95% ethanol, 32.6 g of pure 2-hydroxypropane-1,3-diphthalimide was obtained in long silky crystals (50.6% based on tnOH). When the product is merely being used as a preparative intermediate, a single recrystallization from acetic acid suffices.

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[1] Address correspondence to this author.

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[3] T. G. Appleton and J. R. Hall, *ibid.*, **9**, 1807 (1970).

[4] (a) Part III: T. G. Appleton and J. R. Hall, **10**, 1717 (1971); (b) part V: T. G. Appleton and J. R. Hall, *ibid.*, **11**, 117 (1972).

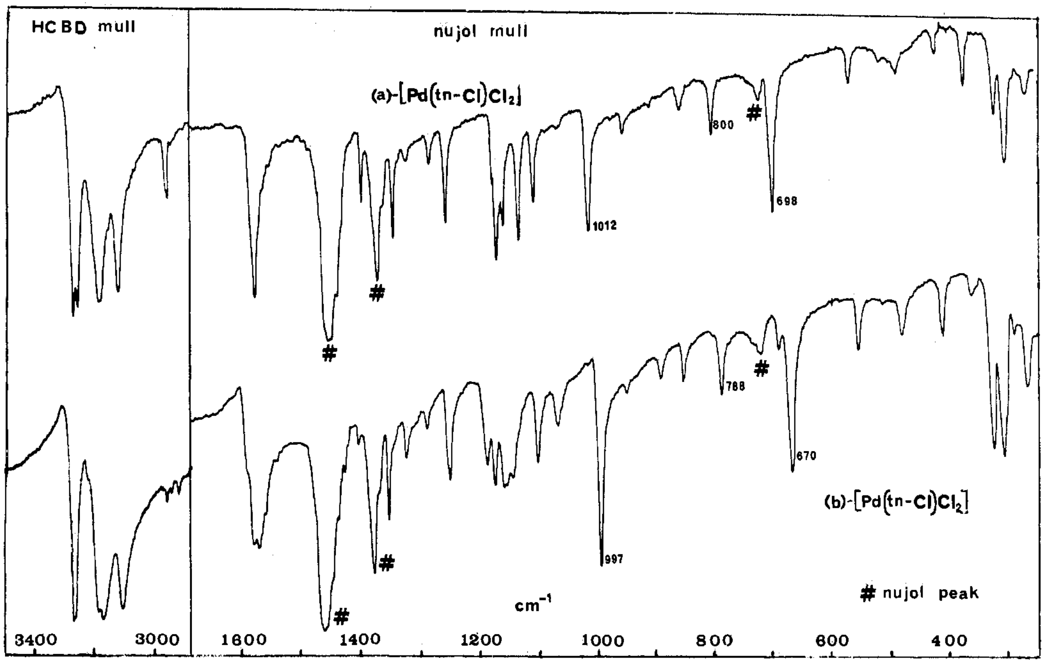

Figure 1.—Infrared spectra of the two forms of $Pd(tnCl)Cl_2$ (HCBD = hexachlorobutadiene).

This diphthalimide was allowed to react with phosphorus pentachloride in benzene, as described by Gabriel and Michels.[5] The product, 2-chloropropane-1,3-diphthalimide, was recrystallized from glacial acetic acid and then from acetone. A boiling mixture of concentrated sulfuric acid and water (volume ratio 14:11) was used to hydrolyze off the phthalyl groups. When all the diphthalimide had dissolved in the minimum volume of hydrolysis mixture, the solution was cooled, the phthalic acid which crystallized was filtered off, and sulfate ions were precipitated from solution by addition of barium chloride solution. The solution was filtered, the filtrate was evaporated nearly to dryness, and excess acetone was added to precipitate $(tnCl)(HCl)_2$ as a white solid. This salt was then recrystallized from boiling 95% ethanol. In a typical reaction sequence, overall yield based on tnOH was 47%. *Anal.* Calcd for $C_3H_{11}Cl_3N_2$: C, 19.9; H, 6.1; N, 15.4; Cl (ionic), 39.1; Cl (covalent), 19.5. Found: C, 19.7; H, 6.4; N, 15.2; Cl (ionic), 38.9; Cl (covalent), 20.0.

2-Bromopropane-1,3-diamine.—The dihydrobromide was prepared from the diphthalimide of tnOH by the method of Mann.[6] *Anal.* Calcd for $C_3H_{11}Br_3N_2$: C, 11.5; H, 3.5; N, 8.9; Br (ionic), 50.8; Br (covalent), 25.4. Found: C, 11.6; H, 3.6; N, 8.8; Br (ionic), 51.0; Br (covalent), 25.4.

Potassium Tetrabromoplatinate(II) and Tetrabromopalladate(II).—K_2PtBr_4 was prepared by reduction of K_2PtBr_6 with hydrazine sulfate, by the method of Shagisultanova.[7]

K_2PdBr_4 was prepared by treating the residue from evaporation of an aqua regia solution of palladium metal several times with concentrated hydrobromic acid, followed each time by evaporation. The resultant moist solid was dissolved in dilute hydrobromic acid and the calculated quantity of potassium bromide was added. Evaporation yielded purple-brown crystals of K_2PdBr_4.

Dihalo(diamine) Complexes of Platinum(II) and Palladium(II). Dichloro(1,3-diaminopropan-2-ol)palladium(II), Pd(tnOH)Cl₂.—Since this complex could not be prepared in the usual way,[2] by addition of HCl to an aqueous solution containing $[Pd(tnOH)_2]Cl_2$ (probably owing to its comparatively high solubility compared with other complexes $Pd(diamine)Cl_2$), the following method was used. Equimolar quantities of aqueous K_2PdCl_4 and tnOH were mixed. The resultant pink-brown precipitate of crude $[Pd(tnOH)_2][PdCl_4]$ was filtered off, washed with water and then acetone, and air-dried. This solid was "recrystallized" from boiling water to give a yellow solid, which was filtered off, washed with a small volume of cold water and then acetone, and air-dried. Typical yield, based on $[Pd(tnOH)_2][PdCl_4]$, was 54%. *Anal.* Calcd for $PdC_3H_{10}Cl_2N_2O$: Pd, 39.8; C, 13.5; H, 3.8; N, 10.5. Found: Pd, 39.6; C, 13.5; H, 3.8; N, 10.4.

Dichloro(1,3-diaminopropan-2-ol)platinum(II), Pt(tnOH)Cl₂.—Addition of free tnOH to an aqueous solution of K_2PtCl_4 usually resulted in a precipitate consisting predominantly of pink $[Pt(tnOH)_2][PtCl_4]$. A sample of crude $Pt(tnOH)Cl_2$ could be obtained in the following way. Aqueous solutions containing 0.86 g of K_2PtCl_4 and 0.448 g of $(tnOH)(HCl)_2$ (molar ratio 1:1.33), the latter being adjusted to pH 8.6 with 1 *N* NaOH solution, were added together. The solution was warmed, a few drops of the NaOH solution being added from time to time to maintain a pH of approximately 9. The disappearance of the pink color of the tetrachloroplatinate ion as the reaction proceeded was masked to some extent by coloration from tars, but by careful observation it was possible to judge when the reaction was nearing completion (no precipitation of complex occurred at this stage). The solution was acidified with HCl and filtered from any small amounts of solid material present. The solution was evaporated to about a third of its original volume and cooled. A 0.1929-g sample of slightly pinkish solid was obtained (white $Pt(tnOH)Cl_2$ contaminated by pink $[Pt(tnOH)_2][PtCl_4]$. Further evaporation yielded 0.2066 g of crude product (total yield 54% based on K_2PtCl_4). The crude product was purified by reaction with silver nitrate solution to give a solution of $[Pt(tnOH)(H_2O)_2](NO_3)_2$.[2] The solution was concentrated to small volume (necessary because $Pt(tnOH)Cl_2$ is more soluble than other complexes of this type) and concentrated hydrochloric acid was added. $Pt(tnOH)Cl_2$ precipitated out as a white solid, was filtered off, washed rapidly with ammonia solution, cold water, and acetone, and air-dried. *Anal.* Calcd for $PtC_3H_{10}Cl_2N_2O$: C, 10.1; H, 2.8; N, 7.9; Cl, 19.9. Found: C, 10.1; H, 3.0; N, 7.6; Cl, 19.9.

Dichloro(2-chloropropane-1,3-diamine)palladium(II), Pd(tnCl)Cl₂.—Warming an aqueous solution of K_2PdCl_4 with a solution containing excess $(tnCl)(HCl)_2$ (adjusted to pH 9) gave, after dissolution of the initial precipitate, a colorless solution containing $Pd(tnCl)_2^{2+}$.[2] Addition of concentrated HCl to this solution caused precipitation of a yellow solid, which was filtered off, washed, and dried as usual. This product corresponded analytically to the formulation $Pd(tnCl)Cl_2$ (typical yield 68% based on K_2PdCl_4) and gave the infrared spectrum shown in Figure 1a. When it was recrystallized from boiling water, the product, also a yellow solid, gave the spectrum shown in Figure 1b. These two materials will be designated a and b forms, respectively, of $Pd(tnCl)Cl_2$. There are several distinct differences between the spectra. For example, there are changes in the structures of the $-NH_2$ stretching (3100–3400 cm⁻¹) and bending (1500–1600 cm⁻¹) bands and the C–H stretching bands (2900–3000 cm⁻¹), and in the region 1100–1200 cm⁻¹. Bands at 1012,

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(5) H. Gabriel and W. Michels, *Chem. Ber.*, **25**, 3056 (1892).

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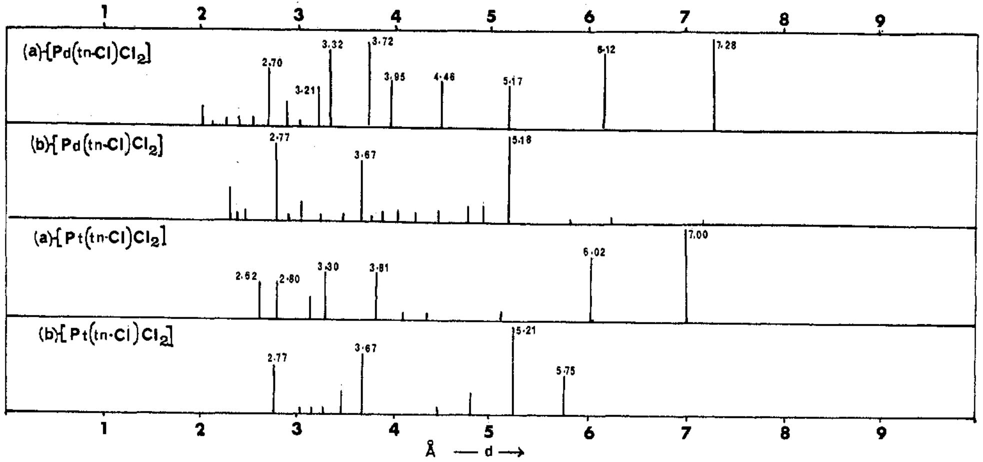

Figure 2.—Schematic representations of X-ray powder diffraction patterns.

800, and 698 cm^{-1} in the spectrum of the a form shift to 997, 788, and 670 cm^{-1}, respectively, for the b form. *Anal.* Calcd for $PdC_3H_9Cl_3N_2$: Pd, 37.2; C, 12.6; H, 3.2; N, 9.8. Found (a form): Pd, 37.6; C, 12.8; H, 3.3; N, 9.6. Found (b form): Pd, 37.2; C, 12.7; H, 3.2; N, 9.7.

Apart from the differences in ir spectra, these two forms differ in their X-ray powder diffraction patterns (Figure 2) and in their thermal stabilities. A sample of a-Pd(tnCl)Cl_2 heated in a glass capillary did not begin to darken noticeably below 224°. As the temperature was increased, the color slowly darkened, and the sample was completely black by 242°. With the b form, definite darkening was noticed at 174–176°, and the sample was completely black by 210°. Further, when samples of the two forms were allowed to stand in an oven at 110°, the a form remained bright yellow with no decomposition over several weeks, but the b form had become gray after a few days. Ir spectra of these samples did not reveal any tendency for one form to change into the other under these conditions.

Dichloro(2-chloropropane-1,3-diamine)platinum(II), Pt(tnCl)-Cl_2.—This complex also exists in two forms, analogous to those obtained for Pd(tnCl)$_2$. When an aqueous solution of K_2PtCl_4 was treated at room temperature with a solution of (tnCl)$(HCl)_2$ adjusted to pH 8.5 with NaOH solution (molar ratio K_2PtCl_4: tnCl is 1:1.3), a precipitate formed which consisted predominantly of yellow a-Pt(tnCl)Cl_2 contaminated with a little b form and with a small amount of pink [Pt(tnCl)$_2$][$PtCl_4$]. Typical yield of this crude product (based on K_2PtCl_4) was 65%. If this product was recrystallized from boiling water (usually slightly acidified with HCl) yellow b-Pt(tnCl)Cl_2 was obtained. The b form was also obtained if the initial preparative reaction mixture was heated or if the preparation was carried out at higher pH (>9). a-Pt(tnCl)Cl_2 could be obtained pure by reacting 1 mol of crude Pt(tnCl)Cl_2 with 2 mol of $AgNO_3$ in water,[2] filtering off the resultant AgCl, and adding HCl to the filtrate, a solution of [Pt(tnCl)$(H_2O)_2$]$(NO_3)_2$. The yellow precipitate of a-Pt(tnCl)Cl_2 was filtered off, washed with aqueous ammonia, water, and acetone, and air-dried. Pure b form was obtained by recrystallization of a form from a large volume of boiling dilute HCl. *Anal.* Calcd for $PtC_3H_9Cl_3N_2$: Pt, 52.1; C, 9.6; H, 2.4; N, 7.4. Found (a form): Pt, 52.0; C, 9.8; H, 2.5; N, 7.5. Found (b form): Pt, 51.9; C, 9.8; H, 2.5; N, 7.5.

The ir spectra of these two forms show differences similar to those observed with Pd(tnCl)Cl_2. For example, a peak occurs at 710 cm^{-1} with the a form, at 690 cm^{-1} with the b form. X-Ray powder photographs (Figure 2) show that a-Pt(tnCl)Cl_2 is isomorphous with a-Pd(tnCl)Cl_2 and that the two b forms are also isomorphous. When samples were heated, the a form became noticeably brown at 155° and then slowly darkened until it was completely black by 200°. With the b form a brown color was not noticed until 222°, and the sample was completely black by 242°. The two forms also differ in their solubilities in water. Rough measurements gave solubilities (27°) of 0.80 g/l. (2.1×10^{-3} mol/l.) and 0.24 g/l. (0.63×10^{-3} mol/l.) for the a and b forms, respectively.

Dibromo(2-chloropropane-1,3-diamine)palladium(II), Pd(tnCl)-Br_2.—This complex was prepared by a method analogous to that used for Pd(diamine)Cl_2.[2,8] A solution of (tnCl)$(HBr)_2$ (prepared by anion exchange from the dihydrochloride) was adjusted to pH 8.6 with sodium hydroxide solution and then added to a solution of K_2PdBr_4 (molar ratio 2.2:1). The solution was stirred until the initial precipitate dissolved and then filtered. To the filtrate was added 2 g of potassium bromide dissolved in the minimum volume of water and then concentrated hydrobromic acid until the solution was acid. When the solution was cooled in ice, bright yellow Pd(tnCl)Br_2 precipitated. It was filtered off, washed with cold water and then acetone, and air-dried. A typical yield, based on K_2PdBr_4, was 32%. *Anal.* Calcd for $PdC_3H_9Br_2ClN_2$: Pd, 28.4; C, 9.6; H, 2.4; N, 7.5. Found: Pd, 28.1; C, 9.7; H, 2.6; N, 7.4. This complex did not appear to exist in more than one form.

Dibromo(2-chloropropane-1,3-diamine)platinum(II), Pt(tnCl)-Br_2.—This complex was prepared by a method analogous to that used for Pt(diamine)Cl_2.[2,9] It exists in two distinct forms. Their X-ray powder diffraction patterns cannot be easily related to those of other tnCl complexes, but the form with a band at 710 cm^{-1} in its ir spectrum has been designated a, and that with a peak at 699 cm^{-1}, b, by analogy with the two forms of Pt(tnCl)-Cl_2 (peaks at 710 and 690 cm^{-1} for a and b forms, respectively). The b form was obtained as a yellow precipitate when a solution of (tnCl)$(HBr)_2$ (adjusted to pH 8.5) was mixed with a solution of K_2PtBr_4 (molar ratio 1.3:1). Typical yield based on K_2PtBr_4 was 74%. b-Pt(tnCl)Br_2 was also obtained when HBr was added to a solution of [Pt(tnCl)$(H_2O)_2$]$(NO_3)_2$ prepared as above. Traces of silver bromide were removed by first washing out residual HBr with cold water, then washing with concentrated sodium thiosulfate solution, and then again with cold water. The b form was also obtained when any sample of Pt(tnCl)Br_2 was recrystallized from boiling water. When higher pH was used in the preparation fron K_2PtBr_4 (≥ 9), samples containing various proportions of a form were obtained, but the maximum proportion in any sample was ~80%. *Anal.* Calcd for $PtC_3H_9Br_2ClN_2$: Pt, 42.1; C, 7.8; H, 2.0; N, 6.1. Found for sample containing 80% a form: Pt, 42.1; C, 7.8; H, 2.0; N, 6.1. Found for the b form: Pt, 42.2: C, 7.9; H, 2.1; N, 6.4.

Dichloro(2-bromopropane-1,3-diamine)palladium(II), Pd(tnBr)-Cl_2.—(tnBr)$(HCl)_2$ was prepared by anion exchange from the dihydrobromide, and an aqueous solution, adjusted to pH 9.2, was used to prepare Pd(tnBr)Cl_2 in the usual way.[2] The yellow solid was obtained in 70% yield based on K_2PdCl_4. *Anal.* Calcd for $PdC_3H_9BrCl_2N_2$: C, 10.9; H, 2.8; N, 8.5. Found: C, 10.8; H, 2.9; N, 8.1. This complex did not appear to exist in more than one form.

Dibromo(2-bromopropane-1,3-diamine)platinum(II), Pt(tnBr)-Br_2.—This was prepared by mixing solutions of (tnBr)$(HBr)_2$ (adjusted to pH 8.5) and K_2PtBr_4. Typical yield was 62%. The complex did not exist in more than one distinct form. It is pale yellow. *Anal.* Calcd for $PtC_3H_9Br_3N_2$: C, 7.1; H, 1.8; N, 5.5; Br, 47.2. Found: C, 7.2; H, 1.7; N, 5.4; Br, 47.1.

Dichloro(trimethylenediamine)platinum(II), Pt(tn)Cl_2.—The

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(8) A. Gutbier and M. Woernle, *Chem. Ber.*, **39**, 2716 (1906).

(9) G. W. Watt and R. E. McCarley, *J. Amer. Chem. Soc.*, **70**, 3315 (1957).

preparation of this complex has been previously described.[2,10] It exists in two distinct forms which could not be easily related to those obtained with tnCl complexes and were designated c and d. When $Pt(tn)Cl_2$ was prepared by addition of free trimethylenediamine to a solution of K_2PtCl_4 at room temperature, the product invariably consisted of predominantly c form, together with a small amount of the second form, d-$Pt(tn)Cl_2$ (5%) (and some pink $[Pt(tn)_2][PtCl_4]$). Addition of HCl to a solution of $[Pt(tn)(H_2O)_2](NO_3)_2$ (prepared as usual by treatment of $Pt(tn)Cl_2$ with $AgNO_3$[2]) at room temperature gave pure c form (after the usual washing with ammonia solution). When $Pt(tn)Cl_2$ was recrystallized from boiling water, products were obtained containing varying proportions of d-$Pt(tn)Cl_2$, often with c and d forms in approximately equal quantities. The largest proportion of d form obtained was ~80%. *Anal.* Calcd for $PtC_3H_{10}Cl_2N_2$: Pt, 57.4; C, 10.6; H, 3.0; N, 8.2; Cl, 20.8. Found for c-$Pt(tn)Cl_2$: Pt, 57.8; C, 10.8; H, 3.0; N, 8.3; Cl, 20.9. Found for a sample containing 80% d form: Pt, 57.5; C, 10.7; H, 3.0; N, 8.1. $Pd(tn)Cl_2$[2] exists in only one form, corresponding (from X-ray powder photographs) to c-$Pt(tn)Cl_2$.

Bis(ammine)(diamine)platinum(II) Complexes. Bis(ammine)(1,3-diaminopropan-2-ol)platinum(II) Salts, $Pt(tnOH)(NH_3)_2^{2+}$.—$[Pt(tnOH)(NH_3)_2]Cl_2$ was formed in the usual way.[2] A suspension of $Pt(tnOH)Cl_2$ in dilute ammonia solution was warmed until all had dissolved, the solution was concentrated to small volume, and a large volume of acetone was added to precipitate $[Pt(tnOH)(NH_3)_2]Cl_2$. It was highly deliquescent, and no analytical results could be obtained.

Addition of a solution of K_2PtCl_4 to a concentrated solution of this complex gave a pink precipitate of $[Pt(tnOH)(NH_3)_2][PtCl_4]$, which was filtered off, washed with cold water and then with acetone, and air-dried. *Anal.* Calcd for $Pt_2C_3H_{16}Cl_4N_4O$: Pt, 59.5; C, 5.5; H, 2.5; N, 8.5; Cl, 21.6. Found: Pt, 59.3; C, 5.6; H, 2.6; N, 8.4; Cl, 21.6.

$Pt(tnCl)(NH_3)_2^{2+}$.—Since evaporation of aqueous solutions of $[Pt(tnCl)(NH_3)_2]Cl_2$ always led to extensive precipitation of $Pt(tnCl)Cl_2$ and because of the susceptibility of the C–Cl bond to hydrolysis and ammonolysis, the following procedure was used to obtain the nitrate salt (the perchlorate tended to be only sparingly soluble). $Pt(tnCl)Cl_2$ (0.246 g) was treated with silver nitrate solution in the usual way[2] to give a solution of $[Pt(tnCl)(H_2O)_2](NO_3)_2$. To the warmed filtered solution were added several drops of concentrated ammonia solution. The solution was evaporated to dryness. Traces of silver salts were removed by boiling aqueous solutions with activated charcoal. The complex $[Pt(tnCl)(NH_3)_2](NO_3)_2$ was isolated by evaporation of its aqueous solution, washed with acetone, filtered off, and dried in a vacuum desiccator over phosphorus(V) oxide. The yield was 0.114 g of colorless crystals or 38% based on $Pt(tnCl)Cl_2$. *Anal.* Calcd for $PtC_3H_{15}ClN_6O_6$: C, 7.8; H, 3.3; N, 18.2; Cl, 7.7. Found: C, 7.5; H, 3.3; N, 18.4; Cl, 7.5.

Addition of a solution of K_2PtCl_4 to a concentrated aqueous solution of this complex gave a violet-pink precipitate of $[Pt(tn)Cl)(NH_3)_2][PtCl_4]$. *Anal.* Calcd for $Pt_2C_3H_{15}Cl_5N_4$: Pt, 57.8; C, 5.3; H, 2.2; N, 8.3; Cl, 26.3. Found: Pt, 57.9; C, 5.3; H, 2.1; N, 8.3; Cl, 26.2.

Bis(diamine) Complexes of Platinum(II) and Palladium(II). Bis(1,3-diaminopropan-2-ol)platinum(II), Salts, $Pt(tnOH)_2^{2+}$.—A sample of $[Pt(tnOH)_2][PtCl_4]$ was prepared from K_2PtCl_4 and free tnOH by the general method described previously for $[Pt(en)_2][PtCl_4]$[11] and $[Pt(tn)_2][PtCl_4]$[2]. This pink solid was suspended in water, excess free tnOH was added, and the mixture was heated and stirred until all had dissolved. The solution was filtered and concentrated to small volume. Addition of excess acetone resulted in the separation of an oil, which was thoroughly washed by decantation with acetone to remove excess tnOH and then was redissolved in the minimum volume of water. The solution was acidified with concentrated HCl, and excess acetone was again added. A solid precipitated which was washed by decantation with a small volume of hot 95% ethanol (to remove brown tars), then filtered off, washed with acetone, and air-dried, giving $[Pt(tnOH)_2]Cl_2$ as a white solid (57%, based on $[Pt(tnOH)_2][PtCl_4]$). *Anal.* Calcd for $PtC_6H_{20}Cl_2N_4O_2$: Pt, 43.7; C, 16.1; H, 4.5; N, 12.6; Cl, 15.9. Found: Pt, 43.3; C, 16.0; H, 4.7; N, 12.4; Cl, 15.9. Addition of K_2PtCl_4 to an aqueous solution caused precipitation of pink $[Pt(tnOH)_2][PtCl_4]$. *Anal.* Calcd for $Pt_2C_6H_{20}Cl_4N_4O_2$: Pt, 54.8; C, 10.1; H, 2.8; N, 7.9; Cl, 19.9. Found: Pt, 54.4; C, 10.3; H, 3.0; N, 8.0; Cl, 20.4.

Although $[Pt(tnOH)_2]Cl_2$ could be obtained as moderately large crystals by slow evaporation of aqueous solutions, or by cooling saturated solutions, attempts to separate the geometrical isomers (Figure 3)[12] of this complex by fractional crystallization were unsuccessful. Mann[6] unsuccessfully attempted to separate the isomers of related complexes.

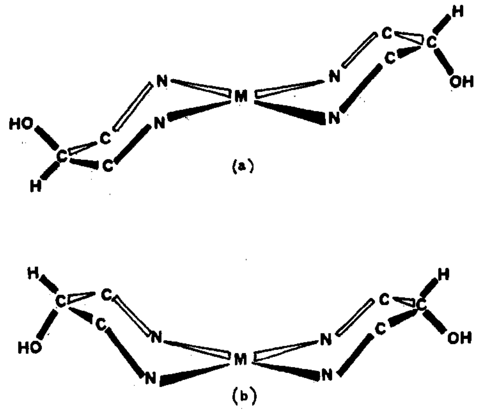

Figure 3.—Geometric isomers of $Pt(tnOH)_2^{2+}$: (a) trans; (b) cis.

Bis(1,3-diaminopropan-2-ol)palladium(II) Salts, $Pd(tnOH)_2^{2+}$.—$[Pd(tnOH)_2]Cl_2$ (a white solid) and $[Pd(tnOH)_2][PdCl_4]$ (a yellow-brown solid) were prepared without difficulty by the usual methods.[2] *Anal.* Calcd for $[Pd(tnOH)_2]Cl_2$, $PdC_6H_{20}Cl_2N_4O_2$: Pd, 29.8; C, 20.2; H, 5.6; N, 15.7. Found: Pd, 29.9; C, 20.3; H, 5.8; N, 15.7. Calcd for $[Pd(tnOH)_2][PdCl_4]$, $Pd_2C_6H_{20}Cl_4N_4O_2$: Pd, 39.8; C, 13.5; H, 3.8; N, 10.5. Found: Pd, 40.0; C, 13.4; H, 3.9; N, 10.4.

Bis(2-chloropropane-1,3-diamine)platinum(II) Salts, $Pt(tnCl)_2^{2+}$.—To prevent contamination with products of hydrolysis and ammonolysis of the CCl bonds, the following procedure was used to obtain the salts of this complex.

$Pt(tnCl)Cl_2$ (0.364 g) was heated with silver nitrate solution in the usual way to give a solution of $[Pt(tnCl)(H_2O)_2](NO_3)_2$. A solution of 0.236 g of $(tnCl)(HCl)_2$ in water passed down a column of Amberlite IRA-400 anion-exchange resin which had been converted to the hydroxide form by treatment with concentrated sodium hydroxide solution. The eluted solution was added to the bis-aquo complex and the mixture was gently warmed for several minutes. A few drops of concentrated hydrochloric acid was added, and the mixture was allowed to cool and then filtered to remove $Pt(tnCl)Cl_2$ (formed from unreacted $Pt(tnCl)(H_2O)_2^{2+}$) and traces of AgCl. The filtrate contained $Pt(tnCl)_2^{2+}$ and $H_2(tnCl)^{2+}$. Addition of K_2PtCl_4 solution caused precipitation of pink $[Pt(tnCl)_2][PtCl_4]$, which was filtered off, washed with cold water and then acetone, and air-dried. A 0.0856-g yield was obtained, or 12% based on $Pt(tnCl)Cl_2$ used. *Anal.* Calcd for $Pt_2C_6H_{18}Cl_6N_4$: Pt, 52.1; C, 9.6; H, 2.4; N, 7.5; Cl, 28.4. Found: Pt, 52.3; C, 9.7; H, 2.3; N, 7.3; Cl, 28.6.

$[Pt(tnCl)_2][PtCl_4]$ (0.0918 g) was warmed with a solution of silver nitrate (molar ratio 1:2). The resultant pink Ag_2PtCl_4 was filtered off, giving a solution of $[Pt(tnCl)_2](NO_3)_2$. Since traces of silver nitrate would be difficult to remove from this salt, the solution was passed down a column of anion-exchange resin in the chloride form. The eluted solution was concentrated and a large excess of acetone was added to precipitate $[Pt(tnCl)_2]Cl_2$. This white powder was washed with acetone and dried in a vacuum desiccator. A 0.0267-g yield was obtained, or 45% based on $[Pt(tnCl)_2][PtCl_4]$. *Anal.* Calcd for $PtC_6H_{18}Cl_4N_4$: C, 14.9; H, 3.8; N, 11.6; Cl, 29.4. Found: C, 15.0; H, 3.7; N, 11.6; Cl, 30.2.

Bis(2-chloropropane-1,3-diamine)palladium(II) Tetrachloropalladate(II), $[Pd(tnCl)_2][PdCl_4]$.—This was obtained in 87% yield by mixing in aqueous solution equimolar quantities of K_2PdCl_4 and $(tnCl)(HCl)_2$ (adjusted to pH 9.0 with NaOH solution).

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[12] If the chelate rings were flattened into the PtN_4 plane, the substituents on the central C atoms of the diamines would be on the same side of this plane for the cis isomer and on opposite sides of it for the trans isomer.

TABLE I

NONELECTROLYTE PLATINUM(IV) COMPLEXES

			Analyses, %										
			Pt		C		H		N		Cl		
Complex	Color	% yield[a]	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Ref[b]
$Pt(en)Cl_2(OH)_2$	Pale yellow	69			6.7	7.3	2.8	2.8	7.8	7.2			12
$Pt(en)Cl_4$	Bright yellow	77	49.1	49.2	6.1	6.5	2.0	2.0	7.1	6.9			12
$Pt(tn)Cl_2(OH)_2$	Pale yellow	79	52.1	52.8	9.6	9.6	3.2	3.3	7.5	7.4	19.0	19.1	
$Pt(tn)Cl_4$	Bright yellow	50	47.5	47.3	8.8	8.8	2.5	2.5	6.8	6.9	34.5	34.7	10
Pt(*meso*-dptn)Cl_4[c]	Bright yellow	73	44.4	44.8	13.7	13.8	3.2	3.3	6.4	6.2	32.3	32.0	
Pt(±dptn)Cl_4[c]	Bright yellow	57	44.4	44.3	13.7	13.9	3.2	3.4	6.4	6.5	32.3	32.5	
$Pt(tnOH)Cl_2(OH)_2$	Pale yellow	61			9.2	9.4	3.1	3.3	7.2	6.9			
$Pt(tnOH)Cl_4$	Bright yellow	77	45.7	45.7	8.4	8.4	2.4	2.4	6.6	6.6	33.2	33.5	
$Pt(tnCl)Cl_2(OH)_2$	Pale yellow	62	47.7	48.1	8.8	8.5	2.7	2.7	6.9	6.7	26.0	26.4	
$Pt(tnCl)Cl_4$	Bright yellow	76[d]	43.8	44.3	8.1	8.1	2.1	2.0	6.3	6.3	39.8	39.7	

[a] Based on Pt(diamine)Cl_2 unless otherwise stated. [b] Where previously prepared. [c] dptn = pentane-2,4-diamine. [d] Based on Pt(diamine)$Cl_2(OH)_2$.

The pink-brown precipitate was filtered off, washed well with water and then acetone, and air-dried. *Anal.* Calcd for $Pd_2C_6H_{18}Cl_6N_4$: Pd, 37.2; C, 12.6; H, 3.2; N, 9.8. Found: Pd, 37.3; C, 12.7; H, 3.2; N, 9.9.

Platinum(IV) Complexes. ***cis*-Dichloro-*trans*-dihydroxo(diamine)platinum(IV) Complexes, Pt(diamine)$Cl_2(OH)_2$.**—These nonelectrolyte complexes were prepared by addition of a small volume of 30% hydrogen peroxide solution to a heated, stirred suspension of Pt(diamine)Cl_2 in water.[11] Vigorous effervescence occurred, and Pt(diamine)$Cl_2(OH)_2$ was formed as a pale yellow precipitate. Warming was continued for 30 min, after which the solution was allowed to cool and then filtered. The pale yellow solid was washed with cold water and then acetone, and air-dried. In some cases, significant amounts of water-soluble side products were formed, reducing the yield of the desired complex. Details of individual complexes are listed in Table I. Some complexes of ligands other than tnOH and tnCl are included since their infrared spectra are relevant to the discussion of the spectra of these complexes.

Tetrachloro(diamine)platinum(IV) Complexes, Pt(diamine)Cl_4.—These complexes could be prepared by warming an aqueous suspension of Pt(diamine)$Cl_2(OH)_2$ with several drops of concentrated HCl.[11] The solid initially dissolved, owing to formation of Pt(diamine)$Cl_2(H_2O)_2^{2+}$ ions, but the solution soon turned bright yellow, and Pt(diamine)Cl_4 precipitated as a bright yellow solid. Alternatively, a heated, stirred supension of Pt(diamine)Cl_2 could be treated directly with hydrogen peroxide and hydrochloric acid.[10] The complex was filtered from the cooled reaction mixture and then washed with cold water, then a small volume of acetone (some of these complexes are appreciably soluble in acetone and some other polar solvents like *N,N'*-dimethylformamide). The complex was then air-dried. Details are given in Table I.

***trans*-Dichlorobis(1,3-diaminopropan-2-ol)platinum(IV) Chloride, [Pt(tnOH)$_2$Cl$_2$]Cl$_2$.**—This complex was obtained in the form of pale yellow sparingly soluble crystals by peroxide oxidation of a solution of [Pt(tnOH)$_2$]Cl_2 in HCl[4a,10,11] (89% yield). *Anal.* Calcd for $PtC_6H_{20}Cl_4N_4O_2$: Pt, 37.7; C, 13.9; H, 3.9; N, 10.8; Cl, 27.4. Found: Pt, 37.3; C, 14.0; H, 4.1; N, 10.8; Cl, 27.1.

***trans*-Dichloro-*cis*-bis(ammine)(1,3-diaminopropan-2-ol)platinum(IV) Chloride, [Pt(tnOH)(NH_3)$_2$Cl$_2$]Cl$_2$.**—This complex was prepared by the general method previously described[4a] for complexes of the type *trans'*-[Pt(diamine)(NH_3)$_2$(Cl'$_2$)]Cl_2 (yellow solid, 64% yield). *Anal.* Calcd for $PtC_3H_{16}Cl_4N_4O$: C, 7.8; H, 3.5; N, 12.2; Cl, 30.8. Found: C, 8.2; H, 3.5; N, 12.4; Cl, 30.8.

Discussion

Existence of Some Complexes, M(diamine)X_2, in Different Forms.—In the Experimental Section, it was mentioned that for a number of complexes of the type M(diamine)X_2 two distinct forms, with different X-ray powder diffraction patterns and ir spectra, are obtained. This behavior seems to be most clearly defined for the M(tnCl)Cl_2. This unusual polymorphism does not seem to be quite unique among coordination compounds (see, for example, the behavior of *mer*-Co(NO_2)$_3$(NH_3)(en)[13,14]). The different crystal structures probably arise from different H-bonded linkages between the molecules. It is possible that the chelate ring conformations could be significantly different in the two forms of a particular complex. It is tempting to speculate that for tnCl complexes one form may correspond to a chair conformation with the chloro group axial, stabilized by intramolecular H bonding, Figure 4, as found for water-soluble complexes in solution (see following paper) and the other form to a chair conformation with the chloro group equatorial. However, for Pt(tn)Cl_2 only one basic type of conformation (chair) could reasonably be expected, so that a different explanation would be necessary for the existence of two forms of this complex.

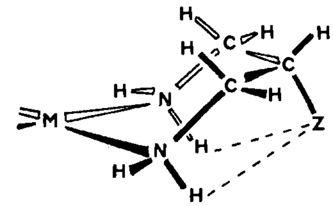

Figure 4.—tnZ chelate ring in chair conformation with Z axial (Z = OH, Cl).

Since the crystal structure of Pt(en)Cl_2 has been found to consist of infinite chains of Pt(en)Cl_2 units with weak electronic interaction between platinum atoms,[15] the possibility of related structures for complexes containing six-membered chelate rings should be considered. Just as the steric hindrance provided by a chair-type conformation would prevent the formation of infinite anion–cation chains in Magnus-type salts,[2] infinite chains would not be possible for complexes Pt(diamine)X_2, where "diamine" is a substituted trimethylenediamine. However, there would be little steric hindrance to close approach of a pair of molecules (Figure 5), and such "molecular pairs" could well be present in the crystal structures of some of these complexes.

Although single-crystal X-ray diffraction would allow the difference between the polymorphic forms of these complexes to be determined, it has not been possible to obtain crystals of suitable quality of these almost insoluble complexes.

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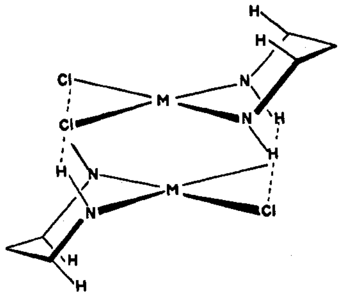

Figure 5.—Possible "molecular pair" in solid Pt(diamine)Cl$_2$.

Tetrachloroplatinate Salts.—In a previous paper,[2] colors of a number of tetrachloroplatinate salts, [Pt(diamine)$(NH_3)_2$][PtCl$_4$] and [Pt(diamine)$_2$][PtCl$_4$], were correlated with the probable ring conformations in the cations. Violet colors indicate some cation–anion electronic interaction; pink colors indicate the lack of such interaction.

The pink color of [Pt(tnOH)$(NH_3)_2$][PtCl$_4$] corresponds to little anion–cation interactions. The chelate ring in this complex probably takes up a chair conformation with the hydroxyl group axial (Figure 4), since such a conformation is preferred for Pt(tnOH)$(NH_3)_2^{2+}$ in solution (see following paper). The axial hydroxyl group would not sterically hinder close anion approach below the PtN$_4$ plane but, by H bonding to the axial amino protons, could hinder formation of N–H···Cl H bonds (probably an important factor when anion–cation proximity is favored).

Although the conformation of Pt(tnCl)$(NH_3)_2^{2+}$ in aqueous solution is analogous to that of the hydroxy compound, this cation gives a violet-pink tetrachloroplatinate. This may correspond to a mixture of two different crystal structures, one with close anion–cation approach and the other without, or to a weak perturbation of the anion in a single-crystal structure.

Of the two geometrical isomers of Pt(tnOH)$_2^{2+}$, the trans isomer (Figure 3) would not permit close anion approach, but this would be possible for the cis isomer. However, [Pt(tnOH)$_2$][PtCl$_4$], which probably contains almost equal quantities of the two isomers, is pink, indicating that close cation–anion approach actually occurs for neither. Analogous geometrical isomers exist for [Pt(tnCl)$_2$][PtCl$_4$], and this salt is also pink.

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Complexes with Six-Membered Chelate Rings. V. Nuclear Magnetic Resonance and Infrared Spectra of Some Complexes of 1,3-Diaminopropan-2-ol and 2-Chloropropane-1,3-diamine with Platinum and Palladium

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Proton magnetic resonance spectra are reported for the compounds (diamine)(HCl)$_2$, Pt(diamine)$(NH_3)_2^{2+}$, [M(tnOH)$_2$]Cl$_2$, [Pt(tnCl)$_2$]Cl$_2$, and *trans*'-[Pt(tnOH)$(NH_3)_2$Cl'$_2$]Cl$_2$ in D$_2$O solutions. The spectra of the complexes are consistent with a preference for a chair-type conformation of the chelate ring with the chloro or hydroxy substituent axial. Such a conformation is probably stabilized by intramolecular hydrogen bonding. Some aspects of the infrared spectra of the complexes M(diamine)Cl$_2$, [M(diamine)$_2$][MCl$_4$], *trans*'-Pt(diamine)Cl$_2$(OH')$_2$, and Pt(diamine)Cl$_4$ are discussed. (M = Pt or Pd, diamine = 1,3-diaminopropan-2-ol, tnOH, or 2-chloropropane-1,3-diamine, tnCl.)

Introduction

X-Ray diffraction studies[1–3] and proton magnetic resonance spectra[4–6] of a number of complexes containing six-membered diamine chelate rings have shown that in many respects the conformational behavior of these rings is analogous to that of the corresponding cyclohexane derivatives. This paper discusses the conformational behavior and some aspects of infrared and pmr spectra of Pt(II), Pd(II), and Pt(IV) complexes of the diamines 1,3-diaminopropan-2-ol (NH$_2$CH$_2$CHOHCH$_2$NH$_2$, tnOH) and 2-chloropropane-1,3-diamine (NH$_2$CH$_2$CHClCH$_2$NH$_2$, tnCl). The chelate rings in these complexes are analogs of cyclohexanol and chlorocyclohexane, respectively.

Experimental Section

Preparation of complexes[7] and instrumentation[4,8] have been previously described. Nmr spectra were run on N-deuterated samples in D$_2$O at 60 MHz using *tert*-butyl alcohol as internal standard, unless otherwise stated. Variable-temperature spectra were run using a V-6040 attachment on the A-60. The 100-MHz spectra were recorded by Dr. S. R. Johns on a Varian HA-100 instrument. Solutions for nmr usually contained about 80 mg/ml. Spectra were not significantly concentration dependent. Chemical shift data are reported on a τ' scale (relative to DSS, 2,2-dimethyl-2-silapentane-5-sulfonate) using τ' 8.77 for *tert*-butyl alcohol in D$_2$O. N-Deuterated b-Pt(tnCl)Cl$_2$ was prepared by recrystallization of Pt(tnCl)Cl$_2$ from boiling D$_2$O.

Results

Proton Magnetic Resonance Spectra.—The pmr spectrum of (tnOH)(HCl)$_2$ at room temperature is

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