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## Complexes with Six-Membered Chelate Rings. I. Preparation of Platinum(II) and Palladium(II) Complexes of Trimethylenediamine and Some Methyl-Substituted Derivatives

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Complexes containing six-membered rings and, for comparison, five-membered rings,  $M(\text{diamine})\text{Cl}_2$ ,  $M(\text{diamine})_2^{2+}$ ,  $M(\text{diamine})(\text{NH}_3)_2^{2+}$ , have been prepared, where  $M = \text{Pt(II), Pd(II)}$ ; diamine = trimethylenediamine, 2-methylpropane-1,3-diamine, pentane-2,4-diamine, neopentanediamine, *meso*-butane-2,3-diamine, and ethylenediamine. The geometric isomers of pentane-2,4-diamine have been reassigned. Some aspects of the infrared spectra of the complexes are discussed. A correlation can be made between structure and color in tetrachloroplatinate salts.

### Introduction

The conformational behavior of six-membered carbocyclic and heterocyclic ring systems has been extensively investigated but little is known of the behavior of six-membered chelate rings, such as would be formed by coordination of trimethylenediamine (propane-1,3-diamine) to a metal ion. Accordingly, some complexes of platinum(II) and palladium(II) with trimethylenediamine and some methyl-substituted derivatives have been prepared, together with some complexes containing five-membered chelate rings for comparison, with a view to studying the pmr spectra of suitable complexes. These pmr spectra are discussed in the following paper.

Drew and Tress<sup>1</sup> prepared a series of trimethylenediamine complexes of platinum(II) and showed them to be analogous in most of their properties to the corresponding ethylenediamine complexes. Apart from this, only a few platinum complexes containing trimethylenediamine derivatives have been prepared.<sup>2-5</sup>

### Experimental Section

**Preparation of Ligands.**<sup>6</sup>—Trimethylenediamine was supplied by L. Light Co.; ethylenediamine, by Unilab. They were used without further purification.

Dihydrochlorides were prepared from free diamines by dissolving the free base in water, adding hydrochloric acid until the solution was acid, evaporating nearly to dryness, and precipitating the diamine dihydrochloride with acetone. These salts may be recrystallized from 95% ethanol. *Anal.* Calcd for  $(\text{tn})(\text{HCl})_2$ ,  $\text{C}_3\text{H}_{12}\text{Cl}_2\text{N}_2$ : C, 24.5; H, 8.2; N, 19.1; Cl, 48.2. Found: C, 24.7; H, 8.5; N, 19.0; Cl, 48.2. Calcd for  $(\text{en})(\text{HCl})_2$ ,  $\text{C}_2\text{H}_{10}\text{Cl}_2\text{N}_2$ : C, 18.1; H, 7.6; N, 21.1; Cl, 53.3. Found: C, 18.1; H, 7.4; N, 20.9; Cl, 53.5.

A free diamine could be obtained from its dihydrochloride by adding saturated aqueous sodium hydroxide solution to a concentrated aqueous solution of the dihydrochloride, separating off the upper diamine layer, drying this over potassium hydroxide, and distilling under vacuum from barium oxide.

**2-Methylpropane-1,3-diamine.**—Diethyl methylmalonate,  $\text{CH}_3\text{CH}(\text{COOC}_2\text{H}_5)_2$ , was prepared by the method of Weiner<sup>7</sup> and converted to the diamide,<sup>8</sup> then to the dinitrile,<sup>9</sup> and finally to the diamine by reduction with sodium in ethanol.<sup>10</sup> The dihydrochloride was a deliquescent white solid. *Anal.* Calcd for  $\text{C}_4\text{H}_{14}\text{N}_2\text{Cl}_2$ : Cl, 44.0. Found: Cl, 43.9.

The overall yield was low, due mainly to a low yield in the diamide dehydration step. It was not possible to reduce the diamide directly using  $\text{LiAlH}_4$  as it is insoluble in ethers, which are used as solvents in these reactions.

**Pentane-2,4-diamine.**—This compound exists in two geometric isomers, *meso* and racemic. A mixture of the two isomers was prepared satisfactorily by reduction of acetylacetone dioxime with sodium in ethanol as described by Dippel.<sup>11</sup> Dippel separated these isomers by converting the diamine to the diacetyl derivative which was dissolved in ethanol. Addition of a large volume of ether precipitated out the  $\alpha$  isomer, leaving the  $\beta$  isomer in solution, to be isolated by evaporation. The acetates were then hydrolyzed to the corresponding dihydrochlorides. A sample obtained by Dippel's method for isolating the  $\alpha$  isomer showed only one methyl doublet in its pmr spectrum in  $\text{D}_2\text{O}$  and was assumed to be pure  $\alpha$ . A sample of " $\beta$  isomer" obtained by Dippel's method was found by pmr, however, to contain 30%  $\alpha$  and 70% of a second component, the  $\beta$  isomer. A much more effective, and convenient, method of separation was by fractional crystallization from ethanol and ethanol-acetone.

In a typical reduction, 30 g of acetylacetone dioxime yielded 32.2 g of crude  $(\text{dptn})(\text{HCl})_2$  (80.6%). The pmr spectrum of this material showed it to contain approximately equal proportions of the two isomers (*cf.* Dippel's estimate of 30:70). The mixture was dissolved in about 600 ml of boiling 95% ethanol. On cooling, the first fraction (8.95 g) was obtained. Its spectrum showed it to be essentially pure ( $\geq 99\%$ )  $\alpha$  isomer. The filtrate was evaporated to approximately 150 ml, then cooled. A second fraction (3.97 g) precipitated out. It contained 95%  $\alpha$  isomer. The filtrate was evaporated nearly to dryness and acetone was added to precipitate out a third fraction (16.6 g) which was found to be 95%  $\beta$  isomer. Further treatment of fraction 2 yielded 2.28 g of pure  $\alpha$  isomer. Pure  $\beta$  isomer, free from small amounts of  $\alpha$ , was more difficult to obtain, but a sample (3.25 g) was eventually isolated by careful precipitation with acetone from an ethanol solution of the third fraction. Both dihydrochlorides are white deliquescent solids. *Anal.* Calcd for  $\text{C}_5\text{H}_{16}\text{Cl}_2\text{N}_2$ : C, 34.3; H, 9.2; N, 16.0; Cl, 40.5. Found for  $\alpha$  isomer: C, 34.3; H, 9.2; N, 15.8; Cl, 40.7. Found for  $\beta$  isomer: C, 34.4; H, 9.1; N, 15.5; Cl, 39.9.

(1) H. D. K. Drew and H. J. Tress, *J. Chem. Soc.*, 1335 (1933).(2) L. Tschugaeff and W. Sokoloff, *Ber.*, **40**, 3461 (1907).(3) F. G. Mann, *J. Chem. Soc.*, 1262 (1928).(4) H. D. K. Drew, F. S. H. Head, and H. J. Tress, *ibid.*, 1549 (1937).(5) C. P. Knop and C. H. Brubaker, Jr., *J. Inorg. Nucl. Chem.*, **9**, 8 (1959).(6) The following abbreviations will be used throughout: tn, propane-1,3-diamine(trimethylenediamine),  $\text{NH}_2(\text{CH}_2)_3\text{NH}_2$ ; metn, 2-methylpropane-1,3-diamine,  $\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$ ; dptn, pentane-2,4-diamine,  $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ ; dan, 2,2-dimethylpropane-1,3-diamine (neopentanediamine),  $\text{NH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$ ; bn, butane-2,3-diamine,  $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NH}_2$ ; en, ethylenediamine,  $\text{NH}_2(\text{CH}_2)_2\text{NH}_2$ .

(7) N. Weiner, "Organic Syntheses," Coll. Vol. 2, Wiley, New York N. Y., 1943, p 279.

(8) R. Meyer and P. Bock, *Justus Liebigs Ann. Chem.*, **347**, 93 (1906).(9) P. Henry, *Jahresber. Fortsch. Chem. Verw. Wiss.*, 639 (1889).(10) H. Strack and H. Fanselow, *Z. Physiol. Chem.*, 159 (1929).(11) C. J. Dippel, *Recl. Trav. Chim. Pays-Bas*, **50**, 525 (1931).

On the basis of a partial resolution of his " $\beta$  isomer" with methoxycamphor, Dippel assigned the racemic structure to this isomer. As we have shown that Dippel's " $\beta$  isomer" probably contained appreciable amounts of  $\alpha$  isomer and because our pmr spectra seemed inconsistent with his assignment, it was important that the question be settled by resolution of one of the pure isomers into enantiomers. The  $\alpha$  isomer was resolved using *d*-tartaric acid, leading us to reverse Dippel's assignment.

**Resolution of ( $\alpha$ -dptn)(HCl)<sub>2</sub>.**—Approximately 1.3 g of free  $\alpha$ -dptn was neutralized with 1.6 g of *d*-tartaric acid in 5 ml of water. After the solution had been allowed to stand, large colorless crystals formed. These were filtered off, washed with a small volume of cold water, then ethanol-water, 95% ethanol, and acetone, and air dried. Specific rotation of this sample (fraction 1, 0.58 g) was +35.4°. Recrystallization from water did not increase the rotation. The filtrate from fraction 1 was evaporated nearly to dryness. When the sides of the beaker were scratched with a glass rod, a microcrystalline solid precipitated. This was filtered as before (fraction 2, 0.34 g,  $\alpha_D$  +32.8°). The filtrate was further evaporated to a colorless oil. Trituration under acetone converted this to a solid, which was filtered, washed with acetone, and dried in a vacuum desiccator over phosphorus(V) oxide. This product was highly deliquescent (fraction 3, 0.74 g,  $\alpha_D$  +13.4°). Because it was difficult to precipitate as a solid, this compound could not be effectively recrystallized.

Fractions 1 and 3 were converted to dihydrochlorides by passing aqueous solutions down a column of Amberlite IRA-400 in the chloride form and evaporating the eluted solutions to dryness. These samples showed specific rotations of +16.3 and -10.6°, respectively. Repetition of this procedure gave similar results.

When the  $\beta$  base was neutralized with *d*-tartaric acid, evaporation of the resultant solution gave an oil, which could be solidified by trituration under acetone. It could not be fractionally crystallized.

**Neopentanediamine.**—The method of Lambert and Lowe<sup>12</sup> was used to prepare 1,3-dinitro-2,2-dimethylpropane, O<sub>2</sub>NCH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NO<sub>2</sub>. To 25.3 g of this product and 60 g of granulated tin was added 20 ml of water and then 50 ml of concentrated hydrochloric acid. The flask was warmed gently under reflux to maintain vigorous evolution of hydrogen, with temporary cooling if frothing became excessive. Further portions of hydrochloric acid were added from time to time until a total of 120 ml had been used. The flask was gently heated 1 hr further; then a saturated aqueous solution containing 100 g of sodium hydroxide was added. The diamine was steam distilled into hydrochloric acid. The resulting solution was evaporated to yield crude (dan)(HCl)<sub>2</sub>. This was dissolved in water and the solution was treated with saturated sodium hydroxide solution. The diamine separated off as a brown oil, which was dried over potassium hydroxide. Vacuum distillation from barium oxide gave 8.3 g of a viscous, colorless liquid. Some of this product was converted to the dihydrochloride, a white deliquescent solid. *Anal.* Calcd for C<sub>5</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>: C, 34.3; H, 9.2; N, 16.0; Cl, 40.5. Found: C, 34.3; H, 9.4; N, 15.9; Cl, 40.1.

This procedure was found by repetition to give variable, sometimes low yields. We found this to be true, however, for other reduction methods attempted.<sup>13</sup>

**Butane-2,3-diamine.**—Dimethylglyoxime was reduced with Raney nickel alloy-sodium hydroxide as described by Dickey, Fickett, and Lucas.<sup>14</sup> The resultant mixture of diamines and amino alcohols was steam distilled into hydrochloric acid. The product obtained by evaporation was dissolved in water and saturated sodium hydroxide solution was added. The oil which separated off was dried over potassium hydroxide and then fractionally distilled under vacuum. No sharp separation between diamine and amino alcohol fractions was obtained, although the more volatile fractions contained greater proportions of diamine. The distillation fractions, all colorless viscous liquids, were dis-

solved separately in water. Each solution was acidified with hydrochloric acid and then evaporated nearly to dryness. Acetone was then added to precipitate out a solid. Each fraction was recrystallized from boiling methanol. The least soluble fractions from each sample were combined together and recrystallized from boiling methanol. Dickey, *et al.*, assigned the *meso* structure to the least soluble component. This sample contained a small (<3%) proportion of another component, detected by nmr, which could not be removed by repeated recrystallization from methanol or ethanol. A 39-g sample of dimethylglyoxime yielded 1.6 g of this dihydrochloride. *Anal.* Calcd for C<sub>4</sub>H<sub>14</sub>Cl<sub>2</sub>N<sub>2</sub>: C, 29.8; H, 8.8; N, 17.4; Cl, 44.0. Found: C, 29.8; H, 8.7; N, 17.3; Cl, 44.2.

**Metal Complexes.**—Potassium tetrachloroplatinate(II) was prepared by the method of Keller.<sup>15</sup> Potassium tetrachloropalladate(II) was prepared by adding the calculated weight of potassium chloride to an aqueous solution of H<sub>2</sub>PdCl<sub>4</sub> prepared in the usual way<sup>16</sup> and evaporating nearly to dryness. The resultant brown crystals were filtered off, washed with ethanol, and air dried.

**Dichloro(diamine)platinum(II) Complexes, Pt(diamine)Cl<sub>2</sub>.**—These complexes are nonelectrolytes, yellow to white in color, all very sparingly soluble in water at room temperature, and more soluble in hot water. In other solvents, solubility is low (*e.g.*, alcohols, *N,N'*-dimethylformamide, acetonitrile) or effectively zero (*e.g.*, chloroform, acetone). Pt(en)Cl<sub>2</sub> was prepared by the method of Basolo, *et al.*<sup>17</sup> Other complexes were prepared by the following procedure.

To a concentrated aqueous solution of K<sub>2</sub>PtCl<sub>4</sub> (1 mol) was added either slightly more than 1 mol of free diamine or an aqueous solution containing 1.3 mol of the appropriate diamine dihydrochloride adjusted to a suitable pH in the range 9–10 with approximately 1 *N* sodium hydroxide solution. With some diamines, precipitation of the desired Pt(diamine)Cl<sub>2</sub> occurred on standing; for others, gentle warming was required. With reactions involving dihydrochlorides, addition of further alkali during the reaction often resulted in precipitation of more solid. Prolonged heating of alkaline solutions caused them to turn brown, but this was reversed by addition of hydrochloric acid. When reaction appeared complete, the solution was cooled, and the resultant solid was filtered off, washed with cold water and then with acetone, and air dried. Products so obtained were usually contaminated by small amounts of the isomeric [Pt(diamine)<sub>2</sub>][PtCl<sub>4</sub>] complexes. In most cases, careful recrystallization from boiling dilute hydrochloric acid was sufficient to remove most of this impurity. Samples quite free from tetrachloroplatinate could be obtained by addition of hydrochloric acid to a solution of [Pt(diamine)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> prepared as described below.<sup>18</sup> Any silver chloride present in the resultant precipitate could be removed by rapid washing with dilute aqueous ammonia solution.

Pt(tn)Cl<sub>2</sub> was found to exist in two distinct forms, depending on conditions of crystallization. This will be discussed with other examples in a later paper.

Some details of preparation, together with analytical results, are given in Table I.

**Dichloro(diamine)palladium(II) Complexes, Pd(diamine)Cl<sub>2</sub>.**—In most of their properties palladium complexes were similar to their platinum analogs. They were prepared by a procedure generally similar to that used for Pd(en)Cl<sub>2</sub>.<sup>19,20</sup> Excess diamine (>2 mol) or neutralized dihydrochloride solution was added to aqueous K<sub>2</sub>PdCl<sub>4</sub> solution. The initial pink to brown precipitate, predominantly [Pd(diamine)<sub>2</sub>][PdCl<sub>4</sub>], redissolved on continued stirring, sometimes aided by warming, to give a solution containing Pd(diamine)<sub>2</sub><sup>2+</sup>, colorless or very pale yellow. This

(12) R. N. Keller, *Inorg. Syn.*, **2**, 247 (1946).

(13) G. B. Kauffman and J. H. Tsai, *ibid.*, **8**, 235 (1966).

(14) F. Basolo, J. C. Bailar, and B. R. Tarr, *J. Amer. Chem. Soc.*, **72**, 2433 (1950).

(15) G. E. Glass, W. B. Schwabacher, and R. S. Tobias, *Inorg. Chem.*, **7**, 2471 (1968).

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

(17) H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J. Chem. Soc.*, 1895 (1932).

(12) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1917 (1947).

(13) J. Rockett and F. C. Whitmore, *J. Amer. Chem. Soc.*, **71**, 3249 (1949).

(14) F. H. Dickey, W. Fickett, and H. J. Lucas, *ibid.*, **74**, 944 (1952).

TABLE I  
DICHLORO(DIAMINE) COMPLEXES

Compound	Color	pH for prepn	% yield	Analyses, %										Ref
				M		C		H		N		Cl		
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Pt(en)Cl <sub>2</sub>	Yellow	fb <sup>a</sup>	60	59.8	59.9	7.4	7.4	2.5	2.5	8.6	8.5	21.7	21.7	b
Pd(en)Cl <sub>2</sub>	Bright yellow	fb	85	44.8	44.6	10.1	10.2	3.4	3.5	11.8	11.6	29.9	30.3	c, d
Pt( <i>meso</i> -bn)Cl <sub>2</sub>	Yellow	10	74	55.1	55.4	13.6	13.6	3.4	3.5	7.9	8.0	20.0	20.2	e
Pt( <i>tn</i> )Cl <sub>2</sub>	Yellow	fb	63	57.4	57.8	10.6	10.8	3.0	3.0	8.2	8.3	20.8	20.9	f
Pd( <i>tn</i> )Cl <sub>2</sub>	Yellow	fb	92	42.3	42.4	14.3	14.4	4.0	3.7	11.1	11.1	28.2	28.3	
Pt( <i>metn</i> )Cl <sub>2</sub>	Yellow	9	34	55.1	55.2	13.6	13.8	3.4	3.6	7.9	7.9	20.0	20.0	g
Pt( <i>meso</i> -dptn)Cl <sub>2</sub>	Yellow	9.1	56	53.0	52.9	16.3	16.4	3.8	3.9	7.6	7.5	19.3	19.4	
Pd( <i>meso</i> -dptn)Cl <sub>2</sub>	Bright yellow	10	63	38.1	38.0	21.5	21.6	5.1	5.1	10.0	9.9	25.4	25.7	
Pt((±)dptn)Cl <sub>2</sub>	Very pale yellow	10	50	53.0	53.1	16.3	16.3	3.8	3.8	7.6	7.7	19.3	19.4	
Pd((±)dptn)Cl <sub>2</sub>	Yellow	10	58	38.1	38.0	21.5	21.1	5.1	5.0	10.0	10.1	25.4	25.2	
Pt( <i>dan</i> )Cl <sub>2</sub>	Yellow	9.1	85	53.0	53.1	16.3	16.3	3.8	3.9	7.6	7.8	19.3	19.4	
Pd( <i>dan</i> )Cl <sub>2</sub>	Bright yellow	10	83	38.1	38.1	21.5	21.5	5.1	5.1	10.0	9.9	25.4	25.4	

<sup>a</sup> fb = free base. <sup>b</sup> F. Basolo, J. C. Bailar, and B. R. Tarr, *J. Amer. Chem. Soc.*, **72**, 2433 (1950). <sup>c</sup> A. Gutbier and M. Woernle, *Ber.*, **39**, 2716 (1906). <sup>d</sup> H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J. Chem. Soc.*, 1895 (1932). <sup>e</sup> M. M. Yakshin and L. I. Baranova, *Zh. Neorg. Khim.*, **5**, 1710 (1960); *Russ. J. Inorg. Chem.*, **5**, 831 (1960). <sup>f</sup> Reference 1. <sup>g</sup> Reference 4.

solution was filtered and concentrated hydrochloric acid was added dropwise until the solution was acid. The solution turned bright yellow (for some ligands slight warming was necessary) and a yellow solid precipitated. If too much acid was added, PdCl<sub>4</sub><sup>2-</sup> tended to form. The precipitate was filtered, washed well with cold water and then acetone, and air dried. These products were generally pure. Sometimes addition of a few more drops of acid to the filtrate resulted in precipitation of more complex.

The complexes may be recrystallized from boiling water. Prolonged boiling of the solutions caused precipitation of small amounts of palladium metal. An alternative method of preparation is by recrystallization of [Pd(diamine)<sub>2</sub>][PdCl<sub>4</sub>] from boiling water to give Pd(diamine)Cl<sub>2</sub>.<sup>20</sup> A sample of Pd(*dan*)Cl<sub>2</sub> was prepared in this way.

Details of preparation and analytical results are given in Table I.

**Bis(diamine) Complexes, [M(diamine)<sub>2</sub>]Cl<sub>2</sub>.**—These were obtained by the action of excess free diamine on a heated and stirred suspension of the corresponding [M(diamine)<sub>2</sub>][MCl<sub>4</sub>] or M(diamine)Cl<sub>2</sub> complexes. Platinum complexes of the former type could be prepared by the method used by Basolo, *et al.*,<sup>17</sup> for [Pt(en)<sub>2</sub>][PtCl<sub>4</sub>]. Samples of [Pd(diamine)<sub>2</sub>][PdCl<sub>4</sub>] suitable for this purpose could be obtained by mixing equimolar quantities of K<sub>2</sub>PdCl<sub>4</sub> and the corresponding base (or dihydrochloride plus sodium hydroxide) in aqueous solution. The resulting solution was filtered and evaporated nearly to dryness. The [M(diamine)<sub>2</sub>]Cl<sub>2</sub> could be precipitated out with excess acetone. The solid was coagulated by warming the suspension, then filtered off, washed with acetone, and dried in a vacuum desiccator. Frequently, the compound still contained some lattice water after this treatment. Alternatively, the solution could be concentrated by evaporation and allowed to cool slowly. In some cases (*e.g.*, [Pt(*tn*)<sub>2</sub>]Cl<sub>2</sub>) quite large crystals could be obtained in this way. If, as sometimes happened, the compound was tinged with brown tars, the color could be removed by washing with a small volume of warm methanol. The small amount of solid which dissolved in the methanol could be reprecipitated if desired with acetone, any colored tars remaining in the methanol-acetone solvent. Tetrachloroplatinate or -palladate salts were precipitated by addition of aqueous solutions of K<sub>2</sub>MCl<sub>4</sub> to solutions of [M(diamine)<sub>2</sub>]Cl<sub>2</sub>. The precipitate was filtered off, washed with cold water and then acetone, and air dried. Details are given in Table II.

In the case of [Pt(*meso*-dptn)<sub>2</sub>]Cl<sub>2</sub>, when an aqueous solution was concentrated and allowed to stand, quite large crystals analyzing for [Pt(*meso*-dptn)<sub>2</sub>]Cl<sub>2</sub>·2H<sub>2</sub>O were obtained (fraction 1, 31% based on Pt(dptn)Cl<sub>2</sub>). After the crystals were filtered off, addition of acetone to the filtrate caused precipitation of a white powder (fraction 2, 49%). The 60-MHz nmr spectra

of these fractions in D<sub>2</sub>O were indistinguishable. Addition of a solution of K<sub>2</sub>PtCl<sub>4</sub> to aqueous solutions of fraction 1 and 2 gave pink and gray-violet precipitates, respectively. The infrared spectra of these precipitates showed slight but definite differences (*e.g.*, a band at 1060 cm<sup>-1</sup> in the spectrum of the pink salt shifts to 1070 cm<sup>-1</sup> in the violet salt). Assignment of isomeric composition to the different fractions will be discussed later, but from the infrared spectra of the tetrachloroplatinates, fraction 1 appears to contain only one isomer; fraction 2, perhaps 20% of this isomer and 80% of the other.

**Bis(amine)(diamine)platinum(II) Complexes.**—Chloride salts, [Pt(diamine)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub>, were obtained by adding several drops of aqueous ammonia solution to a stirred warmed aqueous suspension of Pt(diamine)Cl<sub>2</sub>. When the solid had dissolved, the solution was filtered and evaporated nearly to dryness. The complex was precipitated out with acetone, filtered off, washed with acetone, and dried in a vacuum desiccator over phosphorus(V) oxide. Some of these complexes were quite deliquescent, and some tended to lose ammonia on heating or long standing to re-form Pt(diamine)Cl<sub>2</sub>. These factors made characterization difficult. Evaporation of aqueous solutions to dryness always yielded "glasses." By trituration under acetone, these could be converted into powders.

Tetrachloroplatinate salts were precipitated by mixing concentrated aqueous solutions of [Pt(diamine)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub> and K<sub>2</sub>PtCl<sub>4</sub>. They were filtered off, washed with cold water and then acetone, and air dried.

Perchlorate salts, [Pt(diamine)(NH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, were prepared by reaction of the bis(aquo)(diamine) complexes with ammonia solution. A suspension of 1 mol of Pt(diamine)Cl<sub>2</sub> in the volume of standardized silver perchlorate solution containing 2 mol of AgClO<sub>4</sub> was heated and stirred. Precipitation of silver chloride began immediately and was complete within a few minutes. The mixture was allowed to cool and then was filtered. Any tetrachloroplatinate present was precipitated as the silver salt.<sup>18</sup> The filtrate was a colorless solution containing Pt(diamine)-(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup>, slightly acidic because of dissociation of protons from the coordinated water molecules. The original nonelectrolyte could be regenerated by addition of hydrochloric acid. To the solution of bis-aquo complex was added several drops of concentrated ammonia solution. The solution was then evaporated to dryness on a steam bath. The resultant crystalline solid was dissolved in boiling acetone, the solution was filtered, and excess ether was added to precipitate the complex as a white powder, which was filtered off, washed with ether, and dried in a vacuum desiccator. This procedure helped remove traces of silver salts, and could be repeated if necessary. Unlike the chloride salts, which have low solubility in solvents other than water, the perchlorates are quite freely soluble in dimethyl sulfoxide and dimethylformamide and are moderately soluble in alcohols and

TABLE II  
BIS(DIAMINE) COMPLEXES

Compound	Color	% yield	Based on	Analyses, %										Ref
				M		C		H		N		Cl		
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
[Pt(en) <sub>2</sub> ]Cl <sub>2</sub>	Colorless crystals	85	[Pt(en) <sub>2</sub> ][PtCl <sub>4</sub> ]	50.5	50.1	12.4	12.5	4.2	4.1	14.5	14.9	18.4	18.8	17
[Pt(en) <sub>2</sub> ][PtCl <sub>4</sub> ]	Violet	q <sup>a</sup>	[Pt(en) <sub>2</sub> ]Cl <sub>2</sub>	59.8	59.7	7.4	7.4	2.5	2.5	8.6	8.6	21.7	21.5	17
[Pd(en) <sub>2</sub> ]Cl <sub>2</sub>	Colorless crystals	80	[Pd(en) <sub>2</sub> ][PdCl <sub>4</sub> ]	35.8	35.3	16.1	16.1	5.4	5.4	18.8	18.3	23.8	23.4	20
[Pt(tn) <sub>2</sub> ]Cl <sub>2</sub>	Colorless crystals	87	[Pt(tn) <sub>2</sub> ][PtCl <sub>4</sub> ]	47.1	46.7	17.4	17.4	4.9	5.1	13.5	13.3	17.1	17.4	1
[Pt(tn) <sub>2</sub> ][PtCl <sub>4</sub> ]	Pink	q	[Pt(tn) <sub>2</sub> ]Cl <sub>2</sub>	57.4	57.0	10.6	10.5	3.0	3.0	8.2	8.1	20.8	20.9	1
[Pd(tn) <sub>2</sub> ]Cl <sub>2</sub>	White	82	K <sub>2</sub> PdCl <sub>4</sub> <sup>b</sup>	32.7	32.6	22.1	22.3	6.2	6.5	17.2	16.9	21.8	21.9	
[Pd(tn) <sub>2</sub> ][PdCl <sub>4</sub> ]	Pink-brown	q	[Pd(tn) <sub>2</sub> ]Cl <sub>2</sub>	42.3	42.1	14.3	14.7	4.0	4.3	11.1	11.0	28.2	28.3	
[Pt(meso-dptn) <sub>2</sub> ]Cl <sub>2</sub> ·2H <sub>2</sub> O (fraction 1)	Colorless crystals	31	Pt(meso-dptn)Cl <sub>2</sub> (crude)	38.5	38.8	23.7	23.9	6.4	6.4	11.1	10.8	14.0	14.2	
[Pt(meso-dptn) <sub>2</sub> ][PtCl <sub>4</sub> ]	Pink	q	[Pt(meso-dptn) <sub>2</sub> ]Cl <sub>2</sub> (fraction 1)	53.0	53.2	16.3	16.2	3.8	4.0	7.6	7.7	19.3	19.5	
[Pt(meso-dptn) <sub>2</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O (fraction 2)	White	49	Pt(meso-dptn)Cl <sub>2</sub> (crude)	40.0	39.7	24.6	24.9	6.2	5.9	11.5	11.2	14.5	14.4	
[Pt(meso-dptn) <sub>2</sub> ][PtCl <sub>4</sub> ]	Gray-violet	q	[Pt(meso-dptn) <sub>2</sub> ]Cl <sub>2</sub> (fraction 2)	53.0	52.6	16.3	16.3	3.8	4.0	7.6	7.4	19.3	19.6	
[Pd(meso-dptn) <sub>2</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	White	86	[Pd(meso-dptn) <sub>2</sub> ]-[PdCl <sub>4</sub> ]	26.6	27.0	30.0	30.0	7.6	7.8	14.0	13.7	17.7	18.2	
[Pd(meso-dptn) <sub>2</sub> ][PdCl <sub>4</sub> ]	Bright pink	q	[Pd(meso-dptn) <sub>2</sub> ]Cl <sub>2</sub>	38.1	38.4	21.5	21.6	5.1	5.1	10.0	9.7	25.4	25.9	
[Pt((±)dptn) <sub>2</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	White	65	Pt((±)dptn)Cl <sub>2</sub> (crude)	40.0	40.4	24.6	24.6	6.2	6.1	11.5	11.4	14.5	15.0	
[Pt((±)dptn) <sub>2</sub> ][PtCl <sub>4</sub> ]	Pink	q	[Pt((±)dptn) <sub>2</sub> ]Cl <sub>2</sub>	53.0	52.9	16.3	16.3	3.8	3.8	7.6	7.9	19.3	19.5	
[Pd((±)dptn) <sub>2</sub> ]Cl <sub>2</sub> ·1.5H <sub>2</sub> O	White	82	K <sub>2</sub> PdCl <sub>4</sub> <sup>b</sup>	26.0	26.4	29.4	29.2	7.7	7.6	13.7	13.6	17.3	17.7	
[Pd((±)dptn) <sub>2</sub> ][PdCl <sub>4</sub> ]	Brown	q	[Pd((±)dptn) <sub>2</sub> ]Cl <sub>2</sub>	38.1	38.0	21.5	21.3	5.1	5.2	10.0	10.2	25.4	25.5	
[Pt(dan) <sub>2</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	White	100	Pt(dan)Cl <sub>2</sub>	40.0	40.2	24.6	24.9	6.2	6.3	11.5	11.7	14.5	14.6	
[Pt(dan) <sub>2</sub> ][PtCl <sub>4</sub> ]	Pink	q	[Pt(dan) <sub>2</sub> ]Cl <sub>2</sub>	53.0	53.0	16.3	16.3	3.8	3.9	7.6	7.5	19.3	19.2	
[Pd(dan) <sub>2</sub> ]Cl <sub>2</sub> ·0.5H <sub>2</sub> O	White	60	K <sub>2</sub> PdCl <sub>4</sub> <sup>b</sup>	27.3	27.2	30.8	31.0	7.5	7.5	14.4	13.8	18.2	18.2	
[Pd(dan) <sub>2</sub> ][PdCl <sub>4</sub> ]	Pink	q	[Pd(dan) <sub>2</sub> ]Cl <sub>2</sub>	38.1	38.4	21.5	21.7	5.1	5.1	10.0	10.0	25.6	25.6	

<sup>a</sup> q = quantitative. <sup>b</sup> 1/2 [Pd(diamine)<sub>2</sub>][PdCl<sub>4</sub>].

TABLE III  
BIS(AMMINE)(DIAMINE) COMPLEXES

Compound	Color	% yield	Analyses, %										Ref
			M		C		H		N		Cl		
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
[Pt(en)(NH <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	68	40.0	40.1	4.9	5.5	2.9	3.0	11.5	11.4	14.5	14.6	
[Pt(meso-bn)(NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	White	47	50.3	50.5	12.4	12.8	4.7	4.9	14.4	14.3	18.3	18.4	b
[Pt(meso-bn)(NH <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	51	37.8	36.8	9.3	9.4	3.5	3.2	10.9	11.2	13.7	14.3	
[Pt(bn)(NH <sub>3</sub> ) <sub>2</sub> ][PtCl <sub>4</sub> ]	Violet or red	q <sup>a</sup>	59.6	59.4	7.3	7.6	2.8	2.9	8.6	8.8	21.7	21.7	c, d
[Pt(tn)(NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	White	89	52.1	52.2	9.6	9.8	4.3	4.4	15.0	14.4	18.9	18.5	e
[Pt(tn)(NH <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	73	38.9	38.2	7.2	7.3	3.2	3.3	11.2	11.0	14.1	14.2	
[Pt(tn)(NH <sub>3</sub> ) <sub>2</sub> ][PtCl <sub>4</sub> ]	Violet	q	61.0	60.9	5.6	5.6	2.5	2.6	8.8	8.7	22.2	22.3	e
[Pt(meso-dptn)(NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O	White	q	46.4	46.5	14.3	14.5	5.3	5.3	13.3	13.6	16.9	17.4	
[Pt(meso-dptn)(NH <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	66	36.8	36.0	11.3	11.6	3.8	3.9	10.6	10.1	13.4	13.6	
[Pt(meso-dptn)(NH <sub>3</sub> ) <sub>2</sub> ][PtCl <sub>4</sub> ]·0.5H <sub>2</sub> O	Pink	q	57.6	57.4	8.9	8.9	3.1	3.3	8.3	8.4	20.9	21.1	
[Pt((±)dptn)(NH <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	65	36.8	35.2	11.3	11.4	3.8	4.1	10.6	10.3	13.4	13.3	
[Pt((±)dptn)(NH <sub>3</sub> ) <sub>2</sub> ][PtCl <sub>4</sub> ]·0.5H <sub>2</sub> O	Pink	q	57.6	57.1	8.9	8.8	3.1	2.9	8.3	8.5	20.9	21.2	
[Pt(dan)(NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	White	90	48.5	48.5	14.9	15.0	5.0	5.1	13.9	13.9	17.6	17.7	
[Pt(dan)(NH <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	66	36.8	36.6	11.3	11.4	3.8	3.9	10.6	10.6	13.4	13.7	
[Pt(dan)(NH <sub>3</sub> ) <sub>2</sub> ][PtCl <sub>4</sub> ]	Violet	q	58.4	57.9	9.0	9.0	3.0	3.1	8.4	8.5	21.2	21.0	

<sup>a</sup> q = quantitative. <sup>b</sup> S. Yano, H. Ito, J. Fugita, and K. Saito, *Chem. Commun.*, 460 (1969). <sup>c</sup> M. M. Yakshin and L. I. Baranova, *Zh. Neorg. Khim.*, 5, 1710 (1960); *Russ. J. Inorg. Chem.*, 5, 831 (1960). <sup>d</sup> L. I. Baranova, *Zh. Neorg. Khim.*, 6, 746 (1961); *Russ. J. Inorg. Chem.*, 6, 380 (1961). <sup>e</sup> Reference 1.

acetone. They are insoluble in ether, chloroform, and nitrobenzene. Although there seems to be no great tendency for these compounds to explode at room temperature, a small explosion did occur when a very small quantity of crude [Pt(en)(NH<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was scratched with a glass rod. They decompose explosively on heating. These compounds should be handled in small quantities, with due care. Analyses and other details are given in Table III.

[Pt(meso-bn)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub> with K<sub>2</sub>PtCl<sub>4</sub> solutions usually gave violet precipitates, but on one occasion, a bright red tetrachloroplatinate salt was obtained. The infrared spectra of these two salts were quite different. [Pt(meso-dptn)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub> with K<sub>2</sub>PtCl<sub>4</sub> gave initially a violet precipitate which quickly changed to pale pink. This compound, after drying, analyzed for [Pt(meso-dptn)(NH<sub>3</sub>)<sub>2</sub>][PtCl<sub>4</sub>]·0.5H<sub>2</sub>O.

[Pt((±)dptn)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub> could be obtained as a white solid but on exposure to air almost immediately became an oil. Because of this, no analyses were carried out on this compound. For [Pt(metn)(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>2</sub> and [Pt(metn)(NH<sub>3</sub>)<sub>2</sub>][PtCl<sub>4</sub>] (violet) only platinum analyses were obtained.

*Anal.* Calcd for [PtC<sub>4</sub>H<sub>18</sub>N<sub>4</sub>]Cl<sub>2</sub>: Pt, 50.3. Found: Pt, 50.7. Calcd for [PtC<sub>4</sub>H<sub>18</sub>N<sub>4</sub>][PtCl<sub>4</sub>]: Pt, 59.6. Found: Pt, 59.4.

**N-Deuterated [Pt(tn)<sub>2</sub>][PtCl<sub>4</sub>].**—This was prepared by mixing D<sub>2</sub>O solutions of K<sub>2</sub>PtCl<sub>4</sub> and N-deuterated [Pt(tn)<sub>2</sub>]Cl<sub>2</sub> (see following paper). The precipitate was washed with D<sub>2</sub>O and air dried.

**Analyses.**—C, H, N, and most Cl analyses were performed by the microanalysts in this department. Some analyses of ionic chloride were carried out directly using standard silver nitrate

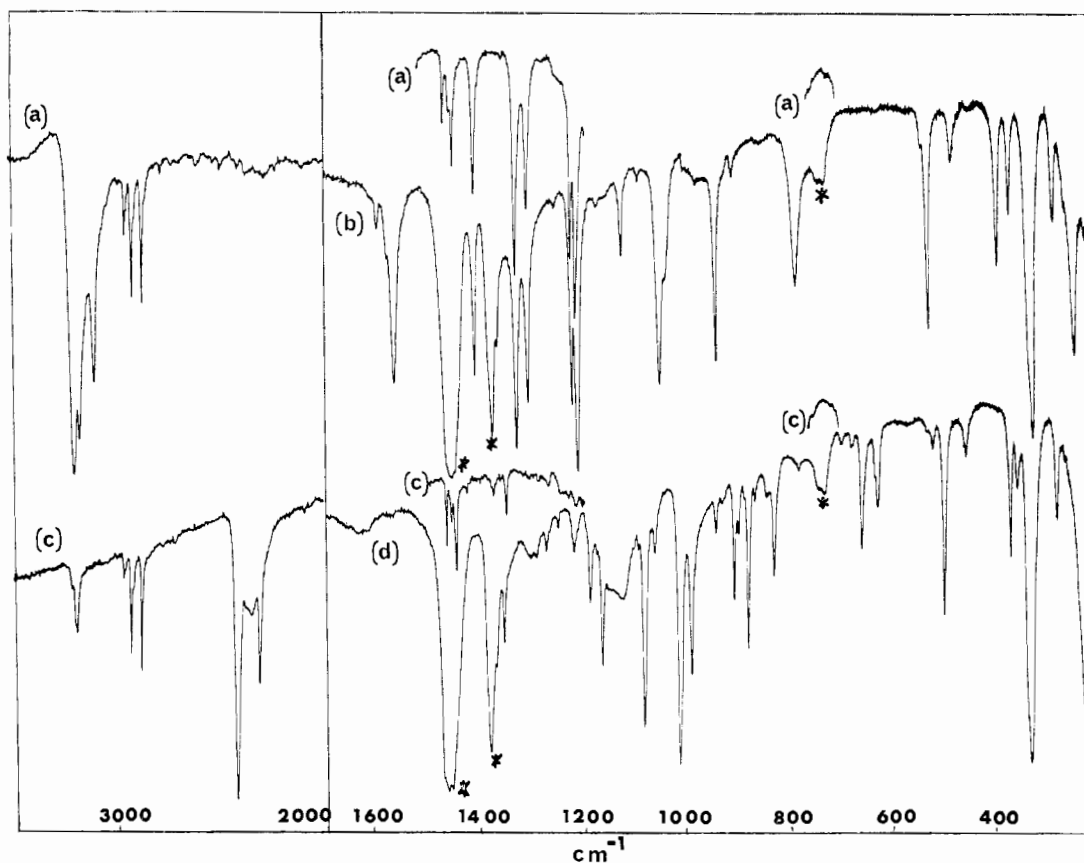


Figure 1.—Infrared spectra of  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$ : (a) hexachlorobutadiene mull; (b) Nujol mull; (c) N deuterated, hexachlorobutadiene mull; (d) N deuterated, Nujol mull. Nujol bands are marked by asterisk.

solutions. Most platinum analyses were performed by adding small quantities of iodine and chloroform to the complex and allowing the mixture to stand at  $100^\circ$  for some hours, followed by careful ignition to constant weight. Palladium analyses and Pt analyses on perchlorates were carried out by ignition with sulfuric acid. The latter usually gave low values.

**Infrared Spectra.**—Most spectra were run on a Perkin-Elmer 457 spectrometer using Nujol and hexachlorobutadiene mulls between potassium bromide disks ( $4000\text{--}400\text{ cm}^{-1}$ ) and on polythene sheeting ( $600\text{--}250\text{ cm}^{-1}$ ). The spectra of  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  and its N-deuterated analog were recorded between cesium iodide disks on a PE-225 spectrometer.

### Discussion

**Infrared Spectra.**—The spectra of complexes of trimethylenediamine and derivatives have many features in common with those of the analogous ethylenediamine complexes<sup>21,22</sup> but are generally more complicated. The following discussion is based partly on the assignments made for ethylenediamine.

For ethylenediamine complexes it was found that halide salts  $[\text{M}(\text{en})_2]\text{X}_2$  gave N-H stretching bands that were generally broader and occurred at lower frequencies than for  $[\text{M}(\text{en})_2][\text{MCl}_4]$  or  $\text{M}(\text{en})\text{Cl}_2$ . This has been attributed to anion-cation interactions in the halide salts.<sup>22</sup> Similar results were obtained with our complexes, and the following remarks apply only to tetrachlorometalates and nonelectrolytes. The spectrum of  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  (Figure 1) illustrates most of the features characteristic of these complexes. Gen-

erally, spectra of corresponding platinum and palladium complexes were very similar, and the spectra of tetrachlorometalates were quite similar to those of the nonelectrolytes. As the complexes are of rather low symmetry, considerable mixing of vibrational modes might be expected. No attempt will be made at a detailed assignment for all the spectra recorded, or for  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$ .

The N-H stretching region ( $3100\text{--}3300\text{ cm}^{-1}$ ) contains three distinct, sharp peaks in all these complexes, with some additional "shoulders" in some cases. The frequencies and relative intensities of these three peaks vary considerably from complex to complex. Only two bands would be expected from asymmetric and symmetric stretching in the  $-\text{NH}_2$  groups. The presence of three bands has been explained for other amine complexes on the basis of a Fermi interaction between the stretching modes and the overtones of the  $-\text{NH}_2$  deformation modes.<sup>23,24</sup> The band pattern may also be influenced by hydrogen bonding within the crystal lattice. In  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  these peaks shift from 3221, 3193, and 3114 to 2406, 2343, and 2304  $\text{cm}^{-1}$ , respectively, on deuteration ( $\nu_{\text{N-H}}/\nu_{\text{N-D}} = 1.34$ , cf. the theoretical value 1.41 for a mode involving only N-H or N-D).

The C-H stretching bands ( $2880\text{--}3000\text{ cm}^{-1}$ ) are

(21) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(22) G. W. Watt and D. S. Klett, *Inorg. Chem.*, **5**, 1278 (1966).

(23) G. W. Watt, B. B. Hutchinson, and D. S. Klett, *J. Amer. Chem. Soc.*, **89**, 2007 (1967).

(24) Yu. Ya. Kharitonov, I. K. Dymina, and T. N. Leonova, *Dokl. Akad. Nauk SSSR*, **173**, 1113 (1967); *Dokl. Chem.*, **173**, 365 (1967).

weak, sharp peaks, again characteristic for each complex. Trimethylenediamine complexes have three peaks in this region. Complexes of ligands containing methyl groups usually give more complex spectra (complexes of ( $\pm$ )-pentane-2,4-diamine are exceptional in giving a three-peak spectrum much less complicated than the spectra of complexes of the *meso* isomer). These peaks do not shift appreciably on N-deuteration.

The  $-\text{NH}_2$  deformation modes give a medium to strong, moderately sharp band, usually with shoulders, in the region 1560–1605  $\text{cm}^{-1}$ . Sometimes there is distinct resolution into two bands. In  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  there is a weak peak at 1598  $\text{cm}^{-1}$  and a medium-intensity peak at 1568  $\text{cm}^{-1}$ . The corresponding peak in the N-deuterated complex is probably that at 1160  $\text{cm}^{-1}$  ( $\nu_{\text{N-H}}/\nu_{\text{N-D}} = 1.34$ ).

The C–H deformation peaks are rather weak (1440–1480  $\text{cm}^{-1}$ ). There is no appreciable shift on N-deuteration. Various  $-\text{NH}_2$  and  $-\text{CH}_2$  wagging and twisting vibrations as well as some skeletal modes occur in the region 1000–1450  $\text{cm}^{-1}$ , making this the most complex region of the spectra. In  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  most of the more intense peaks in this area shift to lower frequencies on deuteration, indicating that they correspond predominantly to vibrations involving the  $-\text{NH}_2$  groups. There is usually at least one medium to strong band in the region 1000–1080  $\text{cm}^{-1}$  (often one band with a shoulder), corresponding to skeletal modes involving C–N stretching. In  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  it occurs at 1048  $\text{cm}^{-1}$ , with a low-frequency shoulder. In the N-deuterated complex the nearest peaks at lower frequencies are at 1006 and 983  $\text{cm}^{-1}$ , which apparently correspond to those at 1328 and 1304  $\text{cm}^{-1}$  in the undeuterated compound. It seems highly probable that this skeletal stretching mode shifts anomalously to higher frequencies (1076  $\text{cm}^{-1}$ ) on N deuteration. This is possible if, in the undeuterated complex, coupling with vibrations involving N–H causes the frequency to be lowered. The lack of such coupling in the deuterated complex would then allow it to occur at a higher “unperturbed” frequency.

There is usually a moderately intense band near 900  $\text{cm}^{-1}$  (935  $\text{cm}^{-1}$  in  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$ ), probably predominantly  $-\text{NH}_2$  twisting. Most complexes show a moderately intense band between 700 and 800  $\text{cm}^{-1}$  (779 in  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$ ), corresponding to  $-\text{NH}_2$  rocking. This shifts at most to 620  $\text{cm}^{-1}$  on N-deuteration (frequency ratio 1.26). This relatively small shift suggests that mixing occurs with modes not involving N–H. As expected, most methyl-substituted derivatives give much more complex spectra in the region 700–1100  $\text{cm}^{-1}$  than the trimethylenediamine complexes.

The intense, sharp peak in  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  at 518  $\text{cm}^{-1}$  corresponds almost certainly to asymmetric metal–nitrogen stretching, the weaker peak at 470  $\text{cm}^{-1}$  probably to symmetric stretching. Slight shifts occur on N deuteration (489 and 445  $\text{cm}^{-1}$ ), indicating some coupling of the stretching modes with  $\text{NH}_2$  modes. The  $\nu_{\text{M-N}}$  bands are unusually intense in this complex. Corresponding bands are discernible for most complexes

in the range 400–600  $\text{cm}^{-1}$ , although assignment is not always easy. The factors causing complications have been discussed for ethylenediamine complexes.<sup>25</sup>

The peaks at 382 and 358  $\text{cm}^{-1}$  and corresponding peaks in other complexes probably represent ring bending modes. They shift slightly on N deuteration (358 and 344  $\text{cm}^{-1}$ ).

Metal–chlorine stretching bands occur just above 300  $\text{cm}^{-1}$  (315  $\text{cm}^{-1}$  in  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$ ). Shift on N deuteration is negligible. There is little frequency difference between  $\text{M}(\text{diamine})\text{Cl}_2$  and  $[\text{M}(\text{diamine})_2][\text{MCl}_4]$  complexes, but in the nonelectrolytes the band is split, often to give shoulders, sometimes well-resolved bands, possibly corresponding to asymmetric and symmetric stretches.

Below 300  $\text{cm}^{-1}$ , there is a band at 272  $\text{cm}^{-1}$  and one at 232  $\text{cm}^{-1}$ , both of which shift slightly on N deuteration (268 and 212  $\text{cm}^{-1}$ , respectively). One, or possibly both, of these bands could correspond to N–M–N bending.

All salts of the type  $[\text{Pt}(\text{diamine})(\text{NH}_3)_2](\text{ClO}_4)_2$  show the expected bands characteristic of perchlorate anions and coordinated ammonia. Each of the diamine hydrochloride salts gives a moderately strong band near 2000  $\text{cm}^{-1}$  characteristic of  $\text{C-NH}_3^+$ , probably a combination of  $-\text{NH}_3$  rocking modes.<sup>26,27</sup>

**Tetrachloroplatinates.**—The “anomalous” colors of tetrachloroplatinates(II) of some platinum–amine complexes, particularly Magnus’ green salt,  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ , have been the subject of much investigation. It now appears well established that these colors result from perturbation of the electrons of the tetrachloroplatinate by those of the cation if, in the crystal structure, the anion and cation are sufficiently close together.<sup>28</sup> The lack of serious steric hindrance by the cation ligands to such close anion–cation approach is a necessary condition for electronic interaction to occur, but not a sufficient one, as demonstrated by the existence of a red form of  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ .

Tetrachloroplatinate salts can be classified into three distinct groups: pink salts, where perturbation of the anion electrons is comparatively small; violet salts, where such perturbation is significant; green salts, where there is comparatively strong interaction associated with infinite anion–cation chains. Of the compounds studied in the present work (Tables II, III), all bis(amine)(diamine)platinum(II) tetrachloroplatinates are violet except for the pink pentanediamine complexes;  $[\text{Pt}(\text{en})_2][\text{PtCl}_4]$  is violet; bis-diamine complexes with six-membered chelate rings are pink, except for one form of  $[\text{Pt}(\textit{meso-dptn})_2][\text{PtCl}_4]$  which is gray-violet. These colors can be rationalized on the basis of the probable structures of the cations.

The  $\text{Pt}(\text{en})_2^{2+}$  ion offers no serious steric hindrance to approach of a  $\text{PtCl}_4^{2-}$  anion above or below the  $\text{PtN}_4$  plane (Figure 2(a)). Some cation–anion interaction

(25) J. R. Durig and D. W. Wertz, *Appl. Spectrosc.*, **22**, 632 (1960).

(26) D. B. Powell, *Spectrochim. Acta*, **16**, 241 (1960).

(27) R. J. Mureinik and W. Robb, *ibid.*, Part A, **24**, 377 (1968).

(28) P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

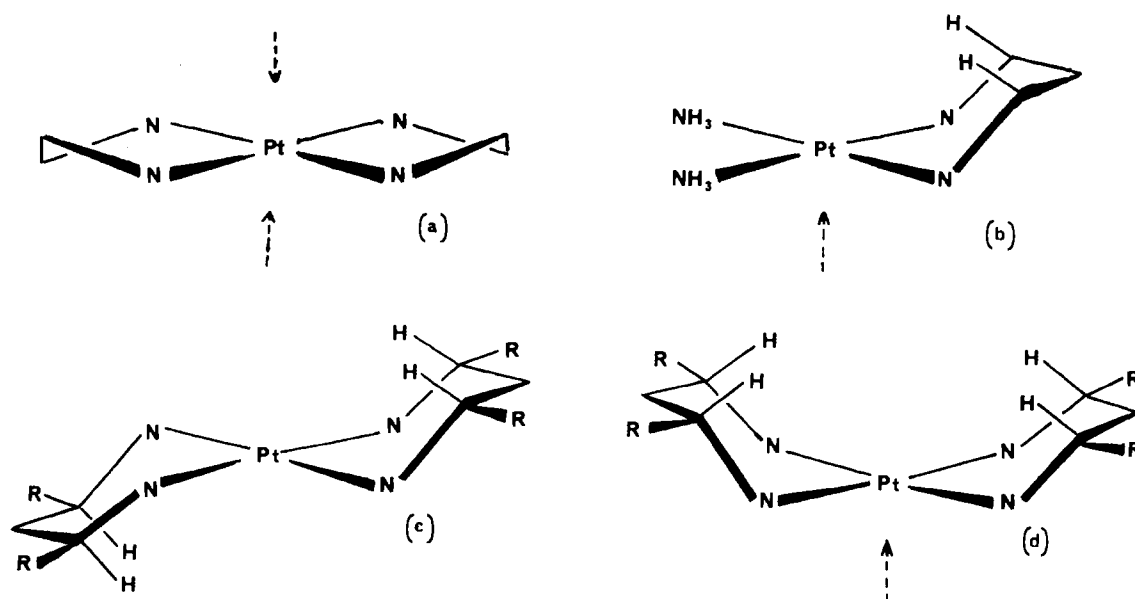


Figure 2.—Probable conformations of cations in tetrachloroplatinate salts.

might be expected (violet color). The conformations of six-membered chelate rings will be discussed more fully in the following paper, but a chair-type conformation is highly probable (Figure 2(b)). In  $\text{Pt}(\text{tn})\text{Cl}_4$  approach of a  $\text{PtCl}_4^{2-}$  anion from above the  $\text{PtN}_4$  plane would be seriously hindered by interaction with the axial hydrogen atoms attached to the  $\alpha$ -carbon atoms, an interaction which does not appear to be greatly relieved by flattening of  $\text{Pt-N-C}$  angles, but there is little hindrance to an approach below the plane. Thus, violet colors would be possible for bis(ammine)-(diamine) complexes. The pentanediamine complexes are exceptional in giving pink tetrachloroplatinates (although a violet color is obtained momentarily for the *meso*-dptn complex). They are also exceptional in that there are methyl groups on the  $\alpha$ -carbon atoms, and the crystal lattice contains water. These factors may contribute to a crystal structure where anion and cation are too distant for interaction to occur.

When a structure with a center of symmetry is one of several differing little in energy, it is usually found that the centrosymmetric structure is favored by the crystal packing.<sup>29</sup> Thus, of the two combinations of chair conformations possible in  $[\text{Pt}(\text{tn})_2][\text{PtCl}_4]$  ( $\text{R} = \text{H}$  in Figure 2(c), (d)), that with a center of symmetry (c) will probably be crystallographically favored. In this

arrangement, close approach of a tetrachloroplatinate anion is hindered both above and below the  $\text{PtN}_4$  plane, and no significant interaction would be expected. This salt is pink. Similarly,  $[\text{Pt}(\text{dan})_2][\text{PtCl}_4]$  and  $[\text{Pt}(\pm\text{dptn})_2][\text{PtCl}_4]$  would be expected to be pink.  $\text{Pt}(\text{meso-dptn})_2^{2+}$  exists in two isomers. Each chelate ring will probably take up the chair conformation with both methyl groups equatorial. This will cause one isomer, the *trans* isomer,<sup>30</sup> to take up the structure illustrated in Figure 2(c) ( $\text{R} = \text{methyl}$ ) and the other (*cis*)<sup>30</sup> that in Figure 2(d) ( $\text{R} = \text{methyl}$ ). Approach of a tetrachloroplatinate ion is hindered for the *trans* isomer, but there is no significant hindrance to approach below the  $\text{PtN}_4$  plane of the *cis* isomer. Therefore the gray-violet salt must correspond to the *cis* isomer and the pink salt to the *trans* isomer (*i.e.*, the less soluble, well-crystallized fraction of  $[\text{Pt}(\text{meso-dptn})_2]\text{Cl}_2$  is predominantly *trans* isomer). Apart from crystal structure determination, there appears to be no other method for assigning the isomers of this complex (although there may well be other methods of distinguishing them—*e.g.*, nmr at high field strengths).

Anion-cation interactions are much less important in Pd-Pd salts than in Pt-Pt compounds, and no attempt has been made to correlate colors of  $[\text{Pd}(\text{diamine})_2][\text{PdCl}_4]$  salts with cation structure.

(29) M. A. Porai-Koshits, *Zh. Neorg. Khim.*, **13**, 1233 (1968); *Russ. J. Inorg. Chem.*, **13**, 644 (1968).

(30) If the chelate ring skeletons were flattened into the  $\text{PtN}_4$  plane, the methyl groups in the two rings would be on the same side of the plane for the *cis* isomer and on opposite sides of the plane for the *trans* isomer.