

# THE *TRANS* EFFECT IN COMPLEX INORGANIC COMPOUNDS

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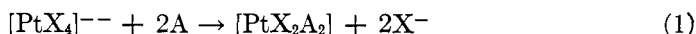
## I. INTRODUCTION

Interesting advances in the chemistry of coördination compounds have been recorded recently, advances which demonstrate the occurrence of directive influences in the reactions of inorganic coördination complexes. Among the known planar complexes, the ones which have led to the most fruitful and interesting results are the platinum(II) complexes. Platinum(II) exhibits square coördination, with resultant stereoisomerism, more readily than does any other metal. Of these platinum compounds, the remarkable stability of the platinum(II) ammines has greatly facilitated their study, for their chemical behavior has been studied by many investigators; the most striking general result of these researches is that there is no evidence that rearrangement of coördinating atoms or groups relative to one another takes place. A *trans*-amine platinum(II) compound, for example, retains its configuration during a series of reactions; the remarkable configurational stability of these compounds is of especial importance, owing to the limited experimental methods for direct determination of the nature of *cis-trans* isomerism (44, 83, 137). In addition, the interconversion of *cis* and *trans* forms of some complex compounds of platinum(II) occurs quite readily (2, 109).

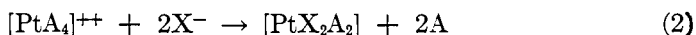
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The fact that dichlorodiammineplatinum(II) exists in two forms led Werner (136) to propose a planar structure for platinum(II) tetracovalent complexes, on the basis of the principles used so successfully by him to account for the structural constitution of the hexacoordinated cobalt(III) ammines. The planar configuration postulated by Werner (136) to explain the existence of the two isomeric compounds of the formula  $[\text{PtCl}_2(\text{NH}_3)_2]$  has been the subject of many chemical investigations, and the structure of divalent platinum compounds has been thoroughly discussed in the excellent review articles by Mellor (92, 93).

The chemical behavior of complex platinum(II) compounds was studied by many early investigators, especially Jorgensen (77) and Peyrone (105). The most important results of their researches followed two lines: (1) When tetrahalogenplatinates(II) are treated with ammonia or amines, salts of the type  $[\text{PtX}_2\text{A}_2]$  are obtained according to the general equation,



(where X = a halide ion and A = ammonia or an amine). (2) If all four coordination positions of platinum(II) are occupied by ammonia or amines, reaction with halide ions produces compounds which are isomeric with the one given in equation 1.

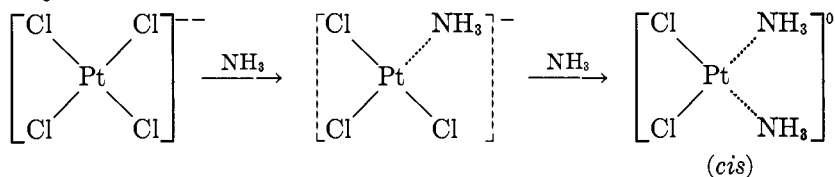


Werner (136) confirmed these observations and first suggested their interpretation.

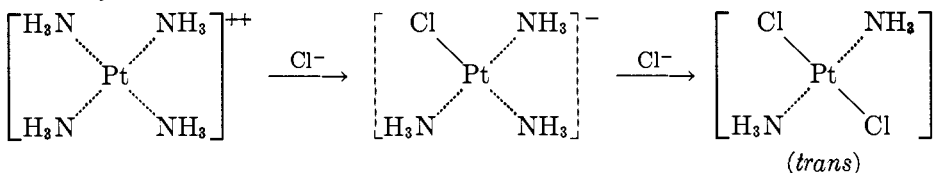
## II. CHEMICAL EVIDENCE FOR DIRECTIVE INFLUENCES IN PLANAR COMPLEXES

Over 100 years ago Peyrone (105) prepared what is now known as the *cis* isomer of dichlorodiammineplatinum; somewhat later Jorgensen (76) obtained the *trans* compound, as shown by the following reactions.<sup>2</sup>

*Peyrone's reaction:*



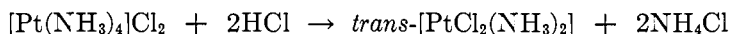
*Jorgensen's reaction:*



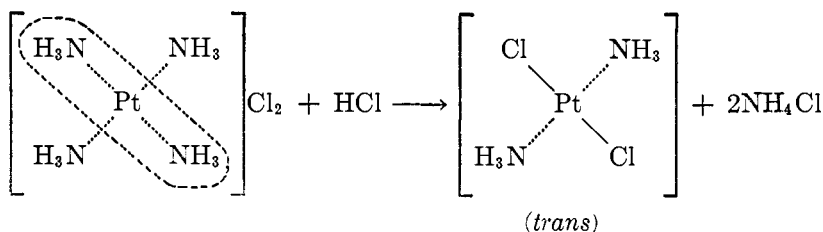
<sup>2</sup> Mellor (93a) states that Werner referred to *cis*- $[\text{Pt}(\text{NH}_3)_2\text{X}_2]$  (X = Cl<sup>-</sup> or any univalent negative ion) as the  $\alpha$ -form and to the *trans*-isomer as the  $\beta$ -form. Much confusion occurs in the literature because of the inconsistent use of the symbols  $\alpha$  and  $\beta$ . Drew and his collaborators revised Werner's usage of  $\alpha$  and  $\beta$ , and some writers have erroneously stated that Werner assumed that  $\alpha$  referred to *trans* positions and  $\beta$  to *cis* positions in the case of the

The conductivity of both isomers in water is very small, and indicates that the compounds are nonelectrolytes undergoing aquation slowly.

Although other investigators introduced arbitrary assumptions to account for the above reactions (34, 35, 37, 77), Werner was able to account for them on the basis of the straightforward and simple assumption of elimination of the coordinating groups *trans* to each other in the coordination sphere of the complex. Thus, when tetraammineplatinum(II) chloride is treated with hydrochloric acid, the *trans* ammonia molecules are replaced by chloride ions.

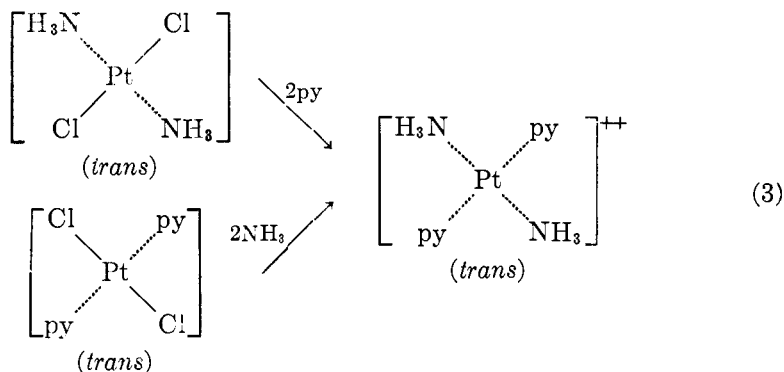


On the basis of Werner's assumption of elimination of groups *trans* to each other, the "trans effect," a designation first proposed by Chernyaev<sup>3</sup> (10), is made clear in the following diagram,<sup>4</sup> where the dotted lines enclose the removed *trans* pair:



The elimination of *cis* ammonia groups would lead to the formation of the corresponding *cis*-dichlorodiammine isomer.

The *trans* effect stipulates that the bond holding a group *trans* to an electronegative or other labilizing group is weakened. This *trans* group is the first to be removed in a substitution reaction, and by this means *cis* and *trans* isomers of four-coordination complexes can be differentiated.



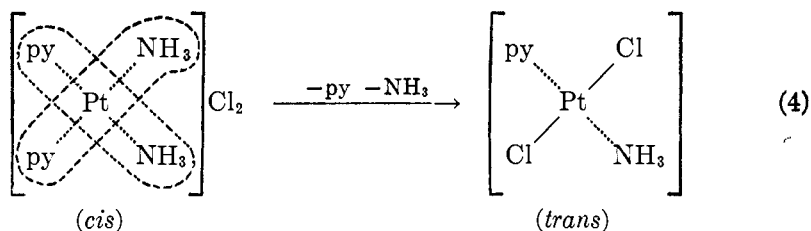
ammines of platinum(II) chloride. To avoid confusion of the nomenclature of these geometrical isomers, only the terms *cis* and *trans* are used in this report.

<sup>3</sup> The transliteration of the Russian names used in this report is in most cases that followed by *Chemical Abstracts*. Some examples in the spelling of the Russian names are: Chernyaev for Tscherniaev, Hel'man for Gelman, and Grinberg for Grunberg.

<sup>4</sup> In formulating these complex compounds a primary (or principal) valence will be indicated by a full line and a secondary (auxiliary or coordinate) valence by a broken line. This distinction is *helpful* in accounting for the resulting charges on the complexes.

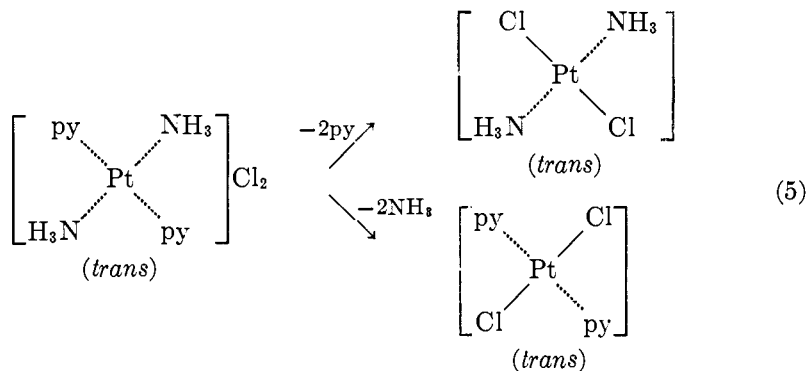
When treated with 2 moles of pyridine (py) *trans*-dichlorodiammineplatinum(II) forms *trans*-dipyridinodiammineplatinum(II), and reaction of the *trans*-dipyridine complex with ammonia leads, as may be expected, to the corresponding *trans* compound.

The results obtained by replacement of groups within the coordination sphere by those outside are especially significant, in that they show further evidence for the *trans* effect. Thus, when solid *cis*-dipyridinodiammineplatinum(II) chloride or its aqueous solution is warmed with concentrated hydrochloric acid, the *trans*-dichloropyridinoammineplatinum nonelectrolyte is obtained.

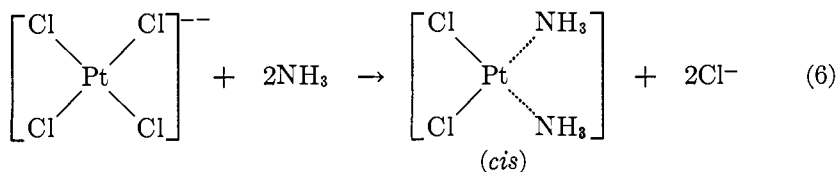


Since only the *trans* compound is obtained, *trans* elimination of ammonia and pyridine must take place, for *cis* elimination of these different groups would result in the formation of *cis*-[PtCl<sub>2</sub>(py)NH<sub>3</sub>], and *cis* elimination of the pyridine groups and of the ammonia groups would lead to the formation of *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] and *cis*-[PtCl<sub>2</sub>(py)<sub>2</sub>], respectively.

Furthermore, similar treatment of the *trans* isomer of dichloropyridinoammineplatinum(II) chloride should result in the formation of only one compound, *cis*-[PtCl<sub>2</sub>(py)(NH<sub>3</sub>)], if *cis* elimination takes place; actually, two compounds are found, indicating *trans* elimination as shown in the following equation:

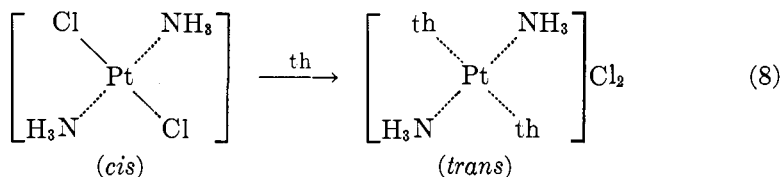
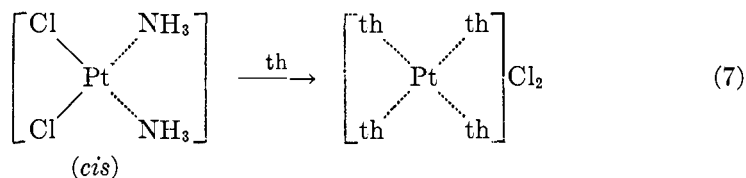


The reaction between the tetrachloroplatinate(II) ion and ammonia forms the *cis*-dichlorodiammine complex, as would be expected according to the *trans* effect.



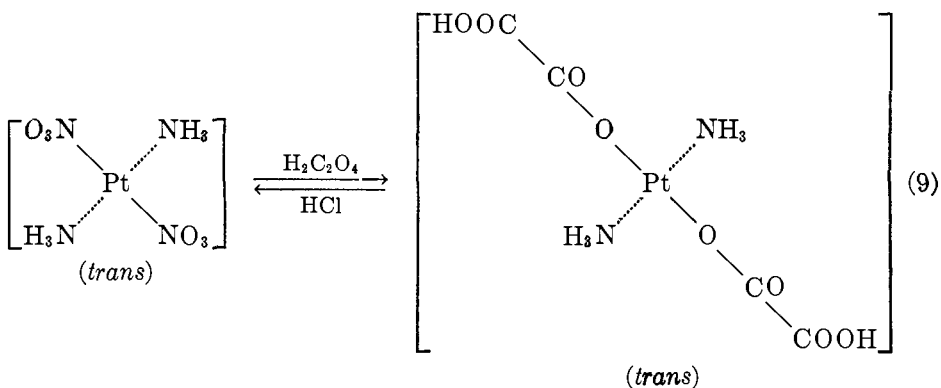
This reaction is typical of many amines, such as ethylamine, pyridine, hydroxylamine, and aniline.

By treating the *cis* and *trans* isomers of  $[\text{PtCl}_2(\text{NH}_3)_2]$  with thiourea (th), Kurnakov (83) obtained the compounds  $[\text{Pt}(\text{th})_4]\text{Cl}_2$  and  $[\text{Pt}(\text{th})_2(\text{NH}_3)_2]\text{Cl}_2$ , respectively.



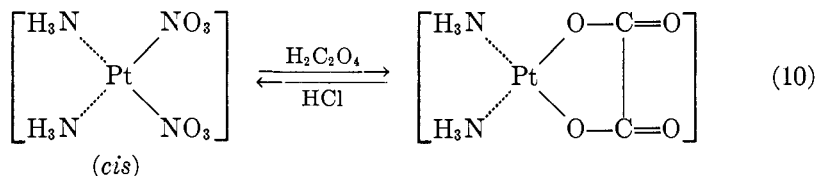
Equation 7 shows that the chlorine groups labilize the ammonia molecules in the *trans* positions, so that all four groups are replaced by the entering substituents. On the other hand, only the coordination bonds of the chloride groups are weakened in the *trans* isomer, resulting in the formation of the corresponding *trans* compound. Furthermore, many platinum(II) compounds of the type  $[\text{PtX}_2\text{A}_2]$  (where A is ammonia or an amine and X is a negative group) react with thiourea to give similar products. Thus, *cis* compounds give complexes of the type  $[\text{Pt}(\text{th})_4]\text{X}_2$  and *trans* isomers give *trans*- $[\text{Pt}(\text{th})_2\text{A}_2]\text{Cl}_2$ . Since the *cis* and *trans* isomers yield different products, the method can be used to differentiate between *cis* and *trans* isomers of platinum(II) complexes. The thiourea reaction is now known as Kurnakov's test and, as pointed out by Mellor (93b), a check of its general applicability with other substances of known configuration, such as the thioether, stilbine, arsine, and phosphine derivatives, would probably repay investigation.

Another significant fact of different character concerning directive influence is that, in spite of the great stability resulting from chelation (33), some groups

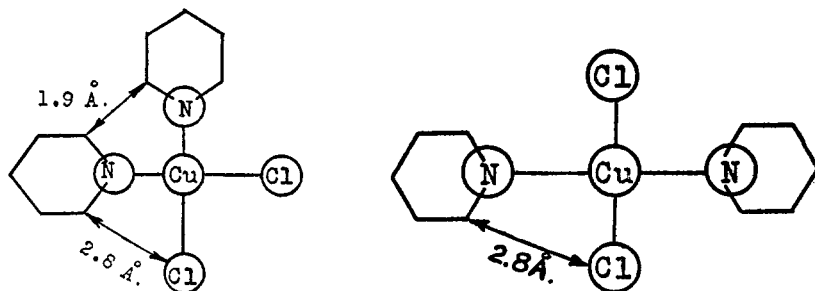


which normally occupy two coördination positions replace only one monodentate group in certain isomers. For example, *trans*-[Pt(NO<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] on reaction with oxalic acid solution yields a compound with the composition [Pt(C<sub>2</sub>O<sub>4</sub>H)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>], and the latter can readily be converted to the original compound by treating with hydrochloric acid.

On the other hand, the bidentate [Pt(C<sub>2</sub>O<sub>4</sub>)(NH<sub>3</sub>)<sub>2</sub>] is obtained by treating the corresponding *cis* compound with oxalic acid solution. These compounds can readily be converted into each other (44).

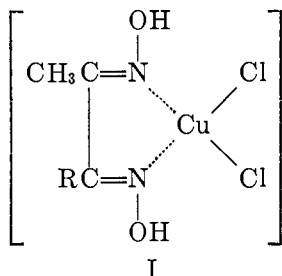


Inspection of equations 9 and 10 reveals the difference between them, for on the basis of the well-known method of Werner (137) for differentiating between the *cis* and *trans* octahedral complexes of cobalt(III), Grinberg (44) postulated that a bivalent coördination group could occupy two coördination positions of planar complexes only if those positions are *cis* to each other. An investigation of the preparation of dichlorodipyridinocopper(II) under a variety of experimental conditions, with the object of discovering the theoretically possible *cis* and *trans* isomers, produced only a single compound (25). From a consideration of the cell dimensions of the compound, which crystallizes well from methyl alcohol, it was found that under all conditions [CuCl<sub>2</sub>(py)<sub>2</sub>] has a planar *trans* configuration. The molecule has a planar *trans* configuration in which the pyridine rings are coplanar (or very nearly so), for with a planar *cis* configuration, the planar arrangement of the pyridine rings is impossible because of the proximity of the two rings (minimum distance 1.9 Å. instead of 3.7 Å.).



In order to obtain the requisite clearance on the basis of the cell dimensions as determined by x-ray methods, a tetrahedral distribution of the coördinating groups is also excluded. A *cis* planar structure requires that the rings be rotated about the nitrogen-copper bonds through approximately 40°, but this would result in the *c*-axis being larger (4.5 Å.) than the experimental value (3.8 Å.).

That the *cis* form of the complex is unstable has been further shown by the reactions of salts of type I with pyridine. Addition of pyridine to a solution of



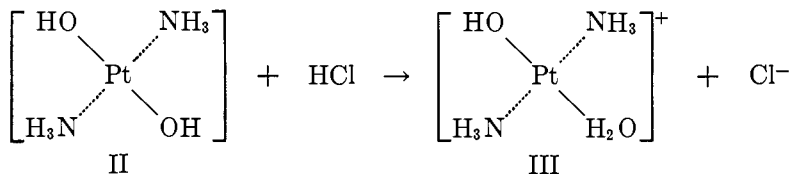
R = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, or C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.

any of these substances in alcohol or acetone displaces the oxime group to form *cis*-[CuCl<sub>2</sub>(py)<sub>2</sub>] initially, but the product isolated is always the planar *trans* compound, [CuCl<sub>2</sub>(py)<sub>2</sub>]. The instability of these planar *cis*-copper(II) complexes is similar to that of the corresponding palladium(II) isomers (52). The four-covalent copper(II) compounds of *cis* configuration, like those of palladium(II), are generally unstable when chelate groups are absent. In these complexes the chelating molecule imposes its steric requirements upon the metal, resulting in the formation of the *cis* isomers. On the other hand, the replacement of the bidentate group by two pyridine molecules imposes steric requirements upon the metal ion, resulting in the formation of the more stable *trans* isomers. It is interesting to note that both a yellow form and a red form of [PdCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] have been shown by chemical and x-ray methods to have a *trans* configuration, their difference in color being due essentially to different structures built up from the same *trans* molecules (89). It is evident that many four-covalent complexes possess a planar configuration, and that this configuration is maintained even when considerable changes are made in the nature of the coördinating groups. On the other hand, there is definite evidence that a change in the principal valency of the central ion of a complex may lead to a change in the spatial distribution of the (same number of) bonds. For example, the configuration of [PtCl(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, in which platinum is four-covalent but also tetravalent, has been shown to be tetrahedral (30). Further, nickel(0) carbonyl, Ni(CO)<sub>4</sub>, has a tetrahedral structure (5). In striking contrast to the planar four-covalent derivatives of divalent copper, some four-covalent copper(I) complexes are tetrahedral. Although silver (I) complexes are planar, those of silver(II) are probably tetrahedral, since Hein and Regler (53) have effected a partial resolution of a silver(I) derivative of 8-hydroxyquinoline by the use of  $\alpha$ -bromo-*d*-camphor- $\pi$ -sulfonate. Attempts to obtain the active isomers, when the optically active agent was removed, failed. These results are of unusual interest, for they indicate that the principal valency of a central ion of a complex may be a factor of importance in deciding the configuration of four-covalent coördination compounds. It is, of course, known that a change in coördination number often accompanies a change in principal valency, resulting in a different spatial distribution of the bonds. Thus, there is abundant

physical and chemical evidence for planar structures in coordination compounds of four-covalent nickel, palladium, and copper, as well as for divalent, four-coordinate beryllium, manganese, iron, cobalt, nickel, copper, and platinum (29, 86, 108, 131, 132). A change in structure with a change in valency has also been observed among derivatives of tin, lead (26), thallium (27), and cobalt (28).

It is assumed in these cases that the central metallic atom regulates the arrangement of the coordinating group, but other considerations, such as the rigidity or size of the coordinating addenda, must also be taken into account (98).

Another significant fact of different character concerning the *trans* effect is that titrations with hydrochloric acid of the isomeric nonelectrolytes of the formula  $[\text{Pt}(\text{OH})_2(\text{NH}_3)_2]$  show the *trans* isomer to be the stronger base (51). In addition, the difference between the first and second hydroxyl ions is much sharper in the *trans* compound, and when the latter is half-titrated in the cold, using phenolphthalein as the indicator, the *trans* complex (III) is obtained. Potentiometric titration of the isomers of  $[\text{Pt}(\text{OH})_2(\text{NH}_3)_2]$  indicates that the



*cis* compound behaves as a monoacid base, but the *trans* isomer, owing to the labilizing influence of the *trans* effect, gives a second dissociation constant (119).

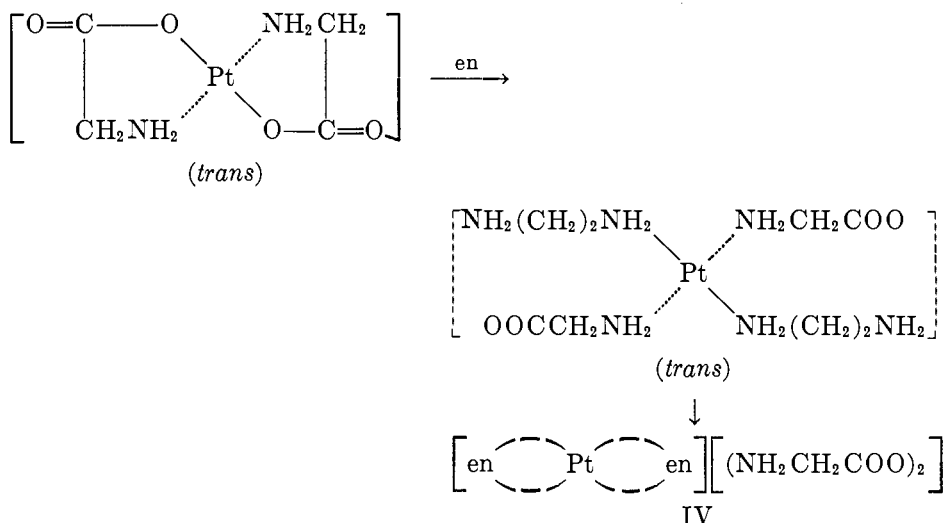
The directive influences in square coordination complexes are of special interest to the theoretical chemist. Furthermore, the question is of importance in relation to the synthesis of coordination compounds. As evidence for the usefulness of the *trans* effect, three isomers of  $[\text{Pt}(\text{NO}_2)(\text{C}_6\text{H}_5\text{N})(\text{NH}_2\text{OH})(\text{NH}_3)]\text{NO}_3$  have been prepared (9). Incidentally, this was the first compound of four-covalent platinum(II) made in which four different groups were coordinated to the platinum atom, and helped to strengthen the theory of square coordination. By utilizing Werner's principle of the *trans* effect, the three possible stereoisomers of  $[\text{Pt}(\text{Br})(\text{Cl})(\text{C}_6\text{H}_5\text{N})(\text{NH}_3)]$  have been prepared (64). Other examples of isomers containing four different groups attached to platinum(II) are  $[\text{Pt}(\text{Cl})(\text{C}_2\text{H}_4)(\text{py})(\text{NH}_3)]\text{NO}_3$  (67) and  $[\text{Pt}(\text{Br})(\text{Cl})(\text{C}_2\text{H}_4)(\text{NH}_3)]$  (61).

### III. CIS-TRANS ISOMERS

The *cis-trans* interconversion of planar four-covalent complexes is well known. Many examples of interconversion of the planar isomers of the nickel-palladium-platinum subgroup take place, but the conversions usually occur only on heating. Although the interconversion is not so readily shown by the true platinum(II) compounds, such as  $[\text{PtCl}_2(\text{NH}_3)_2]$ , the aliphatic sulfide derivatives such as  $[\text{PtCl}_2\{(\text{C}_2\text{H}_5)_2\text{S}\}_2]$  readily undergo conversion at room temperature. The *cis* isomer is partly converted into the *trans* compound on being heated alone or in alcoholic solution. Treating the *cis* compound with aqueous diethyl sulfide, preferably in the warm, causes more complete conversion (2).

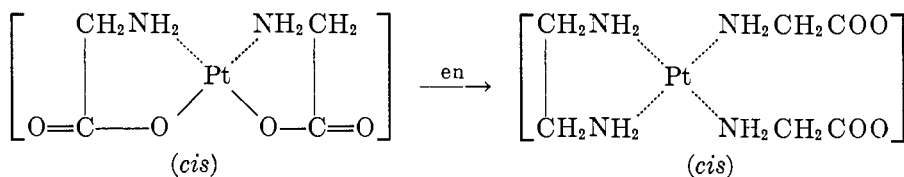


Palladium, like platinum, has been shown to give planar configurations in certain of its four-covalent compounds but, owing to the instability of the *cis* configuration when the coördinating groups are not chelates, interconversion of the isomers is not readily achieved. The reactions between  $[\text{PdCl}_2(\text{NH}_3)_2]$ , ammonia, and sodium nitrite in aqueous solution were investigated by Jonassen and Cull (75) to determine the effect of variations in temperature, concentration of palladium(II) ion, nitrite ion, ammonia, and chloride ion on the products. On the basis of *trans* elimination a mechanism is postulated to explain the observed phenomena. The preparation of *cis*- and *trans*-diglycineplatinum,  $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COO})_2]$ , involving the coördination of the unsymmetrical chelate group, has established the *cis* and *trans* isomerism demanded by theory (108). The chelating glycine group is responsible for the stability of the *cis* compound. On the other hand, the interconversion of the bisbenzylmethylglyoximenickel(II) isomers on heating takes place in spite of the stabilizing tendency of the unsymmetrical chelating groups (131). The two isomers of diglycineplatinum have been obtained in a pure state, and their structures have been confirmed by their reactions with ethylenediamine (131). The *trans* compound in reacting with ethylenediamine breaks the platinum–oxygen linkage and produces first the intermediate *trans* complex and then the ionic complex, IV.



Treatment of IV with hydrochloric acid gives  $[\text{Pt}(\text{en})_2]\text{Cl}_2$ , readily isolated as the platino salt  $[(\text{Pt}(\text{en})_2][\text{PtCl}_4]$ .

The structure of the *cis* compound is confirmed by the following equation:

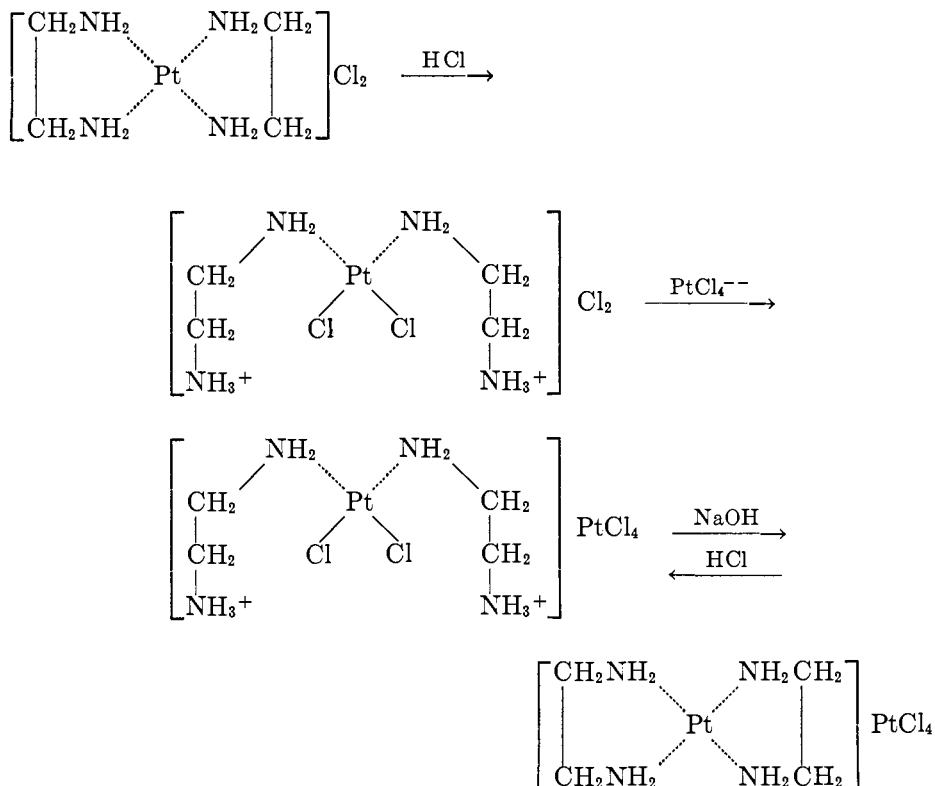


Treatment of the product with hydrochloric acid and  $[\text{PtCl}_4]^{--}$  results in the isolation of the plato salt,  $[\text{Pt}(\text{NH}_2\text{CH}_2\text{COOH})_2(\text{en})][\text{PtCl}_4]$ .

The reaction of  $[\text{PtCl}_4]^{--}$  with an aqueous solution of cold ethylenediamine produces *cis*- $[\text{PtCl}_2(\text{en})]$ , but upon long standing at room temperature or fairly rapidly upon boiling,  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  is obtained. The reaction of *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$  with ethylenediamine gives the diethylenediamine, whether carried out at room temperature or with heating. Furthermore, even when only 1 mole of ethylenediamine is used,  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  is obtained, indicating *trans* elimination of the ammonia molecules and the stability of ethylenediamine as a chelating group (34). In excess  $(\text{PtCl}_4)^{--}$ , the lilac-violet plato salt  $[\text{Pt}(\text{en})_2][\text{PtCl}_4]$  will form.

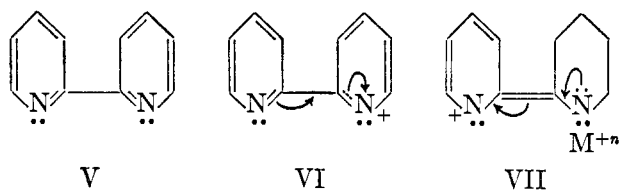
Chelate groups such as ethylenediamine may, however, occupy only one coordination position. It is found that, when treated with hydrochloric acid,  $[\text{Pt}(\text{en})_2]\text{Cl}_2$  eliminates one coordinate bond from each chelate group to give the *cis* dihydrochloride,  $[\text{PtCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+)_2]\text{Cl}_2$  (34). When the latter compound (or its plato salt) is treated with cold sodium hydroxide solution, the coordinating group chelates again, with the loss of 2 moles of hydrogen chloride, re-forming the original compound.

These reactions are formulated by Drew (34) as follows:

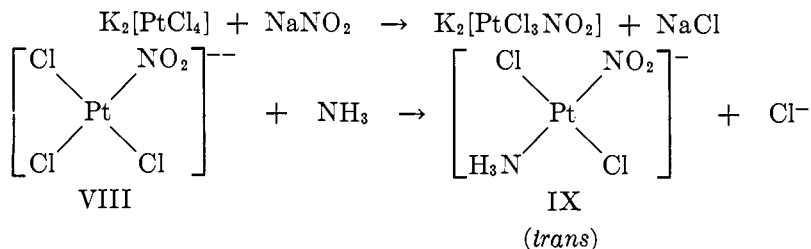


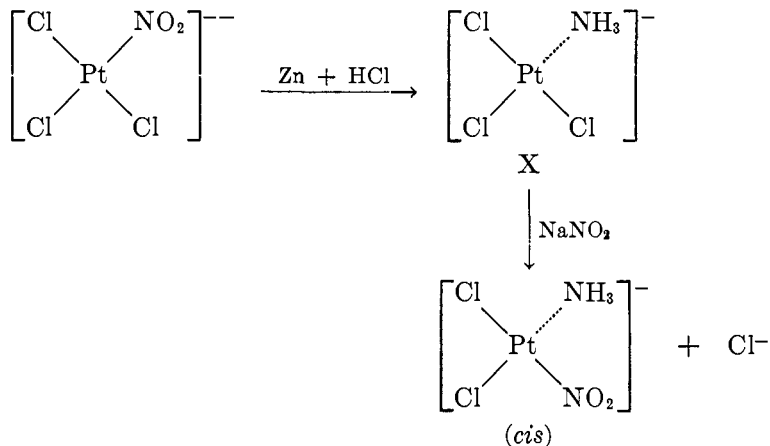
In the case of  $[\text{Pt}(\text{NH}_3)_2(\text{en})]\text{Cl}_2$ , the single chelate group can be opened to give the monohydrochloride,  $[\text{PtCl}_2(\text{NH}_3)(\text{enH})]\text{Cl}$ . This hydrochloride can, in turn, be closed by treatment with sodium hydroxide.

Compounds are also known in which the two amino groups of any one molecule of ethylenediamine are linked to different metallic ions, forming a binuclear complex. The coordination compounds of metallic salts containing  $\alpha, \alpha'$ -dipyridyl (dip) show that this diamine furnishes a chelate group, giving rise to compounds of remarkable stability and sometimes of exceptional color (96). It is of interest to note that, whereas the *cis* dichlorodiammine reacts with the base to form  $[\text{Pt}(\text{dip})(\text{NH}_3)_2]$ , no reaction takes place with the *trans* isomer. The  $\alpha, \alpha'$ -dipyridyl chelating molecule being unable to span the *trans* positions, and to replace both ammonia and chloride, occupies only one position in the coordination sphere. The failure of  $\alpha, \alpha'$ -dipyridyl to coordinate only one position may be explained on the basis of the following formulae.



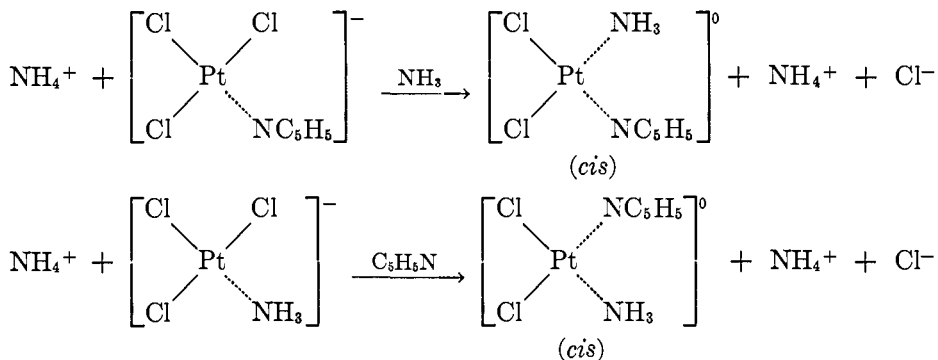
V exists as a resonance hybrid. When  $\alpha, \alpha'$ -dipyridyl acts as a chelate group the resonance hybrids remain entirely equivalent, producing a stable complex. If only one of the nitrogen atoms enters into compound formation with a metal ion  $\text{M}^{n+}$ , however, complex VII is not stable enough to compensate for the decrease in stability due to the loss of resonance energy. Compounds such as ethylenediamine which have no resonance structures, and those like glycine which retain the resonance energy, can coordinate in only one position. The chemical behavior of four-coordination platinum(II) compounds with respect to the varying mobility of the groups attached to the central metallic ion has been studied by Chernyaev and coworkers (9, 11, 13, 14). One of the striking results of their researches is that the order of substitution in some complexes plays an important role. Thus it is found that the reaction of ammonia on  $[\text{PtCl}_3(\text{NO}_2)]^-$  yields *trans*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$ , but on reversing the order of introducing the groups by treating  $[\text{PtCl}_3(\text{NH}_3)]^-$  with sodium nitrite, *cis*- $[\text{PtCl}_2(\text{NO}_2)(\text{NH}_3)]^-$  is formed. When potassium tetrachloroplatinate is used as the starting material, the reactions are as follows:





Owing to the complex nature of the coördination compounds it is difficult to discuss quantitatively the particular affinity of the different coördinating groups for the central metallic ion. Chernyaev (13) has shown, however, that the varying mobility of groups associated with the central platinum(II) ion can be explained quantitatively on the basis of the *trans* effect. The electronegative coördinating ions ( $\text{NO}_2^-$ ,  $\text{SCN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) have a greater labilizing effect on the group in the *trans* position (*trans* effect) than do neutral substituents (ammonia, amines, water, etc.). Furthermore, in the complex compounds of platinum(II) the nitro groups exert a greater *trans* effect than the other negative ions. On the basis of these generalizations an inspection of formula VIII indicates that the chloride ion *trans* to the nitro group is substituted by an ammonia molecule, and one of the *trans* chloride ions is preferentially replaced in formula X.

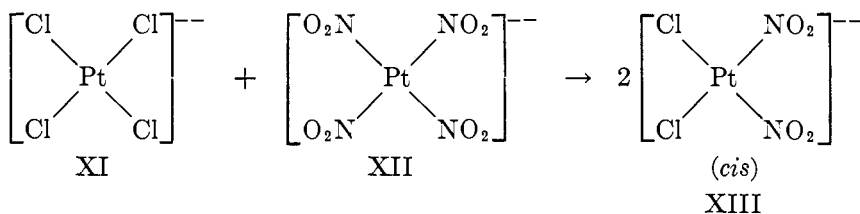
The preparation of geometric isomers using a definite order of entering substituents (57) is shown by the following reactions:



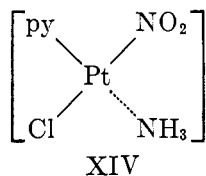
On the other hand, when ethylene is added to a platinum(II) compound containing three negative groups and ammonia in the coördination sphere a *cis* compound is formed, but if ammonia is added to a similar coördination compound with ethylene in place of ammonia, the *trans* isomer is obtained (18).

As further evidence for these generalizations, the results of a series of reactions

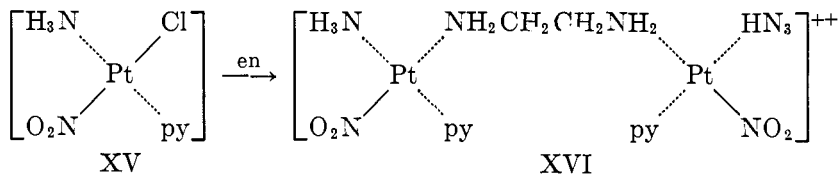
studied by Chernyaev (11) will be mentioned. One of these is that aqueous mixtures of  $K_2[PtCl_4]$  and  $K_2[Pt(NO_2)_4]$  react to give *cis*- $K_2[Pt(NO_2)_2Cl_2]$ .



Hinshelwood (69) has pointed out that the sequence of steps by which most reactions occur is one in which each successive member is of extreme simplicity, involving, for example, the reaction of the fewest molecules, the breaking of a single bond, or the transfer of a single atom or electron from one reacting partner to another. The *cis* compound (formula XIII) is obtained because after one nitro group in XII has been replaced by a chloride ion, another of the pair of *trans* nitro groups is preferentially replaced. The reaction of XI to form XIII can also be explained on the basis of the *trans* effect, for stepwise substitution of two chloride ions by nitro groups produces first *trans*- $[PtCl_2(NO_2)_2]^{-}$ . Then 2 moles of the latter react to form 2 moles of *cis*- $[PtCl_2(NO_2)_2]^{-}$ . Other facts are that aqueous solutions of *trans*- $[PtCl_2(NH_3)_2]$  react with *trans*- $[Pt(NO_2)_2(NH_3)_2]$  to yield *trans*- $[PtCl(NO_2)(NH_3)_2]$ , but the reaction of the corresponding *cis* isomers to produce *cis*- $[PtCl(NO_2)(NH_3)_2]$  requires heating on a water bath for 10 hr., indicating that the displacement of a *cis* group proceeds slowly. Additional evidence for the labilizing of a group *trans* to a negative ion is the reaction of an aqueous solution of *trans*- $[Pt(NO_2)_2(NH_3)(py)]$  and *trans*- $[PtCl_2(NH_3)(py)]$  to give the

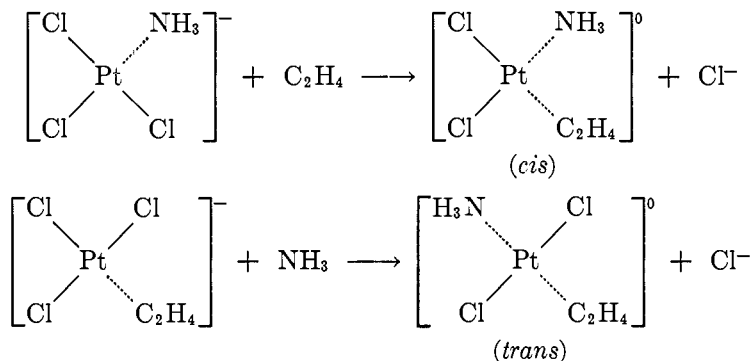


compound shown by structural formula XIV. Finally, it may be mentioned that, since ligands *trans* to a negative group are more labile, the binuclear platinum(II) complex, XVI, can be prepared by the reaction of ethylenediamine with XV (14).



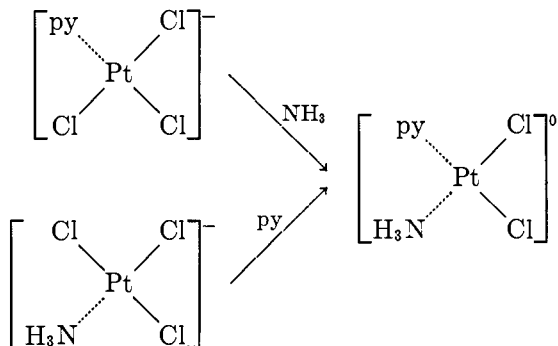
Other interesting examples of a directive influence are found in the platinum(II) complexes containing an unsaturated substance such as ethylene. The fact that alkenes and unsaturated molecules in general can sometimes enter into

complex formation with platinum(II) is now beyond all question, but the mechanism of the linkage remains obscure (78). The order of introduction of the ethylene molecule, as shown by the following equations, has a marked effect on the stereochemistry of the products (16, 63).



These formulas are based on the assumptions that the products are not dimers and that the central metal atom has the covalency of four usually associated with platinum(II) complexes. Furthermore, if it is assumed that ethylene has a strong labilizing effect on the group in the *trans* position, these formulations are in accord with the *trans* effect. Among coordination compounds of platinum, those containing olefins are of especial theoretical interest, owing to the difficulty of establishing an adequate electronic structure.

In many cases the order of substitution in platinum(II) complexes leads to the formation of different products, and these products can be explained on the basis of the *trans* effect. On the other hand, there are many examples in which the order of substitution has no effect, and here too the results are in accord with the principle of *trans* elimination. It does not, for example, make any difference whether  $[\text{PtCl}_3(\text{py})]^-$  is treated with ammonia or  $[\text{PtCl}_3(\text{NH}_3)]^-$  reacts with pyridine (py), for the nonelectrolyte  $[\text{PtCl}_2(\text{py})(\text{NH}_3)]$  is the final product in each case.

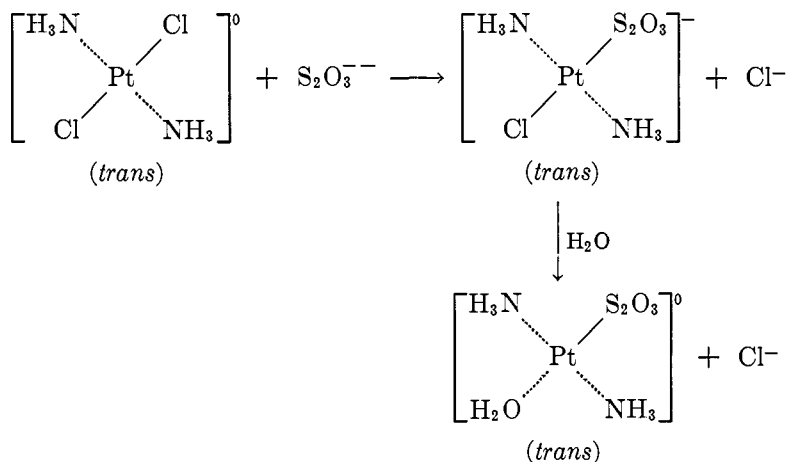


In each anion one of the *trans* chloride ions is preferentially substituted by the incoming group, a result which is to be expected because of the labilizing effect of the *trans* chloride ions.

## IV. PLANAR COÖRDINATION COMPOUNDS

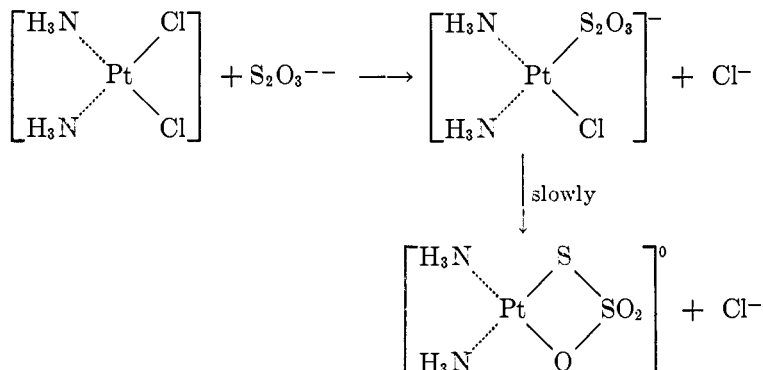
## A. Coördinating groups containing sulfur

The extraordinary coördinating ability of the thiosulfate ion to platinum(II) was indicated by the reaction of excess sodium thiosulfate with potassium tetrachloroplatinate(II) to produce  $\text{Na}_6[\text{Pt}(\text{S}_2\text{O}_3)_4]$  (130). The investigations of Ryabchikov (120, 123, 128) confirmed the strong coördinating ability of the thiosulfate ion, for the chlorine atoms of the  $[\text{PtCl}_4]^{--}$  ion can be replaced two at a time, forming the very stable thiosulfate complexes,  $[\text{Pt}(\text{S}_2\text{O}_3)\text{Cl}_2]^{--}$ ,  $[\text{Pt}(\text{S}_2\text{O}_3)_2]^{--}$ ,  $[\text{Pt}(\text{S}_2\text{O}_3)_3]^{-4}$ , and  $[\text{Pt}(\text{S}_2\text{O}_3)_4]^{-6}$ . The mole ratio of the reactants determines the products, and the thiosulfate ion occupies one or two coördination positions to give platinum(II) its usual coördination number of 4. In occupying two coördination positions, the thiosulfate ion chelates through the electron-rich sulfur and oxygen atoms. The reaction of potassium tetrachloroplatinate with thiourea forms insoluble *trans*- $[\text{PtCl}_2\{\text{SC}(\text{NH}_2)_2\}_2]$ , and addition of sodium thiosulfate causes dissolution with the formation of *trans*- $[\text{Pt}\{\text{SC}(\text{NH}_2)_2\}_2(\text{S}_2\text{O}_3)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ , obtainable as lemon-yellow crystals (121). Molar quantities of solutions of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$  and  $\text{Na}_2\text{S}_2\text{O}_3$  when boiled until no more ammonia is evolved produce, upon precipitation as a yellow oil by ethyl alcohol and slow evaporation over sulfuric acid, *trans*- $\text{Na}_2[\text{Pt}(\text{NH}_3)_2(\text{S}_2\text{O}_3)_2] \cdot 6\text{H}_2\text{O}$ . With respect to the labilizing effect of the thiosulfate group, certain salient facts will be mentioned. One of these is that the group *trans* to the sulfur atom in the thiosulfate complexes is labilized in the same way as in thiourea coördination compounds. When *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$  is treated with sodium thiosulfate, for example, the nonelectrolyte *trans*- $[\text{Pt}(\text{S}_2\text{O}_3)(\text{H}_2\text{O})(\text{NH}_3)_2]$  separates from the solution.



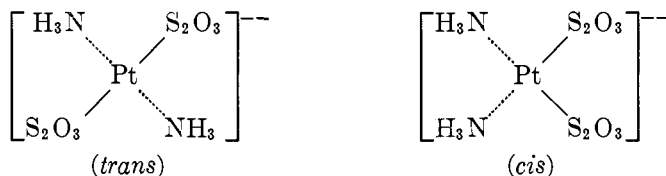
The labilizing effect of the thiosulfate radical causes the *trans* chloride group in the intermediate anion to be replaced by a water molecule. On the other hand, when similar treatment is given to *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ , the intermediate *cis*- $[\text{PtCl}(\text{S}_2\text{O}_3)(\text{NH}_3)_2]^-$  can be isolated as the potassium or sodium salt. If the

intermediate anion is not removed from the solution, however, it slowly forms the yellow, insoluble nonelectrolyte, *cis*-[Pt(S<sub>2</sub>O<sub>3</sub>)(NH<sub>3</sub>)<sub>2</sub>].



The reactions of sodium thiosulfate with the *cis* and *trans* forms of [PtX<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and HC<sub>2</sub>O<sub>4</sub><sup>-</sup>) is of much interest, for if further substantiated with other negative radicals, this would afford a method for distinguishing between the *cis* and *trans* isomers of platinum diammines (125). Further, with excess thiosulfate [Pt(S<sub>2</sub>O<sub>3</sub>)<sub>4</sub>]<sup>-6</sup> is formed from *cis*-[PtX<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>], whereas *trans*-[Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-2</sup> is obtained from the *trans* isomer.

When treated with 2 moles of sodium thiosulfate, *trans*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] forms *trans*-[Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-2</sup>; similar treatment of the *cis* isomer produces *cis*-[Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>].

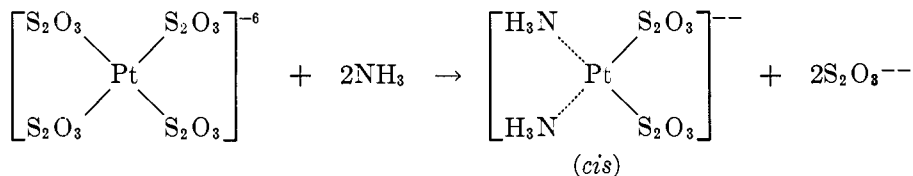


These results are to be expected, since it is well known that the replacement of ammonia molecules by acid radicals does not proceed easily, and although thiosulfate ion in excess can replace all the ammonia groups in the ion [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>++</sup>, the chloride ions in the dichlorodiammine isomers are less firmly held and are replaced first. The *cis* and *trans* isomers of the dithiosulfatodiammineplatinate(II), however, differ markedly in their stability towards excess thiosulfate. The instability of *cis*-[Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-2</sup>, as compared with that of the *trans* isomer, is striking in that the ammonia molecules *trans* to the thiosulfate group of the *cis* compound are labilized and easily replaced in the presence of any slight excess of thiosulfate. On the other hand, the *trans* isomer is stable in the presence of a 2-4 mole excess of thiosulfate. Thiosulfate in larger excess replaces all the ammonia.

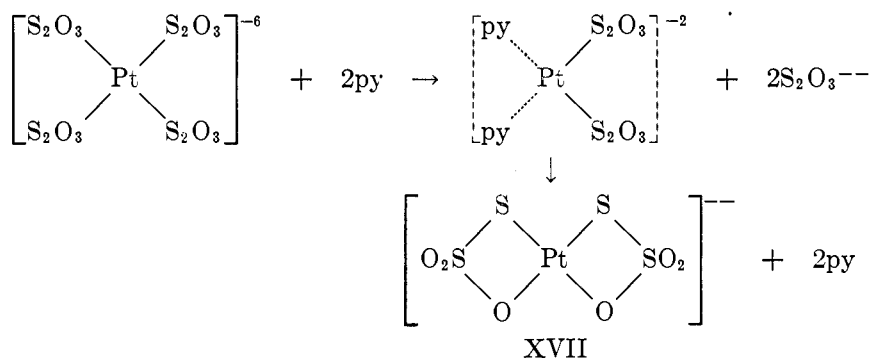
The converse substitution of thiosulfate ions in the coordination sphere by amines is possible, but ammonia and pyridine in excess can replace only two



thiosulfate groups (126). The reaction of  $K_6[Pt(S_2O_3)_4]$  with a saturated solution of ammonia yields the expected *cis*- $K_2[Pt(S_2O_3)_2(NH_3)_2]$ , owing to the *trans* effect of the thiosulfate radicals. On heating  $K_6[Pt(S_2O_3)_4]$  with excess pyridine,

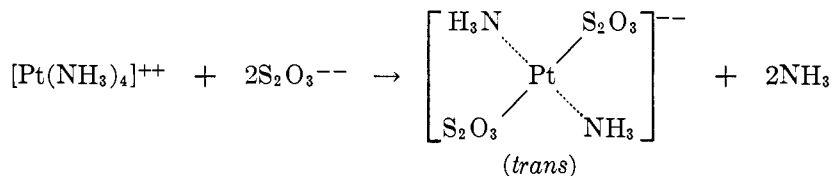


removing the excess amine, and adding alcohol,  $K_2[Pt(S_2O_3)_2]$  is precipitated. Undoubtedly the intermediate *cis*- $K_2[Pt(S_2O_3)_2(py)_2]$  is first formed, but owing to the labilizing influence of the *trans* thiosulfate groups 2 moles of pyridine are lost, forming the chelated anion (XVII). On the other hand, *trans*- $K_2[Pt(S_2O_3)_2(py)_2]$  is very stable.

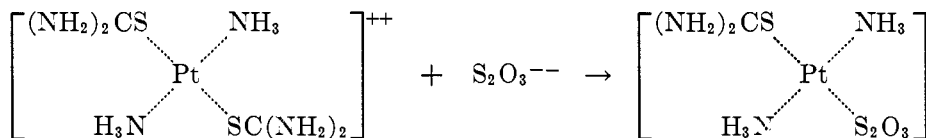


Finally, attention should be called to the fact that *trans*- $H_2[Pt(S_2O_3)_2(NH_3)_2]$ , formed by the action of sulfuric acid on the barium salt of the free acid, is a strong acid and can be titrated quantitatively with alkali.

The following equation indicates the results of *trans* elimination when 2 moles of thiosulfate react in hot solution with 1 mole of  $[Pt(NH_3)_4]Cl_2$ :



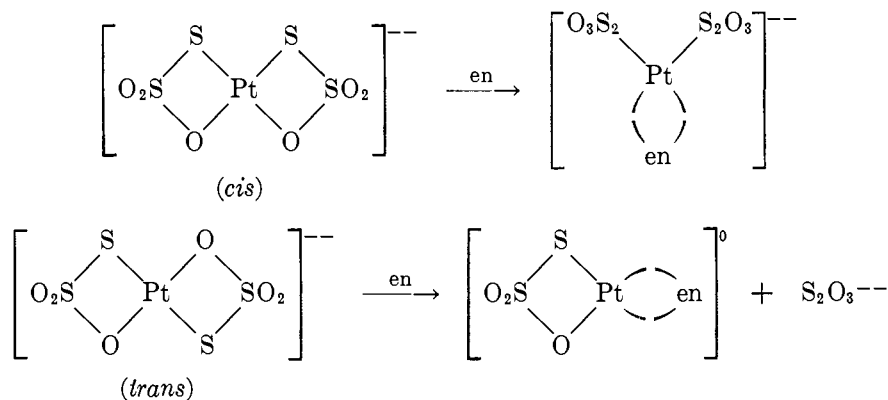
Another particularly interesting reaction illustrating the *trans* effect concerns elimination of a *trans* thiourea in the following reaction (124):



The reason for this displacement is that the *cis* NH<sub>3</sub> groups are strongly stabilized by the thiourea ligands. Hence, the *trans* effect causes the loosening of the *trans* thiourea. Excess thiosulfate causes complete displacement of the thiourea.

The reactions with thiosulfate serve as a method for determining the isomerism of platinum(II) complexes (123, 125). The *cis* form of [PtX<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] (X = NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and HC<sub>2</sub>O<sub>4</sub><sup>-</sup>) reacts with 1 mole of sodium thiosulfate to yield [Pt(S<sub>2</sub>O<sub>3</sub>)(NH<sub>3</sub>)<sub>2</sub>], and the *trans* form yields [Pt(S<sub>2</sub>O<sub>3</sub>)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub>]. If excess thiosulfate is used, [Pt(S<sub>2</sub>O<sub>3</sub>)<sub>3</sub>]<sup>-6</sup> is obtained from the *cis* isomer, and *trans*-[Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> is formed from the *trans* isomer. This technique is analogous to the thiourea reactions of Kurnakov.

The occurrence of *cis-trans* isomers when two unsymmetrical chelate groups are attached to the metallic ion is very common in cationic and neutral platinum(II) complexes (131), but few cases are known of this type of anionic platinum(II) coordination compounds. Of special interest, therefore, are the *cis* and *trans* isomers of [Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>-</sup> prepared by Ryabchikov (127). Reaction of the tetrachloroplatinate(II) ion with thiosulfate ions produces both the *cis* and the *trans* isomer of [Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>-</sup>; separation is effected by the great difference in solubility of the potassium salts. The results obtained by the reaction of the isomers with ethylenediamine are especially significant, in that they permit a distinction between the isomers. Thus, the more soluble (*cis*) isomer reacts with ethylenediamine to produce *cis*-[Pt(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(en)]<sup>-</sup>, whereas the nonelectrolyte [Pt(S<sub>2</sub>O<sub>3</sub>)(en)]<sup>0</sup> is obtained from the *trans* isomer. On the basis that the platinum-oxygen linkages are weaker than the platinum-sulfur linkages, these reactions are shown by the following schematic equations.

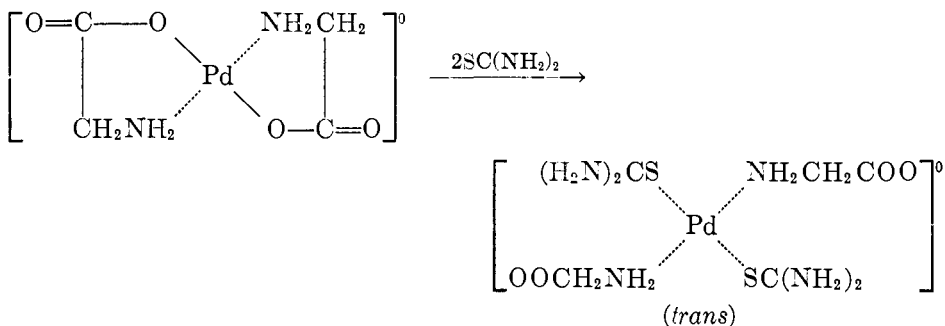


This assumption of the preferential attack of the oxygen coordination positions is reasonable, moreover, owing to the labilizing effect on the oxygen atoms *trans* to the negative sulfur atom of the thiosulfate ion. As further evidence for this conclusion, it may be pointed out that conductometric measurements show that the *trans* form of dithiosulfatoplatinate(II) ion aquates more readily than the *cis* isomer. This effect is explained as being due to the decrease in stability of the platinum-oxygen linkage when in a position *trans* to the platinum-sulfur linkage (138). In all cases in which the thiosulfate ion occupies two coordination

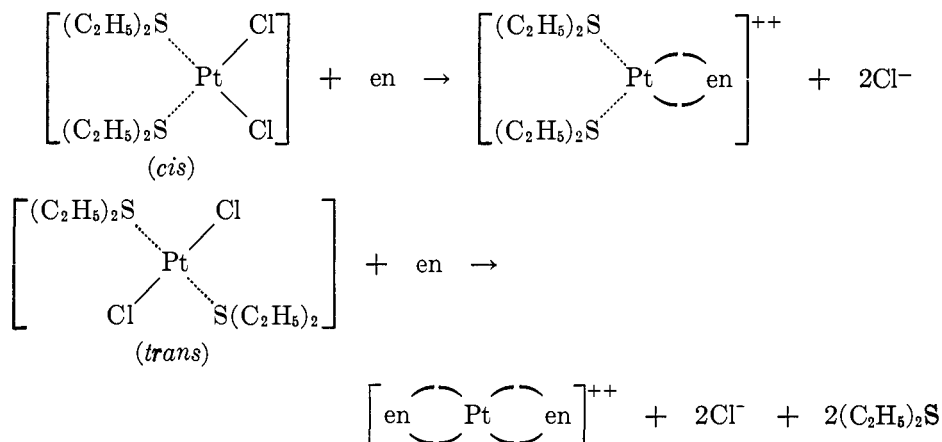
positions, linkage to the platinum(II) takes place through both a sulfur and an oxygen atom.

The reactions of thiosulfate with tetrachloropalladate(II) ion form thiosulfate complexes similar to those with platinum(II) salts. With respect to the general stability of the palladium(II) complexes however, it may be mentioned that only one isomer, the less soluble form of the compound  $K_2[Pd(S_2O_3)_2]$ , has been prepared (129). Furthermore, in contrast to the reactions of tetrachloroplatinate(II), the reaction of equimolar quantities of potassium tetrachloropalladate and sodium thiosulfate precipitates all the palladium as a mixture of palladium sulfide and palladium thiosulfate. These results are in accord with the well-established fact of the lesser stability of palladium coordination compounds.

In spite of the very close similarity between the platinum(II) and palladium(II) coordination compounds, there is a marked difference in some of their chemical properties. For example, nonionic compounds of four-covalent palladium(II) of the type  $[PdA_2X_2]$  rarely exhibit *cis-trans* isomerism, as distinct from the platinum(II) complexes in which the stable *trans* compounds normally occur. Thus, with regard to the thioether compounds of palladium(II) chloride, detailed physical and chemical examination has shown that the single derivative obtained in each case has the *trans* configuration (24). In addition, the relative instability of the palladium(II) complexes compared with the corresponding platinum(II) coordination compounds is noteworthy. Thiourea reacts with *cis*- $[Pd(NH_2CH_2COO)_2]$ , but the red solution obtained at first decomposes to a mixture. On the other hand, the *trans* isomer forms the stable  $[Pd\{SC(NH_2)_2\}_2(NH_2CH_2COO)_2]$ . Kurnakov (127) found that 4 moles of thiourea coordinate with the corresponding *cis* platinum(II) complexes, and 2 moles with the *trans* isomer. If Kurnakov's rule applies to palladium compounds, then the results confirm the *trans* structure.

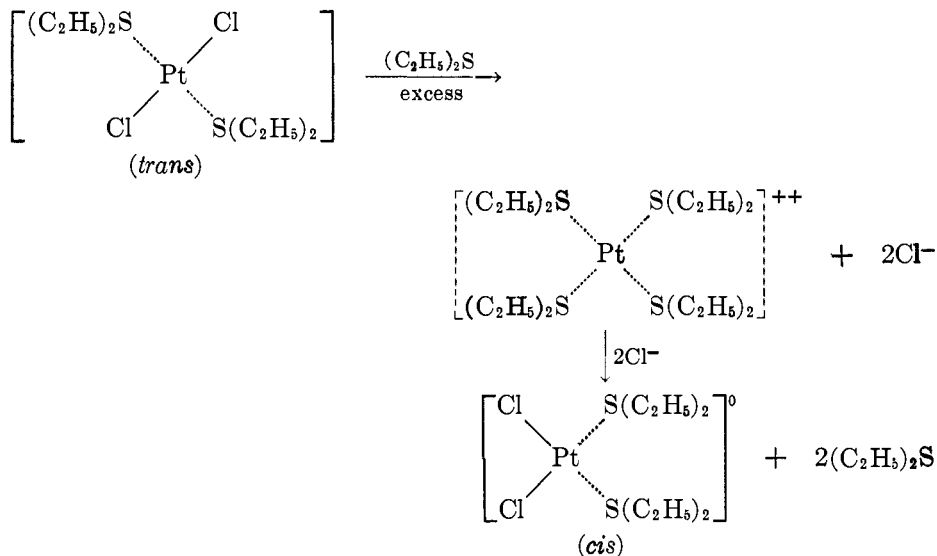


Drew and Wyatt (39) used ethylenediamine as the chelate group to differentiate between *cis* and *trans* isomers of the dithioethers of platinum(II) complexes. When aqueous ethylenediamine acts on *cis*- $[PtCl_2(C_2H_5)_2S)_2]$ , the unstable compound  $[Pt(C_2H_5)_2S)_2(en)]Cl_2$  is formed. This can be obtained as the stable plato salt,  $[Pt(C_2H_5)_2S)_2(en)][PtCl_4]$ . Some  $[PtCl_2(en)_2]$  is obtained as a by-product. On the other hand, when aqueous ethylenediamine acts on the *trans* isomer, the sole product is  $[Pt(en)_2]Cl_2$ , even when less than 1 mole of ethylenediamine is employed.



The *cis* and *trans* forms of the corresponding dimethyl sulfide derivatives have been submitted to a detailed chemical examination by Cox, Saenger, and Wardlaw (24), who draw conclusions substantially in agreement with the results obtained for the diethyl sulfide complexes. Furthermore, x-ray results are in accord with these conclusions. It is interesting to note that the isomers of  $[\text{PtCl}_2(\text{CH}_3)_2\text{S}]_2$  are readily interconvertible. In chloroform solution or on melting, for example, either isomer tends to form an equilibrium mixture, but on warming the solution the formation of the *trans* form is favored.

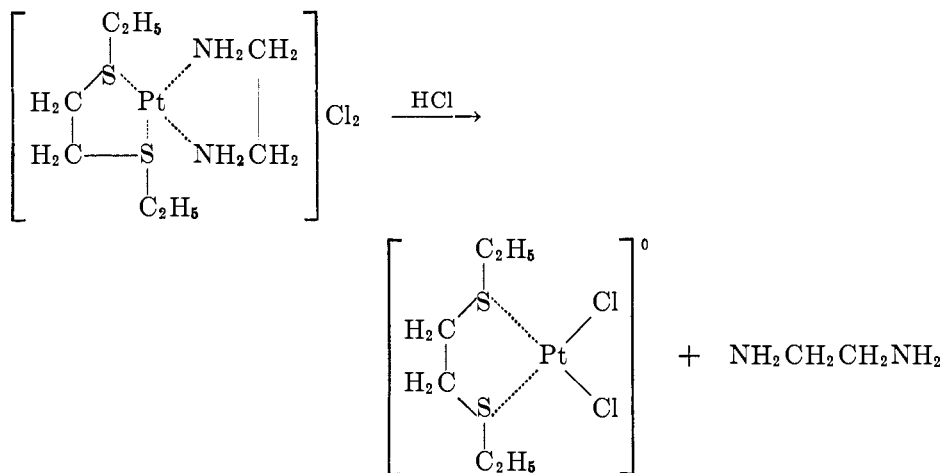
An excess of aqueous ethyl sulfide converts *trans*- $[\text{PtCl}_2(\text{C}_2\text{H}_5)_2\text{S}]_2$  into its *cis* isomer, a reaction which appears to be general for alkyl sulfide compounds of platinum(II) complexes. The change probably takes place through the formation of the unstable tetrasulfide, which loses 2 moles of ethyl sulfide from *cis* positions, indicating the *trans*-directing influence of the diethyl sulfide group (39).



The tetrasulfide complex is known only in aqueous solutions in the presence of excess diethyl sulfide, but the corresponding methyl derivative can be isolated as the moderately stable platino salt.

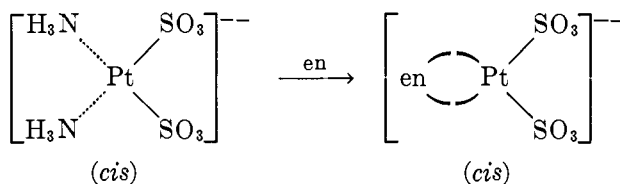
It is probable that the tetraethylplatinum(II) ion would be stable if nitrate or perchlorate ions, poor coordinating ligands, were substituted for the more strongly coordinating chloride ion. In connection with platinum(II) complexes, such as  $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]\text{X}_2$ , where X is a negative ion, it is found that iodide and thiocyanate ions tend to enter the coordination sphere of the complex to a smaller degree than bromide and chloride ions, but that nitrate and sulfate ions have no such tendency (119).

As further evidence for the unusual properties of disulfide complexes of platinum(II), it was found that when  $[\text{Pt}\{\text{S}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2(\text{C}_2\text{H}_5)\text{S}\}(\text{en})]\text{Cl}_2$  is heated with dilute hydrochloric acid, groups *trans* to the sulfur atoms are lost and  $[\text{Pt}\{\text{S}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2(\text{C}_2\text{H}_5)\text{S}\}]\text{Cl}_2$  is obtained.



It is of interest to note that groups are eliminated from the *cis* positions; moreover, the chelating ethylenediamine, which might be expected to be the stronger coordinating group, is expelled (39).

Studies of the isomeric sulfitoammines of platinum(II) by Gurin (72, 74) indicate a high mobility of the ligands in positions *trans* to the sulfite group.



If dimethylglyoxime is used in place of ethylenediamine, the corresponding *cis* compound is obtained. In contrast to these reactions,  $\text{trans}-[\text{Pt}(\text{SO}_3)_2(\text{NH}_3)_2]^{--}$  does not react with ethylenediamine or dimethylglyoxime.

*B. Unsaturated coördinating groups*

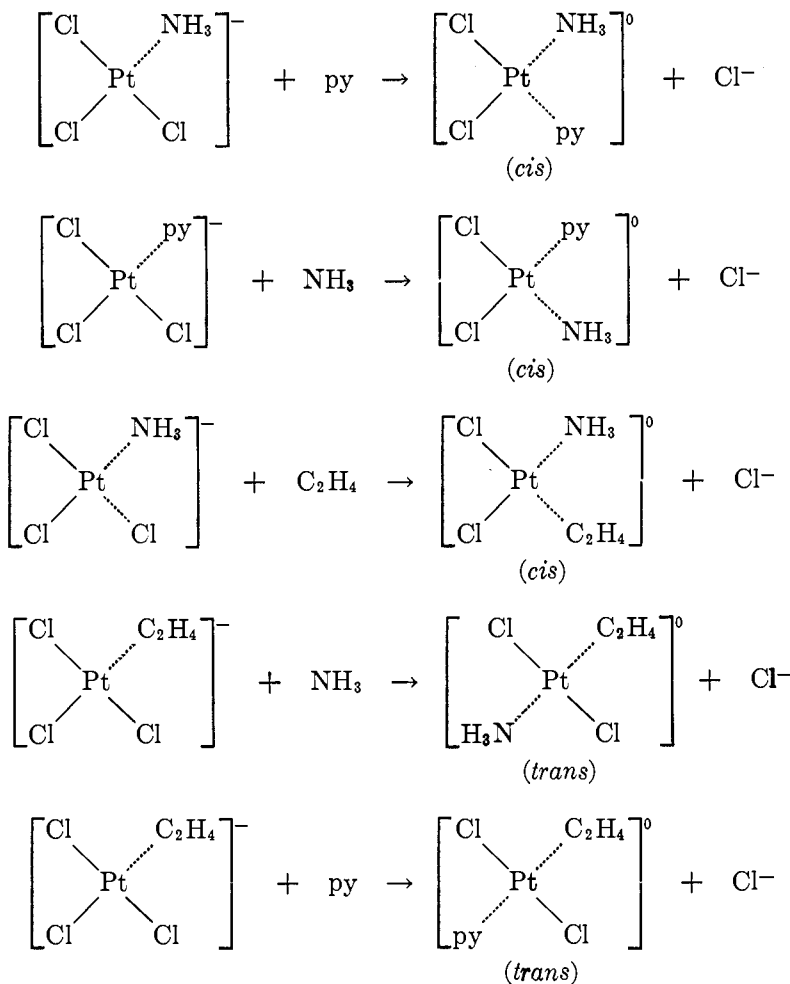
Interesting advances in the chemistry of metallic coördination compounds have been recorded recently, complexes of platinum(II) with unsaturated molecules as ligands having received particular attention. Special interest centers about these complexes, since Zeise (144) reported the ability of olefinic compounds to form complexes of the type  $K[PtCl_3(C_2H_4)] \cdot H_2O$  upon the reduction of platinum(IV) chloride with alcohol.

The ability of unsaturated molecules to form coördination compounds is not limited to hydrocarbons, and many metals can act as the central ion of the coördination complex. Unsaturated acids, alcohols, aldehydes, and esters have been shown to form coördination compounds with metal ions, with the ethylenic linkage functioning as the specific coördinating center. Furthermore, the unsaturated molecule occupies but one coördination position in the complex and, on chemical grounds, no intrinsic difference is apparent between the coördinating ability of an unsaturated molecule such as an alkene and that of a common coördinate molecule such as ammonia (78).

It is now well established that alkenes can act as ligands in complex-salt formation, although the few known stable olefin coördination compounds are largely limited to the platinum complexes. The platinum(II) complexes containing as a coördinating group an unsaturated hydrocarbon are best suited for systematic study, and the relatively great stability of the olefin-platinum linkage permits an unambiguous interpretation of their constitution. As a result, investigations have been limited almost entirely to the platinum(II) coördination compounds. Olefinic complexes of palladium(II), silver(I), and copper(I), as well as less well-defined complexes with other metallic ions, have been recorded (6, 78). Attempts to prepare coördinated complexes of unsaturated molecules with cobalt and nickel complexes were unsuccessful (65).

An excellent comprehensive review of these compounds has been prepared by Keller (78), and the more recent work has been well described by Chatt (6). The concept of the electron-pair bond gives a straightforward and consistent interpretation of many properties of coördination compounds; however, the type of linkage involved in the formation of the olefin coördination complexes is obscure, in that the donor group possesses no extra lone pair of electrons. At any rate, if a lone pair of electrons is available for coördination, it is not apparent in the usual formulation of the olefin molecules. That platinum(II) has a strong tendency to combine with the  $C=C$  group has been shown by Pfeiffer (106), and conclusive evidence is presented that these unsaturated molecules form true coördination compounds.

The unsaturated molecules behave similarly to ammonia and pyridine and occupy only one position about the coördination sphere of the central metal ion of the complex (1). The coördinated unsaturated molecules, however, differ from ammonia and pyridine in that they labilize the groups present in the *trans* position of the planar complexes, in preference to the *cis* ligands. This difference is shown by the following schematic equations, giving corresponding treatment of complexes containing coördinated ammonia with pyridine and with ethylene (16, 17, 57).



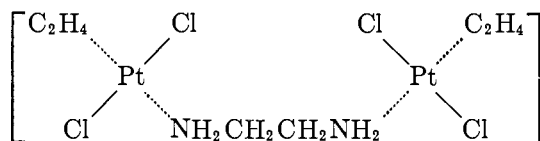
These reactions can be explained on the basis of the *trans* effect, for the ethylene group, as well as negative groups present in the coördination sphere, exhibits a labilizing influence on the group in the *trans* position. Furthermore, the unsaturated compounds of the ethylene series and unsaturated molecules in general exert a directive effect, making the ligand in the *trans* position most labile. Such molecules as propylene, butylene, styrene, amylene, and thiourea also exert a great *trans* effect (55). Butadiene shows a high *trans* effect, but the double bonds in the molecule link with different platinum(II) atoms, forming dinuclear complexes (58).

The stability of ethylene complexes depends upon the other groups present in the coördination sphere of the complex. Some information as to the relative coördinating power of the ligands is provided by Anderson (1) and Hel'man (17, 54, 59).

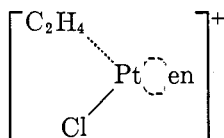
The stability of the complex  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$  decreases by substitution of other univalent anions in place of the chloride ion in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^- >$

$\text{NO}_2^- > \text{CNS}^- > \text{CN}^-$ . With the compound  $[\text{PtX}_2(\text{Am})(\text{C}_2\text{H}_4)]$ , the stability increases in the order:  $\text{Am} = \text{thiourea} < \text{NH}_3 < \text{py} < \text{quinoline}$  ( $\text{X} = \text{CN}^- < \text{CNS}^- < \text{NO}_2^- < \text{I}^- < \text{Br}^-, < \text{Cl}^-$ ). The presence of an excess of any of the anions, except chloride ion, causes replacement of ethylene in the coordination sphere. It is significant that most of the facts concerning the reactions of complexes containing ethylene can be explained on the assumption that this group has a strong *trans* effect, equal to or greater than that of iodide ion and nitrite ion. Substitution of the ethylene molecule itself alters markedly the stability in the order:  $\text{NO} > \text{CO} > \text{styrene} > \text{butadiene} \sim \text{C}_2\text{H}_4 > \text{C}_3\text{H}_6 \sim \text{C}_4\text{H}_8$  (56, 59).

The particularly strong *trans* effect of olefinic ligands was demonstrated by Hel'man (60) on compounds of the type  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$ . A complex of this type can be expected to have a particularly high *trans* effect, since the olefin has as its *cis* neighbor groups which it stabilizes considerably. According to chemical concepts, treatment with ethylenediamine should result in an inner cycle, but this does not happen. Instead, a di- or even a polynuclear compound may form of the type:



If the *cis* chloro groups were not strongly stabilized in the original compound, cyclization by means of ethylenediamine would have resulted in the following product:



The replacement of one olefin in a complex by another under reduced pressure or in solution has been used extensively to estimate their relative stability, but owing to the complex nature of the factors involved, it is difficult to discuss this matter quantitatively (1, 80). Not only are the coordinating tendencies involved but also relative solubilities. The solubilities of the various olefins undoubtedly have a marked effect on the stabilities of the complexes, though, in general, they probably would not change the qualitative order listed above.

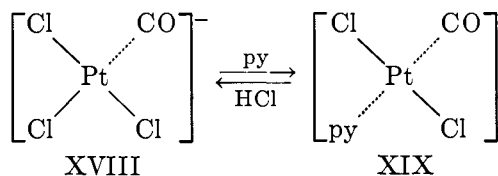
Butadiene shows a high *trans* effect, just as has been observed for ethylene and its homologs, and although both double bonds may be involved in chemical linkage they act separately with different metal atoms (58).

Butadiene, diolefins, and diallyl do not form chelate complexes, and even ethylenediamine fails to do so, producing  $\{[(\text{C}_2\text{H}_4)\text{PtCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)]_2\}$  (59, 68).

Carbon monoxide, like ethylene, is characterized by producing a lability in the group present in the *trans* position of platinum(II) complexes. Any substitu-



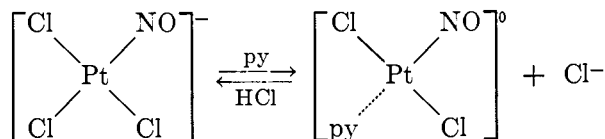
ent introduced into the complex is directed exclusively into the *trans* position, from which it may readily be replaced. Thus,  $K[PtCl_3(CO)]$  (XVIII), produced from the reaction of carbon monoxide in contact with ammonium chloroplatinate-(II), reacts with pyridine to form *trans*- $[PtCl_2(CO)(py)]$  (XIX). The reaction can be reversed by evaporation in hydrochloric acid solution (62).



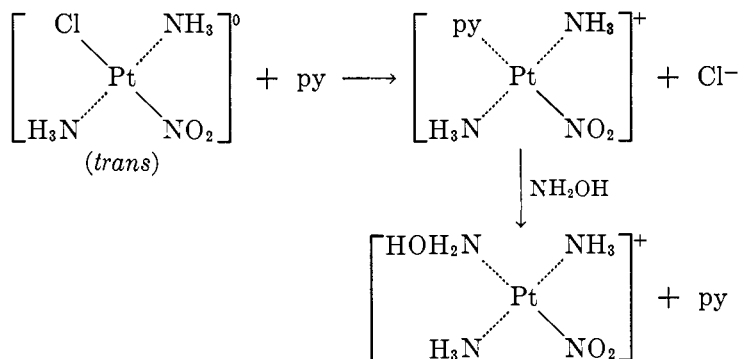
There is ample evidence that carbon monoxide and ethylene play analogous roles in coordination compounds, and this fact may be of significance with respect to the nature of the linkage existing in these complexes (1).

The failure of complex formation of platinum(II) compounds with saturated hydrocarbons indicates that the high *trans* effect of both ethylene and carbon monoxide may be in some manner ascribed to the presence of unsaturated carbon atoms. Moreover, the high *trans* effect of these molecules cannot be attributed to a dipole moment effect (133).

The ability of nitric oxide to enter into complex formation with platinum(II) salts is well established. The interest and importance of this group lie in the fact that the complexes formed are in no way chemically different from the normal coordination compounds, although the mechanism of complex formation is obscure (66). In addition, the NO group has a high *trans* effect, as shown by the following reaction:



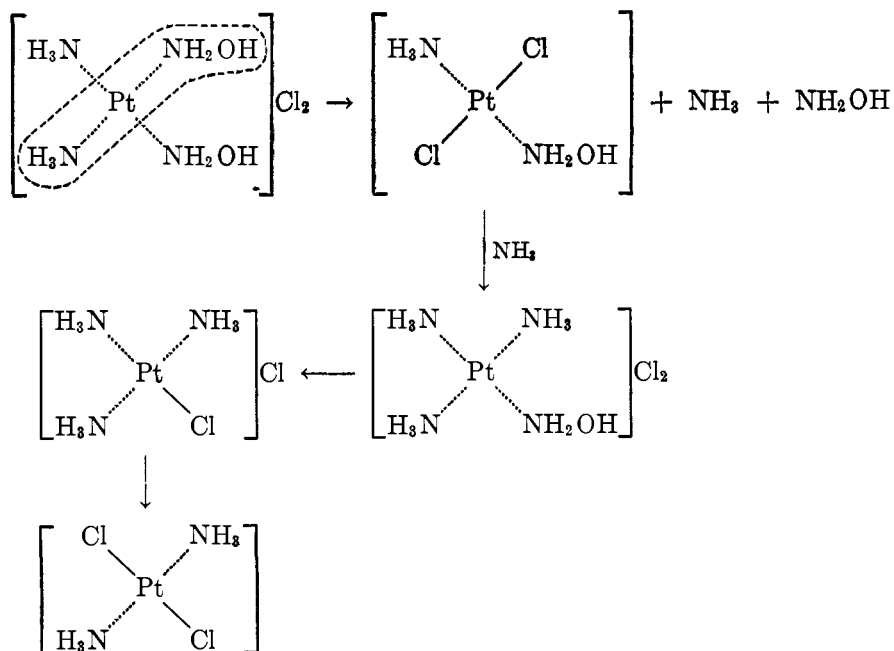
The nitro group also has a high *trans* effect, directing an incoming group to the *trans* position of the coordination sphere, from which it may be readily removed (22).



It is of interest to note that attempts to repeat the work of older chemists in the field of platinum coordination complexes may sometimes lead to somewhat different results. Anderson's (1) preparation of ethyleneplatinum(II) chloride,  $[\text{Cl}_2(\text{C}_2\text{H}_4)\text{Pt}]_2$ , decomposed at  $125\text{--}130^\circ\text{C}$ ., while that prepared by Chatt and Hart (8) decomposed at  $190\text{--}200^\circ\text{C}$ ., a result which may be attributable to the presence of other platinum metals in the older work. It is now known that traces of palladium and rhodium, for example, have a marked effect on the preparation of coordination compounds of platinum.

### C. Hydroxylamine coordinating groups

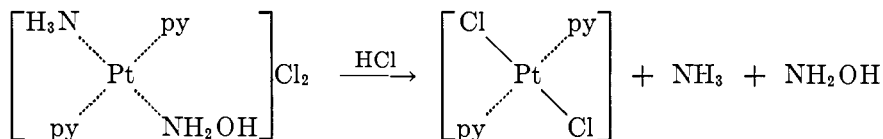
Hydroxylamine, like ammonia, combines with platinum(II) compounds to form a series of complexes which are closely analogous to the metal coordination compounds containing organic amines and sulfides. A systematic investigation was made to elucidate the influence of the progressive substitution of hydroxylamine for ammonia (20). A study of these compounds shows that hydroxylamine plays a role similar to that of ammonia in the platinum(II) complexes. For example,  $[\text{Pt}(\text{NH}_2\text{OH})_4]\text{Cl}_2$  is decomposed by heating with hydrochloric acid to produce *trans*- $[\text{PtCl}_2(\text{NH}_2\text{OH})_2]$ , which is similar in its mode of formation to *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$ . Other results indicate that hydroxylamine is more readily eliminated from the coordinating sphere of complex platinum(II) compounds than ammonia, and elimination reactions of mixed ammonia and hydroxylamines complexes also result in *trans* elimination.



To study further the amines of platinum(II) salts, the reactions of mixed tetraamines of the types  $[\text{PtA}_2\text{A}'_2]\text{Cl}_2$  and  $[\text{PtAA}'\text{A}''_2]\text{Cl}_2$ , where A, A', A'' are

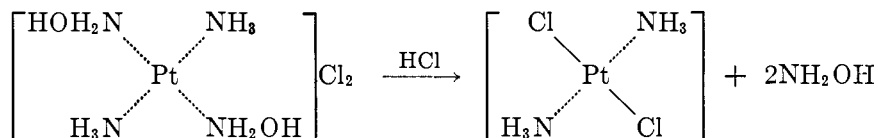
ammonia, pyridine, and hydroxylamine, respectively, were studied (107). The most striking results obtained on decomposing these tetraamines with hydrochloric acid are summarized as follows:

(a) A tetraamine containing one hydroxylamine group loses this group and the ligand in the *trans* position.

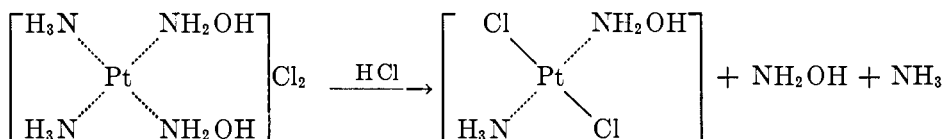


It is significant that the relative weakness of the platinum-hydroxylamine linkage operates in conjunction with the tendency to eliminate the amine group in the *trans* position; this is probably due to the formation of the intermediate compound, *trans*-[PtCl(py)<sub>2</sub>(NH<sub>3</sub>)]Cl.

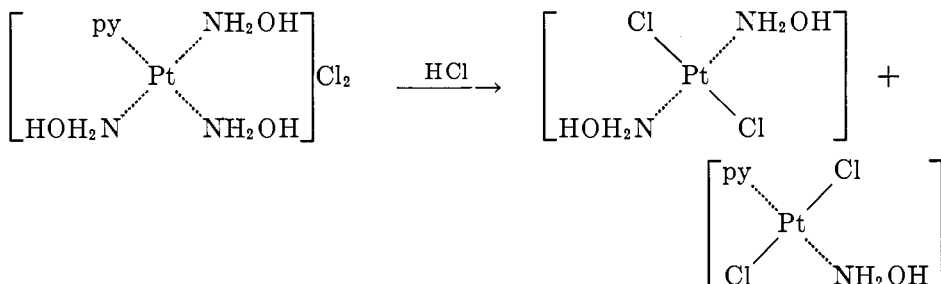
(b) If two *trans* hydroxylamine groups are present, complete or nearly complete elimination of these groups takes place.



(c) A tetraamine containing two hydroxylamine groups in the *cis* positions results in the formation of a mixed *trans* compound, caused by the elimination of *trans* pairs.



(d) A tetraamine containing three hydroxylamine groups gives mixed *trans* amines of the type *trans*-[PtCl<sub>2</sub>(NH<sub>2</sub>OH)<sub>2</sub>] and some *trans*-[PtCl<sub>2</sub>(NH<sub>2</sub>OH)(py)].

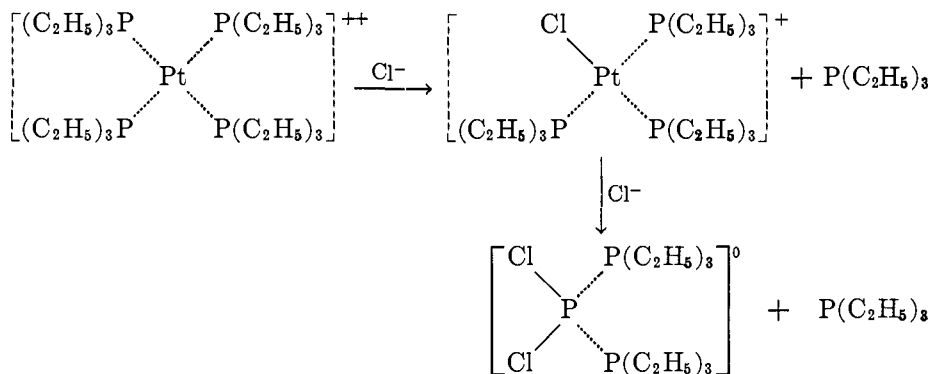


The results of (c) and (d) indicate that *trans* elimination takes place in preference to the complete substitution of the relatively weakly held hydroxylamine groups. The action of ethylenediamine on the mixed *trans* diamines of the type [PtAA'Cl<sub>2</sub>] (where A and A' = ammonia, pyridine, or hydroxylamine) and on

[PtCl<sub>2</sub>(NH<sub>2</sub>OH)<sub>2</sub>] produced in every case, as expected, the sole product [Pt(en)<sub>2</sub>]-Cl<sub>2</sub> (107).

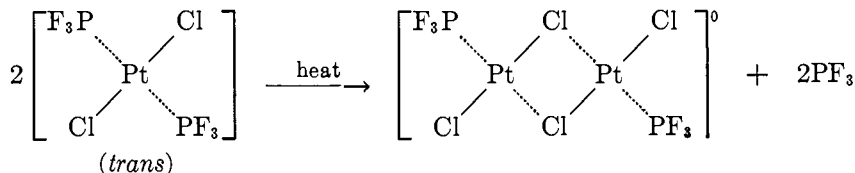
#### D. Coördinating groups containing phosphorus

When an aqueous solution of potassium tetrachloroplatinate is treated with 4 moles of triethylphosphine, the compound [Pt{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}<sub>4</sub>]Cl<sub>2</sub> can not be isolated. Instead, the nonelectrolyte *cis*-[PtCl<sub>2</sub>{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>] is formed (70). Undoubtedly the formation of the *cis* isomer is due to the chloride ions coördinating in place of the triethylphosphine molecules as well as to the labilizing effect of the group in the position *trans* to the triethylphosphine ligand.



If poor coördinating ligands, such as nitrate and perchlorate ions, are used in place of the chloride ion, however, it is very probable that the tetrakis(triethylphosphine) complex can be isolated.

Chatt (7) has prepared the remarkably stable white crystalline complex [PtCl<sub>2</sub>(PF<sub>3</sub>)<sub>2</sub>] by passing phosphorus trifluoride through a plug of powdered platinum(II) chloride in a tube heated to 200°C. This coördination compound, which may be boiled under reflux in a dry atmosphere at atmospheric pressure with only slight deposition of platinum, loses phosphorus trifluoride to produce red [PtCl<sub>2</sub>PF<sub>3</sub>]<sub>2</sub>. Although the structures of these compounds are not given, on the basis of the statement of Chatt that the phosphorus trifluoride ligand is *trans* directing, the reaction may be postulated as follows:



#### E. Substituted pyridine coördinating groups

Investigations of substituted pyridine compounds with platinum(II) compounds have produced some very interesting results. The reaction of potassium tetrachloroplatinate with 2 moles of  $\alpha$ -aminopyridine yields first *cis*-[PtCl<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NH<sub>2</sub>)<sub>2</sub>], as shown by its characteristic reaction with thiourea (114). In contrast to compounds of the type [PtA<sub>2</sub>Cl<sub>2</sub>] (where A = NH<sub>3</sub> or C<sub>5</sub>H<sub>6</sub>N),

which are decomposed by heating to 105–110°C., the corresponding 2-aminopyridine compound is stable. Rubinshtein (115) attributes the unusual stability to hydrogen bonding between the 2-amino groups with the adjacent chlorine atoms, with the pyridine nitrogen atom forming the coördinate bond with platinum(II). As expected on stereochemical grounds 2-aminopyridine does not form chelate complexes with platinum(II) compounds (114).

The reaction of halogen-substituted aminopyridines gives products contrary to those expected on the basis of the principle of *trans* elimination. For example, 2-amino-5-iodopyridine reacts with potassium tetrachloroplatinate to yield *trans*-[PtCl<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>INH<sub>2</sub>)<sub>2</sub>]. It is probable that coördination takes place through the tertiary nitrogen atoms, and steric hindrance prevents formation of the *cis* compound, it being sterically impossible for either the amino groups or the amino group of one ligand and the iodine atom of the other to face each other. Coördination through the iodine atoms of the organic molecule, or other possible arrangements of the substituents, is less probable (116). Furthermore, pyridine readily replaces the 2-amino-5-iodopyridine to yield *trans*-[PtCl<sub>2</sub>(py)<sub>2</sub>] (117).

#### V. MEASUREMENTS OF DIPOLE MOMENT

The usefulness of the dipole moment in investigating the structures of the coördination complexes has been shown by Jensen (70, 71, 73). Since this physicochemical method is concerned with the whole cloud of valency electrons, the symmetrical *trans* isomers of platinum(II) compounds of the type [PtA<sub>2</sub>X<sub>2</sub>] have a center of symmetry and should have a dipole moment closely approaching zero. On the other hand, the corresponding *cis* isomers have no such symmetry and should have high moments. Jensen has verified the validity of these conclusions for a variety of platinum(II) coördination compounds.

Dipole moments were determined for the *cis* and *trans* isomers of thioether derivatives of the type [PtX<sub>2</sub>(SR<sub>2</sub>)<sub>2</sub>] (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, and R = ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, and benzyl). The approximate values (in e.s.u. cm.) of the dipole moment for the chloro and bromo isomers are  $2.4 \times 10^{-18}$  for the *trans* compounds, and  $9 \times 10^{-18}$  for the corresponding *cis* complexes. The dipole moment for *cis*-[PtX<sub>2</sub>R<sub>2</sub>], where X = NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup>, is approximately  $13 \times 10^{-18}$  (70). Measurements of the dipole moment with compounds of the types [PtX<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>], [PtX<sub>2</sub>(R<sub>3</sub>As)<sub>2</sub>], and [PtX<sub>2</sub>(R<sub>3</sub>Sb)<sub>2</sub>] (where X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup> and R = C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, and C<sub>4</sub>H<sub>9</sub>) show that the *trans* compounds have a dipole moment of approximately zero, whereas the *cis* isomers have values of about  $10 \times 10^{-18}$  (71).

Several points of considerable interest have arisen from the investigations of Jensen. It is significant that whereas the various symmetrically substituted *trans* phosphine, arsine, and stibine complexes have a dipole moment of zero, those of the symmetrical sulfides exhibit definite moments which do not vary much among the various compounds. The resultant of each of the three alkyl-metal moments of the coördinating groups is directed along the platinum-metal bond, and in the *trans* compounds should result in a zero moment, regardless of the possibility of free rotation about the platinum-metal bond. The

dipole moment of the thioether complexes in the *trans* compounds, however, may be due to the unshared pair of electrons in the sulfur atoms, resulting in the lack of symmetry. Furthermore, the studies of Mann and Purdie (91) have shown that the stable *trans*-compound  $[\text{PdCl}_2\{\text{S}(\text{C}_2\text{H}_5)_2\}_2]$  has a dipole moment of  $2.27 \times 10^{-18}$  E.S.U. cm., whereas the *trans* compound  $[\text{PdCl}_2\{\text{R}(\text{C}_2\text{H}_5)_3\}_2]$  (R = phosphorus or arsenic) has a moment of about  $1.04 \times 10^{-18}$  E.S.U. cm.

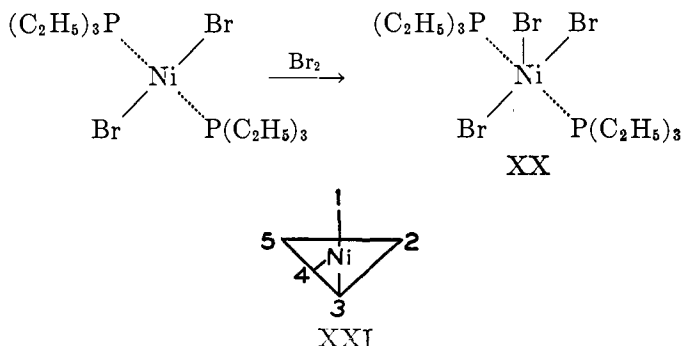
The explanation offered for the higher moment of the sulfur-containing complex, compared with the other two, is that the sulfur atom is at the apex of a tetrahedron and rotates unsymmetrically about the coördinate link to palladium(II), whereas the coördinated phosphorus and arsenic atoms are at the center of a tetrahedron which rotates symmetrically about the coördinate link, joining these elements to the central metal ion of the complex. It is known that in compounds of the type  $\text{CH}_2\text{X}\cdot\text{CH}_2\text{X}$  the two halves of the molecule do not cancel one another, but molecules of this type possess considerable moments, since the rotation of the two halves of the molecule relative to one another gives a mean effective moment. Furthermore, Sutton (91a) suggests that the two ethyl sulfide coördinating groups may rotate relative to each other about the axis formed by the two *trans* coördinate links, and so set up a mean effective moment similar in cause to that of symmetrical dichloroethane. When compounds of the type  $\text{MX}_2\text{Y}_2$  (M = platinum or palladium) are obtained as square complexes in only one form, it is usual to assume that the compound is the *trans* isomer. Thus, the proposal that the three ethyl compounds of the chloro series discussed above are of the *trans* type is strongly supported by the dipole moments. This is not always the case, however, for the only form of the complex  $[\text{PtCl}_2(\text{TeR}_2)_2]$  (R = ethyl) isolated as yet is the *cis* isomer (73). Furthermore, on the basis of dipole-moment measurements, the only known compounds,  $[\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2]$  and  $[\text{PtCl}_2(\text{C}_6\text{H}_5\text{NC})_2]$ , are the *cis* isomers, and these with diethyl telluride or diphenyl telluride produce the corresponding *cis* chloro complexes (73).

The interpretation of structures on the basis of dipole measurements is sometimes further complicated by the influence of solvents, the effect of temperature, and the ready transformation  $\textit{cis} \rightleftharpoons \textit{trans}$  under certain conditions (2, 89). Thus, on being kept in the solid state, or in solution or suspended in alcohol or benzene, *cis*- or *trans*- $[\text{PtCl}_2\{\text{S}(\text{C}_2\text{H}_5)_2\}_2]$  tends to pass into an equilibrium mixture of both. The corresponding dibromides change in a similar manner but the equilibrium mixture is mostly all the *trans* compound, and transformation with the isomeric iodides is even more rapid and complete (2).

#### VI. FIVE-COÖRDINATION COMPLEXES

The mechanism of substitution reactions of four-covalent planar complexes is not known, but an interesting speculation is that reactions take place through the formation of an intermediate five-coördination complex. A coördination number of 5 is unusual, but a few cases such as  $\text{Fe}(\text{CO})_5$  and  $\text{Ru}(\text{CO})_5$  are known in which this unusual coördination number is claimed. Furthermore, in the study of the nickel(II) complexes with tertiary phosphines, Jensen (72) obtained the complex  $[\text{NiBr}_3\{\text{P}(\text{C}_2\text{H}_5)_3\}_2]$ , soluble and monomeric in benzene, by the reaction of *trans*- $[\text{NiBr}_2\{\text{P}(\text{C}_2\text{H}_5)_3\}_2]$  with bromine. Later, the work of Jensen and Ny-

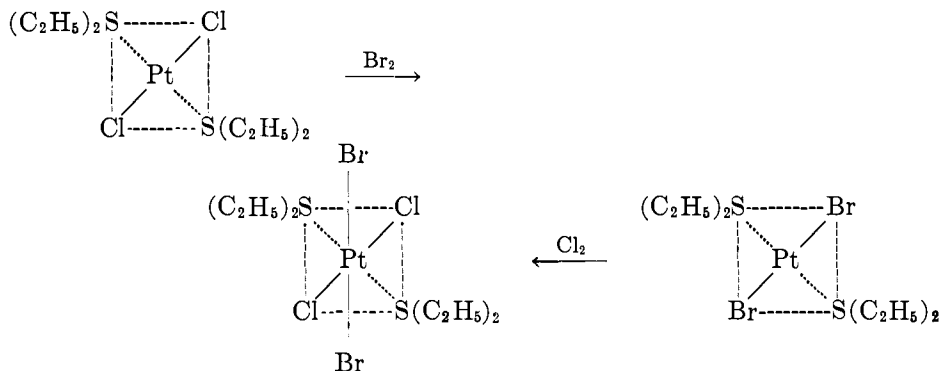
gaard (74) showed the magnetic moment to be 1.72–1.92 Bohr magnetons, compared with 1.73 Bohr magnetons calculated for nickel(III) with covalent bonds. These results indicate the presence of one unpaired electron and suggest the use of  $dsp^3$  bonds in the five-covalent complex. For coordination number 5, the trigonal bipyramid (81) (XX) and the tetragonal pyramid (31) (XXI) are possible (100).



For the compound  $[\text{NiBr}_3(\text{P}(\text{C}_2\text{H}_5)_3)_2]$ , the trigonal bipyramid XXI can exist as three possible isomers in which the  $\text{P}(\text{C}_2\text{H}_5)_3$  group occupies positions (a) 1 and 4, (b) 1 and 2, and (c) 2 and 4. The measured dipole moment of the compound is 2.4 D,<sup>5</sup> and on this basis it is assumed that the configuration is the tetragonal pyramid XXI, since its calculated dipole is about 2–3 D. This is the case if the nickel atom in the complex is in or not far removed from the plane of the base of the tetragonal pyramid. It is possible, however, that a mixture of 1,4 and any other trigonal tripyramid would also result in a dipole moment in accord with the experimental value of 2.4 D. The corresponding five-covalent compounds of platinum(IV) have not been obtained, undoubtedly owing to the great stability of the sixfold coordination complexes.

#### VII. OCTAHEDRAL COMPLEXES

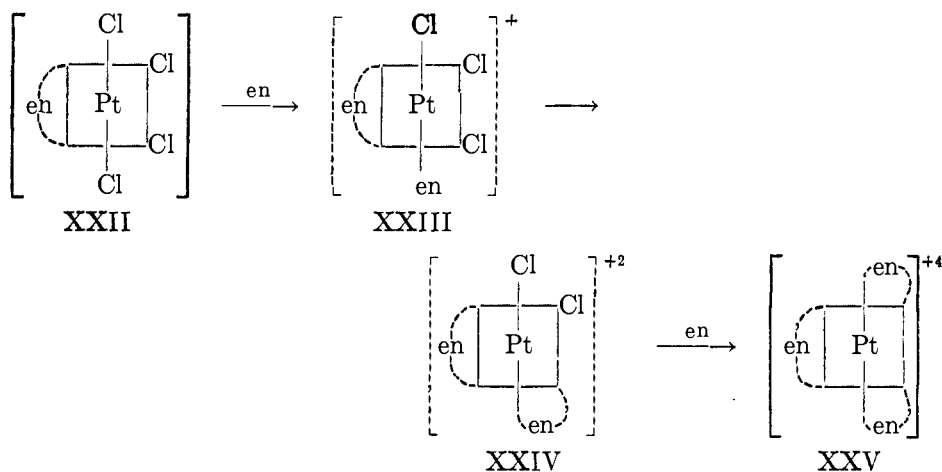
The oxidation of four-coördinate *trans*- $[\text{PtCl}_2(\text{S}(\text{C}_2\text{H}_5)_2)]$  with bromine and of *trans*- $[\text{PtBr}_2\{\text{S}(\text{C}_2\text{H}_5)_2\}_2]$  with chlorine converts the dihalides to one and the same dibromodichloride, having an octahedral configuration (2, 39).



<sup>5</sup> D = Debye unit =  $10^{-18}$  e.s.u. cm.

Owing to the coördination of six groups about the central platinum(IV), the directive influences in this type of coördination compounds are far more complex than in the four-coördinate platinum(II) compounds. No attempt is made in this report to review this interesting field, but reference to several recent contributions to the study of these compounds which provide a wide and useful field of research deserves brief mention.

A study of the preparation and properties of dichlorobis(ethylenediamine)-platinum(IV) chloride was undertaken by Bailar and his students (4). Chemical and physical evidence regarding the compound  $[\text{PtCl}_2(\text{en})_2]\text{Cl}_2$ , which was prepared by the chlorination of  $[\text{Pt}(\text{en})_2]\text{Cl}_2$ , by the reaction of  $[\text{Pt}(\text{OH})_2(\text{en})_2]\text{Cl}_2$  with hydrochloric acid, and by the reaction of  $[\text{Pt}(\text{CO}_3)_2(\text{en})_2]$  with hydrochloric acid, indicates the *trans* configuration for the cation. Furthermore, the following mechanism is suggested for the reaction of ethylenediamine with  $[\text{PtCl}_4(\text{en})]$ :



One of the *trans* chloro groups is more easily displaced than the other two, and the intermediate compound illustrated by XXIII is probably first formed.

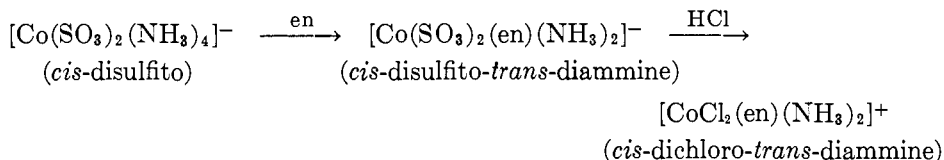
This mechanism has been suggested on the basis of the *trans* effect, since it has been demonstrated that ligands *trans* to a negative group are more labile (101). Conclusive proof of this mechanism would necessitate the isolation of XXIV but, owing to unfavorable solubility relationships and the greater stability of compound XXV, compound XXIV could not be isolated.

The stereochemistry of octahedral complexes presents many difficult problems for which there is no counterpart in the better-known chemistry of carbon. For example, no general methods are known for the determination of the stereochemistry and chemical reactions of ions of the relatively simple type  $[\text{M}(\text{AA})_2\text{b}_2]$  and  $[\text{M}(\text{AA})_2\text{bd}]$  (where AA is a group occupying two coördination positions, and b and d are groups occupying one coördination position). In general it is true that the *cis* compounds are more highly colored and more soluble than the corresponding *trans* isomers, but the great number of exceptions limits the usefulness of this generalization. Furthermore, although differences in reactivity

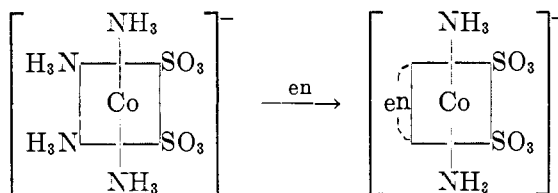


between *cis* and *trans* compounds are known in some cases, examples of these are sufficiently scattered so as to be inadequate for generalization. The problem is further complicated by molecular rearrangements accompanying the synthesis of compounds from complexes of known structure (101).

The principle of the *trans* effect has been especially helpful in the preparation of the three stereoisomeric forms (*cis*-dichloro-*trans*-diammine, *cis*-dichloro-*cis*-diammine, and *trans*-dichloro-*cis*-diammine) of the ion  $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$  (3). For example, preparation of the troublesome *cis*-dichloro-*trans*-diammine  $[\text{CoCl}_2(\text{en})(\text{NH}_3)_2]^+$  was finally obtained according to the following scheme:



The formation of the intermediate sulfite compound is shown by the following schematic representation:



Ethylenediamine replaces the indicated pair of ammonia molecules more readily than the other two, these being the ammonia molecules *trans* to the negative sulfite groups.

The reaction of either *cis*- or *trans*- $[\text{CoCl}_2(\text{pn})_2]\text{Cl}$  (pn = propylenediamine) with potassium thiocyanate forms *trans*- $[\text{Co}(\text{NCS})_2(\text{pn})_2]^+$  (101). Either *cis*- or *trans*- $[\text{CoCl}_2(\text{pn})_2]\text{Cl}$  on reacting with aqueous ammonia yields *trans*- $[\text{CoCl}(\text{pn})_2(\text{NH}_3)]\text{Cl}_2$  and with anhydrous ammonia, *trans*- $[\text{Co}(\text{pn})_2(\text{NH}_3)_2]\text{Cl}_3$ . It is interesting to note that the reaction of aqueous ammonia with the corresponding ethylenediamine series leads to the formation of the *cis* isomer.

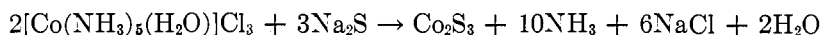
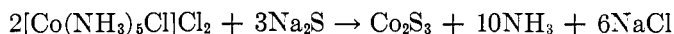
The products of thermal decomposition of  $[\text{Cr}(\text{en})_3](\text{SCN})_3 \cdot \text{H}_2\text{O}$  at  $130^\circ\text{C}$ . and  $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 3.5\text{H}_2\text{O}$  at  $160^\circ\text{C}$ . are, respectively, *trans*- $[\text{Cr}(\text{SCN})_2(\text{en})_2]\text{SCN}$  and *cis*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}$ . In both cases the decomposition is catalyzed to a marked extent by traces of the ammonium salt corresponding to the anion of the complexes (113). The unique catalytic effect suggests that negative ions of the catalysts are involved in the formation of intermediate complexes. It is also noteworthy that *cis*- $[\text{Cr}(\text{SCN})_2(\text{en})_2]\text{SCN}$  is not converted to the *trans* isomer, nor is *trans*- $[\text{CrCl}_2(\text{en})_2]\text{Cl}$  converted to the *cis* isomer.

#### VIII. THERMOCHEMISTRY OF THE TRANS EFFECT

The *trans* effect evidently depends in an important way upon bond-energy relationships within a complex molecule. The methods of thermodynamics, es-

pecially those of thermochemistry, should prove a useful tool in the study of this problem. This was pointed out very early by Michael (95), although this investigator did not concern himself with inorganic coördination compounds, but rather with those of the maleic-fumaric types. Nevertheless his reasoning is as valid for the inorganic complexes.

Lamb and Simmons (85) studied the heats of reaction of the complex cobaltamines without considering the configuration of the complexes. A direct measurement of the heat of reaction was not feasible, because of the slowness of aqution (the transformation chosen for study) and also because of the insoluble nature of the ammine complexes. Instead, the following reactions were chosen:



Any difference in the heat of reaction would be due to the presence of water in the coördination sphere and would provide a measure of bond strength. In this manner, Lamb and Simmons were able to obtain data concerning the various

TABLE I  
Heats of formation of cobalt(III) complexes

IONS	HEATS OF FORMATION	IONS	HEATS OF FORMATION
	<i>kcal.</i>		<i>kcal.</i>
$[\text{Co}(\text{NH}_3)_6]^{+++}$ .....	51.9	$1,6[\text{CoCl}_2(\text{NH}_3)_4]^+$ .....	32.0
$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$ .....	53.1	$1,2[\text{CoCl}_2(\text{NH}_3)_4]^+$ .....	30.2
$[\text{CoCl}(\text{NH}_3)_5]^{++}$ .....	41.7	$1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$ .....	49.3
$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{+++}$ .....	45.0	$1,6[\text{Co}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_4]^{++}$ .....	45.6
$1,6[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$ .....	53.1	$[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ .....	47.0
$1,2[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$ .....	53.9	$[\text{Co}(\text{NO}_2)_6]^{---}$ .....	28.1

heats of reaction and transformation of pentaamminecobalt(III) salts in aqueous solution. It might be noted that Lamb and Marsden (84) attempted to obtain information of the same type from studies of reaction velocities.

This work was continued later by Ovenston and Terrey (103). These authors used the same reaction but studied the tetraamminecobalt(III) salts. Cognizance was taken of the *cis* and *trans* forms, but the data obtained did not permit of any definite conclusions concerning these forms.

Data specifically of interest to a study of the *trans* effect could not be obtained prior to 1926, since it was in that year that Chernyaev (10) clearly defined the nature of this effect. Unfortunately, while most of the theoretical work has centered around the platinum complexes, the greater part of the thermochemical data is concerned with the cobalt coördination compounds.

Yatsimirskii is probably the most active worker in this field. Yatsimirskii and Pankova (141, 142, 143) obtained considerable data on a large number of cobalt(III) complexes. These data were carefully reviewed and amplified by Yatsimirskii (140). Table 1 gives the heats of formation of twelve different cobalt(III) complexes.

Using Hess' Law it is possible to calculate from the data of table 1 a whole series of heat transformations for complex ions and heats of replacement by one group for another. Thus table 2 gives the heat of displacement when a nitro group is displaced by the ligands ammonia, water, and chloride ion.

These effects are rather large, and it becomes evident that the *trans* effect contributes in an important way to the nature of the complex. It should be noted that the *trans* effect in cobalt complexes, as determined thermochemically, differs essentially from a comparable series in the platinum complexes, as determined by chemical substitution. With the cobalt complexes the order is  $\text{NO}_2^- > \text{NH}_3$  and  $\text{H}_2\text{O} > \text{Cl}^-$ .

TABLE 2  
Heats of displacement of nitro group by various ligands in water solution

INITIAL COMPLEX	FINAL COMPLEX	HEAT OF DISPLACEMENT
1. Displacement of $\text{NO}_2^-$ by $\text{NH}_3$		
		<i>kcal.</i>
$1,6[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	0.0
$1,2[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	-0.8
$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	$[\text{Co}(\text{NH}_3)_6]^{+++}$	-1.2
$1,6[\text{Co}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_4]^{++}$	$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{+++}$	-0.6
$1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$	$[\text{CoCl}(\text{NH}_3)_5]^{++}$	-7.6
$[\text{Co}(\text{NO}_2)_6]^{---}$	$[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$	18.9
$[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^+$	$1,2[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	6.9
$1,2[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	$[\text{Co}(\text{NH}_3)_6]^{+++}$	-2.0
2. Displacement of $\text{NO}_2^-$ by $\text{H}_2\text{O}$		
$1,6[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	$[\text{Co}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_4]^{++}$	-7.5
$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{+++}$	-8.1
3. Displacement of $\text{NO}_2^-$ by $\text{Cl}^-$		
$1,6[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$	$1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$	-3.8
$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	$[\text{Co}(\text{Cl})(\text{NH}_3)_5]^{++}$	-11.4
$1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$	$1,6[\text{CoCl}_2(\text{NH}_3)_4]^+$	-17.3

For another series of reactions, it was shown (141) that the bonding strength of anions within the inner sphere of a cobalt(III) complex decreases in the order:  $\text{NO}_2^- > \text{CNS}^- > \text{I}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^-$ .

When nitrite ion is replaced by ammonia, water, or chloride ion, the amount of the heat effect will depend upon the ligand *trans* to the  $\text{NO}_2^-$ . The greatest heat effect is found when the group *trans* to the  $\text{NO}_2^-$  is another  $\text{NO}_2^-$  ligand. If the *trans* partner is ammonia or water, the heat effect is smaller; finally, if the *trans* group is chloride ion (as in  $1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$ ), the smallest heat effect is found. When the displacement is from  $[\text{Co}(\text{NO}_2)_6]^{---}$  a very large heat effect is noted, as is to be expected from the strengthening of the right-angle covalent bonds.

The thermochemical behavior of the cobalt complexes may be explained in

terms of the bonding structure of the inner sphere. The cobalt(III) atom has an octahedral structure and ligands are bonded with the central cobalt atom by means of  $d^2sp^3$  hybridization. The  $d$  bonds are at right angles to each other and opposite each  $d$  bond is a  $p$  bond. Moreover,  $d$  bonding is the most stable, while  $p$  bonding is the least stable. This approach explains the differences in the heats of formation of geometrical isomers. The heat of formation of the croceo ion (where one of the nitro groups is bonded by a  $d$  bond and the second by a  $p$  bond) is less than that of the flaveo ion (where both nitro groups are bonded by  $d$  bonds). Similar considerations may also be applied to the praseo and violeo salts.

Data have already been given to show the heat effects attendant upon the displacement of  $\text{NO}_2^-$  by other groups. Comparable information for the dis-

TABLE 3  
*Heats of displacement of ammonia and water by various substituents in water solution*

INITIAL COMPLEX	FINAL COMPLEX	HEAT OF DISPLACEMENT
1. Displacement of $\text{NH}_3$ by $\text{Cl}^-$		
		<i>kcal.</i>
$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	$1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$	-3.8
$[\text{Co}(\text{NH}_3)_6]^{+++}$	$[\text{CoCl}(\text{NH}_3)_5]^{++}$	-10.2
$[\text{CoCl}(\text{NH}_3)_5]^{++}$	$1,6[\text{CoCl}_2(\text{NH}_3)_4]^+$	-9.7
$[\text{CoCl}(\text{NH}_3)_5]^{++}$	$1,2[\text{CoCl}_2(\text{NH}_3)_4]^+$	-11.5
2. Displacement of $\text{NH}_3$ by $\text{H}_2\text{O}$		
$[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^{++}$	$[\text{Co}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_4]^{++}$	-7.5
$[\text{Co}(\text{NH}_3)_6]^{+++}$	$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{+++}$	-6.9
3. Displacement of $\text{H}_2\text{O}$ by $\text{Cl}^-$		
$[\text{Co}(\text{NO}_2)(\text{H}_2\text{O})(\text{NH}_3)_4]^{++}$	$1,6[\text{Co}(\text{NO}_2)\text{Cl}(\text{NH}_3)_4]^+$	3.7
$[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{+++}$	$[\text{CoCl}(\text{NH}_3)_5]^{++}$	-3.3

placement of other groups is, of course, of great interest, and Yatsimirskii (140) has compiled such information.

These data are, of course, incomplete but an interesting observation can be made. All of these displacements give rise to a negative heat of displacement compared to a positive value of 18.9 kcal. when  $[\text{Co}(\text{NO}_2)_6]^{---}$  is converted to  $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ . This emphasizes that the hexanitrocobalt(III) complex is very stable compared to the initial complexes listed in table 3. Moreover, free energy and other thermodynamic functions may be readily derived from data of this type. Unfortunately this has not, as yet, been done. The advantages of this line of attack are obvious.

Present theory on the *trans* effect is not fully developed, but free-energy data may give us a powerful pragmatic approach to the problem. It becomes even more relevant when we consider Ormont's (102) suggestion that any theory of complex compounds must take the nucleus into account.

Theories regarding shell electrons alone are perhaps insufficient. Moreover, since present theory cannot handle a problem of this magnitude, free energy and other thermochemical data can prove very useful. A determined attempt to amass a great deal of data on the thermochemistry of inorganic complexes will prove very helpful towards the solution of problems concerning their structure.

#### IX. THEORY

Recent advances in the study of the theoretical considerations of the *trans* effect have shown that many factors are involved. Some of these factors are (a) the stereochemistry of the complex involved, (b) the bond forces between the ligands and the central metal ion as well as the possibility of hydrogen bonding and bonding between ligands, (c) polarizability, (d) the activity of the ligand as a reducing agent or its electronegativity, (e) steric hindrance, (f) polymerization phenomena, (g) atomic and molecular radii, (h) dipole moment, (i) resonance and amount of double-bond character, and (j) lability. Even though all of these factors do not necessarily enter into a theoretical discussion of the *trans* effect, they may be sufficiently important to lead to interesting conclusions.

To explain the decomposition reactions of the mixed tetraammines with hydrochloric acid, Werner adopted the arbitrary rule that displacement by the chloride ion meant the loosening of *trans* bonds. This concept assumed that the compounds were stereoisomers and possessed planar configurations. Werner had no proof of this other than the fact that it rendered syntheses predictable. Moreover, this was a radical suggestion at that time, since the stereochemistry of the carbon atom was first investigated and its tetrahedral structure was well established before the planar structure of divalent platinum complexes. Apparently the establishment of the tetrahedral structure of carbon influenced thinking on the subject of divalent platinum. Many authorities first had misgivings as to the validity of the square configuration, a designation proposed by Pauling (104) in connection with his quantum-mechanical treatment of the directed valence bond.

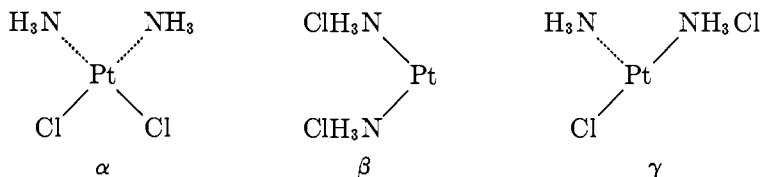
The problem of explaining the existence of *cis* and *trans* compounds, as postulated by Werner, resolves itself initially into deciding whether they are (a) structural or geometrical isomers, (b) polymers, or (c) dimorphs. The possibility of dimorphism was discounted by Cleve, who first emphasized the different chemical behavior of *cis*- and *trans*-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>. It should be pointed out, however, that, even as late as 1935, Mann found that identical complexes may give different x-ray patterns, a result which he thought might be due to dimorphism. However, this explanation is invalid, for a study of absorption spectra eliminates dimorphism as a possibility, since dimorphous substances give identical absorption spectra (94).

The possibility of polymerism provided, for a time, a lively center for discussion. At one time, Werner postulated a tetragonal central atom for divalent platinum. As late as 1932 Drew and his collaborators (36) emphasized that there was no convincing chemical proof for the planar structure. Reihlen (111) believed that platinum(II) complexes could not be completely planar, since he claimed to have resolved the tetraammine salts. This argument was not accepted,

since it could not be proved that the activity was not due to the optically active ligands (36).

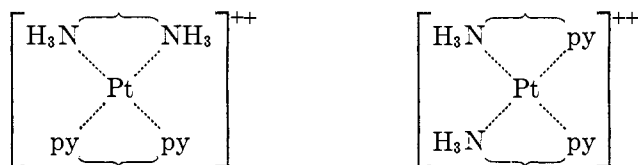
Now, a tetrahedral central atom would involve polymerism rather than isomerism. Reihlen and Nestle (112) found that the molecular weight of *cis*-dichlorodiammineplatinum in liquid ammonia is 258, while the corresponding *trans* compound has a molecular weight of 620. Moreover, evidence from measurements of vapor pressure showed that the *trans* form is the dimeric form of the *cis* compound. In view of the preponderant physical and chemical evidence in favor of *cis-trans* isomerism, these results are puzzling, and it may be conjectured that the liquid ammonia medium caused anomalous polymerization through hydrogen bonding. Also, the possibility of the formation of plato salts was not considered.

Another suggestion was advanced (36) on the basis of the alleged discovery of a third isomer of  $[\text{PtCl}_2(\text{NH}_3)_2]$ . The three possible structural isomers proposed were:



The unusual coordination numbers of 2 and 3 in the  $\beta$ - and  $\gamma$ -forms should be especially noted.

In still another paper on palladium complexes this concept was implemented (38). It is suggested that a pairing of valences takes place much as shown below:



Thus the four bonds to the amine groups of the tetraammines are differentiated into two equivalent pairs which function independently, with a closer relationship existing between members of a pair than between nonmembers.

As pointed out in a succeeding paper (107), however, the preponderant chemical and physical evidence favors a planar structure for four-covalent platinum. This same conclusion was reached by Grinberg (58).

The problem concerning the configuration of four-covalent platinum(II) complexes has been discussed in great detail by Mellor (92, 93) and by Keller (78) in masterful reviews. Any one of a number of structures could account equally well for the *cis-trans* isomerism of  $[\text{PtCl}_2(\text{NH}_3)_2]$ . The four bonds of the platinum might be directed towards (a) the corners of a square or rectangle, (b) the corners of a pyramid on a square or rectangular base, or (c) the corners of a tetragonal or rhombic bisphenoid. Each of these structures has been used to explain some special phenomenon, but the more important evidence, by far, favors the square configuration in which platinum(II) has four-covalent  $dsp^2$  bonds directed to the corners of a square. Were  $sp^3$  orbitals involved, then a tetrahedral structure

would be present. Illustrative of the chemical evidence is Chernyaev's isolation (14) of three compounds of the formula  $[\text{Pt}(\text{NO}_2)(\text{py})(\text{NH}_2\text{OH})(\text{NH}_3)]_2[\text{PtCl}_4]$ ; indicative of the physical evidence are the x-ray diffraction patterns of Cleve's salt and Mangus' salt, among others.

Cox and Preston (23) have carried out x-ray examinations of  $[\text{Pt}(\text{en})_2]\text{Cl}_2$ ,  $[\text{Pd}(\text{en})_2]\text{Cl}_2$ , and  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ; the results give further evidence for the planar distribution of these complexes. In addition, the x-ray results show that the four covalencies are not crystallographically equivalent, only those valencies which are *trans* to each other being equivalent. This applies also to  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ . These authors explain the pairing of the *trans* platinum-nitrogen bonds as being connected with the distribution of shared electrons, and this pairing is presumably due to slight differences in energy between the various subgroups in the same principal quantum group of the central atom. Assuming that the crystallographic results are significant for chemical reactions, the difference between the pairs of valencies lies in the strength of the bond and should be of importance in problems of elimination and substitution. The suggestion is made that the work affords a physical basis for Werner's hypothesis of *trans* elimination of groups from the tetraammines and triammines (37, 107). There appears to be no very simple plausible theoretical reason for "*trans* pairing" in these amine complexes. The entire question of the square complex has been thoroughly discussed elsewhere (92, 93).

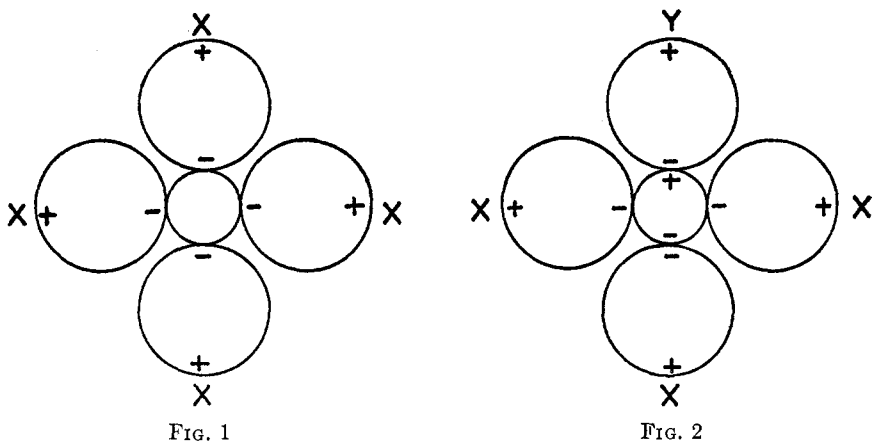
The reality of the *trans* effect for four-covalent platinum(II) depends upon the square configuration. Once this has been established, we are in a position to inquire into the theoretical basis for the *trans* effect. While Werner referred to "*trans* elimination", it remained for Chernyaev (10) to point out the regularity of the *trans* effect. Chernyaev showed that acidic ligands exercise a much higher *trans* effect than do neutral coordinating groups such as ammonia and water. Moreover, a series could be established indicating increasing lability, and, of course, the facts learned empirically in this fashion could be pragmatically tested through the synthesis of new compounds.

Chernyaev (12) essayed the first attempt at a theoretical approach. He recognized that a simple coulombic explanation in the Kossel sense is inadequate. If one considers a platinum complex containing unlike negative ligands, it becomes evident that the negative charge of the groups should exert greater repulsion on a *cis* neighbor than upon a *trans* partner. The result would be labilization of *cis* ligands rather than *trans* groups. This conclusion contradicts experience and therefore other than coulombic forces must be considered.

Grinberg (45) noted that the *trans* effect of the series  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  increases in an order corresponding to their increase in molar refraction; this fact suggested that Fajans' polarizability concept (41) could be employed. This idea was first used by Nekrasov (99) and later more completely formalized by Grinberg. In a complex of the type  $[\text{PtX}_4]^{--}$ , where  $\text{X}^-$  is a halide ion, we have a positive center surrounded by four monovalent negatively charged ions. Mutual polarizability would result in induced dipoles in the anions and in the central ion. Owing to the symmetrical distribution around the central ion (figure 1), the induced dipoles in the central metal ion are compensated and the resultant dipole will be zero.

If, however, a group Y with different polarizability is introduced (figure 2), there will be no mutual compensation, resulting in a dipole in the central ion as well as in the structure as a whole. Furthermore, if Y is a strongly negative or electron-rich group, labilization of the *trans* X group results.

This idea, advanced by Nekrasov and Grinberg, served to indicate a qualitative approach. Later Grinberg (46) offered a more sophisticated explanation on the basis of the following assumptions: (a) The attracting power between the central ion and the coördinating groups depends upon the mutual effect of the ionic charges and the induced dipoles. (b) The magnitude of the dipole moment induced in one component is calculated on the basis that the field caused by the second component is homogeneous and equal to the field formed in the center of the first component. (c) The magnitude of the platinum-chlorine distance is not changed by the entrance of a *trans* neighbor and this distance is assumed to be  $2.33 \times 10^{-8}$  cm., as determined by Dickinson (32) on the basis of an x-ray



examination of potassium tetrachloroplatinate. The polarizability of the chloride ion is assumed to be  $3 \times 10^{-24}$  cm.<sup>3</sup>

Although the polarizability of platinum(II) is not determined directly because there is no direct data of its refraction, it may be estimated using the Lorenz-Lorentz formula (42) and also by difference through known compounds. It is found approximately to be between 9 and 22.6 cm.<sup>3</sup> In the following derivation, however, Grinberg assumes an even more unfavorable value of 4.78 for the ionic refraction of platinum(II), equal to that of silver(I).

Let

- $E_A$  = the field strength of the platinum(II) in the center of the chloro ligand,
- $E_B$  = the field strength of the chloro ligands in the center of the platinum(II) ion,
- $m_{Pt}$  = the induced dipole moment in platinumous ion,
- $m_{Cl}$  = the induced dipole moment in chloride ion, and
- $F_1$  = the total attraction between platinum and chlorine.



Consider the first limiting case, where we have a platinum(II) ion and one chloride ion without a *trans* partner. The chloride ion has about twice the diameter of the platinum ion. Now, field strength at any particular point is the force exerted on a small test charge at this point. The center of the chloride ion represents the test charge. The electric field strength surrounding a charged sphere at a distance  $r$  is given by  $2e/r^2$ . The field strength surrounding a dipole of moment  $m$  is given by  $2m/r^3$ . Thus,

$$E_A = \frac{2e}{r^2} + \frac{2m_{Pt}}{r^3} \text{ (for divalent platinum)}$$

and

$$E_B = -\left(\frac{d}{r^2} + \frac{2m_{Cl}}{r^3}\right) \text{ (for monovalent chlorine)}$$

where  $r$  is the distance between the centers of the platinum and chloride ions.

For the dipole moments,

$$\begin{aligned} m_{Cl} &\equiv \alpha_{Cl} E_A \\ &= \frac{2\alpha_{Cl}}{r^2} \left( e + \frac{M_{Pt}}{r} \right) \end{aligned}$$

$$\begin{aligned} m_{Pt} &\equiv \alpha_{Pt} E_B \\ &= \frac{2\alpha_{Pt}}{r^2} \left( \frac{e}{2} + \frac{m_{Cl}}{r} \right) \end{aligned}$$

where  $\alpha$  is a constant termed polarizability and from the equation may be defined as induced moment divided by the field strength. Making the necessary substitutions we obtain:

$$\begin{aligned} m_{Cl} &= \frac{2\alpha_{Cl} e}{r^2} \cdot \frac{\left(1 + \frac{\alpha_{Pt}}{r^3}\right)}{\left(1 - \frac{4\alpha_{Cl}\alpha_{Pt}}{r^6}\right)} \\ m_{Pt} &= \frac{\alpha_{Pt} e}{r^2} \cdot \frac{\left(1 + \frac{4\alpha_{Cl}}{r^3}\right)}{\left(1 - \frac{4\alpha_{Cl}\alpha_{Pt}}{r^6}\right)} \end{aligned}$$

The total attracting force is given by

$$F_1 = -eE_A + m_{Cl} \frac{dE_A}{dr}$$

leading to

$$F_1 = -\left[ eE_A + m_{Cl} \left( \frac{4e}{r^3} + \frac{6M_{Pt}}{r^4} \right) \right]$$

The quantities in the expression are either measurable or can be estimated with reasonable accuracy. Thus,

$$\begin{aligned} r &= 2.33 \times 10^{-8} \text{ cm. (sum of the two radii),} \\ \alpha_{Cl} &= 3 \times 10^{-24} \text{ cm.}^3, \\ \alpha_{Pt} &= 1.9 \times 10^{-24} \text{ cm.}^3 \text{ and} \\ e &= 4.8 \times 10^{-10} \text{ E.S.U.} \end{aligned}$$

Substituting these values one obtains:

$$m_{\text{Cl}} = 7.4 \times 10^{-18} \text{ E.S.U. cm.}$$

$$m_{\text{Pt}} = 4.0 \times 10^{-18} \text{ E.S.U. cm.}$$

$$E_{\text{A}} = 2.46 \times 10^6 \text{ E.S.U. cm.}^{-2}$$

Therefore

$$F_1 = -30 \times 10^{-4} \text{ E.S.U.}^2 \text{ cm.}^{-2}$$

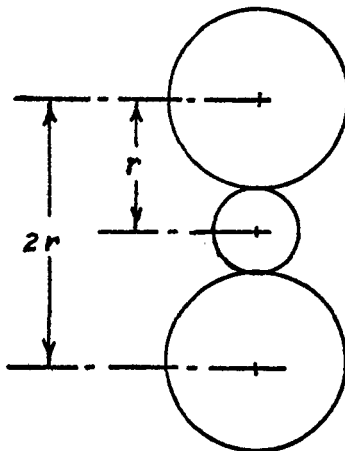


FIG. 3

For the case where we have a *trans* partner (figure 3), consider the upper chloride ion as the test charge and  $E'_{\text{A}}$  the field strength for platinum ion. Here the dipole moment  $m_{\text{Pt}} = 0$ ; therefore

$$E'_{\text{A}} = \frac{2e}{r^2} - \frac{e}{4r^2} - \frac{2m'_{\text{Cl}}}{8r^3}$$

The first term is positive, since it is an attractive term. The second term is due to the repulsive force of the other chloride ion, and hence is negative. The third term is also repulsive and is due to distortion of the second chloride ion. Therefore

$$\begin{aligned} E'_{\text{A}} &= \frac{7e}{4r^2} - \frac{2m'_{\text{Cl}}}{8r^3} \\ m'_{\text{Cl}} &\equiv \alpha_{\text{Cl}} E'_{\text{A}} \\ &= \alpha_{\text{Cl}} \left( \frac{7e}{4r^2} - \frac{2m'_{\text{Cl}}}{8r^3} \right) \\ &= \frac{7e\alpha_{\text{Cl}}}{4r^2} \\ &= \frac{\alpha_{\text{Cl}}}{1 + \frac{\alpha_{\text{Cl}}}{r^3}} \end{aligned}$$

For the total field strength,  $F_2$ , between platinous ion and chloride ion we have:

$$\begin{aligned} F_2 &= -eE'_A + m_{Cl} \frac{dE'_A}{dr} \\ &= -\left[ eE'_A + m'_{Cl} \left( \frac{7e}{2r^3} - \frac{3m'_{Cl}}{4r^4} \right) \right] \end{aligned}$$

Since

$$\begin{aligned} m_{Cl} &= 4.5 \times 10^{-18} \text{ E.S.U. cm.}, \\ E'_A &= 1.5 \times 10^6 \text{ E.S.U. cm.}^{-2}, \text{ and} \\ F_2 &= -13.5 \times 10^{-4} \text{ E.S.U.}^2 \text{ cm.}^{-2} \end{aligned}$$

the ratio

$$\begin{aligned} \frac{F_1}{F_2} &= \frac{-30 \times 10^{-4} \text{ E.S.U. cm.}^{-2}}{-13.5 \times 10^{-4} \text{ E.S.U. cm.}^{-2}} \\ &= 2.2 \end{aligned}$$

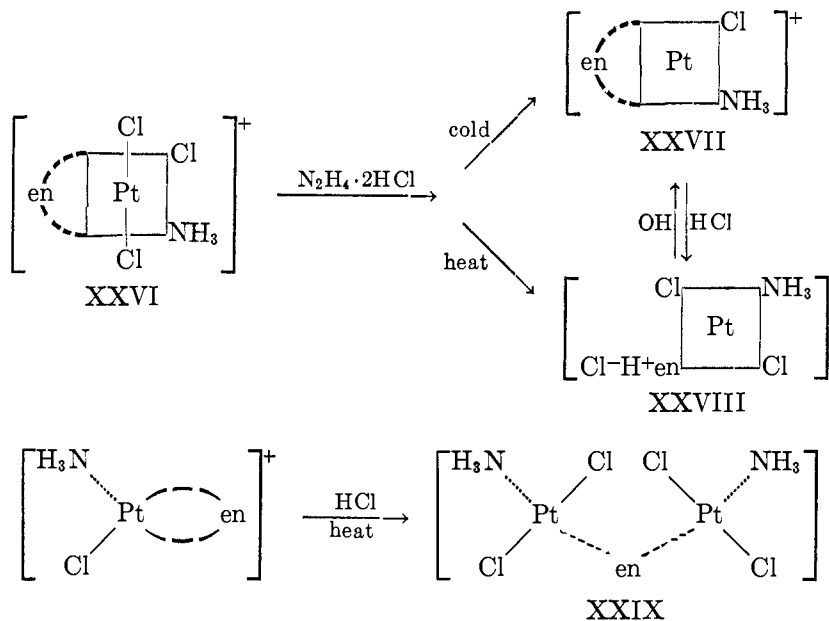
It should be recognized that this ratio assumes the least favorable polarizability for platinous ion. Were the polarizability greater, an even more favorable ratio would result. Now it is true that the assumptions made were not entirely valid. The ionic fields of platinous ion and chloride ion are not homogeneous; also, there are probably exchange forces to consider in addition to those of polarization. Moreover, resonance is not taken into account but is certainly important and is severely decreased by a decrease in symmetry. However, Grinberg was able to estimate the order of magnitude and to show conclusively that the bond with a *trans* partner is weaker than without that partner.

The concept of polarizability gives us several criteria for the existence of the *trans* effect:

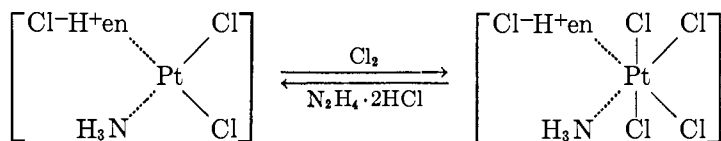
- (a) The *trans* effect can appear only when the central ion is characterized by strong polarization properties.
- (b) The *trans* effect of different coördinating groups is determined by their polarizability.
- (c) The *trans* effect will not only influence the bonding power of groups but also all properties depending upon the degree of polarization. It should be pointed out, however, that since the bonds in platinum(II) complexes are essentially covalent (*dsp*<sup>2</sup>), any idea based solely on polarizability of bonds must be far from complete.

Chernyaev and Fedorova (15) found that reduction of octahedral  $[\text{PtCl}_3(\text{en})(\text{NH}_3)]^+$  with  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$  in the cold produces planar  $[\text{PtCl}(\text{en})(\text{NH}_3)]^+$ . If heat is applied, however, the reduced compound obtained is the nonchelated  $[\text{PtCl}_2(\text{en} \cdot \text{HCl})(\text{NH}_3)]$ . The latter compound can also be obtained slowly by the reaction of the planar chelate complex with hydrochloric acid, with some of the

dinuclear complex,  $[\text{PtCl}_2(\text{NH}_3)(\text{en})(\text{NH}_3)\text{Cl}_2\text{Pt}]$ , also being formed. The reactions are as follows:



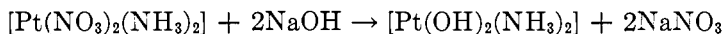
Closure of the ring in **XXVIII** can be easily effected by treatment with alkali or even with pyridine. Oxidation of planar  $[\text{PtCl}_2(\text{en} \cdot \text{HCl})(\text{NH}_3)]$  with chlorine in acid solution gives octahedral  $[\text{PtCl}_4(\text{en} \cdot \text{HCl})(\text{NH}_3)]$ , which on reduction with  $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$  gives the starting planar compound:



Furthermore, when a concentrated solution of  $[\text{Pt}(\text{NO}_2)(\text{en})(\text{NH}_3)]^+$  is heated with hydrochloric acid, the oxidized product  $[\text{PtCl}_4(\text{en} \cdot \text{HCl})(\text{NH}_3)]$  is obtained; with longer heating the ring is closed and  $[\text{PtCl}_3(\text{en})(\text{NH}_3)]\text{Cl}$  is formed. In these transformations the opening of the chelate ring is an example of the *trans* effect. It is likely that the ring opening and proton loss in the presence of a proton acceptor may be explained on the basis of the *trans* effect and its implications of polarizability and dipole moment.

Some interesting and convincing pieces of evidence demonstrating the *trans* effect were obtained through a study of acid and basic strengths of the geometrically isomeric complexes of platinum(II). Grinberg and Ryabchikov (50) pointed out that the degree of dissociation of groups containing a proton, as in  $\text{RH}$ , decreases owing to the influence of a *trans* group, since the latter decreases the field of the central ion and the polarization of the  $\text{RH}$  group. The first dis-

sociation constant of *trans*-[Pt(H<sub>2</sub>O)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>++</sup> is greater than that of the corresponding *cis* complex, since the polarizability (and *trans* effect) of the water is less than that of the ammonia ( $R_{\text{H}_2\text{O}} = 3.71$ ;  $R_{\text{NH}_3} = 5.61$ ). Concerning the second dissociation constants of [Pt(OH)(H<sub>2</sub>O)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, the *cis* complex has a dissociation constant approximately equal to that of the first dissociation constant, since NH<sub>3</sub> is a *trans* partner of H<sub>2</sub>O. In the case of the *trans* complex, however, the dissociation is greatly decreased by the *trans* effect of the hydroxyl group. Furthermore, the hydroxyl group has a strong *trans* effect when *trans* to water in the complex, for in addition to its polarizability, its coulombic forces are significant. Titration of the isomeric bases [Pt(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] with hydrochloric acid shows that the *trans* isomer is a much stronger base and that the difference between the first and second hydroxyl groups is much sharper than in the *cis* base. In terms of the Brønsted definition, the *trans* complex is the stronger base, since the hydroxyl group inhibits the lability of a hydrogen on the hydroxyl group *trans* to it, resulting in an increase in basic properties. Determination of the pH of solutions of the isomeric bases [Pt(OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] shows that the *trans* isomer is the stronger base, especially at higher concentrations (50). Furthermore, the addition of salts containing anions capable of entering the coordination sphere of the *trans* complex causes a decided increase in the alkalinity of the solution. The increase in pH corresponds to the order NO<sub>3</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > Br<sup>-</sup> > CNS<sup>-</sup> > I<sup>-</sup>, with nitrate ion showing the greatest influence. It is interesting to note that the nitrate ion cannot displace the hydroxyl ion but that the reverse reaction



goes to completion and can be used as a quantitative method for the determination of platinum in the complex.

The fundamental equation for the polarizability of a single molecule is

$$m = \alpha E$$

where  $m$  is the electrical moment of the induced dipole (dipole moment) produced by the applied field  $E$  acting on a single molecule, and  $\alpha$  is the polarizability constant. The polarizability of a single molecule is a measure of the ease of displacement of positive and negative charges with respect to each other in an electrical field. If the molecule is not symmetrical, the polarizability or deformability as it may also be called, may vary in different directions. Thus in the case of platinum(II) complexes, major and minor axes of polarization may exist.

The Lorenz-Lorentz equation (42, 135) relates the polarizability,  $\alpha$ , of the atoms of an inert monatomic gas with the refractive index for radiation of infinite wave length:

$$\alpha \equiv \frac{m}{E} = \frac{3}{4\pi N} R_\infty$$

where  $R_\infty$  is the molar refractivity obtained on the basis that the polarizability of hydrogen ion is zero, since this ion consists only of a proton with no extra-

nuclear electrons. This is applicable not only to inert gases but also to ions in solution by determining the refractive index at a series of concentrations and extrapolating to infinite dilution. In this way Grinberg (47) was able to correlate the *trans* effect with the refraction of corresponding groups and found that the extent of polarizability (or the refraction of atoms or ions coordinated to the central ion of a complex) may be taken as a measure of the activity of the *trans* effect. The following listing gives the groups arranged according to effectiveness of *trans* activity, where  $R_\infty$  is the refractivity (41):

Group.....	$\text{ClO}_4^-$	$\text{NO}_3^-$	$\text{SO}_4^{--}$	$\text{H}_2\text{O}$	$\text{NH}_3$	$\text{OH}^-$	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
$R_\infty$ .....	3.30	3.67	3.70	3.71	5.61	5.1	9.0	12.7	19.2

The order agrees approximately with the experimental data and with the sequence of the ability of corresponding groups to form complex compounds with platinum(II) and palladium(II). As indicated above, Grinberg (56) found that the intensity of the *trans* effect in the anion series  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  also increases with molar refraction.

The ligands listed above give reasonably simple reactions and bondings, but relationships may become more complex with other groups. Thus the cyanide ion has a refractive index of 8.66 and should possess a smaller *trans* effect than chloride ion, for example, with its refractive index of 9.0. However, cyanide ion exhibits greater *trans* lability. This is probably partially due to the fact that the cyanide ion is anisotropic and the polarizability about the (coordinating) carbon-nitrogen axis is greater than about the chloride ion. Also, groups which bond through a sulfur atom exhibit a *trans* effect greater than could be expected from the refractive indices of the corresponding groups when referred to the central ion to which they are bound. All of these groups give anomalously large *trans* effects. For thiourea  $R = 22.13$ ; for thiocyanate ion  $R = 17.59$ . If we can assume additivity of refractive indices, we get  $R_S$  (from  $\text{SCN}^-$ ) = 8.93;  $R_S$  (from thiourea) = 10.67. However, these refractivities of the sulfur (which play the role of the bonding agent) are considerably lower than the value of 16 as calculated by Fajans.

Work by Anderson (1), Hel'man (16, 17, 63), and Kharasch and Ashford (79), among others (78), showed that unsaturated ligands such as carbon monoxide and the olefins gave very high *trans* effects. It became apparent that "electron-rich" groups have a very great *trans* influence when they enter the coordination sphere. For example, *cis*- and *trans*- $[\text{PtCl}_2(\text{CO})(\text{NH}_3)]$  were prepared on the basis of the high *trans* effect of the carbonyl group.

Grinberg (47) exploited this idea. He noted that the *trans* effects of ligands are of two general types, depending upon whether or not the coordinating groups have unshared valence electrons. For ions such as chloride, bromide, and iodide, having an inert gas structure, the reducing properties may be associated with their electronegativity, decreasing with electronegativity. In the halogen series iodide ion shows the greatest *trans* influence, with bromide ion more active than chloride ion. Similarly, labilization due to sulfur is greater than that due to oxygen, and that due to phosphorus exceeds labilization due to nitrogen. It is interesting to note, however, that ions of the type  $\text{NO}_2^-$ ,  $\text{SCN}^-$ , and  $\text{S}_2\text{O}_3^{--}$

do not show this property. Instead, for these groups, as well as for neutral "electron-rich" groups of the type of thiourea, ethylene, carbon monoxide, nitric oxide, etc., the reducing power depends mainly on the presence of unused or reserved electrons. This division does not attempt to describe two different mechanisms for reduction, nor can there be a quantitative division. It does point out the fact, however, that unsaturated molecules of the type of ethylene have a greater *trans* influence than do the halogens. In a very real sense the division is artificial, since electronegativity and reducibility are related. Grinberg's conclusion is that a coordinated group exerts *trans* activity because of the presence of labile electrons which can be displaced in the direction of the electron system of the central ion. Once this displacement occurs, polarization of the complex results and a *trans* bond may be loosened.

The electrostatic and polarization approaches, while useful in some instances, are far from correct. The induced dipoles in the central ion, for example, are not sufficiently great to overcome the electrostatic repulsion of two *cis* chlorine atoms. Moreover, this repulsion should labilize *cis* compounds and, in addition, there is much experimental evidence to show that the *trans* effect may be considerable in complexes where polarization is negligible.

Observations of the type that iodide ion is more *trans* labilizing than chloride ion, and that ammonia is more *trans* labilizing than water, suggest that the *trans* effect is greater the less the electronegativity. Also, the less the electronegativity the greater, probably, the covalent character; thus a relationship may exist between covalent character and the *trans* effect. An attack on the ionic or covalent nature of the bonding showed some promise. Yakshin (139) introduced the concept of the "ionic coefficient" or the ratio of total to electronic polarization ( $P/P_E$ ) and found that bonding is more covalent in *trans* than in the corresponding *cis* compounds.

This suggested a quantum-mechanical attack on the problem. It has already been pointed out that Pauling proved the square configuration of platinum(II) complexes by this method. This theoretical argument has been validated through several different techniques; the work of Dickinson (32) was especially clarifying. His x-ray investigation showed that potassium tetrachloroplatinate consists of layers of square complexes alternating with layers of potassium ions. For a structure of this type, and considering the electron configuration of platinum in its normal state wherein each orbital may be occupied either by one electron or by two electrons with opposite spin, it can be shown that bonding must be on the basis of  $dsp^2$  hybridization, resulting in two hybrid covalent bonds at right angles to each other. Syrkin (134) developed this into a satisfying explanation of the *trans* effect, using the theory of directed valences and recognizing that the greatest labilization occurs with those groups *trans* to ligands with the greatest degree of covalent bonding (139).

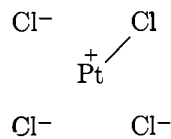
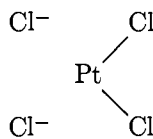
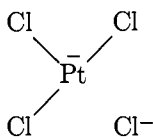
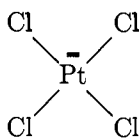
Mellor (92) observed that the study of the magnetic anisotropy of the platinum(II) complexes should be rewarding, and use of this technique again shows the importance of the covalent bond. All of the platinum(II) complexes are diamagnetic, but if the interior sphere contained four chloride ions and one divalent platinum, the platinum would have to give up two free electrons, trans-

forming it into an ion. This makes ionic bonding unlikely. In order to explain the diamagnetism (134), a covalent structure is most reasonable, but for the

TABLE 4  
*Electronic configurations and types of bonding in platinum(II) ions*

ION	ELECTRONIC CONFIGURATION			TYPE OF BONDING
	6d	7s	7p	
Pt <sup>++</sup>				
PtCl <sub>4</sub> <sup>--</sup>				
				<i>dsp<sup>2</sup></i> hybridization; angles = 90°
				<i>dsp</i> hybridization; unsymmetrical plane
				<i>ds</i> hybridization; angle = 90°
				<i>d-orbital</i>

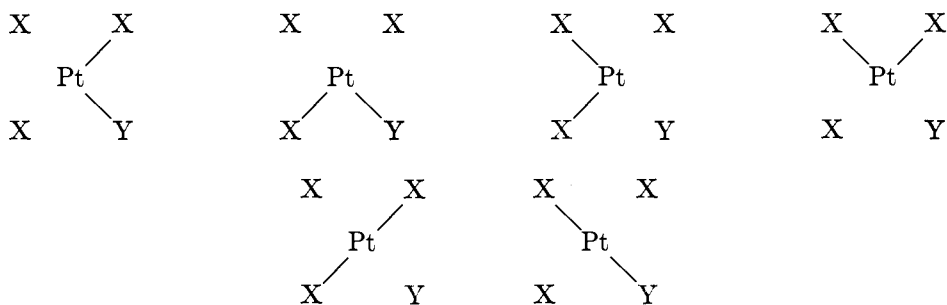
PtCl<sub>4</sub><sup>--</sup> ion, the following structures are compatible with the observed diamagnetism:





The lack of a line in the bonding structure is adopted as a convention to indicate ionic linkage. The last three figures postulate nonequivalence of bonds. The nonequivalence of bonds is now widely accepted in many complexes, but in the  $\text{PtCl}_4^{--}$  ion bonding with all four chloride ions is of equal weight. If a chloride ion is replaced by the ligand  $\text{X}^-$ , the platinum-chlorine and platinum-X bonds become unequal in energy and in covalent character. The electronic configurations of the tetrachloroplatinate(II) ions are given in table 4. The last structure in the table is ruled out, since it indicates that the complex is paramagnetic.

For divalent platinum,  $ds$  valence electrons are available; hence  $ds$  hybridization will result in hybrid covalent bonds at right angles to each other. The restriction that maximum bond strength occurs when the bonds are at right angles is important in consideration of the possible bonding for the internal complex sphere of  $\text{PtX}_3\text{Y}$ :

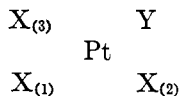


The last two structures are excluded, or at best present to a slight degree, because the bonds are not at right angles. This ability of platinum to give rise to two covalent bonds at right angles must also be correlated with the degree of covalency. It is found that those groups which have the least degree of covalency (the greatest ionic nature) are those which are displaced most readily.

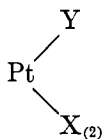
Two cases may be considered for the complex  $\text{PtX}_3\text{Y}$ . In the first case let the  $\text{Pt}-\text{Y}$  bond be more covalent than the  $\text{Pt}-\text{X}$  bond. The four possible structures, excluding other than right-angle bonding, are:



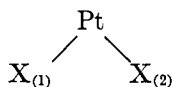
The first two structures involving the strongly covalent  $\text{Pt}-\text{Y}$  bond are the more likely structures, owing to  $ds$  hybridization. This strengthens the covalent nature of the X groups *cis* to the Y and makes the *trans* X groups less covalent. This may be clarified by individual consideration of each X:



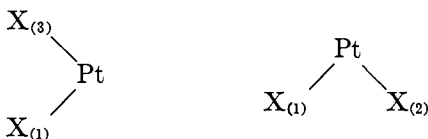
In this formulation  $X_{(2)}$  participates once with the strong covalent bond with Y,



and also once with the weaker covalent bond  $X_{(1)}$ .

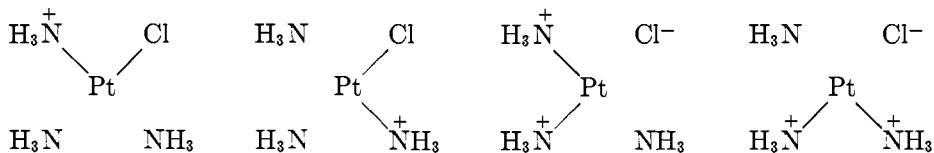


Similarly,  $X_{(1)}$  participates with two weak covalent bonds:



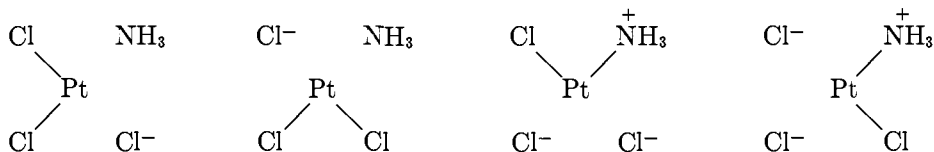
Thus, the  $Pt-X_{(1)}$  bond is less covalent than the other bonds.

These considerations explain Jorgensen's reaction for the complex  $[PtCl(NH_3)_3]^+$ . Here the platinum-chlorine bond is more covalent than the platinum-ammonia bond. The possible structures are:



The first two of these structures are the most likely ones because of the use of the strong platinum-chlorine covalent bond, which in turn strengthens both of the *cis* ammonia groups. In the presence of hydrochloric acid the *trans* ammonia group is labilized and replaced by chloride ion to give *trans*- $[PtCl_2(NH_3)_2]$ .

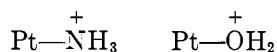
A similar treatment may be given to the complex  $[PtCl_3(NH_3)]^-$ , where the platinum-chlorine bond is again the more covalent. The possible structures are:



Inasmuch as the first two structures do not involve the weaker platinum-ammonia covalent link, they have a higher degree of probability. This in turn means that the three platinum-chlorine bonds are nonequivalent, with the chlorine *trans* to the ammonia bonded to a greater covalent degree, since it participates in two strong covalent bonds. The chlorine ligands *cis* to the ammonia participate in the weaker platinum-ammonia covalent bond and their bonding is not as strong as that which holds the chlorine *trans* to the ammonia. This ex-

plains Peyrone's reaction, with its apparent *cis* elimination. Since the *trans* chlorine ligand participates in two strong covalent structures, its bond is stronger than those which hold the other two chlorine ligands. Therefore it is the *cis* chlorine atoms which are labilized and replaced by ammonia.

Syrkin (134) also considered those factors which determine the degree of covalence of a given bond, since this will affect the tendency towards the *trans* effect. For one type of ligand we have a donor-acceptor relationship, wherein a pair of electrons is donated by one of the atoms (coordinated covalence). As examples of this case we can picture:

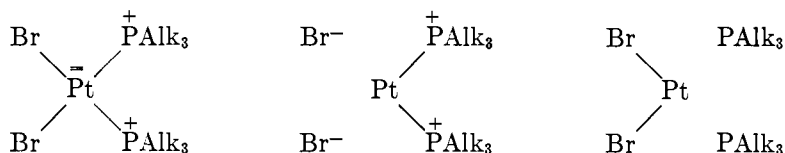


A greater degree of covalence will exist in that case where the unattached pair of electrons is the more readily distributed between the two atoms. It is known that oxygen is more electronegative than nitrogen, attracting electrons more strongly than nitrogen. Consequently the platinum-ammonia bond shows more covalence than the platinum-water bond. Thus, ammonia causes greater labilization of a *trans* group than does water. Similarly, ligands such as  $\text{SAlk}_2$  (where Alk is an alkyl group),  $\text{SC}(\text{NH}_2)_2$ , and  $\text{PAlk}_3$  can be expected to have strong *trans* effects.

It becomes evident, then, that the character of the bond depends upon the negativity (or electronegativity) of the ligand. The degree of covalence increases with decreasing electronegativity, as shown above. Using Mulliken's criterion, as well as ion-potential data, an approximation of electronegativity may be arrived at. When this is not known, the ionization potential for an isoelectric atom may be approximated by the expression,

$$J = az^2 + bz + c$$

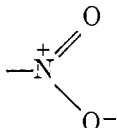
where  $z$  is atomic number and  $a$ ,  $b$ , and  $c$  are constants for any given isoelectric series. As an example of the usefulness of this approach, it is found that platinum and phosphorus are very similar as regards the negative electric charge. This explains Jensen's (70, 71) large dipole moments for *cis*- $[\text{PtBr}_2\{\text{P}(\text{C}_2\text{H}_5)_3\}_2]$  on the basis of the structures



rather than the polar platinum-bromine bond. From this point of view, the ligand  $\text{PAlk}_3$  must strongly labilize groups in the *trans* position. Since sulfur and carbon are only slightly more electronegative than phosphorus, ligands such as  $\text{Alk}_2\text{S}$ , ethylene, propylene, and carbon monoxide should also be strongly *trans* labilizing. This same criterion holds true in any particular series of the periodic table. The electronegative charge decreases in each group of the periodic system from top

to bottom because of the decrease in ionization potential. As an example, iodide ion is the most *trans* labilizing of the halide ions.

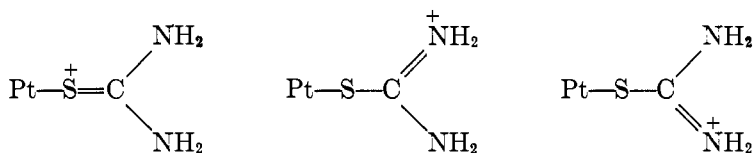
However, the criterion of electronegativity alone is insufficient, since it does not take into account the state of valency. In such cases as the nitro radical,



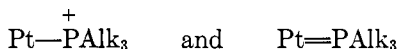
the nitrogen can offer an unpaired electron which can form a purely covalent bond with platinum, resulting in a strong *trans* influence.

Grinberg (46, 47) did not consider resonance in the development of his theory, yet resonance must be important. Of course, any decrease in symmetry will decrease radically the resonance of the structure, and it is known that in structures such as that of potassium tetrachloroplatinate there exists resonance between the ionic and the covalent forms.

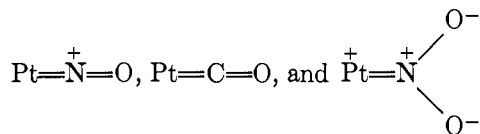
Syrkin (134) explored the relationship of resonance to the *trans* effect. The presence of resonance structures with *d* localization of charge will result in the strengthening of the bond. For platinum-thiourea the resonance structures are:



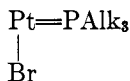
This extra resonance energy adds to the covalent nature of the bond. Similarly, as Pauling (104) has shown, multiple bonding will act in the same direction. The alkyl phosphines may be represented by the formula:



Other possible multiple bond structures are



Thus, structures of the type

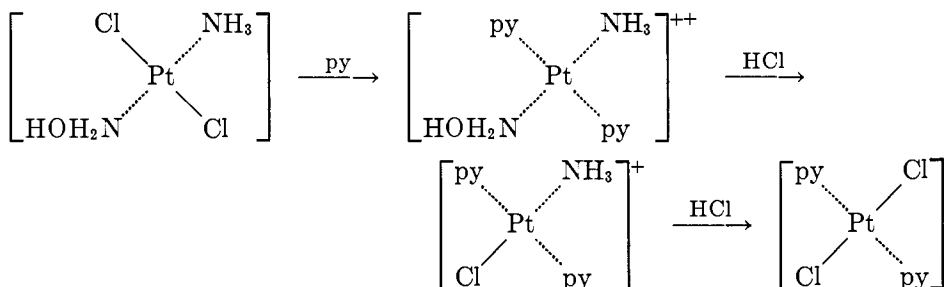


are important for a *trans* effect and the presence of multiple bonds will add to covalent character.

The greater the degree of covalency from any of the causes listed above, the greater will be *cis* stabilization and *trans* labilization, owing to *ds* hybridization and right-angle bonding. It has already been shown how this explains both Pey-

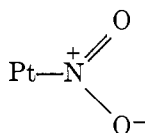
rone's and Jorgensen's reaction. Several other examples are worth discussing.

The following reactions (107), given as a chemical proof for the planar structure of platinum(II) complexes, also demonstrate the operation of the *trans* effect.

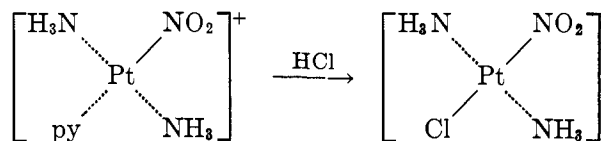


The hydroxylamine is bonded more weakly than the ammonia and is replaced by the chloride ion, which then exerts a strong *trans* effect. Correspondingly, *cis*-[Pt(NH<sub>2</sub>OH)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>++</sup> gives *trans*-[PtCl<sub>2</sub>(NH<sub>2</sub>OH)(NH<sub>3</sub>)] because of the stabilizing effect of chloride ion on its *cis* neighbors.

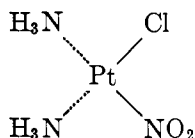
As already pointed out, the nitro group is strongly *trans* directing because of the structure



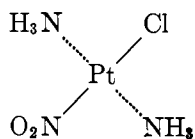
It can therefore be expected to stabilize its *cis* neighbors. Accordingly displacement will occur as follows with this group:



The nitro group is bonded more covalently than the chlorine ligand because of the valence state of the nitrogen atom. Of interest, then, are the reactions undergone by the *cis* and *trans* forms of [Pt(NO<sub>2</sub>)Cl(NH<sub>3</sub>)<sub>2</sub>]. In the *cis* complex

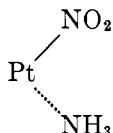


the chlorine atom participates in one structure with the nitro group and in one with ammonia. In the *trans* complex

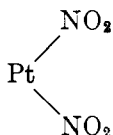


it participates in two structures with ammonia. Since the chloride ion in the *trans* complex does not benefit from hybridization with the more covalent nitro group, as it does in the *cis* complex, it is expected that the chloride ion in the *trans* position should be more labile. Thus, chloride ion may be displaced by ammonia from *trans*-[Pt(NO<sub>2</sub>)Cl(NH<sub>3</sub>)<sub>2</sub>], while the displacement takes place very slowly from the *cis* complex.

Similarly, if we compare *cis*- and *trans*-[Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>], it is evident that in the *trans* combination each nitro ligand participates in two identical structures,

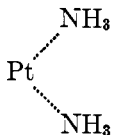


while for the *cis* complex each nitro group participates in one such structure, and in one other structure:



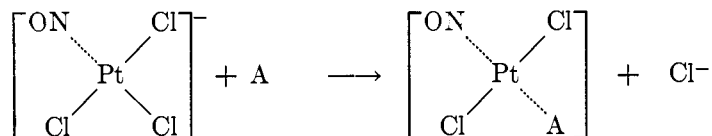
Thus the nitro group in *cis* combination is bonded more strongly. This explains why *trans*-[Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] may eliminate one NO<sub>2</sub><sup>-</sup> in favor of NH<sub>3</sub> or another group. But in the *cis* complex the NO<sub>2</sub><sup>-</sup> ligands are not displaced.

The thiourea (th) reaction may also be satisfactorily explained. The platinum-thiourea bond has a great degree of covalence. In *trans*-[Pt(th)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>++</sup>, each ammonia participates in two structures with thiourea and is stabilized. However, in the *cis* complex there is only one such structure as well as the structure:

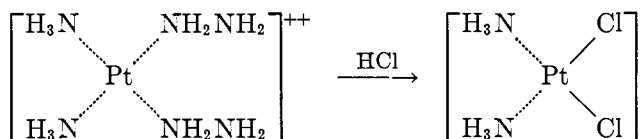


This latter structure is weaker than that which contains a thiourea and therefore when *trans*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] is treated with thiourea, *trans*-[Pt(th)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>++</sup> will result, while the corresponding *cis* complex will give [Pt(th)<sub>4</sub>]<sup>++</sup>. It should be pointed out that in the presence of excess thiourea at elevated temperature, even the *trans* compound yields [Pt(th)<sub>4</sub>]<sup>++</sup>.

The same reasoning can be applied to ligands such as SAlk<sub>2</sub> or PAlk<sub>3</sub>, which form strongly covalent bonds. The work of Hel'man and others on neutral groups such as carbon monoxide, nitric oxide, unsaturated hydrocarbons, etc., is also amenable to treatment. A characteristic reaction is:

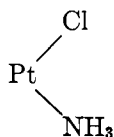


The reaction of Chugaev and Grigor'eva (21) is of especial interest. These authors found that the treatment of *cis*-[Pt(NH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>++</sup> with hydrochloric acid gives the *cis* dichloride:

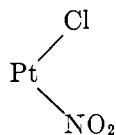


However, at first glance one would expect the *trans* complex to result. Syrkin (134) explains this seeming anomaly in the following way. In the bond Pt—NH<sub>2</sub><sup>+</sup>—NH<sub>2</sub>, one atom of nitrogen remains trivalent and a proton may enter the inner sphere to neutralize the free amino group, giving rise to Pt—NH<sub>2</sub><sup>+</sup>—NH<sub>3</sub>. This weakens the platinum–nitrogen bond, since the strongly positive hydrazine ligand can now attract electrons, and increases the ionic nature of the bond and decreases its covalent nature. Therefore the hydrazine group is bound weakly and may be displaced to give the *cis* complex.

The measure of covalent or ionic bonding determined by the degree of *ds* hybridization, as well as other factors discussed above, explains variations in conductance (19). In *cis*-[PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>] each chloride ion participates in two dissimilar structures, one with another chloride ion and the second with ammonia. In the *trans* complex each chloride ion participates in only one structure, that with two ammonia ligands. Hence the chloride ion in the *cis* complex is bound more covalently than is the chloride ion in the *trans* complex. Therefore the conductance of the *cis* compound should be less than that of the corresponding *trans* complex. Similarly, the *trans* complex gives an immediate precipitate with silver nitrate, while the *cis* complex gives only an opalescence at first. This is demonstrated even more dramatically with *cis*- and *trans*-[Pt(NO<sub>2</sub>)Cl(NH<sub>3</sub>)<sub>2</sub>]. The *trans* compound gives an immediate precipitate with silver nitrate, while the *cis* compound does not even exhibit an initial turbidity. This again is due to the presence of two similar weak structures,



in the *trans* complex, while there is only one of these structures in the *cis* complex in addition to the more strongly stabilizing



The complexes of divalent platinum have been chosen to illustrate the theory of the *trans* effect, because knowledge of these complexes has been more clearly

developed than those of any other metal. The theory is sufficiently well developed so that it becomes a matter of interest to apply it to other complexes. This has been done in only a minor way, though there is ample evidence in favor of the existence of the *trans* effect in these other complexes. Dyatkina (40) has developed these ideas for tetravalent platinum on the basis of  $d^2sp$  bonding.

Examination of the literature shows that an adequate explanation of the *trans* effect has been offered only in the very recent past. A great deal of work, both theoretical and experimental, remains to be done, especially with respect to the study of complexes other than those of divalent platinum. This work should, moreover, be both positive and rewarding, since the problem of the complexes of platinum(II) has been substantially clarified.

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## ADDENDUM

Some fundamental and outstanding work dealing with the *trans* effect has been carried out by Japanese workers but was not available to the authors when the foregoing was written. Of special interest are the extensive studies of absorption spectra of metal coordination compounds by Shibata and coworkers (146; see also 147 and 148). According to Shibata (149), typical metal coordination compounds generally have two absorption bands. The first of these bands lies in the visible region and the second in the ultraviolet. In addition to these two absorption bands, certain metal complexes with negative ligands in *trans* positions have an additional absorption band in the shorter ultraviolet region, designated as a "third band" (146, 151). A much more extensive study of the *trans* effect on the absorption spectrum of metal complexes has been made by Tsuchida and coworkers (151, 152, 155, 156). Tsuchida has shown that a "third band" appears when a pair of negative groups are coordinated in *trans* positions of octahedral or planar complexes (153, 155). The occurrence of a "third band" is independent of (1) the kind and oxidation number of the central ion, (2) the specific nature of the negative *trans* coordinating groups, (3) the charge of the coordination complex, and (4) the configuration of the complex. Thus, cation, anion, and neutral complexes of tetrahedral and planar configurations exhibit a "third

band" (152, 153, 154, 157). The relation between the geometrical configurations of inorganic complexes and their absorption bands has also been studied recently (145, 150).

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