THE STEREOCHEMISTRY OF SQUARE COMPLEXES[1]

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Traditional chemical methods of unravelling questions of molecular structure fail to provide a unique solution to the problem of the structure of bivalent platinum compounds. The various alternative configurations which may be used to explain the phenomena of geometrical and mirror-image isomerism among platinous complexes can be successively narrowed down by different chemical and physical methods of investigation until but one possibility remains—namely, square coördination. The theory of square coördination makes possible the correlation and interpretation of such a large mass of data on the compounds of bivalent platinum and certain other metals that there can be no reasonable doubt of the reality of this type of structure. With the reservation that it applies only to bonds free to arrange, the theory of the directed valence bond makes it clear just what metal atoms are likely to form square bonds.

I. INTRODUCTION

In the design of molecules Nature uses relatively few fundamental units of pattern or configurations, and it is naturally important to know what these are and under what circumstances any particular configuration is likely to be found. We shall here be concerned with the narrow field of stereochemistry which deals with the orientation in space of the four valence bonds of quadricovalent elements. The tetrahedral disposition of four valence bonds about the carbon atom was the first configuration to be discovered, and so widespread did its occurrence eventually prove to be, not only among the compounds of carbon, where it was universal, but also among some forty other elements, that attention to this type of structure long overshadowed that given to an alternative arrangement of four bonds in space—namely, the square arrangement. Indeed, the tetrahedral arrangement proved to be so dominant a feature of molecular architecture that the very existence of the square pattern was,—and, for that matter, in some quarters still is,—a matter of controversy. Nevertheless the evidence on this question has grown steadily over the last few years and the time is opportune for some attempt to evaluate the significance of the square configuration for the stereochemistry of the metals.

In attempting to do this, two main questions will be considered: firstly, how strong is the evidence for the square disposition of valence bonds, and secondly, with what elements and under what circumstances does it occur? In tracing the developments leading to the proof of square coördination, attention will be centered on the compounds of platinous platinum (Pt^{II}), because it is with these that the most abundant and satisfactory evidence has been obtained. Notwithstanding this, there has been a good deal of controversy about the structure

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[1] This article is based largely on the Presidential Address to the Royal Society of New South Wales, April 1, 1942.

of platinum compounds. Some idea of the controversial nature of this field may be gathered from a few excerpts, chosen at random, from the recent literature:

> "Platinum salts combine with an enormous number of inorganic and organic groups or molecules and many of these salts have been known for a hundred years, yet the constitution of the isomeric diammines of the type $[PtA_2X_2]$ is still a subject of controversy" (17).
>
> "It is still an open question whether the experimental work (relating to planar and tetrahedral structures) has been correctly interpreted or not or whether some elements can assume more than one structure" (5).
>
> "In any event, the problem presented by these salts (certain allegedly optically active platinous salts) does not seem to be finally cleared up" (135).

Although, in a certain sense, no scientific problem is ever cleared up, there is reason to believe that the main outlines of the stereochemistry of bivalent platinum are well established and it is hoped to show that the issues raised in these quotations have now been largely settled.

II. THE DISCOVERY OF THE SQUARE CONFIGURATION

It is not surprising that the square configuration was first discovered among the compounds of Pt^{II}, because, as we now know, no other element forms so many compounds which exhibit isomerism on account of this stereochemical characteristic. The two substances primarily concerned with the development of our knowledge in this field,—namely, the α- and β-forms of dichlorodiammineplatinum, $[Pt(NH_3)_2Cl_2]$,—were discovered nearly a century ago, the former by Peyrone (123) and the latter by Reiset (133).[2]

The methods used in their preparation involve two similar processes; the α-compound is made by replacing two chlorine atoms of the $[PtCl_4]^{--}$ ion with ammonia molecules, the β-form by replacing two ammonia molecules of the $[Pt(NH_3)_4]^{++}$ ion with chlorine atoms. The latter operation is effected either by heating solid $[Pt(NH_3)_4]Cl_2$ under carefully controlled conditions or by treating the aqueous solution with concentrated hydrochloric acid; the former, by treating K_2PtCl_4 with aqueous ammonia. There is little doubt that each of the above substitutions proceeds stepwise:

$$[PtCl_4]^{--} \xrightarrow{NH_3} [Pt(NH_3)Cl_3]^{-} \xrightarrow{NH_3} \underset{\alpha}{[Pt(NH_3)_2Cl_2]^{\circ}}$$

$$[Pt(NH_3)_4]^{++} \xrightarrow{Cl^-} [Pt(NH_3)_3Cl]^{+} \xrightarrow{Cl^-} \underset{\beta}{[Pt(NH_3)_2Cl_2]^{\circ}}$$

The intermediate compounds have been isolated and each step has been carried out separately.

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[2] Since the discovery of these compounds, considerable confusion has arisen in regard to their names. They were first known as the chlorides of Peyrone and of Reiset, respectively, and later as plato semi-diammine and platosammine chloride. In 1893 Werner introduced the terms α and β; finally, Drew and his collaborators, for no very good reason, reversed the usage of α and β. In this article Werner's nomenclature will be retained.

The problem of explaining the existence of the α- and β-compounds resolves itself, as a first step, into deciding whether they are (*a*) isomers (structural or geometrical), or (*b*) polymers, or (*c*) dimorphs. These alternatives, though not explicitly formulated by the earlier workers, can, as a result of their work, be narrowed down. The last was eliminated first. Cleve (22), a very active early worker in this field, clearly established the different chemical behavior of the α- and β-forms of $[Pt(NH_3)_2Cl_2]$. By treating each form with a series of reagents, including the appropriate silver salts, he prepared and described new (isomeric) compounds such as the α- and β-forms of $[Pt(NH_3)_2Br_2]$, $[Pt(NH_3)_2I_2]$, $[Pt(NH_3)_2(CN)_2]$, $[Pt(NH_3)_2(NO_3)_2]$, and $[Pt(NH_3)_2(NO_2)_2]$.

Although this and later work leaves no doubt that the α- and β-forms are not just simply different crystalline modifications of the same substance, it is interesting to note recent confirmation along physical lines. Dimorphous molecular crystals contain the same molecules packed in different ways, so that when each crystal structure is broken down by solution in any given solvent, the resulting solutions should be identical, a point which can, for example, be tested by an examination of absorption spectra (105). Small, but definite, differences have been noted in the absorption spectra of the aqueous solutions of the α- and β-forms of $[Pt(NH_3)_2Cl_2]$ (4). There is little doubt that, had chemical and physical tests along these lines been carefully applied, many of the issues created by the announcement of an alleged third (γ) form of $[Pt(NH_3)_2Cl_2]$ (43) would have been avoided.

If we make the assumption that the coördination number of Pt^{II} is four,[3] and experience has shown this to be practically universal, the number of polymers of the empirical composition $[Pt(NH_3)_2Cl_2]_x$ is, for $x > 1$, limited to the following:

1. $[Pt(NH_3)_4][PtCl_4]$ (88)
2. $[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ (122, 124)
3. $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ (23)
4. $[Pt(NH_3)_3Cl]^{-}_{2}[PtCl_4]$ (22)

The α- and β-diammines are distinct from all of these. Anticipating the discussion in a subsequent section, one may add that, with one rather puzzling exception, molecular-weight measurements on α- and β-forms of compounds of the type $[PtA_2X_2]$ (where A = NH_3, pyridine, $C_2H_5NH_2$, etc., and X = Cl, Br, CNS, OH, etc.) show that both forms are monomeric.

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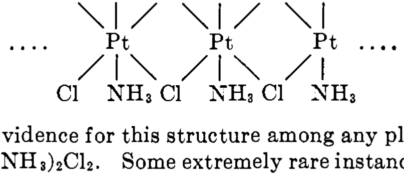
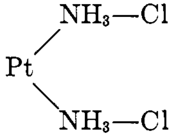
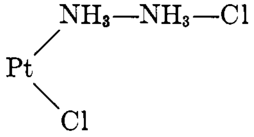
[3] Unless this limitation is specified it would be necessary to consider a structure like:



There is, however, no evidence for this structure among any platinous compounds of the empirical composition $Pt(NH_3)_2Cl_2$. Some extremely rare instances were Pt^{II} may possibly be octahedrally coördinated will be referred to later.

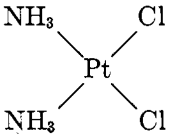
With the elimination of the possibilities (*b*) and (*c*)—polymerism and dimorphism, respectively—the problem now resolves itself into deciding whether the α- and β-diammines are structural or geometrical isomers. One of the first attempts to understand their constitution was made by Cleve (22), who proposed structures which, in the light of the then prevailing theories of valency, seemed plausible enough. They were:

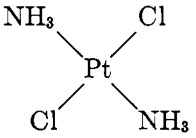

α


β

These formulations, which were also supported by Blomstrand, Jorgensen, and others, implied, of course, that the substances were structural isomers. With present-day knowledge of atomic structure, which enables an upper limit to be placed on the number of covalent bonds that can be formed by first-row elements of the Periodic Table, these structures can be ruled out immediately, since they both involve five covalent bonds to nitrogen. As will appear in the sequel, there are many other reasons for rejecting them. Nevertheless some attempt was made to revive them a few years ago (43) and they are occasionally still seriously discussed in the literature. The revival was the result of an attempt to explain certain reactions of the two compounds but, without going into detail, it can be stated that all these reactions can equally well be explained on an alternative view of their constitution.

While Cleve's formulations of the two compounds are no longer tenable, they served a very useful purpose in focusing attention on the problem of their constitution. Some fifteen years after Cleve's work, Jorgensen (77) set out to determine experimentally whether the assignment of the structures to the α- and β-forms as above had been correct, and in so doing he laid the experimental foundation upon which one of the most important advances in our knowledge of the structure of platinous compounds was made. This was Werner's introduction of the hypothesis of square coördination. Rejecting all previous explanations in terms of structural isomerism, Werner (152) applied to the problem the principles which he so successfully used to account for the constitution of the cobaltic ammines. Realizing that, unlike cobaltic ammines, which were universally characterized by a coördination number of six, the compounds of platinous platinum were always four coördinated, he put forward the idea that the α- and β-diammines were geometrical isomers (*cis* and *trans*), owing their existence to a planar distribution of the four bonds about the platinum atom, as shown below:


α(*cis*)


β(*trans*)

With regular tetrahedral bonds from platinum, two isomeric diammines are not possible. Although it would seem that Werner never at any time explicitly stated that the coplanar bonds were directed towards the corners of a square, it is clear from the diagrams of his classical 1893 paper that he considered them to be so directed. He never stressed the size of the bond angles in the plane, presumably because it was not essential in explaining the geometrical isomerism. Actually, the term "*square* coördination" was first used by Pauling (117) in connection with his quantum-mechanical treatment of the directed valence bond.

Strictly speaking, any one of a number of structures would equally well account for the geometrical isomerism of the α- and β-dichlorodiammines. The four bonds from platinum might be directed towards: (*a*) the corners of a tetragonal or rhombic bisphenoid (figure 1a shows the former); (*b*) and (*c*) the corners of a square (figure 1b) or a rectangle (figure 1c); (*d*) the corners of a tetragonal or rhombic pyramid (figure 1d shows the former). Each one of these alternatives has been introduced from time to time to explain the results of some chemical investigation. Thus, the structure shown in figure 1a was discussed by Rosenheim and Gerb (38) in explaining the existence of certain supposedly optically active platinous and palladous complexes. Drew and his collaborators (44) appear to have had the configurations shown in figures 1a and 1c in mind when formulating the hypothesis of paired coördination links to account for the structure of certain tetrammines. The pyramidal structure, figure 1d, was suggested by Dwyer and Mellor (45) as a means of reconciling results of certain experiments on mirror-image and geometrical isomerism.

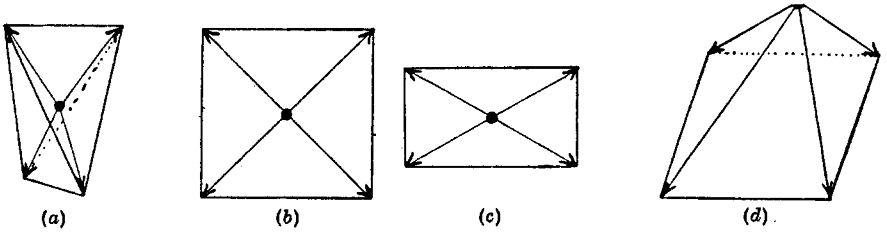


FIG. 1. Possible structures to account for the geometrical isomerism of the α- and β-forms of dichlorodiammineplatinum.

It does not seem to have been widely realized that the results of purely chemical methods of investigation (study of composition, isomerism, reactions, etc.) fail to provide a unique solution to the problem of the structure of platinous compounds and that herein lies the origin of much of the controversy in this field. To distinguish between the alternative structures (figure 1, a to d) it is necessary to have some information about the sizes of the angles between the four platinum bonds. Since the phenomena of geometrical and mirror-image isomerism depend primarily on molecular symmetry, they reveal nothing about the dimensions of bonds or the sizes of the angles between them. For optical activity to appear in the molecule $CR_1R_2R_3R_4$, all that is necessary is that the bonds have a general tetrahedral orientation; there is no need for the angle of the bond

R_1—C—R_2 to be 109°28′,—it might be 140° or more. Similarly, the existence of *cis* and *trans* isomerism among platinous compounds cannot be used to draw any inferences about the size of bond angles; any one of the above models might equally well be used to account for the geometrical isomerism. In view of the impasse which confronts the chemical method, it would perhaps be more logical to pass on to physical methods of studying the problem. This course will not be followed, partly for historical reasons and partly because, although the chemical evidence does not permit a single unequivocal choice, it does allow the alternatives to be narrowed down. This last can be achieved by combining the evidence from the study of geometrical and of mirror-image isomerism. To avoid unnecessary repetition of qualifying statements, the correctness of Werner's hypothesis will be assumed in the following sections dealing with geometrical isomerism.

III. GEOMETRICAL ISOMERISM

A. THE DETERMINATION OF THE CONFIGURATION OF THE DIAMMINES

Having decided that the α- and β-diammines were geometrical isomers, Werner went a step further and by very ingenious reasoning determined which of the two forms was *cis* and which *trans*. The reactions concerned, first studied in detail by Jorgensen (77), may be summarized under two headings:

1. Addition reactions

When treated with two molecules of pyridine, α-dichlorodiammineplatinum forms α-diamminedipyridineplatinous chloride. This latter compound can also be prepared by treating α-dichlorodipyridineplatinum with two molecules of ammonia:

$$\begin{tikzcd}
\underset{\alpha}{[Pt(NH_3)_2Cl_2]} + 2py \arrow[dr] & \\
& \underset{\alpha}{[Pt(NH_3)_2(py)_2]Cl_2} \\
\underset{\alpha}{[Pt(py)_2Cl_2]} + 2NH_3 \arrow[ur] &
\end{tikzcd} \qquad (1)$$

Similar reactions are observed with β-dichlorodiammineplatinum:

$$\begin{tikzcd}
\underset{\beta}{[Pt(NH_3)_2Cl_2]} + 2py \arrow[dr] & \\
& \underset{\beta}{[Pt(NH_3)_2(py)_2]Cl_2} \\
\underset{\beta}{[Pt(py)_2Cl_2]} + 2NH_3 \arrow[ur] &
\end{tikzcd} \qquad (2)$$

2. Elimination reactions[4]

When the solids are heated alone or aqueous solutions of them are warmed with concentrated hydrochloric acid, the α- and β-tetrammines revert to the

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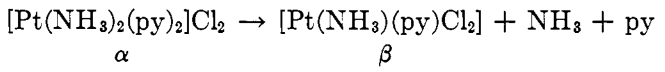
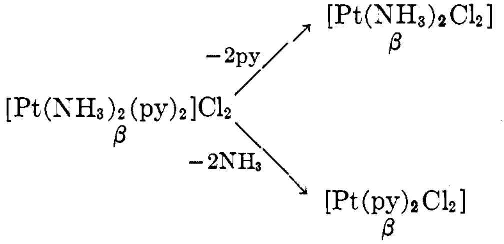
[4] These reactions might also be called substitution reactions if we regard them from the point of view of the complexion only. The names have been used in reference to the molecules as a whole.

dichlorodiammines. Thus α-dipyridinediammineplatinous chloride, when heated, reverts to β-dichloropyridinemonammineplatinum:



$$\underset{\alpha}{[Pt(NH_3)_2(py)_2]Cl_2} \rightarrow \underset{\beta}{[Pt(NH_3)(py)Cl_2]} + NH_3 + py \qquad (3)$$

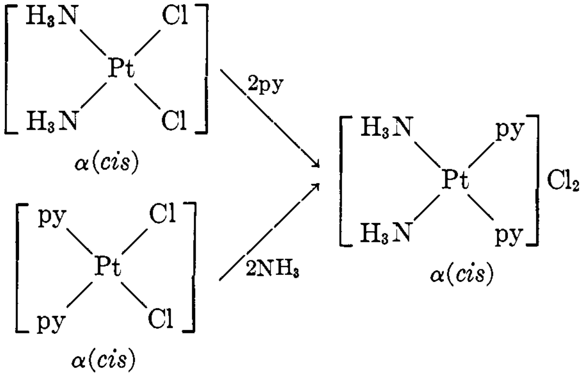
On the other hand, β-dipyridinediammineplatinous chloride gives rise to a mixture of β-dichlorodiammineplatinum and β-dichlorodipyridineplatinum:

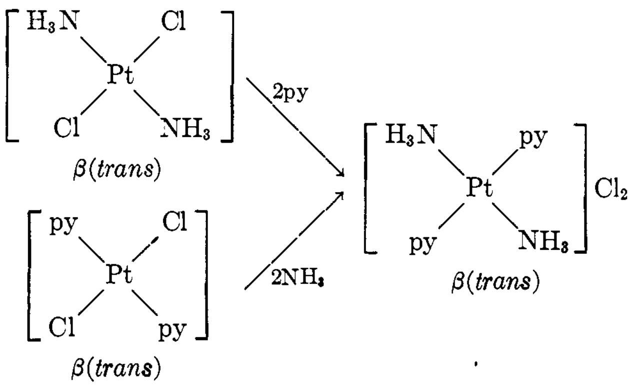


$$\begin{tikzcd} & \underset{\beta}{[Pt(NH_3)_2Cl_2]} \\ \underset{\beta}{[Pt(NH_3)_2(py)_2]Cl_2} \arrow[ur, "-2py"] \arrow[dr, "-2NH_3"'] & \\ & \underset{\beta}{[Pt(py)_2Cl_2]} \end{tikzcd} \qquad (4)$$

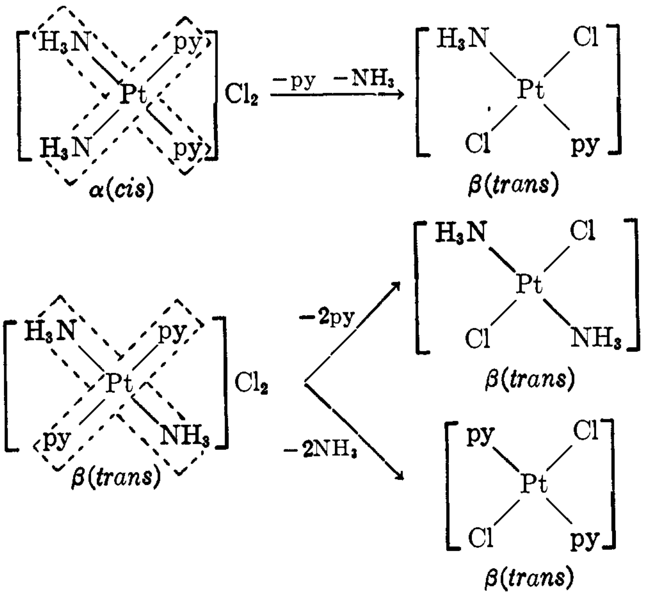
The last reaction has been queried by Reihlen and Nestle (131), but the experimental work of Jorgensen (77) and of Drew *et al.* (44) shows that the reaction which takes place is the one formulated. The products were separated by fractional crystallization and identified by preparing distinctive derivatives. All other addition and elimination reactions have been checked by Drew *et al.*, who used them, not to confirm Werner's hypothesis, but as a basis for the hypothesis of paired coördination links. Suffice it to say that the experimental foundation upon which Werner built his "configuration determination" has stood the test of time.

Whereas Jorgensen was forced to introduce several arbitrary assumptions to account for the above reactions in terms of structural isomerism, Werner was able to account for them in a perfectly straightforward manner with the help of only one further assumption, *viz.*, "*trans* elimination." Werner pictured reactions 1 to 4 as proceeding in the following manner:





In attributing the *cis* structure to the α-compound and the *trans* structure to the β-compound as above, Werner's final conclusions have been anticipated. His argument in support of this assignment is based on the assumption that, in the course of the elimination reactions, pairs of groups in *trans* positions only, are removed. The results of *trans* elimination are made clear in the following diagrams where the dotted lines enclose the eliminated *trans* pairs:



An examination of the structure of α(*cis*)-dipyridinediammineplatinous chloride will show that elimination of pairs of *cis* groups should result in the formation of a mixture of three compounds, *viz.*, $[Pt(NH_3)_2Cl_2]$, $[Pt(py)_2Cl_2]$, and $[Pt(py)(NH_3)Cl_2]$, whereas actually only one, the last, is obtained. On the other hand, *cis* elimination from the β(*trans*)-dipyridinediammine complex should result in the formation of only one compound, *viz.*, $[Pt(py)(NH_3)Cl_2]$; actually two are found, $[Pt(py)_2Cl_2]$, and $[Pt(NH_3)_2Cl_2]$. If we accept the hypothesis of *trans* elimination, all the reactions find consistent interpretation in terms of a *cis* structure for α-[Pt$(NH_3)_2Cl_2$] and a *trans* structure for β-[Pt$(NH_3)_2Cl_2$].

Such then is the experimental foundation upon which Werner, duly acknowledging his debt to Jorgensen, built the planar hypothesis. Yet nearly forty years later, protagonists of the view that the diammines were structural isomers charged Werner with "ignoring the relevant chemical evidence of his predecessors" when dealing with this problem (2).

Perhaps the only weakness in the interpretation of the elimination reactions is that at one stage (elimination from the α(*cis*)-[Pt$(py)_2(NH_3)_2Cl_2$)] it depends on a negative result,—failure to find more than one compound. It is a striking tribute to Werner's remarkable insight into the structure of coördination compounds that all subsequent determinations of the configuration of α- and β-dichlorodiammineplatinum have proved the correctness of his assignment of *cis* and *trans* structures, and at the same time justified his hypothesis of *trans* elimination —at least for these reactions.

B. FURTHER CHEMICAL EVIDENCE CONFIRMING WERNER'S ALLOCATION OF CONFIGURATIONS

With the exception of results from dipole-moment studies and from one or two incomplete x-ray crystal analyses, confirmation of Werner's work on configuration has been obtained along chemical lines.

In the course of extensive investigations of "ammoniacal platinum bases," Cleve (22) reported a very interesting difference in the behavior of the α- and β-forms of [Pt$(NH_3)_2(NO_3)_2$] towards oxalic acid solution: the α-form was converted to a compound with the empirical composition [Pt$(NH_3)_2C_2O_4$]; the β-form to a compound with the composition [Pt$(NH_3)_2(C_2O_4H)_2$]. Some sixty years later Grünberg (60) confirmed these observations and first suggested their interpretation. In doing so he made use of a method developed by Werner in his study of *cis–trans* configurations among the octahedral complexes of Co^{III}. Thus, Grünberg proceeded on the assumption that the $C_2O_4^{--}$ group acted as a bidentate chelate only when it replaced two NO_3 groups in *cis* positions; when it replaced NO_3 groups in *trans* positions, the oxalic acid molecule occupied one coördination position. It is clearly sterically impossible for the $C_2O_4^{--}$ group to span *trans* positions if square bonding is to be maintained.[5]

Since the oxalate group enters α-[Pt$(NH_3)_2(NO_3)_2$] as a bidentate chelate, this form obviously has the *cis* configuration.

Now α-[Pt$(NH_3)_2(NO_3)_2$] is prepared by treating the corresponding (α) chloro compound with silver nitrate, and if it be assumed that the substitution of NO_3 for Cl occurs without change of configuration, then α-[Pt$(NH_3)_2Cl_2$] must also be a *cis*-form, in agreement with Werner's contention. That no change of configuration does occur is shown by the behavior of the oxalato compounds towards hydrochloric acid: the oxalato compound made from *cis*-[Pt$(NH_3)_2(NO_3)_2$] regenerates *cis*-[Pt$(NH_3)_2Cl_2$], while the second oxalato compound regenerates

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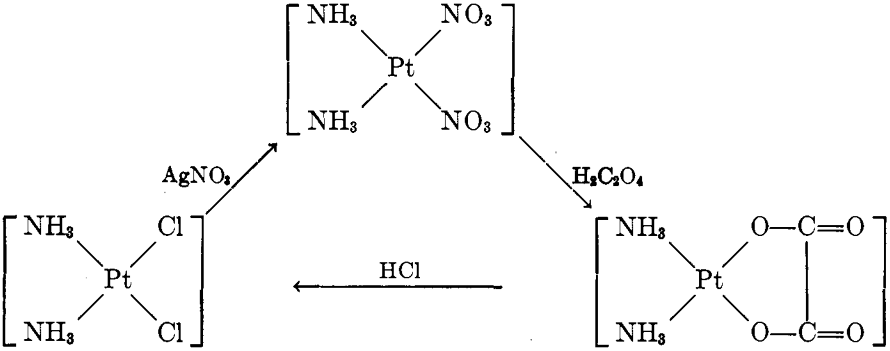
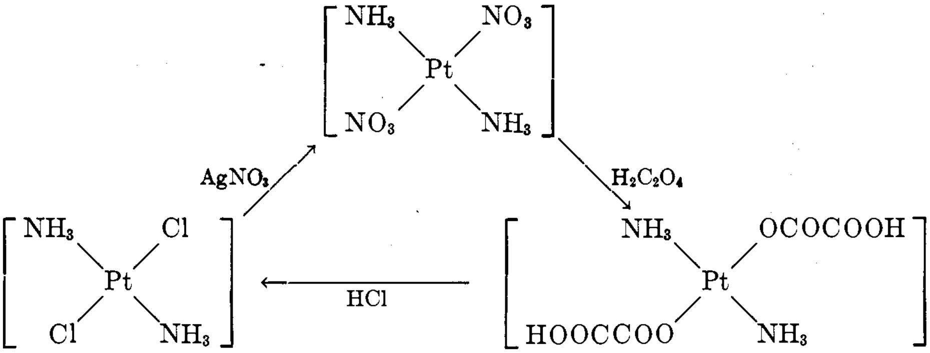
[5] The existence of the so-called *trans*-Pt$(py)_2SO_4$ would seem to be an exception to this statement. The compound is, however, a dihydrate and is probably [Pt$(py)_2(H_2O)_2$]SO_4.

the *trans*-dichloro compound. These reactions may be represented schematically:

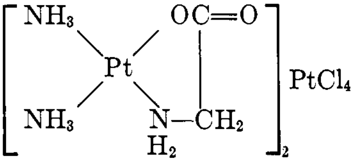


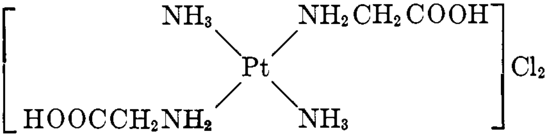


A very similar cycle of reactions has been carried out with α(*cis*)-$[Pt(py)_2Cl_2]$ (43).

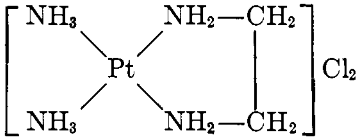
$$\begin{tikzcd}
 & {[Pt(py)_2(OH)_2]} \arrow[dr, "H_2C_2O_4"] & \\
{[Pt(py)_2Cl_2]} \arrow[ur, "Ag_2O"] \arrow[rr, shift left, "Ag_2C_2O_4"] & & {[Pt(py)_2C_2O_4]} \arrow[ll, shift left, "HCl"]
\end{tikzcd}$$

Cis(α)-$[Pt(py)_2Cl_2]$ also reacts with dipyridyl (dipy) to form $[Pt(py)_2dipy]Cl_2$ (114), whereas prolonged boiling of the *trans*(β)-form with alcoholic dipyridyl solution produces no detectable reaction (98). Passing reference only can be made to other work on the configuration of the dichlorodiammines; further confirmatory evidence is to be found in Grünberg and Ptizyn's (61) work on glycine complexes



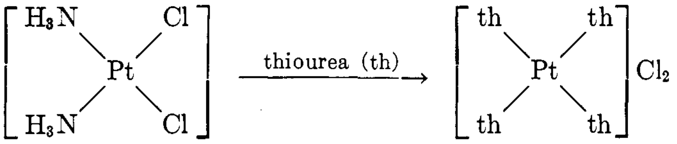


and also in some work by Drew (41), who has shown that α(*cis*)-$[\mathrm{Pt(NH_3)_2Cl_2}]$ reacts with ethylenediamine to form $[\mathrm{Pt(NH_3)_2(NH_2CH_2CH_2NH_2)}]\mathrm{Cl_2}$,

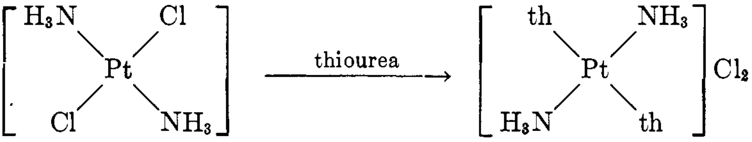


whereas no reaction occurs with the *trans*-form.

Another method of discriminating between *cis*- and *trans*-$[\mathrm{PtA_2X_2}]$ complexes depends on Kurnakow's (82) test, which is based on the reactions:



α(*cis*)



β(*trans*)

These reactions, in themselves, tell one nothing about structure in the sense that the ring-closure reactions do. Kurnakow's test has been very frequently used by Russian workers for deciding on the structure of platinous ammines. It would be interesting to know how widely applicable the test is, and it would be worth while to check it against other substances of known configuration, such as the thioether, stibine, arsine, and phosphine derivatives, described by Jensen (71, 73).

C. RELIABILITY OF THE CHEMICAL METHOD OF DETERMINING CONFIGURATION

A check on the reliability of the chemical method is afforded by dipole-moment measurements, which will be dealt with more fully in a subsequent section. Suffice it to say here that confirmatory evidence from this source has been obtained with *trans*-$[\mathrm{Pt(py)_2Cl_2}]$ and with both forms of $[\mathrm{Pt((C_2H_5)_2S)_2Cl_2}]$. The reactions of α-$[\mathrm{Pt((C_2H_5)_2S)_2Cl_2}]$[6] reported by Angell *et al.* (2) show that it has a *cis* structure; the measured dipole moment of the compound bears this out. Dipole-moment measurements could not, unfortunately, be extended to the ammonia complexes, owing to their limited solubility in non-polar solvents.

One interesting point emerges from all this work and that is the remarkable stability of the configuration of platinous ammines, a circumstance which has greatly facilitated their study. There is no evidence that rearrangement of atoms or groups relative to one another occurs in a dichlorodiammine during

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[6] This compound is referred to as the β-form by Angell and his collaborators.

chemical reaction, that is, a *trans*-compound retains its *trans* configuration through a series of reactions.[7] As Wells (150) has shown in his study of the structure of $Ag[Co(NH_3)_2(NO_2)_4]$, this constancy of configuration is not characteristic of all complexes. It is certainly not characteristic of square palladous complexes which, for some reason as yet unknown, are not as robust, in this sense, as those of platinous platinum.

D. MOLECULAR-WEIGHT DETERMINATIONS ON PtA_2X_2 COMPLEXES

Although all the possible polymeric forms of compounds with the empirical composition $Pt(NH_3)_2Cl_2$ have already been discussed, it is necessary to refer to this topic once again, because one of the first criticisms of the theory of square coördination originated in some work on molecular-weight determinations.

TABLE 1

Molecular weights and melting points of platinous compounds of the type $[PtA_2X_2]$

Jensen (71)

SUBSTANCE	MELTING POINT	MOLECULAR WEIGHT	
		Found	Calculated
	°C.		
trans-$[PtCl_2(Et_2Se)_2]$	60.0	549.0	540.7
cis-$[PtCl_2(Et_2Se)_2]$	74.0	618.0	540.7
trans-$[PtCl_2(Pr_2S)_2]$	80.0	531.0	502.5
cis-$[PtCl_2(Pr_2S)_2]$	85.0	598.0	502.5
trans-$[PtCl_2(Bu_2S)_2]$	60.0	564.0	558.4
cis-$[PtCl_2(Bu_2S)_2]$	84.5	612.0	558.4
trans-$(PtCl_2(i\text{-}Bu_2S)_2]$	110.0	538.0	558.4
cis-$[PtCl_2(i\text{-}Bu_2S)_2]$	138.5	672.0	558.4

Et = ethyl; Pr = propyl; Bu = butyl; *i*-Bu = isobutyl.

From a careful study of the vapor-pressure lowering in liquid ammonia solutions, Reihlen and Nestle (131) showed that *trans*-$[Pt(NH_3)_2Cl_2]$ was dimeric in that solvent. At the same time they showed that both forms (*cis* and *trans*) could be recovered unchanged from liquid ammonia and proved their technique by measurements on known substances. As the authors themselves point out, the dimerism of the *trans*-form does not prove the square hypothesis false. In spite of this and the fact that Fritzmann (53) had shown that both forms of $[Pt\{Se(C_5H_{11})_2\}_2Cl_2]$ were monomeric, Reihlen was so convinced that Werner's interpretation of the structures of the diammines was incorrect that he began a long series of experiments on optical activity, and eventually became one of the chief opponents of the theory of square coördination.

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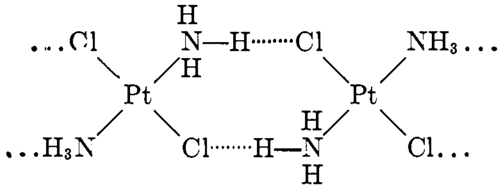
[7] This is, of course, not true of all platinous complexes; it has been reported, for example, that interconversion of *cis*- and *trans*-forms of various thioether complexes occurs quite readily (2).

An ebullioscopic determination of the molecular weight of *trans*-$[Pt(NH_3)_2Cl_2]$ in aqueous solution, admittedly not very accurate (43), shows it to be monomeric in this solvent. King (80) has shown that the molecular weights of both forms of $[Pt(NH_3)_2(OH)_2]$ are normal in aqueous solution. As far as other compounds of the type $[PtA_2X_2]$ are concerned, there is plenty of evidence that both isomeric forms possess normal molecular weights. One may cite the work of Hantzsch (63) on α- and β-$[Pt(py)_2Cl_2]$, of Grünberg (59) on α- and β-$[Pt(NH_3)_2(CNS)_2]$, of Angell *et al.* (2) on α- and β-$[Pt((C_2H_5)_2S)_2Cl_2]$, and finally the very extensive series of measurements by Jensen (71) on a wide range of thioether complexes (table 1). All this work leaves no doubt that the *cis*- and *trans*-compounds are monomeric in the solvents used. In Jensen's work there is some evidence of association of the *cis*-forms, but only to a small degree and in keeping with what one would expect from their higher dipole moment. It is interesting to note, too, the effect of the dipole moments on melting points; of the two, the *cis*-form melts at the higher temperature.

The problem of the dimerism of *trans*-$[Pt(NH_3)_2Cl_2]$ in liquid ammonia still remains. If dipole moment were the principal factor determining association, one would expect the *cis*-form to be the one more associated. Any mechanism of association involving weak hydrogen bonds should operate with both isomers and might reasonably be expected to cause association beyond the dimer stage:



All that can be said at present is that the association of the *trans*-form in liquid ammonia is peculiar to this isomer and to this particular solvent, and, while inexplicable at the moment, it does not weaken the theory of square coördination. The importance of the work of Reihlen and Nestle lies not so much in the peculiarity of the results obtained as in the stimulus it gave to work on the optical activity of platinous compounds, to which we shall now turn.

IV. THE MIRROR-IMAGE ISOMERISM OF PLATINOUS COMPOUNDS

If two unsymmetrical chelate groups such as isobutylenediamine are tetrahedrally coördinated to a central metal atom, the resulting complex may exist in mirror image (figure 2a) but not *cis–trans* forms. On the other hand, if the chelate groups are coplanar, the complex may exist in *cis–trans*, but not mirror-image forms (figure 2b). Finally, if Pt^{II} forms pyramidal bonds, both geometrical (*cis–trans*) and mirror-image isomerism are possible; of the geometrical isomers, the *trans*-form only is capable of existing in mirror-image isomers. Over a number of years, Reihlen and his collaborators, working with various unsymmetrical chelate molecules (see figure 2a), have made repeated claims that they have obtained evidence proving the tetrahedral configuration of Pt^{II}.

Owing to the fact that these claims clash with the main body of evidence, it is necessary to examine them in some detail.

In the first place it must be pointed out that, except in one very doubtful instance, Reihlen and his collaborators have never followed the classical method of establishing a configuration by resolution through to its proper conclusion. That is to say, the allegedly optically active complexes have never been obtained free from the resolving acid (or base). In the one instance (132) where this separation was reported as having been carried out, the observed rotation was so very small (0.06° for a 4-dm. tube) as to be without any special significance. Reihlen's claims, then, rest on the observation that the molecular rotation, [*M*], of a salt like bis(aminomethyl-3-ethyl-4-methylquinoline)platinous α-bromocamphor-π-sulfonate (130) is greater (or less) than that calculated from the α-bromocamphor-π-sulfonate content of the salt. All attempts to obtain an optically active complex free from the acid used for resolution resulted in failure, which was attributed to racemization. In view of the stability of platinous

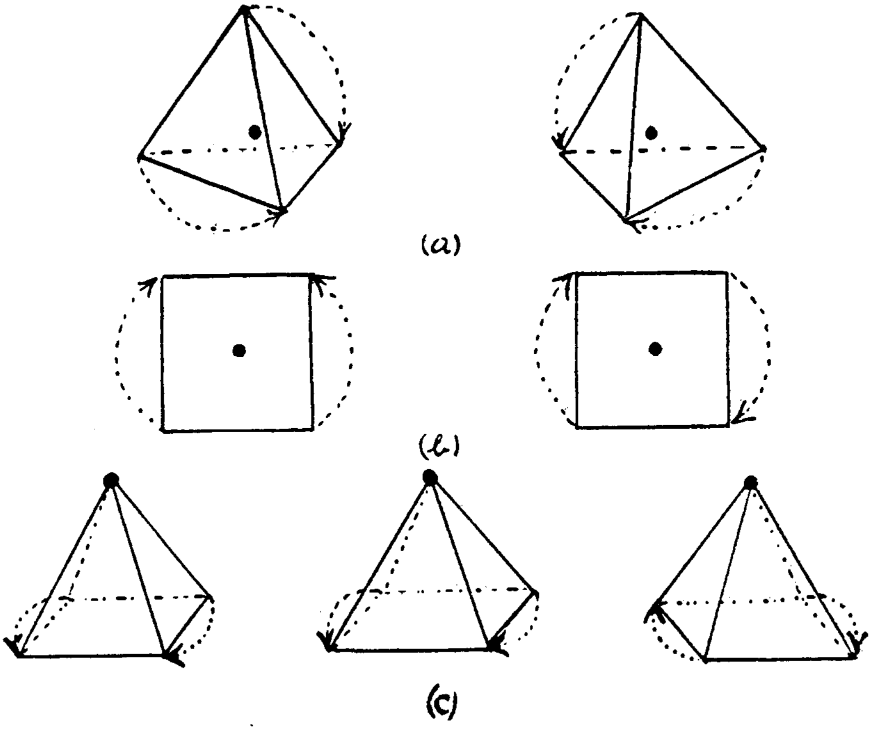
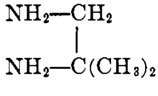


FIG. 2. Possibilities of isomerism when two unsymmetrical chelate groups are coördinated to a central metal atom. The arrow in these diagrams is used to indicate a molecule which by chelation produces an unsymmetrical ring, e.g.,

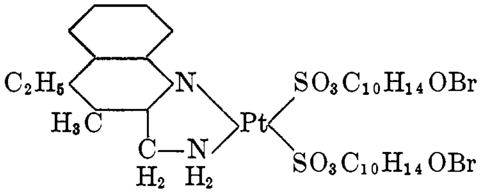


$$\begin{array}{l}NH_2\text{—}CH_2\\ \qquad\ \ |\\ NH_2\text{—}C(CH_3)_2\end{array}$$

complexes, already noted in an earlier section, this explanation is not specially convincing.

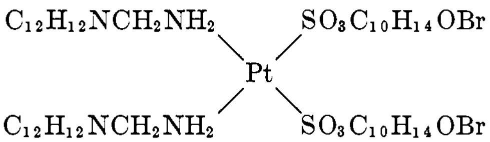
Unsuccessful attempts to obtain optically active platinous complexes have been reported by other workers. Ostromisslensky and Bergman (116) failed with $[PtClNH_3SO_3(py)]^-$, Tscherniaev (144) with $[Pt(NH_2OH)(NH_3)(py)(NO_2)]^+$, and finally Jensen (76) with bis(thiosemicarbazide)- and bis(2-aminomethyl-3-ethyl-4-methylquinoline)platinous ions. Significantly enough, in the last instance Jensen did note rotation differences of the same order as were observed by Reihlen and Huhn (130). However, on attempting to isolate an optically active platinous complex by precipitation with picric acid, Jensen found that the chloroform solution of the resulting picrate was always entirely devoid of optical activity. It is worth noting that several of the compounds upon which attempts at resolution were made have been described in the isomeric forms to be expected from square bonding: thus, two forms of bis(isobutylenediamine)platinous chloroplatinite (42) and bis(phenylethylenediamine-2-aminomethyl-3-ethyl-4-methylquinoline)platinous chloride (132) and three forms of $[Pt(NH_2OH)(NH_3)(py)(NO_2)]^+$ (143, 144) have been isolated. In the belief that Reihlen's resolutions were valid, Dwyer and Mellor (45) suggested a pyramidal structure for the complexes of platinum and palladium with a view to reconciling the findings on optical activity with the known *cis–trans* isomerism. This view is, of course, no longer tenable.

There still remains the question as to what causes the changes in rotation discovered by Reihlen and Jensen. The latter has made the suggestion that the bromocamphorsulfonate molecule becomes attached to the platinum atom itself, either (*1*) by forming the complex I



I

or (*2*) by opening the chelate rings to form II:

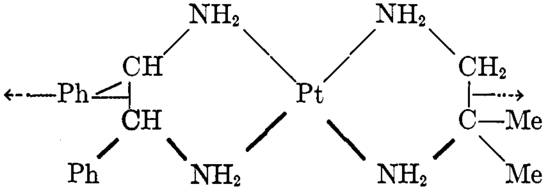


II

Jensen has calculated that contamination of bis(2-aminomethyl-3-ethyl-4-methylquinoline)platinous α-bromocamphor-π-sulfonate with as much as 5 per cent of I makes so very little difference in the analytical figures that it would not be detected. Formation of substance II would not alter the analytical results. Experiment shows (76) that on the addition of hydrochloric acid to bis(2-aminomethyl-3-ethyl-4-methylquinoline)platinous α-bromocamphor-π-sulfonate (which may be contaminated with I or II, or both), the molecular rotation returns to its normal value, i.e., the value for the free bromocamphorsulfonic acid. Jensen explains this behavior as being due to the freeing of the bromocamphorsulfonic acid from I and/or II. Whether we accept Jensen's explanation of the rotation changes or not, the fact remains that none of the foregoing optical evidence can be said to favor the view that Pt^{II} is tetrahedrally coördinated. Rather does it constitute negative evidence for alternative structures, but such evidence is seldom very convincing because we cannot be certain that the cause or causes of the negative result are exactly what we imagine them to be.

The unsatisfactory situation of the resolution work just described has been largely cleared up by Mills and Quibell (111), who were the first to describe stable optically active derivatives of Pt^{II}. Unfortunately, as far as the unequivocal proof of the square structure goes, the work of Mills and Quibell on mirror-image isomerism leaves us in much the same position as does the work on geometrical isomerism; that is to say, their results are quite consistent with the square structure, but they may be explained in terms of other configurations.

As they were doubtful of the interpretation of the work[8] on geometrical isomerism, Mills and Quibell planned and achieved the synthesis of a very ingeniously devised complex which, if planar, would have the symmetry properties required to produce mirror-image isomers. As represented below



the molecule possesses neither a plane nor a center of symmetry and is therefore resolvable. On the other hand, if the chelate group on the left (meso-stilbenediamine) were fixed, while the chelate group on the right were rotated through 90°, so bringing about a tetrahedral distribution of the four bonds to platinum, the molecule as a whole would possess a plane of symmetry. In other words, the molecule with a tetrahedral configuration would no longer be resolvable.

In point of fact, Mills and Quibell were able to isolate, quite free from the resolving acid (*d*-diacetyltartaric), optically active salts whose great stability is entirely in keeping with what is known of the robustness of platinous complexes. And so for the first time the method of resolution was used to provide evidence for the square configuration. In the light of the general body of evidence, more especially the physical, there is no doubt that these optically active complexes

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[8] "Although the frequency with which isomerism occurs in compounds containing a complex of the type A_2PtB_2 gives great weight to Werner's interpretation, yet it is always difficult in dealing with geometrical isomerism to make certain that the isomerism is actually of the nature supposed. There is no such difficulty with mirror image isomerism" (111).

are square, but as Mills and Quibell themselves point out, the results might also have been attributed to a pyramidal arrangement. However, they regarded this last configuration as inherently improbable, pointing out that if it were the explanation of their results, then certain simpler complexes should be resolvable. Inherent improbability is not necessarily a safe argument, as the recent discovery of the pyramidal arrangement of four covalent bonds about Pb^{II} (113) will serve to show.

Summing up the chemical evidence, one may say that it definitely rules out the regular tetrahedral and tetragonal bisphenoidal arrangements, is consistent with the theory of square coördination, but leaves the possibility of pyramidal and rectangular arrangements in doubt. For the final stages of the proof of structure we must turn to physical methods.

V. Raman and Infrared Spectra

In applying Raman and infrared spectra to unravelling problems of molecular structure the procedure is, briefly, as follows: Various molecular models are set up and the modes of vibration of each are systematically examined. According as the modes of vibration produce changes in the degree of polarizability or dipole moment of the molecule, the corresponding vibration frequencies will be responsible for lines in the Raman and infrared spectrum, respectively. The number of lines in each spectrum and the state of polarization of the Raman lines are deduced for each model and the model adopted is the one which gives exact or closest correspondence with the observed spectra. The number of Raman lines alone is not always a certain guide in deciding between alternative structures because there is always the risk that a line, though permitted, may be so faint as to escape detection. In the general case, if reliance is to be placed on structural conclusions, observations must be made on the polarization of the Raman lines and also on the absorption spectrum in the infrared region.

TABLE 2

Raman and infrared spectra of molecules of the type $A(XY)_4$

MODEL	SYMMETRY	RAMAN FREQUENCIES	INFRARED FREQUENCIES	INACTIVE FREQUENCIES	COINCIDENCES
Square	D_{4h}	7 (2)*	6	3	0
Tetrahedral	T_d	8 (2)	4	1	4
Pyramidal (square base)	C_{4v}	15 (4)	9	1	9
Rectangular	D_{2h}	9 (4)	12	2	0
Pyramidal (rectangular base)	C_{2v}	21 (6)	16	0	16

* The figures in parentheses refer to the number of polarized lines.

As far as square complexes are concerned, the simplest spectra are to be expected from an ion like $[PtCl_4]^{--}$ but, owing to difficulties associated with observing the Raman spectra of highly colored solutions, $K_2[PtCl_4]$ has not been investigated. Mathieu (96), who has been mainly responsible for work in this field, has studied the following colorless or nearly colorless compounds:

$Na_2[Pt(CN)_4]$, $Na_2[Pt(NO_2)_4]$, $[Pt(NH_3)_4]Cl_2$, $[Pt(py)_4]Cl_2$, and $[Pt(en)_2]Cl_2$; of these, only the first provided sufficient information for any structural conclusions to be drawn. Observations were made on the number and polarization of the Raman lines and were discussed primarily from the standpoint of square and tetrahedral models. The observed Raman spectrum of $Na_2[Pt(CN)_4]$ comprised six lines, two of which were polarized; these data favor the square structure but do not constitute decisive evidence for it. The position can best be understood by reference to table 2[9], which shows the frequencies to be expected for different models of a molecule of the type $A(XY)_4$ with the atoms AXY collinear. It will be seen at once that the experimental data rule out the last three less symmetrical configurations. A clear-cut distinction between the first two models, in favor of the square structure, is most likely to be obtained by extending observations to the infrared, where the observation of five or more fundamental frequencies would definitely exclude the tetrahedral model. As the position stands, the evidence for the square structure is essentially negative in character; the number of Raman lines does not exceed that predicted for the square model. It is of course always more satisfying to have positive evidence on a point like this and there is a good case for extending work to the infrared.

VI. Evidence from Dipole Moments

Whereas all diatomic molecules of the type A—A are electrically symmetrical and non-polar, those of the type A—B always have a permanent electric moment. In a polyatomic molecule, each bond A—B is associated with a dipole moment which can be treated as a vector quantity, the permanent dipole moment of the molecule as a whole being the vector sum of the individual bond moments. For any molecule with a center of symmetry, the vector sum of the bond dipole moments will be zero, that is, the molecule will have no permanent dipole moment. This is found to be true of a number of molecules whose structures have been ascertained by other means; thus CO_2, SF_6, and *trans*-dichloroethylene are all centrosymmetrical and without permanent dipole moment. In using dipole moments as a test for the presence of a center of symmetry it must be remembered that the converse of the above proposition is not necessarily true, that is to say, there are molecules like CCl_4, with zero dipole moment, which do not have a center of symmetry. However, of the configurations listed on page 153 only two have a center of symmetry; for all the others the vector sum of the dipoles will not, in general, be zero.

Among the dipole studies of metal complexes, those of Jensen (71, 73), dealing with isomerides of the type $[PtA_2X_2]$, have an important bearing on the present discussion. The results of some of Jensen's measurements are set out in table 3, from which it can be seen that the compounds fall into two groups. In the first, where A is represented by various symmetrically substituted arsines, phosphines, and stibines, and X by NO_2, Cl, Br, etc., the moments are either approximately zero or around 8–12 Debye units. The compounds with zero moment are

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[9] I am indebted to Mr. A. Maccoll for the compilation of this table.

obviously the *trans*-forms and those with the large moment, the *cis*-forms. In $PtCl_2((CH_3)_3As)_2$, for example, the resultant of the three As—C bond moments is directed along the Pt—As bond irrespective of whether there is, or is not, rotation about the Pt—As bond. The only reasonable structure for $[PtCl_2((CH_3)_3As)_2]$ which could give zero moment is the *trans*-planar (figure 3).

TABLE 3

Dipole moments of platinous compounds of the type PtA_2X_2

Jensen (71, 73)

COMPOUND	DIPOLE MOMENT	COMPOUND	DIPOLE MOMENT
	Debye units		*Debye units*
trans-$[PtBr_2(Et_3P)_2]$	0	*cis*-$[PtBr_2(Et_3P)_2]$	11.2
trans-$[PtI_2(Et_3P)_2]$	0	*cis*-$[PtI_2(Et_3P)_2]$	8.2
trans-$[PtCl_2(Pr_3P)_2]$	0	*cis*-$PtCl_2(Pr_3P)_2$	11.5
trans-$[PtCl_2(Et_3As)_2]$	0	*cis*-$[PtCl_2(Et_3As)_2]$	10.5
trans-$[PtI_2(Et_3Sb)_2]$	0	*cis*-$[PtCl_2(Et_3Sb)_2]$	9.2
trans-$[PtCl_2(Bu_3P)_2]$	0	*cis*-$[PtCl_2(Bu_3P)_2]$	11.5
trans-$[PtCl_2(Pr_2S)_2]$	2.35	*cis*-$[PtCl_2(Pr_2S)_2]$	9.5
trans-$[PtCl_2(Bu_2S)_2]$	2.35	*cis*-$[PtCl_2(Bu_2S)_2]$	9.2
trans-$[Pt(NO_2)_2(Pr_2S)_2]$	2.48	*cis*-$[Pt(NO_2)_2(Pr_2S)_2]$	13.1
trans-$[PtBr_2(Et_2S)_2]$	2.26	*cis*-$[PtBr_2(Et_2S)_2]$	8.9

Et = ethyl; Pr = propyl; Bu = butyl.

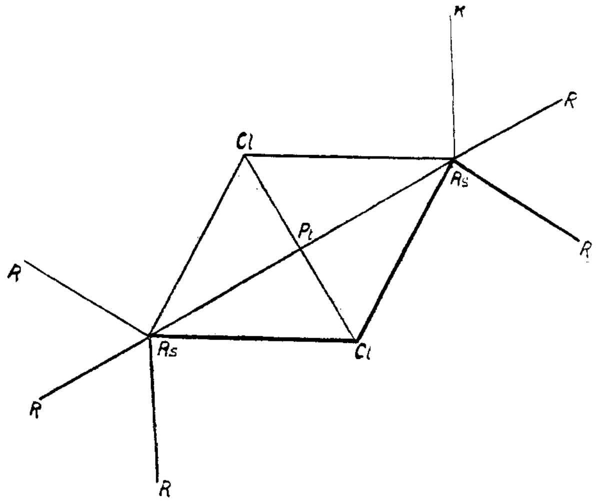
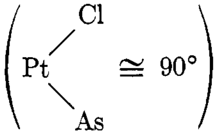


FIG. 3. *Trans*-planar structure for $[PtCl_2((CH_3)_3As)_2]$

In the second group, which comprises the thioether complexes, there is a large difference between the α- and β-forms, the dipole of neither form being zero. However, it is concluded that the compounds with the larger moments are the *cis*-forms and those with the smaller the *trans*-forms. If we make the reasonable assumption that in *trans*-$[Pt((C_2H_5)_2S)_2Cl_2]$ the platinum bonds are coplanar, the small moment of the molecule can be accounted for in terms of the known configuration of tercovalent sulfur. Indeed, the moment of the *trans*-form may be looked upon as supplying further proof that the three sulfur valence bonds are not coplanar. Figure 4 will make it clear that the S—C moments are not directed along the direction of the Pt—S bond, and that the molecule as a whole must have a resultant dipole moment,—in other words, the molecule in figure 4 has a *trans–cis* structure.

Jensen's work provides a neat physical method for determining the configuration of metal complexes and at the same time confirms the results of chemical methods of attack on this problem. More important still, it shows that the complexes are strictly planar, and in fact constitutes one of the strongest pieces of evidence against any suggestion of a pyramidal configuration. From the relevant dipole data it is estimated that the platinum atom cannot, at most, be more than 0.08 Å. from the plane of the four attached groups. Dipole measurements do not tell us what the magnitudes of the Cl—Pt—As bond angles are, and hence do not enable us to say whether the coördination is square



$$\left(Pt\begin{matrix}\diagup Cl\\ \diagdown As\end{matrix}\cong 90^\circ\right)$$

or not. Departures from angles of 90° do not disturb the centrosymmetry of the complex.

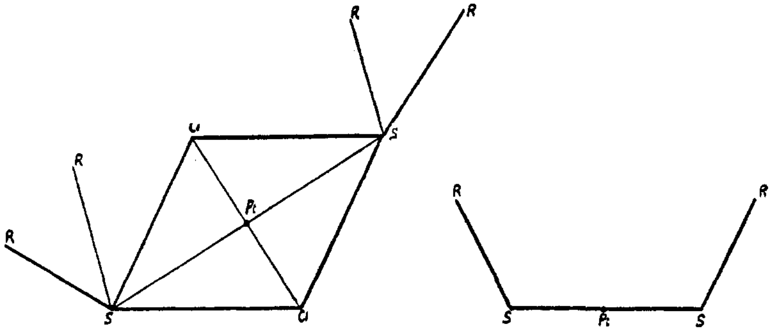


FIG. 4

VII. The Crystal Structure of Platinous Compounds

When based on sufficient reliable intensity data and carried through to completion, x-ray crystal analysis may be looked upon as a final court of appeal in structural problems. Often, however, a crystal may be so complicated and the difficulties associated with its determination so great that only a partial solution can be obtained. Evidence from crystal-structure analyses must therefore be given varying weight according to the completeness of the analysis, always assuming of course that each stage has been reliably determined. Several stages in an analysis may be recognized: (*1*) The determination of the size of the unit cell and the number of molecules contained therein. As a rule the number of molecules per unit cell determines to a large extent the complexity of a structure. If there happen to be a large number of molecules, in themselves fairly complicated, the task may prove extremely difficult, if not impossible, at this stage of the development of x-ray technique. An investigation terminated at the first stage is of little use, although on several occasions attempts have been made to use the fact that one of the dimensions of a unit cell is very small, to prove the existence of some planar structure. Conclusions based on such slender evidence must be accepted with caution, because a small cell dimension may be explained in some other way.[10]

(*2*) The second stage leads to the determination of the space group which describes fully the symmetry of the crystal structure. Once the number of molecules per unit cell and the space group have been determined, it is possible to state the symmetry elements of the molecule itself. By these means the following molecules (or ions) have been shown to have a center of symmetry: (*a*) bis(salicylaldoxime)platinum (25); (*b*) bis(dimethylsulfine)dichloroplatinum (27); (*c*) bis(ethylenediamine)platinous ion (26). In all these instances centrosymmetry is consistent with *trans*-planar structures for the complexes, but not with tetrahedral structures.

(*3*) The third and final step involves finding the exact location of each atom in the unit cell, and as a rule this becomes increasingly difficult as the number of parameters required to fix these positions increases. Relatively few complete structure determinations have been made on platinous compounds and they have, for the most part, been confined to fairly simple structures. Nevertheless the results are of great stereochemical interest. The structures of the following substances have been completely determined and in every instance square complexes have been found:

(1) $K_2[PtCl_4]$ (figure 5)
(2) $[Pt(NH_3)_4]Cl_2H_2O$ (figure 6)
(3) $K_2[Pt(C_2O_2S_2)_2]$ (figure 7)
(4) $PtC_{32}H_{16}N_8$
(5) PtS (figure 8)

The first substance examined was $K_2[PtCl_4]$ (38), which along with K_2PdCl_4 belongs to the tetragonal system and has one molecule per unit cell. Because $K_2[PtCl_4]$ and $[Pt(NH_3)_4]Cl_2$ form the starting materials for the preparation of many of the isomeric ammines discussed earlier and in this sense are key sub-

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[10] Because one of its cell dimensions is small as compared with others, it has been suggested (31) that the compound $Co(py)_2Cl_2$ contains square-coördinated Co^{II}. Magnetic evidence is against this suggestion, and the small cell dimension can be explained on the basis of an octahedral structure (101).

stances, their structure will be discussed in detail. K_2PtCl_4 possesses an unusually simple structure, involving as it does but one parameter, a parameter to fix the position of the chlorine atom in the plane of the platinum atoms, as shown in figure 5. The positions of the potassium and platinum atoms are fixed uniquely by symmetry. In the absence of any crystal faces indicating the contrary, Dickinson assumed that the crystal belonged to the holohedral class and his final structure determination in a sense justified this assumption. Nevertheless it is always useful to have some independent evidence of the absence of lower symmetry in the crystal. Such has been provided by piezoelectric tests (142) and pyroelectric tests (106), both of which show that the crystal does not lack a center of symmetry.

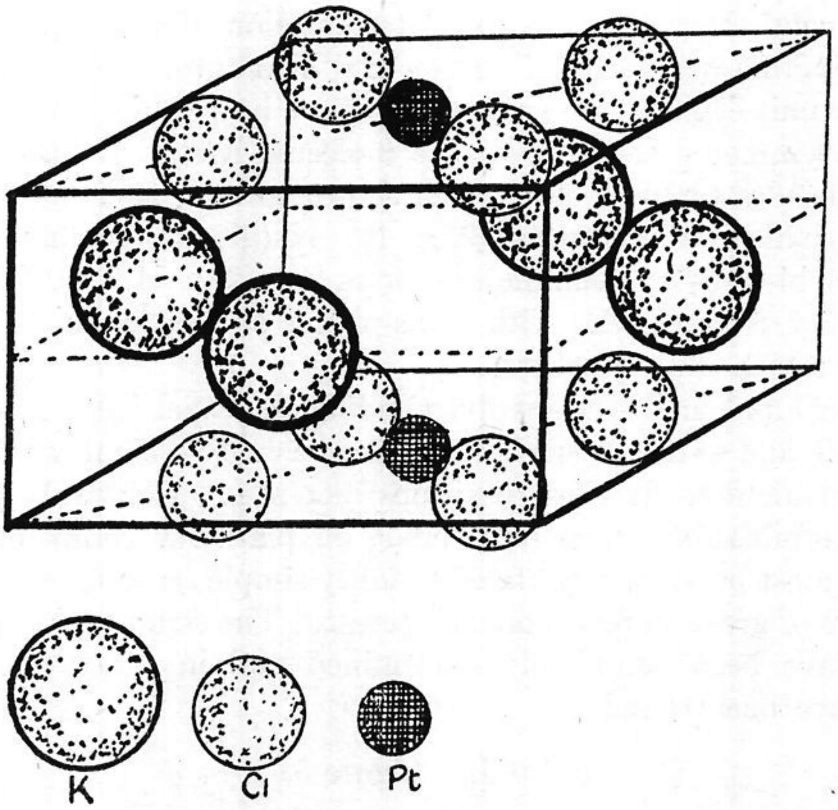

FIG. 5. The structure of $K_2[PtCl_4]$

The isomorphous palladium compound has been reinvestigated with more recently developed x-ray technique by Theilacker (142), and Dickinson's (38) earlier work has been completely confirmed. From his intensity data Theilacker concludes that the palladium atom cannot, at most, be more than 0.2 Å. out of the plane of the four chlorine atoms, and that since this is not much greater than the experimental error it is practically certain that all five atoms are strictly coplanar. If one accepts this evidence for the planar structure of the complex, then it follows immediately from the tetragonal symmetry of the crystal that the four Pt—Cl bonds are at exactly 90°, and that the $PtCl_4^{--}$ complex is definitely square. The stereochemical implications of this crystal structure determination were not at first fully realized. They are, however, most important, because for the first time accurate information of the orientation of the four platinum bonds became available. One or two additional points about the structure are worth noting. Firstly, the strong negative double refraction of the crystal (106) is consistent with the structure attributed to it. Several small discrepancies between observed and calculated intensities in Dickinson's work on K_2PtCl_4 can be explained on the basis of the anisotropic thermal motions of the platinum atoms (66). However, the thermal oscillations of platinum atoms are about fixed mean positions so that no modification of the square structure is required.

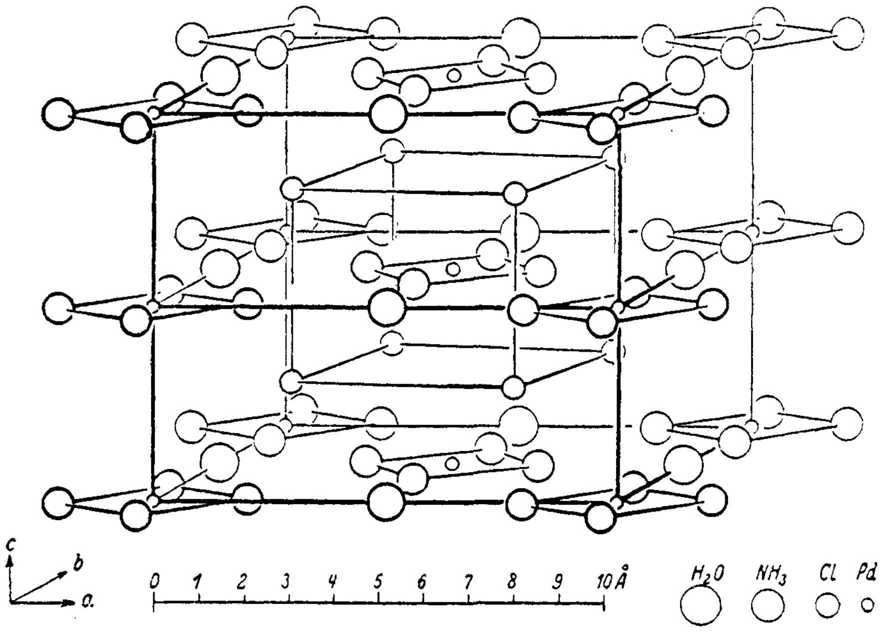

FIG. 6. The structure of $[Pd(NH_3)_4]Cl_2H_2O$ and of $[Pt(NH_3)_4]Cl_2H_2O$ (*Strukturbericht*)

The second relatively simple compound, $[Pt(NH_3)_4]Cl_2H_2O$, was first investigated by Cox (24), who assigned to it a structure the same in essentials as that of K_2PtCl_4,—with the two chloride ions occupying the positions of the two potassium ions and the $[Pt(NH_3)_4]^{++}$ that of $[PtCl_4]^{--}$. Subsequent work has shown that while the essential features of the $[Pt(NH_3)_4]^{++}$ complex are as Cox reported them (the four platinum valences coplanar and directed towards the corners of a square), the structure of the crystal is a little more complicated, requiring for its proper description a two-molecule unit cell (37).[11] The two-molecule cell arises from the small rotations of the $[Pt(NH_3)_4]^{++}$ complexes and chlorine atoms about the c-axis (figure 6). Robertson and Woodward's (136) analysis of platinous phthalocyanine is one of the most extraordinary x-ray analyses carried out to date, but it adds little to the general theme developed here. The phthalo-

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[11] Dickinson's most detailed work actually related to the isomorphous palladous compound $Pd(NH_3)_4Cl_2 \cdot H_2O$.

cyanine molecule is a huge planar molecule and any metal atom attaching itself to it by the four pyrrole nitrogen atoms must do so by coplanar bonds.

In the crystals so far mentioned, the complexes have all belonged to the finite class. In the last crystal of the group, *viz.*, PtS (16), we find a new type,—an infinite complex extending throughout the crystal in three dimensions. Platinum and sulfur maintain a coördination number four by appropriate *sharing* of atoms; a portion of an infinite chain structure can be seen in the unit cell of PtS shown in figure 8.

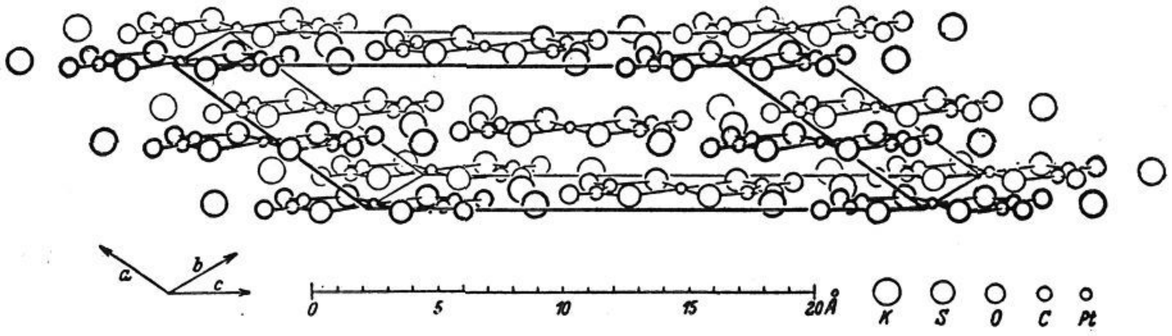


FIG. 7. The structure of $K_2[Pt(C_2O_2S_2)_2]$ (*Strukturbericht*)

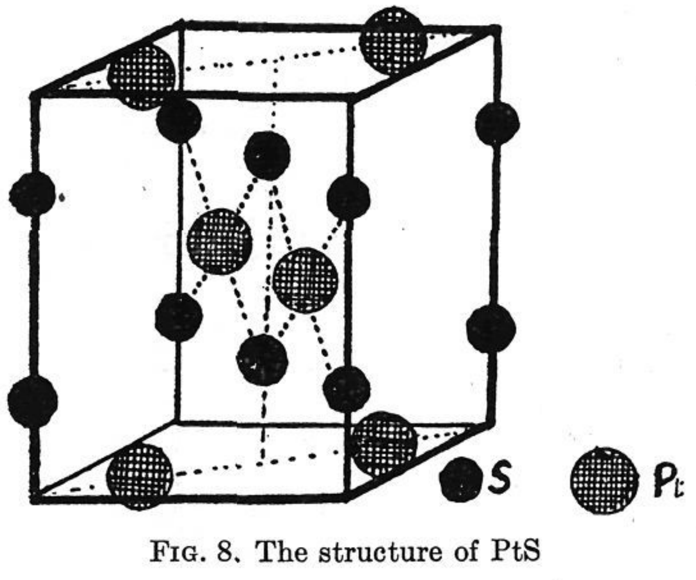


FIG. 8. The structure of PtS

Finally we come to several structures which have not been directly determined but which may be inferred from the complete crystal analysis of an isomorphous crystal. Square-coördinated metal complexes are found in each, and it must suffice merely to list them with the completely analyzed crystal indicated in brackets:

(a)	$Ba[Pt(CN)_4]4H_2O$	$\{(Ba[Ni(CN)_4]4H_2O)\}$	(13)
(b)	$Na_2[Pt(CN)_4]3H_2O$	$\{(Na_2[Ni(CN)_4]3H_2O)\}$	(15)
(c)	$PtCl_2$	$\{PdCl_2\}$	(15)
(d)	PtO	{PdO}	(113)

VIII. SOME OPTICAL PROPERTIES OF THE CRYSTALS OF PLATINOUS COMPOUNDS

Taken by itself, evidence from crystal optics is not specially significant, but in conjunction with other data it may often afford valuable confirmation of the existence of certain structural features in a crystal. It is interesting to recall that von Laue's discovery of the diffraction of x-rays, upon which the science of crystal analysis was built, was in no small measure conditioned by Ewald's theoretical studies of the double refraction to be expected from certain postulated atomic arrangements in crystals. The science of crystal analysis has amply repaid this debt by providing such a wealth of information about atomic arrangements as to enable the formulation of useful correlations between structure and optical properties.

TABLE 4

The birefringence of some platinous compounds

SUBSTANCE	SYMMETRY				DOUBLE REFRACTION	REFERENCES
$K_2[PtCl_4]$	Tetragonal	1.683		1.553	−0.130	(106)
$Ba[Pt(CN)_4]4H_2O$	Monoclinic	1.6706	1.677	1.8982	+0.2276	(153)
$Mg[Pt(CN)_4]7H_2O$	Tetragonal	1.561		1.910	+0.350	(55)
$LiK[Pt(CN)_4]3H_2O$	Orthorhombic	1.6237	1.6278	2.2916	+0.6679	(153)
trans-$[Pt(py)NH_3Cl_2]$	Triclinic	1.653	1.732	>1.79	>−0.137	(56)
cis-$[Pt(py)NH_3Cl_2]$	?	1.624	1.732	>1.79	>−0.166	(56)
$K[PtCl_3C_2H_4]H_2O$	Monoclinic	<1.627		1.717	>−0.090	(78)
$NH_4[PtCl_3C_2H_4]H_2O$	Monoclinic	<1.623		1.702	>?0.079	(78)
$Na_2[Pt(CN_4]3H_2O$	Triclinic				High and negative	(15)
$Sr[Pt(CN)_4]5H_2O$	Monoclinic	1.547	1.613	1.637	−0.090	(12)
$K_2[Pt(COS)_4]$	Monoclinic				Extremely high	(32)
$[Pt(NH_3)_2(NO_2)_2]$	?	1.531	1.779	(1.80)	−0.269	(155)
$[PtNH_3(py)Cl_2]$	?	1.653	1.732	1.79	−0.135	(155)
$[PtNH_3(py)(NO_2)_2]$	?	1.624	1.696	1.750	−0.126	(155)

The striking double refraction of crystals of the isomorphous series $CaCO_3$, $NaNO_3$, and $ScBO_3$, for which the presence of parallel planar XO_3 ions is responsible (10), suggested that similar optical properties would be found among crystals containing square-coördinated Pt^{II}.

According to the results of x-ray analysis the square $[PtCl_4]^{--}$ groups in K_2PtCl_4 are all arranged parallel to 001. If this arrangement is correct, the crystal should show strong negative double refraction, which indeed it does (106). Had the four chlorine atoms been tetrahedrally arranged about the platinum, one would have anticipated a small double refraction of the same order as that found in crystals containing SO_4^{--}, PO_4^{---}, ClO_4^-, etc.

Information about the crystal optics of other platinous compounds is summarized in table 4, from which it can be seen that the double refraction is high throughout. The high double refraction of Zeise's salt, $K[PtC_2H_4Cl_3]$, is interesting; it is not known just how the ethylene is incorporated in the complex, but the complex undoubtedly has a square configuration.

The strength of the double refraction of a crystal will depend on mutual arrangement of any anisotropic units it may contain, being greatest, and negative, when they are all parallel to one another as in $CaCO_3$ and K_2PtCl_4. Certain arrangements of planar groups result in positive double refraction, as in bastnaesite (154); with other arrangements, less probable no doubt, it is conceivable that a very low double refraction could be produced. Thus, while high double refraction undoubtedly indicates the presence of highly anisotropic units in a structure, low double refraction does not necessarily mean that such units are absent. In this connection another situation which may arise must be kept in mind. Double refraction is subject to dispersion,—that is, it varies with wave length,—and one may just happen to choose, for making a measurement, a wave length where the double refraction is low or at a minimum. This point is well brought out in Brasseur and Rassenfosse's recent (12, 15) extensive studies of the crystal optics of a whole series of complex cyanides of the types $Ba[Me(CN)_4]4H_2O$, $Ca[Me(CN)_4]5H_2O$, $Sr[Me(CN)_4]4H_2O$, and $Na_2[Me(CN)_4]3H_2O$, where Me = Pt, Pd, and Ni. Without exception, these substances show high double refraction, and for all except three, $Ba[Pt(CN)_4]4H_2O$, $Mg[Pt(CN)_4]7H_2O$, and $Ca[Pt(CN)_4]5H_2O$, the sign of the double refraction is negative. A complete crystal-structure analysis of $Ba[Ni(CN)_4]4H_2O$ reveals a structure which accords with high negative double refraction. The positive sign of the isomorphous platinum compound is an extremely puzzling anomaly for which no explanation has yet been given. There is little doubt about the observations on the positive sign, since the same results have been reported by several workers. It would seem that Bragg's theory of the origin of double refraction of planar complexes needs further refinement if it is to take account of these platinum compounds.

MAGNETIC ANISOTROPY

Practically nothing has been done on the diamagnetic properties of platinous compounds, but it can reasonably be expected that, like $CaCO_3$, $NaNO_3$, etc., they will show pronounced anisotropy. Some very early observations on $Ca[Pt(CN)_4]5H_2O$ were made by Grailich (58), who reported that the direction of greatest diamagnetic susceptibility is parallel to the *c*-axis of the (orthorhombic) crystal. This would place the plane of the $[Pt(CN)_4]^{--}$ group approximately perpendicular to the *c*-axis, whereas the optical properties suggest a different orientation. The crystal optics of the isomorphous nickel compound, $Ba[Ni(CN)_4]4H_2O$, place the plane of the $[Ni(CN)_4]^{--}$ group approximately parallel to the *c*-axis, in qualitative agreement with the observations on the diamagnetic anisotropy of the platinum compound. Further work, possibly along the lines of that of Born (9) and Hylleraas (68) on quartz and calomel, is needed to clear up the anomalous behavior of these platinum compounds.

IX. DIRECTIVE INFLUENCES IN THE REACTIONS OF SQUARE COMPLEXES

A. *Trans* ELIMINATION

In the light of the crystal-structure determinations of $K_2[PtCl_4]$ and $[Pt(NH_3)_4]Cl_2H_2O$ it is of interest to note at this stage certain features of the reactions involved in the formation of the isomeric diammines. The most important of these is the process of *trans* elimination discovered by Werner. So far, little has been done towards providing a satisfactory understanding of this phenomenon, and all that will be attempted here will be to formulate some of the problems that arise. At the outset it is obvious that *trans* elimination cannot be a perfectly general reaction, because although it provides an explanation of some of the transformations, *cis* elimination must be invoked to explain others.

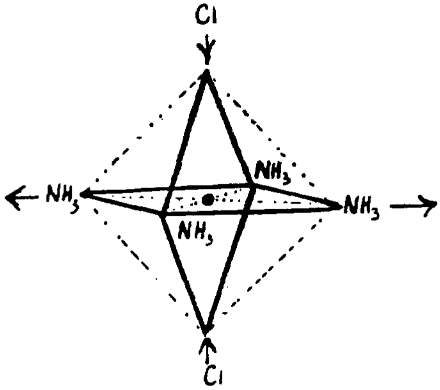


FIG. 9

Let us consider first the reaction responsible for the discovery of *trans* elimination:

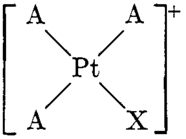
$$[Pt(NH_3)_4]^{++} \xrightarrow{2HCl} \underset{trans}{[Pt(NH_3)_2Cl_2]}$$

If we regard the elimination of the two molecules of ammonia as occurring simultaneously, we might suppose that as the two *trans* molecules depart, two chlorine atoms enter the *trans* octahedral positions to form a new *trans* square complex, as shown in figure 9. But matters are not so simple as this. As already pointed out, the two reactions below proceed stepwise:

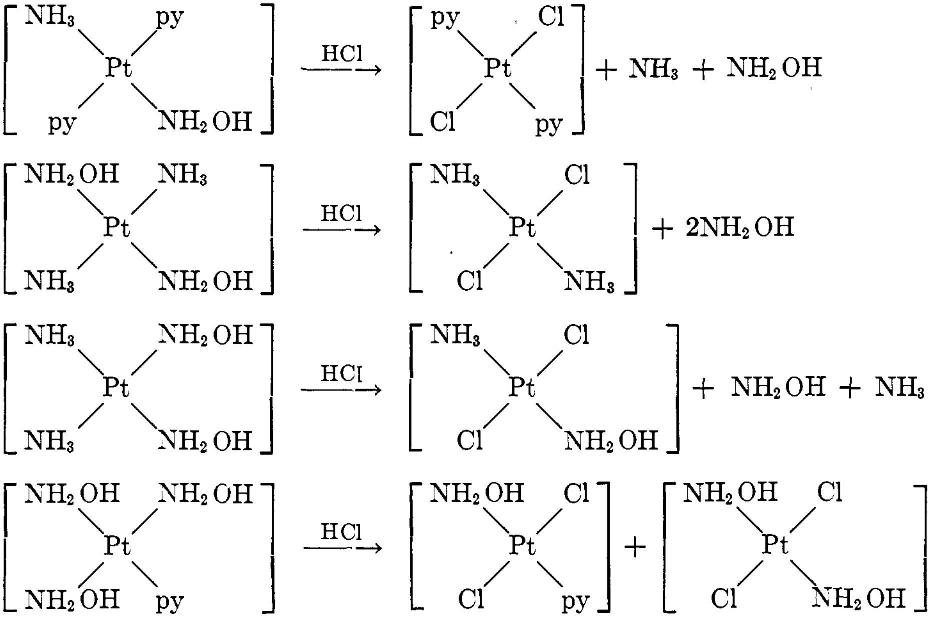
$$[Pt(NH_3)_4]^{++} \xrightarrow{Cl^-} [Pt(NH_3)_3Cl]^+ \xrightarrow{Cl^-} \underset{\beta}{[Pt(NH_3)_2Cl_2]}$$

$$[PtCl_4]^{--} \xrightarrow{NH_3} [PtNH_3Cl_3]^- \xrightarrow{NH_3} \underset{\alpha}{[Pt(NH_3)_2Cl_2]}$$

If the complexes were tetrahedral it would be impossible to account for the two different end products of these reactions. Let us imagine we have a square complex



into which another X is to be substituted for one of the A's. In what circumstances does the first X group direct the second one entering; to the *cis* position as in $[PtNH_3Cl_3]^-$ or to the *trans* position as in $[Pt(NH_3)_3Cl]^+$? At first sight it might seem as though X groups are *trans* directing when present in cationic complexes. Pinkard, Saenger, and Wardlaw (127) have studied very thoroughly the elimination reactions occurring with tetrammines containing ammonia, pyridine, and hydroxylamine, and in every instance the reaction indicates *trans* elimination.



It will be seen that no other X group than Cl was investigated, and as far as the author is aware no systematic work has been done along these lines. However, the behavior of certain nitro palladium compounds is worthy of note. From the evidence available (91) it would seem that the NO_2 group is directed to the *cis* position when it enters the complex $[Pd(NH_3)_3NO_2]^+$ and to the *trans* position when it enters the complex $[Pd(NH_3)(NO_2)_3]^-$, which is just the opposite of the behavior of chlorine in the above platinum complexes.

Two examples will suffice to show that the charge on the complex as a whole is not the factor determining directive influences. When $[Pt(NH_3)_2(dipy)]Cl_2$ is treated with hydrochloric acid, the *cis* ammonia molecules are eliminated. This is perhaps hardly a fair test case, because if ammonia molecules are to be eliminated there is no choice but *cis* elimination. A more convincing case is the one discovered by Jensen (71) who, in the course of his dipole-moment investigations, found that when an aqueous solution of K_2PtCl_4 is treated with four molecules of triethylphosphine, a colorless solution of $[Pt\{P(C_2H_5)_3\}_4]Cl_2$ is formed. This solution on standing deposits *cis*-$[Pt\{P(C_2H_5)_3\}_2Cl_2]$ (μ = 10.7 D) and the only way this latter substance can be formed is by *cis* elimination from $[Pt\{P(C_2H_5)_3\}_4]Cl_2$.

B. *Cis* ELIMINATION

The reaction between ammonia and the $[PtCl_4]^{--}$ ion seems typical of many amines. *Cis* elimination from this ion is known to occur with ethylamine, pyridine, hydroxylamine, aniline, etc., but again the reaction is not a perfectly general one. Some very interesting work in this field has been published by Tscherniaev and his school (57, 145). One of their most important findings is that *order* of substitution plays an important part in some complexes. Thus it was found that when ethylene is passed through Cossa's potassium salt, $K[Pt(NH_3)Cl_3]$, *cis*-$[Pt(NH_3)(C_2H_4)Cl_2]$ is formed. On reversing the order of introduction of the groups, i.e., by treating Zeise's salt, $K[Pt(C_2H_4)Cl_3]$, with ammonia, *trans*-$[Pt(NH_3)(C_2H_4)Cl_2]$ is formed. Similar behavior was observed on substituting carbon monoxide for ethylene, but the effects of ordered substitution are confined to unsaturated substances like ethylene and carbon monoxide. It does not, for example, make any difference whether $K[Pt(py)Cl_3]$ is treated with ammonia or $K[Pt(NH_3)Cl_3]$ with pyridine, *cis*-$[Pt(py)(NH_3)Cl_2]$ is the result. Another interesting but less common example of a directive influence is to be found in the complex ions formed with certain optically active diamines like *l*-cyclopentane-*trans*-1,2-diamine (*l*-cptn). Jaeger and ter Berg (69) have shown that any attempt to introduce a second molecule of the dextro base into [Pt(*l*-cptn)Cl_2] fails; the only compounds obtained were D-[Pt(*l*-cptn)$_2$]Cl_2 and L-[Pt(*d*-cptn)$_2$]Cl_2 where, curiously enough, the sign of the rotation of the complex ions is opposite to that of the constituent optically active bases. These authors found no evidence for the existence of the meso form [Pt(*d*-cptn)(*l*-cptn)]Cl_2. In order to describe the curious propeller-like structure of these optically active complex ions, Jaeger and ter Berg have proposed to call them "pterotactic" complexes.

The preceding examples are sufficient to show that the directive influences in substitution in square complexes present an interesting problem for the theoretical chemist.

X. THE UNIVERSALITY OF THE SQUARE STRUCTURE AMONG PLATINOUS COMPOUNDS

It now remains to consider whether the square structure is universal among Pt^{II} compounds and as characteristic of that atom as the tetrahedral structure is of carbon. The cases put to the test in physical investigation are necessarily few in number. As there is now no doubt about the origin of the geometrical isomerism, a better idea of the extent of the occurrence of the square structure can be gained from a brief survey of isomeric forms. Justification for extrapolating to cover all platinous compounds will be found in the quantum theory of the directed valence bond.

VARIETIES OF ISOMERIC SQUARE COMPLEXES

It is a simple matter to draw up a scheme showing the types of isomeric complexes which are possible on the assumption that Pt^{II} is square coördinated, and it is interesting to see how far these possibilities have been realized in practice. At the same time the scheme will give some idea of the complexity introduced into the chemistry of Pt^{II} by its habit of forming square bonds. All finite mononuclear complexes of quadricovalent Pt^{II} must fall into one or other of these classes: (*a*) $[PtA_4]^{++}$, (*b*) $[PtA_3X]^+$, (*c*) $[PtA_2X_2]^\circ$, (*d*) $[PtAX_3]^-$, (*e*) $[PtX_4]^{--}$.

In the scheme adopted the following symbols have been used:

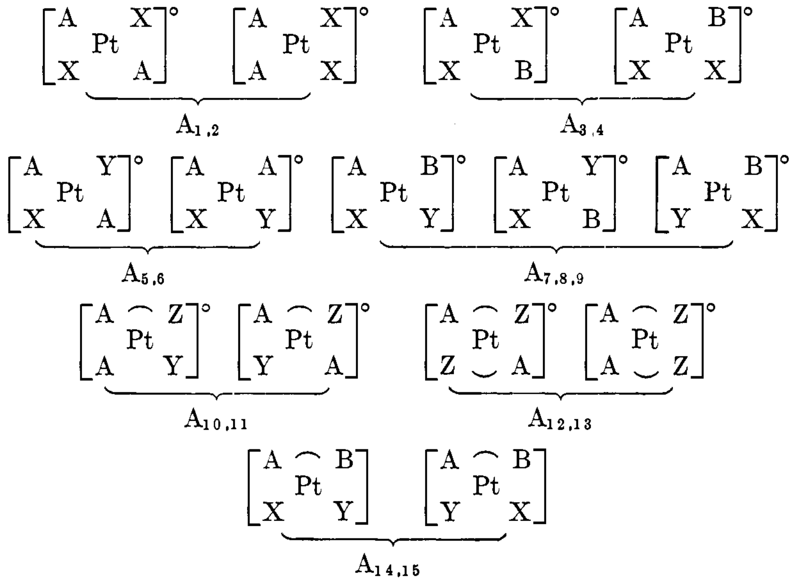
(*1*) A, B, C, etc., to represent neutral molecules, e.g., NH_3, C_5H_5N, NH_2OH, N_2H_4, CH_3NH_2, $C_2H_5NH_2$, $AsCl_3$, $P(CH_3)_3$, $(C_2H_5)_2S$, etc.

(*2*) AB to represent an unsymmetrical bidentate chelate group attached by two coördinate links, e.g., isobutylenediamine.

(*3*) AZ to represent an unsymmetrical chelate group attached by a coördination link and one primary link, e.g., glycine.

(*4*) X, Y, Z, . . . etc., to represent a negatively charged atom or group such as Cl^-, CN^-, NO_2^-, OH^-, etc.

Class A. Non-electrolyte or uncharged complexes

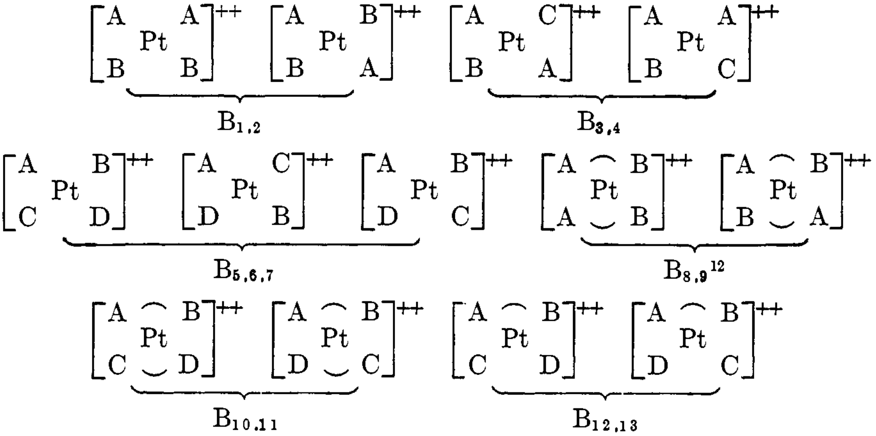


Examples of Class A are the following:

$A_{1,2}$: *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$
$A_{3,4}$: *cis*- and *trans*-$[Pt(NH_3)(py)Cl_2]$ (77)
$A_{5,6}$: *cis*- and *trans*-$[Pt(NH_3)_2(NO_3)OH]$
A_7: $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}I, Cl]$ (121)
$A_{10,11}$: No examples known.
$A_{12,13}$: $[Pt(NH_2CH_2COO)_2]$ (61)
$A_{14,15}$: No examples known.

Numerous examples of classes $A_{1,2}$ and $B_{1,2}$ have been described throughout the literature. On a rough estimate there must be several hundred examples of isomeric forms of all kinds. (Comprehensive lists are to be found in J. W. Mellor's *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 16, Longmans, Green and Company, London (1937), and in Gmelin-Kraut's *Handbuch der anorganische Chemie*, Bd. 5, Teil 3, Heidelberg.)

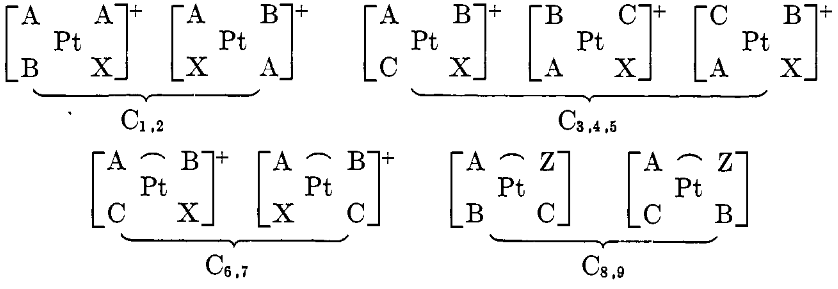
Class B. Divalent cationic complexes



Examples of Class B are the following:

$B_{1,2}$: *cis*- and *trans*-$[Pt(NH_3)_2(py)_2]^{++}$ (77)
$B_{8,9}$: *cis*- and *trans*-$[Pt\{NH_2C(CH_3)_2CH_2NH_2\}_2]^{++}$ (44)
$B_{10,11}$: *cis*- and *trans*-$[Pt(NH_2CH_2CH_2(C_6H_5)NH_2)(C_{12}H_{12}N\cdot CH_2NH_2)]^{++}$ (132)
$B_{12,13}$: *cis*- and *trans*-$[Pt(NH_3)(C_2H_5NH_2)\{NH_2C(CH_3)_2CH_2NH_2\}]^{++}$ (44)

Class C. Monovalent cationic complexes



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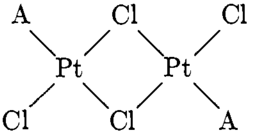
[12] Groups other than unidentate and bidentate have been omitted from this scheme.

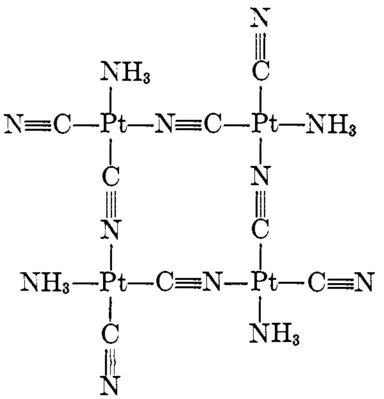
Examples of Class C are the following:

$C_{1,2}$: *cis*- and *trans*-$[Pt(NH_3)_2(NH_2OH)NO_2]^+$ (143, 144)
$C_{3,4,5}$: three isomers of $[Pt(NH_3)(py)(NH_2OH)NO_2]^+$ (143)
No examples of the other classes are known.

A classification along the same lines could be drawn up for anionic classes of the types $[PtX_2Y_2]^{--}$, $[PtX_2YZ]^{--}$ . . . . $[PtAXYZ]^-$, $[PtAX_2Y]^-$, etc., but as only a few examples of isomerism have been recorded in this category and as the classification would simply repeat much of that already given it will not be pursued any further. The scarcity of isomeric forms may well be due to the fact that it is more difficult to make the appropriate substitutions in anionic complexes and also to the fact that the *cis*-forms may not be sufficiently stable. Two substances in this class have, however, been recorded as existing in isomeric forms: namely, $K_2[Pt(S_2O_3)_2]$ (134) and $K_2[Pt(NH_2SO_3)_2Cl_2]$ (79), and no doubt careful search would reveal others. No attempt has been made to draw up a scheme for isomeric polynuclear compounds, mainly because not a single example of isomerism has been found even among those of the simplest type like (1, 72)



Furthermore, the possibilities of isomerism are increased in the more complex polynuclear compounds and few instances of compounds with more than two platinum atoms per molecule have been recorded. The substance with empirical composition $[PtNH_3(CN)_2]_x$, described many years ago by Cleve (22), would probably repay further investigation, since its composition suggests that it may have the following structure:



This survey of isomers would not be complete without some reference to a number of instances where forms in excess of those required by theory have been reported, if only because the existence of these forms has occasionally been used as an argument against the square structure. Jensen (74) has investigated several examples and in each case, except one, he has shown that the alleged third isomer is a mixture of α- and β-forms. The exception noted was the γ-dichlorodiammine of Angell, Drew, and Wardlaw (43) and this proved to be the *trans*-diammine contaminated with a polynuclear complex. No isomers would be expected for the compound $[Pt(dipy)Cl_2]$; nevertheless a yellow and a red form have been reported. As the two forms are indistinguishable chemically, Morgan and Burstall (114, 115) have set them down as dimorphous forms, a conclusion which could be checked by examining the absorption spectra of each of the two forms in a suitable solvent. If, as the observation that the red form is transformed to the yellow in chloroform solution suggests, there is no difference, there would seem to be little doubt that it is a case of dimorphism. At times it is difficult to find chemical differences between truly isomeric complexes, especially those of the type $[Pt(AX)_2]$ and here the absorption test is specially useful, as Lifschitz and Froentjes have shown in their work on the platinous ethyl-thiolactic acid complexes (86).

TABLE 5

CONFIGURATION	NATURE OF EXPERIMENTAL EVIDENCE USED FOR EXCLUDING THE CONFIGURATION
Pyramidal, tetragonal, or rhombic	Dipole moments; Raman and infrared spectra; crystal structure
Tetrahedral (regular)	Geometrical and mirror-image isomerism; Raman and infrared spectra; crystal structure; dipole moments, crystal optics
Bisphenoidal (tetragonal or rhombic)	Mirror-image isomerism; crystal structure; dipole moments
Rectangular	Crystal structure; Raman and infrared spectra

XI. SUMMARY OF EXPERIMENTAL DATA

While the results of the relatively few crystal-structure analyses of platinous compounds must be given great weight, the full force of the argument for the square structure as a general characteristic of Pt^{II} can best be understood from a consideration of the experimental evidence as a whole. This can be most conveniently done by summarizing the data which exclude all but one of the various theoretically possible configurations (table 5). The only reasonable configuration[13] which remains is the square one, and as this can be used to give a consistent explanation of all the observed phenomena it must be considered as established beyond all reasonable doubt.

[13] In the above scheme no provision has been made for the peculiar arrangement of four bonds found in $TeCl_4$ (140) and in the $[IO_2F_2]^-$ ion (67). This configuration is best described as that of a trigonal bipyramid in which one of the three equivalent positions is occupied by an unshared electron pair. It may also be regarded as derived from the tetragonal bisphenoidal configuration by increasing one of the bond angles of the central atom

XII. THEORETICAL EVIDENCE

By the application of general quantum-mechanical principles to the problem of the orientation of chemical bonds Pauling (117) has, on the basis of a single postulate,[14] derived a large number of results of great stereochemical interest. It is perhaps no serious test of the theory of the directed bond that it predicts the square bonding of Pt^{II}, although the general evidence for this latter was not so strong when the theory was first propounded. Nor should it be implied that support for the quantum-mechanical theory of the directed bond comes only from the experimental results dealing with quadricovalent elements. It is, however, necessary to restrict the discussion here to the deductions of the theory relating to such elements. The relevant rules are these: *(1)* Square bonds will be formed whenever dsp^2 orbitals are involved in bond formation. *(2)* Tetrahedral bonds will be formed whenever sp^3 orbitals are involved in bond formation.

Any atom whose structure is such as will permit the use of orbitals, that is any atom with a vacant *d* orbital just within its valence shell, will form square, rather than tetrahedral, bonds, because by so doing a more stable structure will result. The electronic structure of Pt^{II} fulfils just these conditions.

From the numerous examples of square structure already dealt with, and from the above rule, it is a fair inference to conclude that square bonding is as universal among platinous compounds as tetrahedral bonding is among carbon compounds.

NON-PLANAR STRUCTURES

Such an inference does, however, require several qualifications. Firstly, the above bonding rules refer only to electron-pair or covalent bonds. If the difference between the electronegativities of the atoms is sufficiently large, they may be held together by predominantly ionic tetrahedral bonds which do not involve pairing of electrons as in covalent-bond formation. The mere fact of an atom forming square bonds shows that the bonds are covalent, since the configuration of minimum potential energy for four ionic bonds is the tetrahedral one. As will be discussed more fully in the sequel, the magnetic criterion may be used to distinguish between the two bond types. If Pt^{II} formed ionic bonds, i.e., if platinum existed as the Pt^{++} ion in any of its compounds, these should be paramagnetic with susceptibilities corresponding to the presence of two unpaired electron spins. As a matter of actual experience, all platinous compounds examined to date have proved to be diamagnetic, from which we can infer that platinum does not exist in the ionic condition in any of these compounds. About the only likely compounds in which Pt^{II} might be found are those with fluorine, the

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to 180°. It is not, however, a bisphenoidal arrangement. This unusual arrangement of bonds owes its existence to the fact that the unshared electron pair is stereochemically active as in the nitrogen of ammonia, but since there is no parallel between the structures of the valency shells of platinum and tellurium, the configuration has not been included. In any event it is ruled out by the results of Raman spectra and crystal-structure work.

[14] "Of two orbitals in an atom the one which can overlap more with an orbital of another atom will form the stronger bond with that atom and moreover, the bond formed by a given orbital will tend to be in that direction in which the orbital is concentrated" (118).

most electronegative of all elements, but very little is known of such compounds. The few referred to in the literature are by no means well defined, and in no case has any magnetic work been done on them. Nevertheless this possible exception to the general rule must be borne in mind.

Secondly, the bonding rules refer only to compounds in which Pt^{II} has a coördination number four. While this number seems almost universal, there are one or two cases where it may possibly rise to six. Two instances come to mind: The bis(α,β,γ-triaminopropane)platinous ion (90, 92) and the *cis*- and *trans*-forms of bis(acetonitriletetrammine)platinous chloride (147). Doubt has recently been cast on the correctness of the interpretation of the evidence for the last two compounds (83), and in any event all the evidence for octahedral coördination is of a purely chemical nature. Some useful work remains to be done in checking the chemical findings by crystal structure analyses, or by some other means. An octahedral structure has been attributed to $[Pt(NH_3)_4]Cl_2$ (64) but crystal-structure data are definitely against this view.

Finally, it must be emphasized that the quantum-mechanical rules relating to the directed chemical bond refer only to bonds *free to arrange* and that where this condition obtains the bond angles found are very close to those required by theory. Thus, electron-diffraction studies show that in methylene chloride, chloroform, propane, isobutane, and other such molecules the angles between single bonds to carbon are from 109° to 112°, close to the tetrahedral value of 109°28′. Yet there is not the slightest doubt that in cyclopropane the angles between single bonds to carbon are 60°. Permanent bond-angle distortions inherent in the configuration adopted by a molecule are by no means rare (97) and must be allowed for in discussing the stereochemistry of platinum. Crystal-structure analyses reveal bond angles of 90° in $K_2[PtCl_4]$, $[Pt(NH_3)_4]Cl_2$, etc., but there may well arise instances where, under duress, as it were, such large bond-angle distortions may be produced as to alter completely the symmetry of a complex. Two examples of what may be called "forced configurations" will be considered here. The first is the compound β,β',β''-triaminotriethylamineplatinous chloride described by Mann and Pope (93). If platinum is regarded as having a coördination number of four, then it is sterically impossible for it to be square coördinated here (see figure 10).

Platinum might conceivably be octahedrally coördinated in this compound, and without a crystal analysis it is difficult to eliminate this possibility with any degree of certainty. The same objection does not apply to compounds containing bis-3,3′,5,5′-tetramethyl-4,4′-dicarbethoxydipyrromethene (figure 11).

Porter (129) has shown that if this substituted pyrromethene, with methyl groups in the α-positions, functions as a bidentate chelate group,—and the evidence is that with many metals it does,—then any attempt on the part of the chelate to assume a planar configuration is prevented by steric hindrance. The α methyl groups (asterisked in figure 11) must clash. The clashing is more serious than might be gathered from the figure. In redrawing it with the appropriate dimensions (figure 12), the extent of the overlapping of the methyl groups is indicated by horizontal shading. It should be pointed out that, owing to resonance in the pyrrole ring, the α methyl groups and the ring would normally be coplanar. Under stress the methyl groups might be bent to some small extent out of the plane of the pyrrole ring, but because of the large van der Waals'

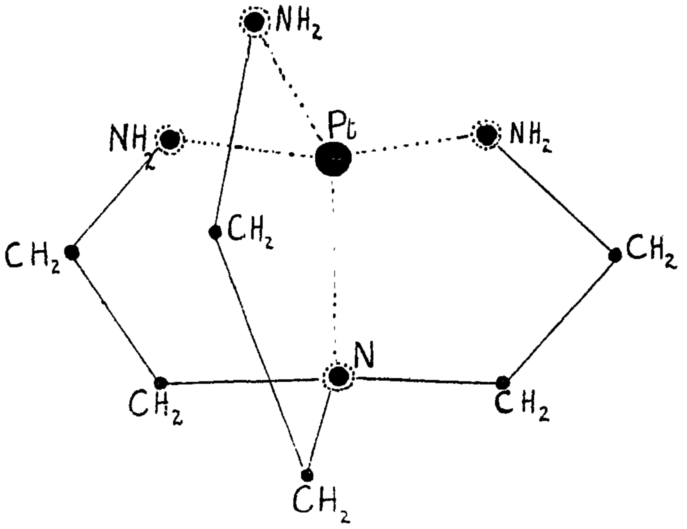

FIG. 10. β,β',β''-Triaminotriethylamineplatinous chloride

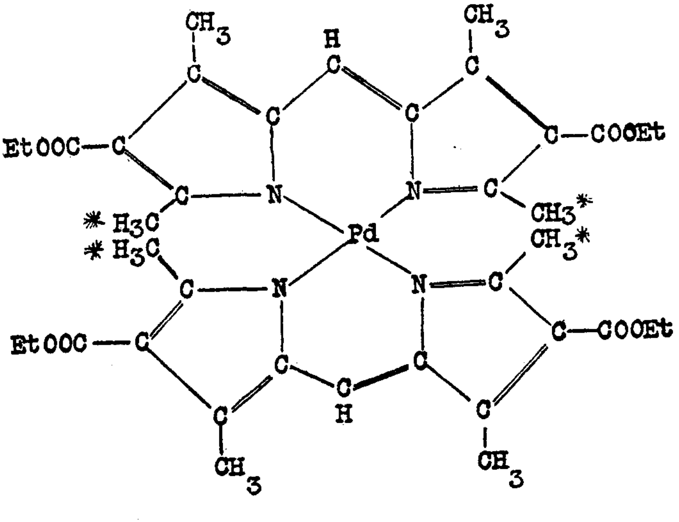

FIG. 11

radius of the methyl group, 2 Å., no amount of distortion of the C—CH_3 could accommodate chelating dipyrromethene groups in square-coördinated positions. By assuming that the methyl groups remain in the plane of the pyrrole rings, and that all the distortion occurs in the CH_3—N bonds, a rough calculation shows that the distortion amounts to about 40° (103).

Although quite a number of metal derivatives of this dipyrromethene have been described, curiously enough the platinum derivative does not appear among them. However, the palladium compound has been prepared (104, 129) and there is little doubt that platinum can also form a compound.

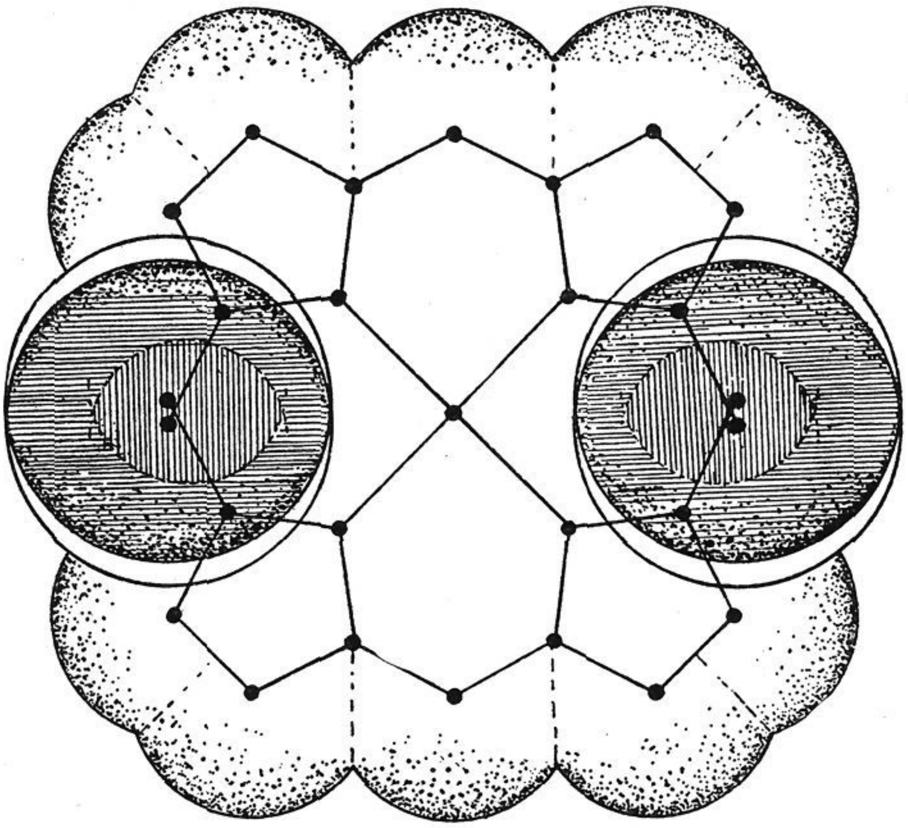

FIG. 12

XIII. INCIDENCE OF TNE SQUARE CONFIGURATION AMONG OTHER METAL COMPLEXES

The metals for which square coördination is theoretically possible are those whose electronic structures permit the use of dsp^2 orbitals in bond formation, that is to say, those which have a vacant d orbital within the valence shell. The elements which fulfil this condition are confined to the three transition series of the Periodic Table. Table 6, drawn up primarily (120) to show the magnetic moments predicted for the transition elements in different stereochemical configurations, will be used as a basis for discussion. This table is taken (modified) from the paper by Pauling and Huggins (120). It should be explained that the magnetic dipole moment of an atom arises from the existence in it of unpaired electron spins; the magnitude of the moment, in Bohr magnetons (the units employed in the table), is given by the expression $\mu = \sqrt{n(n+2)}$, where n is the number of unpaired spins. For diamagnetic substances $n = 0$.

Several interesting features of table 6 call for comment. In the first place it will be seen that the magnetic distinction between ionic, tetrahedral, and square coördination can be made only with elements in horizontal rows 6, 7, 8, and 9. Secondly, although square coördination is theoretically possible with any element of the three transition series, it has actually been found with very few (shown in heavy type), and these are confined to the relatively small portion of the table marked off with a heavy line. It is significant that the square structure is most common among elements with zero or one unpaired electrons ($\mathrm{Pt^{II}}$, $\mathrm{Pd^{II}}$, $\mathrm{Au^{III}}$, $\mathrm{Ni^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Cu^{II}}$, $\mathrm{Ag^{II}}$), very rare or doubtful among those with two or three ($\mathrm{Fe^{II}}$, $\mathrm{Mn^{II}}$), and, as far as is known, non-existent among those with the maximum number possible, four. The numbers of unpaired electrons just quoted refer of course to the different atoms in the square-coördinated condition. The same tendency to assume configurations with small numbers of unpaired electrons is to be seen among the diamagnetic complexes of Co, Pt, Pd, and Ir, which are invariably octahedral.[15] These observations may be summarized in a general rule which states that, when a metal atom of the transition series forms a covalent complex, it tends to assume that configuration (tetrahedral, square, octahedral, etc.) which involves the least possible number of unpaired electrons.

TABLE 6

Predicted magnetic moments of complexes containing transition elements

	THE IRON GROUP	THE PALLADIUM GROUP	THE PALATINUM GROUP	NUMBER OF ELECTRONS IN d SHELL ($3d$, $4d$, OR $5d$)	FOR IONIC OR sp^3 (TETRAHEDRAL) BONDS	FOR FOUR dsp^2 (SQUARE) BONDS	FOR SIX d^2sp^3 (OCTAHEDRAL) BONDS
1	$\mathrm{K^{I}Ca^{II}Sc^{III}Ti^{IV}}$	$\mathrm{Rb^{I}Sr^{II}Y^{III}Zr^{IV}}$ $\mathrm{Nb^{V}Mo^{VI}}$	$\mathrm{Cs^{I}Ba^{II}\text{-}Hf^{IV}Ta^{V}}$ $\mathrm{W^{VI}}$	0	0.00	0.00	0.00
2	$\mathrm{V^{IV}}$	$\mathrm{Nb^{IV}Mo^{V}}$	$\mathrm{W^{V}}$	1	1.73	1.73	1.73
3	$\mathrm{V^{III}Cr^{IV}}$	$\mathrm{Mo^{IV}Ru^{VI}}$	$\mathrm{W^{IV}Os^{VI}}$	2	2.83	2.83	2.83
4	$\mathrm{V^{II}Cr^{III}Mn^{IV}}$	$\mathrm{Mo^{III}}$		3	3.88	3.88	3.88
5	$\mathrm{Cr^{II}Mn^{III}Fe^{IV}}$	$\mathrm{Mo^{II}Ru^{IV}}$	$\mathrm{Os^{IV}}$	4	4.9	4.9	2.83
6	$\mathbf{Mn^{II}}\mathrm{Fe^{III}Co^{IV}}$	$\mathrm{Ru^{III}}$	$\mathrm{Os^{III}Ir^{IV}}$	5	5.91	3.88	1.73
7	$\mathbf{Fe^{II}}\mathrm{Co^{III}}$	$\mathrm{Ru^{II}Rh^{III}Pd^{IV}}$	$\mathrm{Ir^{III}Pt^{IV}}$	6	4.90	2.83	0.00
8	$\mathbf{Co^{II}}\mathrm{Ni^{III}}$	$\mathrm{Rh^{II}}$	$\mathrm{Ir^{II}}$	7	3.88	1.73	
9	$\mathbf{Ni^{II}}$	$\mathrm{Rh^{I}}\mathbf{Pd^{II}}\mathrm{Ag^{III}}$	$\mathbf{Pt^{II}Au^{III}}$	8	2.83	0.00	
10	$\mathbf{Cu^{II}}$	$\mathbf{Ag^{II}}$		9	1.73		
11	$\mathrm{Cu^{I}Zn^{II}Ge^{IV}}$	$\mathrm{Ag^{I}Cd^{II}In^{III}}$	$\mathrm{Au^{I}Hg^{II}Ti^{III}Pb^{IV}}$ $\mathrm{Bi^{V}}$	10	0.00		

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[15] If the results of the incomplete x-ray study (34) of $\mathrm{Pt(CH_3)_3Cl}$ are correct, this compound should have a magnetic moment of 4.9 Bohr magnetons, which, in view of the data so far available for platinum compounds, is very unlikely. Platinum is most likely octahedrally coördinated in this compound, as in $\mathrm{Pt(CH_3)_4}$ (118).

The usefulness of a theory is determined largely by the extent to which its predictions check satisfactorily with experiment. In this respect the quantum theory of the directed valence bond has fared well. For example, it predicted (117) that the diamagnetic complexes of Ni^{II} and Au^{III} would have the square structure; in both instances crystal analyses and other investigations have amply borne this out.

Where definite evidence for square coördination has been found for any element it may be assumed that it will be found in this condition generally, unless (*1*) the element is octahedrally coördinated, (*2*) steric effects cause bond-angle distortion, (*3*) marked electronegativity differences produce predominantly ionic (tetrahedral) binding. It is true that some elements, notably Fe^{II} and Mn^{II}, are so very sensitive to this last factor that they are seldom square coördinated. On the other hand, the above provisos rarely have to be invoked for Pt^{II}, Pd^{II}, Cu^{II}, and Au^{III}.

XIV. SQUARE-COMPLEX FORMATION WITH METALS OTHER THAN PLATINUM

A. PALLADIUM

This element resembles platinum very closely except in one respect. Neither the geometrical nor the optical isomers of Pd^{II} retain their configurations with the same tenacity as those of Pt^{II}. Geometrical isomerism is confined, so far as the observations go, to neutral complexes. In summarizing the evidence for Pd^{II} and the metals to follow, the nature of the investigation will first be indicated and then the compound in which the square structure has been found.

Crystal structure: $K_2[PdCl_4]$ (38, 142); PdO (87); $[Pd(NH_3)_4]Cl_2$ (37); $K_2[Pd(COS)_4]$ (32); $[((CH_3)_2S)_2PdCl_2]$ (27); PdS (54); $PdCl_2$ (151); $[((CH_3)_3As)_2PdBr_2]$ (95); $[(NH_3)_2Pd(C_2O_4)]$ (91).

Geometrical isomerism: Cis- and *trans*-forms of benzylmethylglyoximepalladium (46); *cis-* and *trans*-bisglycinepalladium (98, 128); *cis-* and *trans*-dichlorodiamminepalladium (62); *cis-* and *trans*-$[(NH_3)_2Pd(NO_2)_2]$ (91).

Optical isomerism: Isobutylenediaminestilbenediaminepalladous salts (84).

Dipole moments: $[PdCl_2(AsR_3)_2]$ (94); $[PdCl_2((C_2H_5)_3Sb)_2]$ (73).

Crystal optics: $K_2[PdCl_4]$ (98); $Ba[Pd(CN)_4]4H_2O$ (12), etc.

Magnetic susceptibilities: $K_2[PdCl_4]$, etc. (70).

B. NICKEL

This is the first element so far considered for which there is evidence of both the square and tetrahedral configuration, although it must be admitted that the evidence for the latter is as yet rather meager. Theory predicts a square covalent structure for diamagnetic, and an ionic tetrahedral structure for paramagnetic complexes. The former prediction has been abundantly verified, as the following summary shows:

Crystal structure: $K_2[Ni(COS)_4]$ (32); $Ba[Ni(CN)_4]4H_2O$ (13); $Na_2[Ni(CN)_4]\cdot 3H_2O$ (15); bis(*N*,*N′*-dipropyldithiocarbamate)nickel (125).

Geometrical isomerism: Bis(methylglyoxime)nickel (146); bis(benzylmethylglyoxime)nickel (141); bis(thiosemicarbazide)nickelous sulfate (75); nickel salicylaldimine (81).

Dipole moments: $[NiBr_2((C_2H_5)_3P)_2]$ ($\mu = 0$) and related compounds (73); nickel glyoximes (20); nickel salicylaldimine (81).

Crystal optics: $K_2[Ni(CN)_4]$ (107); $Ba[Ni(CN)_4]$ (12), etc.

Magnetic susceptibilities: Nickel ethyldithiocarbamate, etc. (19); a wide range of nickel complexes (102); bis(phenylethylenediamine)nickel chloride, etc. (85).

All the compounds mentioned above are diamagnetic. On the assumption that the magnetic criterion for distinguishing configurations is valid, a study (102) has been made of the factors which determine whether nickel will be tetrahedrally or square coördinated. This study shows that differences between the electronegativity of the nickel and the atoms linked to it play a major rôle; if these differences are large, the bonds are predominantly ionic in character and the structure is tetrahedral. All complexes in which Ni^{II} is bound to four oxygen atoms, as in bis(salicylaldehyde)nickel for example, are paramagnetic. There is also evidence that extensive deflection of bond directions, which in the absence of steric influences would be expected to assume the square orientation, results in a marked change of bond character (104). The bond changes from one of predominantly covalent character to one of predominantly ionic character. The difference in stability of the two configurations must at times be relatively small, as there are instances where the one complex may under some conditions be diamagnetic and under other not very different conditions paramagnetic (85, 86). A notable characteristic of diamagnetic nickel compounds is that they show little tendency to assume sixfold coördination. Paramagnetic nickel compounds with a coördination number of four, on the other hand, quite readily take up two additional atoms or groups to assume the octahedral configuration (47).

It is very interesting to note a similar kind of behavior in ionic Fe^{II} complexes with coördination number four (ferrohemoglobin, etc.), where the change to a diamagnetic octahedral covalent Fe^{II} complex can be readily brought about. The metals which easily form square bonds could not well play the same rôle as Fe^{II} in the blood pigments.

Paramagnetic and diamagnetic nickel compounds lend themselves to studies on the correlation between bond character and absorption spectrum and one or two interesting results have been reported (109). The method of procedure was to compare the absorption of a nickel organic coördination compound with that of the organic molecule from which it was derived, comparisons being made in the same solvent throughout. A marked difference in the two magnetic types was found. Thus, diamagnetic complexes in which the four atoms linked to nickel are two oxygen and two nitrogen atoms exhibit the following features: (*a*) bands of the coördinated molecule, slightly displaced, usually to longer wave lengths; (*b*) one or more bands[16] of appreciable intensity (sometimes with a molecular extinction coefficient approaching 7000) not found in the metal-free

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[16] French, Magee, and Sheffield (52) state that one band only was found by Mills and Mellor, but two bands were actually recorded for both bis(salicylaldoxime)nickel and ethylenediamine-formylcamphor nickel, the weaker having a maximum at 6200 Å. (109).

molecule. These latter bands must be attributed to the presence of the nickel atom in the complex. On the other hand, in the range 6500 to 2500 Å., paramagnetic complexes of nickel show no band, or at least no band of appreciable intensity comparable to (*b*) above, which can be attributed to nickel. Only a relatively limited range of complexes has been examined so far and it is therefore premature to make any generalization.

The tetrahedral configuration for Ni^{II}

Apart from magnetic data, the evidence which has been brought forward to prove the existence of this alternative structure is confined to two lines of approach. There is first of all Jensen's observation (75) that paramagnetic $[Ni((C_2H_5)_3P)_2(NO_3)_2]$ has a large electric dipole moment which presumably arises from a tetrahedral arrangement of the attached groups rather than from the less stable *cis*-planar arrangement. Secondly, there are the data of French and Corbett (51) on the rotatory dispersion and absorption of paramagnetic nickel formylcamphor. The argument used here was that since nickel formylcamphor showed the Cotton effect in a band (maximum at 3172 Å.), the nickel atom must be a center of asymmetry and therefore tetrahedrally coördinated. From the work of Mills and Mellor (109) there is some doubt as to whether the band at 3172 Å., in which the Cotton effect occurs, can be attributed to the presence of nickel atom in the complex.

In any event it has been shown (97) that ethylenediamine-formylcamphor nickel, which is diamagnetic in the solid state, also shows the Cotton effect in a band (maximum 6200 Å.) which definitely arises from the presence of the nickel atom, since it is absent from the ethylenediamine-formylcamphor itself. From the regularities noted earlier (109) this band is to be associated with covalently bound nickel. French, Magee, and Sheffield (52) have recently reported that ethylenediamine-formylcamphor nickel when dissolved in methyl alcohol is paramagnetic with a moment of 1.9 Bohr magnetons, an observation which must mean that there is an equilibrium between nickel in the two different magnetic conditions.[17] An added complication arises from the fact that some of the nickel may become octahedrally coördinated, in which case it would be magnetically indistinguishable from ionically bound nickel. Although it is unlikely that nickel becomes octahedrally coördinated by the attachment of two ethyl alcohol molecules, it has yet to be shown that the optical effects under discussion are due to tetrahedrally coördinated nickel.

C. GOLD (Au^{III})

In the trivalent condition gold undoubtedly forms square bonds, but it is extremely doubtful whether it does so in the monovalent condition. Further

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[17] Attempts have been made to repeat the observation in this laboratory but the solubility of the compound in methyl alcohol is so small that the difference between the magnetic susceptibility of solvent and solution could not be measured with any accuracy. Ethylenediamine-formylcamphor nickel is much more soluble in pyridine, but even in this solvent the susceptibility of the compound did not appear to be very different from its value for the solid (99).

work substantiating the claims of Dothie, Llewellyn, Wardlaw, and Welch (39) is needed before it can be accepted that Au^{I} can be grouped with Au^{III}.

It is noteworthy that no geometrically isomeric auric compounds have been observed, in spite of the definite searches made for them.

Crystal structure: $K[AuBr_4]2H_2O$ (36); $[C_2H_5AuBr_2]_2$ (16); $[(C_3H_7)_2AuCN]_4$ (126); $Cs_2Au_2Cl_6$ (50).

Crystal optics: $[N(C_2H_5)_4][AuCl_4]$, $K[AuBr_4]2H_2O$ (107).

D. SILVER (Ag^{II})

The only instance so far described is argentic picolinate. An incomplete x-ray analysis of this substance made by Cox, Wardlaw, and Webster (33) shows the presence of square complexes.

E. COPPER (Cu^{II})

An outstanding characteristic of copper is that it is much less sensitive to electronegative differences (from a stereochemical viewpoint) than its close neighbors like Ni^{II}, Co^{II}. Several hydrated salts of copper are known, from crystal analyses, to form square complexes, e.g., $CuCl_22H_2O$, $K_2CuCl_42H_2O$, and $CuSO_45H_2O$. No diamagnetic hydrated nickel chloride or sulfate has been reported.

It is very doubtful whether any tetrahedral cupric complexes have yet been found. Arguing by analogy, Mills and Gotts (110) concluded that cupribenzoylpyruvic acid had a tetrahedral structure. It is practically certain that the analogy does not hold.

Large numbers of internal copper complexes containing unsymmetrical chelate groups have been described throughout the literature, and it is extraordinary that so few geometrical isomers have been discovered. One can only conclude that *cis*-isomers must be so unstable as to be incapable of existing for any length of time, or that no special efforts have been made to isolate isomeric forms.

Crystal structure: $CuCl_22H_2O$ (65); $K_2CuCl_42H_2O$ (21); copper diketone (35); $CuSO_45H_2O$ (8); CuO (148); $Cu(py)_2Cl_2$ (28).

Geometrical isomerism: $[Cu_2Cl_3\{(Ph_2Me)_3As\}_3]$ (100); cupric polymethylene bis-imino-acid complexes (138); cupric picolinate (33).

F. COBALT (Co^{II})

The only evidence to date comes from magnetic susceptibility measurements which show that certain internal complexes have a moment corresponding to the existence of one unpaired electron, the number to be expected for a square structure. Magnetic data show that α- and β-$Co(py)_2Cl_2$ are not square forms.

Magnetic susceptibilities: Bis(benzildioxime)cobalt (18); many other internal complexes (103); $[Co(py)_2Cl_2]$ (7, 101).

G. RHODIUM (Rh^{II})

All attempts to prepare square rhodous complexes have so far resulted in failure (99), but Dwyer and Nyholm (48) have described a number of complexes of bivalent rhodium in all of which the Rh^{II} appears to be octahedrally coördinated. They are, without exception, diamagnetic (98).

H. IRON (Fe^{II}) AND MANGANESE (Mn^{II})

Many compounds have been examined (99) in the hope of finding evidence for the square configuration, but without success. Such compounds appear to be very rare, and the only ones reported to date are ferrous and manganous phthalocyanine (139). Several years ago, Cox, Shorter, Wardlaw, and Way (31), on the basis of a determination of unit-cell dimensions, reported that manganous dipyridine chloride $[Mn(py)_2Cl_2]$ had the *trans* square structure. This was subsequently shown to conflict with the magnetic data, which indicated that manganese in this compound was definitely in the ionic condition (101). An alternative octahedral structure was suggested as a way of explaining the small cell dimensions. The structure attributed to the $Mn(H_2O)_4^{++}$ ion in $K_2Mn(SO_4)_2 4H_2O$ (3) is almost certainly incorrect.

I. IRIDIUM, OSMIUM, AND RUTHENIUM

As already pointed out, iridium, platinum, and palladium, etc. in the higher valence states are invariably octahedrally coördinated. It is only in the lower valence states, as in IrCl, for example, that iridium is likely to have the square structure. The empirical composition of diamagnetic Ir^{II} compounds suggests a coördination number of six for iridium even in this low valence state (99). It seems very unlikely that square structures will be found for Os^{II} and Ru^{II}, since the general tendency among platinum metals is to form complexes with the lowest possible magnetic moments. The predicted magnetic moment for square complexes of Os^{II} and Ru^{II} is 2.83 Bohr magnetons. In practice it is found that the compounds of Os^{II} and Ru^{II} are diamagnetic and have a coördination number of six. It should be mentioned, however, that the diamagnetism of compounds of Rh^{II} and Ir^{II} does not accord with the moments predicted for these atoms in table 6 and that there is other evidence for the breakdown of the predictions for heavy atoms like those of the platinum metals (98).

J. ELEMENTS OUTSIDE THE TRANSITION SERIES

Before concluding this survey, some reference must be made to cases where square coördination has been claimed for atoms not listed in table 6 as capable of forming dsp^2 bonds. The evidence for square Tl^I and Au^I (30) rests mainly on the smallness of one of the dimensions (39) of the unit cell in certain of their compounds and cannot therefore be considered as very satisfactory. With regard to earlier claims relating to a square structure for Cd^{II} (11) and Sn^{II} (29), all that need be said here is that the most recent crystal-structure analyses show that these elements are octahedrally coördinated (89).

It was once believed that the α- and β-forms of $[Te(CH_3)_2I_2]$ were *cis–trans* planar isomerides (149), but Drew (40) claims to have shown this explanation to be untenable. The β-form is said to be a molecular compound: $[TeMeI_3]$ $[TeMe_3I]$. Nevertheless, if the bond orientation discovered by Stevenson and

Schomaker (140) in $TeCl_4$ occurs also in $[Te(CH_3)_2I_2]$, as it most probably does, then it is theoretically possible for the latter compound to exist in three geometrically isomeric forms. It would be interesting to know whether it is possible to synthesize isomeric forms of the appropriate compounds of tellurium (and possibly also selenium and arsenic) in which the unshared electron pair of these atoms is stereochemically active.

Lastly, there is an element outside the transition series which does form bonds directed to the corners of a square but not through the agency of dsp^2 orbitals. In the complex ion $[ICl_4]^-$ (112) the iodine atom has two stereochemically active unshared electron pairs in octahedral positions, a structure, which so far as is known at present, is unique.

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