

# THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS

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The stereochemistry of carbon has been investigated so extensively that stereochemistry is commonly considered as a chapter in the study of organic compounds. This thought was so firmly fixed in the minds of the preceding generation that many chemists felt that Werner's resolutions of metal amines into optical antipodes depended upon the fact that he used organic amines (such as ethylenediamine) as coördinating groups. Werner's postulate that the hexammine metal ion is octahedral was universally accepted only after he had resolved an ion containing no carbon.

More recently, x-ray investigations, electron-diffraction studies, dipole-moment measurements, and other physicochemical methods have greatly extended our knowledge of the spatial relationships of the atoms of inorganic, as well as organic, compounds. The important principles of stereochemistry, however, are still those which were discovered through the study of organic compounds, and which, in some cases, have been shown to be applicable to other elements having four tetrahedral valences. But the tetravalent elements are not necessarily tetrahedral, and it is quite probable that some of them are planar, at least in certain types of compounds. The hexavalent elements are evidently octahedral, and present several times as many possibilities for isomerism and intramolecular rearrangement as do the compounds of carbon. Very little is known about the stereochemistry of elements having coördination numbers greater than six, but the relationships must be extremely complex.

The complexity of the stereochemistry of inorganic compounds makes it difficult to establish generalizations and to formulate theories on the basis of observations of these compounds. On the other hand, we have here an extremely useful tool for testing the theories of the organic stereochemist. A theory may describe the behavior of a tetrahedral molecule very well, but if it cannot predict behavior in molecules of other structures, it is in error in some particular. Moreover, when working with the complex inorganic compounds, it is possible to achieve conditions which cannot be achieved with the carbon compounds. Thus, it is possible to com-

pare the stereochemical properties of analogous compounds of different elements; it is possible to vary the valence of the central atom of the complex; and it is possible to achieve optical activity when the center of asymmetry is attached to two or more identical univalent groups.

No attempt is made in this paper to discuss the stereochemistry of the complex inorganic compounds completely. A few of the more important problems which have been reported are described here in the hope of stimulating interest in this investigational field.

#### TETRACOVALENT METALS

The question of the spatial distribution of the valences of the tetravalent elements has received a great deal of attention and has inspired an enormous amount of research. It is well known that the valences of carbon, nitrogen, sulfur, and many other tetravalent elements are arranged tetrahedrally, and there seems to be no substantial evidence that the valences of the elements named are ever otherwise. Among certain of the tetravalent metals, the case is not nearly so simple, since there is evidence for the existence of both tetrahedral and planar structures for several of them. It is still an open question whether the experimental work has been incorrectly interpreted or whether some elements can assume more than one structure.

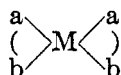
The fact that dichlorodiammineplatinum exists in two forms led Werner (88) to propose a planar arrangement of the four valences of the platinum atom. His interpretation was unchallenged until 1926, when Reihlen and Nestle (73) carried out molecular weight determinations of the two forms (cryoscopically in liquid ammonia) and found one of them to be dimolecular. Werner's fundamental postulate was upheld, however, by Hantzsch's (28) discovery that both forms of  $[\text{Pt}(\text{py})_2\text{Cl}_2]$  (py = pyridine) are monomolecular in phenol and by Grünberg's demonstration (25) of the monomolecular structure of both forms of  $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$ . Dozens of pairs of such isomers have been studied. There seems little reason to doubt that planar structures exist for several of the metallic elements, though some of the cases reported have been found to be in error.<sup>1</sup>

The supposition of planar structures for the tetravalent platinum, palladium, and nickel ions is supported by several x-ray studies. Dickinson (16) has shown the anions of  $\text{K}_2\text{PtCl}_4$  and  $\text{K}_2\text{PdCl}_4$  to be planar, and Cox (10) has reported that the four nitrogens of  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$  are in the same plane as the platinum atom. X-ray investigations of many other compounds of nickel, palladium, and platinum have confirmed these discoveries (11).

<sup>1</sup> For example, Drew, Pinkard, Preston, and Wardlaw (20) have shown that the pallado-diammines exist in only one series, and that the supposed isomeric series (40) is actually polymeric.

The discovery of three isomers of  $[\text{Pt}(\text{NH}_3)(\text{NH}_2\text{OH})(\text{C}_6\text{H}_5\text{N})(\text{NO}_2)]\text{NO}_2$  (84) further confirms the planar arrangement of the valences of the platinum ion. Incidentally this is the only compound of tetravalent platinum known in which four different groups are coordinated to the platinum atom.

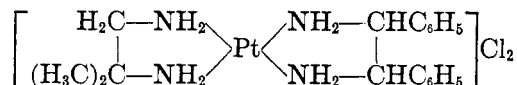
Still further support for the planar structure of these complexes of platinum, palladium, and nickel is deduced from the existence of isomeric forms of chelated spiran compounds of the type



The tetrahedral structure postulates mirror-image isomers; the planar structure postulates *cis-trans* isomers, differing in physical and chemical properties, but having no optical activity. Actually, several cases of such geometric isomerism are known. Dwyer and Mellor have obtained isomeric forms of bisantibenzylmethylglyoximeplatinous chloride (23) and the corresponding palladium salt (24) differing in color, melting point, solubility, and stability. To see whether these compounds have a planar or pyramidal structure, Dwyer and Mellor attempted to resolve them—one of them would be optically active if the molecule is pyramidal—but were unable to prepare salts of optically active acids.

Other examples of unsymmetrical chelate compounds which have been obtained in *cis* and *trans* forms are to be found in the work of Grünberg and Ptizyn (27), Pinkard, Sharratt, Wardlaw, and Cox (65), Sugden (83), Drew and Head (18) and many others.

Mills and Quibell (61) have recently demonstrated in a most ingenious way that the valences of platinum are not tetrahedral. They prepared *meso*-stilbenediaminoisobutylenediaminoplatinous chloride

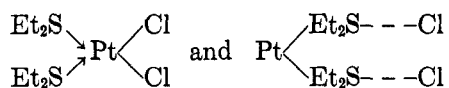


by the successive action of isobutylene diamine and *meso*-stilbenediamine on potassium chloroplatinite. If the valences of the platinum be in a plane, this compound will have no plane of symmetry and must be optically active. If, on the other hand, the valences of the platinum form a regular tetrahedron, the molecule will possess a plane of symmetry. Actually, the compound was resolved into isomers of high optical stability. On the basis of atomic radii considerations, Mills and Quibell have deduced that for this compound, the planar arrangement actually produces less strain in the molecule than does the tetrahedral.

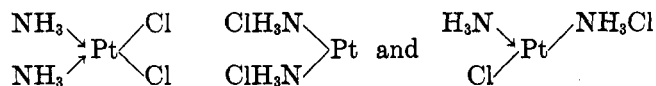
Jensen (35) has recently determined the dipole moments of several compounds of the type  $PtX_2(SR_2)_2$ , where X represents Cl, Br, I,  $NO_2$ , or  $NO_3$ , and R represents ethyl, propyl, isopropyl, butyl, isobutyl, secondary-butyl, or benzyl. The  $\alpha$ (*trans*)-compounds give values of about  $2.4 \times 10^{-18}$  e.s.u., the  $\beta$ (*cis*)-compounds containing halogen values of  $9 \times 10^{-18}$  e.s.u., and the  $\beta$ -compounds containing nitrite and nitrate values of  $13 \times 10^{-18}$  e.s.u. While these results are in accord with Werner's configuration determinations, it is significant that the  $\alpha$ -compounds do not have zero moment. The moment of  $2.4 \times 10^{-18}$  e.s.u. may be reconciled with the planar arrangement by assuming that the valence angles of the sulfur atom are tetrahedral and that the R groups all lie on one side of the plane. However, it is difficult to understand how this unsymmetrical structure would be maintained.

Finally, it should be pointed out that Pauling (64) has shown on strictly theoretical grounds that divalent nickel, palladium, and platinum should have planar structures. His views have been given partial confirmation by the work of Sugden (83), who has studied the isomeric forms of nickel benzylmethylglyoxime. It should be emphasized that the foregoing statements refer only to the metals in the divalent state. Brockway and Cross (9) have pointed out that Pauling's calculations indicate a tetrahedral structure for neutral nickel and they have shown, by electron-diffraction studies, that nickel carbonyl is probably tetrahedral. Cox and Webster (13) have made an x-ray study of trimethylplatonic chloride,  $(CH_3)_3PtCl$ , in which the platinum is tetravalent and quadrivalent. The molecule is not planar, and is presumably tetrahedral.

The recent work of Drew and his associates deserves some mention, for it strikes at the theory of planar distribution of the bonds, and indeed at the coordination theory itself. Angell, Drew, and Wardlaw (1) have examined the isomeric forms of  $Pt\{(C_2H_5)_2S\}_2Cl_2$  and concluded that they are structural isomerides with formulas



Drew, Pinkard, Wardlaw, and Cox (21) have reported the discovery of a third isomer of  $Pt(NH_3)_2Cl_2$  and have ascribed the formulas



to these compounds. Their work has been criticized by Rosenblatt and Schleede (76), and their interpretation by Bassett (6) and by Jensen (36).

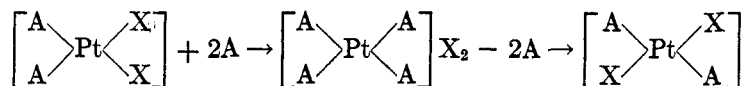
Lifschitz and Froentjes (48) believe they have found support for Drew's formulas, but Jensen (37) feels that their results are fully explained on the basis of Werner's formulas. If the formulas proposed are correct, the assumption of planar configuration for the platinum atom has no support. Drew and his coworkers have therefore abandoned it, and have proposed a new theory to account for the reactions of the isomers (17, 19, 22). They suppose that the four valences are grouped in two pairs, the members of each pair being more closely related to each other than they are to those of the other pair. These rather revolutionary proposals cannot be accepted until they have been substantiated by further work.

Several methods have been devised for distinguishing between the *cis* and *trans* isomers. The well-known method of Werner (89), while lacking a theoretical basis, has proven very useful. Grünberg (26) has postulated that a divalent group can occupy two coördination positions only if those positions are *cis* to each other, and that if this group be displaced by two univalent groups, they will occupy the same positions. Thus  $\alpha$ -[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and [Pt(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)] can readily be converted into each other. The  $\beta$ -[Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>], however, yields an acid oxalate [Pt(NH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>H)<sub>2</sub>] when treated with oxalic acid. The  $\alpha$ -form is therefore the *cis* isomer and the  $\beta$ -form the *trans* isomer. Glycine, ethylenediamine, and other groups which normally occupy two coördination positions can be used in place of oxalic acid.

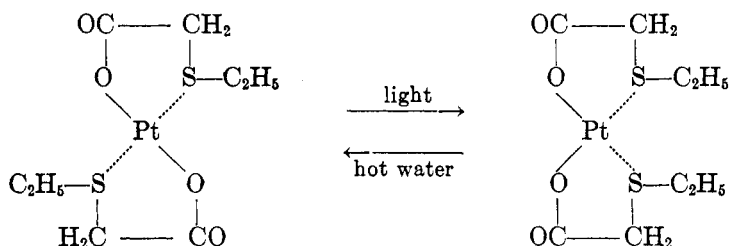
Kurnakow (42) has reported that many platinous salts of the type [PtA<sub>2</sub>X<sub>2</sub>] (A is ammonia or an amine, and X is a negative ion) react with thiourea, the *cis* salts giving compounds of the type [Pt{CS(NH<sub>2</sub>)<sub>2</sub>}<sub>4</sub>]X<sub>2</sub> and the *trans* giving [Pt{CS(NH<sub>2</sub>)<sub>2</sub>}<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]X<sub>2</sub>.

The two types of salts can often be distinguished by differences in properties. The *cis* salts are usually darker in color, more soluble, and have lower melting points.

In some cases the *cis* form changes to the *trans* form very readily. In other cases continued heating is required to effect the change. Thus *cis*-di(triethylphosphine)dichloroplatinum changes to the *trans* form upon heating to 100°C. in a sealed tube with alcohol. In accordance with Werner's principle of "*trans* elimination" the *cis* forms of the type PtA<sub>2</sub>X<sub>2</sub> can be changed to *trans* by adding and removing two molecules of the amine

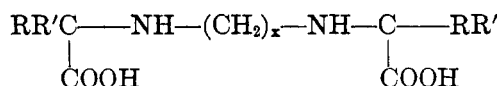


Ramberg (67) has observed that the *cis* and *trans* isomers of platinous ethyl thioglycolate can be readily interconverted.

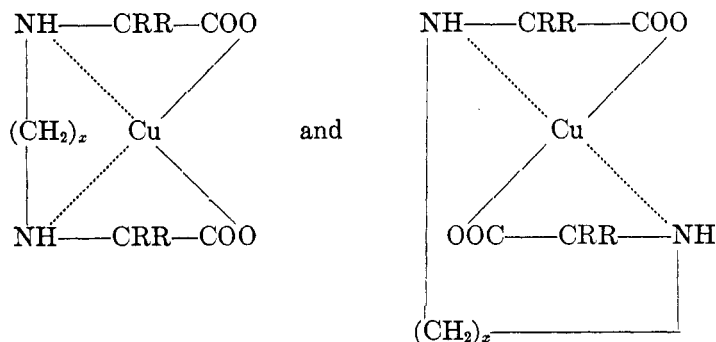


This work has been criticized by Reihlen and Nestle (74), who hold that the platinum is tetrahedral, and that the existence of two forms is due to the presence of the two asymmetric sulfur atoms.

N. Schlesinger (79) has prepared salts of copper with *bis*( $\alpha$ -imino) acids of the type



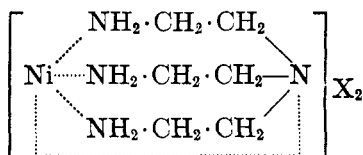
Acids containing two or three methylene groups give water-soluble, blue compounds, those containing ten give insoluble violet compounds, and those containing five or seven give mixtures of the two types. Schlesinger explained these as *cis-trans* isomers.



Obviously the "*cis*" is the blue form, and the "*trans*" the violet form. Reihlen (69), however, has called attention to the fact that, since nitrogen is tetrahedral, the copper either is not planar in these compounds or is subject to great strain. He explains the existence of isomers in the following way: If the  $-\text{CH}_2-$  groups lie "inside" the two nitrogen atoms, a bridge of two or three can span the distance between the nitrogen atoms. If the hydrogen atoms lie "inside" the nitrogens and the  $-\text{CH}_2-$  groups "outside," a bridge of at least seven methylene groups is required.

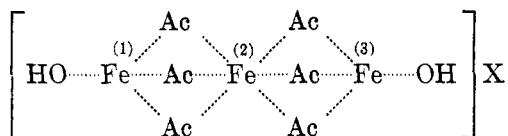
Cox and his coworkers (12, 15) have recently carried out x-ray studies on several complex compounds of bivalent copper, and have found that the four coordinated groups lie in the same plane with the copper.

It is firmly established that the valences of some of the tetravalent elements are non-planar. Compounds of carbon, sulfur, boron, and many other elements exist in optically active forms, which precludes the possibility of a planar arrangement. Even those elements which have been shown to have a planar arrangement must be able also to assume a non-planar configuration. The nickel, platinum, and palladium  $\beta$ ,  $\beta'$ ,  $\beta''$ -triaminotriethylamine salts of Mann and Pope (53) are almost certainly non-planar. The nickel compound has been shown to be monomeric; consequently it probably has the structure (70)



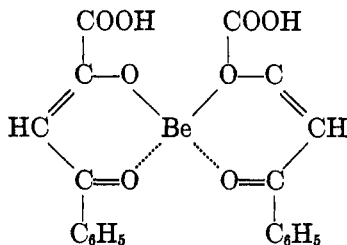
Cox and Webster (14), in reporting the results of x-ray studies on these nickel salts, have pointed out that there is no evidence to show that they are not "pseudo salts" containing hexavalent nickel.

Reihlen (68) pointed out long ago that Werner's formulas for basic ferric and chromic acetates



indicate a three-dimensional configuration. Each of the triplets of acetate groups fills the three corners of a face of the central octahedron. Metal atoms 1 and 3 are therefore centers of three-dimensional figures or are parts of the face of the octahedron, which seems unlikely.

The tetrahedral configuration implies asymmetry and optical activity for certain types of compounds. A considerable amount of work has been done on the resolution of inorganic complex compounds of tetravalent elements. Lowry and Burgess (49) observed that the beryllium salt of benzoylcamphor mutarotates in certain organic solvents. Mills and Gotts (60) prepared beryllium, zinc, and copper compounds of benzoylpyruvic acid:



The beryllium compound was resolved through the brucine salt, and the brucine was precipitated by dimethylaniline. The material so obtained racemized in a few minutes. The brucine salt of the zinc compound and the strychnine salt of the copper compound were shown to mutarotate.

Apparently the first attempt to resolve compounds of tetravalent platinum was made by Rosenheim and Händler (78). The compounds which they studied were too unstable to give positive results. Reihlen and his coworkers had somewhat better success. Reihlen and Hühn (71) resolved the *bis*-(1,2-isobutylenediamine)-platinous and -palladous ions and the *bis*-(2-aminomethyl-3-methyl-4-ethylquinoline)-platinous, -palladous, and -nickel ions through the  $\alpha$ -bromocamphor- $\pi$ -sulfonates. They prepared  $\alpha$ -phenylethylenediamine-(2-aminomethyl-3-methyl-4-ethylquinoline)platinous salts (72) and were able to fractionate the  $\alpha$ -bromocamphor- $\pi$ -sulfonate. Reihlen, Seipel, and Weinbrenner (75) prepared and resolved *l*- $\alpha$ -phenylethylenediaminedipyridylplatinous salts and other similar salts. Rosenheim and Gerb (77) resolved the *bis*(2,3-diaminotoluene)-platinous and -palladous ions. In no case, however, have the nickel, platinous, or palladous salts been obtained in optically active form after the removal of the resolving agent. The results are, therefore, not entirely certain.

Hein and Regler (30) have recently reported that crystallization of *bis*-(8-hydroxyquinoline)argentate  $\alpha$ -bromocamphor- $\pi$ -sulfonate yields fractions of different rotatory power.

Hantzsch and Rosenblatt (29) have suggested that the tetrammine platinum compounds are not true salts of the type  $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ , but are octahedral "pseudo salts"  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$  in which the platinum is hexacovalent. In ionizing solvents, the chlorine atoms are expelled from the complex, as chloride ions, by the entrance of solvent molecules. Evidence for the existence of such pseudo salts is found in the abnormally low conductivity of  $\text{Pt}(\text{pyridine})_4(\text{SCN})_2$  and similar salts in alcohol, and in the fact that several of these salts show different absorption spectra in solvents which form solvates than in those which do not. It should be mentioned in this connection that divalent platinum is undoubtedly hexacovalent in



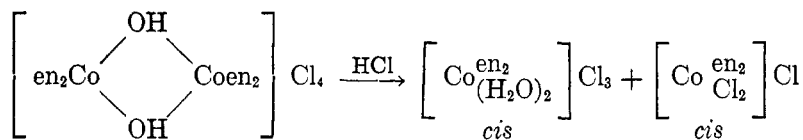
some compounds. By assuming the octahedral structure for the tetramine, the theory accounts for both geometric and optical isomerism.

#### HEXACOVALENT METALS

The stereochemistry of the hexacovalent metals is remarkably complex and very little has been done to unravel the problems it presents. This is largely due, no doubt, to experimental difficulties. Methods of synthesizing even the simple compounds are quite empirical, and it is as yet impossible to build very complex molecules of known configuration. Even if it were possible to synthesize the desired compounds, the problem of determination of configuration would still have to be met. The complexity of the problem is evident from the fact that a molecule in which six different groups are coordinated to the central atom should exist (assuming the octahedral theory) in thirty different configurations,—fifteen pairs of mirror-image isomers. The elementary state of our knowledge of the problem can be seen from the following considerations: The two simplest cases in which isomerism are possible are those in which (1) two coordinated groups are alike, but different from the other four, and (2) two groups are unlike and different from the other four. It is possible to synthesize many compounds of each type and in most cases to tell which is *cis* and which is *trans*. For the closely related compounds of the types  $[MA_2b_2]$  and  $[MA_2bc]$  (A represents a group occupying two coordination positions) it is also possible to distinguish between the *cis* and the *trans*, and in some cases to resolve the *cis* forms into optical antipodes. Resolution is likewise possible for compounds of the type  $[MA_3]$ . Beyond these simplest types, our knowledge is very slight. Compounds of other types have been described, but in most cases their configurations are not known.

Several methods are available for determining the configurations of the compounds of the types  $[Ma_4b_2]$  and  $[MA_2b_2]$ . Isomerism in these cases is apparently impossible when a group occupying two coordination positions is substituted for the groups b. Werner assumed (91) that the compound formed in such case has the *cis* configuration, and that if the doubly bound group be replaced by two singly bound groups (b) these will be *cis* to each other. For example, carbonato tetrammine cobaltic salts react with hydrochloric acid to give purple dichloro salts. These must be *cis*. The green isomeric dichloro salts, therefore, have the *trans* configuration. If we substitute other bases for ammonia, or other halogens for chlorine, the green and purple colors persist, and indicate the configurations of these compounds.

The doubly bridged dinuclear complexes can also be used for determinations of configuration. These are assumed to be joined in the *cis* positions, and when broken, *cis* compounds are formed.



(In these formulas "en" represents ethylenediamine.)

*Cis* compounds of certain types are resolvable into optical antipodes, but *trans* compounds are not. This furnishes an absolute method of determining configurations for molecules of the types  $[\text{MA}_2\text{b}_2]$  and  $[\text{MA}_2\text{bc}]$ .

The *cis* compounds are usually but not always more soluble, less stable, and more intensely colored than the *trans* compounds. The *cis* compounds also have a greater electric moment than the *trans*.

In many cases it is possible to change a *cis* compound to the *trans*, or *vice versa*. Thus, *cis*-dinitrodiethylenediaminocobaltic nitrite changes to the *trans* isomer when its water solution is boiled for a long time. *Trans*-dichlorodiethylenediaminocobaltic chloride changes to the *cis* form on heating in water. The presence of acid, however, causes the reverse change to take place. Reactions in which coordinated groups are displaced often lead to changes in configuration. Werner (91) made an extended study of this phenomenon, but as yet we know very little about it. A few of Werner's results are presented in table 1.

No general rules can be drawn from these results. Reactions 1 and 2, 6 and 7, 8 and 9, and 12 and 13 show that the configuration of the product has no relationship to the configuration of the original material. The last pair mentioned is the most striking, for change of configuration takes place in both reactions. This case has been subjected to a detailed study (7). Several bases were used to carry out the reaction, and the conditions of temperature and concentration were varied over a wide range, but the result in every case was the same as Werner reported. In some cases, however, the conditions of the experiment affect the relative amounts of the two isomeric products very markedly.

To explain these results Werner assumed (90) that the incoming group is subjected to the attractive force of the central ion, and that this attractive force is exerted in a definite direction which determines what position the group shall occupy. The group which is least firmly bound is expelled, and there is no connection between the positions of the incoming and outgoing groups. This problem is certainly in need of further study.

The complex inorganic compounds lend themselves well to the study of optical rotatory power. Many of them are simple in structure, have absorption bands in the visible region, and have very high rotatory powers. Studies of the rotatory power of these compounds have been made by Jaeger<sup>2</sup> (32), Lifschitz (45), Johnson (38, 39), and others, and many in-

<sup>2</sup> For a summary of his results see reference 32.

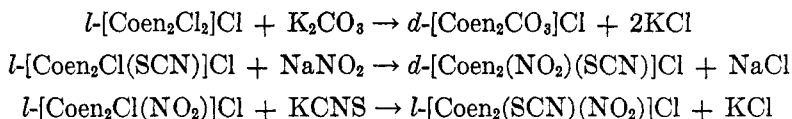
TABLE I  
*Results obtained by Werner in a study of changes in configuration*

REACTION	STARTING MATERIAL		REAGENT	PRODUCT	RATIO OF	
	cis	trans			cis	trans
1		+	Liquid NH <sub>3</sub>	[Coen <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>3</sub>	20	1
2	[Coen <sub>2</sub> Br <sub>2</sub> ]Br	+	Liquid NH <sub>3</sub>	[Coen <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>3</sub>	6	1
3	[Coen <sub>2</sub> Cl(SCN)]SCN	+	Liquid NH <sub>3</sub>	[Coen <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> (SCN)]Cl(SCN)	2	1
4	[Coen <sub>2</sub> Br(SCN)]Br	+	Liquid NH <sub>3</sub>	[Coen <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> (SCN)]Br <sub>2</sub>	1	2
5	[Coen <sub>2</sub> Br(SCN)]ClO <sub>4</sub>	+	Liquid NH <sub>3</sub>	[Coen <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> (SCN)](ClO <sub>4</sub> )Br	2	1
6	[Coen <sub>2</sub> (SCN)(NH <sub>3</sub> )X <sub>2</sub>	+	KSCN	[Coen <sub>2</sub> (SCN) <sub>2</sub> ]SCN		*
7	[Coen <sub>2</sub> (SCN)(NH <sub>3</sub> )X <sub>2</sub>	+	KSCN	[Coen <sub>2</sub> (SCN) <sub>2</sub> ]SCN	**	*
8	[Coen <sub>2</sub> (NH <sub>3</sub> )Cl]X <sub>2</sub>	+	AgOH	[Coen <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> (OH)]X <sub>2</sub>		*
9	[Coen <sub>2</sub> (NH <sub>3</sub> )Cl]X <sub>2</sub>	+	AgOH	[Coen <sub>2</sub> (SCN)(OH)]X <sub>2</sub>		*
10	[Coen <sub>2</sub> (SCN)Cl]Cl	+	NH <sub>4</sub> OH	[Coen <sub>2</sub> (SCN)(OH)]Cl	*	*
11	[Coen <sub>2</sub> (SCN)Cl]Cl	+	KSCN	[Coen <sub>2</sub> (SCN) <sub>2</sub> ]SCN		*
12	[Coen <sub>2</sub> Cl <sub>2</sub> ]Cl	+	KOH	[Coen <sub>2</sub> (H <sub>2</sub> O)(OH)]X <sub>2</sub>	*	*
13	[Coen <sub>2</sub> Cl <sub>2</sub> ]Cl	+	Concd. NH <sub>4</sub> OH	[Coen <sub>2</sub> (H <sub>2</sub> O)(OH)]X <sub>2</sub>		*

\* = chiefly; \*\* = quantitatively.

teresting facts have been brought to light. Johnson has deduced from atomic structure considerations that not all compounds of the type  $[MA_3]$  are resolvable. The trioxalato salts of cobalt and chromium which are held together by "electron bonds" have been resolved, but those of manganese and iron have not, and, according to Johnson, are incapable of resolution, since they are held together by "ionic bonds."

In an effort to find a relationship between configuration and direction of rotation, Werner (92) carried out many transformations involving optically active compounds:



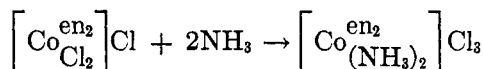
He assumed that no change in configuration took place during these reactions, and formulated structures in accord with this assumption. The results of resolution of some of the compounds mentioned gives some evidence for this view.  $[\text{Coen}_2\text{Cl}(\text{SCN})]\text{Cl}$ ,  $[\text{Coen}_2\text{Cl}(\text{NO}_2)]\text{Cl}$ , and  $[\text{Coen}_2(\text{NO}_2)(\text{SCN})]\text{Cl}$  were resolved through fractionation of the  $d$ - $\alpha$ -bromocamphor- $\pi$ -sulfonates. Werner assumed that the complex ions of the same configuration form in each case the less soluble salt with the active acid. The results obtained agree with those derived from the first assumption, for the  $l$ - $[\text{Coen}_2\text{Cl}(\text{SCN})]^+$ ,  $d$ - $[\text{Coen}_2\text{Cl}(\text{NO}_2)]^+$ , and  $d$ - $[\text{Coen}_2(\text{NO}_2)(\text{SCN})]^+$  ions crystallized with the bromocamphorsulfonate in the first fractions. Werner has applied these principles to other cases as well. Jaeger (33) has criticized these views, and has sought to relate configuration to sign of rotation by a study of the crystal forms of the compounds in question. From studies of the optical absorption and rotation of many optically active complex salts, Mathieu (54) has found some support for Werner's rule relating configuration and solubility of the diastereoisomers.

Several methods of correlating configuration with sign of rotation have been suggested recently. Werner Kuhn (41) has deduced absolute configurations of both organic and inorganic compounds from the theory of the origin of optical rotation. Mathieu (55) has suggested that the study of circular dichroism leads to a determination of configuration. Tsuchida, Kobayashi, and Nakamura (86) have reported that when finely-powdered quartz is shaken with solutions of certain racemic complex compounds, it preferentially adsorbs one antipode, compounds of the same configuration being preferentially adsorbed by quartz of a given sign of rotation. The method may also be used to determine whether a given compound is "cis" or "trans". Thus, when a solution of chloroamminobisdimethylglyoxime cobalt is shaken with the quartz powder, the supernatant liquid

is optically active (87). The complex compound must therefore have the *cis* configuration.

Werner's assumption that atoms or groups in the complex ion are always displaced by others without change of configuration is certainly wrong, for it has been shown (2) that silver carbonate reacts with *l*-dichlorodiethylenediaminocobaltic chloride to give *l*-carbonatodiethylenediamino salts, while potassium carbonate gives the dextrorotatory product. A more recent study (4) has shown that an excess of silver carbonate gives the levorotatory product, while a deficiency gives the dextrorotatory salt. It is interesting to consider this result in the light of the suggestions of Bancroft and Davis (5). From a study of the reaction of bases with halo-succinic acids, they have concluded that the degree of inversion is a function of the acidity of the solution. Such an explanation may not hold in this case, for silver carbonate, like potassium carbonate, is basic. However, the greater the quantity of silver carbonate employed, the higher the negative rotation of the product, while potassium carbonate always gives a dextrorotatory product.

Inversion occurs also when ammonia reacts with dichlorodiethylenediaminocobaltic chloride to form the diammino salt (3):



At the boiling point of liquid ammonia, and at lower temperatures, the product has the same sign of rotation as the original material (0.1 per cent solutions, D line for the dichloro salt and E line for the diammine), but at room temperature or higher, the sign of rotation is reversed. A little of the *trans* salts is always formed, the amount varying with the conditions of the experiment, but it is not yet known what factors control this change.

The fact that inversion can take place in this reaction is very interesting, for it throws some light upon a recent theory of the Walden inversion. Olson (63) and Polanyi (8, 56) have suggested (on the basis of the reactions of organic molecules) that inversion accompanies *every* reaction. If the reaction takes place in one step, the initial and final products have opposite configurations; if it takes place in two steps, inversion takes place twice, and the product has the same configuration as the original salt, etc. In this case two chlorine ions, occupying identical positions in the molecule, are displaced by ammonia molecules. It seems logical to suppose that the same mechanism functions in displacing the two ions. There must, then, be an even number of steps in the complete process, and according to the theory, inversion could not take place. (Formation of the *trans* salts could take place through the steps *cis* → *cis* → *trans* and race-

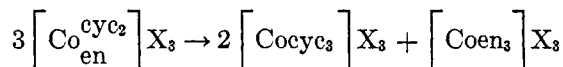
mization through the steps *cis* → *trans* → *cis*). If the two chlorine atoms are not displaced in the same way, inversion may take place.

Meisenheimer's theory of the Walden inversion (57, 59) postulates that the incoming group attaches itself to the face of the tetrahedron opposite the group to be expelled. For the octahedral model, there is no face opposite a corner, but there are four "opposite" faces all equidistant from each corner. If we consider that the incoming group may attach itself to any one of these four faces, the theory of Meisenheimer will predict complete racemization, as a study of the model will show.

If optically active groups are introduced into molecules of the type [MA<sub>3</sub>] some remarkably interesting properties appear. Jaeger and Blumendal (34) have worked with *trans*-1,2-cyclopentylenediamine (cyc). For the complex ion consisting of three molecules of this base and a metal ion, eight stereoisomeric forms are theoretically possible,—*Dddd*, *Dlll*, *Dddl*, *Ddll*, *Lddd*, *Llll*, *Lddl*, *Ldll* (*D* and *L* represent the configurations of the complex ion and *d* and *l* the configurations of the base). For the cobalt and rhodium complexes Jaeger and Blumendal obtained only two compounds,—*Dlll* and *Lddd*. The asymmetry of the base has induced asymmetry in the complex, so that we have a partially asymmetric synthesis.

When racemic  $\left[ \text{Co} \begin{array}{c} \text{en}_2 \\ \text{Cl}_2 \end{array} \right] \text{Cl}$  was treated with racemic cyclopentylenediamine,  $\left[ \text{Co} \begin{array}{c} \text{en}_2 \\ \text{cyc} \end{array} \right] \text{Cl}_3$  was formed. Resolution gave only two of the four possible isomers,—*Dl* and *Ld*. When the levo form of the base was used, however, both of the possible isomers were formed,—*Dl* and *Ll*.

Jaeger and Blumendal also prepared the compound  $\left[ \text{Co} \begin{array}{c} \text{cyc}_2 \\ \text{Cl}_2 \end{array} \right] \text{Cl}$ , using the racemic base. Of the three theoretically possible isomers of the *trans* configuration (*dd*, *ll*, *dl*), only two seemed to form,—*dd* and *ll*. These, on being heated in water, gave the corresponding *cis* forms. For both the *cis* and the *trans* forms, the rotation of the complex was opposite to that of the free base. Attempts were made to introduce the levo base into the complex containing the dextro base, and *vice versa*, but the expected compounds, if formed at all, decomposed to a mixture of the more symmetrical types. The same effect was observed when ethylenediamine was introduced into the molecule:



Evidently the desired compounds were formed in this case, but were too unstable to be separated from the solution.

In building up complexes containing 1,2-propylenediamine (pn) still another complexity is introduced, for in addition to being optically active,

propylenediamine is unsymmetrical. Smirnof (82, see also 85) prepared the platonic and cobaltic tripropylenediamino salts, and observed that it is not possible to have both the levo and dextro base in the same complex ion. Here again the rotation of the complex is opposite that of the base. Smirnof did not detect any isomerism due to the unsymmetrical nature of the propylenediamine molecule.

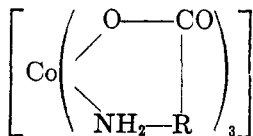
These results hint that a molecule of the type  $\left[ M \begin{smallmatrix} l_2 \\ x_2 \end{smallmatrix} \right]$  (where  $l$  is a levo-rotatory base such as cyclopentylendiamine or propylenediamine and  $x$  is a univalent group) might react more readily with another molecule of the levo base than with a molecule of the dextro base. If this is the case, a molecule of the complex, treated with an excess of the racemic base, might react with the levo component, leaving the dextro component uncombined, and thus effect a resolution of the base. Several attempts to produce such an effect have been made in the author's laboratory,<sup>3</sup> but positive results have not yet been achieved.

Werner and Smirnof (96) investigated the case of *cis*-ethylenediamino active propylenediamino-dinitrocobaltic salts. The complex may be either *D* or *L*, the propylenediamine may be either *d* or *l*, and for the *cis* form the methyl group of the propylenediamine molecule may be either adjacent to the plane containing the nitro groups or distant from it. If all of the possibilities are realized, eight isomers will exist. Werner and Smirnof succeeded in obtaining all of them, thus confirming the predictions of the octahedral theory in a most brilliant manner. The two *trans* salts were also isolated.

Hürlimann (31) investigated the active dipropylenediaminocobaltic salts. Of the great number of isomers possible, only four seem to form,—namely, two pairs of optical antipodes. In one of the pairs the propylenediamine molecules have the same configuration; in the other, they are of opposite configuration. No isomerism due to the position of the methyl group could be detected. None of the six possible *trans* salts was found.

These phenomena have no counterpart in the stereochemistry of carbon. It is quite possible that further study in this field would yield results of great value to stereochemistry.

Ley and his coworkers (43, 44) have studied some amino acid chelate compounds of the type

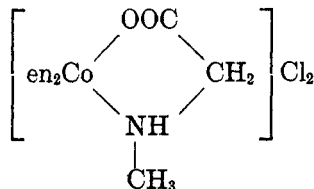


<sup>3</sup> This work has been done by Dr. J. H. Balthis, Mr. C. A. Stiegman, and Mr. E. H. Huffman.

Each of the glycine, alanine, and picolinic compounds exists in two forms (one violet and one red) in one of which the nitrogen atoms are all *cis* to each other (1:2:3), while in the other two nitrogen atoms are *trans* to each other (1:2:6). No method of distinguishing between them has been developed. Both the violet and the red forms are asymmetric, but cannot be resolved as they do not form salts. Chelated amino acid salts of platinum and chromium were also prepared. Using *d*-alanine, Lifschitz (46) obtained three forms of the cobalt salt,—two violet and one red. The two violet forms are supposed to be diastereoisomers, *Dddd* and *Lddd*. If this explanation is correct, there should be two red forms also. Lifschitz did not isolate them, but he obtained evidence for their existence.

Shibata and his colleagues (80, 81) studied the catalytic oxidation of certain racemic amino acids in the presence of optically active complex compounds and reported that one isomer of the amino acid is oxidized faster than the other. They attribute this to an "enzyme-like action" of the inorganic complex. An alternative explanation would be that one form of the amino acid becomes part of the complex, while the other does not. Subsequent oxidation might destroy one or the other. Pugh's results (66) are not entirely in accord with those of Shibata.

In a metal ammine, each nitrogen atom may be considered the center of a "secondary" complex. This was strikingly illustrated by Meisenheimer, Angermann, Holsten, and Kinderlen (58), in demonstrating the tetrahedral nature of the nitrogen atom. Sarcosine-diethylenediamine-cobaltic chloride



was converted to the bromocamphorsulfonate, which upon crystallization yielded two forms, evidently (Co - N±) and (Co + N±). The second, upon recrystallization from water, gave a salt with a molecular rotation (for the D line) of +2290°. This gradually decreased to +2020°, which is the value for the (Co + N±) form. Two of the other three isomers were obtained in the impure state. Their rotations changed in solution to that of the nitrogen racemic compound.

The same principle is illustrated in the resolution of ( $\beta, \beta'$ -diaminodiethyl sulfide monohydrochloride)tetrachloroplatinum,

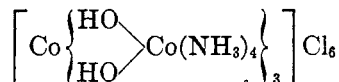




Only one isomer was obtained; evidently it is much more stable than the others, and is formed preferentially. There was some evidence of optical activity, but the results in this regard are not definite.

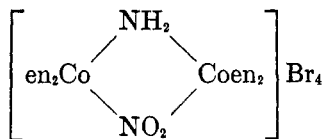
Morgan and Main-Smith (62) demonstrated that ethylenediaminobisacetylacetonone (abbreviated "ec") acting in the enol form,  $\text{CH}_3 \cdot \text{C}(\text{OH}) : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{C}(\text{OH}) \cdot \text{CH}_3$ , can occupy four coordination positions. All five of the possible stereoisomers of the compound  $[\text{Coec}(\text{NH}_3)_2]\text{Br}$  were obtained. The most stable form is the one in which the ammonia molecules occupy the *trans* positions; the other forms, which comprise two pairs of mirror images, all change over to it on standing. Morgan and Main-Smith later attempted to duplicate their own work, even in another laboratory and using new apparatus, but were unable to prepare any but the stable form.

The polynuclear complexes offer many interesting problems in stereochemistry, but very little research work has been done in this field since the time of Werner. The tetranuclear tri-(tetramminodiolcobaltic)cobaltic chloride



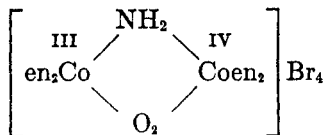
is the most interesting of these compounds from the historical point of view, for the resolution of this purely inorganic substance (94) furnished final proof of the correctness of the octahedral theory.

A polynuclear complex may contain more than one center of asymmetry. Thus, in tetraethylenediamino- $\mu$ -amminonitrodicobaltic bromide



there are two asymmetric cobalt atoms, and Werner (93) was able to obtain dextro, levo, and meso forms. The active forms were converted to the meso form by heating in solution. The fact that the meso form was completely inactive led Werner to the conclusion that there is no essential difference between "primary" and "secondary" valences. Lifschitz (47) does not agree with this conclusion.

In the peroxo salt



the two cobalt atoms differ in valence, so the compound should exist in four forms. Werner (95) isolated two of these,—the ones in which the cobalt atoms are both dextro, or both levo. Starting with the active material, Werner prepared several other optically active dinuclear complexes. These are presented in table 2. It is to be observed that all of the compounds obtained in these reactions have rotations opposite in sign to that of the original material. The rotations, also, are much smaller than that of the original  $\mu$ -amino-peroxo salt. It is not clear whether this is due to a difference in structure or to partial racemization during the

TABLE 2  
Reactions of  $l$ - $\left[ \begin{array}{c} \text{NH}_2 \\ \text{en}_2\text{Co} \diagdown \quad \diagup \text{Coen}_2 \\ \text{O}_2 \end{array} \right] \text{X}_4$   
 $[\alpha] = -840^\circ$ ;  $[M] = -6854^\circ$

NO.	REAGENT	PRODUCT	$[\alpha]$	$[M]$
1	$\text{NH}_3$	$\left[ \begin{array}{c} \text{III} \quad \text{NH} \quad \text{IV} \\ \text{en}_2\text{Co} \diagdown \quad \diagup \text{Coen}_2 \\ \text{O}_2 \end{array} \right] \text{X}_3$	$+160^\circ$	$+1372^\circ$
2	$\text{HX}$	$\left[ \begin{array}{c} \text{HX} \\ \text{III} \quad \text{NH} \quad \text{IV} \\ \text{en}_2\text{Co} \diagdown \quad \diagup \text{Coen}_2 \\ \text{O}_2 \end{array} \right] \text{X}_3$	$+192^\circ$	$+1625^\circ$
3	$\text{NaI}$	$\left[ \begin{array}{c} \text{III} \quad \text{NH}_2 \quad \text{III} \\ \text{en}_2\text{Co} \diagdown \quad \diagup \text{Coen}_2 \\ \text{OH} \end{array} \right] \text{X}_4$	$+110^\circ$	$+990^\circ$
4	$\text{HNO}_2$	$\left[ \begin{array}{c} \text{III} \quad \text{NH}_2 \quad \text{III} \\ \text{en}_2\text{Co} \diagdown \quad \diagup \text{Coen}_2 \\ \text{NO}_2 \end{array} \right] \text{X}_4$	$+158^\circ$	$+1311^\circ$
5	$\text{SO}_2$	$\left[ \begin{array}{c} \text{III} \quad \text{NH}_2 \quad \text{III} \\ \text{en}_2\text{Co} \diagdown \quad \diagup \text{Coen}_2 \\ \text{SO}_4 \end{array} \right] \text{X}_3$	$+200^\circ$	$+1384^\circ$

reactions. Werner believed that the valence of the central atom was important in determining the magnitude of rotation, as the compounds containing one tetravalent cobalt atom have somewhat larger rotations than the others. The data, however, are insufficient to support this hypothesis.

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