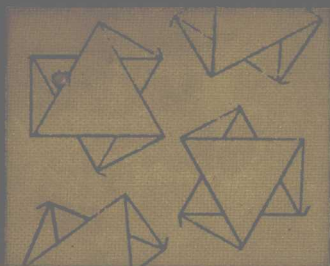


Stereochemistry of Optically Active Transition Metal Compounds



Stereochemistry of Optically Active Transition Metal Compounds

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FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

Alfred Werner used the classical approach to prove his intuitive ideas concerning the stereochemistry of coordination compounds. After Werner's death there was little interest in inorganic stereochemistry for a long period. One of the groups which helped to revive interest in this field and to keep it active for many years was that of John C. Bailar, Jr. at the University of Illinois. We are pleased that he consented to write Chapter 1, for this volume as a personal account of his years in research. It is particularly appropriate since he was honored at the ACS/CSJ Meeting in Hawaii in observance of his 75th birthday.

Optical activity was very important in finally convincing Werner's critics of his theories concerning the stereochemistry of coordination compounds. The study of these optically active compounds has yielded increasingly detailed stereochemical information with improvements in theory and instrumentation and a significant increase in the research effort. The developments in ligand field theory, theories of optical activity, the classical Corey-Bailar paper (*see* Chapter 1, Ref. 26) on conformational effects, and the establishment of absolute configurations for a large number of metal complexes (*see* Chapter 2) have been important in stimulating the development of the stereochemistry of metal complexes.

Major activities in the study of inorganic stereochemistry are now spread throughout the world. The first joint ACS/CSJ Chemical Congress in Hawaii provided an opportunity to bring together many active investigators from the United States, Japan, and Australia. It has been 25 years since the absolute configuration of the first metal complex was determined; the contributions to this symposium are representative of the achievements in this field since that time.

The volume begins with some historical background, the opening lectures of the original symposium, and an invited paper on organometallic chemistry. Stereochemical assignments depend on definitive x-ray work and this work provides a basis for linking theory to experiment. Important new theoretical developments should aid our understanding of and stimulate new work in the study of optically active metal compounds. The stereochemical bases for stereoselectivity in square planar and octahedral complexes and in asymmetric hydrogenation are presented as well as other aspects of synthesis and stereoselectivity. Bioinorganic topics include microbial iron transport compounds and metal ion interactions with azoproteins. Various contributions to CD spectra and the effect of

solvent on the spectra are considered. Photoacoustic detection of CD and stereochemical description and notation also are discussed and should be instructive for workers in the field. The volume is representative of current work in the stereochemistry of optically active compounds of transition metals.

We acknowledge the splendid cooperation of the contributors to the symposium and to this volume. Their efforts and those of the ACS Books Department staff in helping to publish the book soon after the symposium were crucial. We hope that this work will be useful to those active in the field and in arousing further interest in inorganic stereochemistry and its applications.

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January 15, 1980

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Research in the Stereochemistry of Cobalt Complexes

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Stereochemistry, long the backbone of coordination chemistry, is still a major area for investigation and discovery. The methods of studying it have changed, and perhaps because of that, the emphasis on the topics under investigation has changed. Synthetic chemistry has been displaced by, or better, augmented by, physical methods. Both approaches are important and both contribute to the growth of our knowledge. It is most appropriate that we should hold a symposium on the stereochemistry of complexes and compare notes on what is being done in the countries which are represented at this meeting. In introducing the symposium, I should like to recount some developments of the nearly fifty years that I have been involved in this field. Most of the work which I shall describe was done by my students -- not that I think that their work is better than that of others, but because I know it better, and it serves to illustrate some interesting aspects of what I think of as the synthetic approach. Space alone would preclude discussing any more.

My entrance into the field of inorganic stereochemistry was brought about in an unusual way. As an organic chemist, my interest lay chiefly in isomerism and isomeric rearrangements. One day in a class in general chemistry which I was teaching, there was a discussion of the hydrolysis of antimony trichloride, which leads to the precipitation of the oxychloride, SbOCl . One of the students referred to this as "antimony hypochlorite". While I was correcting his impression that " OCl " always represents a hypochlorite, it occurred to me that the hypochlorite of a metal in the +1 oxidation state would be isomeric with the oxychloride of that metal in the +3 state. This was the first time I had ever imagined that inorganic compounds could exist in isomeric forms, and it was an exciting idea. That very day, I began efforts to prepare the two isomers of TlOCl , only to discover that thallous hypochlorite cannot exist, for the cation is easily oxidized and the anion is a strong oxidizing agent. However, the idea of inorganic isomers persisted and my thinking and reading soon led to the postulation of many other cases; for example,

selonosulfate and thioselenate, phosphonium nitrate and ammonium metaphosphate and hydroxylamine nitrite and ammonium nitrate. Of course, one cannot go very far in looking for isomers in inorganic chemistry without discovering the whole, rich field of coordination compounds. And if one can have isomeric rearrangements in organic molecules, why not in the complexes of cobalt, too? It was thus that I became an inorganic chemist.

The stereochemistry of coordination compounds was a part of chemical thinking much earlier than is generally assumed. For example, as early as 1875, van Hoff suggested that compounds containing six groups attached to a central metal atom are at the corners of an octahedron and that geometric isomers should exist for suitably substituted cases (1). However, it was Alfred Werner who demonstrated that this is indeed the case, and also that the four covalent platinum(II) compounds are coplanar. In those early days, the multitude of sophisticated techniques which we now enjoy was not known, and deductions as to structure had to be made mostly on the basis of synthesis and other chemical evidence. Progress was slow, for this kind of structure determination requires a great deal of imagination and more experimental work than determination of structure by modern methods.

Consider, for example, Werner's ingenious determination of the structures of *cis*- and *trans*-[Pt(NH₃)₂Cl₂] (2), and his demonstration of the octahedral structure of six-coordinate complexes through the optical resolution of [Co(en)₂(NH₃)X]²⁺ (X = Cl, Br) (3). We are now able, by modern techniques, not only to perform these demonstrations quickly, but, in the case of chiral complexes, to show the actual configurations of the isomers (4,5).

After Werner's death in 1919, there was little activity in the field of stereochemistry of coordination compounds. An exception is found in the work of Yuji Shibata, who had been one of Werner's students, and who continued with excellent stereochemical work when he returned to Japan. His work on the enzyme-like activity of cobalt complexes furnishes especially interesting examples of stereoselectivity and of the catalytic action of such compounds (6). T. P. McCutcheon and V. L. King, Americans who had done their theses on stereochemical topics under Werner's guidance, did not continue in that field. King, who actually performed the first resolution of an asymmetric complex (7), went into industrial work. McCutcheon became a member of the faculty at the University of Pennsylvania and did research on complex compounds, but not on their stereochemistry.

In a long paper which he published in 1912 (8), Werner described many *cis-trans* rearrangements which cobalt(III) compounds undergo during replacement reactions. He also described some reactions of optically active complexes, which give optically active products, such as the one shown by the equation



He had no way of knowing whether this reaction involved an inversion of configuration, but on the basis of such studies, he suggested a mechanism for the famous Walden inversion of organic chemistry, postulating that the central atom of a chiral molecule exerts a directive influence.

Some years later, Robert Auten, an undergraduate student at the University of Illinois, achieved an optical inversion in the reaction just mentioned (9). Patterning his work on that of Walden, Auten used silver carbonate instead of potassium carbonate and obtained a levo-rotatory carbonate complex. It was soon found that the choice of carbonate is not the important factor, and Dwyer, Sargeson and Reid, in Australia, showed that the pH of the solution is the deciding factor (10). After his initial success, Auten looked for inversions in the reactions of the dichloro complex with oxalate and nitrite, but did not find them. It is most fortunate that he tried the carbonate reaction first, for otherwise, we would have concluded that optical inversions do not take place in the reactions of cobalt complexes, and probably would not have tried carbonate.

Werner's directions for the resolution of the dichloro complex are very simple and quite specific, but when Auten repeated them, he obtained no crystals of the diastereo isomer at all. Several trials all gave negative results. Upon reflection, Auten realized that laboratories in Europe are not heated as much as ours in America, so he repeated Werner's directions with the solution cooled to 16°. This gave an excellent yield of pure product. Every chemist knows that sometimes repetition of another's work does not give good results; many do not understand, however, that the difficulty may lie in a minor change in conditions.

It was soon found that an inversion takes place also in the reaction



the configuration of the final product depending upon the temperature at which the reaction takes place (11). This seems to be a somewhat more complicated reaction than the one with carbonate, for it proceeds in two distinctly visible steps with sharp changes in color, and in each step the product may have the original configuration, the mirror image one, or the trans configuration. The rotations observed for the diammine were very small, but were confirmed by observations made by several different people and even by secretly having the observers check the same sample repeatedly. The results are shown in Table I.

Table I.
Reaction of Ammonia with levo-[Co(en)₂Cl₂]Cl to yield
[Co(en)₂(NH₃)₂]Cl₃

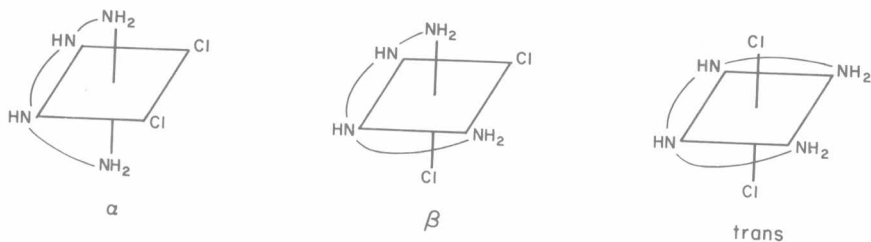
Reagent	Temperature	Ratio cis/trans in product	[α] _D
Liquid NH ₃ (solution)	-77°	2.5/1	-32°
Liquid NH ₃ (solution)	-38°	2.85/1	-22°
Liquid NH ₃ (solution)	+25°	3.7/1	+18°
Gaseous NH ₃	+80°	∞	+38°

In the reaction at 80°, the complex remained solid throughout the reaction. Evidently very little rearrangement of any sort took place, for the value of [α]_D for an authentic sample of dextro [Co(en)₂(NH₃)₂]Cl₃ was +50°. The discovery of inversion in this reaction was somewhat surprising, even to the investigators, for it had been assumed that the two steps would follow the same mechanism, so that any inversion that took place in the first step would be counterbalanced by an inversion in the second. However, Earl Greenwood was not able to get an inversion in the reaction (12)



so it was assumed that inversion takes place only in the replacement of the first chloro group. Ronald Archer later showed that this is, indeed, the case (13).

Closely related to this is the much later work of Eishin Kyuno and Laurence Boucher (14), who studied the reactions of the triethylenetetramine complex, [Co(trien)Cl₂]Cl. The complex cation of this substance exists in three stereoisomeric forms



both the α and β forms being asymmetric and resolvable. Treatment with base converts the dextro-α-form into its levo-β-isomer.

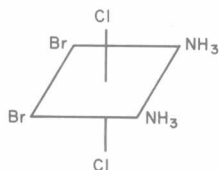
We once thought that all of these rearrangements result from the abstraction of a proton from a coordinated amine and the motion of the resulting negatively charged amine group from

one corner of the octahedron to an adjacent one. This may not be the case, however, for Archer and his students at the University of Massachusetts have observed an inversion in a reaction of an octahedral complex in which there are no acidic protons (15).

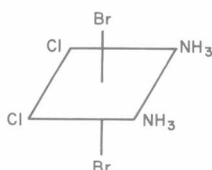


Another stereochemical problem concerns the preparation of octahedral complexes of known configuration.

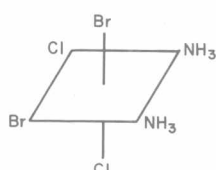
The Russian chemists, who are masters in the manipulation of platinum complexes, have done interesting work in this area. For example, Chernyaev and Krasovskaya (16) prepared all five isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{Br}_2]$:



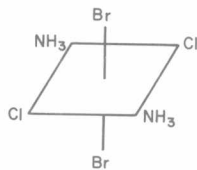
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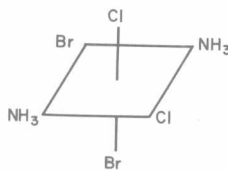
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III

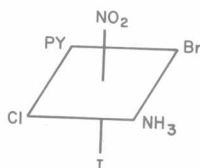


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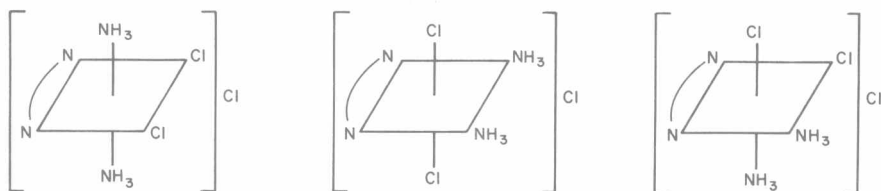
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Dr. Anna Gel'man (now usually transliterated as Hel'man) and her colleagues have also done elegant work of this type and have succeeded in making the compound



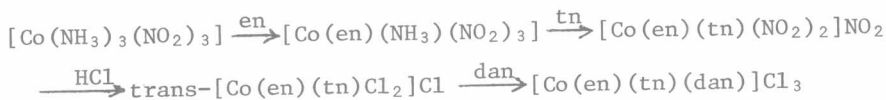
in which the position of each group is firmly established (17). This substance is chiral, but evidently no attempt has been made to resolve it. Platinum lends itself readily to these involved syntheses, for the trans effect in the reactions of planar platinum(II) complexes allows the preparation of isomers which offer good starting places for the formation of the desired octahedral platinum(IV) compounds. It is unfortunate that Dr. Hel'man has not continued her very interesting research on the synthesis of compounds containing a multiplicity of unidentate groups, for it is excellent work. For some years now she has been involved in the chemistry of actinide elements.

The preparation of three isomers of $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$ by Peppard (18), I think, ranks in importance with those just mentioned.



In these syntheses, Peppard had to rely on the very weak trans effect in the cobalt complex $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]^-$. The cis-dichloro-cis-diammineethylenediaminecobalt(III) ion is asymmetric, and Peppard partially resolved it into its enantiomeric forms by adsorption on quartz ground to 100 mesh. This method of resolution is frequently, but not always, effective. Before it can be fully utilized, we will need to learn a great deal more about the principles of adsorption. The preparation of Peppard's isomer's is particularly interesting because cobalt(III) complexes rearrange easily, whereas the platinum compounds do not.

Another case involving cobalt complexes was studied by Work (19), who prepared, among others, a compound containing three different bidentate amines--ethylenediamine, trimethylenediamine, and neopentanediamine, $[\text{Co}(\text{en})(\text{tn})(\text{dan})]\text{Cl}_3$, by following and extending a synthesis first described by Werner (20):



The last step was accomplished through the catalytic influence of decolorizing carbon, a method first used by Bjerrum (21) and developed by Work (22). Doubtless, this synthesis now could

be performed more easily through the elegant tris-carbonato method developed by Mori and his colleagues (23).

A great deal could be learned by further synthetic studies of unusual complexes of platinum and cobalt, as well as other metals, but the syntheses are long and multistep and few chemists have the patience to attempt them. Knowledge gained by work on the complexes of one metal can be used only indirectly in studies of another; the chemistries of the complexes of cobalt(III) and chromium(III), for example, are quite different, although these substances closely resemble each other in physical properties.

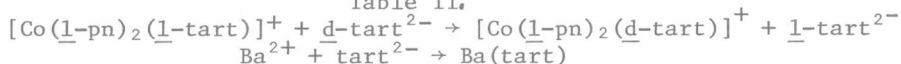
Another topic of interest in the stereochemistry of coordination compounds is that of stereoselective reactions. The first case of this was discovered by Tschugaieff (Chugaev) and Sokoloff in 1907 (24). They prepared the tris-1,2-propanediamine-cobalt(III) complex from racemic propylenediamine and found that the ions obtained contained molecules of only the levo- or only the dextro- base, and that the presence of these in the complex forced an overall asymmetry upon it. Thus, they obtained [Dlll] and [Lddd] complexes, where the capital letters represent the rotation of the complexes, and the small letters, the rotation of the molecules of coordinated base. Many people have worked in this field since, and a good deal has been learned. Dwyer, Sargeson, and members of their groups have been particularly productive in this field. The subject was discussed in detail by Jaeger (25), who prepared tris-(trans-1,2-cyclopentanediamine) rhodium(III) and cobalt(III) ions, and found that, using the racemic base, only two of the possible isomers, (Dlll and Lddd), were formed in each case. Even if only one or two molecules of the optically active base were used along with a symmetrical base, as in $[\text{Co}(\text{en})_2(\text{cptdin})]^{3+}$ and $[\text{Co}(\text{en})(\text{cptdin})_2]^{3+}$, a stereoselective effect was observed. Likewise, efforts to prepare trans- $[\text{Co}(\text{l-cptdin})(\text{d-cptdin})\text{Cl}_2]^+$ were without avail. Jaeger was of the opinion that this stereospecificity was dependent upon the symmetry of the complexes--the more symmetrical the molecule, the greater its stability. It is now generally agreed, however, that the formation of some isomers in preference to others depends upon the conformations of the chelate rings. This concept is largely due to Professor E. J. Corey (26).

The complexes of propylenediamine (1,2-propanediamine) offer a somewhat more complicated picture than those of trans-cyclopentanediamine, for the propylenediamine molecule not only contains an asymmetric carbon atom, but is also unsymmetrical. Werner reported the isolation of all eight of the possible isomers of cis- $[\text{Co}(\text{en})(\text{pn})(\text{NO}_2)_2]^+$, and this was supported by the work of Cooley and Liu (27), who obtained four isomers of cis- $[\text{Co}(\text{en})(2,3\text{-bn})(\text{NO}_2)_2]^+$ and four cis- $[\text{Co}(\text{en})(\text{iso-bn})(\text{NO}_2)_2]^+$. (2,3-bn = racemic $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NH}_2$; iso-bn = $\text{NH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$). The isomers containing 2,3-butylenediamine proved to be of unequal stability--in fact, in the early experiments, only three

isomers were obtained, and, to isolate the fourth, the experiment had to be repeated, using milder conditions.

In the early belief that these reactions were completely stereospecific, we felt that the reaction of $[\text{Co}(\text{l-pn})_2\text{Cl}_2]^+$ with carbonate could not give an optical inversion under any experimental conditions. This is, of course, not true, as was soon shown by the work of McReynolds (28) and Sister Mary Martinette Hagan (29). In a cobalt complex containing asymmetric ligands, one form is preferred, but both forms can and do exist. In the same belief, we hoped that stereospecific effects could be used in the resolution of racemic potential ligands. This does give partial resolution, as shown by the work of Johnson (30), Jonassen and Gott (31,32) and Hamilton (33). Hamilton's results, shown in Table II, indicate this clearly.

Table II.



Time of Standing with Ba^{2+} (hours)	Yield of Ba tart (g)	$[\alpha]_D$ of Recovered Tartaric Acid
0	4.7	-6°
0.2	1.5	0°
0.5	0.6	$+7.5^\circ$
2	0.9	$+7.5^\circ$
4	1.6	$+7.5^\circ$
18	0.5	$+12^\circ$
72	0.2	$+10^\circ$
10.0 (theoretical)		

He treated $[\text{Co}(\text{l-pn})_2\text{CO}_3]\text{Cl}$ with a 100% excess of racemic tartaric acid to form the complex $[\text{Co}(\text{l-pn})_2\text{tart}]^+$. The addition of an excess of barium hydroxide to the solution gave an immediate precipitate of barium tartrate which was removed from the solution, and which was shown to contain an excess of l-tartrate. The filtrate, upon standing, gave more precipitate, which was removed at intervals, and was found to contain tartrate of varying rotatory power, but always dextro. Attempts to improve the stereoselectivity by using very bulky asymmetric ligands, such as phenylethylenediamine, have not improved the situation (34).

The first stereoselective syntheses of coordination compounds were performed by Jonassen and Huffman (35) who treated $[\text{Co}(\text{en})_2\text{CO}_3]^+$ with d-tartaric acid. This gave a mixture of D- and L- $[\text{Co}(\text{en})_2\text{d-tart}]^+$, which, upon treatment with ethylenediamine at 50° , gave a 70% yield of D- $[\text{Co}(\text{en})_3]^{3+}$. Either the two tartrato isomers were formed in unequal amounts, or the less