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ALFRED WERNER'S RESEARCH ON GEOMETRICALLY ISOMERIC COORDINATION COMPOUNDS

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CONTENTS

ABBREVIATIONS

A, B, C	monodentate ligands; charge indicated by superscript Roman numerals
$\overline{AA}$, $\overline{BB}$, $\overline{CC}$	symmetrical bidentate ligands; charge indicated by superscript Roman numerals

$\overline{AB}$	unsymmetrical bidentate ligand
en	the bidentate ligand ethylenediamine, $H_2NCH_2CH_2NH_2$
pn	the bidentate ligand propylenediamine, $H_2NCH_2CH(CH_3)NH_2$
tn	the bidentate ligand trimethylenediamine, $H_2NCH_2CH_2CH_2NH_2$

A. INTRODUCTION

This article is the last in a series of four dealing with various aspects of the research of Alfred Werner, the founder of coordination chemistry[1]. In the words of Sykes and Weil[2]: "It is fitting once again to give credit to the work of Werner and his students, which continues to dominate the background of the field despite the corrections and elaborations which have now been made." Like the previous articles on polynuclear complexes[3], structural isomerism[4] and optically active complexes[5], the viewpoint in this review is largely "historical". In some cases Werner's results have been related to later developments, but this article is not intended to complete with recent reviews or with standard treatments of the subject[6—16]. Literature summaries can be found in *Gmelin's Handbuch*[17,18] and Pascal's *Traité*[19] and reproducible preparative procedures[20—41] and significant papers by Werner[42] and others[43] in English translation are also available.

In 1832 Berzelius "proposed to call substances of the same composition but different properties *isomeric*, from the Greek ἰσομερῆς (composed of equal parts)"[44]. Although isomerism is sometimes divided into several types, basically there are only two types — (1) structural or position isomerism and (2) stereoisomerism or space isomerism. Structural or position isomerism[4] results from differences in the arrangement of atoms or groups of atoms in the molecules (constitution). In other words, an actual difference in bonding exists between the different isomers. Stereoisomerism or space isomerism results from differences in the spatial arrangement of atoms or groups of atoms (configuration). In other words, the same bonding is present in the different isomers, but the bonds are oriented differently in space. Stereoisomerism, in turn, is subdivided into geometric isomerism and optical isomerism[5].

The highlights of Werner's research on geometric isomerism are summarized in his magnum opus, *Neuere Anschauungen*[45]. His earlier work, up to about 1903, is also described in his other and less well-known text, *Lehrbuch der Stereochemie*[46]. Beginning with Werner's very first paper on the coordination theory[47], the phenomenon of isomerism has played a prominent role in his work and thought, and a complete listing of all his articles involving isomerism would include most of his contributions to coordination chemistry. Key papers, in which much of his work found elsewhere[48—85] is summarized, include his Berlin lecture of November 3rd, 1906 before the Deutsche Chemische Gesellschaft[86], his paper on stereoisomeric salts in the Adolf Lieben *Festschrift* of the same year[87], his 1911 paper on spatial rearrangement in reactions of stereoisomers[88] and last, but not least, the longest paper that he ever wrote, his monumental 272-page article of 1912 on stereoisomeric cobalt compounds[89]. In this last and most extensive compendium Werner[89] listed 27 series of cobalt compounds that had been obtained in two stereoisomeric series.

Shortly after Werner had received the Nobel Prize, the progressive and degenerative illness that eventually claimed his life made its appearance, and as early as 1915 he was forced to give up his lecture duties (ref. 1, Chap. 15). Consequently, Werner did not publish some of his work that was carried out during the decade of the 1910s. Because Paul Karrer, Werner's successor at the Chemisches Institut der Universität Zürich, soon turned his interest to problems of organic chemistry, these results remained buried in Werner's students' dissertations, many of the titles of which are so general as to give little hint of their contents. Hence a prominent feature of this review is the citation of more than fifty[90–146] of the two hundred odd dissertations written by Werner's Doktoranden or Doktorandinnen (a surprisingly large proportion of Werner's students were women). Only a fraction of Werner's students' dissertations were available to the present author, and, considering Werner's central role in coordination chemistry, it would be of great value to contemporary coordination chemists if at least a detailed list of the contents of all the dissertations were somehow made available to them.

B. GEOMETRIC ISOMERISM AND PROOF OF THE OCTAHEDRAL CONFIGURATION

From his earliest work on coordination compounds[47], Werner recognized that, contrary to common belief, isomerism was an important and frequently encountered phenomenon in inorganic chemistry and that it could provide insight into the structure of complex compounds. His remarks in the first edition (1905) of *Neuere Anschauungen* are typical:

""The concept of isomerism has only minor significance in the inorganic field, especially since only a few cases of isomerism are known," is an assertion which is repeatedly found in the most diverse variations in the publications of the last decade and which is occasionally still found repeated today without any proof for its justification.... The compounds in the inorganic field, with the exception of the simple bases, acids and salts, are of very complex composition; furthermore, they are synthetically either very difficult to obtain or their mode of formation gives no information about their constitution. It is therefore important that the appearance of important isomeric phenomena gives us the means of fathoming the involved structure of these complicated compounds.

That the concept of isomerism actually has great significance in inorganic chemistry also and that the number of isomeric phenomena is no small one will be seen from the following. First, it should be emphasized that inorganic isomerisms are more varied than organic ones, since they do not originate from a unified principle but rather must be attributed to varied and in part still not wholly recognized causes." (Ref. 45a, pp. 158—159.)

The details of Werner's proof for the octahedral configuration of cobalt(III) have been given elsewhere[10,43,147,148]. Here we need only mention that the method used, viz. "isomer counting", did not originate with Werner. Yet the technique of comparing the number and type of isomers actually prepared with the number and type theoretically predicted for various configurations probably reached the height of its development with Werner's work. By this method he was able not only to discredit completely the Blomstrand—Jørgensen chain theory but also to demonstrate unequivocally that tripositive cobalt possesses an octahedral configuration rather than another possible symmetrical arrangement such as hexagonal planar or trigonal prismatic.

Although compounds containing complexes of type MA_6 and MA_5B should occur in only one form for each of the configurational possibilities, compounds of types such as MA_4B_2, MA_4BC, $M(\overline{AA})_2B_2$ or $M(\overline{AA})_2BC$ should exist in two forms for an octahedral configuration but in three forms for the other two configurations, and consequently most of Werner's synthetic attempts involved compounds of these types. In most cases the number and type of isomers actually prepared corresponded to the theoretical expectations for the octahedral arrangement, but there were a few exceptions, and Werner required more than two decades to accumulate a definitive proof for his structural ideas.

For example, the first and still probably the best known case of inorganic geometric isomerism was discovered in 1890 by Werner's primary scientific adversary Sophus Mads Jørgensen not among simple tetraammines MA_4B_2 but among salts of the $M(\overline{AA})_2B_2$ type. In 1889 Jørgensen (ref. 149, p. 15) first described green salts of composition $[Co(en)_2Cl_2]X$ (see Section D(iii)(a)(5)), completely analogous to the previously known praseo salts of Gibbs and Genth[150], $[Co(NH_3)_4Cl_2]X$ (see Section D(iii)(f)(2)), which he therefore called ethylenediaminedichloropraseo salts. In the following year Jørgensen (ref. 151, pp. 448—53) observed that evaporation of a neutral aqueous solution of ethylenediaminedichloropraseo chloride produced an isomeric violet compound which he called ethylenediaminedichlorovioleo chloride. He regarded the difference in color as due to *structural* isomerism connected with the linking of the two ethylenediamine molecules, whereas Werner correctly regarded the compounds as *stereoisomers*, differing only in the spatial orientation of the bonding (violeo, *cis*; praseo, *trans*).

If this type of isomerism were merely a geometric consequence of the octahedral structure as Werner maintained, it should also be observed among simple tetraammines MA_4B_2 which do not contain ethylenediamine. Yet for compounds $[Co(NH_3)_4Cl_2]X$, only one series, the above-mentioned praseo was known[150]. Jørgensen, a confirmed empiricist, quite correctly criticized Werner's theory on the ground that it implied the existence of unknown compounds. It was not until 1907 that Werner[71] finally succeeded in synthesizing the unstable, highly crucial violeo tetraammines, *cis*-$[Co(NH_3)_4Cl_2]X$ (see Section D(iii)(f)(2)), which were a necessary consequence of his theory but not of the Blomstrand—Jørgensen chain theory[147,152]. His Danish opponent thereupon immediately conceded defeat.

The second case of geometric isomerism among coordination compounds was likewise discovered by Jørgensen. In 1875 Gibbs[153] had prepared the yellow croceo salts of composition $[Co(NH_3)_4(NO_2)_2]X$ (see Section D(iii)-(f)(1)). In 1894 Jørgensen (ref. 154, p. 159) discovered the isomeric flavo compounds. Once again, he attributed the isomerism to *structural* causes (difference in the bonding of the NO_2 groups to the cobalt atom), while Werner correctly maintained that the salts were *stereoisomers* (flavo, *cis*; croceo, *trans*). Through the years Werner made a concerted effort to prepare various series of geometrically isomeric pairs of compounds which supported his stereochemical views and which were not explicable according to the rival Blomstrand—Jørgensen chain theory.

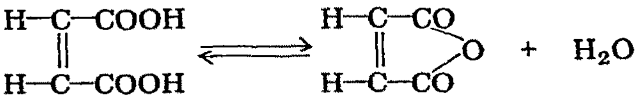
Even though the discovery of the long-sought violeo salts convinced Jørgensen that his own views and those of his mentor Blomstrand could not be correct, Werner's success in preparing two, and only two, isomers for compounds of the types mentioned was not sufficient to prove conclusively his proposed octahedral configuration. Despite such "negative" evidence, it could still be argued logically that failure to isolate a third isomer for these compounds did not necessarily prove their nonexistence. A more "positive" proof was necessary, and this proof, which involved the resolution into optical isomers of certain types of asymmetric coordination compounds containing chelate groups, has been discussed in detail elsewhere[43,147,148]. Suffice it to say that by 1912, in the opening lines of his longest paper Werner was able at long last to announce triumphantly:

> "The investigations of stereoisomeric cobalt compounds have occupied us longer than we originally intended, primarily because for a long time it was not possible to discover conclusive evidence for the steric concept and unambiguous methods for the determination of configuration. It was therefore necessary to accumulate a very extensive collection of factual data before positive experimental foundations for the solution of these problems could be attained. This has now been accomplished, and the experimental results published in this article demonstrate that both problems have finally been solved." (Ref. 89, p. 1.)

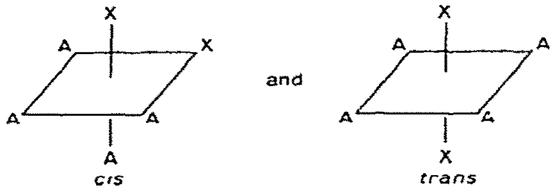
C. ASSIGNMENT OF CONFIGURATION

From the inception of his coordination theory[47,50], Werner was concerned with the problem of assigning configurations to each isomer of given isomer pairs for both coordination numbers four and six. In other words, he devised methods for deciding which isomer was *cis* and which was *trans*. Basically, the methods devised were similar to those used in organic chemistry to assign structures to geometrically isomeric ethylene compounds[155]. Both methods depend on the determination of the genetic relationships between one of the isomers and the corresponding cyclic compounds.

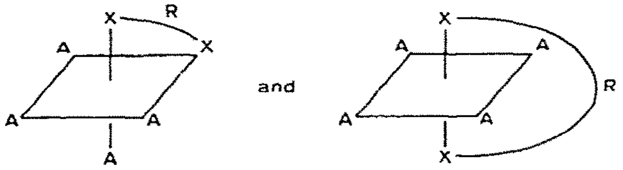
The compound for which the *cis* configuration is to be proven should be preparable from a closed ring compound or should be convertible into a compound of a known closed ring constitution. The simplest organic example is the case of fumaric acid and maleic acid[155]. The latter is considered to be the *cis* form because it forms a cyclic anhydride, which on hydrolysis regenerates maleic acid.



Similarly, among stereoisomeric cobalt compounds it is obvious that since

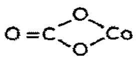


chelate groups can only span adjacent positions on the octahedron, ring closure between the two X atoms can occur easily for the *cis* isomer but only with great difficulty, if at all, for the *trans* isomer. The strict analogy with the



ethylene compounds can be made more obvious if we compare with the organic compounds the relative positions of the groups in the octahedral plane in which two A groups and two X groups are found.

Werner assumed that in the carbonatotetraammine salts, $[Co(NH_3)_4CO_3]X$, the carbonate group forms a four-membered ring with the cobalt atom and



that consequently the two oxygen atoms bonded to the cobalt atom are in the *cis* positions. He therefore concluded that, when diaquotetraammine salts are formed from the carbonato compound by the action of dilute mineral acids, the two water molecules enter the *cis* positions.

$$[Co(NH_3)_4CO_3]X + 2HX + H_2O \rightarrow cis\text{-}[Co(NH_3)_4(H_2O)_2]X_3 + CO_2\uparrow$$

Since similar replacements among stereoisomeric cobalt complexes are known in many cases to be accompanied by rearrangement, Werner's choice of this reaction as a starting point for configurational determinations was an extremely fortunate one. In some cases, Werner confirmed these configurational assignments by resolution experiments — *cis* isomers were resolved, while all efforts to resolve *trans* isomers resulted in failure, as would be expected from the octahedral configuration. Although other, more dependable methods for determining configuration of isomers have since been developed (ref. 15, pp. 187—97), Werner's assignments by classical chemical methods have in most cases withstood the test of time. The ways in which Werner determined isomer configurations will be given in connection with the individual compounds, which will now be considered.

D. COBALT COMPLEXES

(i) *Trivalent complexes, [M]X₃*[78,87,89]

(a) *Type* $[Co(\overline{AA})_2B_2]X_3$

(1) $[Co(en)_2(NH_3)_2]X_3$. Before May, 1906, when Werner wrote his first article on these compounds[87], he had already described isomeric series of compounds containing the complex MA_4B_2, but in all these previous cases B had always been an "acid residue" (negative group). With his discovery of the first stereoisomeric diamminebis(ethylenediamine)cobalt(III) salts[87], Werner concluded that the existence of geometric isomers does not require that anions be directly coordinated to the central atom. These brown to reddish yellow salts (ref. 17, pp. 85—9; ref. 18, pp. 395—6; ref. 19, pp. 452—4; refs. 59, 95, 87, 115; ref. 89, pp. 22—3, 199—205) exist in *cis* and *trans* forms which are differentiated by their solubilities; the *cis* compounds are easily soluble, while the *trans* compounds are difficultly soluble, a difference in solubility similar to that of the corresponding diaquo and aquoammine salts.

A mixture of both series is formed by the action of liquid ammonia on *trans*-$[Co(en)_2Cl_2]X$, *cis*- or *trans*-$[Co(en)_2Br_2]X$, *trans*-$[Co(en)_2(NH_3)Cl]X_2$, *cis*- or *trans*-$[Co(en)_2(NH_3)Br]X_2$, and *cis*- or *trans*-$[Co(en)_2(NO_3)_2]X$. The isomers are separated almost quantitatively by precipitation of the *trans* compound by $Na_2S_2O_6$ from the aqueous solution of the evaporated residue, while the *cis* compound is precipitated from the resulting filtrate as the polyiodide. The salts may be differentiated by boiling with $CoCl_2$ and treating the solution with concentrated HCl whereupon different chlorocobaltates(II) are formed; the *cis* series gives an intensely green, anhydrous compound, while the *trans* series gives a brown, hydrated compound.

The configuration of the two series was arrived at by oxidation of the $[Co(en)_2(NCS)_2]X$ salts (see Section D(iii)(a)(7))[59,95], but in Werner's first article on the diammine compounds, the configurational assignment was incorrectly reversed because of an initially incorrect assignment of configuration to the diisothiocyanato compounds[59,95]. The easily soluble *cis* series is obtained by oxidation of *cis*-$[Co(en)_2(NCS)_2]X$ with H_2O_2, while the difficultly soluble *trans* series forms from oxidation of *trans*-$[Co(en)_2(NH_3)NCS]X_2$ with H_2O_2 or *trans*-$[Co(en)_2(NCS)_2]X$ with Cl_2. Bailar and Work[156a] later obtained the *trans* compounds by action of ammonia on *cis*-$[Co(en)_2Cl_2]Cl$ in the presence of activated charcoal. The compounds do not isomerize in aqueous solution[157]. Werner and Shibata[158] confirmed the configurational assignment by resolving the *cis* isomers into optical antipodes, and others[159–162] have also investigated the optically active compounds.

(2) *$[Co(en)_2(H_2O)_2]X_3$*. For the diaquobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 118—21; ref. 18, pp. 393—5; ref. 19, pp. 539—540; ref. 66; ref. 89, pp. 13—14, pp. 86—96; ref. 117), which are similar to the diaquotetraammine salts (see Section D(i)(c)(1)), the *trans* salts are brownish red, while the *cis* salts are an intense fire-red, less soluble than the *trans* salts and on heating with alkali are converted into the *trans* salts. In aqueous solution the salts of both series give an acidic reaction because of the formation of the hydroxoaquobis(ethylenediamine)cobalt(III) ion (see Section D(ii)(a)(7)).

$$[Co(en)_2(H_2O)_2]^{3+} + H_2O \rightarrow [Co(en)_2(H_2O)OH]^{2+} + H_3O^+$$

This reaction explains the fact that treatment of a solution of the *trans* salt with KI precipitates not *trans*-$[Co(en)_2(H_2O)_2]I_3$ but rather *trans*-$[Co(en)_2(H_2O)OH]I_2$. Similarly, the action of pyridine or alkali on solutions of the salts of both series precipitates the corresponding hydroxoaquo compounds, which on treatment with mineral acids regenerate the original isomeric diaquo compounds. A thorough spectrophotometric and electrochemical investigation[163] of the following equilibria in aqueous solution

$$\begin{tikzcd}
\textit{cis}\text{-}[Co(en)_2(H_2O)_2]^{3+} + H_2O \arrow[r, shift left] \arrow[dd, shift left] & \textit{cis}\text{-}[Co(en)_2(H_2O)OH]^{2+} + H_3O^+ \arrow[l, shift left] \arrow[dd, shift left] \arrow[dr, shift left, "H_2O"] & \\
 & & \textit{cis}\text{-}[Co(en)_2(OH)_2]^{+} + 2H_3O^+ \arrow[ul, shift left] \\
\textit{trans}\text{-}[Co(en)_2(H_2O)_2]^{3+} + H_2O \arrow[r, shift left] \arrow[uu, shift left] & \textit{trans}\text{-}[Co(en)_2(H_2O)OH]^{2+} + H_3O^+ \arrow[l, shift left] \arrow[uu, shift left] \arrow[dr, shift left, "H_2O"] & \\
 & & \textit{trans}\text{-}[Co(en)_2(OH)_2]^{+} + 2H_3O^+ \arrow[ul, shift left]
\end{tikzcd}$$

permitted calculation of the different equilibrium constants (ref. 14a, p. 387, ref. 164). Various studies of absorption spectra of the compounds have been made[157,165–167], and their chromatographic adsorption on activated alumina has been utilized in separating the *cis* and *trans* isomers (ref. 168, p. 1208).

The fire-red salts have been assigned the *cis* configuration on the basis of their preparation from compounds containing rings, which necessarily must possess the *cis* configuration*. For example, the *cis* salts may be prepared by

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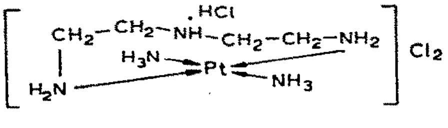
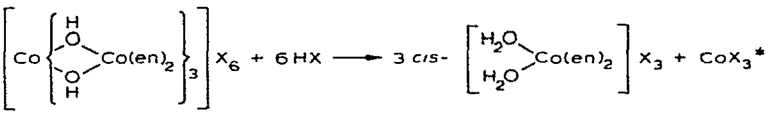
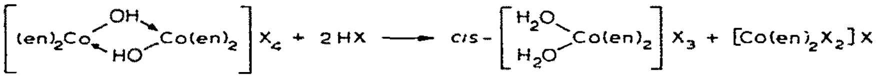
* Bailar has recently prepared a compound containing a chelate spanning the *trans* positions, viz.



the action of dilute mineral acids on $[\mathrm{Co(en)_2CO_3}]\mathrm{X}$ salts, which are known in only one form, which has been confirmed as the *cis* form by resolution of $[\mathrm{Co(en)_2CO_3}]\mathrm{X}$ salts[169–172]. This configurational assignment is corroborated by formation of the salt by the action of mineral acids on tris[bis(ethylenediamine)-μ-dihydroxo-cobalt(III)]cobalt(III) salts. Here the two hydroxo groups, which must be *cis* to each other, are converted into the aquo groups simply by adding a proton without leaving the molecule. Further confirmation of the configurational assignment comes from the preparation of the fire-red salts by cleavage with concentrated mineral acids of μ-dihydroxobis[bis(ethylenediamine)cobalt(III)) salts, in which the *cis*-hydroxo groups are likewise converted into diaquo groups by addition of a proton.

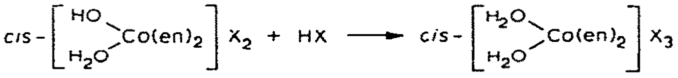


$$\left[\mathrm{Co}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co(en)_2}\right\}_3\right]\mathrm{X_6} + 6\,\mathrm{HX} \longrightarrow 3\ cis\text{-}\left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co(en)_2}\right]\mathrm{X_3} + \mathrm{CoX_3}^{*}$$



$$\left[\mathrm{(en)_2Co}\begin{matrix}\mathrm{OH}\\ \mathrm{HO}\end{matrix}\mathrm{Co(en)_2}\right]\mathrm{X_4} + 2\,\mathrm{HX} \longrightarrow cis\text{-}\left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co(en)_2}\right]\mathrm{X_3} + [\mathrm{Co(en)_2X_2}]\mathrm{X}$$

and from their similar preparation from the *cis*-hydroxoaquo salts (see Section D(ii)(a)(7)) (ref. 173, p. 75). The *trans* salt is similarly obtained by the action of concentrated mineral acids on *trans*-hydroxoaquo compounds. Both the *cis* and *trans* compounds react with $\mathrm{HNO_2}$ to give the corresponding unstable dinitrito stereoisomers (see Section D(iii)(a)(3)), which rearrange to yield the stable dinitro isomers (see Section D(iii)(a)(2)). In this way the fire-red salts give the *cis*-dinitro (flavo) salts, while the brownish red salts give the *trans*-dinitro (croceo) salts, a further proof of configuration.



$$cis\text{-}\left[\begin{matrix}\mathrm{HO}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co(en)_2}\right]\mathrm{X_2} + \mathrm{HX} \longrightarrow cis\text{-}\left[\begin{matrix}\mathrm{H_2O}\\ \mathrm{H_2O}\end{matrix}\mathrm{Co(en)_2}\right]\mathrm{X_3}$$

(b) Type $[\mathrm{Co}(\overline{\mathrm{AA}})_2\mathrm{BC}]\mathrm{X_3}$

(1) $[\mathrm{Co(en)_2(NH_3)H_2O}]\mathrm{X_3}$. The aquoamminebis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 112–13; ref. 18, pp. 402–3; ref. 19, pp. 473–4; ref. 40; ref. 89, pp. 21–2, pp. 185–92) correspond to the $[\mathrm{Co(NH_3)_5H_2O}]\mathrm{X_3}$ (roseo) salts in which four molecules of ammonia have been replaced by two molecules of ethylenediamine, and they are formed in a manner analogous to that of the roseo salts. They are also closely related to the stereoisomeric haloamminebis(ethylenediamine) salts (see Section D(ii)(a)(4) and (5)), from which they are formed by action of aqueous potassium hydroxide or moist,

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* $\mathrm{CoX_3}$ probably does not exist. The equation is Werner's (ref. 89, p. 14).

freshly prepared silver oxide, which produces the hydroxoammine salts.

$$[Co(en)_2(NH_3)X]X_2 + KOH \rightarrow [Co(en)_2(NH_3)OH]X_2 + KX$$

$$2[Co(en)_2(NH_3)X]X_2 + Ag_2O + H_2O \rightarrow 2[Co(en)_2(NH_3)OH]X_2 + 2AgX$$

which are then converted into the aquoammines by acidifying the solution.

$$[Co(en)_2(NH_3)OH]X_2 + HX \rightarrow [Co(en)_2(NH_3)H_2O]X_3$$

The kinetics of the reaction have been investigated by Tobe and others[157, 174,175]. In all cases, a partial rearrangement takes place, so that a mixture of both *cis* and *trans* isomers is always obtained. Conversion is much greater with KOH than with Ag_2O. Separation of the two isomers is accomplished by conversion to the bromide or nitrate salt; the salts of the *trans* series are much less soluble in water than are those of the *cis* series, a solubility difference that is also observed in the diaquo series (see Section D(i)(a)(2)).

The two stereoisomeric series of aquoammine salts are differentiated and their configurations assigned by their reactions with concentrated HCl, which yield the corresponding isomers of the $[Co(en)_2(NH_3)Cl]X_2$ series (see Section D(ii)(a)(4)), characterized as dithionates, and by their reactions with $NaNO_2$ in acetic acid solution, which yield the corresponding isomers of the $[Co(en)_2(NH_3)NO_2]X_2$ (see Section D(ii)(a)(1)), also characterized as dithionates (ref. 89, pp. 186, 188). Werner and King[73,130] confirmed the *cis* configuration of the more soluble series by converting optically active *cis*-$[Co(en)_2(NH_3)Br]Br_2$ to optically active *cis*-$[Co(en)_2(NH_3)H_2O]Br_2NO_3$ by heating with silver nitrate (ref. 73, pp. 1889, 1896). Racemization of the nitrate occurs slowly in solution (ref. 176, p. 698).

(c) Type $[CoA_4B_2]X_3$[87]

(1) $[Co(NH_3)_4(H_2O)_2]X_3$. The salts of this series (ref. 17, pp. 113—118; ref. 18, pp. 390—393; ref. 19, pp. 533—538; refs. 27, 87; ref. 89, pp. 13—14) were called roseotetrammine salts because of their red color. Although they were first discovered by Vortmann[177,178], their constitution as hexaammines in which two molecules of ammonia had been replaced by two molecules of water was first established by Jørgensen (ref. 179, p. 288). Werner (ref. 89, pp. 13, 14) recognized that along with the series $[Co(NH_3)_5H_2O]X_3$, $[Co(NH_3)_3(H_2O)_3]X_3$, and $[Co(NH_3)_2(H_2O)_4]X_3$, they form a transition series (Übergangsreihe) between pure ammines and pure hydrates. In general, their colors are closer to those of the halopentaammine (purpureo) salts than to those of the aquopentaammine (roseopentaammine) salts, but in properties they resemble the hexaammine (luteo) and aquopentaammine (roseopentammine) salts (ref. 179, p. 288). Job[180] proved that in the chloride and sulfate salts the two water molecules were bonded in the inner coordination sphere.

The diaquotetraammines are less stable than the aquopentaammines and are easily converted to anionoaquo salts by replacement of one of the coordinated water molecules by an acid radical (ref. 19, p. 534). In the solid state, this reaction is rapid at 100°C (ref. 179, p. 288) and slower at room temperature (ref. 88, p. 875; ref. 89, p. 46). The transformation into the anionoaquo salt is favored by the presence of the free acid[181]. This transformation is preceded in solution by an instantaneous hydrolysis with formation of hydronium ions and hydroxoaquo ions (see Section D(ii)(b)(1)), the latter of which is in equilibrium with dihydroxo ions (ref. 182, p. 132; ref. 183, p. 388; ref. 184; ref. 185, p. 282).

Theoretically the diaquotetraammines should exhibit geometric isomerism, but most of the salts exist in only one form. Because of their formation from *cis* complexes, e.g. carbonatotetraammines, their easy transformation into polynuclear complexes, e.g. tris[tetraammine-μ-dihydroxo-cobalt(III)]cobalt(III) salts (ref. 186, p. 2117), and the similarity of their absorption spectra to those of the *cis*-diaquobis(ethylenediamine) salts (see Section D(i)(a)(2))[187] they are assumed to possess the *cis* configuration, and this was the only form known to Werner. However, after Werner's death, a second (*trans*) form was found for the sulfate[188] and nitrate[189].

The *cis*-sulfate is prepared by the action of dilute sulfuric acid on $[Co(NH_3)_4CO_3]_2SO_4$, followed by precipitation with ethanol (ref. 179, p. 288). Several acid salts and mixed salts[190,191] are known, and the system $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 - - H_2SO_4 - - H_2O$ has been investigated[181,192,193]. The *trans*-sulfate is prepared by heating *trans*-$[Co(NH_3)_4(H_2O)NO_2](NO_3)_2$ (see Section D(ii)(a)(8)) with nitric acid, redissolving the resulting precipitate in 4 *N* H_2SO_4, and precipitating the monohydrated product at 0°C with ethanol [188]. The compound is more soluble than the *cis* isomer and possesses a much greater hydrolysis constant. The absorption spectra have been determined (ref. 194, p. 71).

The *cis*-nitrate is prepared by treating carbonatotetraamminecobalt(III) nitrate or carbonate with dilute or concentrated nitric acid (ref. 178; ref. 179, p. 280; refs. 195, 196). The *trans*-nitrate is obtained from a solution of the *cis*-nitrate, which consists of an equilibrium mixture of both isomers, by precipitation with 50% HNO_3. The product is washed with ethanol and ether, dried in a desiccator, and reprecipitated several times from water at 5°C by addition of HNO_3 until the absorption spectrum, which differs from that of the *cis* isomer, no longer changes[189]. The equilibrium constant for the isomerization has been determined[189].

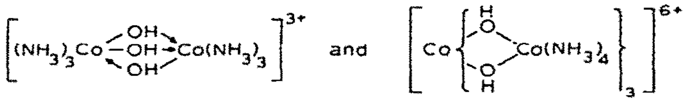
(d) Type $[CoA_3B_3]X_3$

(1) $[Co(NH_3)_3(H_2O)_3]X_3$. The bluish red triaquotriammine salts (ref. 17, pp. 122—3; ref. 18, p. 402; ref. 19, p. 641; ref. 25, p. 111; ref. 197, p. 2678; ref. 74, p. 216) are prepared by the aquation of $[Co(NH_3)_3(NO_3)_3]$ (ref. 154, p. 187; ref. 191, p. 284; ref. 197, p. 2675) or $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (dichro chloride) (ref. 154, p. 187; ref. 182; ref. 187), and they resemble the halo-

pentaammine (purpureo) salts. Less stable than the diaquotetraammines (see Section D(i)(c)(1)), they hydrolyze strongly in aqueous solution, and various determinations of the acid dissociation constant of the $[Co(NH_3)_3(H_2O)_3]^{3+}$ ion have been made (ref. 14a, p. 387; ref. 182, pp. 124, 130, 133; ref. 184; ref. 198, p. 96). One of the three water molecules is readily lost[199], e.g.

$$[Co(NH_3)_3(H_2O)_3]^{3+} + Cl^- \rightarrow [Co(NH_3)_3(H_2O)_2Cl]^{2+} + H_2O$$

Of the triaquotriammines, only the chloride exists in two stereoisomeric forms. Werner (ref. 197, p. 2678) prepared the bright reddish violet (*cis*; 1, 2, 3) form by allowing $[Co(NH_3)_3(NO_3)_3]$ to stand in water containing acetic acid, strongly cooling the resulting solution, and precipitating the product with HCl saturated at 0°C. The dark violet (*trans*; 1, 2, 6) form is prepared by acidifying an aqueous solution of green $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (dichro salt) (see Section D(iii)(i)(1)) with HCl and evaporating in vacuo (ref. 187, pp. 14, 15, 17). It is unstable in aqueous solution and is converted into the corresponding *cis* isomer. The absorption spectra of the two isomers are different and resemble those of the corresponding isomeric diaquobis(ethylenediamine) salts (see Section D(i)(a)(2)) (ref. 187; ref. 200, p. 86). The configurational formulas of both isomers were given by Werner (ref. 74, p. 216). In basic solution the *cis* isomer "polymerizes" to a mixture of



while the *trans* isomer does not give this reaction[187].

(ii) Divalent complexes, $[M]X_2$

(a) [Type $(Co(\overline{AA})_2BC]X_2$

The following six series of salts, $[Co(en)_2(NH_3)A]X_2$ (where A = NO_2, NO_3, F, Cl, Br or NCS) may be considered to be derived from the aniono-pentaammine (purpureo) salts, $[Co(NH_3)_5A]X_2$, by replacement of four molecules of ammonia with two molecules of ethylenediamine. They resemble the anionopentaammines in method of preparation, viz. by treating $[Co(en)_2(NH_3)H_2O]X_3$ or $[Co(en)_2(NH_3)B]X_2$ salts with excess ion A. In some cases, they may be prepared from $[Co(en)_2B_2]X_2$ by replacing one B ion with an ammonia molecule. They differ from the anionopentaammines by existing in geometrically isomeric forms. In some cases, the configuration of the *cis* isomers has been confirmed by resolution into optically active antipodes (see ref. 5 for details).

(1) $[Co(en)_2(NH_3)NO_2]X_2$. The brownish yellow stereoisomeric nitroamminebis(ethylenediamine) salts (ref. 17, pp. 139—41; ref. 18, pp. 466—8; ref. 19, pp. 515—16; ref. 89, pp. 23, 216—28) were prepared by Werner (ref.

89, pp. 23, 216—28) in several different ways, and therefore their configurations and relationships to other series of stereoisomeric cobalt complexes are well known. The *cis* salts are generally much more soluble and deeper in color than the *trans* salts, except that the dithionate, which is the most suitable salt for differentiating the two isomeric series, exhibits the reverse behavior in solubility and color. The *cis*-dithionate is only slightly soluble in hot water and crystallizes from it in small golden-yellow plates, whereas the *trans*-dithionate is easily soluble in boiling water and crystallizes on cooling in well-defined, silky, lustrous prisms. The two series may also be differentiated by evaporating with concentrated hydrochloric acid and treating the resulting chloroammine salts (see Section D(ii)(a)(4)) with sodium dithionate; the resulting *cis*-$[Co(en)_2(NH_3)Cl]S_2O_6$ forms compact crystals, while the *trans* compound forms long needles. The configuration of the *cis*-nitroammines has also been confirmed by resolution of the bromocamphorsulfonates into optically active forms (ref. 5; ref. 89, p. 216; ref. 144, p. 55).

Werner prepared the *cis* salts by the following four methods, of which the first is the most common.

(1) Action of nitrous acid on *cis*-aquoammine salts (see Section D(i)(b)(1)).

$$cis\text{-}[Co(en)_2(NH_3)H_2O]X + HNO_2 \rightarrow cis\text{-}[Co(en)_2(NH_3)NO_2]X_2 + HX + H_2O$$

(2) Action of silver nitrite on *cis*-chloroammine salts (see Section D(ii)(a)-(4)).

$$cis\text{-}[Co(en)_2(NH_3)Cl]X_2 + AgNO_2 \rightarrow cis\text{-}[Co(en)_2(NH_3)NO_2]X_2 + AgCl\downarrow$$

(3) Action of ammonia on *trans*-dinitro salts (see Section D(iii)(a)(2)).

$$trans\text{-}[Co(en)_2(NO_2)_2]X + NH_3 \rightarrow cis\text{-}[Co(en)_2(NH_3)NO_2]NO_2X$$

(4) Oxidation of *cis*-nitroisothiocyanato salts (see Section D(iii)(d)(4)) with 30% hydrogen peroxide.

$$cis\text{-}[Co(en)_2NO_2(NCS)]X + HX + 2H_2O + 4O \rightarrow cis\text{-}[Co(en)_2(NH_3)NO_2]X_2 + CO_2\uparrow + H_2SO_4$$

Werner prepared the *trans* salts in quantitative yields by the action of liquid ammonia on either the *trans*-chloronitro chloride (see Section D(iii)(d)(3))

$$trans\text{-}[Co(en)_2(NO_2)Cl]Cl + NH_3(l) \rightarrow trans\text{-}[Co(en)_2(NH_3)NO_2]Cl_2$$

or the *trans*-nitratonitro nitrate

$$trans\text{-}[Co(en)_2(NO_2)NO_3]NO_3 + NH_3(l) \rightarrow trans\text{-}[Co(en)_2(NH_3)NO_2](NO_3)_2$$

or by the action of silver nitrite on the *trans*-chloroammine chloride (see Section D(ii)(a)(4)).

$$trans\text{-}[Co(en)_2(NH_3)Cl]Cl + AgNO_2 \rightarrow trans\text{-}[Co(en)_2(NH_3)NO_2]Cl + AgCl\downarrow$$

By use of these methods Werner prepared the *cis*- and *trans*- bromides, iodides, nitrates and dithionates as well as the *cis*-chloride, sulfate and bromide—nitrate and the *trans*-thiocyanate. On warming with $NaNO_2$ or KSCN, concentrated aqueous solutions of the salts of both series liberate ammonia, a reaction facilitated with KOH in the case of the *trans* compounds.

(2) *$[Co(en)_2(NH_3)NO_3]X_2$*. The orange—red stereoisomeric nitratoamminebis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 147—8; ref. 18, p. 468; ref. 19, pp. 516—17; ref. 89, pp. 214—16; ref. 175, p. 3783) are formed by evaporation of the corresponding stereoisomeric aquoammine nitrates (see Section D(i)(b)(1)) with nitric acid.

$$cis\text{- or } trans\text{-}[Co(en)_2(NH_3)H_2O](NO_3)_3 \rightarrow cis\text{- or } trans\text{-}[Co(en)_2(NH_3)NO_3](NO_3)_2 + H_2O$$

In the preparation of the *trans* salt, small amounts of the *cis* isomer are also formed simultaneously by steric rearrangement. The mixture can be separated by conversion to the dithionates since the *cis*-dithionate is much less soluble in water than is the *trans*-dithionate. The configuration can be determined by evaporating aqueous solutions with concentrated hydrochloric acid, whereupon the corresponding chloroammine salts (see Section D(ii)(a)(4)) are formed. Liquid ammonia converts the salts of both series to a mixture of *cis*- and *trans*-diamminebis(ethylenediamine)cobalt(III) salts (see Section D(i)-(a)(1)) because of a steric rearrangement.

(3) *$[Co(en)_2(NH_3)F]X_2$*. The red stereoisomeric fluoroamminebis(ethylenediamine)cobalt(III) salt (ref. 17, p. 149; ref. 18, p. 468; ref. 19, p. 511; ref. 132) were first prepared by Werner's Doktorand Heinrich Seibt, and almost all the data on these little-investigated compounds appears in Seibt's dissertation[132]. The fluoride of the series is prepared by shaking a solution of *cis*- or *trans*-$[Co(en)_2(NH_3)H_2O]Br_3$ (see Section D(i)(b)(1)) with freshly precipitated silver oxide and evaporating the filtrate to dryness in the presence of excess hydrofluoric acid. The configuration of the original aquoammine bromide is retained; the *cis* isomer yields the *cis*-fluoroammine (ref. 132, pp. 71—5), and the *trans* isomer, the *trans*-fluoroammine (ref. 132, pp. 69—70). Seibt prepared the *cis*- and *trans*-bromides and dithionates and the *cis*-perchlorate, nitrate and thiocyanate from the corresponding fluorides by metathesis. The *cis* isomers are darker in color than the *trans* isomers, but the absorption spectra of both series are almost identical (ref. 129, pp. 92—3). The configuration of the *cis* series has been confirmed by converting (+)-*cis*-$[Co(en)_2(NH_3)Cl]Cl_2$ (see Section D(ii)(a)(4)) into the corresponding optically active (+)-*cis*-$[Co(en)_2(NH_3)F](NO_3)_2$[201—203].

(4) *$[Co(en)_2(NH_3)Cl]X_2$*. The first chloroamminebis(ethylenediamine)—cobalt(III) salt (ref. 17, pp. 159—63; ref. 18, pp. 468—70; ref. 19, pp. 511—13; ref. 89, pp. 20—21, 164—76) was the *cis*-chloride, prepared by Jørgensen

(ref. 151, p. 453) by evaporating *trans* (praseo)-$[Co(en)_2Cl_2]Cl$ (see Section D(iii)(a)(5)) with the calculated amount of aqueous ammonia.

trans-$[Co(en)_2Cl_2]Cl + NH_3 \rightarrow$ *cis*-$[Co(en)_2(NH_3)Cl]Cl_2$

He viewed the series as chloropentaammine (purpureo) salts in which four molecules of ammonia had been replaced by two molecules of ethylenediamine, and he therefore called them amminediethylenediaminechloropurpureo salts. Werner (ref. 88; ref. 89, pp. 20—1, 164—76) prepared the corresponding *trans* compounds by first preparing *trans*-$[Co(en)_2Cl(NCS)]X$ salts (see Section D(iii)(d)(5)) by the action of potassium thiocyanate on *trans* (praseo)-$[Co(en)_2Cl_2]Cl$ (see Section D(iii)(a)(5)), and oxidizing the *trans*-chloroisothiocyanato compounds with hydrogen peroxide.

trans-$[Co(en)_2Cl(NCS)]X + 4O + HX + 2H_2O \rightarrow$ *trans*-$[Co(en)_2(NH_3)Cl]X_2$

$+ CO_2\uparrow + H_2SO_4$

Since the —NCS group was oxidized to NH_3 without breaking the Co—N bond, Werner regarded the compounds which he discovered as *trans* compounds and therefore Jørgensen's isomeric compounds as *cis* compounds. Together with his American Doktorand Victor L. King[130], Werner (ref. 73, p. 1890) proved this configurational assignment by resolving Jørgensen's compound by means of silver-(+)-α-bromocamphor-π-sulfonate[148c]. This historic first resolution of a coordination compound (1911) unequivocally proved Werner's proposed octahedral configuration for cobalt(III) and led directly to his being awarded the Nobel Prize in chemistry (1913)[84]. Werner also devised three additional methods for preparing the *trans*-chloride: (1) heating the *trans*-nitroammine chloride (see Section D(ii)(a)(1)) with concentrated hydrochloric acid.

trans-$[Co(en)_2(NH_3)NO_2]Cl_2 + HCl \rightarrow$ *trans*-$[Co(en)_2(NH_3)Cl]Cl_2 + HNO_2$

(2) action of a solution of ammonia in absolute methanol on the *trans*-dichloro chloride (see Section D(iii)(a)(5)), a reaction which also yields some *cis* isomer.

trans-$[Co(en)_2Cl_2]Cl + NH_3 \rightarrow$ *trans* (and *cis*-)-$[Co(en)_2(NH_3)Cl]Cl_2$

and (3) heating the *trans*-aquoammine chloride (see Section D(i)(b)(1)) with concentrated hydrochloric acid.

trans-$[Co(en)_2(NH_3)H_2O]Cl_3 \rightarrow$ *trans*-$[Co(en)_2(NH_3)Cl]Cl_2 + H_2O$

The chloroammines are bluish red in color, the *trans* compounds being a little more blue than the corresponding *cis* compounds, but not enough to differentiate the two series. The salts of the two series can be distinguished by formation of the sparingly soluble dithionates; the *cis*-dithionate forms compact crystals, while the *trans*-dithionate forms long needles. Another differentiating reaction is the behavior with liquid ammonia; the *trans* compounds dissolve easily and react to form a mixture of the two isomeric diammine compounds, with the *cis* isomer predominating.

trans-$[Co(en)_2(NH_3)Cl]X_2 + NH_3(l) \rightarrow$ *cis*- and *trans*-$[Co(en)_2(NH_3)_2Cl]X_2$

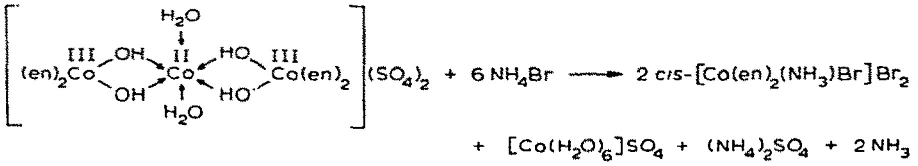
whereas the *cis* compounds are insoluble in liquid ammonia and do not react. Werner[89] prepared the *cis*- and *trans*-chlorides, dithionates, chloride—perchlorates, nitrites and nitrates as well as the *trans*-chloride—bisulfate and dichromate. The coordinated ammonia in chloroammine salts is easily replaced by the nitro group. For example, concentrated aqueous solutions of both *cis*- and *trans*-$[Co(en)_2(NH_3)Cl](NO_2)_2$ evolve ammonia at room temperature (more quickly on warming) and form first *trans*-$[Co(en)_2(NO_2)Cl]X$ (see Section D(iii)(d)(3)) and then *trans*-$[Co(en)_2(NO_2)_2]X$ (croceo salt) (see Section D(iii)(a)(2))[89]. Similarly, the coordinated ammonia in chloroammine salts can be replaced by the isothiocyanato group. Heating the *trans*- salt with KSCN produces *trans*-$[Co(en)_2Cl(NCS)]SCN$ (see Section D(iii)(d)(5)), while heating the *cis* salt produces *trans*-$[Co(en)_2(NCS)_2]SCN$ (see Section D(iii)-(a)(7))[89]. The conductivity (ref. 64, p. 337) and absorption spectra (ref. 129, pp. 84, 89; ref. 160; ref. 204, pp. 38, 58; ref. 205, p. 429; ref. 206, p. 31; ref. 207; ref. 208, p. 246) of the chloroammines have been determined by Werner and others.

(5) *$[Co(en)_2(NH_3)Br]X_2$*. The stereoisomeric bromoamminebis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 176—8; ref. 18, pp. 470—1; ref. 19, pp. 514—15; ref. 40; ref. 89, pp. 20—1, pp. 176—85; ref. 137) are very similar to the corresponding chloroammine salts (see Section D(ii)(a)(4)). The *cis* compounds are purplish blue, and the *trans* compounds are blue—violet. The *cis* salts are especially easy to prepare, and a variety of preparative methods are available[89].

(1) Action of concentrated ammonia on the *trans*-dibromo bromide (see Section D(iii)(a)(6)), whereby rearrangement takes place.

trans-$[Co(en)_2Br_2]Br + NH_3 \rightarrow$ *cis*-$[Co(en)_2(NH_3)Br]Br_2$

(2) Action of ammonium bromide on the trinuclear complex bis[bis-(ethylenediamine)-di-μ-hydroxo-cobalt(III)]diaquocobalt(II) sulfate (ref. 209, pp. 4429—33; ref. 210, p. 41).



(3) Action of hydrobromic acid on the *cis*-nitroammine bromide (see Section D(ii)(a)(1)).

cis-$[Co(en)_2(NH_3)NO_2]Br_2 + HBr \rightarrow$ *cis*-$[Co(en)_2(NH_3)Br]Br_2 + HNO_2$

(4) Action of hydrobromic acid on the *cis*-aquoammine bromide (see Sec-on D(i)(b)(1)).

s-$[Co(en)_2(NH_3)H_2O]Br_3 \overset{\Delta}{\rightarrow}$ *cis*-$[Co(en)_2(NH_3)Br]Br_2 + H_2O$

he first two methods are especially suitable for the preparation of the com-ounds in large quantities. Werner established the *cis* configuration of this ries by resolution with silver-α-(+)-bromocamphor-π-sulfonate[5,73,130,211,212].

The *trans* compounds can be obtained by the following three methods, of hich the first was used by Werner to establish the *trans* configuration.

(1) Oxidation of the *trans*-bromoisothiocyanato salts (see Section D(iii)-l)(6)) with hydrogen peroxide.

ans-$[Co(en)_2Br(NCS)]Br + 4O + 2H_2O \rightarrow$ *trans*-$[Co(en)_2(NH_3)Br]BrHSO_4 + CO_2\uparrow$

(2) Action of concentrated hydrobromic acid on the *trans*-aquoammine romide (see Section D(i)(b)(1)).

ans-$[Co(en)_2(NH_3)H_2O]Br_3 \rightarrow$ *trans*-$[Co(en)_2(NH_3)Br]Br_2 + H_2O$

(3) Action of hydrobromic acid on the *trans*-nitroammine salts (see Sec-on D(ii)(a)(1)).

ans-$[Co(en)_2(NH_3)NO_2]Br_2 + HBr \rightarrow$ *trans*-$[Co(en)_2(NH_3)Br]Br_2 + HNO_2$

The two series can be distinguished by formation of the slightly soluble ithionates, of which the *cis* salt forms short, compact crystals, while the *ans* compound forms long, fine needles. Furthermore, the *cis*-dithionate issolves easily in concentrated hydrobromic acid to form the easily soluble romide, while the *trans*-dithionate remains unchanged. Werner[89] prepared ie *cis*- and *trans*-bromides, nitrates and dithionates as well as the *cis*-hloride, bromide—nitrate and tetrachloroplatinate(II) and the *trans*-iodide nd perchlorate. The absorption spectra of the bromoammines closely esemble those of the corresponding hydroxopentaammines, exhibiting one and[129,213], situated at 550 nm and disymmetric (ref. 160; ref. 208, p. 246; f. 213).

(6) *$[Co(en)_2(NH_3)NCS]X_2$*. Because of their many genetic relationships) other series, the isothiocyanatoamminebis(ethylenediamine)cobalt(III) lts (ref. 17, pp. 183—5; ref. 18, p. 471; ref. 19, pp. 517—18; ref. 88, . 876; ref. 89, pp. 23, 49—55; 205—13) have played an important role in etermining configurations and ascertaining rearrangements. Their colors ary from brick—red to brown—red. They are prepared by the action of liquid mmonia on *cis*- or *trans*-$[Co(en)_2Cl(NCS)]X$ (see Section D(iii)(d)(5)) or *is*- or *trans*-$[Co(en)_2Br(NCS)]X$ (see Section D(iii)(d)(6)). A mixture of both *is* and *trans* isomers is obtained, regardless of which isomeric haloisothio-

cyanato salt is used as starting material. Werner[89] investigated the ratio of the isomers formed in these mixtures and found it to be dependent upon the anion outside the coordination sphere.

Since the *trans*-thiocyanate is much less soluble than the *cis*-thiocyanate, the isomers are easily separated. In both series the NCS group is bonded to the cobalt atom through the nitrogen atom, and oxidation with hydrogen peroxide, followed by evaporation with hydrochloric acid proceeds with retention of configuration to give the corresponding isomers of $[Co(en)_2(NH_3)_2]X_3$ (see Section D(i)(a)(1)). Since the *cis*-diammine salts are very soluble and the *trans*-diammine salts are only slightly soluble, this oxidation has been used to differentiate and assign configurations to the isomeric isothiocyanatoammines. Werner[89] prepared the *cis*- and *trans*-thiocyanates and iodides as well as the *cis*-dithionate and thiocyanate—chloride and the *trans*-bromide, perchlorate and thiocyanate—bromide. Evaporation of either *cis*- or *trans*-$[Co(en)_2(NH_3)NCS]X_2$ with hydrochloric acid gives the corresponding isomeric $[Co(en)_2(NH_3)Cl]X$ salts. All the isothiocyanatoammines give yellow addition compounds with silver nitrate of the type $[Co(en)_2(NH_3)(NCSAg)_2]X_2$, which, according to Chamberlain and Bailar[335], are much less stable than Werner reported.

Werner's assignment of configuration was confirmed not by the resolution of the *cis* isomers per se but by his Doktorand Rudolf van Arx's conversion of optically active (+)— and (—)-*cis*-$[Co(en)_2(NH_3)Cl]ClO_4$ (see Section D(ii)(a)(4)) to the corresponding active *cis*-$[Co(en)_2(NH_3)NCS]Cl$ with liquid ammonia (ref. 142, p. 55). von Arx isolated the active chloride, bromide, nitrate, nitrite, perchlorate and thiocyanate (ref. 142, pp. 64—73). The absorption spectra of the *cis*- and *trans*-iodides are almost identical[204], and the spectra of other salts have been determined[160,214]. The compounds exhibit strong anomalous rotatory dispersion[160,166,214,215].

An apparent error regarding a supposedly isomeric series of the type $[Co(en)_2(NH_3)B]X_2$ might be mentioned at this point. In Werner's lengthy paper of 1912 (ref. 89, p. 7), the series $[Co(en)_2(NH_3)OH]X_2$ is listed as No. 20 in a list of 27 compound types for which two stereoisomeric series were obtained. The series is not mentioned again in the experimental section of the paper, and although other authors, probably repeating Werner's error, cite it as existing in both *cis* and *trans* forms (ref. 7, p. 24; ref. 13, p. 73), Gmelin (ref. 18, p. 466) and Pascal (ref. 19, p. 515) list only a *cis* series.

(7) *$[Co(en)_2(H_2O)OH]X_2$*. The hydroxoaquobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 127—9; ref. 18, pp. 459—60; ref. 19, pp. 554—5; ref. 67; ref. 89, pp. 14—15, 96—102; ref. 173, p. 74) are very similar to the corresponding tetraammine compounds (see Section D(ii)(b)(1)) except that among the latter isomerism is confined to the case of one salt. They are also closely related to the diaquobis(ethylenediamine) salts (see Section D(i)(a)(2)), from which they may be prepared by removal of one mole of acid caused by the action of ammonia, pyridine or aqueous alkali[67].

$$cis\text{- or } trans\text{-}[Co(en)_2(H_2O)_2]X_3 + NH_3 \rightarrow cis\text{- or } trans\text{-}[Co(en)_2(H_2O)OH]X_2 + NH_4X$$

The hydroxoaquo salts, in turn, can be reconverted to the diaquo salts by the action of acid.

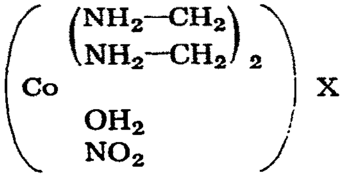
$$cis\text{- or } trans\text{-}[Co(en)_2(H_2O)OH]X_2 + HX \rightarrow cis\text{- or } trans\text{-}[Co(en)_2(H_2O)_2]X_3$$

Since these reactions involve only the loss or gain of a proton by the complexes and no metal—ligand bonds are broken, the *cis*-hydroxoaquo salts are formed from the *cis*-diaquo salts, and the *trans*-hydroxoaquo salts are formed from the *trans*-diaquo salts. Furthermore, by action of $NaNO_2$ in concentrated acetic acid solution both series form unstable $[Co(en)_2(ONO)_2]X$ salts (see Section D(iii)(a)(3)), which rearrange to form isomeric stable $[Co(en)_2(NO_2)_2]X$ salts (see Section D(iii)(a)(2)). In this way, the brownish red (*cis*) hydroxoaquo salts form *cis* (flavo)-$[Co(en)_2(NO_2)_2]X$ salts, and the bluish red (*trans*) hydroxoaquo salts form *trans* (croceo)-$[Co(en)_2(NO_2)_2]X$ salts. Hydroxoaquo salts may also be obtained by the hydrolysis of chloroaquo salts (ref. 89, pp. 45, 97; ref. 216, pp. 240, 252, 255, 257—9), by aquation of anionohydroxo salts or by hydrolysis and aquation of dianiono or carbonato salts (ref. 173, p. 74; ref. 217, p. 79; ref. 217a). They are also formed as a byproduct in the preparation of $[Co(en)_2(A)Cl]X_2$ compounds (where A is an organic amine)[218], and the bromide and sulfate may be prepared from *trans*-$[Co(en)_2Cl_2]Cl$ with a strongly basic anion exchange resin[219]. The hydroxoaquo compounds, which are obtained from *cis*- or *trans*-$[Co(en)_2(NO_2)_2]X$, *cis*- or *trans*-$[Co(en)_2(NCS)_2]X$ or *cis*- or *trans*-$[Co(en)_2NO_2(NCS)]X$ by treatment with KOH solution, reportedly possess the *cis* configuration[167].

The hydroxoaquo salts react weakly alkaline to litmus and liberate ammonia from ammonium salts. However, they do not precipitate Ag_2O from $AgNO_3$ solution, and they do not absorb CO_2 either in solution or in the solid state. In acetic acid solution these otherwise sparingly soluble salts easily dissolve to form diaquo salts, but addition of KBr, KI or KSCN to these solutions reprecipitates the hydroxoaquo salts. On the basis of these properties, Werner (ref. 67; ref. 89, pp. 14, 96; ref. 220) considered them to be not true bases but salts in which the hydroxo group is bonded directly to the cobalt atom[221]. As discussed above, the hydroxoaquo ion is easily transformed into the diaquo ion by the action of acid, and the equilibrium constants for the transformation into the diaquo and dihydroxo ions have been determined (see Section D(i)(a)(2))[163].

(8) *$[Co(en)_2(H_2O)NO_2]X_2$*. First mention of the nitroaquobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 143—4; ref. 18, pp. 461—2; ref. 19, p. 555; ref. 89, pp. 56, 253—4; ref. 222) in Werner's published work does not appear until 1911 (ref. 222, p. 3273), but apparently he had been working on this series many years earlier, for in a letter of December 13th, 1897 to his friend and former fellow student Arturo Miolati[223] he wrote:

"For the present, I still want to let you know that I have very probably found the two geometrically isomeric series



$$\left(\mathrm{Co}\begin{matrix}\left(\begin{matrix}\mathrm{NH_2{-}CH_2}\\ \mathrm{NH_2{-}CH_2}\end{matrix}\right)_2\\ \mathrm{OH_2}\\ \mathrm{NO_2}\end{matrix}\right)\mathrm{X}$$

with whose investigation I am presently occupied."

Although these compounds exist in two stereoisomeric series, the salts are all extremely soluble, and consequently Werner was able to isolate only a sulfate, to which he assigned the *trans* configuration because on warming with concentrated hydrochloric acid it formed *trans*-$[Co(en)_2(NO_2)Cl]X$ (see Section D(iii)(d)(3)).

Although both *cis* and *trans* isomers of $[Co(en)_2(H_2O)NO_2]X_2$ exist, salts of the *cis* series were not isolated by Werner in the solid state but were later prepared by others[224]. In solution the *cis* and *trans* isomers are converted into each other; the *cis* form predominates in the resulting mixture[225]. Werner confirmed his assignment of configuration by obtaining the (+)- and (—)-chlorides in aqueous solution by aquation of the corresponding optically active chloronitro compounds (see Section D(iii)(d)(3)) (ref. 5; ref. 222, pp. 3273, 3276; ref. 226, p. 457; ref. 227, p. XXI).

(9) *$[Co(en)_2(H_2O)Cl]X_2$*. The chloroaquobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 168—70; ref. 18, pp. 463—4; ref. 19, pp. 551—3; ref. 41; ref. 89, pp. 17—19, 121—30; ref. 173, p. 71) should theoretically exist in two stereoisomeric configurations but, with the sole exception of the chloride (ref. 217, pp. 256—7), only one series of salts (bluish red) are known. Werner (ref. 89, p. 121), however, specifically tried to prepare a second isomeric series but without success. The salts, which correspond completely to the analogous tetraammines (see Section D(ii)(b)(3)) and the analogous bromoaquo salts, are more stable than these compounds in aqueous solution. However, slowly in the cold and more rapidly at higher temperatures, the $[Co(en)_2\text{-}(H_2O)Cl]^{2+}$ ion is partially transformed into the $[Co(en)_2(H_2O)_2]^{3+}$ ion (see Section D(i)(a)(2)), accompanied by a hydrolysis reaction[214,228—230].

The chloroaquo compounds are formed by the action of water on *trans*-$[Co(en)_2Cl_2]X$ (see Section D(iii)(a)(5)), and Werner assigned them the *cis* configuration. Regardless of the configuration of the starting material, Werner always obtained the same bluish red (*cis*) compounds. He ascribed this to the fact that the *trans*-haloaquo salts change very easily into the *trans*-dihalo salts and since the *trans*-$[Co(en)_2Cl_2$ or $Br_2]X$ salts (see Section D(iii)(a)(5) and (6)) always form the *cis* series on entry of water into the coordination sphere, the *cis*-haloaquo salts should be produced. Furthermore, careful treatment of the haloaquo salts with hydrochloric acid gives mainly *cis* (violeo) salts.

$$cis\text{-}[Co(en)_2(H_2O)Cl]Cl_2 \xrightarrow{HCl} cis\text{-}[Co(en)_2Cl_2]Cl + H_2O \qquad (1)$$

$$cis\text{-}[Co(en)_2(H_2O)Cl]Br_2 \xrightarrow{HCl} cis\text{-}[Co(en)_2(Cl)Br]Br + H_2O \qquad (2)$$

$$cis\text{-}[Co(en)_2(H_2O)Br]Cl_2 \xrightarrow{HCl} cis\text{-}[Co(en)_2(Cl)Br]Cl + H_2O \qquad (3)$$

$$cis\text{-}[Co(en)_2(H_2O)Br]Br_2 \xrightarrow{HCl} cis\text{-}[Co(en)_2Br_2]Br + H_2O \qquad (4)$$

Identical series of compounds were formed from reactions (2) and (3). Werner recognized that such substitution reactions cannot always be used for determining configuration because of the possibility of rearrangements. In this case, however, he believed rearrangement to be improbable because other transformations of the haloaquo salts always give *cis* compounds. For example, chloroaquo and bromoaquo salts give *cis*-$[Co(en)_2(H_2O)OH]X$ salts (see Section D(ii)(a)(7)) on treatment with NH_3 or KOH. Also, both series yield *cis*(flavo)-$[Co(en)_2(NO_2)_2]X$ salts (see Section D(iii)(a)(2)) on treatment with $NaNO_2$. Treatment of both series with a small amount of concentrated ammonia converts them to the corresponding halohydroxo salts (Section D(iii)(d)(1)).

$$cis\text{-}[Co(en)_2(H_2O)Cl \text{ or } Br]X_2 + NH_3 \rightarrow cis\text{-}[Co(en)_2(OH)Cl \text{ or } Br]X + NH_4X,$$

which closely resemble in color the violeo (*cis*)-$[Co(en)_2Cl_2$ or $Br_2]X$ salts (Section D(iii)(a)(5) and (6)). If the halohydroxo salts are dissolved in warm water, the solution becomes red, and the *cis*-$[Co(en)_2(H_2O)OH]X_2$ salts soon crystallize. Finally, Werner observed that since concentrated aqueous ammonia converts *trans*-$[Co(en)_2Cl_2$ or $Br_2]X$ into *cis*-$[Co(en)_2(NH_3)Cl$ or $Br]X_2$ and, since H_2O and NH_3 are completely analogous, he concluded that the products of the action of H_2O on *trans*-$[Co(en)_2Cl_2$ or $Br_2]X$ correspond to the *cis*-$[Co(en)_2(NH_3)Cl$ or $Br]X_2$ salts and are therefore *cis* compounds. Werner's assignment of configuration (ref. 89, pp. 13, 121) was confirmed by the resolution of the chlorohydroxo compounds reported in the unpublished dissertation of his Swiss Doktorand Hermann Fischlin[143] by means of ammonium (+)-bromocamphor-π-sulfonate. The salts exhibit anomalous rotatory dispersion[143] and the Cotton effect[215]. Bailar and Peppard[172] consider the chloride, which is dextrorotatory for Na_D light, to be the (—)-compound.

Werner obtained the bluish red (*cis*) chloride by the action of cold concentrated hydrochloric acid on the sulfate (ref. 89, p. 121) or by aquation of *trans*-$[Co(en)_2Cl_2]Cl$ (ref. 88, p. 875; ref. 89, p. 46; ref. 231). It is very soluble in water, giving a violet—red solution whose spectra have been measured[165, 228, 232]. The grayish green *trans*-chloride was not obtained until 1924 and was prepared by precipitating with a mixture of ethanol and ether a solution of *trans*-$[Co(en)_2(OH)Cl]Cl$ (see Section D(iii)(d)(1)) in hydrochloric acid[216]. It crystallizes with one molecule of water, and both this molecule as well as the molecule of coordinated water are lost slowly with simultaneous entry of chlorine into the complex on heating to 80° C in vacuo. In solution both the *cis* and *trans* compounds isomerize to an equilibrium mixture of the two forms[157,217a,229,230]. Only one form (*cis*) appears to be known for the other haloaquo series, $[Co(en)_2(H_2O)Br]X$ (ref. 17, p. 179; ref. 18, p. 464; ref. 19, pp. 553—4) and $[Co(en)_2(H_2O)F]X_2$ (ref. 18, pp. 462—3).

(10) *$[Co(en)_2(H_2O)NCS]X_2$*. The isothiocyanatoaquobis(ethylenediamine)-cobalt(III) salts (ref. 17, pp. 185—6; ref. 18, p. 466; ref. 19, p. 556; ref. 89, pp. 20, 153—64) occur in two stereoisomeric series — salmon-pink (*cis*) and violet (*trans*). Both series are formed from the corresponding $[Co(en)_2(OH)NCS]X$ salts (see Section D(iii)(d)(2)) (which may be formed from the corresponding $[Co(en)_2Cl(NCS)]X$ salts (Section D(iii)(d)(5)) by the action of concentrated NH_3), by addition of mineral acids, and both series give with $AgNO_3$ brightly colored, stable addition compounds, which Werner formulated as $[Co(en)_2(H_2O)NCSAg]X_2(NO_3)$ and which give no precipitate of AgCl on addition of HCl. Werner[89] proved the compounds to contain Co—NCS bonding in both series by oxidizing them with H_2O_2 and evaporating with HCl, whereupon the yellow—red salts gave *cis*-$[Co(en)_2(NH_3)Cl]Cl_2$ and the violet salts, *trans*-$[Co(en)_2(NH_3)Cl]Cl_2$ (see Section D(ii)(a)(4)). He also assigned them configurations on the basis of their behavior on heating with hydrochloric acid; the red salts give red (*cis*)-$[Co(en)_2Cl(NCS]X$ salts, and the violet salts give violet (*trans*)-$[Co(en)_2Cl(NCS)]X$ salts. Treatment of *cis*-$[Co(en)_2(H_2O)NCS]X_2$ with HNO_2 gives *cis*-$[Co(en)_2(NO_2)NCS]X$ (see Section D(iii)(d)(4)), while similar treatment of the *trans* compounds yields *trans*-$[Co(en)_2(ONO)NCS]NO_2$, which slowly changes to the isomeric nitro compound, *trans*-$[Co(en)_2(NO_2)NCS]NO_2$. Werner's assignment of configuration was confirmed when he obtained the *cis*-$[Co(en)_2(H_2O)NCS]X_2$ compounds in optically active form, not by resolution but by aquation of the corresponding $[Co(en)_2Cl(NCS)]X$ salts (ref. 139; ref. 226, p. 459; ref. 227, p. XI).

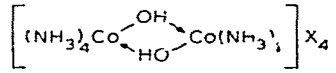
(b) Type $[CoA_4BC]X_2$

The anionoaquotetraamminecobalt(III) compounds can be considered to be derived from the diaquotetraammines by substitution of a mononegative anion for one of the two coordinated water molecules. They are prepared by this process or by aquation of dianionotetraammines. They are characterized by their ease of aquation with formation of the diaquo compounds. In general, stereoisomerism is less prevalent among these compounds than among the corresponding ethylenediamine compounds.

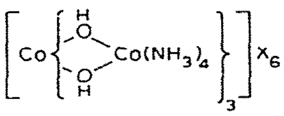
(1) *$[Co(NH_3)_4(H_2O)OH]X_2$*. The hydroxoaquotetraamminecobalt(III) salts (ref. 17, pp. 125—7; ref. 18, pp. 453—4; ref. 19, pp. 546—8; ref. 233) are blue to purple—red and are derived from diaquotetraammines by substitution of one of the constitutional water molecules by a hydroxo group. Accordingly, they are prepared by the action of ammonia or pyridine on diaquotetraammines. The first compound of the series to be prepared was the sulfate,

discovered by Jørgensen[234], who regarded it as a basic sulfate of the diaquo series. The correct constitution of the series was recognized by Werner[233], who prepared the sulfate, chloride, bromide, nitrate and dithionate.

Like all hydroxo complexes, the hydroxoaquotetraammines give a basic reaction in aqueous solution and liberate ammonia from ammonium salts. However, they do not precipitate Ag_2O from $AgNO_3$ solution[221,233]. The compounds are characterized by a great instability. For example, heating the solid salts or treating them with acetic anhydride leads to loss of water and formation of

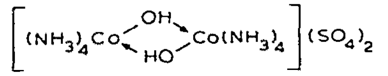

$$\left[(NH_3)_4Co\begin{matrix}OH\\HO\end{matrix}Co(NH_3)_4\right]X_4$$

salts[235–237], a reaction which led Werner to assign them the *cis* configuration (ref. 235, p. 4437). The compounds are even more unstable in aqueous solution; they undergo hydrolysis to form hydronium ions and dihydroxotetraammine ions, a reaction followed by slow "polymerization". Thus in the cold and in the dark a solution of the sulfate[233] or nitrate[234] changes from red to violet with formation of


$$\left[Co\left\{\begin{matrix}\overset{H}{O}\\\underset{H}{O}\end{matrix}Co(NH_3)_4\right\}_3\right]X_6$$

The salts readily form anionoaquo- or dianionotetraammines. For example, the action of hydrochloric acid produces[234] $[Co(NH_3)_4(H_2O)Cl]Cl_2$, while a current of CO_2 precipitates this same salt, leaving $[Co(NH_3)_4CO_3]Cl$ in solution[233].

Only the sulfate occurs in two stereoisomeric forms, of which the bright violet (*cis*) form was known to Werner (ref. 71, p. 4820; ref. 233). It was not until 1935 when ter Horst (ref. 188, p. 265) obtained the supposedly *trans*-sulfate by mixing a solution of $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ with $Ba(OH)_2$ and extracting the reaction mixture at 0° C with water. While heating the *cis*-sulfate gives


$$\left[(NH_3)_4Co\begin{matrix}OH\\HO\end{matrix}Co(NH_3)_4\right](SO_4)_2$$

(ref. 235, p. 4437), heating the *trans*-sulfate to 80°C in a current of dry air yields an insoluble polymeric complex $[Co(NH_3)_4(OH)SO_4]_n$ (ref. 188, p. 267). The absorption spectra of aqueous solutions have been measured (ref. 194, p. 71).

(2) $[Co(NH_3)_4(H_2O)NO_2]X_2$. Our knowledge of the nitroaquotetraamminecobalt(III) salts (ref. 17, pp. 141–3; ref. 18, pp. 454–5; ref. 19, p. 548; refs. 238–41) is rather confused. They were first discovered by Jørgensen[238], who described them as generally yellow salts except for the

chloride, bromide, tetrachloroaurate(III) and tetrachloroplatinate(II), which are red. He viewed them as nitropentaammine (xantho) salts in which one molecule of NH_3 had been replaced by one of H_2O, and he therefore called them aquoxantho salts. The salts are generally prepared by aquation of $[Co(NH_3)_4(NO_2)Cl]X$ (see Section D(iii)(d)(3)) or $[Co(NH_3)_4(NO_2)OH]X$ salts. In 1900 Werner (ref. 59, pp. 114, 120, 122) and his English assistant Alfred Rudolph Klien[239] described new yellow salts of the nitroaquo series. In 1907 Werner (ref. 240, pp. 4124, 4126; ref. 241, p. 4129) succeeded in preparing the chloride and bromide as very unstable, yellow salts which, on standing or more quickly in solution, were converted into Jørgensen's red compounds. Werner and Herty[64] measured the freezing-point depression of the chloride in aqueous solution. Werner regarded the yellow salts as true aquoxantho salts, $[Co(NH_3)_4(H_2O)NO_2]X_2$ (X = Cl or Br), and the red salts as "esohydrates" (compounds in which the water molecules are not part of the coordination sphere), viz. $[Co(NH_3)_4(NO_2)X]X \cdot H_2O$ (X = Cl or Br), in other words, a case of what he called "hydrate isomerism" (ref. 4, pp. 169—72). Jørgensen[238], Meyer and Gröhler[242] and Matsuno[243], however, considered the yellow and red series to be stereoisomers. In addition to the yellow normal sulfate, $[Co(NH_3)_4(H_2O)NO_2]SO_4$, prepared by Jørgensen (ref. 238, p. 297), a red acid sulfate, supposedly $[Co(NH_3)_4(H_2O)NO_2](HSO_4)_2$, has been described[242]. On the basis of a comparison of color, solubility and crystallizability with those of the corresponding $[Co(en)_2(H_2O)NO_2]X_2$ salts (see Section D(ii)(a)(8)), Meyer and Rampoldt[223] regarded the red salts as *trans* compounds.

Yalman and Kuwana[189] prepared the brown *cis*-nitrate by allowing *cis*-$[Co(NH_3)_4(H_2O)ONO](NO_3)_2$ to stand for several days at room temperature, and King and Mistry[244] prepared it by metathesis of the *cis*-sulfate with $Ba(NO_3)_2$. In solution, the *cis*-nitroaquo nitrate is slowly transformed into the isomeric *trans* compound. Hydrochloric acid converted it into *trans*-$[Co(NH_3)_4Cl_2]Cl$, nitric acid at 80°C, to $[Co(NH_3)_4(H_2O)_2]X_3$, sodium nitrite in slightly acidic solution, to *cis* (flavo)-$[Co(NH_3)_4(NO_2)_2]X$. These three reagents, on the other hand, react with the *trans*-nitrate to give $[Co(NH_3)_4(NO_2)Cl]X$, $[Co(NH_3)_4(H_2O)NO_3]X$, and *trans* (croceo)-$[(Co(NH_3)_4(NO_2)_2]X$, respectively. A number of other salts of both the *cis* and *trans* series have been prepared[245—250]. The enthalpy of formation of the *trans*-$[Co(NH_3)_4(H_2O)NO_2]^{2+}$ ion has been determined[251], and a spectrophotometric investigation of its conversion into $[Co(NH_3)_4(OH)NO_2]^+$ and H_3O^+ has been made[252].

(3) *$[Co(NH_3)_4(H_2O)Cl]X_2$*. The chloroaquotetraamminecobalt(III) salts (ref. 17, pp. 166—8; ref. 18, pp. 455—7; ref. 19, pp. 544—6; ref. 27, pp. 233—4; ref. 35) are violet and correspond completely to the $[Co(en)_2(H_2O)Cl]X_2$ salts (see Section D(ii)(a)(9)). Their constitution was explained by Jørgensen (ref. 253, p. 211; ref. 254, p. 465), who correctly regarded them as chloropurpureo salts, $[Co(NH_3)_5Cl]X_2$, in which one molecule of NH_3 was

replaced by one molecule of H_2O. By conductometric titration with $Ba(OH)_2$ Job (ref. 255, p. 111) proved that the water molecule was bonded within the coordination sphere.

Except for the chloride, the salts of this series occur in only one configuration, which is supposedly *cis*. The absorption spectrum of solutions of the chloride, almost identical with that of *cis*-$[Co(NH_3)_4(H_2O)_2]Cl_3$ (see Section D(i)(c)(1)), is very similar to that of *cis*-$[Co(en)_2(H_2O)_2]Cl_3$ (see Section D(i)(a)(2)) and $[Co(NH_3)_5Cl]Cl_2$ (ref. 129, pp. 96, 97; ref. 187, pp. 18, 19; ref. 204, p. 53; ref. 213, p. 10; ref. 256, pp. 367, 371, 372; refs. 257, 258). Furthermore, oxalic acid reacts with the chloride to produce $[Co(NH_3)_4C_2O_4]Cl$, which must necessarily possess a *cis* configuration (ref. 231, p. 171). For configurational evidence on the basis of substitution reactions see Section D(ii)(a)(9).

In solution, the chloroaquo salts quickly undergo aquation to form the diaquo salts, and the rate constant for the reaction

$$[Co(NH_3)_4(H_2O)Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_4(H_2O)_2]^{3+} + Cl^-$$

has been measured[214,259,260]. That their solutions contain the chloroaquo ion for only a short time has been shown by measurements of conductance (ref. 52, p. 236; ref. 187; refs. 261, 262), congelation point[261] and flocculating power[243]. The chlorine in the complex does not react with $AgNO_3$ if the solution is cold and freshly prepared (ref. 253, p. 211; refs. 262, 263).

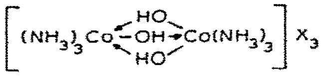
Most chloroaquo salts are prepared from the crude *cis* chloride, which is obtained by air oxidation of an ammoniacal solution containing[35,253,254] $CoCl_2$ and $(NH_4)_2CO_3$. The *cis*-chloride may also be prepared by aquation of *trans* (praseo) $[Co(NH_3)_4Cl_2]Cl$ (ref. 88, p. 877; ref. 89, pp. 46, 56), the action of malonic acid on $[Co(NH_3)_4(H_2O)_2]Cl_3$ or $[Co(NH_3)_4(H_2O)OH]Cl_2$ (ref. 231, pp. 167, 171), the action of hydrochloric acid on $[Co(NH_3)_4(OH)_2]OH$ (ref. 264) or dehydration of solid $[Co(NH_3)_4(H_2O)_2]Cl_3$ in air at 40°C (ref. 88, p. 875; ref. 89, p. 46). By agitation of *trans*-$[Co(NH_3)_4Cl_2]Cl$ in the presence of its saturated solution, ter Horst (ref. 188, p. 269) obtained an isomeric chloride, which she considered to be the *trans* isomer. It is darker and more soluble than the *cis* isomer. In contact with the mother liquor, it is slowly reconverted to its *cis* isomer. Tsuchida (ref. 265, pp. 722, 730, 733) studied the formation and isomerization spectrophotometrically and determined the rate constants for the reactions

$$\textit{trans-}[Co(NH_3)_4Cl_2]Cl + H_2O \rightarrow \textit{trans-}[Co(NH_3)_4(H_2O)Cl]Cl_2$$
$$\rightarrow \textit{cis-}[Co(NH_3)_4(H_2O)Cl]Cl_2$$

(c) Type $[CoA_3B_2C]X_2$

(1) *$[Co(NH_3)_3(H_2O)_2Cl]X_2$*. The chlorodiaquotriamminecobalt(III) salts (ref. 17, pp. 170—1; ref. 18, p. 477; ref. 19, pp. 642—3; ref. 27, p. 255) are violet except for the bromide, which is blue. They closely resemble the $[Co(NH_3)_4(H_2O)Cl]X_2$ salts and are derived from these by replacement of one

NH_3 molecule by a H_2O molecule. They are very unstable in solution and readily undergo aquation; for this reason the conductivities of their dilute solutions are much greater than would be expected for a dipositive complex[187]. Treatment with mineral acids yields $[Co(NH_3)_3(H_2O)X_2]X$ salts ($[Co(NH_3)_3(H_2O)Cl_2]Cl$, dichro chloride, in the case of HCl, see Section D(iii)(j)(1)) (ref. 54; ref. 395, p. 418; ref. 429, p. 4703). Treatment of the violet sulfate (ref. 430, p. 4838) or selenate (ref. 263, pp. 357, 381, 382) with aqueous KBr yields


$[(NH_3)_3Co(OH)_3Co(NH_3)_3]X_3$

salts, a transformation which would seem to corroborate Werner's assumption (ref. 74, p. 218) of a *cis*(1, 2, 3) configuration for the violet salts.

Of the series only the sulfate is known to exist in two forms. The violet form can be prepared by letting a cold aqueous solution of $[Co(NH_3)_3(H_2O)Cl_2]HSO_4$ stand for several hours (ref. 395, p. 421) or by adding H_2SO_4 to this solution on the water bath (ref. 54, p. 158; ref. 187, p. 4). The blue—gray sulfate was prepared by Werner (ref. 54, p. 156) by dissolving $[Co(NH_3)_3(H_2O)Cl_2]HSO_4$ in cold water, filtering quickly and treating the indigo—blue solution with ethanol. Triturating the violet sulfate with conc. HCl yields violet $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$, while the same treatment of the blue—gray sulfate gives gray $[Co(NH_3)_3(H_2O)Cl_2]Cl$. As previously mentioned, Werner (ref. 74, p. 218) considered the violet sulfate to possess the *cis*(1, 2, 3) configuration[54]. He assigned the *trans*(1, 2, 6) configuration to the blue—gray sulfate. In opposition to this, on the basis of the absorption spectrum of the violet sulfate, which was very similar to that of *trans*-$[Co(en)_2(H_2O)_2]X_3$ salts, Matsuno (ref. 187, pp. 4, 15) assigned it the *trans*(1, 2, 6) configuration.

(iii) Monovalent complexes, [M]X

(a) Type $[Co(\overline{AA})_2B_2]X$ *(ref. 144)*

(1) $[Co(en)_2(N_3)_2]X$. The diazidobis(ethylenediamine)cobalt(III) salts (ref. 18, p. 505; ref. 19, p. 603; refs. 127, 146, 266) provide an excellent example of important research data that lie buried among the unpublished dissertations of Werner's students. According to Gmelin (ref. 18, p. 505) and Pascal (ref. 19, p. 603), the only research carried out on these compounds is the work of Strecker and Oxenius published in 1934[266]. Yet, as early as 1912, Salomea Lorie, one of Werner's numerous Polish Doktorandinnen, prepared a red salt $[Co(en)_2(N_3)_2]N_3$, which she believed to be a *trans* compound since it was produced by the action of sodium azide on *trans*-$[Co(en)_2Cl_2]Cl$ (ref. 127, p. 57 ff.). Shortly thereafter (1913—15) J. Ernst Zollinger, a Swiss Doktorand of Werner's, in his doctoral dissertation[146], reinvestigated Fräulein Lorie's work and succeeded in preparing the bromide (p. 81), sulfate (p. 82), chloride (p. 82), iodide (p. 83) and perchlorate (p. 84) of her red series. By

the action of NaN_3 on *cis*-$[Co(en)_2(NH_3)H_2O]X_3$ (see Section D(i)(b)(1)) he was able to prepare a series of deep blue compounds[146] (iodide, p. 69; nitrate, p. 71; bromide, p. 72; chloride, p. 74; azide, p. 75; dithionate, p. 76; thiocyanate, p. 77; and perchlorate, p. 78) isomeric with her red series. Actually a mixture of both series resulted, from which the blue salts were prepared. Because of World War 1, Zollinger's dissertation was not completed until 1921. Since rearrangements are known to occur during substitution reactions among cobalt complexes, Zollinger disputed Lorie's assignment of configuration and, on the basis of color and solubility (he assumed that *trans* compounds are generally deeper in color and less soluble than the corresponding *cis* compounds, a rather risky assumption), he assigned the red series the *cis* configuration and the blue series the *trans* configuration (ref. 146, p. 84). He attempted to confirm his configurational assignment by treating optically active (+)-*cis*-$[Co(en)_2(NH_3)H_2O](NO_3)_2ClO_4$ with NaN_3 and KI in an attempt to prepare (+)-*cis*-$[Co(en)_2(N_3)_2]I$, but because of the optical density of the solution his results were inconclusive.

In 1934 Strecker and Oxenius[266], completely unaware of Lorie's[127] and Zollinger's[146] work, prepared red—brown *cis*-$[Co(en)_2(N_3)_2]N_3$ by heating a solution of *trans*-$[Co(en)_2Cl_2]N_3$ with NaN_3. By repeated distillation of HN_3 with $[Co(en)_2CO_3]Cl$ they obtained the green *trans*-azide. The *cis*-azide is converted to the *trans*-azide on standing[266a,b,c]. Both compounds explode on heating and decompose in hot water.

(2) *$[Co(en)_2(NO_2)_2]X$*. The dinitrobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 216—22; ref. 18, pp. 505—10; ref. 19, pp. 597—600; ref. 27, pp. 243—5; ref. 28, p. 97; refs. 34, 38, 39, 60, 61; ref. 89, pp. 24, 247—51; refs. 104, 106, 204; ref. 268, p. 72; ref. 269) were among the first stereoisomers discovered by Werner and his students. The two stereoisomeric series, both yellowish brown and completely analogous in constitution and chemical behavior to the corresponding $[Co(NH_3)_4(NO_2)_2]X$ (*cis*, flavo; *trans*, croceo; see Section D(iii)(f)(1)), were first described in the dissertation[104] of Werner's first woman Doktorandin, Edith Humphrey, and in the first articles[60,61] in his series, Über Isomerien bei anorganischen Verbindungen. Werner[60,61] first (1901) believed them to be nitrito compounds but later, after discovering the true nitrito compounds (1907) (ref. 66, p. 264; ref. 68, p. 771; refs. 107, 117), he designated them nitro compounds. Like the corresponding tetraammines the NO_2 groups in the ethylenediamine compounds are "masked". Werner[60,61] found that the conductance of their aqueous solutions showed the presence of a monovalent complex cation.

The *cis* salts crystallize without water of crystallization and are less soluble and darker in color than the *trans* salts. In contrast with the tetraammines, interconversions between the two isomeric series occur. On heating, hydrochloric acid converts the *cis* salts to green *trans*-$[Co(en)_2Cl_2]X$ (see Section D(iii)(a)(5)) but the *trans* salts to red *trans*-$[Co(en)_2(NO_2)Cl]X$ (see Section D(iii)(d)(3))[60,61]. However, with the *cis*-nitrate, Werner (ref. 89, p. 248 ff.)

was able to isolate the intermediate red *cis*-[$Co(en)_2(NO_2)Cl$]X salt. With both series, HNO_3 replaces only one NO_2 group, and liquid NH_3 produces no change. The absorption spectra of both series are almost identical except in the far ultraviolet (ref. 204, p. 41 ff., ref. 270).

According to Werner (ref. 66, p. 264) the isomeric dinitro salts are formed by the action of $NaNO_2$ on the corresponding isomers of [$Co(en)_2Cl_2$]X or [$Co(en)_2(NO_2)Cl$]X or by the action of ethylenediamine on M[$Co(NH_3)_2$·$(NO_2)_4$]. He suggested the action of ethylenediamine on $K_3[Co(NO_2)_6]$ as the best preparation for a mixture of the isomeric [$Co(en)_2(NO_2)_2$]NO_2 salts, which are used for preparation of the other members of the series. Other methods are also available. Werner assigned the configurations to the dinitro salts on the basis of their methods of preparation. For example, nitrous acid converts the two stereoisomeric diaquobis(ethylenediamine) series (see Section D(i)(a)(2)) to the stereoisomeric dinitrobis(ethylenediamine) series (see Section D(iii)(a)(3)), whose configurations are assured since by treating them with dilute mineral acids they can be reconverted to the corresponding diaquo salts. On standing, the dinitrito salts are converted to the corresponding dinitro salts, which have the same configuration as that of the dinitrito salt from which they are formed (ref. 89, p. 24).

$$\textit{cis- or trans-}[Co(en)_2(H_2O)_2]X_3 \xrightleftharpoons[HX]{HNO_2} \textit{cis- or trans-}[Co(en)_2(ONO)_2]X \rightleftharpoons \textit{cis- or trans-}[Co(en)_2(NO_2)_2]X$$

Werner (1911) confirmed his assignment of configuration by resolving the flavo (*cis*) dinitro salts into optically active antipodes with (+)-camphorsulfonic acid and (+)-bromocamphorsulfonic acid[5,38,136,267]. With his Swiss Doktorand Jakob Bosshart[271], he[272] also later (1914) resolved these salts by preferential crystallization with "seed crystals" of (+)-[$Co(en)_2C_2O_4$]X.

(3) *[$Co(en)_2(ONO)_2$]X.* The dinitritobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 225—6; ref. 18, pp. 510—11; ref. 19, p. 600; ref. 68; ref. 89, pp. 24, 247) are brick-red to brownish red in color and exist in two stereoisomeric series. They were first prepared by Werner[68] by the action of $NaNO_2$ on [$Co(en)_2(H_2O)_2$]X_3 salts (see Section D(i)(a)(2)) in acetic acid solution. The *cis*-diaquo salts gave the *cis*-dinitrito salts, and the *trans*-diaquo salts gave the *trans*-dinitrito salts. Werner[68] prepared the nitrates, bromides, iodides and dithionates of both series as well as the *trans*-chloride and thiocyanate. The *cis*-nitrate has since been prepared from *cis*-[$Co(en)_2(NO_2)Cl$]X salts (see Section D(iii)(d)(3)) by the action of Ag^+ followed by NO_2^- by Adell[273—5], who also investigated the kinetics of the conversion to the dinitro compounds.

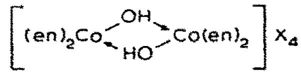
The dinitrito salts are stable in acetic acid solution; dilute mineral acids, however, immediately liberate HNO_2 and reform the diaquo salts from which the dinitrito salts were originally prepared (see Section D(iii)(a)(2)). In the solid state, both series are converted on standing into the corresponding dinitro salts, which are stable toward mineral acids. In this manner, the dinitrito salts prepared from the *cis*-diaquo salts give brownish yellow dinitro compounds, which are identified as *cis* (flavo) salts by yielding a mixture of *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ on treatment with conc. HCl. On the other hand, the dinitrito salts prepared from the *trans*-diaquo salts give bright yellow dinitro compounds, which are identified as *trans* (croceo) salts by yielding red *trans*-$[Co(en)_2(NO_2)Cl]Cl$ on treatment with conc. HCl. Both *cis* and *trans* isomers of a series of compounds intermediate between the dinitro and dinitrito salts, viz. $[Co(en)_2(NO_2)ONO]X$ have been prepared[275,276], and the *cis* series has been resolved[277], but these compounds were unknown to Werner.

(4) *$[Co(en)_2F_2]X$*. The difluorobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 227—8; ref. 18, pp. 512—13; ref. 19, pp. 589—90; ref. 132, pp. 53—66) are described in the doctoral dissertation of Werner's student Heinrich Seibt (ref. 132, pp. 53—66), who prepared the *cis*- and *trans*-nitrates and iodides and the *trans*-fluoride, chloride, bromide, perchlorate, dithionate and thiocyanate. The *trans*-fluoride is prepared by the action of HF on $[Co(en)_2CO_3]OH$. Repeated evaporation of an aqueous solution of the green *trans*-fluoride, followed by addition of NH_4NO_3 to the solution, precipitates the red *cis*-fluoride. An acid fluoride, *trans*-$[Co(en)_2F_2]HF_2$, has been reported by Matoush and Basolo[201,202], by the action of a current of air on a solution obtained by dissolving $CoCO_3$ in HF and adding ethylenediamine. They confirmed Seibt's assignment of configuration by treating (—)-*cis*-$[Co(en)_2Cl_2]Cl$ dissolved in an ethanol—HF mixture, with $AgNO_3$, and thus obtaining optically active (+)-*cis*-$[Co(en)_2F_2]NO_3$. They also resolved the racemic *cis*-nitrate by means of dibenzoyltartaric acid and studied its rotatory dispersion. Basolo et al.[278] have measured the rates of acid and base hydrolysis of the *trans*-difluoro compounds and compared them with those of the corresponding dichloro and dibromo complexes. The absorption spectra of the difluoro salts have been studied by various workers (ref. 129, pp. 92, 93; refs. 201, 202, 270, 279, 280).

(5) *$[Co(en)_2Cl_2]X$*. As we have already seen (Section B), the dichlorobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 235—43; ref. 18, pp. 514—27; ref. 19, pp. 590—5; ref. 89, pp. 15—16, 104—10) constitute the oldest known case of geometric isomerism among octahedral complexes and probably the best known example of *cis*—*trans* isomerism among inorganic complexes in general. Both the green *trans* (praseo) (ref. 149, p. 15) and the violet *cis* (violeo) (ref. 151, p. 448) series were first prepared by Jørgensen. He obtained the former by heating the praseo acid chloride, *trans*-$[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}2H_2O$, which he prepared by adding concentrated HCl to an air-oxidized aqueous mixture of $CoCl_2$ and ethylenediamine (ref. 149, p. 16). He obtained violeo salts by repeated evaporation of the praseo salts. Numerous preparative methods for both series are available (ref. 27, pp. 237—9; ref. 28, p. 62; ref. 29,

pp. 140—2; ref. 32, pp. 11—13, 96—9; ref. 33; ref. 60; ref. 89, pp. 104—10; ref. 173, pp. 68, 70; ref. 281). Jørgensen claimed that the two series were structural isomers produced by different bondings within the ethylenediamine molecule, whereas Werner, beginning with his very first article on the coordination theory (ref. 47, p. 298) insisted that they were *cis—trans* stereoisomers[60], and the compounds thus played an important role in the history of coordination chemistry. Another theory of their constitution was later advanced by Friend[282] and opposed by Turner[283], but as is well known, Werner's views prevailed.

Werner assigned the violeo salts the *cis* configuration by preparing them by treating with concentrated HCl cobalt complexes containing closed rings such as $[Co(en)_2CO_3]X$, $[Co(en)_2SO_3]X$ and



$$\left[(en)_2Co\begin{smallmatrix}OH\\ HO\end{smallmatrix}Co(en)_2\right]X_4$$

He confirmed this assignment of configuration by resolving them by means of ammonium (+)- and (—)-bromocamphor-π-sulfonates[284]. The resolution has been repeated by Bailar and Auten[33,170], and resolutions by means of (+)- and (—)-quartz have been reported[285,286].

The two chlorine atoms in both series of $[Co(en)_2Cl_2]X$ salts are not detectable by $AgNO_3$ in the cold. By cryoscopic and conductance measurements, Werner and Herty[64] showed that their solutions contained a unipositive cation. Like the dichlorotetraammines, the dichlorobis(ethylenediamine) salts undergo aquation in solution, as shown by changes in color (ref. 149, p. 15), absorption spectra[213,228], molecular conductance[64] and flocculating power[243]. This "hydrolysis", which has been studied by numerous workers[229—231,287—297], is dependent upon the nature of the anions present and occurs in two steps, (i) and (ii).

$$cis\text{- or } trans\text{-}[Co(en)_2Cl_2]^+ + H_2O \rightarrow cis\text{-}[Co(en)_2(H_2O)Cl]^{2+} + Cl^- \qquad (i)$$

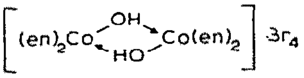
(a slow reaction, which, however, is more rapid for the *cis*- than for the *trans*-dichloro compound[297]).

$$cis\text{-}[Co(en)_2(H_2O)Cl]^{2+} + H_2O \rightarrow cis\text{-}[Co(en)_2(H_2O)_2]^{3+} + Cl^- \qquad (ii)$$

Aside from their color, the *cis*- and *trans*-$[Co(en)_2Cl_2]X$ compounds differ in a number of properties such as absorption spectra[129,165,214,228,232,270,279,280,298—302], and ionic mobility[303]. Like the *trans*-$[Co(en)_2Br_2]X$ salts and unlike the *trans*-$[Co(NH_3)_4Cl_2]X$ salts, the *trans* compounds tend to form acid salts; e.g. in addition to Jørgensen's *trans*-$[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}2H_2O$ (ref. 149, p. 15) and Werner's acid salt, formulated as *trans*-$[Co(en)_2Cl(HCl)(H_2O)_2Cl_2$ (ref. 89, p. 53), an entire series of acid salts with dibasic organic acids has been prepared[304]. *trans*-$[Co(en)_2Cl_2]X$ salts react immediately with concentrated aqueous NH_3 to give *trans*-$[Co(en)_2(NH_3)Cl]X_2$ salts (see Section D(ii)(a)(4)), while the *cis* compounds dissolve only on heating with formation of *trans*-$[Co(en)_2(H_2O)OH]X_2$ salts (see Section D(ii)(a)(7)) (ref. 89, pp. 44, 97). The *cis*-dichlorobis(ethylenediamine) salts are converted into the *trans* salts on heating in acid solution, while the reverse reaction occurs on evaporating neutral solutions of the *trans* salts[181]. Numerous studies have been made of the isomerization reaction[157,281,291,232,302,305–312] as well as of substitution reactions[156,161,162,216,225,313–317]. *cis*-$[Co(en)_2Cl_2]Cl$ has been separated from its *trans* isomer by ion exchange[318] and paper chromatography[319,320].

(6) *$[Co(en)_2Br_2]X$*. The dibromobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 250—3; ref. 18, pp. 530—3; ref. 19, pp. 595—7; ref. 89, pp. 16—17, 110—17) are completely analogous to the corresponding dichloro compounds (see Section D(iii)(a)(5)). The *cis* (violeo) salts are violet to slate gray and show no tendency to form acid salts. The *trans* (praseo) salts are yellow—green and tend to form acid salts. The salts are unstable in aqueous solution and are converted into aquo salts. By the action of concentrated acids, the *cis* salts are converted into *trans* salts, while the *trans* salts are converted into *cis* salts on evaporation of *neutral* aqueous solutions. Both series give a mixture of *cis*- and *trans*-$[Co(en)_2(NH_3)_2]X_3$ (see Section D(i)(a)(1)) on treatment with liquid ammonia (ref. 88; ref. 89, p. 52).

The *trans* salts were first obtained by Jørgensen[151] by evaporating *trans*-$[Co(en)_2Cl_2]Cl$ with HBr or by triturating it with Ag_2O and evaporating the resulting solution with HBr. Since some decomposition occurred by the use of HBr, Werner (ref. 89, p. 110) devised alternate methods for the preparation of the *trans* salts by air oxidation of a solution containing $CoBr_2$ and ethylenediamine. He was the first to prepare the violeo salts by evaporating solutions of *trans* salts. He[89] also prepared violeo salts by the action of HBr on ring-containing complexes such as $[Co(en)_2CO_3]Br$, $[Co(en)_2SO_3]Br$ and



$$\left[(en)_2Co\begin{matrix}OH\\HO\end{matrix}Co(en)_2\right]Br_4$$

(ref. 210, p. 95), and he cited these methods of preparation as evidence for a *cis* configuration. Werner's assignment of configuration was confirmed by Bailar and Peppard[172], who resolved the *cis*-bromide by means of α-bromo-(+)-camphor-π-sulfonic acid.

The absorption spectra of the *cis* and *trans* salts in solution differ considerably (ref. 129, p. 90; ref. 157; ref. 232, pp. 23, 42; refs. 279, 280, 321). In aqueous solution, both isomers undergo aquation; for example, the *cis*-bromide forms *cis*-$[Co(en)_2(H_2O)Br]Br_2$ instantaneously and *cis*-$[Co(en)_2(H_2O)_2]Br_3$ in half an hour[243]. The conversion of *trans*-$[Co(en)_2Br_2]^+$ into *cis*-$[Co(en)_2Br_2]^+$ is five times more rapid than the corresponding isomerization of the dichloro complexes[157, 229, 230]. For the $[Co(en)_2I_2]^+$ ion, a *trans*-iodide[279] and a *cis*-periodide[322] have been reported, but Werner did not investigate this series.

(7) *[Co(en)$_2$(NCS)$_2$]X*. The yellow—red to dark red diisothiocyanatobis-(ethylenediamine)cobalt(III) salts (ref. 17, pp. 254—7; ref. 18, pp. 543—6; ref. 19, pp. 601—2; ref. 89, pp. 22, 192—9; refs. 68, 69, 102, 107) were first prepared in 1900 by Werner and Bräunlich (ref. 59, pp. 95, 123; ref. 95), but their constitution and configuration were incorrectly assigned because of their anomalous behavior on oxidation with chlorine, which led Werner to believe them to be structural isomers (thiocyanato, —SCN vs. isothiocyanato, —NCS). Werner later (1912) (ref. 89, pp. 22, 41, 192) showed the two series to be *cis* and *trans* stereoisomers, both containing the isothiocyanato group bonded to the cobalt atom through nitrogen. The less soluble salts, previously described as *trans*-dithiocyanato salts[59,95], gave on oxidation with Cl_2 *trans*-[Co(en)$_2$Cl$_2$]X salts; on oxidation with HNO_3 followed by evaporation with HCl they gave *trans*-[Co(en)$_2$Cl$_2$]X salts; and, on oxidation with H_2O_2, followed by evaporation with HCl they gave *cis*-[Co(en)$_2$(NH$_3$)-Cl]X salts. On the other hand, the more soluble salts, previously described as *cis*-diisothiocyanato salts gave on the same treatments *trans*-[Co(en)$_2$(NH$_3$)$_2$]-X$_3$; mainly *trans*-[Co(en)$_2$(NH$_3$)Cl]X and a little *trans*-[Co(en)$_2$(NH$_3$)$_2$]X$_3$; and *trans*-[Co(en)$_2$(NH$_3$)$_2$]X$_3$, respectively. From this and his knowledge of spatial rearrangements[88], Werner concluded that the less soluble salts were the *cis* isomers and the more soluble salts were the *trans* isomers.

The diisothiocyanato salts are formed by the action of the thiocyanate ion on various bis(ethylenediamine)cobalt(III) complexes. Most salts of the *cis* series are prepared from the *cis*-chloride, which is obtained by evaporating a solution of *cis*-isothiocyanatonitro salts (see Section D(iii)(d)(4)) with hydrochloric acid, followed by cooling (ref. 89, pp. 195, 239).

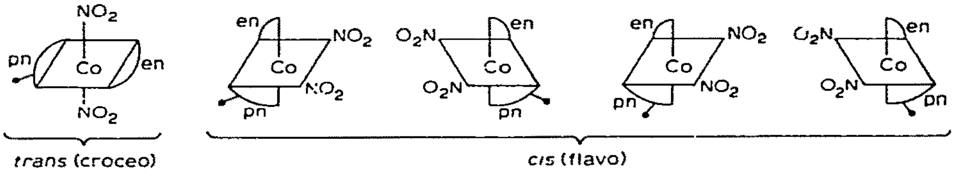
$$\textit{cis}\text{-}[Co(en)_2(NO_2)NCS]X + 2HCl \rightarrow \textit{cis}\text{-}[Co(en)_2(NCS)_2]Cl + \textit{trans}\text{-}[Co(en)_2Cl_2]Cl + 2HNO_2$$

Most *trans* salts are prepared from the *trans*-thiocyanate, which is obtained by air oxidation on the water bath of a concentrated aqueous solution of $Co(SCN)_2$ and ethylenediamine[323]. Werner and Bräunlich (ref. 59, p. 125 ff.) obtained a mixture of the *cis*- and *trans*-thiocyanates by treating a solution of *trans*-[Co(en)$_2$Cl$_2$]Cl with KSCN; the salts of the two series were separated by taking advantage of their different solubilities. Werner prepared the *cis*- and *trans*-chlorides, bromides, iodides, nitrates and thiocyanates as well as the *cis*-dithionate and sulfate and the *trans*- hydrogensulfate. Numerous other salts, including those with complex anions have been described by others[263,321,322,324—335]. The *cis*- and *trans*-diisothiocyanato salts can be differentiated by means of their absorption spectra[214,336—338] and separated by cation exchange[318] and paper chromatography[320].

(b) *Type [Co($\overline{AA}$)($\overline{AB}$)C$_2$]X*

(1) *[Co(en)(pn)(NO$_2$)$_2$]X*. Coordination compounds containing optically

active bidentate ligands are of great stereochemical interest because they involve types of isomerism for which there are no counterparts in the organic realm (ref. 5, pp. 34—5). Of all optically active unsymmetrical ligands, the one most extensively investigated is still propylenediamine (1,2-diaminopropane). Werner published four papers[69,70,339,340] on complexes of this ligand, and such complexes were the topics for the dissertations of a number of his Doktoranden[97,102,103,119,135,140,341—343]. The only conclusive proof of isomerism caused by the position of the methyl group on a coordinated molecule was presented by Werner and Smirnoff[339,344] in the very first article in *Helvetica Chimica Acta*, a journal founded largely through Werner's efforts. Their resolution with silver α-(+)-bromocamphor-π-sulfonate of *cis*-[Co(en)(pn)$(NO_2)_2$]Br contains both asymmetric cobalt and asymmetric carbon and hence illustrates a new and complicated type of isomerism. The isomerism possible in this compound arises from three causes: (1) *cis* (flavo)-*trans* (croceo) geometric isomerism, (2) ligand isomerism ((+)-pn or (—)-pn), and (3) structural isomerism caused by the unsymmetrical nature of the pn ligand (*cis* isomer only). In the *cis* (flavo) series, the methyl group can be situated either near to the plane of the two nitro groups or distant from this plane. Werner distinguished these isomers as α (prisms) and β (needles). Neglecting the optical isomerism of the propylenediamine, five isomers can be distinguished (↑ = methyl group).



Inasmuch as the propylenediamine molecule can exist in (+)- and (—)-forms, the number of isomers shown should be doubled.

trans-(+)-pn
trans-(—)-pn
cis-α-(+)-pn-(+)-Co
cis-α-(+)-pn-(—)-Co
cis-α-(—)-pn-(+)-Co
cis-α-(—)-pn-(—)-Co

cis-β-(+)-pn-(+)-Co
cis-β-(+)-pn-(—)-Co
cis-β-(—)-pn-(+)-Co
cis-β-(—)-pn-(—)-Co

It is a tribute to Werner's octahedral model that such isomers were predictable and a tribute to his experimental skill that he was able to isolate all ten optically active isomers of dinitro(propylenediamine)(ethylenediamine)cobalt(III) bromide even though he was unable to assign unambiguous structures to all of these (ref. 17, pp. 223—5; ref. 18, p. 583; ref. 19, pp. 612—13; refs. 339, 345—347). By the action of ethylenediamine on an aqueous solution of trinitrotriamminecobalt(III) (prepared by heating Erdmann's potassium salt, K *trans*-$[Co(NH_3)_2(NO_2)_4]$), Werner (ref. 339, p. 9) prepared trinitroammine(ethylenediamine)cobalt(III).

$$[Co(NH_3)_3(NO_2)_3] + en \rightarrow [Co(en)(NH_3)(NO_2)_3] + 2NH_3$$

By the action of optically active propylenediamine on this compound, he obtained a mixture of *cis* (flavo) and *trans* (croceo) salts of dinitro(propylenediamine)(ethylenediamine)cobalt(III) nitrite.

$$[Co(en)(NH_3)(NO_2)_3] + pn \rightarrow [Co(en)(pn)(NO_2)_2]NO_2 + NH_3$$

The *cis* isomer was separated by addition of ethanol, and the *trans* isomer was recovered by concentrating the mother liquor. In addition to the ten bromides, Werner[339] prepared the (+)- and (—)- sulfates and thiocyanates of the *cis*-(+)-pn and *cis*-(—)-pn series as well as the nitrites and chlorides of the *trans*-(+)-pn and *trans*-(—)-pn series. Those complexes whose activity is due to the cobalt atom exhibit the Cotton effect, while those whose activity is due to the propylenediamine molecule do not[215,298]. The products of the reaction between $[Co(en)(NH_3)(NO_2)_3]$ and (—)-propylenediamine have recently been separated chromatographically and shown to contain six of Werner and Smirnoff's isomers[348].

(c) *Type* $[Co(\overline{AB})_2C_2]X$

(1) $[Co(pn)_2(NO_2)_2]X$. The yellow dinitrobis(propylenediamine)cobalt(III) salts (ref. 18, pp. 550—5; ref. 19, pp. 614—15; refs. 349—351) should theoretically exist in numerous isomeric forms; not only is *cis*—*trans* isomerism possible due to the positions of the nitro groups, but because of the dissymmetry of the propylenediamine molecule three forms would then be possible for the *cis* ion and two for the *trans* ion; furthermore, the propylenediamine molecules could exist in three possible forms — (+), (—) or racemic (+)(—). However, not all combinations are of equal stability, a phenomenon known as stereospecificity — the fact that coordination compounds containing optically active ligands exist in only certain preferred strereoisomeric configurations rather than in all the possible forms (ref. 5; ref. 15, pp. 220—2).

The dinitro compounds were investigated by several of Werner's Doktoranden[103,119,140,341], especially by Hugh Edmund Watts[341], a young Englishman, and Hans Hürlimann[140], scion of a famous Zürich brewery family. The compounds may be prepared by treating $[Co(pn)_2Cl_2]X$ salts (see Section D(iii)(c)(2)) with[349] $AgNO_2$. Regardless of whether *cis*- or *trans*-dichloro compounds are used as starting materials, a mixture of *cis*- and *trans*-dinitro isomers is obtained[103]. A similar mixture of isomers is obtained by treating $[Co(NH_3)_3(NO_2)_3]$ with propylenediamine[350]. The following compounds were prepared: *cis* (ref. 140) — NO_2^-, NO_3^-, Cl^-, ClO_4^-, Br^-, I^-, SO_4^{2-}, $S_2O_6^{2-}$, SCN^-, (+)-camphorsulfonate (ref. 341) and bromocamphorsulfonate (ref. 341), *cis*-(+)-pn (ref. 341) — NO_2^-, NO_3^-, Cl^-, Br^-, SO_4^{2-}, and $S_2O_6^{2-}$ (ref. 140); *cis*-(—)-pn (refs. 140, 341) — NO_2^-, NO_3^-, Cl^-, Br^-, SO_4^{2-} and $S_2O_6^{2-}$; *cis*-(+)-Co (ref. 140) — NO_3^-, Br^-, I^-, SO_4^{2-}, $S_2O_6^{2-}$ and (—)-bromocamphorsulfonate; *cis*-(—)-Co (ref. 140) — NO_3^-, Br^-, I^-, SO_4^{2-}, $S_2O_6^{2-}$, SCN^- and (—)-bromocamphorsulfonate; *trans*-(—)-pn (refs. 349, 350) — NO_2^-; *trans* (ref. 166) — Cl^-.

(2) *[Co(pn)₂Cl₂]X*. The dichlorobis(propylenediamine)cobalt(III) salts (ref. 17, pp. 243—4; ref. 18, pp. 555—9; ref. 19, p. 614; ref. 27, p. 239; ref. 70; ref. 89, pp. 47, 48, 53; ref. 103) theoretically should exhibit the same isomerism expected for the dinitro compounds (see Section D(iii)(c)-(1)). Werner and Fröhlich[70,103], who first prepared these compounds, predicted the existence of four inactive *trans* series and six inactive *cis* series, of which two *trans* series and three *cis* series should be resolvable. They prepared salts of the violet *cis* and green *trans* series with racemic propylenediamine, each series in only one form. The compounds correspond in color and chemical behavior to the *cis*(violeo)- and *trans*(praseo)-$[Co(en)_2Cl_2]X$ salts (see Section D(iii)(a)(5)) but are more soluble and less stable. The conversion of the *trans* series into the *cis* series by evaporation of the neutral aqueous solution occurs more easily but incompletely since even the slightest trace of acid causes the reconversion of *cis* salts to *trans* salts. In alcoholic solution complete conversion of the *cis* ion into the *trans* ion occurs[312]. The *cis* salts are much less stable than their ethylenediamine analogues and are obtained pure only with difficulty. Because of their instability they cannot be purified by dissolving and reprecipitating, and they have not been resolved into optical isomers.

The *trans*-acid chloride is prepared by oxidizing with air an aqueous solution containing $CoCl_2$ and propylenediamine, heating the solution with concentrated HCl, and concentrating the solution (ref. 70, p. 2228; ref. 89, p. 53; ref. 103). The *trans*-chloride is obtained from an alcoholic solution of the *trans*-acid chloride by addition of ether. Evaporating a solution of the *trans*-chloride to dryness and heating the residue to 105° yields the *cis* chloride (ref. 70, p. 2233; ref. 103). Werner[70,103] also prepared the *cis*-dithionate and the *trans*-nitrate, bromide, silver sulfate—silver nitrate double salt (ref. 89, p. 48), hydrogensulfate, thiocyanate (ref. 89, p. 47), permanganate, hexacyanoferrate(III), tetrachloroaurate(III), tetrachloroplatinate(II) and hexachloroplatinate(IV). By analogous methods, other workers have prepared *cis*- and *trans*-chlorides containing optically active propylenediamine[312,315,317,341,347,349,350,352—356]. Of the six forms possible for the *cis*-$[Co(pn)_2Cl_2]^+$ ion (if the position isomerism depicted in Section D(iii)(b)(1) is disregarded), rotatory dispersion studies[357,358] have shown that the only stable forms are (+)-Co-((—)-pn)₂ and (—)-Co-((+)-pn)₂.

(d) *Type $[Co(\overline{AA})_2BC]X$*

(1) *[Co(en)₂(OH)Cl]X*. The chlorohydroxobis(ethylenediamine)cobalt-

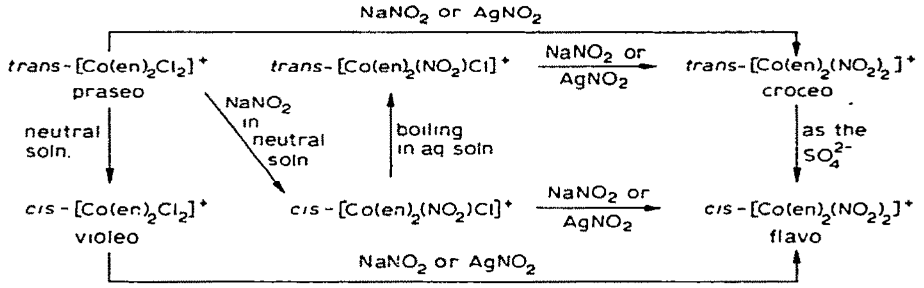
(III) salts (ref. 17, pp. 259—60; ref. 18, pp. 527—8; ref. 19, pp. 606—7) exist in only one series — *cis* (dark violet) — discovered by Werner (ref. 89, pp. 18, 122, 130), who obtained the bromide by the action of ammonia on *cis*-$[Co(en)_2(H_2O)Cl]Br_2$ (see Section D(ii)(a)(9)). Werner's assignment of configuration was confirmed by one of his Swiss Doktoranden, Hermann Fischlin[143], who treated optically active *cis*-$[Co(en)_2(H_2O)Cl]Br_2$ with a 1 : 1 mixture of concentrated NH_3 and absolute ethanol and obtained the corresponding active bromides of the chlorohydroxo series, which he was able to convert into the active nitrates, which racemize rapidly and exhibit anomalous rotatory dispersion and the Cotton effect (ref. 143, pp. 44, 46; ref. 215, p. 46). However, Meisenheimer and Kiderlen (ref. 216, pp. 241, 255), by action of diethylamine on *trans*-$[Co(en)_2Cl_2]Cl$, obtained a pigeon-gray chloride, which they considered to belong to the *trans* series. Its rate of aquation in solution was found to be ten times that of the *trans*-dichloro salt[229]. Pearson et al.[359] claim that the *trans*-chlorohydroxo salts are unknown in the solid form and are stable in solution to only a limited extent. However Baldwin et al.[217a] report *trans*-$[Co(en)_2(OH)Cl]Cl \cdot H_2O$ as a well-defined compound.

(2) *[Co(en)$_2$(OH)NCS]X*. Only one isothiocyanatohydroxobis(ethylenediamine)cobalt(III) salt (ref. 17, pp. 266—267; ref. 19, p. 611; ref. 89, pp. 59, 154, 155) is known in the pure state. Werner (ref. 89, p. 158) obtained the brownish red thiocyanate by the action of concentrated KOH solution on either *trans*-$[Co(en)_2Cl(NCS)]CNS$, *trans*-$[Co(en)_2(NCS)_2]Cl$ or *cis*-$[Co(en)_2Cl(NCS)]NO_3$. The compound dissolves in water giving an alkaline reaction. Since vigorous oxidation with HNO_3 or slow oxidation with 30% H_2O_2, each followed by evaporation with HCl, yielded *trans*-$[Co(en)_2(NH_3)Cl]Cl_2$, Werner concluded that the compound contained Co—NCS bonding and possessed the *trans* configuration. He was unable to isolate individual salts of the *cis* series, but by treating *cis*- or *trans*-$[Co(en)_2Cl(NCS)]X$ salts with concentrated NH_3, he obtained a red solution apparently containing the *cis* salts in solution (ref. 89, pp. 59, 154). By triturating *trans*-$[Co(en)_2Cl(NCS)]_2S_2O_6$ with concentrated NH_3 and adding ethanol to the resulting red solution. Werner obtained a mixture of *cis*-$[Co(en)_2(OH)NCS]X$ salts as a bright red precipitate. From an aqueous solution of this mixture he obtained a crystalline *cis*-dithionate by addition of acetic acid.

(3) *[Co(en)$_2$(NO$_2$)Cl]X*. Werner and his students were the first to prepare the *cis* (bright red)[63,105] and *trans* (brownish red)[60] stereoisomeric chloronitrobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 261—3; ref. 18, pp. 528—30; ref. 19, pp. 607—8; refs. 62, 63; ref. 89, pp. 25, 251—2) by the action of $NaNO_2$ on *trans*-$[Co(en)_2Cl_2]X$. Because compounds containing Co—N bonds are usually yellow or brown while those with Co—O bonds are usually red, Werner[62,63] initially believed these salts to be nitrito (Co—ONO) compounds, but he later (ref. 68, p. 768) decided that they were nitro

($Co—NO_2$) compounds. The Cl and NO_2 groups are not detectable by the usual ionic reactions. The various *cis* salts are prepared from the *cis*-chloride, which is obtained by the action of $NaNO_2$ on a neutral solution of *trans*-[Co(en)$_2$Cl$_2$]Cl (see Section D(iii)(a)(5))[60,62-63]. The various *trans* salts are prepared from the *trans*-nitrate, which is obtained as a precipitate by addition of NH_4NO_3 to the mother liquor from the preparation of the *cis*-chloride[62,63] Werner[62,63,89] prepared the *cis*- and *trans*-nitrites, nitrates (and a *trans*-acid nitrate), chlorides, iodides and thiocyanates as well as a *cis*-bromide and hydrogensulfate.

The characteristic reactions of the chloronitro salts and their relations to the dichloro (see Section D(iii)(a)(5)) and dinitro (see Section D(iii)(a)(2)) salts can be summarized as follows (ref. 60, p. 1715). The chloronitro isomers



can also be distinguished by the action of HCl, which converts the *cis* salts into a mixture of *cis*- and *trans*-[Co(en)$_2$Cl$_2$]X salts but has no effect on the *trans* salts, and by the action of liquid ammonia, which has no effect on the *cis* salts but converts the *trans* salts to *trans*-[Co(en)$_2$(NH$_3$)Cl]X$_2$ salts (see Section D(ii)(a)(4)). Werner's assignment of configuration, based on the above transformations (ref. 60, p. 1715), was confirmed by his resolution of the *cis* series by means of ammonium (+)-camphorsulfonate and (+)-bromocamphorsulfonate (ref. 134, pp. 34—44; refs. 222, 226). The resolution illustrates an unusual case of mutarotation, similar to that observed with dextrose (ref. 5, p. 112). Werner converted the optically active salts to the corresponding active *cis*-[Co(en)$_2$(H$_2$O)NO$_2$]X$_2$ (see Section D(ii)(a)(8)), *cis*-[Co(en)$_2$(NO$_2$)$_2$]X (see Section D(iii)(a)(2)), or *cis*-[Co(en)$_2$(NO$_2$)NCS]X (see Section D(iii)(d)(4)) salts by the action of water, $NaNO_2$ or KSCN, respectively. Absorption spectra have been measured[160,166,208,214,270,303,360—363], and substitution reactions have been studied[275,364,365] for both the inactive and active chloronitro salts. The *cis* and *trans* isomers have been separated by paper chromatography[320], and the racemic chloride has been resolved on starch[366].

(4) *[Co(en)$_2$(NO$_2$)NCS]X*. The isothiocyanatonitrobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 269—71; ref. 18, pp. 546—7; ref. 19, pp. 611—12; ref. 59; ref. 89, pp. 23—4, 157, 228—46; refs. 96, 105, 109, 111, 134, 367) occur in two series — *cis*, brownish yellow, and the more soluble *trans*, dark

brown — which can be differentiated by the solubilities of their sulfates. The *cis* salts are prepared from the *cis*-chloride, which is obtained by heating an aqueous solution of the *cis*-chloronitro thiocyanate containing acetic acid (see Section D(iii)(d)(3)) (ref. 89, pp. 231, 240; ref. 367).

$$cis\text{-}[Co(en)_2(NO_2)Cl]SCN \xrightarrow{\Delta} cis\text{-}[Co(en)_2(NO_2)NCS]Cl$$

The *cis* salts can also be prepared by the action of KSCN on *cis*-$[Co(en)_2(NO_2)Cl]X$ salts or by the action of $NaNO_2$ on *cis*-$[Co(en)_2Cl(NCS)]X$ salts (see Section D(iii)(d)(5)). The *trans* salts are obtained from the *trans*-thiocyanate, which is obtained by treating *trans*-$[Co(en)_2(NH_3)NO_2]X_2$, (Section D(ii)(a)(1)), *trans*-$[Co(en)_2(NO_2)Cl]X$ (Section D(iii)(d)(3)), or *trans*-$[Co(en)_2(NO_2)NO_3]X$ salts with KSCN. Werner[89] prepared the *cis*- and *trans*-nitrites, nitrates, chlorides, bromides, iodides and thiocyanates as well as the *cis*-sulfate, perchlorate and dithionate and the *trans*-$[Co(en)_2(NO_2)NCS]NO_3 \cdot AgNO_3$, which he formulated as *trans*-$[Co(en)_2(NO_2)NCSAg](NO_3)_2$.

The isomeric isothiocyanatonitro series may be differentiated in three ways: (1) oxidation with H_2O_2 of the *cis* salts gives largely *cis* (flavo)-$[Co(en)_2(NO_2)_2]X$ and a little *cis*-$[Co(en)_2(H_2O)NO_2]X_2$, while the *trans* salts give only *trans*-$[Co(en)_2(H_2O)NO_2]X_2$ salts; (2) oxidation of the *cis* salts with HNO_3, followed by evaporation with HCl, gives *trans*-$[Co(en)_2Cl_2]X$, while the *trans* salts give *trans*-$[Co(en)_2(NO_2)Cl]X$ salts; (3) heating the *cis* salts with concentrated HCl gives *cis*-$[Co(en)_2Cl(NCS)]X$ salts, while the *trans* salts remain unchanged. Werner cited the oxidation of the *cis* salts with H_2O_2 as proof of an isothiocyanato (Co—NCS) structure but, because of the weaker bonding of the —NCS group in the *trans* compounds, this could not be proven for that series. Werner and Gerb[63,105,367] first believed that the salts were nitrito (Co—ONO) compounds, but Werner later designated them as nitro (Co—NO_2) compounds (ref. 89, pp. 162, 163), thus differentiating them from the true nitrito salts, $[Co(en)_2(ONO)NCS]X$ ($X = NO_2$ or SCN), for which only one isomeric form has been found. Werner established his assignment of configuration by preparing optical isomers of the *cis* series, not by resolution, but by treatment of the optically active *cis*-$[Co(en)_2(NO_2)Cl]X$ salts (see Section D(iii)(d)(3)) with KSCN (ref. 222, pp. 3274, 3278; refs. 222, 226, 227). The optically active nitrites, nitrates, chlorides, bromides, iodides, perchlorates, thiocyanates, (+)-sulfate and (+)-$[Co(en)_2(NO_2)NCSAg](NO_3)_2$ were isolated and are described in the dissertations of two of Werner's Russian students, Efim Gurewitsch (ref. 134, pp. 44—50) and Ida Wilbuschewitsch (ref. 144, pp. 44—59). Absorption spectra for various salts of both isomeric series have been measured[160,167,208,215,362,363,368].

(5) *$[Co(en)_2Cl(NCS)]X$*. The chloroisothiocyanatobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 271—5; ref. 18, pp. 547—9; ref. 19, pp. 608—9; ref. 27, p. 240; ref. 88, p. 876; ref. 89, pp. 19—20, 131—44) exist in two series; the *cis* salts are bluish pink, soluble only with difficulty, and in aqueous

solution are quickly converted into *cis*-$[Co(en)_2(H_2O)NCS]X_2$ salts (see Section D(ii)(a)(10)), while the *trans* salts are violet, easily soluble and stable in aqueous solution. The *cis* salts are prepared from the *cis*-chloride, which is obtained either by treating *cis*-$[Co(en)_2(NO_2)NCS]Cl$ with concentrated HCl (ref. 89, p. 141), by heating a solution of *trans*-$[Co(en)_2Cl_2]Cl$ with KSCN, cooling and removing the precipitated *cis*-chloride (ref. 89, pp. 133, 139) or by stirring an aqueous suspension of *trans*-$[Co(en)_2Cl_2]SCN$ with strips of sheet nickel or zinc (ref. 142, p. 48). The *trans* salts are prepared from the *trans*-thiocyanate, which is obtained by heating a concentrated solution of *cis*- or *trans*-$[Co(en)_2Cl_2]X$ with KSCN, cooling, filtering off the *cis*-$[Co(en)_2Cl(NCS)]SCN$ and precipitating the *trans*-thiocyanate from the filtrate with solid KSCN (ref. 59, p. 154; ref. 68, p. 778; ref. 89, pp. 57, 132—6, 169, 175). Werner[59,68,89] prepared the *cis*- and *trans*-chlorides, bromides, perchlorates and dithionates, the *cis*-sulfate and the *trans*-iodide, thiocyanate, dichromate and double nitrate $[Co(en)_2Cl(NCSAg)](NO_3)_2$. His Swiss student Rudolf von Arx[142] and his Russian student Wera Tupizina[139] resolved the *cis* series by means of ammonium bromocamphorsulfonate, isolating the (+)- and (—)-*cis*-nitrite, nitrate, chloride, bromide, iodide, perchlorate, dithionate and thiocyanate (ref. 215, p. 46; ref. 226). The compounds exhibit strong anomalous rotatory dispersion and the Cotton effect[215]. Absorption spectra for the optically active and optically inactive compounds were measured by several of Werner's students (ref. 129, pp. 90, 94; ref. 142; ref. 232, p. 41) and others[160,166,205,206,208,214,301 316,335,369].

In both isomeric series, the coordinated chlorine atom is easily replaced by bromine, the hydroxyl group (by the action of NH_3), the thiocyanate or nitro groups or ammonia (by the action of liquid NH_3). Except in the case of the NO_2 group, these substitutions are accompanied by a partial rearrangement to the other isomeric form. As with most other isothiocyanato complexes, the chloroisothiocyanato compounds form addition compounds with $AgNO_3$ (ref. 88; ref. 89, pp. 38, 39, 142; ref. 139, p. 28). Oxidation of the *trans* compounds with H_2O_2, followed by evaporation with HCl, yields *trans*-$[Co(en)_2(NH_3)Cl]Cl_2$, while the *cis* compounds yield *trans*-$[Co(en)_2Cl_2]Cl$ if the solution is freshly prepared; if the solution has been allowed to stand, *cis*-$[Co(en)_2(NH_3)Cl]Cl$ is the product (ref. 88; ref. 89, pp. 38, 59, 142; ref. 144, p. 44). The *cis* and *trans* isomers have been separated by paper chromatography[320].

(6) *$[Co(en)_2Br(NCS)]X$*. The bromoisothiocyanatobis(ethylenediamine)-cobalt(III) salts (ref. 17, pp. 275—6; ref. 18, p. 549; ref. 19, pp. 610—11; ref. 89, pp. 145—53) exist in two stereoisomeric series. The *cis* salts are bluish red, very unstable in aqueous solution, undergoing aquation, especially on warming[370], and are consequently difficult to isolate.

$$cis\text{-}[Co(en)_2Br(NCS)]^+ + H_2O \rightarrow cis\text{- and } trans\text{-}[Co(en)_2(H_2O)NCS]^{2+} + NCS^-$$

Evaporation of the resulting solution with HBr regenerates *cis*- and *trans*-[Co-

$(en)_2Br(NCS)]Br$. The *trans* salts are blue, much more stable and consequently easy to isolate. A mixture of both series is formed by the action of KSCN on *trans*-$[Co(en)_2Br_2]Br$ (see Section D(iii)(f)(3)). The *cis* salts are also formed by the action of HBr on *cis*-$[Co(en)_2(H_2O)NCS]X_2$ salts, and the *trans* salts may also be prepared by the action of HBr on *trans*-$[Co(en)_2(OH)NCS]X$ salts. Werner[89] prepared the *cis*- and *trans*-bromides and dithionates as well as the *cis*-nitrate and sulfate and the *trans*-perchlorate and thiocyanate. Absorption spectra of the *trans*-bromide (ref. 129, p. 94) and its solution undergoing aquation (ref. 370, pp. 1697, 1700) have been measured.

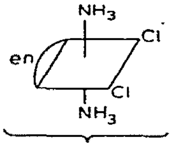
Ammonia reacts with either the *cis* or *trans* salts to give a mixture of *cis*- and *trans*-$[Co(en)_2(NH_3)NCS]X_2$ salts. Oxidation of the *trans* salts with H_2O_2 followed by evaporation with HBr, yields *trans*-$[Co(en)_2(NH_3)Br]Br_2$ but, if the solution is concentrated, the NCS group is completely oxidized off, and *trans*-$[Co(en)_2Br_2]Br$ results. Similar oxidation of the *cis* salts always yields only *trans*-$[Co(en)_2Br_2]Br$. Werner proved isothiocyanato (Co—NCS) bonding by carrying out this oxidation and evaporation on aqueous solutions of *cis*-$[Co(en)_2Br(NCS)]X$ salts that had been aquated to *cis*- and *trans*-$[Co(en)_2$-$(H_2O)NCS]X_2$ salts; he thus obtained *cis*- and *trans*-$[Co(en)_2(NH_3)Br]Br$, with the *cis* compound predominating. Furthermore, since *cis*-$[Co(en)_2(NO_2)$-$NCS]X$ salts can be converted to *cis*-$[Co(en)_2(NH_3)NO_2]X_2$ salts by oxidation with H_2O_2, the abnormal behavior of *cis*-$[Co(en)_2Br(NCS)]X$ salts on oxidation with H_2O_2 must be due to the labilizing effect of the *cis*-bromine atom on the isothiocyanato group.

(7) *[Co(en)₂ClBr]X.* The bromochlorobis(ethylenediamine)cobalt(III) salts (ref. 17, pp. 265—6; ref. 18, p. 533; ref. 19, p. 606; ref. 41; ref. 89, pp. 57, 117—21) were first obtained by Werner as an isomeric mixture of the bromides either by the action of concentrated HBr on *cis*-$[Co(en)_2(H_2O)Cl]$-Br_2 (see Section D(ii)(a)(9)) or by dehydration of this compound at 110°C (ref. 89, pp. 57, 118). Only the *cis* isomer could be obtained pure, since the *trans* isomer was contaminated with *trans*-$[Co(en)_2Br_2]Br$. The bromochloro compounds are intermediate in color between the dichloro and dibromo compounds. The *cis* salts are violet—gray to slate—gray, while the *trans* salts are green. On heating with HBr, the *cis* salts yield *trans*-$[Co(en)_2Br_2]Br$ (ref. 88; ref. 89, p. 121; ref. 228, p. 332). Werner[89] prepared the *cis*- and *trans*-nitrates and dithionates, the *cis*-bromide, and the *trans*-thiocyanate. Werner and Tschernoff[371] confirmed Werner's assignment of configuration by the resolution of the *cis* series with ammonium (+)- and (—)-bromocamphorsulfonates. They isolated the nitrates, chlorides, bromides, sulfates and dithionates of both enantiomeric forms. In solution, the salts readily undergo aquation with complete loss of optical activity within 30—60 min. The absorption spectra, optical rotatory dispersion and circular dichroism of the compounds have been measured[160,176,208,214,279,363].

(e) *Type* $[Co(\overline{AA})B_2C_2]X$

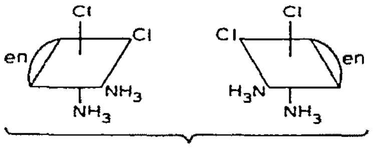
(1) *$[Co(en)(NH_3)_2Cl_2]X$.* In the posthumous fourth (1920) edition of *Neuere Anschauungen* (ref. 45d, p. 371), edited by Paul Karrer, the compound series $[Co(en)(NH_3)_2Cl_2]X$ is cited as the only example of the type $[M(en)(NH_3)_2AB]$ to be resolved. (Actually, the compound is an example of the type $[M(en)(NH_3)_2AA]$ but, at any rate, it would be the sole example resolved by Werner of a complex containing only one molecule of a bidentate ligand.) The citation may be an error, for it does not appear in the third edition[45c], published in 1913 when Werner was in full possession of his faculties, or in the posthumous fifth edition (1923) edited by Paul Pfeiffer[45e]. Nevertheless, Werner did prepare compounds of this type, so the possibility of his resolving them cannot be discounted.

Compounds of type $[Co(en)(NH_3)_2Cl_2]X$ exist in three isomeric forms, one of which is theoretically resolvable (ref. 17, pp. 245—6; ref. 18, pp. 581—2; ref. 19, pp. 581—2).



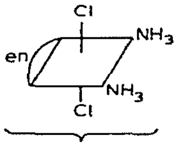
I

2,3-dichloro-1,6-diammine
cis-trans
blue



II

1,2-dichloro-3,6-diammine
cis-cis
violet



III

1,6-dichloro-2,3-diammine
trans-cis
green

Werner and one of his Doktoranden, Franz Chaussy*, prepared the chloride, nitrate, iodide, bromide, thiocyanate, hydrogensulfate and dithionate of Series III, the bromide and dithionate of Series II and the carbonato complex related to Series II, $[Co(en)(NH_3)_2CO_3]Cl$ (ref. 89, pp. 254—64). By treatment with ethylenediamine, they converted trinitrotriamminecobalt(III) to trinitroammine(ethylenediamine)cobalt(III).

$$[Co(NH_3)_3(NO_2)_3] + en \rightarrow [Co(en)NH_3(NO_2)_3] + 2NH_3$$

which they treated with HCl to give dichloroaquoammine(ethylenediamine)-cobalt(III) chloride.

$$[Co(en)NH_3(NO_2)_3] + 3HCl + H_2O \rightarrow [Co(en)NH_3(H_2O)Cl_2]Cl + 3HNO_3$$

Treatment of the latter compound with NH_3, followed by evaporation with

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* Even though Chaussy's dissertation[118] of 1909 may contain more details than the published paper[89] it antedates Werner and King's work[73] of 1911 and could therefore not involve any successful resolution, the details of which must be sought elsewhere.

HCl, gave the desired green *trans-cis* chloride.

$$[Co(en)NH_3(H_2O)Cl_2]Cl + NH_3 \rightarrow \textit{trans-cis-}[Co(en)(NH_3)_2Cl_2]Cl + H_2O$$

By the action of K_2CO_3 on the *trans-cis* chloride, they obtained the corresponding carbonato compound.

$$\textit{trans-cis-}[Co(en)(NH_3)_2Cl_2]Cl + K_2CO_3 \rightarrow \textit{cis-cis-}[Co(en)(NH_3)_2CO_3]Cl + 2KCl$$

which, on treatment with cold fuming HCl, gave the violet *cis-cis*-chloride.

$$\textit{cis-cis-}[Co(en)NH_3)_2CO_3]Cl + 2HCl \rightarrow \textit{cis-cis-}[Co(en)(NH_3)_2Cl_2]Cl + CO_2\uparrow + H_2O$$

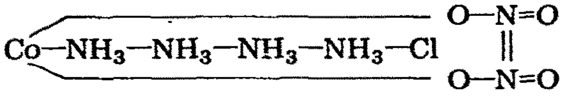
They recognized the two series as *trans*-dichloro and *cis*-dichloro, respectively, analogous to the corresponding praseo and violeo $[Co(en)_2Cl_2]X$ salts, and they predicted (ref. 89, p. 255) the existence of a second *cis* series, I, discovered twenty-eight years later by Bailar and Peppard[372], who prepared the chloride, bromide, iodide, thiocyanate and α-bromo-(+)-camphor-π-sulfonate. Bailar and Peppard[372] also prepared the chloride and bromide of Series II and the chloride of Series III. Lobanov later prepared the periodates[373] of both Series II and III and an iodate—iodic acid addition compound[374] of Series III. Bailar and Peppard[372] prepared the carbonato carbonates ($[Co(en)(NH_3)_2CO_3]_2CO_3$) of Series I and II and attempted to resolve them by shaking solutions with (+)- or (—)-quartz. The carbonate related to Series II was partially resolved; the solution racemized completely in 3 minutes at 90°C or in 3 days at room temperature. Bailar and Peppard[372] also prepared the bromide and thiocyanate of a dibromo complex $[Co(en)(NH_3)_2Br_2]X$ corresponding to Series III. The rate of aquation of the Series III chloro chloride has been determined[294].

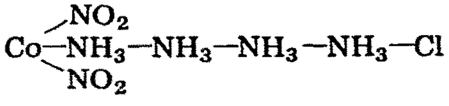
(f) *Type* $[CoA_4B_2]X$.

(1) $[Co(NH_3)_4(NO_2)_2]X$. The yellow dinitrotetraamminecobalt(III) salts (ref. 17, pp. 205—16, 321—2; ref. 18, pp. 480—7; ref. 19, pp. 568—73; ref. 89, pp. 29, 31, 53, 247) represent the second longest known case of geometric isomerism among coordination compounds. Consequently, they have been extensively investigated, and numerous preparative procedures have appeared in the literature (ref. 22, pp. 179—183; ref. 24, pp. 447—8; ref. 26, pp. 537—9, 547; ref. 27, pp. 245—8; ref. 28, pp. 62—3, 97). The reddish yellow *trans* compounds were first prepared by air oxidation of a solution of $CoCl_2$ containing NH_4Cl, NH_3 and $NaNO_2$ in 1875 by Wolcott Gibbs[153], who named them croceo salts, while the brownish yellow *cis* compounds were first prepared by treating $[Co(NH_3)_4CO_3]X$ salts with $NaNO_2$ in 1894 by Jørgensen (ref. 154, pp. 159, 189), who named them flavo salts. The two series correspond completely to the $[Co(en)_2(NO_2)_2]X$ salts (see Section D(iii)(a)(2)).

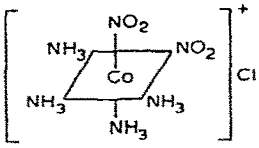
Both series of compounds were found to possess similar properties. The two nitro groups are "masked" within the coordination sphere; they are not removed during metathetical reactions, and they resist the action of dilute acids. Further evidence for the strong bonding of the NO_2 groups to the cobalt atom is the existence of the complex in solution as a monopositive ion, as demonstrated by cryoscopic measurements by Werner[64] and others[375], by measurements of conductance by Werner (ref. 48, p. 46) and others (ref. 262; ref. 375, p. 2652; ref. 376; ref. 377, p. 57; ref. 378, p. 2360; ref. 379, p. 2109), by combined studies of transport numbers and conductances (ref. 380, p. 345; ref. 381, p. 86; ref. 382, p. 127) and by measurements of flocculating power on colloidal solutions[243].

Concentrated HCl converts the croceo salts to *trans*-$[Co(NH_3)_4(NO_2)Cl]Cl$ (see Section D(iii)(h)(1)), whereas with the flavo salts, both NO_2 groups are replaced, resulting in either[383] *cis*(violeo)-$[Co(NH_3)_4Cl_2]Cl$ or *trans*(praseo)-$[Co(NH_3)_4Cl_2]Cl$ (see Section D(iii)(f)(2))[154,189,262]. Because of this difference in the reactivity of the NO_2 groups in the two series, Jørgensen regarded them as structural isomers[4], considering croceo salts as nitro (Co—NO_2) compounds and flavo salts as nitrito (Co—O—N=O) compounds.

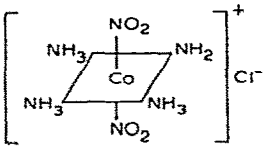

flavo


croceo

Werner (ref. 46, p. 336; ref. 60; ref. 89, pp. 24, 37) argued that flavo salts could not be nitrito compounds since $[Co(en)_2(ONO)_2]X$ salts (see Section D(iii)(a)(3)) had been prepared and found to exhibit entirely different properties, being red and acid-sensitive*. He thus considered both flavo and croceo salts to be true nitro compounds, differing only in the orientation of these groups in space, i.e. *cis*—*trans* stereoisomers.



flavo (*cis*)



croceo (*trans*)

Jørgensen felt that Werner was being inconsistent in agreeing with him that xantho ($[Co(NH_3)_5NO_2]X_2$) and isoxantho ($[Co(NH_3)_5ONO]X_2$) salts were structural isomers, yet insisting that flavo and croceo salts were stereoisomers rather than structural isomers. If the isomerism arose as a consequence of

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* Yalman and Kuwana[189], by action of HNO_2 on $[Co(NH_3)_4CO_3]NO_3$ followed by addition of $NaNO_2$, have prepared a true nitrito compound, *cis*-$[Co(NH_3)_4(ONO)_2]NO_3$, which in aqueous solution is slowly converted into the flavo nitrate, *cis*-$[Co(NH_3)_4(NO_2)_2]NO_3$.

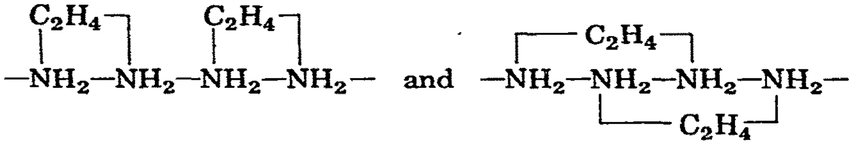
purely geometric considerations, Jørgensen argued that other isomer pairs of type MA_4B_2 should exist. Furthermore, he pointed out that Werner's formulation of the croceo salt as a *trans*-dinitro compound required the two nitro groups to be identical, yet one of these groups is attacked much more readily by hydrochloric acid than the other. Misinterpreted evidence based on salt interconversions led Jørgensen to postulate that flavo and croceo salts belong to the praseo and violeo series, respectively (ref. 255, p. 463), in direct opposition to Werner's views (ref. 50, p. 182), which were based on direct conversion of praseo salts to croceo salts using sodium nitrite. Subsequently, Werner's theory of rearrangements[89] explained many such inconsistencies. Although Werner's view of the flavo—croceo isomerism eventually prevailed, other explanations were also offered[384,385].

The *cis* salts are generally much more soluble than the *trans* salts. The two series can be distinguished by the action of various reagents[154], in addition to the concentrated HCl mentioned above. For example, 50% HNO_3 converts the *cis*-nitrate to *cis*-$[Co(NH_3)_4(H_2O)_2](NO_3)_3$ and the *trans*-nitrate to[189] *trans*-$[Co(NH_3)_4(H_2O)NO_2](NO_3)_2$. Furthermore, $(NH_4)_2C_2O_4$ or H_2SiF_6 gives a precipitate with the *cis* salts but not with the *trans* (ref. 154; ref. 254, p. 468). In the catalytic decomposition of H_2O_2, the *trans* salts are more active than the *cis*[386]. The *cis* and *trans* isomers have been separated by ion exchange chromatography[387]. The absorption spectra, both in solution and in the solid state, are very similar for both series (refs. 129, 166, 213; ref. 256, p. 366; refs. 301, 376, 388—393). The *cis* or *trans* structures are preserved during metathetical reactions, and it has not yet been found possible to convert one series directly into the other.

(2) *$[Co(NH_3)_4Cl_2]X$*. The dichlorotetraamminecobalt(III) salts (ref. 17, pp. 228—33; ref. 18, pp. 488—90; ref. 19, pp. 563—6; refs. 53, 71; ref. 89, pp. 15—16, 102—4; ref. 90) have played a crucial role in the development of coordination chemistry (ref. 47, pp. 40—41), and numerous preparative procedures are available (ref. 26, p. 546; ref. 27, pp. 241—3; ref. 28, pp. 67—8; ref. 30, pp. 1536—7). The compounds correspond completely to the previously discovered corresponding ethylenediamine compounds but are much less stable. Our consideration of the $[Co(NH_3)_4Cl_2]X$ salts therefore logically begins with the dichlorobis(ethylenediamine) compounds.

As we have already seen (p. 4), the best known example of *cis—trans* isomerism among coordination compounds was first observed in 1889 by Jørgensen[149,151,394,395] not among simple tetraammines but among the violeo and praseo salts of the formula $[Co(en)_2Cl_2]X$ (see Section D(iii)-(a)(5)). In his very first paper on the coordination theory (ref. 47, p. 40), Werner, in discussing the violeo and praseo salts, stated: "This interesting isomerism is the first confirmation of the conclusions resulting from the octahedral formulas." He regarded these compounds as *cis* and *trans* stereoisomers, respectively, and felt that the isomerism was merely a geometric consequence of the octahedral structure.

Jørgensen, on the other hand, disagreed with this view, formulated the compounds as $\overset{.Cl}{\underset{.Cl}{Co}}\cdot en\cdot en\cdot X$, and considered the difference in color as due to structural isomerism connected with the linking of the two ethylenediamine molecules, a situation that could not occur among the simple tetraammines: "Whereas the diatomic group $(NH_3)_4$ can be conceived as composed in only one manner, $-NH_3\cdot NH_3\cdot NH_3\cdot NH_3-$, the diatomic group $(NH_2C_2H_4NH_2)_2$ can be conceived as composed in two ways, viz.



$-NH_2-NH_2-NH_2-NH_2-$ and $-NH_2-NH_2-NH_2-NH_2-$

(ref. 396, footnote on pp. 16—17). ... only one conclusion seems possible, namely that such a difference between praseo and violeo salts as we find among the cobalt ethylenediamine salts does not occur among the cobalt ammonia salts." (Ref. 395, p. 409.)

Werner, however, repeatedly insisted that praseo—violeo isomerism should exist among compounds of type $[Co(NH_3)_4Cl_2]X$, which do not contain ethylenediamine. As the time only the praseo salts of this series were known, and the missing violeo salts became a major point of contention between the two adversaries. Jørgensen felt justified in criticizing Werner's theory on the grounds that it predicted the existence of many compounds that were then unknown. Although the simple violeo salts were the most famous of such "nonexistent" compounds, they were by no means the only ones; Jørgensen lists more than a dozen series of such compounds (ref. 395, pp. 410—11).

Among the simple tetraammines not containing ethylenediamine, only NO_2 and SO_3 isomers were known, and it could be argued that such compounds were not stereoisomers but rather structural isomers caused by the difference in the linking of the NO_2 and SO_3 groups. Until 1906, all cases of stereoisomerism among MA_4B_2 type compounds had involved acid radicals (anions) for either A or B, which, according to Werner, were bound to the central metal ion by primary valence bonds (Hauptvalenzen), while the remaining groups were bonded by secondary valence bonds (Nebenvalenzen). In that year, however, Werner[87] was able to announce the preparation of MA_4B_2 stereoisomers of formula $[Co(en)_2(NH_3)_2]X_3$ (see Section D(i)(a)(1)), in which all ligands were bound to the central metal ion by secondary valence bonds, thus demonstrating that the occurrence of stereoisomerism is independent of whether or not acid radicals are bound directly to the central metal ion. But the missing violeo salts remained unknown.

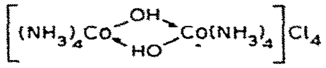
The preparation of these compounds posed a difficult and challenging synthetic problem, for they rapidly undergo aquation to form chloroaquo salts unless the temperature is kept low and the hydrochloric acid concentration is kept high. Under the circumstances, it is understandable that immediately after his successful preparation of these elusive compounds, even before submitting the manuscript to Paul Jacobson, editor of *Berichte der Deutschen Chemischen Gesellschaft*, Werner (on November 13th, 1907) jubilantly informed Jørgensen of his discovery:

> "I am taking the liberty of sending you in the same mail a sample of the long-sought ammonia—violeo series $[Cl_2Co(NH_3)_4]Cl$ and hope that you too will take pleasure in it."

When Jørgensen learned of the preparation of these compounds, whose existence was a necessary consequence of the coordination theory but not of the Blomstrand—Jørgensen chain theory, he promptly acknowledged the validity of Werner's views.

The first dichlorotetraammine salt to be discovered was the green praseo (*trans*) chloride, prepared by Gibbs and Genth[150] in 1857 by the decomposition of $[Co(NH_3)_5H_2O]_2(SO_4)_3$. Rose (ref. 397, p. 44) later prepared the same compound by air oxidation of an ammoniacal $CoCl_2$ solution and assigned it the formula $Co(NH_3)_4Cl_3 \cdot H_2O$. Vortmann (ref. 177, p. 1454; ref. 178, pp. 1893, 1896) prepared the praseo nitrate, chloride and $HgCl_2$ double salt. The most extensive investigations of the praseo series were carried out in 1897 by Jørgensen[395] and by Werner and one of his earliest Doktoranden, Arnold Klein[90]. Jørgensen[395] prepared the chloride by dissolving in H_2SO_4 either $[Co(NH_3)_4(H_2O)Cl]Cl_2$ or $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ and adding concentrated HCl. Werner and Klein (ref. 53, p. 29) prepared the acid sulfate, which is the easiest compound of the series to obtain in the pure state, by the action of concentrated HCl on $[Co(NH_3)_4CO_3]Cl$, followed by treatment with H_2SO_4. They[53] also prepared the praseo chloride, bromide, iodide, fluoride, nitrate, nitrite, thiocyanate, dichromate, hexacyanoferrate(III), hexacyanochromate(III), tetrachloroaurate(III), tetrachloroplatinate(II) and hexachloroplatinate(IV).

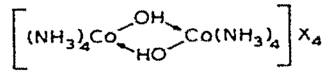
The blue violeo (*cis*) dichlorotetraammines were first prepared in 1907 by Werner[71], who treated



$$\left[(NH_3)_4Co\begin{matrix}OH\\HO\end{matrix}Co(NH_3)_4\right]Cl_4$$

with hydrochloric acid saturated with HCl gas at —12°C. Werner thus obtained the *cis*-chloride, bromide, iodide, sulfate and dithionate. Treatment of carbonatotetraamminecobalt(III) chloride with concentrated aqueous HCl produces only a small yield of violeo chloride, but in 1912 Werner (ref. 89, pp. 103, 104) described an improved procedure involving the action of absolute ethanol saturated with HCl gas at 0°C on $[Co(NH_3)_4CO_3]Cl$. The product is always contaminated with the praseo (*trans*) isomer. Pure violeo salts are usually prepared by means of the insoluble *cis*-dithionate. Duval[383] has reported the preparation of isomerically pure *cis*-$[Co(NH_3)_4Cl_2]Cl$ in quantitative yield by the action of concentrated HCl on *cis*(flavo)-$[Co(NH_3)_4(NO_2)_2]NO_3$ at −10°C*.

Werner's assignment (ref. 89, p. 104) of a *cis* configuration for the violeo dichlorotetraammines (ref. 12, p. 291; ref. 13, pp. 283—4) was based on their preparations from the ring-containing — and therefore *cis* — compounds, $[Co(NH_3)_4CO_3]X$ and



$$\left[(NH_3)_4Co\overset{OH}{\underset{HO}{\rightleftarrows}}Co(NH_3)_4\right]X_4$$

and the reasoning is similar to that for the *cis*-$[Co(en)_2Cl_2]X$ compounds (see Section D(iii)(a)(5)). Werner's resolution of the more stable *cis*-$[Co(en)_2Cl_2]X$ salts[284], to which the violeo tetraammines are strictly analogous, supports his configurational assignment. Further configurational proof was furnished by Stelling's X-ray spectroscopic investigations[398,399], according to which complexes that exist in two stereoisomeric forms show different X-ray absorption spectra of the chlorine atoms.

The dichlorotetraammines are unstable in aqueous solution and undergo aquation, which is accompanied by changes in color. The blue solutions of the violeo salts rapidly become violet[71], while the originally green solutions of the praseo salts become violet gradually or more rapidly when warmed[53]. The aquation can be followed by measurements of conductivity (ref. 52, p. 231; ref. 400), of flocculating power[243], and by spectrophotometry[256,265,401], and the kinetics for the *trans* compounds have been studied[294,355,359]. In general, the *trans* dichloro salts are converted into *trans*-$[Co(NH_3)_4(H_2O)_2]X_3$ salts, with intermediate formation of *trans*-$[Co(NH_3)_4(H_2O)Cl]X_2$ salts[243,265,401]. Only the *trans*-acid sulfate does not undergo aquation (ref. 52, p. 231). In the presence of concentrated acids the violeo salts are converted into the praseo salts. The two series of salts have been separated chromatographically on alumina[402,403].

(g) Type $R[Co(\overline{AA})_2B_2^{II})$

(1) $R[Co(en)_2(SO_3)_2]$. The configuration of the disulfitobis(ethylenediamine)cobaltate(III) salts (ref. 17, pp. 302—3; ref. 18, p. 534; ref. 19, p. 638; ref. 112, pp. 43—51; ref. 268, pp. 77, 79) is not completely established. According to Gmelin (ref. 17, pp. 302—3) and Pascal (ref. 19, p. 638), only two salts have been prepared: (1) the yellow anhydrous ammonium salt, obtained in 1923 by Riesenfeld[403,404] by the action of aqueous ethylenediamine on

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* The methods of preparation cited in this paragraph are lacking in reproducibility, and a reproducible synthesis for the ammonia—violeo salts would be highly desirable. The present author and his students have spent considerable time in checking all these syntheses and have obtained either low yields or no product at all. The author welcomes correspondence from anyone with expertise on these important compounds.

$NH_4[Co(NH_3)_4(SO_3)_2]$ (see Section D(iii)(h)(1)); and (2) the reddish brown sodium trihydrate, obtained in 1925 by Klement[405] by treating an aqueous solution of $[Co(en)_2CO_3]Cl$ with solid $NaHSO_3$. Since Riesenfeld[404] prepared a dihydrated stychnine salt from the ammonium salt but was unable to resolve it, he assigned the ammonium salt the *trans* configuration. Klement[405], who was unable to obtain either a strychnine or brucine salt, assigned the *cis* configuration to his sodium salt because of its preparation from the carbonatobis(ethylenediamine) salt, which is necessarily *cis*.

Nearly four decades later Baldwin[406] reported an anhydrous sodium salt, designated *cis*, obtained by the action of a saturated Na_2SO_3 solution on *cis*-$[Co(en)_2(H_2O)NCS]S_2O_6$ (see Section D(ii)(a)(10)) and a yellow trihydrated sodium salt, designated *trans*, obtained by the action of excess Na_2SO_3 on a concentrated aqueous solution of *trans*-$[Co(en)_2Cl_2]Cl$. Babaeva and Baranovskii[407] obtained the same *trans*-sodium salt by the action of Na_2SO_3 on *trans*-$[Co(en)_2(NO_2)Cl]NO_3$ (see Section D(iii)(d)(3)) and confirmed Baldwin's assignment of configuration by measurement of infrared spectra. It would appear from these data that the founder of coordination chemistry played no part in the investigation of these compounds, but this assumption would be incorrect.

Eighteen years before Riesenfeld's work[403] of 1923, Marie Pokrowska, a Russian Doktorandin of Werner's, in her unpublished doctoral dissertation (ref. 112, pp. 43—51) of 1905, reported the preparation of several disulfitobis(ethylenediamine)cobaltate(III) salts, some of which seem not to have been prepared since that time. She assigned no configuration to her salts (presumably *trans*), but in the case of the sodium and potassium salts she attempted to prepare isomeric compounds but without success.

By boiling *trans*-$[Co(en)_2Cl_2]Cl{\cdot}HCl$ with Na_2SO_3, Pokrowska obtained compact orange—yellow crystals of the trihydrated sodium salt (ref. 112, pp. 43—6). In contrast with Baldwin's work[406], she was unable to prepare the salt from acid-free *trans*-$[Co(en)_2Cl_2]Cl$. In attempts to prepare an isomeric salt, treatment of *cis*-$[Co(en)_2Cl_2]Cl$ with Na_2SO_3 in the cold did not result in a recrystallizable product, and treatment on heating yielded $[Co(en)_2SO_3]Cl$. By boiling $[Co(en)_2SO_3]Cl{\cdot}\frac{1}{2}H_2O$ with aqueous K_2SO_3, Pokrowska (ref. 112, pp. 46—8) obtained the orange—yellow salt $K[Co(en)_2(SO_3)_2]{\cdot}5H_2O$, apparently not described elsewhere. She also obtained the same compound by boiling *trans*-$[Co(en)_2Cl_2]Cl{\cdot}HCl$ with aqueous K_2SO_3. Her attempt to prepare an isomeric salt by treating *cis*-$[Co(en)_2Cl_2]Cl$ with K_2SO_3 also resulted in the formation of the same potassium salt. By boiling Rb_2SO_3 with aqueous $[Co(en)_2SO_3]Cl{\cdot}\frac{1}{2}H_2O$, she obtained orange—yellow $Rb[Co(en)_2(SO_3)_2]{\cdot}3\frac{1}{2}H_2O$, not described elsewhere (ref. 112, pp. 48—9) and, by an analogous process, she obtained the yellow—orange salt $NH_4[Co(en)_2(SO_3)_2]{\cdot}3\frac{1}{2}H_2O$.

(h) Type $R[CoA_4B_2^{II}]$

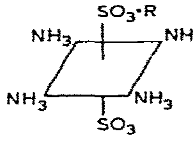
(1) *$R[Co(NH_3)_4(SO_3)_2]$*. The disulfitotetraamminecobaltate(III) salts (ref.

17, pp. 300—2; ref. 18, pp. 492—3; ref. 19, pp. 636—7; refs. 94, 372) exist in two stereoisomeric series, which differ in color, solubility and reactions, but which cannot be directly interconverted. The series of sparcely soluble brown salts was reported simultaneously in 1898 in the same issue of the Zeitschrift für anorganische Chemie by Hofmann and Reinsch[408] and by Werner and Grüger[56], who reported a sodium salt with one[408], two[56,408—412], or three[409] molecules of water of hydration, trihydrated[56,404,405,408,409,413,414] and anhydrous[404,408,409] ammonium salts, a dihydrated rubidium salt[56] and an anhydrous potassium salt[56]. Numerous double salts of this series, the constitutions of which are hypothetical, are known, including ammonium salts with[415] $(NH_4)_2SO_3$ and $BaSO_3$, an ammonium salt[56] with Li_2SO_3, a cesium salt[56] with $(NH_4)_2SO_3$, a barium salt[415] with $BaSO_3$, a cobalt(II) salt[56,415] with $CoSO_4$, and a cobalt(III) salt[56,415,416] with $Co_2(SO_4)_3$. According to Hofmann and Jenny[409], the compounds of this series possess the *cis* configuration. From the lack of the third (*trans*) absorption band in the dihydrated sodium salt, Shimura[411] confirmed the *cis* structure, a conclusion corroborated by infrared spectroscopy, which also showed that the SO_3 groups are bonded to the Co atom through the S atoms[412]. The *cis* structure of the ammonium salt was confirmed by the action of ethylenediamine, which substituted only two molecules of ammonia[405].

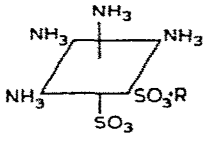
The second or *trans* series of salts, reddish yellow and more soluble than the first series, was discovered in 1901 by Hofmann and Jenny, who prepared tetrahydrated sodium[409] and ammonium salts[409,414]. Riesenfeld[404] also prepared an anhydrous ammonium salt. Yellow and brown sodium salts with variable water content have been prepared[407] and assigned the *trans* configuration[411,412]. A brown trihydrated ammonium salt was prepared by Bailar and Peppard[372], who considered it to belong to the *cis* series, an assignment challenged by Shimura[411], who reported that its spectrum is almost identical with that of the brown *trans*-sodium salt.

Although the discovery of the second (*trans*) series is credited to Hofmann and Jenny[409], who also apparently first assigned configurations to the salts, a letter of Werner dated May 5th, 1898 with the salutation "Geehrter Herr Professor" (presumably Hofmann) suggests that Werner or Hofmann may have isolated the second series three years earlier:

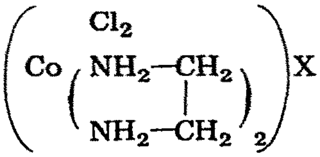
> "I herewith thank you for your kind letter and express my pleasure at our meeting in the experimental area. I am completely of your opinion with regard to the identity you suggest for the compounds in question.
>
> Now it would be a great satisfaction to me if you would take the trouble to undertake a detailed investigation of the two series of isomeric compounds and for the following reason.
>
> I am firmly convinced that the two compounds are stereoisomeric in accordance with the following schematic formulas.



and

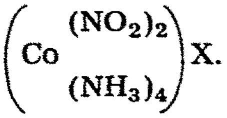


analogous to the dichlorodiethylenediamine salts



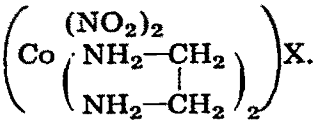
$\left(\mathrm{Co}\begin{matrix}\mathrm{Cl_2}\\ \left(\begin{matrix}\mathrm{NH_2{-}CH_2}\\ |\\ \mathrm{NH_2{-}CH_2}\end{matrix}\right)_2\end{matrix}\right)\mathrm{X}$

and the dinitrotetrammine salts



$\left(\mathrm{Co}\begin{matrix}\mathrm{(NO_2)_2}\\ \mathrm{(NH_3)_4}\end{matrix}\right)\mathrm{X}.$

In addition we have found and thoroughly investigated two new series, namely,



$\left(\mathrm{Co}\begin{matrix}\mathrm{(NO_2)_2}\\ \left(\begin{matrix}\mathrm{NH_2{-}CH_2}\\ |\\ \mathrm{NH_2{-}CH_2}\end{matrix}\right)_2\end{matrix}\right)\mathrm{X}.$

Their publication is to take place soon.

Since in the whole question of explaining these isomeric phenomena I could be regarded as being prejudiced because of my theoretical developments, it would be of the greatest importance if the detailed investigation of one such case of isomerism could come from a completely uninvolved quarter, and since you have found the two sulfito series, this would offer the best opportunity for this."

The two series can be distinguished by the colors developed[408,409] on treatment with conc. HCl or conc. H_2SO_4 as well as by the rate of their photolysis, which is more rapid for the *cis* salt[44]. The brown *cis*-sodium and ammonium salts can be prepared by the action of Na_2SO_3 or NH_4HSO_3 in ammoniacal solution on $[Co(NH_3)_4CO_3]Cl$. The corresponding *trans* salt can be prepared by the action of SO_2 or $NaHSO_3$ on an ammoniacal solution of a cobalt(II) salt, after oxidation by a current of air.

(i) Type $[CoA_4BC]X$

(1) $[Co(NH_3)_4(NO_2)NCS]X$. The isothiocyanatonitrotetraamminecobalt(III) salts (ref. 17, pp. 267—8; ref. 18, p. 503; ref. 19, p. 579; ref. 27, p. 248; refs. 59, 68, 96, 107) exist in two series — one, yellowish brown and the other bright pink. The yellow series was first prepared in 1900 by Werner and Klien [59,96] by the action of KSCN on $[Co(NH_3)_4(NO_2)Cl]X$ or *trans*(croceo)-$[Co(NH_3)_4(NO_2)_2]X$ salts. The isomeric pink salts were prepared in 1907 by Werner and Zinggeler[68,107], starting from the nitrite, which was formed by heating $[Co(NH_3)_4(H_2O)NCS](NO_2)_2$ to about 79°C. At first, Werner[68] considered the two series to be examples of "salt isomerism", i.e. structural isomers differing in the bonding of the SCN group (Co—NCS vs. Co—SCN). Later, however, because of analogy with the corresponding ethylenediamine compounds, $[Co(en)_2(NO_2)NCS]X$ (see Section D(iii)(d)(4)), Werner (ref.

89, p. 38) considered both series to be isothiocyanato (Co—NCS) compounds and regarded them as *cis* and *trans* isomers, but he did not assign them configurations. On careful oxidation with Cl_2, the pink series maintains its Co—N bonding and gives $[Co(NH_3)_5NO_2]X_2$ salts (xantho). The yellow series has since been identified as *trans* by visible[417] and infrared[418] spectroscopy of Werner and Klien's chloride (ref. 59, p. 111), and the pink series as *cis* by visible spectroscopy[417] of Werner and Zinggeler's bromide (ref. 68, p. 777).

Of the yellow series, Werner and Klien[59] prepared the chloride, bromide, iodide, polyiodide, nitrate, hydroxide, thiocyanate and dinitrooxalatodiamminecobaltate(III) as well as a double chloride with $HgCl_2$ and an addition compound of the chloride with $AgNO_3$ similar to the $AgNO_3$ addition compounds formed by other isothiocyanato complexes. Treatment of the chloride with HCl gives *trans*(praseo)-$[Co(NH_3)_4Cl_2]Cl$; with Cl_2 followed by evaporation, the chloride gives $[Co(NH_3)_4(NO_2)Cl]Cl$ (ref. 59, p. 111). Cryoscopic and conductometric studies of the yellow salts have shown the existence of a monopositive cation in solution[59], and solubilities have been determined for both series of salts[419,420]. Of the pink series, Werner and Zinggeler[68] prepared the nitrite, nitrate, bromide, iodide and dinitrooxalatodiamminecobaltate(III). Others have prepared the perchlorate[420] and picrate[420] (no configurations given), the *cis*-bromate[250], the *cis*-periodate[421], the *trans*-thiocyanate[422] and, from the *trans*-chloride, an iodate which Lobanov[249] considers to be *cis*, but which Shimura[417] maintains is *trans*.

(j) Type $[CoA_3BC_2]X$

(1) $[Co(NH_3)_3(H_2O)Cl_2]X$. Dichloroaquotriamminecobalt(III) chloride (ref. 17, pp. 246—8; ref. 18, pp. 579—80; ref. 19, p. 644; ref. 27, pp. 252—3, 255; ref. 36) was first prepared in 1874 by Rose (ref. 397, p. 42), who called it Dichrochlorid because of its dichroism. Its constitution was explained by Werner (ref. 50, p. 161) on the basis of its conductivity; he considered it as *trans*(praseo)-$[Co(NH_3)_4Cl_2]Cl$, in which one molecule of NH_3 has been replaced by one molecule of H_2O. This conclusion was confirmed chemically by Jørgensen (ref. 395, p. 420) and Werner (ref. 54, pp. 146, 153) by the preparation of a nitrate and especially by the preparation of an acid sulfate and a silver sulfate salt $[Co(NH_3)_3(H_2O)Cl_2]SO_4Ag$, which are characteristic of praseo salts. All the coordinated chlorine in these gray—green salts is precipitated completely in the cold with silver salts (ref. 154, p. 187) because of the great instability of the $[Co(NH_3)_3(H_2O)Cl_2]^+$, which rapidly undergoes aquation, as shown by a change in color of the originally green solutions to blue and then to violet. This reaction is also shown by the change in conductivity (ref. 49, p. 517; ref. 50, p. 167; ref. 64, p. 346) and the identity of the resulting spectra with those of $[Co(NH_3)_3(H_2O)_2Cl]X_2$ and $[Co(NH_3)_3(H_2O)_3]X_3$ salts (ref. 187, pp. 3, 15, 18; ref. 423, p. 92).

Rose (ref. 397, p. 42) prepared the grayish green chloride by heating an oxidized, ammoniacal, aqueous $CoCl_2$ solution until $Co(OH)_3$ separated, adding excess HCl, and allowing the salt to crystallize. It may also be prepared by treating $[Co(NH_3)_3(NO_3)_3]$ (ref. 154, p. 187) or $[Co(NH_3)_3(NO_2)_3]$ (ref. 263, p. 357; ref. 395, p. 418) with HCl. The chloride appears to exist in two modifications: (1) large, black, lustrous, very stable crystals with pronounced dichroism (bright red, dark green), and (2) thin, hexagonal, unstable, non-dichroic tablets (ref. 154, p. 188; ref. 182, p. 122; ref. 254, p. 476). X-ray absorption spectra[299] have failed to show any difference between these modifications. X-ray investigations of the chloride prepared according to Jørgensen (ref. 395, p. 418) and Meyer et al. (ref. 263, p. 357) have confirmed that the two chlorine atoms are in the *trans* positions (ref. 398, p. 652; ref. 424).

In addition to the gray—green form, the chloride also exists in a gray form prepared in 1897 by Werner (ref. 54, p. 157) by triturating blue—gray $[Co(NH_3)_3(H_2O)_2Cl]SO_4$ several times with conc. HCl until the sulfate ion has been removed. With mineral acids the compound gives the same products as the gray—green dichro chloride, with which, however, it is not identical. According to Matsuno (ref. 187, p. 4), the gray chloride is the *cis* salt and the gray—green chloride the *trans* salt. However, the two chlorides could not be differentiated with certainty by X-ray absorption spectra[299], so stereoisomerism may not actually occur in this series.

(k) Type $[CoA_2B_2C_2]X$.

(1) $[Co(NH_3)_2(H_2O)_2Cl_2]X$. The green dichlorodiaquodiamminecobalt(III) salts (ref. 17, pp. 248—9; ref. 18, p. 580; ref. 19, p. 662) can be regarded as derived from the *trans*(praseo)-$[Co(NH_3)_4Cl_2]X$ salts by replacing two NH_3 molecules with two H_2O molecules. Werner[50,54,425] prepared two chlorides as well as the nitrate, hydrogensulfate and nitrite of the series. A hydrogenselenate (ref. 263, p. 359) and oxalate (ref. 426, p. 154) are also known. The salts dissolve in water to give a green solution, which soon becomes blue, then violet and finally red, because of aquation to $[Co(NH_3)_2(H_2O)_3Cl]X_2$ and $[Co(NH_3)_2(H_2O)_4]X_3$ salts *[50,54,425], a reaction confirmed by measurements of increasing conductivity (ref. 52, p. 233) and precipitation values for As_2S_3 sols (ref. 243, p. 13). The configuration of the hydrogensulfate has been determined by absorption measurements; since the spectrum for this compound agrees with that of *cis*-$[Co(en)_2(H_2O)_2)]Cl_3$ and deviates from that of *trans*-$[Co(en)_2(H_2O)_2]Cl_3$, Matsuno (ref. 187, pp. 9, 12, 21) assumed that the two H_2O molecules are *cis*, the two NH_3 molecules are *cis*, and the two Cl atoms are *trans*[427].

The chloride exists in two modifications, which Werner (ref. 54, p. 152) believed are probably stereoisomers. He offered no proof for this assumption

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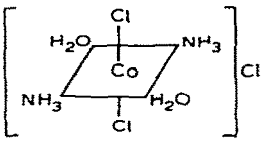
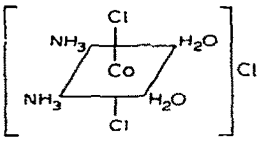
* Compounds of type $[MA_2B_2C_2]X$ can theoretically exist in five isomeric forms ((1) *trans, trans, trans*; (2) *trans, cis, cis*; (3) *cis, trans, cis*; (4) *cis, cis, trans*; and (5) *cis, cis, cis*), the last of which is asymmetric. The various color changes which $[Co(NH_3)_2(H_2O)_2Cl_2]X$ undergoes in solution may possibly be due to isomerization as well as to aquation — different isomers with different rates of aquation may be present (John C. Bailar, Jr., personal communication, July 15, 1974).



and



and assigned no configurations to the compounds. He promised to establish their configurations more definitely but apparently never did so. Werner may have been referring to these compounds or the two chlorides in the previous section when he wrote to his former mentor Arthur Hantzsch on November 6th, 1896: "We have found very interesting geometric isomers in the cobalt series — caused by the different position of water molecules in the octahedron."

The "green-soluble" chloride (Diaquochloropraseochlorid) may be prepared by treating $K[Co(NH_3)_2(NO_2)_4]$ with conc. H_2SO_4 followed by slow addition of conc. HCl (ref. 50, p. 172) or by treating $NH_4[Co(NH_3)_2(NO_2)_4]$ with conc. HCl and a stream of HCl gas at 0°C (ref. 425, p. 1540; ref. 427, pp. 10, 16; ref. 428, p. 448). Werner (ref. 50, p. 172) prepared the "blue-soluble" chloride by triturating $[Co(NH_3)_2(H_2O)_3Cl]SO_4$ several times with conc. HCl and washing the salt free of acid. This compound is a green powder and readily dissolves in water to give a blue solution. The "green-soluble" chloride, on the other hand, gives an initially emerald-green solution, which quickly becomes indigo-blue, then violet and on dilution red (ref. 50, p. 173).

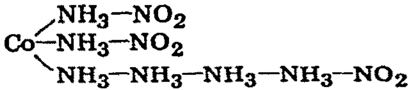
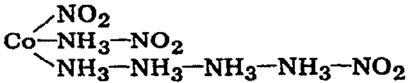
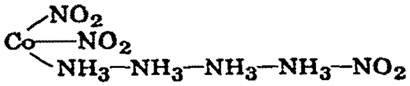
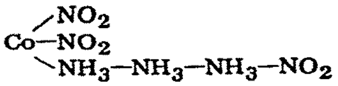
(iv) Nonelectrolytic Complexes, [M]

(a) Type $[CoA_3B_3]$

(1) $[Co(NH_3)_3(NO_2)_3]$. Trinitrotriamminecobalt(III) is the most important and easiest to prepare of the nonelectrolytic cobalt triammines, which played a most prominent role in the supersession of the Blomstrand—Jørgensen chain theory by Werner's coordination theory[147,148]. It was first prepared as flat needles in 1866 by Erdmann[431], then in 1875 as rhombic tablets by Gibbs (ref. 153, p. 14), and numerous preparations from various starting materials are available (ref. 17, pp. 304—6; ref. 18, pp. 586—91; ref. 19, pp. 649—50; ref. 22, pp. 183—4; ref. 23, p. 129; ref. 24, p. 488; ref. 25, pp. 110—11; ref. 26, pp. 539—41; ref. 27, pp. 262—3; ref. 31, pp. 189—90; ref. 37). For the hexaammines, pentaammines and tetraammines, the electrolytic character as predicted by both Jørgensen's and Werner's formulations are in complete agreement, but for the triammines, Jørgensen's theory predicted the presence of two ions, whereas Werner's theory required these compounds to be nonelectrolytes (ref. 47, p. 274).

Thus the conductivities of the triammines became an important and bitterly contested issue in the Werner—Jørgensen controversy. Measurements by Werner (ref. 48, p. 48; ref. 52, p. 227) and others of electrical conductivity (ref. 375, p. 2656; ref. 377, p. 55; ref. 432, p. 414) and freezing-point

TABLE 1

Class of compound	Blomstrand-Jørgensen Formula	No. of ions	Werner Formula	No. of ions
Hexaamines MA_6	 $Co\begin{cases}NH_3-NO_2\\NH_3-NO_2\\NH_3-NH_3-NH_3-NH_3-NO_2\end{cases}$	4	$[Co(NH_3)_6](NO_2)_3$	4
	$\downarrow -NH_3$		$\downarrow -NH_3$	
Pentaammines MA_5B	 $Co\begin{cases}NO_2\\NH_3-NO_2\\NH_3-NH_3-NH_3-NH_3-NO_2\end{cases}$	3	$[Co(NH_3)_5NO_2](NO_2)_2$	3
	$\downarrow -NH_3$		$\downarrow -NH_3$	
Tetraammines MA_4B_2	 $Co\begin{cases}NO_2\\NO_2\\NH_3-NH_3-NH_3-NH_3-NO_2\end{cases}$	2	$[Co(NH_3)_4(NO_2)_2]NO_2$	2
	$\downarrow -NH_3$		$\downarrow -NH_3$	
Triammines MA_3B_3	 $Co\begin{cases}NO_2\\NO_2\\NH_3-NH_3-NH_3-NO_2\end{cases}$	2	$[Co(NH_3)_3(NO_2)_3]$	0

depression (ref. 375, p. 2675; ref. 432, p. 415) of $[Co(NH_3)_3(NO_2)_3]$ solutions showed the compound to be a nonelectrolyte.

Although the conductivity of $[Co(NH_3)_3(NO_2)_3]$ clearly agreed with Werner's formulation for its *constitution*, unfortunately the existence of isomerism for this compound was not clearly established, and therefore he was unable to prove his *configuration* for this compound. At one time Werner (ref. 50, p. 173; ref. 432a, p. 26) believed that the compound prepared by Erdmann[431] was the *cis* isomer and the compound prepared by Gibbs (ref. 153, p. 14) was the *trans* compound, but Jørgensen (ref. 433, pp. 180, 182) believed them to be different crystallographic modifications of the same compound. In a letter of November 24th, 1896 to his friend and former fellow student Arturo Miolati[223], Werner admitted that Jørgensen might be correct, and he did not dispute the point.

In this case, the phenomenon of "polymerization isomerism", a type of structural isomerism first defined by Werner (ref. 4, pp. 163—5), resulted in misinterpretations and cases of mistaken identity. In fact, the classic and best known example of this type of isomerism cited by Werner involved the nine known compounds of empirical formula $Co(NH_3)_3(NO_2)_3$. The large number of such isomers resulted in uncertainties as to which compounds were actually the monomolecular *cis* or *facial* (1, 2, 3) and *trans* or *peripheral* (1, 2, 6) isomers of $[Co(NH_3)_3(NO_2)_3]$, predicted by Werner's coordination theory. Since the existence of two and only two nonelectrolytic isomers of zero conductivity were required by Werner's theory, the confusion in this case enabled Jørgensen to attack the new theory. In fact, the uncertainties were not cleared up until very recently. Although Gmelin (ref. 17, pp. 304—6; ref. 18, pp. 586—91) and Pascal (ref. 19, pp. 649—50) list detailed data for the two isomers, according to MacDermott and Barfoed[434], the numerous claims[37,254,383,435—446] for the isolation of the *facial* (1, 2, 3) isomer of $[Co(NH_3)_3(NO_2)_3]$ required by Werner's theory are all without foundation, and the compound most commonly assigned this configuration is actually[444] *trans*-$[Co(NH_3)_4(NO_2)_2]$*trans*-$[Co(NH_3)_2(NO_2)_4]$. Only the *peripheral* (1, 2, 6) isomer has been positively identified (ref. 206, p. 44; refs. 157, 199, 254, 351; ref. 439, p. 475; refs. 447—9). Apparently, $[Co(NH_3)_3(NO_2)_3]$, like other $[Co(NH_3)_3X_3]$ and especially $[Cr(NH_3)_3X_3]$ compounds, exists in only one configuration.

(b) Type $[CoA_3B^{II}C^{I}]$

(1) $[Co(NH_3)_3(C_2O_4)NO_2]$. Nitrooxalatotriamminecobalt(III) (ref. 17, p. 313; ref. 19, p. 652; ref. 27, p. 257; ref. 74, pp. 216, 218, 236) exists in two stereoisomeric forms. By the action of $NaNO_2$ on $[Co(NH_3)_3(H_2O)C_2O_4]NO_3$ (ref. 54, p. 164), Werner obtained bright, brick-red, scaly, water-insoluble crystals with a greasy luster (ref. 74, p. 236). According to their method of formation, Werner believed that this compound corresponded to violet $[Co(NH_3)_3(C_2O_4)Cl]$ (see Section D(iv)(b)(2)), and he therefore assigned it the *cis* (1, 2, 3) configuration (ref. 74, p. 218). By the action of $H_2C_2O_4$ on $[Co(NH_3)_3(NO_2)_3]$, he also obtained brownish red, compact, prismatic crystals, which were about twenty times more soluble in water than those of the isomeric brick-red compound (ref. 74, p. 236). He considered the brownish red compound to possess the *trans* (1, 2, 6) configuration. The influence of neutral salts on the rate of the photolysis of the *trans* compound has been measured (ref. 450, p. 55), but otherwise these compounds seem to have received little attention. Nevertheless, Werner (ref. 74, pp. 216) considered the existence of these isomers and the corresponding chlorooxalatotriammine isomers (see Section D(iv)(b)(2)) to be extremely important, since they constituted the long-sought geometric isomers of type MA_3B_3 required by his postulated octahedral configuration. Until that time (1914), only two pairs of compounds had been described, which exhibited this type of isomerism, viz. the trinitrotrihydroxocobaltates(III), $R[Co(OH)_3(NO_2)_3]$ (ref. 451) and red and violet trisglycinatocobalt(III), $[Co(NH_2CH_2COO)_3]$ (refs. 452, 453), for which, unfortunately, there were no criteria for assignment of configuration. Werner's oxalato isomers, on the other hand, not only supported his octahedral configuration by their very existence but also supported it further by his ability to assign configurations to them.

(2) $[Co(NH_3)_3(C_2O_4)Cl]$. Chlorooxalatotriamminecobalt(III) (ref. 17, p. 313; ref. 19, p. 652; ref. 25, p. 544; ref. 26, p. 147; ref. 27, pp. 257—8; ref.

74, pp. 216, 217, 234, 235), like the corresponding nitro compound, also exists in two stereoisomeric forms. By the action of $H_2C_2O_4$ on *trans*-$[Co(NH_3)_3(H_2O)Cl_2]Cl$ (dichro chloride) (see Section D(iii)(j)(1)), Jørgensen (ref. 428, p. 434) in 1896 prepared indigo blue, water-insoluble rhombic tablets of a compound $[Co(NH_3)_3(C_2O_4)Cl]\cdot\frac{1}{2}H_2O$. Werner (ref. 74, pp. 217, 234) showed that the water was not contained in the coordination sphere since heating the compound at 80°C removed it without causing any change in the color or character of the compound. Werner prepared the water-insoluble, isomeric, reddish violet compound, which contained one water molecule of hydration, in two ways (ref. 72, pp. 230, 231): (1) by allowing $[Co(NH_3)_3(H_2O)C_2O_4]Cl$ to stand for a long time (12 years!)

$$[Co(NH_3)_3(H_2O)C_2O_4]Cl \rightarrow [Co(NH_3)_3(C_2O_4)Cl] + H_2O$$

and (2) by converting the indigo blue chloride into the corresponding aquo nitrate with silver nitrate

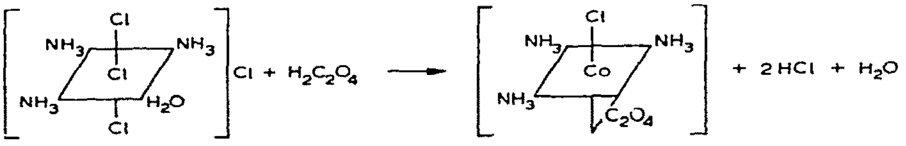
$$\underset{\text{indigo blue}}{[Co(NH_3)_3(C_2O_4)Cl]\cdot\tfrac{1}{2}H_2O} + AgNO_3 + H_2O \rightarrow cis\text{-}[Co(NH_3)_3(H_2O)C_2O_4]NO_3 + AgCl\downarrow + \tfrac{1}{2}H_2O$$

and warming this with hydrochloric acid

$$cis\text{-}[Co(NH_3)_3(H_2O)C_2O_4]NO_3 + HCl \rightarrow \underset{\text{reddish violet}}{[Co(NH_3)_3(C_2O_4)Cl]\cdot H_2O} + HNO_3$$

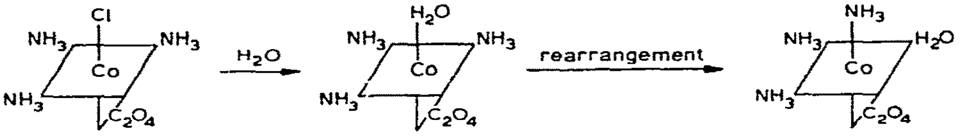
In this compound too, the water molecule is not contained in the coordination sphere since heating at 110°C removed it without altering the color or character of the compound. Although the indigo blue compound can be converted into its reddish violet isomer through the $[Co(NH_3)_3(H_2O)C_2O_4]^+$ intermediate, the reverse conversion is not possible (ref. 72, pp. 217, 235).

Werner (ref. 72, pp. 217, 218) assigned the indigo blue chloride the *trans* (1, 2, 6) configuration and the reddish violet chloride the *cis* (1, 2, 3) configuration since the former results from the action of oxalic acid on dichro chloride (ref. 428, p. 434).



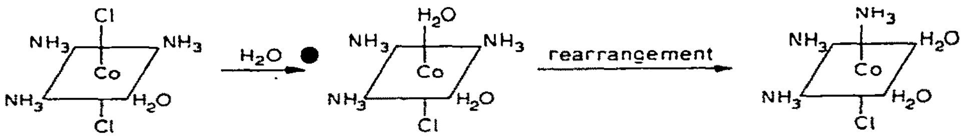
trans (1,2,6) *trans* (1,2,6) indigo blue

This configurational assignment agrees with the colors of the compounds, for among the $[Co(en)_2Br(NCS)]X$ salts (see Section D(iii)(d)(6)) the *trans* salts are blue, while the *cis* salts are reddish lilac. The conversion of indigo blue $[Co(NH_3)_3(C_2O_4)Cl]\cdot\frac{1}{2}H_2O$ into *cis*-$[Co(NH_3)_3(H_2O)C_2O_4]X$ salts, which Werner used as the first step in his preparation of the reddish violet chloride, occurs with rearrangement of an ammonia molecule.



trans (1,2,6) *trans* (1,2,6) *cis* (1,2,3)

This reaction is analogous to the action of water on *trans*-$[Co(NH_3)_3(H_2O)Cl_2]HSO_4$, which first produces blue-gray (*trans*)-$[Co(NH_3)_3(H_2O)_2Cl]SO_4$, which in turn is converted on standing in aqueous solution into its isomeric violet (*cis*) compound (see Section D(ii)(c)(1)).



trans (1,2,6) *trans* (1,2,6) *cis* (1,2,3)

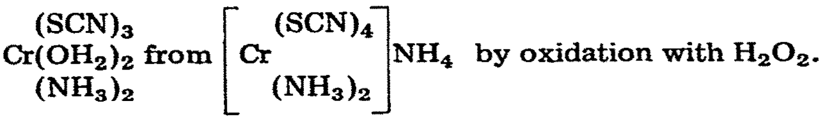
E. CHROMIUM COMPLEXES

(1) Nonelectrolytes

(a) Type $[CrA_2BC_3]\cdot H_2O$

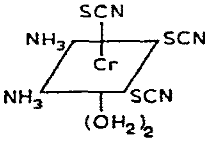
(1) $[Cr(NH_3)_2H_2O(SCN)_3]\cdot H_2O$. In a letter dated April 12th, 1897 to his friend, sometime collaborator and former fellow student Arturo Miolati[223], Werner wrote:

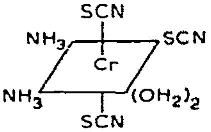
"At the end of the semester we were able to record another beautiful success. As is known, Nordenskjöld has prepared a compound



$$\begin{matrix}(SCN)_3\\ Cr(OH_2)_2\\ (NH_3)_2\end{matrix}\ \text{from}\ \left[Cr\begin{matrix}(SCN)_4\\ \\ (NH_3)_2\end{matrix}\right]NH_4\ \text{by oxidation with}\ H_2O_2.$$

We have now succeeded in obtaining a compound isomeric with it by oxidation with nitric acid. With ammonium thiocyanate both isomers again give Reinecke's ammonium salt — thus they must be isomeric and in fact stereoisomeric according to the following formulae.



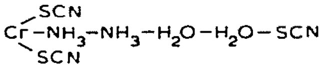


Thus we have here the first representatives of stereoisomeric chromium compounds. The [illegible] double water molecule seems to have acid properties, just like the water molecule in platinic chloride* (even though less). In order to be informed about this I should now like to ask you to determine as soon as possible the molecular conductivities of the 2 preparations I am sending you at the same time.

Preparation I is the Nordenskjöld, preparation II, our new compound."

Miolati apparently never carried out the conductivity measurements that Werner requested; the last article on which they collaborated was their paper[52] of 1896**. The facts in the literature concerning Werner's supposed isomers are as follows (ref. 456, pp. 222—4; ref. 457, p. 487).

In 1892, by oxidizing Reinecke's salt, $NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$ with 3% H_2O_2, Otto Nordenskjöld (ref. 458, p. 137) prepared purple, hexagonal plates of a water-soluble compound of the composition $Cr(NH_3)_2(SCN)_3\cdot 2H_2O$, to which, in accordance with the Blomstrand—Jørgensen chain theory, he assigned the structure



$$\mathrm{Cr}\begin{matrix}\diagup \mathrm{SCN} \\ -\mathrm{NH_3}-\mathrm{NH_3}-\mathrm{H_2O}-\mathrm{H_2O}-\mathrm{SCN} \\ \diagdown \mathrm{SCN}\end{matrix}$$

i.e. Reinecke's salt in which two SCN groups have been replaced by two water molecules, and the name Chromodiammindiaquorhodanid. In a later, more detailed investigation, undertaken in order to establish the constitution of Reinecke's salt, Werner and his German Doktorand Georg Richter[92] prepared Nordenskjöld's compound by oxidizing Reinecke's salt by several methods — electrolysis, $KClO_3$ in HCl solution, or with warm 1 : 1 HNO_3 (ref. 55, pp. 268—73). Furthermore, by oxidizing Reinecke's salt with 1 : 2 HNO_3, they also prepared (ref. 55, pp. 273—4) a red compound (designated as the β form), which was isomeric with Nordenskjöld's compound (designated as the α form) but which was much less soluble and gave different precipitation reactions (ref. 55, pp. 274—6). Werner and Richter established the fact that both the α (ref. 55, pp. 271—2) and the β form (ref. 55, p. 274) were nonelectrolytes, not by the conductivity data that Werner had hoped to obtain from Miolati but by cryoscopy. Since the behavior of the two trithiocyanatodiaquodi-

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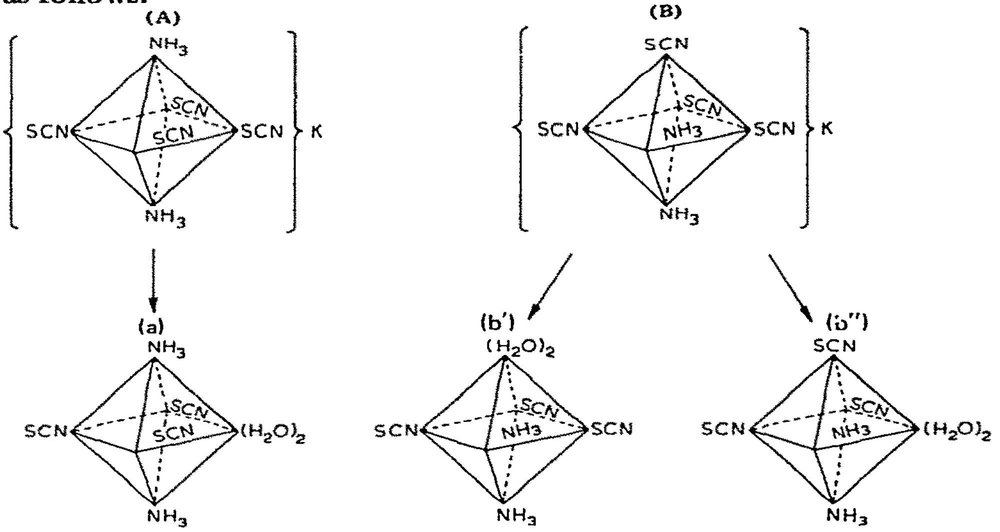
* Miolati[454,455] was later to prepare all members except the fourth of the transition series $H_2[PtCl_6]$, $H_2[Pt(OH)Cl_5]$, $H_2[Pt(OH)_2Cl_4]$, $H_2[Pt(OH)_3Cl_3]$, $H_2[Pt(OH)_4Cl_2]$, $H_2[Pt(OH)_5Cl]$ and $H_2[Pt(OH)_6]$. The second and third members of this series can be considered to be hydrated platinum(IV) chlorides, viz. $PtCl_4\cdot HCl\cdot H_2O$ and $PtCl_4\cdot 2H_2O$, respectively.

** In numerous letters Werner asked Miolati to collaborate on various projects, always with negative results. For example, on May 29th, 1897 he wrote: "On April 12th I sent you two stereoisomeric chromium compounds for investigation; however, have had no news from you about this, did you receive them? We have carried out the molecular weight investigations, both compounds are "$i = 1$." Miolati rarely answered Werner's letters, but, perhaps in attempts to assuage his guilty conscience, he sometimes sent Werner gifts of Italian fruit.

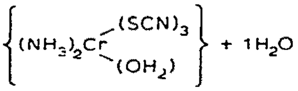
ammine compounds showed them to have the same constitution and therefore ruled out *structural* isomerism Werner and Richter (ref. 55, p. 259) considered them to be *stereoisomers* of the MA_3B_3 type. Because these two isomers were obtained by oxidation of Reinecke's salt, which was easily and quantitatively recovered from them by treatment with KSCN

$$\left[(NCS)_3Cr\begin{matrix}(OH_2)_2\\(NH_3)_2\end{matrix}\right] + KSCN \longrightarrow K\left[(NCS)_3Cr\begin{matrix}SCN\\(NH_3)_2\end{matrix}\right] + 2H_2O$$

Werner and Richter (ref. 55, p. 259) assumed that three SCN groups and two NH_3 molecules were bonded to the chromium atom and that the sixth coordination position was occupied by a double water molecule (Doppelwassermolekül). According to Werner's theory, if the two NH_3 molecules in Reinecke's salt were in the *trans* positions (A), replacement of one SCN group by a double water molecule would yield only one trithiocyanato compound (a), whereas if the two NH_3 molecules in Reinecke's salt were in the *cis* positions (B), replacement of one SCN group by a double water molecule would yield two isomeric trithiocyanato compounds (b′, 1, 2, 6; and b″, 1, 2, 3). Werner and Richter (ref. 55, p. 259) therefore assigned the α and β forms the configurations b′ and b″, without specifying which form has which configuration. They also assigned to Reinecke's salt the *cis* structure (B), a conclusion which X-ray diffraction measurements (ref. 459; ref. 460, p. 324) have shown to be incorrect; Reinecke's salt has the two NH_3 molecules in the *trans* positions (ref. 457, pp. 244—5). Werner and Richter's configurational assignments are as follows.



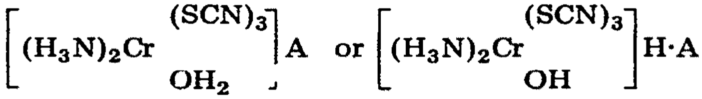
Although Werner considered the existence of the two isomeric trithiocyanato compounds and their genetic relationship to Reinecke's salt to provide strong support for his coordination theory, he does not seem to have published anything further about them until 1902 when, in an article on tetraaquodiammine- and dianionodiaquodiamminechromium(III) compounds [461], published with his English Doktorand and assistant James L. Klien[462], he cites the fact that since in the oxidation of Reinecke's salt to form the α-trithiocyanato compound[55,458] now formulated as



$$\left\{(NH_3)_2Cr\begin{matrix}(SCN)_3\\(OH_2)\end{matrix}\right\} + 1H_2O$$

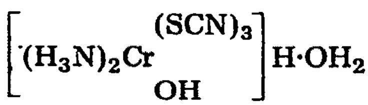
(there is no mention of isomerism), one SCN group is completely oxidized away, its bonding to the chromium atom must be through the sulfur atom (ref. 461, p. 280; ref. 462, p. 49). By oxidizing the α compound with bromine, Werner and Klien obtained $[Cr(NH_3)_2(H_2O)_2Br_2]Br$ (ref. 461, p. 285), and they therefore concluded that all the SCN groups in the α compound and in Reinecke's salt as well are bonded to the chromium atom through the sulfur atom. This conclusion is in contradiction to more recent X-ray diffraction[459, 460,463–465] and infrared spectroscopic studies (ref. 466; ref. 467, p. 41) of $R[Cr(NH_3)_2(SCN)_4]$ salts and studies of related compounds (ref. 468, p. 82), which show Cr—NCS (isothiocyanato) bonding.

Except for the preparation of an addition compound $[Cr(NH_3)_2H_2O(SCN)_3]_4 \cdot Cd(NO_3)_2$ (ref. 113, p. 68), Werner did not return to the trithiocyanato compounds until 1916, when in a paper with J.A. Siemssen devoted completely to the compound (apparently the α form; there is no mention of isomerism)[76], he attempted to provide a more complete configurational proof for the admittedly unusual double water molecule (Bisaquogruppe). In addition to citing the replacement of both water molecules by a single thiocyanate in the conversion of the compound back to Reinecke's salt, Werner and Siemssen[76] showed that one water molecule can be replaced by a molecule of various amines (pyridine, aniline, α-picoline, collidine, quinaldine, brucine, strychnine, ethylenediamine and piperidine) and that therefore one of the two water molecules must contain an acidic hydrogen atom. Since the amines are very easily removed from the resulting oxonium salts, which they formulated as



$$\left[(H_3N)_2Cr\begin{matrix}(SCN)_3\\OH_2\end{matrix}\right]A \quad \text{or} \quad \left[(H_3N)_2Cr\begin{matrix}(SCN)_3\\OH\end{matrix}\right]H\cdot A$$

(where A is an organic amine), they formulated the trithiocyanato compound as an acid with the constitution



$$\left[(H_3N)_2Cr\begin{matrix}(SCN)_3\\OH\end{matrix}\right]H\cdot OH_2$$

Except in his first article on the trithiocyanatodiaquo compounds[55], Werner apparently never mentioned the β form or the occurrence of stereoisomerism.

In his discussions of geometric isomerism among chromium compounds in the 3rd and 4th editions of *Neuere Anschauungen* (ref. 45b, pp. 284—5; ref. 45c, pp. 354—5; ref. 45d, pp. 364—6), Werner mentions only the ethylenediamine compounds investigated by Paul Pfeiffer. In the 5th (posthumous) edition, Pfeiffer also mentions the dioxalatochromates prepared by Werner et al.[75] in 1914 (see Section E(ii), (iii), (iv)). Inasmuch as, since Werner's time, only measurements of absorption spectra (ref. 469, p. 355) of the trithiocyanatodiaquodiammine have been made and inasmuch as Pfeiffer (ref. 470, footnote on p. 4256), who occupies a rank in the coordination chemistry of chromium similar to Werner's in that of cobalt, has cast doubt on Werner's alleged isomerism, a reinvestigation of Werner's compounds seems in order.

(ii) Monovalent anions

(a) Type $R[CrA_2(\overline{BB})_2^{II}]$

(1) $R[Cr(H_2O)_2(C_2O_4)_2]$. In 1914, together with his Zürcher Doktorand Hans Surber, Werner published a long article on dioxalato compounds of chromium[75], which are also described in Surber's dissertation[138]. The dioxalatodiaquochromate(III) ion (ref. 7, p. 49; ref. 25, pp. 114—15; ref. 26, pp. 387—90; ref. 31, pp. 91—3, 179—81; ref. 45e, pp. 358—60; ref. 75, pp. 295—307; ref. 138, pp. 28—36, 69, 72—86; ref. 457, pp. 497—8; ref. 471, pp. 413—15, 461—2, 502—03, 658—62, 737, 767, 773, 790, 817, 830, 847, 863, 934; ref. 472) forms a large number of well-crystallized salts with various cations. Their constitution was established by Rosenheim and Cohn[472] and by Werner and Surber[75]. The salts occur in two geometrically isomeric series — *cis*, reddish violet and *trans*, pinkish red — which are formed by the reduction of dichromates by oxalic acid, whereby the formation of the particular reaction product is controlled by the conditions of the reaction (ref. 75, p. 297; ref. 473, p. 219). Werner and Surber prepared the following *trans* salts (ref. 75, pp. 295—304; ref. 138, pp. 72—82) — K, Na, Li, Rb, Cs, NH_4, Ca, Sr, Ba, Ag, Mg, Pb, Zn and ethylenediamine — and the following *cis* salts — K, NH_4, Rb and Cs (ref. 75, pp. 304—07; ref. 138, pp. 82—6).

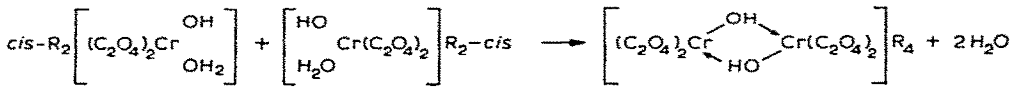
The mechanism of the formation of the $[Cr(H_2O)_2(C_2O_4)_2]^-$ ion from $[Cr(H_2O)_6]^{3+}$ and $C_2O_4{}^{2-}$ ions (ref. 474, p. 232) has been established by polarographic[475,476], conductometric[475] and spectrophotometric[476,477] measurements. Its formation by reduction of CrO_3 by excess $H_2C_2O_4$ in aqueous solution[478] and the kinetics of its formation by aquation of the $[Cr(C_2O_4)_3]^{3-}$ ion[479,480] and by cleavage of the $[(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2]^{4-}$ ion[481] have also been investigated.

In aqueous solution the equilibrium between the *cis*- and *trans*-$[Cr(H_2O)_2(C_2O_4)_2]^-$ ions lies almost completely on the side of the *cis* isomer; pure crystals of the sparcely soluble potassium *trans* salt are formed by slow evaporation of the solution at room temperature, whereas the potassium *cis* salt is obtained by cooling the hot solution[482]. The kinetics of the isomerization reaction have been studied (ref. 15, pp. 198, 211; ref. 474, p. 229; ref. 483). *Trans* salts isomerize to *cis* salts by the action of Na_2CO_3; the reverse isomerization occurs in the presence of HCl. The absorption spectra of the *cis* and *trans* compounds are similar but differ greatly in intensity[482–484].

The *cis* salts are generally less hydrolyzed in water and are more soluble than the corresponding *trans* salts. Their dilute aqueous solutions are reddish violet, while their concentrated solutions exhibit red—blue dichroism. Solutions of the *trans* salts are red and not dichroic when freshly prepared; on long standing or short heating they become green or blue and form trioxalatochromates(III). Solutions of both *cis* and *trans* salts give an acidic reaction. Treatment of the *cis* salts with aqueous NH_3 or KOH gives *cis*-$[Cr(H_2O)OH(C_2O_4)_2]^{2-}$ salts (green), while similar treatment of the *trans* salts gives *trans*-$[Cr(H_2O)OH(C_2O_4)_2]^{2-}$ salts (red or brown) (see Section E(iii)(a)(1)).

$$cis\text{- or } trans\text{-}[Cr(H_2O)_2(C_2O_4)_2]^- + OH^- \rightarrow cis\text{- or } trans\text{-}[Cr(H_2O)OH(C_2O_4)_2]^{2-} + H_2O$$

In the case of the *cis* but not the *trans* salts, further loss of water molecules with formation of the di-μ-hydroxo-bis(dioxalatochromate(III)) ion occurs, a reaction which Werner called Verolung (ref. 75, p. 267; ref. 485). Werner



$$cis\text{-}R_2\left[(C_2O_4)_2Cr\begin{matrix}OH\\OH_2\end{matrix}\right] + \left[\begin{matrix}HO\\H_2O\end{matrix}Cr(C_2O_4)_2\right]R_2\text{-}cis \longrightarrow \left[(C_2O_4)_2Cr\begin{matrix}OH\\HO\end{matrix}Cr(C_2O_4)_2\right]R_4 + 2H_2O$$

used the "olation" (Verolung) reaction to assign configurations to the salts (ref. 75, pp. 267—8). The pinkish to dark red *trans* salts are very stable, but only the alkali metal salts can be recrystallized from water. When heated to 140° C they lose both coordinated water molecules and become green. The relationship between the $[Cr(H_2O)_2(C_2O_4)_2]^-$ salts and related oxalato complexes is shown schematically in Fig. 1 (ref. 7, p. 52; ref. 75, p. 270; ref. 138, p. 59; ref. 471, p. 412).

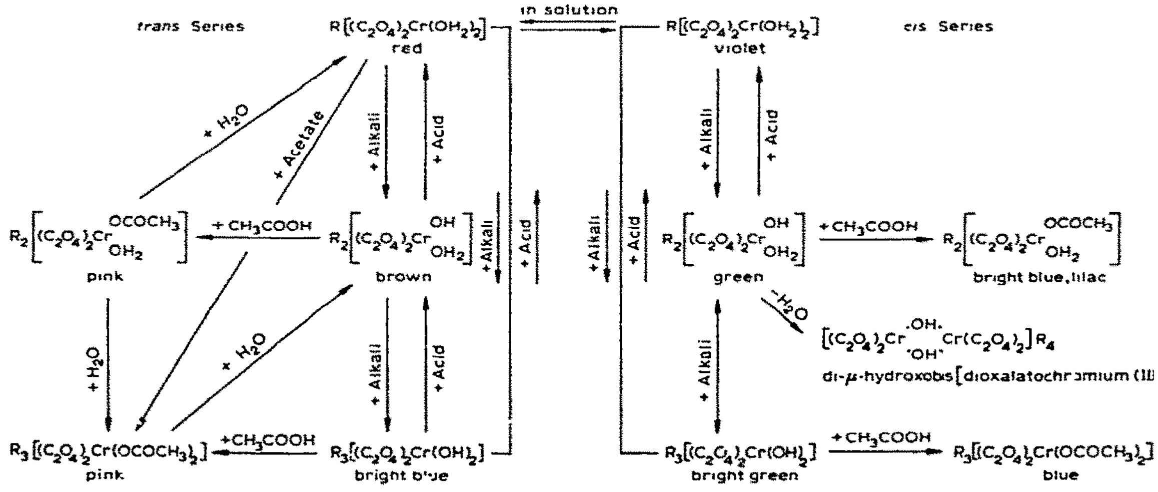


Fig. 1.

The commonest and best known dioxalatodiaquochromate(III) is the potassium salt, which, together with the sodium salt, is used in tanning (ref. 486, pp. 162—4). The dark red potassium *trans* salt, known as Croft's salt or red potassium chromioxalate and crystallizing with two, three of four molecules of water, was prepared in 1842[487] but was known much earlier. Croft[488,489] prepared it by heating $H_2C_2O_4$ with $K_2Cr_2O_7$ at 200° C. Rosenheim (ref. 490, pp. 209, 213) prepared it by treating $H_3[Cr(C_2O_4)_3]$ with $K_2C_2O_4$. In addition to being studied by Alfred Werner, it was also investigated by the English chemist E.A. Werner[491,492]. Proof of the coordinative bonding of the $C_2O_4{}^{2-}$ ion to the chromium atom in Croft's salt has been obtained by absorption spectra measurements[493], and its structure has been determined by X-ray diffraction[494,495]. The lilac-colored potassium *cis* salt, which crystallizes with two or three molecules of water, was first prepared by Werner (ref. 75, pp. 304, 308; ref. 232, p. 52) by allowing a moistened mixture of $H_2C_2O_4 \cdot 2H_2O$ and $K_2Cr_2O_7$ to react, by cooling a warm solution of the *trans* salt, or by treating solid K_2 *cis*-$[Cr(H_2O)OH(C_2O_4)_2] \cdot 2H_2O$ (see Section E(iii)(a)(1)) with dilute mineral acids.

(iii) Divalent anions

(a) Type $R_2[CrAB(\overline{CC})_2{}^{II}]$

(1) $R_2[Cr(H_2O)OH(C_2O_4)_2]$. The stereoisomeric dioxalatohydroxoaquochromates(III) (ref. 7, pp. 48—9; ref. 25, p. 115; ref. 45e, p. 360; ref. 75, pp. 307—18; ref. 138, pp. 36—45, 69, 86—101; ref. 457, p. 500; ref. 471, pp. 415, 462, 503, 672—3, 737—8, 767, 773, 830, 847, 863) were first prepared by Werner and Surber[75,138], who prepared the *cis* and *trans* salts of K, NH_4, Cs, Ca, Ba and Ag as well as the Rb *cis* salt and the *trans* salts of Na, Li, Sr and Zn (ref. 75, pp. 307—18; ref. 138, pp. 86—101). The salts are formed from the corresponding isomeric $R[Cr(H_2O)_2(C_2O_4)_2]$ salts by treatment with aqueous NH_3 or KOH (see first eqn. under Section E(ii)(a)(1)), and the kinetics of formation have been determined[475—477]. The *trans* salts are brown or brownish red, crystalline and stable, while the *cis* salts are bright green or dark green, crystalline and not very stable. Dilute mineral acids immediately reconvert the *trans* salts to red *trans*-$[Cr(H_2O)_2(C_2O_4)_2]^-$ salts and the *cis* salts to violet *cis*-$[Cr(H_2O)_2(C_2O_4)_2]^-$ salts. Aqueous solutions of the salts of both series give an alkaline reaction and are not very stable. Solutions of *trans* salts are brown when freshly prepared but gradually become green, more quickly on warming or on addition of alkali. Solutions of *cis* salts are green and on warming undergo an irreversible "olation" (Verolung) to form the binuclear $[(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2]^{4-}$ ion (see second equation under Section E(ii)(a)(1)), a reaction which Werner cited as evidence for a *cis* configuration (ref. 75, pp. 267—8). The relationship between the $[Cr(H_2O)OH(C_2O_4)_2]^{2-}$ salts and related oxalato complexes is shown in Fig. 1.

(2) $R_2[Cr(H_2O)OCOCH_3(C_2O_4)_2]$. Only a few salts of the dioxalatoacetatoaquochromate(III) ion (ref. 7, p. 49; ref. 45e, p. 360; ref. 75, pp. 323—5; ref. 138, pp. 50—1, 69, 106—10; ref. 457, p. 501; ref. 471, pp. 503, 412, 416, 847), first prepared by Werner and Surber[75,138], are known. Only the Ba salt (with $7H_2O$) is known in both stereoisomeric forms (ref. 75, pp. 324—5; ref. 471, p. 847). Werner and Surber also prepared the *trans* salts of Na (ref. 75, p. 323; ref. 471, p. 503) and Ag (ref. 75, pp. 324—5). Salts of the *cis* series are red—lilac, and those of the *trans* series are blue—lilac. The compounds are derived formally and experimentally by replacement of the OH group in $R[Cr(H_2O)OH(C_2O_4)_2]$ salts by the $OCOCH_3$ group. The Ba *cis* salt is prepared by treating the $Ba[Cr(H_2O)OH(C_2O_4)_2]$ salt with acetic acid, while the corresponding *trans* salt is obtained by treating $Na_3[Cr(OCOCH_3)_2(C_2O_4)_2]$ (see Section E(iv)(a)(2)) with acetic acid and adding $Ba(OCOCH_3)_2$ solution. The salts of both series are stable only in the solid state; even in cold water they are converted into $R[Cr(H_2O)_2(C_2O_4)_2]$ salts. With ammonia, the *cis* salts assume a bright green color, while the *trans* salts give a grayish brown color. With acetic acid, the *cis* salts dissolve to yield a bluish violet solution, while the *trans* salts form a pink solid salt (ref. 75, p. 323). Also see Fig. 1.

(iv) Trivalent anions

(a) Type $R_3[CrA_2{}^{I}(\overline{BB})_2{}^{II}]$

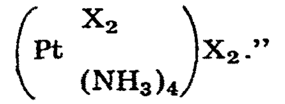
(1) $R_3[Cr(OH)_2(C_2O_4)_2]$. Like the previous series, in the case of the dioxalatodihydroxochromates(III) only a few salts are known (ref. 7, p. 49; ref. 45e, p. 360; ref. 138, pp. 45—9, 69, 101—6; ref. 457, pp. 507—8; ref. 471, pp. 415—16) — the *cis* and *trans* Ag salt (ref. 75, pp. 321—2), the *cis* Ca salt (ref. 75, p. 322; ref. 471, p. 817) and the *trans* K (ref. 75, p. 320; ref. 471, p. 673) and Pb salts (ref. 75, p. 321; ref. 471, p. 934), all prepared by Werner and Surber by treatment of the corresponding $R_2[Cr(H_2O)OH(C_2O_4)_2]$ with alkali, whereby the last aquo ligand is deprotonated. The differences between the *cis* and *trans* isomers of this series are less pronounced than those among the salts containing aquo ligands. The bright blue to green *trans* salts are not very stable and are converted into *trans*-$[Cr(H_2O)_2(C_2O_4)_2]^-$ salts by mineral acids and into pink *trans*-$[Cr(OCOCH_3)_2(C_2O_4)_2]^{3-}$ salts (see Section E(iv)(a)(2)) by CH_3COOH. The bright green *cis* salts are even less stable than the *trans* compounds. They are converted into *cis*-$[Cr(H_2O)_2(C_2O_4)_2]^-$ salts by mineral acids and into blue *cis*-$[Cr(OCOCH_3)_2(C_2O_4)_3]^{3-}$ salts by CH_3COOH. On ageing, aqueous solutions of the *cis* salts polymerize to form trinuclear and tetranuclear ions (ref. 474, p. 234; ref. 485). See Fig. 1.

(2) $R_3[Cr(OCOCH_3)_2(C_2O_4)_2]$. Only two salts of the dioxalatodiacetatochromate(III) ion (ref. 7, p. 50; ref. 45e, p. 360; ref. 457, p. 511; ref. 471, pp. 503, 412, 416) are known — the sodium *trans* salt (ref. 75, p. 326) and

the silver *cis* and *trans* salts (ref. 75, p. 327), both prepared by Werner and Surber (ref. 138, pp. 51—3, 69, 110—13). The isomeric salts are formed by the action of CH_3COOH and H_2O on the corresponding $R_3[Cr(OH)_2(C_2O_4)_2]$ salts or by the action of metal acetates in large excess on the corresponding $R[Cr(H_2O)_2(C_2O_4)_2]$ salts. The *cis* salts are blue, while the *trans* salts are bright red. Both series are stable only in the solid state, and the behavior toward water is known only with the *trans* salts, which are converted partially into *trans*-$[Cr(H_2O)OCOCH_3(C_2O_4)_2]^{2-}$ and *trans*-$[Cr(OH)_2(C_2O_4)_2]^{-}$ salts; the former react in turn to give *trans*-$[Cr(H_2O)_2(C_2O_4)_2]^{-}$ salts. See Fig. 1.

F. PLATINUM COMPLEXES

In the previously mentioned letter to Miolati of May 29th, 1897 (see Section E(i)(a)(1)), Werner wrote:

> " We have also found stereoisomeric platinum compounds of the formula
>
> 
>
> $$\left(Pt\begin{matrix}X_2\\ (NH_3)_4\end{matrix}\right)X_2."$$

In his first paper on the coordination theory (ref. 47, p. 319), Werner stated: "Until now only one series of these compounds is known", and he was obviously anxious to discover the second series, which would provide additional support for his theory.

In a letter of May 5th, 1898 to an unidentified "Geehrtester Herr Professor", Werner probably referred again to the same isomers:

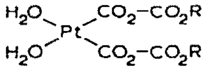
> "As a scientific result I am able to inform you that we have found an octahedral stereoisomerism of platinum, which until now had been observed in cobalt and have thus taken an important step in the experimental foundation of the theory."

Unfortunately, Werner's report, as revealed in these letters, of his discovery of stereoisomerism among the $[Pt(NH_3)_4X_2]X_2$ salts or among any other compounds of platinum(IV) is not confirmed in any of his fourteen articles on the platinum metals[51,58,496—507], six of which[51,58,496,497,501,505] are specifically devoted to platinum. In his two classic articles (ref. 48, pp. 49—52, 54—5; ref. 49, pp. 507—10) on the conductivity of coordination compounds, published jointly with Miolati[223], he gives conductivity data for a number of platinum(II) and platinum(IV) compounds — cationic, nonelectrolytic and anionic — but nowhere does he indicate any stereoisomerism of the type mentioned. Of course, the geometric isomerism of *cis* (platosemidiammine chloride)- and *trans* (platosammine chloride)-$[Pt(NH_3)_2Cl_2]$ (ref. 48, pp. 49—50) and of *cis* (platinisemidiammine chloride)- and *trans* (platiniammine chloride)-[Pt-

$(NH_3)_2Cl_4]$ (ref. 48, pp. 51—2) discussed in these articles and which played such a prominent role in Werner's first paper on the coordination theory (ref. 47, pp. 50, 63—79) were discovered by others in 1844 (ref. 508, p. 6; ref. 509, p. 1103; ref. 510, p. 418; ref. 511), 1850 (ref. 512, p. 279; ref. 513, p. 308; ref. 514) and 1870 (ref. 514; ref. 515, p. 783; ref. 516, p. 58; ref. 517), respectively. In Werner and Miolati's second paper (ref. 49, p. 510) are found the two classic V-shaped conductivity curves for the transition series (Übergangsreihen) between ammines and double salts for both platinum(II) ($[Pt(NH_3)_4]Cl_2$ to $K_2[PtCl_4]$) and platinum(IV) ($[Pt(NH_3)_6]Cl_4$ to $K_2[PtCl_6]$), with no mention of isomerism. Details on the conductivity of *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$ (Platindiamminchlorid) are given in their first paper (ref. 48, pp. 54—5), also with no mention of isomerism. The closest that Werner may have come to preparing compounds of the type $[Pt(NH_3)_4X_2]X_2$ is possibly his preparation of *trans*-$[Pt(pn)_2Cl_2]Cl_2$ (ref. 340, pp. 236, 241) and *trans*-$[Pt(pn)_2Br_2]Cl_2$ (ref. 340, p. 237), both of which occur in only one form. In short, for a full century since its discovery[518,519] in 1838, the only form of $[Pt(NH_3)_4Cl_2]Cl_2$ known was the *trans* isomer (Gros' chloride). It was not until 1938 that the Russian chemist Ilya Ilyich Chernyaev, of *trans* effect fame, succeeded in preparing the *cis* isomer[520,521]. Until the laboratory notebooks of Werner or of his students, which have apparently not been preserved, are examined, the nature of Werner's stereoisomers of $[Pt(NH_3)_4X_2]X_2$ will probably remain an enigma.

Another series of researches on alleged stereoisomerism of platinum compounds still remains unsettled — his studies "On a Peculiar Class of Platinum Compounds and the So-called Isomeric Platosoxalic Acids (Über eine eigentümliche Klasse von Platinverbindungen und die sogenannten isomeren Platosaxalsäuren)[51]. Since simple platinum oxalates do not exist, the yellow crystals described in 1779 by Bergman (ref. 522, p. 265) were probably $Na_2[Pt(C_2O_4)_2]$. The chemistry of the complex oxalatoplatinates (ref. 523, pp. 121—3; ref. 524, pp. 774—6), however, is generally considered to begin with Döbereiner's work[525] of 1833, in which he dissolved sodium platinate in a hot solution of oxalic acid and obtained a reddish copper-colored sodium oxalatoplatinate(II) (ref. 523, pp. 161—2; ref. 524, pp. 784—5). If, however, the compound is crystallized from alkaline solution, yellow isomeric crystals are obtained[525—529]. Since both the platinum and the oxalate group were "masked" in the compounds, the constitution of the salts was assumed to be $Na_2[Pt(C_2O_4)_2]\cdot 4H_2O$. Apparently isomeric yellow and reddish copper-colored compounds were found in the cases of the potassium (ref. 523, pp. 199—200; ref. 524, p. 793), ammonium (ref. 523, p. 222), magnesium (ref. 523, p. 264; ref. 524, p. 804), calcium (ref. 523, pp. 274—5; ref. 524, p. 807), and cobalt salts (ref. 523, pp. 332).

In his first paper on the coordination theory (ref. 47, pp. 317—18) Werner cited this peculiar isomerism (eigentümliche Isomerie) of these Platosoxalsäuren in order to support his proposed square planar configuration for platinum(II). Since the potassium and ammonium salts contain two molecules of water that cannot be removed without decomposition, Werner assumed that these molecules were coordinated to the platinum atom. He considered the two series to be stereoisomeric, and, on the basis of analogies of colors with platinum(II) compounds of known configurations, an admittedly risky procedure with numerous exceptions, he assigned them the following configurations.



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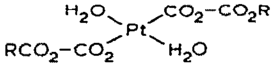
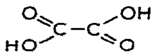


dark red series (*cis*) pale yellow series (*trans*)

Werner's view of these compounds as stereoisomers of formula $K_2[Pt(H_2O)_2(C_2O_4)_2]$ was disproved by Söderbaum (ref. 530, p. 47), who found that both the yellow and copper-colored salts could be dehydrated without change in properties and that the original salts could be re-formed by uptake of water.

At the time of his first paper on the coordination theory, Werner had apparently not done any experimental work on these compounds, but shortly thereafter he assigned the problem to his Swiss Doktorand Friedrich Fassbender[91], and in 1896 they published their results[51], which unfortunately include no experimental details such as analyses. Together with his American Doktorand Emil Grebe[93], Werner, in 1899, published a second paper on the topic with experimental details[58]. In these papers, they reported unstable red salts of a third type which are formed by complete oxidation of the yellow salts and which readily revert to the copper-colored salts. Such salts were formulated as platinum(IV) compounds, e.g. $R_2[Pt(C_2O_4)_2Cl_2]$ (ref. 51, p. 52; ref. 58, pp. 379, 384), and related compounds, e.g. $R_2[Pt(C_2O_4)_2O]$ were found by others (ref. 531, p. 129). Werner concluded that the copper-colored salts were not isomeric with the yellow salts but were instead mixed platinum(II)—platinum(IV) addition compounds, $XR_2[Pt(C_2O_4)_2]\cdot R_2[Pt(C_2O_4)_2O]$ (ref. 51, p. 51; ref. 58, p. 380; ref. 93, p. 10). Blondel (ref. 531, p. 136), however, disagreed that the copper-colored salts contained platinum(IV); instead he considered them as acid salts of the type $3R_2[Pt(C_2O_4)_2]\cdot H_2[Pt(C_2O_4)_2]$.

Since he no longer considered the yellow and the copper-colored salts to have the same composition, Werner (ref. 51, p. 52) withdrew his earlier explanation for their stereoisomerism (ref. 47, pp. 317—18). He noted that "the complete explanation of the . . . rather complicated relationships must, however, be relinquished to later investigations" (ref. 58, p. 382). Agreement has still not been reached on the relationship between the two series of compounds. While the yellow salts are generally considered to be $R_2[Pt(C_2O_4)_2]\cdot 2H_2O$, the constitution of the copper-colored compounds has not been completely explained. In an interesting study of infrared absorption spectra of oxalic acid and 48 metal oxalates, Douvillé et al. (ref. 493; ref. 524, p. 775) concluded that, contrary to the principle of free rotation about a single bond, oxalic acid can exist in geometrically isomeric forms



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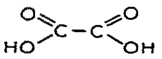
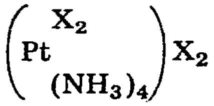


trans (usual commercial form) *cis* (isolated from H_2SO_4 solution)

They therefore attributed the isomerism of the platinum compounds in question to the isomerism of the coordinated oxalic acid (ligand isomerism); according to them, the yellow compounds contain *cis*-oxalic acid and the copper-colored compounds contain *trans*-oxalic acid. On the other hand, Yamada (ref. 532, pp. 146—7) considered the copper-colored compound to consist of chains involving both platinum(II) and platinum(IV).

In closing this section, it should be noted that in the discussions of isomerism among platinum(II) compounds in his *Lehrbuch der Stereochemie* (published in 1904) (ref. 46, pp. 337—48), Werner cited the Platosoxalsäuren (ref. 46, p. 347), but in all the editions of *Neuere Anschauungen* (first edition published in 1905) (ref. 45a, pp. 182—5; ref. 45b, pp. 286—9; ref. 45c, pp. 357—60; ref. 45d, pp. 367—9; ref. 45e, pp. 362—4), he did not mention these compounds. In his discussions of isomerism among platinum(IV) compounds in the *Lehrbuch* (ref. 46, pp. 349—50), Werner specifically states: "Among compounds of the formula



$$\left(\mathrm{Pt}\begin{matrix}X_2\\ (NH_3)_4\end{matrix}\right)X_2$$

. . . isomerism was until now not observed" (ref. 46, p. 349). In *Neuere Anschauungen* (ref. 45b, p. 286; ref. 45c, pp. 355—7; ref. 45d, pp. 366—7; ref. 45e, pp. 360—1), Werner makes no mention of isomerism among $[Pt(NH_3)_4X_2]X_2$ salts.

From his preparations and characterizations of the numerous stereoisomeric cobalt complexes (see Section D), Werner was able to draw a number of general conclusions which he summarized in his long paper of 1912 (ref. 89, pp. 25—72). To treat these in detail or to attempt to evaluate them critically in the light of more recent work would require a separate article. Therefore, in the following sections some of Werner's more important generalizations will be touched upon, with no pretense of completeness.

G. INFLUENCE OF THE COMPOSITION OF THE COMPLEX ON THE EXISTENCE OF STEREOISOMERIC COBALT COMPLEXES

Werner noted that the *cis* complexes of the ammonia series are much less easily formed and are more easily converted into the *trans* complexes than are those of the ethylenediamine series (ref. 89, p. 25). For example, in comparing $[Co(NH_3)_4Cl_2]X$ (Section D(iii)(f)(2)) with $[Co(en)_2Cl_2]X$ (Section D(iii)(a)(5)), the *cis* (violeo) compounds of the first series are formed in much smaller yields from the corresponding carbonato compound and are much more quickly converted into *trans* compounds by acids than are those of the second series. Furthermore, the stability of the *cis*-$[Co(en)(NH_3)_2Cl_2]X$ series (Section D(iii)(e)(1)) lies between that of the *cis*-$[Co(NH_3)_4Cl_2]X$ series and the *cis*-$[Co(en)_2Cl_2]X$ series. The nature and perhaps the size of the coordinated halogen also affect the stability of stereoisomers. For example, while both stereoisomers exist in the $[Co(en)_2Cl_2]X$ (Section D(iii)(a)(5)) and $[Co(en)_2Br_2]X$ series (Section D(iii)(a)(6)), Werner was unable to obtain the *cis*-$[Co(NH_3)_4Br_2]X$ series or either stereoisomeric $[Co(NH_3)_4I_2]X$ or $[Co(en)_2I_2]X$ salts (*cis*-$[Co(en)_2I_2]I_3$ has since been prepared (ref. 322, p. 372)).

As in organic chemistry, steric factors have a pronounced effect on the stability of complexes, especially in regard to ring size, an effect noted earlier by the Russian chemist Lev Aleksandrovich Chugaev (also transliterated as Tschugaeff)[533,534] in his so-called rule of rings[535]. In agreement with Chugaev's observations, Werner found that complexes with six-membered rings were less stable than those containing five-membered rings. For example, although he obtained both *cis* and *trans* isomers of $[Co(en)_2Cl_2]X$ (Section D(iii)(a)(5)) and $[Co(pn)_2Cl_2]X$ (Section D(iii)(c)(2)), he was able to obtain only the green *trans*-$[Co(tn)_2Cl_2]X$ salts (ref. 17, p. 245; ref. 18, p. 562; ref. 19, p. 615; ref. 89, p. 270; refs. 536, 537) from $[Co(tn)_2CO_3]X$ salts (ref. 17, p. 285; ref. 18, p. 562; ref. 19, p. 633; ref. 89, p. 271; ref. 538). Furthermore, he could obtain no cobalt complexes at all with alkylenediamines which form seven- or eight-membered rings, such as tetramethylenediamine or pentamethylenediamine*. Similar generalizations held true for potentially coordinating bivalent acid radicals. Although Werner prepared crystalline compounds of type $[Co(en)_2Z]X$ where $Z = SO_3^{2-}$ (ref. 89, pp. 81—6), CO_3^{2-} (ref. 89, pp. 72—7), $C_2O_4^{2-}$ (ref. 89, pp. 77—9) or malonate (ref. 89, pp. 79—81), he obtained only syrups that solidified to glassy solids from dicarboxylic acids forming seven-membered rings such as succinic, malic or tartaric acids.

H. RELATIONSHIP OF SOLUBILITY TO THE CONSTITUTION AND CONFIGURATION OF COBALT COMPLEXES

Werner's generalizations on this topic were extremely tentative and were based on only a relatively small number of cases (ref. 89, pp. 29—31). He concluded that, for a given transition series of coordination compounds, the solubility increases with the increasing number of ionizable anions. In other words, solubility parallels conductivity in a series such as $[Co(NH_3)_6](NO_2)_3$, $[Co(NH_3)_5NO_2](NO_2)_2$, *cis*- and then *trans*-$[Co(NH_3)_4(NO_2)_2]NO_2$, [Co-

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* According to Dr. J.C. Bailar, Jr., (personal communication to G.B. Kauffman, July 15, 1974) Hiroshi Ogino has recently obtained compounds containing 4-, 6-, 8- and 10-membered rings in dimethyl sulfoxide solution.

$(NH_3)_3(NO_2)_3]$ and $K[Co(NH_3)_2(NO_2)_4]$, falling from a maximum with $[Co(NH_3)_6](NO_2)_3$ to a minimum with $[Co(NH_3)_3(NO_2)_3]$ and rising again with[539] $K[Co(NH_3)_2(NO_2)_4]$.

For geometrically isomeric organic compounds, the *cis* compounds are often more soluble than the *trans* compounds. Werner found a similar relationship between solubility and configuration for coordination compounds, but this regularity was sometimes disturbed in cases of those compounds for which aquation occurs. Isomer pairs for which the *cis* compound is more soluble than the *trans* compound included $[Co(NH_3)_4(NO_2)_2]X$ (X = Cl, NO_3, or $\frac{1}{2}$ SO_4), $[Co(en)_2(NO_2)_2]NO_3$, $[Co(en)_2Cl_2]X$ ($X = NO_3$ or I), $[Co(en)_2(NO_2)Cl]NO_3$, $[Co(en)_2(NH_3)_2]X_3$ and $[Co(en)_2(H_2O)_2]X_3$. An exception was found in the case of $[Co(en)_2(NO_2)_2]I$, for which the *trans* isomer is more soluble than the *cis* isomer.

I. RELATIONSHIP OF COLOR TO THE CONSTITUTION AND CONFIGURATION OF COBALT COMPLEXES

Since Werner published several articles on the color of organic compounds[540] and the theory of mordant dyes[541,542], it is not surprising that he sought regularities between the color of complexes and their constitution and configuration (ref. 89, pp. 31—7), and the dissertations of a number of his Doktoranden and Doktorandinnen were devoted to studies of absorption spectra of complexes[129,204,232,543]. He observed that the cobalt atom possessed chromophoric properties, and he investigated the effect of various coordinated groups on the colors of the compounds. He recognized that groups in the second sphere also influence the color but much less so than those coordinated in the first sphere, and he (ref. 89, p. 31) promised to examine this effect in a later article, but he apparently never did. He also began an extensive investigation of the absorption spectra of the ammines of chromium, rhodium, iridium, etc., in order to compare the effect of altering the elementary chromophore. He hoped "to be able to communicate the results in the near future", but he apparently never did (ref. 89, p. 37).

Considering the influence on the color of the atom bonded directly to the cobalt atom, Werner arranged the commonest donor atoms in the order of increasing color imparted to the complex, viz. C, N, S, O, Cl, Br and I. He further expanded this series by considering the manner in which another element with bathochromic (color-deepening) action influences the atom coordinated to the cobalt atom.

$$\underbrace{\text{CN, CO}}_{\text{carbon}} \quad \underbrace{\text{NO}_2\text{, en, NH}_3\text{, NCS}}_{\text{nitrogen}} \quad \underbrace{\text{SO}_3}_{\text{sulfur}} \quad \underbrace{\text{OH}_2\text{, ONO, O-acyl, OH}}_{\text{oxygen}} \quad \underbrace{\text{Cl, Br, I}}_{\text{halogen}}$$

He noted that groups bonded to cobalt through nitrogen impart colors from light yellow to dark brown, e.g. the transition series $[Co(NH_3)_6]X_3$ (gold—yellow) to $R_3[Co(NO_2)_6]$ (brown). Amines impart colors similar to those imparted by ammonia. Among nitrogen donors, the nitro group (yellow color) shows the greatest stability toward alteration by the influence of other coordinated groups. Of all the nitrogen donor ligands, the —NCS group displaces the color the most towards the red.

Since most sulfito salts of cobalt are brown, Werner concluded that in its effect on color sulfur acts in the same direction as nitrogen*. He also noted that ligands bonded to cobalt through oxygen deepen the color considerably; as a case in point, he cited the series $[Co(NH_3)_6]X_3$ (yellow), $[Co(NH_3)_5H_2O]X_3$ (brick-red), $[Co(NH_3)_4(H_2O)_2]X_3$ (blue—red) and $[Co(NH_3)_3(H_2O)_3]X_3$ (blue). The color-deepening effect of the oxygen donor atom with respect to the nitrogen donor atom is apparent from the colors of the structurally isomeric[4] series $[Co(en)_2(NO_2)_2]X$ (Section D(iii)(a)(2)) (yellow—brown) and $[Co(en)_2(ONO)_2]X$ (Section D(iii)(a)(3)) (brick—red). Halogen atoms produce the strongest deepening of color, and the effect increases with the atomic weight. The bathochromic action of ligands is usually greater for the *trans* than for the *cis* configuration (ref. 7, p. 67; ref. 89, pp. 34—7; ref. 543), as the following example shows.

$$\begin{tikzcd} & {[Co(en)_2(NH_3)NCS]X_2} \arrow[dl] \arrow[dr] & \\ \textit{cis} & \text{brick—red} & \textit{trans} \\ {[Co(en)_2Cl(NCS)]X} & & {[Co(en)_2Cl(NCS)]X} \\ \text{red} & & \text{violet} \\ {[Co(en)_2Br(NCS)]X} & & {[Co(en)_2Br(NCS)]X} \\ \text{red} & & \text{indigo—blue} \end{tikzcd}$$

Others, such as Werner's onetime associate Israel Lifschitz, have related the color of complexes to their structures. Lifschitz et al.[545] reported results with nickel(II), and Pauling[546] has discussed the concept.

J. REACTIONS OF COBALT COMPLEXES

(i) Difference in reaction properties of stereoisomers

Probably one of the oldest observed differences in reaction between stereoisomeric compounds was the difference between the products formed by the action of hydrochloric acid on *cis* (flavo)- and *trans* (croceo)-$[Co(NH_3)_4(NO_2)_2]X$ salts, viz. *trans* (praeso)-$[Co(NH_3)_4Cl_2]Cl$ and *trans*-$[Co(NH_3)_4(NO_2)Cl]Cl$ (see Section D(iii)(f)(1)). From this Werner concluded that groups coordinated in the *cis* position have a lesser bonding strength than those in the *trans* positions. He and his students often encountered this effect, e.g. among the stereoisomers of $[Co(en)_2(NO_2)_2]X$ (Section D(iii)(a)(2)) and $[Co(en)_2NO_2(NCS)]X$ salts (Section D(iii)(d)(4)). In Werner's own words, "it has

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* Because bonding of cobalt through two oxygen atoms usually causes a red color and the color of $[Co(en)_2SO_3]X$ salts are brown, Werner (ref. 89, p. 81) concluded that the bidentate SO_3 ligand was bonded through a sulfur atom, a conclusion with which Duff[544] agreed. Baldwin[406], however, adduced evidence that the hydrated chloride has the constitution $[Co(en)_2(SO_3)Cl]\cdot H_2O$, which forms $[Co(en)_2(H_2O)SO_3]Cl$ in aqueous solution.

frequently caused unpleasant surprises and difficulties for us in the elucidation of constitutional and configurational problems" (ref. 89, p. 38).

An important case in point involved the thiocyanato (—SCN) and isothiocyanato(—NCS) groups, which Werner frequently used in the determination of the constitution and configuration of complexes. Operating on the assumption that oxidation of coordinated —NCS yields coordinated NH_3, whereas oxidation of coordinated —SCN, followed by treatment with acid, results in replacement of the —SCN group by the acid anion, Werner and Bräunlich (ref. 59, pp. 95, 123; ref. 95) mistakenly concluded that the more soluble $[Co(en)_2Cl(NCS)]X$ salts were —NCS compounds and the less soluble $[Co(en)_2Cl(NCS)]X$ salts were —SCN compounds, i.e., that the two series were structural isomers rather than *stereoisomers*. Later Werner (ref. 89, pp. 22, 41, 192) realized that the difference in reactivity of the compounds on oxidation was caused by the lesser bond strength of *cis*-NCS groups as compared to *trans*-NCS groups, and he correctly identified the two series as *trans*- and *cis*-isothiocyanates, respectively (see Section D(iii)(a)(7)). Similar reasoning allowed Werner to assign correct configurations to each of the geometrically isomeric pairs of $[Co(en)_2NH_3(NCS)]X_2$ (Section D(ii)(a)(6)), $[Co(en)_2Cl(NCS)]X$ (Section D(iii)(d)(5)), and $[Co(en)_2Br(NCS)]X$ salts (Section D(iii)(d)(6)).

In other cases, it is the *trans* group that is bonded less strongly to the cobalt atom than the *cis* group. For example, according to Werner, while liquid ammonia has no effect on the *cis* isomers of chloroamminebis(ethylenediamine)* (Section D(ii)(a)(4)) and chloronitrobis(ethylenediamine) salts (Section D(iii)(d)(3)), the *trans* isomers react readily:

$$trans\text{-}[Co(en)_2(NH_3)Cl]Cl_2 + NH_3(l) \rightarrow cis\text{- and } trans\text{-}[Co(en)_2(NH_3)_2]Cl_3{}^*$$

$$trans\text{-}[Co(en)_2(NO_2)Cl]Cl + NH_3(l) \rightarrow trans\text{-}[Co(en)_2(NH_3)NO_2]Cl_2$$

(ii) Intramolecular reactions

Werner (ref. 89, p. 45) recognized that among intramolecular reactions of cobalt-ammines that involve the evolution of ammonia or water the reaction depends upon the nature of the anion present outside the coordination sphere. In his own words, "a pronounced selective affinity of the central cobalt atom strives to pull into the first sphere the acid radicals that are bound in the second sphere" (ref. 89, p. 47). For example, whereas heating solutions of the chloride, bromide, and nitrate of the *cis*-chloroammine-bis-(ethylenediamine) series produces no reaction, heating the nitrite and thio-

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* According to Bailar, Haslam, and Jones[161], (—)-*cis*-$[Co(en)_2Cl_2]Cl$ reacts with liquid NH_3 to form primarily *cis*-$[Co(en)_2(NH_3)_2]Cl_3$ with a small amount of the *trans* isomer ($[Co(en)_2(NH_3)Cl]Cl_2$) is the intermediate. At or below the boiling point of liquid NH_3, the product has the same sign of rotation as the original material, but at 25° C or above, optical inversion occurs and the sign of rotation is reversed.

cyanate results in the evolution of ammonia:

$$\textit{cis-}[\mathrm{Co(en)_2(NH_3)Cl}]\mathrm{X_2} \xrightarrow{\Delta} \textit{trans-}[\mathrm{Co(en)_2Cl(X)}]\mathrm{X} + \mathrm{NH_3}\uparrow \ (\mathrm{X{=}NO_2} \text{ or } \mathrm{NCS})$$

The anions which displace the ammonia in these intramolecular reactions are characterized by the great strength of their bonding to cobalt. Similar reactions in which water rather than ammonia is evolved occur among aquo complexes. For example, the following reaction occurs when the solid salts are kept for a long time.

$$\textit{cis-} \text{ or } \textit{trans-}[\mathrm{Co(en)_2(H_2O)_2}]\mathrm{X_3} \rightarrow \textit{cis-}[\mathrm{Co(en)_2X_2}]\mathrm{X} + 2\mathrm{H_2O} \ (\mathrm{X{=}Cl} \text{ or } \mathrm{Br})$$

If the diaquo chloride is not entirely free of acid, the green *trans* salt is formed instead of the violet *cis* salt.

Intramolecular reactions also occur in which anions are mutually substituted. For example, if acid-free *trans*-dichlorobis(ethylenediamine)cobalt(III) nitrite is touched with a drop of water, the color changes from green to yellow—red.

$$\textit{trans-}[\mathrm{Co(en)_2Cl_2}]\mathrm{NO_2} \rightarrow \textit{cis-}[\mathrm{Co(en)_2(NO_2)Cl}]\mathrm{Cl}$$

Light as well as moisture seems to exert a catalytic effect on reactions of this type.

Werner (ref. 89, p. 48) postulated that intermediate products that he was unable to isolate are formed in the rearrangement of one isomer to the other. Examples of *trans* to *cis* and *cis* to *trans* isomerizations which occur on evaporating the aqueous solution include

$$\textit{trans-}[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl} \rightarrow \textit{cis-}[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$$

$$\textit{cis-}[\mathrm{Co(en)_2(NO_2)Cl}]\mathrm{Cl} \rightarrow \textit{trans-}[\mathrm{Co(en)_2(NO_2)Cl}]\mathrm{Cl}$$

(iii) Addition compounds

Werner considered addition compounds of cobalt-ammine salts with metal salts to be of great importance in understanding the course of chemical transformations, and he studied a number of them in detail (ref. 89, pp. 49—53). The most stable of such compounds are formed between isothiocyanato compounds and silver nitrate, and their formation is often accompanied by a pronounced change in color.

$$\underset{\text{bright brick—red}}{\textit{cis-}[\mathrm{Co(en)_2(NH_3)NCS}]\mathrm{S_2O_6}} + \mathrm{AgNO_3} \rightarrow \underset{\text{pale yellow}}{\textit{cis-}[\mathrm{Co(en)_2(NH_3)NCSAg}]\mathrm{NO_3{\cdot}S_2O_6}}$$

In some cases, two molecules of the silver salt may be added.

$$\underset{\text{orange}}{\textit{trans-}[\mathrm{Co(en)_2(NH_3)NCS}](\mathrm{ClO_4})_2} + 4\mathrm{AgNO_3} \rightarrow \underset{\text{yellow}}{\textit{trans-}[\mathrm{Co(en)_2(NH_3)NCSAg_2}](\mathrm{NO_3})_4{\cdot}\mathrm{H_2O}} + 4\mathrm{AgClO_4}$$

In many of these addition compounds, the silver is bonded nonionically and quite strongly to the isothiocyanate group, and addition of hydrochloric acid to the solution does not precipitate silver chloride. The stable silver salts of the isothiocyanato complexes were easily investigated, and their existence led Werner to seek to prepare addition compounds of other aniono cobalt salts, which, however, were of lesser stability. The commonest and longest known of such compounds is the acid chloride obtained in the preparation of *trans*-$[Co(en)_2Cl_2]Cl$, viz. $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ or $[Co(en)_2Cl(ClH)(H_2O)_2]Cl_2$ (ref. 149, p. 15). Other addition compounds of chloro, bromo and nitro complexes include $[Co(en)_2Br(BrH)(H_2O)_2]Br_2$, $[Co(NH_3)_4Cl(ClAg)]SO_4$, $[Co(en)_2Cl(Cl_3Bi)]SO_4$ and *cis*-$[Co(NH_3)_4(NO_2)(O_2NM)](NO_3)_2$, where M=K or Rb.

(iv) Spatial rearrangements in substitution reactions

Unlike substitution reactions of platinum(II) or platinum(IV) complexes, those of cobalt(III) complexes are often accompanied by rearrangement, Werner (ref. 88; ref. 89, pp. 54—8) divided substitution reactions (Ersatzreaktionen) into three types: (1) intercalation reactions (Einlagerungsreaktionen), (2) displacement reactions (Verdrängungsreaktionen) and (3) replacement reactions (Substitutionsreaktionen).

An intercalation reaction is one in which water or ammonia enters the coordination sphere and the anion whose place it has taken becomes indirectly bonded in the second sphere, e.g.

$$[Co(en)_2Br(NCS)]Br + NH_3 \rightarrow [Co(en)_2(NH_3)NCS]Br_2$$

and

$$[Co(en)_2Cl_2]Cl + H_2O \rightarrow [Co(en)_2(H_2O)Cl]Cl_2$$

Werner established the fact that many intercalation reactions occur without change of configuration, but that in others rearrangements occur. Werner tabulated the ratios of the yields of the two stereoisomers formed in these reactions (ref. 89, pp. 55—6) and found that they depended upon reaction conditions such as temperature and dilution. He promised to continue this research (ref. 89, p. 56), but he soon became engrossed in optically active coordination compounds[5], the study of which occupied most of the remainder of his career.

A displacement reaction involves the expulsion of ammonia or water from a complex and its replacement by an anion which enters the coordination sphere, e.g.

$$[Co(en)_2(NH_3)Cl](NO_2)_2 \rightarrow [Co(en)_2(NO_2)Cl]NO_2 + NH_3\uparrow$$

and

$$[Co(en)_2(H_2O)Cl]Cl_2 \rightarrow [Co(en)_2Cl_2]Cl + H_2O$$

These reactions, which are the reverse of the intercalation reactions, often occur with rearrangement, and Werner tabulated the ratios of the two stereoisomers formed (ref. 89, p. 57).

A replacement reaction involves the replacement of one coordinated anion by another, e.g.

$$[Co(en)_2Cl_2]X + KNO_2 \rightarrow [Co(en)_2(NO_2)Cl]X + KCl$$

For these reactions, which often occur with rearrangement, Werner also tabulated the ratios of the two stereoisomers formed (ref. 89, p. 59). He emphasized that the ratios tabulated for the three types of substitution reactions were qualitative only. It is obvious that no conclusions can be drawn from Werner's results. Since some of the substitution reactions studied by Werner yield products which are known to undergo isomerization, the observed isomeric ratios may not be direct consequences of the reactions. Some of these reactions have been reinvestigated using spectrophotometric techniques[225] to determine the ratio of the isomers in situ immediately following the reactions. These results agree well with Werner's observations.

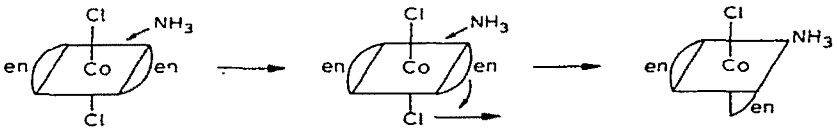
K. THEORY OF THE COURSE OF SUBSTITUTION REACTIONS

Rearrangements occur frequently in organic chemistry, and Werner, who was trained as an organic chemist[547] under Arthur Hantzsch and who carried out experimental or theoretical research on organic rearrangements[548–561] throughout his career, particularly the Beckmann rearrangement[551–555,560,561] and the Walden inversion (ref. 89, pp. 68—72; refs. 556, 557), naturally attempted to explain the course of rearrangements among coordination compounds (refs. 83, 88; ref. 89, pp. 58—65; ref. 114). He recognized the similarity between inorganic and organic substitution reactions and postulated that they occurred by similar mechanisms (ref. 89, p. 58). Today, when entire volumes are devoted to the mechanisms of inorganic reactions[14], Werner's ideas may seem primitive, but, because of their influence on later workers, they are well worth examining.

In attempting to explain the course of substitution reactions, Werner asked and answered two questions. (1) What causes require rearrangements? (2) How does the rearrangement take place? In answering the first question, Werner rejected the prevalent suggestion that rearrangement takes place because the isomer that is ultimately formed is more stable than the isomer that should be formed by normal substitution without rearrangement, His tabulated results proved that differences in stability of the stereoisomers cannot possibly control the occurrence of rearrangements. For the same reason, Werner also rejected the view that rearrangements occur because the group that is being substituted is removed from the coordination sphere and the resulting vacant position stays occupied long enough for the other coordinated groups to rearrange to a more stable configuration whereupon the substituting group enters the newly formed vacancy.

Instead, Werner based his theory of substitution reactions[88] on his very early idea, first expressed in his Habilitationsschrift (1891)[562], that affinity is a variously divisible, attractive force emanating from the center of an atom and acting equally in all directions. According to his new theory, the cobalt atom exerts an attraction on the anions in the second sphere, which therefore tend to enter the first sphere. The magnitude of this attraction depends on the nature of the anions, and when these are directly bonded to cobalt they are held with the greatest strength. The direction of the attraction to the groups in the second sphere varies with the composition and structure of the complex ion, and Werner assumed that this attraction is greater towards certain directions than towards others. Therefore, the directions favored by affinity determine the position occupied by the group entering the first sphere from the second. Since the complex into which this group enters is coordinatively saturated, the entry of this new group must be accompanied by an expulsion of one of the other coordinated groups. The group that is bonded the most weakly is expelled, regardless of the position occupied by the entering group. Therefore, the position occupied by the entering group is independent of that vacated by the departing group and is dependent only on the reaction direction caused by the attraction emanating from the central cobalt atom.

With the aid of his theory, Werner explained the course of various substitution reactions such as the conversion of *trans*-$[Co(en)_2Cl_2]Cl$ to *cis*-$[Co(en)_2(NH_3)Cl]Cl_2$ with aqueous ammonia. On the basis of electrostatics (ref. 563, p. 783), the negative nitrogen atom of the ammonia molecule approaches the octahedron so as to maintain the maximum distance from the electronegative chlorine atoms, i.e. in the plane of the ethylenediamine molecules. Werner depicted the course of the reaction as follows (ref. 89, p. 63).



Werner concluded this section of his paper with the statement:

"I therefore believe that by these explanations I have developed a new conception of the course of substitution reactions, to which the displacement, intercalation, and replacement reactions belong, that is satisfactory in every direction, simple and abundantly confirmed by the experimental results. According to this new conception, spatial rearrangement is no anomaly but a phenomenon established in the course of the reaction." (Ref. 89, p. 65.)

L. CONCLUSION

An unidentified "northern colleague" of Werner's once told him that his proposal of the coordination theory had been "an ingenious impudence" (eine geniale Frechheit)[564], for at the time of its inception (1893)[47], the twenty-two-year-old Werner's theory was largely without experimental verification, being based to a great extent on the data of Werner's primary scientific adversary, Sophus Mads Jørgensen. Werner, however, was not only the primary theoretician of coordination chemistry but also its greatest experimentalist. He devoted the remaining quarter-century of his career to an experimental search for the unknown compounds, whose existence would support his theory. Foremost among these, until his discovery of optically active coordination compounds in 1911[5], were the geometric isomers of cobalt and chromium, the study of more than four dozen series of which has been discussed in this paper. Werner's studies of these isomeric series not only laid the foundations for the stereochemistry of coordination compounds but also provided him with data for understanding the mechanisms of inorganic reactions, a currently important research area of which he may justly be considered the founder.

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