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ALFRED WERNER'S RESEARCH ON OPTICALLY ACTIVE COORDINATION COMPOUNDS

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CONTENTS

ABBREVIATIONS

en	the bidentate ligand ethylenediamine, $NH_2CH_2CH_2NH_2$
acac	acetylacetonate anion
prac	propionylacetonate anion
tn	trimethylenediamine, $NH_2(CH_2)_3NH_2$

A. INTRODUCTION

A review article devoted primarily to the research efforts of one man is unusual, but when the field is coordination chemistry, and the man in question is Alfred Werner, its founder[1], the limitation in the scope of such an article is more apparent than real. Consequently, although this article is limited primarily to Werner's achievements, it should nevertheless provide a wide coverage of the most important and fundamental problems in optical isomerism. Also, in the words of Sykes and Weil[2], referring to polynuclear compounds but true of optical isomers as well, "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." The viewpoint in this review is largely "historical", and no pretense is made as to coverage of the contemporary literature. In some cases Werner's results have been related to later developments, but this article is not intended to compete with recent reviews or with standard treatments of the subject[3-16]. Summaries of the literature can be found in *Gmelin's Handbuch*[17-23] and Pascal's *Traité*[24-29], and reproducible preparative procedures[30-57] and significant papers by Werner[58] and others[59] in English translation are also available.

The highlights of Werner's research on optical isomerism are summarized in his magnum opus, *Neuere Anschauungen*, beginning with third (1913) edition[60]. His work on optically active cobalt complexes is described in his twelve-paper series (1911-1914), *Zur Kenntnis des asymmetrischen Kobaltatoms*[61-72] and three additional papers[73-75], and his work on optically active chromium complexes is found in his three-paper series (1911-1912), *Über Spiegelbildisomerie bei Chromverbindungen*[76-78]. His work on rhodium comprises two papers[79,80], while one article each is devoted to iron[81], platinum[82], and iridium[83]. Werner also discussed various aspects of his work on compounds of a number of metals in review articles and in published and unpublished lectures[84-98]. Because many of the compounds resolved by Werner were first prepared in racemic form by him and his students, reference will also be made here to a number of his other articles[99-123].

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 1910's and which often concerned optical isomerism. Because Paul Karrer, Werner's successor at the Chemisches Institut der Univeristät 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 sixty[124-184] of the two hundred odd dissertations written by Werner's *Doktoranden* or *Doktorandinnen* (a surprisingly large proportion of Werner's students were women).

Such dissertations are of value to today's chemists for both the positive and negative information that they contain. For positive results on compounds resolved by Werner and his students, which have never appeared in the open literature, see Miscellaneous Compounds (Section B(v)) and $M_3[Rh(C_2O_4)_3]$ (Section E(i) (b)). Unsuccessful resolutions were of two types — (1) proof that *trans* compounds are not resolvable, e.g. the attempted resolutions with ammonium (+)-bromocamphorsulfonate* of the *trans* isomers of $[Co(en)_2Cl_2]Cl$ (p. 44 of Wera Tupizina's (1915) dissertation[172]), $[Co(en)_2(NO_2)_2]$-NO_2 (pp. 44-45), $[Co(en)_2(NH_3)_2]Cl_3$ (pp. 45-46), $[Co(en)_2(C_5H_5N)Br]Br_2$ (pp. 46-48), and $[Co(en)_2(C_5H_5N)NH_3]Br_3$ (pp. 48-49), and (2) attempted resolutions of potentially

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* Because of possible confusion of *observed rotations* (*d* for dextrorotatory and *l* for levorotatory) with *D* and *L*, where the capital letters refer to *absolute configurations*, a preferable system for designating the *observed rotation* of optical isomers is the notation (+) for a dextrorotatory isomer and (−) for a levorotatory isomer.

resolvable compounds, e.g. the attempted preparation of optically active *cis*-$[Co(en)_2(NCS)_2]X$ by treatment of active *cis*-$[Co(en)_2(NCS)Cl]X$ with KNCS (pp. 39–40), ref. 172), *cis*-$[Co(en)_2(NCS)_2]SO_4$ with barium (+)-bromocamphorsulfonate or the free acid (pp. 40–42), and *cis*-$[Co(en)_2(NCS)_2]X$ with (+)-$[Co(en)_2(NO_2)_2]NO_2$ (pp. 42–43), or the attempted resolution of the *cis*-$[Cr(H_2O)(OH)(C_2O_4)_2]^{2-}$ ion by spontaneous crystallization, diastereoisomer formation (with strychnine, brucine, cinchonine, cinchonidine, quinine, quinidine, and the (+)- and (−)-$[Co(en)_3]^{3+}$ ions in various solvent media), esterification with active alcohols, or biochemical methods, contained in Hans Surber's (1915) dissertation (ref. 171, pp. 56-57). 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.

The concepts of asymmetry and optical activity, although introduced fairly late into inorganic chemistry, have played venerable and central roles in organic chemistry. In fact if modern organic chemistry is considered to commence with Friedrich Wöhler's synthesis of urea[185] in 1828, then Jean Baptiste Biot's discovery of optical activity[186] in 1812 antedates the very genesis of this field. Moreover, LeBel[187] and van't Hoff's[188] concept of the tetrahedral carbon atom (1874), which constitutes the foundation of organic stereochemistry, was proposed primarily in order to explain the optical isomerism investigated by Louis Pasteur and others. It is to Alfred Werner, however, that we owe the introduction of the concept of optical activity into coordination chemistry[1,58,189,190].

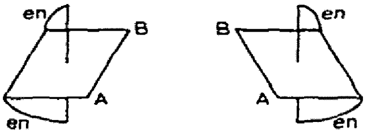
Although it is true that compounds containing asymmetric atoms other than carbon, e.g. nitrogen[191], phosphorus[192], sulfur[193], selenium[194], tin[195], and silicon[196], had been resolved before Werner and King's resolution, all these cases had involved atoms of tetrahedral configuration. Werner's work, on the other hand, involved a compound of the proposed, but as yet unproven octahedral configuration. As a result of this work, the eminent English stereochemist Sir Gilbert T. Morgan was able to state in his obituary of Werner[197] that "the spatial configuration of the co-ordination complex with six associating units is now as firmly established as that of the asymmetric tetrahedral carbon atom." Werner's indirect proof has been amply corroborated by direct X-ray diffraction studies.[59]

The resolution of optically active coordination compounds, which John Read, a former *Doktorand* of Werner's, has called[198] a "stereochemical achievement of the first order", was Werner's greatest experimental triumph. This feat, which "shook chemistry to its innermost foundations"[199], gained for the coordination theory the widespread recognition for which Werner had been striving so long. Nor was the theory's founder neglected, for two years later, largely in recognition of "the most brilliant confirmation of [his] stereochemical views"[200], as Lifschitz has described the resolution, Werner was awarded the Nobel Prize in chemistry.

Unfortunately, we do now know exactly when Werner first realized that one of the geometric consequences of his octahedral model was molecular asymmetry for certain types of complexes containing chelate ligands or when he first recognized that a resolution of such compounds would provide an elegant and definitive proof of his stereochemical views. Contrary to common belief, no mention of this topic appears in his first paper[99] on the coordination theory. Werner's first published work in the field of optical activity (1899) dealt with the resolution of an organic compound, *trans*-hexahydrophthalic acid[103,124]. In the same year, in a paper dealing with oxalatobis(ethylenediamine)cobalt(III) salts[100], $[Co(en)_2C_2O_4]X^*$, Werner apparently mentioned for the first time in print the possibility of optical isomerism among coordination compounds. A dozen years of work involving what others might have considered insurmountable difficulties were to elapse before his insightful prediction was fulfilled[61,201,202].

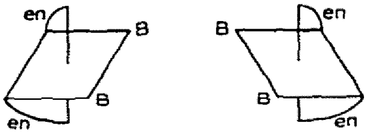
For mononuclear complexes Werner distinguished three types of asymmetry:

(1) Asymmetry involving an asymmetric metal atom, as exemplified by ions of the *cis*-$[M(en)_2AB]$ type.



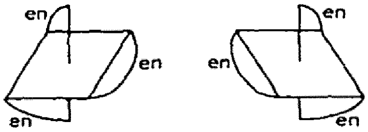
This type contains two nonsuperimposable tetrahedra (M, en, A, B), and the first coordination compounds resolved[61] belong to this class.

(2) Molecular asymmetry I (*Molekül-Asymmetrie I*)[62], as exemplified by ions of the *cis*-$[M(en)_2B_2]$ type.



According to Werner, since such octahedra cannot be regarded as containing two nonsuperimposable tetrahedra, they do not contain an asymmetric cobalt atom, but the octahedron as a whole is asymmetric.

(3) Molecular asymmetry II (*Molekül-Asymmetrie II*)[65], as exemplified by ions of the $[M(en)_3]$ type.



These octahedra, consisting of only one type of metal atom and one type of bidentate ligand, likewise cannot be regarded as containing two nonsuperimposable tetrahedra. Werner considered types (1), (2), and (3) to represent acidopentaammines, diacidotetraammines, and hexaamines, respectively, since in compounds of these types five, four, and six groups, respectively, were bound to the central metal atom by secondary valences (*Nebenvalenzen*). We shall now examine Werner's contributions to the field of optical activity according to the type of compound. The discussions follow in approximate chronological order within each type.

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[*] Although these salts were not the first coordination compounds to be resolved, Werner did succeed in resolving them[66,71] in 1912.

B. COBALT COMPLEXES

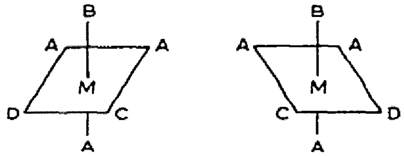
(*i*) *Type* $M(en)_2AB$

(*a*) cis-$[Co(en)_2(NH_3)Cl]X_2$ *and* cis-$[Co(en)_2(NH_3)Br]X_2$

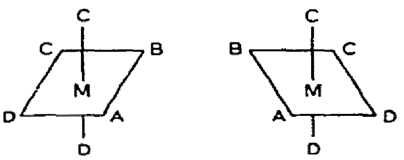
The first person to resolve a coordination compound was Victor L. King (1886-1958), an American chemist, who received his doctorate *summa cum laude* under Werner in 1912 (ref. 58, pp. 157-158; ref. 150). According to King's laboratory notebook (January 1910) (ref. 203, pp. 2-10), the compound that he was assigned to resolve was carbonatobis-(ethylenediamine)cobalt(III) bromide, $[Co(en)_2CO_3]Br$. Although King's results on the unsuccessful attempts to resolve this compound with silver (+)-bromocamphor-π-sulfonate were never published, they are found in his dissertation (ref. 150, pp. 39-40).

King was, of course, successful in resolving not this compound but the *cis*-chloro- and bromoamminebis(ethylenediamine)cobalt(III) salts[61]. All attempts to prepare optical isomers of the $[Co(en)_2CO_3]^+$ ion by diastereoisomer formation with optically active anions were unsuccessful until in 1912, together with another American, the late Thomas P. McCutcheon, who was the present author's instructor in general chemistry at the University of Pennsylvania, Werner was finally able to synthesize such compounds by the action of potassium carbonate on optically active *cis*-$[Co(en)_2Cl_2]^+$ salts[66], a reaction which is discussed later (Section B(ii)(b) and (c)). Similar reactions have since been investigated by Bailar et al.[204-206]

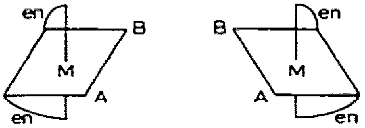
In his classic paper with King, the first in a series of twelve papers entitled *Zur Kenntnis des asymmetrischen Kobaltatoms* ("Toward an understanding of the asymmetric cobalt atom")[61], Werner used stereochemical arguments reminiscent of van't Hoff's famous paper[188] of 1874 on the asymmetric carbon atom. After citing several consequences of the octahedral hypothesis that are amenable to experimental verification, such as the occurrence of complex ions $[MA_5B]$ in only one form and the occurrence of complex ions $[MA_4B_2]$ (refs. 105, 117) and $[MA_4BC]$ (refs. 104, 106, 107) in two isomeric series, Werner discussed a much more decisive proof—the existence of the optical isomers required by the octahedral model. For the complex $[MA_3BCD]$ in which the three A's or B, C and D occupy the three corners of an octahedral face (*cis*; 1, 2, 3), the mirror images are not superimposable.



The same is true of the complex $[MABC_2D_2]$ if the groups are arranged in the following manner.



The number of different groups that are required to produce molecular asymmetry is reduced considerably when the coordinated groups are united by bridges, i.e. when monodentate groups are replaced by bidentate groups*. Werner demonstrated that if the groups CC and DD in the last structure are each replaced by a molecule of ethylenediamine, the molecular asymmetry is maintained in the resulting complex *cis*-$[MAB(en)_2]$ †. Consequently, compounds with this structure should contain an asymmetric central atom and should therefore be resolvable into optically active antipodes



The most widely used resolution method, Pasteur's diastereoisomer formation[207], although general in principle, often failed in practice, largely because naturally occurring optically active acids and bases are weak and their salts are not very stable in solution. In the same year in which the coordination theory was published, Kipping and Pope[208] has synthesized the strong acids, (+)-camphorsulfonic acid and (+)-bromocamphorsulfonic acid, from naturally occurring (+)-camphor and thus had provided the stereochemist with a series of versatile resolving agents. It was the silver salt of the latter compound that brought Werner his widely acclaimed success‡.

The first series of coordination compounds to be resolved were the *cis* isomers of $[Co(en)_2(NH_3)Cl]X_2$ (ref. 17, pp. 159–163; ref. 18, pp. 468–470); ref. 24)§. The results were published[61] along with those for $[Co(en)_2(NH_3)Br]X_2$ (with Ernst Scholze, Ph.D., Universität Zürich, 1911) (ref. 17, pp. 176–178; ref. 18, p. 470; refs. 24, 37, 170). The salts of the bromoammine series were easier to resolve because their diastereoisomeric (+)-bromocamphorsulfonates exhibit a great difference in solubility. For both series, the (+)-bromocamphorsulfonate of the (+)-form, which is less soluble than that of the (—)-form, crystallizes out first. The diastereoisomers were converted into the bromides either through intermediate conversion to the dithionate or directly by grinding with concentrated hydrobromic acid. For the bromides, Werner obtained the specific rotations, $[\alpha]_C = \pm 43°$ (chloroammine) and $\pm 46.25°$ (bromoammine).

Contrary to Werner's expectations, the compounds proved to be remarkably resistant to racemization in solution, both on prolonged standing at room temperature and even on heating to incipient boiling. He was able to interconvert various salts within each series without loss of activity. Even more remarkably, he succeeded in replacing the coordinated bromine atom in the bromoammine bromide with water

$$cis\text{-}[Co(en)_2(NH_3)Br]Br_2 + 3\ AgNO_3 + H_2O \rightarrow cis\text{-}[Co(en)_2(NH_3)H_2O](NO_3)_3 + 3\ AgBr$$

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* As a matter of fact, no one has yet succeeded in resolving a complex containing monodentate groups only.

† Werner had already developed experimental criteria for distinguishing *cis* from *trans* isomers[121].

‡ Although Werner used the method of Kipping and Pope[209], improved syntheses for (+)-bromocamphorsulfonic acid and its salts have since been reported[210–212].

§ These compounds were discovered in 1890 by Sophus Mads Jørgensen, Werner's principal scientific adversary (ref. 213, pp. 454, 459). It is one of those ironies of history that many of the compounds which played crucial roles in the victory of the coordination theory over the Blomstrand–Jørgensen chain theory were first prepared by Jørgensen himself[214,215].

and he found that the resulting aquoamminebis(ethylenediamine) salts were optically active (ref. 121, pp. 21, 186, 188; ref. 149).

According to Werner, the investigation proved that "metal atoms can act as central atoms of stable, asymmetrically constructed molecules [and] that pure molecular compounds can also occur as stable mirror image isomers, whereby the difference between valence compounds and molecular compounds, which is still frequently maintained, disappears entirely" (ref. 61, p. 1890). Moreover, it confirmed "one of the most far-reaching conclusions of the octahedral formula". King considered the resolution to be "the last proof for the octahedral formula assumed by A. Werner" (ref. 150, p. 59). He attributed the optical activity to mirror image isomerism rather than exclusively to the presence of an asymmetric atom. "Whereas until now only a few carbon compounds with such steric structure are known, a considerable number of such metal-ammines have already been successfully prepared" (ref. 150, p. 59).

Improvements in instrumentation which occurred in the first decade of the present century may have played the largest role in Werner's success[216,217]. Before this time, polarimeters, color filters, and light sources were still in too primitive a state to permit easy observation of the deeply colored solutions with which Werner was forced to work. It was only shortly before the time of Werner's success that the Schmidt and Haensch Model No. 8142 polarimeter became commercially available. This instrument, which brought Werner his long-sought success, was based upon the specifications of Hans Heinrich Landolt[218,219] and included several new features of importance for measuring small rotations, especially the Lippich *Halbschatten* (half-shadow) device[220,221], which better defined the uniform gray appearance midway between the extinctions of the two halves of the field and thus increased the precision in determining the zero points.

Another factor that may have proved crucial was Werner's choice of the wavelength of the light used for his measurements[217]. Most of the rotations at that time were measured at the wavelength of the sodium *D*-line produced by thermal excitation (589 nm), but the intense color of Werner's solutions would have rendered use of this wavelength difficult. At about the time of Werner and King's success, Landolt had described the use of filters to obtain different wavelengths. By employing a pair of colored solutions (crystal violet and potassium chromate) as a filter for his Nernst projection lamp[222,233], Werner obtained a light of optical mass-center 665.3 nm, very close to the wavelength of the Fraunhofer *C*-line (656.3 nm), and all of his optical rotation values[61] are reported as $[\alpha]_C$ rather than $[\alpha]_D$.

"Whenever Werner opened up a new field, he expanded it with unbelievable speed." This statement[199] of Paul Karrer has been amply confirmed by Werner's investigations of optically active complexes, for once Werner and King[61] had found the key to the resolution of complexes in 1911, a large number of articles describing additional resolutions appeared from Werner's institute with great rapidity. Within eight years, he and his students had resolved more than forty series of complexes. As will be seen below (Section B(iii)(a)), Werner even repaid his debt to Pasteur by using optically active inorganic octahedral complexes, which had been resolved by means of organic substances, to resolve in turn dimethylsuccinic acid[122,165] and diphenylsuccinic acid[176], both organic tetrahedral compounds. These numerous resolutions by Werner and his students will now be discussed, but in much less detail than the historic resolution by Werner and King.

(*b*) cis-$[Co(en)_2(NH_3)H_2O]X_3$

Both the *cis*- and *trans*-aquoammine compounds are red and are prepared by the action of potassium hydroxide solution on the corresponding haloammine compounds (ref. 17, pp. 112–113; ref. 18, pp. 402–403; ref. 24; ref. 121, pp. 185–192; ref. 149). As mentioned in Section B(i)(a), Werner and King converted a solution of the active bromoammine bromide to one of the active aquoammine compounds by heating with silver nitrate (ref. 61, pp. 1889, 1896), but no details were given, and the solid compound was apparently never isolated. They (ref. 61, p. 1896) only reported a rotation of 0.25° for a 0.8% solution of "aquated" (+)-*cis*-$[Co(en)_2(NH_3)Br]Br_2$ in a 2-dm tube in order to show that the resulting (+)-*cis*-$[Co(en)_2(NH_3)H_2O]^{3+}$ salt was optically active. From these data, the specific rotation $[\alpha]_C$ should equal +15.62°. The only other citations by Werner of these compounds are in a lecture given before the Société Chimique de France on May 24th, 1912 (ref. 90, p. XXI), where he gives an $[\alpha]$ value of +124° for $[Co(en)_2(NH_3)H_2O]X_3$ and in *Neuere Anschauungen* (ref. 60(a), p. 362; ref. 60(b), p. 382) with the value $[M]$ = +392°. Tupizina in her dissertation (ref. 172, pp. 14, 23) reports a value of $[M]$ = +700°. More recent measurements at wavelengths from 440-650 nm of the optical rotation, circular dichroism, and absorption spectra of a solution of the (+)-nitrate prepared by Werner's method were obtained by Mathieu (ref. 224, p. 698).

(*c*) cis-$[Co(en)_2(NO_2)Cl]X$

Werner was the first to prepare both the *cis* (bright red)[107,121,131] and *trans* (brownish red)[104,121] forms of the chloronitro compounds by the action of sodium nitrite 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 and Zinggeler initially believed these salts to be nitrito (Co-ONO) compounds, but they later (ref. 112, p. 768; ref. 133) decided that they were nitro ($Co-NO_2$) compounds. The configurations of the isomers were confirmed by Werner's resolution of the *cis* series[63,84,161].

Werner's resolution of these compounds, described in the third paper of his series on the asymmetric cobalt atom[63], illustrates an unusual case of mutarotation, similar to that observed with dextrose in the organic field. He isolated the (–)-nitrate and the (+)- and (–)-chlorides and iodides (ref. 17, pp. 261–263; ref. 18, pp. 490–491; ref. 24). He found that, on standing, $[\alpha]_D$ for the (+)-chloride rose from an initial value of +20° to a constant value of +52°, accompanied by a change in color from red to yellow*. Both effects were due to the rapid aquation reaction

$$[Co(en)_2(NO_2)Cl]Cl + H_2O \rightarrow [Co(en)_2(H_2O)NO_2]Cl_2$$

which caused difficulties when silver (+)-camphorsulfonate and (+)-bromocamphorsulfonate were used for the fractional crystallization of the diastereoisomers. Werner therefore used the ammonium salts, which rapidly precipitated the diastereoisomers. By heating the active chlorides with $NaNO_2$, Werner obtained the corresponding active flavo compounds, (+)- or (–)-*cis*-$[Co(en)_2(NO_2)_2]X$, which were isolated as the perchlorate salts. By the action of KSCN on the (–)-chloride, Werner obtained active (–)-$[Co(en)_2(NO_2)NCS]X$ (see ref. 161).

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* The value eventually fell to zero after a week because of autoracemization.

(*d*) cis-$[Co(en)_2(H_2O)NO_2]X_2$

Although both *cis* and *trans* isomers of nitroaquobis(ethylenediamine)cobalt(III) salts exist, salts of the *cis* series were not isolated by Werner in the solid state (ref. 17, pp. 143–144; refs. 24, 121). Solid compounds, however, were later prepared by others (ref. 18, pp. 461–462; ref. 225). Of the optically active *cis* series Werner described only the (+)- and (−)-chlorides, which he obtained in aqueous solution by aquation of the corresponding chloronitro compounds (see previous section) (ref. 63, pp. 3273, 3276; ref. 84, p. 457; ref. 90, p. XXI). He reported the following values of the specific rotation $[\alpha]$ for the (+)- and (−)-salts for red, yellow, and white light, respectively: +31°, −35°; +52°, −48°; +52°, −55°. The compounds racemized only slowly, but the solutions became completely inactive after a week. Werner also prepared an insoluble polyiodide, from which he prepared an active iodide, but he gave no details or numerical data (ref. 63, pp. 3273, 3276). Tupizina (ref. 172, pp. 14, 23) reports $[M] = +196°$ for *cis*-$[Co(en)_2(H_2O)NO_2]X_2$.

(*e*) cis-$[Co(en)_2(NO_2)Br]X$

The optical isomers of the bromonitro series are described in the dissertations of two of Werner's *Doktoranden*, Alexander Fraenkel[155] and Otto Dätwiler (ref. 17, p. 264; ref. 18, p. 533; refs. 24, 178). Resolution was accomplished by means of ammonium (+)- or (−)-camphorsulfonate, and the chlorides, bromides, iodides, nitrates, perchlorates, sulfates, peroxydisulfates, dithionates, and thiocyanates were isolated (ref. 178, pp. 31–49). The specific rotations are approximately the same as those of the corresponding chloronitro compounds (Section B(i)(c)), but in aqueous solution the activities quickly increase to maximum values caused by the formation of nitroaquo salts (see previous section). The salts exhibit anomalous rotatory dispersion and the Cotton effect (ref. 226; ref. 227, p. 247; ref. 228, pp. 473, 484; ref. 229).

(*f*) cis-$[Co(en)_2(NO_2)NCS]X$

The *cis* salts are brownish-yellow, while the *trans* salts are dark brown; the two series can be differentiated by the solubilities of their sulfates (ref. 17, pp. 269–271; ref. 18, pp. 546–547; refs. 24, 102; ref. 121, pp. 157, 230–245; refs. 126, 131, 134, 137, 230). Werner and Gerb first believed that the salts were nitrito compounds[107,131,230], but Werner later designated them as true nitro compounds (ref. 121, pp. 162, 163). The *cis* compounds can be prepared by the action of KNCS on *cis*-$[Co(en)_2(NO_2)Cl]X$ (see Section B(i)(c)). The *cis* configuration was established by the preparation of optical isomers, not by resolution, but by treatment of the optically active *cis*-$[Co(en)_2(NO_2)Cl]X$ with KNCS (ref. 63, pp. 3274, 3278; refs. 84, 90, 161). The optically active nitrites, nitrates, chlorides, bromides, iodides, perchlorates, thiocyanates, and perchlorates were isolated and are described in the dissertation of one of Werner's numerous female *Doktorandinnen*, Ida Wilbuschewitsch (ref. 182, pp. 44–59). The active bromides ($[\alpha]_D = \pm 100°$) exhibit anomalous rotatory dispersion and the Cotton effect (ref. 226, p. 146; ref. 227, p. 246).

(*g*) cis-$[Co(en)_2BrCl]X$

The *cis* (violet-gray to slate gray) (ref. 121, pp. 57, 118, 120) and *trans* (green) salts (ref. 121, p. 119) of this series were first prepared by Werner by the action of concentrated HBr on *cis*-$[Co(en)_2(H_2O)Cl]Br_2$ or by dehydration of this compound at 110°C.

Werner and Tschernoff, in the eighth article in the series on the asymmetric cobalt atom[68], confirmed the configuration of the violet-gray series by resolution of the compounds with ammonium (+)- and (−)-bromocamphorsulfonates. The nitrates, chlorides, bromides, sulfates, and dithionates of both enantiomeric forms were isolated (ref. 17, pp. 265–266; ref. 18, p. 533; refs. 24, 38). For the bromide, $[Co(en)_2BrCl]Br\cdot H_2O$, the specific rotations $[\alpha]^{20^\circ}$ for white light were found to be +148° ((+)-salt) and −155° ((−)-salt). In solution, salts of the chlorobromo series readily undergo aquation with complete loss of optical activity within 30–60 minutes.

(*h*) cis-$[Co(en)_2(NH_3)NO_2]X_2$

The salts of both stereoisomeric nitroammine series are brownish-yellow, but the *cis* salts are more soluble and deeper in color than the *trans* salts, except for the dithionates, for which these relationships are reversed. The compounds, first isolated by Werner and Boës (ref. 121, pp. 55, 59, 168, 216–228; ref. 146), are usually prepared by the action of $NaNO_2$ or HNO_2 on *cis*-$[Co(en)_2(NH_3)H_2O]X_3$, but other preparative methods are available (ref. 17, pp. 139–141; ref. 18, pp. 466–468; ref. 24). The two series may be differentiated by means of the dithionates. The configuration of the salts of the *cis* series was confirmed by resolution. This work was not published by Werner, but it appears in the dissertation of Ida Wilbuschewitsch (ref. 182, pp. 55–60), who "oxidized"* (+)- or (−)-*cis*-$[Co(en)_2(NCS)NO_2]NO_3$ with 30% H_2O_2 and precipitated the corresponding diastereoisomers with ammonium (−)- or (+)-bromocamphorsulfonate, respectively. Treatment of the diastereoisomers with HBr yielded the (+)- and (−)-bromides ($[\alpha]_C = \pm 20^\circ$; $[\alpha]_D = \pm 50^\circ$; $[\alpha]_E = \pm 150^\circ$). The enantiomers exhibit a pronounced anomalous rotatory dispersion[182] and the Cotton effect[226].

(*i*) cis-$[Co(en)_2(H_2O)Cl]X_2$

Although compounds of this formula should theoretically exist in two stereoisomeric configurations, only one series of salts (blue-red) is known (ref. 17, pp. 168–170; ref. 18, p. 460; ref. 24)**. Werner identified these as the *cis* compounds by means of their colors and substitution reactions (ref. 121, pp. 17, 46, 56, 121–125; ref. 120, p. 875; refs. 149, 158, 184). The most conclusive proof, however, was provided by their resolution by means of ammonium (+)-bromocamphor-Π-sulfonate. This work was not published but appeared in the dissertation of one of Werner's *Doktoranden*, Hermann Fischlin[179], who isolated both (+)- and (−)-forms of the chloride, bromide, sulfate, selenate, oxalate, and dithionate. The salts exhibit anomalous rotatory dispersion[179] and the Cotton effect[226]. The specific rotation $[\alpha]_D$ for the active bromide was found to be ±215° (ref. 179; ref. 75, p. 117). Bailar and Peppard[206] consider the chloride, which is dextrorotatory for Na_D light, to be the (−)-compound. Treatment with ammonia converts the active chloroaquo salts into the corresponding optically active chlorohydroxo salts (ref. 179, p. 42) (see the following section), while treatment with acetylacetone or propionylacetone converts them

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* Although Werner considered this reaction with H_2O_2 an oxidation, none of the elements involved (N, C, or S) undergoes a change in oxidation number, and the reaction is more properly an aquation and protonation: $NCS^- + H_2O + H^+ \rightarrow NH_3 + COS$.

** The sole exception is the chloride, which also exists in a gray-green (*trans*) form (ref. 231, pp. 256, 257), which can be converted into the more stable blue-red *cis* form[232].

into the corresponding optically active acetylacetonatobis(ethylenediamine) and propionylacetonatobis(ethylenediamine) salts[75] (see Section E(ii)(f)).

(j) cis-$[Co(en)_2(OH)Cl]X$

Like those of the previous series, these compounds exist in only one series, the *cis* (dark violet) salts (ref. 17, pp. 259-260; ref. 18, pp. 527-528; ref. 24; ref. 121, pp. 18, 122, 130). Only the chloride exists in a pigeon-gray (*trans*) form (ref. 231, pp. 241, 255). The *cis* compounds were not resolved per se, but by treatment of active *cis*-$[Co(en)_2(H_2O)Cl]Br_2$ (see previous section) with a 1:1 mixture of concentrated ammonia and absolute ethanol. Fischlin[179] obtained the corresponding active bromides of the chlorohydroxo series, which he was also able to convert into the active nitrates. For the nitrates, which exhibit anomalous rotatory dispersion (ref. 179, pp. 44, 46) and the Cotton effect (ref. 226, p. 46), $[\alpha]_D = +530°(+)$ and $-542°(-)$. The values are only approximate and quickly decrease because of autoracemization. According to Pearson et al.[233], $[Co(en)_2(OH)Cl]X$ salts are unknown in the solid form and are stable in solution to only a limited extent.

(k) cis-$[Co(en)_2(NCS)Cl]X$

The *trans*-chloroisothiocyanato salts are violet, easily soluble, and stable in aqueous solution, while the *cis* salts are bluish pink, soluble only with difficulty, and in aqueous solution are quickly converted into isothiocyanatoaquo salts (see next section). At first (1899), Werner et al. (ref. 102, p. 154; ref. 125) erroneously considered the $[Co(en)_2(NCS)Cl]X$ salts, obtained by the action of KNCS on *trans*-$[Co(en)_2Cl_2]Cl$, as thiocyanato compounds, but later (1912) Werner realized that they were isothiocyanato compounds (ref. 17, p. 271-275; ref. 18, pp. 547-549; refs. 24, 121; ref. 120, p. 876). The *cis* chloride was resolved by Wera (Vera) Tupizina, a young Russian *Doktorandin* of Werner, by means of ammonium bromocamphorsulfonate[84,172]. She isolated both antipodes of the chloride, bromide, iodide, nitrite, nitrate, perchlorate, dithionate, and thiocyanate[172]. The compounds exhibit strong anomalous rotatory dispersion and the Cotton effect[226]. Absorption spectra for the compounds were measured by several of Werner's students[149,177,184]. Treatment of the (−)-salts with $NaNO_2$ produces (+)-$[Co(en)_2(NO_2)NCS]X$ salts. In aqueous solution, the optically active compounds are converted into the corresponding active *cis*-$[Co(en)_2(H_2O)NCS]X_2$ salts[84].

(l) cis-$[Co(en)_2(H_2O)NCS]X_2$

Both series of isothiocyanatoaquo compounds are formed by action of mineral acids on the corresponding isothiocyanatohydroxo compounds; the *cis* salts are yellow-red, whereas the *trans* salts are violet (ref. 17, pp. 185-186; ref. 18, p. 466; ref. 24). Werner proved[121] the compounds to contain Co-NCS bonding in both series by "oxidizing" them with H_2O_2, evaporating them with HCl, and obtaining *cis*- or *trans*-$[Co(en)_2(NH_3)Cl]Cl_2$. The *cis* compounds were obtained in optically active form, not by resolution, but by aquation of the corresponding chloroisothiocyanato compounds (see previous section; ref. 84, p. 459; ref. 90, p. XI; ref. 172). Absorption spectra, rotatory dispersion, and circular dichroism have been measured (ref. 224, p. 696).

(*m*) cis-$[Co(en)_2(NH_3)NCS]X_2$

Werner first prepared the brick-red to brownish red isothiocyanatoammine salts in two stereoisomeric series by treating the corresponding isomers of $[Co(en)_2(NCS)Cl]X$ or $(Co(en)_2(NCS)Br]X$ with liquid ammonia (ref. 17, pp. 183–185; ref. 18, p. 471; ref. 24; ref. 121, pp. 49-55, 205–213; ref. 120, p. 876; ref. 172, pp. 38–39). The series are separated by means of the thiocyanates, the *cis* compound being much more soluble than the *trans*. Werner showed that the compounds contained Co–N rather than Co–S bonding since on "oxidation" with H_2O_2 they yielded the corresponding $[Co(en)_2(NH_3)_2]^{3+}$ compounds. The *cis* compounds were not resolved per se, but Werner's *Doktorand* Rudolf von Arx converted the optically active (+)- and (−)-*cis*-$[Co(en)_2(NCS)Cl]ClO_4$ (see Section B(i)(k)) to the corresponding active *cis*-$[Co(en)_2(NH_3)NCS](NCS)Cl$ with liquid ammonia (ref. 177, p. 55). He also isolated the active chloride, bromide, nitrite, nitrate, perchlorate, and thiocyanate (ref. 177, pp. 64–73). The compounds exhibit strong anomalous rotatory dispersion (ref. 177, p. 55; refs. 226, 228, 234).

(*ii*) *Type* $M(en)_2B_2$

(*a*) cis-$[Co(en)_2(NO_2)_2]X$

The dinitrobis(ethylenediamine)cobalt(III) salts can be prepared by the action of ethylenediamine on $K_3[Co(NO_2)_6]$ and by other methods (ref. 17, pp. 216–222; ref. 18, pp. 505-509; ref. 24; ref. 32, pp. 243-247; refs. 39–42, 104, 105, 121, 130, 132, 158). They exist in two stereoisomeric series, *cis* (flavo) and *trans* (croceo). Werner[104,105] first (1901) believed them to be nitrito compounds but later, after discovering the true nitrito compounds (1907) (ref. 111, p. 264; ref. 112, p. 771; refs. 133, 140), he designated them nitro compounds.

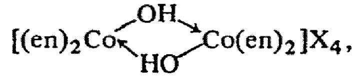
In the second paper[62] of his series "Toward an understanding of the asymmetric cobalt atom", Werner resolved compounds of the *cis*-$[Co(en)_2(NO_2)_2]X$ (flavo) series by a combination of two resolving agents[84,163]. With the flavo salts, which led to Werner's postulation of molecular asymmetry I, (+)-camphorsulfonic acid forms a less soluble (−)-salt, whereas α-(+)-bromocamphorsulfonic acid forms a less soluble (+)-salt. In this way, Werner was able to avoid the use of the sulfonic acid derivatives of the uncommon (−)-camphor. All attempts to resolve salts of the *trans*-$[Co(en)_2(NO_2)_2]X$ (croceo) series ended in failure although crystalline camphorsulfonates were obtained. This result lent further weight to the octahedral hypothesis, which predicted that the *cis*, and only the *cis*, form should be resolvable. It simultaneously added resolvability as a new and powerful weapon to the arsenal of the stereochemist seeking to determine the configuration of isomeric complexes.

Werner isolated both antipodes of the chloride, bromide, iodide, nitrate, perchlorate, sulfate, and thiocyanate[62]. He later (1914)[71] resolved (±)-*cis*-$[Co(en)_2(NO_2)_2]X$ compounds by preferential crystallization with "seed crystals" of (+)-$[Co(en)_2C_2O_4]X$ (see Section B(ii)(d)). Dwyer and Garvan[40] have also accomplished the resolution by means of potassium (+)-tartratoantimonate(III) (tartar emetic), and Kuroya et al.[235] have reported the asymmetric adsorption of the dissolved compounds on powdered quartz[236]. Measurements of rotatory dispersion and the Cotton effect have also been made on the optically active compounds (ref. 227, pp. 246, 250; ref. 228, pp. 487, 489; refs. 237, 238).

(*b*) cis-[$Co(en)_2Cl_2$]X

The dichlorobis(ethylenediamine)cobalt(III) salts 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. 239, p. 15) and violet *cis* (violeo) (ref. 213, p. 448) series were first prepared by Jørgensen. He obtained the latter from solutions of the former by repeated evaporation. Numerous preparative methods for both series are available (ref. 17, pp. 235–243; ref. 18, pp. 514–524; ref. 24; ref. 32, pp. 237–239; refs. 43, 84, 121, 136). 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. 99, p. 298) insisted that they were *cis–trans* stereoisomers, and the compounds thus played an important role in the history of coordination chemistry. Another theory of their constitution was later advanced by Friend[240] and opposed by Turner[241], but, as is well known, Werner's views prevailed.

Werner proved the *cis* configuration of the violeo salts by preparing them through treating with hydrochloric acid cobalt complexes containing closed rings such as

$[Co(en)_2CO_3]X$, $[Co(en)_2SO_3]X$, and  $[(en)_2Co\overset{OH}{\underset{HO}{\rightleftarrows}}Co(en)_2]X_4$, but more conclusively by resolving them in the fourth paper[64] in his series *Zur Kenntnis des asymmetrischen Kobaltatoms*, in which he isolated both enantiomers of the chloride, bromide, sulfate, and dithionate[68]. The resolution has since been repeated by Bailar[43], and resolutions by means of (–)-quartz[242] and (+)-quartz[243] have been reported.

Since coordinated chlorine atoms appear to be replaced by water when silver salts are used as resolving agents, Werner resolved the *cis*-$[Co(en)_2Cl_2]X$ compounds by use of the ammonium salts of (+)- and (–)-bromocamphor-π-sulfonic acids[64]. Although the active salts are perfectly stable in the dry state, they racemize rapidly in solution, losing all activity within a few hours, and forming chloroaquo and diaquo salts. Nevertheless, in some cases, Werner observed that not only could the coordinated chlorine atoms be replaced by other ions without loss of activity but that some reactions of inorganic complexes proceeded with a change in the sign of rotation. Thus when the (–)-chloride* was allowed to react with potassium carbonate in aqueous solution, the (+)-carbonato chloride was obtained.

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

At first glance, one might erroneously conclude that this reaction is an inorganic counterpart of the well-known organic Walden inversion[147,164,244–247]

$$\mathrm{HOOC{-}CH_2{-}CHCl{-}COOH} \xrightleftharpoons[\mathrm{PCl_5}]{\mathrm{KOH}} \mathrm{HOOC{-}CH_2{-}CHOH{-}COOH}$$

(+)- or (–)-chlorosuccinic acid (–)- or (+)-malic acid

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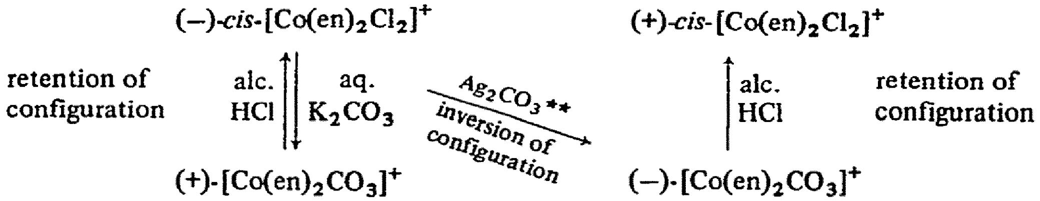
* Now that the absolute configuration of this complex has been determined, Werner's designation “*l*” should be replaced by “D”.

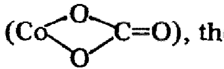
Yet Werner was astute enough to realize that the sign of rotation is not determined simply by the absolute configuration of a complex and that consequently a change in the sign of rotation need not be attributed to an inversion of configuration[*].

On the basis of reactions involving the least soluble bromocamphorsulfonate diastereoisomers of the *cis*-$[Co(en)_2(NCS)Cl]^+$ and *cis*-$[Co(en)_2(NO_2)Cl]^+$ ions with NO_2^- and NCS^- ions, respectively, Werner[90] concluded that displacement reactions always occur with retention of configuration. Although Werner's general conclusion was incorrect, his belief that the reaction observed between (−)-*cis*-$[Co(en)_2Cl_2]Cl$ and potassium carbonate was not a true inversion was a correct one. The first example of a "Walden inversion" among inorganic compounds was not discovered until 1934 by Bailar and Auten[204,249,250]



Circular dichroism (ref. 228, p. 497) and rotatory dispersion[224,229] studies showed that the reaction of the chloro complex with potassium carbonate first observed by Werner actually takes place with retention of configuration, whereas the reaction with Ag_2CO_3 results in inversion (S_N2 displacement process). Another Walden inversion occurs when (−)-*cis*-$[Co(en)_2Cl_2]Cl$ is treated with liquid ammonia[251], and the phenomenon is currently of great research interest[249,250].

(*c*) $[Co(en)_2CO_3]X$

Since the carbonate ion is easily replaceable by other anions and it forms a ring with the cobalt atom , these bluish red compounds exist only in the *cis* configuration, and consequently, together with the carbonatotetraammine compounds, they have served for configurational determinations of diacido and diaquo tetraammines and diaquobis(ethylenediamine) compounds (ref. 17, pp. 283, 284; ref. 18, pp. 536–538; ref. 24; ref. 32, pp. 229, 230; ref. 121, pp. 72–79; ref. 145). Absorption spectra relating these series have been especially important in such structure-proofs (ref. 149, pp. 98, 99; ref. 158, pp. 39, 40; refs. 252, 253). Werner prepared the racemic carbonatobis(ethylenediamine) compounds by heating solutions of *trans*-dichloro compounds with sodium carbonate or potassium carbonate (ref. 121, pp. 72–79). Since King and other students of Werner were unable to resolve $[Co(en)_2CO_3]X$ compounds by diastereoisomer formation, Werner and McCutcheon obtained the desired optically active compounds by heating solutions of

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[*] As a pertinent example, Werner's (−)-*cis*-$[Co(en)_2Cl_2]^+$ ion, which he found to be levorotatory toward cadmium red light (644 nm)[64], was later found to be dextrorotatory toward sodium light (590 nm)[248].

[**] Bailar and others later found that Ag^+ is unnecessary; addition of base is sufficient to produce inversion[250a,b,c].

optically active *cis*-dichloro chloride with potassium carbonate and reported this in the sixth paper[66] of the series *Zur Kenntnis des asymmetrischen Kobaltatoms.*

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

They found that the rotation of the active salts was opposite in sign from that of the dichloro compounds from which they were prepared. The chlorides, for which they obtained the value $[\alpha]_C = \pm 350°$, became inactive when heated in solution to 90°C. At room temperature the activity of a chloride solution fell to one-half its initial value. Werner and McCutcheon also isolated the optically active iodides and dithionates.

The optically active isomers have since been prepared by reactions similar to those used by Werner and McCutcheon[204-206]. Resolutions by means of selective adsorption on powdered quartz[235] or on starch[254] have been reported. Measurements of circular dichroism, rotatory dispersion, and the Cotton effect have also been made[227-229].

(*d*) $[Co(en)_2C_2O_4]X$

These extremely stable yellow-red to brown-red compounds exist only in the *cis* form and are similar to the corresponding carbonato salts (ref. 17, pp. 288-291; ref. 18, pp. 538-539; ref. 24; ref. 100, pp. 150-157; ref. 121, p. 77). Even on prolonged boiling in solution, aquation does not occur. Werner and McCutcheon (ref. 66, pp. 3286-3287) obtained the optically active salts by heating solutions of the optically active *cis*-dichloro chloride with potassium oxalate

$$(+)\text{- or }(-)\text{-}cis\text{-}[Co(en)_2Cl_2]Cl + K_2C_2O_4 \rightarrow (-)\text{- or }(+)\text{-}[Co(en)_2C_2O_4]Cl + 2\ KCl$$

As was the case with the carbonato compounds, the rotation of the active salts was opposite in sign from that of the dichloro compounds from which they were prepared. The antipodes were found to be extremely stable, and racemization did not occur on warming the solution. Werner and McCutcheon also prepared the optically active iodide and nitrate. The optically active oxalato compounds have since been obtained by others[204,206] and the stable antipodes used in turn to resolve other coordination compounds[44]. Resolutions have also been accomplished by adsorption on quartz[235,242] and measurements of rotatory dispersion and the Cotton effect have been made[227-229,238].

In the eleventh article of the series *Zur Kenntnis des asymmetrischen Kobaltatoms*[71,159], Werner and Bosshart reported not only their development of a new method of resolution—preferential crystallization (ref. 8, p. 332)—but also their finding that the previous rotation values[66] for the active oxalato salts were too low. Addition of a "seed" crystal of (+)-$[Co(en)_2C_2O_4]Br$ to a concentrated solution of (±)-$[Co(en)_2C_2O_4]Br$, followed by addition of ethanol and ether, produced a precipitate of pure (+)-$[Co(en)_2C_2O_4]Br$. The (–) salt was then recovered from the solution. The optically active chlorides, iodides, nitrates, perchlorates, dithionates, and thiocyanates were also isolated.

Werner showed that the method was not limited to salts of the same series or even of the same metal by his use of "seed" crystals of (+)-$[Co(en)_2C_2O_4]X$ in resolving (±)-*cis*-$[Co(en)_2(NO_2)_2]X$ (resolved the previous year)[62] and (±)-*cis*-$[Cr(en)_2C_2O_4]X$. The chromium compounds had previously resisted all attempts at resolution. Any isomorphous "seed" crystal may be used, but the new method is applicable only when the active salts are much less soluble than the racemic salt. Marcel Delépine[255,256] later used a similar process in developing his method of "active racemates", which has been used not only for the resolution of racemic mixtures but also for the determination of relative configurations. Relatively little work has been done with the technique of preferential crystallization, largely because of the success of other methods, yet Werner's method possesses considerable potential as a method of resolution and configurational determination[257].

(e) cis-$[Co(en)_2(NH_3)_2]X_3$

The brown to red-yellow diamminebis(ethylenediamine)cobalt(III) salts exist in two stereoisomeric series, one easily soluble (*cis*) and one difficultly soluble (*trans*) (ref. 17, pp. 85-89; ref. 18, pp. 395-396; refs. 24, 102, 110, 121, 125, 138, 143, 152). A mixture of compounds of both series is obtained by the action of liquid ammonia on *cis*-$[Co(en)_2Cl_2]X$, *cis*- and *trans*-$[Co(en)_2Br_2]X$, *trans*-$[Co(en)_2(NH_3)Cl]X$, or *cis*- and *trans*-$[Co(en)_2(NH_3)Br]X$. Werner established the configurations of the isomeric series from their preparations by oxidation of the corresponding isomers of the diisothiocyanato compounds, but because of a mistake in the configurational determination of the latter compounds (ref. 110, p. 65), the designations of the configurations of the diammine compounds are reversed in his paper of 1906 (ref. 110, p. 79). Werner later corrected his error (ref. 121, p. 78), and his configurational assignments were confirmed by his preparation, with Shibata, of optically active *cis* compounds in the seventh paper of the series *Zur Kenntnis des asymmetrischen Kobaltatoms*[67].

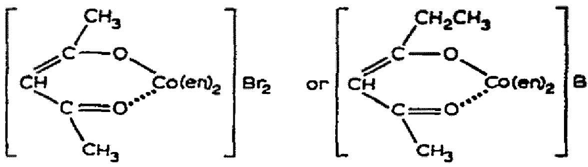
Because all attempts to resolve racemic *cis*-$[Co(en)_2(NH_3)_2]X_3$ salts by means of active acids had ended in failure, Werner and Shibata[67] converted active *cis*-$[Co(en)_2(NH_3)Br]X_2$ salts[61] into the corresponding active diammine salts by treatment with liquid ammonia.

$$cis\text{-}[Co(en)_2(NH_3)Br]X_2 + NH_3 \rightarrow cis\text{-}[Co(en)_2(NH_3)_2]X_2Br$$

Since the first complex contains an asymmetric cobalt atom, whereas the second shows molecular asymmetry I, the reaction indicates that a transition from one type to the other is possible. The active chlorides, bromides, iodides, perchlorates, and nitrates were isolated, and the preparations have since been repeated by others[251,258]. Measurements of rotatory dispersion and the Cotton effect have been made by Werner's students[177,226] and by others[228,234,259]

(f) $[Co(en)_2(acac)]X_2$ and $[Co(en)_2(prac)]X_2$

Werner was the first to prepare a metal β-diketonate compound[108], but since his day a large number of such compounds have been prepared[260]. In the last article he published before his death, Werner, together with his Russian *Assistentin* Sophie Matissen[74,151], found new evidence for his long-held view (1901) that metallic salts of diketones should be viewed as inner complex salts in which a β-diketonate anion occupies two coordination positions[108]. They succeeded in introducing the anion of the simplest β-diketone, acetylacetone, into the coordination compound $[Co(en)_2(H_2O)OH]Br_2$ in place of the two coordinatively monovalent groups H_2O and OH. Attempts to resolve the resulting $[Co(en)_2(acac)]Br_2$ were unsuccessful, but by treating (+)- and (−)-*cis*-$[Co(en)_2(H_2O)Cl]Br_2$ (see Section B(i)(i)) with the calculated amount of aqueous KOH, Werner et al.[75], Schwyzer[181] and Karrer[180] obtained solutions of the corresponding optically active *cis*-$[\mathrm{Co(en)_2(H_2O)OH}]\mathrm{Br_2}$. By warming these solutions with acetylacetone or propionylacetone, they obtained the corresponding optically active salts



(ref. 17, pp. 187–189; refs. 24, 75)

They isolated the chlorides, bromides, iodides, nitrates, perchlorates, peroxydisulfates, and thiocyanates of the first series and the iodides, nitrates, perchlorates, and peroxydisulfates of the second series. The red compounds are extremely stable, and the solutions can be evaporated to dryness without racemization. The salts exhibit anomalous rotatory dispersion and the Cotton effect.[75,226]

(*iii*) *Type* $M(en)_3$

(*a*) $[Co(en)_3]X_3$

These brownish yellow compounds, first prepared by Jørgensen (ref. 239, pp. 8–15), can be obtained by oxidation of cobalt(II) salts in aqueous ethylenediamine or by heating acidopentaamminecobalt(III) salts with aqueous ethylenediamine (ref. 17, pp. 73–80; ref. 18, pp. 351–369; ref. 24; ref. 32, pp. 186–188; ref. 34, p. 1538; ref. 35, pp. 93, 100; refs. 36, 45–47). In the fifth paper of his series *Zur Kenntnis des asymmetrischen Kobaltatoms* (ref. 36, pp. 66-74; refs. 65, 169), Werner reported his success in resolving $[\mathrm{Co(en)_3}]\mathrm{X_3}$ salts, designated as examples of molecular asymmetry II, by crystallization of the chloride tartrate or bromide tartrate, one of the few cases among inorganic complexes in which tartaric acid proved useful as a resolving agent, the other case being the structurally similar $[\mathrm{Rh(en)_3}]\mathrm{X_3}$. The active salts of this series were found to be extremely stable, and Werner and Basyrin later used them in the resolution of dimethylsuccinic acid[122,165]. Other workers[47,50,256,261–226] have since utilized this technique of using stable optically active complexes as resolving agents. Werner regarded the resolution of tris(ethylenediamine)cobalt(III) salts as particularly important in that it furnished culminating proof for the correctness of the octahedral configuration, for it ruled out the hexagonal planar and trigonal prismatic configurations*, which would possess a plane of symmetry for compounds of type $[\mathrm{M}(\overline{\mathrm{AA}})_3]$. It also demonstrated that optical activity does not require the linkage of *different* groups to the central atom, and it explained the optical activity and enantiomorphism of many minerals (Schweinfurt green and apatites) which may be regarded as constitutionally similar to $[\mathrm{M(en)_3}]$ salts, i.e. basic polynuclear salts[116] of types such as $\left[\mathrm{M}\left(\begin{smallmatrix}\mathrm{HO}\\ \mathrm{HO}\end{smallmatrix}\mathrm{M}\right)_3\right]\mathrm{Xy}$ or $\left[\mathrm{M}\left(\begin{smallmatrix}\mathrm{RO}\\ \mathrm{RO}\end{smallmatrix}\mathrm{M}\right)_3\right]\mathrm{Xy}$.

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* Coordination compounds with the trigonal prismatic configuration were discovered more than a half-century later[267].

Werner[65] isolated the optically active chlorides, bromides, and nitrates. His resolution was repeated by Jaeger, who isolated the optically active iodides, perchlorates, and thiocyanates[268,269]. The optically active tris(ethylenediamine)cobalt(III) salts have been extensively investigated (ref. 18, pp. 351–369; refs. 158, 238) and a number of additional resolutions by various methods have been reported (ref. 36, pp. 66–74; refs. 47, 242, 243, 254, 263, 270, 271). Studies of optical rotatory dispersion and circular dichroism[5,272,273] have also been made. In 1955, by means of anomalous X-ray diffraction, Saito et al.[274–276] established the absolute configuration of the dextrorotatory ion as $D(+)\text{-}[Co(en)_3]^{3+}$.

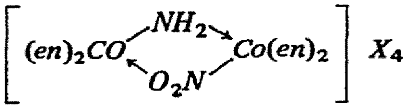
(b) $K_3[Co(C_2O_4)_3]$

Oxalate chelation has long been used as a diagnostic tool in coordination chemistry, and consequently the complex oxalates have been extensively investigated[227]. In fact, more resolution and racemization studies have been made of oxalate complexes than of any other class of coordination compounds. A wide variety of methods is available for preparing the well-known deep green potassium trioxalatocobaltate(III) (ref. 24; ref. 30, pp. 115–116; ref. 31, p. 550; ref. 33, p. 75; refs. 45–50, 278). This compound was the third of the complex oxalates to be resolved by Werner, being preceded by the corresponding chromium(III)[78] and rhodium(III)[80] compounds.

In 1915, Hans Biland, one of Werner's Swiss *Doktoranden*, resolved $K_3[Co(C_2O_4)_3]$ by means of strychnine, but the results of his dissertation[166] were never published. Several years later Jaeger and Thomas (ref. 5, pp. 113–120; refs. 279, 280) first demonstrated the method of spontaneous crystallization of antipodes from a racemic mixture of a complex by crystallizing this compound above 13.2°C and mechanically separating the optical antipodes (ref. 8, p. 331). In practice, however, the standard technique of fractional crystallization of the strychnine diastereoisomers has been used[256,279–282]. Partial resolution on optically active quartz has been reported[242]. Selective decomposition of the antipodes by circularly polarized light was investigated with negative results by Jaeger and Berger[283], but partial resolution by this method has been claimed by Tsuchida et al.[284]. More recent resolutions with optically active complex cations, e.g. $(-)\text{-}[Ni(o\text{-}phen)_3]^{2+}$ (refs. 50, 263, 285) and $(-)\text{-}[Co(en)_3]^{3+}$ (ref. 266) are simpler and yield higher optical activity values. Both antipodes of the $[Co(C_2O_4)_3]^{3-}$ ion racemize rapidly in solution[166,286,287] and even in the solid state[282], and numerous racemization studies have been carried out[166,282,286–288]. Optical rotatory dispersion measurements have been used to determine the absolute configuration of the trioxalatocobaltate(III) ion[281,282,289].

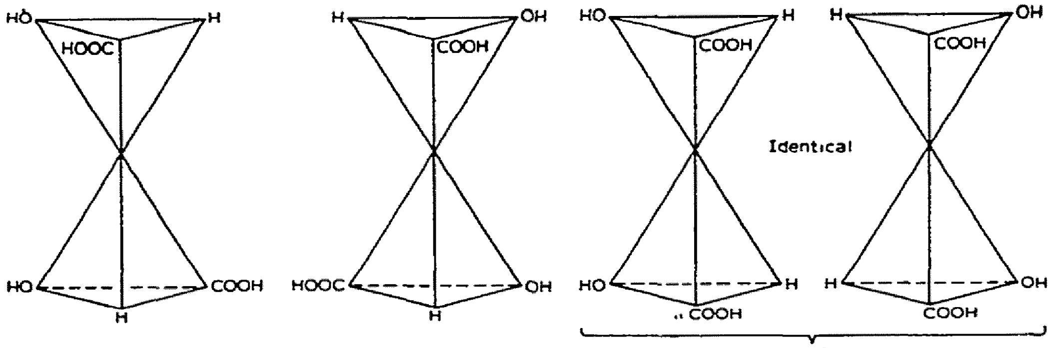
(iv) *Polynuclear complexes*

(a)

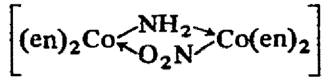


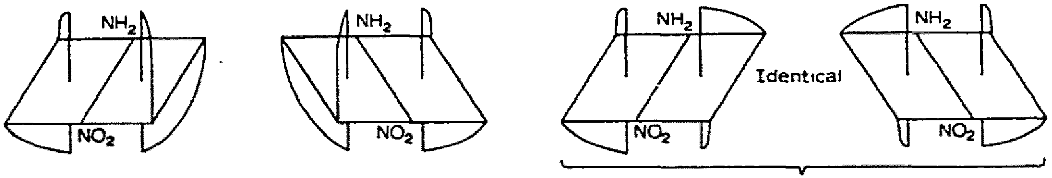
$$\left[(en)_2Co\begin{smallmatrix}NH_2\\ O_2N\end{smallmatrix}Co(en)_2\right]X_4$$

The ninth paper in Werner's cobalt series[69,91] was particularly noteworthy not only in that it proved that polynuclear[290] as well as mononuclear complexes could be resolved but also in that it demonstrated the theoretically predicted analogy between compounds containing two asymmetric carbon atoms and polynuclear complexes with two metal atoms, another striking confirmation of his octahedral hypothesis. In complete analogy with tartaric acid, HOOC·C*HOH·C*HOH·COOH, which, in addition to the racemic (±) form, also exists in (+)- and (–)-enantiomers and in an internally compensated nonresolvable (meso) form.



(+)-form (–)-form meso–form

Werner was able to demonstrate experimentally for the brown binuclear complex  $\left[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\rightarrow\\ \leftarrow\mathrm{O_2N}\end{smallmatrix}\mathrm{Co}(\mathrm{en})_2\right]X_4$ (ref. 17, pp. 360-361; ref. 18, p. 627; ref. 24), the existence of a racemic (±) form, (+)- and (–)-enantiomers, and an internally compensated, nonresolvable (meso) form



(+)-form (–)-form meso–form

for the bromide, iodide, thiocyanate, and (+)-bromocamphorsulfonate[*]. Resolution was accomplished with silver (+)-bromocamphorsulfonate, and treatment of the diastereoisomers with concentrated hydrobromic acid yielded the bromides (active with $5H_2O$, $[\alpha]$ for white light = ±164°, inactive with $6H_2O$, $[\alpha] = 0°$). The optically active compounds were also prepared[70,157] from the optically active μ-amido-μ-peroxo compounds by treatment with HNO_2.

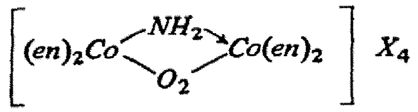
According to the coordination theory, the two cobalt atoms in these complexes should not be structurally identical since one is bound by a principal valence to NO_2 and by a secondary valence to NH_2 and the other vice versa. The inactivity of the meso-form, however, indicates that the two cobalt atoms exhibit no difference even in their action on the plane of polarized light and that the NH_2 and NO_2 groups are symmetrically located with

---

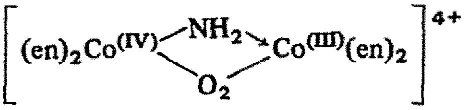
[*] I am indebted to Dr. John C. Bailar, Jr., for pointing out that complexes bridged by NO_2 cannot be symmetrical and that Werner was therefore incorrect in his reasoning (The bridge is M–N–O–M, not M–O–N–O–M); (see, e.g. U. Thewalt and R.E. Marsh, *Inorg. Chem.*, 9 (1970) 1604–1610).

respect to the cobalt atoms. Consequently, Werner concluded that "no essential difference can exist between principal and secondary valence bonds" (*"kein prinzipieller Unterschied zwischen Haupt- und Nebenvalenzbindungen bestehen kann"*) (ref. 69, p. 3676) a statement which he also made on other occasions[70,291].

(*b*)



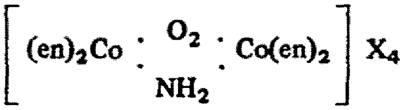
The next polynuclear ion to be resolved by Werner, in the tenth paper of his cobalt series[70], the ion regarded by him as the tetrakis(ethylenediamine)-μ-amido-μ-peroxo-cobalt(III)cobalt(IV) ion



first described by him in 1910 (ref. 17, pp. 352–353; ref. 18, pp. 624–625; refs. 24, 119), presented several interesting problems. Because the two octahedra comprising the complex contained asymmetric cobalt atoms ($[M(en)_2AB]$ type) and were also different in that Werner considered them to contain cobalt atoms in different oxidation states ((III) and (IV)), he predicted the existence of four optically active isomers—(1) (+)-[$Co^{(III)}$],(+)-[$Co^{(IV)}$], (2) (−)-[$Co^{(III)}$],(−)-$Co^{(IV)}$], (3) (+)-[$Co^{(III)}$],(−)-[$Co^{(IV)}$], and (4) (−)-[$Co^{(III)}$],(+)-[$Co^{(IV)}$]* (according to the concept of resonance, the last two combinations are identical, and only three possibilities exist). By diastereoisomer formation with silver (+)- and (−)-bromocamphorsulfonates, Werner isolated in low yield two optically active forms for the bromide, nitrate, and dithionate. The active salts were stable in aqueous solution, but the rotation fell to zero after a week's standing.

A letter of July 16th, 1911 from Werner to his assistant, Dr. Aegidius Tschudi, shortly after King's first success shows that Werner had worked on these compounds for several years before publishing his results.

"Your congratulations on the asymmetric cobalt made me very happy, and I can tell you that meanwhile we have resolved some more cobalt-ammines, e.g., the ones that you found in your private laboratory—series containing two cobalt atoms



$$\left[(en)_2Co \; \overset{O_2}{\underset{NH_2}{:\;\;:}} \; Co(en)_2\right]X_4$$

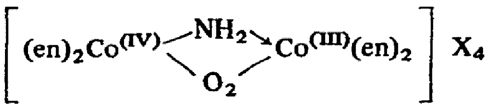
with 4-valent cobalt.

---

* If both octahedra were structurally similar, an internally compensated, nonresolvable (meso) form should be theoretically possible.

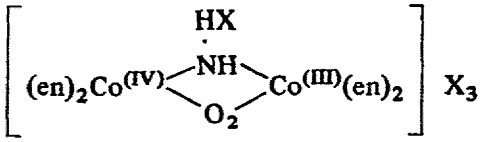
The series rotates to an extraordinary extent; according to our determinations to date, the specific rotation is ca. ±280°*. i.e., it corresponds to the highest rotation values found for carbon compounds. Of course we are working feverishly."

Werner[119] regarded these green (paramagnetic) salts



$$\left[(en)_2Co^{(IV)}\begin{matrix}NH_2\\O_2\end{matrix}Co^{(III)}(en)_2\right]X_4$$

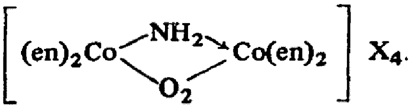
as "valence isomers" (a particular kind of structural isomer)[292] of the red, diamagnetic salts



$$\left[(en)_2Co^{(IV)}\begin{matrix}HX\\ \cdot \\ NH\\O_2\end{matrix}Co^{(III)}(en)_2\right]X_3$$

(see Section B(iv)(c)), and a number of polynuclear cobalt complexes which contain $-O_2-$ bridges exist in green (paramagnetic) and red (diamagnetic) series. In a private communication of June 21, 1946 to Prof. John C. Bailar, Jr., Dr. E.O. Brimm (ref. 293, p. 100) suggested that, because all the complexes which, according to Werner, contained "tetrapositive cobalt" also contained $-O_2-$ bridges, the magnetic evidence cited on behalf of Werner's $Co^{(IV)}$ state could be explained equally well by assuming these compounds to contain the superoxide group (O_2^-) and tripositive cobalt. It was not until twenty years later that this view was confirmed experimentally[290,294–297].

Werner transformed the active salts of the



$$\left[(en)_2Co\begin{matrix}NH_2\\O_2\end{matrix}Co(en)_2\right]X_4.$$

series into salts of other series in order to see if the activity persisted and to observe the effect of substitution on rotatory power. By allowing the parent compound to react with various reagents, he obtained products, each of which possessed a rotation of opposite

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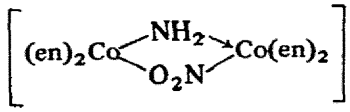
* Werner later[70,157] obtained considerably higher values, e.g., $[\alpha]_D^{20} = \pm 840°$, $[M]_D^{20} = \pm 6854°$ for the compound

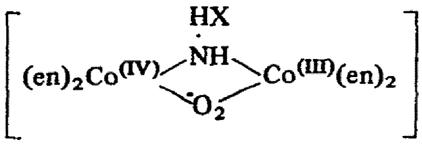
$$\left[(en)_2Co\begin{matrix}NH_2\\O_2\end{matrix}Co(en)_2\right]Br_4\cdot 5H_2O$$

He suggested that the valence of the central atom has a marked influence on the magnitude of the optical activity inasmuch as the rotations for binuclear complexes containing only trivalent cobalt are much smaller than those observed for these compounds.

sign and smaller magnitude than that of the starting material*. In this way he prepared optically active compounds formulated by him as follows.

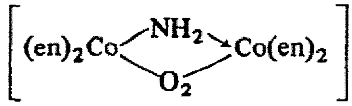


$\left[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O_2N}\end{smallmatrix}\mathrm{Co(en)_2}\right]X_4$ (previously resolved in ref. 69; see Section B(iv)(a));



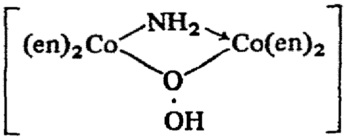
$\left[(\mathrm{en})_2\mathrm{Co^{(IV)}}\begin{smallmatrix}\mathrm{HX}\\ \cdot\\ \mathrm{NH}\\ \mathrm{O_2}\end{smallmatrix}\mathrm{Co^{(III)}(en)_2}\right]X_3$

later formulated[298] as

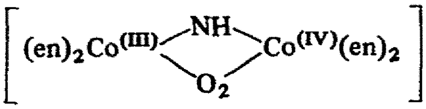


$\left[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{smallmatrix}\mathrm{Co(en)_2}\right]X_3\cdot HX$

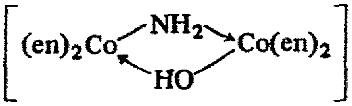
but actually[294]



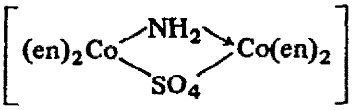
$\left[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O}\\ \cdot\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co(en)_2}\right]X_4$ (see Section B(iv)(c));



$\left[(\mathrm{en})_2\mathrm{Co^{(III)}}\begin{smallmatrix}\mathrm{NH}\\ \mathrm{O_2}\end{smallmatrix}\mathrm{Co^{(IV)}(en)_2}\right]X_4$ (see Section B(iv)(d));



$\left[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{HO}\end{smallmatrix}\mathrm{Co(en)_2}\right]X_4$ (see Section B(iv)(e)); and



$\left[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{SO_4}\end{smallmatrix}\mathrm{Co(en)_2}\right]X_3$ (see Section B(iv)(f))

These preparations, which proceed without racemization, represent the first examples of oxidation-reduction reactions among optically active complexes. A number of similar redox reactions have since been demonstrated[299,300].

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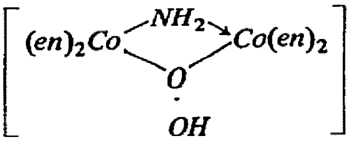
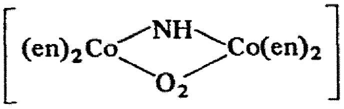
* Later rotatory dispersion studies have shown the generic configuration of the products to be the same as that of the reactant[252].

(c) 

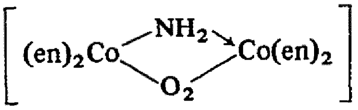
$\left[(en)_2Co{<}^{NH_2}_{O\cdot OH}{>}Co(en)_2\right]X_4$

These red, diamagnetic salts were first prepared by Werner by careful neutralization of



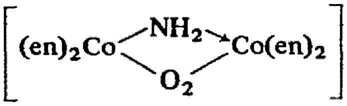
$\left[(\mathrm{en})_2\mathrm{Co}{<}^{\mathrm{NH}}_{\mathrm{O_2}}{>}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X}_3$ (Section B(iv)(d))

with mineral acids (ref. 17, pp. 350–351; ref. 18, pp. 624–625; refs. 24, 119, 301). These unstable compounds give a strongly acidic reaction in aqueous solution and are converted into



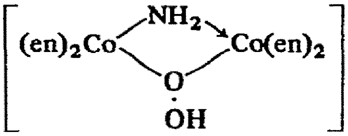
$\left[(\mathrm{en})_2\mathrm{Co}{<}^{\mathrm{NH_2}}_{\mathrm{O_2}}{>}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X}_4$ (Section B(iv)(b)).

Werner considered the two series to be "valence isomers" (ref. 119, p. 7). Thompson and Wilmarth[298] later considered the compounds to be acid salts



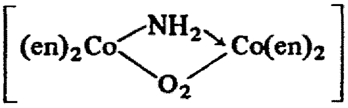
$\left[(\mathrm{en})_2\mathrm{Co}{<}^{\mathrm{NH_2}}_{\mathrm{O_2}}{>}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X}_3\cdot\mathrm{HX}$

but Thewalt and Marsh[294] showed them to contain hydroperoxide bridges,



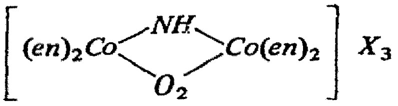
$\left[(\mathrm{en})_2\mathrm{Co}{<}^{\mathrm{NH_2}}_{\mathrm{O\cdot OH}}{>}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X}_4$

Werner[70,157] prepared the optically active bromides of this series by treating optically active



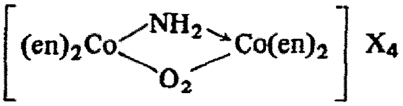
$\left[(\mathrm{en})_2\mathrm{Co}{<}^{\mathrm{NH_2}}_{\mathrm{O_2}}{>}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{Br}_4$

with concentrated aqueous ammonia, cooling, and adding concentrated HBr. From these, he prepared the active dithionates by metathesis.

(*d*) 

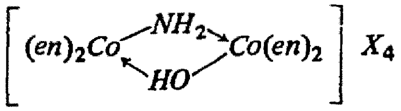
$$\left[(en)_2Co\begin{matrix}NH\\ O_2\end{matrix}Co(en)_2\right]X_3$$

Werner was the first to prepare these brown salts from the green, paramagnetic



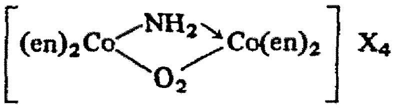
$$\left[(\mathrm{en})_2\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X_4}$$

compounds by removing one molecule of HX with NH_3 (ref. 17, pp. 349-350; ref. 18, p. 623; ref. 24; ref. 119, pp. 74–76; ref. 301). Werner et al. prepared the optically active iodides from the optically active μ-amido-μ-superoxo iodides by this method (ref. 70, pp. 1963, 1973; ref. 157).

(*e*) 

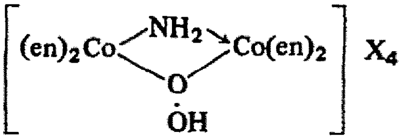
$$\left[(en)_2Co\begin{matrix}NH_2\\ HO\end{matrix}Co(en)_2\right]X_4$$

These red salts were first prepared by Werner by reduction with HI of either the green



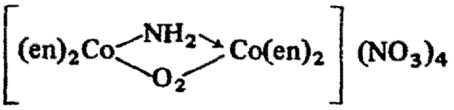
$$\left[(\mathrm{en})_2\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X_4}$$

or the red



$$\left[(\mathrm{en})_2\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O}\\ \mathrm{\dot{O}H}\end{matrix}\mathrm{Co}(\mathrm{en})_2\right]\mathrm{X_4}$$

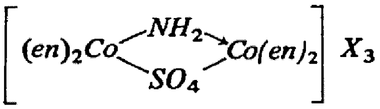
(ref. 17, p. 356; ref. 18, p. 626; refs. 24, 90; ref. 119, p. 76; ref. 301). Werner, Kuh and Wüst prepared the (+)-iodide ([α], apparently for the Na *D* line = +110°) from

(–)- 

$$(-)\text{-}\left[(\mathrm{en})_2\mathrm{Co}\begin{matrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{matrix}\mathrm{Co}(\mathrm{en})_2\right](\mathrm{NO_3})_4$$

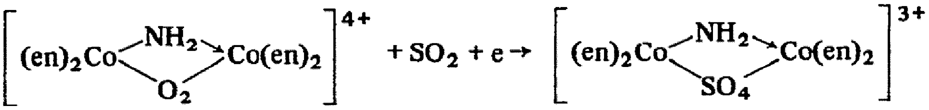
by conversion to the polyiodide, which in turn was converted into the iodide by treatment with $Na_2S_2O_3$ (ref. 70, pp. 1964, 1977; ref. 157).

(f)



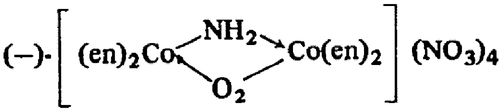
$$\left[(en)_2Co\begin{matrix}NH_2\\SO_4\end{matrix}Co(en)_2\right]X_3$$

These bright red salts were first prepared by Werner from the corresponding μ-amido-μ-superoxo salts by treatment with sulfur dioxide



$$\left[(en)_2Co\begin{matrix}NH_2\\O_2\end{matrix}Co(en)_2\right]^{4+} + SO_2 + e \rightarrow \left[(en)_2Co\begin{matrix}NH_2\\SO_4\end{matrix}Co(en)_2\right]^{3+}$$

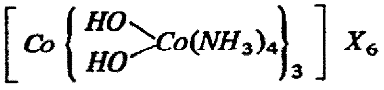
a reaction that Werner misinterpreted as a "reduction" of one "cobalt(IV)" atom to the trivalent state (ref. 17, pp. 342–343; ref. 18, p. 628; ref. 24; ref. 119, p. 77). Although Werner, Kuh and Wüst were able to isolate a (+)-bromocamphorsulfonate diastereoisomer from the racemic bromide, conversion of this to the corresponding nitrate resulted only in inactive salts (ref. 70, p. 1976; ref. 157). Consequently, they reduced



$$(-)\text{-}\left[(en)_2Co\begin{matrix}NH_2\\O_2\end{matrix}Co(en)_2\right](NO_3)_4$$

with SO_2 and obtained the (+)-nitrate ([α] apparently for the Na D line = +200°) (ref. 70,, pp. 1965, 1977). The salts exhibit large rotatory dispersion[70,301].

(g)



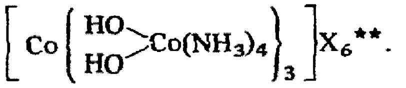
$$\left[Co\left\{\begin{matrix}HO\\HO\end{matrix}Co(NH_3)_4\right\}_3\right]X_6$$

Although the complexes that Werner had resolved up to 1914 represented a remarkable variety of compound types, they all possessed one common characteristic – they all contained carbon. Even though the symmetrical carbon-containing ligands (ethylenediamine, dipyridyl, or oxalate ion) are themselves optically inactive, those chemists still antagonistic toward Werner's views stubbornly maintained that the optical activity of these compounds was in some way due to the presence of these ligands. By such devious reasoning, they were able to cast doubt on the validity of his octahedral configuration for $Co^{(III)}$, $Cr^{(III)}$, $Rh^{(III)}$, and $Fe^{(II)}$.

For this reason, the twelfth and last article[72] in Werner's series on the asymmetric cobalt atom was a particularly welcome and satisfying one to him, since it served to vindicate his octahedral concept for even his most sceptical contemporaries[94,97]. In his own words, the investigation proved that "carbon-free inorganic compounds can also exist as mirror image isomers" and that therefore "the difference still existing between carbon compounds and purely inorganic compounds disappears" (ref. 72, p. 3087). At last Werner had experimentally verified a belief that he had held for many years.

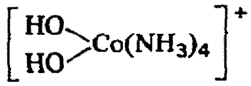
The brown, lustrous tetranuclear tris[tetraammine-μ-dihydroxo-cobalt(III)]cobalt(III)·

salts were first discovered and named "*Anhydrobasische Tetrammindiaquodiamminkobaltsalze*" by Jørgensen[302] in 1898 (ref. 17, pp. 370–372; ref. 18, pp. 630–631; ref. 24; ref. 34, pp. 267–268; ref. 51)*. In 1907 Werner et al.[114] showed that they possessed the constitution



$$\left[\mathrm{Co}\left\{\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}>\mathrm{Co(NH_3)_4}\right\}_3\right]\mathrm{X_6}^{**}.$$

Since they are thus structurally similar to $[\mathrm{M(en)_3}]\mathrm{X}_n$ salts with



$$\left[\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}>\mathrm{Co(NH_3)_4}\right]^{+}$$

ions in place of ethylenediamine molecules, they should be capable of existing in non-superimposable mirror image forms.

Werner[72] succeeded in resolving the bromides by diastereoisomer formation with silver (+)-bromocamphorsulfonate, but the process was extremely tedious because of the small differences in solubility between the diastereoisomers. Optical measurements were hindered by rapid racemization and the deep color of the solutions. Rotations were measured in 50% aqueous acetone solutions in order to minimize racemization. The highest values found were $[\alpha]_{560} = -4500°$, $[M]_{560} = -47{,}475°$ for the pure (−)-bromide and $[\alpha]_{560} = +1050°$, $[M]_{560} = +11{,}109°$ for the (+)-bromide. Although the structure of these compounds has not yet been determined by X-ray diffraction, the structure of the corresponding ethylenediamine cation has been so determined and found to agree with Werner's formulation[303]. To the present day, with the sole exception of F.G. Mann's resolution[304] of Na-*cis*-$[\mathrm{Rh(H_2O)_2\{SO_2(NH_2)_2\}_2}]$, Werner's resolution[72] of

$$\left[\mathrm{Co}\left\{\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}>\mathrm{Co(NH_3)_4}\right\}_3\right]\mathrm{X_6}$$

remains the only example of the resolution of a completely carbon-free coordination compound and marks his crowning achievement in coordination chemistry.

(*v*) *Miscellaneous compounds*

In *Neuere Anschauungen*, Werner mentioned three series of cobalt compounds that he claimed to have resolved, but he gave no details concerning the resolutions, which are not cited in either *Gmelins Handbuch*[17, 18] or Pascal's *Nouveau Traite*[24]. These details are probably contained (in the third case, they definitely are contained) in unpublished dissertations of Werner's students, thus underscoring the need for making these results available to all coordination chemists. Two of the three cases involved later work by John C. Bailar, Jr., dean of American coordination chemists, whose knowledge of the literature is second to none. Although Bailar was familiar with Werner's published results pertinent to his own studies, his work would undoubtedly have been facilitated had he been acquainted with Werner's unpublished results. These three cases are illustrative

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* See footnote § on p. 6.

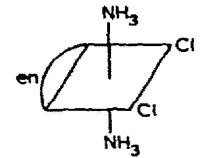
** For a discussion of Werner's reasons for assigning this configuration see ref. 290, pp. 357–358.

rather than exhaustive; a thorough study of Werner's students' dissertations would probably disclose additional similar examples.

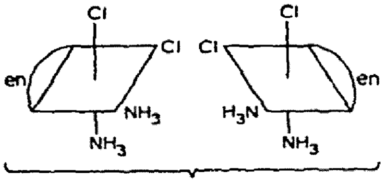
(*a*) [*Coen*$(NH_3)_2Cl_2$]*X*

In the posthumous fourth (1920) edition of *Neuere Anschauungen* (ref. 60(b); p. 371), edited by Paul Karrer, the compound series $[\mathrm{Coen(NH_3)_2Cl_2}]X$ is cited as the only example of the type $[\mathrm{Men(NH_3)_2AB}]$ to be resolved. (Actually, the compound is an example of the type $[\mathrm{Men(NH_3)_2AA}]$, 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[60(a)], published in 1913 when Werner was in full possession of his faculties, or in the posthumous fifth edition (1923) edited by Paul Pfeiffer[60(c)]. Nevertheless, Werner did prepare compounds of this type, so the possibility of his resolving them cannot be discounted.

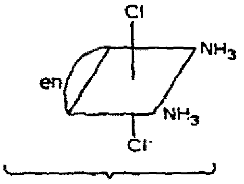
Compounds of type $[\mathrm{Coen(NH_3)_2Cl_2}]X$ exist in three isomeric forms, one of which is theoretically resolvable (ref. 17, pp. 245-246; ref. 18, pp. 581-582; ref. 24, pp. 581-582).



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, $[\mathrm{Coen(NH_3)_2CO_3}]\cdot$Cl (ref. 121, pp. 254-264). They recognized the two series as *trans*-dichloro and *cis*-dichloro, respectively, and they predicted (ref. 121, p. 255) the existence of a second *cis* series, I, discovered twenty-eight years later by Bailar and Peppard[305], who prepared the chloride, bromide, iodide, thiocyanate, and α-bromo-(+)-camphor-π-sulfonate. Bailar and Peppard[305] also prepared the chloride and bromide of Series II and the chloride of Series III. Lobanov later prepared the periodates[306] of both Series II and III and an iodate-iodic acid addition compound[307] of Series III. Bailar and Peppard[305] prepared the carbonato carbonates ($[\mathrm{Coen(NH_3)_2CO_3}]_2\mathrm{CO_3}$) 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[305] also prepared the bromide and thiocyanate of a dibromo complex $[\mathrm{Coen(NH_3)_2Br_2}]X$ corresponding to Series III. The rate of aquation of the series III chloro chloride has been determined[308].

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* Even though Chaussy's dissertation[142] of 1909 may contain more details than the published paper[121], it antedates Werner and King's work[61] of 1911 and could therefore not involve any successful resolution, the details of which must be sought elsewhere.

(b) cis-$[Co(en)_2(NH_3)NH_2OH]X_3$ *and* cis-$[Co(en)_2(NH_2OH)Br]X_2$

In the third, fourth, and fifth editions of *Neuere Anschauungen* (ref. 60(a), p.365; ref. 60(b), p. 376; ref. 60(c), p. 368), Werner claims to have resolved compounds of the $[Co(en)_2(NH_3)NH_2OH]X_3$ series (obviously *cis*, although they are not so specified) and gives a value of $[\alpha]_D = 112°$ ($[M]_D = 545°$) (no sign of rotation specified), a value that is also quoted in a published lecture of 1912 (ref. 90, p. XIV). Yet Werner gives no details of the resolution or even of the preparation of the racemic compounds, and they are not listed in either *Gmelins Handbuch*[17,18] or Pascal's *Nouveau Traité*[24]. In the published literature, the only hydroxylamine-containing cobalt complexes prepared by Werner are the series $[Co(NH_2OH)_6]X_3$, described by Werner and Berl[109,309] in 1905.

In the fourth and fifth (but not the third) editions of *Neuere Anschauungen* (ref. 60(b), p. 375; ref. 60(c), 368), Werner lists compounds of the series $[Co(en)_2(NH_2OH)Br]X_2$ (obviously *cis*) as being resolved but gives no details or rotations here or in any of his other publications. The compounds are not listed in *Gmelins Handbuch*[17,18]or Pascal's *Nouveau Traité*[24]. However, the closely related compound[310] $[Co(en)_2(NH_2OH)Cl]Cl_2$ was used by Werner and Berl[109] in their preparation of $[Co(NH_2OH)_6]X_3$. Details of the preparation and resolution of both *cis*-$[Co(en)_2(NH_3)NH_2OH]X_3$ and *cis*-$[Co(en)_2(NH_2OH)Br]X_2$ are probably given in the dissertation (1913) of one of Werner's Polish *Doktoranden*, Chil Szaja Borzekowski[154], which was completed two years after Werner and King's historic resolution, but this work was not available to the present author.

(c) $[Co(en)_2tn]X_3$ *and* $[Co(tn)_3]X_3$

In the fourth and fifth (but not the third) editions of *Neuere Anschauungen* (ref. 60(b), pp. 372, 376; ref. 60(c), pp. 367, 368), Werner lists compounds of the two series $[Co(en)_2tn]X_3$ and $[Co(tn)_3]X_3$ as being resolved and cites rotation values of $[\alpha]_D = 85°$ ($[M]_D = 622°$) and $[\alpha]_D = 74°$ ($[M]_D = 550°$) for the iodides of the two series, respectively. Although Werner mentioned complexes of cobalt with trimethylenediamine in a 1906 lecture[311] and cited $[Co(en)_2tn]X_3$ as a resolved series in a lecture of 1912 (ref. 90, p. XIV), neither series is mentioned elsewhere in his publications, and his work on these compounds is not cited in *Gmelins Handbuch* (ref. 18, pp. 370, 397) or Pascal's *Nouveau Traité*. Among Werner's publications, the only trimethylenediamine complexes whose preparations are described are *trans*-$[Co(tn)_2(NO_2)_2]X$, where X = NO_2, Cl, Br or I (ref. 17, p. 222; ref. 121, pp. 264–269), *trans*-$[Co(tn)_2Cl_2]X$, where X = Cl or $\frac{1}{2}PtCl_6$ (ref. 17, p. 245; ref. 18, p. 562; ref. 121, p. 269-271), and $[Co(tn)_2CO_3]Cl$ (ref. 17, p. 562; ref. 121, pp. 271-272; ref. 312).

Full data on the resolved series in question, however, are found in the 1914 dissertation[160] of Werner's Norwegian *Doktorand*, Johannes Flood, who describes the preparation of his starting materials *trans*-$[Co(tn)_2(NO_2)_2]NO_2$ (ref. 160, p. 31) and *trans*-$[Co(tn)_2Cl_2]Cl$ (ref. 160, p. 31), both previously prepared by Werner and Lindenberg (ref. 121, pp. 265-266, 269-271), and then goes on to describe the preparations of the apparently new series $[Co(tn)_3]X_3$, where X = Cl, Br, I, ClO_4, SO_4, CO_3, NO_3 or NCS (ref. 160, pp. 32-39), $[Co(en)_2tn]X_3$, where X = I or NO_3 (ref. 160, pp. 44-45, p. 48), and the compound $[Co(tn)_2CO_3]I \cdot H_2O$ (ref. 160, p. 50). For his resolutions, Flood employed silver (+)-tartrate. After encountering difficulties in resolving the chlorides and bromides, he resolved $[Co(tn)_3]I_3$, obtaining rotation values of $[\alpha]_D = +74°$ or $-71°$ and $[\alpha]_C = +36°$ or $-35°$ (ref. 160, pp. 40–43). For $[Co(en)_2tn]I_3$, another difficult resolution, he obtained values of $[\alpha]_D = +85°$ or $-82°$ and $[\alpha]_C = +40°$ or $-38°$ (ref. 160, pp. 46–48). By metathesis with silver nitrate, he converted the active iodide into the active nitrate, $[\alpha]_D = +100.5°$ or $-80°$ and $[\alpha]_C = +40°$ or $-35°$ (ref. 160, pp. 48–49). Although Lindenberg's dissertation[139] of 1906 could not possibly contain a description of any successful resolutions of additional trimethylenediamine complexes, such data might be contained in the 1917 dissertation of Emil Lüscher[174]. In their paper (1946), "Some coordination compounds of cobalt containing trimethylenediamine and neopentanediamine"[313], Bailar and Work prepared *trans*-$[Co(tn)_2Cl_2]Cl$, $[CoentnCl_2]Cl$, $[Co(tn)_3]Cl$, and $[Co(en)_2tn]Cl_3$. They were aware of Werner and Lindenberg's published work but not of Flood's unpublished dissertation.

C. CHROMIUM COMPLEXES

(*i*) *Type M(en)$_2$B$_2$*

(*a*) cis-$[Cr(en)_2Cl_2]X$

From the very beginning of his studies of optical activity, Werner did not limit himself to complexes of cobalt[85–87,89,90]. Less than four months after receiving the manuscript describing the first resolution of a complex[61], the editor of *Berichte* received from Werner a manuscript[76] describing the resolution of *cis*-$[Cr(en)_2Cl_2]X$ (molecular asymmetry I), where X = Cl, Br or NO_3. This, the first article in his three-paper series *Über Spiegelbild-isomerie bei Chromverbindungen*, preceded the paper describing the corresponding cobalt compound[64] by two weeks. Werner achieved the resolution of the racemic chromium compound, first prepared by Pfeiffer (ref. 19, pp. 190–196; ref. 25; ref. 32, pp. 222–224; ref.4, p. 1356; ref. 35, pp. 93, 99; refs. 52, 135; ref. 314, p. 294; refs. 315, 316) by diastereoisomer formation with ammonium (+)-bromocamphorsulfonate. Werner thus showed that optical activity among complexes is not confined to those of cobalt and that chromium(III), like cobalt(III), possesses an octahedral configuration. The rotation, however, is apparently dependent on the central atom as well as on the ligands, for he found that the values were less than those for the corresponding cobalt salts, a conclusion that was confirmed in his later study of tris(ethylenediamine)chromium(III) salts[77] (molecular asymmetry II).

(*b*) $[Cr(en)_2C_2O_4]X$

These compounds were first described in the dissertation of Werner's student Heinrich Schwarz[135]. Since they must be *cis* compounds because of the bidentate oxalate group, Pfeiffer et al.[315] used them for determining the configuration of related chromium (III) compounds (ref. 19, pp. 202–204; ref. 25; ref. 32, pp. 227–229; ref. 123, pp. 223–225; refs. 167, 171). Werner's attempts to resolve the $[Cr(en)_2C_2O_4]X$ compounds by the usual resolving agents were unsuccessful. Unlike the corresponding cobalt compounds (see Section B(ii)(d)), which could be resolved by treatment of active *cis*-$[Co(en)_2Cl_2]^+$ salts with $K_2C_2O_4$, the chromium compounds yielded only racemic mixtures. However, by the method of preferential crystallization (see B(ii)(d)) in which (+)-$[Co(en)_2C_2O_4]Br$ was added to a solution of racemic $[Cr(en)_2C_2O_4]Br$, Werner and Bosshart[71] were able to isolate both antipodes of the latter compound. Resolution was subsequently accomplished[228,287] by the action of $(NH_4)_2C_2O_4$ on (+)-*cis*-$[Cr(en)_2Cl_2]Cl$, and a partial separation of the antipodes on levorotatory quartz has also been claimed[242]. More recently the direct resolution of the racemic bromide with potassium (−)-ethylenediaminetraacetatocobaltate(III) has been reported[265].

(*ii*) *Type* $M(en)_3$

(*a*) $[Cr(en)_3]X_3$

Tris(ethylenediamine)chromium(III) salts were discovered by Werner's former student and assistant, Paul Pfeiffer, in 1900, and a variety of preparative methods are available (ref. 19, pp. 67–87; ref. 25; ref. 32, pp. 172–175; ref. 34, pp. 1354–1356; refs. 53–57; ref. 314, p. 286; refs. 315, 317). Although Werner's attempts to resolve these compounds with tartrates, camphorsulfonates, and bromocamphorsulfonates were unsuccessful, diastereoisomer formation with sodium (+)-nitrocamphorate proved satisfactory and led to the isolation of optically active iodides and thiocyanates[77]. The same method[169] was also used for resolving $[Rh(en)_3]X_3$. The resolution of the tris(ethylenediamine)chromium(III) ion has been attempted by others[318–320] using various methods, including partial chromatographic separations on optically active quartz[242,321] and potato starch (ref. 254, p. 100). Numerous measurements of optical rotation have been made[227,237,281].

(*b*) $K_3[Cr(C_2O_4)_3]$

This compound, sometimes called Gregory's salt, has been known since 1839 (ref. 25, pp. 508–510; ref. 31, p. 386; ref. 34, p. 1372; ref. 35, p. 56; refs. 44, 48, 322, 323) and is similar to, but less stable than, the corresponding cobalt(III) compound. Werner's resolution of $K_3[Cr(C_2O_4)_3]$ in 1912 by means of strychnine in ethanol solution[78,148] possesses the double historical distinction of being the first resolution of both a complex anion and of a complex that did not contain nitrogen. The aqueous solution loses its activity very rapidly, and in 1¼ h Werner found that the rotation had fallen to zero. The loss occurs more slowly in acetone solution. The compound has since been resolved more effectively by means of optically active cationic coordination compounds as resolving agents, e.g. (+)-$[Ni(o\text{-phen})_3]^{2+}$ (ref. 263) or (−)-$[Co(en)_3]^{3+}$ (ref. 266).

The chromium complex racemizes so rapidly in aqueous solution that it has been resolved by a second-order asymmetric transformation[44]. In connection with the $[Cr(C_2O_4)_3]^{3-}$ ion, Werner was the first to suggest that complexes may racemize by an intramolecular process, a mechanism which has since been shown to be correct by means of oxalate exchange studies[324,325]. He proposed that one end of a chelate group breaks free of the central atom yielding a pentacoordinate intermediate in which there is either a plane of symmetry or at least a reasonable probability of forming either antipode when the free end of the chelate re-forms a bond with the central atom[78]. A number of alternative mechanisms have since been suggested for such racemizations[287,288,326–328].

D. IRON COMPLEXES

(*i*) *Type M(en)*$_3$

(*a*) [*Fe(dipyridyl)*$_3$]*X*$_2$

The red tris(α,α′-dipyridyl)iron(II) complexes are easily prepared and have been known since 1888 (ref. 26, p. 361; refs. 329–335). They are of great analytical importance[336–339] their pink coloration making α,α′-dipyridyl one of the most sensitive and specific reagents for iron(II). The iron(II)-(III)-α,α′-dipyridyl system is also one of the best known redox systems, and α,α′-dipyridyl is a well-known redox indicator for the determination of iron. It has also been used as a spot test reagent, and the complex, being soluble in both water and organic solvents, has been utilized in colorimetric and spectrophotometric determinations[336,337,339].

Werner apparently intended to make a thorough study of optical isomerism in iron compounds, for his only article on the topic, *Über Spiegelbild-Isomerie bei Eisenverbindungen*[81,168], is subtitled *Vorläufige Mitteilung* (Preliminary Communication). By means of ammonium (+)-tartrate, Werner was able to prepare the (−)-$[Fe(dipy)_3]^{2+}$ diastereoisomer, from which he isolated the (−)-bromide ($[\alpha]_D = -520°$) and (−)-iodide ($[\alpha]_D = -440°$). No optically active salts of the (+)-series were prepared. The salts of the (−)-series racemize rapidly in solution, losing all activity within a few hours, and an intramolecular mechanism seems likely. The rate of racemization is also greater than that of dissociation[340].

Werner's resolution proved that iron(II), like cobalt(III) and chromium(III), possesses an octahedral configuration. $[Fe(dipy)_3]X_2$ salts were the first optically active complexes of a divalent element to be resolved; all complexes resolved previously had contained trivalent ions (Co or Cr) as central atoms. Furthermore, they were the first complexes resolved that did not contain ethylenediamine. For iron(II) salts, the new compounds proved remarkably stable to atmospheric oxidation—an excellent illustration of stabilization by coordination, a phenomenon that has been widely utilized in the synthesis of compounds containing elements in unusual and ordinarily unstable oxidation states[293].

E. RHODIUM COMPLEXES

(*i*) *Type M(en)*$_3$

(*a*) [*Rh(en)*$_3$]*X*$_3$

The tris(ethylenediamine)rhodium(III) compounds are extremely stable, easily prepared, colorless salts that were first prepared by Werner[79] in 1912, specifically for the purpose of attempting their resolution (ref. 21, pp. 104–105, 113–118; refs. 27, 55). The racemic as well as the optically active compounds are completely isomorphous with the corresponding cobalt(III), chromium(III), and iridium(III) compounds[279,341–343].

In the first of his two papers entitled *Über Spiegelbild-Isomerie bei Rhodium-Verbindungen*[79], Werner not only established the existence of mirror image isomerism and the octahedral configuration for another metal—the first case among the platinum metals—but he also enunciated a valuable empirical rule for determining the generic configuration of optically active complexes, a principle which he later developed and extended[90] and which has become known as Werner's solubility method. Together with the rotatory dispersion technique developed by Mathieu, Werner's method is probably the most important means for determining the relative configuration of complexes.

It has already been shown that Werner realized that the absolute configuration of a complex cannot be directly determined from the sign of rotation[64,90]. Some other configurational criterion was therefore needed. According to Werner's solubility rule, all antipodes of a corresponding type which give the least soluble diastereoisomer with a given resolving agent have the same absolute configuration, regardless of the sign of rotation. Applying this rule to the resolution of the tris(ethylenediamine) complexes of tripositive cobalt, chromium, and rhodium by means of (+)-nitrocamphorates and (+)-tartrates, Werner concluded that the (+)-$[Co(en)_3]^{3+}$, (+)-$[Cr(en)_3]^{3+}$, and (–)-$[Rh(en)_3]^{3+}$ cations possess the same absolute configuration. The Dutch stereochemist, Francis Mauritius Jaeger, together with Blumendal, first criticized this theory* and attempted to disprove Werner's rule[344], but Jaeger subsequently acknowledged its validity and actually used it himself to determine the relative configurations of optically active complexes[319,345,346].

Werner[79] isolated the optically active chlorides, iodides, and thiocyanates, while others have isolated the (–)-enantiomorphs of the bromide and nitrate (ref. 256; ref. 279, p. 198; ref. 343, p. 249; refs. 347, 348). The active compounds are very stable; no noticeable change in activity occurs after months of standing at room temperature or on heating or in the presence of acids (ref. 79, p. 1229; ref. 349). Numerous studies of rotatory dispersion and the Cotton effect have been made (ref. 281; ref. 349, p. 85), and the absolute probable configuration of the tris(ethylenediamine)rhodium(III) ion has been determined (ref. 21, pp. 104–105). Optically active racemates also exist (ref. 21, pp. 117–118; ref. 347).

(b) $M_3[Rh(C_2O_4)_3]$

The trioxalatorhodates were discovered in 1899 and are stable, water-soluble compounds (ref. 21, pp. 83–85; refs. 27, 350). In 1914 Werner and Poupardin[80] resolved the potassium salt with strychnine nitrate and then also isolated the sodium, rubidium, and barium salts. They found the optical rotations to be smaller than those of the trioxalatochromates. The rhodium salts are much more stable than the corresponding chromium compounds and do not racemize appreciably even in hot solution. Measurements of rotatory dispersion[184,281], circular dichroism (ref. 5, p. 125) and the Cotton effect[351] have been made.

Werner and Poupardin[80] claimed that cooling a hot concentrated solution of the racemic mixture produced hemihedral crystals of (+)- and (–)-$K_3[Rh(C_2O_4)_3]$, which they were able to separate mechanically with the aid of a microscope. Jaeger[352] was unable to duplicate their results with this compound, but he and Thomas were able to resolve $K_3[Co(C_2O_4)_3]$ into its optical antipodes in a similar manner[279,280], the first example of

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* "This view is quite arbitrary because, in general, solubility is a so highly complicated and constituent property of matter that, even where we seem to have established rules for homologous series, sometimes most unexpected and surprising exceptions spring up. This makes these rules quite illusory" (ref. 5, p. 92).

the successful application of Pasteur's method of spontaneous crystallization to complexes. Additional resolutions have since been devised, using the (+)-tris(*o*-phenanthroline)nickel(II)[263] and the (−)-tris(ethylenediamine)cobalt(III)[266] cations as resolving agents.

Some question has arisen about the number of molecules of water of crystallization contained in optically active $K_3[Rh(C_2O_4)_3]$. Whereas Werner and Poupardin[80] and Jaeger (ref. 279, pp. 262, 265) claimed only one molecule, Charonnat[353] and Delépine (ref. 256, p. 1258), on the basis of isomorphism with the corresponding iridium salt whose water content was well established, claimed two molecules. Werner considered his resolution to be evidence for an octahedral configuration for rhodium(III) with coordination number 6, whereas Charonnat[353], on the basis of the formula $K_3[Rh(H_2O)_2(C_2O_4)_3]$, proposed a coordination number of 8, together with a structure that would require two additional isomers, which have never been found.

The citation in Tupizina's dissertation (ref. 172, pp. 15, 24) of resolved $[Rh(en)_2(C_2O_4)]X$ ($[\alpha] = +153°$ to $+275°$) has already been mentioned in the Introduction.

F. PLATINUM COMPLEXES

(*i*) *Type* $M(en)_3$

(*a*) $[Pt(en)_3]X_4$

Ethylenediamine that is coordinatively bonded to platinum(IV) readily loses protons, and thus the $[Pt(en)_3]^{4+}$ ion gives an acidic reaction in solution (ref. 22, pp. 470–474; refs. 28, 353, 354). In the first paper[82] of a projected but never continued series, "*Über Spiegelbildisomerie bei Platinverbindungen*", Werner was the first to describe the preparation of the tris(ethylenediamine)platinum(IV) salts. He resolved the chloride, iodide, thiocyanate, and nitrate by means of ammonium (+)- and (−)-tartrate[82]. This resolution simultaneously showed that mirror image isomerism could exist among coordination compounds of tetrapositive elements and confirmed the octahedral configuration proposed for $Pt^{(IV)}$ by Werner in 1893 (ref. 99, p. 297 et seq.), a configuration that has since been amply corroborated by numerous subsequent resolutions[355–357].

G. IRIDIUM COMPLEXES

(*i*) *Type* $M(en)_2B_2$

(*a*) cis-$[Ir(en)_2(NO_2)_2]X$

These colorless, very stable salts were first prepared and resolved by Werner and Smirnoff and described in a posthumous publication (ref. 22, pp. 167–169; refs. 29, 83). Although the action of ethylenediamine on $[IrX_6]^{2-}$ compounds yielded only dark uncrystallizable syrups, the action of ethylenediamine on $Na_3[IrCl_2(NO_2)_4] \cdot 2H_2O$ yielded a mixture of $[Ir(en)_2(NO_2)_2]X$ and $[Ir(en)_3]X_3$. The mixture was isolated as the mixed iodides and separated by treatment with silver α-(+)-camphorsulfonate, whereupon the (+)-$[Ir(en)_2(NO_2)_2]^+$ salt separated first. The filtrate was converted to bromide, treated with silver α-(−)-camphorsulfonate, yielding the (−)-$[Ir(en)_2(NO_2)_2]^+$ salt, and addition of KBr to the filtrate precipitated racemic $[Ir(en)_3]Br_3$.

The new dinitro compounds closely resemble the *cis*-$[Ir(NH_3)_4(NO_2)_2]X$ salts first prepared by Werner and de Vries[118,141]. The optically active bromides, perchlorates, and nitrates of the dinitro series were prepared. The nitro groups are bonded so strongly that evolution of NO_2 occurs only after heating for several hours with concentrated sulfuric acid. In the visible portion of the spectrum the compounds exhibit normal rotatory dispersion.

Werner and Smirnoff's resolution of $[Ir(en)_2(NO_2)_2]X$ simultaneously proved that the compounds possessed the *cis* configuration (no *trans* compounds were isolated) and, together with the resolution of $[Ir(en)_3]X_3$, confirmed the octahedral configuration for iridium complexes proposed in 1914 by Delépine[358].

(*ii*) *Type* $M(en)_3$

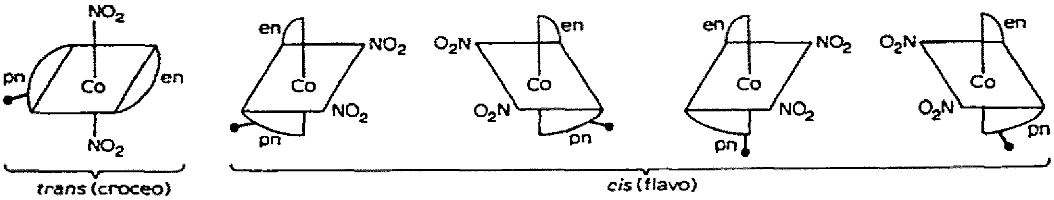
(*a*) $[Ir(en)_3]X_3$

The colorless, very stable, easily soluble salts of this series closely resemble the $[Ir(NH_3)_6]X_3$ salts first prepared by Palmaer (ref. 22, p. 148–151; refs. 29, 359). Werner and Smirnoff[83] resolved the racemic bromide described above (Section G(i)(a)) by treatment with sodium α-nitro-(+)-camphorate. They isolated the optically active bromides, iodides, perchlorates, and nitrates. They found that the rotatory power corresponds to the analogous compounds of $Rh^{(III)}$ and $Pt^{(IV)}$ and is greater than for the simultaneously resolved $[Ir(en)_2(NO_2)_2]X$ salts. Their resolution confirmed the octahedral configuration proposed by Delépine[358] for iridium complexes. Delépine and Charonnat's "active racemate" method[347] and Mathieu's rotatory dispersion studies[237,349] confirmed Werner's solubility rule and showed that the (–)-$[Ir(en)_3]^{3+}$ ion possesses the same configuration as the (+)-$[Co(en)_3]^{3+}$, (+)-$[Cr(en)_3]^{3+}$ and (–)-$[Rh(en)_3]^{3+}$ ions.

H. COMPLEXES WITH OPTICALLY ACTIVE LIGANDS

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. The first of such compounds, $[Co((+)\text{- or }(-)\text{-}pn)_3]X_3$, were prepared by Chugaev and Sokolov[360,361] fours years before Werner and King's historic resolution. The Russian chemists isolated only two of the twenty-four possible optically active combinations. No effect of the position of the methyl groups in the propylenediamine could be found nor has it been yet found. Stereospecificity, the fact that coordination compounds containing optically active ligands exist in only certain preferred stereoisomeric configurations rather than in all the possible forms, has since been studied in depth by many workers (ref. 10, pp. 220–222; refs. 276, 362–370). It has been used both to prepare optically active complexes and to resolve coordinating agents.

Of all optically active unsymmetrical ligands, the one most extensively investigated is still propylenediamine (1,2-diaminopropane). Werner published four papers[73,101,113,115] on complexes of this ligand, and such complexes were the topics for the dissertations of a number of his *Doktoranden*[127–129,144,153,162,173,175,183]. The only conclusive proof of isomerism caused by the position of the methyl group on a coordinated molecule was presented by Werner and Smirnoff[73,98] in the very first article in *Helvetica Chimica Acta*, a journal founded largely through Werner's efforts. Their resolution 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 (I = 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 even though he was unable to assign unambiguous structures to all of these (ref. 17, pp. 223-225; ref. 18, p. 583; refs. 371-373). The products of the reaction between [$Coen(NH_3)(NO_2)_3$] and (–)-propylenediamine have recently been separated chromatographically and shown to contain six of Werner and Smirnoff's isomers[374].

A similar complex containing two active propylenediamine molecules was investigated by two of Werner's *Doktoranden*, Hugh Edmund Watts[153], a young Englishman, and Hans Hürlimann[175], scion of a famous Zürich brewery family. Although the *cis*-[Co((+)- or (–)-pn)$_2$(NO_2)$_2$]$^+$ ions should exist in twelve forms, Watts and Hürlimann were able to isolate only two optically active isomers. The complex has since been reinvestigated by O'Brien et al.[375], who, on the basis of rotatory dispersion studies, concluded that Hürlimann's isomer must have had the *trans* configuration. Experiments on compounds similar to those of Hürlimann were carried out by Cooley et al.[376].

I. CONCLUSION

During his last years, then, Werner devoted himself almost exclusively to studies of the compounds which had brought him the Nobel Prize and had proved beyond the shadow of a doubt his stereochemical views. Without the impetus of his octahedral hypothesis, who would have thought of looking for optical activity among compounds such as the trioxalato salts $R^{I}_{3}[M^{III}(C_2O_4)_3]$, previously regarded merely as double salts $3R^{I}_{2}C_2O_4 \cdot M^{III}_{2}(C_2O_4)_3$, similar to the alums? Werner's investigations of the optically active coordination compounds of cobalt, chromium, rhodium, iridium, and iron underlie much of the more recent and sophisticated studies of the thermodynamics, kinetics, visible, ultraviolet and infrared spectra, rotatory dispersion, circular dichroism, ligand exchange, racemization, and absolute configuration of these and similar compounds. Although some of his methods of resolution have been improved and his specific rotation values for many complexes have been shown to be too low, it must always be remembered that Werner was the pioneer who first opened the door to a previously unsuspected field. In his last works, he stood on the threshold of an extremely complicated research area—the investigation of optically active coordination compounds containing optically active ligands. Had the powerful, creative trend of his life not been cut short by his untimely death, there is no telling what Alfred Werner might have accomplished in this field.

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REFERENCES

1 G.B. Kauffman, *Alfred Werner–Founder of Coordination Chemistry*, Springer-Verlag, Berlin, 1966.
2 A.G. Sykes and J.A. Weil, *Progr. Inorg. Chem.*, 13 (1970) 1–106, p. 2.
3 A.W. Stewart, *Stereochemistry*, Longmans, Green and Co., London, 1st edn., 1907, 2nd edn., 1919.
4 G. Wittig, *Stereochemie*, Akademische Verlagsgesellschaft, Leipzig, 1930, Chap. 3.
5 F.M. Jaeger, *Spatial Arrangements of Atomic Systems and Optical Activity; Methods, Results and Problems of Precise Measurements at High Temperatures; The Constitution and Structure of Ultramarines*, McGraw-Hill, New York, 1930, Part 1.
6 P. Pfeiffer, Komplexverbindungen, in K. Freudenberg (Ed.), *Stereochemie: Eine Zusammenfassung der Ergebnisse, Grundlagen und Probleme*, Franz Deuticke, Leipzig, 1933, pp. 1200–1377.
7 W.C. Fernelius, Structure of coordination compounds, in R.E. Burk and O. Grummitt (Eds.), *Chemical Architecture*, Interscience, New York, 1948, Chap. 3, pp. 85, 91, 92.
8 F. Basolo, Stereoisomerism of hexacovalent atoms, in J.C. Bailar, Jr. (Ed.), *The Chemistry of the Coordination Compounds*, Reinhold, New York, 1956, pp. 308–353.
9 F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, John Wiley, New York, 1st edn., 1958, 2nd edn., 1967.
10 R.G. Wilkins and M.J.G. Williams, The isomerism of complex compounds, in J. Lewis and R.G. Wilkins (Eds.), *Modern Coordination Chemistry*, Interscience, New York, 1960, pp. 174–228.
11 M.M. Jones, *Elementary Coördination Chemistry*, Prentice-Hall, Englewood Cliffs, N. J., 1964, Chap. 6.
12 S. Kirschner, Optically active coordination compounds, in W.L. Jolly (Ed.), *Preparative Inorganic Reactions*, Interscience, New York, 1964, Chap. 2.
13 T.M. Lowry, *Optical Rotatory Power*, Dover Publications, New York, 1964.
14 B.E. Douglas, *Advan. Chem. Ser.*, 62 (1967) 357–365.

15 A.M. Sargeson, Optical phenomena in metal chelates, in F.P. Dwyer and D.P. Mellor (Eds.), *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964, Chap. 5.
16 C.L. Hawkins, *Absolute Configuration of Metal Complexes*, Wiley-Interscience, New York, 1971.
17 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 58, Part B, Verlag Chemie, Berlin, 1930.
18 *Gmelins Handbuch der Anorganischen Chemie*, System No. 58, Part B, Ergänzungsband, Lieferung 2, Verlag Chemie, Weinheim/Bergstrasse, 1964.
19 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 52, Part C, Verlag Chemie, Weinheim/Bergstrasse, 1965.
20 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 59, Part B, Lieferung 2, Verlag Chemie, Weinheim/Bergstrasse, 1930, pp. 329–330.
21 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 64, Verlag Chemie, Weinheim/Bergstrasse, 1938 (reprint 1955).
22 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 68, Part D, Verlag Chemie, Weinheim/Bergstrasse, 1957.
23 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 67, Verlag Chemie, Weinheim/Bergstrasse, 1939.
24 P. Job, Complexes du cobalt trivalent, in P. Pascal (Ed.), *Nouveau Traité de Chimie Minérale*, Vol. 18, Masson, Paris, 1959, pp. 413–737.
25 R. Duval and C. Duval, Complexes du chrome, in P. Pascal (Ed.), *Nouveau Traité de Chimie Minérale*, Vol. 14, Masson, Paris, 1959, pp. 415–551.
26 C. Duval, Sels et complexes du fer, in P. Pascal (Ed.), *Nouveau Traité de Chimie Minérale*, Vol. 18, Masson, Paris, 1959, pp. 1–221.
27 P. Poulenc and G. Ciepka, Rhodium, in P. Pascal (Ed.), *Nouveau Traité de Chimie Minérale*, Vol. 19, Masson, Paris, 1958, pp. 282–464.
28 C. Duval, Platine, in P. Pascal (Ed.), *Nouveau Traité de Chimie Minérale*, Vol. 19, Masson, Paris, 1958, pp. 657–731.
29 M. Delépine, Iridium, in P. Pascal (Ed.), *Nouveau Traité de Chimie Minérale*, Vol. 19, Masson, Paris, 1958, pp. 465–575.
30 A. King, *Inorganic Preparations: A Systematic Course of Experiments*, rev. edn., George Allen & Unwin, London, 1950, pp. 115–116.
31 W.G. Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, Cambridge, 1954.
32 G.G. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publishing Co., New York, 1962.
33 D.N. Grindley, *An Advanced Course in Practical Inorganic Chemistry*, Butterworths, London, 1964, p. 75.
34 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd edn., Academic Press, New York, 1965, Vol. 2.
35 G. Pass and H. Sutcliffe, *Practical Inorganic Chemistry*, Chapman and Hall, London, 1968.
36 R.J. Angelici, *Synthesis and Technique in Inorganic Chemistry*, W.B. Saunders Co., Philadelphia, 1969, p. 66.
37 M.L. Tobe and D.F. Martin, *Inorg. Syn.*, 8 (1966) 198–202.
38 J.W. Vaughn and R.D. Lindholm, *Inorg. Syn.*, 9 (1967) 163–166.
39 H.F. Holtzclaw, Jr., D.P. Sheetz and B.D. McCarty, *Inorg. Syn.*, 4 (1953) 176–179.
40 F.P. Dwyer and F.L. Garvan, *Inorg. Syn.*, 6 (1960) 195–197.
41 E.P. Harbulak and M.J. Albinak, *Inorg. Syn.*, 8 (1966) 196–198.
42 J.H. Worrell, *Inorg. Syn.*, 13 (1972) 195–202.
43 J.C. Bailar, Jr., *Inorg. Syn.*, 2 (1946) 222–225.
44 G.B. Kauffman, N. Sugisaka and I.K. Reid, *J. Chem. Educ.*, 41 (1964) 461–462.
45 J.B. Work, *Inorg. Syn.*, 2 (1946) 221–222.
46 J.A. Broomhead, F.P. Dwyer and J.W. Hogarth, *Inorg. Syn.*, 6 (1960) 183–186.
47 J.A. Broomhead, F.P. Dwyer and J.W. Hogarth, *Inorg. Syn.*, 6 (1960) 186–188.
48 J.C. Bailar, Jr. and E.M. Jones, *Inorg. Syn.*, 1 (1939) 35–38, p. 37.
49 G.B. Kauffman, L.T. Takahashi and N. Sugisaka, *Inorg. Syn.*, 8 (1966) 207–211.
50 G.B. Kauffman and L.T. Takahashi, *J. Chem. Educ.*, 39 (1962) 481–483.
51 G.B. Kauffman and R.P. Pinnell, *Inorg. Syn.*, 6 (1946) 176–179.
52 C.L. Rollinson and J.C. Bailar, Jr., *Inorg. Syn.*, 2 (1946) 200–202.
53 C.L. Rollinson and J.C. Bailar, Jr., *Inorg. Syn.*, 2 (1946) 196–200.
54 D. Berman, G. Bokerman and R.W. Parry, *Inorg. Syn.*, 10 (1967) 35–42, p. 40.

55 F. Galsbøl, *Inorg. Syn.*, 12 (1970) 269–280.

56 R.D. Gillard and P.R. Mitchell, *Inorg. Syn.*, 13 (1972) 184–186.

57 W.N. Shepard, *Inorg. Syn.*, 13 (1972) 233.

58 G.B. Kauffman, *Classics in Coordination Chemistry, Part I: The Selected Papers of Alfred Werner*, Dover Publications, New York, 1968.

59 G.B. Kauffman, *Classics in Coordination Chemistry, Part II: Selected Papers (1798–1935)*, Dover Publications, New York, in press.

60 A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischem Chemie*, Friedrich Vieweg, Braunschweig, (a) 3rd edn., 1913, pp. 360–370; (b) 4th edn., P. Karrer (Ed.), 1920, pp. 370–382; (c) 5th edn., P. Pfeiffer (Ed.), 1923, pp. 365–377.

61 A. Werner and V.L. King, *Ber. Deut. Chem. Ges.*, 44 (1911) 1887–1898. For a discussion of this paper and an English translation by G.B. Kauffman see ref. 58, pp. 155–173.

62 A. Werner, *Ber. Deut. Chem. Ges.*, 44 (1911) 2445–2455.

63 A. Werner, *Ber. Deut. Chem. Ges.*, 44 (1911) 3272–3278.

64 A. Werner, *Ber. Deut. Chem. Ges.*, 44 (1911) 3279–3284.

65 A. Werner, *Ber. Deut. Chem. Ges.*, 45 (1912) 121–130.

66 A. Werner and T.P. McCutcheon, *Ber. Deut. Chem. Ges.*, 45 (1912) 3281–3287.

67 A. Werner and Y. Shibata, *Ber. Deut. Chem. Ges.*, 45 (1912) 3287–3293.

68 A. Werner and G. Tschernoff, *Ber. Deut. Chem. Ges.*, 45 (1912) 3294–3301.

69 A. Werner, *Ber. Deut. Chem. Ges.*, 46 (1913) 3674–3683.

70 A. Werner, H. Kuh and P. Wüst, *Ber. Deut. Chem. Ges.*, 47 (1914) 1961–1979.

71 A. Werner and J. Bosshart, *Ber. Deut. Chem. Ges.*, 47 (1914) 2171–2182.

72 A. Werner, *Ber. Deut. Chem. Ges.*, 47 (1914) 3087–3094. For a discussion of this paper and an English translation by G.B. Kauffman see ref. 58, pp. 175–184.

73 A. Werner, *Helv. Chim. Acta*, 1 (1918) 5–32.

74 A. Werner and S. Matissen, *Helv. Chim. Acta*, 1 (1918) 78–84.

75 A. Werner, J.E. Schwyzer and W. Karrer, *Helv. Chim. Acta*, 4 (1921) 113–129.

76 A. Werner, *Ber. Deut. Chem. Ges.*, 44 (1911) 3132–3140.

77 A. Werner, *Ber. Deut. Chem. Ges.*, 45 (1912) 865–869.

78 A. Werner, *Ber. Deut. Chem. Ges.*, 45 (1912) 3061–3070.

79 A. Werner, *Ber. Deut. Chem. Ges.*, 45 (1912) 1228–1236.

80 A. Werner and J. Poupardin, *Ber. Deut. Chem. Ges.*, 47 (1914) 1954–1960.

81 A. Werner, *Ber. Deut. Chem. Ges.*, 45 (1912) 433–436.

82 A. Werner, *Vierteljahresschr. Naturforsch. Ges. Zuerich*, 62 (1917) 553–564.

83 A. Werner and A.P. Smirnoff, *Helv. Chim. Acta*, 3 (1920) 472–486.

84 A. Werner, *Arch. Sci. Phys. Natur.*, [4] 32 (1911) 457–467.

85 A. Werner, *Chem.-Ztg.*, 44 (1912) 401.

86 A. Werner, Über die asymmetrisch gebauten chemischen Moleküle, in *Universität Zürich, Festgabe zur Einweihung der Neubauten, 18. April 1914*, Schulthess, Zürich, 1914, pp. 65–79

87 A. Werner, Über spiegelbildisomere Metallverbindungen, *Lecture*, Karlsruhe, 1911.

88 A. Werner, Über optisch-aktive Kobaltverbindungen, *Lecture before the Zürcher Chemische Gesellschaft*, Zürich, July, 1911 and the *Schweizerische Naturforschende Gesellschaft*, Solothurn, Switzerland, August 1st, 1911.

89 A. Werner, Über neue optisch-isomere Metallverbindungen, *Lecture before the Schweizerische Chemische Gesellschaft*, Basel, March 2nd, 1912.

90 A. Werner, Sur les composés métalliques à dissymétrie moléculaire, *Lecture before the Société Chimique de France*, Paris, May 24th, 1912, *Bull. Soc. Chim. Fr.*, [4] 11, No.14 (1912) I XXIV. For an English translation, see *Amer. Chem. J.* 48 (1912) 314–336.

91 A. Werner, Über Verbindungen mit zwei asymmetrischen Kobaltatomen, *Lecture before the Verein Deutscher Chemiker*, Freiburg im Breisgau, Germany, May 29th, 1912.

92 A. Werner, *Lecture on coordination compounds (Title unknown) before the Dansk Kemisk Forening*, Copenhagen, December 6th, 1913.

93 A. Werner, Über die Konstitution und Konfiguration von Verbindungen höherer Ordnung, Nobel lecture, Stockholm, December 11, 1913, in *Les Prix Nobel en 1913*, P.-A. Norstedt, Stockholm, 1914; *Naturwissenschaften*, 2 (1914) 1–7; *Sur la Constitution et la Configuration des Combinaisons d'Ordre elévé*, Editions de la Revue Politique et de la Revue Scientifique, Paris, n. d., [1914]; *J. Chim. Phys. Physicochim. Biol.*, 12 (1914) 133–152; On the constitution and configuration of compounds of higher order, in Nobel Foundation (Ed.), *Nobel Lectures in Chemistry, 1901–1921*, Elsevier, Amsterdam, 1966, pp. 256–269.

94 A. Werner, *Chem.-Ztg.*, 38 (1914) 793.

95 A. Werner, Neue Ergebnisse der Spaltungsversuche mit anorganischen Verbindungen, *Lecture held before the Schweizerische Chemische Gesellschaft*, Neuchâtel, Switzerland, May 2, 1914, in *Ansprachen zu Ehren des Herrn Prof. Dr. Werner gehalten bei der Versammlung vom 2. Mai 1914 in Neuenberg*, Imprimerie Th. Eberhard, Lausanne, Switzerland, 1914, pp. 35–47; *Arch. Sci. Phys. Natur.*, 37 (1914) 455.

96 A. Werner, Über anorganische Konstitutions- und Konfigurationsfragen, *Lecture held before the Naturforschende Gesellschaft Zürich*, June 8th, 1914.

97 A. Werner, Sur l'activité optique de composés chimiques sans carbone, *Lecture held before the Société Chimique de France*, Paris, August 17th, 1914, *C. R. Acad. Sci.*, 159 (1914) 426–429.

98 A. Werner, Über eine neue Isomerieart bei Kobaltverbindungen und Kobaltverbindungen mit asymmetrischem Kobalt und Kohlenstoff, *Lecture before the Schweizerische Naturforschende Gesellschaft*, Geneva, September 14th, 1914.

99 A. Werner, *Z. Anorg. Chem.*, 3 (1893) 267–330; reprinted as *Beitrag zur Konstitution anorganischer Verbindungen*, P. Pfeiffer (Ed.), Ostwald's Klassiker der exakten Wissenschaften No. 212, Akademische Verlagsgesellschaft, Leipzig, 1924. For a discussion of this paper and an English translation by G.B. Kauffman, see ref. 58, pp. 5–88.

100 A. Werner and A. Vilmos, *Z. Anorg. Chem.*, 21 (1899) 145–158.

101 A. Werner, W. Spruck, W. Megerle and J. Pastor, *Z. Anorg. Chem.*, 21 (1899) 201–242.

102 A. Werner, H. Müller, R. Klien and F. Bräunlich, *Z. Anorg. Chem.*, 22 (1899) 91–157.

103 A. Werner and H.E. Conrad, *Ber. Deut. Chem. Ges.*, 32 (1899) 3046–3055.

104 A. Werner, *Ber. Deut. Chem. Ges.*, 34 (1901) 1705–1719.

105 A. Werner and E. Humphrey, *Ber. Deut. Chem. Ges.*, 34 (1901) 1719–1732.

106 A. Werner, *Ber. Deut. Chem. Soc.*, 34 (1901) 1733–1738.

107 A. Werner and L. Gerb, *Ber. Deut. Chem. Ges.*, 34 (1901) 1739–1745.

108 A. Werner, *Ber. Deut. Chem. Ges.*, 34 (1901) 2584–2593.

109 A. Werner and E. Berl, *Ber. Deut. Chem. Ges.*, 38 (1905) 893–899.

110 A. Werner, F. Bräunlich, E. Rogowina and C. Kreutzer, Über raumisomere Hexamminsalze, in *Festschrift Adolf Lieben zum fünfzigjährigen Doktorjubiläum und zum siebzigsten Geburtstage von Freunden, Verehren und Schülern gewidmet*, C.F. Winter'sche Verlagsbuchhandlung, Leipzig, 1906, pp. 197–218; reprinted in *Justus Liebigs Ann. Chem.*, 351 (1907) 65–86.

111 A. Werner and G. Jantsch, *Ber. Deut. Chem. Ges.*, 40 (1907) 262–271.

112 A. Werner and E. Zinggeler, *Ber. Deut. Chem. Ges.*, 40 (1907) 765–788.

113 A. Werner and K. Dawe, *Ber. Deut. Chem. Ges.*, 40 (1907) 789–799.

114 A. Werner, E. Berl, E. Zinggeler and G. Jantsch, *Ber. Deut. Chem. Ges.*, 40 (1907) 2103–2125.

115 A. Werner and A. Fröhlich, *Ber. Deut. Chem. Ges.*, 40 (1907) 2225–2235.

116 A. Werner, *Ber. Deut. Chem. Ges.*, 40 (1907) 4441–4449.

117 A. Werner, *Ber. Deut. Chem. Ges.*, 40 (1907) 4817–4825. For a discussion of this paper and an English translation by G.B. Kauffman, see Ref. 58, pp. 141–154.

118 A. Werner and O. de Vries, *Justus Liebigs Ann. Chem.*, 364 (1909) 77–127.

119 A. Werner, *Justus Liebigs Ann. Chem.*, 375 (1910) 1–144. An English translation by G.G. Christoph, California Institute of Technology, Pasadena, *On Polynuclear Metal-Ammines*, is available from University Microfilms, Ann Arbor, Michigan, as Order No. 70–12, 256 (1969).

120 A. Werner, *Ber. Deut. Chem. Ges.*, 44 (1911) 873–882.

121 A. Werner, *Justus Liebigs Ann. Chem.*, 386 (1912) 1–272.

122 A. Werner and M. Basyrin, *Ber. Deut. Chem. Ges.*, 46 (1913) 3229–3232.

123 A. Werner, E. Bindschedler, E. Blatter, C. Sackur, H. Schwarz and H. Surber, *Justus Liebigs Ann. Chem.*, 405 (1914) 212–241.

124 H.E. Conrad, *Über optisch aktive Hexahydrophthalsäuren, Dissertation*, Universität Zürich, 1898.

125 F. Bräunlich, *Über Dirhodanatokobaltiake und Strukturisomerie bei anorganischen Verbindungen, Dissertation*, Universität Zürich, 1899.

126 A.R. Klien, *Über die Bindefestigkeit der negativen Reste in den Kobalt-, Chrom- und Platinammoniaken. Über eine neue Nitritorhodanatotetraminkobalt-Reihe, Dissertation*, Universität Zürich, 1899.

127 J. Pastor, *Ueber Propylendiamin-Metallsalze, Dissertation*, Universität Zürich, 1900.

128 K. Dawe, *Ueber Hexamminmetallsalze und Dirhodanatokobaltiake, Dissertation*, Universität Zürich, 1901.

129 A. Fröhlich, *Ueber Propylendiaminverbindungen, Dissertation*, Universität Zürich, 1901.
130 E. Humphrey, *Über die Bildungsstelle der Metalle in ihren Verbindungen und über Dinitrodiäthylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1901.
131 L. Gerb, *Zur Kenntnis der Diaethylendiamin-Kobalti-Verbindungen, Dissertation*, Universität Zürich, 1902.
132 C. Popovici, *Ueber isomere Dinitrodiaethylendiamincobalt-Verbindungen, Dissertation*, Universität Zürich, 1902.
133 E. Zinggeler, *Ueber Rhodankobaltsalze, Dissertation*, Universität Zürich, 1902.
134 N. Goslings, *Ueber Carbonato- und Rhodanatonitrokobaltiake, Dissertation*, Universität Zürich, 1903.
135 H. Schwarz, *Über die Beziehungen zwischen Metallammoniaken und komplexen Salzen, Dissertation*, Universität Zürich, 1903.
136 P. Larisch, *Über die Abhängigkeit der Löslichkeit von der Anzahl der Ionen bei den Kobalt-Chrom-, Rhodium-, Iridium- und Platin-Ammoniaken, Dissertation*, Universität Zürich, 1904.
137 C. Rix, *Über Aethylendiaminkobaltiake, Dissertation*, Universität Zürich, 1904.
138 C. Kreutzer, *Über geometrisch isomere Hexamminreihen und Nitrito-nitrato-diaethylendiamin-Kobalt-Verbindungen, Dissertation*, Universität Zürich, 1906.
139 G. Lindenberg, *Über Trimethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1906.
140 G. Jantsch, *Untersuchungen über Koordinationsverbindungen, Dissertation*, Universität Zürich, 1907.
141 O. de Vries, *Over Complexe Iridiumverbindungen, Dissertation*, Rijks-Universiteit te Leiden, 1908.
142 F. Chaussy, *Über Stereoisomerie bei Dichloroaethylendiamindiamminkobaltisalzen, Dissertation*, Universität Zürich, 1909.
143 R. Hartmuth, *Über Nitro- und Nitritosalze, Dissertation*, Universität Zürich, 1909.
144 D. Miklosich, *Ueber isomere Dinitrodipropylendiaminkobaltverbindungen, Dissertation*, Universität Zürich, 1909.
145 J. Rapiport, *Über Karbonatosalze der Diaethylendiaminkobaltreihe, Dissertation*, Universität Zürich, 1909.
146 W.E. Boës, *Nitro- und Nitritoverbindungen der Metallammoniake, insbesondere der Kobaltiake, Dissertation*, Universität Zürich, 1910.
147 H.A. Tschudi, *Zur Kenntnis der Walden'schen Umkehrung, Dissertation*, Universität Zürich, 1910.
148 E. Blatter, *Über komplexe Verbindungen mit Oxalsäure, Dissertation*, Universität Zürich, 1912.
149 A. Gordienko, *Untersuchungen über die Beziehungen zwischen Farbe und Konstitution chemischer Verbindungen, Dissertation*, Universität Zürich, 1912.
150 V.L. King, *Über Spaltungsmethode und ihre Anwendung auf komplexe Metall-Ammoniakverbindungen, Dissertation*, Universität Zürich, 1912.
151 S. Matissen, *Zur Kenntnis der inneren Komplexsalze, Dissertation*, Universität Zürich, 1912.
152 R. Šamánek, *Über die Einwirkung von Ammoniak und Pyridin auf Dichlorodiaethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1912.
153 H.E. Watts, *Ueber Kobaltiake mit assymmetrischen Kohlenstoffatomen, Dissertation*, Universität Zürich, 1912.
154 C.S. Borzekowski, *Ueber optisch-aktive, hydroxylaminhaltige Kobaltiake, Dissertation*, Universität Zürich, 1913.
155 A. Fraenkel, *Ueber optisch-aktive Bromo-nitro-diaethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1913.
156 F. Niemand, *Über optisch-aktive Kobaltammoniake, Dissertation*, Universität Zürich, 1913.
157 P. Wüst, *Zur Kenntnis der mehrkernigen Kobaltiake, Dissertation*, Universität Zürich, 1913.
158 J. Angerstein, *Ueber die Absorptionsspektren von Metallammoniaken, Dissertation*, Universität Zürich, 1914.
159 J. Bosshart, *Anomale Erscheinungen bei der Spaltung von Racemverbindungen, Dissertation*, Universität Zürich, 1914.
160 J. Flood, *Ueber Hexamminsalze mit zweiwertigen Diaminen im Komplex, Dissertation*, Universität Zürich, 1914.
161 E. Gurewitsch, *Ueber optisch aktive Chloro-nitro- und Nitro-isorhodanato-diaethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1914.
162 N. Helberg, *Isomere Propylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1914.
163 R. Hessen, *Ueber optisch-aktive Dinitrodiaethylendiamin-Kobaltisalze, Dissertation*, Universität Zürich, 1914.
164 G. Toepke, *Über die Waldensche Umkehrung, Dissertation*, Universität Zürich, 1914.

165 M. Basyrin, *Ueber Spaltung der Dikarbonsäuren und über optisch aktive Dimethylbernsteinsäuren, Dissertation*, Universität Zürich, 1915.

166 H. Biland, *Optisch aktive Trioxalokobaltiake, Dissertation*, Universität Zürich, 1915.

167 W. Bremy-Schulthess, *Untersuchungen über Oxalodiäthylendiaminchromisalze, Dissertation*, Universität Zürich, 1915.

168 L. Karpf, *Komplexe Eisenverbindungen, Dissertation*, Universität Zürich, 1915.

169 L.L. Lehrfeld, *Zur Kenntnis der optisch-aktiven Triäthylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1915.

170 A. Müller, *Ueber Bromammindiäthylendiaminkobaltisalze und daraus dargestellte Reihen, Dissertation*, Universität Zürich, 1915.

171 H. Surber, *Stereo-Isomerie bei Dioxalo-Chromiaten, Dissertation*, Universität Zürich, 1915.

172 W. Tupizina, *Untersuchungen über die optische Aktivität von Kobaltverbindungen, Dissertation*, Universität Zürich, 1915.

173 A. Bertossa, *Über Diaethylendiamin-l-propylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1916.

174 E. Lüscher, *Ueber Pentammin- und Hexamminsalze mit Imidazol und Trimethylendiamin, Dissertation*, Universität Zürich, 1917.

175 H. Hürlimann, *Ueber optisch aktive Dinitro-l-propylendiamin-d-propylendiamin-Kobaltisalze, Dissertation*, Universität Zürich, 1918.

176 N. Zaremba, *Die optisch-aktiven s-Diphenylbernsteinsäuren, Dissertation*, Universität Zürich, 1918.

177 R. von Arx, *Ueber aktive Isorhodanatoammindiaethylendiamin-Kobaltisalze, Dissertation*, Universität Zürich, 1919.

178 O. Dätwiler, *Zur Kenntnis der optisch-aktiven cis-Bromonitrodiaethylendiamin-Kobaltisalze, Dissertation*, Universität Zürich, 1919.

179 H. Fischlin, *Ueber optisch aktive Chloro-aquodiaethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1919.

180 W. Karrer, *Ueber optisch inaktive und aktive Diathylendiaminkobaltpropionylacetonatosalze, Dissertation*, Universität Zürich, 1919.

181 J.E. Schwyzer, *Ueber Acetylacetonatodiaethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1919.

182 I. Wilbuschewitsch, *Ueber Diacido-diaethylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1919.

183 A. Tommasi, *Über optisch-aktive Propylendiaminkobaltisalze, Dissertation*, Universität Zürich, 1920.

184 C. Schleicher, *Über Absorptionsspektren von Komplexsalzen, Dissertation*, Universität Zürich, 1921.

185 F. Wöhler, *Pogg. Ann. Phys. Chem.*, 12 (1828) 253–256.

186 J.B. Biot, *Mem. Inst. Fr., Cl. Sci., Mat., Phys.*, 13, 1 (1812) 1.

187 J.A. Le Bel, *Bull. Soc. Chim. Fr.*, [2] 22 (1874) 337–347. An English translation appears in G.M. Richardson, *Foundations of Stereochemistry*, American Book Co., New York, 1901, pp. 49–59 and in O.T. Benfey, *Classics in the Theory of Chemical Combination*, Dover Publications, New York, 1963, pp. 161–171.

188 J.H. van't Hoff, *Voorstel tot Uitbreiding der Tegenwoordig in de Scheikunde Gebruikte Structuurformules in de Ruimte*, J. Greven, Utrecht, 1874. An English translation appears in G.M. Richardson, *Foundations of Stereochemistry*, American Book Co., New York, 1901, pp. 37–46 and in O.T. Benfey, *Classics in the Theory of Chemical Combination*, Dover Publications, New York, 1963, pp. 151–160.

189 G.B. Kauffman, *Chemistry*, 39 (12) (1966) 14–18.

190 G.B. Kauffman, *Educ. Chem.*, 4 (1967) 11–18.

191 W.J. Pope and S.J. Peachey, *J. Chem. Soc., London*, 75 (1899) 1127–1131; W.J. Pope and A.W. Harvey, *J. Chem. Soc., London*, 79 (1901) 828–841; H.O. Jones, *J. Chem. Soc., London*, 83 (1903) 1400–1421; 85 (1904) 223–234.

192 J. Meisenheimer and L. Lichtenstadt, *Ber. Deut. Chem. Ges.*, 44 (1911) 356–359.

193 S. Smiles, *J. Chem. Soc., London*, 77 (1900) 1174–1179; W.J. Pope and S.J. Peachey, *J. Chem. Soc., London*, 77 (1900) 1072–1075.

194 W.J. Pope and A. Neville, *J. Chem. Soc., London*, 81 (1902) 1552–1563.

195 W.J. Pope and S.J. Peachey, *Proc. Chem. Soc., London*, 16 (1900) 42, 116.

196 F.S. Kipping, *J. Chem. Soc., London*, 91 (1907) 209–240; B.D.W. Luff and F.S. Kipping, *J. Chem. Soc., London*, 93 (1908) 2090–2098.

197 G.T. Morgan, *J. Chem. Soc., London*, 117 (1920) 1639–1648.

198 J. Read, *Humour and Humanism in Chemistry*, G. Bell, London, 1947, pp. 262–296.

199 P. Karrer, Prof. Alfred Werner, in *Neue Zürcher Zeitung*, No, 1804, Erstes Morgenblatt, Feuilleton, p. 1, November 21st, 1919; reprinted in *Vierteljahresschr. Naturforsch. Ges. Zuerich*, 64 (1919) 851–854.

200 J. Lifschitz, *Z. Elektrochem.*, 26 (1920) 514–529.

201 For a detailed discussion of the experimental work leading to the first resolution of optically active coordination compounds and speculations concerning the work see ref. 58, pp. 155–158, and G.B. Kauffman, *Isis*, 64 (1974).

202 V.L. King, *J. Chem. Educ.*, 19 (1942) 345.

203 This book is preserved in the Chemistry Laboratory Library at Dartmouth College, Hanover, New Hampshire, from which King received his bachelor's degree in 1907.

204 J.C. Bailar, Jr. and R.W. Auten, *J. Amer. Chem. Soc.*, 56 (1934) 774–776.

205 J.C. Bailar, Jr., F.G. Jonelis and E.H. Huffman, *J. Amer. Chem. Soc.*, 58 (1936) 2224–2226.

206 J.C. Bailar, Jr. and D.F. Peppard, *J. Amer. Chem. Soc.*, 62 (1940) 820–823.

207 L. Pasteur, *C. R. Acad. Sci.*, 35 (1852) 176–183.

208 F.S. Kipping and W.J. Pope, *J. Chem. Soc., London*, 63 (1893) 548–604.

209 F.S. Kipping and W.J. Pope, *J. Chem. Soc., London*, 67 (1895) 354–368, p. 356.

210 W.J. Pope and J. Read, *J. Chem. Soc., London*, 97 (1910) 2199–2206, p. 2200.

211 H. Regler and F. Hein, *J. Prakt. Chem.*, 148 (1937) 1–4.

212 G.B. Kauffman, *J. Prakt. Chem.*, [4] 33 (1966) 295–297.

213 S.M. Jørgensen, *J. Prakt. Chem.*, [2] 41 (1890) 440–459.

214 G.B. Kauffman, *J. Chem. Educ.*, 36 (1959) 521–527.

215 G.B. Kauffman, *Chymia*, 6 (1960) 180–204.

216 R. Huber, *Schweiz. Chem.-Ztg.*, 7 (1920) 73–80.

217 Y. Shibata and R.E. Lyle, personal communications to G.B. Kauffman.

218 H. Landolt, *Ber. Deut. Chem. Ges.*, 28 (1895) 3102–3104.

219 H. Landolt, *Ber. Deut. Chem. Ges.*, 29 (1896) 2404.

220 F. Lippich, *Z. Instrumentenk.*, 2 (1882) 167.

221 F. Lippich, *Z. Instrumentenk.*, 14 (1894) 326.

222 H.W. Nernst, *Z. Elektrochem.*, 6 (1899) 41.

223 H.W. Nernst, *Z. Elektrochem.*, 7 (1900) 373.

224 J.-P. Mathieu, *Bull. Soc. Chim. Fr.*, [5] 4 (1937) 687–700.

225 J. Meyer and O. Rampoldt, *Z. Anorg. Chem.*, 214 (1933) 1–15.

226 J. Lifschitz, *Z. Phys. Chem.*, 105 (1923) 27–54.

227 T. Bürer, *Helv. Chim. Acta*, 46 (1963) 242–255.

228 J.-P. Mathieu, *Bull. Soc. Chim. Fr.*, [5] 3 (1936) 463–475, 476–498.

229 J.G. Brushmiller, E.L. Amma and B.E. Douglas, *J. Amer. Chem. Soc.*, 84 (1962) 3227–3233.

230 L. Gerb, *Zh. Russ. Fiz.-Khim. Obshchest., Chast. Khim.*, 37 (1905) 43.

231 J. Meisenheimer and E. Kiderlin, *Justus Liebigs Ann. Chem.*, 438 (1924) 217–278.

232 J. Brüll, *C. R. Acad. Sci.*, 202 (1936) 1584–1586; 204 (1937) 349–352.

233 R.G. Pearson, R.E. Meeker and F. Basolo, *J. Amer. Chem. Soc.*, 78 (1956) 2673–2676.

234 F. Basolo, *J. Amer. Chem. Soc.*, 72 (1950) 4393–4397.

235 H. Kuroya, M. Aimi and R. Tsuchida, *J. Chem. Soc. Jap.*, 64 (1943) 995–998.

236 L.F. Druding and G.B. Kauffman, *Coord. Chem. Rev.*, 3 (1968) 409–428.

237 J.-P. Mathieu, *C. R. Acad. Sci.*, 199 (1934) 278–280.

238 M.J. Albinak, D.C. Bhatnagar, S. Kirschner and A. J. Sonnessa, The effects of optically inactive ions on the rotatory dispersion of asymmetric complex ions, in S. Kirschner (Ed.), *Advances in the Chemistry of the Coordination Compounds*, Macmillan, New York, 1961, pp. 154–172.

239 S.M. Jørgensen, *J. Prakt. Chem.*, [2] 39 (1889) 1–26.

240 J.A.N. Friend, *J. Chem. Soc., London*, 109 (1916) 715–722, p. 717. For a discussion and an edited version of this paper by G.B. Kauffman, see ref. 59.

241 E.E. Turner, *J. Chem. Soc., London*, 109 (1916) 1130–1134.

242 G.K. Schweitzer and C.K. Talbott, *J. Tenn. Acad. Sci.*, 25 (1950) 143–147.

243 R. Tsuchida, M. Kobayashi and A. Nakamura, *J. Chem. Soc. Jap.*, 56 (1935) 1339–1345.

244 P. Walden, *Ber. Deut. Chem. Ges.*, 26 (1893) 210–215.

245 P. Walden, *Ber. Deut. Chem. Ges.*, 28 (1895) 2766–2773.

246 P. Walden, *Ber. Deut. Chem. Ges.*, 29 (1896) 133–138.

247 P. Walden, *Optische Umkehrerscheinungen (Waldensche Umkehrung)*, F. Vieweg, Braunschweig, 1919.

248 W.R. Matoush and F. Basolo, *J. Amer. Chem. Soc.*, 78 (1956) 3972–3976.

249 J.C. Bailar, Jr., *Chem. Zvesti*, 19 (1965) 153–160 (in English).
250 J.C. Bailar, Jr., *Rev. Pure Appl. Chem.*, 16 (1966) 91–101.
250a L.J. Boucher, E. Kyuno and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 86 (1964) 3656–3660.
250b E. Kyuno, L.J. Boucher and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 87 (1965) 4458–4462.
250c E. Kyuno and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 88 (1966) 1120–1124.
251 J.C. Bailar, Jr., J.H. Haslam and E.M. Jones, *J. Amer. Chem. Soc.*, 58 (1940) 2226–2227; E. Kyuno and J.C. Bailar, Jr., *J. Amer. Chem, Soc.*, 88 (1966) 1125–1128.
252 Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, 37 (1915) Article 2, pp. 12, 13.
253 K. Matsuno, *J. Coll. Sci., Imp. Univ. Tokyo*, 41 (1921) Article 10, p. 20.
254 H. Krebs, J. Diewald, H. Arlitt and J.A. Wagner, *Z. Anorg. Chem.*, 287 (1956) 98–105.
255 M. Delépine, *Bull. Soc. Chim. Fr.*, [4] 29 (1921) 656–669.
256 M. Delépine, *Bull. Soc. Chim. Fr.*, [5] 1 (1934) 1256–1266.
257 R.M. Secor, *Chem. Rev.*, 63 (1963) 297–309.
258 J.C, Bailar, Jr., *Chem. Rev.*, 19 (1936) 67–87, p. 79.
259 J.-P. Mathieu, *C. R. Acad. Sci.*, 201 (1935) 1183–1184.
260 J. P. Fackler, Jr., *Advan. Chem. Ser.*, 62 (1967) 580–589.
261 J.C. Bailar, Jr., C.A. Stiegman, J.H. Balthis and E.H. Huffman, *J. Amer. Chem. Soc.*, 61 (1939) 2402–2404.
262 J.C. Bailar, Jr., H.B. Jonassen and A.D. Gott, *J. Amer. Chem. Soc.*, 74 (1952) 3131–3134.
263 F.P. Dwyer and A.M. Sargeson, *J. Phys. Chem.*, 60 (1956) 1331–1332.
264 G.B. Kauffman and L. T. Takahashi, *Inorg. Syn.*, 8 (1966) 227–232.
265 J.W. Vaughn and D.J. Walkwitz, *Inorg. Chem.*, 5 (1966) 1082–1083.
266 J.W. Vaughn, V.E. Magnuson and G.J. Seiler, *Inorg. Chem.*, 8 (1969) 1201–1202.
267 H.B. Gray, R. Eisenberg and E.I. Stiefel, *Advan. Chem. Ser.*, 62 (1967) 641–650
268 F.M. Jaeger, *Akad. Amsterdam Versl.*, 23 (1914–1915) 1305–1311.
269 F.M. Jaeger, *Z. Kristallogr. Mineral.*, 55 (1915) 209–248.
270 H. Krebs and R. Rasche, *Z. Anorg. Chem.*, 276 (1954) 236–246.
271 V. Carassiti, *Ann. Chim. (Rome)*, 46 (1956) 1112–1120; 47 (1957) 1337–1358; 48 (1958) 167–176; *J. Phys. Chem.*, 55 (1958) 120–125.
272 F. Woldbye, Technique of optical rotatory dispersion and circular dichroism, in H.B. Jonassen and A. Weissbarger (Eds.), *Technique of Inorganic Chemistry*, Interscience, New York, 1965, Vol. 4, p. 249–368.
273 R.D. Gillard, *Progr. Inorg. Chem.*, 7 (1966) 215.
274 Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Crystallogr.*, 8 (1955) 723–730; *Bull. Chem. Soc. Jap.*, 30 (1957) 795–798.
275 R. Pepinsky, *Rec. Chem. Progr.*, 17 (1956) 145–189, p. 176.
276 E.J. Corey and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 81 (1959) 2620–2629.
277 K.V. Krishnamurty and G.M. Harris, *Chem. Rev.*, 61 (1961) 213–246.
278 *Gmelins Handbuch der Anorganischen Chemie*, 8th edn., System No. 58, Part A, Verlag Chemie, Berlin, 1932, pp. 420–425; System No. 58, Part A, Ergänzungsband, Verlag Chemie, Weinheim/Bergstrasse, 1961, pp. 792–797.
279 F.M. Jaeger, *Rec. Trav. Chim. Pays-Bas. Belg.*, 38 (1919) 250.
280 F.M. Jaeger and W. Thomas, *Proc. Kon. Ned. Akad. Wetensch.*, 21 (1919) 693–706.
281 W. Kuhn and J. Bein, *Z. Phys. Chem., Abt. B*, 24 (1934) 335; *Z. Anorg. Allg. Chem.*, 216 (1934) 321–348.
282 C.H. Johnson and A. Mead, *Trans. Faraday Soc.*, 29 (1933) 625; 31 (1938) 1621.
283 F.M. Jaeger and G. Berger, *Rec. Trav. Chim. Pays-Bas*, 40 (1921) 153.
284 R. Tsuchida, A. Nakamura and M. Kobayashi, *J. Chem. Soc. Jap.*, 56 (1935) 1335–1338.
285 G.B. Kauffman, L.T. Takahashi and N. Sugisaka, *Inorg. Syn.*, 8 (1966) 207–211.
286 N.W.D. Beese and C.H. Johnson, *Trans. Faraday Soc.*, 31 (1935) 1632.
287 E. Bushra and C.H. Johnson, *J. Chem. Soc., London*, (1939) 1937.
288 M. Billardon, *J. Chim. Phys. Physicochim. Biol.*, 61 (1964) 1070–1075.
289 W. Kuhn and R. Rometsch, *Helv. Chim. Acta*, 27 (1944) 1080.
290 For a review of Werner's research on polynuclear coordination compounds see G.B. Kauffman, *Coord. Chem. Rev.*, 9 (1973) 339–363.
291 J. Lifschitz, *Z. physik. Chem.*, 114 (1925) 490.
292 G.B. Kauffman, *Coord. Chem. Rev.*, 11 (1973) 161–188.
293 J. Kleinberg, *Unfamiliar Oxidation States and Their Stabilization*, University of Kansas Press, Lawrence, 1950.

294 U. Thewalt and R.E. Marsh, *J. Amer. Chem. Soc.*, 89 (1967) 6364. See also *Chem. Eng. News*, (Nov. 27, 1967) 38–39.
295 R.E. Marsh and W.P. Schaefer, *Acta Crystallogr., Sect. B*, 24 (1968) 246–251.
296 W.P. Schaefer, *Inorg. Chem.*, 7 (1968) 725–731.
297 W.P. Schaefer and R.E. Marsh, *J. Amer. Chem. Soc.*, 88 (1966) 178–179.
298 L.R. Thompson and W.K. Wilmarth, *J. Phys. Chem.*, 56 (1952) 5–9.
299 F.P. Dwyer and E.C. Gyarfas, *J. Proc. Roy. Soc. N. S. W.*, 83 (1949) 134, 174–176, 263–265.
300 F.P. Dwyer and E.C. Gyarfas, *Nature (London)*, 166 (1950) 481.
301 J.-P. Mathieu, *Bull. Soc. Chim. Fr.*, [5] 5 (1938) 105–113.
302 S.M. Jørgensen, *Z. Anorg. Chem.*, 16 (1898) 184–197.
303 U. Thewalt, unpublished work; D. Dixon, R.E. Marsh and W.P. Schaefer, unpublished work.
304 F.G. Mann, *J. Chem. Soc., London*, (1933) 412.
305 J.C. Bailar, Jr. and D.F. Peppard, *J. Amer. Chem. Soc.*, 62 (1940) 105–109.
306 N.I. Lobanov, *Zh. Neorg. Khim.*, 7 (1962) 48–51; *Russ. J. Inorg. Chem.*, 7 (1962) 23–25.
307 N.I. Lobanov, *Zh. Neorg. Khim.*, 2 (1957) 1035–1039, p. 1038; *Russ. J. Inorg. Chem.*, 2 (1957) 81–89, p. 87.
308 R.G. Pearson, C.R. Boston and F. Basolo, *J. Phys. Chem.*, 59 (1955) 304–308.
309 W. Feldt, *Ber. Deut. Chem. Ges.*, 27 (1894) 401–406.
310 J. Brigando, *Bull. Soc. Chim. Fr.*, (1957) 211–218, p. 212.
311 A. Werner, Untersuchungen über anorganische Konstitutions- und Konfigurations-Fragen, *Lecture before the Deutsche Chemische Gesellschaft*, Berlin, Nov. 3rd, 1906, published in *Ber. Deut. Chem. Ges.*, 40 (1907) 15–69, p. 60.
312 J.E. Boyle and G.M. Harris, *J. Amer. Chem. Soc.*, 80 (1958) 782–787.
313 J.C. Bailar, Jr. and J.B. Work, *J. Amer. Chem. Soc.*, 68 (1946) 232–235.
314 P. Pfeiffer, *Z. Anorg. Chem.*, 24 (1900) 279–304.
315 P. Pfeiffer, P. Koch, G. Lando and A. Trieschmann, *Ber. Deut. Chem. Ges.*, 37 (1904) 4255–4290.
316 P. Pfeiffer and R. Stern, *Z. Anorg. Chem.*, 58 (1908) 228–256.
317 P. Pfeiffer, *Beitrag zur Chemie der Molekülverbindungen, Habilitationsschrift*, Universität Zürich, 1902.
318 H.L. Schläfer and H. Seidel, *Z. Phys. Chem. (Frankfurt am Main)*, 16 (1958) 1–13.
319 F.M. Jaeger, *Bull. Soc. Chim. Fr.*, [5] 4 (1937) 1201–1220.
320 F.M. Jaeger, *Nachr. Ges. Wiss. Goettingen, Math.-Phys. Kl., Fachgruppe 3*, [2] 1 (1934–1938) 199–213.
321 G. Karagunis and G. Coumoulos, *Prakt. Akad. Athenon*, 13 (1938) 414–418; *Nature (London)*, 142 (1938) 162–163; *Atti. Congr. Int. Chim., 10th Roma, 1938*, Vol. 2, pp. 278–282.
322 A. Bussy, *Ann. Chem. Pharm.*, 29 (1839) 312.
323 H. Croft, *J. Prakt. Chem.*, 27 (1842) 431; *Phil. Mag.*, 21 (1842) 197.
324 F.A. Long, *J. Amer. Chem. Soc.*, 61 (1939) 570–572.
325 F.A. Long, *J. Amer. Chem. Soc.*, 63 (1941) 1353–1357.
326 P. Rây and N. Dutt, *J. Indian Chem. Soc.*, 20 (1943) 81.
327 J.C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 8 (1958) 165–175, p. 171.
328 M. Billardon, *J. Chim. Phys. Physicochim. Biol.*, 62 (1965) 273–280.
329 F. Blau, *Ber. Deut. Chem. Ges.*, 21 (1888) 1077–1078.
330 F. Blau, *Monatsh. Chem.*, 19 (1898) 651.
331 L.A. Welo, *Phil. Mag.*, [7] 6 (1928) 505–508.
332 R. Kuhn and A. Wassermann, *Justus Liebigs Ann. Chem.*, 503 (1933) 203–232.
333 F.M. Jaeger and J.A. van Dijk, *Proc. Kon. Ned. Akad. Wetensch.*, 37 (1934) 333–336.
334 F.M. Jaeger and J.A. van Dijk, *Z. Anorg. Chem.*, 227 (1936) 273–327.
335 C. Ferrari, *Gazz. Chim. Ital.*, 67 (1937) 604–608; *Ann. Chim. Appl.*, 27 (1937) 479–482.
336 K. Yamasaki, *Bull. Chem. Soc. Jap.*, 12 (1937) 390–394.
337 K. Yamasaki, *Bull. Chem. Soc. Jap.*, 15 (1940) 461–465.
338 F.W. Cagle, Jr. and G.F. Smith, *Anal. Chem.*, 19 (1947) 384–385.
339 P. Läuger, S. Fallab and H. Erlenmeyer, *Helv. Chim. Acta*, 37 (1954) 1050.
340 F. Basolo, J.C. Hayes and H.M. Neumann, *J. Amer. Chem. Soc.*, 76 (1954) 3807–3809.
341 F.M. Jaeger, *Chem. Weekbl.*, 14 (1917) 706.
342 F.M. Jaeger, *Akad. Amsterdam Versl.*, 26 (1917–1918) 166.
343 F.M. Jaeger, *Proc. Kon. Ned. Akad. Wetensch.*, 20 (1917) 244–262, p. 258.
344 F.M. Jaeger and H.B. Blumendal, *Z. Anorg. Allg. Chem.*, 175 (1928) 161.
345 F.M. Jaeger, *Proc. Kon. Ned. Akad. Wetensch.*, 40 (1937) 2–11, 108, 406, 574.

346 F.M. Jaeger and L. Bijkerk, *Proc. Kon. Ned. Akad. Wetensch.*, 40 (1937) 116.
347 M. Delépine and R. Charonnat, *Bull. Soc. Fr. Mineral.*, 53 (1930) 73–84.
348 F.M. Jaeger, *Akad. Amsterdam Versl.*, 26 (1917–1920) 157.
349 J.-P. Mathieu, *J. Chim. Phys., Rev. Gen. Colloides*, 33 (1936) 78–96.
350 E. Leidié, *C. R. Acad. Sci.*, 129 (1899) 1251.
351 J.-P. Mathieu, *C. R. Acad. Sci.*, 198 (1934) 1600.
352 F.M. Jaeger, *Proc. Kon. Ned. Akad. Wetensch.*, 20 (1917) 263–279, p. 264.
353 R. Charonnat, *Ann. Chim. (Paris)*, [10] 16 (1931) 152.
354 A.A. Grinberg and Kh.I. Gil'dengershel, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1948) 479–492.
355 A.P. Smirnoff, *Helv. Chim. Acta*, 3 (1920) 177.
356 I.I. Chernyaev, *Izv. Inst. Izuch. Platiny Drugikh Blagorod. Metal., Akad. Nauk SSSR*, 6 (1928) 40.
357 I.I. Chernyaev, *Izv. Inst. Izuch. Platiny Drugikh Blagorod. Metal., Akad. Nauk SSSR*, 8 (1931) 37.
358 M. Delépine, *C. R. Acad. Sci.*, 159 (1914) 239–241.
359 W. Palmaer, *Z. Anorg. Chem.*, 10 (1895) 376.
360 L.A. Chugaev and W. Sokolov, *Ber. Deut. Chem. Ges.*, 40 (1907) 173–181, p. 177.
361 L.A. Chugaev and W. Sokolov, *Ber. Deut. Chem. Ges.*, 42 (1909) 55–58.
362 J.C. Bailar, Jr., *Rec. Chem. Progr.*, 10 (1949) 17.
363 F.P. Dwyer, F.L. Garvan and A. Shulman, *J. Amer. Chem. Soc.*, 81 (1959) 290–294.
364 F.P. Dwyer and F.L. Garvan, *J. Amer. Chem. Soc.*, 81 (1959) 1043–1045.
365 F.P. Dwyer and A.M. Sargeson, *J. Amer. Chem. Soc.*, 81 (1959) 5269–5272.
366 F.P. Dwyer and A.M. Sargeson, *J. Amer. Chem. Soc.*, 81 (1959) 5272–5274.
367 F.P. Dwyer and F.L. Garvan, *J. Amer. Chem. Soc.*, 82 (1961) 2610–2615.
368 F.P. Dwyer, *Aust. J. Sci.*, B24 (1961) 97–103.
369 F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1958, pp. 289–302.
370 D.H. Busch, D.W. Cooke, K. Swaminathan and Y.A. Im, The stereochemistry and mechanism of some reactions of ethylenediaminetetraacetatocobaltate (III) and propylenediaminetetraacetatocobaltate(III), in S. Kirschner (Ed.), *Advances in the Chemistry of the Coordination Compounds*, Macmillan, New York, 1961, pp. 139–153.
371 W. Kuhn and A. Szabo, *Z. Phys. Chem., Abt. B*, 15 (1932) 59–73, p. 69.
372 J.-P. Mathieu, *C. R. Acad. Sci.*, 215 (1942) 325–327.
373 J.-P. Mathieu, *Ann. Phys. (Leipzig)*, [11] 19 (1944) 335–354, pp. 340, 341.
374 L.A.P. Kane-Maguire and T.E. MacDermott, *Inorg. Chem.*, 7 (1968) 769–771.
375 T.D. O'Brien, J.P. McReynolds and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 70 (1948) 749–755.
376 W.E. Cooley, C.F. Liu and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*, 81 (1959) 4189–4195.