

A STEREOCHEMICAL ACHIEVEMENT OF THE FIRST ORDER: ALFRED WERNER'S RESOLUTION OF COBALT COMPLEXES, 85 YEARS LATER

George B. Kauffman, California State University, Fresno

Listen, old man; take my advice.
Give me the cobalt in a thrice.
Though Hell and Devil say me nay,
I shall resolve cobalt today (1).

With these words the Old One (*der Alte*, i.e., Werner) challenges the King of the Spirits (*Geisterkönig*). Spurning the tempting gifts offered him by the King, he approaches the giant blue octahedron with a cry of "I want to resolve cobalt" (*Ich will das Kobalt spalten*). He tears one side of it away with his axe, removes the *d*-form, and spins it on his little finger. As everyone joyfully shouts, "It rotates, it rotates!" (*Es dreht, es dreht!*), *der Alte* removes the *l*-form from the other side of the octahedron and spins it on his little finger in the direction opposite to the *d*-form.

Now that the momentous task has been accomplished, all the participants face the audience and triumphantly sing the final chorus to the melody of *Das Studium der Weiber*:

From early morn 'till night so late
We'll just rotate, rotate, rotate,
Until the world and all therein
Rotating spins to oblivion (2).

So ends the anonymous 1911 *Weihnachtskommers* (traditional student Christmas party) playlet in verse, *Drehen und Spalten* (Rotating and Resolving) (3), whose authorship the late Nobel Chemistry laureate Paul Karrer (Ph.D., Universität Zürich, 1911) admitted to me. It



Alfred Werner (1866-1919) from George B. Kauffman, "Alfred Werner-Founder of Coordination Chemistry," Berlin-Heidelberg-New York: Springer 1966, Frontispiece

purports to tell in mock-heroic fashion the story of the first successful resolution of an optically active coordination compound, a problem that had occupied Alfred Werner (4) and a series of his students "over a period of

some nine years" (5), according to his American *Doktorand* Victor L. King (1886-1958) (Ph.D., Universität Zürich, 1912) (6), who finally solved the problem. King, who was accustomed to being greeted on the streets of Zürich with the inquiry, "Nun, dreht es schon?" (Well, does it rotate yet?), recalls how he walked into Werner's office with the long-awaited news. Werner "leaned back in his chair, smiled, and said not a single word" (5).

All the students knew that something extraordinary must have happened when the always punctual Werner failed to appear at his 5 P.M. lecture. A young student appeared, announcing that the lecture had been canceled. Werner, fearing that the optical antipodes might racemize, worked late into the night with King, making many derivatives and measuring their rotations. But his fear was unfounded, for the enantiomorphs proved to be remarkably resistant to racemization in solution, both on prolonged standing and even on heating to incipient boiling (7).

Werner atypically but elatedly accosted casual acquaintances to tell them of his greatest experimental triumph – a "stereochemical achievement of the first order. (8)" Peter Debye offered his own personal account (9):

One early afternoon, when I went from the lake to the Physics Institute after lunch, Werner hailed me from the opposite side of the Rämistrasse. It turned out that he wanted to talk to me about the fact that he had succeeded in making a coordination compound which showed rotation of the plane of polarization. I was very much interested indeed but did not quite understand why he talked to me, since we had had no scientific discussions at all before that time.

The concepts of asymmetry and optical activity, although introduced fairly late into inorganic chemistry, have played a central role in organic chemistry. If modern organic chemistry is considered to begin in 1828 with Friedrich Wöhler's synthesis of urea, then Jean Baptiste Biot's discovery of optical activity in 1812 antedates the very genesis of this field. Furthermore, Le Bel and van't Hoff's concept of the tetrahedral carbon atom in 1874, which constitutes the foundation of stereochemistry, was proposed primarily to explain the optical isomerism investigated by Louis Pasteur and others. It is to Werner, however, that we owe the systematic introduction of the concept of optical activity into coordination chemistry.

Although compounds containing asymmetric atoms other than carbon, e.g., nitrogen, phosphorus, sulfur, selenium, tin, and silicon, had been resolved before

Werner and King's resolution, all these compounds had involved atoms of tetrahedral configuration (10). Werner's work, on the other hand, involved a compound of the octahedral configuration, which he had proposed in his first paper on the coordination theory (1893) (11) but which was still unproven. As a result of this work, "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" (12).

The resolution of optically active coordination compounds, a feat that "shook chemistry to its innermost foundations" (13), gained for Werner and his coordination theory the widespread recognition for which he had been striving so long. In 1913, two years later, largely because of this "most brilliant confirmation of [his] stereochemical views" (14), Werner was awarded the Nobel Prize in Chemistry "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry" (15).

Werner's Earlier Research on Optical Activity

Contrary to common belief, Werner did not mention optical activity in his first paper on the coordination theory (11). It was not until 1899, the same year in which he accomplished his first resolution – that of the organic compound, *trans*-hexahydrophthalic acid – with his assistant Hermann Erich Conrad (Ph.D., Universität Zürich, 1898) (16) – that he and A. Vilmos considered for the first time in print the fact that molecular asymmetry for certain types of complexes containing chelate ligands (17) is a geometric consequence of his postulated octahedral configuration (18):

Thus, for the oxalatodiethylenediaminecobalt salts [modern, bis(ethylenediamine)oxalatocobalt(III) salts (19) and similar compounds, we may predict a new type of isomerism which belongs to the class of asymmetry isomerism, of which until now the usual carbon asymmetry and the molecular asymmetry of the inositols [cyclohexanhexanols] are known (19).

The first evidence that Werner had recognized that resolution of such compounds would provide an elegant, definitive proof of his stereochemical views and that he was actually attempting to resolve them is found in a letter of February 20, 1897 to Arturo Miolati antedating this paper by two years (20):

At present we are searching for asymmetrically constructed cobalt molecules. Will it be successful?

King's estimate of the time that Werner had spent on unsuccessful resolutions was thus a conservative one.

More than a decade after this letter, success still eluded Werner, but he had not abandoned his goal (21):

I see from your beautiful paper in the *Berichte* that you have been more successful in resolving propylenediamine than we have. Now I wish to ask you whether you would permit me to use the active propylenediamine in the investigation of compounds $[(O_2N)_2C_6H_4]X$, of which we have already obtained five inactive series.

Further proof of continuing activity in the field is a sample in the Werner collection of complexes labeled "Resolution experiment on $[CoCO_3en_2]Br$ [en = ethylenediamine] by means of silver *d*-tartrate, 20/I. 1908, Dubsy" (22). It was on this compound that King began experimental work on first arriving in Zürich (23), but after a year of unsuccessful attempts at resolution, he abandoned it.

Werner and King's Resolution

Werner chose the most widely used method of resolution, Pasteur's diastereomer formation, which often failed because the naturally occurring optically active acids and bases then available for use as resolving agents were weak and their salts were not very stable in solution. Kipping and Pope's synthesis from naturally occurring (+)-camphor of resolving agents that are strong acids or bases, such as (+)-camphorsulfonic and (+)-bromocamphorsulfonic acids, provided Werner and King with the agent that finally brought them success (24).

The resolution involved two series of complexes – the *cis*-amminechlorobis(ethylenediamine)cobalt(III) salts, $[CoCl(NH_3)en_2]X_2$ (with King) and the corresponding *cis*-bromo- salts, $[CoBr(NH_3)en_2]X_2$ (with Werner's *Privat-Assistent* Ernst Scholze, Ph.D., Universität Zürich, 1911) (25). The latter series is easier to resolve because of the greater difference in solubility between the diastereomers that are formed with the resolving agent, silver (+)-3-bromo-9-camphorsulfonate. For both series the (+)-bromocamphorsulfonate of the (+)-antipode is less soluble than that of the (-)-antipode.

According to King's laboratory notebook (Ref. 23, p. 21, undated but sometime between April and June 12, 1911), "With the Bromoammine *Reihe* [series] the dextro salt falls right out and no fractionation is necessary." King later recalled (5):

I shall never forget the day that the optically active isomers were first attained. In connection with this work, I had been carrying out some 2000 fraction-

ations and had been studying Madame Curie's work on radium for that purpose. After having made these 2000 separate fractional crystallizations which proved that the opposite ends of the system were precisely alike and that we had to do something more drastic, I proposed increasing the dissimilarity of the diastomers [*sic*] by using brom camphor sulfonic acid as a salt-forming constituent having extremely high optical activity. When this was tried, the isomers in the form of these salts literally fell apart.

A solution of the chloro- or bromo- racemic salt was treated with a solution of the resolving agent, whereupon the (+)(+)-diastereomer precipitated and was removed by filtration (26). The (-)-dithionate was precipitated from the mother liquor by addition of sodium dithionate. The recrystallized (+)(+)-diastereomer was treated with concentrated hydrochloric acid to yield a precipitate of the (+)-chloride, while the (-)-chloride was precipitated by grinding the (-)-dithionate with concentrated hydrochloric acid, followed by cooling. The procedure is reproducible (27) and has been modified and simplified for use as a classic experiment for the undergraduate inorganic laboratory (28).

The resolution, which Werner considered to confirm "one of the most far-reaching conclusions of the octahedral formula," proved that "metal atoms can act as central atoms of stable, asymmetrically constructed molecules [and] that pure molecular compounds [coordination compounds] can also occur as stable mirror image isomers, whereby the difference between valence compounds [ordinary compounds], which is still frequently maintained, disappears entirely" (26). According to King, it was "the last proof for the octahedral formula assumed by A. Werner" (29).

Werner's numerous contributions to coordination chemistry sometimes tend to obscure the fact that he was trained under Arthur Hantzsch as an organic chemist with an emphasis on stereochemistry, was originally called to Universität Zürich to teach organic chemistry, and was not assigned the main lecture in inorganic chemistry until the winter semester 1902/03 (Ref. 4, pp. 38-39). It was not until 1898, when his reputation was firmly established in coordination chemistry, that the number of his inorganic articles – 21 – reached that of his organic papers (30).

Therefore the question as to why it took Werner so long to succeed in resolving coordination compounds is not only an interesting but a legitimate one (31). Many anionic complexes such as oxalato compounds, which contain the chelate ligand with which Werner first considered the possibility for optical isomerism (17), racemize readily; and he might have achieved resolutions of

these compounds without recognizing them. The most common resolving agents such as (+)-tartaric acid are unsuccessful in the case of most coordination compounds, and the resolving agent that eventually proved to be successful – (+)-3-bromo-9-camphorsulfonic acid – was not readily available at the time. Because its synthesis was a long and tedious process, Werner probably did not try it until he had exhausted all other possibilities. Furthermore, recent improvements in instrumentation may have played a great role in Werner's success. It was only shortly before Werner achieved his long-sought success with the Schmidt & Haensch Model No. 8142 polarimeter that this instrument, whose new features for measuring small rotations such as the Lippich half-shadow (*Halbschatten*) device increased the precision in determining the zero points with the deeply colored solutions with which he had to work. Although at the time optical rotations were measured at the sodium D-line wavelength, the intense colors of Werner's solutions must have made use of this wavelength difficult. Around the time of Werner's success Hans Heinrich Landolt introduced the use of filters to obtain different wavelengths, and Werner reported all his optical rotation values as $[\alpha]_C$ rather than $[\alpha]_D$. Finally, the resolution of optical isomers in the absence of exact directions is as much an art as a science.

Rather than asking why it took Werner so long, perhaps we should marvel that he succeeded in the time that he did. Considering the possible variety of coordination compounds and choice of resolving agents, instruments, and wavelengths as well as the highly specific experimental conditions sometimes required, it is not unlikely that, even for someone with Werner's experimental skill and chemical intuition, many years of hard work might have been needed to solve the problem. In short, an extensive Edisonian trial-and-error approach was necessary, and the large number of possible experiments to be attempted rendered the possibility of success small. In any case, Werner's conclusive proof of an octahedral configuration for cobalt(III) by the resolution of certain coordination compounds was due to his persistent belief in his own ideas and his unrelenting attempts to prove them, despite what others might have found to be insurmountable experimental obstacles.

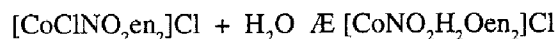
Further Resolutions

It is a repeating historical scenario that whenever anything substantially new is being attempted, much time and effort are required to discover the first successful example; thereafter, numerous examples are quickly and

readily developed. Thus a long period of search is followed by several years of fruitful and prolific productivity. As Paul Karrer expressed it in the present case, "Whenever Werner opened up a new field, he expanded it with unbelievable speed" (13). Once Werner had discovered the means of resolving coordination compounds, a large number of papers describing resolutions of additional complexes – more than forty series within eight years – appeared with great speed from his institute. Together with Michael Basyrin (Ph.D., Universität Zürich, 1915), he even repaid his debt to Pasteur by using optically active inorganic complexes, which he had resolved with organic resolving agents, to resolve an organic compound, dimethylsuccinic acid (32).

In the second article in his 12-part series "Toward an Understanding of the Asymmetric Cobalt Atom" (33) Werner resolved compounds of the *cis*-[Co(NO₂)₂en₂]X (flavo) series by a combination of two resolving agents – (+)-camphorsulfonic acid, which forms a less soluble (-)-salt, and (+)-3-bromocamphor-9-sulfonic acid, which forms a less soluble (+)-salt. In this way he was able to avoid using the sulfonic acid derivatives of the uncommon (-)-camphor. All his attempts to resolve salts of the corresponding *trans*-[Co(NO₂)₂en₂]X (croceo) series were unsuccessful, in support of his octahedral hypothesis, which predicted that only the *cis*- and not the *trans*- isomer should exist in asymmetric forms. It also added resolvability as a new and powerful weapon to the arsenal of the stereochemist seeking to determine the configuration of geometrically isomeric complexes.

In Werner's third paper in the series (34) the resolution of *cis*-[CoClNO₂en₂]X by means of ammonium (+)-camphorsulfonate and ammonium (+)-bromocamphorsulfonate provided an unusual case of mutarotation, similar to that observed with dextrose among organic compounds, caused by a rapid aquation reaction:



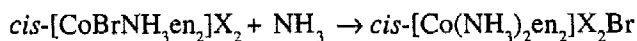
Because coordinated chlorine atoms appear to be replaced by water when silver salts are used as resolving agents, in his fourth paper in the series (35) Werner used ammonium (+)- and (-)-bromocamphorsulfonates to resolve *cis*-[CoCl₂en₂]X. Although stable in the dry state, the active salts racemized in solution to form inactive aquachloro and diaqua salts. Yet in some cases Werner was able to replace coordinated chlorine atoms with other atoms without loss of optical activity. He also observed that some reactions proceed with a change in the sign of rotation, but he realized that the sign of rotation of a

complex is not determined simply by its absolute configuration and that consequently a change in sign need not be attributed to an inversion of configuration.

In the fifth paper in the series (36) Werner resolved $[\text{Coen}_3]\text{X}_3$ salts 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 that of the structurally similar $[\text{Rhen}_3]\text{X}_3$ (37). He regarded the resolution of tris(ethylenediamine)cobalt(III) salts as particularly important because it furnished conclusive proof for the correctness of the octahedral configuration, in that it eliminated the hexagonal planar and trigonal prismatic configurations, which would possess a plane of symmetry for compounds of type $[\text{M}(\text{AA})_3]$. It also demonstrated that optical activity does not require the linkage of *different* groups to the central atom, and it explained the optical activity of many minerals such as basic polynuclear salts which may be regarded as constitutionally similar to $[\text{Men}_3]$ salts (38).

All attempts to resolve by diastereomer formation with optically active anions the salts with which King began his work, *viz.*, $[\text{CoCO}_3\text{en}_2]\text{X}$, were unsuccessful. Therefore in the sixth paper of the series (39) Werner, together with the late Thomas Potter McCutcheon, who was my general chemistry instructor at the University of Pennsylvania in 1948, synthesized optically active $[\text{CoCO}_3\text{en}_2]\text{X}$ by the action of potassium carbonate on optically active *cis*- $[\text{CoCl}_2\text{en}_2]\text{X}$ salts, a reaction later investigated by Bailar (40) and others. Werner and McCutcheon also prepared optically active $[\text{CoC}_2\text{O}_4\text{en}_2]\text{X}$ by reaction of active *cis*- $[\text{CoCl}_2\text{en}_2]\text{X}$ with potassium oxalate rather than by resolution of the racemic mixture (39). In attempting the latter Werner developed a new method of resolution – preferential crystallization (21b), a procedure currently used in Japan to produce L-glutamic acid in tonnage quantities.

Because all attempts to resolve *cis*- $[\text{Co}(\text{NH}_3)_2\text{en}_2]\text{X}_3$ salts by means of optically active acids had ended in failure, in the seventh paper of the series Werner and Shibata (41) converted optically active *cis*- $[\text{CoBrNH}_3\text{en}_2]\text{X}_2$ salts (26) into the corresponding active diammine salts by treatment with liquid ammonia:



In the eighth paper of the series (42) Werner and Tschernoff resolved *cis*- $[\text{CoBrClen}_2]\text{X}$ salts by precipitation with ammonium (+)- and (-)-bromo camphorsulfonates. In solution the active salts undergo

aquation with complete loss of activity within 30-60 minutes.

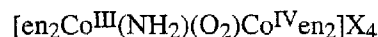
In the ninth paper of the series (43, 44) Werner proved that polynuclear as well as mononuclear complexes could be resolved, demonstrating his theoretically predicted analogy between compounds containing two asymmetric carbon atoms and polynuclear complexes with two metal atoms, another striking confirmation of his octahedral hypothesis. In complete analogy with tartaric acid, Werner prepared



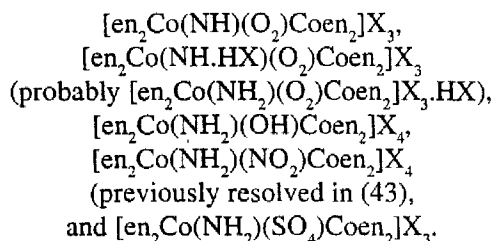
in a racemic (+)(-) form; (+)- and (-)-enantiomers; and an internally compensated, nonresolvable *meso* form.

According to the coordination theory, the two cobalt atoms in these binuclear complexes should not be structurally identical because one is bonded by a principal valence (*Hauptvalenz*) to NO_2 and by a secondary valence (*Nebenvalenz*) to NH_2 and the other vice versa. However, the inactivity of the *meso* form 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 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*) (43), a statement that he also subsequently made on other occasions.

In the tenth paper of the series (45) Werner, together with Hedwig Kuh (Ph.D., Universität Zürich, 1912) and Paul Wüst (Ph.D., Universität Zürich, 1913), resolved



(previously prepared in (46)) into three forms – (+),(+); (-),(-); and (+),(-) (His formulations with $\text{Co}(\text{IV})$ are now known to be incorrect; the two cobalt atoms are equivalent and tripositive, and the O_2 is a superoxide bridge). By allowing the parent compound to react with various reagents, he also obtained the following optically active compounds:



In the eleventh paper of the series (18b) Werner and Jakob Bosshart (Ph.D., Universität Zürich, 1914) used preferential crystallization to resolve $[\text{CoC}_2\text{O}_4\text{en}_2]\text{X}$, the series in which he first predicted the possibility of optical isomerism (19). By adding a "seed" crystal of (+)- $[\text{CoC}_2\text{O}_4\text{en}_2]\text{Br}$ to a concentrated solution of racemic- $[\text{CoC}_2\text{O}_4\text{en}_2]\text{Br}$, followed by addition of alcohol and ether, they obtained a precipitate of pure (+)- $[\text{CoC}_2\text{O}_4\text{en}_2]\text{Br}$. They then recovered the (-)-isomer from the solution.

The Final and Unequivocal Proof

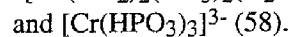
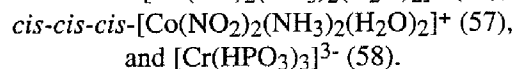
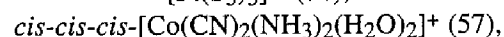
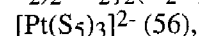
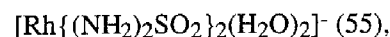
Although the complexes that Werner had resolved up to this time (1914) represented a remarkable variety of compound types, they all possessed one common characteristic – they all contained carbon. Even though the symmetrical carbon-containing ligands (ethylenediamine, bipyridyl, or oxalate ion) are themselves optically inactive, any chemists opposed to Werner's views might maintain that the optical activity of the resolved complexes was in some way due to the presence of these ligands and thus cast doubt on the validity of the octahedral configuration for not only cobalt(III) but also for chromium(III), rhodium(III), and iron(II), whose complexes Werner had also resolved.

For this reason, the twelfth and last article in Werner's series on the asymmetric cobalt atom (47) was a particularly satisfying and welcome one, for it vindicated his octahedral concept for even his most skeptical contemporaries (48-50). In his own words, the resolution proved that "carbon-free inorganic compounds can also exist as mirror image isomers" (47) and that therefore "the difference still existing between carbon compounds and purely inorganic compounds disappears" (47). Finally, he had verified experimentally a conviction that he had held for many years – there is no essential difference between organic and inorganic chemistry.

It is ironic that the completely inorganic tetranuclear tris[tetraammine- μ -dihydroxocobalt(III)]cobalt(III) salts that Werner and his female *Doktorandin* Sophie Matissen (Ph.D., Universität Zürich, 1912) succeeded in resolving were first prepared by Jørgensen (51), whom Werner graciously acknowledged in his Nobel acceptance address. With Ernst Berl (Ph.D., Universität Zürich, 1911), Ernst Zinggeler (Ph.D., Universität Zürich, 1902), and Gustav Jantsch (Ph.D., Universität Zürich, 1907), Werner had showed that they possess the constitution $[\text{Co}\{(\text{OH})_2\text{Co}(\text{NH}_3)_4\}_3]\text{X}_6$ (52). They are thus struc-

turally similar to $[\text{Men}_3]\text{X}$ salts with the inorganic $[(\text{OH})_2\text{Co}(\text{NH}_3)_4]^+$ ions in place of the organic ethylenediamine molecules and should therefore be capable of existing in optically active forms.

The resolution of the bromides with silver (+)-bromocamphorsulfonate was very tedious because of the slight differences in solubility between the diastereomers. Optical rotation measurements were difficult because of the dark color of the solutions and were made in 50% aqueous acetone to minimize the rapid racemization. Nevertheless, a modified form of the resolution is reproducible (53) and has been adapted as an undergraduate laboratory experiment (54). Since Werner's classic resolution only five other completely carbon-free inorganic complexes have been resolved, *viz.*,



Conclusion

From the inception of his studies of optical activity, Werner did not limit himself to the complexes of cobalt. He succeeded in resolving coordination compounds of chromium(III), iron(II), rhodium(III), iridium(III), and platinum(IV), which are discussed elsewhere (59). He continued his research with cobalt to include complexes with optically active unsymmetrical ligands. For example, he and his assistant A. P. Smirnov (60) resolved *cis*- $[\text{Co}(\text{NO}_2)_2\text{enpn}]\text{Br}$; this compound illustrated a new and complicated type of isomerism, which arises from three causes – (1) *cis* (flavo) geometric isomerism, (2) ligand isomerism ((+)-pn or (-)-pn), and (3) structural isomerism caused by the unsymmetrical nature of the pn ligand (*cis* isomer only). It is a tribute to Werner's octahedral model that he could predict the existence of ten optically active isomers of this complex and a tribute to his experimental skill that he was able to isolate them even though he was unable to assign unambiguous structures to all of them.

In his last article (61), published with Jeanne Elisabeth Schwyzer (Ph.D., Universität Zürich, 1919) and Walter Karrer (Ph.D., Universität Zürich, 1919), more than a year after his premature death, Werner confirmed his view that β -diketonate anions occupy two coordination positions (62, 63) by preparing optically active acetylacetonatobis(ethylenediamine)cobalt(III) and propionylacetonatobis(ethylenediamine)cobalt(III) salts.

Thus, during his last years, Werner devoted himself almost exclusively to the optically active complexes that had proved his stereochemical views and had brought him the Nobel Prize in Chemistry. His studies of these complexes underlie much of the more recent and sophisticated studies of the thermodynamics; kinetics; visible, ultraviolet, infrared, NMR, and EPR spectra; rotatory dispersion; circular dichroism; ligand exchange; racemization; absolute configuration; and other aspects of these and similar compounds. Although some of his resolution methods have been improved upon, and his specific rotation values have proved to be too low, he was a true pioneer who first opened a previously unsuspected field. In his last works he stood on the threshold of an extremely complex area of research – the study of optically active coordination compounds containing optically active ligands. If his creative and fruitful life had not been cut short by his death at the early age of 53, Alfred Werner certainly would have made many significant contributions to this field.

ACKNOWLEDGMENT

The author is indebted to the referees for helpful comments and suggestions.

REFERENCES AND NOTES

1. "Hör, Alter, ich rate dir wirklich sehr,
Gib mir das Kobalt gutwillig her.
Nicht Hölle und Teufel sollen mich halten,
Noch heute will ich das Kobalt spalten."
2. "Ja, vom Morgen bis Abend spät,
Wird jetzt nur noch gedreht, ja gedreht,
Bis die ganze grosse Welt
Sich drehend in Ohnmacht fällt."
3. *Drehen und Spalten: Tragikomisches Volksspiel in einem Akt*, Weihnachtskommers der Universitäts-Chemiker, 15. Dezember 1911, Dissert.-Druckerei Gebr. Leemann & Co., Zürich-Selnau, 1911. For excerpts translated into English see G. B. Kauffman and H. K. Doswald, "Paul Karrer—Rotating and Resolving: A Tragicomic Popular Play," *Chemistry*, **1974**, 47(2), 8-12. The entire playlet was performed in English at the van't Hoff–Le Bel Centennial Symposium, 168th National Meeting, American Chemical Society, Atlantic City, NJ, September 11-12, 1974 with George B. Kauffman in the role of Werner and with a cast of internationally distinguished chemists, including a Nobel laureate. It was also performed at the California State University, Fresno, May 14, 1974; the Australian National University, Canberra, December, 1975; and a meeting of the Penn-Ohio Border Section, American Chemical Society, Youngstown, OH, February 20, 1976.
4. G. B. Kauffman, *Alfred Werner: Founder of Coordination Chemistry*, Springer-Verlag, New York, 1966.
5. V. L. King, "A Rough but Brilliant Diamond," *J. Chem. Educ.*, **1942**, 19, 345.
6. For biographical information on King see G. B. Kauffman, *Classics in Coordination Chemistry, Part I: The Selected Papers of Alfred Werner*, Dover, New York, 1968, pp. 157-158.
7. G. B. Kauffman, "The First Resolution of a Coordination Compound," in O. B. Ramsay, Ed., *van't Hoff–Le Bel Centennial*, American Chemical Society, Washington, DC, 1975, pp. 126-142.
8. J. Read, *Humour and Humanism in Chemistry*, G. Bell & Sons, London, 1947, p. 264. John Read, the historian of chemistry, received his Ph.D. under Werner in 1907 with an organic stereochemical dissertation.
9. P. Debye, letter to George B. Kauffman, December 4, 1963.
10. G. B. Kauffman and I. Bernal, "Overlooked Opportunities in Stereochemistry. Part II. The Neglected Connection between Metal-Ammines (Alfred Werner) and Organic Onium Compounds (William Jackson Pope)," *J. Chem. Educ.*, **1989**, 66, 293-300.
11. A. Werner, "Beitrag zur Konstitution anorganischer Verbindungen," *Z. Anorg. Chem.*, **1893**, 3, 267-330. For an annotated English translation see Ref. 6, pp. 9-88.
12. G. T. Morgan, "Alfred Werner," *J. Chem. Soc.*, **1920**, 117, 1639-1648.
13. P. Karrer, "Prof. Alfred Werner," *Neue Zürcher Zeitung*, No. 1804, Erstes Morgenblatt, November 21, 1919, Feuilleton p. 1; reprinted in *Vierteljahresschrift der Naturforschenden Gesellschaft in Zürich*, **1919**, 64, 851-854.
14. I. Lifschitz, "Alfred Werner," *Z. Elektrochem.*, **1920**, 26, 514-529. Israel Lifschitz received his *venia legendi* (the right to lecture) with a *Habilitationsschrift* (a paper embodying the results of original and independent postdoctoral research) at Universität Zürich in 1911.
15. Nobel Foundation, *Nobel Lectures Including Presentation Speeches and Laureates' Biographies: Chemistry, 1901-1921*, Elsevier, Amsterdam, 1966, p. 253. Werner received the following nominations for the Nobel Prize: 1907, Eugen Bamberger; 1908, Adolf von Baeyer, Luigi Balbiano, E. Grandmougin, Georg Lunge, and Frederic P. Treadwell; 1911, Otto Dimroth, A. F. Holleman, and Paul Walden; 1912, Emil Fischer, Arnold Lang, Johannes Thiele, and Edgar Wedekind; and 1913, Svante A. Arrhenius, who also nominated Theodore W. Richards (the 1914 winner): Emil Fischer, Arthur R. Hantzsch, Werner's *Doktorvater*, and Paul Sabatier (the 1912 winner). All the 1912 and 1913 nominators except Fischer in 1911 specifically cited Werner's work on optical activity. In both 1912 and 1913 Friedrich Rose and Hans Rupe nominated Werner, but because their nominations were received after the February 1 deadlines in both years they were disallowed (information and letters of nomi-

- nation, courtesy of Kai-Inge Hillerud, Secretary to the Nobel Archives Committee, the Royal Swedish Academy of Sciences). See also E. Crawford, J. L. Heilbron, and R. Ullrich, *The Nobel Population 1901-1937: A Census of the Nominators and Nominees for the Prizes in Physics and Chemistry*, Office for History of Science and Technology, University of California, Berkeley, CA, Office for History of Science, Uppsala University, Uppsala, 1987, pp. 174, 176, 177, 186-195.
16. A. Werner and H. E. Conrad, "Über die optisch aktiven Transhexahydroptalsäuren," *Ber. Dtsch. Chem. Ges.*, **1899**, *32*, 3046-3055.
 17. Although Werner's isolation of the long-sought, unstable *cis*-tetraamminedichlorocobalt(III) salts (violeto salts), *cis*-[CoCl₂(NH₃)₄]X (A. Werner, "Über 1.2-Dichlorotetrammin-kobaltisalze (Ammoniakvioleosalze)," *Ber. Dtsch. Chem. Ges.*, **1907**, *40*, 4817-4825; for an annotated English translation see Ref. 6, pp. 144-154) convinced his primary scientific adversary Sophus Mads Jørgensen (1837-1914) that the Blomstrand-Jørgensen chain theory could not be correct (G. B. Kauffman, "Sophus Mads Jørgensen and the Werner-Jørgensen Controversy," *Chymia*, **1960**, *6*, 180-204), Werner's success in preparing two and only two isomers for complexes of types MA₄B₂ and MA₃B₃ was not sufficient to prove the octahedral configuration. In spite of such "negative" evidence, it could be argued that failure to isolate a third isomer did not necessarily prove its non-existence. The resolution of asymmetric coordination compounds would provide Werner with the "positive" proof that he needed.
 18. A. Werner and A. Vilmos, "Beitrag zur Konstitution anorganischer Verbindungen. XVII. Über Oxalato-diäthylendiaminkobaltisalze (CoC₂O₄en₂)X," *Z. anorg. Chem.*, **1899**, *21*, 145-158, p. 147.
 19. These salts were not the first coordination compounds to be resolved, but Werner succeeded in resolving them in 1912 and 1914 - (a) A. Werner and T. P. McCutcheon, "Zur Kenntnis des asymmetrischen Kobaltatoms. VII.," *Ber. Dtsch. Chem. Ges.*, **1912**, *45*, 3281-3287; (b) A. Werner and J. Bosshart, "Zur Kenntnis des asymmetrischen Kobaltatoms. XI. Über Oxalato-diäthylendiamin-kobaltisalze und eine neue Spaltungsmethode für racemische anorganische Verbindungen," *Ber. Dtsch. Chem. Ges.*, **1914**, *47*, 2171-2182.
 20. Werner's former fellow doctoral student, friend, and collaborator on the classical conductance studies of coordination compounds - the first published experimental work in support of his coordination theory (A. Werner and A. Miolati, "Beiträge zur Konstitution anorganischer Verbindungen, I. Abhandlung," *Z. physik. Chem.*, **1893**, *12*, 35-55; "Beiträge zur Konstitution anorganischer Verbindungen, II. Abhandlung," *Z. physik. Chem.*, **1894**, *14*, 506-521; for annotated English translations see Ref. 6, pp. 92-139). For a biography see G. B. Kauffman, "Arturo Miolati (1869-1956)," *Isis*, **1970**, *61*, 241-253.
 21. (a) A. Werner, letter to Lev Aleksandrovich Chugaev (1873-1922), the Russian chemist who was an enthusiastic proponent of his coordination theory, November 15, 1907. (b) For a biography see G. B. Kauffman, "Terpenes to Platinum: The Chemical Career of Lev Aleksandrovich Chugaev," *J. Chem. Educ.*, **1963**, *40*, 656-665.
 22. Jean V. Dubsy (1882-1946) received his Ph.D. under Werner's supervision in 1908 and served as his assistant. For a biography see F. Jursík and G. B. Kauffman, "J. V. Dubsy and His Participation in Werner's Coordination Theory," in G. B. Kauffman, Ed., *Coordination Chemistry: A Century of Progress*, American Chemical Society, Washington, DC, 1994, pp. 58-67.
 23. V. L. King, *Nachweis des Oktaheder Formels der Kobaltiake: Arbeit für Ph.D., Zürich, 1910-1912*, p. 2. This laboratory notebook is preserved in the Chemistry Department Library at Dartmouth College, Hanover, NH, from which King received his bachelor's degree in 1907.
 24. F. S. Kipping and W. J. Pope, "Studies of the Terpenes and Allied Compounds. The Sulphonic Derivatives of Camphor," *J. Chem. Soc.*, **1893**, *63*, 548-604. Werner used their procedure, but improved syntheses have since been devised, e.g., G. B. Kauffman, "A Rapid, Simplified Synthesis of α -Bromo-*d*-camphor- π -sulfonic Acid and Its Salts," *J. prakt. Chem.*, **1966**, [4] *33*, 295-297.
 25. These compounds, like many of the complexes that Werner used to support his coordination theory and discredit the rival Blomstrand-Jørgensen chain theory, was first prepared by Jørgensen ("Ueber Metalldiaminverbindungen. VII. Ammin-Aethylendiamin-Chloropurpureokobaltsalze," *J. prakt. Chem.*, **1890**, [2] *41*, 453-459).
 26. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. I.," *Ber. Dtsch. Chem. Ges.*, **1911**, *44*, 1887-1898; for an annotated English translation see Ref. 6, 159-173.
 27. G. B. Kauffman and E. V. Lindley, Jr., "Resolution of the *cis*-Bromoamminebis(ethylenediamine)cobalt(III) Ion," *Inorg. Syn.*, **1976**, *16*, 93-97.
 28. G. B. Kauffman and E. V. Lindley, Jr., "A Classic in Coordination Chemistry: A Resolution Experiment for the Inorganic Laboratory," *J. Chem. Educ.*, **1974**, *51*, 424-425.
 29. V. L. King, "Über Spaltungsmethoden und ihre Anwendung auf komplexe Metall-Ammoniakverbindungen," Dissertation, Universität Zürich, J. J. Meier, Zürich, 1912, p. 59.
 30. G. B. Kauffman, "Alfred Werner's Research in Organic Stereochemistry," *Die Naturwissenschaften*, **1976**, *63*, 324-327.
 31. G. B. Kauffman, "The Discovery of Optically Active Coordination Compounds: A Milestone in Stereochemistry," *Isis*, **1975**, *66*, 38-62.
 32. A. Werner and M. Basyrin, "Über die optisch aktiven Dimethyl-bernsteinsäuren," *Ber. Dtsch. Chem. Ges.*, **1913**, *46*, 3229-3232.

33. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. II.," *Ber. Dtsch. Chem. Ges.*, **1911**, *44*, 2445-2555.
34. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. III.," *Ber. Dtsch. Chem. Ges.*, **1911**, *44*, 3272-3278.
35. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. IV.," *Ber. Dtsch. Chem. Ges.*, **1911**, *44*, 3279-3284.
36. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. V.," *Ber. Dtsch. Chem. Ges.*, **1912**, *45*, 121-130.
37. A. Werner, "Über Spiegelbildisomerie bei Rhodium Verbindungen. I.," *Ber. Dtsch. Chem. Ges.*, **1912**, *45*, 1228-1236.
38. A. Werner, "Zur Konstitution basischer Salze und analog konstituierte Komplexsalze. I.," *Ber. Dtsch. Chem. Ges.*, **1907**, *40*, 4441-4449.
39. A. Werner and [T. P.] McCutcheon, "Zur Kenntnis des asymmetrischen Kobaltatoms. VI.," *Ber. Dtsch. Chem. Ges.*, **1912**, *45*, 3281-3287.
40. J. C. Bailar, Jr. and R. W. Auten, "The Stereochemistry of Complex Inorganic Compounds. I. The Walden Inversion as Exhibited by Diethylenediaminocobaltic Compounds," *J. Am. Chem. Soc.*, **1934**, *56*, 774-776. D. D. Brown, Christopher K. Ingold, and Ronald S. Nyholm ("Mechanism, Kinetics, and Stereochemistry of Octahedral Substitutions. Part I. Edge-displacement as a Hypothesis Linking Mechanism with the Stereochemistry of Substitution," *J. Chem. Soc.*, **1953**, 2674-2680) suggested that Bailar should not refer to his discovery as a Walden inversion because it implied an octahedral type inversion analogous to the familiar umbrella inversion of tetrahedral carbon.
41. A. Werner and Y. Shibata, "Zur Kenntnis des asymmetrischen Kobaltatoms. VII.," *Ber. Dtsch. Chem. Ges.*, **1912**, *45*, 3287-3293.
42. A. Werner and G. Tschernoff, "Zur Kenntnis des asymmetrischen Kobaltatoms. VIII.," *Ber. Dtsch. Chem. Ges.*, **1912**, *45*, 3294-3301.
43. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. IX.," *Ber. Dtsch. Chem. Ges.*, **1913**, *46*, 3674-3683.
44. A. Werner, "Über Verbindungen mit zwei asymmetrischen Kobaltatomen," lecture, Verein Deutscher Chemiker, Freiburg im Breisgau, Germany, May 29, 1912.
45. A. Werner, H. Kuh, and P. Wüst, "Zur Kenntnis des asymmetrischen Kobaltatoms. X.," *Ber. Dtsch. Chem. Ges.*, **1914**, *47*, 1961-1979.
46. A. Werner, F. Salzer, M. Pieper, J. Fürstenberg, S. Malmgren, M. Grigorieff, A. Grün, E. Bindschedler, and E. Welti, "Über mehrkernige Metallammoniate. X.," *Ann.*, **1910**, *375*, 1-144.
47. A. Werner, "Zur Kenntnis des asymmetrischen Kobaltatoms. XII. Über optische Aktivität bei kohlenstofffreien Verbindungen," *Ber. Dtsch. Chem. Ges.*, **1914**, *47*, 3087-3094. For an annotated English translation see Ref. 6, pp. 177-184.
48. A. Werner, "Neue Ergebnisse der Spaltungsversuche mit anorganischen Verbindungen," in *Schweizerische Chemische Gesellschaft: Ansprachen zu Ehre des Herrn Prof. Dr. Werner gehalten bei der Versammlung vom 2. Mai 1914 in Neuenberg*, Imprimerie Th. Eberhard, Lausanne, Switzerland, 1914, pp. 35-47 (in German); *Archives des Sciences physiques et naturelles*, **1914**, *37*, 455 (in French).
49. A. Werner, "Über anorganische Konstitutions- und Konfigurationsfragen," lecture, Naturforschende Gesellschaft Zürich, Zürich, June 8, 1914.
50. A. Werner, "Sur l'activité optique de composés chimiques sans carbone," lecture, Société Chimique de France, Paris, August 17, 1914; *Compt. rend.*, **1914**, *159*, 426-429.
51. S. M. Jørgensen, "Zur Konstitution der Kobalt-, Chrom-, und Rhodiumbasen. X. Mitteilung," *Z. Anorg. Chem.*, **1898**, *16*, 184-197. For a more recent synthesis see G. B. Kauffman and R. P. Pinnell, "Tris[tetrammine- μ -dihydroxo-cobalt(III)]cobalt(III) Sulfate 4-Hydrate," *Inorg. Syn.*, **1960**, *6*, 176-179.
52. A. Werner, E. Berl, E. Zinggeler, and G. Jantsch, "Über mehrkernige Metallammoniate. III. Über Dodekamminhexoltetrakobaltisalze und Hexaäthylendiaminhexoltetrakobaltisalze: $\{Co[(HO)_2CoA_4]_3\}X_6$," *Ber. Dtsch. Chem. Ges.*, **1907**, *40*, 2103-2125.
53. T. Yasui, T. Ama, and G. B. Kauffman, "Resolution of the Dodecaamminehexa-m-hydroxo-tetracobalt(III) Ion," *Inorg. Syn.*, **1992**, *29*, 169-174.
54. T. Yasui, T. Ama, and G. B. Kauffman, "The Resolution of a Completely Inorganic Coordination Compound: A Modified Classic Experiment for the Inorganic Laboratory," *J. Chem. Educ.*, **1989**, *66*, 1045-1048.
55. F. G. Mann, "The Complex Metallic Salts of Sulfamide," *J. Chem. Soc.*, **1933**, 412-419.
56. R. D. Gillard and F. L. Wimmer, "Inorganic Optical Activity," *J. Chem. Soc., Chem. Comm.*, **1978**, 936-937.
57. S. Shimba, S. Fujinami, and M. Shibata, "Preparation of a Novel Amminebromocyno[1,4,7-triazacyclononane]cobalt(III) Complex," *Chem. Lett.*, **1979**, 783-784.
58. J. Podlaha and M. Ebert, "Triphosphitochromic Acid," *Nature (London)*, **1960**, *188*, 657-658; *Zh. Neorgan. Khim.*, **1962**, *7*, 2185-2191 (in Russian); "Triphosphite Chromic Acid," *Russ. J. Inorg. Chem. (Engl. transl.)*, **1962**, *7*, 1130-1136.
59. G. B. Kauffman, "Alfred Werner's Research on Optically Active Coordination Compounds," *Coord. Chem. Rev.*, **1974**, *12*, 105-149.
60. A. Werner, "Über eine neue Isomerieart bei Kobaltverbindungen und Verbindungen mit asymmetrischen Kobalt und Kohlenstoff," *Helv. Chim. Acta*, **1918**, *1*, 5-32; also lecture with the same title,

Schweizerische Naturforschende Gesellschaft, Geneva, September 14, 1915.

61. A. Werner, J. E. Schwyzer, and W. Karrer, "Optisch-aktive Kobaltsalze mit β -Diketonreste im Komplex," *Helv. Chim. Acta*, **1921**, *4*, 113-129.
62. A. Werner, "Über Acetylacetonverbindungen des Platins," *Ber. Dtsch. Chem. Ges.*, **1901**, *34*, 2584-2593.
63. A. Werner and S. Matissen, "Zur Konstitution der inneren Metallkomplexsalze," *Helv. Chim. Acta*, **1918**, *1*, 78-84.

ABOUT THE AUTHOR

George B. Kauffman, Professor of Chemistry at California State University, Fresno, is the author or editor of 16 books and more than 1400 papers, reviews, and

encyclopedia articles on chemistry, the history of chemistry, and chemical education. A Dexter Awardee (1978), he has long been active in ACS affairs, serving HIST as Symposium Chairman (1966, 1968, 1970, 1993), Program Chairman (1967-1970), and Division Chairman (1969-1970). A Guggenheim fellow and Contributing Editor of five journals, he recently became the first recipient of the President's Medal of Distinction, the highest nondegree award presented by CSUF. His other honors include CSU System Outstanding Professor, MCA Catalyst Award, ACS Pimentel Award in Chemical Education, Marc-Auguste Pictet Medal, and Chugaev, Kurnakov, and Chernyaev Medals of the USSR Academy of Sciences.

American Chemists and Chemical Engineers

Volume 2

Wyndham D. Miles and Robert F. Gould, Editors

269 New biographical sketches, each fully referenced by 40 contributors. Includes many early chemists who started teaching "natural science," which later branched into chemistry, physics, botany, and so on; 37 born before 1800; 10 college presidents; 14 original ACS members; 4 charter members of AIChE; 19 who saw Civil War service; 7 historians of chemistry.

360 pages, including 67-page name and subject index.

Price: \$23.00, postpaid in US and Canada. Additional \$2.00 elsewhere.

Name: _____

Address: _____

Send to:
Gould Books
20 Forest Brook Rd.,
Guilford, CT 06437