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ALFRED WERNER'S RESEARCH ON STRUCTURAL ISOMERISM

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CONTENTS

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. Werner played such a central and monopolistic role in coordination chemistry that his name is virtually synonymous with the field. Even today, more than a half-century after his death, coordination compounds, particularly metal–ammines, are known as Werner complexes, and the coordination theory, the theoretical and practical basis for the field, is colloquially called Werner's theory.

Consequently, although this article on structural isomerism is limited primarily to Werner's achievements, it should nevertheless provide a wide coverage of the most important and fundamental problems in this area and be of use to practicing chemists as well as to historians of science

The viewpoint in this review is largely "historical", in the sense that no pretense is made as to coverage of the contemporary literature. Although in some cases Werner's results have been related to later developments, this article is in no way intended to compete with the excellent recent reviews of what is probably the best investigated type of structural isomerism, viz linkage isomerism[2–5], or with the standard treatments in various textbooks and reference works[6–11] English translations of significant papers by Werner[12] and others[13] on some of the compounds cited in the present article are also available

In 1832 Berzelius "proposed to call substances of the same composition but different properties *isomeric*, from the Greek ἰσομερῆς (composed of equal parts)"[14], and the concept of isomerism was born Although isomerism is sometimes divided into several types, basically there are only two types – (1) structural or position isomerism, and (2) stereoisomerism or space isomerism Structural or position isomerism results from differences in the arrangement of atoms or groups of atoms in the molecules (constitution) In other words, an actual difference in bonding exists between the different isomers Stereoisomerism or space isomerism results from differences in the spatial arrangement of atoms or groups of atoms (configuration) In other words, the same bonding is present in the different isomers, but the bonds are oriented differently in space Stereoisomerism[15–23], in turn, is subdivided into geometric isomerism and optical isomerism[24], which do not concern us here.

Although of the two main types of isomerism encountered among coordination compounds stereoisomerism has been the most extensively investigated, the more neglected structural isomerism has also been of great importance in providing a brilliant confirmation for Werner's coordination theory. From the very inception of his theory, Werner was well aware of the existence of structural isomers Magnus's Green Salt[25], $[Pt(NH_3)_4][PtCl_4]$, and the dichlorodiammines[26–28] of platinum(II), *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$, later to be classed by Werner as polymerization isomers, are mentioned in Werner's first publication[29] on complexes (1893) In Werner's second study of conductivity[30] with Miolati (1894), the two mentioned Jørgensen's[31] eight polymerization isomers of $[Co(NH_3)_3(NO_2)_3]$, and they measured the conductivities of four of them. Yet it was not until 1899 that Werner and Vilmos[32] drew a sharp distinction between stereoisomers *(räumliche Isomeren)* and structural isomers *(Koordinationsisomeren)* (not to be confused with his later use of the latter term for the particular type of structural isomers listed below in Sect. D).

Strictly speaking, isomers must contain the same numbers of the same atoms differently arranged, i e. they must possess the same molecular weights. For the phenomenon exhibited by compounds in which the relative numbers of atoms in the two compounds are the same but the absolute numbers are different, Berzelius[14,33] coined the term *polymerism*★ Inas-

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★The classical example of this phenomenon and the one cited by Berzelius is the case of the two hydrocarbons olefiant gas or ethylene (C_2H_4, then written CH_2) and butylene (C_4H_8, then written C_2H_4) Another familiar pair of such "polymers" is acetylene (C_2H_2) and benzene (C_6H_6), the latter compound, incidentally, can actually be obtained by polymerization of the former.

much as Werner considered such "polymers" as isomers and it has become general practice to do so, Werner's classification and nomenclature, as given in his magnum opus, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*[34], beginning with its first edition (1905), will be used in the present article. Not only did Werner devise a classification system for structural isomers but also he and his students prepared many such isomers for the first time or improved syntheses for known isomers. Despite occasional overlap of the various types of isomerism, Werner's classification has proven extremely useful. Alternative classifications are mentioned briefly in Sect. L.

B. POLYMERIZATION ISOMERISM OR COORDINATION POLYMERIZATION ISOMERISM *(KOORDINATIONSPOLYMERIE)*

Werner used this term to denote compounds with the same empirical formula but with formula weights that are different multiples of the same formula weight (refs. 34a, pp. 159–162, 34b, pp. 252–256, 34c, pp. 319–324; 34d, pp. 328–333, 34e, pp. 330–335, 35, p. 6). The term is used in a formal sense only and is not intended to imply that any of the isomers are related by actual polymerization processes. In other words, the fact that the compounds happen to have the same composition may be regarded as purely fortuitous – as a coincidence, so to speak. As would be expected from the great differences in structure among such compounds, their properties differ widely in physical and chemical properties.

The classic and best known example cited first by Werner is that of the nine known compounds* of empirical formula $Co(NH_3)_3(NO_2)_3$

Compound	Formula weight multiple	
(1) $[Co(NH_3)_3(NO_2)_3]$ (refs. 36, 37, 38, p. 302, 39, 40, p. 174, 41, p. 166, 42, 43) Trinitrotriamminecobalt(III)	1	
(2) $[Co(NH_3)_6][Co(NO_2)_6]$ (ref. 31, p. 177) Hexaamminecobalt(III) hexanitrocobaltate(III)	2	
(3) $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$ (refs. 31, p. 180, 39, p. 183, 30, p. 514) Dinitrotetraamminecobalt(III) tetranitrodiamminecobaltate(III)	2	Stereoisomers (*cis* and *trans*) of both the cation and anion are theoretically possible, they actually exist in the case of the cation, but the anion is known only in the *trans* form

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* Actually many more isomers are theoretically possible if one considers the unknown ion *cis*-$[Co(NH_3)_2(NO_2)_4]^{2-}$ (only the *trans* isomer is known) as well as nitro–nitrito isomerism (See linkage isomerism, Sect. I)

Compound	Formula weight multiple	
(4) $[Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2$ (ref. 31, p 177) Nitropentaamminecobalt(III) tetranitrodiamminecobaltate(III)	3	The anion is known only in the *trans* form
(5) $[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$ (ref 31, p. 177) Hexaamminecobalt(III) tetranitrodiamminecobaltate(III)	4	The anion is known only in the *trans* form
(6) $[Co(NH_3)_4(NO_2)_2]_3[Co(NO_2)_6]$ (ref. 31, p. 178) Dinitrotetraamminecobalt(III) hexanitrocobaltate(III)	4	The cation exists in stereoisomeric forms (*cis* and *trans*)
(7) $[Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$ (ref. 30, p 514) Nitropentaamminecobalt(III) hexanitrocobaltate(III)	5	

Such isomerism is obviously not limited to complexes of cobalt A similar example among chromium compounds cited by Werner and Jovanovits[44] was the series of isomers of empirical formula $Cr(NH_3)_3(SCN)_3$. simple formula weight (1) $[Cr(NH_3)_3(SCN)_3]$, double formula weight (2) $[Cr(NH_3)_6][Cr(SCN)_6]$, (3) $[Cr(NH_3)_4(SCN)_2][Cr(NH_3)_2(SCN)_4]$, triple formula weight (4) $[Cr(NH_3)_5SCN][Cr(NH_3)_2(SCN)_4]_2$; quadruple formula weight (5) $[Cr(NH_3)_6][Cr(NH_3)_2(SCN)_4]_3$, (6) $[Cr(NH_3)_4(SCN)_2]_3[Cr(SCN)_6]$, and quintuple formula weight (7) $[Cr(NH_3)_5SCN]_3[Cr(SCN)_6]_2$ One of the oldest known examples of polymerization isomerism is the series of platinum(II) compounds of empirical formula $Pt(NH_3)_2Cl_2$. simple formula weight (1) *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ (refs 26–28); double formula weight (2) $[Pt(NH_3)_4][PtCl_4]$ (Magnus's Green Salt, the first platinum–ammine to be discovered)[25], triple formula weight (3) $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ (ref 45), and (4) $[Pt(NH_3)_3Cl]_2[PtCl_4]$ (refs 46–48) Among other cases of polymerization isomerism involving compounds prepared by Werner and his students may be listed

(1) $Cr(H_2O)_6][Cr(H_2O)_4Cl_2](SO_4)_2 \cdot 2H_2O$ (ref 49), isomeric with $[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$ (Recoura's Sulfate)[50], and

(2) $Cr(H_2O)_3F_3]$, isomeric with $[Cr(H_2O)_6][CrF_6]$ (both prepared by Werner and Costachescu)[51]

In some cases, the phenomenon of polymerization isomerism has resulted in misinterpretations and cases of mistaken identity. For example, the large number of such isomers of empirical formula $Co(NH_3)_3(NO_2)_3$ resulted in uncertainties as to which compounds were actually the monomolecular isomers *cis*- and *trans*-$[Co(NH_3)_3(NO_2)_3]$, predicted by Werner's coordination theory Inasmuch as the existence of two and only two non-electrolytic isomers of zero conductivity were required by Werner's theory, the confusion in this case enabled Jørgensen to attack the new theory In fact, the uncertainties were not cleared up until very recently. According to MacDermott and Barfoed[52], the various claims for the isolation of the *facial* (1,2,3) isomer of [$Co(NH_3)_3(NO_2)_3$] required by Werner's theory[53–63] are all without foundation, and the compound most commonly assigned this configuration is actually *trans*-[$Co(NH_3)_4(NO_2)_2$] *trans*-[$Co(NH_3)_2(NO_2)_4$][59]. Only the *meridional* (1,2,6) isomer has been identified (refs 60, 61, p 475).

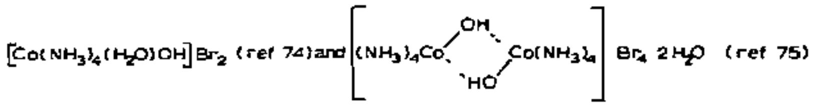
Another recent case typifying erroneous conclusions based on polymerization isomerism is that of the yellow and red compounds of empirical formula $Ir\{(C_2H_5)_2S\}_3Cl_3$, assumed by their discoverers[64] to be *cis* and *trans* isomers (1933) Thirty years later[65], measurements of dipole moment, electrolytic conductance, electrophoresis, visible and ultraviolet absorption and reflectance spectra, and NMR spectra later confirmed the yellow form to be *cis*(1,2,3)-[$Ir\{(C_2H_5)_2S\}_3Cl_3$ but showed the red form to be a polymerization isomer, *trans*-[$Ir\{(C_2H_5)_2S\}_4Cl_2$] *trans*-[$Ir\{(C_2H_5)_2S\}_2Cl_4$] The preparation of a third isomer has been claimed by Fritsman and Krinitskii[66], but no details or properties are given. This compound might possibly be the true *trans* isomer. An analogous case of polymerization isomerism occurs[67] with [$Ir(R_3As)_3Cl_3$], where one of the two forms is monomeric, while the other is the electrolyte [$Ir(R_3As)_4Cl_2$] [$Ir(R_3As)_2Cl_4$].

C NUCLEAR POLYMERIZATION ISOMERISM *(KERNPOLYMERIE)*

This type of isomerism is not mentioned by Werner in the first edition of his *Neuere Anschauungen*[34a], and in the second edition (ref 34b, pp. 259–260) it is mentioned under "Polymerism Phenomena of Another Type" (*"Polymerieerscheinungen anderer Art"*). In the third (ref 34c, pp 324–325) and fourth editions (ref 34d, pp 333–334), it is considered a separate type of isomerism, but in the fifth edition, Paul Pfeiffer, the editor, merely considers it under "Polymeric Compounds" (*"Polymere Verbindungen"*) (ref. 34e, p. 345) It is so closely related to the previous type of isomerism (Coordination Polymerization Isomerism) that many workers make no distinction between the two In nuclear polymerization isomerism, not only is one compound a "polymer" of the other, but also one complex cation is a "polymer" of the other or can be formed from it by a polymerization reaction At least one of the isomeric compounds is polynuclear[68] and involves a bridged structure

Two pairs of isomers, all prepared by Werner, will suffice to illustrate this type of isomerism

The second compound, tris[tetraammine-di-μ-hydroxocobalt(III)] cobalt(III) halide, was the first completely inorganic coordination compound to be resolved[72] Werner's resolution of this compound, first prepared, ironically enough, by his scientific adversary Jørgensen[73], provided the final, unequivocal proof for his coordination theory and the octahedral configuration of cobalt



$$[Co(NH_3)_4(H_2O)OH]Br_2 \text{ (ref 74) and } \left[(NH_3)_4Co\overset{OH}{\underset{HO}{\rightleftarrows}}Co(NH_3)_4\right]Br_4\ 2H_2O \text{ (ref 75)}$$

The cation of the first compound can theoretically exist in *cis* and *trans* configurations, but only the *cis* cation has been found Werner postulated this configuration from the fact that the monomeric compound could "polymerize" to form the dinuclear complex, which, in turn, could be cleaved to re-form the monomer. In this case, the terminology chosen by Werner seems particularly justified inasmuch as the compounds are interconvertible by polymerization and depolymerization

An example which Karrer and Werner[76,77] believed to belong to this type of isomerism was the case of the red and black compounds of empirical formula $[Co(NH_3)_5NO]X_2$ originally discovered by Sand and Genssler[78,79] Werner and Karrer believed that the black isomer was the monomeric nitrosopentaammine compound $[Co(NH_3)_5NO]X_2$ and the red isomer was the binuclear compound $[Co_2(NH_3)_{10}(N_2O_2)]X_4$ These compounds are discussed in Sect J because for many years they were believed to exemplify the phenomenon of valence isomerism The compounds are now believed to be polymerization isomers

Like the polymerization isomers to which they are closely related, the physical and chemical properties of nuclear polymerization isomers differ greatly from each other

D. COORDINATION ISOMERISM *(KOORDINATIONSISOMERIE)*

Isomerism of this type, possible for salts in which both the cation and anion are complex and in which either central metal atom can act as a coordination center for the ligands involved, arises from the different distribution of the ligands with respect to the coordination centers (refs 34a, pp. 165–169, 34b, pp. 260–265, 34c, pp 328–333; 34d, pp 337–342, 34e, pp 325–330, 35, p. 7) If two different metals are involved, isomers of the type $[MA_x][M'B_x]$, $[M'A_x][MB_x]$, or any combination between these extremes are possible A few examples should suffice

(1) $[Co(NH_3)_6][Cr(CN)_6]$ (ref 80) and $[Cr(NH_3)_6][Co(CN)_6]$ (refs 81, p 31, 82, p 42)

(2) $[Cu(NH_3)_4][PtCl_4]$ (ref 83) and $[Pt(NH_3)_4][CuCl_4]$ (refs 84, 85)

(3) $[Co(en)_3][Cr(C_2O_4)_3]$[*] (ref. 82), $[Co(en)_2C_2O_4][Cr(en)(C_2O_4)_2]$ (ref 82), $[Cr(en)_2C_2O_4][Co(en)(C_2O_4)_2]$ (ref 82), and $[Cr(en)_3][Co(C_2O_4)_3]$ (ref 82)

It is not necessary, however, for the metal ion in the cation and anion to be different As examples, Werner cites the following pairs

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[*] en = ethylenediamine

(1) $[Co(NH_3)_6][Co(NO_2)_6]$ (ref. 31, pp. 177, 180) and $[Co(NH_3)_4(NO_2)_2]$-$[Co(NH_3)_2(NO_2)_4]$ (ref. 31, pp. 177, 180)

(2) $[Pt(NH_3)_4][PtCl_4]$ (Magnus's Green Salt)[25] and $[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$ (ref. 86)

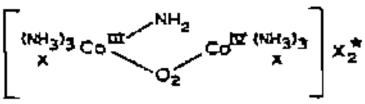
Such isomers may involve differences in oxidation state and thus in configuration as well.

(1) $[Pt^{II}(NH_3)_4][Pt^{IV}Cl_6]$ (refs. 27a, p. 429, 87, 88) and $[Pt^{IV}(NH_3)_4Cl_2][Pt^{II}Cl_4]$ (ref. 27a, p. 429, 87)

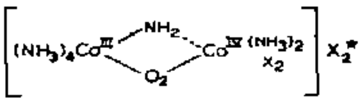
(2) $[Pt^{II}(py)_4][Pt^{IV}Cl_6]$ † (refs. 89, 90, p. 26, 91) and $[Pt^{IV}(py)_4Cl_2][Pt^{II}Cl_4]$ (refs. 90, p. 49, 92)

E. COORDINATION POSITION ISOMERISM *(KOORDINATIVE STELLUNGSISOMERIE)*

Werner first defined this type of isomerism in 1910, and it appears in *Neuere Anschauungen* beginning with the third edition (refs. 34c, pp. 340–341, 34d, pp. 350, 351, 34e, pp. 328, 329). This isomerism, which Werner regarded as analogous to the familar substitution or position isomerism of organic chemistry CH_3-CHX_2 (ethylidene chloride) and CH_2X-CH_2X (ethylene chloride), occurs among dinuclear compounds in which different distributions of the ligands about the two coordination centers are possible (refs. 35, pp. 7, 8, 30, 32, 107, 111, 93). For example, of the complexes



and



where X = Cl or Br, the first or symmetrical salts are grayish green and difficultly soluble in water, while the second or unsymmetrical salts are brownish green and easily soluble. The two series of salts are very different in chemical properties.

F. STRUCTURAL ISOMERISM *(STRUKTURISOMERIE)*

We have used this term to refer to the overall type of isomerism that is different from stereoisomerism. The term is also used to refer to the type of isomerism known as salt isomerism or linkage isomerism (Sect. I). However, Werner (refs. 34a, p. 176, 34b, pp. 275, 276, 34c, pp. 339, 340, 34d, pp. 349, 350, 34e, p. 342) used this term to denote the type of isomerism exemplified by the compounds $H_2N \cdot NO_2$ (nitramide) and $\overset{H}{HO} \cdot N \cdot NO$ (nitrosohydroxylamine). As examples of this type of isomerism among coordination compounds, Werner cited three pairs of complexes[98] which involve the thiourea–ammonium thiocyanate

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† py = pyridine

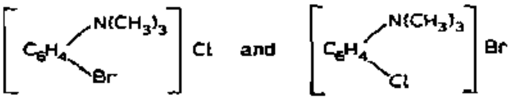
* Although Werner formulated these substances as peroxo (O_2^{2-}) compounds containing one atom of tripositive cobalt and one atom of tetrapositive cobalt, recent work has shown them to contain superoxo (O_2^-) bridges and two tripositive cobalt atoms[68,94–97]

isomerism analogous to the classical urea—ammonium cyanate isomerism first observed by Wohler[99]

(1) $[(NH_2)_2CS]_2 \cdot Hg(SCN)_2$ and $(NH_4SCN)_2 \cdot Hg(SCN)_2$
(2) $[(NH_2)_2CS]_2 \cdot Co(SCN)_2$ and $(NH_4SCN)_2 \cdot Co(SCN)_2$
(3) $[(NH_2)_2CS]_2 \cdot Zn(SCN)_2$ and $(NH_4SCN)_2 \cdot Zn(SCN)_2$

G IONIZATION METAMERISM *(IONISATIONSMETAMERIE)*

This type of isomerism, in which compounds of the same composition yield different ions in aqueous solution, was the first of the structural (as opposed to stereo) types to be singled out by Werner (1897) (ref. 41, p 145) for special attention although he did not give it a specific name at that time. In the first (1905) edition of *Neuere Anschauungen* (ref 34a, pp 172, 173), he designated the phenomenon *ionization isomerism (Ionisationsisomerie)*, but in his lecture *Untersuchungen uber anorganische Konstitutions- und Konfigurations-Fragen* given before the Deutsche Chemische Gesellschaft in Berlin on November 3rd, 1906 (ref. 100, p 33), he changed the name to *ionization metamerism (Ionisationsmetamerie)* because the name *Ionisationsisomerie* had previously been used by his teacher Arthur Hantzsch for another isomeric phenomenon In the second and later editions of *Neuere Anschauungen* (refs 34b, pp 269–271, 34c, pp 336–338, 34d, pp 345–347, 34e, pp 338–340), Werner used the term *Ionisationsmetamerie* He regarded it as analogous to the isomerism exhibited by the pair of organic compounds



The classic example is the pair of isomers of empirical formula $Co(NH_3)_5Br \cdot SO_4$ prepared by Jørgensen, viz red-violet $[Co(NH_3)_5Br]SO_4$ (ref 101) and red $[Co(NH_3)_5SO_4]Br$ (ref. 102) The first compound gives an immediate precipitate with aqueous barium chloride but not with aqueous silver nitrate, while the second compound exhibits the reverse behavior Since this type of isomerism occurs frequently among metal–ammines, we shall limit ourselves to a few of the cases in which Werner was experimentally involved

$[Co(NH_3)_4(NO_2)Cl]Cl$ (ref 61, p 468) (red) and $[Co(NH_3)_4Cl_2]NO_2$ (ref 103) (green)
$[Co(en)_2(NO_2)Cl]Cl$ (ref 104) (red) and $[Co(en)_2Cl_2]NO_2$ (refs 105, 106) (green)
$[Co(en)_2(NO_2)Cl]NO_2$ (ref 104) (red) and $[Co(en)_2(NO_2)_2]Cl$ (ref 107) (yellow-brown)
$[Co(en)_2(NO_2)Cl]SCN$ (ref 104) (red), $[Co(en)_2(NO_2)SCN]Cl$ (ref 108) (red-brown) and $[Co(en)_2(SCN)Cl]NO_2$ (ref 109) (brown-violet)

A peculiar variation on this type of isomerism is the pair
$[Co(NH_3)_5SO_3]NO_3$ (ref 110) and $[Co(NH_3)_5NO_2]SO_4$ (ref. 31, p 172)

H. HYDRATE ISOMERISM *(HYDRATISOMERIE)*

This type of isomerism arises from the different possible modes of bonding of water in coordination compounds, viz. (1) as coordinated water within the complex ion or (2) as water of crystallization bonded outside the coordination sphere. Werner called these two types of compounds *aquo salts (Aquosalze)* and *eso hydrates (Esohydrate)*, respectively. Such isomerism may also be regarded as a special case of ionization isomerism, although in most cases the anions in the isomers differ not in kind but only in number. Water, of course, is the most widely used solvent, and hence isomers involving differently bonded water molecules are the most common. O'Brien[9] preferred to regard this type of isomerism as a special case of what he called *solvate isomerism*, and he mentioned the possibility of such isomers in which alcohols, amines, or ammonia take the place of water molecules.

The classic example of hydrate isomerism, the first type of structural isomerism to be given a specific name (1901) by Werner (refs. 34a, pp. 169–172, 34b, pp. 265–269, 34c, pp. 333–335, 34d, pp. 342–345, 34e, pp. 335–338, 111), is furnished by the three chromium(III) chlorides of empirical formula $CrCl_3 \cdot 6H_2O$. It was these intriguing compounds, already considered in his first (1893) paper on the coordination theory (ref. 29, p. 290), that marked Werner's entry into the field of chromium complexes, an area to whose study he was to devote a dozen and a half papers[49,51,111–126].

Werner applied to these hydrates of chromium(III) chloride the same type of physicochemical methods that had done yeoman service in elucidating the constitution of the metal–ammines (conductivity measurements, cryoscopic molecular-weight determinations, and behavior toward aqueous silver nitrate). As a result, he proposed[111] the formulae $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ for the so-called Recoura's gray[127,128] and green[128–130] chromium chlorides, respectively.[*] Kinetic studies of the aquation of the green isomer to the violet isomer[†] led Niels Bjerrum to predict the existence of an intermediate compound containing the $[Cr(H_2O)_5Cl]^{2+}$ ion. A story by Bjerrum concerning this chloropentaaquochromium(III) chloride that he discovered[145–149] will give some insight into Werner's modus operandi and illustrate the speed and efficacy of his simple and direct technique.

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[*] Werner also proposed the formulae $[Cr(H_2O)_4Cl_2]Cl$ (ref. 111) and $[Cr(H_2O)_4Cl_2]Cl \cdot 6H_2O$ ($[Cr(OH_2 \cdot H_2O)_4(Cl \cdot H_2O)_2]Cl$) (ref. 113) for Godefroy's[131,132] hydrates $CrCl_3 \cdot 4H_2O$ and $CrCl_3 \cdot 10H_2O$, respectively. Furthermore, together with his assistant Robert Huber[49,125], he prepared a new green chromium chlorosulfate isomeric with Recoura's green chlorosulfate[133,134]. Based on its reactions, he claimed that the new compound was a double salt $[Cr(H_2O)_4Cl_2][Cr(H_2O)_6](SO_4)_2 \cdot 2H_2O$ similar to the alums, a view with which the Danish physical chemist Niels Bjerrum[135,136] concurred. However, when Werner proposed the same formula for Recoura's chlorosulfate itself, Bjerrum, who believed it to be $[Cr(H_2O)_5Cl]SO_4 \cdot H_2O$, disagreed. Although the chemistry of these chromium compounds is far from simple, Bjerrum's formulation seems to be correct.

[†] Although the system $[Cr(H_2O)_6]^{3+}$–$[Cr(H_2O)_5Cl]^{2+}$–$[Cr(H_2O)_4Cl_2]^{+}$ is probably more intricate than Werner believed, his proposed equilibria still offer the best simple explanation for a complicated phenomenon[137–144].

"When I came to Zurich [May–June, 1907] I had a short time before published a paper on a new chromic chloride with only one coordinatively bound chlorine atom [[$Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$] In order to be able to check this result Werner asked me to prepare a small amount of it, but instead of carrying out a titration with silver nitrate in order to test it, he only treated a small amount of it on a watch glass with sulfuric acid and in this way prepared a chloridesulfate, which he at once recognized as the so-called Recoura's chlorosulfate [[$Cr(H_2O)_5Cl]SO_4 \cdot H_2O$] Thus in the course of a few minutes he had acquired the conviction that the substance was really a new monochlorochromic chloride [refs 1, p. 63, 150] "

Actually, in solution the three aquated chromium(III) chlorides are interconvertible and the initially green solution changes in color to violet in the course of several days according to the equilibria[143]

$$[Cr(H_2O)_4Cl_2]Cl \overset{\text{rapid}}{\rightleftharpoons} [Cr(H_2O)_5Cl]Cl_2 \overset{\text{slow}}{\rightleftharpoons} [Cr(H_2O)_6]Cl_3$$

Recoura's Green Chloride	intermediate chloride predicted by Werner and isolated by Bjerrum	Recoura's Violet Chloride
emerald-green	blue-green	

Silver nitrate precipitates from the three compounds one-third, two-thirds, and all of the chlorine, respectively It is indeed a remarkable coincidence that each of the three solid hydrates contains the exact number of water molecules needed to maintain the constant total number six required to make the compounds isomeric The commercial product is the dichlorotetraaquo salt, and syntheses for the other two isomers have been devised (refs 148, 149, 153, pp 102, 103, 154) Werner proposed that the "excess" water molecules in the dichlorotetraaquo and chloropentaaquo compounds are bonded indirectly in the complex cation as $[Cr(H_2O)_4(Cl \cdot H_2O)_2]Cl$ and $[Cr(H_2O)_5(Cl \cdot H_2O)]Cl_2$, respectively. The lattice structures of $[Cr(H_2O)_6]Cl_3$ (ref 151) and *trans*-$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (ref 152) have been determined by X-ray crystallography.

Relationships similar to those among the three hydrates of chromium(III) chloride also exist between the two hexahydrates of chromium(III) bromide (ref 34e, p 336) From a solution of the blue isomer all the bromine is immediately precipitated by silver nitrate, whereas from a solution of the green isomer the bromine is only partially precipitated

$[Cr(H_2O)_6]Br_3$	and	$[Cr(H_2O)_4Br_2]Br \cdot 2H_2O$
hexaaquochromium(III) bromide		dibromotetraaquochromium(III) bromide
blue		green

Werner (ref. 155, p 344) proved the formulation of the green isomer by preparing the difficultly soluble salt $[Cr(H_2O)_4Br_2][Co(NH_3)_2(NO_2)_4]\cdot 2H_2O$

Werner's student Paul Pfeiffer[156], together with M Tapuach, discovered a number of cases of hydrate isomerism among other chromium complexes

(1) $[Cr(H_2O)_4(py)_2]Br_3\cdot 2H_2O$ and $[Cr(H_2O)_2(py)_2Br_2]Br\cdot 4H_2O$
(2) $[Cr(H_2O)_2(py)_2Cl_2]Cl$ and $[Cr(H_2O)(py)_2Cl_3]\ H_2O$
(3) $[Cr(en)_2(H_2O)_2]Br_3$ and $[Cr(en)_2(H_2O)Br]Br_2\ H_2O$ (ref. 157)

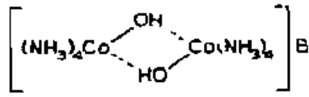
Hydrate isomerism is, of course, not limited to chromium compounds, witness the following four cases recognized by Werner among the complexes of cobalt

(1) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (ref 103) and $[Co(NH_3)_4Cl_2]Cl\cdot H_2O$ (ref. 111, p 1587)
violet green
(2) $[Co(NH_3)_3(H_2O)_2Cl]Br_2$ (ref. 158) and $[Co(NH_3)_3(H_2O)ClBr]Br\cdot H_2O$ (ref 158)
violet brown
(3) $[Co(NH_3)_4(H_2O)Cl]Br_2$ (ref 159) and $[Co(NH_3)_4Br_2]Cl\cdot H_2O$ (ref 160, p 215)
violet green
(4) $[Co(NH_3)_4(NO_2)Cl]Cl\cdot H_2O$ (ref 161) $\rightleftarrows$ $[Co(NH_3)_4(H_2O)(NO_2)]Cl_2$ (ref. 161)
red yellow-brown

The two compounds listed as (3) above are also examples of ionization isomers because in solution they yield different anions (see Sect G) The two compounds listed as (4) above are especially interesting because the red *eso hydrate*, on dissolution in water, is immediately transformed into the yellow-brown *aquo salt* The reaction is reversible, for the red *eso hydrate* can be precipitated from the resulting solution of the *aquo salt* by addition of potassium chloride

In the fifth edition of Werner's *Neuere Anschauungen* (ref 34e, pp 337, 338), Pfeiffer cites as a case of what he calls ***hydrate polymerism (Hydratpolymerie)*** the interconvertible pair of compounds

$[Co(NH_3)_4(H_2O)OH]Br_2$ (ref 74) and



$Br_4\ 2H_2O$ (ref 75)

The dinuclear compound has twice the molecular weight of the mononuclear compound In the earlier editions of *Neuere Anschauungen*, Werner had classified these compounds as examples of nuclear polymerization isomerism *(Kernpolymerie)* (see Sect C, p 166)

I SALT ISOMERISM, STRUCTURAL ISOMERISM, OR LINKAGE ISOMERISM *(SALZISOMERIE)*

Although this type of isomerism was called *salt isomerism* by Werner (refs 34a, pp 173–176, 34b, pp 271–275, 34c, pp. 338, 339, 34d, pp 347–349, 34e, pp. 340, 341, 100, p. 34), it has also been referred to as *structural isomerism*[8,9], a term that Werner reserved for isomers of the type listed in Sect F of this paper Since we have used the term *structural isomerism* to refer to the general type of isomerism exhibited by all the compounds treated in the present review and since the term *linkage isomerism* has now almost universally come into use, we shall use the term *linkage isomerism* in this paper. Of all the types of isomerism discussed in this article, linkage isomerism is probably the one most extensively investigated in recent years. The examples cited here are illustrative rather than exhaustive, and articles[2,4] reviewing the topic should be consulted for further examples and detailed information.

It is a well known fact of organic chemistry that tautomeric acids can give rise to two series of covalent isomeric derivatives, e.g. $\mathrm{R{-}N}\genfrac{}{}{0pt}{}{\nearrow\mathrm{O}}{\searrow\mathrm{O}}$ (nitro compounds) and R—O=N=O (nitrites), R—C≡N (nitriles) and R—N=C (isonitriles), R—O—C≡N (cyanates) and R—N=C=O (isocyanates), R—S—C≡N (thiocyanates) and R—N=C=S (isothiocyanates). Such isomerism, of course, cannot exist for ionic salts of these acids, but the phenomenon would be expected to occur among complexes containing these anions as ligands, i.e. covalently linked to a metal atom. Ligands which contain more than one coordinating group are known as *ambidentate*[3,5], and if only one of these donor groups can coordinate with a given metal at one time, linkage isomers, differing only in the mode of attachment of the ligand to the metal, are possible[2].

One isomer (xanthocobaltic chloride)[162] of the first pair of linkage isomers, was isolated in 1852, but the second isomer (isoxanthocobaltic chloride) was not isolated until 1894 (ref. 31, pp. 168–174). In 1899 Werner[109] mistakenly believed that he had prepared several series of isomers exemplifying thiocyanato–isothiocyanato isomerism, and he referred to this isomerism as structural isomerism. In his first (1905) edition of *Neuere Anschauungen* (ref. 34a, pp. 173–176), he cited these compounds as examples of what he then and henceforth called salt isomerism. It is strange that he did not mention the xantho and isoxantho isomers. However, he did cite them in the second edition (ref. 34b, pp. 274, 275). Little conclusive work on linkage isomerism was performed until the 1960's, but since that time more than thirty pairs of isomeric compounds have been synthesized and characterized by physicochemical methods[4]. Most of these have been synthesized by relying on mechanistic, electronic, and steric considerations. These compounds involve primarily six ambidentate ligands.

(i) M-NO₂ and M-ONO isomers (refs. 4, pp. 225–228, 5, pp. 216–220)

As already stated, the first and best known case of linkage isomerism among complexes, and until recently the only substantiated case, was first observed by Jørgensen, who isolated an unstable red salt of empirical formula $CoCl_2 \cdot NO_2 \cdot 5NH_3$ (refs. 31, pp. 168–174, 163, p. 149), which he called isoxantho cobaltic chloride because it was isomeric with the yellow xantho salt discovered by Wolcott Gibbs[162,164] in November, 1852 and published by Gibbs and Genth[165–167] in 1856.

Because of the stability and color of the xantho compound, Jørgensen regarded it as a nitro compound involving a Co—N bond; the isoxantho compound he regarded as a nitrito compound involving a Co–O bond Werner and Zinggeler[168] formulated these compounds as $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$, respectively, and also prepared other compounds exhibiting the same type of isomerism such as *cis*-$[Co(en)_2(NO_2$ or $ONO)_2]X$ (ref. 168), *trans*-$[Co(en)_2(NO_2$ or $ONO)_2]X$ (ref 168) and *trans*-$[Co(NH_3)_2(py)_2(NO_2$ or $ONO)_2]X$ (ref 168). Although some workers[169,170] have expressed doubt as to the existence of distinct xantho and isoxantho isomers, such isomerism has definitely been verified (refs 171–176, 177, pp 409–418), and studies of the isomerization reaction have been made Thus the nitropentaammine and nitritopentaammine of cobalt(III) constitute the most extensively studied case of linkage isomerism, and reproducible syntheses and isomerization reactions for these compounds have been devised and used as undergraduate laboratory experiments (refs 153, pp 105, 106, 178–180). The xantho and isoxantho cobalt compounds remained the only confirmed case of linkage isomerism until 1962, when the corresponding nitritopentaammines of rhodium(III), iridium(III) and platinum(IV) were synthesized for the first time, and their isomerization to the nitropentaammines was studied[181]

$$[Rh(NH_3)_5ONO]^{2+} \rightleftarrows [Rh(NH_3)_5NO_2]^{2+}$$
$$[Ir(NH_3)_5ONO]^{2+} \rightleftarrows [Ir(NH_3)_5NO_2]^{2+}$$
$$[Pt(NH_3)_5ONO]^{3+} \rightleftarrows [Pt(NH_3)_5NO_2]^{3+}$$

More recently, the unstable nitrito isomers $[Ni(Me_2en)_2(ONO)_2]$ and $[Ni(Et_2en)_2(ONO)_2]$ have been detected in solution but were not isolated[182] In short, the nitrito group remains one of the most versatile ambidentate ligands[183] ★

(ii) M-CN and M-NC isomers (refs 3, 4, pp 233, 234, 5, p 215)

The first clear-cut case of isomerism involved pseudohalogen salts Until Wohler[186] had analyzed silver cyanate and found its composition to be identical with that found by Liebig[187] for silver fulminate, it was considered axiomatic that substances with the same composition had to be identical[188]. As a result of Wohler's discovery, Berzelius[14] proposed the concept of isomerism, as mentioned in the Introduction

Although bifunctionality is known for halogens and many pseudohalogens, it is most prominent for cyanide and it influences the structures, properties, and reactions of cyanide derivatives In the older literature cyanide linkage isomers were often proposed, but definitive evidence for their existence has been fairly recent[3]. Examples include $[Co(CN)_5(CN$ or $NC)]^{3-}$ (refs. 189, 190) and $[Cr(H_2O)_5(CN$ or $NC)]^{2+}$ (ref 191), in both cases the unstable M-NC isomer was detected in solution but was not isolated. It was not until 1967 that

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★ A new type of isomerism *(conformational isomerism)*, which lies outside the scope of this paper, has recently been discovered[52,184] for the yellow and brown isomers of $[Co(en)NH_3(NO_2)_3]$, originally isolated by Werner and Grun[185] isocyano (M-NC) complexes that do not isomerize to the cyano (M-CN) form were reported[192] These linkage isomers, which constitute the first mononuclear N-bonded cyanide complexes ever isolated, were

cis-α-$[Co(tren)(CN)_2]ClO_4$ and *cis*-α-$[Co(tren)(NC)_2]ClO_4$
light yellow deep yellow

where tren is the tetradentate ligand triethylenetetramine

Pseudohalides, like halides themselves, can form bridges and consequently lead to the formation of polymers The first recorded inorganic complex, Prussian Blue, contains such bridges[3] In 1965 Shriver et al [193] predicted and discovered linkage isomerism in the compound $K[FeCr(CN)_6]$ (containing $Cr^{III}-C\equiv N-Fe^{II}$), which on heating isomerizes to $K[CrFe(CN)_6]$ (containing $Cr^{III}-N\equiv C-Fe^{II}$) In 1968 cyanide linkage isomerism was found to occur in the solid state for the polymeric complex $Fe_3[Cr(CN)_6]_2$ (ref 194) A total of four distinct structures exist, two intermediate stages were detected between the two linkage isomers $Fe^{2+}-N\equiv C-Cr^{3+}$ and $Cr^{3+}-N\equiv C-Fe^{2+}$.

(iii) M-SCN and M-NCS isomers (refs 4, pp 228–231, 5, pp 205–210)

In the last (1899) of his papers[109] to appear in the *Zeitschrift für Anorganische Chemie**, Werner believed that he had encountered salt isomerism, i e. linkage isomerism, involving thiocyanate ligands In fact, it was for such isomers rather than for the longer known nitro–nitrito isomers that he originated the term *Salzisomerie* For complexes of formula $[Co(en)_2(NCS)_2]X$, he obtained two series of compounds, an easily soluble one and a difficultly soluble one Since oxidation with chlorine converted the first series to *trans*-$[Co(en)_2(NH_3)_2]Cl_3$, he assumed that in these compounds the thiocyanate nitrogen is bonded directly to the cobalt atom, i e these are isothiocyanato compounds Similar treatment converted the second series to *trans*-$[Co(en)_2Cl_2]Cl$, in which the thiocyanate group had been removed by complete oxidation, and Werner supposed that these compounds contained Co–S bonds, i e they were true thiocyanate compounds In 1907, Werner and Zinggeler[168] reported a similar case of supposed linkage isomerism for compounds of formula $[Co(NH_3)_4(NO_2)SCN]X$ Finally, in 1912, on the basis of oxidation studies involving hydrogen peroxide and fuming nitric acid in addition to the previously employed chlorine, Werner (ref 196, pp 22, 41–43, 192–194) admitted that he was in error and that these compounds were stereoisomers, not structural isomers In all cases of thiocyanate coordination[109,168,197], the ligand was coordinated as isothiocyanate, i e through the ni-

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* After 1899 most of Werner's papers appeared in *Berichte der Deutschen Chemischen Gesellschaft* probably because he no longer approved of the philosophy underlying *Zeitschrift für Anorganische Chemie* In a letter of June 23rd, 1904, to Richard Lorenz, editor of the *Zeitschrift*, Werner resigned from the editorial board because that journal had "gradually developed so strongly in the physico-chemical direction that it no longer meets the needs and expectations of the pure inorganic chemist"[195]

trogen. The easily soluble "diisothiocyanato" compounds were found to be *trans* isomers, and the sparingly soluble "dithiocyanato" compounds the corresponding *cis* isomers.

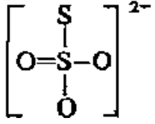
Since Werner's day, chemists have learned that the thiocyanate ion forms both thiocyanato and isothiocyanato complexes depending upon the central metal atom, but until recently it was believed that for a given metal atom, only one type of complex could exist[198–208]. Then in 1961, Turco and Pecile[209] observed that for palladium(II) and platinum(II) complexes, coordinated thiocyanate ion is either S- or N-bonded, depending upon the other ligands present. Their discovery that the presence of other ligands in the coordination sphere can affect the nature of the metal–thiocyanate bond provided the impetus for much of the current interest in ambidentate ligands[5]. Acting on Turco and Pecile's observation, Basolo et al.[210,211] were able to synthesize thiocyanato–isothiocyanato linkage isomers of $[Pd\{(C_6H_5)_3As\}_2(SCN)_2]$ and $[Pd(2,2'\text{-bipyridine})_2(SCN)_2]$. Once again, another of Alfred Werner's predictions had been fulfilled. The monopoly of xantho–isoxantho compounds on what was once the least familiar type of complex isomerism was broken, and numerous thiocyanato–isothiocyanato linkage isomers were soon prepared, e.g. $[Pd(N,N,N',N'\text{-tetraethyldiethylenetriamine})NCS]^+$ (refs. 212, 213), $[Cd(NCS)_4]^{2-}$ (refs. 214–216), $[Mn(CO)_5SCN]$ (ref. 217), $[Pd(Bu^n_3As)_2(SCN)_2]$ (ref. 218), $[Rh(NH_3)_5NCS]^{2+}$ (refs. 219, 220), $[Ir(NH_3)_5NCS]^{2+}$ (refs. 220, 221), $[Cr(H_2O)_5NCS]^{2+}$ (refs. 222, 223), $[(C_5H_5)Fe(CO)_2NCS]$ (ref. 224), $[(C_5H_5)Mo(CO)_3NCS]$ (ref. 224) and $[Pd\{P(OMe)_3\}_2(NCS)_2]$ (ref. 225). The isomers of $[Pd(4,7\text{-diphenyl-1,10-phenanthroline})(SCN)_2]$ (ref. 226) and $[Cu(\text{triethylenetetramine})(NCS)(SCN)]$ (ref. 227) involve both M-SCN and M-NCS bonding in the same molecule. A case in which all three possible linkage isomers are known, for a complex containing two thiocyanate groups, is provided by $[CuL(SCN)(NCS)]$, $[CuL(SCN)_2]$, and $[CuL(NCS)_2]$, where L is the bidentate ligand (2-pyridyl)amine[228].

(iv) M-SeCN and M-NCSe isomers (refs. 4, pp. 234, 235, 5, pp. 210–214)

Virtually no research was carried out on the ambidentate selenocyanate ligand until the 1960's. The first pair of linkage isomers to be isolated[229,230] was $[Pd(N,N,N',N'\text{-tetraethyldiethylenetriamine})(SeCN\text{ or }NCSe)][B(C_6H_5)_4]$; this cation represented the first example of the dependence of the bonding mode of an ambidentate ligand on the nature of a non-coordinated group[230].

(v) M-SSO$_3$ and M-OS$_2$O$_2$ isomers

Another potentially ambidentate ligand is the thiosulfate ion. Since it possesses the structure



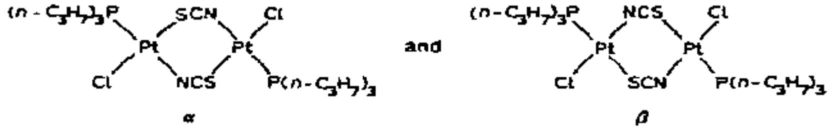
either a sulfur atom or an oxygen atom could theoretically function as a donor in forming a coordination compound, thus leading to linkage isomerism. Such isomerism has been reported[231] for the compound $H_4[Co(S_2O_3)(CN)_5]$, which was said to exist in gold and brown forms More recently, linkage isomers of the $[Co(NH_3)_5S_2O_3]^+$ ion have been detected by kinetic and spectral data from electron transfer studies[232-234]. The mixture of isomers was initially isolated in the solid state

(vi) M-OSO₂ and M-SO₃ isomers (ref 4, pp 236, 237)

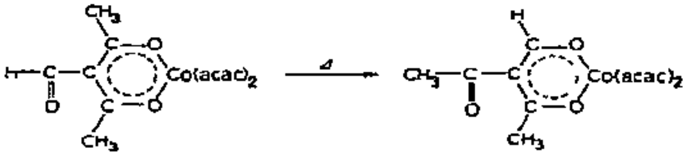
The only published information (ref 2, p. 298) on sulfite linkage isomers is based upon an incorrect quotation of D.R Stranks by R T.M. Fraser. Stranks was said to have prepared the unstable pink O-bonded $[Co(NH_3)_5OSO_2]^+$, but this species was not isolated nor was any evidence presented that would point to its existence in solution[230] Only the stable yellow-brown S-bonded species is known[235].

(vii) Miscellaneous isomers (ref 4, pp. 237, 238)

"Linkage isomerism involving bridging groups is rare. In addition to the polymeric cyanide compounds[193,194] cited above (Sect. I (*ii*)), the dinuclear compounds [236,237], α- and β-$[Pt_2(SCN)_2Cl_2\{P(C_3H_7)_3\}_2]$, first believed to be structural isomers and then stereoisomers, were finally shown by X-ray analysis to be linkage isomers[238-240]



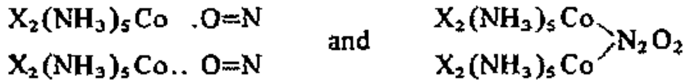
In 1901, Werner[241] discovered the acetylacetonate complex K[Pt(acac)₂Cl]. Although several distinct bonding and structural types involving acetylacetone and its enolate anion are known[242], linkage isomers involving chelating ligands are still rare Both linkage isomers have been isolated[243] in the isomerization reaction



J VALENCE ISOMERISM *(VALENZISOMERIE)*

According to Werner (ref 34d, p 382), "Valence isomerism is predicated upon the fact that in the isomers the same molecular components are linked by different valences. In one isomer the radicals in question are linked to a definite atom by secondary valences *(Nebenvalenzen)*, while the bonding in the other isomer results from primary valences *(Hauptvalenzen)*." All the examples of this type of isomerism cited originally by Werner (refs. 34a, pp. 185–187, 34b, pp. 290, 291, 34c, pp. 370–373, 34d, pp. 382–385, 34e, pp. 377–379; 35, pp. 6,7) have been disproved or shown to be isomers of a different type. Indeed, since no essential difference, but only an artificial one, exists between primary and secondary valences, as Werner himself readily admitted, such isomerism is meaningless (ref. 10, pp. 172, 173). Nevertheless, these isomers present a number of interesting problems, and we shall now briefly examine the history of three of them.

The most frequently cited example of valence isomerism now appears to be a case of polymerization isomerism (ref. 177, pp. 408–412). The nitrosopentaammines corresponding to the dimolecular formula $[(NO_2)_2\{Co(NH_3)_5\}_2]X_4$ were found to occur in two series, an unstable black one and a stable red one, to which their discoveres, Sand and Genssler[78,79] assigned the formulae

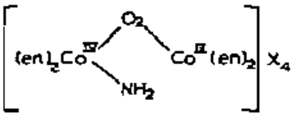


$$\begin{matrix} X_2(NH_3)_5Co\ .O{=}N \\ X_2(NH_3)_5Co..\ O{=}N \end{matrix} \quad \text{and} \quad \begin{matrix} X_2(NH_3)_5Co \\ X_2(NH_3)_5Co \end{matrix}\!\!>\!N_2O_2$$

Werner and Paul Karrer, his successor as head of the Chemisches Institut der Universitat Zurich[76,77], reinvestigated Sand's compounds and concluded that the red salts were dimolecular, $[Co_2N_2O_2(NH_3)_{10}]X_4$, but that the black salts were monomolecular, $[Co(NH_3)_5NO]X_2$. Since that time, these perplexing compounds have been the subject of numerous experimental studies[246–261]. The results of many of these have led to conflicting interpretations. On the basis of several measurements of magnetic susceptibility[244–248], which apparently showed the black isomer to be paramagnetic and the red isomer to be diamagnetic, a new type of isomerism – "electronic isomerism" – was proposed and the following structural formulae were assigned. $[Co^{II}(NH_3)_5(NO)^0]X_2$ (black) and $[Co^{III}(NH_3)_5(NO)^-]X_2$ (red)[249]. Others[248,250] suggested that Werner and Karrer's formulations should be reversed and that the red salt was a mononuclear compound and the black salt a dinuclear compound. However, the mononuclear structure attributed to the red salts[251] was not confirmed experimentally. Asmussen et al.[252] showed that previous magnetic measurements were incorrect because of the presence of cobalt(II) impurities, salts of both the red and black series were diamagnetic. Miki et al.[253] believed the compounds to be linkage (nitro–nitrito) isomers.

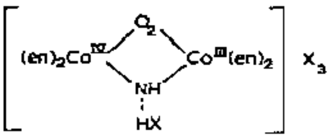
Recent studies have confirmed Werner and Karrer's assignment of a dinuclear structure to the red salt. Thus, Brintzinger and Plessing[256] reported an ionic weight of 380 for the ion of this salt. Ardon[257], by means of the elution rate of the red salt from a cation-exchange resin, showed that the ion had a +4 charge, and conductivity studies by Feltham[258] have shown the red isomer to be a 4:1 electrolyte. The monomeric salt is believed to contain Co–NO bonding, while the dinuclear salt is thought to contain an $ONNO^{2-}$ ion of some configuration between the cobalt atoms[259,260]. Reproducible preparations for both compounds have been published[261,262].

Of a second pair of valence isomers cited by Werner (ref. 35, p. 18)



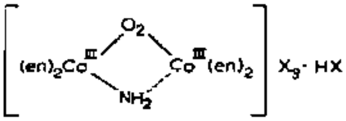
green, neutral reaction

and

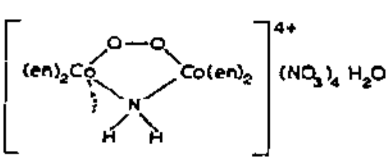


red, acid reaction

the second compound has been shown not to be isomeric with the first at all. Instead, it was found to contain only tripositive cobalt, and Thompson and Wilmarth[263] formulated it as the acid salt of the one-electron reduction product of the first, viz

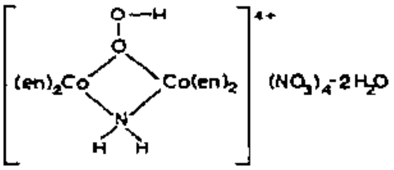


Thewalt and Marsh[95] later showed for the nitrates of the two series that the green paramagnetic compound contains a superoxo (O_2^-) bridge, while the red diamagnetic compound contains a hydroperoxide (OOH^{2-}) bridge[68]



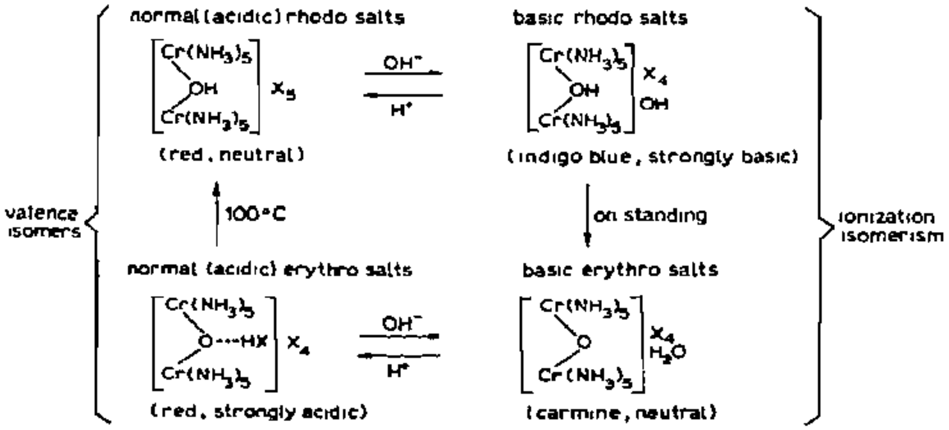
green, paramagnetic

and

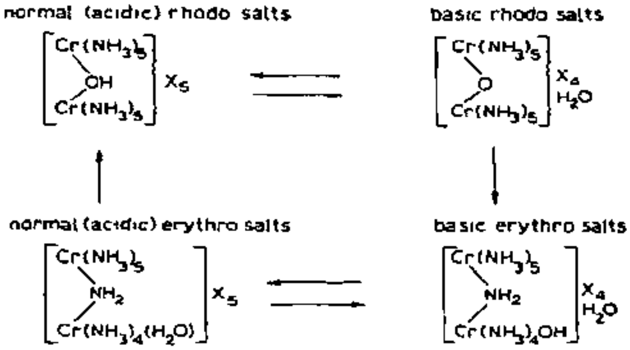


red, diamagnetic

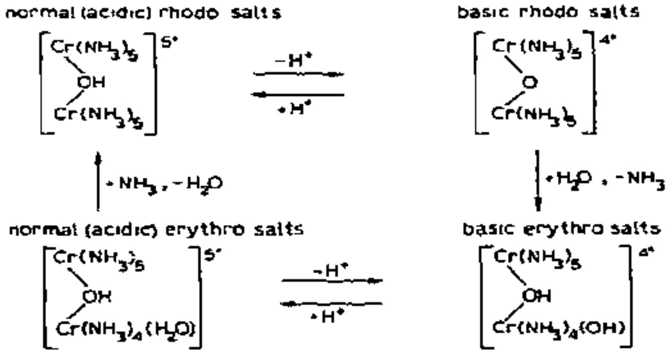
A third case of valence isomerism cited by Werner (ref 34d, p 383) concerns the so-called rhodo and erythro salts of chromium, first discovered in 1882 by Jørgensen[264–266] The relationships of these compounds to each other and to their basic salts, together with their properties and Werner's constitutional formulae, are best shown schematically as



In 1937, these compounds were reinvestigated by Jensen[267], who, by use of X-ray powder pattern techniques, found the rhodo and erythro bromides to be isomorphous Since no difference actually exists between primary and secondary valences, the formulae proposed for the normal rhodo and erythro salts are identical Consequently, Jensen proposed the following formulation to explain the isomeric relationships



More recently, on the basis of analytical data, degradation reactions, and measurements of acidity constants and magnetic susceptibilities, Wilmarth et al [268] have concluded that the rhodo and erythro ions are not isomeric at all, and they reformulated the situation as



The alleged isomerism had been predicated upon Jørgensen's incorrect nitrogen analyses for the erythro compound Inasmuch as Jensen analyzed the erythro bromide for chromium and bromine only, he naturally did not detect the replacement of an ammonia molecule by water Wilmarth et al [268] used both Dumas and Kjeldahl analyses to show that the erythro ion contained nine rather than ten nitrogen atoms The conversion of a hydroxo bridge to an oxo bridge, as in the formation of basic rhodo salts from normal rhodo salts, is readily detectable by dramatic changes in the near-ultraviolet spectra[269-272]

K COORDINATION NUMBER ISOMERISM *(KOORDINATIONSZAHLISOMERIE)*

This type of isomerism is not yet mentioned in any of the standard textbooks It was proposed by Werner in an unpublished, but complete, 10-page, double-spaced, typewritten manuscript "*Über Koordinationszahl 'acht' und über die wechselnde Koordinationszahl*", found by the present author among Werner's papers in Zurich[124] In this manuscript Werner describes the preparation, properties, and constitution of a series of supposedly octacoordinate chromium complexes which remains unreported in the literature up to the present day He cited the following pair of compounds as isomers containing the same metal with different coordination numbers

$[Cr(en)_2Cl_2]Cl \cdot H_2O$	and	$[Cr(en)_2(H_2O)Cl_3]$
Pfeiffer[273]		Werner
coordination number 6		coordination number 8

On heating, the latter compound is transformed into the anhydrous form of the former compound

On the basis of preliminary reflection spectra[274], the compound formulated by Werner as $H[Cr(en)_2Cl_4]$ has been tentatively identified as octahedral 1, 2, 3-$[Cr(en)(enH)Cl_3]Cl$, in which one molecule of ethylenediamine is bidentate, but the other (protonated) one is monodentate[275] The coordination number would thus appear to be 6, not 4, and the compounds do not exemplify Werner's proposed type of isomerism The aquo compound would presumably be 1,2,3-$[Cr(en)(enH)Cl_3]OH$, and the type of isomerism exhibited would be ionization isomerism[124]

L OTHER CLASSIFICATIONS

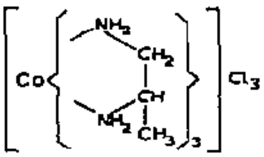
Other workers have defined additional types of isomerism such as ligand isomerism, ring size isomerism, summation isomerism, and electronic isomerism (ref 9, pp 271–273)

Ligand isomerism arises from isomerism within the ligands themselves, e.g the two trios of isomers

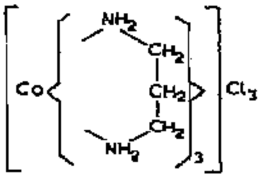
$[Co(en)_2(CH_3C_6H_4NH_2)Cl]Cl_2$ (ref 276), where $CH_3C_6H_4NH_2$ = *o*-, *m*-, or *p*-toluidine

$[Pt(NH_2C_6H_4COOH)_2Cl_2]$ (ref 277), where $NH_2C_6H_4COOH$ = *o*-, *m*-, or *p*-aminobenzoic acid

Ring size isomerism is illustrated by the pair of isomers[278]



propylenediamine forms 5-membered rings



trimethylenediamine forms 6-membered rings

Summation isomerism is illustrated by compounds in which entirely different groups are coordinated to the central atom, but the sum of all the atoms is constant, e g [278]

$$[Co(NH_2CH_2CH_2CH_2CH_2NH_2)(NH_2CH_2CH_2NH_2)Cl_2]^+ \text{ and } [Co(NH_2CH_2CH_2CH_2NH_2)_2Cl_2]^+$$

Electronic isomerism has already been mentioned in connection with the black and red "valence isomers" of the compounds of empirical formula $Co(NH_3)_5NOCl_2$ (Sect 3)

As we have seen from the examples in this article, Werner's classification of structural isomerism is so thorough and detailed that the sheer number of the types defined is almost overwhelming at first sight Even Paul Pfeiffer, in his fifth edition of *Neuere Anschauungen*[34e], reduces the number of different types of isomerism by combining several Since most cases of structural isomerism arise from the different permutations and combinations of ligands and metal atoms, Martin and Martin[279] propose a classification of such isomerisms into three main types (1) *coordination-sphere isomerism*, which arises because of different distributions of ligands inside and outside the coordination sphere and includes Werner's hydrate, ionization, and valence isomerisms, (2) *distribution isomerism*, which is due to different distributions of a set of ligands about two or more coordination centers and includes Werner's polymerization, coordination, and coordination position isomerisms, and (3) *ligand isomerism*, which includes Werner's salt isomerism Regardless of whether or not such proposals eventually supersede Werner's original classification, his scheme, which for many years provided a fruitful frame of reference for research in the field, will undoubtedly retain its place in the annals of coordination chemistry.

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