高等学校教材

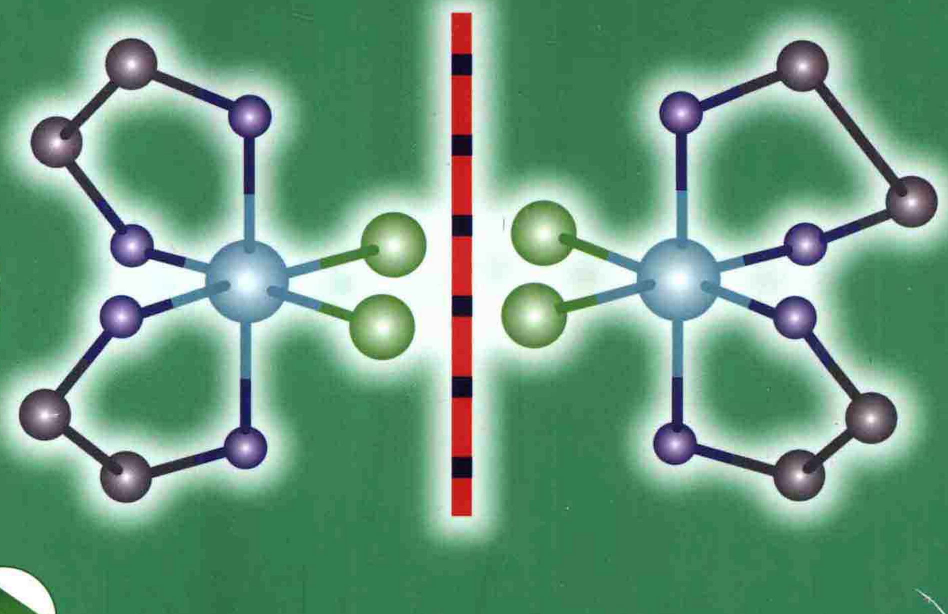
配位化学

Coordination Chemistry

（双语版）

第二版

李晖 编著



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·北京·

本书是在作者多年的双语教学实践和思考的基础上编撰而成的，是一本适应当前国内高等院校化学专业教学需要和21世纪人才培养新需求的教科书。

全书共分五章，第1、2章简介了配位化学的发展、基本概念和基本理论，第3章为配合物结构的谱学研究方法，第4、5章为配合物的物理化学性质和反应性。

本书可作为高等院校化学及相关专业高年级本科生和研究生的教材，也可供化学教师及科研工作者参考。

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前　言

本书自2006年出版以来，受到了高校师生和广大读者的欢迎，至2010年底已经发行了上万册。这也反映出配位化学在化学、生命科学、材料学等相关专业的教学和科研中的重要性和强烈需求。

近五年来，作者在配位化学的教学与科研过程中，深深体会到配位化学的迅速发展及其与其他学科领域的交叉与融合，尤其是与超分子化学的相互渗透。因此，在第二版中，作者觉得不得不将超分子化学的一些基本概念编入到教材中（第1、2章）。同时，X-射线衍射技术（包括粉末衍射和单晶衍射）在物质结构分析中的重要性也被每年大量报道的新颖配合物的晶体结构所证实，说明X-射线衍射技术已成为研究配合物结构的最重要的方法。所以，将X-射线衍射的基本原理编入第3章。同时，鉴于分子轨道理论在复杂配位化合物的成键与结构应用中的局限性，将原第2章中的这部分内容进行了适当的删减。第4、5章没有做明显的改动，并不是这部分没有新的发展，而是因为一方面时间有限，没有充足的精力做太多的改动；另一方面，第二版应该保持第一版的主要特色。

第二版的修订与编撰同样得到了很多人的帮助与支持，我的女儿施如菲作为加州大学尔湾分校（UC Irvine）化学生物学专业的学生，对超分子化学和配位化学具有浓厚的兴趣，为第二版的修订提出了很多中肯的建议，我的博士研究生汤贝贝为第二版的中英文校对付出了辛勤的劳动，出版社的编辑也为本版的出版付出了大量的心血。在此作者谨向他们表示衷心的感谢。

由于时间仓促及作者水平有限，书中的不妥和疏漏之处在所难免，敬请专家和读者指正。

李晖
于北京理工大学化学学院
2011年6月

第一版前言

无机化学、有机化学、分析化学和物理化学等都是经典的化学学科分支。配位化学作为无机化学和有机化学的交叉领域，迄今已有一百多年的历史。配位化学的兴起和迅速发展不仅给古老的无机化学带来了生机，也为化学领域中其他分支学科的发展开辟了更广阔的天地。20世纪80年代后期发展起来的超分子化学与配位化学之间更有着紧密的联系，可以看成是广义的配位化学（游效曾院士在全国配位化学会议上的报告）。因此，配位化学已经成为化学领域中的重要分支，是与材料科学、生命科学、物理学等众多学科相互渗透、高度融汇的重要学科领域。

目前，许多高等院校都为化学及相关专业的高年级本科生和研究生开设了配位化学课。也有一些配位化学的专著出版，如游效曾院士的《配位化合物的结构和性质》等。但尚未有合适的教材适应当前相关层次的教学。作者在多年配位化学的教学实践过程中，收集了大量的资料，结合作者多年的国内外的科研经历，编撰了这本双语教材。

本教材有以下几个特点。

（1）英、中双语是本教材的首要特点。作为自然科学的学习，英语是一种非常重要的工具，是我们了解国际最新发展动态的重要窗口，作为21世纪的大学生和研究生，对英语熟练地听、说、读、写已是一项基本要求。教育部也大力提倡在高等教育中运用双语教学。本教材正是为适应这一新的需求而编撰的。而且，本教材在北京理工大学的高年级本科生和研究生教学中，深受学生欢迎，已取得了良好的教学效果。

（2）深入浅出，重点突出，是本教材的另一特点。配位化学是一门相当成熟的学科，有着一整套的新理论、新概念、新方法和新反应等。本教材以配位化学中最为重要的概念、理论、方法和性质为主体，层次分明地展开叙述。对于涉及量子化学的内容，如分子的对称性——群论、分子轨道理论和配位场理论等部分，只给出结论并注重这些结论在解决化学问题中的应用，而不涉及量化计算。

（3）选材新颖，具有时代性，是本教材的第三个特点。将配位化学一些新近发展的成果融入到教材和整个教学实践中一直是作者努力的方向，但由于配位化学的发展非常迅速，所以，也不太可能囊括所有的最新研究成果，只能适当地编入一些材料，以便读者进一步跟踪有关发展动态。

本书在编撰过程中得到了多方的支持，尤其是研究生——郭明、田红、何飞跃，本科生白萌等为本书的中文输入和制图付出了辛勤的劳动，化学工业出版社的编辑在本书的出版过程中提供了有益的建议和大量的帮助。在此谨向他们表示衷心的感谢。

由于时间仓促及作者水平有限，书中不妥之处，敬请读者批评指正。使用过程中如有问题可与作者联系，E-mail：lihui@bit.edu.cn。

李晖

北京理工大学理学院化学系

2005年9月

Contents

Chapter 1 An Introduction To Coordination Chemistry

1. 1 The History of Coordination Chemistry

1. 1. 1 The Origin of Coordination Chemistry

One of the most productive areas of research in the twentieth century was Alfred Werner's development of coordination chemistry. It is a measure of Werner's impact on the realm of inorganic chemistry that the number, variety, and complexity of coordination compounds continues to grow even as we pass the centennial anniversary of his original work.

The first coordination compound was most likely prepared in the late 1700s by Tassaert, a French chemist. He observed that ammonia combined with a cobalt ore to yield a reddish brown product. Over the next century, many compounds were synthesized and characterized, but little progress was made in formulating and accounting for their molecular structures (Fig 1.1). The discovery and explanation of coordination compounds should be viewed against the larger picture of progress in understanding atomic structure, the periodic table, and molecular bonding.

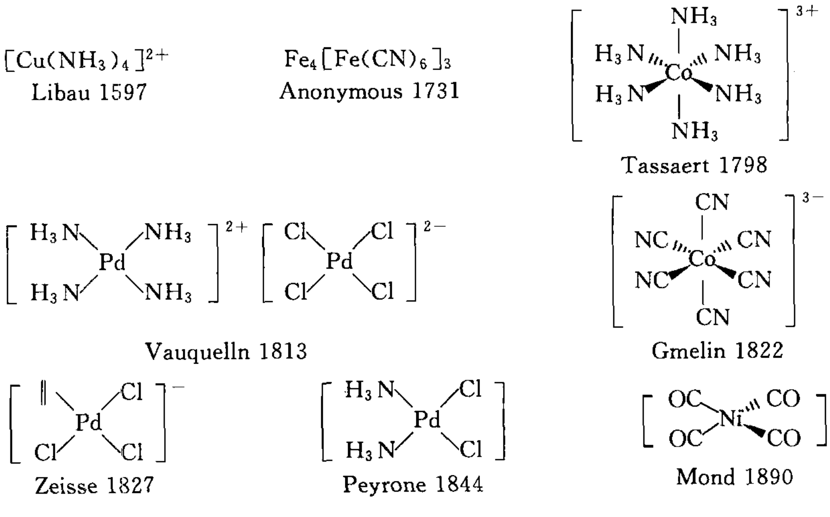


Fig 1. 1 Some important compounds as landmarks in inorganic chemistry

The contributions of Proust and Lavoisier led Dalton to formulate the first concrete atomic theory in 1808. Mendeleev published his first periodic table in 1869. With the discoveries of X rays, radioactivity, electrons, and the nucleus at the beginning of the twentieth century, the modern quantum-mechanical picture of the atom started to emerge in the 1920s. This model gives a theoretical explanation for atomic line spectra and the modern periodic table. However, no theoretical basis was developed to satisfactorily account for these wondrous compounds at that time.

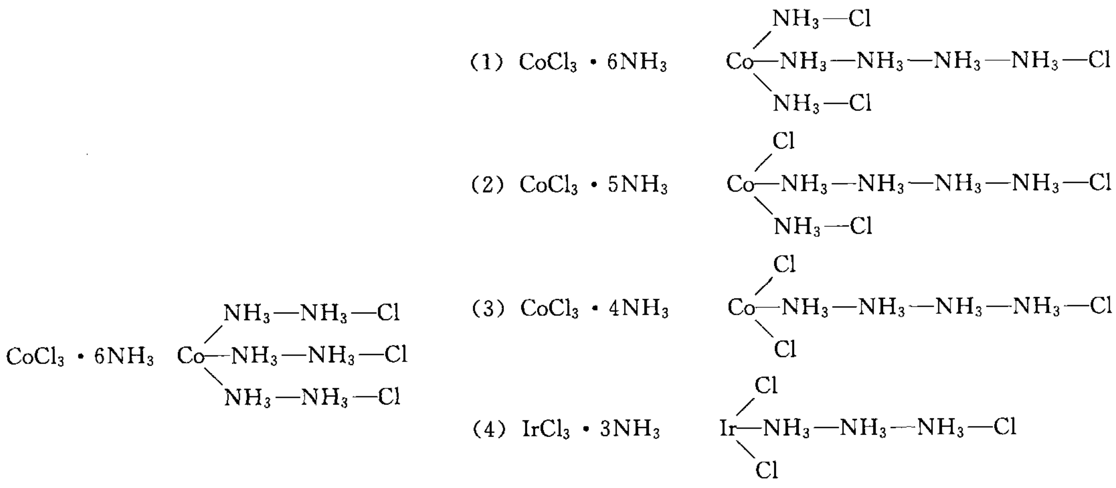
Given the success of organic chemists in describing the structural units and fixing atomic valences found in carbon-based compounds, it was natural that these ideas be applied to the ammonates. The results, however, were disappointing; for example, considering the typical data for the cobalt ammonate chlorides listed in the Table 1.1. The formulas used in the last few decades of the nineteenth century indicated the ammonia-to-cobalt mole ratio but left the nature of the bonding between them to the imagination. This uncertainty was reflected in the dot used in the formula to connect, for example, $CoCl_3$ to the appropriate number of ammonias. Conductivities measured when these compounds were dissolved in water are given qualitatively, which was just then starting to be taken as a measure of the number of ions produced in solution. The "number of chloride ions precipitated" was determined by the addition of aqueous silver nitrate, as represented in (equation 1.1):

Table 1.1 The cobalt ammonate chlorides

Formula	Conductivity	No. of Cl^- ions precipitated
$CoCl_3 \cdot 6NH_3$	High	3
$CoCl_3 \cdot 5NH_3$	Medium	2
$CoCl_3 \cdot 4NH_3$	Low	1
$IrCl_3 \cdot 3NH_3$	Zero	0

$$AgNO_3(aq) + Cl^-(aq) \longrightarrow AgCl(s) + NO_3^-(aq) \qquad (1.1)$$

Now how might you explain such data? In 1869, Christian Wilhelm Blomstrand firstly formulated his theory to account for the cobalt ammonate chlorides and other series of ammonates. He produced a picture of $CoCl_3 \cdot 6NH_3$ have shown in Fig 1.2 (a).



(a) Blomstrand's representation of $CoCl_3 \cdot 6NH_3$ (b) Jϕrgensen's representations of four members of the series with the iridium subsitituted for the intended cobalt in compound (4)

Fig 1.2 Representations of the cobalt ammonate chlorides by Blomstrand and Jørgensen

Based on the prevailing ideas of that time, this was a perfectly reasonable structure. The divalent ammonia he proposed was consistent with a view of ammonium chloride written as H—NH_3—Cl. The valence of 3 for cobalt was satisfied and nitrogen atoms were chained together much like carbon in organic compounds. The three monovalent chlorides were far enough removed from the cobalt atom to be available to be precipitated by aqueous silver chloride.

In 1884, S. M. Jørgensen proposed some amendments to his mentor's picture (Table 1.2). First, he had new evidence that correctly indicated that these compounds were monomeric. Second, he adjusted the distance of the chloride groups from the cobalt to account for the rates at which various chlorides were precipitated. The first chloride is

Table 1.2 The historical setting of coordination compounds

Atomic structure and the periodic table	Molecular structure and bonding	Coordination chemistry
1750		
1774: Law of conservation of matter: Lavoisier 1799: Law of definite composition: Proust		1798: First cobalt ammonates observed: Tassaert
1800		
1808: Dalton's atomic theory published in *New System of Chemical Philosophy*	1830: The radical theory of structure: Liebig, Wöhler, Berzelius, Dumas (organic compounds composed of methyl, ethyl, etc, radicals) 1852: Concept of valence: Frankland (all atoms have a fixed valence) 1854: Tetravalent carbon atom: Kekulé	1822: Cobalt ammonate oxalates prepared: Gmelin 1851: $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5NH_3$, and other cobalt ammonates prepared: Genth, Claudet, Fremy
1859: Spectroscope developed: Bunsen and Kirchhoff 1869: Mendeleev's first periodic table organizes 63 known elements	1874: Tetrahedral carbon atom: Le Bel and Van't Hoff	1869: Chain theory of ammonates: Blomstrand
1885: Balmer formula for visible H spectrum	1884: Dissociation theory of electrolytes: Arrhenius	1884: Amendments to chain theory: Jørgensen
1894: First "inert gas" discovered 1895: X-rays discovered: Roentgen 1896: Radioactivity discovered: Becquerel		1892: Werner's dream about coordination compounds
1900		
1902: Discovery of the electron: Thomson 1905: Wave-particle duality of light: Einstein 1911: α-particle/gold foil experiment; nuclear model of the atom: Rutherford 1913: Bohr model of the atom (quantization of electron energy) 1923: Wave-particle duality of electrons: De Broglie 1926: Schrödinger quantum-mechanical atom (electrons in orbitals about nucleus; electron spectroscopy explained as transitions among orbitals)	1923: Electron-dot diagrams: Lewis 1931: Valence-bond theory: Pauling, Heitler, London, Slater Early 1930s: Molecular orbital theory: Hund, Bloch, Mulliken, Hückel 1940: Valence-shell electron-pair repulsion (VSEPR) theory: Sidgwick	1902: Three postulates of coordination theory proposed: Werner 1911: Optical isomers of *cis*-$[CoCl(NH_3)(en)_2]X_2$ resolved: Werner 1914: Non-carbon-containing optical isomers resolved: Werner 1927: Lewis ideas applied to coordination compounds: Sidgwick 1933: Crystal field theory: Bethe and Van Vleck
Modern periodic table including trends in periodic properties	Modern concepts of chemical bonding	Modern coordination theory

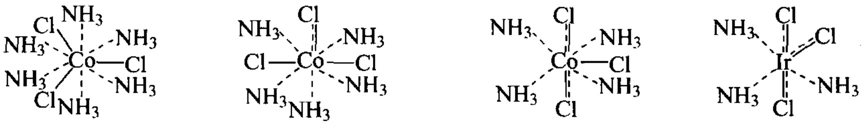
precipitated much more rapidly than the others and so was put farther away and therefore less under the influence of the cobalt atom. His diagrams for the first three cobalt ammonate chlorides are shown in Fig 1. 2 (b). Note that, in the second compound, one chloride is now directly attached to the cobalt, therefore, unavailable to be precipitated by silver nitrate. In the third compound, two chlorides are similarly pictured. These changes are significant. It appeared that the Blomstrand-Jørgensen theory was on the right track.

But was there a compound with only three ammonias? As shown in Fig 1. 2 (b) (4), the theory predicted that it should exist and, furthermore, should have one ionizable chloride. But this critical compound was not available. After considerable time and effort, the analogous iridium ammonate chloride was found to be a neutral compound with no ionizable chlorides. The theory was in trouble.

1. 1. 2 The Modern Coordination Chemistry—Werner Coordination Chemistry

Alfred Werner (1866—1919), as a young unsalaried lecturer in organic chemistry, was torn between organic and inorganic chemistry. His first contributions (the *stereochemistry*, or spatial arrangements, of atoms in nitrogen compounds) were in the organic field, but so many intriguing inorganic questions were being raised in those days. He observed the difficulties that inorganic chemists were having in explaining coordination compounds, and he was aware that the established ideas of organic chemistry seemed to lead only into blind alleys and dead ends. In 1892, his coordination theory came to him. But his new theory broke with the earlier traditions, and he had essentially no experimental proof to support his ideas. Werner's theory was considered to be audacious fiction. Werner spent the rest of his life directing a systematic and thorough research program to prove that his intuition was correct.

Werner decided that the idea of a single fixed valence could not apply to cobalt and other similar metals. Working with the cobalt ammonates and other related series involving chromium and platinum, he proposed instead that these metals have two types of valence, a primary valence and a secondary valence. The primary, or ionizable, valence corresponded to what we call today the *oxidation state*; for cobalt, it is the 3+ state. The secondary valence is more commonly called the *coordination number*; for cobalt, it is 6. Werner maintained that this secondary valence was directed toward fixed geometric positions in space.



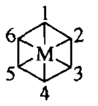
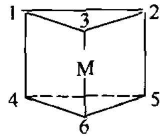
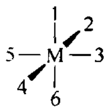
(1) $CoCl_3 \cdot 6NH_3$ (2) $CoCl_3 \cdot 5NH_3$ (3) $CoCl_3 \cdot 4NH_3$ (4) $IrCl_3 \cdot 3NH_3$

Fig 1. 3 Werner's representations of the cobalt ammonate chlorides. The solid lines represent groups that satisfy the primary valence or oxidation state (3+) of cobalt, and the dashed lines represent those that satisfy the secondary valence, or coordiantion number (6). The secondary valence occupies fixed positions in space

Fig 1. 3 shows Werner's early proposals for the bonding in the cobalt ammonates. He said that the cobalt must simultaneously satisfy both its primary and secondary valences. The solid lines show the groups that satisfy the primary valence. The dashed lines, always directed toward the same fixed positions in space, showing how the secondary valence was satisfied. In compound (1), all three chlorides satisfy only the primary valence, and the six ammonias satisfy only the secondary. In compound (2), one chloride must do double duty and help satisfy both valences. The chloride that satisfies the secondary valence (and is directly bound to the Co^{3+} ion) was concluded to be unavailable for precipitation by silver nitrate. Compound (3) has two chlorides doing double duty and only one available for precipitation. Compound (4), according to Werner, should be a neutral compound with no ionizable chlorides. This was exactly what Jørgensen had found with the iridium compound.

Werner next turned to the geometry of the secondary valence (or coordination number). As shown in Table 1. 3, six ammonias about a central metal atom or ion might assume one of several different common geometries, including hexagonal planar, trigonal prismatic, and octahedral. The table compares some information about the predicted and actual number of isomers for a variety of substituted coordination compounds.

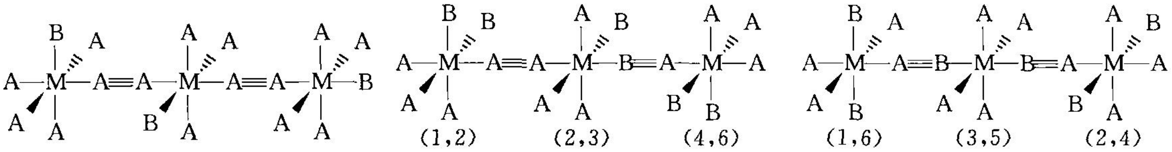
Table 1. 3 The number of actual versus predicted isomers for three different geometries

	Geometries of Coordination Number 6			
	Hexagonal planar	Trigonal prism	Octahedral	
				
Formula	No. of predicted isomers (numbers in parentheses indicate position of the B ligands)			No. of actual isomers
MA_5B	One	One	One	One
MA_4B_2	Three	Three	Two	Two
	(1,2)	(1,2)	(1,2)	
	(1,3)	(1,4)	(1,6)	
	(1,4)	(1,6)		
MA_3B_3	Three	Three	Two	Two
	(1,2,3)	(1,2,3)	(1,2,3)	
	(1,2,4)	(1,2,4)	(1,2,6)	
	(1,3,5)	(1,2,6)		

A few comments about the information in this table needed to be given before discussing. (1) The symbols for the compounds use M for the central metal and A's and B's for the various ligands. (2) The numbers in parentheses for each isomer refer to the relative positions of the B ligands.

Isomers are defined here as compounds that have the same numbers and types of chemical bonds but differ in the spatial arrangements of those bonds (A more detailed discussion of isomers is presented in the following sections).

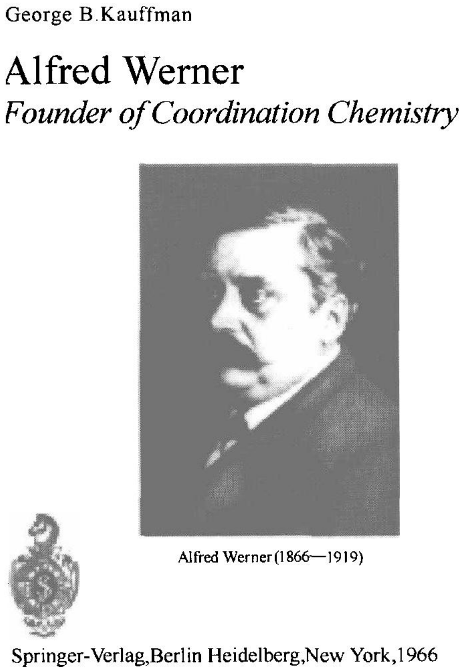
For the MA_5B case in Table 1. 3, only one isomer could actually be prepared experimentally, a result consistent with all three of the proposed geometries. For the MA_4B_2 case, however, Werner could prepare only two isomers (Fig 1. 4). For the octahedral case, this actual number matched the possible number, but for the hexagonal planar and trigonal prism cases, there were three possible isomers. Assuming that Werner had not missed the preparation of an isomer someplace along the line, the data indicated that the "fixed positions in space" for six ligands is octahedral. The same type of analysis for the MA_3B_3 case gives a similar result. Only the octahedral configuration gives the same number of isomers as were actually prepared.



(a) MA_5B (b) MA_4B_2 (Isomer 1) (c) MA_4B_2 (Isomer 2)

Fig 1.4 Equivalent configurations for some octahedral isomers

Given these results, Werner could predict that two isomers would be found for the $CoCl_3 \cdot 4NH_3$ case. These proved somewhat difficult to prepare, but in 1907 Werner was finally successful. He found two isomers, one a bright green and the other a violet color. By comparing the actual number of known isomers with the number that should exist for various geometries, Werner concluded that the six ligands in the cobalt ammonates were in an octahedral arrangement. So, the coordination theory was growing stronger.


George B.Kauffman

Alfred Werner

Founder of Coordination Chemistry

Alfred Werner(1866—1919)

Springer-Verlag,Berlin Heidelberg,New York,1966

Fig 1.5 A copy of the cover of book《Alfred Werner—Founder of Coordination Chemistry》

All of this goes to demonstrate, as so often is the case in science. Sometimes, we need to take risks. We must occasionally follow our intuitions and advocate a new and sometimes poorly supported way of thinking about a phenomenon in order to make a truly revolutionary advance. Blomstrand and Jørgensen tried to extend the established ideas of organic chemistry to account for the newer coordination compounds. In doing so, one could argue, they actually impaired progress in the understanding of this branch of chemistry. The trick, of course, is to know when to stick to the established ideas and when to break away from them. Werner chose the latter course. 20 years later in 1913, he received the Nobel Prize in chemistry.

At the start of the 20th century, inorganic chemistry was not a prominent field until Werner studied the metal-amine complexes such as $[Co(NH_3)_6Cl_3]$—Werner compound. He is a founder of coordination chemistry. Fig 1.5 is a copy of the cover of book《Alfred Werner—Founder of Coordination Chemistry》.

1.1.3 Extending Coordination Chemistry—Supramolecular Chemistry

Supramolecular chemistry refers to the area of chemistry that focuses on the the weaker and reversible non-covalent interactions between molecules. These non-covalent interactions include hydrogen bonding, π-π stacking, electrostatic effects, hydrophobic forces and Van der Waals forces. Recently, the coordination bonding in coordination complexes of metal is accepted as an important force in supramolecular chemistry. At this point, the supramolecular chemistry can be considered as extended coordination chemistry. The concepts such as molecular self-assembly, molecular recognition, preorganization, and macro-