Chapter 2
False Labor: Inorganic Chemistry in the Late Nineteenth-Early Twentieth Centuries

Those of us who were familiar with the state of inorganic chemistry in universities twenty to thirty years ago will recall that at that time it was widely regarded as a dull and uninteresting part of the undergraduate course….that the opportunities for research in inorganic chemistry were few, and that in any case the problems were dull and uninspiring; as a result, relatively few people specialized in this subject.

Ronald Nyholm, *The Renaissance of Inorganic Chemistry* (1956)

The previous chapter paints a rather bleak portrait of inorganic chemistry in the late 1800s. However, both chemists and historians have pointed to a significant upgrade in status—using terms such as revival, rebirth, renaissance—taking place even before the turn of the century. One historian commented in 1906: "If we glance back over the labors of the last 50 or 60 years, we recognize that organic chemistry has gone on preponderating more and more over inorganic…. A review of the chemical literature of the last 10 or 20 years shows very clearly the revived influence of inorganic chemistry as an incentive to research" [1]. H. N. Stokes, an important American chemist of the time,[1] published a lengthy *Science* article in 1899 entitled "The Revival of Inorganic Chemistry" [2]. (It should be noted, however, that he followed it with "The Revival of Organic Chemistry" [3], acknowledging that many might find *that* topic "almost facetious.") There is no question that many important advances that took place in the late nineteenth through the first part of the twentieth centuries played a crucial role in the evolution of inorganic chemistry as an independent subfield. Nonetheless, it would be incorrect to apply so momentous a term as "rebirth" to this early period.

Before surveying those developments, I offer a brief comment on the appropriateness of terms. It is true that research in what we would now call inorganic chemistry languished during the greater part of the nineteenth century and began to grow again towards the end. However, it does not seem quite accurate to call that a "*re*birth" or "renaissance" of the *field* of inorganic chemistry. Such a field never existed as a distinct entity; the earlier researches were part of chemistry *tout court*.

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1 Henry Newlin Stokes (1859–1942) was a chemist with the US Geological Survey and Bureau of Standards, and served a term as President of the ACS around the turn of the century, before turning to philosophy, becoming a leader of the Theosophical Society.

J. A. Labinger, *Up from Generality*, SpringerBriefs in History of Chemistry,
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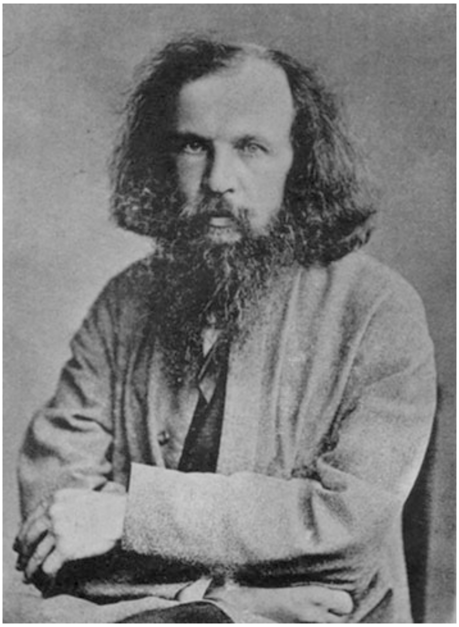

Fig. 2.1 Dmitry Mendeleev (1834–1907), date unknown. His discovery of the Periodic Law is arguably the most important (eligible) contribution in chemistry that was never recognized with a Nobel Prize (Image courtesy of the University of Pennsylvania Library's Edgar Fahs Smith Memorial Collection)

Fred Basolo makes a similar point, with regard to similar mid-twentieth century characterizations: "Everyone talks about the renaissance of inorganic chemistry…. Actually, I'm inclined to call it the "birth" of inorganic chemistry because renaissance means that you're coming back to something that has already been done" [4]. Be that as it may, I will bow to common practice and continue to apply "revival", "renaissance," etc. to all (real and/or perceived) upgrades in status.

The first (and foremost) advance, of course, was the work culminating in the 1870s with Mendeleev's (Fig. 2.1) Periodic Table. Many historians have proclaimed its significance: "It is with the construction of the Periodic Table that the story of 1800s inorganic chemistry begins" [5]. "[Inorganic chemistry], so long over-shadowed by organic chemistry, so long but little more than a collection of almost un-connected facts, subordinate to analytical and technical chemistry and to mineralogy, is gradually, and especially since the discovery of the Periodic Law, rising to the rank of an independent and important division of our science" [3]. "The Periodic Law…stimulated the study of Inorganic Chemistry, which had been rather neglected in the second half of the nineteenth century owing to the great specialization in Organic Chemistry" [6].

All of that is true; but in the last source cited we also read "The development in *general* chemistry during the twentieth century originated in the Periodic Law" (my italics) [6]. The Periodic Table is unquestionably a *sine qua non* for any systematic study of the chemistry of the elements; but its evolution really belongs to general, not inorganic, chemistry. Or, better put, it solidified the *conflation* of general and inorganic chemistry, rather than advancing inorganic chemistry as a distinct, respected subfield. Mendeleev himself held the title of "Professor of

General (Inorganic) Chemistry" at the University of St. Petersburg [7]! Russell comments: "It [the Periodic Table] also provided for inorganic chemistry its first great generalization….But it is all too easy to overstate its importance for suggesting lines of research….Indeed, it is not going too far to say that the most important discoveries in inorganic chemistry for the rest of the century not only owed little to the Periodic Table but actually offered it an embarrassing challenge" [8].

In any case, the preponderance of late nineteenth century inorganic studies, though more systematic than before Mendeleev, remained largely descriptive and phenomenological. There was not much interest or activity in the more explanatory mode that organic chemists had established. "In 1910 many specialists in inorganic chemistry still thought that the atomic and molecular hypothesis was only a fiction….Although molecular structures had had an impact on organic chemistry, they had remained relatively peripheral in inorganic chemistry, which was more concerned with the variety of elements that entered into compounds than with the structures built by molecules" [9].

To be fair, it must be acknowledged that many of the founders of physical chemistry were at least equally skeptical of the utility, let alone the reality, of atoms and molecules. But those skeptics *did* construct their science upon an alternative philosophical framework, based on energetics [10], whereas inorganic chemistry of the time had little in the way of comparable intellectual underpinnings to offer. The one exception—and the most significant advance in the field around the turn of the twentieth century—is to be found in the work of Alfred Werner (Fig. 2.2).

Werner has been claimed as a national by the Germans, French and Swiss. He was born in Mulhouse while Alsace was still part of France, remained there after it was seized in the Franco-Prussian War of 1870 (and even served in the German army); but he spent most of his career as an independent researcher in Zurich, coming to the University of Zurich (initially as an organic chemist!) in 1893. By then he had already taken an interest in coordination compounds, which at the time were poorly (if at all) understood, especially with regard to constitution and structure [11]. The existence of a number of series of species, each containing a metal in combination with the same constituents but in varying numbers, was very hard to reconcile with well-established laws of proportions and valency.

For example, cobalt-ammine-chloride compounds of formulae $Co(NH_3)_xCl_3$ were known for $x = 3$, 4, 5 and 6, all of different colors. Cobalt was considered to be trivalent, which was taken to mean that it could only bond to three entities; how could that be made compatible with the known compositions? Before Werner, the dominant model was that of Jørgensen,[2] who had proposed the chain structures shown in Fig. 2.3. These did correctly capture *some* of the known chemical

[2] Sophus Mads Jørgensen (1837–1914), a Danish chemist who made many of the early important *experimental* discoveries in coordination chemistry, but fought a long rear-guard action against Werner's conceptual interpretation, until finally acknowledging the latter's triumph in the early twentieth century.

Fig. 2.2 Alfred Werner (1866–1919), the father of coordination chemistry, at the time he received the 1913 Nobel Prize in Chemistry (Image downloaded from Wikimedia Commons, in the public domain)

behavior, notably the varying number of ionizable chloride ions. Those at the end of the chains were assumed to be ionizable, whereas those attached directly to cobalt were not. However, there were clear anomalies; the case where x = 3 (i.e., $Co(NH_3)_3Cl_3$) should behave much like that for x = 4 in Jørgensen's model, but the former is entirely *non*-ionic, while the latter readily liberates one Cl^- ion [12].

In a groundbreaking series of papers beginning in 1893 [13], Werner completely reformulated these and related species. First he introduced a distinction between groups directly bonded to the central metal atom and those affiliated only by ionic forces. In due course these came to be called inner- and outer-sphere interactions, respectively, with the former eventually termed "ligands" (by Stock in 1916 [14]). He further recognized that the "magic" number was not three, the valency (in traditional usage) of cobalt, but rather *six*, the characteristic "coordination number" of trivalent cobalt. The complexes of Fig. 2.3 would thus be represented instead as $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_3Cl]Cl_2$, and $[Co(NH_3)_6]Cl_3$, where the Cl's outside the brackets are ionizable. He then extended this concept to include spatial representation, postulating an octahedral arrangement of six groups around a central atom as the obvious analog of the organic chemist's tetrahedron, and observed that certain compositions should exist as more than one structural isomer, as shown (for x = 4) in Fig. 2.4. Even more dramatically, he recognized that certain arrangements of ligands could give rise to the possibility of optical isomerism, a phenomenon previously deemed unique to the organic realm. All of these predictions were already known (or were soon shown) to be consistent with experimental finding [8, 12].

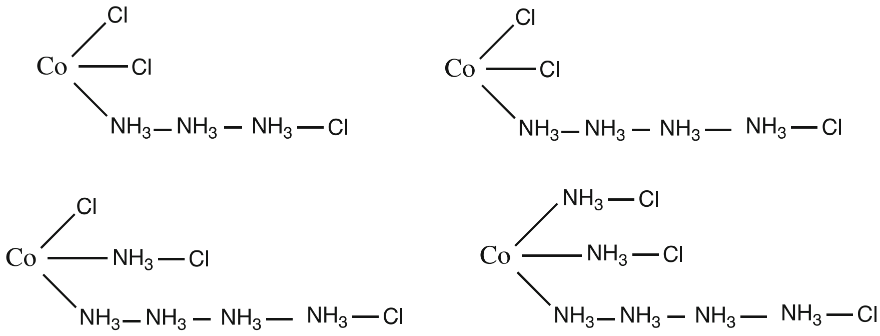

Fig. 2.3 Jørgensen's chain structure model for the $Co(NH_3)_xCl_3$ series

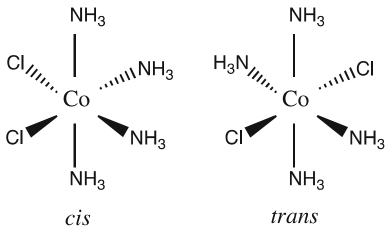

Fig. 2.4 The two isomers of $[Co(NH_3)_4Cl_2]Cl$ (the ionic Cl's are not shown)

Werner's work *has* been characterized by some as an early renaissance (or, as Basolo would prefer, a "naissance") of inorganic chemistry. For example, "The progress in carbon chemistry outshone that made in other areas until the 1890s, when new discoveries and theories relating to coordination compounds signalled the coming of age of inorganic chemistry" [15]. On the other hand, Russell describes the period quite differently: "It was simply not true that coordination complexes played a key role in inorganic chemistry either then [just before the First World War] or for 40 years ahead. What Werner did do in his own fairly short lifetime was to convince people that *in this area*…his theory was a satisfactory explanation" (italics in the original) [8].

George Kauffman, a leading Werner scholar, has suggested that Werner's management style may have been part of the reason that his work did not ignite a major expansion of the field: "[O]ne might also wish to ponder whether it was [his] high degree of regulation and supervision which may have prevented the formation of a Werner school….Perhaps the impact of Werner's powerful, authoritarian personality and the impression of his control and mastery of his field deterred most of those who had worked with him from any thought of following in his footsteps" [16]. In any case, while there is no doubt that Werner's work lies at the very center of the emergence of inorganic chemistry as an intellectually respected field, the preponderance of evidence, as we shall see, shows that no such emergence took place until *much* later—about 40 years later, as Russell says.

Nonetheless, Werner's contemporaries were already beginning to show *some* renewed interest in the field. The most notable development was the founding of the first journal devoted to the topic, the *Zeitschrift für anorganische Chemie* (*ZAC*), in 1892. The very first issue includes an editors' note, offering a rationale for a new journal, which begins (my translation[3]) [17]:

> At present, reports of inorganic chemistry research submitted for publication are dispersed among a very large number of domestic and foreign journals; they appear as strangers among the ever-increasing number of works in the field of chemistry of carbon compounds. This situation is inconsistent with the current importance of inorganic chemistry, which in recent decades has emerged from the confines of its narrowly defined science to take part in the resolution of questions which are of great significance for chemistry in general.

It is not at all clear to me what they might have meant by "emerged from the confines of its narrowly defined science." In what way was the *purview* of inorganic chemistry constrained in the earlier nineteenth century, or less so towards the end? Examination of the technical content of that first issue doesn't help much; of the 34 articles a large fraction deal with matters that could well be considered at least as appropriate for "chemistry in general" rather than specifically inorganic. The two longest, by Harvard chemist T. W. Richards, are on determining the atomic weight of copper with greater precision; another is on the phenomenon of coal dust explosions! Like the Periodic Table, the introduction of this journal perhaps does more to blur any distinction between general and inorganic chemistry than to help secure the latter's standing.

To bolster that argument, we need only look at the subsequent history of the *title* of this journal. In 1915, it became known as *Zeitschrift für anorganische und allgemeine Chemie* (*ZAAC*: journal of inorganic *and* general chemistry); in 1943 it reverted to the original *ZAC*; and then in 1950, back again to *ZAAC*, which remains its title to this day. According to one of the current editors, the first shift was largely the initiative of the editor at that time, who was personally very interested in a broad range of topics such as metallurgy, and induced the publishers to change the name; the second was brought about by the president of the Deutsche Chemische Gesellschaft, who wanted to keep inorganic and physical chemistry strictly separate, and was able to force his preferences upon the editors by virtue of his good connections with the Nazi regime. After the war, that move was reversed [18].

To be sure, *ZAC* (and later *ZAAC*) did publish many papers that play an important part in the continuing development of inorganic chemistry, including much of Werner's early work, as well as a good deal of the next major European figure in inorganic chemistry, Alfred Stock (1876–1946). But Werner ceased publishing in *ZAC* in 1899 (after that date most of his work appeared in

[3] "Die Mitteilungen über anorganisch-chemische Untersuchungen sind bis jetzt in einer sehr grossen Ansahl von in- und ausländischen Zeitschriften verstreut zur Veröffentlichung gelangt; sie erscheinen als Fremdlinge unter der immer mehr wachsenden Anzahl von Arbeiten aus dem Gebiete der Chemie der Kohlenstoffverbindinungen. Diese Stellung entspricht nicht der heutigen Bedeutung der anorganische Chemie, denn diese ist im Laufe der letzten Decennien aus dem engen Rahmen einer rein beschreibenden Naturwissenschaft herausgetreten und nimmt Teil an der Entscheidung von Fragen, welche für die allgemeine Chemie von hoher Bedeutung sind."

Berichte [11]), and resigned from its editorial board, feeling that the journal had moved away from inorganic chemistry in favor of physical chemistry [19]. (On the other hand, Stock published almost exclusively in *Berichte* until around 1925, only after then using *ZAC* for a portion of his output.)

Stock enjoyed a long career of investigations into the chemistry of main group elements, primarily boron and silicon, at several German universities (Breslau, Berlin, Karlsruhe), and developed much of the methodology needed to work with such species, many of which are volatile, air-sensitive and/or toxic. He was particularly noted for his introduction of vacuum line techniques (which, unfortunately for him, entailed usage of large quantities of mercury: he suffered terribly from mercury poisoning for the last several decades of his life). But even a (rather hagiographic) scientific biography does not credit his work as amounting to a renaissance; rather it proposes that "his own life's work…laid the sure foundation of a *future* renaissance in inorganic chemistry" (my italics) [20].

Of course there were other important inorganic chemists during the first half of the twentieth century, most of them also in Germany. I will not undertake an extensive survey, but will just mention Walter Hieber (1895–1976), whose research program, primarily at the Technische Hochschule München, essentially created the topic of metal carbonyl chemistry, bringing it from a small handful of "peculiar compounds" to a highly populated class of metal complexes, extending to virtually all the transition metals. Like Stock's work, Hieber's studies played a crucial role in subsequent developments [21].

Outside of Germany we find much less evidence of revitalized interest in the field. Of course there *were* advances during this period that, like the Periodic Table, were absolutely essential for further progress in systematizing inorganic chemistry, particularly the contributions to the understanding of the nature of chemical bonds made by two American chemists: Gilbert N. Lewis (1875–1946) and Linus Pauling (1901–1994) [22]. Their work was seminal: one chemist/historian recalls that a popular exam question in the years before Pauling was "Is inorganic chemistry a largely closed and finished subject?" [23]. But neither of these giants was really associated with the field of inorganic chemistry. Lewis always called himself a physical chemist, while Pauling's title at Caltech, which varied over the years, never included any reference to inorganic chemistry. Indeed, he said that any interest he had in inorganic (and organic, for that matter) chemistry was "almost entirely from the structural point of view" [24].

Like the other milestones examined in this chapter—the Periodic Table, Werner's work on coordination compounds, the establishment of the first dedicated journal, Stock's work on main group compounds—the work of Lewis and Pauling did not result in any *immediate* improvement of the status of inorganic chemistry. To be sure, that *was* to come, as a farsighted turn-of-the-century commentator opined: "It is not to be expected, nor is it to be desired, that inorganic chemistry will at once sweep organic chemistry from its position of preeminence. The causes to which this is due may outlast our generation, but that the inorganic tide is rising, and that this branch will finally attain its due position, cannot be doubted" [2]. But any birth (or rebirth) announcement of inorganic chemistry before the middle of the twentieth century would have to be considered as decidedly premature.

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