

THE JOINT PAPERS OF PAUL KARRER AND ALFRED WERNER

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At a symposium in the History of Chemistry Division in San Francisco, during an interesting paper by Professor J. S. Siegel (1), a comment was made in passing that Karrer worked for Alfred Werner for three years, but his work was never published. The comment was notable, considering what we had known of the productivity of both persons. It also seemed uncharacteristic of Werner, who was known to care for his students (2). It seems appropriate to review briefly the background of both persons before determining why the statement might or might not be correct.

Alfred Werner (1866-1919)

Werner's background is amply provided elsewhere (3-5). Briefly, it may be noted that in 1892 at the University of Zürich he was faced with producing a *Habilitations-schrift*, a requirement for a position in a German-speaking university. He awoke one night, brewed coffee, and started writing; and by the afternoon of the next day Werner had finished describing the basis of coordination theory of inorganic compounds (6). He was subsequently made a *Privatdozent* and in 1893 assumed the chair of chemistry at Zürich. An energetic mentor, he attracted an international group of students, both men and women. By 1911 he was only 45, but was "quite gray haired and very fat" (7). In 1913 he received the Nobel Prize. The onset of arteriosclerosis was evident according to Dr. Yuji Shibata (7). On October 15, 1919, Werner was forced to resign from his teaching and laboratory duties, and he died exactly one month later (8).

Paul Karrer (1889-1971)

Karrer's academic history is presented in an official summary below (9). Karrer worked with Werner from 1908-1911, received his D. phil. for a dissertation titled "Untersuchungen über Valenzisomerie beim Kobalt" (9). He served as an assistant in 1912. His postdoctoral research in chemistry with Paul Ehrlich at the Georg Speyer Haus, Frankfurt-am-Main, extended for a period of six years (10). Subsequently, he became a Reader at Zürich in 1918 and a Professor in 1919 (9, 10). He was a co-recipient of the Nobel Prize in Chemistry (1937) "for his investigations of carotenoids, flavins and Vitamins A and B₂" (10). He later was Rector at Zürich, 1950-51 (9).

What follows is the entry for Dr Karrer from the Matrikeledition of the University of Zürich (9):

• **18286** phil.II Chemie WS1908KarrerPaul*1889mTeufenthalAGCHtechn.Abt.Kts.schule Aarau (Mat. zgn.)ohne Zgn.29.06.1911 ; (prom. StAZ U 110 e.15)* 21.04.1889 , Wg. Leonhardstr. 12 bei Stähelin ; 1911 Dr.phil.II, Diss. "Untersuchungen über Valenzisomerie beim Kobalt" (J`verz.1910/11 Nr.176), 1919-59 Ordinarius f.Chemie a.d.Univ.Zürich, Rektor 1950/51, 1937 Nobelpreis, Constaffler, oo Lene Frölich (1890-1972), + 18.06.1971: UFS 1983 S.733 ; J`ber.Univ.Zch.1971/72 ; SL III 763E: Dr. Paul K` , Birkenhof, Aarau

In the view of some, Paul Karrer and Paul Pfeiffer were the only two of Werner's 200 doctoral students who really attained notable success, and Pfeiffer was the only one who remained in the field of coordination chemistry.

It is also important to note that Karrer had a high regard for Werner, about whom he remarked (4):

Alfred Werner was a model teacher. The clarity and logic of his thinking made his lectures enjoyable hours.

It seems highly unlikely that he would have had this high regard, had none of his work been published.

Plausible Reasons

There could be at least five reasons for the validity of the statement about Werner/Karrer publications.

First, Werner was very busy (5, 11). He had ten productive years, from 1893-1913, before the onset of his illness became truly debilitating. Reportedly, 52 papers were authored by him alone, and 75 were co-authored with associates (11). There was a total of 200 thesis investigations that were made under his inspiration and supervision (5).

Second, poor health would have impacted not only his productivity but his priorities as well. Accordingly, it is reasonable to assume that not every dissertation would be published.

Third, focus could have been a factor. There were two major challenges. Werner was faced with providing convincing evidence of the validity of his view of the constitution and configuration of coordination compounds over the so-called chain theory. Perhaps the most significant critic was noted Danish chemist Sophus Mads Jørgensen (1837-1914), who would not be convinced until Werner succeeded in presenting the existence of the two geometric isomers of $[(Cl_2(NH_3)_4Co)^+]$. This feat, achieved in 1907, was taken as evidence of the octahedral structure that Werner had proposed (12). A second challenge was concerned with the resolution of asymmetric cobalt complexes, a series, "Toward an Understanding of the Asymmetric Cobalt Atom," and a

dozen papers on this topic appeared in *Berichte* between 1911 and 1914 (13, 14).

Fourth, the pattern of authorship varies among researchers. Our mentor, the late Dr. W. Conard Fernelius, believed whoever wrote the first draft of a paper became the senior author, and this was true of the five papers that we, between us, co-authored with Fernelius.

Werner followed a different course in publication. He was senior author on most if not all his papers, and he was either the sole author or appeared to be in many other publications. But he would give credit in an interesting way to those who had done the experimental work. The American Victor L. King was the codiscoverer of optically active coordination compounds in 1911; yet the first paper in the series (13) shows Werner as the sole author on the title page (p 1887).

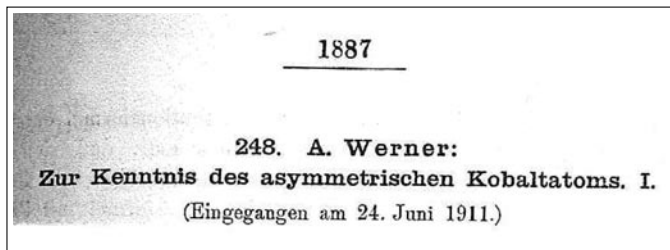
On page 1890, under the experimental section (Experimenteller Teil), he gives credit "von V. L. King" to his experimental colleague (see below).

This pattern is one that we have observed in more than one of Werner's "solo" papers; but the point remains, unless one examines all of the solo papers, one could miss a "joint paper," i.e., one in which Paul Karrer appears as an active participant, one that we would regard as a joint effort.

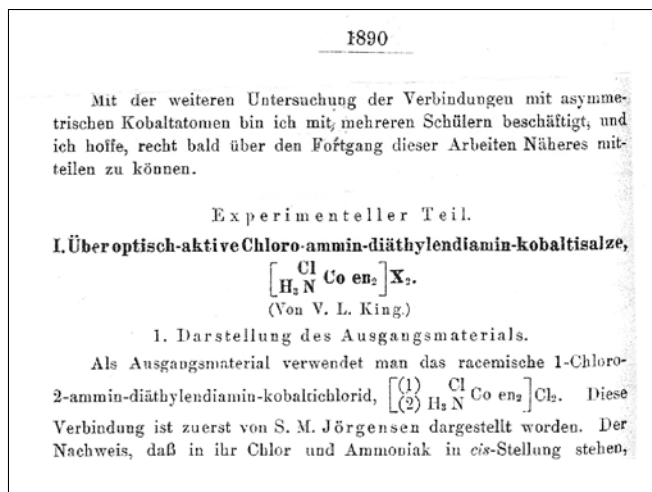
Fifth, delayed publication is a plausible reason that Karrer's dissertation would not have appeared, owing to the onset of Werner's terminal illness.

Success, perhaps

We did in fact find reference to joint publications, or in fairness, other persons did. Karrer (14) provided an obituary of Werner that included a bibliography described



Portion of title page from Ref. 13

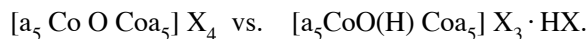


Portion of page from p 1890 of Ref. 13

as “extensive but not complete” (11). F. R. Morral (11) provided a list of papers by Werner, which includes one coauthored by Karrer (published in 1918) and a posthumous publication by Werner with J. E. Schwyzer and “P. Karrer” (published in 1921). The first paper (15) provides proof that Karrer’s work with Werner was, in fact, published. The second paper (16) contains a misprint, as the third author listed is “Walter Karrer” on the actual opening page.

When Werner became seriously ill in 1915, his academic activities were taken over by Paul Pfeiffer and Paul Karrer (17), who assisted Werner upon his return from Frankfurt to the University of Zürich.

There is, however, a matter of interpretation. One may note that the paper cited (15) is an example of *ligand isomerism*, i.e., the nitric oxide molecule could potentially coordinate through N or O. Karrer’s dissertation appears to be on a different subject, “Untersuchungen über Valenzisomerie beim Kobalt” (9). Valence isomerism refers to the fact that the two isomers differ with respect to an atom inside vs. outside the coordination sphere. A good example would be the two compounds below (a refers to a unidentate ligand, e.g. NH₃):



Up to this point, we have not found a paper that specifically refers to this type of isomerism, and it was not listed in the examples of isomerism cited by Morgan (3).

We did, however, find reference to a joint paper involving Werner and P. Karrer (15) and to one co-authored by Schwyzer and “W.” Karrer (16). We also found that Karrer was respectful of Werner in Karrer’s writings, and that he was a dedicated friend and colleague. We should like to think that we have corrected a misunderstanding in an otherwise fascinating presentation.

REFERENCES AND NOTES

1. J. S. Siegel, “Paul Karrer as Patriarch of Zurich” presented in the Division of the History of Chemistry Symposium “Classic Chemistry Books of the Twentieth Century: Organic Chemistry” at the 232nd ACS National Meeting, San Francisco, CA, September 10, 2006, HIST 08.
2. W. H. Brock. *The Chemical Tree*, W W. Norton and Co., New York, 2000; originally published as *The Norton History of Chemistry*, 1992, 591.
3. G. T. Morgan, “Alfred Werner,” *J. Chem. Soc.*, **1920**, 117, 1639-1648.

4. P. Karrer, “Alfred Werner (1866-1919) in memoriam,” *Helv. Chim. Acta*, **1966**, 49, E1-E16.
5. P. Pfeiffer, “Alfred Werner,” *J. Chem. Educ.*, **1928**, 5, 1090-1098.
6. A. Werner. “Beitrag zur Konstitution anorganischer Verbindungen,” *Z. Anorg. Chem.*, **1894**, 3, 267 -330.
7. Y. Shibata, “Some Personal Recollections of Alfred Werner,” in G. B. Kauffman, *Werner Centennial*, Adv. Chem, Ser. 62, American Chemical Society, Washington, DC, 1967, 1-2.
8. G. B. Kauffman, *Classics in Coordination Chemistry, Part I: The Selected Papers of Alfred Werner*, Dover Publications, New York, 1968, 4.
9. Matrikeledition der Universität Zürich. Student number 18286. Karrer, Paul [<http://www.matrikel.unizh.ch/pages/799.htm>; accessed October, 2006]
10. “Paul Karrer. The Nobel Prize in Chemistry 1937 including Biography,” in *Nobel Foundation, Nobel Lectures: Including Presentation Speeches and Laureates’ Biographies: Chemistry, 1922-1941*, Elsevier, Amsterdam, London, New York, 1966, 449-450 [http://nobelpriz.org/nobel_prizes/chemistry/laureates/1937/karrer-bio.html; accessed April, 2007]
11. F. R. Morral, “Alfred Werner and Cobalt Complexes,” in: G. B. Kauffman, *Werner Centennial*, Adv. Chem, Ser. 62, American Chemical Society, Washington, DC, 1967, 70-77.
12. A. Werner, “Über 1,2-Dichloro-tetrammin-kobaltisalze (Ammoniakvioleosalze),” *Ber. Dtsch. Chem. Ges.*, **1907**, 40, 4817-4825.
13. A. Werner, “Zur Kenntnis des asymmetrischen Kobaltatoms. I,” *Ber. Dtsch. Chem. Ges.*, **1911**, 44, 1887-1898.
14. P. Karrer, “Alfred Werner,” *Helv. Chim. Acta*, **1920**, 3, 196-224.
15. A. Werner and P. Karrer, “Über Nitroso-pentamminkobaltisalze,” *Helv. Chim. Acta*, **1917**, 1, 54-78.
16. A. Werner, J. E. Schwyzer, and W. Karrer, “Ueber einige optisch-aktive Kobaltsalze mit β-Diketonresten im Komplex,” *Helv. Chim. Acta*, **1921**, 4, 113-129.
17. E. Berl, “Some Recollections of Alfred Werner,” *J. Chem. Educ.*, **1942**, 19, 153-154.

ABOUT THE AUTHORS

The authors are members of the Department of Chemistry at the University of South Florida, Tampa, where Dean Martin is Distinguished University Professor Emeritus and Barbara Martin is Assistant Professor (Courtesy). They have shared interest in chemistry of coordination compounds, and co-authored a monograph on the subject in 1964, and are the co-authors of over 40 other publications.