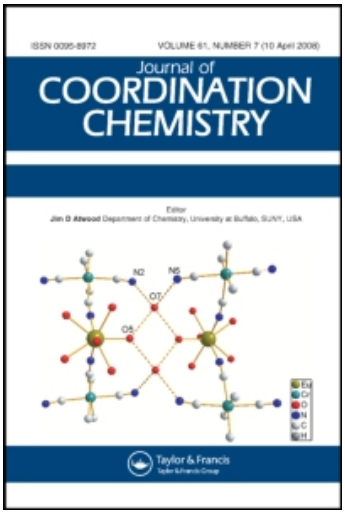

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Ligand: Origin and Dissemination

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HISTORICAL NOTE

Ligand: Origin and Dissemination

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The term *ligand*, which occurs so frequently in the pages of this journal, was first proposed by Alfred Stock (1876–1946) in the published version of a lecture on the hydrides of silicon presented at Berlin on November 27, 1916 before the Kaiser-Wilhelm-Institut für Chemie:

Affinity is the expression for the firmness with which one element binds other elements or radicals (generally: "Ligands" (*ligare* [Latin], to bind); the introduction of a word hitherto lacking simplifies the manner of expression for this immediately clear concept). *Valence* (*Valenz*) means the unit of force which can bind a univalent ligand; positive valencies bind negative ligands, negative valencies bind positive ligands.[1]

Having proposed this definition in the context of silicon chemistry, not, it should be stressed, in the context of coordination compounds, Stock made no further use of the term *ligand* in the paper nor did he use it frequently in later experimental papers.

For more than a decade after Stock's proposal, none of the classical monographs on coordination chemistry employed the term.[2] Although a commission of the Deutsche Chemische Gesellschaft (R. Lorenz, R. J. Meyer, S. Meyer, P. Pfeiffer, A. Rosenheim, and A. Stock), appointed to deal with the nomenclature of inorganic chemistry, recommended in its published rules[3] the use of a Roman numeral (the Stock number) to designate the "valence" (oxidation state) of an element, the term *ligand* was absent in this preliminary report.

The proposal was submitted by Stock at the Hauptversammlung des Vereins deutscher Chemiker (Nürnberg, 1925), and from the appearance of *ligand* in the German literature since 1927 one can deduce that the term was included in his report. The fourth edition of Ephraim's distinguished textbook, *Anorganische Chemie*[4] (1929) adopted the word in introducing the elements of Periodic Group IV and referred to Stock explicitly as its originator. By 1930, therefore, the word *ligand* had become widely used in German publications,[5] including the monographs on stereochemistry by Goldschmidt and Freudenberg,[6] and it was even adopted by the Japanese coordination chemist, Ryūtarō Tsuchida, when writing in English on the spectrochemical series in a Japanese journal.[7]

After World War I the Union Internationale de Chimie Pure et Appliquée (UIC) was established, without Germany as a member and with French as its official language. After meetings in 1926 and 1929 an

UIC Commission on the Nomenclature of Inorganic Chemistry, first appointed in 1921, adopted a proposal[8] containing detailed rules for naming coordination compounds by use of Stock numbers; the term *ligand*, however, was not used.[9] At a 1936 meeting the commission (H. Remy, W. P. Jorissen, M. Delépine, and F. Fichter; the English member, Clarence Smith, was absent) drafted a proposal adopted at the Tenth Congress of the UIC (Rome 1938). (Here A. Damiens and H. Bassett had replaced Delépine and Smith.) The German version, containing the word *ligand*, was published in 1940.[10] However, in translating this German report, Bassett rendered *ligands* as "attached atoms or groups",[11] just as the French had done in 1937.[9] His decision may have been influenced by the outbreak of World War II and the absence of the word in English textbooks, Patterson's *German–English Dictionary for Chemists*,[12] and *Chemical Abstracts*, where it did not appear until the Sixth Collective Index (1957–61). Since Bassett's translation was used in the American version[13] with only minor amendments of spelling and footnotes, not surprisingly the word was omitted in Scott's 1943 review of inorganic nomenclature.[14]

On the other hand, there seems to have been less reluctance to take *ligand* into other languages either directly from German usage or from the German version of the 1938 Rules. In the mid-1930s K. A. Jensen introduced *ligand* into Danish[15] after first using it in a German paper on platinum complexes.[16] On Jensen's suggestion, Jannik Bjerrum adopted the word in 1941 in the context of discussions of stepwise equilibria, e.g., a "step system consisting of a central group M and n ligands A" and "ligand effect".[17] In this way, together with Tsuchida, Bjerrum became the first to use *ligand* in an influential English publication. His use of the term was immediately accepted by some Swedish chemists, but English-speaking chemists did not use it extensively until the 1950s.

How then did the long-neglected *ligand* suddenly become so widespread in English? A decisive factor was undoubtedly the first post-war meeting in London in 1947 of the revived International Union (retitled the International Union of Pure and Applied Chemistry, IUPAC) whose Commission on the Nomenclature of Inorganic Chemistry used *ligand* in a 1949 review paper.[18] Following further meetings of the Commission, an extended set of rules for inorganic nomenclature was prepared and presented as "Tentative Rules" at a 1953 conference in Stockholm. The contents of the new rules and the official definition of *ligand* were therefore known four years before they were finally adopted by the IUPAC Council at the 1957 conference in Paris and published as *Nomenclature of Inorganic Compounds 1957*.[19] However, by this time, largely as a result of the large number of American and British chemists who had worked with Jannik Bjerrum, the extensive use of the term at the first four International Conferences on Coordination Chemistry (Welwyn, 1950; Copenhagen, 1953; Amsterdam, 1955; and Rome, 1957), and the advent of ligand field theory, *ligand* was already an established term in the English chemical literature.

A detailed and fully documented account of the origin and dissemination of the term *ligand* of interest to historians of science is found in a recent article in *Ambix*.[20]

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7. R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388 (1938).
8. *Rapport du Comité de Travail de Réforme de la Nomenclature de Chimie Minérale, Paris, 1926.*
9. After 1930, when Germany had been readmitted to the UIC, a collaboration between the International and German commissions on nomenclature was initiated, and a French translation of the German proposal was published by R. J. Meyer (*Helv. Chim. Acta*, **20**, 159 (1937), p. 171). This contains the phrase "ordre des

constituants liés à l'atome central" for the original "Reihenfolge der Liganden". Clearly, *ligand* was not acceptable as a French term.
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20. W. H. Brock, K. A. Jensen, C. K. Jørgensen and G. B. Kauffman, *Ambix*, **28**, 171.