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THE DEVELOPMENT OF COMPLEX AND COORDINATION CHEMISTRY IN DENMARK

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In his book "Die Chemie der Jetztzeit" of 1869 C.W. Blomstrand in Lund, Sweden, made the assumption that the ammonia in metal ammine compounds, on account of its nitrogen atom, can act as a divalent radical and thus is able to form chains between the central metal atom and the anions of the complex salt, chains similar to the methylene series in organic molecules. Blomstrand's ideas inspired S.M. Jørgensen in Copenhagen, who in 1878 began his extensive and important investigations of the ammine compounds of trivalent cobalt, chromium and rhodium, mainly published in J. prakt. Chem. and in Z. anorg. Chem. in the years until 1899. Guided by Blomstrand's chain theory Jørgensen was able to write formulae for all of the complexes that he had prepared until it was found that tetraammine salts existed in two isomeric forms. This isomerism could not easily be explained by the Blomstrand–Jørgensen theory, and it found its first natural explanation after Alfred Werner had put forward his coordination theory in 1893. Werner's theory was, at the time of its appearance, supported by only rather sparse experimental material, and it is understandable that Jørgensen did not realize the advantages of the new ideas. In a series of valuable experimental investigations he tried to show that Werner's assumptions could not be true; he was first convinced of the inability of the Blomstrand–Jørgensen chain theory to compete with the new theory when, in 1911, Werner succeeded in resolving the violo ethylenediamine salt *cis*-$[Coen_2Cl_2]Cl$ in optical antipodes and still more impressed when Werner in 1914 succeeded in resolving the purely inorganic carbon-free brown salt $[Co\{(OH)_2Co(NH_3)_4\}_3](NO_3)_6$. His students, especially Odin T. Christensen and S.P.L. Sørensen, continued his experimental work up to the end of the 19th century.

In the years 1906–1918 Niels Bjerrum, guided by Werner's theory, studied chromium and gold complexes by physical–chemical methods and thereby made fundamental contributions to solution chemistry. Thus, kinetically and spectrophotometrically, he proved the existence of the monochloro chromium(III) complex in solutions and prepared salts of this hitherto unknown complex. In hydrolysis studies of the hexaaquachromium(III) ion he dis-

tinguished between the instantaneous formation of the aquahydroxo complexes and the slow formation of the polynuclear complexes. In the robust thiocyanato chromium(III) system he proved that all six thiocyanate complexes existed in solution and by chemical analysis he was able to estimate values for their stability constants. Further, as an addition to a study of the stability constants and redox equilibria in the gold thiocyanate system he showed the existence of free thiocyanogen. His papers were mainly published in Z. anorg. Chem. and Z. phys. Chem.

In the thirties and forties of this century studies in coordination chemistry were continued in Copenhagen mainly by Jannik Bjerrum, Kai Arne Jensen and R.W. Asmussen. Jannik Bjerrum in his book "Metal Ammine Formation in Aqueous Solution", gave the theoretical and experimental basis for determining the successive stability constants of labile complexes in solution. For the ammonia and ethylenediamine complexes he was able to prove the existence of all the intermediate complexes between the metal aqua ion and the coordinatively saturated complex. Kai Arne Jensen prepared numerous complex salts and distinguished between *cis* and *trans* complexes by dipole measurements. His experimental work, mainly published in Z. anorg. Chem. in the thirties, gave strong support to the correctness of Alfred Werner's theory; for the planar structure of the coordinatively tetravalent platinum(II) complexes as well as for the analogous diamagnetic nickel(II) and palladium(II) complexes. R.W. Asmussen studied the magnetochemical properties of transition metal complexes, thereby solving several constitution problems. Together with Bjerrum and Jensen he took the initiative to organize what was really the first International Conference on Coordination Chemistry in Copenhagen in 1953.

In the following years C.J. Ballhausen, Chr. Klixbüll Jørgensen and Claus Schäffer made important contributions to ligand field theory, and in recent times the young generation of Danish chemists has continued to contribute to all fields of coordination chemistry, after the second world war almost exclusively in the English language.