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Structure and Bonding

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Optical Spectra and Chemical Bonding in Transition Metal Complexes

Special Volume II dedicated to Professor Jørgensen

Volume Editor:
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The series *Structure and Bonding* publishes critical reviews on topics of research concerned with chemical structure and bonding. The scope of the series spans the entire Periodic Table. It focuses attention on new and developing areas of modern structural and theoretical chemistry such as nanostructures, molecular electronics, designed molecular solids, surfaces, metal clusters and supramolecular structures. Physical and spectroscopic techniques used to determine, examine and model structures fall within the purview of Structure and Bonding to the extent that the focus is on the scientific results obtained and not on specialist information concerning the techniques themselves. Issues associated with the development of bonding models and generalizations that illuminate the reactivity pathways and rates of chemical processes are also relevant.

As a rule, contributions are specially commissioned. The editors and publishers will, however, always be pleased to receive suggestions and supplementary information. Papers are accepted for *Structure and Bonding* in English.

In references *Structure and Bonding* is abbreviated *Struct Bond* and is cited as a journal.

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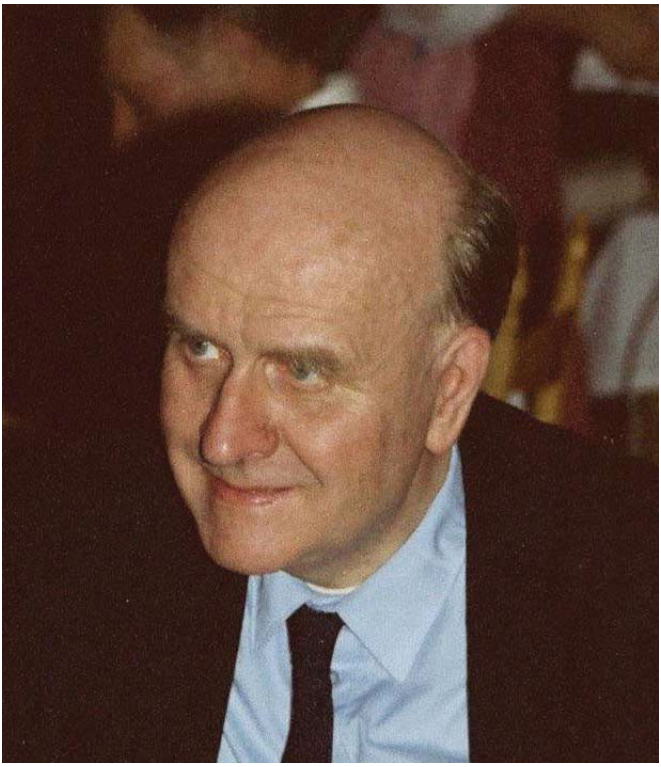
Foreword

Axel Christian Klixbüll Jørgensen was a "Polyhistor", one of the very few in the highly specialized science of our time. His interests and contributions in chemistry covered the whole Periodic Table. This statement demonstrates the breadth of his interests, however, it also sheds light on the constraints of chemistry which deals with a large, yet limited number of elements. It is not surprising that Jørgensen went beyond these limits, exploring the probable or plausible chemistry of yet unknown elements and elementary particles such as quarks. Even chemistry itself did not place rigid limits on his mind, he was able to transfer his chemical concepts to scientific problems far beyond the normal such as in astrophysics.

"Structure and Bonding" is intimately associated with the name C.K. Jørgensen both as initiator and author over several decades. The appearance of a special edition in memory of this great scientist is a self-evident prolongation of his many contributions to the success of this series.

We owe a debt of thanks to Dr. Thomas Schönherr for his efforts in setting up this special edition. The scientific contributions reflect some of the outstanding impact on the understanding of chemistry stimulated by Jørgensen's thoughts as well as by his opening of new research areas. As an innovation in "Structure and Bonding", a number of personal notes have been added in order to give some impression of the method of thinking and communicating that was so characteristic of Jørgensen. These notes will be a reminder to all those who knew him and they will convey to those who never met him what was so special about this great man.

Stuttgart, September 2003 Arndt Simon



Axel Christian Klixbüll Jørgensen (1931–2001)

Axel Christian Klixbüll Jørgensen

1931 Born in Aalborg, Denmark, 18th April
1950 Graduation from high school (Abitur). Beginning of studies at the University of Copenhagen. The aim was a candidatus magisterii (cand. mag.), which would qualify him as a Danish high school teacher
1953 Teaching assistant at the Technical University of Denmark, Copenhagen
1954 Cand. mag. in chemistry, mathematics, astronomy and physics with chemistry as the main subject, University of Copenhagen
1957 Doctor philosophiae, University of Copenhagen, thesis: *Energy Levels of Complexes and Gaseous Ions, Gjellerup, Copenhagen, Denmark*
1957 Marriage to Micheline Prouvez
1959 Head of Office for Fundamental Research, Division of the Scientific Businesses, NATO, Paris
1961 Director of the Group of Theoretical Inorganic Chemistry, Cyanamid European Research Institute, Cologny, Geneva (until 1968)
1962 Books: *Absorption Spectra and Chemical Bonding in Complexes, Pergamon, Oxford, England. Orbitals in Atoms and Molecules, Academic Press, London, England*
1963 Book: *Inorganic Complexes, Academic Press, London, England*
1965 Member of the Royal Danish Academy of Sciences and Letters
1966 Editor of *Structure and Bonding* (until 1989)
1968 Invited to be Professor at the University of Geneva
1969 Book: *Oxidation Numbers and Oxidation States, Springer-Verlag, Berlin*
1970 Chair of Physical Chemistry at the University of Geneva
1971 Book: *Modern Aspects of Ligand-Field Theory, Amsterdam, North-Holland*
1974 Chair of Inorganic and Analytical Chemistry at the University of Geneva
1977 Book: *Lasers and Excited States of Rare Earth (with Renata Reisfeld), Springer-Verlag, Berlin*
1978 Death of his wife Micheline
1983 Doctor *honoris causa* from the Philosophical Faculty of the University of Zürich
1997 Professor Emeritus at the University of Geneva
2001 His death on 9th of January

Preface

The present volume of Structure and Bonding is the second one dedicated to the memory of C. K. Jørgensen by providing accounts of the present stage of development of a number of the most important areas of chemical spectroscopy to which he made influential contributions.

While Volume 106 included personal recollections of Jørgensen by his friends and colleagues, the present Volume 107 is restricted to original work.

Chemical spectroscopy signifies the conceptual area where chemistry and spectroscopy meet. In the early days of ligand-field theory, where a fusion with the molecular orbital theory of inorganic complexes happened, synergy helped our striving for understanding structure, bonding and spectroscopy. While structure and bonding are mostly conceived as static properties, spectroscopy is a collective word describing the many associated dynamic properties. The synergy arises when these dynamic properties are projected onto parameter spaces covering the semi-empirical parameters whose values are obtained by holding together the spectroscopic results and the expressions of theoretical modeling. The fact that regular and chemically transparent behavior was almost invariably found in these parameter values not only placed chemical spectroscopy in the front line of chemical science for more than a decade, but also allowed it to stay alive for at least 50 years.

The subfields of chemical spectroscopy to which Jørgensen made pioneering contributions are well represented in the present volume of Structure and Bonding. One only need to cast a brief look at the titles of the works to be reminded of the width of Jørgensen's writing.

Boulon gives us the opportunity to look back at CKJ's first series of papers: "Studies of Absorption Spectra" from 1955–56 where he pioneered the idea that 3*d* and 4*f* ions ought to be looked at in a similar way. CKJ was one of the few scientists who remained faithful to this idea in a productive way. Most other people remained attached either to the *d* or the *f* camp. CKJ was also the first to suggest (1963) that the ligand-field part of the structure of the *f-f* spectra of rare earth complexes was due to covalency in spite of the fact that it was smaller than the fine structure due to spin orbit coupling. In this context he saw that the σ. Part of the molecular orbital model that Yamatera had developed for the ligand field of orthoaxial 3*d* complexes could be applied easily to high-symmetry rare earth systems. This vision of his led to the Angular Overlap Model (AOM, 1965).

Gütlich, van Koningsbruggen and Renz bring us up to date with the ramifications of the spin cross-over phenomenon, which has its origin in the early recog-

nition of complexes of the same metal ion in the same oxidation state but with different total spins. This recognition could be qualitatively explained by the Pauling hybridization theory of *d*-period complexes, the theory that had been governing this part of chemistry for two decades at the time when ligand fields entered the chemical scene (around 1950). The ligand-field plus interelectronic repulsion model, which is the essence of ligand-field theory for *d*-electron complexes, was able to quantify the occurrence of the different total spins parametrically, and for cubic complexes the transition from the low spin to the high spin situation would depend on the internal field strength, which could be defined as the ratio between the cubic ligand-field parameter Δ and Jørgensen's spin pairing energy parameter *D*. CKJ was the first to see the potential of the ligand-field theory as compared with that of hybridization, and he was the only chemist who had the courage to criticize Pauling's work. The rate at which the development took place can be interestingly illustrated by the fact that approximately at the time when CKJ wrote his last solo-authored book about chemical spectroscopy (1971), Pauling's latest edition of "The Nature of the Chemical Bond" hardly, if at all, mentioned the revolution that this part of science had undergone over the last 20 years.

Lever and Gorelsky remind us about three other facets of Jørgensen's initiatives. They discuss spectra of ruthenium complexes making us recall that CKJ was the first to demonstrate (1956) that the ligand-field model, which at that time was thought of mostly as a purely electrostatic model, could be used to interpret also the *d*-*d* spectra of 4*d* and 5*d* complexes, which at that time were thought of as being definitely much more covalent than those of the 3*d* series. Moreover, these authors concentrate on non-innocent ligands, a concept coined by Jørgensen to cover the ligands whose complexes cannot be characterized by a preponderant d^q configuration. Finally, their focus is charge transfer spectra, an area of spectra which CKJ insisted upon calling electron transfer spectra when he made his early (1959) and remarkably detailed contributions to their interpretation on the basis of the d^q configuration concept. Clearly, the Lever-Gorelsky spectra are not "innocent" enough to adhere to Jørgensen's vocabulary[1].

Morita, Buddhudu, Rau, and Murakami's work on energy transfers in rare earth nanoporous xerogels and sol-gel SiO_2 glasses illuminates the last two decades of Jørgensen's active life. During this time he was given an extraordinary opportunity to unite his legendary overview of rare earth chemistry and spectra and his practical theoretical skill in his close collaboration with Professor Renata Reisfeld, an expert on solar-energy, whose sol-gel glasses made up their favorite subject material.

Nolet, Beaulac, Boulanger, and Reber write about intensity borrowing in *d*-*d* spectra including the spin-forbidden transitions, subjects to which CKJ made pioneer contributions in 1956. In this context, one cannot help mentioning again Jørgensen's spin pairing energy parameter, which was not only useful in making his electron transfer transitions in complexes of different central ions commensurable, but also in general for parameterizing the electron repulsion part of the ligand-field model.

[1] see Vol. 106, p. 13 – 14

Reinen and Atanasov use DFT to combine the Angular Overlap Model with vibronic coupling in addressing the subjects of *s*-*d* and *s*-*p* mixing. The relevance of these orbital interactions had been foreseen by CKJ as early as 1955 and 1971, respectively. The intermixing of *s* and *d* was unfortunately introduced in an incorrect context, but this is the exception that proves the rule that he made remarkably few mistakes. However, the case illustrates the symbiosis of Jørgensen's life and writing which could have been a disaster but actually became an enrichment of our subject and of our community: when Jørgensen had an idea, he was not himself if events that were not under his control prevented him from writing about it before sunset. In his book referred to above, CKJ discussed *s*-*p* mixing in the context of main group stereochemistries.

Riesen treats hole-burning spectroscopy of complexes and thereby opens up for the future of Jørgensen's science. Finally, Anthon, Bendix and Schäffer exemplify how the values of the semi-empirical parameters of ligand-field theory can be obtained by computation using the commercially available Kohn-Sham DFT program package in a constrained way. At least one of these authors feels sad that he cannot enjoy Jørgensen's skeptical remarks about the almost mysterious fact that the procedure described here works so well.

CKJ interrelated concepts as well as phenomena. He saw analogies and connections. He always did things differently. He was altogether different and, therefore, controversial. He was inspiring, but with his unimaginable ability to read fast, he was also inspired by the whole chemical community, and again here, he was special because he could be inspired even by thoughts which he did not fully understand. He certainly had his own intuitive approach.

Copenhagen, March 2004 C. E. Schäffer

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