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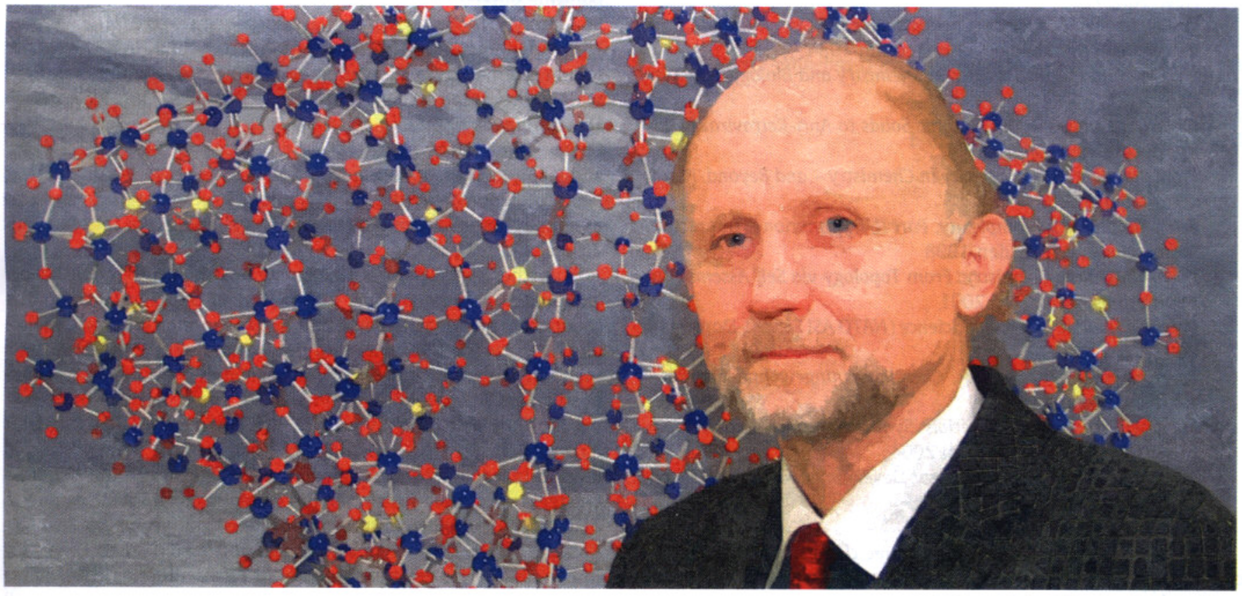
Preface

Protagonists in Chemistry: Achim Müller



Artwork by Norma Langohr

Professor Achim Müller from the University of Bielefeld (Germany) is a remarkable personality of today's chemistry and natural science. His basic facts are: born February 14, 1938 and brought up in Detmold (at that time Principality of Lippe, Germany). After his studies of Chemistry and Theoretical Physics he obtained his Ph.D. degree under the supervision of Professor Oskar Glemser in 1965 from the University of Göttingen with a thesis on experimental thermochemistry and already two years later his *venia legendi* with a Habilitation thesis on the theory of molecular vibrations from the same university. In 1971, he became Associate Professor of Inorganic Chemistry at the University of Dortmund and in 1977 he was appointed as Full Professor at the University of Bielefeld, where he is as Professor emeritus successfully active today, heading a research group which has become a world center of excellence in Inorganic Chemistry. He received but subsequently declined an invitation to succeed Professor F. Seel at Saarbrücken in 1982. Although it is evident from many of the contributions to this special issue, that Achim Müller has had a profound influence on the field of polyoxometalate chemistry, we should also recognize the evolution of the work of this highly creative scientist – *inorganic chemist* would be a too restrictive label for him, Michael Pope once said.

That Achim Müller has published his research output (ca. 900 papers, among them more than 50 reviews) in more than 100 journals and 13 edited volumes reveals an amazing breadth of his interests and abilities. His *curriculum vitae* lists the following areas:

- Preparative and Analytical Transition Metal Chemistry
- Nano-Science
- Solution and Encapsulation Chemistry (e.g. related to vesicle formation, artificial cell–cations' interactions and confined water)
- Magnetochemistry
- Structural Chemistry
- Materials Chemistry
- Bioinorganic Chemistry
- Biological N_2-Fixation (microbiological and biochemical investigations)
- Heterogeneous Catalysis (Hydrodesulfurization, HDS)
- Electronic Structure of Transition Metal Compounds

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- Molecular Physics (theory of heavy atom isotope effects on molecular constants; isotope rules)
- Vibrational Spectroscopy (matrix isolation spectroscopy; gas phase band contour analysis; resonance Raman effect)
- Philosophy of Science
- Public Understanding of Science

The titles of the edited volumes resulting from symposia organized by him reveal the scope and their interdisciplinary nature:

- *Spectroscopy in Chemistry and Physics:* Modern Trends, Amsterdam 1980
- *Transition Metal Chemistry – Current Problems of General, Biological and Catalytical Relevance*, Weinheim 1981
- *Matrix Isolation Spectroscopy*, Dordrecht 1981
- *Nitrogen Fixation: The Chemical–Biochemical–Genetic Interface*, New York 1983
- *Sulfur: Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology*, Amsterdam 1984
- *Electron and Proton Transfer in Chemistry and Biology*, Amsterdam 1992
- *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Dordrecht 1994
- *From Simplicity to Complexity in Chemistry – and Beyond, Part I*, Wiesbaden 1996
- *From Simplicity to Complexity, Part II, Information – Interaction – Emergence*, Wiesbaden 1998
- *Polyoxometalate Chemistry: From Topology via Self Assembly to Applications*, Dordrecht 2001
- *Polyoxometalate Molecular Science (NATO ASI Series)*, Dordrecht 2003
- *Facetten einer Wissenschaft: Chemie aus ungewöhnlichen Perspektiven*, Weinheim 2004
- *The Chemistry of Nanomaterials: Synthesis, Properties and Applications, Vols. 1–2*, Weinheim 2004
- *Nanomaterials Chemistry: Recent Developments and New Directions*, Weinheim 2007

Until about 1990 most of his *inorganic chemistry* research concerned transition metal thioanions and metal sulfido clusters, an area in which his group is acknowledged for pioneering work, examples are polysulfidic species like $Mo_2S_{12}^{2-}$, $Mo_3S_{13}^{2-}$, $W_3S_9^{2-}$, the ferredoxin model $[Fe_4S_4(SH)_4]^{2-}$ and the introduction of thioanions MS_4^{2-} as ligands in transition metal chemistry. This work also naturally emerged to the research in hydrodesulfurization catalysis of MoS_2 based heterogeneous catalysts and the microbiological and biochemical investigations of the biological nitrogen fixation, also basing on FeMo sulfide clusters in protein matrices. Quite recently the group succeeded to identify and characterize a protein responsible for the storage of Mo via polyoxometalate units. In both emerging fields the achievements received international recognition.

However, it is within the past twenty years that Achim and his coworkers have produced their most spectacular and really breathtaking contributions to chemistry. Beginning with a series of papers in the early 1990's on the structures and magnetic properties of polyoxovanadate anions that exhibited an unusual and surprising host–guest chemistry – *anions enclosed in anions*. Fascinated by the topological implications of polyoxometalate structures, they began to explore the systematic synthesis of more and more elaborate and unusual assemblies. This includes the templating of polyvanadate structures by small inorganic anions, and the studies of the unusual magnetic behavior of the subsequent mixed valence vanadates. Moving to molybdates his group prepared the already large $Mo_{57}V_6$ and $Mo_{57}Fe_6$ mixed valence oxoanions. Recognizing the polymolybdate building blocks common to these and the previously discovered $Mo_{36}O_{112}^{8-}$ anion, they began to devise ways of constructing even larger assemblies. The first of these was the amazing Mo_{154} "Bielefeld giant wheel" of 1995 which has attracted worldwide attention in both the scientific and the lay press. It took almost two years of intensive work to determine the charge and protonations of this cluster ion to establish the correct chemical formula since classical analytical methods did not provide a sufficient accuracy. They then proceeded to show that this anion was not the result of an accidental synthesis, but that similar species were present in the poorly-understood *molybdenum blue* solutions known to the scientific community since the early work of Carl Wilhelm Scheele in the seventies and eighties of the eighteenth century. They have since isolated several other derivatives, among them a larger Mo_{176} wheel and the Mo_{248} by capping these wheels. Later, the Bielefeld team prepared a huge cluster which they call a "nano-hedgehog" because of its shape and as it has an outer layer of oxygen atoms pointing outwards. Philip Ball called it a "blue lemon". It contains 368 molybdenum atoms and is actually the size of a protein. "Bringing inorganic chemistry to life", states Nina Hall. The cluster has an internal cavity 2.5 nanometers wide and 4 nanometers long which encapsulates about 400 water molecules. The electron-rich structure is deep blue in color – due to delocalised electrons. It is believed that such structures could be used as selective catalysts, similar to zeolites, or as nanoreactors. Achim Müller's aim has thus been to explore how the functionality of such materials could be explored through tuning the structure by varying the reaction conditions and reagents.

A further spectacular achievement was the synthesis of hollow icosahedral polymolybdates making use of building blocks of the required pentagonal, trigonal and linear symmetry to form *molecular quasicrystals*, a term applicable also to the ring shaped clusters mentioned above. These so called *keplerates* (reminding of Johannes Keplers *Mysterium Cosmographicum*) could be sized by replacing Mo^{V}_2 linking units by Fe^{III} (i.e. Mo_{132} to $Mo_{72}Fe_{30}$), the latter a neutral cluster with 150 unpaired electrons. The team succeeded both to incorporate the Keggin anion as a guest into the $Mo_{72}Fe_{30}$ cluster, an example for some kind of *Molecular Darwinism*, and to assemble these clusters into two-dimensional arrays by Fe–O–Fe linkages. "$Fe^{III}{}_{30}Mo^{VI}{}_{72}$" is a spherical antiferromagnet. Especially interesting is the geometry of the 30 Fe^{III} centers as they define an icosidodecahedron, a unique Archimedean solid having all edges equal. The cluster is an example of a zero-dimensional system that shows magnetic ordering at low T. The linking of Fe^{III} triangles causes fascinating frustrations comparable to those of the well known Kagomé lattices. Corresponding clusters with Cr^{III} and VO^{2+} as linking units have also been investigated.

Another striking example for unexpected and intriguing magnetic properties was the "$V^{IV}{}_{15}$ "Though the cluster shows a rather high symmetric distribution of 15 magnetic V^{IV} centers (ground state = 1/2), it has layers of different magnetization and, therefore, interesting related properties. Because of the rather large size and low spin state (decreasing dipolar interactions) it was considered in the literature as a candidate for the observation of quantum oscillations (Dobrovitski et al., Phys. Rev. Lett. 84 (2000) 3458). Quite recently this could be confirmed experimentally by Achim and his collaborators from Grenoble and Be'er Sheva (Bertaina et al., Nature 453 (2008) 203).

His recent work further involves probing and controlling water structures inside the giant rings and balls, and demonstrating the existence of the hydrogen-bonded polyhedra that have been postulated for models of bulk water. Further surprises were the observation of the formation of multi-nanometer-sized unprecedented vesicles bounded by the polymolybdate rings and balls with hydrophilic surfaces. This work implied a new solute state of inorganic ions. Another topic of his actual interest is related to porous capsules comprising of perspectives for *chemistry under confined* *conditions*, artificial cell- environment interactions and understanding the principles of *porosity* on a molecular level.

Achim introduced us to the unusual characteristics of polyoxometalates, and he has opened up new ways of thinking about these substances which indeed have properties and applications unmatched by any other group of compounds by drawing attention to relationships with other fields of human enquiry. A real scholar, experienced by some thousands chemistry students in Göttingen, Dortmund and Bielefeld. He enjoys high prestige in the scientific community and worldwide recognition demonstrated through six honorary degrees (Wroclaw, Sibiu, Cluj, Russ. Acad. Sci., Paris, La Plata); a series of named lectureships and prizes, e.g. at the Universities of Arizona, Kentucky, South Carolina, and at Texas A&M University; the Alfred-Stock Prize, the Gay-Lussac/Humboldt Prize and the Sir Geoffrey Wilkinson Prize; Emerson Center Award, Emory University, Atlanta (USA); Lewis Lecture, University of Cambridge (UK); Elhuyar-Goldschmidt Prize, Spanish Royal Society of Chemistry; Wilhelm Manchot-Forschungsprofessur, Technische Universität München; Jean Perrin Lecture, Paris and the Centenary Prize, Royal Society of Chemistry, London, not to forget his election to numerous national and international academies and scientific societies. Some fifty postdocs, visiting professors and Humboldt awardees have been attracted to Bielefeld undertaking collaborative and truly interdisciplinary research with him. The existence of the Center for Interdisciplinary Research at Bielefeld has allowed Achim to bring together chemists, physicists, biologists, mathematicians, and philosophers for a series of workshops. Many of the edited volumes cited above emerged from events organized by him at this Center.

Although the *PROTAGONISTS IN CHEMISTRY* volumes are designed to celebrate the lifework more or less at the end of this time, it is clear that Achim shows no signs of acknowledging this transition. This is continuing to be an exciting time for him and his group, and we are sure that he will continue to be recognized. His homepage http://www.uni-bielefeld.de/chemie/ac1/will keep everybody up to date.

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