

Foreword



Professor Achim Müller

Although it is evident from 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 remarkably creative scientist—"inorganic chemist" is too restrictive a label. The basic career facts are these: a Ph.D. at Göttingen in Experimental Thermochemistry with Professor Oskar Glemser in 1965, followed by Habilitation (Vibrational Spectroscopy) only two years later; appointment as Associate Professor at the University of Dortmund in 1971, and thence to the Chair of Inorganic Chemistry I at Bielefeld in 1977, where he has since remained. He received but subsequently declined an invitation to succeed Professor F. Seel at Saarbrücken in 1982.

That Achim Müller has published his research output (ca. 700 papers and reviews) in more than 70 journals reveals the astonishing breadth of his interests and abilities. His curriculum vitae lists the following areas: Chemistry of Transition Metals; Supramolecular Inorganic Chemistry; Nano-Sciences; Inorganic Structural Chemistry; Bioinorganic Chemistry; Biological Nitrogen Fixation (microbiological and biochemical investigations); Heterogeneous Catalysis (hydrodesulfurization); Structure and

Electronic Structure of Transition Metal Compounds; Molecular Physics (theory of heavy atom isotope effects on molecular constants); Vibrational Spectroscopy (matrix isolation spectroscopy; gas phase band contour analysis; resonance Raman effect); Philosophy of Science; Popularized Science. His papers and especially his review articles are carefully crafted and written with a distinctive style and flair that is unfortunately rarely seen today in the scientific literature.

Until about 1990 most of his *inorganic chemistry* research concerned transition metal thioanions and thiometal clusters, an area in which he is an acknowledged pioneer with the characterization of species like $\text{Mo}_2\text{S}_{12}^{2-}$, $\text{Mo}_3\text{S}_{13}^{2-}$, $\text{W}_3\text{S}_9^{2-}$, the simple ferredoxin model $[\text{Fe}_4\text{S}_4(\text{SH})_4]^{2-}$, and the introduction of thiometalates, MS_4^{2-} , as ligands in coordination chemistry. This work also naturally led to research programs in hydrodesulfurization catalysis and microbiological and biochemical investigations of biological nitrogen fixation, fields in which he already has some 40 publications. But it is within the past 10–15 years that Achim has produced his most spectacular, indeed breathtaking, contributions to chemistry, for which he has received well-deserved international recognition. This includes three honorary degrees; named lectureships 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; election to numerous international honorary societies, most recently the Academia Scientiarum et Artium Europaea. Some fifty postdoctorals and visiting professors have been attracted to Bielefeld, and he undertakes collaborative research programs that are truly interdisciplinary.

Beginning with a series of papers in the early 1990's on the structures and magnetic properties of polyoxovanadate anions that exhibited unusual host-guest chemistry—*anions enclosed within anions*—Achim “discovered” the unusual characteristics of polyoxometalates, and embraced this field with the enthusiasm of a convert to the True Faith. Characteristically, 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. The existence of the Center for Interdisciplinary Research at Bielefeld, has allowed him to bring together chemists, physicists, biologists, mathematicians, and philosophers (not to mention musicians and science writers) for a series of symposia. The titles of the edited volumes resulting from recent symposia reveal their interdisciplinary nature : “Electron and Proton Transfer in Chemistry and Biology” (1992), “Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity” (1994), “From Simplicity to Complexity in Chemistry—and Beyond, Part I” (1996), “From Simplicity to Complexity, Part II, Information–Interaction–Emergence”

(1998), “Polyoxometalate Chemistry: From Topology via Self Assembly to Applications” (2001). Fascinated by the topological implications of polyoxometalate structures, Achim began to explore the systematic synthesis of more and more elaborate and unusual assemblies. This led initially to the templating of polyvanadate structures by small inorganic anions, and to the unusual magnetic behavior of the subsequent mixed valence vanadates. Moving to molybdates he soon had prepared the unprecedentedly large mixed valence Mo_{57}V_6 and $\text{Mo}_{57}\text{Fe}_6$ oxoanions. Recognizing the polymolybdate building blocks common to these and the previously-discovered $\text{Mo}_{36}\text{O}_{112}^{8-}$ anion, he began to devise ways of constructing even larger assemblies. The first of these was the astonishing Mo_{154} “big wheel” of 1995 which has attracted worldwide attention in the scientific and lay press. Achim then proceeded to show that this anion was not the result of a random accidental synthesis, but that similar species were present in the long-known and poorly-understood “molybdenum blue” solutions. He has since isolated several other derivatives, a larger (Mo_{176}) wheel, and more recently the Bielefeld “hedgehog” with 368 molybdenum atoms. An even more spectacular achievement in my view was the designed synthesis, à la Buckminster Fuller, of hollow icosahedral polymolybdates making use of building blocks of the required pentagonal, trigonal and linear symmetry. The resulting “keplerates” could be sized by replacing Mo_2^{V} linking units by $\text{Fe}^{\text{III}}(\text{Mo}_{132}$ to $\text{Mo}_{72}\text{Fe}_{30})$ —the latter a neutral cluster with 150 unpaired electrons! But the story does not end here; it proves to be possible both to incorporate the Keggin anion as a guest in the $\text{Mo}_{72}\text{Fe}_{30}$ cluster and to demonstrate assembly of these clusters into two-dimensional arrays by Fe–O–Fe linkages. Results such as these justify the long-held claims of polyoxometalate chemists that these complexes provide the link between molecular and nanoscopic materials.

Although this volume is designed to celebrate the traditional age of retirement, it is clear that Achim shows no signs of acknowledging this transition. And why should he? His current work involves probing *and controlling* water structures inside the Bielefeld rings and balls, and demonstrating the existence of the hydrogen-bonded polyhedra that have been postulated for models of bulk water. Further surprises are in store with recent observations of multi-nanometer-sized aqueous micelles bounded by the polymolybdate rings. This is an exciting time for inorganic chemists, and we can expect that Achim Müller will continue to be a major influence.

Michael Pope

“The creation of something new is not accomplished by the intellect.... . The creative mind plays with the objects it loves.”

Carl Jung

