Crystallography in *Structural Chemistry*

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Abstract This anniversary article has three functions: It marks Volume 25 of our journal; it honors 2014, the International Year of Crystallography; and it celebrates the centennial from the birth of a great crystallographer, Aleksandr I. Kitaigorodskii.

Keywords A. I. Kitaigorodskii · History of X-ray crystallography · Generalized crystallography · Gas-phase electron diffraction · Quasicrystals

Introduction

Our journal, *Structural Chemistry*, is completing its 25th volume this year; it seems recent that we marked the twentieth anniversary of this publication [1]. The goal of our journal has not changed since its inception; viz., to provide a venue for high-quality research reports and overviews in diverse areas of the ever expanding discipline of structural chemistry. The year 2014 is the International Year of Crystallography, and we are happy to note that

crystallography has constituted a substantial portion of the papers we have published. Lately, the emphasis of our crystallographic contributions has changed. We have moved away from publishing mere structure reports toward more comprehensive papers, including such that deal with the foundations of crystallography and the various approaches to the determination of crystal and molecular structures. During the past quarter century the foundations of crystallography have broadened and it has increasingly become the science of structures. Following a brief historical introduction, I am singling out a few contributions from these 25 volumes for illustration, but this sampling is indeed a sampling only and is far from a comprehensive coverage.

X-ray crystallography

In the November 14, 1912, issue of *Nature*, the British scientist A. E. H. Tutton reported [2]: “During a visit to Munich at the beginning of August last the writer was deeply interested in some extraordinary photographs which were shown to him by Prof. von Groth, the *doyen* of the crystallographic world, and professor of mineralogy at the university of that city. They had been obtained by Dr. M. Laue, assisted in the experiments by Herren W. Friedrich and P. Knipping, in the laboratory of Prof. A. Sommerfeld in Munich, by passing a narrow cylindrical beam of Röntgen rays through a crystal of zinc blende, the cubic form of naturally occurring sulphide of zinc, and receiving the transmitted rays upon a photographic plate. They consisted of black spots arranged in a geometrical pattern, in which a square predominated, exactly in accordance with the holohedral cubic symmetry of the space-lattice attributed by crystallographers to zinc blende.” It seems

Dedication This Editorial is dedicated to the memory of Aleksandr I. Kitaigorodskii (1914–1985). He was a unique thinker, an original scientist, and a versatile human being. He uncovered a general principle of how molecules build up crystal structures, and he predicted correctly the relative frequencies of occurrence of the various space groups among crystal structures at the time when relatively few organic crystal structures had been yet determined. His teachings live on in his papers and monographs and in the scientific and pedagogical activities of his pupils and their pupils.

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Aleksandr I. Kitaigorodskii in his laboratory at the Institute of Element-organic Compounds (INEOS) of the Soviet (now Russian) Academy of Sciences, Moscow. Photograph courtesy of the late Erlen Fedin. (Kitaigorodskii's name is spelled in a variety of ways in the scientific literature: Kitaigorodskii, Kitaigorodsky, Kitaigorodski, Kitaigorodskij, depending on the approach to transliterating his name from the Russian original.)

that Tutton recognized the broader significance of what he saw, “Crystallography thus affords to its sister science Chemistry the first visible proof of the accuracy of Dalton’s atomic theory, and now enters into a new sphere of still greater usefulness. ... Crystallography has thus become an exact science leading us to a practical knowledge of the hitherto mysterious world where Dalton’s atoms and molecules reign supreme.”

I hasten to note that crystallography had existed as a science long before the Munich experiments. Two hundred years before Dalton and three hundred years before the Munich experiment, Johannes Kepler discussed the shape and inner structure—in today’s terms, the atomic arrangement—of crystals. He did this in his Latin-language treatise, *Strena, seu De Nive Sexangula* of 1611, which was published in English translation in 1966 [3]. Kepler presented arrangements of closely packed spheres. Incidentally, Dalton invoked the image of close packing of spheres in his work on gas absorption [4]. The history of classical crystallography from Kepler to Laue is a shining page in science history.

Laue had initiated the experiments because P. P. Ewald, a doctoral student in physics, had raised the possibility of X-ray scattering by crystals in his dissertation. Ewald completed his thesis earlier in 1912 and turned to Laue with his query. Ewald’s genius connected the propagation of electromagnetic radiation and the supposed internal structure of crystals. He assumed that if the crystal is looked at as a regular arrangement of resonators, and the distance between these resonators would be commensurate

with the wavelength of the radiation, there should be a diffraction phenomenon, and it should be possible to observe it. He consulted Max Laue (as he was then), and the experiment mentioned above followed. The significance of the experiment was immediately recognized in Max von Laue’s Nobel Prize in 1914 (by then, “von,” because his father received hereditary nobility in 1913).

Direct methods

The Nobel laureate mathematician turned crystallographer Herbert Hauptman (1917–2011) described in the pages of *Structural Chemistry* [5] the development of X-ray crystallography to which he and Jerome Karle (1918–2013) [6] contributed in a seminal way by proposing and working out the direct methods of structure analysis. Hauptman and the physical chemist Karle shared the Nobel Prize in Chemistry in 1985. They solved the so-called phase problem using mathematical techniques [7–9]. Their discovery and the discoveries of others made it possible for X-ray crystallography to expand toward larger systems than before and to increase the accuracy of structure determination. David Sayre (1924–1912) was another outstanding contributor to the solution of the phase problem and he gave a detailed critical analysis in this journal of how it happened [10].

Isabella Karle was one of the pioneers in applying the direct methods for actual structure determinations. She and Jerome had utilized their vast experience in modernizing a less well-known technique of structure determination, gas-phase (often, simply, gas) electron diffraction (GED) [11]. Some of the intricacies of the structure analysis of GED were helpful in developing the direct methods. At this point, it is proper to stress that the term crystallography has become synonymous with the science of structure; thus, it embraces structural studies in gases and liquids as well. The development of the gas-electron-diffraction technique has also received exposure in our periodical *Structural Chemistry* [12, 13]. Beside gases, the electron diffraction technique has also been used extensively for the analysis of solid structures. An outstanding contribution to electron crystallography is mentioned here as it was applied for a broad range of materials [14]. The development of holographic methods was among the recent technical innovations in crystallography, on the road toward structure determination with atomic resolution [15].

Biological macromolecules

The crystallographic investigation and structure determination of biological macromolecules was one of the most

spectacular scientific achievements of the twentieth century in which X-ray crystallography played a pivotal role. Linus Pauling's triumph in discovering the alpha-helix structure of proteins served as useful example in a host of research projects [16]. Pauling's accumulation and utilization of structural data was a key element in his success. The discovery of the double helix structure of DNA was a spectacular application of Pauling's model-building approach [17]. Pauling's attitude, however, was less than welcoming toward the cyclol hypothesis, which came up in the quest for protein structures. Further support for the rejection of this hypothesis appeared recently from theoretical calculations [18]. The ultimate utilization of the quest for biomolecular structures will be the fascinating approach of personalized medicine toward which the mapping of the human genome constituted a great stride [19].

Generalized crystallography and quasicrystals

Our journal has paid much attention to generalized crystallography—a term much cultivated by Alan L. Mackay—expressing the structure of science [20]. In particular, this interpretation of crystallography went beyond the classical system of 230 three-dimensional space groups. Here we quote only a small set of contributions that paid homage to Mackay and his concepts and extended the realm of structure considerations to non-classical constructions [21–23]. This area of crystallography overlaps with nanoscience and nanotechnology, molecular biology, and condensed state physics.

A specific area of non-classical crystallography is quasicrystals. The history of their discovery and the barriers its concept had to overcome before acceptance by some of the leading scientists was most instructive [24–26]. In particular, Ref. 25 anticipated the high recognition for the quasicrystal discovery just a few months before Dan Shechtman's Nobel Prize was announced in October 2011.

The structures of quasicrystals have remained a puzzle in many aspects, but the accomplishments in the area have also been most impressive. The time has come to discuss quasicrystal structures at the atomic level [27]. Steurer and Deloudi took up the challenge of describing quasicrystals consisting of clusters, and found packing principles for them [28].

Fundamental concepts

Finally, a sampler of papers follow to represent studies of rather general character that belong to the expanded interpretation of crystallography. They cover a wide range of topics, but all examine questions related to fundamental

features or concepts of structure. Above we mentioned a paper about quasicrystal clusters. Ilyushin communicated a comprehensive study of clusters in general, their self-organization, and described geometrical modeling of nanocluster precursors, building up a hierarchical system [29]. Malenkov investigated the possibility of understanding the regularities of non-crystalline substances on the level of their inherent structures. The concept of inherent structures and the history of the development of this concept are exposed [30]. Shevchenko carries a similar question to philosophical depths. He follows the process of structures building up from fundamental configurations to clusters and to the whole structures. He finds unity in the basic principles of hierarchical construction regardless whether the final structure is periodic or aperiodic [31]. Efforts to find the concept universal optimum and general principles of “inorganic genes” directed Shevchenko and Krivovichev to investigate paulingite-related zeolites and minerals [32].

Meyer investigated the notions of size and shape separately and in combination; he showed the advantage in considering them “wedded” [33]. He involved molecular volume, surface area, packing densities and other properties in the discussion, and used the example of aromatic organic compounds for the application of his conclusions. One of the conditions influencing molecular size is temperature. For molecules with high degree of deformation motion, the size may expand considerably at elevated temperatures. Varga et al. examined the extent of such expansion as a function of temperature [34]. For this, intricacies of intramolecular motion and its anharmonicity have to be taken into account. The concerted use of experimental data and computational results yielded noteworthy conclusions.

There have been valuable attempts to uncover regularities and trends in the variations of various properties of related substances. Slovokhotov, Batsanov, and Howard analyzed the trends in melting temperatures and boiling temperatures of organic compounds [35]. Their observations supported the notion of molecular van der Waals symmetry developed earlier by the authors. They thus seemed to transfer successfully information about molecular properties to information about bulk properties.

In 2007, a rather unusual contribution was published in *Structural Chemistry* by an unusual scientist. The late John E. Scott was professor of chemical morphology at the Department of Chemical Morphology, University of Manchester, UK. His research field was the structure and function of various polysaccharides that constitute building blocks in our body. As he taught, “Our shape is defined and maintained by the connective tissues (skin, tendons, cartilages, blood vessels, etc.) or more precisely by their extracellular matrices. These highly ordered supramolecular organisations are

modules of protein fibrils held together by elastic carbohydrate strings” [36]. His review covered a broad range of structural studies on a variety of polysaccharides involving various experimental techniques as well as molecular modeling and computer simulations. Scott’s studies served as one of the inspirations for us to look more into the structural intricacies of a particular polysaccharide, hyaluronic acid, called also hyaluronan [37]. Lately, this substance has gained great visibility and fame for its presence in relatively great concentrations in some specific areas of the human body (such as, for example, the vitreous, the umbilical cord, the joints, and in the skin); for its most efficient clinical use; and for its popularity as an anti-aging agent in cosmetics. It has interesting structural features, including a double-helix configuration with intramolecular hydrogen bonding, not unlike the double helix of DNA.

In this overview, already a few studies have been mentioned in connection with developing a systems approach to inorganic structures. David Brown’s work on chemical topology belongs to this domain of inquiries. He singled out three components in the description of structures [38]. They are the properties of atoms participating in the structure; the three-dimensional space hosting the structure; and the topology describing the structure. He analyzed the relevant topologies and concluded that this analysis together with electrostatic theory and augmented with empirical observation led to a helpful model comprising of localized chemical bonding.

Geometry and models are most useful ingredients of structural chemistry and in particular, structural inorganic chemistry [39]. The geometrical model has been utilized in the description of molecular systems although its utility has limitations; the more rigid the system the better it works. Geometrical modeling has helped uncovering molecular structures from the simplest systems to the most intricate biological macromolecules. In this connection, the areas surveyed included: the technique of gas-phase electron diffraction; the notion of “experimental error” in quantum chemical calculations; precision and accuracy; the application of qualitative models, such as the VSEPR model; the investigation of isomerism; chirality; and molecular packing in organic substances.

AI Kitaigorodskii and molecular packing

The degree of understanding of molecular packing has been an evolving measure in our understanding how molecules, atoms, and ions build crystal structures. Aleksandr Kitaigorodskii made outstanding contributions to this question. Although he could not fully solve it; he was among the first who asked this pivotal question. He was an extraordinary scientist as well as human being [40]. He

pioneered the observation that the distances between molecules showed a characteristic constancy in diverse classes of organic substances. This observation helped him formulate the concept of molecular shape from which it was natural to pose the question about molecular packing in crystals. This fundamental question arose simultaneously in the minds of more than one scientist, which is not a rare occurrence in science history. In 1940, Linus Pauling and Max Delbrück published a note about interactions between molecules assigning precedence for interactions between parts that are complementary to each other rather than parts that are identical with each other [41]. This notion could be applied directly to considerations about molecular packing although Kitaigorodskii developed his ideas independently from Pauling and Delbrück.

Kitaigorodskii communicated his ambitious research program in a brief paper in 1945 in a then still existing English-language Soviet journal [42]. Kitaigorodskii declared in this paper that in a molecular crystal, “the mutual location of molecules is determined by the requirements of the most close-packing.” The packing of molecules in organic crystals remained his leitmotif throughout his scientific career and he opened up a new area in crystal chemistry. With painstaking and systematic work, Kitaigorodskii determined the frequency distribution of molecular crystals among the 230 three-dimensional space groups. Later observations on hundreds of thousands experimentally determined crystal structures confirmed the correctness of his predictions. The importance of complementary arrangements has proved a basic governing factor in the structure of molecular crystals.

Kitaigorodskii had a spectacular initial career; he was successful in original research, in popularizing science, in building a research center, in developing a great school of pupils, and in gaining international recognition. He was less successful in gaining official recognition in his home country where his free spirit and irreverence toward authority gained him enemies and generated jealousy. We remember Aleksandr Kitaigorodskii as a great contributor to the science of chemical structures, a devoted teacher, and a unique human being.

We at *Structural Chemistry* recognized the importance of Kitaigorodskii’s oeuvre from the beginning of our publication. Soon after the inception of this journal, in 1992, we initiated a special issue to honor his memory. An excellent collection of papers came together; of them, a few remembered Kitaigorodskii the scientist and the man, and most were outstanding research contributions. Unfortunately, by the time the collection was ready for publication, a crisis had developed about our journal and the survival of the journal was uncertain for some time before a change in publishers could be arranged. In the meantime, as we wanted to be sure that the special collection of papers

honoring Kitaigorodskii would not be lost we had to find an alternate venue for bringing it out. It happened to be *Acta Chimica Hungarica—Models in Chemistry* of the Hungarian Academy of Sciences. This venue saved the collection, but it also meant a reduced visibility, the more so, because *Acta Chimica Hungarica* soon ceased to exist. This is also, why I mention this special collection with emphasis in this Editorial [43].

Trends

Recently we have reviewed the Nobel Prizes awarded for discoveries in the domains of structural chemistry [44, 45]. It needs to be stressed that science history cannot be compiled on the basis of Nobel Prizes as they are often accidental and sometimes the award gives succumb to demands of fashion. Nonetheless, it is noteworthy that structural chemistry, directly or indirectly, figures conspicuously often in the award-winning achievements. Table 1 in Ref. 45 listed 19 Nobel Prizes related to structural chemistry, awarded through 2011. If extended to two more years available as of July 2014 when this account is being written, the 2013 Nobel Prize in Chemistry “for the development of multi-scale models for complex chemical systems” should be added, because the application of this approach is aimed at solving structural problems. Thus, during the last six decades, 20 Nobel Prizes were related to structural chemistry. Even a superficial browsing of these 20 awards shows that at least half of them were related to crystallography if it is taken in the modern sense as the structure of science.

Crystallography is as old as science itself; this is so if we consider the appearance of “scientific” crystallography from Kepler’s treatise on the snowflakes. Moreover, the “science” of crystals could be dated at the first moment when a crystalline substance was distinguished from an amorphous body. Alan Mackay used this telling example from *Kama Sutra* of Vatsayana that in the India of the sixth century, the courtesans had to learn some basics of mineralogy in order to distinguish real crystals from paste [20].

Contemplating about the development of crystallography during the past decades, a shift is noteworthy from ordered structures toward less ordered ones. The initial success of X-ray crystallography originated to great extent from the enormous amount of routine determinations of ordered structures. However, at certain point this also became a barrier to further development, because many scientists were hesitant to extend the realm of their inquiry toward less ordered structures. Between the two world wars, it was still possible to divide large research areas among a few scientists. Thus, for example, the two outstanding British crystallographers J. Desmond Bernal and

William Astbury decided to delineate their research areas. In Bernal words: “I took the crystalline substances and he [Astbury] the amorphous or messy ones. At first it seemed that I must have the best of it but it was to prove otherwise. ... It may be paradoxical that the more information-carrying methods should be deemed the less useful to examine a really complex molecule but this is so as a matter of analytical strategy rather than accuracy” [46].

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