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book reviews

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Crystalline Molecular Complexes and Compounds. Vol. 1 and 2. By F. H. Herbstein. Pp. xxviii + 1273. Oxford: Oxford University Press, 2005. Price (hardback) GBP 125.00. ISBN 0-19-852660-1.

Intermolecular interactions are of fundamental importance for the formation and assembly of supramolecular structures. In this context, crystals form a unique environment for the study of intermolecular interactions, since these interactions are spatially and temporally stable in crystals. At the same time, crystal structure analysis permits primary insight into the geometrical aspects of such interactions and through analysis of a large variety of crystalline binary adducts a wealth of structure-forming principles beyond the covalent bond becomes accessible. A further consequence is that the forces stabilizing these interactions are generally anisotropic and directed. With the present book all of these aspects have been brought together.

In Crystalline Molecular Complexes and Compounds an enormous amount of information and structural detail has been compiled, and still the author himself believes that only some 20% of all the crystal structures of binary adducts found entry into the two volumes. Volume 1 deals with molecular complexes, while Volume 2 looks at molecular compounds. The distinction is made by the author in such a way that all those binary adducts whose structures are determined predominantly by $A\cdots B$ interactions, whereby A and B are two chemically different entities, are classified as molecular compounds. The book is further subdivided into six parts, each of which consists of several, consecutively numbered chapters.

Part I prepares the ground for the adapted classification of binary adducts and defines the borders; this material is followed by a historical outline. These chapters, like all others in the book, are preceded by a short summary and a copy of the table of contents pertinent to the chapter. Since the chapters are all finely structured, the reader finds easily an entry point into any topic. This somewhat compensates for the rather short subject index.

Part II, Moieties within Molecules, begins the series of chapters, which discuss particular types of binary adducts, and deals with classical enclosure species like crown ethers and cryptands but also many more complex host molecules (Chapter 3). Throughout this and all subsequent chapters the crystal structures discussed are all referenced to the original publication and the corresponding refcode of the CSD, which enables readers with direct access to the Cambridge Structural Database to retrieve the molecular structures. The section dealing with hemicarcerands and hemicarceplexes also highlights one of the strengths of this book. Not only are the crystal structures of these compounds discussed, but the reader is introduced to theoretical calculations and spectroscopic measurements that have been applied to the complexation and decomplexation processes. Chapter 4 focuses on the cyclodextrins, in particular α-, β- and γ-cyclodextrins, while the final chapter of this part brings examples of the crystal chemistry of oligonucleotides. It is not the intention of the author to compete with the specialist monographs in this area, but a book like the present one would be incomplete without discussing these prominent bio-organic examples.

Part III is entitled Host–Guest Inclusion Complexes and as such covers, in four chapters, the very many aspects of this rich class of complexes. The author has structured this part on one hand into tunnel and clathrate inclusion complexes, and on the other hand into hosts of greater and lesser versatility, referring to those hosts able to form two or more different host structures. The section on tunnel inclusion complexes also discusses in some detail the diffraction properties of these complexes, since here one encounters regularly ordered host structures which combine with disordered guest molecules to give rise to diffuse scattering. The final chapter of Part III is concerned with intercalation complexes, of which three representative examples have been chosen, namely graphite, tantalum sulfide and zirconium phosphate and phosphonate, extending the scope of molecular complexes somewhat.

Part IV, Packing Complexes. This part is also the final chapter of Volume 1 and comprises a variety of rather different chemical structures. Common to all of them is that neither interactions of the type $A\cdots A$ (the host) nor of the type $A\cdots B$ as in the molecular compounds are predominant. Instead this part ranges from structures with Z' larger than one, treating conformational isomers as binary adducts, to various binary adducts of buckminsterfullerenes.

In Volume 2 the emphasis is transferred from particular classes of compounds to modes of interactions, in particular the detailed analysis of donors and acceptors.

Part V, Molecular Compounds with Localized Interactions. The first chapter concentrates mainly on nitrogen, oxygen and sulfur as donors of lone-pair electrons (n-donor) in combination with s-, σ^*-, p- and π^* acceptors for which a large number of representative crystal structures have been selected. This is followed by a discussion of localized π-donor systems such as olefins and aromatics, and s-acceptors (transition metal cations, in particular silver) as well as p-acceptors like antimony. A chapter on hydrogen-bonded complexes and compounds concludes this part, which includes a very useful section on graph theory for the description of hydrogen-bond patterns and leads to a detailed discussion on framework structures.

Part VI, Molecular Compounds with Delocalized Interactions, finally takes the reader into the large field of charge-transfer complexes. The five chapters of this part give an account of the chemical structures of donor and acceptor molecules in charge-transfer complexes and discuss not only their crystal structures, but also the spectroscopic implications following from the formation of these compounds and the subsequent charge transfer. A whole chapter is dedicated to the crystal chemistry of mixed stack π–π^* molecular compounds, followed by a further chapter on the crystal physics focusing on phase transitions in these mixed stack π–π^* molecular compounds. The final chapter of this part, Volume 2, and the book looks at segregated-stack π-molecular compounds, with their characteristic feature of forming parallel stacks of donor molecules and acceptor molecules.

In conclusion, Crystalline Molecular Complexes and Compounds is a must for every structural chemist, as it compiles and categorizes not only the presently available wealth of information on crystalline binary adducts but also provides insight into the principles responsible for the formation and stability of these adducts. Certainly Crystalline Molecular Complexes and Compounds makes no easy reading, but then this has not been the intention of the author in the first place. Rather, the book is a formidable compilation of the structural chemistry of binary adducts with more than 600 figures and over 200 tables and will serve as a desk top reference for some time.

Christian W. Lehmann

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim an der Ruhr
Germany