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BOOK REVIEW

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Book Review of Inorganic 3D Structures

Inorganic 3D Structures. Edited by Angel Vegas (Instituto de Química Física "Rocasolano" CSIC, Madrid, Spain). From the series, Structure and Bonding, 138. Edited by D. M. P. Mingos. Springer: Heidelberg, Dordrecht, London, New York. 2011. xvi + 202 pp. $259. ISBN 978-3-642-20340-4.

Three-dimensional inorganic structures are generally described in terms of a classical model in which smaller cations reside in the interstitial voids of an array of anions. Not surprisingly, this description fails to predict or rationalize all but the simplest of structures containing anions. This latest installment of the "Structure and Bonding" series provides an alternative to this approach, based on two postulates: (1) The formation of cation arrays created by electron transfer to more electronegative atoms and resulting in anionic "pseudoatoms or pseudomolecules" provides an adequate description of an inorganic structure, and (2) the structure of a metal oxide is determined by the structure of the elemental metal or corresponding alloy.

The second postulate results from the theoretically challenging observation that a large number of metal oxides have structures remarkably similar to those of the elemental metals/alloys in the oxides. This observation has led to an extension of the Zintl–Klemm concept, originally designed for semimetallic alloys, to encompass structures that have traditionally been classified as more or less ionic. As a descriptive scheme, the "Extended Zintl–Klemm Concept" (EZKC) appears to rationalize a large number of structures within the limits of the relatively crude assumptions upon which it is based.

There are many examples of the application of the concept throughout the book. The third chapter is especially representative of the EZK approach, illustrating both its strengths and weaknesses. In this chapter, the author "dissects" the crystal structure of $FeLi[PO_4]$ as an illustration of the utility of this approach. The "alloy" analog here is FeLiP, which has the same structure as FeS. The EZK formalism invokes transfer of an electron from Li to P, resulting in the formation of P^- (pseudosulfur), which is allegedly close enough to a sulfur atom to result in the creation of the Fe-pseudo-S lattice with Li^+ in the voids. The oxide structure is then compared to that of the alloy analog, and the similarities in the two structures are pointed out by the author. There are also differences in the structures, however: the lithium ions do not occur at the same locations. They are coplanar in FeLiP but not in $FeLi[PO_4]$. The author rationalizes this with the transfer of a second electron from Fe to create P^{2-} (pseudochlorine) in FeLiP, thus forcing the structure to mimic the planar rock-salt structure of LiCl. It is not clear where the Li-pseudo-Cl structure ends and the Fe-pseudo-S structure begins. More importantly, this points out an inherent weakness in electron-counting schemes. To some extent, structures can be rationalized by "creating" the appropriate pseudoatom/pseudomolecule, with virtually no experimental or theoretical evidence that such species might actually exist.

The large number of structures treated in the volume indicates that the extended Zintl–Klemm approach provides a useful descriptive alternative to the classical ionic model. Vegas, the editor of this volume, begins the third chapter by appropriately pointing out that the classical ionic model is often used to describe and "understand" crystal structures but, in reality, leads to little "understanding." He then concludes the chapter with the following statement: "The Extended Zintl–Klemm Concept, applied to any cation array, appears as the most useful tool for both, [*sic*] description and understanding of structures." This depends to some degree on the definition of "understand", but the many examples in the book shed little light on any physical aspects that might provide a more conceptual and rigorous elucidation of the electronic structure of inorganic materials. Indeed, this book may be most useful to theoreticians, providing a number of observed relationships and trends that clearly demand further study.

There is much to be digested in this book, despite its 200-page length. The hypotheses put forth are provocative enough that they demand a clear narrative. Unfortunately, the book lacks such clarity. It is full of details and descriptions, but the reader is left to his or her own devices in order to make any logical connections. The necessary roadmap is absent in either the introductions or conclusions of the five chapters, the last three of which are either authored or coauthored by Vegas. He is a strong proponent of the EZKC approach, and it is not surprising that this is a central theme in the book. There are many useful references cited throughout the book, and although many are dated, the subject matter requires a review of the literature that spans a great deal of the inorganic chemistry of the past several decades.

I would recommend this book for library purchase, but the price is probably too steep for anyone not specifically interested in the extended Zintl–Klemm formalism.

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