

range of compounds are $F_{1/2}$ and $F_{1/3}$ which have 84.3 and 82.7% of entries, respectively, within the 10% error boundary. Furthermore, the percentages of Z_{est} calculated for $F_{1/2}$ and $F_{1/3}$ relationships within 5% error boundary are higher than the percentage obtained using the KL expression and the 10% error boundary.

Despite the fact that the boron volume is bigger than average for period 2, remarkably good agreement is obtained for its compounds using $F_{1/2}$ and $F_{1/3}$ (91.5 and 94.1% within 10% error bounds). For silicon compounds, the values are also acceptable with 79.6 and 73.3% within 10% error bounds, respectively.

In order to assess the effects of atoms from different periods, modified $F_{1/2}$ and $F_{1/3}$ expressions have been applied to a set of 164 crystal structures having two or more X elements from different periods in their formulae. In these new expressions, the increase in A will depend on the number of atoms of each period, excluding the H and second period atoms, so that these elements do not produce an increase in the initial value of A . ΔA will be the ratio between the increment produced for the atoms of each period and the summation of atoms from the third to the fifth period.

$$\Delta A = \frac{\sum[(p-2)/D]N_p}{\sum N_p}, \quad (5)$$

where $D = 2$ for $F_{1/2}$ and $D = 3$ for $F_{1/3}$. In this expression, $p > 2$ and $\sum N_p$ is the number of non-H atoms excluding those belonging to the second period. We now have:

$$Z_{\text{est}} = \frac{V/(A + \Delta A)}{BN_{\text{H}} + \sum C_p N_p}, \quad (6)$$

where $A = 12$, $B = 1/2$, $C_p = p/2$ for $F_{1/2}$ and $A = 14$, $B = 1/3$, $C_p = (p+1)/3$ for $F_{1/3}$.

Results for 'mixed-period' compounds show that agreement between Z_{est} and Z (from CSD) is worse than that obtained for compounds with X atoms of the same period, but it is still acceptable (>55% of entries with an error less than 10%) and clearly better than for the KL expression (<20%).

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Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (R. F. Bryan, Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, Virginia 22901, USA). As far as practicable, books will be reviewed in a country different from that of publication.

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Reactivity in molecular crystals. Edited by Y. OHASHI. Pp. xii + 348. Weinheim: VCH Verlagsgesellschaft, and Tokyo: Kodansha, Ltd, 1993. Price DM 198.00. ISBN 3-527-29098-2 (Weinheim), 4-06-206228-3 (Tokyo).

This volume is a description of the results of a project on the 'analysis and control of reactions in molecular crystals', sponsored by the Japanese Ministry of Education, Science and Culture from 1988 to 1990. The planned project was quite broad in scope, ranging from theoretical approaches to the prediction of crystal structures to the development of a laboratory X-ray diffractometer utilizing Weissenberg geometry and equipped with sensitive imaging plates, capable of collecting complete intensity data sets in 1-2 h. The major emphasis of the project was on a series of chemical investigations, often combined with X-ray crystallography, into specific solid-state reactions. All the contributors - crystallographers, chemists and physicists - are from Japanese educational and research institutions.

Despite compromises, presumably made in order to provide a detailed report on the overall project, the book contains much interesting and innovative solid-state chemistry. However, because of many omissions (e.g. analysis of hydrogen-bonding patterns, effects of dopants) and under-representations (solid-state NMR, energy calculations), it cannot be considered as a comprehensive review of that field. It reads as a collection of 22 reports from a variety of research laboratories, with an almost equal variety in terms of significance and achievement. It is a minor irritation that the authors of the various sections that make up most chapters are not given in the main text but have to be identified by name from the Table of Contents and, by full affiliation, from a separate page.

Chapter 1 (23 pp.) provides a brief but very readable review of efforts to calculate crystal structures from energy considerations, followed by a description of a molecular dynamics approach to the structure of benzene. This is the shortest chapter in the book, testifying to the clear emphasis on experimental methods in the overall project.

The second chapter (90 pp.) describes a number of fairly brief contributions from laboratories working on spectroscopic approaches to solid-state reactivity. The methods used include high-resolution electron spectromicroscopy, EXAFS and

excitation energy studies, and this section contains the single solid-state NMR study described. For crystallographers, the most interesting section in this chapter will likely be that devoted to the development of the high-speed diffractometer mentioned above.

The next three chapters (Ch. 3, 61 pp., Ch. 4, 25 pp. and Ch. 5, 73 pp.) are devoted to chemical and crystallographic studies of solid-state processes in a variety of systems. The major contributions described here are those of Ohashi and coworkers on the racemization of solid cobaloxime complexes, and of Hasegawa and colleagues on the solid-state photochemistry of unsymmetrically substituted diolefin crystals. Much of the work of these two important research groups has been reviewed elsewhere, but this update is welcome. Ohashi describes three modes of racemization in crystals of differently substituted cobaloxime complexes and analyzes them in terms of crystal structures, reaction cavities and reaction pathways. The racemization of one complex over a 10 h period was monitored by four X-ray data sets, some obtained in 45 min, and without a synchrotron! The detailed studies of the Hasegawa group on the polymerization of diolefin crystals are well known to organic solid-state chemists. The clear and comprehensive description of the topochemical principles involved, the extensive use of crystal structure analysis and the use of mixed crystals and complexes reveal a very impressive research effort. The entire Chapter 4 is a review by Toda of the work in his laboratory on carrying out organic chemical reactions by grinding together the solid reactants. While containing descriptions of many new findings, this chapter will probably be of limited interest to most crystallographers, and suffers from a rather encyclopedic approach to the cataloging of results with little in the way of introduction and an absence of any concluding remarks on overall significance or future directions.

The final chapter (Ch. 6, 67 pp.), entitled 'Reactivity and crystal structure', includes descriptions of five fairly unrelated projects, ranging from the influences of substituents on polymer properties, the structures of bilayers formed by azolipids, to the reactivity of thiathiophthenes and other hypervalent sulfur compounds.

In summary, this volume provides a good overview of recent activity in solid-state organic chemistry in Japan. Much of this

work is of major significance, and there are many examples of interdisciplinary approaches involving both crystallography and chemistry. For these reasons, the volume would be a useful addition to any chemical or crystallographic library. However, on account of the omissions and inadequate coverage of certain topics mentioned earlier, it cannot be recommended as a comprehensive description of the present status of the field internationally.

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Books Received

The following books have been received by the Editor. Brief and generally uncritical notices are given of works or marginal crystallographic interest; occasionally, a book of fundamental interest is included under this heading because of difficulty in finding a suitable reviewer without great delay.

Transition metal chemistry. The valence shell in d-block chemistry. By M. GERLOCH and E. C. CONSTABLE. Pp. xi + 211. Weinheim: VCH Verlagsgesellschaft, 1994. Price (soft cover) DM 58.00. ISBN 3-527-29219-5. Early in the authors' preface this book is offered as 'an outline of a theoretical structure for transition metal chemistry at an elementary (early to mid UK degree) level that hopefully provides a consistent viewpoint of this widely varying and fascinating subject' and later as 'an attempt to bring together in a single yet non-simplistic way many important bonding and theoretical principles that hopefully make more sense of this wide and fascinating subject'. The book is described by the publisher as 'eminently readable'.