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Estimate of two general relationships between the number of atoms and the volumes of the unit cells of compounds containing only non-metallic p-block elements.

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Abstract

Compounds with the general formula $C_aH_bN_cO_dX_x$ (where X = boron and/or a non-metallic element of the third to fifth period; $b \geq 1$; $a, c, d, e \ldots x \geq 0$) have been studied using the Cambridge Structural Database as a source of data and a search tool. Two relationships between the volume (V) and the number of formula units (Z) in the unit cell have been established that account for the individual contributions of elements to the cell volume in terms of their element period number. The two improved relationships have 84.3 and 82.7% of entries, respectively, within the 10% error boundary, and they are more accurate than other expressions described in the literature.

Introduction

Empirical relationships are often of considerable value in many areas of science. An interesting crystallographic example is the estimation of Z, the number of formula units in the crystallographic unit cell, using the Kempster & Lipson (1972) relationship, hereafter referred to as KL, which has often been used in the crystal structure determination of organic and organometallic compounds:

$$Z_{est} = (V/18)/N, \qquad (1)$$

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where N is the number of non-H atoms per formula unit and $V(\text{Å}^3)$ is the volume of the unit cell. However, (1) leads to some important differences between Z and Z_{est} for many compounds and there have been attempts to improve this expression by taking into account the contribution of H atoms (Srinavasan & Rajan, 1975).

Previously (Román, Guzmán-Miralles & Luque, 1993), we analysed organic compounds containing elements of the second period, except boron, and two expressions ($F_{1/2}$ and $F_{1/3}$) were obtained which take into account the different contributions of H and non-H atoms. Thus,

$$Z_{est} = (V/A)/(BN_H + CN), \qquad (2)$$

where $A = 12$, $B = 1/2$ for $F_{1/2}$, and $A = 14$, $B = 1/3$ for $F_{1/3}$. N_H is the number of H atoms per formula unit, and B is their 'contribution factor' to the unit-cell volume. The contribution factor from non-H atoms of the second period, C, was taken as 1. Elements belonging to high periods were excluded from this study since their volumes are larger than those of the second period.

The aim of the present study is to develop a general expression that can also be applied to compounds containing larger non-metallic p-block elements. A total of 2303 crystal structures, of general formula $C_aH_bN_cO_dX_x$ (where X = B or any non-metallic element of the third to fifth period), were taken as the starting point for this study.

Data selection

Experimental information for this work was taken from the Cambridge Structural Database (CSD) version 5.04 of October 1992 containing 102 585 entries (Allen *et al.*, 1991). In order to obtain a number of entries that fully represent each periodic table subgroup, the following criteria have been used:

(1) crystal structures determined by X-ray and neutron diffraction and published from 1970 to 1992 were selected;

(2) $R \leq 0.05$ for most groups, but for As, I, Se and Te compounds, the limit $R \leq 0.10$ was used due to the low number of crystal structures reported for these compounds;

(3) crystal structures determined at $T \leq 293$ K were also included in the survey.

The original list of hits was edited by hand to remove duplicate entries and local *FORTRAN* programs were used to analyse the information retrieved. CSD reference codes for the 2303 entries used in this work are given in the supplementary material.*

Results and discussion

Intuitively, it seems obvious that (1) can be improved by expanding N to a form:

$$N = N_a + N_b + N_c + \ldots$$

for different element types a, b, c, ..., just as the formula weight is built up of contributions from the individual weights of those different atoms. Elements belonging to the same period have similar size, so that we may assign to them the same contribution factor (C_p).

In order to establish the contribution factor (C_p) for each period, we have considered the relationship between the magnitude of the atomic volume and the number of the period in which the element is placed. The values of covalent radii employed are the standard values used to establish the intramolecular connectivity in CSD entries (*CSD User Manual*, 1992).

It may be seen that radii for B and Si are higher than the mean radius for elements in their period. However, these elements are included in this analysis. The ratio between the average covalent radius of the elements from a period p and the second period is near $p/2$ when $p = 2$, 3, and $(p + 1)/3$ when $p = 2$, 4, 5. Because of this, the contribution factor (C_p) for all elements of a period p will be $(p + 1)/3$ for $F_{1/3}$ and $p/2$ for $F_{1/2}$.

The results with these contribution factors are better than those obtained using the KL expression. However, in many cases, it is observed that Z_{est} calculated with these two new expressions are bigger than Z (taken from CSD). Thus, the results can be improved by an increase in the A value.

To establish how much the A value must be modified (A_p), a scattergram of the total number of atoms $[Z(C_pN_p + BN_H)]$ versus the cell volume V has been calculated for

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* Tables, figures and a list of the CSD reference codes of the 2303 crystal structures used in this work classified by periods and elements has been deposited with the IUCr (Reference AB0323). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

each period analysed (Fig. 1). A_p^{-1} is the slope of the straight line plotted. The results show that the increase in the A value (ΔA) and period number are approximately related.

$$A_p = 12 + \Delta A; \quad \Delta A \simeq (p - 2)/2$$

$$A_p = 14 + \Delta A; \quad \Delta A \simeq (p - 2)/3.$$

Then, expression (2) may be modified to (3) and (4):

$$Z_{est}(F_{1/2}) = \frac{V/\{12 + [(p - 2)/2]\}}{(1/2)N_H + \Sigma(p/2)N_p} \tag{3}$$

$$Z_{est}(F_{1/3}) = \frac{V/\{14 + [(p - 2)/3]\}}{(1/3)N_H + \Sigma[(p + 1)/3]N_p} \tag{4}$$

The new $F_{1/2}$ and $F_{1/3}$ formulae, as well as the KL equation (1), have been used to analyse the whole data set in terms of boundary error values of 5 and 10% as in our previous paper (Román, Guzmán-Miralles & Luque, 1993). Fig. 2 shows the results obtained when the compounds under study were examined by period.

An element-by-element analysis of the results obtained from the two improved relationships and from the KL expression shows that the agreement is rather poor for the latter expression with only 52.1% of entries having a relative error between Z (taken from CSD) and Z_{est} of less than 10%. The most accurate relationships over a larger
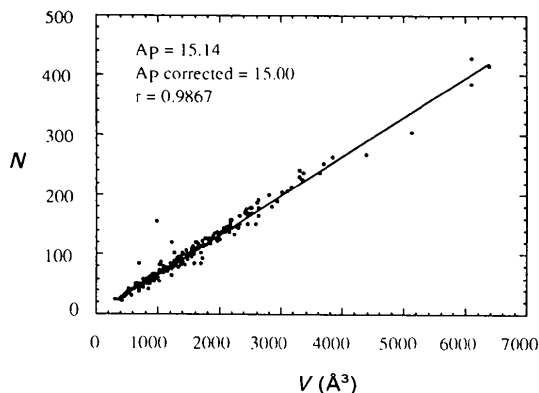

Fig. 1. Scattergram of the total number of atoms $N = [Z(C_pN_p + BN_H)]$ *versus* the cell volume for $F_{1/3}$ expression and period 5.
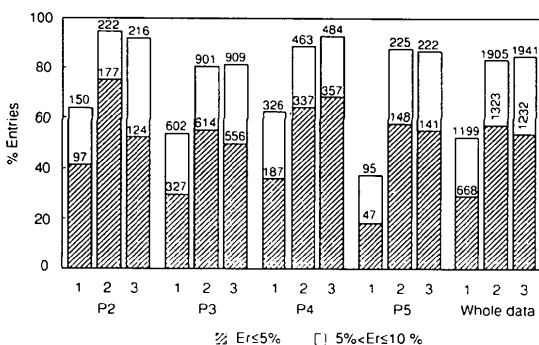

Fig. 2. Stack histogram of % compounds within the error boundary *versus* period, for the (1) KL, (2) $F_{1/3}$ and (3) $F_{1/2}$ expressions.

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.

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

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

$$Z_{est} = \frac{V/(A + \Delta A)}{BN_H + \Sigma C_p N_p}, \qquad (6)$$

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.

Acta Cryst. (1994). B50, 629–630

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