



## Ion-molecular Crystals as Inclusion Compounds: Van der Waals Contacts in Ionic Carbonates

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### Abstract

Among Cambridge substances, which always include “organic” carbon, i.e., carbon contained in molecules or molecular ions, ion-molecular crystals (particularly, carbonates or alkaline-earth and alkaline metals) are of special interest. Some of such carbonates contain pronounced van der Waals (vdw) contacts between oxygen atoms of carbonate groups. Thus, agglomerates (layers or columns) formed by contacting carbonate groups arise (columns being connected in a frame), and in the cavities between these agglomerates cations are situated. The structure looks like an inclusion compound, the carbonate groups being hosts and the cations being guests. To discuss this question we used the refined value of vdw radius of oxygen which was obtained by statistical treatment of 8200 crystal structures from Cambridge Structural Database (CSD) and is equal to 1.53 Å for the O···O contacts. Hence the length of a normal supporting vdw contact O···O is  $3.06 \pm 0.15$  Å. Such contacts are present in MgCO<sub>3</sub> and CaCO<sub>3</sub> (calcite) and in  $\alpha$ -Na<sub>2</sub>CO<sub>3</sub>. There are contacts O···O that are even shorter (2.74–2.81 Å) in CaCO<sub>3</sub> (aragonite), SrCO<sub>3</sub>, BaCO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub>. So it is possible to suppose the existence of specific (partly covalent) contacts O···O in these substances. In  $\beta$ -Na<sub>2</sub>CO<sub>3</sub>, all forms of K<sub>2</sub>CO<sub>3</sub>, Rb<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> the vdw contacts of CO<sub>3</sub> groups are absent; therefore they are ionic (not inclusion) compounds.

### Introduction

An overwhelming majority of known individual substances can be regarded as molecular, i.e., formed by molecules. When speaking about molecular crystals we suppose that a molecule is a relatively stable finite group of atoms that are more firmly bound with one another than with atoms belonging to other such groups. Interatomic bonds in molecules are mainly covalent. Interactions between atoms of adjacent molecules have van der Waals or ionic nature; sometimes they are strengthened by hydrogen bonds.

Molecular crystal structures can be homomolecular ( $n = 1$ ) or heteromolecular ( $n \geq 2$ ), where  $n$  is the number of kinds of molecules taking part in crystal formation. If molecules of one kind are simply monoatomic ions, we come to ion-molecular crystals. Such ions can be anions (mainly halogen ions) or cations (alkaline or alkaline-earth metals). Bonds formed by other metals are more or less covalent.

In the present work we are dealing with so-called Cambridge structures. These are substances that always include “organic” carbon, i.e., carbon atoms contained in molecules or molecular ions; such structures are collected in Cambridge Structural Database (CSD). They can be subdivided into organic or “purely organic” (containing only organogenic elements: C, H, N, O, F, Cl, Br, I, S, Se, Te, P, As, Si,

B) and semi-organic (containing metals and/or metalloids in addition to C and other organogenic elements).

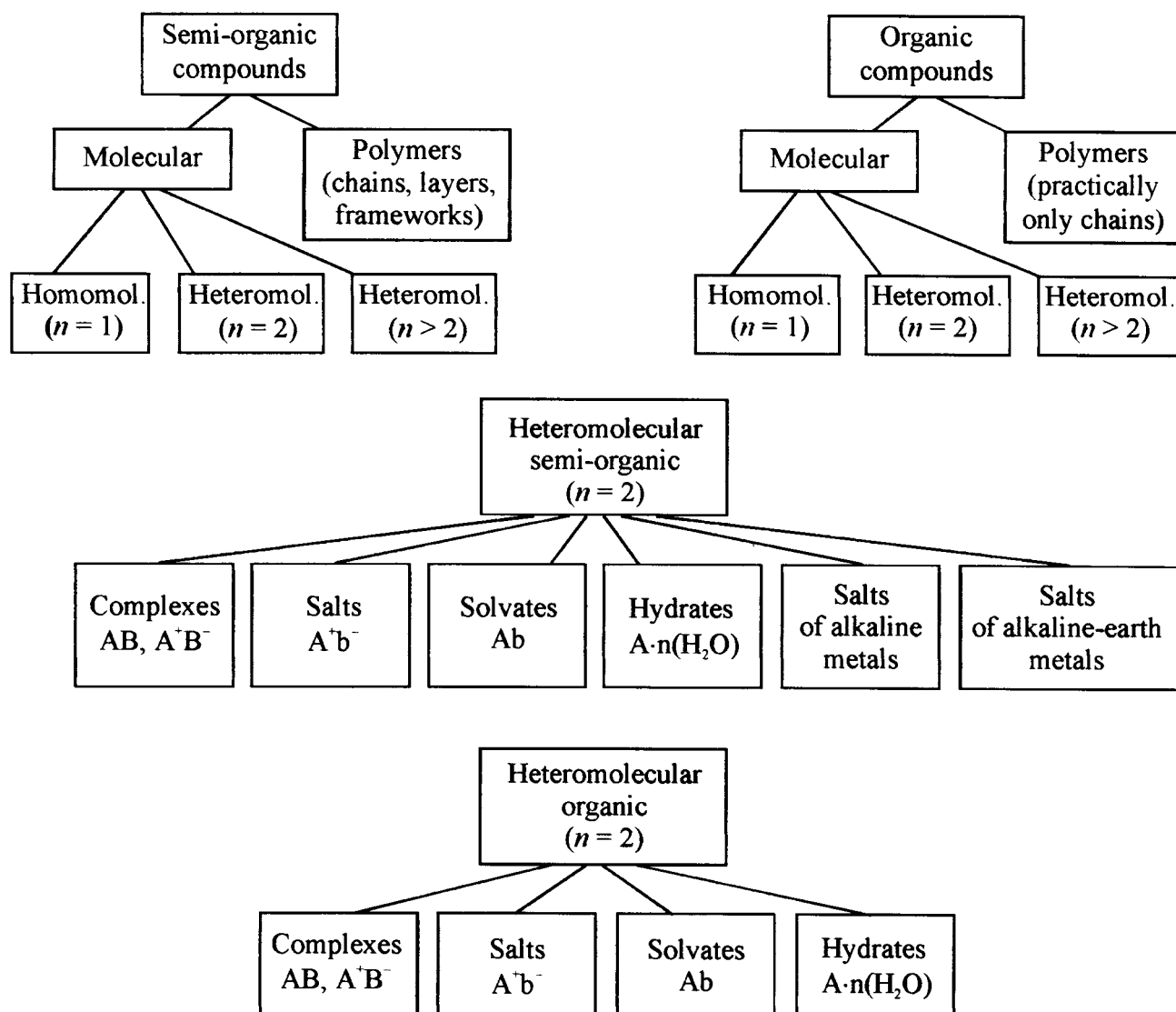
A statistical treatment [1, 2] of the Cambridge structures makes it possible to subdivide them into crystal chemistry classes as shown in Scheme 1.

The majority of ion-molecular crystals in CSD are salts of alkaline and alkaline-earth metals, for example, formates, acetates, oxalates etc. Obviously, carbonates of these metals must be ranked among substances of this type. However, they are not included in CSD; apparently, it is a misunderstanding. Nevertheless, we consider ionic carbonates as ion-molecular CSD structures.

Since carbonates of alkaline and alkaline-earth metals were regarded as molecular crystals, for their consideration it was convenient to use some major methods developed in organic crystal chemistry. These are the concept of structural classes and the theory of close packing.

The main purpose of this work was to present the range of ionic carbonates as a logical sequence of structures. It was interesting to show that some of them contain pronounced van der Waals contacts between oxygen atoms of carbonate groups. Thus, the agglomerates formed by carbonate groups arise and in the cavities between these agglomerates cations are situated. In the considered carbonates two variants are realised. First, CO<sub>3</sub> groups form layers, cations are intercalated. Second, CO<sub>3</sub> groups form columns, the latter are connected (also by short O···O contacts) forming a frame

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Scheme 1.

Table 1. Carbonates of alkaline-earth metals

| Substances (literature)                 | Structural class                                   | Unit cell dimensions (Å)                   | <i>t</i> (°C) |
|---|--|--|---------------|
| MgCO <sub>3</sub> [3]                   | $R\bar{3}c$ , $Z = 6$ ( $\bar{3}$ ; 32)            | $a = 4.637$ , $c = 15.023$                 | Room          |
| CaCO <sub>3</sub> calcite [4]           | $R\bar{3}c$ , $Z = 6$ ( $\bar{3}$ ; 32)            | $a = 4.990$ , $c = 17.061$                 | -33           |
| CaCO <sub>3</sub> aragonite [5]         | $Pnma$ , $Z = 4$ ( $m$ ; $m$ )                     | $a = 5.740$ , $b = 4.961$ ,<br>$c = 7.957$ | Room          |
| CaMg(CO <sub>3</sub> ) <sub>2</sub> [6] | $R\bar{3}$ , $Z = 3$ ( $\bar{3}$ ; $\bar{3}$ ; 32) | $a = 4.87$ , $c = 16.003$                  | Room          |
| SrCO <sub>3</sub> [7]                   | $Pnma$ , $Z = 4$ ( $m$ ; $m$ )                     | $a = 5.997$ , $b = 5.090$ ,<br>$c = 8.358$ | 20            |
| BaCO <sub>3</sub> [7]                   | $Pnma$ , $Z = 4$ ( $m$ ; $m$ )                     | $a = 6.428$ , $b = 5.313$ ,<br>$c = 8.896$ | 20            |

Table 2. Carbonates of alkaline metals

| Substances<br>(literature)                     | Structural<br>class  | Unit cell<br>dimensions (Å)  | <i>t</i><br>(°C) |
|--|--|--|------------------|
| Li <sub>2</sub> CO <sub>3</sub> [8]            | <i>C2/c</i> , <i>Z</i> = 4 (1; 2)  | <i>a</i> = 9.359, <i>b</i> = 4.973,<br><i>c</i> = 6.198, $\beta$ = 114.83° | Room             |
| $\alpha$ -Na <sub>2</sub> CO <sub>3</sub> [9]  | <i>P6<sub>3</sub>/mmc</i> , <i>Z</i> = 2<br>( <i>3m</i> , $\bar{6}m2$ ; $\bar{6}m2$ )  | <i>a</i> = 5.200, <i>c</i> = 6.500   | 500              |
| $\alpha$ -K <sub>2</sub> CO <sub>3</sub> [10]  | <i>P6<sub>3</sub>/mmc</i> , <i>Z</i> = 2<br>( $\bar{3}m$ , $\bar{6}m2$ ; $\bar{6}m2$ ) | <i>a</i> = 5.700, <i>c</i> = 7.160   | 425              |
| $\beta$ -Na <sub>2</sub> CO <sub>3</sub> [11]  | <i>C2/m</i> , <i>Z</i> = 4((2/ <i>m</i> ) <sup>2</sup> , <i>m</i> ; <i>m</i> )         | <i>a</i> = 9.01, <i>b</i> = 5.237,<br><i>c</i> = 6.312, $\beta$ = 96.83°   | 400              |
| $\gamma$ -Na <sub>2</sub> CO <sub>3</sub> [12] | <i>C2/m</i> , <i>Z</i> = 4 (modulated)   | <i>a</i> = 8.900, <i>b</i> = 5.240,<br><i>c</i> = 6.040, $\beta$ = 101.20° | 20               |
| $\beta$ -K <sub>2</sub> CO <sub>3</sub> [13]   | <i>C2/c</i> , <i>Z</i> = 4 ( $\bar{1}$ , 2; 2)   | <i>a</i> = 5.675, <i>b</i> = 9.920,<br><i>c</i> = 7.018, $\beta$ = 96.80°  | 310              |
| $\gamma$ -K <sub>2</sub> CO <sub>3</sub> [14]  | <i>P2<sub>1</sub>/c</i> , <i>Z</i> = 4 (1 <sup>2</sup> ; 1)                            | <i>a</i> = 5.640, <i>b</i> = 9.800,<br><i>c</i> = 6.80, $\beta$ = 98.80°   | Room             |
| Rb <sub>2</sub> CO <sub>3</sub> [15]           | <i>P2<sub>1</sub>/c</i> , <i>Z</i> = 4 (1 <sup>2</sup> ; 1)                            | <i>a</i> = 5.870, <i>b</i> = 10.120,<br><i>c</i> = 7.330, $\beta$ = 97.65° | Room             |
| Cs <sub>2</sub> CO <sub>3</sub> [15]           | <i>P2<sub>1</sub>/c</i> , <i>Z</i> = 4 (1 <sup>2</sup> ; 1)                            | <i>a</i> = 6.120, <i>b</i> = 10.270,<br><i>c</i> = 8.140, $\beta$ = 95.85° | Room             |

with cations in cavities. Such structures look like inclusion compounds, the carbonate groups being hosts and the cations being guests. However, not all ionic carbonates can be described in this manner.

### List of considered carbonates and their structural classes

The structural class is the space group of symmetry plus the list of orbits (systems of equivalent positions) occupied by atoms or by some atomic groups; each orbit is indicated by the point group showing the site symmetry; in addition the number of formula units per unit cell (*Z*) is included in the symbol of class. In ionic carbonates we deal with site symmetry of cations and carbonate groups. For example, the structural class of calcite is *R* $\bar{3}c$ , *Z* = 6 ( $\bar{3}$ ; 32); this means that the space group is *R* $\bar{3}c$  with a rhombohedral lattice, there are six formula units per hexagonal unit cell, the Ca atoms occupy an orbit with the site symmetry  $\bar{3}$ , CO<sub>3</sub> groups occupy another orbit with the site symmetry 32.

In Tables 1 and 2 the considered carbonates with their structural classes are listed; *t* is a temperature at which the X-ray investigation was performed. Figures 1–6 show the main crystal structures and their most important peculiarities.

### Van der Waals contacts in ionic carbonates

There is a substantial flaw in the traditional approach to the description and interpretation of such structures: only ionic bonds between oxygen and the cations are taken into account while van der Waals (vdw) interactions between carbonate

groups are ignored. Yet using calcite and aragonite as examples one can see that these interactions play an important structuring role and affect the properties.

The shape, the effective form of the CO<sub>3</sub> groups is similar to that of organic molecules, and the structure of the sublayer of the CO<sub>3</sub> groups in calcite clearly demonstrates the postulates of the theory of close molecular packing (in particular the “bump-to-hollow” principle).

It is very common to describe the calcite crystal structure using analogy with NaCl or isostructural CaO. However, the layer of CO<sub>3</sub> groups in calcite (Figure 1) and the dense hexagonal layer of equal spheres (for example, of atoms O in CaO) are not similar. The calcite layers, being typical for organic substances, are connected with Ca—O bonds in a fairly complicated way which is usual for inorganic compounds (particularly, for polytypes) (Figure 2).

Even more clearly vdw interactions manifest themselves in aragonite (Figure 3). There are columns formed by CO<sub>3</sub> groups and wells between these columns. In the wells Ca ions are situated. An important peculiarity of the structure of aragonite is that the wells are blocked up because there are short vdw contacts O···O between adjacent columns. So the cavities containing Ca ions alternate with the blocks formed by closely interacting O atoms along each well.

Carbonates of alkaline-earth metals provide a classical example of *morphotropy*, i.e., of a change of the structural type in a sequence of related chemical compounds. MgCO<sub>3</sub> belongs to the calcite type; in the case of CaCO<sub>3</sub> two polymorphs (calcite and aragonite) are realised; SrCO<sub>3</sub> and BaCO<sub>3</sub> are isostructural with aragonite. Under ordinary conditions aragonite is unstable and gradually turns into calcite [6]. It is remarkable that a very small admixture of strontium can stabilise the structure of aragonite [6]. This, probably, can be explained by the fact that the hollows occupied by

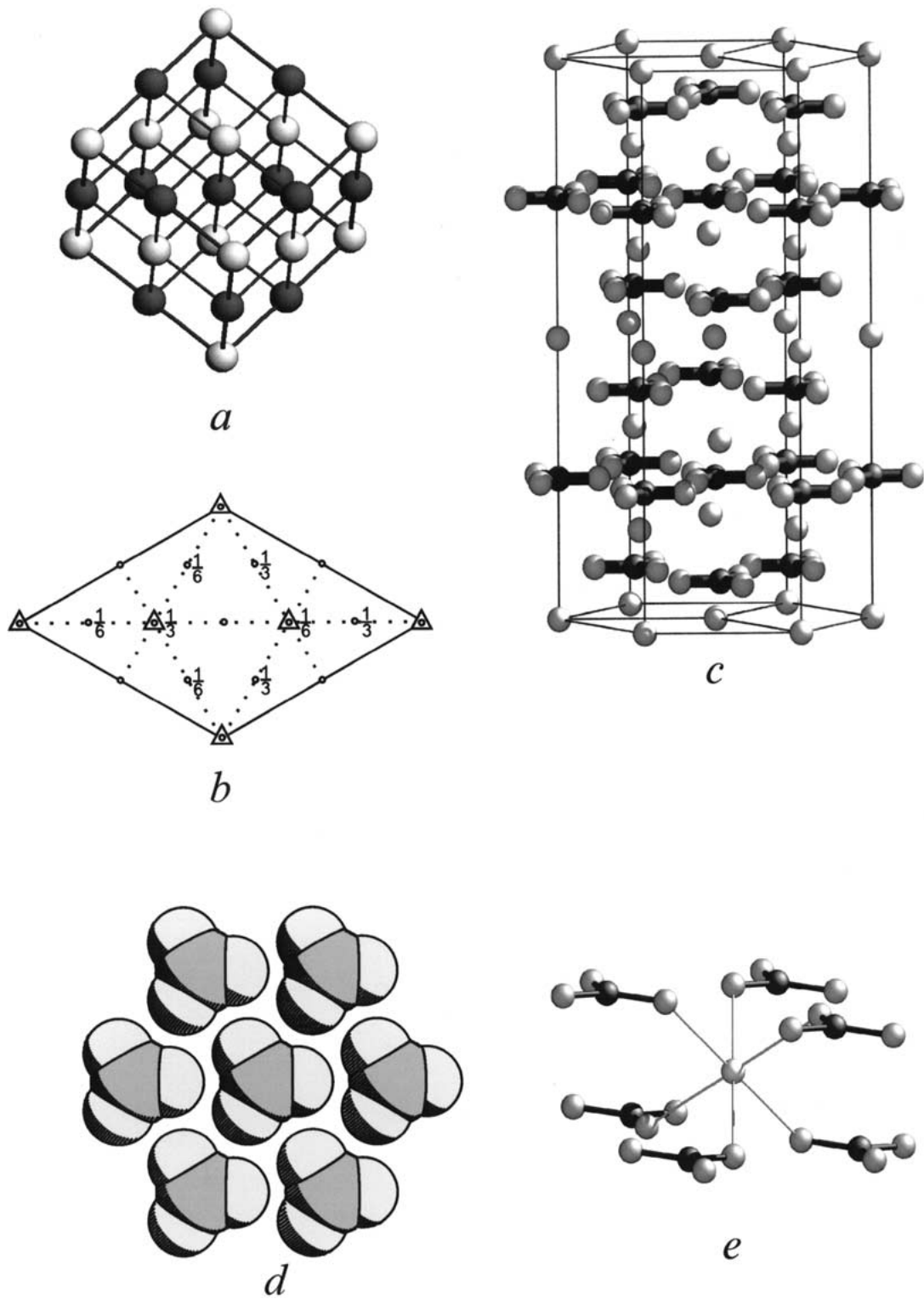


Figure 1. Crystal structure of calcite  $\text{CaCO}_3$  and its comparison with the CaO structure: (a) CaO, (b) space group  $R\bar{3}c$  (c) calcite, (d) a layer of  $\text{CO}_3$  groups, (e) coordination of Ca.



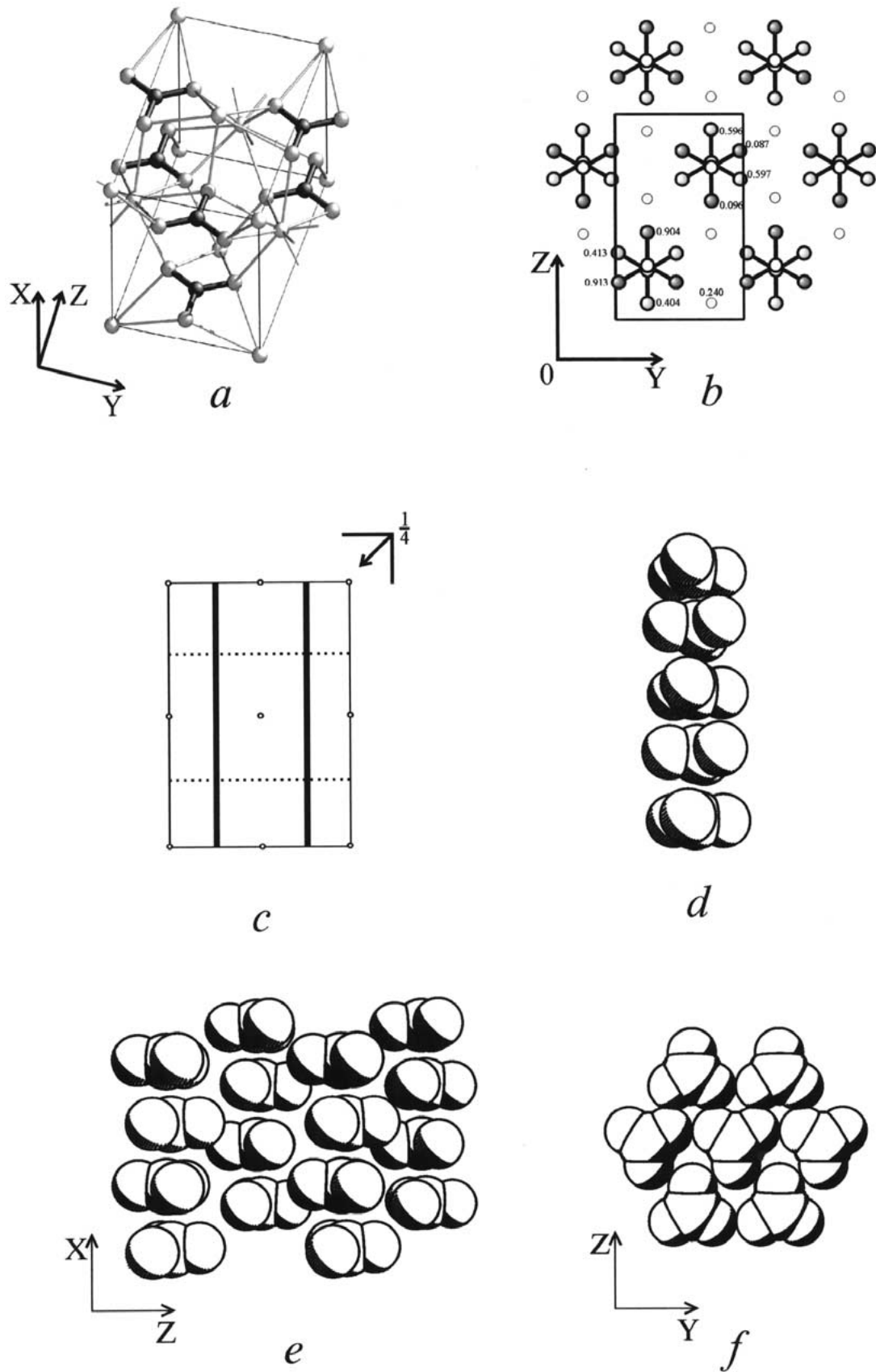


Figure 3. Crystal structure of aragonite  $\text{CaCO}_3$ : (a) view of the structure, (b) projection onto the  $YZ$  plane, atomic co-ordinates  $x/a$  are shown, (c) planes of symmetry in the  $Pnma$  group (projected onto the  $YZ$  plane), (d) a column of  $\text{CO}_3$  groups, (e) a layer of  $\text{CO}_3$  groups parallel to the  $XZ$  plane, (f) projection of  $\text{CO}_3$  groups along the axes of the columns.

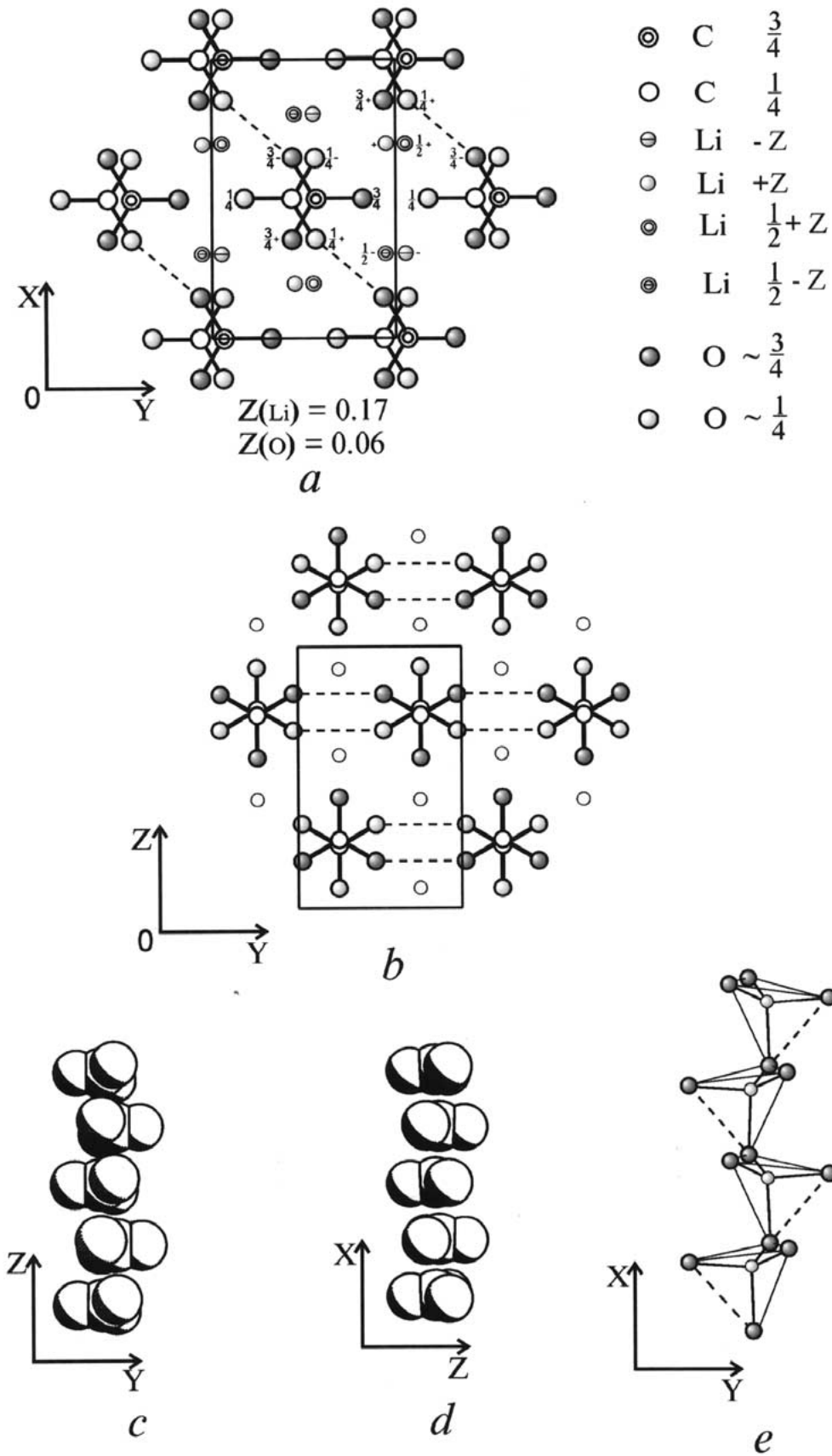


Figure 4. Crystal structure of  $\text{Li}_2\text{CO}_3$ : (a) projection along the Z axis, on the right – symbols of atoms with their levels, (b) structure of aragonite (for comparison), (c) a column of  $\text{CO}_3$  groups, (d) a column of  $\text{CO}_3$  groups in aragonite, (e) a chain of  $\text{LiO}_4$  tetrahedra.

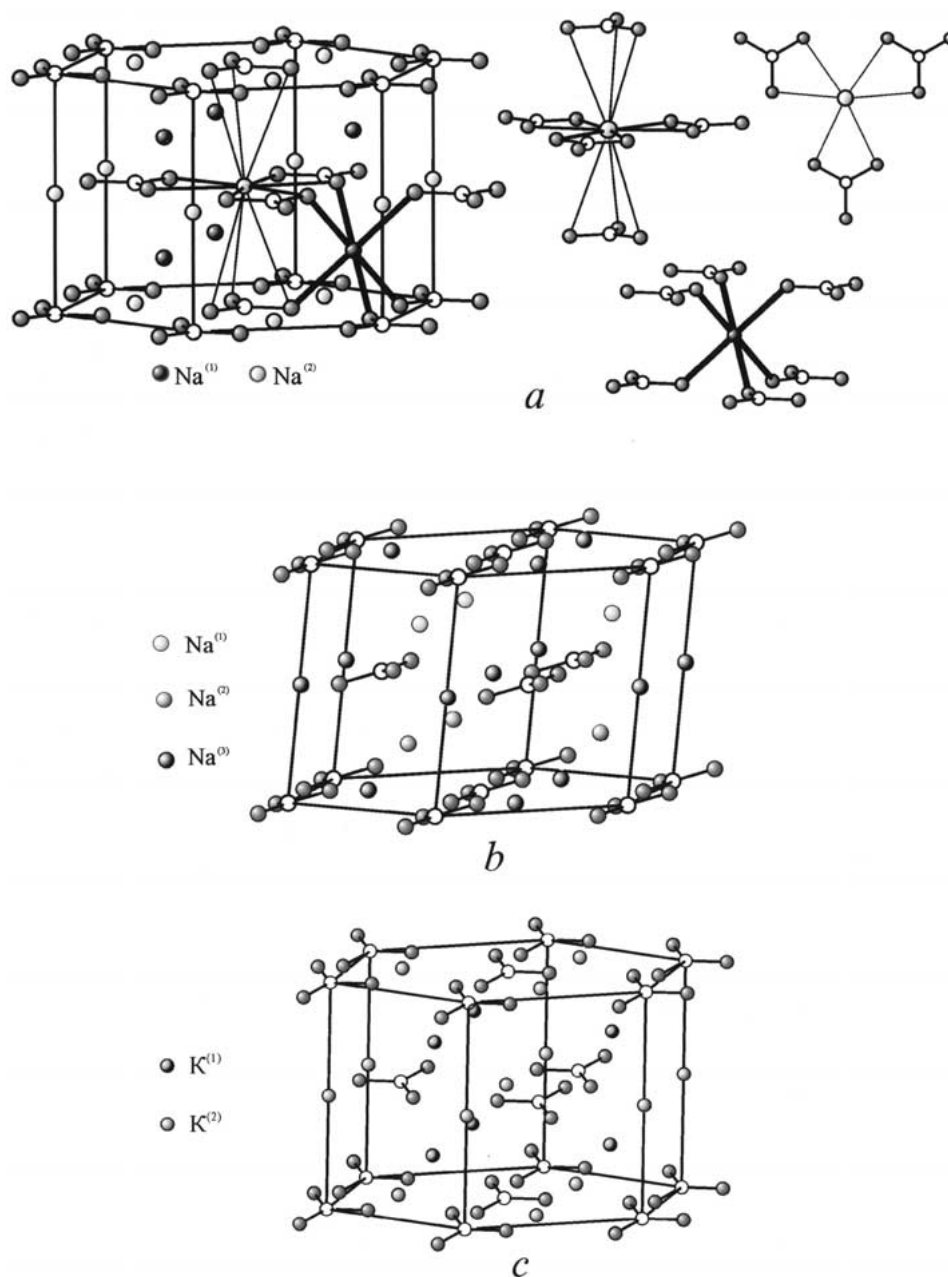


Figure 5. High-temperature structures  $\alpha$ - $\text{Na}_2\text{CO}_3$  (a),  $\beta$ - $\text{Na}_2\text{CO}_3$  (b),  $\beta$ - $\text{K}_2\text{CO}_3$  (c). The co-ordination of Na is shown for  $\alpha$ - $\text{Na}_2\text{CO}_3$ .

perature, but vdw contacts of  $\text{CO}_3$  groups can not appear.  $\beta$ - $\text{K}_2\text{CO}_3$  (Figure 5) and  $\gamma$ - $\text{K}_2\text{CO}_3$  are also monoclinic; however, other ways of distortion of the initial hexagonal structure of  $\alpha$ - $\text{Na}_2\text{CO}_3$  occur in both of them (see Table 2). The structure of  $\beta$ - $\text{Na}_2\text{CO}_3$  is obtained from the structure of  $\alpha$ - $\text{Na}_2\text{CO}_3$  by a  $\sim 16^\circ$  rotation of the  $\text{CO}_3$  groups belonging to the same sublayer about the direction that is perpendicular to axis Y; while rotating, the  $\text{CO}_3$  groups remain in plane  $m$ . The  $\text{CO}_3$  groups of adjacent sublayers are rotated about the same direction, but in the opposite sense. A different transformation takes place when  $\alpha$ - $\text{K}_2\text{CO}_3$  changes into  $\beta$ - $\text{K}_2\text{CO}_3$ ; the  $\text{CO}_3$  groups are rotated about axes 2 (through  $23^\circ$ ). As a result, the structures of  $\beta$ - $\text{Na}_2\text{CO}_3$  and  $\beta$ - $\text{K}_2\text{CO}_3$  have different symmetry.  $\gamma$ - $\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  are isostructural and vdw contacts of  $\text{CO}_3$  groups are absent in these substances.

The information concerning vdw contacts is clear enough, if the shortest distances  $\text{O} \cdots \text{O}$  are calculated. Such data are given in Table 3. Two types of forces are present in the considered ionic carbonates: ionic bonds  $\text{M}-\text{O}$  (always) and vdw contacts  $\text{O} \cdots \text{O}$  (sometimes). The mean lengths  $\text{M}-\text{O}$  in the nearest surroundings of the M cation was divided by the sum of ionic radii  $r_{\text{M}} + r_{\text{O}}$  taken from Pauling's book [16]. The ratio  $\langle \text{M}-\text{O} \rangle / r_{\text{M}} + r_{\text{O}}$  can characterise the closeness of the shortest  $\text{M}-\text{O}$  bonds to ionic nature. From Table 3 one can see that this ratio is always close to 1 and, consequently, the bonds are approximately ionic. As to contacts  $\text{O} \cdots \text{O}$ , we need the value of the oxygen vdw radius to discuss the problem.

In scientific publications there are several systems of vdw atomic radii of organogenic elements [17–19]. Unfortunately all of them are not completely satisfactory. For



Table 3. Ionic bonds M—O and distances O···O in considered carbonates

| MCO <sub>3</sub>              | $\frac{\langle M-O \rangle}{r_M+r_O}$ | O···O (Å) | M <sub>2</sub> CO <sub>3</sub>            | $\frac{\langle M-O \rangle}{r_M+r_O}$ | O···O (Å) |
|-------------------------------|---------------------------------------|-----------|---|---------------------------------------|-----------|
| MgCO <sub>3</sub>             | 1.05                                  | 3.03      | Li <sub>2</sub> CO <sub>3</sub>           | 0.98                                  | 2.91      |
| CaCO <sub>3</sub> (calcite)   | 0.98                                  | 3.26      | $\alpha$ -Na <sub>2</sub> CO <sub>3</sub> | 1.00                                  | 2.98      |
| CaCO <sub>3</sub> (aragonite) | 1.06                                  | 2.74      | $\alpha$ -K <sub>2</sub> CO <sub>3</sub>  | 0.98                                  | 3.27      |
| SrCO <sub>3</sub>             | 1.04                                  | 2.81      | $\beta$ -Na <sub>2</sub> CO <sub>3</sub>  | 1.04                                  | 3.17      |
| BaCO <sub>3</sub>             | 1.01                                  | 2.93      | $\gamma$ -K <sub>2</sub> CO <sub>3</sub>  | 1.01                                  | 3.50      |

example, the radii given by Zefirov and Zorkii [17, 18] are not confirmed by a thorough statistical treatment using CSD. Some other works do not contain any clear definition of atomic vdw radii as mean statistical values that follow from the theory of close packing of molecules. Such a definition was given by Zefirov and Zorkii [17, 18]; it is based on the concept of “supporting contacts”. They are those shortest atom-atom intermolecular contacts which form a space system of contacting molecules; usually only one atom-atom contact from each contact molecule-molecule is taken into account. In the system of contacting molecules each molecule is supported by no less than six other molecules; so its position is stable and the close packing arises. Now a new refinement of vdw radii performed by us using CSD is in progress. Below we give some preliminary results that were necessary for this work.

First of all, it concerns the oxygen vdw radius ( $R_O$ ). The  $R_O$  values recommended by numerous authors are rather different (the review on this question was given in [20]). The smallest of them is 1.29 Å in [17], though there are also values that are larger than 1.50 Å. Our latest results (obtained with the assistance of M. Rotyakov) are shown in Figure 6. They give reasons to believe that the  $R_O$  values can differ in the atom-atom contacts of different types. Moreover, the distribution of contacts of the given type (O···O or O···C) can be bimodal; we mean it can be a superposition of two maxima. Perhaps, the shape of the distribution of the C···O supporting contacts is bimodal and contains two Gaussian maxima; their positions correspond to  $2\sqrt{R_C R_O}$  (as is was taken in [17] and in earlier works by these authors), where  $R_C = 1.75$  Å,  $R_O = 1.35$  Å and 1.50 Å. (We give preliminary approximate values with an accuracy of 0.05 Å). The O···O distribution is bimodal as well. The second maximum of this distribution gives  $R_O = 1.53$  Å in good agreement with the C···O distribution; the first maximum is evidently false because it corresponds to H-bonds in which the H atoms were not localized by X-ray method.

Thus, we are inclined to accept that  $R_O$  equal to about 1.35 Å is suitable for some contacts C···O (and indeed some of these contacts were the source of the value taken by Zefirov and Zorkii [17]). The value  $R_O = 1.53$  Å is to be accepted for the O···O contacts. So the normal “supporting” O···O vdw distances are equal to 3.06 Å.

Returning to carbonates let us mention that distances within  $2\sqrt{R_X R_Y} \pm 0.15$  Å are regarded as normal vdw contacts X···Y [17]. However, sometimes significantly shorter distances X···Y occur in crystals. They are

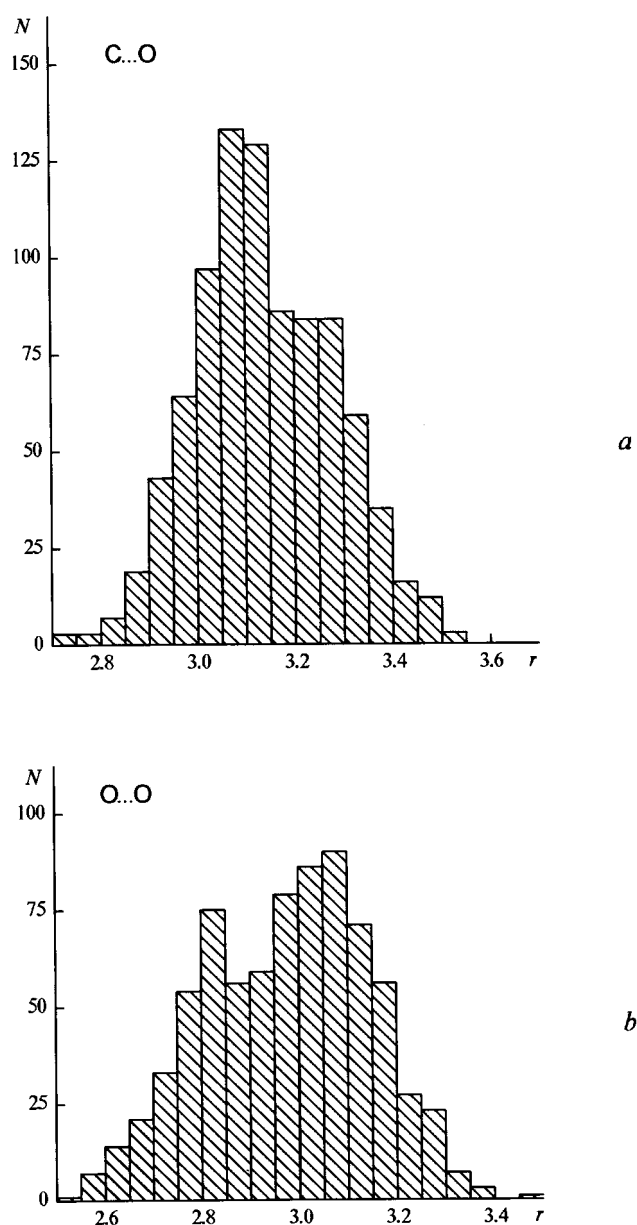


Figure 6. Distributions of supporting atom-atom intermolecular contacts C···O (a) and O···O (b) obtained using 8200 organic crystal structures taken from CSD.  $r$ , length of contact,  $N$ , number of contacts.

regarded as “specific”, in other words, they generate stronger bonding than normal  $X \cdots Y$  contacts. It is accepted that specific vdw contacts correspond to partly covalent interactions. The well-known example is specific interactions  $\text{Cl} \cdots \text{Cl}$  and other interactions  $\text{Hal} \cdots \text{Hal}$  in crystals of halogens and in some halogenorganic compounds. However, specific contacts are not numerous and do not generate special maxima in distributions of contacts.

To conclude the discussion of Table 3 let us examine it from this point of view. The distances close to 3.06 Å are present in  $\text{MgCO}_3$  and  $\text{CaCO}_3$  (calcite) and in  $\alpha\text{-Na}_2\text{CO}_3$ . Thus, we see the agglomerates of contacting  $\text{CO}_3$  groups in these substances. There are contacts  $\text{O} \cdots \text{O}$  that are even shorter (2.74–2.81 Å) in  $\text{CaCO}_3$  (aragonite),  $\text{SrCO}_3$ ,  $\text{BaCO}_3$  and  $\text{Li}_2\text{CO}_3$ . So it is reasonable to suppose the existence of specific (partly covalent) contacts  $\text{O} \cdots \text{O}$  in these carbonates. In  $\beta\text{-Na}_2\text{CO}_3$ , all forms of  $\text{K}_2\text{CO}_3$ ,  $\text{Rb}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  the vdw contacts between  $\text{CO}_3$  groups are absent; therefore these crystals are normal ionic (not inclusion) compounds.

## Conclusions

It was demonstrated that in all carbonates of alkaline-earth metals and in some carbonates of alkaline metals there are vdw contacts  $\text{O} \cdots \text{O}$  forming the agglomerates of  $\text{CO}_3$  groups, while cations are situated in the hollows imitating inclusion compounds (host–guest) similar to intercalates or cryptates. If such structures are available even among carbonates, they must occur and be common among many other salts with organic molecular anions. This opens a new interesting field of crystal chemistry analysis.

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