On Si—O—Si Configurations in Silicates

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From an analysis of the experimentally determined Si—O—Si geometry in a number of silicates it is concluded that the determining factors are very often the almost constant distances Si—O (bonded) and Si$\cdots$Si (non-bonded). The Si$\cdots$Si distance does not change if the 'anion' is varied (nitrides, carbides), and is the same as in small molecules. Relationships between Si—O lengths and Si—O—Si angles are deduced.

Introduction

A conspicuous feature of silicate chemistry is the large angle (typically $\sim$145°) at an O atom bridging two SiO_4 tetrahedra. Particularly striking in this respect are the high- and low-cristobalite forms of SiO_2. In principle, the Si—O—Si angle θ in these structures can be varied from 180 to 109·47° (or even less, subject to the constraint of O$\cdots$O repulsions) by concerted rotations of SiO_4 tetrahedra, and without any distortion of the tetrahedra (O'Keeffe & Hyde, 1976). In fact, however, $\theta \simeq 145$° in these compounds, although a simple model of covalent bonding would lead one to expect a value close to 109° (and a simple ionic model to 180°).

One interpretation of this large bond angle invokes $d_\pi-p_\pi$ bonding of Si and O (Cruickshank, 1961), but this approach is not entirely satisfactory [see O'Keeffe & Hyde (1976) and Glidewell (1973) for discussions]. An alternative approach invokes repulsive interaction between the Si atoms. With 'non-bonded' or 'one-angle' radii derived by Glidewell (1975), developing earlier work by Bartell (1960), it was possible to calculate T—O—T' angles (T and T' are tetrahedrally coordinated atoms) in good agreement with the observed values for a number of binary and ternary compounds with cristobalite structures (O'Keeffe & Hyde, 1976). The basic assumption of this latter approach is that for example Si—O—Si angles are determined by Si$\cdots$Si contacts. This assumption has several implications that can be used to test its validity: they are explored in this paper, which is concerned with all silicates and all forms of silica.

Si$\cdots$Si distances in silicates and other compounds

If our basic assumption is correct, an examination of the Si$\cdots$Si distances in silicates in which the Si are joined by a bridging O atom should reveal that they cluster around a constant value. There may, however, be some structures [such as thortveitite, $Sc_2Si_2O_7$ (Smolin, Shepelev & Titov, 1973)] in which values of θ as large as 180° are observed, and in which Si$\cdots$Si contacts are clearly not achieved. The distribution of observed Si$\cdots$Si distances should therefore be skew, with a tail at larger distances.

We have taken Si$\cdots$Si distances from well-refined structures [including all those compiled by Gibbs, Hamil, Louisnathan, Bartell & Yow (1972), and low-tridymite (Kato & Nukui, 1976)], but have made no
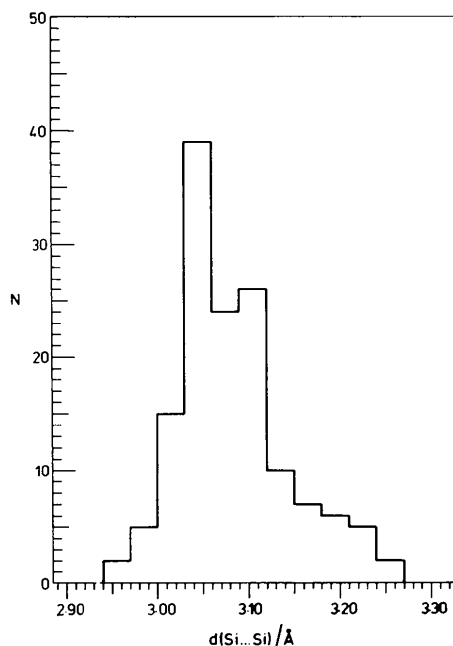

Fig. 1. Histogram showing the distribution of 141 nearest-neighbour Si$\cdots$Si in various silicates and silicas.

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effort to be either comprehensive or systematic. The distribution of distances (all recorded; 141 in number) is plotted as a histogram in Fig. 1. There is a pronounced peak at ∼3·06 Å, and the distribution is clearly skew as anticipated. From these data we deduce the 'one-angle' radius of Si to be 1·53 Å (*cf.* 1·55 Å deduced by Glidewell, 1975).

The data in Fig. 1 are for oxides. Recently, the structures of a number of binary and ternary Si nitrides have been reported: α-Si_3N_4 (Marchand, Laurent, Lang & Le Bihan, 1969; Kohatsu & McCauley, 1974), β-Si_3N_4 (Borgen & Seip, 1961), $LiSi_2N_3$ (David, Laurent, Charlot & Lang, 1973), $MgSiN_2$ (David, Laurent & Lang, 1970), $MnSiN_2$ (Winterberger, Marchand & Maunaye, 1977) and Si_2N_2O (Idrestedt & Brosset, 1964). In these compounds SiN_4 tetrahedra (SiN_3O in the last) are joined by a bridging N atom, with the Si—N—Si angle equal to ∼120°. The average Si···Si distance is 3·01 Å (mean of 33 independent values). Thus it appears that in the nitrides as well as the oxides the same non-bonded Si···Si distance determines the geometry.

We note, without comment, that in SiC the bond angle is 109° 28', as required by the diamond structure, and that here the Si···Si distance is 3·075 Å.

The discussion so far has been restricted to non-molecular, crystalline solids. But similar values for Si···Si are reported for vitreous silica: 3·00 to 3·10 Å (Zarzycki, 1957; Eitel, 1964; Narten, 1972). Furthermore, very nearly the same Si···Si distances are to be found in *molecules* with bridging N or O atoms. Thus, in Glidewell's (1973) review, five molecules [*e.g.* $(SiH_3)_2O$] with Si—O—Si groups are cited for which the mean Si···Si distance is 3·10 ± 0·04 Å; for eleven molecules with Si—N—Si groups [*e.g.* $(SiH_3)_2NH$] the mean Si···Si distance is 3·06 ± 0·05 Å. In disilylmethane, $(SiH_3)_2CH_2$, the Si···Si distance is 3·15 Å (Almenningen, Seip & Seip, 1970).

Si—O—Si angles and Si—O lengths

The variation of bond angle θ and bond length l in silicates has been much discussed. In particular the question of whether there is any correlation between θ and l has been the subject of controversy (Baur, 1971, 1977; Taylor, 1972; Gibbs *et al.*, 1972). We examine this question in the light of the hypothesis of Si···Si interaction.

The Si···Si distance d, and l and θ are related by

$$l = (d/2) \operatorname{cosec}(\theta/2).* \qquad (1)$$

If Si···Si contact occurs, so that d is essentially constant (∼ 3·06 Å), then a strong correlation between l and θ is predicted. On the other hand, for those

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* In scalene Si—O—Si triangles, l is taken as the average of the two different Si—O lengths.

structures in which θ is somehow constrained to be large, Si···Si contacts do not occur; and one would not expect any correlation between θ and l. In that case θ is determined by structural requirements (as in thortveitite) and l, at least in part, by the bonding of O atoms to cations additional to the Si atoms − *i.e.* by the bond-strength variation $\Delta p(O)$ of the O atoms (Baur, 1971). [In this context it is unimportant whether a covalent or an ionic description of the bonding is employed (Gibbs *et al.*, 1972).] Hence the situation at small values of θ is quite different from that at large values; but the boundary between small and large has to be determined. A reasonable guess is that the division between the two regimes is at $l \simeq 1·60$ Å: an average for the unconstrained forms of silica − α- and β-quartz, -cristobalite and -tridymite, in which each O atom is coordinated by two Si atoms only − when $d \simeq 3·06$ Å and hence, by equation (1), $\theta \simeq 145°$. Accordingly, the data have been divided into two sets: A for $\theta > 145°$, and B for $\theta < 145°$. (We excluded several structures in which uncertainty in the O atom parameters precluded accurate calculation of the bond angles.)

For both sets of data the dependence of l upon $\operatorname{cosec}(\theta/2)$ was investigated. For set A (comprising 43 data) l does not depend on θ: the result of a linear regression analysis $[l = a + b \operatorname{cosec}(\theta/2)]$ is that $a = 1·58$, and $b = 0·03$ with a standard deviation $\sigma(b) = 0·16$. The correlation coefficient was $r = 0·03$. For set B (comprising 80 data) a dependence of l on θ is clearly indicated: the relevant parameters are now $a = 0·76$, $b = 0·81$, $\sigma(b) = 0·16$ and $r = 0·66$. These lines and the individual data are plotted in Fig. 2.
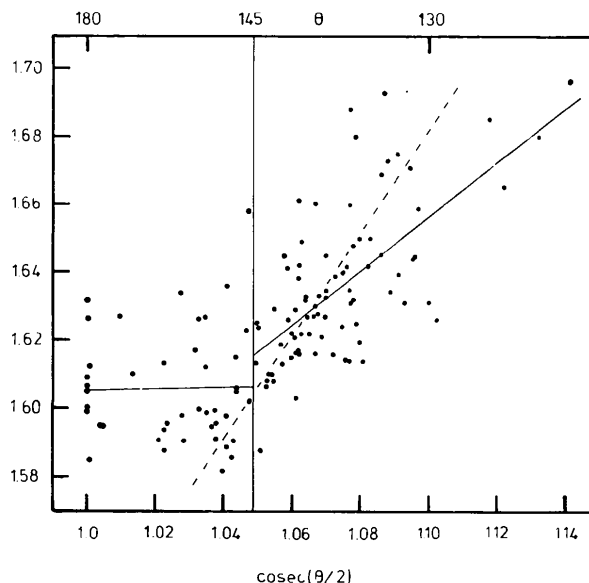

Fig. 2. A graph of Si—O length l *versus* $\operatorname{cosec}(\theta/2)$, where θ is the Si—O—Si angle. The data have been divided into two sets at the vertical line $\theta = 145°$. The other full lines are the best linear relations $l = a + b \operatorname{cosec}(\theta/2)$ for each set. The broken line is for $l = (d/2) \operatorname{cosec}(\theta/2)$ with $d = 3·06$ Å.

[While the present paper was being completed we received a manuscript from Baur (1977) in which he analysed 79 pairs of θ and l, all but four of which were for $\theta > 142°$. He found that there was, at best, a very weak correlation between θ and l; and concluded that, at the 2·5% risk level, one could reject the hypothesis that θ and l were correlated. If the four data at low θ were not included the null hypothesis could be accepted even more confidently. These conclusions are consistent with our own.]

For set B the results of the linear regression analysis are not in agreement with equation (1), which requires $a = 0, b = 1·53$ (shown as a broken line in Fig. 3). The significantly lower slope b suggests that d is not strictly constant, but decreases somewhat at smaller θ (larger l). Thus, in the extreme example of Li_2SiO_3 (Hesse, 1977) the relevant data are $\theta = 124·1°, l = (1·681 + 1·678)/2$ Å and $d = 2·967$ Å. The bridging $O(2)$ is also connected to two Li atoms at the unusually long distance of 2·170 Å. [Normal distances for four-coordination are $d(Si-O) = 1·64, d(Li-O) = 1·97$ Å (Shannon, 1976).] Thus, the $O(2)Si_2Li_2$ tetrahedron involves four $M-O$ bonds all of which are abnormally long, i.e. in tension. This must reflect the difficulty of fitting two Si and two Li atoms around an O atom, this difficulty arising from the non-bonded interactions between the M atoms. The tension in the $M-O$ bonds is balanced by compression of the $M\cdots M$ distances. Omission from set B of the four points in the top right part of Fig. 2 does not significantly change the calculated regression line, suggesting that this effect (compression of $Si\cdots Si$) is real; and that it also occurs at higher angles, though to a lesser extent.

Hence, a high value of l will be associated with a *low* value of d. On the other hand, if the $Si\cdots Si$ interaction were unimportant and d is determined only by θ, then a high value of l would mean a *high* value of d.

Further confirmation of the compression effect comes from a comparison of the structures of Li_2SiO_3 and (the isostructural) Si_2LiN_3. Both contain the anion-centred Si_2Li_2 tetrahedron but, in the nitride, the $M-N$

distances are normal $[d(Li-N) = 2·04, d(Si-N) = 1·70$ Å; calculated for four-coordination 2·05 and 1·72 Å respectively]. Hence there is no tension in these bonds, and one would expect a normal $Si\cdots Si$ distance. The observed value is $d = 3·08_6$ Å, in accordance with this expectation. The relaxation in the nitride is because the bonds to N are slightly longer than those to O.

Additivity of 'one-angle radii'

'One-angle radii' for many different elements can be derived in the way used here for Si: a set of such radii appropriate to tetrahedral oxides is in preparation. We give just one example here to illustrate that $A\cdots B$ distances are at least approximately equal to the sum of the radii for A and B. Of those atoms commonly coordinated by four O atoms, boron has the smallest radius. The mean of 21 $B\cdots B$ distances in borates with tetrahedrally coordinated B is 2·52 Å, so that we deduce a one-angle radius of 1·26 Å for tetrahedrally coordinated B. {In dimethyl boric anhydride, $[(CH_3)_2B]_2O$, the $B\cdots B$ distance is 2·59 Å (Gundersen & Vahrenkamp, 1976).} Together with the one-angle radius of 1·53 Å for Si, one would predict a $B\cdots Si$ contact distance of 2·79 Å in borosilicates. The average of 16 $B\cdots Si$ distances taken from recently refined structures of six borosilicates is 2·80 Å. In $(SiH_3)_2NBF_3$, $B\cdots Si = 2·78$ Å (and $Si\cdots Si = 3·07$ Å) (Robiette, Sheldrick & Sheldrick, 1970).

Discussion

It must be pointed out that the limiting $Si\cdots Si$ distance of twice the non-bonded/one-angle radius applies only to situations in which the Si atoms are bonded to just one common atom. When there are two common atoms (cation coordination polyhedra sharing edges to produce rings of four atoms, $Si-X-Si-X$) the distance apart is significantly smaller. Thus, in stishovite (SiO_2 with the rutile structure) the short $Si\cdots Si$ distance is only 2·66 Å (Baur & Khan, 1971).

We have already pointed out that, in fact, neither the $Si\cdots Si$ distance nor the $Si-O$ length is strictly constant. However, it may be supposed that departures from the mean values are symptomatic of strain in a crystal structure. One can thus calculate the value of an unstrained $Si-O-Si$ angle as indicated in Fig. 3, or indeed of $T-O-T'$ angles in general. We have shown (O'Keeffe & Hyde, 1976) that bond angles calculated in this way are close to those observed in crystals with the cristobalite structures.

It is also clear that in silicates the $O\cdots O$ distances are considerably greater than twice the non-bonded radius of O $[\sim 1·12$ Å; cf. Glidewell (1975) who gives 1·13 Å]. Hence, we must conclude that the detailed geometry of silicates is largely determined by $Si\cdots Si$
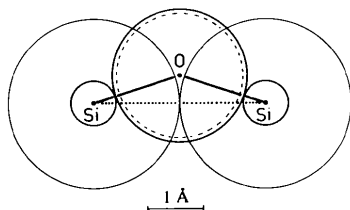

Fig. 3. An 'unstrained' $Si-O-Si$ group with $l(Si-O) = 1·61$ Å (sum of the ionic radii for Si in four-coordination and O in two-coordination) and $d(Si\cdots Si) = 3·06$ Å. Heavier circles represent ionic radii (Shannon, 1976); lighter circles represent 'one-angle' or 'non-bonded' radii (full for Si, broken for O). The heavy, full lines represent the $Si-O$ bonds, and the heavy dotted line the contact distance $d(Si\cdots Si)$. The bond angle $Si-O-Si$ is $2\sin^{-1}[3·06/(2 \times 1·61)] = 144°$.

and Si—O contacts, but not by O···O contacts. [The frequent occurrence in oxides of O atom arrangements approximating to a close-packed geometry is not a consequence of O···O contact, but arises in a quite different context (O'Keeffe, 1977).] The importance of Si···Si contact is illustrated in the crystal chemistry of the pyroxenes, and we cannot do better than quote Bragg & Claringbull (1965a): 'The Si—Si distance in a single chain, 3·05 Å, is the same for all three structures [diopside, pigeonite and clinoenstatite]. The difference in the shapes of the chains is the result of slight rotation about the Si—O$_1$ direction without change in the relative positions of the Si atoms...'*

A configuration of regular, corner-connected SiO$_4$ tetrahedra well-suited to Si···Si contact is in rings of four. This point is illustrated by Fig. 4, where the Si···Si distances for some symmetrical rings of tetrahedra are shown [based on l(Si—O) = 1·60 Å]. The widespread occurrence of configurations close to those of II and III in the figure is to be explained in terms of

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* Other, similarly relevant, quotations occur in the literature, particularly in discussions of thermal vibrations in systems of corner-connected tetrahedra, cf. below and, for example, McDonald & Cruickshank (1967) on vibrations in the P$_2$O$_7$ group in Na$_4$P$_2$O$_7$.10H$_2$O.

the favourable Si···Si distances. Significantly, it turns out that configurations suitable for SiO$_4$ tetrahedra are equally suitable for alternate SiO$_4$ and AlO$_4$ tetrahedra: the bond lengths and non-bonded radii are different for Al—O—Al [Al—O = 1·73, Al···Al = 3·30 Å (to be published)] and Si—O—Si, but their ratios, bond length/non-bonded radius, are almost identical, viz. 1·04$_8$ and 1·04$_6$ respectively, and hence their bond angles also: θ(Al) = 145·2, θ(Si) = 145·9°.

The Si$_8$O$_{20}$ configuration shown in Fig. 5(a) (cf. Bragg & Claringbull, 1965a) is particularly appropriate to Si···Si contact, the Si···Si distance being 3·08 Å for the perfectly regular figure (with l = 1·60 Å). Examples of its occurrence are in Linde molecular sieve type A (Bragg & Claringbull, 1965b) and in ekanite, Ca$_2$ThSi$_8$O$_{20}$ (Mokeeva & Golovastikov, 1966). In Fig. 5(b) spheres centred at the Si atoms, and with a radius equal to the one-angle radius of Si, are sketched in.

It is topologically impossible to construct an infinite, three-dimensional network consisting only of rings of four SiO$_4$ tetrahedra sharing corners. [This follows
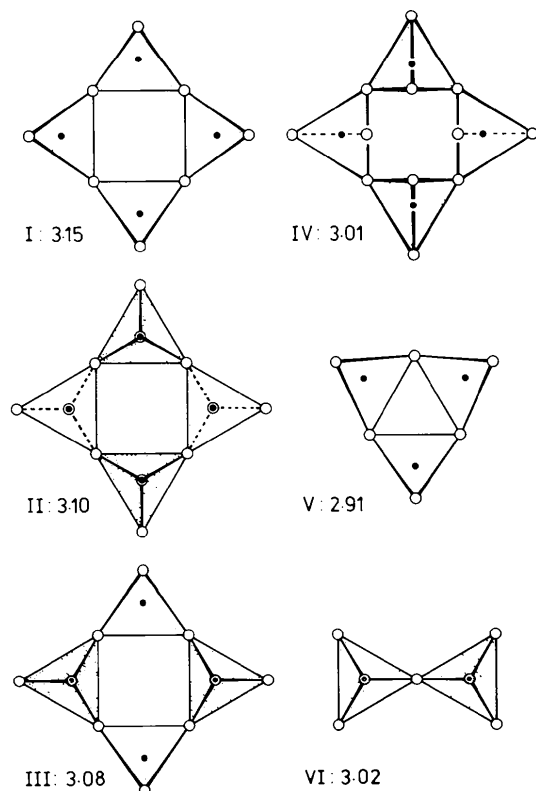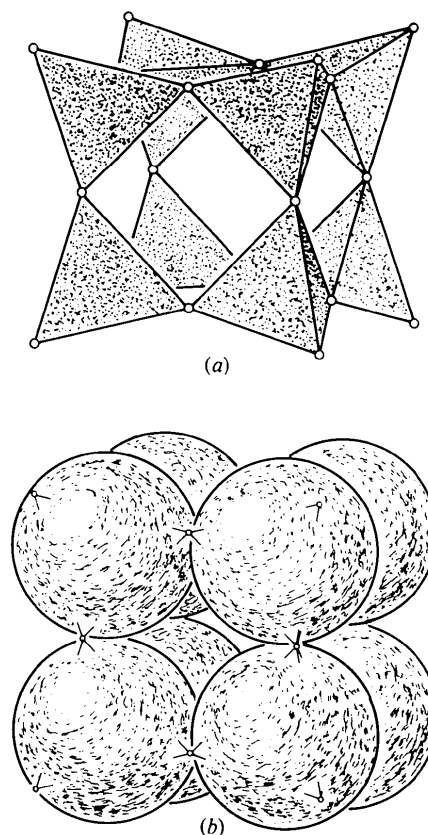

Fig. 4. Various symmetrical arrays of corner-connected SiO$_4$ tetrahedra. The smaller, filled circles are Si, the larger, open circles are O. The quantities are distances d(Si···Si) in Å for regular tetrahedra, and l(Si—O) = 1·60 Å.

Fig. 5. Two representations of the same Si$_8$O$_{20}$ structure unit: (a) the conventional one, with SiO$_4$ tetrahedra (the circles are O atoms); (b) with spheres of radius equal to the one-angle radius of Si (1·53 Å) centred at the Si positions. In (b) each sphere is almost in contact with its three nearest-neighbour spheres (cf. Fig. 4, I) if the Si$_8$ is a perfect cube. (Note the barely emergent vertices of the tetrahedra.)

from a consideration of four-connected nets (Wells, 1975).] However, two-dimensional nets of rings of four tetrahedra are possible [and occur, for example, in the structures of red HgI_2 and $SrZnO_2$ (Wells, 1975)]. Their absence in silicates may be understood, as it is easy to show that such layers must involve very short $Si \cdots Si$ distances (small Si—O—Si angles).

In this paper we have been content to present the facts concerning $Si \cdots Si$ distances, bond lengths and angles; and it appears as if $Si \cdots Si$ contacts are occurring in silicates. The physical reality that this corresponds to remains to be determined. It is difficult to separate a $Si \cdots Si$ interaction potential from the other interatomic interactions in a crystal, but there are at least two theoretical investigations of some relevance.

Pantelides & Harrison (1976) discussed SiO_2 in terms of a very simple model involving Si sp^3 and O p orbitals. [They claim that involvement of Si $3d$ orbitals can be safely neglected, cf. Tossell (1975).] Not surprisingly, the minimum-covalent-energy bond angle was found to be 90°. Of interest though is that the addition of an electrostatic (Madelung) energy term made very little difference (bond angle now 100°). These authors concluded that there must be a large short-range $Si \cdots Si$ repulsion term that contributes ~0·3 MJ mol⁻¹ to the total energy. [The heat of atomization (bond energy × 4) of quartz is 1·85 MJ mol⁻¹.]

Striefler & Barsch (1975) analysed the lattice dynamics of quartz with the aid of a force-constant model. Direct $Si \cdots Si$ interactions were not included, and it was found that the experimental data required an Si—O—Si bending force constant almost twice as large as that for O—Si—O bending. In view of the fact that, in silicates, the Si—O—Si angles show a much wider range of values than O—Si—O angles, it seems plausible that $Si \cdots Si$ interactions are contributing to the stiffness of the Si—O—Si group.

Summary and conclusion

In this paper we have made the following observations.

(a) In silicates the $Si \cdots Si$ non-bonded distance is, almost invariably, at least as constant as the Si—O bonded distance.

(b) To the same approximation the $Si \cdots Si$ distance in nitrides and carbides is the same as in oxides.

(c) Distances (bonded and non-bonded) in small molecules do not differ significantly from those in non-molecular crystals.

(d) Si—O—Si angles, which range from ~122 to 145°, can be interpreted as being determined by a combination of Si—O and $Si \cdots Si$ interactions. Small, correlated variations in the Si—O and $Si \cdots Si$ distances (due to stress) account for all but the largest bond angles.

(e) Observed $Si \cdots Si$ and (e.g.) $B \cdots B$ distances can be used to predict $B \cdots Si$ distances accurately.

(f) $O \cdots O$ distances in oxides are variable and are usually significantly greater than twice the one-angle radius appropriate for O.

The above observations are based solely upon the analysis of experimentally determined structures. They suggest, at a minimum level of interpretation, that a useful structural principle is to consider silicate structures as determined primarily by Si—O and $Si \cdots Si$ interactions, but not by $O \cdots O$ interactions. The same sort of principle is expected to hold for many other oxide (and nitride etc.) crystal [and molecular, cf. Glidewell (1975)] structures – a possibility that we are exploring. At a higher level of interpretation, the results suggest that a re-examination of the role of non-bonded interactions in determining the structures of ionic crystals should be rewarding. However, we feel that this task should await the analysis of more experimental data. In particular we wish to emphasize at this stage that we suggest only that one-angle radii can be of use in analysing and predicting structural details. This is in exactly the same spirit that ionic radii were first used by Bragg (1920), who originally proposed a set quite different from those currently in vogue. In a subsequent revision (Bragg, 1926) he emphasized that it had 'as its sole justification its convenience as a means of summarizing observed *distances* and of making possible a first approximation to the relative positions of atoms in a structure...' (our italics). We feel that subsequent neglect of this caution resulted in a too-literal interpretation of ionic radii as a true measure of ion size, and consequently to some incorrect structural principles, such as the role of anion packing referred to above, and the radius-ratio rules for determining cation coordination. (These last points will be taken up in subsequent papers.)

The similarity in local geometry between molecules and non-molecular crystals suggests that there is no fundamental difference in bonding in the two classes of compound, and that we should adopt a unified treatment for both. Here we are re-iterating a viewpoint long advocated by Sanderson (1971).

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The Crystal Structure of Cadmium Dihydrogenphosphite Monohydrate

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$Cd(H_2PO_3)_2.H_2O$ is triclinic, space group $P\bar{1}$, with $a = 6.772$ (2), $b = 7.523$ (4), $c = 7.982$ (3) Å, $\alpha = 113.70$ (4), $\beta = 110.69$ (3), $\gamma = 95.26$ (4)°, $Z = 2$. The structure was refined to $R = 0.033$ for 1186 counter reflections. It contains two distorted octahedra, connected on one edge, with central Cd atoms |Cd–O 2.263 (3) to 2.351 (3) Å|, and two phosphite anions connected by a hydrogen bond |P–O 1.494 (3) to 1.569 (3) Å, O–H···O 1.09 (6), 1.58 (7) Å, 173 (6)°|.

Introduction

The study of the title compound was undertaken as part of an investigation of H_3PO_3–$M(H_2PO_3)_2$–H_2O systems. The Cd compound was selected because it was assumed to contain a polyorthophosphite anion (Ebert & Čipera, 1966), which has not yet been studied structurally.

Experimental

The sample was prepared by reaction of phosphorous acid with cadmium phosphite under conditions following from the solubility diagram of the H_3PO_3–$CdHPO_3$–H_2O system at 25°C (Eysseltová, 1975). The cell dimensions were determined by least squares from 15 reflection angles measured on an automatic