Reports of the Academy of Sciences of the USSR

1961

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR

1961. Volume 138, No. 1

CRYSTALLOGRAPHY

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ON INTERATOMIC DISTANCES AND THE NATURE OF Si–O BONDS IN SILICATES

(Presented by Academician N. V. Belov, 17 IX 1960)

It is usually considered ($^{1-3}$) that the interatomic distances in all silicates retain approximately the same value, 1.60 Å (^{3}). However, numerous X-ray structural data convincingly show that the length of the Si–O bond varies within rather wide limits, 1.5–1.8 Å. Here we give a theoretical justification for this and show that, alongside the "average" distances between Si and O atoms usual for oxygen compounds of silicon, in silicates there are also "short" and "long" ones, whose presence is due to the different nature of the siloxane bond Si–O.

The oxygen atoms bonded to silicon, as has already been noted earlier (^{4}), occur in silicates either in the form of a monovalent ion O^-, or they form a second covalent bond with another atom as well, being, for example, a bridge between two silicon atoms.

The length of the Si–O bond in SiO_2 and in organosilicon compounds is indeed distinguished by its constancy: 1.63 ± 0.03 Å (^{3,5,6}). This distance is 0.20 Å shorter than the 1.83 Å calculated from the covalent radii of Pauling–Huggins (^{7}). Such a shortening cannot be explained by a significant ionic character of the Si–O bond ($\sim 40\%$) (^{8}), since introducing the corresponding correction (^{9}) for the difference in electronegativities of the silicon and oxygen atoms leads to a value of 1.77 Å, again exceeding the experimental value by 0.14 Å. At present it has been firmly established ($^{10-14}$) that the shortening of the Si–O bond is due to its partial double-bond character, of the order of 30% (^{8}), owing to the formation of an additional donor-acceptor p_π–d_π bond through overlap between the vacant $3d$-orbital of silicon (acceptor atom) and the free $2p$-orbital of oxygen (donor atom, possessing an unshared pair of electrons).

The degree of p_π–d_π bonding between Si and O atoms is determined by the electron-acceptor properties of the silicon atom, which depend on the substituents attached to it, and also by the electron-donor properties of oxygen. Thus, for example, the presence at the silicon atom of electron-attracting chlorine atoms increases the order of the Si–O bond (15), as a result of which the nucleophilic properties of the oxygen atom are greatly reduced.

$$\text{Cl}-\text{Si}-\ddot{\text{O}}^-$$

The presence at the silicon atom of electron-repelling groups (+*I*-effect), on the contrary, leads to a decrease in the double-bond character of the Si–O bond owing to a decrease in the electron-acceptor properties of the silicon atom and increases its ionic character:

$$\text{R} \rightarrow \text{Si} \rightarrow \text{O}^-.$$

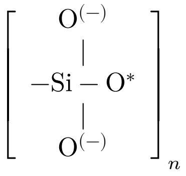
Both effects (a decrease in the degree of p_π–d_π bonding and an increase in the ionicity of the bond) compensate each other to one degree or another, so that no noticeable change in the length of the Si–O bond occurs in this case.

It must be said that the influence of such substituents as chlorine atoms or alkyl radicals is too small to change the Si–O bond order to such an extent that it would cause its shortening or lengthening by an amount exceeding the error of ordinary measurements (0.02–0.05 Å). Thus, for example, the interatomic Si–O distance in $\text{Cl}_3\text{SiOSiCl}_3$ and $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ proves to be practically the same: 1.64 ± 0.05 Å (5). It is precisely for this reason that in many oxygen compounds of silicon we deal with an “average” value of the Si–O bond length, 1.63 ± 0.03 Å.

Nevertheless, there exist substituents possessing powerful electron-repelling properties. These are negatively charged anionic substituents (for example, an “active” oxygen ion-atom O^-), the electron displacement from which is due both to the +*I*- and to the +*M*-effect

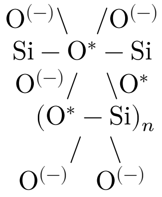
$$\overset{..}{\text{O}}^{(-)} \longrightarrow \text{Si} \longrightarrow \text{O}—$$

The presence of such substituents at the silicon atom must hinder the formation of a p_π—d_π-bond with the bridging (“inactive”) oxygen atom. Therefore one should expect that the distance between the silicon atoms and the bridging oxygen (O*) in linear (A) and cyclic (B) metasilicates, and also in pyrosilicates (C) and silicates of spatial structure (D), should be greater than the “average” value.*

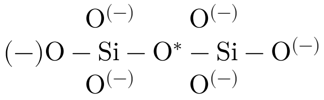


$\left[-\overset{O^{(-)}}{\underset{O^{(-)}}{Si}}-O^*\right]_n$

A



B



$(-)O-\overset{O^{(-)}}{\underset{O^{(-)}}{Si}}-O^*-\overset{O^{(-)}}{\underset{O^{(-)}}{Si}}-O^{(-)}$

C

Table 1 illustrates that this is indeed so. The data in the table, borrowed from the most reliable literature sources, clearly

Table 1

Interatomic Si–O distances in silicates

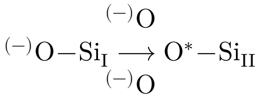
Silicate	Anion structure	Interatomic distance in Å: “long” Si–O*	Interatomic distance in Å: “short” Si–O$^{(-)}$
Na_2SiO_3	A	1.68	1.57
$MgSiO_3$, enstatite	A	1.63	1.53
$CaMgSiO_3$, diopside	A	1.76	1.54
$Na_2Zr(Si_3O_9)\cdot 2H_2O$, catapleite	B, $n = 1$	1.73	1.50
$BaTi(Si_2O_9)$, benitoite	B, $n = 1$	1.65	1.59
$Zn_4(OH)_2(Si_2O_7)\cdot H_2O$, hemimorphite	C	1.72 (1.81)	1.60 (1.58)
$CaFeAl_2(Si_2O_7)(SiO_4)O(OH)$, epidote	C	1.67	1.51
$Ca_2Zn(Si_2O_7)$, hardystonite	C	1.70	1.54
$Ca_{10}Mg_2Al_4Si_9O_{34}(OH)$, vesuvianite	C	1.86	1.28 (?)
$Na_2Al_2Si_2O_{10}\cdot 2H_2O$, natrolite	D	1.80	1.51
$Ca_4(Si_2O_5)_4\cdot KF\cdot 8H_2O$, apophyllite	D	1.75	1.54
$KAlSi_3O_8$, sanidine	D	1.75	1.59

Silicate	Anion structure	Interatomic distance in Å: "long" Si–O*	Interatomic distance in Å: "short" Si–O$^{(-)}$
Average . . .		1.73	1.54

show that the distance between the bridging oxygen atom and the silicon atoms bonded to it, which are also bonded to O^- anions, greater than the "average" and is 1.73±0.1 Å. This distance is close to the length of a purely single Si–O bond, calculated from covalent radii with a correction for the difference in electronegativities of Si and O, 1.77 Å. In individual cases, even practically "pure" σ-bonds Si–O of length 1.75–1.78 Å occur in silicates; the presence in them of p_π—d_π bonding is unlikely.

On the other hand, the tabular data indicate that in silicates there are also "short" Si–O bonds, joining the silicon atom to a negatively charged anionic oxygen atom possessing an excess lone pair of electrons. The latter contributes substantially to the formation of a p_π—d_π bond between oxygen and silicon, since negatively charged groups, as a rule, tend to increase their covalency ($+M$ effect). Therefore in silicates there are Si–O bonds that are practically double, as is shown by the agreement of their length (1.54 ± 0.05 Å) with that calculated from covalent radii for the double bond Si=O (1.53 Å), using the "ionic" correction $-0.09(\chi_O - \chi_{Si})$ (9). The order of such a Si–O^- bond, calculated by Pauling' s equation (8), is approximately 1.9. Strangely enough, no one has so far paid attention to this circumstance, and in almost all literature sources (except the work of N. V. Belov (16)) the constancy of the Si–O bond length in silicates (1.60 Å) and its order, not exceeding 1.2–1.3 (6,7), are indicated.

It is interesting to note that the powerful electron-repelling effect of anionic substituents attached to the silicon atom may lead not only to lengthening of the Si_I—O^* bond, but also to shortening of the neighboring bridging bond O^*—Si_{II}. This is caused by the fact that strong ionization of the Si_I—O^* bond, which gives rise to a large effective negative charge on the oxygen atom, leads to strengthening of the p_π—d_π bond between the atoms O^* and Si_{II}, especially if the electron-donor effect of the substituents bound to the latter is less than that of those joined to the Si_I atom.



$$\overset{^{(-)}O}{\underset{^{(-)}O}{^{(-)}O-Si_I}} \longrightarrow O^*-Si_{II}$$

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* In the structural formulas of silicate anions given here, the minus signs are put in parentheses, since they d

Such inequality of the bridging Si–O* bonds is observed, for example, in beryl (1.68 and 1.54 Å), wollastonite (1.76 and 1.48 Å), benitoite (1.65 and 1.46 Å), and natrolite (1.80 and 1.50 Å).

The presence, at the central silicon atom located in the silicon-oxygen tetrahedron (with sp^3 hybridization), of several p_π—d_π Si–O bonds, close in order to double bonds, is improbable. This can be explained by the fact ([17]) that if the 3d orbitals of silicon are oriented so as to ensure maximal interaction with the π-orbital of one of the oxygen atoms, then they are positioned unfavorably with respect to the other oxygen atoms.

Therefore p_π—d_π bonding of the central silicon atom with several oxygen atoms is possible when its 3d orbitals are oriented either in a way that does not lead to maximal interaction with any one of the oxygen atoms, or in a way leading to the greatest overlap with the π-orbital of one (or partly two) oxygen atoms. One or another character of the distribution of p_π—d_π bonds is determined both by the number of anionic oxygen atoms and by the nature of the cations bound to them. Competition (gem-conjugation) may even arise between anionic oxygen atoms, leading to strengthening of one p_π—d_π bond and weakening of another.

It is noteworthy that in orthosilicates containing isolated $(SiO_4)^{4-}$ ions, the electron-donor effect of the anionic oxygen atoms and the nonuniform distribution of p_π—d_π bonds may lead to disruption of the symmetry of the silicate anion through lengthening of one part of the Si–O bonds and shortening of another. Thus, for example, in olivine the interatomic distances between silicon and oxygen are 1.789, 1.895, 1.603, and 1.603 Å ([16]).

Summarizing what has been said above, we arrive at the conclusion that Si–O bonds can be divided into three types. "Long"σ-bonds with a considerable degree of ionicity (1.73 ± 0.1 Å) connect a bridging oxygen atom with two (sometimes with one) silicon atoms, which are, in addition, bonded to anionic substituents ($-O^-$, etc.). The degree of p_π—d_π bonding in this case is reduced to a minimum. Anionic negatively charged oxygen atoms can be joined to a silicon atom by "short" bonds (1.53 ± 0.05 Å), approaching, owing to the additional formation of a p_π—d_π bond, in their order (~ 1.9) double bonds. The remaining interatomic Si–O distances are "intermediate" (1.63 ± 0.05 Å) and correspond to a bond order of 1.2-1.3 and to its ionic character of $\sim 40\%$.

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Received
25 VI 1960

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Note: Figure translations are in progress. See original paper for figures.