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Bond Angle Distortions in Silicate Tetrahedra

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O–Si–O bond angles related to coordination edges shared with M site polyhedra in silicates with the clinopyroxene, olivine and garnet structures are compared with calculated electrostatic potentials due to the M site metals. The repulsion between the M and Si atoms is proportional to the *ideal* ionic charge (or valence) of the M atoms rather than to the effective ionic charge calculated from electronegativity data, and this is ascribed to an inhomogeneous charge density on metal atoms.

Introduction

The stereochemistry of the tetrahedral portion of silicates has been the subject of much discussion in recent years (Brown & Gibbs, 1970; Baur, 1971; Gibbs, Hamil, Louisnathan, Bartell & Yow, 1972; Louisnathan & Gibbs, 1972*a*, *b*). It is recognized that the sharing of coordination edges with larger polyhedra is the principal cause of bond-angle distortion in these tetrahedra and a significant contributor to bond-length distortion, although this effect has not been investigated quantitatively.

In discussing distortions in the M site coordination polyhedra of olivine, clinopyroxene and amphibole Fleet (1974) has developed the classic work of Pauling (1929, 1960) suggesting that the repulsive force experienced by an M atom from an edge-related M atom would be proportional to the electrostatic potential $Z_{\text{eff}}/(\text{M–O})$, where Z_{eff} is the effective atomic charge on the first M atom. When an M site polyhedron shares a coordination edge with a Si, O tetrahedron it is distorted through accommodation of the shorter tetrahedral edge and this distortion is intensified by apparent repulsion between the edge-related M and Si atoms.

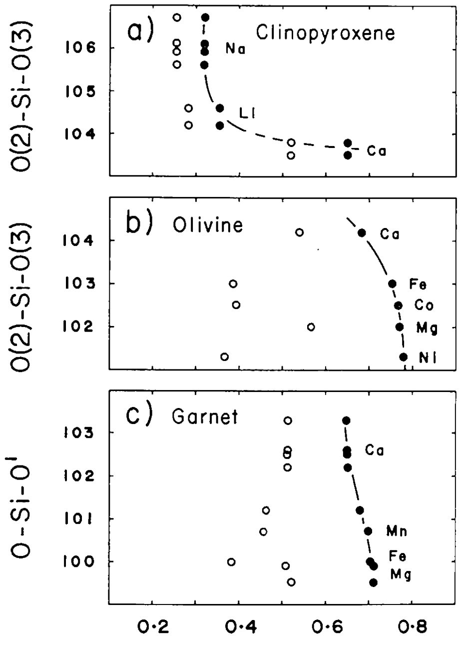

Fig. 1. Variation of tetrahedral bond angle with the electrostatic potentials $Z_{\text{eff}}/(\text{M–Si})$ (open circles) and $Z/(\text{M–Si})$ (closed circles) for (*a*) $C2/c$ clinopyroxene; (*b*) olivine; (*c*) garnet. M site atoms are indicated.

In the present study, for silicates with the $C2/c$ clinopyroxene, olivine and garnet structures, the tetrahedral bond-angle distortion associated with a shared edge is compared with the electrostatic potentials $Z_{\text{eff}}/(\text{M–Si})$ and $Z/(\text{M–Si})$, where Z_{eff} is the effective atomic charge on the M site atom, calculated from electronegativity data (Fleet, 1974), Z is the ideal ionic charge on the M site atom and M–Si is the undistorted M–Si distance calculated with the ideal tetrahedral bond angle and the effective ionic radii of Shannon & Prewitt (1969).

Data

In the structure of $C2/c$ clinopyroxene the Si, O tetrahedron shares two non-equivalent edges of the face parallel to (100) with the M(2) coordination polyhedron. Data for the O(2)–Si–O(3) bond angle of eight clinopyroxenes (Clark, Appleman & Papike, 1969, Table 13) are presented in Fig. 1(*a*). O(3^{i}), one of the oxygens forming the second shared edge, is relatively distant from the M(2) atom. In fact, it is not usually included in the coordination polyhedron of Li. The O(3)–Si–O(3^{i}) bond angles are correspondingly larger than the O(2)–Si–O(3) bond angles and vary in a less systematic way with the calculated electrostatic potentials.

The Si, O tetrahedron in the olivine structure shares all three edges forming the face parallel to (100), two with the M(1) octahedron and one with the M(2) octahedron. The tetrahedral bond angles affected are O(2)–Si–O(3) and O(3)–Si–O(3^{i}), respectively. The O(2)–Si–O(3) bond-angle data of five end-member orthosilicates (Louisnathan & Gibbs, 1972*b*, Table 1) are used in the present study [Fig. 1(*b*)]. The corresponding O(3)–Si–O($3^{\rm i}$) bond angles are larger, the repulsive force between the M(2) atom and Si being reduced by the movement of the M(2) atom away from the shared edge (Fleet, 1974).

The Si, O tetrahedron in the garnet structure shares two opposite, equivalent edges with the eightfold coordinated X site metals. The O–Si–O$^{\rm i}$ bond-angle data used in Fig. 1(*c*) are taken from the study of Novak & Gibbs (1971, Table 9).

Discussion

Rather surprisingly the decrease in tetrahedral bond angle (Fig. 1) shows a better correlation with Z/(M–Si) than $Z_{\rm eff}$/(M–Si), the bond angle, $Z_{\rm eff}$/(M–Si) distributions for the olivine and possibly the garnet structures tending to show separate populations for the transition and non-transition metals.

In the previous publication (Fleet, 1974) the O(1)–M–O($1^{\rm i}$) bond angle of *C*2/*c* clinopyroxene, which is related to a shared edge between two M(1) site octahedra, was compared with $Z_{\rm eff}$/(M–O). The correlation obtained although feeble was considered encouraging. However, in the light of the present study I have compared O(1)–M–O($1^{\rm i}$) with Z/(M–M) and, once again, the correlation between distortion and apparent distorting force is much better for electrostatic potential data based on ideal ionic charges (Fig. 2).

A possible explanation for these discrepancies is that the atomic charge acting in the interbonded areas of a metal atom is not necessarily the same as that in the bonded areas. Atomic charge is basically a function of the extent to which the valence and non-bonded electrons screen the fraction of nuclear charge left unscreened (uncompensated) by the filled electron shells. For a heteropolar bonded metal the valence electron density is greatest along the bonded directions. Hence, even a metal with a calculated $Z_{\rm eff}$ of zero will tend to have a net positive charge in interbonded areas. A sphere about a non-transition metal with the effective ionic radius would be a heterogenous potential surface, perhaps even negative in bonded areas but positive in interbonded areas. The extent to which this effect is compensated by a perturbation of the electron density in the filled electron shells (or of the electric field due to these electrons) is unknown. If this compensation does not occur the charge acting in the interbonded areas would be related more closely to the valence of the metal than to the covalence (and the electronegativity difference) of the metal–ligand bonds. Certainly in the absence of such an explanation we have to question either the electronegativity values used in the calculation of $Z_{\rm eff}$ or the assumption that the shortening of shared coordination edges results from electrostatic repulsion between the metal atoms.

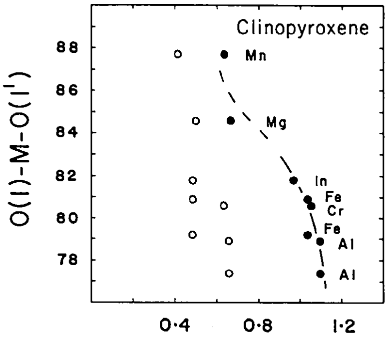

Fig. 2. Variation of octahedral bond angle with the electrostatic potentials $Z_{\rm eff}$/(M–M) (open circles) and Z/(M–M) (closed circles) for *C*2/*c* clinopyroxene. M site atoms are indicated.

This hypothesis tends to contradict the suggestion of Pauling (1960, p. 562) that the shortening of shared coordination edges is not consistent with extensive covalent bonding. Also, in transition metals the distribution of the *d* orbitals may be a complicating factor. However, it has been noted (Fleet, 1974, 1975) that for coordination octahedra the electrons in t_{2g} orbitals do not appear to screen atomic charges along the edge-related metal–metal directions. We can only surmise at this time that either they have low screening efficiencies because the orbitals are diffuse or they tend to occupy preferentially the orbital lobes which do not project along metal–metal directions.

The evidence presented in this study then suggests that the atomic charge causing repulsion between M and Si atoms related by shared coordination edges is proportional to Z (or M atom valence) rather than $Z_{\rm eff}$. Naturally the charge experienced by an edge-related Si atom will be reduced further owing to screening by the valence electrons on the oxygens forming the shared edge. In addition the bond-angle variations appear more sensitive to the distance parameter in the electrostatic potential expressions than to Z. There are marked inflexion points where a change in valence state occurs [Li to Ca, Fig. 1(*a*); also Mg to In, Fig. 2] suggesting that the atomic charges actually experienced by Si [and M(1) atoms] are not in proportion to the ideal ionic charges.

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The Crystal Structure of the γ-Lactone of 2,2-Dimethyl-3,4-dihydroxy-5-phenylvaleric Acid: a Degradation Product of Neoantimycin

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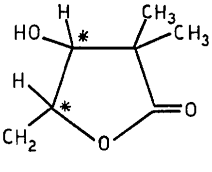
The γ-lactone of 2,2-dimethyl-3,4-dihydroxy-5-phenylvaleric acid, $C_{13}H_{16}O_3$, crystallizes in the space group $P2_1$ with $a=8{\cdot}373$ (4), $b=6{\cdot}373$ (3), $c=11{\cdot}234$ (5) Å, $\beta=97{\cdot}85$ (8)°, $Z=2$. Data for 820 reflexions were collected on a Siemens automated diffractometer. The crystal structure was solved by direct methods; refinement was carried out by full-matrix least-squares procedures including anisotropic thermal parameters. The lactone ring is puckered at the β-carbon atom which deviates by about 0·47 Å from the best plane formed by the four remaining atoms. The relative configuration of the two adjacent asymmetric carbon atoms of the molecule is *RR* (or *SS*). The molecules are held together in the crystal by hydrogen bonds (O···O 2·76 Å) along twofold axes.

Introduction

Recently, the structure of neoantimycin, an antibiotic obtained from *Streptoverticillum orinoci* has been determined by chemical and spectroscopic methods (Cassinelli, Grein, Orezzi, Pennella & Sanfilippo, 1967; Caglioti, Misiti, Mondelli, Selva, Arcamone & Cassinelli, 1969). Acidification of an alkaline solution of hydrolysed neoantimycin yields the γ-lactone of 2,2-dimethyl-3,4-dihydroxy-5-phenylvaleric acid



The molecule contains two adjacent asymmetric carbon atoms. The relative configuration of these atoms has not been determined so far. In order to solve this configurational problem and to gain more information on the structure of the antibiotic itself we undertook the X-ray single-crystal analysis of the title compound.

Experimental

Accurate cell constants were obtained by a least-squares treatment of 15 high-angle reflexions recorded with Cu Kα radiation.

Crystal data

$C_{13}H_{16}O_3$, F.W. 220·3, space group $P2_1$, $a=8{\cdot}373$ (4), $b=6{\cdot}373$ (3), $c=11{\cdot}234$ (5) Å, $\beta=97{\cdot}85°$ (8), $U=593{\cdot}8$ Å^3, $D_m=1{\cdot}23$ g cm^{-3}, $D_c=1{\cdot}233$ g cm^{-3} for $Z=2$,