Table 4. *Fit to the measured data of urea–oxalic acid* $(1:1) x = K_0 + K_1 T + K_2 T^2$

x	K_0	$K_1 (\times 10^3)$	$K_2 (\times 10^6)$	P^*
a	12·885 (3)	0·32 (3)	0·96 (7)	0·9999
b	6·610 (3)	0·04 (3)	0·27 (6)	0·9988
c	6·625 (4)	0·57 (4)	0·63 (9)	0·9999
β	89·92 (4)	7·3 (4)	5·9 (9)	0·9999

* P is the correlation coefficient between measured and calculated unit-cell dimensions.

Table 5. *Direction cosines of the principal components of the expansion tensor (in columns) relative to the crystal axes of urea–oxalic acid* (1:1) *at room temperature*: 295 (1) K

The last column gives the direction cosines of the normal to ($\bar{1}01$).

a_1	a_2	a_3	
0·81	0·00	−0·59	−0·47
0·00	1·00	0·00	0·00
0·55	0·00	0·83	0·90

containing the hydrogen bonds, of the expansion tensor are comparable with the expansion tensor of oxamide, which also has a two-dimensional hydrogen-bonding network (de With, 1977).

Since the compound is an addition compound, one expects the bond lengths and angles to not differ significantly between the title compound, urea–oxalic acid (2:1), oxalic acid dihydrate and urea. Data on these compounds are given in Table 3, which shows that there is a fair agreement of bond lengths and angles in the different compounds. Some of the differences found, however, are significant from a crystallographic point of view. These differences, particularly in the urea molecules, may be due to differences in hydrogen bonding in the different compounds.

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SHORT COMMUNICATION

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Variabilities in interatomic distances and angles involving BeO4 tetrahedra. By DIBYENDU GANGULI, *Central Glass & Ceramic Research Institute, Calcutta 700032, India*

Abstract

Variations in Be–O bond lengths have been found to be related to a large extent to corresponding variations of bond strength received by Be-bonded oxygens in 23 inorganic structures (r value for regression of Δd on $\Delta p_o = +0.70$). An inverse relationship between Be–O lengths and Be–O–Si angles (in 17 beryllosilicates) is also largely valid when values of Be–O lengths uninfluenced by tetrahedral edge-sharing are considered ($r = -0.59$). Be–O bonds unconnected with other tetrahedral atoms are rare, but the known ones are also relatively shorter than Be–O($\rightarrow T$) lengths. Because $d-p$ π-bonding can be ignored for Be–O bonds and Be–O–T angles, their variations seem to indicate a more generalized applicability of the 'extended electrostatic valence rule'.

Variations in individual and average T–O distances and T–O–T angles (T = tetrahedral cation) have been known to exhibit, specially in the case of silicates and aluminosilicates, the following trends (Baur, 1961, 1971; Brown, Gibbs &

Ribbe, 1969; Brown & Gibbs, 1970): (i) directly propor-
tional relationship between bond-length and bond-strength
variations ($\Delta d \propto \Delta p_o$); (ii) inverse relationship between T—O
bond-length and T—O—T bond-angle variations; and (iii)
relative shortness of T—O(nbr) bonds (oxygen attached to
only one T cation) compared to T—O($\to T$) lengths. Trends
(ii) and (iii) follow from the d–p π-bonding model (Brown,
Gibbs & Ribbe, 1969); however, Baur's (1961, 1971)
extended electrostatic valence rule, expressed in trend (i),
claims all these trends to be its corollaries, though current
work (Baur, 1977) tends to minimize the importance of trend
(ii).

Variations in interatomic distances and angles involving
BeO_4 tetrahedra seem interesting from the above viewpoints
because (a) the average Be—O bond should be more ionic
than the average Si—O bond and, hence, more responsive to
Baur's rule, and (b) the effect of d–p π-bonding can be
ignored in the case of Be—O bonds (Brown & Gibbs, 1970).
Compliance with the trends (i) to (iii) in the case of Be—O
bonds should, therefore, indicate wider applicability of the
extended electrostatic valence rule.

Discussion

Relevant data on 23 natural and synthetic inorganic
compounds were collected from the literature (Table 1) for
testing trend (i); these structure types showed, in contrast to
the clearly defined structural groups examined by Baur
(1971), wide variations. Standard deviations of the Be—O
lengths also varied widely (0·003–0·09 Å). In spite of these
inherent constraints, the correlation coefficient (r) for the
regression of Δd on Δp_o (Fig. 1) was found to be +0·70,
indicating a high level of significance (0·1%) of the inter-
dependence of the two parameters, as suggested by Baur's

rule. A feature not encountered among the silicates was the
frequent occurrence of edge-sharing among the tetrahedra
(here BeO_4) with themselves, or with other polyhedral
elements; this was at least partly responsible for an increase
in Be—O (edge-sharing) lengths in most of the cases (e.g.
epididymite, eudidymite). The edge-sharing oxygens, again,
took part in smaller Be—O—X angles (X = Be, or other
mono- to trivalent cations) and O—O distances than corner-
sharing oxygens and, hence, connected themselves to addi-
tional cations for valence-balance necessity and also to
nullify the effect of O—O respulsion. Thus, in most of the
cases, oxygens constituting shared polyhedral edges had rela-
tively long Be—O contacts, and were also those receiving the
highest bond strength, which fitted nicely with Baur's rule.

Be—O—Si angles were common among the beryllo-
silicates, varying mostly in the narrow range 120–140°. The
corresponding Be—O bond lengths, however, exhibited a
wide scatter. Many of these Be—O distances were affected by
the phenomenon of edge-sharing, while the corresponding
Be--O—Si angles did not undergo a proportional change
because the edge-sharing never involved the SiO_4 tetrahedra.
Therefore, the regression analysis in this case had to be
performed on values uninfluenced by BeO_4–TO_4 edge-
sharing, where the bond-length increase was expected to be a
maximum (Fig. 2); this led to an r value of −0·59 (0·1%
level of significance), confirming thereby the inverse trend
(ii).

Be—O—Be angles were mostly clustered in two groups,
with oxygens common to edge-sharing Be_2O_6 groups
(leading to relatively smaller angles), or corner-sharing
Be_2O_7 groups. In $La_2Be_2O_5$ and $Y_2SiBe_2O_7$, on the other
hand, BeO_4 tetrahedra shared edges with La and Y polyhedra
respectively. These two structures, again, had relevant bond
lengths and angles very different from the general trend; their
influence on the regression of Be—O length on Be—O—Be

Table 1. *Structures used for examining bond-strength
variations* (Δp_o) *of Be-bonded oxygens with corresponding
Be—O bond-length variations* (Δd) *in individual structures*
(*see Fig.* 1)

| Structure	Reference
Anhydrous beryl	Gibbs, Breck & Meagher (1968)
Anhydrous emerald	Gibbs, Breck & Meagher (1968)
Aminoffite	Coda, Rossi & Ungaretti (1967)
Asbecasite	Cannillo, Giuseppetti & Tadini (1969)
Bavenite	Cannillo, Coda & Fagnani (1966)
Beryllium oxide	Smith, Newkirk & Kahn (1964)
Chrysoberyl	Farrell, Fang & Newnham (1963)
Epididymite	Robinson & Fang (1970)
Euclase	Mrose & Appleman (1962)
Eudidymite	Fang, Robinson & Ohya (1972)
Hambergite	Zachariasen, Plettinger & Marezio (1963)
Helvite	Holloway, Giordano & Peacor (1972)
Herderite	Lager & Gibbs (1974)
Hurlbutite	Lindbloom, Gibbs & Ribbe (1974)
Hydrous beryl	Gibbs, Breck & Meagher (1968)
Hydrous emerald	Gibbs, Breck & Meagher (1968)
$La_2Be_2O_5$	Harris & Yakel (1968)
γ-Li_2BeSiO_4	Howie & West (1974)
$NiYb_2Be_2Si_2O_{10}$	Foit & Gibbs (1975)
Phenakite	Zachariasen (1972)
Tugtupite	Danø (1966)
Väyrynenite	Mrose & Appleman (1962)
$Y_2SiBe_2O_7$	Bartram (1969)
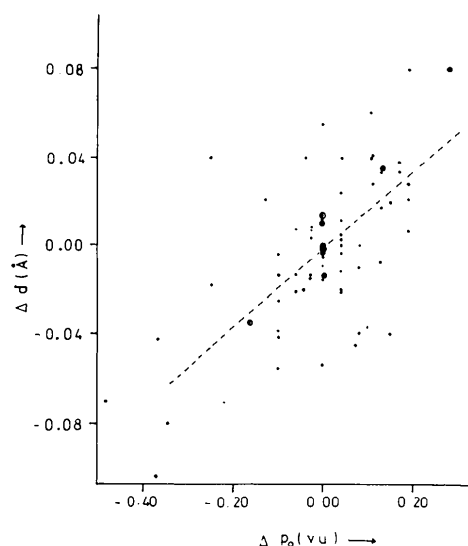
Fig. 1. Scatter diagram showing deviations of Be—O bond lengths
(Δd) *versus* corresponding deviations of bond strength received
by Be-bonded oxygens (Δp_o), both from average values, in 23
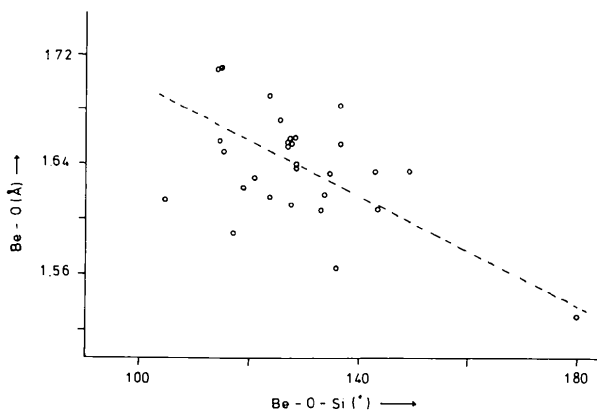inorganic structures. Large dots indicate superimposition of
two or more values.

Fig. 2. Scatter diagram showing variations in Be—O bond length *versus* corresponding Be—O—Si bond-angle variations in beryllo-silicate structures referred to in Table 1 (except epididymite, eudidymite and γ-Li$_2$BeSiO$_4$ for eliminating BeO$_4$–TO$_4$ edge-sharing effect), and the following additional compounds: leifite (Coda, Ungaretti & Della Giusta, 1974); meliphanite (Dal Negro, Rossi & Ungaretti, 1967); leucophanite (Cannillo, Giuseppetti & Tazzoli, 1967); chkalovite (Simonov, Egorov-Tismenko & Belov, 1975).

angle was, however, unusually large because the total number of values available in the literature was rather small. With the exclusion of these two values, the r value for the above regression turned out to be -0.81.

Very few structures considered in this survey contained Be—O(nbr) bonds because such oxygens remained in most cases severely underbonded (beryllium supplied only 0.50 valence units). However, in Y$_2$SiBe$_2$O$_7$, La$_2$Be$_2$O$_5$, NiYb$_2$Be$_2$-Si$_2$O$_{10}$ and herderite the Be—O(nbr) bonds were also the shortest, confirming trend (iii), though bavenite provided an exceptional Be—O(nbr) bond which was the longest of the four; this oxygen received a bond strength of 1.00 valence units from a hydrogen atom and, hence, could afford not to be linked with a tetrahedral silicon and still more than compensate its valence (Cannillo, Coda & Fagnani, 1966).

The observations indicate that the variations in individual and average Be—O lengths and Be—O—T (T = Be, Si) angles fall in line to a large extent with the trends exhibited by silicate and aluminosilicate T—O and T—O—T systems, as outlined earlier. As d–p π-bonding (Brown, Gibbs & Ribbe, 1969) can be ignored in the case of Be—O—T systems, the results obtained seem to point towards a more generalized validity of Baur's (1961, 1971) extended electrostatic valence rule.

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