reflexions to the data sets, as in the case of $K_3[Co(CN)_6]$, is not possible.

The implication of these results is that the partial symmetry operations of the OD groupoid symbol are to be regarded as approximate rather than exact and that the degree to which they are obeyed varies from structure to structure. Ďurovič (1974) has suggested that the more ordered the crystal, the less it complies with the ideal OD model. Although this is consistent with $K_3[Cr(CN)_6]$, which exhibited well-defined maxima on exceedingly weak streaks, it is by no means consistent with $K_3[VO(CN)_5]$ for which the streaks were more or less continuous and without well-defined maxima. Similarly, it would seem somewhat difficult to reconcile this suggestion with preliminary results from the refinement of diaquobis(salicylato)copper(II) (Jagner, Hazell & Larsen, 1975) which indicate that the partial symmetry operations are preserved more exactly in the monoclinic $MDO_2$ structure than in the orthorhombic $MDO_1$ structure, both structures having been solved from the same crystal. Obviously, more evidence is needed before the extent to which the partial symmetry operations relax can be classified and suitably interpreted.

From a practical point of view, since it is usually necessary to impose some sort of constraint, at least during the initial stages of refinement, in order to obtain convergence, it would seem more appropriate to preserve the partial symmetry operations of the OD groupoid symbol, even if these constraints are later released, than to more or less arbitrarily select one or more parameters to be fixed. In those cases where there is little difference between the constrained and unconstrained models, constrained refinement does, of course, yield bond distances and angles with smaller standard deviations.

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# The Crystal Structure of Calcium Orthoborate: a Redetermination

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Single crystals of $Ca_3(BO_3)_2$ have been obtained from the melt. The compound crystallizes in the rhombohedral system, space group $R\bar{3}c$, with six formula units in the hexagonal cell of dimensions $a_H = 8{\cdot}6377$ (8) and $c_H = 11{\cdot}849$ (2) Å. The final $R$ is 0·016, and $R_w$ is 0·024. The $BO_3$ group appears to be non-planar with a B–O distance of 1·3836 (5) Å and an O–B–O angle of 119·95 (4)°. The calcium atom is surrounded by eight nearest oxygens forming a distorted square-antiprism. The $\delta_p$ half-normal probability plot analysis applied to positional and thermal parameters obtained by Schuckmann [*Neues Jb. Miner. Mh.* (1969). **3**, 142–144] against those calculated in this work indicates that the least-squares calculated standard deviations are underestimated by a factor of 1·7.

## Introduction

As a part of a programme to gain an understanding of the structural principles of anhydrous borates, we have undertaken the determination of the crystal structure of calcium orthoborate.

This structure has been reported by Schuckmann (1969) to a good degree of accuracy, and we have undertaken the present investigation for the following reasons:

(1) To verify the non-planarity of the $BO_3$ triangle observed by Schuckmann.

(2) To obtain more accurate bond lengths for the orthoborate group. It is evident that the nature, charge and size of a cation can modify the regular geometry of the $BO_3$ group. Only in a few compounds, *e.g.* $LuBO_3$ (Abrahams, Bernstein & Keve, 1971) and the title compound, is the original threefold symmetry of the orthoborate anion maintained. In the first case, the ability of the $Lu^{3+}$ cation to form covalent bonds with oxygen atoms can cause, in some way, a redistribution of the original electrical charge in the $BO_3^{3-}$ anion, implying a change in the B–O bond length. However, in the present case this ability to form covalent bonds decreases, so that the influence of the $Ca^{2+}$ cation over the $BO_3$ anion could be neglected, and its real charge distribution would thus be maintained; hence, our interest in obtaining very precise results.

(3) We were encouraged by Professor S. C. Abrahams to apply the half-normal probability plot analysis to the thermal and positional parameters obtained in our work and to those obtained by Schuckmann in order to estimate the bias in parameters from the precision values.

## Experimental

Calcium orthoborate was prepared by heating a mixture of $CaCO_3$ and $B_2O_3$ ($3CaCO_3:B_2O_3$), in a Pt crucible, from room temperature up to 800°C. The compound, identified as $Ca_3(BO_3)_2$ by X-ray powder diffraction (Schäfer, 1968), was heated above the melting point (1479°C) (Carlson, 1932) and poor-shaped, colourless single crystals were obtained by slowly decreasing the temperature.

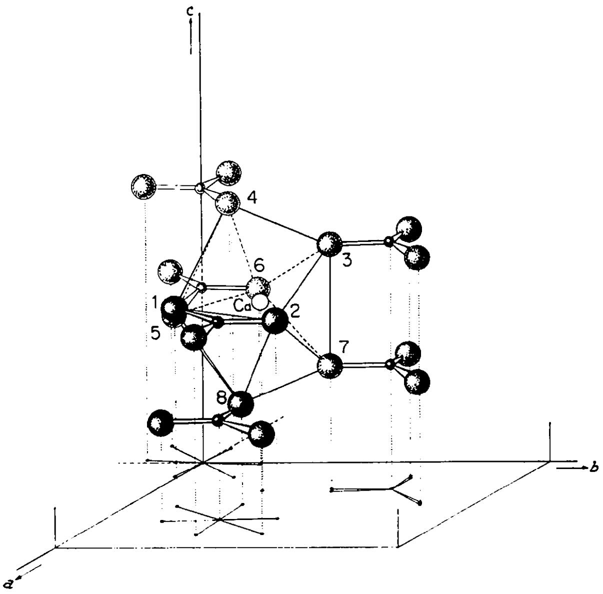

Fig. 1. Atomic arrangement showing the $BO_3$ units and the coordination polyhedron around the Ca atom.

The crystals were identified again by chemical analysis of calcium, X-ray powder diffraction and infrared spectroscopy (Weir & Schröder, 1964).

The previously reported values of the lattice constants (Schäfer) were used to index the powder pattern and more accurate values of cell parameters were obtained by least-squares refinement of the $2\theta$ values measured on a powder diffractometer using silicon as internal standard.

A quasi-spherical crystal ($R=0{\cdot}3$ mm) was used to measure all reflexions within one hemisphere of reciprocal space for $\theta \leq 30°$. The intensities were measured in the $\omega$–$2\theta$ scan mode on a Philips 1100 four-circle diffractometer, using Mo $K\alpha$ radiation monochromated by graphite ($\lambda=0{\cdot}7107$ Å).

The intensities were corrected by Lorentz and polarization factors. No absorption correction was applied since the absorption effect was negligible.

Crystal data are given in Table 1.

Table 1. *Crystal data for calcium orthoborate*

$Ca_3(BO_3)_2$. F.W. 237·62
Rhombohedral; $Z_H=6$
$a_H=8{\cdot}6377$ (8) Å
$c_H=11{\cdot}849$ (2) Å
$V=765{\cdot}60$ (15) Å$^3$
$D_m=3{\cdot}05$; $D_x=3{\cdot}09$ g cm$^{-3}$
$\mu$(Mo $K\alpha$) = 30·3 cm$^{-1}$
Space group $R\bar{3}c$ (No. 167)

## Solution and refinement of the structure

The structure was solved by three-dimensional Patterson and Fourier syntheses using the mean values for the 544 independent reflexions. Of these, 64 were considered as unobserved by the criterion $I_{\text{meas}} \geq 2\sigma(I)$.

From the interpretation of the Patterson map, the Ca atoms were located at the 18(*e*) site $(x,0,\frac{1}{4})$ around the heliocoidal axis. The light atoms were easily recognized in a Fourier map based on the phases given by the heavy atom. The B atoms are located at the 12(*c*) site $(0,0,z)$ while the oxygens occupy the 36(*f*) general position, forming a triangle around the B atom.

At this stage, neutral atomic scattering factors (Cromer, 1965) were assumed and unit weights were assigned to the reflexions for the least-squares procedure. The structure was refined by the full-matrix least-squares method.

The isotropic refinement yielded an $R$ value of 0·080 which was reduced to 0·074 when the thermal parameters were varied anisotropically.

The structure refinement was continued assuming several models for the electrical charges on the atoms and the following sets of atomic scattering factors were tried: (1) B,O,Ca (Cromer, 1965); (2) B,$O^-$,$Ca^{2+}$

(Cromer, 1965);* (3) B, O, Ca (Cromer & Mann, 1968); (4) B, $O^-$, $Ca^{2+}$ (Cromer & Mann, 1968).

In every model, anomalous dispersion coefficients for the calcium atom were used (Cromer & Liberman, 1970).

Two weighting schemes were tried: Firstly $w_1 = 1/\sigma^2(F_{\rm meas})$ with $\sigma^2(F_{\rm meas})$ from counting statistics allowing for crystal and diffractometer instabilities. The second scheme was based on a normal distribution fit to $w\Delta^2$ giving rise to weights $w_2 = 1/\{[(0{\cdot}398 + 0{\cdot}0165F_{\rm obs})^2]\,[5{\cdot}637 - 12{\cdot}876(\sin\theta/\lambda) + 7{\cdot}66(\sin\theta/\lambda)^2]\}$.

The best convergence was obtained by using the $f$ curves of B, $O^-$ and $Ca^{2+}$ (Cromer & Mann, 1968) and the second weighting scheme, the reflexions considered as unobserved being omitted from the least-squares refinement. The maximum value for the ratio of final shifts to the estimated standard deviation was 0·002 for the $x$ coordinate of the Ca atom.

Next, the non-centrosymmetric group $R3c$ was tested for every model and was rejected in the least-squares refinement. As a final check, $\Delta F$ syntheses were calculated for all the cases, confirming the choice of the charged-atom model.

After the last cycle, secondary extinction was corrected (Stout & Jensen, 1968), with a $g$ coefficient of $1{\cdot}584 \times 10^{-3}$, and the $R$ value became $R = 0{\cdot}016$, $R_m = 0{\cdot}015$, $R_w = 0{\cdot}024$, where $R_m = \sum m\,||F_o| - |F_c||/\sum m|F_o|$ and $R_w = \sum w[||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, $m$ being the multiplicity of a reflexion in the reciprocal space and $w$ the weight assigned to each reflexion.†

The positional and thermal parameters are shown in Table 2.

### Description and discussion of the structure

The structure can be described in terms of Ca columns, almost coincident with the $3_1$ axis, delimiting hexagonal prismatic holes around the threefold axes on which the $BO_3^{3-}$ anions are located. These orthoborate groups are coupled through a centre of symmetry.

The calcium atoms are surrounded by eight nearest oxygens, forming a distorted polyhedron (Fig. 1) in which the only symmetry element is a twofold axis passing through the Ca atom. Thus there are only four different Ca–O distances (Table 3) ranging from 2·347 to 2·733 Å (2·488 Å average).

Fig. 1 shows a view of this coordination polyhedron which is in between a distorted square antiprism and a triangular dodecahedron (Lippard & Russ, 1968).

Since the $BO_3$ groups are situated on the threefold axis, all three oxygen atoms are equivalent by symmetry with a B–O distance of 1·3836 (5) Å. The O–B–O angle is 119·95 (4)°.

The distance between two centrosymmetric $BO_3$ triangles is 2·787 Å and the non-centrosymmetric triangles are twisted 7·99° with respect to each other and separated by a distance of 3·137 Å.

The best least-squares plane has been calculated (Schomaker, Waser, Marsh & Bergman, 1959) for the $BO_3$ group. The deviations of atoms from this plane are: $\Delta_B = 0{\cdot}023$ Å and $\Delta_O = -0{\cdot}008$ Å, with a value of $\chi^2 = 535{\cdot}3$, confirming the non-planarity of the $BO_3^{3-}$ anion observed by Schuckmann.

No thermal correction has been applied to the interatomic distances and angles reported in Table 3.

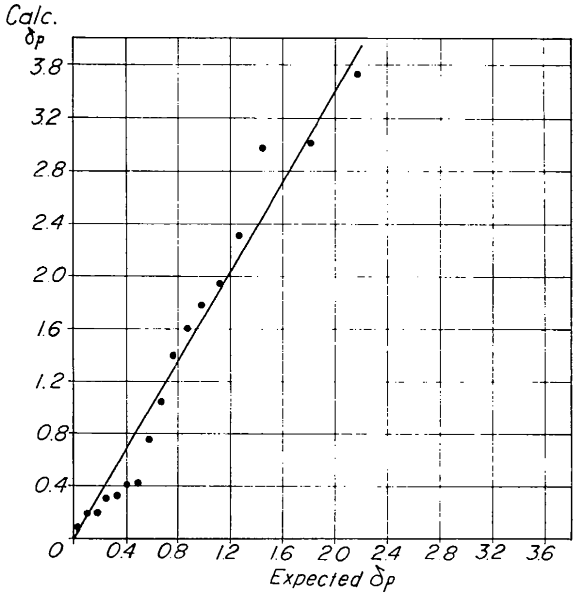

Fig. 2. Half-normal $\delta_p$ probability plot of positional and thermal parameters comparing the Schuckmann values with those derived in the present work. Calculated $\delta_{pi} = ||p(1)_i| - |p(2)_i||/|\sigma^2 p(1)_i + \sigma^2 p(2)_i|^{1/2}$.

Table 2. *Final atomic parameters for* $Ca_3(BO_3)_2$

In the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$ the symmetry requirements are: for $B$, $U_{11} = U_{22} = 2U_{12}$, $U_{13} = U_{23} = 0$; for Ca, $U_{12} = \frac{1}{2}U_{22}$, $U_{13} = \frac{1}{2}U_{23}$. The standard deviations are those obtained in the least-squares refinement.

| | (*a*) Fractional coordinates | | | (*b*) Anisotropic thermal parameters ($\times 10^5$) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x/a$ | $y/b$ | $z/c$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
| B | 0 | 0 | 0·11761 (13) | 645 (19) | 645 (19) | 774 (69) | 323 (10) | 0 | 0 |
| O | 0·16624 (6) | 0·01297 (6) | 0·11496 (6) | 650 (12) | 788 (13) | 1541 (37) | 411 (9) | −235 (12) | −50 (12) |
| Ca | 0·35814 (1) | 0 | $\frac{1}{4}$ | 563 (7) | 665 (6) | 1064 (19) | 332 (3) | 56 (2) | 111 (4) |

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* In this case, the $O^-$ scattering factors (not reported by Cromer) from *International Tables for X-ray Crystallography* were used.

† The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30877 (4 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Interatomic distances* (Å) *and valence angles* (°)

| | | | |
|---|---|---|---|
| BO$_3$ unit | | | |
| B–O | 1·384 (1) | O–B–O | 119·95 (4) |
| Eight-coordination polyhedron | | | |
| Ca—O(1) | 2·440 (1) | O(2)–O(1)–O(4) | 88·37 (4) |
| Ca—O(2) | 2·431 (1) | O(2)–O(1)–O(8) | 66·93 (4) |
| Ca—O(3) | 2·347 (1) | O(5)–O(1)–O(8) | 74·36 (3) |
| Ca—O(4) | 2·732 (1) | O(1)–O(2)–O(3) | 97·43 (4) |
| | | O(1)–O(2)–O(8) | 66·93 (4) |
| O(1)–O(2) | 2·395 (1) | O(7)–O(2)–O(8) | 57·69 (3) |
| O(1)–O(4) | 3·543 (1) | O(7)–O(2)–O(8) | 49·48 (3) |
| O(1)–O(5) | 2·797 (1) | O(2)–O(3)–O(4) | 92·57 (4) |
| O(1)–O(8) | 3·056 (1) | O(2)–O(3)–O(7) | 69·10 (3) |
| O(2)–O(3) | 3·037 (1) | O(1)–O(4)–O(3) | 79·74 (3) |
| O(2)–O(7) | 3·543 (1) | O(1)–O(5)–O(8) | 56·15 (3) |
| O(2)–O(8) | 3·056 (1) | O(2)–O(7)–O(3) | 53·21 (3) |
| O(3)–O(4) | 2·797 (1) | O(2)–O(7)–O(8) | 56·15 (3) |
| O(3)–O(7) | 3·205 (1) | O(1)–O(8)–O(2) | 46·14 (3) |
| | | O(1)–O(8)–O(5) | 49·48 (3) |
| | | O(2)–O(8)–O(7) | 74·36 (4) |

The oxygen atoms are labelled as in Fig. 1. The standard deviations have been corrected with the half-normal probability plot coefficient.

The present results have been tested against Schuckmann's (1969) data. The resulting $\delta_p$-half-normal probability plot is shown in Fig. 2 using theoretical moduli of normal observations calculated for small samples (Hamilton & Abrahams, 1972). All the $\delta_p$ terms lie on an acceptably linear array, with a slope of 1·7, indicating that the majority of the $\delta_p$ values have a random normal distribution of errors but the pooled standard deviations in the difference between corresponding parameters are underestimated by a factor of 1·7. Although the differences between our results and those of Schuckmann are not significant, a slightly higher degree of accuracy has been achieved in this work.

The corrected values for the B–O bond length are $d_{B-O} = 1{\cdot}380$ (2) Å (Schuckmann) and $d_{B-O} = 1{\cdot}384$ (1) Å (this work). This value, in agreement with the 1·38 Å predicted by Shannon & Prewitt (1969), is in our opinion the most accurate B–O bond length reported to date for the BO$_3$ group.

Throughout this work, the X-RAY system of programs was used (Stewart, Kundell & Baldwin, 1970). We gratefully acknowledge the interest of Professor S. C. Abrahams in the development of this work. Thanks are also due to the staff of C.P.D. del Ministerio de Educación y Ciencia for the facilities provided on the 1108 UNIVAC computer. One of us (A.V.) also acknowledges a research grant from M.E.C., Spain.

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