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The Refinement of MDO Structures

By Rita Grønbæk Hazell and Susan Jagner

*Department of Inorganic Chemistry, Aarhus University, DK-*8000 *Aarhus C, Denmark*

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Four MDO structures have been refined with and without constraints with respect to the partial symmetry operations of their OD groupoid symbols. The results indicate that these partial symmetry operations are of approximate rather than exact nature.

During an investigation of the structures of some nitrosyl and cyanide complexes of transition metals, several compounds crystallizing with disordered crystal structures have been encountered. The disorder is of OD type (Dornberger-Schiff, 1966), *i.e.* the structures can be described in terms of ordered, equivalent layers whose mode of stacking is disordered. There are many phenomena by which such structures may be recognized, the most usual being the presence of diffuse streaks in reciprocal space, owing to the non-periodicity in the stacking direction.

Following the methods proposed by Dornberger-Schiff (1966), it has been possible to solve the crystal structures of several such compounds (Svedung & Vannerberg, 1968; Jagner, 1970; Vannerberg, 1970; Vannerberg, 1972; Jagner & Vannerberg, 1973; Jagner, Ljungström & Vannerberg, 1974; Jagner, 1975). In the determination of an OD structure it is customary first to deduce the OD groupoid symbol from the systematic absences afforded by the discrete reflexions and diffuse streaks. This symbol gives the total symmetry of any pair of consecutive layers, *i.e.* the partial symmetry operations within a single layer and those which convert one layer into the next. It thus characterizes the whole family of structures in which the compound crystallizes. Following the determination of the superposition structure from the discrete, or 'family', reflexions, one or more of the ordered extreme structures, or 'structures of maximum degree of order', MDO, (Dornberger-Schiff, 1966) is then determined by including the intensities of the streaks measured at the relevant reciprocal lattice points. Normally, the intensity distribution on the streaks is such that only one of the possible MDO structures can be determined with any precision.

The least-squares refinement of MDO structures is often problematic, owing to large correlations between parameters related in the superposition structure, and, in order to stabilize the refinement, it has usually proved necessary to hold one or more parameters fixed. Quite apart from the practical necessity of constraining in order to obtain convergence, it would seem logical that the partial symmetry operations of the OD groupoid symbol should be preserved if they have any exact meaning. Such symmetry operations are rarely all accounted for by the space group of the MDO structure.

In order to test the appropriateness of the use of constraints in the refinement of MDO structures, rerefinement of three such structures has been undertaken. The results of the refinement of a fourth MDO structure, $K_4[V(CN)_6]$, in which the partial symmetry operations of the layer had been constrained in the original refinement (Jagner, 1975), have been included for the purpose of comparison.

All refinement was carried out with the full-matrix least-squares program *LINUS* (Busing, Martin & Levy, 1962; Coppens & Hamilton, 1970), with scattering factors due to Cromer & Mann (1968). Unit weights were assigned to all reflexions, the family and non-family reflexions being scaled with separate scale factors. The different models were tested by means of *R* factor tests (Hamilton, 1965), with the approximation due to Pawley (1970).

Example 1: $K_3[Cr(CN)_6]$ (*Jagner, Ljungström & Vannerberg*, 1974)

The family of structures in which $K_3[Cr(CN)_6]$ crystallizes is characterized by the OD groupoid symbol:

$$\begin{array}{l} Pma(n) \\ \{c_2 n_{2,1/2}(n_{1/2,\,1})\}\ . \end{array}$$

The ordered orthorhombic structure (MDO_1) was determined from 372 family reflexions (*hkl*, $h=2n$) and 322 non-family reflexions (*hkl*, $h=2n+1$). The MDO_1 structure has a unit cell with $a=8{\cdot}5256\,(9)$, $b=10{\cdot}6000\,(12)$, and $c=13{\cdot}6840\,(13)$ Å, space group *Pcan*, $Z=4$. The Cr atom and one K atom occupy special positions 4(*c*), whereas all other atoms occupy the general position $\pm(x,y,z;\ \frac{1}{2}-x,\frac{1}{2}-y,\frac{1}{2}+z;\ \frac{1}{2}-x,\frac{1}{2}+y,\bar{z};\ x,\bar{y},\frac{1}{2}-z)$.

Three modes of refinement were investigated. In the first (I), the partial symmetry operations of the OD groupoid symbol were preserved for all atoms by introducing the extra equivalent positions: $\pm(\frac{1}{4}-x,y,z;\ \frac{1}{4}+x,\frac{1}{2}-y,\frac{1}{2}+z;\ \frac{1}{4}+x,\frac{1}{2}+y,\bar{z};\ \frac{1}{4}-x,\bar{y},\frac{1}{2}-z)$. In other words, Cr, K(1), K(2), C(1) and N(1) were constrained to lie on the mirror planes indicated in Fig. 1, while C(2) and C(3) and N(2) and N(3) were related by these planes. It is seen that all the partial symmetry operations of the OD groupoid symbol are preserved by inserting the mirror plane of the layer. This refinement (47 parameters) yielded $R=0{\cdot}056$ ($R_w=0{\cdot}056$), where R and R_w are defined as $R=\sum\limits_i w_i^{1/2}|F_i|_o-|F_i|_c/\sum\limits_i w_i^{1/2}|F_i|_o$ and $R_w=[\sum\limits_i w_i(|F_i|_o-|F_i|_c)^2/\sum\limits_i w_i|F_i|_o^2]^{1/2}$. In the second refinement (50 parameters), the partial mirror plane of the layer was assumed to apply to K(1) and to the $[Cr(CN)_6]^{3-}$ ion, but not to K(2). Cr, K(1), N(1), N(2), C(1) and C(2) were thus refined with the equivalent positions employed in refinement (I), while K(2) was refined with the equipoints of *Pcan*. Refinement (II) yielded $R=0{\cdot}054$ and $R_w=0{\cdot}055$. Finally, the constraints were released and refinement (III) was carried out in *Pcan* (76 parameters), an R of 0·047 ($R_w=0{\cdot}050$) being obtained. The scale factors for the family and non-family reflexions differed by less than one-tenth of a standard deviation in the three cases.

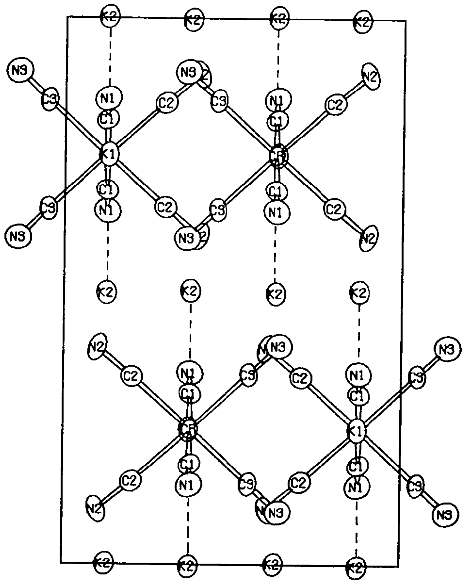

Fig. 1. Projection of a unit cell of the MDO_1 structure of $K_3[Cr(CN)_6]$ along [010]. The *a* axis is horizontal. The partial mirror planes of the OD layers are indicated with dotted lines.

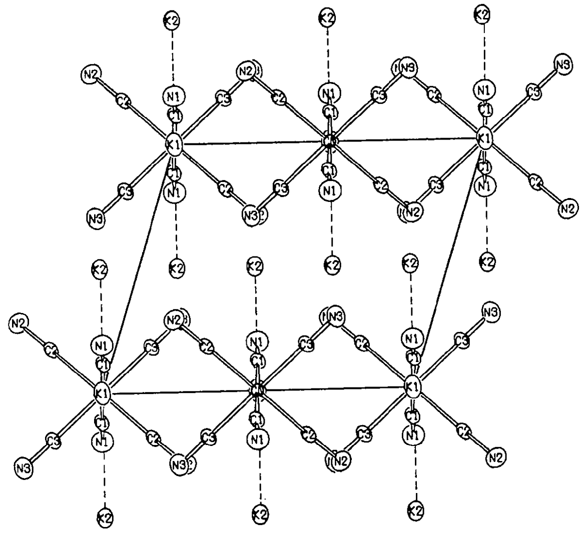

Fig. 2. Projection of the MDO_2 structure of $K_3[Co(CN)_6]$ along [010]. The *a* axis is horizontal and the unit cell is indicated with full lines. The partial mirror planes of the OD layers are indicated with dotted lines.

The results of R factor tests on the R_w values obtained for the different models are given in Table 1. It is evident that the addition of 29 extra parameters in going from the constrained to the completely unconstrained model leads to a highly significant improvement in the agreement between observed and calculated structure factors. Although the model in which K(2) is released from the partial mirror plane of the layer is more appropriate than that in which the mirror plane is preserved for all atoms, it is inferior to the completely unconstrained model. The original refinement (Jagner *et al.*, 1974) was stabilized by holding x_{Cr} fixed at 0·125. This resulted in an R of 0·046 ($R_w=0{\cdot}049$), *i.e.* lower R and R_w values were obtained with 75 parameters as compared with 76 parameters in the unconstrained refinement.

Table 1. *R factor tests on the three different models investigated for* $K_3[Cr(CN)_6]$

The models I, II and III are as described in the text. $\mathscr{R}_{\text{exp}}=R_{w,p}/R_{w,q}$.

Model				$\mathscr{R}_{b,n-m,\alpha}$		
p/q	$\mathscr{R}_{\text{exp}}$	b	$n-m$	$\alpha=0{\cdot}05$	$\alpha=0{\cdot}01$	$\alpha=0{\cdot}001$
I/III	1·1295	29	618	1·0343	1·0400	1·0472
I/II	1·0235	3	644	1·0055	1·0078	1·0112
II/III	1·1035	26	618	1·0313	1·0369	1·0437

Example 2: $K_3[Co(CN)_6]$ (*Vannerberg*, 1972)

$K_3[Co(CN)_6]$ crystallizes as a family of structures characterized by the same OD groupoid as $K_3[Cr(CN)_6]$ (see Example 1). The MDO_2 structure [$a=8{\cdot}367$ (6), $b=10{\cdot}363$ (8), $c=6{\cdot}994$ (10) Å, $\beta=107{\cdot}40$ (4)°, space group $P2_1/a$, $Z=2$] was solved from 461 family reflexions and 184 non-family reflexions and originally refined without constraints (I; 77 parameters) to $R=0{\cdot}069$ ($R_w=0{\cdot}075$). The Co and one K atom occupy the special positions 2(*a*) and 2(*c*), respectively, while all other atoms occupy the general position 4(*c*), *i.e.* $\pm(x,y,z;\ \tfrac{1}{2}+x,\tfrac{1}{2}-y,z)$.

As for $K_3[Cr(CN)_6]$, two additional models were investigated. The unit cell of the MDO_2 structure contains a single layer whose symmetry, *Pma*(*n*), was preserved (II) by introducing the extra equivalent positions $\pm(z/2-x,y,z;\ \tfrac{1}{2}+z/2-x,\tfrac{1}{2}-y,z)$; see Fig. 2. The z coordinates of the atoms situated on the mirror plane were refined while the x coordinates were reset to $x=0{\cdot}25z$. Similarly, the β_{12} and β_{13} parameters of these atoms were reset to $\beta_{12}=0{\cdot}25\beta_{23}$ and $\beta_{13}=0{\cdot}25\beta_{33}$, respectively. The constrained refinement (46 parameters) yielded $R=0{\cdot}073$ ($R_w=0{\cdot}080$). In the third refinement (III; 49 parameters), K(2) was released from the mirror plane of the layer and refined with the equipoints of $P2_1/a$, while the remaining atoms were constrained so that the layer mirror plane was preserved. This yielded $R=0{\cdot}073$ ($R_w=0{\cdot}080$).

The space group of the MDO_2 structure does not require that the reflexion condition $hk0$: $h+k=2n$ (indexed according to $a=8{\cdot}37$, $b=10{\cdot}36$ and $c=13{\cdot}34$ Å) used in the derivation of the OD groupoid symbol (Vannerberg, 1972) be preserved. Twenty such reflexions with $F_o=0{\cdot}0$ were therefore inserted in the data set with unit weights and the three models were re-investigated. Finally, constrained and unconstrained refinement was repeated, double weight being assigned to these zero reflexions. The results of R factor tests on the different models are given in Table 2. There were no significant differences between the factors scaling the family and non-family reflexions in the different refinements.

Table 2. *R factor tests on the different models investigated for* $K_3[Co(CN)_6]$

The models I, II and III are as described in the text. *A* denotes the original data set, *B* the data set containing zero reflexions with unit weight, and *C* the data set containing zero reflexions with double weight. $\mathscr{R}_{\text{exp}}=R_{w,p}/R_{w,q}$.

	Model				$\mathscr{R}_{b,n-m,\alpha}$		
	p/q	$\mathscr{R}_{\text{exp}}$	b	$n-m$	$\alpha=0{\cdot}05$	$\alpha=0{\cdot}01$	$\alpha=0{\cdot}001$
	II/I	1·0619	31	568	1·0394	1·0458	1·0538
A	II/III	1·0040	3	596	1·0059	1·0084	1·0121
	III/I	1·0577	28	568	1·0362	1·0424	1·0501
	II/I	1·0562	31	588	1·0380	1·0442	1·0519
B	II/III	1·0030	3	616	1·0057	1·0082	1·0117
	III/I	1·0530	28	588	1·0350	1·0410	1·0484
C	II/I	1·0474	31	588	1·0380	1·0442	1·0519

As can be seen from Table 2, for the original data set the unconstrained model must be considered to provide a significantly better agreement between observed and calculated structure factors. The release of K(2) alone does not, however, yield significant improvement. It is, moreover, apparent that the constrained model can be forced to yield significantly better agreement between observed and calculated structure factors by increasing the weight assigned to the systematically absent $hk0$: $h+k=2n$ reflexions.

Example 3: $K_3[VO(CN)_5]$ (*Jagner & Vannerberg*, 1973)

$K_3[VO(CN)_5]$ crystallizes with a disordered structure characterized by the OD groupoid symbol:

$$\begin{gathered} P(n)m2_1 \\ \{(n_{\bar{1}/2,1})a_2 2_1\} \end{gathered}$$

the **a** direction being that of non-periodicity. The MDO_1 structure [$a=13{\cdot}4700$ (12) Å, $b=8{\cdot}5292$ (6) Å, $c=9{\cdot}7818$ (15) Å, space group $Pna2_1$, $Z=4$] was determined from visually estimated film data [292 family reflexions (hkl, $k=2n$) and 235 non-family reflexions (hkl, $k=2n+1$)]. All atoms occupy general positions.

In the original refinement the V and K atoms were assigned anisotropic temperature factors while the ligand atoms were assumed to vibrate isotropically. A repeat of this refinement with unit weights (I; 81 parameters) yielded $R=0{\cdot}082$ and $R_w=0{\cdot}090$. The positional and thermal parameters were then constrained to comply with the partial symmetry operations of the OD groupoid symbol by introducing the extra equipoints: $x,\frac{1}{4}-y,z$; $\bar{x},\frac{3}{4}+y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{3}{4}-y,$

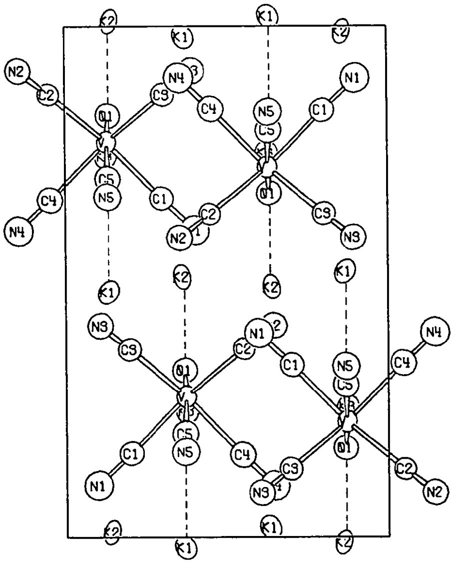

Fig. 3. Projection of a unit cell of the MDO_1 structure of $K_3[VO(CN)_5]$ along [001]. The b axis is horizontal. The partial mirror planes of the OD layers are indicated with dotted lines.

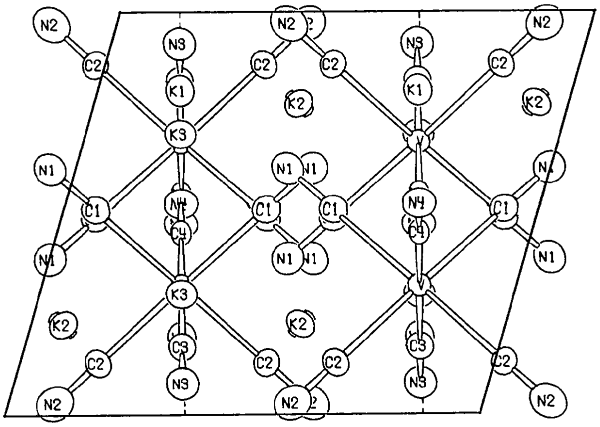

Fig. 4. Projection of a unit cell of the MDO_2 structure of $K_4[V(CN)_6]$ along [010]. The a axis is horizontal. The partial mirror planes of the OD layer are indicated with dotted lines.

$\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{4}+y,z$, anisotropic temperature factors being included for all atoms. K(1) and K(2) could either be situated on the layer mirror plane indicated in Fig. 3 or placed as a single general position in the layer. The former arrangement (II; 79 parameters) yielded $R=0\cdot089$ ($R_w=0\cdot096$), while the latter gave $R=0\cdot129$ ($R_w=0\cdot145$) and was therefore rejected. As in the case of $K_3[Cr(CN)_6]$, the addition of the partial mirror plane of the layer was sufficient to preserve both the layer and the inter-layer partial symmetry operations.

Owing to the small number of data available, the completely unconstrained refinement with anisotropic temperature factors for all atoms (136 parameters) failed to converge and yielded an R of 0·14. The structure was therefore refined without extra symmetry constraints but with isotropic temperature factors for all atoms (III; 61 parameters). This yielded $R=0\cdot098$ and $R_w=0\cdot108$. Finally, K(1) and K(2) were released from the mirror plane of the layer and were refined with the equipoints of $Pna2_1$, while the remaining atoms were constrained as in refinement (II). This yielded $R=0\cdot085$ and $R_w=0\cdot091$ (85 parameters). The scale factors in all four refinements differed by less than one standard deviation.

The results of R factor tests on the different models are given in Table 3. It is evident that the constrained model (II) is significantly better than the unconstrained model in which all atoms are assumed to have isotropic temperature factors (III). It is, on the other hand, inferior to the original model (I). When K(1) and K(2) are released from the mirror plane constraint, (IV), there is significant improvement in the agreement between observed and calculated structure factors compared with that provided by the constrained refinement (II). This indicates that the unconstrained model with anisotropic temperature factors for all atoms would be favoured could it be realized. For the data available the original model without extra symmetry constraints but with isotropic temperature factors for the ligand atoms would seem to be the most appropriate.

Example 4: $K_4[V(CN)_6]$ (*Jagner*, 1975)

$K_4[V(CN)_6]$ crystallizes with a disordered structure characterized by the OD groupoid symbol:

$$\begin{gathered} Pma(b) \\ \{c_2 n_{2,\bar{1}/2}(n_{1/2,1})\} \end{gathered}$$

the **c** direction thus being that of non-periodicity.

Table 3. *R factor tests on the different models investigated for* $K_3[VO(CN)_5]$

Models I, II, III and IV are as described in the text. $\mathscr{R}_{\rm exp}=R_{w,p}/R_{w,q}$.

Model				$\mathscr{R}_{b,n-m,\alpha}$		
p/q	$\mathscr{R}_{\rm exp}$	b	$n-m$	$\alpha=0\cdot05$	$\alpha=0\cdot01$	$\alpha=0\cdot001$
II/I	1·0693	2	446	1·0047	1·0070	1·0111
III/II	1·1230	18	448	1·0321	1·0388	1·0473
II/IV	1·0516	6	442	1·0140	1·0187	1·0248
III/IV	1·1810	24	442	1·0410	1·0485	1·0580
III/I	1·2009	20	446	1·0351	1·0421	1·0509

The MDO_2 structure ($a=8\cdot5770$ (6), $b=21\cdot5271$ (26), $c=7\cdot5270$ (8) Å, $\beta=106\cdot55$ (1)°, space group $P2_1/a$, $Z=4$) was determined from 641 family reflexions (hkl, $h=2n$) and 116 non-family reflexions (hkl, $h=2n+1$), measured on the streaks, $hk\zeta$, at the reciprocal lattice points corresponding to the monoclinic unit cell. All atoms occupy the general position 4(*e*), *i.e.* $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,z)$.

The MDO_2 structure, which contains a single OD layer, was constrained to have $Pma(b)$ symmetry (see Fig. 4) by the introduction of the following equivalent positions: $\pm(x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,z;\ \frac{1}{4}+z/2-x,y,z;\ \frac{3}{4}+z/2-x,\frac{1}{2}-y,z)$. The z coordinates of the atoms situated on the mirror plane, *i.e.* K(1), K(3), V, C(3), N(3), C(4) and N(4), were refined, while the x coordinates were reset to $x=\frac{1}{8}+z/4$. Similarly, β_{12} and β_{13} for these atoms were reset to $\beta_{12}=0\cdot25\beta_{23}$ and $\beta_{13}=0\cdot25\beta_{33}$, respectively. The refinement converged to an R of 0·053 ($R_w=0\cdot055$). On release of the constraints, R dropped to 0·049 ($R_w=0\cdot051$). The scale factors in the two refinements differed by less than one-half a standard deviation.

The hypothesis that the constrained refinement (89 parameters) provided a more appropriate model than the unconstrained refinement (155 parameters) was tested by means of an R factor test. The R factor ratio ($R_{w,\rm constr.}/R_{w,\rm unconstr.}=1\cdot0734$) indicated that, although the hypothesis could be rejected at the 0·05 probability level ($\mathscr{R}_{66,602,0.05}=1\cdot0702$), it could not be rejected at the 0·01 level ($\mathscr{R}_{66,602,0.01}=1\cdot0784$). The introduction of 66 extra parameters thus resulted in a barely significant improvement in the agreement between observed and calculated structure factors.

Conclusions

Only in the case of $K_4[V(CN)_6]$ does refinement in which the positional and thermal parameters are constrained to comply with the partial symmetry operations of the OD groupoid symbol yield a model justifiable on a statistical basis for a normal data set. For $K_3[Co(CN)_6]$ such a model is acceptable if systematically absent reflexions not required by space-group symmetry are given double weight. This is, of course, a reasonable assignment, bearing in mind that photographs of substances crystallizing with OD structures usually have to be considerably over-exposed in order that the OD groupoid symbol can be determined with certainty. For $K_3[Cr(CN)_6]$ and $K_3[VO(CN)_6]$, models based only on the space-group symmetries of the MDO_1 structures yield the most satisfactory agreement between observed and calculated structure factors. Since the systematic absences from which the OD groupoid symbols are derived are all required by the space groups of these structures, the addition of zero 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

By A. Vegas, F. H. Cano and S. García-Blanco

Instituto de Química-Física 'Rocasolano', CSIC Serrano 119, *Madrid*-6, *Spain*

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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 δ_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.