

## The Crystal Structure of Potassium Binoxalate

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The structure of potassium binoxalate,  $\text{KHC}_2\text{O}_4$ , has been redetermined using 1266 data collected on a diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. Absorption, secondary-extinction and anomalous-dispersion corrections were applied. The hydrogen atom was located in a difference map. Least-squares refinement included anisotropic temperature parameters for all atoms and converged with a final  $R$  index of 0.027. The material crystallizes in space group  $P2_1/c$  with  $Z=4$ . Comparison with previous results [Pedersen, B. F. *Acta Chem. Scand.* (1968), **22**, 2953] prompted a remeasurement of lattice constants using a Straumanis camera. Final values are  $a=4.3043$  (2),  $b=12.8334$  (2),  $c=7.6322$  (2) Å and  $\beta=102.01$  (2)°. These results confirm the conclusion of Pedersen that the hydrogen bond [O...O distance = 2.523 (2) Å] has an asymmetric potential.

### Introduction

Hendricks (1935) published the crystal data for potassium binoxalate, choosing space group  $P2_1/n$  with  $Z=4$ . The crystal structure was published by Pedersen (1968). This investigation was undertaken in ignorance of Pedersen's work in order to examine the hydrogen bond. As the acid salt of a monobasic acid with one molecule per asymmetric unit, this compound might be expected to exhibit a short hydrogen bond whose hydrogen position would not be subject to ambiguities introduced by crystallographic symmetry. [For a review of this subject, see Ibers (1965).]

### Experimental

A supply of the compound was purchased from Amend Drug and Chemical Company. A single crystal in the shape of a triangular prism 0.22 (3) mm in length was selected from a portion recrystallized from aqueous solution. The base of the prism was approximately an isosceles right triangle with legs 0.42 (3) mm in length. The crystal was mounted with the fiber axis approximately parallel to one of the legs (the  $a$  axis). It was aligned on a Picker diffractometer equipped with a graphite monochromator and molybdenum  $K\alpha$  radiation. The lattice constants, set I of Table 1, corresponding to a cell with space group  $P2_1/c$ , were used for data collection. These lattice constants are the result of a least-squares fit to eleven  $2\theta$  values greater than 49°, measured using a take-off angle of 0.5° and a narrow vertical slit. Data were collected in the  $\theta$ - $2\theta$  scan mode out to 61° in  $2\theta$  using a scan rate of

2° per min and a 20 sec count time for each background. Aluminum foil attenuators were automatically inserted when the counting rate exceeded 7000 counts per sec during the scan. The intensities of three standard reflections, collected every fifty reflections, held constant throughout the data collection. 1266 unique reflections were collected.

Table 1. *Lattice constants*

Set I contains the initial values obtained from diffractometer measurements. Set II contains the values of Pedersen (1968). Set III lists the values obtained by remeasurement on a precision Weissenberg camera of 10 cm diameter in which the film is placed asymmetrically (Straumanis's principle).

	I	II	III
$a$	4.2992 (4) Å	4.319 Å	4.3043 (2) Å
$b$	12.827 (1)	12.890	12.8334 (2)
$c$	7.6202 (8)	7.660	7.6322 (2)
$\beta$	101.93 (1)°	101.96°	102.01 (2)°
$\rho_{\text{calc}}(\text{g.cm}^{-3})$	2.070	2.040	2.064
$T$	21 ± 2°C		24 ± 2°C

$\rho_{\text{meas}} = 2.066 \text{ g.cm}^{-3}$  (Hendricks, 1935).

Raw intensities were corrected for background in the usual manner. Variances,  $\sigma^2(I)$ , were obtained from counting statistics with an additional intensity-dependent term,  $(pI)^2$ , where  $p$  was estimated from analysis of the standards to be 0.016. Intensities and variances were corrected for Lorentz-polarization and absorption effects. Absorption corrections were made using the method of De Meulenaer & Tompa (1965) with an absorption coefficient of 11.6  $\text{cm}^{-1}$ . Transmission factors ranged from 0.80 to 0.75.

\* Contribution No. 4369.

## Structure determination and refinement

The position of the potassium atom was readily determined from a three-dimensional Patterson map. Interpretation of this map with the aid of a two-dimensional superposition down a on the potassium

positions permitted location of all other non-hydrogen atoms. The initial structure-factor calculation gave an  $R$  index, defined as  $\sum |F_o| - |F_c| / \sum |F_o|$ , of 0.23. Form factors for  $K^+$ , C and O were taken from *International Tables for X-ray Crystallography* (1962). The hydrogen atom was located in a difference map following three

Table 2. Positional and thermal parameters

Parameters for K(1) to C(7) are multiplied by  $10^5$ ; parameters for H(8) are multiplied by  $10^3$ . Anisotropic temperature factors are expressed as:

$$\exp \{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})\}.$$

E.s.d.'s are in parentheses. Atom labels and origin differ from those of Pedersen (1968), the latter by a shift of  $a/2$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
K(1)	31310 (6)	6917 (2)	22748 (3)	3687 (18)	268 (2)	1039 (5)	-41 (6)	-890 (13)	-53 (3)
O(2)	120668 (21)	43564 (4)	35043 (12)	3496 (46)	286 (5)	1085 (16)	-71 (22)	-905 (42)	-157 (12)
O(3)	135885 (20)	27013 (7)	33318 (12)	3237 (46)	323 (5)	1253 (16)	484 (24)	-1787 (43)	-107 (14)
O(4)	74914 (23)	40010 (7)	4916 (13)	5418 (64)	294 (5)	1459 (19)	430 (28)	-3089 (56)	-5 (15)
O(5)	83928 (20)	22947 (7)	8711 (12)	2778 (44)	267 (5)	1076 (15)	130 (22)	-1125 (40)	-156 (13)
C(6)	118102 (23)	34712 (8)	28604 (13)	2215 (49)	290 (6)	715 (16)	-64 (25)	-435 (44)	41 (14)
C(7)	89823 (24)	32766 (8)	12652 (14)	2483 (50)	278 (6)	795 (16)	135 (27)	-605 (46)	-63 (15)
H(8)	676 (5)	225 (1)	-2 (3)	110 (21)	1 (1)	35 (6)	-8 (8)	46 (19)	0 (4)

Table 3. Observed and calculated structure factors including e.s.d.'s for the observed values ( $\times 10^2$ )

The final value of the secondary-extinction parameter (equation 3, Larson, 1967) is  $2.1(1) \times 10^{-5} e^{-2}$ .

$h$	$k$	$l$	$F_o$	$F_c$	$e.s.d.$	$h$	$k$	$l$	$F_o$	$F_c$	$e.s.d.$
0	0	0	1000	1000	0	0	0	0	1000	1000	0
0	0	1	120	120	0	0	0	1	120	120	0
0	0	2	240	240	0	0	0	2	240	240	0
0	0	3	360	360	0	0	0	3	360	360	0
0	0	4	480	480	0	0	0	4	480	480	0
0	0	5	600	600	0	0	0	5	600	600	0
0	0	6	720	720	0	0	0	6	720	720	0
0	0	7	840	840	0	0	0	7	840	840	0
0	0	8	960	960	0	0	0	8	960	960	0
0	0	9	1080	1080	0	0	0	9	1080	1080	0
0	0	10	1200	1200	0	0	0	10	1200	1200	0
0	0	11	1320	1320	0	0	0	11	1320	1320	0
0	0	12	1440	1440	0	0	0	12	1440	1440	0
0	0	13	1560	1560	0	0	0	13	1560	1560	0
0	0	14	1680	1680	0	0	0	14	1680	1680	0
0	0	15	1800	1800	0	0	0	15	1800	1800	0
0	0	16	1920	1920	0	0	0	16	1920	1920	0
0	0	17	2040	2040	0	0	0	17	2040	2040	0
0	0	18	2160	2160	0	0	0	18	2160	2160	0
0	0	19	2280	2280	0	0	0	19	2280	2280	0
0	0	20	2400	2400	0	0	0	20	2400	2400	0
0	0	21	2520	2520	0	0	0	21	2520	2520	0
0	0	22	2640	2640	0	0	0	22	2640	2640	0
0	0	23	2760	2760	0	0	0	23	2760	2760	0
0	0	24	2880	2880	0	0	0	24	2880	2880	0
0	0	25	3000	3000	0	0	0	25	3000	3000	0
0	0	26	3120	3120	0	0	0	26	3120	3120	0
0	0	27	3240	3240	0	0	0	27	3240	3240	0
0	0	28	3360	3360	0	0	0	28	3360	3360	0
0	0	29	3480	3480	0	0	0	29	3480	3480	0
0	0	30	3600	3600	0	0	0	30	3600	3600	0
0	0	31	3720	3720	0	0	0	31	3720	3720	0
0	0	32	3840	3840	0	0	0	32	3840	3840	0
0	0	33	3960	3960	0	0	0	33	3960	3960	0
0	0	34	4080	4080	0	0	0	34	4080	4080	0
0	0	35	4200	4200	0	0	0	35	4200	4200	0
0	0	36	4320	4320	0	0	0	36	4320	4320	0
0	0	37	4440	4440	0	0	0	37	4440	4440	0
0	0	38	4560	4560	0	0	0	38	4560	4560	0
0	0	39	4680	4680	0	0	0	39	4680	4680	0
0	0	40	4800	4800	0	0	0	40	4800	4800	0
0	0	41	4920	4920	0	0	0	41	4920	4920	0
0	0	42	5040	5040	0	0	0	42	5040	5040	0
0	0	43	5160	5160	0	0	0	43	5160	5160	0
0	0	44	5280	5280	0	0	0	44	5280	5280	0
0	0	45	5400	5400	0	0	0	45	5400	5400	0
0	0	46	5520	5520	0	0	0	46	5520	5520	0
0	0	47	5640	5640	0	0	0	47	5640	5640	0
0	0	48	5760	5760	0	0	0	48	5760	5760	0
0	0	49	5880	5880	0	0	0	49	5880	5880	0
0	0	50	6000	6000	0	0	0	50	6000	6000	0
0	0	51	6120	6120	0	0	0	51	6120	6120	0
0	0	52	6240	6240	0	0	0	52	6240	6240	0
0	0	53	6360	6360	0	0	0	53	6360	6360	0
0	0	54	6480	6480	0	0	0	54	6480	6480	0
0	0	55	6600	6600	0	0	0	55	6600	6600	0
0	0	56	6720	6720	0	0	0	56	6720	6720	0
0	0	57	6840	6840	0	0	0	57	6840	6840	0
0	0	58	6960	6960	0	0	0	58	6960	6960	0
0	0	59	7080	7080	0	0	0	59	7080	7080	0
0	0	60	7200	7200	0	0	0	60	7200	7200	0
0	0	61	7320	7320	0	0	0	61	7320	7320	0
0	0	62	7440	7440	0	0	0	62	7440	7440	0
0	0	63	7560	7560	0	0	0	63	7560	7560	0
0	0	64	7680	7680	0	0	0	64	7680	7680	0
0	0	65	7800	7800	0	0	0	65	7800	7800	0
0	0	66	7920	7920	0	0	0	66	7920	7920	0
0	0	67	8040	8040	0	0	0	67	8040	8040	0
0	0	68	8160	8160	0	0	0	68	8160	8160	0
0	0	69	8280	8280	0	0	0	69	8280	8280	0
0	0	70	8400	8400	0	0	0	70	8400	8400	0
0	0	71	8520	8520	0	0	0	71	8520	8520	0
0	0	72	8640	8640	0	0	0	72	8640	8640	0
0	0	73	8760	8760	0	0	0	73	8760	8760	0
0	0	74	8880	8880	0	0	0	74	8880	8880	0
0	0	75	9000	9000	0	0	0	75	9000	9000	0
0	0	76	9120	9120	0	0	0	76	9120	9120	0
0	0	77	9240	9240	0	0	0	77	9240	9240	0
0	0	78	9360	9360	0	0	0	78	9360	9360	0
0	0	79	9480	9480	0	0	0	79	9480	9480	0
0	0	80	9600	9600	0	0	0	80	9600	9600	0
0	0	81	9720	9720	0	0	0	81	9720	9720	0
0	0	82	9840	9840	0	0	0	82	9840	9840	0
0	0	83	9960	9960	0	0	0	83	9960	9960	0
0	0	84	10080	10080	0	0	0	84	10080	10080	0
0	0	85	10200	10200	0	0	0	85	10200	10200	0
0	0	86	10320	10320	0	0	0	86	10320	10320	0
0	0	87	10440	10440	0	0	0	87	10440	10440	0
0	0	88	10560	10560	0	0	0	88	10560	10560	0
0	0	89	10680	10680	0	0	0	89	10680	10680	0
0	0	90	10800	10800	0	0	0	90	10800	10800	0
0	0	91	10920	10920	0	0	0	91	10920	10920	0
0	0	92	11040	11040	0	0	0	92	11040	11040	0
0	0	93	11160	11160	0	0	0	93	11160	11160	0
0	0	94	11280	11280	0	0	0	94	11280	11280	0
0	0	95	11400	11400	0	0	0	95	11400	11400	0
0	0	96	11520	11520	0	0	0	96	11520	11520	0
0	0	97	11640	11640	0	0</					

cycles of isotropic least-squares refinement. Subsequent refinement incorporated the hydrogen form factor of Stewart, Davidson & Simpson (1965), and a correction for the anomalous dispersion of potassium [for Mo  $K\alpha_1$ ,  $\Delta f' = 0.235^*$  (Cromer & Liberman, 1969)]. This least-squares procedure minimized the function  $\sum w(F_o^2 - F_c^2)^2$  where the weights  $w$  were taken as  $1/\sigma^2(F_o^2)$ . Refinement was ended after convergence with an  $R$  index of 0.027 and a goodness-of-fit of 2.5. The optimized parameters totalled 74 and included anisotropic temperature factors for all atoms and a secondary-extinction coefficient (Larson, 1967).

Final values of the parameters are listed in Table 2. Table 3 contains values of the observed and calculated structure factors for each reflection. A final difference map in the average plane of the binoxalate ion showed residual electron density in the C-C and C-O bonds of 0.5 and 0.2  $e.\text{\AA}^{-3}$  respectively. The standard deviation of electron density is estimated to be 0.1  $e.\text{\AA}^{-3}$ .

\* This value, taken from preliminary results, is larger than the revised value (Cromer & Liberman, 1970) by some 0.05 e.

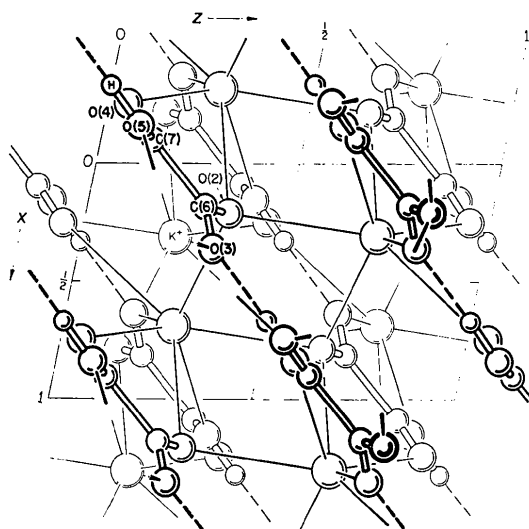


Fig. 1. The structure projected on (010).

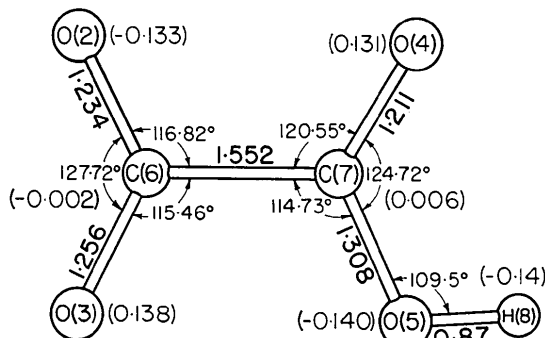


Fig. 2. Bond distances ( $\text{\AA}$ ) and angles for the binoxalate anion. Deviations ( $\text{\AA}$ ) from the mean plane are given in parentheses.

tion of electron density is estimated to be 0.1  $e.\text{\AA}^{-3}$ .

It was at this point that Pedersen's work on this compound came to our attention. With the exception of some of the temperature coefficients of the potassium atom, none of our parameters differ from those of Pedersen by more than three of her e.s.d.'s (which are nearly ten times as large as ours). The difference in temperature factors for potassium (Pedersen's are systematically smaller than ours) may be due to her neglect of anomalous dispersion [ $\Delta f' = 0.365$  for Cu  $K\alpha_2$  (Cromer & Liberman, 1970)]. Comparison of lattice constants (Table 1) showed Pedersen's values (set II) to be systematically  $\frac{1}{2}\%$  larger than our initial values (set I). This discrepancy prompted a remeasurement of the cell dimensions using a Straumanis camera and copper radiation. Two crystals were used. Thirty-one measurements were obtained from the  $h0l$  zone; 74 were obtained from the  $0kl$  zone. The results of a least-squares regression are listed as set III of Table 1. We use these values in all subsequent calculations. Differences between sets I and III may in part be due to temperature; however, set I is considered to be less reliable in view of the limited number of observations, the limited  $2\theta$  range, and the potential for systematic errors such as, for example, errors in  $2\theta_0$  and  $\chi_0$ . No explanation is available for the discrepancy between sets II and III.

## Results and discussion

Fig. 1 is a representation of the structure viewed down  $b$ . Fig. 2 shows bond distances and angles for the binoxalate ion. Fig. 3 is a view of the binoxalate group showing the coordination of each oxygen atom. Fig. 4 shows the coordination polyhedron of the potassium ion.

As pointed out by Pedersen, the structure is composed of layers of anions and cations parallel to  $(10\bar{2})$ , the plane of the observed cleavage. Binoxalate ions are hydrogen bonded together in chains with an  $O(3)\cdots O(5)$  hydrogen-bond distance of 2.523 (2)  $\text{\AA}$ . Adjacent binoxalate chains within layers are held together by coordination to potassium ions. Potassium coordination is sevenfold; the next shortest  $K\cdots O$  distance in this compound is 3.394 (2)  $\text{\AA}$ . There are no close intermolecular contacts between oxygen atoms; the shortest distance is 3.113 (2)  $\text{\AA}$  between  $O(3)$  and  $O(5)$  in adjacent layers.

In agreement with Pedersen, the binoxalate anion is found to be twisted about its C-C bond. The angle between carboxylate planes is  $13.92 \pm 0.15^\circ$ . Standard deviations for distances and angles involving non-hydrogen atoms only are estimated at 0.002  $\text{\AA}$  and  $0.12^\circ$ ; those for distances and angles including a hydrogen atom are 0.02  $\text{\AA}$  and  $1.2^\circ$ . Not shown in these figures are hydrogen bond angles  $O(5)-H(8)\cdots O(3)$  of  $173.4^\circ$  and  $H(8)-O(5)\cdots O(3)$  of  $4.3^\circ$ .

Thermal ellipsoids in Fig. 3 and 4 are drawn at the 50% probability level; major axes of all the heavy

atoms are roughly perpendicular to the average binoxalate plane. While the intermediate axis of the hydrogen ellipsoid (Fig. 3) is in the same direction as the major axes of the heavy atoms and has a similar amplitude, the major hydrogen axis is parallel to the direction of the hydrogen bond. Mean square amplitudes of apparent vibration along the principal axes of the hydrogen ellipsoid are 0.11 (2), 0.08 (1) and 0.006 (8) Å<sup>2</sup>. Standard deviations for the orientation of this ellipsoid, expressed in terms of angular displacements about each of these principal axes, are 6.6, 4.9 and 20° respectively. [This formulation of the uncertainties in the orientation of thermal ellipsoids has recently been suggested by Lindblom, Marsh & Waser (1972).] Although the amplitude of the minor axis is not significantly different from zero, neither is it significantly different from the amplitudes of the minor and intermediate axes of the heavy atoms. The large angular uncertainty associated with the minor axis reflects the near equality of the amplitudes of the other two axes.

The shape of the hydrogen ellipsoid seems to be characteristic of oxalate hydrogen bonds (Hodgson & Ibers, 1969; Delaplane & Ibers, 1969). As pointed out by Brown (1969), the shape is probably less indicative

of thermal motion than of deficiencies in the model. In particular the elongation in the direction of the hydrogen bond may well represent polarization of the electron distribution about the hydrogen atom.

Despite these peculiarities, the centroid of the hydrogen ellipsoid is within two standard deviations of its location after isotropic refinement and the hydrogen atom is, without doubt, covalently bonded to O(5). The hydrogen bond was found to be somewhat longer than had been anticipated; however, the conclusion of Pedersen that the hydrogen-bond potential is asymmetric is confirmed.

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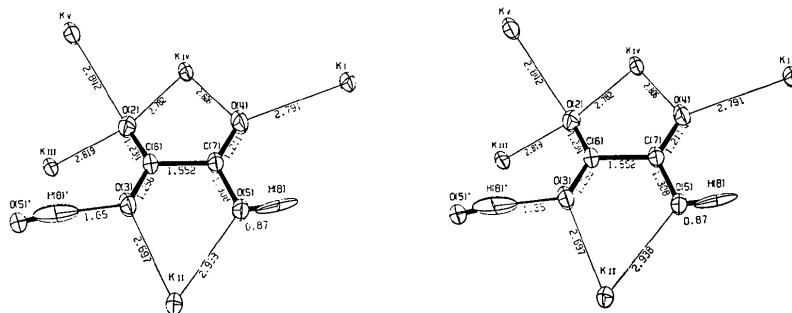


Fig. 3. Stereo projection of the binoxalate group showing the coordination of each oxygen. Distances are in Å.

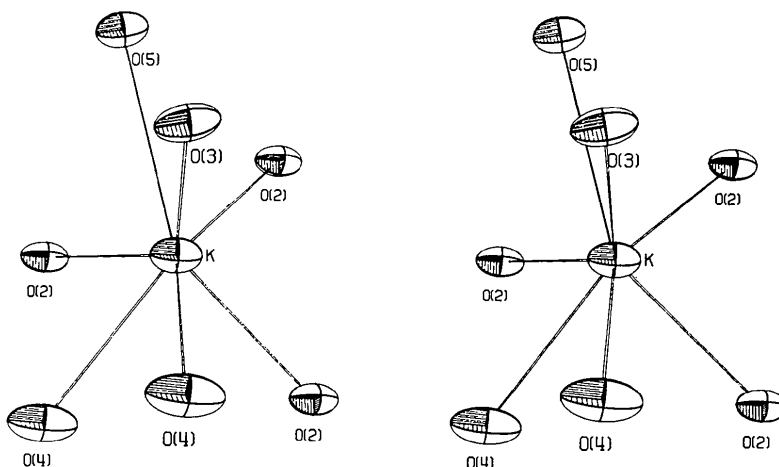


Fig. 4. The coordination polyhedron of the potassium ion.

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## Variations and Covariances of the Anisotropic Temperature Parameters\*

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It is proposed that, in reporting results of crystal structure refinements that include anisotropic temperature parameters, the covariances involving the temperature parameters be expressed in terms of the following six parameters: the lengths of the three principal axes of the vibrational ellipsoids and the orientational angles about these three axes. Equations are presented for deriving the covariances that relate to these new parameters from the covariances given in terms of the primary parameters  $B_{kl}$ .

In reporting the results of a crystal structure analysis that includes adjustments of anisotropic thermal parameters, it is the common practice to list the magnitudes  $U_{ii}$  ( $i=1,2,3$ ) of the principal axes of a vibrational ellipsoid and the direction cosines of these axes relative to a crystal coordinate system with axes  $a_j$ . Thus, twelve quantities – three  $U_{ii}$ 's and nine direction cosines – are presented, of which only six are independent, because of the constraints on the cosines. Along with these twelve derived parameters are often presented their associated standard deviations (and sometimes covariances as well). The three standard deviations  $\sigma(U_{ii})$  of the magnitudes of the principal axes are readily interpretable. It is more difficult, however, to understand the meaning of the nine standard deviations associated with the direction cosines, not only because of the constraints among them but also because of the difficulty of visualization. We suggest here an alternative approach to presenting the uncertainties in the orientations of the principal axes. In particular, we suggest that these uncertainties be represented as uncertainties in the angular displacements  $\alpha_i$  ( $\alpha_1 \equiv \alpha$ ,  $\alpha_2 \equiv \beta$ ,  $\alpha_3 \equiv \gamma$ ) of the ellipsoid around its principal axes. For example, the quantity  $\sigma(\gamma)$  in Fig. 1 represents the uncertainty of orientation of the ellipsoid with respect to a rotation about the eigenvector  $c$ . Note that while  $\alpha = \beta = \gamma = 0$ , the variances and covariances relating to these angles need not be zero.

To derive expressions for variances and covariances

that involve  $\alpha$ ,  $\beta$ , and  $\gamma$ , we presume that the temperature parameters  $B_{kl}$  have been transformed to the coordinate system in which the coordinate axes are parallel to the eigenvectors of the  $B_{kl}$ . This is achieved by a similarity transformation that diagonalizes  $B_{kl}$  (see, for example, Rollett & Davies, 1955; Waser, 1955; Busing & Levy, 1958) by means of a matrix  $G_{jl}$ ,

$$U_{ij} = \sum_k \sum_l G_{ik} G_{jl} B_{kl} = V_i \delta_{ij}. \quad (1)$$

The  $\delta_{ij}$  are Kronecker deltas, and the  $U_{ij}$  are the diagonalized values of the temperature parameters; we have found it convenient to introduce the new symbols,  $V_i = U_{ii}$ .† Variances and covariances are attached to all parameters  $U_{ij}$  including those that are zero. The covariance matrix associated with the  $U_{ij}$  is related to that associated with the  $B_{kl}$  by

$$\begin{aligned} \text{cov}(U_{ij}, U_{kl}) &= \sum_{a,b,c,d} \frac{\partial U_{ij}}{\partial B_{ab}} \frac{\partial U_{kl}}{\partial B_{cd}} \text{cov}(B_{ab}, B_{cd}) \\ &= \sum_{a,b,c,d} G_{ia} G_{jb} G_{kc} G_{ld} \text{cov}(B_{ab}, B_{cd}). \quad (2) \end{aligned}$$

† Important aspects of these matters, including the transformation to main axes in oblique crystal systems, were recently summarized by Cerrini (1971). The matrices  $G_{ik}$  in (1) depend, of course, on whether covariant or contravariant (or mixed) tensor components are chosen; but our results do not depend on the details of the  $G_{ik}$ , and we also do not use index positions to distinguish between covariant, contravariant, or mixed components.

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