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Appendix

Proof of the relations (7) for the case of constraints being applied

Let F be any non-singular linear transformation, and let $Q_F = F^T Q F$, and $A_F = F^T A F$; then we obtain

$$Q_F^{-1} A_F = F^{-1} Q^{-1} A F; \lambda_i \{Q_F^{-1} A_F\} = \lambda_i \{Q^{-1} A\}. \quad (A1)$$

With Q positive-definite and symmetric we can always find a matrix F such that $Q_F = I$ (where I is the unit matrix). (One possible way to determine F according to $Q_F = I$ is outlined by Sparks, 1961.) With $Q_F = I$ we have

$$\begin{aligned} Q^{\text{red-1}} A^{\text{red}} &= (R^T Q R)^{-1} R^T A R \\ &= (R^T F^T F^{-1} Q_F F^{-1} R)^{-1} R^T F^T F^{-1} A_F F^{-1} R \\ &= (S^T S)^{-1} S^T A_F S \end{aligned}$$

by using $S = F^{-1} R$. Hence the following relation holds for the eigenvalues:

$$\lambda_i \{Q^{\text{red-1}} A^{\text{red}}\} = \lambda_i \{(S^T S)^{-1} S^T A_F S\}. \quad (A2)$$

Moreover, with $Q_F = I$ and with (A1) we have

$$\lambda_i \{Q^{-1} A\} = \lambda_i \{A_F\}. \quad (A3)$$

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Hydrogen Bond Studies. XXIII.* The Crystal Structure of Potassium Hydrogen Diformate

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The crystal structure of potassium hydrogen diformate has been determined at room temperature from three-dimensional single-crystal X-ray data. The crystals are orthorhombic, space group *Pbca*, with eight $\text{KH}(\text{HCOO})_2$ units in a unit cell with the dimensions $a = 17.708$, $b = 7.510$, $c = 7.377$ Å. Least-squares refinements with allowance for anisotropic thermal motion gave a final discrepancy index of 0.073. Two crystallographically non-equivalent formate groups are linked into a dimer by a short hydrogen bond (2.45 Å). The potassium ions occur in puckered layers perpendicular to the a axis. The charged dimers and the metal ions are joined by ionic interaction, and the structure is built up of alternating layers of potassium ions and formate dimers. Each potassium ion is surrounded by eight oxygen atoms at the vertices of a distorted square antiprism (K–O distances: 2.77–3.06 Å). The C–O bond lengths in one of the non-equivalent formate groups are 1.24 and 1.25 Å, and in the other 1.22 and 1.26 Å. The corresponding O–C–O angles are 124 and 125°.

Introduction

Several acid salts of monocarboxylic acids with alkali metals have been studied by Speakman and co-workers

If we now make use of a proof given in another paper (Scheringer, 1965a, Appendix), the relations (7) follow from (A2) and (A3).

Proof of the relations (7) for the case of the parameters forming a subset

As Q^{-1} is positive-definite and symmetric, $Q^{-1}A$ is also positive-definite. Let $Q^{\text{red-1}}$ be a non-correlated principal submatrix of Q^{-1} , and A^{red} the corresponding principal submatrix of A (A^{red} generally is correlated), then $Q^{\text{red-1}}A^{\text{red}}$ is a principal submatrix of $Q^{-1}A$. According to the Sturm–Hurwitz theorem (*cf.* Scheringer, 1965b) the maximum (minimum) eigenvalue of a positive-definite matrix is always larger (smaller) than or equal to the maximum (minimum) eigenvalue of any principal submatrix. Hence the relations (7) hold.

References

- FARAG, M. S. (1954). *Acta Cryst.* 7, 117.
LINNIK, J. W. (1961). *Die Methode der kleinsten Quadrate in moderner Darstellung*, p.184. Berlin: VEB Deutscher Verlag der Wissenschaften.
SCHERINGER, C. (1963). *Z. Kristallogr.* 119, 273.
SCHERINGER, C. (1965a). *Acta Cryst.* 19, 513.
SCHERINGER, C. (1965b). *Acta Cryst.* 19, 504.
SCHERINGER, C. (1966). *Acta Cryst.* 20, 319.
SCHERINGER, C. (1968). *Acta Cryst.* In the press.
SPARKS, R. A. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p.170. Oxford, London, New York, Paris: Pergamon Press.

(*e.g.* Golič & Speakman, 1965). The negative ions in these compounds are linked as dimers by short hydrogen bonds which in some cases have been regarded as symmetrical. As potassium hydrogen diformate, $\text{KH}(\text{HCOO})_2$, is one of the simplest acid salts a determination of its structure is of interest. Moreover, this

* Part XXII: Liminga & Mehlsen Sørensen (1967).

study is part of the systematic investigations of hydrogen bonds formed with carboxyl or carboxylate groups which is in progress at this institute.

The melting-point diagram of the system HCOOK–HCOOH (Kendall & Adler, 1921) shows the existence of the solid compounds HCOOK. n HCOOH ($n=1,2,3$). Only the 1:1 compound has a congruent melting point. The present paper is concerned with the determination of the crystal structure of this compound based on three-dimensional X-ray data collected at room temperature.

Experimental

KH(HCOO) $_2$ was prepared according to Groschuff (1903) by dissolving recrystallized potassium formate in formic acid during heating. The salt crystallized as thin plates which were found to be unsuitable for X-ray work. After recrystallization several times from ethanol (99.5%) the salt was carefully melted and sealed in a thin-walled glass capillary (0.2 mm in diameter). The observed melting point agreed with that reported earlier, 108.6° (Kendall & Adler, 1921).

A cylindrical single crystal (diameter 0.2 mm and length 1.5 mm) was used for the X-ray analysis. It was grown from the polycrystalline mass by moving an electrically heated wire slowly along the capillary, using one of the original crystals as a seed.

The crystal was rotated about the c axis, which deviated by 22° from the capillary axis. Multiple-film (five), equi-inclination Weissenberg photographs for the seven layers $0 \leq l \leq 6$ were taken with Ni-filtered Cu K radiation. The number of independent reflexions recorded was 960, which corresponds to about 85% of the reflexions within the copper reflexion sphere. However, 170 of these were too weak to be measured. The relative intensities of the reflexions were obtained by visual comparison with a calibrated intensity scale. The intensity range was 1 to 6000. The data were corrected for Lorentz and polarization effects. Absorption correction was applied by the program DATAP2, written by Coppens, Leiserowitz & Rabinovich (1965). The cylindrical crystal had to be approximated by a regular 12-sided prism since the program requires a crystal description in terms of plane faces. The irradiated volume was not constant during the rotation as the cylinder and the rotation axes did not coincide, and the crystal was longer than the diameter of the X-ray beam. However, a constant mean value for the irradiated volume was used in the absorption correction. The linear absorption coefficient for Cu $K\alpha$ radiation, μ , is 86.9 cm $^{-1}$.

Space group and unit cell

The diffraction symmetry and systematic absences indicated the orthorhombic space group $Pbca$ (no. 61, *International Tables for X-ray Crystallography*, 1952). As shown below, the structure can be described satisfactorily in this space group with the atoms in general eightfold positions.

The dimensions of the unit cell were determined from a powder photograph taken in a Guinier–Hägg focusing camera using Cr $K\alpha_1$ radiation ($\lambda = 2.28962 \text{ \AA}$) with silicon as an internal standard ($a = 5.43054 \text{ \AA}$ at 25°C). From θ values for 43 measured reflexions the cell parameters were calculated by the method of least squares using the program CELSIUS. The cell parameters together with their estimated standard deviations are:

$$\begin{aligned} a &= 17.7079 \pm 0.0009 \text{ \AA} \\ b &= 7.5096 \pm 0.0004 \\ c &= 7.3774 \pm 0.0004 \end{aligned}$$

Unit-cell volume = 981.05 Å 3 . With eight formula units in the unit cell the calculated density is 1.76 g.cm $^{-3}$. An experimental determination of the density was not made.

Determination of the atomic coordinates

The position of the potassium atom was derived from the Harker vectors of a three-dimensional Patterson synthesis (the inter-layer scale factors were based on the relative exposure times). The four oxygen atoms and the two carbon atoms were readily located in the subsequent three-dimensional electron density maps. All atoms occupy general eightfold positions of the space group $Pbca$.

The atomic coordinates thus obtained were improved in series of three-dimensional electron density calculations. Further refinement was made by the method of least squares. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights, w were calculated according to the expression

$$w = 1/(a + |F_o| + c|F_o|^2),$$

with $a = 5.0$ and $c = 0.015$. Reflexions too weak to be measured were given zero weight. After several cycles of refinement the discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.104. Unobserved reflexions were omitted in all calculations of R values.

A three-dimensional difference synthesis was now calculated in order to locate the hydrogen atoms. Only reflexions with $\sin \theta / \lambda$ less than 0.5 Å $^{-1}$ were used. No definite peaks corresponding to the expected positions of the hydrogen atoms could be found. Coordinates for hydrogen in the two independent HCOO $^-$ groups (regarded as planar) were calculated assuming the O–C–H angles in each formate group to be equal and the C–H distance to be 1.09 Å (*Tables of Interatomic Distances*, 1965). The third hydrogen atom was assumed to be symmetrically situated in the hydrogen bond.

Another two cycles of least-squares refinements were performed. The three hydrogen atoms were included with fixed parameters and Debye–Waller factors of 6 Å 2 . Now the R value dropped to 0.101.

The difference synthesis indicated anisotropy in the thermal motion of potassium, oxygen and carbon atoms. Anisotropic refinements were therefore performed. The inter-layer scale factors were fixed to the

values obtained from the final isotropic refinement, and an overall scale factor was refined. The parameters for all atoms but the hydrogen atoms were varied. The total number of parameters varied increased from 35 to 64. After three cycles of refinement the R value was 0.073. In the last cycle all shifts were less than one tenth of the standard deviations. Finally, another difference synthesis was calculated (hydrogen atoms not included) but the hydrogen atoms could still not be located.

For the Fourier calculations a program designated DRF was used. The least-squares calculations were performed with the full-matrix program, LALS. Reference to the programs used has been made by Nahringer (1967).

Tables 1 and 2 list the atomic coordinates and thermal parameters with standard deviations obtained from the final least-squares refinement. The observed and calculated structure factors are listed in Table 3. The atomic scattering factors used were those for K^+ , and

neutral O, C, and H, respectively. Dispersion corrections for oxygen and potassium were included. (*International Tables for X-ray Crystallography*, 1962, pp. 202, 214).

Table 1. *Atomic coordinates with standard deviations*

Standard deviations for potassium are multiplied by 10^5 , for other atoms by 10^4 .

	x	y	z
K	0.46296 (6)	0.43735 (15)	0.28430 (17)
O(1)	0.1564 (2)	0.0774 (6)	0.0795 (6)
O(2)	0.0544 (2)	0.2829 (5)	0.4858 (6)
O(3)	0.2922 (2)	0.0584 (7)	0.0209 (7)
O(4)	0.4009 (2)	0.1260 (6)	0.1478 (6)
C(1)	0.1229 (3)	0.3164 (7)	0.4765 (8)
C(2)	0.3321 (3)	0.1257 (7)	0.1441 (9)
Hydrogen atoms			
C(1):H(1)	0.156	0.251	0.371
C(2):H(2)	0.302	0.189	0.259
O(1), O(3):H(3)	0.224	0.068	0.050

Table 2. *Thermal parameters with standard deviations*

All values are multiplied by 10^4 . The expression used is: $\exp[-(\beta_{11}h^2 + \dots + \beta_{12}hk + \dots)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	21 (1)	125 (2)	124 (4)	9 (1)	-10 (1)	-21 (3)
O(1)	21 (1)	205 (9)	160 (10)	6 (5)	-18 (5)	120 (14)
O(2)	20 (1)	169 (8)	166 (10)	-21 (5)	-16 (5)	45 (14)
O(3)	22 (1)	285 (12)	218 (12)	17 (6)	-23 (6)	-192 (18)
O(4)	18 (1)	180 (8)	213 (11)	0 (5)	-6 (5)	-51 (15)
C(1)	19 (1)	118 (8)	132 (13)	0 (6)	-6 (6)	19 (16)
C(2)	18 (1)	141 (9)	173 (15)	7 (6)	17 (6)	11 (18)

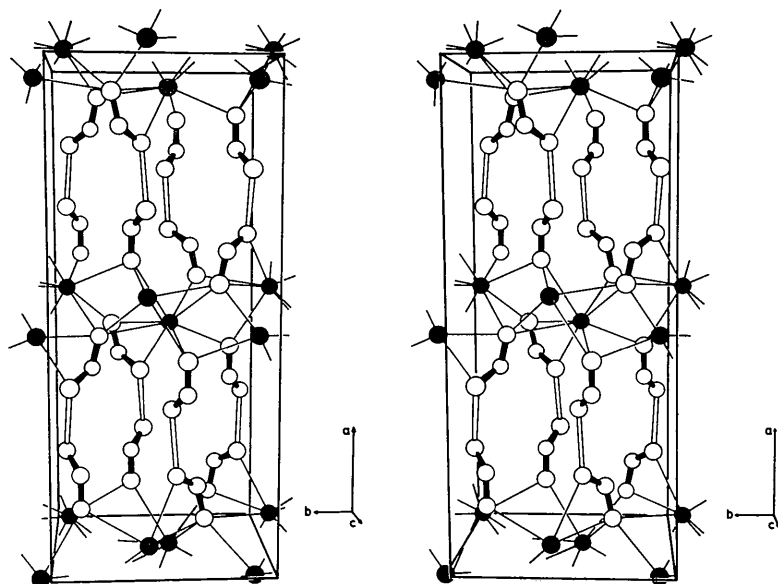


Fig. 1. A stereoscopic pair of drawings showing the hydrogen bonding pattern and the ionic contacts between the formate dimers and potassium ions. Hydrogen atoms are omitted. Covalent bonds are filled, hydrogen bonds are open and ionic bonds are drawn as single lines. The potassium ions are filled. The view is approximately along the c axis. This and the other figures were drawn with the program *ORTEP*.

Table 3. Observed and calculated structure factors

An asterisk indicates reflexions which were too weak to be measured. The F_o values for these are given as (1/√2)F_{min} for the reflexion in question.

A large multi-column table with 26 columns of data, each column representing a different reflection (h, k, l). The columns are labeled with h, k, l, |F_o|, and |F_c|. The data values are numerical, often in scientific notation or with decimal points, representing structure factor magnitudes. Asterisks indicate reflections that were too weak to be measured.

Parallel with these refinements another series was run with data not corrected for absorption. The final Debye-Waller factors were about 0.5 \AA^2 lower than in the first case and the scale factors applied to F_o were accordingly smaller. The differences in the final atomic coordinates were less than one standard deviation, and consequently bond lengths and angles were not significantly affected by absorption.

Description and discussion of the structure

General

A stereoscopic illustration of the structure is given in Fig. 1. Fig. 2 shows the formate dimer and its ionic contacts with potassium. The environment of a potassium ion is given in Fig. 3. Bond distances and angles with standard deviations are listed in Table 4.

The structure consists of K^+ and $\text{H}(\text{HCOO})_2^-$ ions. The potassium ions form infinite puckered layers which are perpendicular to the a axis and located at $x=0$ and $\frac{1}{2}$. The two crystallographically non-equivalent formate groups are joined in a zigzag shaped dimer by a short hydrogen bond of $2.447 \pm 0.006 \text{ \AA}$ (*cf.* Fig. 2). The direction of this dimer is approximately parallel to the a axis, *i.e.* perpendicular to the layers of potassium ions. The shortest distance between atoms in adjacent dimers is 3.21 \AA . The charged dimers are linked to the metal ions by ionic interactions and the structure is thus built up of alternating layers of potassium ions and formate dimers (*cf.* Fig. 1).

The formate groups

The planes through the non-equivalent formate groups form an angle of about 110° with each other and approximately 2 and 3° , respectively, with the hydrogen bond direction. The $\text{C}(1)\text{--O}(1)$ and $\text{C}(1)\text{--O}(2)$ bond lengths are 1.251 and 1.240 \AA , and the $\text{C}(2)\text{--O}(3)$ and $\text{C}(2)\text{--O}(4)$ distances are 1.257 and 1.220 \AA ($\sigma = 0.006\text{--}0.008 \text{ \AA}$, *cf.* Table 4). The corresponding O--C--O bond angles are $124.1 \pm 0.5^\circ$ and $125.3 \pm 0.6^\circ$, respectively. In ammonium formate (Nahringbauer, 1968), the formate group has similar dimensions: C–O bond

lengths 1.232 and 1.239 \AA (without thermal correction, $\sigma = 0.007 \text{ \AA}$), and O--C--O angle 126.3° ($\sigma = 0.6^\circ$).

In earlier structure determinations differences between the dimensions of ionized and non-ionized carboxyl groups have been reported (for references *cf.* Hahn, 1957). The C–O distances from C(2) differ significantly, which may indicate that this group is less

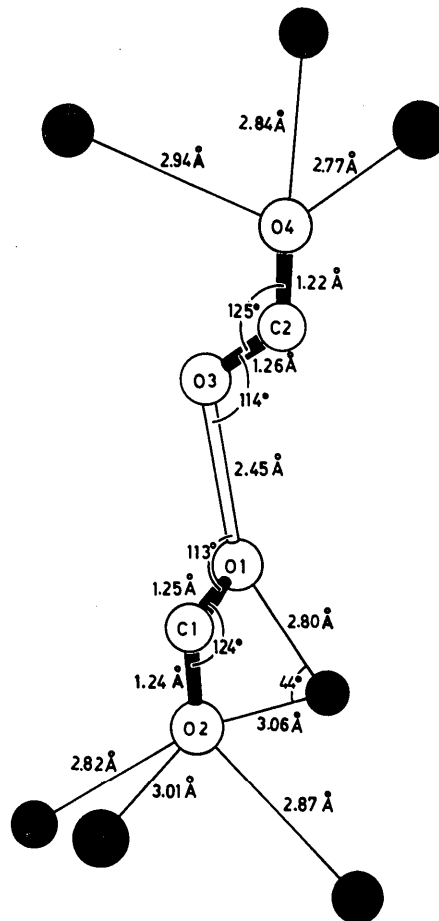


Fig. 2. The formate dimer and its ionic contacts with potassium. The view is along the b axis.

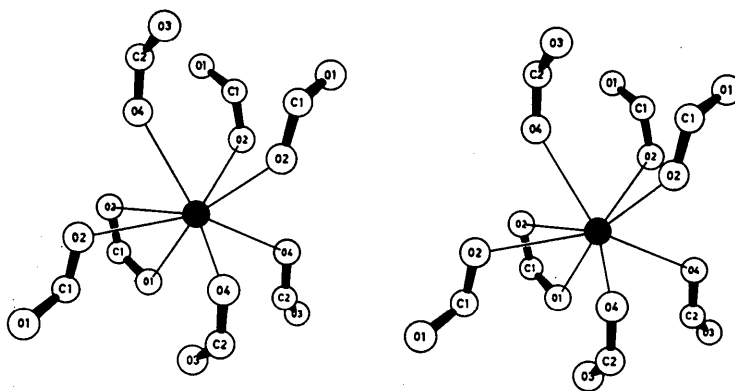


Fig. 3. A stereoscopic pair of drawings showing the environment of the potassium ion. The orientation is the same as in Fig. 1, with the view approximately perpendicular to the two quadrangles of the coordination polyhedron.

ionized than the other. In rubidium hydrogen bisglycollate (Golič *et al.*, 1965), and potassium hydrogen di-*p*-nitrobenzoate (Shrivastava & Speakman, 1961) only one of the two carboxyl groups was supposed to be ionized. However, in these compounds the difference in the C–O distances was much more pronounced.

The environment of the potassium ion

The potassium ion has eight oxygen neighbours at the vertices of a distorted square antiprism. The K–O distances range from 2.773 to 3.059 Å ($\sigma=0.004$ – 0.005 Å, *cf.* Table 4) with a mean value of 2.888 Å. These data are in good agreement with those earlier reported for eight-coordinated potassium (*International Tables for X-ray Crystallography*, 1962, p.258). As seen from Fig.3 there is a considerable distortion of the coordination polyhedron. Two of the coordinating oxygen atoms belong to the same formate group and the angle O–K–O is here only $43.8 \pm 0.1^\circ$, whereas it should be 70.5° in an undistorted square antiprism. The plane of this chelate ligand passes very close to the central potassium ion. None of the atoms deviates from the least-squares plane by more than 0.03 Å. A similar situation was found in potassium hydrogen maleate (Darlow & Cochran, 1961).

It is interesting to note that the number of ionic contacts to potassium is different for the two formate groups: O(1) and O(2), joined to C(1), has one and four potassium neighbours, respectively. In the other formate group, O(4) makes three K–O contacts and O(3) none (*cf.* Fig.2). For a further discussion of this point, see below.

The distance between the potassium atoms in adjacent antiprisms is 3.569 Å when they have one quadrangle in common and 4.010 Å when the common side is triangular. In the cases that only one edge is shared there are two potassium–potassium distances, 4.495 and 4.639 Å respectively. All standard deviations are less than 0.003 Å. The first distance, 3.569 Å, is much shorter than the potassium–potassium contacts re-

ported in *e.g.* potassium hydrogen maleate: 4.466, 4.572, and 4.578 Å ($\sigma=0.003$ Å) (Darlow *et al.*, 1961), where adjacent coordination polyhedra (distorted cubes) share edges. A comparison with potassium–potassium distances in other compounds is difficult to make as the potassium–oxygen coordination is rather different in these compounds.

The hydrogen bonding

In formic acid there is one active hydrogen per formate group and infinite chains are formed in the structure (Holtzberg, Post & Fankuchen, 1953). In the present compound, however, there are only half as many hydrogen atoms available for hydrogen bonding and only dimers $\text{H}(\text{HCOO})_2^-$ can be formed.

The hydrogen bond in the $\text{H}(\text{HCOO})_2^-$ dimer, 2.447 ± 0.006 Å, is close to the value reported in the related compound $\text{NaH}(\text{CH}_3\text{COO})_2$, 2.444 ± 0.010 Å (Speakman & Mills, 1961). The hydrogen bonds in formic acid (Holtzberg *et al.*, 1953), and acetic acid (Jones & Templeton, 1958) are considerably longer, 2.58 and 2.61 Å respectively. This is of course to be expected as the hydrogen bond accepting power of an ionized carboxyl group is considerably greater than that of the corresponding acid. Another example is the hydrogen bond between a carboxyl and a carboxylate group in $\text{K}(\text{C}_2\text{O}_4\text{H})(\text{C}_2\text{O}_4\text{H}_2) \cdot 2\text{H}_2\text{O}$, 2.51 Å (Haas, 1964) as compared to the hydrogen bond in oxalic acid, 2.71 Å (Cox, Dougill & Jeffrey, 1952).

The angles between the hydrogen bond and the adjacent C–O bonds, 113 and 114° , are close to the corresponding angles in $\text{NaH}(\text{CH}_3\text{COO})_2$, 111° (two equivalent ones) (Speakman & Mills, 1961), and in $\text{K}(\text{C}_2\text{O}_4\text{H})(\text{C}_2\text{O}_4\text{H}_2) \cdot 2\text{H}_2\text{O}$, 114 and 116° (Haas, 1964). The angles for the last compound have been calculated from the coordinates reported by Haas.

The hydrogen bond length in $\text{H}(\text{HCOO})_2^-$ is close to the upper limit suggested for a symmetrical bond. In most of the acid salts investigated by Speakman and collaborators the acidic residues in the dimer have been

Table 4. Bond distances and angles with standard deviations

Covalent bonds		Angles	
C(1)–O(1)	1.251 (7) Å	O(1)–C(1)–O(2)	124.1 (0.5)°
C(1)–O(2)	1.240 (6)	O(3)–C(2)–O(4)	125.3 (0.6)
C(2)–O(3)	1.257 (8)		
C(2)–O(4)	1.220 (6)		
Hydrogen bond			
O(1)···O(3)	2.447 (6) Å	C(1)–O(1)···O(3)	113.4 (0.4)°
		C(2)–O(3)···O(1)	113.6 (0.4)
Ionic bonds			
K···O(4)	2.773 (4) Å		
K···O(1)	2.803 (4)		
K···O(2)	2.817 (4)		
K···O(4)	2.840 (4)		
K···O(2)	2.870 (4)		
K···O(4)	2.937 (5)		
K···O(2)	3.006 (4)		
K···O(2)	3.059 (4)		

crystallographically symmetry related. This is not the case in the present compound, which also shows an apparent difference between the two hydrogen-bridged formate groups. As mentioned previously, the distances C(2)–O(3) and C(2)–O(4) differ significantly in contrast to C(1)–O(1) and C(1)–O(2) which are of about the same length (*cf.* Table 4). Furthermore, the number of ionic contacts to potassium is different: one formate group has 4+1 whereas the other has 3+0 potassium–oxygen contacts.

According to the facts given above there may be a tendency towards less ionization in one of the groups than in the other. This has important bearings on the symmetry character of the hydrogen bond in the dimer.

As mentioned earlier the positions of the hydrogen atoms have not been located experimentally. Naturally nothing definite can be said about the character of the hydrogen bond from the X-ray data. Attempts will be made to attack this problem with other methods.

The authors are indebted to Dr I. Olovsson for his great interest in this work and for valuable discussions and suggestions. Many thanks are also due to Mr H. Karlsson and Mrs M. Hillberg for their skilful technical assistance.

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The Crystal Structure of $\text{La}_2\text{Be}_2\text{O}_5$ *

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The crystal structure of $\text{La}_2\text{Be}_2\text{O}_5$ has been derived and refined from Mo $K\alpha$ X-ray diffraction data. The *C*-centered monoclinic unit cell with $a_0=7.536$, $b_0=7.348$, $c_0=7.439$ Å, $\beta=91^\circ 33'$ contains four formula weights. The atomic arrangement in this equilibrium phase consists of a three-dimensional framework of cornersharing beryllium–oxygen tetrahedra with lanthanum atoms irregularly coordinated to ten oxygen atoms. The structure is compared with those of other oxide compounds containing beryllium and, in particular, with the structures of the recently reported nonequilibrium phases $\text{Ca}_{12}\text{Be}_{17}\text{O}_{29}$ and Y_2BeO_4 .

Introduction

The work described in this paper is part of a continuing study of binary oxide compounds that contain beryllia as a member. We have previously reported the crystal

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References

- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.
 COX, E. G., DOUGILL, M. W. & JEFFREY, G. A. (1952). *J. Chem. Soc.* p.4854.
 DARLOW, S. F. & COCHRAN, W. (1961). *Acta Cryst.* **14**, 1250.
 GOLIČ, L. & SPEAKMAN, J. C. (1965). *J. Chem. Soc.* p.2521.
 GROSCHUFF, E. (1903). *Ber. dtsh chem. Ges.* **36**, 1783.
 HAAS, D. J. (1964). *Acta Cryst.* **17**, 1511.
 HAHN, T. (1957). *Z. Kristallogr.* **109**, 438.
 HOLTZBERG, F., POST, B. & FANKUCHEN, I. (1953). *Acta Cryst.* **6**, 127.
International Tables for X-ray Crystallography (1952). Vol. I. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JONES, R. E. & TEMPLETON, D. H. (1958). *Acta Cryst.* **11**, 484.
 KENDALL, J. & ADLER, H. (1921). *J. Amer. Chem. Soc.* **43**, 1470.
 LIMINGA, R. & MEHLSSEN SØRENSEN, A. (1967). *Acta Chem. Scand.* **21**, 2669.
 NAHRINGBAUER, I. (1967). *Acta Cryst.* **23**, 956.
 NAHRINGBAUER, I. (1968). *Acta Cryst.* **B24**, 565.
 SHRIVASTAVA, H. N. & SPEAKMAN, J. C. (1961). *J. Chem. Soc.* p.1151.
 SPEAKMAN, J. C. & MILLS, H. H. (1961). *J. Chem. Soc.* p.1164.
Tables of Interatomic Distances and Configuration in Molecules and Ions (1958). Special Publication No.11, 109. London: The Chemical Society.

structures of the compounds $\text{Ca}_{12}\text{Be}_{17}\text{O}_{29}$ and Y_2BeO_4 (Harris & Yakel, 1966, 1967). Unusual trigonal beryllium–oxygen coordinations appeared in these probably metastable crystals which we could form only by quenching from the liquid state.

In both $\text{Ca}_{12}\text{Be}_{17}\text{O}_{29}$ and Y_2BeO_4 , the heavy cations have a large radius (0.99 and 0.97 Å, respectively) relative to those in the known equilibrium compounds