

The Crystal Structure of Lithium Hydrogen Phthalate Dihydrate, Containing a Very Short Hydrogen Bond

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(Received 8 April 1974; accepted 20 November 1974)

Crystals of $\text{LiH}(\text{C}_8\text{H}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$ are orthorhombic (space group $Pnma$) with $a = 16.837$ (2), $b = 6.822$ (1), $c = 8.198$ (2) Å, $Z = 4$, $\rho = 1.4677$ g cm⁻³. The crystal structure was determined by Patterson syntheses. Full-matrix least-squares refinement with anisotropic temperature parameters for the non-hydrogen atoms converged to an R index of 0.040. The hydrogen phthalate ion is found to be planar. The carboxyl groups are linked by an extraordinarily short intramolecular hydrogen bond (2.385 Å). The Li ion is found in tetrahedral coordination.

Introduction

Lithium hydrogen phthalate dihydrate, $\text{LiH}(\text{C}_8\text{H}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$, was first described by Smith, Sturm & Ely (1935). In order to give an interpretation of the physical properties (Haussühl, 1975) in terms of the crystal structure a structure analysis was carried out.

The crystal structures of some other hydrogen orthophthalates have already been determined: $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$ (Okaya, 1965), $\text{NH}_4\text{H}(\text{C}_8\text{H}_4\text{O}_4)$ (Okaya & Pepinsky, 1957) and $\text{CuH}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ (Cingi, Guastini, Musatti & Nardelli, 1969). Of interest in all these crystals is the packing of the hydrogen phthalate ions, the relative arrangement of the two carboxyl groups, and the formation of hydrogen bonds.

Experimental

$\text{LiH}(\text{C}_8\text{H}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$ is orthorhombic. The density (flotation method), the lattice constants at 20°C (single-crystal diffractometer) and the space group were determined by Haussühl (1973) (any piezoelectric effect was not observable). The lattice constants were redetermined in the course of this work by the Guinier technique and a least-squares procedure. Silicon was used as a calibrating substance.

$$\begin{array}{ll} \rho = 1.4694 \text{ g cm}^{-3} & \rho_x = 1.4677 \text{ g cm}^{-3} \\ a = 16.837 \text{ (2) \AA} & \text{Space group } Pnma \\ b = 6.822 \text{ (1)} & Z = 4 \\ c = 8.198 \text{ (2)} & \end{array}$$

Because $Z = 4$ the hydrogen phthalate ion occupies a special position on the mirror planes. The crystal used for the intensity measurements was nearly spherically ground and had a diameter of about 0.6 mm. The intensities of 1209 independent reflexions in the range $0.1 < \sin \theta / \lambda < 0.66$ were gathered by a Siemens automatic diffractometer with $\text{Mo K}\alpha$ radiation. Each of

these values is an average of four measurements of equivalent reflexions. Since the linear absorption coefficient was only 1.3 cm^{-1} the intensities were not corrected for absorption. 214 reflexions with $F_o < 1.0$ were treated as 'less thans'.

Determination and refinement of the structure

All computing work was carried out by the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). In the refinement procedure the F_o values were weighted with the reciprocal standard deviation of the respective F_o . Direct methods failed in the attempt to obtain a structure model, whereas a sharpened Patterson synthesis clearly revealed the C and O atoms. The positions of the Li ions and the H atoms were found by a difference Fourier synthesis. Full-matrix least-squares refinement was carried out with isotropic H and anisotropic C, O and Li temperature parameters. The F_o values of six reflexions ($|F_o| > 75.0$) turned out to be appreciably lower than the respective F_c values (most probably because of extinction). Without these and without 214 'less thans' the refinement led to a weighted R value of 0.040.*

The atomic parameters and temperature factors with their standard deviations are given in Table 1.

Discussion

Description of the structure

The hydrogen phthalate and lithium ions have positions on the mirror planes at $y = 0.25$ and 0.75 . The

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30797 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^5$)

Standard deviations given in parentheses refer to the least significant digits in the parameter values. The temperature factor is of the form $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \times 10^{-5}]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4603 (1)	2500	5454 (2)	174 (6)	1052 (44)	690 (29)	0	-29 (11)	0
C(2)	4235 (1)	2500	3924 (3)	224 (7)	1689 (53)	932 (34)	0	-96 (13)	0
C(3)	4659 (2)	2500	2486 (3)	390 (10)	2011 (58)	663 (33)	0	-127 (15)	0
C(4)	5475 (1)	2500	2539 (3)	376 (11)	1875 (56)	694 (33)	0	138 (15)	0
C(5)	5857 (1)	2500	4032 (3)	215 (8)	1619 (53)	944 (34)	0	83 (13)	0
C(6)	5441 (1)	2500	5510 (2)	176 (7)	1038 (45)	684 (29)	0	10 (11)	0
C(7)	4018 (1)	2500	6861 (2)	173 (7)	1361 (49)	949 (32)	0	38 (11)	0
C(8)	5969 (1)	2500	6995 (2)	172 (7)	1377 (49)	916 (31)	0	-73 (11)	0
O(1)	3308 (1)	2500	6574 (2)	158 (5)	3716 (60)	1556 (32)	0	44 (10)	0
O(2)	4260 (1)	2500	8341 (2)	235 (6)	3529 (59)	731 (24)	0	96 (10)	0
O(3)	5675 (1)	2500	8427 (2)	239 (6)	3605 (60)	698 (23)	0	-85 (10)	0
O(4)	6701 (1)	2500	6823 (2)	167 (5)	2480 (46)	1318 (29)	0	-93 (10)	0
O(5)	2101 (1)	4917 (2)	4763 (2)	308 (5)	2782 (37)	2561 (33)	-87 (14)	-107 (12)	1300 (28)
Li	2220 (2)	2500	5985 (5)	230 (13)	1930 (89)	1048 (60)	0	-51 (23)	0

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	4969 (17)	2500	8492 (37)	3.49 (65)
H(2)	3663 (14)	2500	3871 (88)	1.18 (49)
H(3)	4384 (15)	2500	1455 (29)	1.26 (49)
H(4)	5783 (13)	2500	1593 (27)	0.90 (48)
H(5)	6404 (14)	2500	4034 (29)	1.00 (48)
H(6)	2497 (18)	5441 (36)	4327 (31)	5.12 (73)
H(7)	1700 (19)	5383 (43)	4446 (34)	6.53 (92)

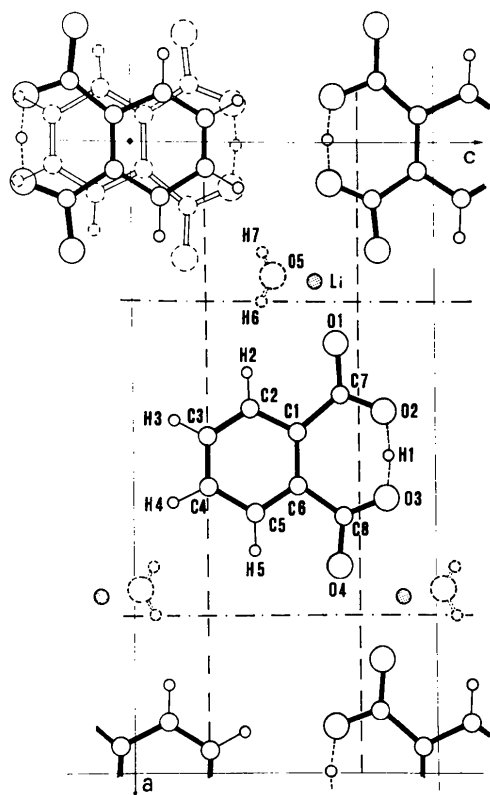


Fig. 1. Section through the unit cell at $y=0.25$ (mirror plane). Atoms O(5) (at $y=0.008$ and 0.492), H(6) and H(7) not lying on the mirror plane are dashed. The position of one particular hydrogen phthalate ion lying on the mirror plane at $y=0.75$ is outlined by faint contours in the upper left part of the figure.

H₂O molecules are located in between these planes at nearly $y=0$ and 0.5 . The atomic arrangement is illustrated in Fig. 1. The distance of the mirror planes, *i.e.* of adjacent layers of the planar hydrogen phthalate ions is $b/2=3.411$ Å. The bond distances and angles within the hydrogen phthalate ion are given in Fig. 2. Fig. 3 shows a stereoscopic view of the hydrogen phthalate ion; the atoms are represented by their thermal ellipsoids (50% probability).

The geometrical arrangement in the crystal structure is characterized by the formation of flat ribbons of neighbouring hydrogen phthalate ions extending in the *c* direction, each ion within one ribbon having the same orientation (Fig. 1). Adjacent ions are separated by the following distances: O(2)–H(3) 2.561 (24), O(2)–C(3) 3.464 (3), O(3)–H(4) 2.601 (22), O(3)–C(4) 3.388 (3) Å. Parallel to such a ribbon another ribbon with opposite orientation of the molecules is packed, the centres of the hydrogen phthalate ions coinciding approximately in the projection along *b* (faint ion in Fig. 1). Thus, walls parallel to (100) are formed, connected in the *a* direction by the Li ions and the water molecules.

The LiO₄ tetrahedron and the water molecule

The lithium ion is surrounded by four oxygen atoms: O(1), O(4'), O(5), and O(5^m) [the latter being generated from O(5) by the mirror plane]. These oxygens form a distorted tetrahedron lying symmetrically to the mirror plane. The Li–O distances, the O–O distances, and the O–Li–O angles are as follows.

Li–O(1)	1.895 (4) Å	O(1)–O(4')	3.008 (2) Å
Li–O(4')	1.998 (4)	O(1)–O(5)	3.009 (2)
Li–O(5)	1.940 (3)	O(4')–O(5)	3.317 (2)
Li–O(5 ^m)	1.940 (3)	O(5)–O(5 ^m)	3.298 (2)
O(1)–Li–O(4')	101.2 (2)°	O(4')–Li–O(5)	114.8 (2)°
O(1)–Li–O(5)	103.4 (2)	O(5)–Li–O(5 ^m)	116.4 (2)

The water molecule forms two very weak hydrogen bonds from O(5) to O(4'') and to O(2'') (see Fig. 4) with distances 2.978 (2) and 3.116 (2) Å respectively. The angles O(5)–H(6)–O(4'') and O(5)–H(7)–O(2'')

are both found to be about 164° . As frequently observed in X-ray investigations, the distances O(5)–H(6) and O(5)–H(7), 0.836 (29) and 0.790 (31) Å respectively, are lower than the 'real' distances. Angle H(6)–O(5)–H(7) is $111 (3)^\circ$. The bisector of the O(5) lone-pair electrons is directed approximately toward the Li ion.

The distance Li–O(4') is found to have a comparatively large value, presumably because O(4') is also involved in the 2.978 Å hydrogen bond to O(5^{iv}) (see Fig. 4) whereas distance Li–O(1) is found to be small because O(1) is connected only to the Li ion.

The intramolecular hydrogen bond

The flat configuration of the hydrogen phthalate ion with an O(2)–O(3) distance of 2.385 (2) Å is realized by means of a 'very short' intramolecular hydrogen bond. This is one of the shortest O...H...O hydrogen bonds hitherto observed. The only crystal structure reported to possess a hydrogen bond of similarly short length is caesium hydrogen trifluoroacetate (Golić & Speakman, 1965) with an O–O distance of 2.38 (3) Å.

However, the standard deviation is rather high in this case. The structure of $\text{CuH}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ also exhibits an intramolecular hydrogen bond [2.422 (6) Å] which is longer than the bond in the present crystal, presumably because the anion is not planar in that case. A further example of a short intramolecular hydrogen bond [2.398 (3) Å] was found in the crystal structure of quinolinic acid (Kvick, Koetzle, Thomas & Tagusagawa, 1974). The molecular structure of quinolinic acid resembles that of the anion investigated in the present paper: one C atom of the benzene ring [C(5)] is replaced by a N atom.

As in other hydrogen chelates such as potassium hydrogen maleate (Peterson & Levy, 1958) and potassium hydrogen chloromaleate (Ellison & Levy, 1965) the O...H...O bond is constrained by the 'pincer action' of the quasi-rigid anion. The benzene ring provides an additional reinforcement for the framework of the ion when compared with the smaller and more flexible maleate ion. This might explain why the hydrogen bond in the hydrogen phthalate anion is shorter

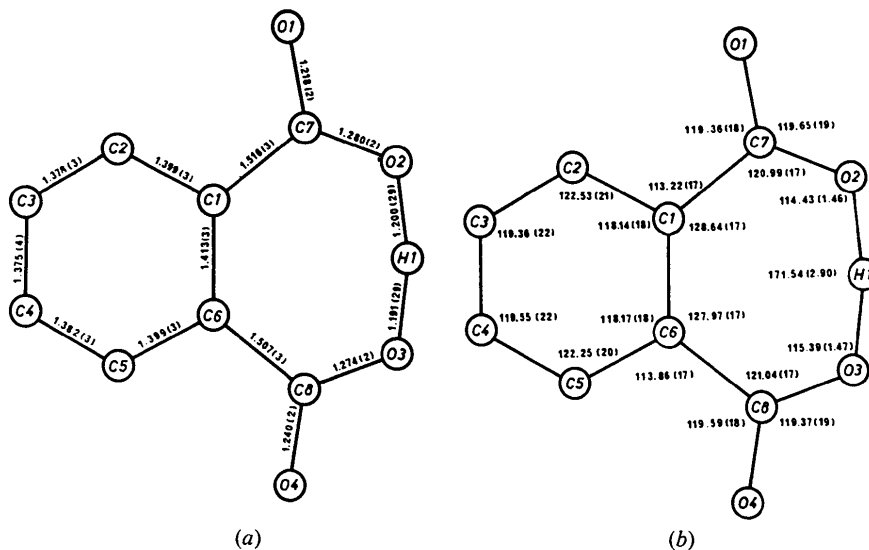


Fig. 2. (a) Bond lengths and (b) angles in the hydrogen phthalate ion.

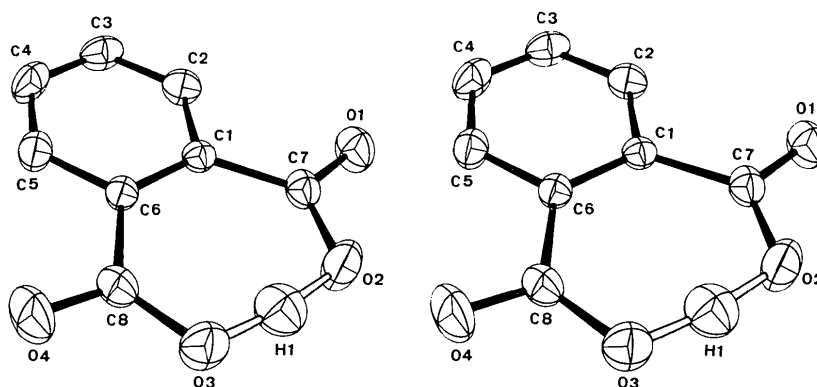


Fig. 3. Stereoscopic thermal ellipsoid plot of the hydrogen phthalate ion (drawn by ORTEP, Johnson, 1965).

than those found in the two crystals mentioned above [2.437 (4) and 2.403 (27) Å]. The spatial restraint results in a strain modifying distances and angles in the phthalate ion. As an indication that the present hydrogen-bond length is shorter than the equilibrium distance, repulsive forces expand the chelates of the orthophthalate ion. By this action the bond length C(1)–C(6) is increased to 1.413 (3) Å whereas C(3)–C(4) is decreased to 1.375 (4) Å. As a further consequence, the angles deviate appreciably from 120°. In contrast, in the strainless $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$ the C–C bond lengths show only small deviations from an average value of 1.388 Å and the C–C–C angles are nearly equal to 120° (Okaya, 1965). Inserting the distances which are found usually and on average in aromatic compounds (C–C=1.39 Å, C–C–C=120°) and in carboxyl groups (Hahn, 1957) [C(1)–C(7)=1.50, C(7)–O(2)=1.26 Å, angle C(1)–C(7)–O(2)=117°, assuming a double-bond character of 50% for the C–O bonds] into the planar phthalate ion geometry, yields an O(2)–O(3) distance of 1.52 Å. The strain thus enlarges the distance by approximately 0.86 Å.

Apparently an appreciable amount of energy is consumed for the deformation of the anion. In the lattice-energy balance, however, the energy gain resulting from the close packing of flat molecules in a layer-like fashion seems to compensate for the energy loss due to the planarity of the anion.

Similar distortions arise in the structures of $\text{CuH}_2(\text{C}_8\text{O}_4\text{H}_4)_2 \cdot 2\text{H}_2\text{O}$ and of quinolinic acid.

In the nomenclature of Speakman (1972), this hydrogen bond is of type *A*, because the dimensions of the two carboxyl groups are similar, or more strictly of pseudo type *A*, because there does not exist a symmetry element ($\bar{1}$ or 2) at the midpoint of the hydrogen bond.

Since the determination of the hydrogen position by means of X-rays is very inaccurate, it is not possible to decide whether the hydrogen bond is symmetric or not from the experimental results. Although some authors state that such short hydrogen bonds are very probably symmetric, examples are known (Schlemper, Hamilton & La Placa, 1971; Kvik, Koetzle, Thomas & Tagusagawa, 1974) where the O...H distances differ significantly even in the case of very short hydrogen bonds [2.420 (5) Å and 2.398 (3) Å respectively]. From

a theoretical point of view the potential in a very short hydrogen bond is characterized by a broad, nearly flat minimum (Schlemper *et al.*, 1971). Therefore, the position of the hydrogen is sensitive to small perturbations in the environment. Although the geometrical arrangement of the atoms within the molecule is rather symmetrical with respect to the hydrogen bond, the environment in the crystal structure is very asymmetrical (Fig. 1): O(2) is involved in the weak hydrogen bond to O(5), but O(3) has no such contact. Furthermore, O(1) and O(4) are differently linked to the Li ion. Therefore, in the present structure also an asymmetric hydrogen bond seems probable. This question will be answered in a later neutron diffraction study.

The planarity of the hydrogen phthalate ion

$\text{LiH}(\text{C}_8\text{H}_4\text{O}_4) \cdot 2\text{H}_2\text{O}$ is the first example of a structure containing a planar hydrogen phthalate anion the possible existence of which was predicted by Speakman (1972) in his review article (p. 169). In phthalic acid (Nowacki & Jaggi, 1957), in $\text{KH}(\text{C}_8\text{H}_4\text{O}_4)$, $\text{NH}_4\text{H}(\text{C}_8\text{H}_4\text{O}_4)$ and in $\text{CuH}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ the angles between the two carboxyl planes and the plane of the benzene ring have the following values: (34.0, 34.0°), (31.7, 75.4°), (21, 65°) and (16.5, –19.0°).

The question why the anion is planar in lithium hydrogen phthalate but not so in the other salts is very difficult to answer. Presumably, the low coordination number of the Li ion and the additional water content might favour such geometry. In K and NH_4 hydrogen phthalate, the coordination number is six. Each cation is linked to four different anions, two of them contributing two oxygens of the same COO group. In order to realize a largely uniform octahedral environment of oxygens around the cations, the COO groups have to be rotated appropriately. In lithium hydrogen phthalate, however, a Li ion has contacts only with two oxygens which are part of two different anions; the other two oxygens of the coordination sphere belong to water molecules which are associated only with this particular Li ion. Therefore, no necessity exists for rotating the COO groups. On the other hand, a minimum of free energy seems to be achieved by a layer-like arrangement of planar molecules on the mirror plane, in accordance with the close-packing concept.

Thermal motion

The principal axes of the thermal ellipsoids and their direction cosines (Fig. 3) are summarized in Table 2. A rigid-body treatment of the whole hydrogen phthalate ion failed. The program *TLS* (Schomaker & Trueblood, 1968) yielded one negative eigenvalue for the libration tensor, apparently because the COO groups librate independently around the C–C bond. The libration of the frame of C atoms, however, could be determined, if the O atoms were excluded from refinement. (They were taken into account, however, in fixing the molecules' centre of gravity.) Thus, the fol-

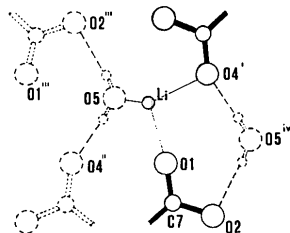


Fig. 4. Environment of the Li ion. Atoms lying on the mirror plane at $y=0.25$ are identified by full lines, others by dashed lines. Heights of O(5) and O(5') are $y=0.492$, and $y=-0.008$, respectively, those of other dashed C and O atoms $y=0.75$.

Table 2. Lengths (\AA) and direction cosines (relative to the crystallographic axes) of the principal axes of the thermal ellipsoids

Values are $\times 10^3$.

C(1)	149	571	0	821
	157	0	1000	0
	162	-821	0	571
C(2)	159	696	0	718
	197	718	0	-696
	199	0	1000	0
C(3)	143	242	0	970
	218	0	1000	-0
	241	970	0	-242
C(4)	144	-279	0	960
	210	0	1000	0
	238	960	0	279
C(5)	160	-746	0	666
	193	666	0	746
	195	0	1000	0
C(6)	152	-316	0	949
	156	0	1000	0
	159	949	0	316
C(7)	155	952	0	-306
	179	0	1000	0
	182	306	0	952
C(8)	148	877	0	480
	180	-0	1000	0
	184	480	0	-877
O(1)	149	-995	0	101
	231	101	0	995
	296	0	1000	0
O(2)	146	-474	0	881
	193	881	0	474
	288	0	1000	0
O(3)	145	408	0	913
	192	-913	0	408
	291	0	1000	0
O(4)	149	962	0	274
	216	-274	0	962
	242	0	1000	0
O(5)	195	079	-793	604
	208	989	138	052
	340	125	-593	-795
Li	175	822	0	569
	195	-569	0	822
	213	0	1000	0

lowing principal components of the L tensor [in ($^\circ$)²] were calculated (standard deviations in parentheses):

$$L_1 = 5.9 (1.4), \quad L_2 = 10.7 (8), \quad L_3 = 15.2 (3).$$

The principal axes are oriented nearly parallel to the cell edges, and the indices refer to the appropriate crystallographic axes. The librational amplitudes are: 2.4, 3.3, and 3.9 $^\circ$, respectively. The components of the T tensor are (in \AA^2):

$$T_1 = 0.024 (1), \quad T_2 = 0.021 (2), \quad T_3 = 0.023 (1).$$

The effective screw translations do not exceed 0.0005 \AA . The standard deviation of the U_{ij} is 0.0018 \AA^2 .

An upper limit of the hydrogen-bond length as corrected for thermal motion was obtained by the fol-

lowing procedure. The components of the thermal-motion tensors of O(2) and O(3), as determined from the refinement, were diminished by the tensor components which result solely from the rigid-body translation T and libration L of the molecule. Using the remaining tensor components and assuming an independent motion of the oxygens according to Busing & Levy (1964) an upper limit for the O(2)-O(3) distance of 2.4044 (7) \AA was determined.

An interpretation of the physical properties of lithium hydrogen phthalate dihydrate with respect to its crystal structure will be given by Haussühl (1975).

We are indebted to Professor Dr S. Haussühl for suggesting this work and for supplying crystal material. We also thank Professor Dr Th. Hahn for helpful discussions and consultations. Thanks are also due to Drs R. Reeber and M. S. Madhava for reading the manuscript. The diffractometer was supplied by the Deutsche Forschungsgemeinschaft. Calculations were carried out at the Rechenzentrum der TH Aachen.

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