

## The Carvoxime System. II. X-ray Study of *l*-Carvoxime (m.p. 72°C)

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*l*-Carvoxime (m.p. 72°C) is monoclinic,  $P2_1$ , with  $a = 10.24$  (1),  $b = 11.67$  (1),  $c = 8.54$  (2) Å,  $\beta = 103.1$  (1)°,  $Z = 4$ . The structure was determined from 1043 independent intensities with  $I \geq 2.5\sigma(I)$  measured with Mo  $K\alpha$  radiation on a diffractometer, and refined by block-diagonal least squares to  $R = 0.039$ . The packing is essentially the same as in *dl*-carvoxime. The rotational arrangements of the isopropenyl groups are significantly different in the two independent molecules and deviate from that found in the *dl*-compound.

### Introduction

The present study is part of a programme which aims at a better understanding of the thermodynamic properties of the system *d*-carvoxime + *l*-carvoxime. In Part I (Oonk & Kroon, 1976) the crystal structure of *dl*-carvoxime ( $C_{10}H_{15}NO$ ) has been described; Baert & Fouret (1975) solved it independently. In this contribution we report the details of the crystal structure analysis of *l*-carvoxime, while, in the near future, we hope to communicate on mixed crystals of composition between *d* (or *l*) and *dl*.

The striking resemblance between the crystal data of *l*-carvoxime and those of *dl*-carvoxime suggests that the crystals are isostructural. This similarity extends to the X-ray intensity statistics. The latter is demonstrated by the comparison of  $\langle F(h0l)^2 \rangle_{l=2n+1} / \langle F(h0l)^2 \rangle_{l=2n}$ : for *dl*-carvoxime this ratio is zero as a consequence of space-group symmetry, and for *l*-carvoxime a value as low as 0.06 is found.

### Experimental

Transparent plate-shaped crystals (m.p. 72°C) were obtained from a methanol-water solution by slow evaporation. Because of the volatility of the compound, a crystal,  $0.8 \times 0.4 \times 0.3$  mm, was sealed in a glass capillary. Crystal data are presented in Table 1; the cell dimensions were calculated from the settings of 14 reflexions on a Nonius four-circle automatic diffractometer (Zr-filtered Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å).

Table 1. *Crystal data*

$C_{10}H_{15}NO$ , monoclinic, $P2_1$	F.W. 165.23
$a = 10.24$ (1) Å	$V = 994.0$ Å <sup>3</sup> , $Z = 4$
$b = 11.67$ (1)	$D_x = 1.104$ g cm <sup>-3</sup>
$c = 8.54$ (2)	$D_m = 1.108$
$\beta = 103.1$ (1)°	$\mu(\text{Mo } K\alpha) = 0.84$ cm <sup>-1</sup>

Intensities for 2276 reflexions for the unique portion of the reciprocal lattice with  $\sin \theta / \lambda < 0.65$  Å<sup>-1</sup> were measured with the same equipment by the  $\omega$ - $2\theta$  scan method and a scan width of  $0.37 + 0.92 \tan \theta$ . The scan speed was varied to achieve 1000 counts above background, with a maximum scan time of 120 s. Only 1043 reflexions had  $I \geq 2.5\sigma(I)$  and these were used for the structure determination. The data were corrected for the Lorentz-polarization effects, but not for absorption.

The X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) modified and implemented by the Dutch X-ray system group was used for most calculations.

### Structure determination

The structure was solved by the multisolution procedure of Main, Woolfson & Germain (1971). After anisotropic block-diagonal least-squares refinement the difference map revealed all H atoms. The refinement was continued with the H vibrational parameters constrained to the isotropic thermal parameters of the atoms to which they are bonded. The scattering factors for the heavy atoms were those of Cromer & Mann (1968), for H those of Stewart, Davidson & Simpson (1965). Unit weights were used throughout. During the last cycle the largest parameter shifts were  $0.7\sigma$  for the heavy and  $1.8\sigma$  for the H atoms. The absolute values of peaks and troughs in the final difference synthesis did not exceed  $0.09$  e Å<sup>-3</sup>.

It appeared that the geometry of the isopropenyl group C(18)C(19)C(20) deviated from what would be expected from bond-order considerations. Since from a semi-block-diagonal refinement it appeared that a strong correlation exists between the parameters of the isopropenyl groups of the two independent molecules, the parameter-shift procedure of Bhuiya &

Stanley (1964) was applied to these six C atoms. However, the resulting coordinates did not depart significantly from those obtained by least squares. Final parameters are listed in Table 2 ( $R=0.039$ ).

### Discussion of the structure

The expected similarity of the *dl*-carvoxime and *l*-carvoxime structures is confirmed and can be seen in Fig. 1. The conformations of the isopropenyl groups

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31770 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

of the two independent molecules are such that the loss of mirror symmetry caused by the presence of only one antipode is partially compensated. The pseudosymmetrical relation is illustrated in Fig. 2. From this figure it is also clear that three conformations of the carvoxime molecule are now known. Since most of the conformational differences are accounted for by the rotational arrangements of the isopropenyl groups, Newman projections along the C(4)–C(8) bonds are given (Fig. 3).

Bond distances and angles are listed in Table 3.

Apart from the isopropenyl group C(18)C(19)C(20) there are no striking differences from the geometry of carvoxime found in *dl*-carvoxime. The geometry of this particular isopropenyl group at first sight might point to partial conformational disorder (the existence

Table 2. Atomic parameters

The e.s.d.'s are in parentheses and refer to the least significant digit(s).

(a) Heavy atoms. The positional parameters are  $\times 10^4$ . The thermal parameters are in the form

$$T = \exp(-2\pi^2/100 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} h_i h_j a_i^* a_j^*)$$

The key to the numbering can be inferred from Fig. 1.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
O(1)	3448 (3)	4750 (3)	7224 (5)	6.5 (2)	5.1 (2)	10.7 (3)	1.0 (2)	1.6 (2)	0.0 (2)
N(1)	4364 (4)	5593 (4)	7988 (5)	6.1 (3)	5.5 (2)	6.9 (3)	0.9 (2)	0.7 (2)	-0.3 (2)
C(1)	4721 (5)	7541 (5)	8584 (7)	5.2 (3)	6.4 (3)	7.3 (4)	0.5 (3)	1.0 (3)	-1.3 (3)
C(2)	3860 (5)	6600 (4)	7854 (6)	5.7 (3)	5.4 (3)	5.7 (3)	1.2 (2)	1.6 (2)	0.4 (2)
C(3)	2476 (5)	6860†	6883 (6)	5.7 (3)	5.5 (3)	7.1 (4)	0.8 (3)	0.7 (3)	-0.5 (3)
C(4)	1962 (5)	8049 (4)	7202 (6)	5.9 (3)	5.5 (3)	5.8 (3)	1.5 (2)	0.9 (3)	0.1 (3)
C(5)	3030 (6)	8933 (5)	7166 (8)	7.3 (4)	5.2 (3)	12.3 (5)	0.9 (3)	1.3 (4)	0.2 (3)
C(6)	4334 (6)	8597 (5)	8278 (8)	6.8 (4)	5.5 (3)	11.9 (5)	0.1 (3)	1.2 (4)	-2.1 (3)
C(7)	6076 (6)	7223 (5)	9653 (8)	6.5 (4)	9.0 (5)	9.6 (5)	0.6 (3)	-0.3 (3)	-2.3 (4)
C(8)	623 (5)	8275 (5)	6079 (7)	6.5 (4)	6.6 (4)	7.7 (4)	2.5 (3)	0.3 (3)	-0.9 (3)
C(9)	417 (8)	9036 (7)	4909 (9)	11.2 (6)	12.6 (6)	9.7 (5)	4.3 (5)	-0.4 (4)	2.9 (5)
C(10)	-485 (7)	7548 (7)	6406 (11)	6.6 (4)	10.5 (6)	19.3 (8)	1.6 (4)	-1.4 (5)	0.0 (6)
O(2)	3340 (4)	9221 (3)	1696 (5)	6.5 (2)	5.1 (2)	12.9 (3)	-0.7 (2)	1.0 (2)	1.4 (2)
N(2)	4251 (4)	8422 (3)	2574 (6)	5.3 (2)	5.0 (3)	8.6 (3)	-0.6 (2)	1.0 (2)	0.5 (2)
C(11)	4548 (5)	6555 (4)	3647 (6)	4.4 (3)	7.1 (3)	6.1 (3)	-0.3 (2)	0.9 (2)	-0.6 (3)
C(12)	3720 (5)	7430 (4)	2677 (6)	5.1 (3)	5.1 (3)	5.7 (3)	-0.5 (2)	1.1 (2)	-0.2 (2)
C(13)	2270 (5)	7158 (4)	1935 (6)	5.0 (3)	5.4 (3)	6.5 (3)	-1.3 (2)	0.5 (2)	0.9 (3)
C(14)	2137 (5)	5882 (4)	1421 (6)	5.2 (3)	6.5 (3)	6.3 (3)	-1.4 (3)	0.8 (3)	0.1 (3)
C(15)	2693 (5)	5129 (4)	2900 (6)	5.7 (3)	4.7 (3)	7.5 (4)	-0.9 (2)	0.9 (3)	0.5 (3)
C(16)	4064 (5)	5516 (4)	3753 (6)	5.8 (3)	5.6 (3)	7.4 (4)	-0.4 (3)	0.2 (3)	0.8 (3)
C(17)	5954 (5)	6890 (5)	4559 (7)	5.5 (3)	8.3 (4)	8.6 (4)	-0.7 (3)	-0.6 (3)	-1.0 (3)
C(18)	715 (5)	5546 (5)	626 (7)	6.6 (4)	7.5 (4)	7.3 (4)	-2.5 (3)	-0.7 (3)	1.2 (3)
C(19)	499 (8)	4772 (7)	-544 (10)	10.0 (6)	14.0 (7)	13.8 (7)	-3.8 (5)	-1.7 (5)	-4.2 (5)
C(20)	-357 (7)	6017 (7)	1246 (10)	6.1 (4)	13.1 (7)	18.2 (8)	-2.1 (4)	0.1 (5)	-0.4 (6)

(b) H atoms. Positional parameters are  $\times 10^3$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$B(\text{\AA}^2)$		<i>x</i>	<i>y</i>	<i>z</i>	$B(\text{\AA}^2)$
H(O1)	389 (4)	414 (4)	722 (5)	7.9	H(O2)	382 (5)	972 (4)	175 (6)	8.8
H(C3)	182 (4)	617 (4)	709 (5)	6.7	H(C13)	200 (4)	768 (4)	86 (5)	6.6
H'(C3)	249 (4)	683 (4)	580 (5)	6.7	H''(C13)	175 (4)	725 (4)	290 (5)	6.6
H(C4)	176 (4)	794 (4)	838 (5)	6.7	H(C14)	277 (4)	571 (4)	67 (5)	7.0
H(C5)	282 (5)	976 (4)	746 (5)	9.1	H(C15)	275 (4)	437 (4)	243 (5)	6.9
H'(C5)	319 (5)	887 (4)	596 (6)	9.1	H''(C15)	204 (4)	513 (4)	375 (5)	6.9
H(C6)	489 (5)	935 (4)	897 (5)	8.9	H(C16)	463 (4)	490 (4)	451 (5)	6.7
H(C7)	664 (5)	691 (4)	894 (6)	9.2	H(C17)	589 (5)	760 (4)	541 (5)	8.3
H'(C7)	645 (5)	790 (4)	1029 (6)	9.2	H''(C17)	628 (5)	618 (4)	539 (5)	8.3
H''(C7)	585 (5)	672 (4)	1076 (6)	9.2	H''(C17)	659 (5)	695 (4)	373 (6)	8.3
H(C9)	102 (5)	971 (5)	475 (6)	12.2	H(C19)	141 (5)	452 (5)	-102 (6)	12.2
H'(C9)	-56 (5)	904 (5)	405 (6)	12.2	H''(C19)	-30 (5)	447 (5)	-83 (6)	12.2
HC(10)	-29 (6)	671 (5)	582 (7)	13.9	H(C20)	-16 (6)	662 (5)	242 (7)	13.9
H'(C10)	-118 (6)	771 (5)	564 (7)	13.9	H''(C20)	-121 (6)	547 (5)	124 (7)	13.9
H''(C10)	-69 (6)	787 (5)	775 (7)	13.9	H''(C20)	-61 (6)	640 (5)	25 (8)	13.9

† Parameter restricted.

of two conformations, differing by 180°, and not occurring in the same proportion). On the other hand, in the absence of disorder in this group, its geometry may be explained as the result of intramolecular overcrowding, since the very short contact H'(C13)

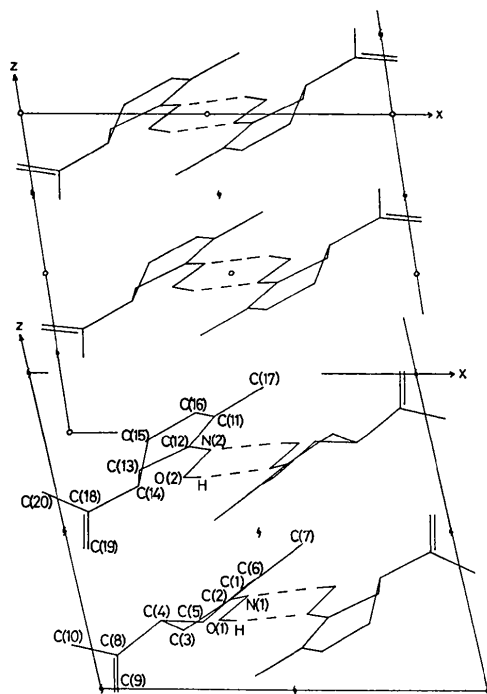


Fig. 1. Projection along *b* of the structures of *dl*-carvoxime (upper part) and *l*-carvoxime (lower part). Of the H atoms, only those of the oxime groups are depicted.

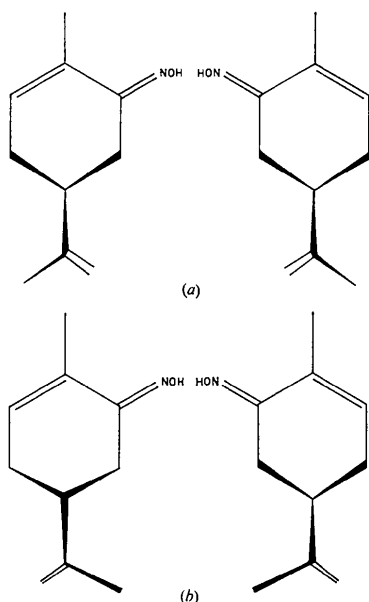


Fig. 2. (a) The mirror-image relation between the antipode molecules of *dl*-carvoxime. (b) The pseudo mirror-image relation between the two independent molecules of *l*-carvoxime.

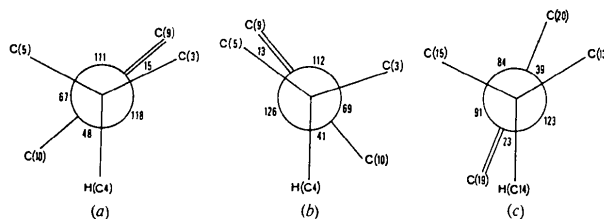


Fig. 3. Newman projections along C(4)-C(8) bonds of the carvoxime molecules having the *l*-carvoxime configuration in (a) *dl*-carvoxime, (b) *l*-carvoxime (molecule I), (c) *l*-carvoxime (molecule II).

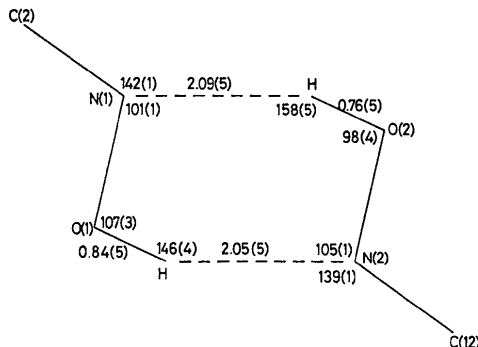


Fig. 4. Hydrogen-bond geometry in the structure of *l*-carvoxime. Distances are in Å, angles in degrees.

Table 3. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

For geometries involving H atoms only mean values are given with their corresponding standard deviations (see also Fig. 4).

N(1)-O(1)	1.413 (5)	O(1)-N(1)-C(2)	112.7 (4)
C(2)-N(1)	1.278 (6)	N(1)-C(2)-C(1)	117.5 (4)
C(1)-C(2)	1.457 (7)	N(1)-C(2)-C(3)	123.2 (4)
C(2)-C(3)	1.502 (6)	C(1)-C(2)-C(3)	119.2 (4)
C(3)-C(4)	1.530 (6)	C(2)-C(3)-C(4)	113.9 (3)
C(4)-C(5)	1.508 (8)	C(3)-C(4)-C(5)	109.7 (4)
C(5)-C(6)	1.505 (8)	C(4)-C(5)-C(6)	110.6 (5)
C(1)-C(6)	1.302 (7)	C(5)-C(6)-C(1)	124.0 (5)
C(1)-C(7)	1.525 (7)	C(6)-C(1)-C(2)	120.0 (4)
C(4)-C(8)	1.508 (7)	C(6)-C(1)-C(7)	123.0 (5)
C(8)-C(9)	1.318 (9)	C(2)-C(1)-C(7)	117.0 (5)
C(8)-C(10)	1.493 (10)	C(3)-C(4)-C(8)	110.2 (4)
		C(5)-C(4)-C(8)	115.2 (4)
		C(4)-C(8)-C(9)	124.5 (6)
		C(4)-C(8)-C(10)	113.7 (5)
		C(9)-C(8)-C(10)	121.8 (6)
N(2)-O(2)	1.408 (5)	O(2)-N(2)-C(12)	113.1 (4)
C(12)-N(2)	1.291 (6)	N(2)-C(12)-C(11)	117.8 (4)
C(11)-C(12)	1.459 (6)	N(2)-C(12)-C(13)	123.3 (4)
C(12)-C(13)	1.510 (6)	C(11)-C(12)-C(13)	118.8 (4)
C(13)-C(14)	1.551 (7)	C(12)-C(13)-C(14)	109.6 (4)
C(14)-C(15)	1.538 (7)	C(13)-C(14)-C(15)	108.9 (4)
C(15)-C(16)	1.498 (7)	C(14)-C(15)-C(16)	111.0 (4)
C(11)-C(16)	1.321 (7)	C(15)-C(16)-C(11)	124.7 (4)
C(11)-C(17)	1.524 (7)	C(16)-C(11)-C(12)	120.1 (4)
C(14)-C(18)	1.512 (7)	C(16)-C(11)-C(17)	121.7 (4)
C(18)-C(19)	1.328 (10)	C(12)-C(11)-C(17)	118.1 (4)
C(18)-C(20)	1.432 (10)	C(13)-C(14)-C(18)	112.9 (4)
		C(15)-C(14)-C(18)	111.1 (4)
		C(14)-C(18)-C(19)	119.5 (6)
		C(14)-C(18)-C(20)	118.4 (5)
		C(19)-C(18)-C(20)	121.9 (6)
C-H	1.06 (2)		
C-C( <i>sp</i> <sup>3</sup> )-H	107.5 (10)		
C-C( <i>sp</i> <sup>2</sup> )-H	119 (2)		
H-C( <i>sp</i> <sup>3</sup> )-H	112 (3)		
H-C( <i>sp</i> <sup>2</sup> )-H	120 (6)		

$\cdots\text{H}(\text{C}20)$  of 2.05 Å would be even less if the angle  $\text{C}(14)\text{--}\text{C}(18)\text{--}\text{C}(20)$  had the expected value of  $115^\circ$  rather than the observed  $118^\circ$ .

The most dominant feature in the packing is the hydrogen-bond formation  $\text{O--H}\cdots\text{N}$  which is essentially the same as in the *dl*-compound, although the six-membered ring, which is planar within 0.15 Å, has lost its centre of symmetry (Fig. 4). The distances  $\text{O}(1)\cdots\text{N}(2)$  and  $\text{O}(2)\cdots\text{N}(1)$  are 2.793 (5) and 2.806 (6) Å respectively.

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## Compounds with Perovskite-Type Slabs. II. The Crystal Structure of $\text{Sr}_2\text{Ta}_2\text{O}_7$

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The crystal structure of  $\text{Sr}_2\text{Ta}_2\text{O}_7$  has been determined from three-dimensional X-ray diffraction data and refined to a conventional *R* value of 0.036 for 697 observed reflexions.  $\text{Sr}_2\text{Ta}_2\text{O}_7$  crystallizes in the orthorhombic space group *Cmcm*, with  $a=3.937$  (6),  $b=27.198$  (6),  $c=5.692$  (7) Å and  $Z=4$ . The crystal is essentially isostructural with  $\text{Sr}_2\text{Nb}_2\text{O}_7$ , having a structure composed of perovskite-type slabs parallel to (010). There are two independent Ta atoms surrounded octahedrally by O atoms. The  $\text{Ta}(1)\text{--}\text{O}$  and  $\text{Ta}(2)\text{--}\text{O}$  distances range from 1.87 (1) to 2.16 (1) Å and 1.89 (1) to 2.07 (1) Å respectively. The  $\text{Sr}(2)$  atom is surrounded by 12 O atoms with distances ranging from 2.70 (3) to 2.85 (1) Å. The  $\text{Sr}(1)$  atom near the boundary of a slab is surrounded by six O atoms in the same slab and two O atoms in the neighbouring slab with distances ranging from 2.47 (1) to 3.27 (1) Å.

#### Introduction

Recently, some  $\text{A}_2\text{B}_2\text{O}_7$  compounds were revealed to form a structural family characterized by the perovskite-type slabs in their structures. Examples are  $\text{Ca}_2\text{Nb}_2\text{O}_7$  (Scheunemann & Müller-Buschbaum, 1974),  $\text{Sr}_2\text{Nb}_2\text{O}_7$  (Ishizawa, Marumo, Kawamura & Kimura, 1975) and  $\text{La}_2\text{Ti}_2\text{O}_7$  (Gasperin, 1975). Though crystals of  $\text{Sr}_2\text{Ta}_2\text{O}_7$  had been supposed to have a tetragonal pyrochlore-type structure with  $a=10.63$ ,  $c=10.91$  Å (Ismailzade, 1958), it was found by Nanamatsu, Kimura & Kawamura (1975) that the symmetry and the cell dimensions rather suggest a close similarity in the structure to  $\text{Sr}_2\text{Nb}_2\text{O}_7$ .  $\text{Sr}_2\text{Ta}_2\text{O}_7$  is paraelectric at room temperature, having a markedly lower ferroelectric phase transition temperature ( $-107^\circ\text{C}$ ) than  $\text{Sr}_2\text{Nb}_2\text{O}_7$  ( $1342^\circ\text{C}$ ),  $\text{La}_2\text{Ti}_2\text{O}_7$  ( $\sim 1500^\circ\text{C}$ ) and  $\text{Ca}_2\text{Nb}_2\text{O}_7$  ( $> 1500^\circ\text{C}$ ) (Nanamatsu *et al.*, 1975). Therefore, the crystal structure of  $\text{Sr}_2\text{Ta}_2\text{O}_7$  at room temperature is expected to afford important information on the structures of the paraelectric phases of these compounds.

#### Experimental

Transparent, colourless crystals were synthesized from a 2:1 mixture of  $\text{SrCO}_3$  and  $\text{Ta}_2\text{O}_5$  with a floating-zone technique. From Weissenberg photographs, the crystal was found to have orthorhombic symmetry, and systematic absences,  $h+k$  odd in  $hkl$  and  $l$  odd in  $h0l$ , restricted the possible space groups to *C2cm* (No. 40), *Cmc2<sub>1</sub>* and *Cmcm*. Since the crystal is paraelectric at room temperature, the space group *Cmcm* seemed to be most plausible, and has been justified in the course of the structure determination. The cell dimensions were determined from 15  $2\theta$  values in the range between  $20$  and  $70^\circ$  measured with  $\text{Cu K}\alpha$  radiation on a powder diffractometer, by the least-squares procedure. The crystal data are given in Table 1.

Intensities were collected on a four-circle diffractometer (Philips PW 1100) with  $\text{Mo K}\alpha$  radiation from a graphite monochromator. A crystal with dimensions of about  $0.166 \times 0.024 \times 0.166$  mm was used. The  $\omega$ - $2\theta$  scan technique was employed with a scanning speed of  $4^\circ \text{min}^{-1}$  in  $\omega$ . In all, 697 independent reflexion