

The Crystal and Molecular Structure of β -Pyrazincarboxamide

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β -Pyrazincarboxamide crystallizes in the space group $P2_1/c$ with unit-cell dimensions $a=14.372$ (7), $b=3.711$ (3), $c=10.726$ (5) Å and $\beta=101.92$ (5)°. The structure was solved on the basis of 813 observed independent reflexions by the aid of the symbolic addition procedure and refined by the full-matrix least-squares method, including anisotropic temperature factors and the use of a weighting scheme, to a final R_1 index of 0.055. The molecules have a closely planar pyrazine ring, and the carboxamide group, which is also planar, deviates 3.2° from the plane of the ring. The molecules exist as dimers formed by hydrogen bonds between carboxamide groups, the dimers being linked together in chains by other weaker hydrogen bonds between the carboxamide groups.

Introduction

Pyrazincarboxamide (pyrazine-2-carboxamide) has four different crystal modifications as shown by Tamura, Kuwano & Sasada (1961). The crystal structure of α -pyrazincarboxamide, abbreviated α -PCA, was solved and refined by Takaki, Sasada & Watanabé (1960). While the crystal structures of α - and δ -pyrazincarboxamide are formed by simple sheets of molecules, the structure of β -pyrazincarboxamide (hereafter called β -PCA) is supposed to be of the two-dimensional sheet type, also referred to as the 'herring bone' packing, as suggested by Takaki *et al.* (1960). No detailed structure analysis has so far been published for the β -, γ - and δ -forms. A knowledge of the structures of these crystal modifications would be of interest in order to understand the existence of four apparently stable forms and to relate their structures to those of other carboxamides. The results of the determination of the structure of β -PCA are given in the present paper, and the structure of the δ form will be described in a following paper.

Experimental

Crystals of β -PCA were obtained by recrystallization of commercial pyrazincarboxamide using the method described by Tamura *et al.* (1961). The crystals were small, thin prisms showing frequent twinning, and most often linked together in long chains. The crystallographic data are:

β -Pyrazine-2-carboxamide, $C_5H_5N_3O$; F.W. 123.11; m.p. 188°C; monoclinic; $Z=4$; $\lambda(\text{Cu } K\alpha_1)=1.5405$ Å.

$$\begin{aligned} a &= 14.372 \pm 0.007 \text{ \AA} \\ b &= 3.711 \pm 0.003 \\ c &= 10.726 \pm 0.005 \\ \beta &= 101.92 \pm 0.05^\circ \end{aligned}$$

Volume of the unit cell: $V=559.64$ Å³

Density, calculated with $Z=4$: $D=1.461$ g.cm⁻³;

Absorption coefficient for $\lambda(\text{Cu } K\alpha)$ ($=1.5418$ Å):

$\mu=9.24$ cm⁻¹

Systematic absences: $h0l$ when l odd and $0k0$ when k odd;

Space group: $P2_1/c$; $F(000)=256$.

Intensities were initially measured by the aid of a manually operated Siemens diffractometer equipped with an Eulerian cradle, using Ni-filtered Cu radiation, a pulse-height discriminator and a scintillation counter. The crystals are slightly unstable and it was therefore necessary to use two specimens for the complete data collection. These specimens were of the following dimensions 0.15 × 0.23 × 0.06 mm and 0.13 × 0.30 × 0.10 mm, having μR_{max} values of 0.13 and 0.16 respectively. No absorption corrections were made in the measured intensities. The crystal was mounted with the b axis parallel to the ϕ axis of the Eulerian cradle. The normal beam equatorial 2θ scan method with symmetrical A and fixed χ settings was used for intensity measurements in the 2θ range 0 to 158°. Neglecting all intensities with $\sigma(\Delta I/I) > 1.0$ this set of data consisted of 852 independent reflexions. The intensity measurements were at a later stage in the structure determination repeated using a Picker automatic four circle diffractometer. The dimensions of the third crystal were 0.09 × 0.21 × 0.04 mm corresponding to a value of μR_{max} of 0.11. The mounting of the crystal and the scanning method were the same as in the former case. Intensities were measured in the 2θ range 0 to 128° using symmetrical A setting only. Applying the $\sigma(\Delta I/I) > 1.0$ criterion on this set and taking the mean values of the two scaled intensity sets gave a final data set consisting of 813 independent reflexions.

The structure factors were derived from the measured intensities by means of a data reduction program. This program corrected also for the reduction in the

integrated intensities of two standard reflexions $2\bar{1}2$ and $1\bar{1}1$, which were measured at frequent intervals (after every 15 to 20 reflexions). Lorentz and polarization factor corrections were introduced simultaneously. Conversion of absolute F values to the corresponding E values was carried out using the formula:

$$E_h^2 = F_h^2 / \varepsilon \sum_{j=1}^N f_{jh}^2.$$

In the case of the space group $P2_1/c$, $\varepsilon = 1$ except when h is $h0l$ or $0k0$. The statistical averages for the E values are as follows:

	Experi- mental	Centric	Acentric
$\langle E \rangle$	0.752	0.798	0.886
$\langle E^2 - 1 \rangle$	1.047	0.968	0.736
$\langle E ^2 \rangle$	0.991	1.000	1.000

The distribution of the normalized structure factors gives 0.73% with $|E| > 3.0$, 5.1% with $|E| > 2.0$ and 26.4% with $|E| > 1.0$. The theoretical values for a centric crystal having randomly distributed atoms are 0.3, 4.6 and 31.7% respectively.

Determination of the structure

The structure of β -PCA was solved by using the symbolic addition procedure described by Karle & Karle

(1963). The origin was chosen by assigning signs to three suitable linearly independent reflexions. Three more reflexions were specified with given letter symbols. The reflexions, thus selected, had relatively large $|E|$ values and occurred in a large number of interactions in the \sum_2 relationship given by:

$$sE_h \approx s \sum_k E_k \cdot E_{h-k}$$

where s means 'sign of'. The six reflexions used for a start are listed in Table 1.

Table 1. *The basic set of normalized structure factor amplitudes for the application of the \sum_2 relationship*

h	k	l	$ E $	Sign
2	$\bar{1}$	$\bar{1}$	2.51	+
3	0	$\bar{1}0$	4.31	+
8	$\bar{1}$	4	2.87	+
11	$\bar{1}$	5	3.03	+A
4	$\bar{1}$	9	2.72	+B
11	$\bar{1}$	6	2.42	+C

Starting with a selection of 129 reflexions having $|E| \geq 1.5$ the \sum_2 formula was applied in an iterative process using the program *SYMBOL*. The probability limit of accepting a sign was $P+(h) > 0.98$ based on the formula by Cochran & Woolfson (1955) $P+(h) \approx \frac{1}{2} + \frac{1}{2} \tanh(\sigma_3 \cdot \sigma_2^{-3/2} |E_h| \sum_k E_k \cdot E_{h-k})$. The signs of

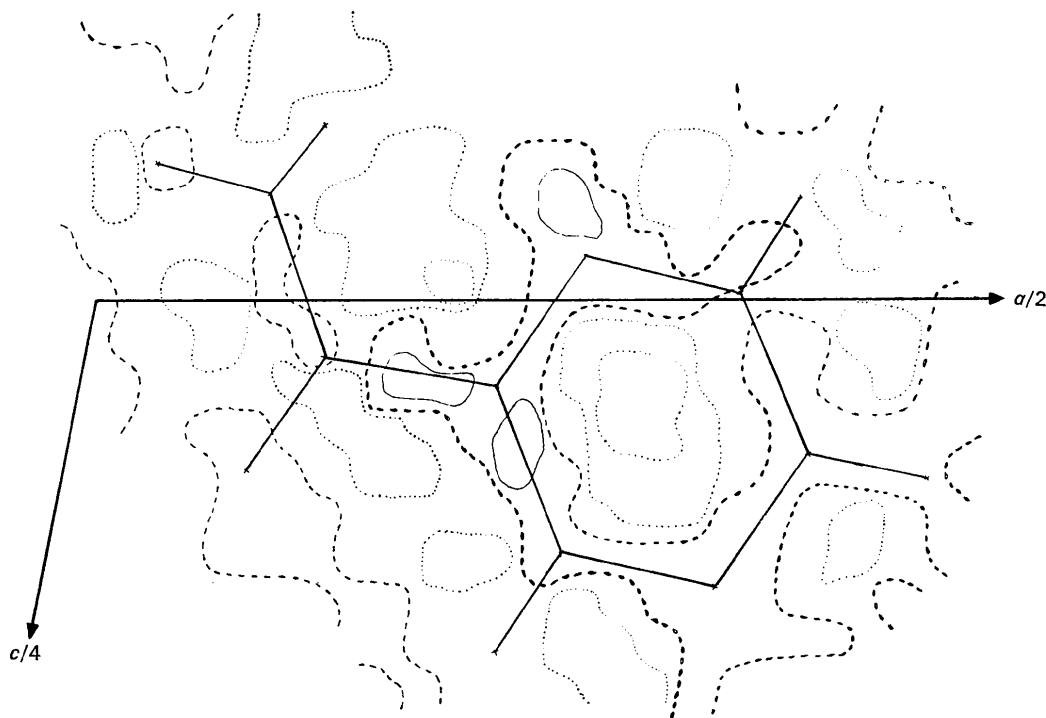


Fig. 1. Final difference map of β -PCA calculated in the molecular plane. The zero contour is shown by dashed lines, negative contours by dotted lines and positive contours by full lines at intervals of $0.07 \text{ e.}\text{\AA}^{-3}$ (average value of three Fourier map sections).

Table 2. Final atomic parameters of β -PCA

The thermal parameters are defined by the expression:

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

The positional and thermal parameters for the non-hydrogen atoms have been multiplied by 10^4 , and the positional parameters for the hydrogen atoms by 10^3 .

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	2670 (2)	4916 (7)	-306 (2)	30 (1)	528 (21)	46 (2)	2 (4)	5 (1)	-2 (6)
C(2)	2321 (2)	6146 (8)	670 (2)	28 (1)	391 (22)	51 (2)	-8 (5)	8 (1)	4 (6)
C(3)	2860 (2)	6169 (9)	1898 (3)	32 (1)	624 (27)	52 (3)	-1 (6)	9 (2)	-13 (7)
N(4)	3758 (2)	5018 (8)	2173 (2)	31 (1)	771 (26)	51 (2)	1 (5)	3 (1)	10 (7)
C(5)	4105 (2)	3816 (9)	1192 (3)	28 (1)	576 (26)	67 (3)	11 (5)	8 (2)	30 (7)
C(6)	3565 (2)	3737 (9)	-33 (3)	36 (1)	564 (26)	57 (3)	10 (5)	15 (2)	-16 (7)
C(7)	1324 (2)	7668 (9)	410 (3)	30 (1)	465 (25)	64 (3)	-9 (5)	6 (2)	6 (7)
N(8)	846 (2)	7471 (9)	-787 (3)	32 (1)	869 (29)	65 (3)	35 (5)	2 (2)	-19 (8)
O(9)	1017 (1)	9033 (7)	1291 (2)	34 (1)	770 (22)	72 (2)	44 (4)	11 (1)	-35 (6)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(3)	261 (2)	704 (10)	261 (3)	3.9 (0.8) Å ²
H(5)	479 (2)	298 (9)	137 (3)	3.3 (0.7)
H(6)	380 (2)	290 (9)	-75 (3)	3.4 (0.7)
H(8')	109 (3)	658 (13)	-134 (4)	5.7 (1.1)
H(8'')	21 (3)	829 (12)	-101 (4)	6.0 (1.0)

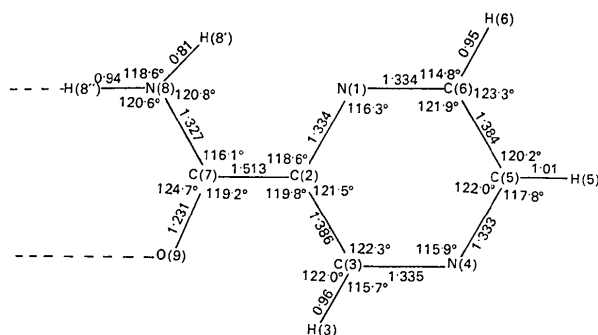
123 other reflexions were indicated by a combination of letters or the sign +. The numbers of relationships among the symbols were as follows:

$$\begin{array}{ll} - = + & 95 \\ + A = + & 5 \\ - A = + & 5 \\ + B = + & 190 \\ + B = + & 79 \\ + AB = + & 39 \end{array} \quad \begin{array}{ll} - AB = + & 118 \\ + C = + & 3 \\ - C = + & 209 \\ + BC = + & 2 \\ + ABC = + & 2 \\ - ABC = + & 2. \end{array}$$

The most probable signs of *A*, *B* and *C* appear from these relations to be *A* = -, *B* = + and *C* = -. The calculation of a three-dimensional *E* map based on the derived phases clearly revealed the structure of the molecule and the approximate positions of the heavier atoms. All the 129 signs used in the calculation of this map later proved to be correct.

Refinement of the structure

The structure was refined by means of the full-matrix least-squares refinement program minimizing the function $\sum w(|F_o| - K|F_c|)^2$. The atomic scattering factors for O, N and C were as given by Doyle & Turner (1968), and for H by Stewart, Davidson & Simpson (1965). The initial atomic positions were obtained from the *E* map. Two cycles of refinement, in which the scattering factor of carbon was used for all the heavier atoms, lowered the *R*₁ index from a value of 33.4 to 20.0%. The *R*₁ index is as usual: $\sum ||F_o| - K|F_c|| / \sum |F_o|$. Two more cycles, in which the isotropic *B*'s for the heavier and included atoms were varied, made it possible to distinguish between the oxygen atom, the nitrogen atoms and the carbon atoms.

Fig. 2. Bond lengths (Å) and bond angles (°) in β -PCA.

The atomic coordinates, and the isotropic and anisotropic temperature factors were then successively refined giving a total reduction of the *R*₁ index from a value of 17.0% to 10.1%. A difference map calculated at this stage revealed the positions of all the five hydrogen atoms. The atomic coordinates of the hydrogen atoms were refined in the next three cycles, together with the scale factor, and this led to a value of the *R*₁ index of 7.2%.

Inspection of the strongest reflexions indicated that the 102 reflexion was seriously affected by extinction and this reflexion was therefore removed from the data set. The refinement was continued varying all coordinates and anisotropic thermal parameters of the heavier atoms and coordinates and isotropic *B*'s of the hydrogen atoms. The *R*₁ index stopped at a value of 6.8%, the refinement being up to this stage based on the data obtained with the manual diffractometer. The further refinement was from now on based on mean values of the two sets of data from the manual diffractometer and the automatic diffractometer. Two cycles of refinement reduced the *R*₁ index to a value of 5.7%. In a final cycle the weighting scheme proposed by Cruickshank (1965) was introduced as follows:

$$w_1 = (0.0057|F_o|^2 - 0.074|F_o| + 0.75)^{-1}$$

and

$$w_2 = (0.022|F_o| + 0.36)^{-1}$$

below and above the threshold value $|F_0| = 13.0$ respectively. The final value of the R_1 index was 5.5%. A difference map was calculated. This is reproduced in Fig. 1 and shows that there are no distinct maxima of any height left. A tendency to positive values around the positions of the ring atoms may be observed.

The atomic coordinates and thermal parameters are given in Table 2 together with their estimated standard deviations. The observed and the calculated structure factors are listed in Table 3.

Discussion

Molecular structure

The calculated bond lengths and bond angles of β -PCA with their estimated standard deviations are given in Table 4, and are also indicated in Fig. 2. All bond lengths except those containing O(9), N(8) or H were corrected for thermal motion using the libration correction method proposed by Cruickshank (1956). The difference between the u_{ij} values for O(9)

Table 3. Observed and calculated structure factors for β -PCA

The columns are $h, l, |F_0|$ and F_c .

h	l	$ F_0 $	F_c
0 0 0	0 0 0	13.0	13.0
0 0 1	0 0 1	13.0	13.0
0 0 2	0 0 2	13.0	13.0
0 0 3	0 0 3	13.0	13.0
0 0 4	0 0 4	13.0	13.0
0 0 5	0 0 5	13.0	13.0
0 0 6	0 0 6	13.0	13.0
0 0 7	0 0 7	13.0	13.0
0 0 8	0 0 8	13.0	13.0
0 0 9	0 0 9	13.0	13.0
0 0 10	0 0 10	13.0	13.0
0 0 11	0 0 11	13.0	13.0
0 0 12	0 0 12	13.0	13.0
0 0 13	0 0 13	13.0	13.0
0 0 14	0 0 14	13.0	13.0
0 0 15	0 0 15	13.0	13.0
0 0 16	0 0 16	13.0	13.0
0 0 17	0 0 17	13.0	13.0
0 0 18	0 0 18	13.0	13.0
0 0 19	0 0 19	13.0	13.0
0 0 20	0 0 20	13.0	13.0
0 0 21	0 0 21	13.0	13.0
0 0 22	0 0 22	13.0	13.0
0 0 23	0 0 23	13.0	13.0
0 0 24	0 0 24	13.0	13.0
0 0 25	0 0 25	13.0	13.0
0 0 26	0 0 26	13.0	13.0
0 0 27	0 0 27	13.0	13.0
0 0 28	0 0 28	13.0	13.0
0 0 29	0 0 29	13.0	13.0
0 0 30	0 0 30	13.0	13.0
0 0 31	0 0 31	13.0	13.0
0 0 32	0 0 32	13.0	13.0
0 0 33	0 0 33	13.0	13.0
0 0 34	0 0 34	13.0	13.0
0 0 35	0 0 35	13.0	13.0
0 0 36	0 0 36	13.0	13.0
0 0 37	0 0 37	13.0	13.0
0 0 38	0 0 38	13.0	13.0
0 0 39	0 0 39	13.0	13.0
0 0 40	0 0 40	13.0	13.0
0 0 41	0 0 41	13.0	13.0
0 0 42	0 0 42	13.0	13.0
0 0 43	0 0 43	13.0	13.0
0 0 44	0 0 44	13.0	13.0
0 0 45	0 0 45	13.0	13.0
0 0 46	0 0 46	13.0	13.0
0 0 47	0 0 47	13.0	13.0
0 0 48	0 0 48	13.0	13.0
0 0 49	0 0 49	13.0	13.0
0 0 50	0 0 50	13.0	13.0
0 0 51	0 0 51	13.0	13.0
0 0 52	0 0 52	13.0	13.0
0 0 53	0 0 53	13.0	13.0
0 0 54	0 0 54	13.0	13.0
0 0 55	0 0 55	13.0	13.0
0 0 56	0 0 56	13.0	13.0
0 0 57	0 0 57	13.0	13.0
0 0 58	0 0 58	13.0	13.0
0 0 59	0 0 59	13.0	13.0
0 0 60	0 0 60	13.0	13.0
0 0 61	0 0 61	13.0	13.0
0 0 62	0 0 62	13.0	13.0
0 0 63	0 0 63	13.0	13.0
0 0 64	0 0 64	13.0	13.0
0 0 65	0 0 65	13.0	13.0
0 0 66	0 0 66	13.0	13.0
0 0 67	0 0 67	13.0	13.0
0 0 68	0 0 68	13.0	13.0
0 0 69	0 0 69	13.0	13.0
0 0 70	0 0 70	13.0	13.0
0 0 71	0 0 71	13.0	13.0
0 0 72	0 0 72	13.0	13.0
0 0 73	0 0 73	13.0	13.0
0 0 74	0 0 74	13.0	13.0
0 0 75	0 0 75	13.0	13.0
0 0 76	0 0 76	13.0	13.0
0 0 77	0 0 77	13.0	13.0
0 0 78	0 0 78	13.0	13.0
0 0 79	0 0 79	13.0	13.0
0 0 80	0 0 80	13.0	13.0
0 0 81	0 0 81	13.0	13.0
0 0 82	0 0 82	13.0	13.0
0 0 83	0 0 83	13.0	13.0
0 0 84	0 0 84	13.0	13.0
0 0 85	0 0 85	13.0	13.0
0 0 86	0 0 86	13.0	13.0
0 0 87	0 0 87	13.0	13.0
0 0 88	0 0 88	13.0	13.0
0 0 89	0 0 89	13.0	13.0
0 0 90	0 0 90	13.0	13.0
0 0 91	0 0 91	13.0	13.0
0 0 92	0 0 92	13.0	13.0
0 0 93	0 0 93	13.0	13.0
0 0 94	0 0 94	13.0	13.0
0 0 95	0 0 95	13.0	13.0
0 0 96	0 0 96	13.0	13.0
0 0 97	0 0 97	13.0	13.0
0 0 98	0 0 98	13.0	13.0
0 0 99	0 0 99	13.0	13.0
0 0 100	0 0 100	13.0	13.0

and N(8) was more than three times the standard deviation of the calculated values.

Table 4. Bond lengths and bond angles of β -PCA

The standard deviation is set three times higher than the e.s.d. values.

	Uncorrected	Corrected
N(1)–C(2)	1.331 Å	1.334 (3) Å
C(2)–C(3)	1.383	1.386 (4)
C(3)–N(4)	1.333	1.335 (3)
N(4)–C(5)	1.331	1.333 (3)
C(5)–C(6)	1.381	1.384 (4)
C(6)–N(1)	1.333	1.334 (3)
C(2)–C(7)	1.512	1.513 (3)
C(7)–N(8)	1.327 (4)	
C(7)–O(9)	1.231 (3)	
C(3)–H(3)	0.96	
C(5)–H(5)	1.01	
C(6)–H(6)	0.95	
N(8)–H(8')	0.81	
N(8)–H(8'')	0.94	
H(8'')–N(8)–H(8')	118.6°	
H(8'')–N(8)–C(7)	120.6	
H(8')–N(8)–C(7)	120.8	
O(9)–C(7)–N(8)	124.7 (3)	
N(8)–C(7)–C(2)	116.1 (4)	
C(2)–C(7)–O(9)	119.2 (4)	
C(7)–C(2)–N(1)	118.6 (4)	
C(7)–C(2)–C(3)	119.8 (4)	
N(1)–C(2)–C(3)	121.5 (3)	
C(2)–C(3)–N(4)	122.3 (4)	
C(2)–C(3)–H(3)	122.0	
H(3)–C(3)–N(4)	115.7	
C(3)–N(4)–C(5)	115.9 (4)	
N(4)–C(5)–C(6)	122.0 (3)	
N(4)–C(5)–H(5)	117.8	
H(5)–C(5)–C(6)	120.2	
C(5)–C(6)–N(1)	121.9 (4)	
C(5)–C(6)–H(6)	123.3	
H(6)–C(6)–N(1)	114.8	
C(6)–N(1)–C(2)	116.3 (4)	
C(5)–C(2)–C(7)	{ 176.8 (4)	
	{ 3.2 (4)	

The average values of the bond lengths in the pyrazine ring of β -PCA are 1.334 and 1.385 Å for the C–N and C–C bond respectively. The maximum deviation of the individual values from the average is 0.001 Å, which cannot be considered as significant. Somewhat larger fluctuations, possibly significant, were found in the structure of α -PCA by Takaki *et al.* (1960). The value of the C–N bond length found in this work, 1.334 Å, is slightly shorter than that found for α -PCA *i.e.* 1.348 Å and for picolinamide: 1.342 Å by Takano, Sasada & Kakudo (1966). The value of the C–C bond length 1.385 Å is in good agreement with those of α -PCA and picolinamide 1.383 and 1.379 Å respectively. Bennett, Davidson, Harding & Morelle (1971) report for the C–N bond length of DL-histidine hydrochloride, having a five-membered ring, an average value of 1.355 Å for DL-crystals and 1.345 Å for L-crystals, both cases showing a considerable spread of the individual values. The C–C bond length in the ring

is in this case 1.355 Å for DL-crystals and 1.386 Å for L-crystals.

The bond lengths within the amide group found in this work may also be compared with the corresponding bonds in the structure of α -PCA and picolinamide as follows:

	C(2)–C(7)	C(7)–N(8)	C(7)–O(9)
β -PCA	1.513 Å	1.327 Å	1.231 Å
α -PCA	1.503	1.312	1.244
picolinamide	1.515	1.330	1.241

The agreement between the values for β -PCA and picolinamide is very good. There are, however, small but probably significant differences between the values for β -PCA and those for α -PCA, indicating that the resonance between the amide group and the pyrazine ring, giving some double bond character of the C(2)–C(7) bond, is less pronounced in β -PCA than in α -PCA. The C=O double bond in the β -PCA molecule, 1.231 Å, is thus somewhat shorter than the corresponding bond in α -PCA which is 1.241 Å. It is, however, stated from infrared absorption studies by Tamura & Kuwano (1962) that the C=O bond of the four modifications of PCA, that is the α -, β -, γ - and δ -modifications, have a different construction. A C=O distance comparable to that found in β -PCA is reported for dihydronicotinamide (DHNA) by Ammon & Jensen (1967), thus 1.230 (2) Å.

The C–N distance found here in the amide group of β -PCA: 1.327 (3) Å is comparable to the value of 1.328 (6) Å found in cyclopropanecarboxamide (CCA) by Long, Maddox & Trueblood (1969), and a value of 1.334 (17) Å in acetamide, reported by Hamilton (1965). The value of 1.513 (3) Å for the C(2)–C(7) bond in β -PCA is also close to 1.509 Å found for the corresponding bond in DHNA. The C–H and the N–H bond lengths in β -PCA are on the average 0.97 and 0.87 Å respectively, and these values are closely the same as those found in α -PCA. The mean values of the C–N–C and N–C–C bond angles of the pyrazine ring found in this work are $116.2 \pm 0.4^\circ$ and $121.9 \pm 0.4^\circ$ respectively. The former value is in good agreement with that found by Chatar Singh (1965) for the C–N–C angle as a weighted mean value for six-membered heterocyclic compounds without extra-annular attachment to the ring nitrogen, *viz.* $115.7 \pm 0.2^\circ$, while the latter value is comparable with the mean value of 7 N–C–C bond angles of 121.1° found in pyridine rings as given by Sasada, Takano & Kakudo (1964). The corresponding values found in α -PCA were 115.8 and 122.1° respectively. The other bond angles of β -PCA have all reasonable values and agree closely with those found for α -PCA, especially for the bond angles within the pyrazine ring. The C(7) carbon atom of the side chain lies closely in the plane of the ring, as may be seen from the last angle of Table 4, *viz.* angle C(5)–C(2)–C(7) $176.8 \pm 0.4^\circ$; thus the carboxamide group deviates about 3.2° from the ring plane, as compared with 5° in the structure of α -PCA.

The best plane through the pyrazine ring calculated according to Blow (1960) is given by:

$$0.35975x + 0.92029y - 0.15380z + 3.13276 = 0.$$

There are no significant deviations of the ring atoms from this plane. The mean plane through the whole molecule is similarly given by:

$$0.38401x + 0.90826y - 0.16614z + 3.21143 = 0.$$

The deviations from this plane are, however, appreciable: -0.0327 \AA for C(2), -0.0462 \AA for C(3), 0.0309 \AA for C(5), 0.0241 \AA for C(6), -0.0220 \AA for N(8) and 0.0597 \AA for O(9). The C(2), C(7), N(8) and O(9) atoms of the carboxamide group lie in the plane:

$$0.41049x + 0.89051y - 0.19617z + 3.19979 = 0$$

without significant deviations from this plane.

Crystal structure

The projection of the structure of β -PCA along the b axis is shown in Fig. 3. The molecules are connected by N(8)–H(8'')–O(9) hydrogen bonds of lengths 2.92 \AA , forming dimers across the centre of symmetry. This feature is common to structures of many compounds containing a carboxamide group, e.g. α -PCA and

picolinamide. The difference in structure between the α -form and the β -form of PCA is, however, obvious, when the bonds linking the dimers together are being considered. In α -PCA the strongest intermolecular bond between dimers is found between the nitrogen atom of the carboxamide group and a nitrogen atom belonging to the pyrazine ring of a neighbouring molecule; thus N(1)–H(8)–N(8) is found to be 3.14 \AA in α -PCA. In β -PCA the strongest bond between dimers is, on the contrary, found between an amide nitrogen atom and the oxygen atom of the amide group of an adjacent molecule. In this respect the structure and the molecular packing of β -PCA is similar to that found for picolinamide (Takano *et al.*, 1966) and in tetradecanamide by Turner & Lingafelter (1955). The hydrogen bond, linking the dimers together to form endless chains running along the c -axis direction, is apparently much weaker in β -PCA than in picolinamide, as the N(8)–H(8'')–O(9) distance is found to be 3.24 \AA in the former case, while a value of 3.01 \AA was found in the latter case. The N–H...O hydrogen bonds in tetradecanamide were reported as 2.99 and 2.93 \AA for intradimer and interdimer bonds respectively. The next nearest contacts between atoms of different dimers of β -PCA are N(4)–H(6): 2.47 \AA ,

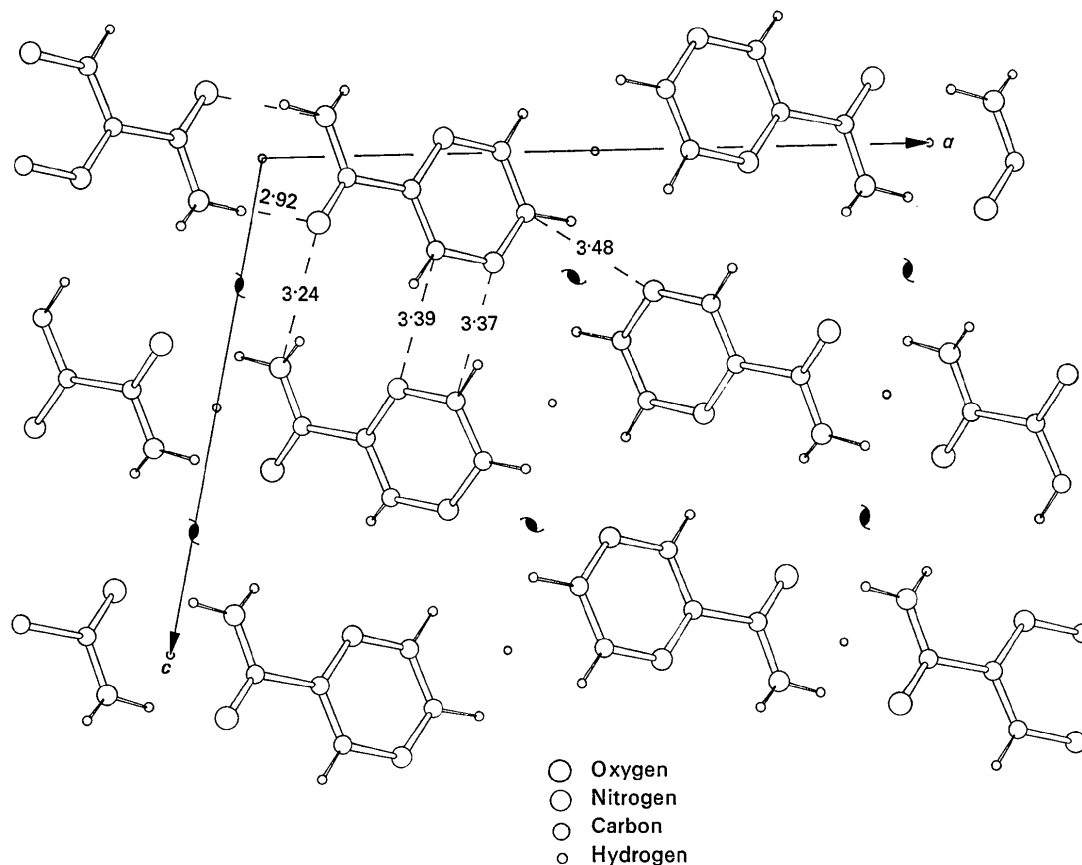


Fig. 3. Packing of the molecules in the structure of β -PCA as viewed down the b axis. Dashed lines indicate intradimer and interdimer hydrogen bonds.

N(1)–H(3): 2.49 Å and N(4)–H(5): 2.58 Å, which are all shorter than the sum of the van der Waals radii of the participants. These contacts would, however, correspond to 'bond lengths' of N(4)···H(6)–C(6) of 3.37 Å, N(1)···H(3)–C(3): 3.39 Å and N(4)···H(5)–C(5): 3.48 Å and can hardly be considered as hydrogen bonds.

The average intermolecular C–C, C–O and C–N distances are 3.49, 3.54 and 3.50 Å and the corresponding shortest approaches are 3.44, 3.38 and 3.37 Å respectively. The values may be compared to the average C–C and C–N intermolecular distances found in α -PCA, which were 3.54 and 3.44 Å, with lowest values of 3.54 and 3.44 Å respectively.

Thermal motion

An analysis of the thermal vibration parameters for β -PCA gave values of the translational and rotational vibration tensors T_{ij} and L_{ij} as given in Table 5, indicating a similar behaviour of the molecules as found in the structure of α -PCA. As might have been expected the largest oscillation was found around the axes connecting the C(2) and the C(5) atoms, showing a value of 3.8°. The oscillations around the *b* and *c* axes are 1.2 and 1.0° respectively. The corresponding values for α -PCA were 5.7° around C(2)–C(5) axis, 2.6° around the *b* axis and 2.2° around the *c* axis. The values of the T_{ij} 's and L_{ij} 's are comparable to those reported for α -PCA.

Table 5. Values of T_{ij} (10^{-2} Å²) and L_{ij} (deg²)

$$T = \begin{pmatrix} 2.63 & 0.22 & 0.33 \\ & 3.29 & 0.00 \\ & & 2.06 \end{pmatrix}$$

$$L = \begin{pmatrix} 1.4 & -2.4 & 0.5 \\ & 14.4 & -1.0 \\ & & 1.0 \end{pmatrix}$$

The sets of thermal vibration parameters given in Table 2 have been transformed to u_{ij} values referring to a new set of molecular orthogonal axes m_1 , m_2 and m_3 defined in such a way that m_1 passes through C(2) and C(5), the transverse axis m_2 passes through C(2) and lies in the molecular plane, and m_3 passes through C(2) but is perpendicular to the molecular plane. In Table 6, these observed u_{ij} 's are compared to u_{ij} values calculated from the translational and rotational vibration tensors T_{ij} and L_{ij} . The thermal motions

of O(9) and N(8) do not seem to follow the rigid body assumption, and these atoms have therefore not been included in this comparison. The average deviation in observed u_{ij} 's is 0.19, standard deviation in calculated u_{ij} 's 0.29 and the average deviation between calculated and observed u_{ij} 's 0.24. As may be seen from Table 6 the thermal motions are fairly isotropic for the atoms considered, having u_{ij} values ranging from 4.59, 3.90 and 3.04 ($\times 10^{-2}$) Å² for N(4) to 2.95, 2.58 and 2.84 ($\times 10^2$ Å² for the C(2) atom for u_{11} , u_{22} and u_{33} respectively. The thermal motion analysis, given in Table 6, indicates almost identical thermal movements of the atoms in the structure of β -PCA as in that of α -PCA.

The following programs were used on a UNIVAC 1108:

DATARED (1970), a program for deriving $|F|$ values from observed intensities.

SCALIN (1970), a program for the conversion of F values to the corresponding E values.

SIGMA 2, a program for the listing of all possible Σ_2 relations.

SYMBOL (1969), a program for the iterative use of Σ_2 relations. These four programs were written by J. A. Hjortås of this Institute.

FOUFU 1, a Fourier summation program.

LSFIV 4, a full-matrix least-squares program based on the Oak Ridge program *ORFLS* (TM-305) by Busing, Martin & Levy.

PAFVO 1, a function and error program based on the Oak Ridge program *ORFFE* (TM-306) by Busing, Martin & Levy.

BEPLA 1, a program for calculating best planes. These programs were written by O. Borgen & B. Mestvedt, the first one (*FOUFU 1*) in cooperation with J. Finjord (Technical Reports 52, 45, 47 and 40, Institute of Physical Chemistry, NTH).

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Table 6. Observed and calculated u_{ij} values for β -PCA (in 10^{-2} Å²)

	u_{11}		u_{22}		u_{33}		u_{12}		u_{13}		u_{23}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
N(1)	3.41	3.41	3.27	3.34	2.66	2.59	0.34	0.30	0.11	0.16	-0.24	0.12
C(2)	2.95	3.10	2.58	3.29	2.84	2.74	-0.11	0.22	0.09	0.08	0.09	0.0
C(3)	3.99	4.18	3.57	3.37	2.88	2.77	0.53	0.48	-0.21	-0.11	-0.14	-0.22
N(4)	4.58	4.49	3.90	3.48	3.04	3.14	1.09	0.72	0.42	0.43	-0.27	-0.20
C(5)	3.34	3.55	3.48	3.43	3.77	3.68	0.67	0.58	0.43	0.21	0.34	-0.05
C(6)	3.59	3.56	3.96	3.38	2.99	3.17	0.24	0.41	-0.53	-0.24	0.09	0.06
C(7)	3.37	2.93	2.87	3.34	3.67	3.77	0.04	0.10	0.24	0.02	-0.04	0.11

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Crystal and Molecular Structure of Bis(amidoxalato-*O,O*)-cobalt(II) Tetrahydrate

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The crystals of bis(amidoxalato-*O,O*)-cobalt(II) tetrahydrate are monoclinic, space group $P2_1/c$. The unit-cell constants are: $a = 5.640$ (5), $b = 13.734$ (12), $c = 7.414$ (6) Å; $\beta = 109.8$ (2)°, $Z = 2$. The three-dimensional intensity data have been measured on a single-crystal automated diffractometer. The structure has been solved by Fourier methods and refined by least-squares methods ($R = 3.7\%$). The structure consists of *trans*-octahedral metal complexes with amidoxalato anion forming chelate pentatomic rings with the amidic oxygen and one carboxylic oxygen as donor atoms. The remaining positions of the octahedron are occupied by water molecules. The complexes are held together by a three-dimensional network of hydrogen bonds. In the ligand the $C_{sp^2}-C_{sp^2}$ distance $C(4)-C(2) = 1.550$ (9) Å, has been found, which is longer than expected for bonds between two sp^2 hybridized carbon atoms.

Introduction

As part of the research on the properties of ligands capable of forming pentatomic chelate rings with divalent metals (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971), we have now determined the crystal structure of bis(amidoxalato-*O,O*)-cobalt(II) tetrahydrate.

Experimental

Preparation

The crystals can be obtained by evaporation of an aqueous solution of cobalt carbonate and amidoxalic acid in stoichiometric ratio.

Crystal data

Compound: Bis(amidoxalato-*O,O*)cobalt tetrahydrate, $\text{Co}(\text{H}_2\text{N}-\text{CO}-\text{COO})_2 \cdot 4\text{H}_2\text{O}$.
 Formula weight: 307.09.

Crystal class: monoclinic prismatic.

Unit-cell parameters (determined from rotation and Weissenberg photographs and refined on an automated single-crystal diffractometer, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å):

$a = 5.640$ (5), $b = 13.734$ (12), $c = 7.414$ (6) Å;

$\beta = 109.8$ (2)°; $V = 540.3$ Å³; $Z = 2$;

$D_x = 1.89$, $D_m = 1.88$ g.cm⁻³;

$\mu(\text{Mo } K\alpha) = 154.25$ cm⁻¹; $F(000) = 314$.

Space group: $P2_1/c$ ($C_{2h}(5)$ -No. 14) from systematic absences.

Intensity data

The intensity data were collected on a single-crystal automated Siemens diffractometer on line with a Siemens 304/P computer using Zr-filtered Mo $K\alpha$ radiation and the $\omega-2\theta$ scan technique. A thin tablet crystal of approximate dimensions $0.045 \times 0.180 \times 0.210$ mm was aligned with its [010] axis along the ϕ axis of the diffractometer and all the reflexions with $2\theta < 58^\circ$ were collected. Intensities of 1436 independent reflexions were measured and 833 of them, having $I > 2\sigma(I)$, were used in the crystal analysis.

Calculations

Usual corrections except that for absorption have been applied. The observed factors have been put on an absolute scale by Wilson's (1942) method. Atomic form factors of Cromer & Mann (1968) for non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atom have been employed. The structure has been solved by Patterson and Fourier

* Or diaquobis(amidoxalato-*O,O*)-cobalt(II) dihydrate, $[\text{Co}(\text{H}_2\text{N}-\text{CO}-\text{COO})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O}$.