Crystal data for two enkephaline peptides. By M. Cotrait and S. Geoffre, Laboratoire de Cristalloigraphie, Université de Bordeaux I, 351 Cours de la Libération, 33405 Talence, France

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The two enkephaline Tyr-Gly-Gly (I) and Phe-Met (II) peptides have been crystallized with the following crystal data: (I) space group $P_{21}2_12_1$ or $P_{22}2_1$ ($Z=4$); $a=9.549(3)$, $b=8.073(2)$, $c=18.424(5)$ Å; (II) space group $I4_1$ ($Z=8$); $a=b=23.891(4)$, $c=5.589(3)$ Å.

Introduction

Enkephalines are endogenous pentapeptides isolated from mammalian brain with morphin-like activity. The amino acid sequence of the major component, Met-enkephalin is Tyr-Gly-Gly-Phe-Met. The conformation of the molecule has been proposed in solution by NMR spectroscopy (Roques, Garbay-Jauregui-Berry, Oberlin, Anteneus & Lala, 1976) and in vacuum by means of empirical energy calculations (Isogai, Nemethy & Scheraga, 1976). We intended to solve the crystal structures of the Tyr-Gly-Gly and Phe-Met peptides, as part of Met-enkephaline.

Crystal data

The two peptides were purchased from Bachem Biochemicals; Tyr-Gly-Gly was crystallized from water–methanol mixtures and Phe-Met from methanol solutions (thin needle-shaped crystals with square section).

Unit-cell dimensions and their associated standard deviations were derived from least-squares fits to the angular settings of about ten reflections on a Siemens four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å, $T=20^\circ$C). Densities were determined by flotation. The crystal data for both compounds are given in Table 1.

Table 1. Crystal data

<table>
<thead>
<tr>
<th>Peptide</th>
<th>Space group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tyr-Gly-Gly</td>
<td>$P_{21}2_12_1$ or $P_{22}2_1$</td>
<td>9.549(3)</td>
<td>8.073(2)</td>
<td>18.424(5)</td>
<td>1414</td>
<td>4</td>
</tr>
<tr>
<td>Phe-Met</td>
<td>$I4_1$</td>
<td>23.891(4)</td>
<td>23.891(4)</td>
<td>5.589(3)</td>
<td>3190</td>
<td>8</td>
</tr>
</tbody>
</table>

Results

As far as Tyr-Gly-Gly is concerned there is a space-group ambiguity which has not been yet quite cleared. There is a clear systematic absence for the $[00l]$ row. Along the $[0k0]$ row, the 010 reflection only is present. On the $[h00]$ row, reflections with $h$ odd are present though they are all weak or very weak. So the space group could be $P_{22}2_1$ or $P_{21}2_12_1$, and we tried to solve the structure in both groups.

Diffracted intensities from Phe-Met crystals are very weak owing to the small dimensions of the crystals (0.1 × 0.1 × 1 mm) and the quite high thermal scattering ($B_M \approx 6.5$ Å$^2$ from a Wilson plot); the Bragg angle $\theta$ was then limited to 50°. On the other hand, the crystals were of too poor quality to permit a structure determination.

We plan to determine the Phe-Met crystal structure when better and bigger crystals are obtained.

* In which case $h$ and $k$ as well as $a$ and $b$ should be exchanged according to the international conventions.

References


Crystal data for an ilmenite variety of calcium stannate CaSnO$_3$. By B. Durand, Laboratoire de Chimie Minérale 3, Université Claude Bernard, 69621 Villeurbanne, France and H. Loiseleur, Laboratoire de Chimie Analytique 2, Université Claude Bernard, 69621 Villeurbanne, France

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An ordered ilmenite phase of the stannate CaSnO$_3$ is evidence from powder patterns. The hexagonal and rhombohedral unit-cell parameters are respectively: $a=5.497(1)$, $c=15.287(6)$ Å, $Z=6$ and $a=6.000(2)$ Å, $\alpha=54.42(3)^\circ$, $Z=2$; $D_m=5.16$, $D_a=5.17$ g cm$^{-3}$.

Origin of specimen

Calcium stannate CaSnO$_3$ was prepared by a double decomposition reaction between the lithium tin oxide Li$_2$SnO$_3$ and the eutectic (CaCl$_2$·1·13 NaCl):

$$\text{Li}_2\text{SnO}_3 + \text{CaCl}_2 - 1·13 \text{NaCl} \xrightarrow{600^\circ\text{C}} \text{CaSnO}_3 + 2\text{LiCl} + 1·13 \text{NaCl}.$$
After cooling, the alkaline salts were removed by washing with water.

**Chemical characterization**

The compound was analysed for calcium content by a gravimetric method and an EDTA titration, and for tin content by a redox method. The analytical results are given below.

<table>
<thead>
<tr>
<th></th>
<th>Ca %</th>
<th>Sn %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>19.38</td>
<td>57.38</td>
</tr>
<tr>
<td>Found</td>
<td>19.42</td>
<td>57.40</td>
</tr>
</tbody>
</table>

**Crystal geometry**

The powder X-ray photograph obtained with a Guinier camera \( R = 57 \rho m, \lambda(Cu K\alpha) = 1.5418 \) Å showed the compound to be hexagonal with reflections only possible for \(-h + k + l = 3n\). It shows a great similarity to the ilmenite pattern. The unit-cell parameters were refined by a least-squares method minimizing \( 2(\sin^2 \theta_k - \sin^2 \theta_h) \) for the 16 reflections indicated by an asterisk in Table 1. Intensities were measured with a Philips goniometer \( \lambda(Cu K\alpha) \) by scanning each peak. In Table 1 are reported the reflections which could be seen on the powder X-ray photograph. The 125 reflection (hexagonal indexing) could be detected only on the goniometric recording \( d_e(125) = 1.549 \) Å, \( I/I_o < 2 \).

The experimental density was determined pycnometrically in xylene.

**Ilmenite structure corroboration**

An atomic-parameter least-squares refinement method, in space group R3 gave reliability factors \( R = 0.046 \) for structure factors and \( R = 0.092 \) for intensities. Resulting relative coordinates are: \( x_{Sn} = 0.1553(7), x_{Ca} = 0.367(2) \) and for the O atom \( x = 0.553(4), y = -0.040(4), z = 0.200(4) \). Bond lengths are: \( Ca-O = 2.29(2) \) and \( 2.56(3) \) Å, \( Sn-O = 2.01(2) \) and \( 2.06(2) \) Å. The method and detailed results will be published later.

**Comparison with other results**

Different crystalline varieties of the double oxide CaSnO₃ are already known (Selme & Croissant, 1960; Smith & Welch, 1960). A perovskite variety was prepared by heating a mixture of the oxides CaO and SnO₂ at 1200°C (Colin, 1963). The ilmenite variety prepared by a double decomposition reaction was unknown. It is a metastable phase which transforms into the perovskite structure by annealing at 900°C. Such a transformation is irreversible and causes a volume decrease of 7.15% (ilmenite \( V = 265.7 \) Å³; perovskite \( V = 246.7 \) Å³).

Other ilmenite-structure stannates are known. CdSnO₃ and MgSnO₃ can be obtained by pyrolysis of the hydroxystannates CdSn(OH)₆ and MgSn(OH)₆ (Morgenstern-Badarau, Poix & Michel, 1964; Lévy-Clément, Morgenstern-Badarau, Billiet & Michel, 1967). But the pyrolysis of CaSn(OH)₆ leads only to the perovskite form of CaSnO₃ (Coffeen, 1953).

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**References**


