On the Crystal Structure of Cesium Bismuth Iodide

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In connection with solubility studies of \( \text{BiO}_3^– - \text{BiOI} \) in 1 M and 3 M (H,Na) (ClO\(_4\),I) as a function of \([\text{H}^+\]) and \([\text{I}^-]\), the structure of cesium bismuth iodide has been investigated and a preliminary report is given in this note.

Crystals were prepared by allowing a solution of cesium nitrate to diffuse into a solution of 14 g sodium iodide and approximately 0.8 g bismuth(III) oxide in 4.3 M acetic acid.

Weissenberg photographs corresponding to the reflections 0kI – 5kI and h00 have been recorded, using CuK\(\alpha\) radiation. The crystals are of hexagonal symmetry and from the systematically absent reflections, the space group was determined to be either No. 186 – \( P6_3mc \), No. 190 – \( P6_2c \), or No. 194 – \( P6_3mmc \). The cell dimensions, as calculated from the Weissenberg data, are \( a = b = 8.3 \) Å and \( c = 21.0 \) Å. The volume of the unit cell is thus approximately 1290 Å\(^3\). Assuming a cell content of two formula units, a calculated density of 4.70 g/cm\(^3\) is obtained, which seems reasonable.

From three-dimensional Patterson calculations, based on the 0kI – 5kI intensities, the bismuth atoms were found to occupy the four-fold position \( 4(f) \) in \( P6_3/mmc \) (No. 194) with \( z = 0.155 \). The positions of the iodine and cesium atoms were then deduced from successive electron density calculations. A preliminary three-dimensional least squares refinement of the structure was performed giving an \( R \) value of 0.21, and the resulting parameters are listed in Table 1. Since the linear absorption coefficient is as high as 1450.7 cm\(^{-1}\) no significance can be assigned to the temperature factors until an absorption correction has been performed.

From the structure determination it was found that the crystals contain \( \text{[Bi}_3\text{I}_5]^{2-} \) ions which may be described in terms of two distorted octahedra joined by a common face. The bismuth atoms lie on one six-fold inversion axis and one three-fold rotation axis, the rotation plane and the inversion centre being situated halfway between the two bismuth atoms. The six-fold inversion axis generates the positions of six iodine atoms, \( I_1 \), and the three-fold rotation axis the positions of three iodine atoms, \( I_2 \) (cf. Fig. 1). The distance between the bismuth atoms is 4.0 Å and the bismuth-iodine distances are 2.9 Å (Bi – I\(_1\)) and 3.3 Å (Bi – I\(_2\)). The distance between the planes through the I\(_1\)-triangles is 7.1 Å.

A complete three-dimensional refinement, based on intensities corrected for absorption effects, is in progress, and a detailed presentation of the structure of \( \text{Cs}_3\text{Bi}_3\text{I}_5 \) will soon be published in Acta Chem. Scand.

The authors wish to thank Professor Georg Lundgren for valuable discussions and for his criticism of this paper. Many thanks are also due to Susan Jagner M.A., fillic., of this Department for revising the English text.

Table 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>B (in Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4(f)</td>
<td>1/3</td>
<td>2/3</td>
<td>0.155</td>
<td>0.141</td>
</tr>
<tr>
<td>I(_1)</td>
<td>12((k))</td>
<td>0.161</td>
<td>0.322</td>
<td>0.081</td>
<td>1.339</td>
</tr>
<tr>
<td>I(_2)</td>
<td>6(h)</td>
<td>0.508</td>
<td>0.016</td>
<td>1/4</td>
<td>0.944</td>
</tr>
<tr>
<td>Cs(_3)</td>
<td>2(b)</td>
<td>0</td>
<td>0</td>
<td>1/4</td>
<td>2.712</td>
</tr>
<tr>
<td>Cs(_6)</td>
<td>4(f)</td>
<td>1/3</td>
<td>2/3</td>
<td>-0.081</td>
<td>2.831</td>
</tr>
</tbody>
</table>

Fig. 1. The \( \text{Bi}_3\text{I}_5^{2-} \) ion in the crystals of \( \text{Cs}_3\text{Bi}_3\text{I}_5 \).

SHORT COMMUNICATIONS

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N-Isothiocyanatoamines

V. Conversion of
N-Isothiocyanatodisopropylamine to
Seleno- and Tellurothiocarbazic Acid
Derivatives

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Recently,¹ the synthesis and infrared spectra of several dithio- and diseleno-
carbazic acids have been described and their dipolar structure established. N,N-
Diisopropylthiocarbazic acid (I), which became of interest in connection with our
studies on N-isothiocyanatodisopropylamine,² proved to be readily available
from N,N-disopropylhydrazine and carbon disulfide by a closely related method.

\[
\begin{align*}
\text{(I-C}_3\text{H}_7\text{)}\text{N}_2\text{H}_2 & + \text{CS}_2 + \text{KOH} \rightarrow \text{H}_2\text{O} \\
[\text{(I-C}_3\text{H}_7\text{)}\text{N}_2\text{NH-CSS}^-] K^+ & \rightarrow \text{H}^+ \\
\text{(I-C}_3\text{H}_7\text{)}\text{NH}^+ & \text{NH-CSS}^-
\end{align*}
\]

Replacement of carbon disulfide in this synthesis by CSSe or CSTe would furnish
the title compounds. Both these starting materials, however, are unstable and dif-
ficult to prepare. To circumvent these preparative difficulties, we decided to in-
vestigate the reaction between N-isothio-
cyanatodisopropylamine and H₂Se or
H₂Te. The first reaction proceeds according
to the following scheme.

\[
\text{(I-C}_3\text{H}_7\text{)}\text{N}_2\text{NCS} + \text{H}_2\text{Se} \rightarrow \text{II}
\]

The assignment to I and II of the dipolar structures shown followed from their
infrared spectra (KBr). In the high
frequency region, the strong bands originating
from the NH⁺ stretching vibrations
were observed in the 2500—3000 cm⁻¹
range and the NH stretching vibrations are
(as a result of the neighbouring positive charge) characteristically¹ around 3100
cm⁻¹. The lower frequency regions were
nearly identical, apart from two absorptions
in the regions 1000—1050 cm⁻¹ and
600—700 cm⁻¹. These bands have been
assigned to the antisymmetrical and sym-
metrical CSS⁻ stretching vibrations for
dithiocarbazic acids.¹ Consistently with
this, we assign the bands at 1048 and 1017
cm⁻¹ in I and II, respectively, to the
antisymmetrical CXS⁻ vibrations and the
bands at 680 or 650 and 660 or 624 cm⁻¹
to the corresponding symmetrical modes.

If an ethanolic solution of II is oxidized
for some time with air, the corresponding
diselenide (III) is formed.

\[
\text{[I-C}_3\text{H}_7\text{]}\text{N}_2\text{NH-CSS}^-\text{Se}^- \quad \text{III}
\]

By treating N-isothiocyanatodisopropylamine with hydrogen telluride we
obtained, instead of the expected tel-
luorothiocarbazic acid, the tellurium analo-
gue of III (IV). The reason for the failure
to observe the intermediate tellurothio-
carbazic acid is at present obscure,
especially if the strongly reducing prop-
erties of hydrogen telluride are taken into
account. It cannot a priori be decided
whether III and IV have the diselenide
and ditelluride structures, respectively,
instead of being disulfides, though chemical
reasoning argues for the former alternative.
However, the infrared spectra support the

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