Tris(ethylenediamine)cobalt(III) nonaiododibismuthate

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Tris(ethylenediamine)cobalt(III) nonaiododibismuthate
Andrea M. Goforth, Rachael E. Hipp, Mark D. Smith, LeRoy Peterson Jr and Hans-Conrad zur Loye
The asymmetric unit of the title compound, [Co(C$_2$H$_8$N$_2$)$_3$][Bi$_2$I$_9$], crystallizes in the orthorhombic space group Cmc$_2$1. The asymmetric unit contains half of a [Co(en)$_3$]$^{3+}$ cation (en is ethylenediamine) and half of a [Bi$_2$I$_9$]$^{3-}$ anion. Both species are located on mirror planes, requiring the [Co(en)$_3$]$^{3+}$ cation to be present as a statistically disordered mixture of both enantiomeric forms. Crystals were grown solvothermally from an ethanol–water solvent mixture using rac-[Co(en)$_3$I$_3$] and bismuth triiodide as starting materials. The compound is a rare example of a mixed-metal halobismuthate material.

Comment

The chemistry of the bismuth(III) halides, or halobismuthate materials, has been extensively explored, due to the promising physical characteristics that such compounds often exhibit, including semiconductivity, luminescence and second-order non-linear optical activity (Eickmeier et al., 1999; Goforth et al., 2004; Mitzi & Brock, 2001; Mousdis et al., 1998; Papa- vassiliou et al., 1995; Zhu et al., 2003). In general, these materials consist of a complex halobismuthate anion (connected BiX$_n$ polyhedra) and an organic counter-cation. However, we have been interested in the synthesis of new halobismuthate materials which have a metal-containing cation in addition to the metal-containing anion. Such compounds may display new and interesting physical properties resulting from the synergistic interaction of more than one metal-containing species in the same compound. The title compound, [Co(en)$_3$][Bi$_2$I$_9$], (I), represents one of the first halobismuthate materials having a transition metal coordination cation as the charge-balancing species.
metal-organic papers

Fig. 1 displays the crystal packing of (I) viewed along [110], where it is observed that columns of the cations alternate with columns of the anions in a chessboard fashion.

Experimental

BiI₃ (0.15 mmol, 88.5 mg) and rac-[Co(ethylenediamine)₃]I₃ (0.05 mmol, 31 mg) were weighed and placed in a 23 ml Teflon-lined autoclave with absolute ethanol (5 ml) and distilled water (5 ml) as the reaction solvents. The autoclave was subsequently sealed and heated at a rate of 1 K min⁻¹ to 433 K. The temperature was held at 433 K for 2 d before it was decreased, at a rate of 0.1 K min⁻¹, to 343 K, where it was then held for 6 h. Finally, the temperature was decreased at a rate of 0.1 K min⁻¹ to room temperature. Red-orANGE crystals of (I) were isolated from the reaction and a suitable single crystal was selected for the X-ray diffraction experiment.

Crystal data

\[ [\text{Co(C}_2\text{H}_8\text{N}_2)_3][\text{Bi}_2\text{I}_9] \]

Mo-Kα radiation

Cell parameters from 8193 reflections

\( a = 12.5267 (6) \text{ Å} \)
\( b = 17.2768 (8) \text{ Å} \)
\( c = 13.8644 (7) \text{ Å} \)
\( V = 3000.6 (3) \text{ Å}^3 \)
\( Z = 4 \)
\( D_x = 3.983 \text{ Mg m}^{-3} \)

Data collection

Bruker SMART APEX CCD area-detector diffractometer

\( \theta_{	ext{max}} = 26.4^\circ \)
\( h = -15 \rightarrow 15 \)
\( k = -18 \rightarrow 21 \)
\( l = -17 \rightarrow 17 \)

Refinement

Refinement on \( F^2 \)

\( R[F^2 > 2\sigma(F^2)] = 0.030 \)
\( wR(F^2) = 0.071 \)
\( S = 1.04 \)

3216 reflections

102 parameters

H-atom parameters constrained

Absolute structure: Flack (1983), with 1535 Friedel pairs

Flack parameter: -0.021 (5)

Table 1

<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₁–I₁</td>
</tr>
<tr>
<td>Bi₁–I₃</td>
</tr>
<tr>
<td>Bi₁–I₂</td>
</tr>
<tr>
<td>Bi₁–I₄</td>
</tr>
<tr>
<td>Bi₂–I₆</td>
</tr>
<tr>
<td>Bi₂–I₅</td>
</tr>
<tr>
<td>Bi₂–I₄</td>
</tr>
<tr>
<td>I₁–Bi₁–I₁’</td>
</tr>
<tr>
<td>I₁–Bi₁–I₃</td>
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<tr>
<td>I₁–Bi₁–I₁</td>
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<tr>
<td>I₁’–Bi₂–I₄’</td>
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<td>I₁–Bi₁–I₄</td>
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<td>I₁’–Bi₂–I₄’</td>
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<tr>
<td>I₁’–Bi₂–I₄</td>
</tr>
</tbody>
</table>

Symmetry code: (i) \( -x, y, z \).
Due to the cation disorder, only the Co, Bi and I atoms were refined with anisotropic displacement parameters; C and N atoms were refined isotropically. One distance restraint [C1A–N1A = 1.50 (1) Å] was necessary to maintain a reasonable distance between these atoms. H atoms for each disorder component were placed in geometrically idealized positions, with C–H = 0.96–0.99 Å and N–H = 0.90 Å, and included as riding atoms, with Uiso(H) = 1.2Uiso(C,N). The highest peak is located 0.84 Å from atom I6 and the deepest hole is located 0.87 Å from Bi2.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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References