Tris(ethylenediamine)cobalt(III) nonaiodo-dibismuthate

Andrea M. Goforth,[a] Rachael E. Hipp,[a] Mark D. Smith,[a] LeRoy Peterson Jr[b] and Hans-Conrad zur Loye[a]*

[a]Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA, and [b]Department of Chemistry, Francis Marion University, Florence, South Carolina 29501, USA

Correspondence e-mail: zurloye@sc.edu

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 $Cmc2_1$. 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; Papavassiliou *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.

(I)
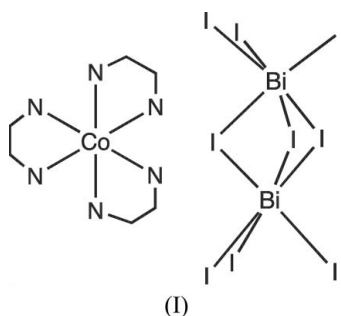
Single crystals of (I) were isolated from the solvothermal reaction of rac-[Co(en)$_3$]I$_3$ and BiI$_3$ and were studied by single-crystal X-ray diffraction. The asymmetric unit of the compound contains half of an independent [Co(en)$_3$]$^{3+}$ cation and half of a [Bi$_2$I$_9$]$^{3-}$ anion, both of which are located on
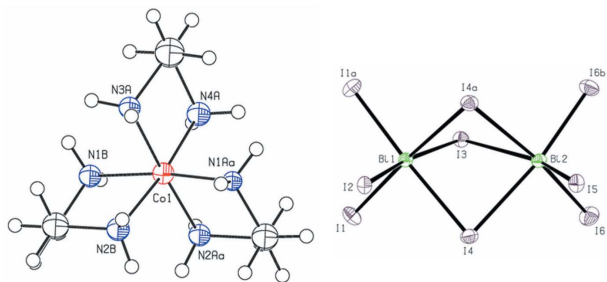
Figure 1
Plots of the components of (I), showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Only the symmetry-independent part of the [Co(en)$_3$]$^{3+}$ cation is shown.
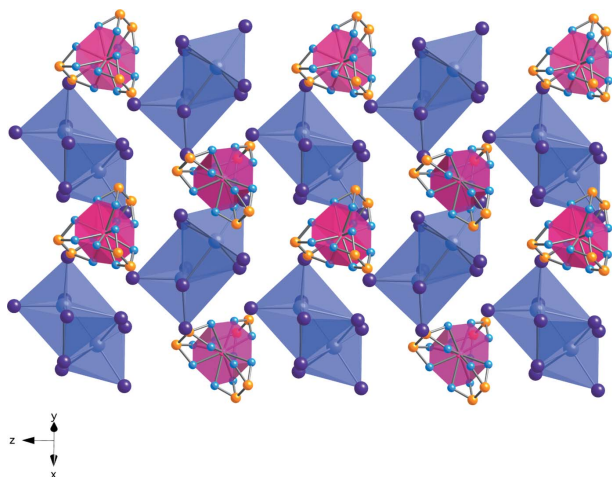

Figure 2
A view along [110] of the crystal packing in (I). Bi polyhedra are shown in blue, I atoms as purple spheres, C atoms as yellow spheres, N atoms as small blue spheres and Co atoms as pink spheres. Both disorder components of the [Co(en)$_3$]$^{3+}$ cation are shown.

crystallographic mirror planes (Fig. 1). Both the Δ and Λ enantiomers of the cation are present in the structure, and they are statistically disordered throughout the crystal structure across the mirror plane passing through C3A/C4A and Co1. The atomic positions of Co and all C atoms (C1–C4) are common to both enantiomeric cations; only the N atoms distinguish the two enantiomers.

The [Bi$_2$I$_9$]$^{3-}$ anion is well known in bismuth iodide chemistry, and the majority of the bond distances and angles of the anion in (I) are comparable with those found in other compounds containing the same ion. In the present structure, however, the Bi2—I3 distance of 3.5462 (11) Å is significantly longer than the average bridging Bi—I distances (approximately 3.2 Å) observed in other [Bi$_2$I$_9$]$^{3-}$-containing compounds. (Bowmaker *et al.*, 1997; Eickmeier *et al.*, 1999; Goforth *et al.*, 2004; Lazarini, 1987; Zhu *et al.*, 2003). For (I), the average terminal Bi—I distance is 2.987 Å, the average bridging Bi—I distance is 3.282 Å, and the *cis* angles range from 75.12 (2) to 98.75 (2)°. Likewise, the [Co(en)$_3$]$^{3+}$ cation is well known (Wang *et al.*, 2004; Nakashima *et al.*, 2003), and the bond distances and angles of the cation in (I) are within the expected ranges (Table 1).

Fig. 2 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

BiI$_3$ (0.15 mmol, 88.5 mg) and *rac*-[Co(ethylenediamine)$_3$]I$_3$ (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

[Co(C$_2$H$_8$N$_2$)$_3$][Bi$_2$I$_9$]	Mo-$K\alpha$ radiation
$M_r = 1799.30$	Cell parameters from 8193
Orthorhombic, $Cmc2_1$	reflections
$a = 12.5267$ (6) Å	$\theta = 2.4$–$26.4°$
$b = 17.2768$ (8) Å	$\mu = 21.51$ mm^{-1}
$c = 13.8644$ (7) Å	$T = 150$ (1) K
$V = 3000.6$ (3) Å^3	Plate, red–orange
$Z = 4$	$0.14 \times 0.08 \times 0.04$ mm
$D_x = 3.983$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3216 independent reflections
	3129 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$\theta_{max} = 26.4°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.206$, $T_{max} = 0.423$	$k = -18 \rightarrow 21$
12584 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 28.8217P]$
$wR(F^2) = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3216 reflections	$\Delta\rho_{max} = 1.76$ e Å^{-3}
102 parameters	$\Delta\rho_{min} = -1.36$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983), with 1535 Friedel pairs
	Flack parameter: -0.021 (5)

Table 1
Selected geometric parameters (Å, °).

Bi1—I1	2.9179 (8)	Bi2—I3	3.5462 (11)
Bi1—I3	2.9912 (11)	Co1—N4A	1.928 (17)
Bi1—I2	3.2398 (12)	Co1—N1A	1.940 (16)
Bi1—I4	3.2486 (8)	Co1—N2A	1.950 (18)
Bi2—I6	2.8815 (8)	Co1—N1B	1.961 (17)
Bi2—I5	2.9088 (10)	Co1—N3A	1.976 (17)
Bi2—I4	3.3435 (8)	Co1—N2B	2.026 (17)
I1—Bi1—I1^i	94.83 (4)	I6—Bi2—I6^i	96.73 (4)
I1—Bi1—I3	95.56 (2)	I6—Bi2—I5	95.04 (2)
I1—Bi1—I2	92.82 (2)	I6—Bi2—I4	89.46 (2)
I3—Bi1—I2	167.61 (3)	I6^i—Bi2—I4	171.94 (3)
I1—Bi1—I4	89.09 (2)	I5—Bi2—I4	89.53 (2)
I1^i—Bi1—I4	176.04 (2)	I4—Bi2—I4^i	83.93 (3)
I3—Bi1—I4	84.58 (2)	I6—Bi2—I3	98.75 (2)
I2—Bi1—I4	86.44 (2)	I5—Bi2—I3	159.16 (3)
I4—Bi1—I4^i	86.98 (3)	I4—Bi2—I3	75.12 (2)

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 U_{iso}(H) = 1.2U_{iso}(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*.

References

Bowmaker, G. A., Harrowfield, J. M., Junk, P. C., Skelton, B. W. & White, A. H. (1997). *Aust. J. Chem.* **51**, 285–291.
Bruker (2001). *SMART* (Version 5.625), *SAINT-Plus* (Version 6.22) and *SADABS* (Version 2.05). Bruker AXS Inc., Madison, Wisconsin, USA.
Eickmeier, H., Jaschinski, B., Hepp, A., Nuß, J., Reuter, H. & Blachnik, R. (1999). *Z. Naturforsch. Teil B*, **54**, 305–313.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Goforth, A. M., Smith, M. D., Peterson, L. Jr & zur Loye, H.-C. (2004). *Inorg. Chem.* **43**, 7024–7031.
Lazarini, F. (1987). *Acta Cryst.* C**43**, 875–877.
Mitzi, D. B. & Brock, P. (2001). *Inorg. Chem.* **40**, 2096–2104.
Mousdis, G. A., Papavassiliou, G. C., Terzis, A. & Raptopoulou, C. P. (1998). *Z. Naturforsch. Teil B*, **53**, 927–931.
Nakashima, T., Mishiro, J., Ito, M., Kura, G., Ikuta, Y., Matsumoto, N., Nakajima, K. & Kojima, M. (2003). *Inorg. Chem.* **42**, 2323–2330.
Papavassiliou, G. C., Koutselas, I. B., Terzis, A. & Raptopoulou, C. P. (1995). *Z. Naturforsch. Teil B*, **50**, 1566–1569.
Sheldrick, G. M. (2000). *SHELXTL*. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Wang, Y., Yu, J., Pan, Q., Du, Y., Zou, Y. & Xu, R. (2004). *Inorg. Chem.* **43**, 559–565.
Zhu, X.-H., Mercier, N., Frère, P., Blanchard, P., Roncali, J., Allain, M., Pasquier, C. & Riou, A. (2003). *Inorg. Chem.* **42**, 5330–5339.