Tetrakis[2-(2-pyridyl)pyridinium] tetra-μ_3-iodo-hexa-μ_2-iodo-dodeca-iodohexabismuthate and bis[tris(2,2′-bipyridine)ruthenium(II)] di-μ_4-iodo-octa-μ_2-iodo-dodecaiodohexa-bismuthate

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Crystals of the title compounds were grown solvothermally in an ethanol–water solvent mixture using ruthenium triiodide, 2,2′-bipyridine and bismuth triiodide as starting materials. Tetrakis[2-(2-pyridyl)pyridinium] tetra-μ_3-iodo-hexa-μ_2-iodo-dodecaiodohexabismuthate, $(C_{10}H_9N_2)_4[Bi_6I_{22}]$, crystallizes in the triclinic space group $P\bar{1}$ and is the major reaction product. The asymmetric unit of this compound consists of half a centrosymmetric $[Bi_6I_{22}]^{4-}$ anion and two independent 2,2′-bipyridinium cations. The minor product of the reaction is bis[tris(2,2′-bipyridine)ruthenium(II)] di-μ_4-iodo-octa-μ_2-iodo-dodecaiodohexabismuthate, $[Ru(C_{10}H_8N_2)_3]_2[Bi_6I_{22}]$, which also crystallizes in the triclinic space group $P\bar{1}$. For this compound, the asymmetric unit consists of one full $[Ru(2,2′-bipyridine)_3]^{2+}$ cation and half a centrosymmetric $[Bi_6I_{22}]^{4-}$ anion. Although both compounds contain a centrosymmetric $[Bi_6I_{22}]^{4-}$ anion, the polyhedral arrangement of the distorted BiI_6 octahedra in the two compounds is quite different, and the anion of the latter compound has not previously been observed in iodobismuthate chemistry.

Comment

The chemistry of main group halometallate materials has been of interest to chemists and materials scientists for some time, due to their promising physical characteristics and their interesting structural diversity. With respect to the physical properties, behaviors such as semiconductivity, luminescence and second-order non-linear optical activity have been observed in this family of materials (Papavassiliou et al., 1995; Zhu et al., 2003; Mitzi & Brock, 2001; Mousdis et al., 1998). The main group halometallate materials display extensive structural diversity, as the anionic inorganic component ranges

from discrete clusters (zero-dimensional) to polymeric structures (one-, two- or three-dimensional) depending on the main group metal and on the specific synthetic conditions employed. To date, main group halometallate materials based on Cu^I (Yu et al., 2003), Sn^{II} (Xu & Mitzi, 2003), Sb^{III} (Mousdis et al., 1998), Te^{IV} (Ryan & Xu, 2004), Pb^{II} (Zhu et al., 2003) and Bi^{III} (Mousdis et al., 1998; Eickmeier et al., 1999; Lindsjo et al., 2005) have been synthesized and structurally characterized.
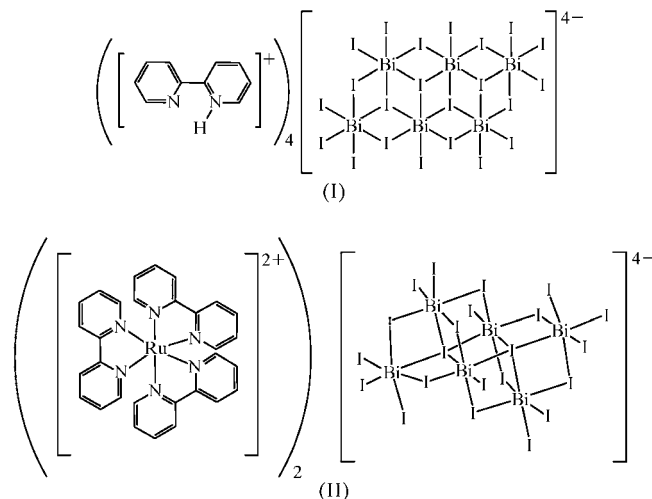
We have been interested in the synthesis of new main group halometallate materials containing Bi^{III} and have been successful in the synthesis of many new iodobismuthate(III) materials having either organic or inorganic cations for charge balance (Goforth et al., 2004; Goforth, Gardinier et al., 2005; Goforth, Peterson et al., 2005). Many halobismuthate compounds have been synthesized by us and others, and most of these compounds contain either discrete anions (of varying sizes) or one-dimensional polymeric anions. In either case, the anion is generally composed of connected BiI_6 polyhedra, which are corner-, edge- or face-sharing. The number of
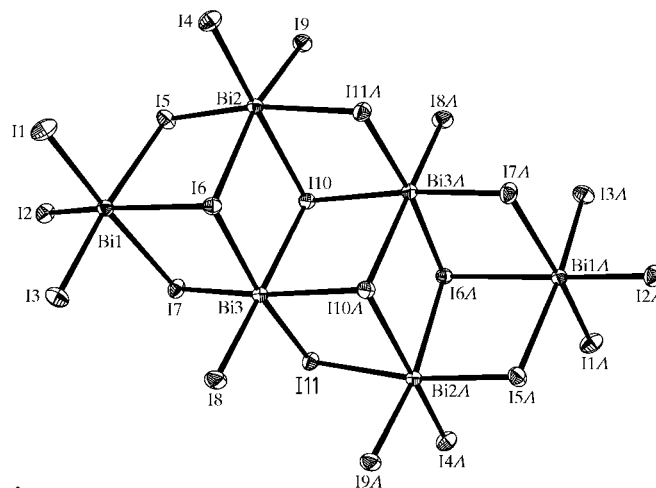

Figure 1
A view of the $[Bi_6I_{22}]^{4-}$ anion of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The cation was refined isotropically and is not shown. [Symmetry code: (i) $1-x, -y, 1-z$.]

metal-organic compounds

connected polyhedra, and the mode of connectivity and the spatial arrangement of these polyhedra, may vary within a given metal halide system, *e.g.* iodobismuthates, such that one can envision a large number of possible halometallate anion structures. In fact, certain synthetic conditions, such as cation size and geometry, solvent system and reagent stoichiometry, may be adjusted to affect the identity of the iodobismuthate anion (Eickmeier *et al.*, 1999; Goforth, Peterson *et al.*, 2005; Krautscheid, 1994).

While the vast majority of iodobismuthate materials known to date have contained an organic cation for charge balance, our group has recently demonstrated that a *d*-metal coordination cation is a viable charge-balancing species for iodobismuthate anions and that the use of such cations may lead to new iodobismuthate anions (Goforth, Gardinier *et al.*, 2005;
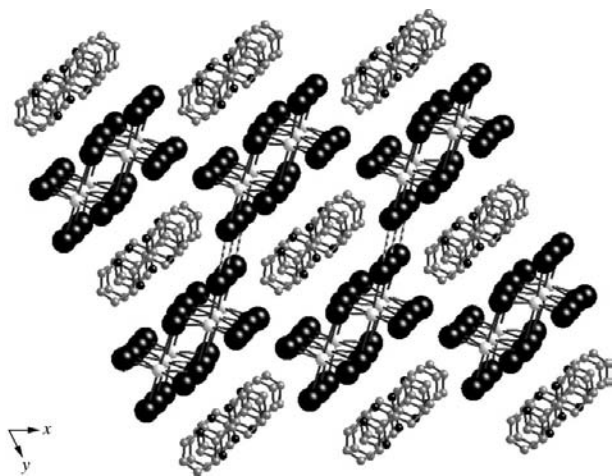
Figure 2
An [001] view of the crystal packing in (I). I···I interactions less than or equal to the sum of the van der Waals radii are indicated as two-tone bonds. Bi atoms are shown as light-grey spheres, I atoms as large black spheres, C atoms as dark-grey spheres and N atoms as small black spheres. H atoms are not shown.

Goforth, 2005). We report here the synthesis and single-crystal X-ray structures of two cocrystallizing iodobismuthate compounds, one of which has a coordination cation for charge balance while the other has an organic counter-cation. Both compounds contain $[Bi_6I_{22}]^{4-}$ anions. However, the polyhedral arrangements of the six BiI_6 octahedra in the two compounds differ.

The title compounds, $[H(2,2'-bipy)]_4[Bi_6I_{22}]$ {$[H(2,2'-bipy)]^+$ is protonated 2,2'-bipyridine}, (I), and $[Ru(2,2'-bipy)_3]_2$-$[Bi_6I_{22}]$, (II), were synthesized solvothermally from RuI_3, 2,2'-bipyridyl and BiI_3 in aqueous ethanol (50% *v/v*) using a 1:3:3 molar ratio. Crystals of (I) were isolated as the major phase, and crystals of both (I) and (II) were characterized by single-crystal X-ray diffraction. The structure of (II) reveals that the compound contains a novel $[Bi_6I_{22}]^{4-}$ anion that has not previously been reported in iodobismuthate chemistry, and this anion is discussed in detail following the structure description of (I).

Compound (I) crystallizes in the triclinic space group $P\bar{1}$ and contains two crystallographically independent 2,2'-bipyridinium cations and half of a $[Bi_6I_{22}]^{4-}$ iodobismuthate anion in the asymmetric unit. For the structure solution, the 2,2'-bipyridinium cations were refined isotropically, due to disorder. Anisotropic refinement of the cations resulted in unreasonable ellipsoids for these atoms, most probably due to unresolved disorder in the form of the N atoms oriented in the opposite direction. N-atom positions were assigned based on the magnitude of the U_{iso} parameter, but are uncertain due to the disorder and probably represent only the major orientation. The positions of nitrogen-bound protons were not calculated or located. However, they are necessary to maintain charge neutrality for the compound. The atoms of the $[Bi_6I_{22}]^{4-}$ anion were refined anisotropically. The centrosymmetric anion consists of six BiI_6 octahedra, which are connected such that two sets of three *trans* edge-sharing octahedra share five *cis* edges (Fig. 1). The arrangement of the six BiI_6 octahedra in (I) is a known arrangement of the $[Bi_6I_{22}]^{4-}$ anion. For example, the $[Bi_6I_{22}]^{4-}$ anions of
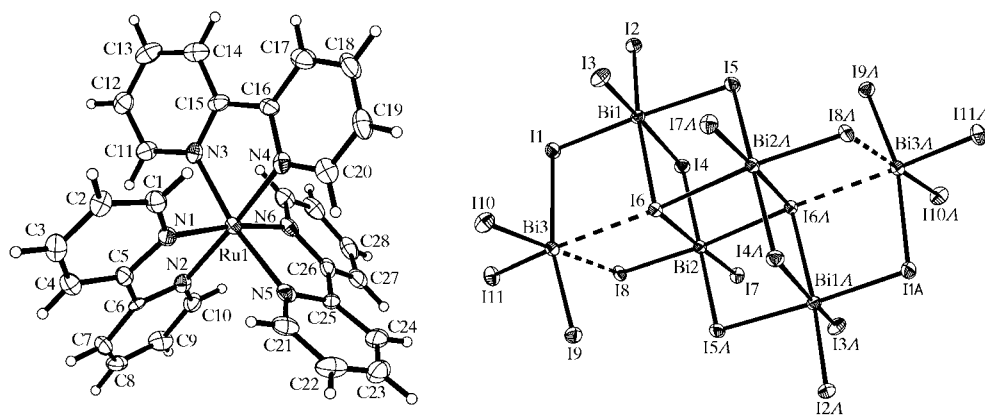
Figure 3
A view of the components of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms as small spheres of arbitrary radii. In order to assist the distinction of the Bi_4I_{16} cluster core from the pendant BiI_3 units, two of the three long bonds are drawn as dashed lines. The third, Bi3—I1, is drawn as a solid line. [Symmetry code: (ii) $1 - x$, $1 - y$, $1 - z$.]

[(THF)$_6$Na]$_4$[Bi$_6$I$_{22}$] (THF is tetrahydrofuran; Krautscheid, 1994), (EtMe$_2$PhN)$_4$[Bi$_6$I$_{22}$] (Eickmeier *et al.*, 1999) and (H$_2$TMDP)$_2$[Bi$_6$I$_{22}$] {[H$_2$TMDP]$^{2+}$ is 1,3-bis(4-piperidinio)propane; Goforth, Peterson *et al.*, 2005} have the same polyhedral connectivity as the anion of (I), and the bond distances and angles of the anion of (I) are comparable with those determined for these compounds. The average terminal Bi—I distance in (I) is 2.8793 Å, the average Bi—μ_2-I distance is 3.1491 Å and the average Bi—μ_3-I distance is 3.3177 Å. The *cis* I—Bi—I angles in (I) range from 82.350 (13) to 100.270 (17)° and the *trans* angles from 163.460 (16) to 176.741 (16)°.

When the structure of compound (I) is viewed along [001] (Fig. 2), stacks of [H(2,2′-bipy)]$^+$ cations and rows of [Bi$_6$I$_{22}$]$^{4-}$ anions are observed. Weak I···I bonding interactions between [Bi$_6$I$_{22}$]$^{4-}$ anions of neighboring rows are also observed [I3···I9^i = 3.739 (1) Å and I8···I8^{ii} = 3.732 (1) Å; symmetry codes: (i) $x - 1$, $y + 1$, z; (ii) $-x$, $1 - y$, $1 - z$; van der Waals radius of I = 1.98 Å and I···I ≥ 3.96 Å; Bondi, 1964], and when these interactions are taken into account, the structure may be viewed as an array of weakly bonded inorganic chains, with organic cations situated above and below the chains.

Compound (II) crystallizes in the triclinic space group $P\bar{1}$ and contains the well known tris-chelate cation [Ru(2,2′-bipy)$_3$]$^{2+}$ and a novel arrangement of the [Bi$_6$I$_{22}$]$^{4-}$ anion (Fig. 3). The bond distances and angles of the cation are normal [2.044 (6)–2.067 (6) Å; Biner *et al.*, 1992]. Due to the crystallographic inversion symmetry in the crystal, both the Λ and Δ enantiomers of the cation are present in the structure.

The centrosymmetric [Bi$_6$I$_{22}$]$^{4-}$ anion of (II) consists of a central Bi$_4$I$_{16}$ core (containing atoms Bi1 and Bi2), with two BiI$_3$ units (containing atom Bi3) connected to the core by three relatively long Bi—I bonds [3.3268 (6), 3.4311 (6) and 3.5484 (5) Å; Fig. 3]. Alternatively, the BiI$_3$ units can be considered as part of very distorted Bi3I$_6$ octahedra, each of

which shares two *cis* edges with the Bi$_4$I$_{16}$ cluster core. The bond lengths and angles of the Bi$_4$I$_{16}$ core are within the normal ranges and are comparable with those found in previously reported [Bi$_4$I$_{16}$]$^{4-}$ anions (Goforth, Gardinier *et al.*, 2005). The average terminal Bi—I distance is 2.897 Å and the average Bi—μ_2-I distance is 3.166 Å.

Considering the pendant BiI$_3$ units of the anion, an unusual bonding feature of the anion of compound (II) is the presence of an essentially μ_4-bridging iodide ligand. However, the average Bi—μ_4-I distance of 3.397 Å is within the reported ranges for Bi—μ_3-I distances in related compounds (Feldmann, 2003), further supporting the description of the anion as a Bi$_4$I$_{16}$ core with two pendant BiI$_3$ groups. In fact, many of the larger known discrete iodobismuthate anions may be considered to be based on Bi$_4$I$_{16}$ cores, either joined with one or more pendant BiI$_3$ units {as in [Bi$_5$I$_{19}$]$^{4-}$ (Krautscheid, 1994), or the typical arrangement of [Bi$_6$I$_{22}$]$^{4-}$ (Eickmeier *et al.*, 1999; Pohl *et al.*, 1994; Goforth, Peterson *et al.*, 2005; Krautscheid, 1994)}, or connected to another such core through a single edge {as in [Bi$_8$I$_{30}$]$^{6-}$ (Feldmann, 2003)}. The *cis* I—Bi—I angles of the anion of (II) range from 78.39 (1) to 103.69 (2)° and the *trans* angles from 159.65 (2) to 177.02 (2)°, where the largest deviations from the ideal octahedral angles are observed in the Bi3 polyhedron.

A [100] view of the crystal packing in compound (II) is shown in Fig. 4, where it can be seen that the discrete anions are arranged in layers which are interleaved by layers of the cations. As in compound (I), the discrete anions in (II) are close enough to one another in space that certain I atoms of neighboring anions are closer than the sum of their van der Waals radii (see above), thus leading to the formation of very weak I···I bonding interactions [I10···I3^i = 3.834 (1) Å and I11···I7^{ii} = 3.957 (1) Å; symmetry codes: (i) $1 - x$, $1 - y$, $-z$; (ii) $-x$, $1 - y$, $z - 1$]. When the I···I interactions are taken
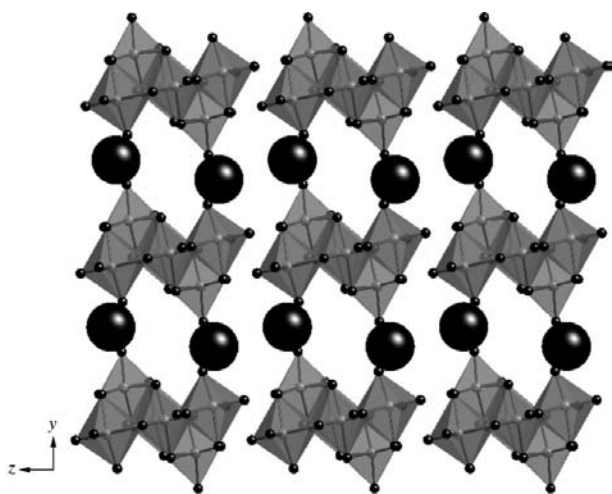

Figure 4
A [100] view of the crystal packing in (II). Bi polyhedra are shown in grey, I atoms as small black spheres and [Ru(2,2′-bipy)$_3$]$^{2+}$ cations as large black spheres.
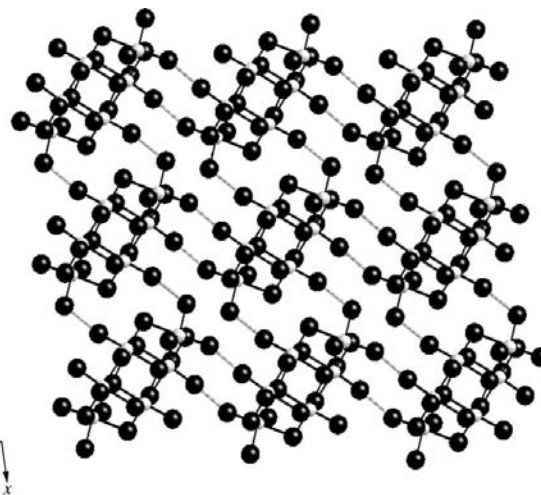

Figure 5
An [010] view of a single pseudo-two-dimensional anionic layer in (II). I···I interactions less than or equal to the sum of the van der Waals radii are indicated as two-tone bonds. Bi atoms are shown as light-grey spheres and I atoms as black spheres.

into consideration, the anionic component of the structure may be viewed as an array of weakly bonded two-dimensional sheets, which lie in the *ac* plane (Fig. 5). These pseudo-two-dimenional sheets may have an interesting consequence in terms of dimensionality-dependent optical properties, *i.e.* quantum confinement behavior, in that they serve to extend the dimensionality of the discrete anionic component (Ryan & Xu, 2004). Experiments aimed at isolating the phase-pure compound for optical measurements are in progress.

While it is reasonable to believe that compounds (I) and (II) contain anions of different polyhedral arrangements because they crystallize with different cations, it is also of interest to note that we have prepared another iodo-bismuthate compound, *viz.* [Ru(2,2′-bipy)$_3$]$_2$[Bi$_4$I$_{16}$] (Goforth, Gardinier *et al.*, 2005), which contains the same [Ru(2,2′-bipy)$_3$]$^{2+}$ cation as compound (II). However, [Ru(2,2′-bipy)$_3$]$_2$[Bi$_4$I$_{16}$] was synthesized from [Ru(2,2′-bipy)$_3$]I$_2$ tetra-hydrate and BiI$_3$, rather than from RuI$_3$, BiI$_3$, and 2,2′-bipyridine. Thus, it may be concluded that several reaction conditions, including choice of starting materials and nature of the counter-cation, simultaneously affect the identity of the iodobismuthate anion formed. The anion of [Ru(2,2′-bipy)$_3$]$_2$[Bi$_4$I$_{16}$] is the same as the Bi$_4$I$_{16}$ core in the [Bi$_6$I$_{22}$]$^{4-}$ anion of compound (II).

Experimental

BiI$_3$ (175 mg, 0.3 mmol; Alfa Aesar, 99.999%), 2,2′-bipyridine (54 mg, 0.3 mmol; Acros, 99+%) and RuI$_3$ (48 mg, 0.1 mmol; Aldrich, reagent grade) were placed in a 15 ml glass pressure vessel (Ace glass) and covered with aqueous ethanol (10 ml, 50% *v/v*). The reaction vessel was subsequently sealed with a threaded Teflon plug (with a back-seal FETFE O-ring; Ace glass) and heated at rate of 0.1 K min^{-1} to 433 K, where the temperature was held for 5 d. At the end of this period, the vessel was cooled at a rate of 0.1 K min^{-1} to 353 K and this temperature was maintained for 6 h, after which the reaction vessel was cooled to room temperature at a rate of 0.1 K min^{-1}. Red–orange blocks of (I), red–orange prisms of (II) and a red–orange polycrystalline material were isolated from the reaction. Suitable red–orange crystals were selected for the structure determinations of (I) and (II).

Compound (I)

Crystal data

(C$_{10}$H$_9$N$_2$)$_4$[Bi$_6$I$_{22}$]	$V = 2071.2$ (2) Å^3
$M_r = 4674.45$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 3.748$ Mg m^{-3}
$a = 11.3334$ (6) Å	Mo $K\alpha$ radiation
$b = 12.9913$ (7) Å	$\mu = 20.93$ mm^{-1}
$c = 15.7999$ (9) Å	$T = 150$ (1) K
$\alpha = 78.7780$ (10)°	Block, orange
$\beta = 79.5200$ (10)°	$0.12 \times 0.11 \times 0.08$ mm
$\gamma = 66.0230$ (10)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	27864 measured reflections
	9709 independent reflections
ω scans	8250 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$R_{int} = 0.039$
$T_{min} = 0.501$, $T_{max} = 1.000$	$\theta_{max} = 27.7°$
(expected range = 0.094–0.187)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 1.7243P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.085$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.03$	$\Delta\rho_{max} = 1.83$ e Å^{-3}
9709 reflections	$\Delta\rho_{min} = -2.90$ e Å^{-3}
223 parameters	
H-atom parameters constrained	

Compound (II)

Crystal data

[Ru(C$_{10}$H$_8$N$_2$)$_3$][Bi$_6$I$_{22}$]	$V = 2489.0$ (2) Å^3
$M_r = 5184.92$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 3.459$ Mg m^{-3}
$a = 12.7346$ (7) Å	Mo $K\alpha$ radiation
$b = 13.6135$ (7) Å	$\mu = 17.72$ mm^{-1}
$c = 14.5978$ (8) Å	$T = 150$ (1) K
$\alpha = 91.3800$ (10)°	Block, red
$\beta = 100.0770$ (10)°	$0.18 \times 0.14 \times 0.10$ mm
$\gamma = 92.0100$ (10)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	23253 measured reflections
	10135 independent reflections
ω scans	8993 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$R_{int} = 0.033$
$T_{min} = 0.686$, $T_{max} = 1.000$	$\theta_{max} = 26.4°$
(expected range = 0.117–0.170)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 2.3445P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 1.41$ e Å^{-3}
10135 reflections	$\Delta\rho_{min} = -1.37$ e Å^{-3}
461 parameters	Extinction correction: *SHELXL97* (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.000139 (15)

For compound (I), all atoms of the anion were refined with anisotropic displacement parameters. H atoms bonded to C atoms were placed in geometrically idealized positions and included as riding atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). No N-bound H atoms were located or calculated. The highest residual electron-density peak is located 0.57 Å from C13 and the deepest hole is located 2.88 Å from I5. For compound (II), H atoms were placed in geometrically idealized positions and included as riding atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The highest residual electron-density peak is located 0.93 Å from Bi3 and the deepest hole is located 0.54 Å from I4.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3025). Services for accessing these data are described at the back of the journal.

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