Tetrakis[2-(2-Pyridyl)Pyridinium] Tetra-$\mu_3$-Iodo-Hexa-$\mu_2$-Iodo-Dodecaiodohexabismuthate and Bis[Tris(2,2'-Bipyridine)Ruthenium(II)] Di-$\mu_4$-Iodo-Octa-$\mu_2$-Iodo-Dodecaiodohexabismuthate

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**Publication Info**
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Received 25 May 2006
Accepted 5 July 2006
Online 11 August 2006

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-μ₂-iodo-hexa-μ₂-iodo-dodecaiodohexabismuthate, \( \text{C}_{10} \text{H}_{14} \text{N}_{2} \text{I}_{2} \)\(_4\)[Bi₄I₂₂], crystallizes in the triclinic space group \( P\overline{1} \) and is the major reaction product. The asymmetric unit of this compound consists of half a centroymmetric \( \text{Bi}_4\text{I}_{22}^{-} \) anion and two independent 2,2′-bipyridinium cations. The minor product of the reaction is bis[tris(2,2′-bipyridine)ruthenium(II)] di-μ₄-iodo-octa-μ₂-iodo-dodecaiodohexabismuthate, \( [\text{Ru}(\text{C}_1\text{H}_2\text{N}_2)_{3}]_{2}\text{[Bi}_4\text{I}_{22}] \), which also crystallizes in the triclinic space group \( P\overline{1} \). For this compound, the asymmetric unit consists of one full \( [\text{Ru}(2,2′-\text{bipyridine})]_{2}^{4-} \) cation and half a centroymmetric \( \text{Bi}_4\text{I}_{22}^{-} \) anion. Although both compounds contain a centroymmetric \( \text{Bi}_4\text{I}_{22}^{-} \) anion, the polyhedral arrangement of the distorted Bi₄ 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; Moudis 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 \( \text{Cu}^3 \) (Yu et al., 2003), \( \text{Sn}^\text{III} \) (Xu & Mitzi, 2003), \( \text{Sb}^\text{III} \) (Moudis et al., 1998), \( \text{Te}^\text{IV} \) (Ryan & Xu, 2004), \( \text{Pb}^\text{II} \) (Zhu et al., 2003) and \( \text{Bi}^\text{III} \) (Moudis et al., 1998; Eickmeier et al., 1999; Lindsjö et al., 2005) have been synthesized and structurally characterized.

We have been interested in the synthesis of new main group halometallate materials containing \( \text{Bi}^\text{III} \) 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, Gardnier 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 \( \text{Bi}_4 \) polyhedra, which are corner-, edge- or face-sharing. The number of

Figure 1

A view of the \( \text{Bi}_4\text{I}_{22}^{-} \) 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) \( 1-x, -y, 1-z \).]
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; Goforth, 2005). We report here the synthesis and single-crystal X-ray structures of two co-crystallizing iodobismuthate compounds, one of which has a coordination cation for charge balance while the other has an organic counter-ion. Both compounds contain [Bi$_6$I$_{22}$]$^{4+}$ anions. However, the polyhedral arrangements of the six Bi$_6$ octahedra in the two compounds differ.

The title compounds, [H(2,2’-bipy)][Bi$_6$I$_{22}$] and [H(2,2’-bipy)]$^+$ is protonated 2,2’-bipyridine], (I), and [Ru(2,2’-bipy)$_3$]$_2$- [Bi$_6$I$_{22}$], (II), were synthesized solvothermally from RuI$_3$, 2,2’-bipyridyl and Bi$_3$I$_6$ 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$_6$I$_{22}$]$^{4+}$ 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 $P\overline{1}$ and contains two crystallographically independent 2,2’-bipyridinium cations and half of a [Bi$_6$I$_{22}$]$^{4+}$ 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$_6$I$_{22}$]$^{4+}$ anion were refined anisotropically. The centrosymmetric anion consists of six Bi$_6$ 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 Bi$_6$ octahedra in (I) is a known arrangement of the [Bi$_6$I$_{22}$]$^{4+}$ anion. For example, the [Bi$_6$I$_{22}$]$^{4+}$ anions of
metal-organic compounds

\[(\text{THF})_n\text{Na}[\text{Bi}_4\text{I}_{12}]\] (THF is tetrahydrofuran; Krautschkeid, 1994), \((\text{EtMe}_3\text{PhN})_n[\text{Bi}_4\text{I}_{12}]\) (Eickmeier et al., 1999) and \((\text{H}_2\text{TMMDP})_n[\text{Bi}_4\text{I}_{12}]\) \([\text{H}_2\text{TMMDP}]^{2+}\) is 1,3-bis(4-piperidino)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–I distance is 3.1491 Å and the average Bi–I–Bi 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 \([\text{H}(2,2’-\text{bipy})]^+\) cations and rows of \([\text{Bi}_4\text{I}_{12}]^{2+}\) anions are observed. Weak \(I–\cdot–I\) bonding interactions between \([\text{Bi}_4\text{I}_{12}]^{2+}\) anions of neighboring rows are also observed \(I_3–I_9 = 3.739 (1) \text{ Å} \text{ and } I_8–I_{10} = 3.732 (1) \text{ Å}; \text{ symmetry codes: } (i) x–1, y+1, z; (ii) x, 1–y, 1–z; \text{ van der Waals radius of } I = 1.98 \text{ Å and } I_\text{..I} = 3.96 \text{ Å; Bondi, 1964)}\), 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 \(P\overline{1}\) and contains the well known tris-chelate cation \([\text{Ru}(2,2’-\text{bipy})_3]^{2+}\) and a novel arrangement of the \([\text{Bi}_4\text{I}_{12}]^{2+}\) anion (Fig. 3). The bond distances and angles of the cation are normal \(2.044 (6)–2.067 (6) \text{ Å; Biner et al., 1992})\). Due to the crystallographic inversion symmetry in the crystal, both the \(\Lambda\) and \(\Delta\) enantiomers of the cation are present in the structure.

The centrosymmetric \([\text{Bi}_4\text{I}_{12}]^{2+}\) anion of (II) consists of a central \(\text{Bi}_4\text{I}_{12}\) core (containing atoms Bi1 and Bi2), with two \(\text{Bi}_3\) units (containing atom Bi3) connected to the core by three relatively long Bi–I bonds \(3.3268 (6), 3.4311 (6) \text{ and } 3.5484 (5) \text{ Å; Fig. 3})\). Alternatively, the \(\text{Bi}_3\) units can be considered as part of very distorted \(\text{Bi}_3\text{I}_6\) octahedra, each of which shares two \(\text{cis}\) edges with the \(\text{Bi}_4\text{I}_{16}\) cluster core. The bond lengths and angles of the \(\text{Bi}_4\text{I}_{16}\) core are within the normal ranges and are comparable with those found in previously reported \([\text{Bi}_4\text{I}_{16}]^{2+}\) anions (Goforth, Gardiner et al., 2005). The average terminal Bi–I distance is 2.897 Å and the average Bi–I–Bi–I distance is 3.166 Å.

Considering the pendant \(\text{Bi}_3\) units of the anion, an unusual bonding feature of the anion of compound (II) is the presence of an essentially \(\mu_4\)-bridging iodide ligand. However, the average Bi–I–Bi distance of 3.397 Å is within the reported ranges for Bi–I–Bi distances in related compounds (Feldmann, 2003), further supporting the description of the anion as a \(\text{Bi}_4\text{I}_{16}\) core with two pendant \(\text{Bi}_3\) groups. In fact, many of the larger known discrete iodobismuthate anions may be considered to be based on \(\text{Bi}_4\text{I}_{16}\) cores, either joined with one or more pendant \(\text{Bi}_3\) units [as in \([\text{Bi}_4\text{I}_{16}]^{2+}\) (Krautschkeid, 1994), or the typical arrangement of \([\text{Bi}_4\text{I}_{12}]^{2+}\) (Eickmeier et al., 1999; Pohl et al., 1994; Goforth, Peterson et al., 2005; Krautschkeid, 1994)], or connected to another such core through a single edge [as in \([\text{Bi}_4\text{I}_{16}]^{2+}\) (Feldmann, 2003)]. The \(\text{cis}\) \(\text{I}–\text{Bi}–\text{I}\) angles of the anion of (II) range from 78.39° (1) to 103.69° (2) and the \(\text{trans}\) angles from 159.65° (2) to 177.02° (2), where the largest deviations from the ideal octahedral angles are observed in the \(\text{Bi}_3\) polyhedron.

A [010] 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 \(I\cdot–I\) bonding interactions \([I10–I3’ = 3.834 (1) \text{ Å and } I11–I7’ = 3.957 (1) \text{ Å; symmetry codes: } (i) x–1, y–1, z–1; (ii) –x, 1–y, z–1\)] and \(I1\cdot–I1\) interactions are taken.

![Figure 4](image-url)

**Figure 4**
A [010] view of the crystal packing in (II). Bi polyhedra are shown in grey. I atoms as small black spheres and \([\text{Ru}(2,2’-\text{bipy})_3]^{2+}\) cations as large black spheres.

![Figure 5](image-url)

**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-bonded Bi atoms. 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-dimensional 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 iodobismuthate compound, viz. \( \text{[Ru}(2,2'\text{-bipy})_2\text{]}[[\text{Bi}_2\text{I}_8]] \) (Gofforth, Gardiner et al., 2005), which contains the same \( \text{[Ru}(2,2'\text{-bipy})_2\text{]} \) cation as compound (II). However, \( \text{[Ru}(2,2'\text{-bipy})_2\text{]}[[\text{Bi}_2\text{I}_8]] \) was synthesized from \( \text{[Ru}(2,2'\text{-bipy})_2\text{]}\text{II} \) tetrahydrate and \( \text{Bi}_3 \), rather than from \( \text{RuI}_3 \), \( \text{Bi}_3 \), 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 \( \text{[Ru}(2,2'\text{-bipy})_2\text{]}[[\text{Bi}_2\text{I}_8]] \) is the same as the \( \text{Bi}_2\text{I}_8 \) core in the \( \text{Bi}_2\text{I}_3 \) anion of compound (II).

Experimental

\( \text{Bi}_3 \) (175 mg, 0.3 mmol; Alfa Aesar, 99.999%) and \( \text{Al}\text{I}_3 \) (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-saw FETTEF O-ring; Ace glass) and heated at a 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\(^{-1}\) to 353 K. 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**

\( \text{(C}_0\text{H}_2\text{N}_2\text{)}_2\text{[Bi}_2\text{I}_8] \)

- \( M_r = 4674.45 \)
- Triclinic, \( P\bar{1} \)
- \( a = 11.3334 \) (6) Å
- \( b = 12.9915 \) (7) Å
- \( c = 15.7999 \) (9) Å
- \( \alpha = 78.7790 \) (10°)
- \( \beta = 79.5200 \) (10°)
- \( \gamma = 66.0230 \) (10°)

**Data collection**

- Bruker SMART APEX CCD area-detector diffractometer
- \( 27864 \) measured reflections
- \( 9709 \) independent reflections
- \( 8250 \) reflections with \( \theta > 2\theta(I) \)
- \( R_{int} = 0.039 \)
- \( \theta_{max} = 27.7° \)

Refinement

- **Refinement on \( F^2 \)**
  - \( R(F^2) = 0.036 \)
  - \( wR(F^2) = 0.085 \)
  - \( S = 1.03 \)
  - 9709 reflections
  - 223 parameters
  - H-atom parameters constrained

- **Parameters**
  - \( w = 1/\left[\sigma^2(F_e^2) + (0.0369P^2) + 1.7343P \right] \)
  - where \( P = (F_e^2 + 2F_c^2)/3 \)
  - \( \langle \sigma\rangle_{max} = 0.001 \)
  - \( \Delta \sigma_{max} = 1.83 \) e Å\(^{-3}\)
  - \( \Delta \rho_{min} = -2.90 \) e Å\(^{-3}\)

**Compound (II)**

**Crystal data**

\( \text{[Ru}(C_0\text{H}_2\text{N}_2\text{)}_2\text{][Bi}_2\text{I}_8] \)

- \( M_r = 5184.92 \)
- Triclinic, \( P\bar{1} \)
- \( a = 12.7346 \) (7) Å
- \( b = 13.6135 \) (7) Å
- \( c = 14.9578 \) (8) Å
- \( \alpha = 91.3800 \) (10°)
- \( \beta = 100.0770 \) (10°)
- \( \gamma = 92.0100 \) (10°)

**Data collection**

- Bruker SMART APEX CCD area-detector diffractometer
- \( 10135 \) independent reflections
- \( 8993 \) reflections with \( \theta > 2\theta(I) \)
- \( R_{int} = 0.033 \)
- \( \theta_{max} = 26.4° \)

**Refinement**

- **Refinement on \( F^2 \)**
  - \( R(F^2) = 0.032 \)
  - \( wR(F^2) = 0.070 \)
  - \( S = 1.02 \)
  - 10315 reflections
  - 461 parameters
  - H-atom parameters constrained

- **Parameters**
  - \( w = 1/\left[\sigma^2(F_e^2) + (0.0252P^2) + 2.3445P \right] \)
  - where \( P = (F_e^2 + 2F_c^2)/3 \)
  - \( \langle \sigma\rangle_{max} = 0.001 \)
  - \( \Delta \sigma_{max} = 1.41 \) e Å\(^{-3}\)
  - \( \Delta \rho_{min} = -1.37 \) e Å\(^{-3}\)
  - Extinction correction: \( SHELXL97 \)
  - Exinction 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 \( U_{eq}(H) = 1.2U_{eq}(C) \). 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 \( U_{eq}(H) = 1.2U_{eq}(C) \). 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: SHELX97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 2000); software used to prepare material for publication: SHELXL.

Financial support for this work was provided by the National Science Foundation through grant Nos. CHE: 0314164 and CHE: 0315152.
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.

References
