J|A|C|S
ARTICLES

Structural Diversity and Thermochromic Properties of Iodobismuthate Materials Containing d-Metal Coordination Cations: Observation of a High Symmetry $[Bi_3I_{11}]^{2-}$ Anion and of Isolated I^- Anions

Andrea M. Goforth,*,[†,§] Meredith A. Tershansy,[†] Mark D. Smith,[†] LeRoy Peterson, Jr.,[‡]
Jennifer G. Kelley,[‡] William J. I. DeBenedetti,[§] and Hans-Conrad zur Loye*,[†]

Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208, United States, Department of Chemistry, Francis Marion University, Florence, South Carolina 29501, United States, and Department of Chemistry, Portland State University, Portland, Oregon 97201, United States

Received September 24, 2010; E-mail: zurloye@mail.chem.sc.edu; agoforth@pdx.edu

Abstract: Six new inorganic−organic salts, all containing iodobismuthate anions and d-metal coordination cations, were synthesized solvothermally from reactions of bismuth iodide, a transition metal (M) nitrate salt (M = Co, Fe or Zn), and a heterocyclic, chelating organic ligand: 1,10-phenanthroline (1,10-phen), 3,4,7,8-tetramethyl-1,10-phenanthroline (TMphen), or 2,2′:6′,2′′-terpyridine (tpy). All six compounds were structurally analyzed by single crystal X-ray diffraction, including variable temperature crystallographic analysis to monitor for structural changes. Furthermore, those containing novel anions and achieved in high yield were additionally characterized by solid-state UV visible spectroscopy at room temperature. $[Co(1,10\text{-phen})_3][Bi_3I_{11}]$ (**1**), $[Fe(1,10\text{-phen})_3][Bi_3I_{11}]$ (**2**), and $[Zn(1,10\text{-phen})_3][Bi_3I_{11}]$ (**3**) are isostructural. They crystallize in the monoclinic space group $P2_1/n$ and contain the unprecedented iodobismuthate anion, $[Bi_3I_{11}]^{2-}$, which exhibits near D_{3h} symmetry and has an unusual arrangement of three cis face-sharing BiI_6 octahedra. $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (**4**), which crystallizes in the trigonal space group $P\text{-}31c$, and $[Co(tpy)_2]_2[Bi_2I_9][I]$ (**5**) and $[Zn(tpy)_2]_2[Bi_2I_9][I]$ (**6**), which are isostructural and crystallize in the monoclinic space group $C2/c$, contain the discrete binuclear $[Bi_2I_9]^{3-}$ anion, common in previously reported iodobismuthate compounds. In addition they contain unusual isolated I^- anions, which are rarely encountered in iodobismuthate phases. Compounds **1**−**6** show constitutional similarities while utilizing different organic ligands and illustrate the sensitive dependence of reaction conditions on the identity of the halometalate anion formed. Additionally, all six compounds and the starting material BiI_3 are thermochromic; the origin of this behavior is spectroscopically and crystallographically investigated.

Introduction

Many research groups have been interested in the chemistry of main group halometalate materials due to the wide structural diversity observed in this family of materials and due to the interesting optical and electronic properties, including nonlinear optical behavior, absorption and luminescence thermochroism, and semiconductivity, that have been observed in such systems.[1−7] Particularly, many solid-state, main group halometalate materials have UV−visible absorption spectra with absorption edges in the visible, which have led to their classification as low-dimensional semiconductors.[2,8−14] Consequently, these materials have been of interest in the study of dimensionally restricted optical properties (i.e., confinement effects),[2,8] especially since the metal halide anion is typically of lower dimensionality than the corresponding parent metal halide.[15] In addition to the possibility of comparing the optical properties of lower dimensional species to those of higher dimensional, bulk semiconducting materials, numerous previous studies have shown that within a given metal halide system, e.g., iodobismuthates, it is possible to produce anions of both different dimensionalities and different

---

[†] The University of South Carolina.
[§] Portland State University.
[‡] Francis Marion University.

(1) Mercier, N.; Louvain, N.; Bi, W. *Cryst. Eng. Commun.* **2009**, *11*, 720.
(2) Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1.
(3) Bi, W.; Louvain, N.; Mercier, N.; Luc, J.; Rau, H.; Kajzar, F.; Sahraoui, B. *Adv. Mater.* **2008**, *20*, 1013.
(4) Louvain, N.; Mercier, N.; Boucher, F. *Inorg. Chem.* **2009**, *48*, 879.
(5) Bi, W.; Mercier, N. *Chem. Commun.* **2008**, 5743.
(6) Tershansy, M. A.; Goforth, A. M.; Gardinier, J. R.; Smith, M. D.; Peterson, L., Jr.; zur Loye, H.-C. *Solid State Sci.* **2007**, *9*, 410.
(7) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220.
(8) Mousdis, G. A.; Papavassiliou, G. C.; Terzis, A.; Raptopolou, C. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1998**, *53*, 927.
(9) Mitzi, D. B.; Brock, P. *Inorg. Chem.* **2001**, *40*, 2096.
(10) Knutson, J. L.; Martin, J. D. *Inorg. Chem.* **2005**, *44*, 4699.
(11) Xu, Z.; Mitzi, D. B. *Inorg. Chem.* **2003**, *42*, 6589.
(12) Zhu, X.-H.; Mercier, N.; Frère, P.; Blanchard, P.; Roncali, J.; Allain, M.; Pasquier, C.; Riou, A. *Inorg. Chem.* **2003**, *42*, 5330.
(13) Liu, B.; Xu, L.; Guo, G.-C.; Huang, J.-S. *J. Solid State Chem.* **2006**, *179*, 1611.
(14) Papavassiliou, G. C.; Koutselas, I. B.; Terzis, A.; Raptopolou, C. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1995**, *50*, 1566.
(15) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Butterworth-Heinemann: Oxford, UK, 1998.

10.1021/ja108278j

sizes by variation of the synthetic conditions. Thus, it should be possible to synthesize compounds having a variety of halometalate anions within a single metal halide system in order to systematically investigate the effects of the size and dimensionality of the inorganic component upon the optical properties of the material. Factors known to affect the size, polyhedral connectivity (arrangement), and dimensionality of the inorganic metal halide anion include choice of reagents, reagent stoichiometry, solvent system, crystallization conditions, and size, charge, and charge density of the countercation.[1,5,13,16−22]

To date, numerous halometalate materials based on the main group metals Cu(I), Ag(I), Pb(II), Sn(II), Sb(III), Bi(III), Te(IV), and others have been synthesized and structurally characterized.[1,2,8,10−12,22−30] These compounds may be represented by the general formula $[A_a(M_mX_x)]$, where A represents a cation, M represents a main group metal, and X represents a halide ligand (a, m, and x represent the stoichiometry of the compound). The halometalate anion is composed of MX_n polyhedra ($X = Cl$, Br, or I; n is an integer, typically 6), which may be isolated or condensed by corner-, edge-, or face-sharing of the polyhedra. While most halometalate materials contain zero-dimensional, discrete anions, it is worth mentioning that some halometalates have extended structures with two- or three-dimensional anions; however, higher order polymers are far less common than zero- and one-dimensional anion structures. Several review papers,[1,2] which survey a large population of halometalate compounds, have addressed synthetic rationale in achieving higher dimensional anions. However, such a survey is beyond the scope of this paper, and, in practice, experimental results do not usually support straightforward anion engineering in these systems. With respect to the cation, the vast majority of compounds have contained a simple organic cation, e.g., alkyammonium cations, as charge balance for the inorganic halometalate anion.

Our group has been interested in the synthesis, structural determination, and optical properties of new materials containing iodobismuthate anions.[6,22,26,27,31−33] Though numerous iodobismuthate materials have been reported in the literature, iodobismuthate compounds having a metal-containing cation are comparatively rare;[20,26,29,31,33−39] furthermore, many of these examples possess a bismuth-containing cation as charge balance for the iodobismuthate anion.[31,35−39] Herein, we present the solvothermal syntheses, diffuse reflectance UV−visible spectroscopy, and single crystal X-ray structures of several new iodobismuthate materials that possess a d-metal coordination cation as the charge balancing species; we have determined that the use of such cations can lead to novel iodobismuthate anions and unusual structures. Specifically, we discovered the new, relatively high symmetry iodobismuthate anion, $[Bi_3I_{11}]^{2-}$, which has an unusual arrangement of three mutually cis face-sharing octahedra, in the isostructural compounds $[M(1,10\text{-phenanthroline})_3][Bi_3I_{11}]$ (M = Co (**1**), Fe (**2**), and Zn (**3**)). The occurrence of the $[Bi_3I_{11}]^{2-}$ anion is unprecedented and adds a fundamentally new binary anion to bismuth halide chemistry. While similar anions are known in lead[40,41] and cadmium halide[42,43] compounds, the observation of $[Bi_3I_{11}]^{2-}$ represents an important new development in bismuth halide chemistry.

Additionally, the crystal structures of related compounds, $Co[(3,4,7,8\text{-tetramethyl-1,10-phenanthroline})_3]_2[Bi_2I_9][I]$ (**4**) and $[M(2,2'{:}6,2''\text{-terpyridine})_2]_2[Bi_2I_9][I]$ (M = Co (**5**), or Zn (**6**)), synthesized by minor variation of the reaction conditions producing **1**−**3**, are reported. These structures contain highly unusual, isolated I^- anions, which are rarely encountered in iodobismuthate phases and which represent a new charge compensation mode in bismuth halide chemistry. These structures illustrate the sensitive dependence of the identity of the iodobismuthate anion on the specific reaction conditions, particularly on the identity of the cation. All six compounds display thermochromism, and the origin of thermochromic behavior is investigated by single crystal X-ray diffraction of **1** at several temperatures.

Experimental Section

Synthesis of $[M(1,10\text{-Phenanthroline})_3][Bi_3I_{11}]$ (M = Co (1), Fe (2), Zn (3)). The series of compounds having the general formula $[M(1,10\text{-phen})_3][Bi_3I_{11}]$ (M = Co (**1**), Fe (**2**), or Zn (**3**); 1,10-phen = 1,10-phenanthroline) was synthesized solvothermally. BiI_3 (0.3 mmol, 176 mg, Alfa Aesar, 99.999%), 1,10-phen (0.3 mmol, 54 mg, Acros, 99+%), and 0.1 mmol of a metal nitrate salt (29 mg $Co(NO_3)_2 \cdot 6H_2O$ (MCB, reagent grade), 40 mg $Fe(NO_3)_3 \cdot 9H_2O$ (Alfa Aesar, 98+%), or 30 mg $Zn(NO_3)_2 \cdot 6H_2O$ (Fisher, reagent grade)) were weighed and placed in 15 mL glass pressure vessels (Ace glass) with 10 mL of aqueous ethanol as the reaction solvent (50% v/v). The glass vessels, supported upright in beakers, were sealed with threaded Teflon plugs (having back seal FETFE o-rings)

---

(16) Eickmeier, H.; Jaschinski, B.; Hepp, A.; Nuβ, J.; Reuter, H.; Blachnik, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1999**, *54*, 305.

(17) Cornia, A.; Fabretti, A. C.; Grandi, R.; Malavasi, W. *J. Chem. Crystallogr.* **1994**, *24*, 277.

(18) Clegg, W.; Errington, R. J.; Fisher, G. A.; Green, M. E.; Hockless, D. C. R.; Norman, N. C. *Chem. Ber.* **1991**, *124*, 2457.

(19) Carmalt, C. J.; Farrugia, L. J.; Norman, N. C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1995**, *50*, 1591.

(20) Krautschied, H. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1559.

(21) Feldmann, C. *J. Solid State Chem.* **2003**, *172*, 53.

(22) Goforth, A. M.; Peterson, L., Jr.; Smith, M. D.; zur Loye, H.-C. *J. Solid State Chem.* **2005**, *178*, 3529.

(23) Yu, J.-H.; Jia, H.-B.; Pan, L.-Y.; Yang, Q.-X.; Wang, T.-G.; Xu, J.-Q.; Cui, X.-B.; Liu, Y.-J.; Li, Y.-Z.; Lu, C.-H.; Ma, T.-H. *J. Solid State Chem.* **2003**, *175*, 152.

(24) Tershansy, M. A.; Goforth, A. M.; Smith, M. D.; zur Loye, H.-C. *Cryst. Eng. Commun.* **2008**, *10*, 833.

(25) Burns, M. C.; Tershansy, M. A.; Ellsworth, J. M.; Khaliq, Z.; Peterson, L., Jr.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2006**, *45*, 10437.

(26) Goforth, A. M.; Gardinier, J. R.; Smith, M. D.; Peterson, L., Jr.; zur Loye, H.-C. *Inorg. Chem. Commun.* **2005**, *8*, 684.

(27) Goforth, A. M.; Smith, M. D.; Peterson, L., Jr.; zur Loye, H.-C. *Inorg. Chem.* **2004**, *43*, 7042.

(28) Ryan, J. M.; Xu, Z. *Inorg. Chem.* **2004**, *43*, 4106.

(29) Tershansy, M. A.; Goforth, A. M.; Peterson, Jr., L.; Burns, M. C.; Smith, M. D.; zur Loye, H.-C. *Solid State Sci.* **2007**, *9*, 895.

(30) Chai, W.-X.; Wu, L.-M.; Li, J.-Q.; Chen, L. *Inorg. Chem.* **2007**, *46*, 1042.

(31) Tershansy, M. A.; Goforth, A. M.; Smith, M. D.; zur Loye, H.-C. *J. Chem. Cryst.* **2008**, *38*, 453.

(32) Tershansy, M. A.; Goforth, A. M.; Smith, M. D.; Peterson, L., Jr.; zur Loye, H.-C. *Acta Crystallogr.* **2006**, *E62*, m2987.

(33) Goforth, A. M.; Tershansy, M. A.; Smith, M. D.; Peterson, L., Jr.; zur Loye, H.-C. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2006**, *C62*, m381.

(34) Lindsjo, M.; Fischer, A.; Kloo, L. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1497.

(35) Rogers, R. D.; Bond, A. H.; Aguinaga, S.; Reyes, A. *J. Am. Chem. Soc.* **1992**, *114*, 2967.

(36) Feldmann, C. *Inorg. Chem.* **2001**, *40*, 818.

(37) Kubiak, R.; Ejsmont, K. *J. Mol. Struct.* **1999**, *474*, 275.

(38) Bowmaker, G. A.; Junk, P. C.; Lee, A. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1998**, *51*, 293.

(39) Carmalt, C. J.; Farrugia, L. J.; Norman, N. C. *Z. Anorg. Allg. Chem.* **1995**, *621*, 47.

(40) Krautscheid, H.; Vielsack, F. *Z. Anorg. Allg. Chem.* **1997**, *623*, 259.

(41) Krautscheid, H.; Vielsack, F. *J. Chem. Soc., Dalton Trans.* **1999**, 2731.

(42) Waskowska, A.; Lis, T.; Krzewska, U.; Czapla, Z. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1768.

(43) Kurawa, M. A.; Adams, C. J.; Orpen, A. G. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2008**, *E64*, m960.

and heated at a rate of 0.1 °C/min to 160 °C in a programmable furnace. The temperature was held at 160 °C for three days before it was decreased, at a rate of 0.1 °C/min, to 70 °C where it was then held for 6 h. Finally, the temperature was decreased at a rate of 0.1 °C/min to room temperature. Dark red, bar-shaped single crystals and red polycrystalline material were isolated from each of the three separate reactions. Both the crystals and the polycrystalline materials are stable in air upon removal of the mother liquors by vacuum filtration. For **2**, it is noteworthy that the Fe(III) starting material was reduced to Fe(II) during the synthesis; however, this is not unexpected under the reducing conditions of hydrothermal reactions. Powder X-ray diffraction on the bulk solid isolated directly from the reaction of **1** revealed that the polycrystalline material is not of the same phase as the single crystals. However, the yield of single crystals is good in all three cases, and phase-pure samples of **1**, **2**, and **3** are readily obtained by manual separation of the single crystals from the polycrystalline material using metal sieves of appropriate mesh. Phase purity is demonstrated for **1** by powder X-ray diffraction (Figure S1, Supporting Information) and for compounds **1**, **2**, and **3** by elemental analysis. The yield of single crystals was estimated for compound **1**. In a typical reaction producing **1**, 190 mg of solid product is obtained. Estimating that crystals of **1** comprise 95% of the solid product by mass (with the remaining 5% being the unidentified, red polycrystalline material) the yield of **1** based on Bi^{3+} is 25%. A phase-pure sample of each of the three compounds was manually separated as described above, ground to a fine powder, and used for diffuse reflectance UV−visible absorption spectroscopy. Elemental analyses were also performed on manually separated single crystalline samples of the compounds by Desert Analytics (Tucson, AZ). Anal. Calcd (%) for **1**: $C_{36}H_{24}Bi_3CoI_{11}N_6$: C, 16.49; H, 0.92; N, 3.20. Found for **1**: C, 16.55; H, 0.94; N, 3.10. Anal. Calcd (%) for **2**: $C_{36}H_{24}Bi_3FeI_{11}N_6$: C, 16.51; H, 0.92; N, 3.21. Found for **2**: C, 16.66; H, 1.21; N, 3.31. Anal. Calcd for **3**: $C_{36}H_{24}Bi_3I_{11}N_6Zn$: C, 16.45; H, 0.92; N, 3.20. Found for **3**: C, 16.41; H, 0.87; N, 3.17.

UV−Visible Spectroscopy Measurement of 1, 2, and 3. Diffuse reflectance UV−visible spectroscopy measurements for compounds **1**, **2**, and **3** were made on an Ocean Optics USB-2000 fiber optic spectrometer equipped with a diffuse reflectance probe and a 45° sample stage; the measurements were conducted at room temperature. A white PTFE standard (Ocean Optics WS-1) was used as the reference material. Both a reference spectrum and a dark spectrum were recorded prior to the measurement of each compound, and a measurement of the reflected light was then acquired for each by the spectrometer operating in absorbance mode. For reference of these compounds to the starting material, the absorption spectrum of BiI_3 was acquired in the same way.

Synthesis of [Co(3,4,7,8-Tetramethyl-1,10-phenanthroline)$_3$]$_2$[Bi$_2$I$_9$][I] (4). Bismuth triiodide (0.3 mmol, 176 mg, Alfa Aesar, 99.999%), $Co(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 29 mg, MCB, reagent grade), and 3,4,7,8,-tetramethyl-1,10-phenanthroline (hereafter, TMPhen; 0.1 mmol, 70 mg, Acros, 99+%) were weighed and placed in a 15 mL glass pressure vessel (Ace glass) with 10 mL of deionized water as the reaction solvent. The glass tube, supported in a beaker, was sealed with a threaded Teflon plug (having a back seal FETFE O-ring) and heated at a rate of 0.1 °C/min to 180 °C. The temperature was held at 180 °C for seven days before it was decreased, at a rate of 0.1 °C/min, to 90 °C where it was then held for 6 h. Finally, the temperature was decreased at a rate of 0.1 °C/min to room temperature. Fine orange, air-stable needles and orange, air-stable polycrystalline material were obtained from the reaction and a suitable single crystal was selected for the X-ray diffraction analysis. Though this synthesis consistently resulted in single crystals of **4**, the synthesis could not be optimized to produce crystals large enough for manual separation from the polycrystalline material. Thus, compound **4** was characterized by single crystal X-ray diffraction only.

Synthesis of [M(2,2′:6,2″-Terpyridine)$_2$]$_2$[Bi$_2$I$_9$][I] (M = Co (5) or Zn (6)). Bismuth triiodide (0.3 mmol, 176 mg, Alfa Aesar, 99.999%), 2,2′:6,2″-terpyridine (hereafter, tpy; 0.3 mmol, 70 mg, Sigma Aldrich, >98.5% purity), and 0.1 mmol of a metal nitrate salt (29 mg $Co(NO_3)_2 \cdot 6H_2O$ (MCB, reagent grade) or 30 mg $Zn(NO_3)_2 \cdot 6H_2O$ (Fisher, reagent grade)) were weighed and placed in a 15 mL glass pressure vessel (Ace glass) with 10 mL of aqueous ethanol (50% v/v) as the reaction solvent. The glass vessels, supported in glass beakers, were sealed with a threaded Teflon plug (having a back seal FETFE O-ring) and heated at a rate of 0.1 °C/min to 160 °C. The temperature was held at 160 °C for five days before it was decreased, at a rate of 0.1 °C/min, to 80 °C where it was then held for 6 h. Finally, the temperature was decreased at a rate of 0.1 °C/min to room temperature. Air-stable, red-orange block crystals of **5** or orange plate-like crystals of **6**, in addition to air-stable orange polycrystalline material, were obtained from the reactions and a suitable single crystal of each was selected for X-ray diffraction analysis. The syntheses producing **5** and **6** are highly reproducible; however, due to their small size and plate-like morphology, respectively, phase-pure samples consisting entirely of single crystals of the compounds could not be manually isolated. Therefore, optical property measurements were not made on the two compounds.

Single Crystal Structure Determinations. [M(1,10-phen)$_3$][Bi$_3$I$_{11}$] (M = Co (1), Fe (2), Zn (3)). X-ray intensity data for **1** were collected on a red needle at 294(1) (**a**), 200(1) (**b**), 150(1) (**c**, **d**) and 100(1) K (**e**) on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å).[44] For the 150(1) K data set, the I(10) ligand site was modeled both as a split site (**c**) and as a single site (**d**). Minor improvement of the *R*-factors was observed when the I(10) site was modeled as a split position {R1, wR2 [$(I > 2(\sigma)I)$, **c**] = 0.0428, 0.0807; and R1, wR2 [$(I > 2(\sigma)I)$, **d**] = 0.0435, 0.0829}. For the remaining data sets, the I(10) ligand site was modeled only as a split position. For all data sets, raw frame integration and Lp corrections were performed with SAINT+.[44] Final unit cell parameters were determined by least-squares refinement of all reflections with $I > 5(\sigma)I$ from the respective data sets. For each experiment, analysis of the data showed negligible crystal decay during collection. The data were corrected for absorption effects with SADABS.[44] Direct methods structure solution, difference Fourier calculations, and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[45] Data collection and refinement statistics for structure solutions **1a**−**e** are listed in Tables S1−S5, Supporting Information.

For **1**, one of the 11 independent halide positions appeared unusual when it was refined anisotropically. In each structure, anisotropic refinement of I(10) resulted in an elongated, “cigar-shaped” displacement ellipsoid together with large nearby residual electron density along the elongated axis of the ellipsoid, ca. 0.5 Å from the primary I(10) position. Refinement of the I(10) site occupation factor resulted in negligibly small deviation from unity. When the nearby residual electron density peak was included, and the occupancies of both this site [I(10)B] and the primary I(10) position [I(10)A] were refined freely, the resulting sum of both occupancies was close to unity. This feature was taken as evidence for a split position occupied solely by iodine. For refinement, only the major position was refined anisotropically; the minor position was refined isotropically. At all measured temperatures, the split position model always resulted in a flatter difference map and a 1−2% decrease in the R1 values. For compounds **2** and **3**, similar crystallographic determinations were performed with similar results to those of **1**. The final refined I(10)A/I(10)B fractions (at 150(1) K) are as follows: (**1**) 0.91(1)/0.09(1); (**2**) 0.92(1)/0.08(1); (**3**) 0.93(1)/0.07(1).

---

(44) SMART Version 5.625, SAINT+ Version 6.45 and SADABS Version 2.05, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2001.

(45) SHELXTL Version 6.14, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2000.

Table 1. Data Collection and Refinement Statistics for the Single Crystal X-ray Structures of Compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{36}H_{24}Bi_3CoI_{11}N_6$	$C_{36}H_{24}Bi_3FeI_{11}N_6$	$C_{36}H_{24}Bi_3I_{11}N_6Zn$	$C_{96}H_{96}Bi_2Co_2I_{10}N_{12}$	$C_{60}H_{44}Bi_2I_{10}N_{12}Co_2$	$C_{60}H_{44}Bi_2I_{10}N_{12}Zn_2$
formula weight	2622.38	2919.3	2628.82	3222.67	2737.89	2750.77
crystal system	monoclinic	monoclinic	monoclinic	trigonal	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{3}1c$	$C2/c$	$C2/c$
a (Å)	14.9220(6)	14.9899(6)	15.0198(6)	17.8037(3)	28.007(1)	28.007(1)
b (Å)	21.1086(9)	20.9181(9)	21.0316(9)	17.8037(3)	12.4528(6)	12.5205(6)
c (Å)	17.3631(7)	17.2302(7)	17.3527(7)	19.0141(8)	20.7886(1)	20.738(1)
α (deg)	90	90	90	90	90	90
β (deg)	96.491(1)	97.224(1)	96.633(1)	90	94.213(1)	93.819(1)
γ (deg)	90	90	90	120	90	90
V (Å^3)	5434.0(4)	5359.8(4)	5444.9(4)	5219.5(3)	7229.6(5)	7255.8(6)
Z	4	4	4	2	4	4
density (mg/m^3)	3.205	3.246	3.207	2.051	2.515	2.518
μ (mm^{-1})	16.267	16.453	16.37	6.68	9.62	9.789
temperature (K)	150(1)	150(1)	150(1)	294(2)	150(1)	150(1)
residuals ($I > 2(\sigma)I$): R1, wR2	0.0428, 0.0807	0.0318, 0.0676	0.0354, 0.0716	0.0377, 0.0906	0.0342, 0.0672	0.0342, 0.0672
residuals (all data): R1, wR2	0.0556, 0.0850	0.0403, 0.0709	0.0464, 0.0756	0.0553, 0.1008	0.0438, 0.0708	0.0438, 0.0708

[Co(3,4,7,8-Tetramethyl-1,10-phenanthroline)$_3$]$_2$[Bi$_2$I$_9$][I] (4) and [M(2,2′:6,2″-Terpyridine)$_2$]$_2$[Bi$_2$I$_9$][I] (M = Co (5) or Zn (6)). X-ray intensity data were collected on single crystals of compounds **4**−**6** at 294(2) K (**4**) or at 150(1) K (**5** and **6**) on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.71073$).[44] Raw data frame integration and Lp corrections were performed with SAINT+.[44] Final unit cell parameters were determined by least-squares refinement of all reflections with $I > 5(\sigma)I$ from the respective data sets. Analysis of the data sets showed negligible crystal decay during collection in each case. All data sets were corrected for absorption effects by SADABS.[44] Direct methods structure solution, difference Fourier calculations, and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[45] The structure solutions of **4**−**6** are described in Results and Discussion; however, noteworthy features of these crystallography experiments are described below. CIFs are also deposited with the Cambridge Crystallographic Data Centre (CCDC) and have been allocated the deposition numbers CCDC 286133−286137 (**1a**−**e**), CCDC 790687−790689 (**2**−**4**), and CCDC 609279−609280 (**5**, **6**).

For **4**, no appreciable scattering was observed above 2θ ∼ 45° due to the thin needle morphology of all available single crystals. Structure solutions of **5** and **6** were routine. Table 1 lists data collection and refinement statistics for **1**−**6**. Selected interatomic distances and angles for the compounds are listed in Tables S6−S11, Supporting Information.

Results and Discussion

Synthesis of the Compounds. [Co(1,10-phen)$_3$][Bi$_3$I$_{11}$] (**1**), [Fe(1,10-phen)$_3$][Bi$_3$I$_{11}$] (**2**), [Zn(1,10-phen)$_3$][Bi$_3$I$_{11}$] (**3**), [Co(TMphen)$_3$]$_2$[Bi$_2$I$_9$][I] (**4**), [Co(tpy)$_2$]$_2$[Bi$_2$I$_9$][I] (**5**), and [Zn(tpy)$_2$]$_2$[Bi$_2$I$_9$][I] (**6**) were synthesized solvothermally using similar reaction conditions in all cases. For all reactions, a 3:3:1 molar ratio of BiI$_3$:organic ligand:metal nitrate was employed. However, slightly different reaction temperatures, heating times, and reaction solvents were necessary to achieve X-ray quality single crystals for each of the compounds.

The [M(1,10-phen)$_3$][Bi$_3$I$_{11}$] compounds were all synthesized under identical reaction conditions, and the three compounds are isostructural. However, when TMPhen was used as the organic ligand under the same conditions used to produce the [M(1,10-phen)$_3$][Bi$_3$I$_{11}$] compounds, poor quality single crystals were obtained. In order to produce X-ray quality single crystals, the heating temperature was increased from 160 to 180 °C, the reaction time was increased from three to seven days, and a more polar solvent was used (100% water vs 50% aqueous ethanol). The resulting compound contained a tris chelate dication, analogous to those in the [M(1,10-phen)$_3$][Bi$_3$I$_{11}$] compounds, but a different iodobismuthate anion. An additional feature of the resulting compound, [Co(TMphen)$_3$]$_2$[Bi$_2$I$_9$][I], is the presence of isolated I$^-$, a feature which is not observed in the compounds based on the 1,10-phen ligand. When the tpy ligand was used under the same conditions used to produce the [M(1,10-phen)$_3$][Bi$_3$I$_{11}$] compounds, small, poor quality single crystals were also obtained. Changing only the reaction time, higher quality crystals suitable for single crystal X-ray analysis were produced. [Co(tpy)$_2$]$_2$[Bi$_2$I$_9$][I] and [Zn(tpy)$_2$]$_2$[Bi$_2$I$_9$][I] contain the same two anions as [Co(TMphen)$_3$]$_2$[Bi$_2$I$_9$][I] and a similar d-metal coordination dication, which consists of two, tridentate chelating ligands rather than three, bidentate chelating ligands. Though it cannot conclusively be stated that the major factor influencing the identity of the inorganic iodobismuthate anion is the choice of the cation precursors, the choice of organic ligand is perhaps the most significant change in the reaction conditions presented here, particularly when the syntheses of **1**−**3** are compared to the syntheses of **5** and **6**, which, other than the ligand, only differed in the reaction time. Other studies of iodobismuthate chemistry have indicated that some of the major factors affecting the identity of the iodobismuthate anion include cation geometry, cation size and charge density, solvent choice, the relative stoichiometry and concentration of reactants, and the presence of additional reagents.[1,5,13,16−22] However, it is difficult to separate all of these factors so that definitive trends may be observed, and general predictability of the size and dimensionality of the inorganic anion is currently lacking, although features of the cation (size, geometry, charge, and charge density) seem to be the major determinant.[1]

Structural Description of the Compounds. X-ray crystallographic analysis revealed that [Co(1,10-phen)$_3$][Bi$_3$I$_{11}$] (**1**), [Fe(1,10-phen)$_3$][Bi$_3$I$_{11}$] (**2**), and [Zn(1,10-phen)$_3$][Bi$_3$I$_{11}$] (**3**) are isostructural compounds, which crystallize in the monoclinic space group $P2_1/n$. For compounds **1**−**3**, the asymmetric units consist of one [M(1,10-phen)$_3$]$^{2+}$ cation and one [Bi$_3$I$_{11}$]$^{2-}$ anion. Both the cation and the anion of the compounds are generated in situ during the course of the solvothermal reactions, and both the Λ- and the Δ-enantiomers of the tris chelate cations are present in the structures. With respect to the cations, one enantiomer is crystallographically generated from the other due to the specific symmetry of the compounds. The cations of the compounds are well-known, and in all cases have appeared in numerous other crystallographically characterized salts. How-

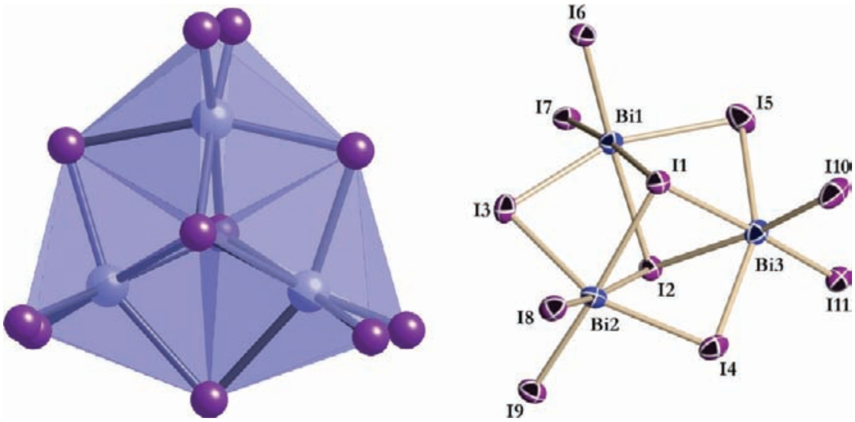

Figure 1. Two views of the nearly D_{3h} symmetric $[Bi_3I_{11}]^{2-}$ anion of $[M(1,10\text{-phen})_3][Bi_3I_{11}]$ (M = Co (**1**), Fe (**2**), or Zn (**3**)). Only the major position of the I(10) ligand is shown. The same atomic numbering scheme was used for the anions of all three compounds. Bi atoms, blue; I atoms, purple.

ever, the $[Bi_3I_{11}]^{2-}$ anion has not yet been reported in iodobismuthate chemistry.

In the $[Bi_3I_{11}]^{2-}$ anions of **1**−**3** (Figure 1), three BiI_6 octahedra are connected to give the *nearly* D_{3h} symmetric (idealized point symmetry) anion in which each octahedron shares one face with each of the two others. The two shared faces of each octahedron are cis with respect to one another, leading to the formation of a discrete anionic cluster, rather than an oligomeric chain structure where trans faces are shared, as in the anions of $[Bi(dpmu)_6][Bi_3I_{12}]$ and $(PPh_4)_3[Bi_5I_{18}]$ (dpmu = *N*,*N′*-dimethylpropylene, Ph = C_6H_5).[39,46] While this particular cluster composition (A_3B_{11}) and arrangement has been observed in $[Cd_3Cl_{11}]^{5-}$,[42,43] $[Pb_3I_{11}]^{5-}$ (not isolated, but as a repeat unit of 1-D polymer chains)[40,41] and in some alkali metal suboxides (e.g., $[O_3Cs_{11}]$),[15,47] it should be noted that the tendency of BiI_6 octahedra to engage in face-sharing is rather uncommon relative to the tendency to engage in edge- or corner-sharing arrangements of the polyhedra; the exception is $[Bi_2I_9]^{3-}$, which is common in iodobismuthate chemistry and consists of only two, face-sharing BiI_6 octahedra. Three sets of Bi−I bonds are present in the $[Bi_3I_{11}]^{2-}$ cluster. For brevity, we only discuss bonding in the anion of compound **1** here; although very similar bond lengths and angles occur in compounds **2** and **3**, they are explicitly listed in Tables S7 and S8. The terminal Bi−I average distance of 2.891 Å, the Bi−μ_2-I average distance of 3.181 Å and the Bi−μ_3-I average distance of 3.286 Å are comparable in length to bonds of the same type in other iodobismuthate compounds.[16,21] The cis I−Bi−I angles of the $[Bi_3I_{11}]^{2-}$ cluster range from 78.02(3)° to 102.45(3)°, and the trans I−Bi−I angles range from 154.66(3)° to 176.10(3)°. With respect to the trans angles, it should be noted that these angles fall into two distinct sets: the smaller set involving only μ_2-bridging iodide ligands (average = 155.9°) and the larger set involving both a μ_3-bridging and a terminal iodide ligand (average = 173.2°). The smaller set is located on the horizontal mirror plane of the cluster (assuming idealized D_{3h} symmetry), and the significant deviation of these angles from the ideal trans angle is a direct result of the cis face-sharing arrangement of the three BiI_6 octahedra. The average Bi···Bi distance in the cluster is 4.26 Å, and this is comparable to Bi···Bi distances found in the linear, face-sharing $[Bi_3I_{12}]^{3-}$ anions of $[Bi(dmpu)_6][Bi_3I_{12}]$ (dmpu = *N*,*N′*-dimethylpropylene) and $[CH_2{=}C(C_6H_4\text{-}4\text{-}NO_2)CH_2NMe_3]_3[Bi_3I_{12}]$ (3.99−4.25 Å)[39] and much longer than those found in α-Bi (3.07 and 3.53 Å).[15]

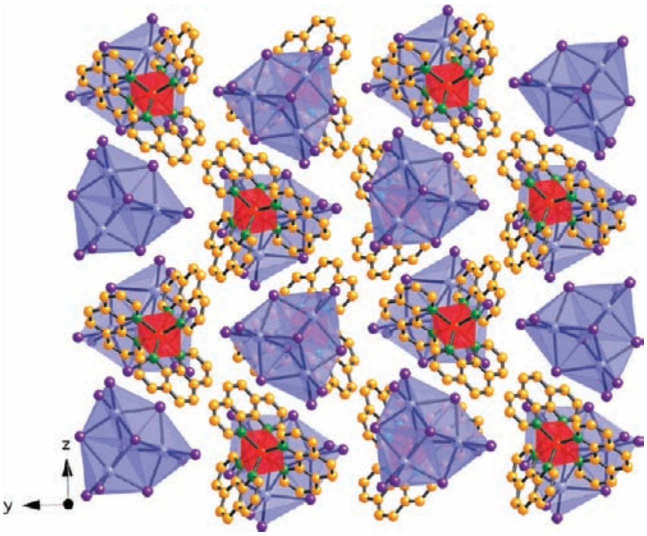

Figure 2. [100] view of the crystal packing in $[M(1,10\text{-phen})_3][Bi_3I_{11}]$ (M = Co (**1**), Fe (**2**), or Zn (**3**)). M, red polyhedra; C, yellow spheres; N, green spheres; Bi, blue polyhedra; I, purple spheres. H atoms not shown.

The crystal packing of $[Co(1,10\text{-phen})_3][Bi_3I_{11}]$, which is representative of the crystal packing in compounds **1**−**3**, is shown in Figure 2. When the compound is viewed along [100], rows consisting of alternating cations and anions are observed. Despite being separated from one another by the cations along [100], the anions are closer than twice the van der Waals radius of *I* (vdW(I) = 1.98 Å),[48] leading to I···I interactions, and consequently weakly bonded anionic chains extending along [010] (3.912 Å in **1**, 3.835 Å in **2**, 3.925 Å in **3**, all at 150(1) K). Figure 3 shows the 1-D anionic chains of $[Co(1,10\text{-phen})_3][Bi_3I_{11}]$ with red lines connecting iodine ligands from different clusters that are closer than twice the van der Waals radius of I. In other iodometalate compounds, I···I interactions are said to extend the dimensionality of the inorganic component of the structure, potentially extending electronic conductivity pathways;[4,9,13,27,28,33] experimental and theoretical investigations have supported this hypothesis.[4,9] Selected interatomic distances and angles for compounds **1**−**3** are listed in Tables S6−S8, respectively.

---

(46) Pohl, S.; Peter, M.; Haase, D.; Saak, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1994**, *49*, 741.

(47) Simon, A. *Coord. Chem. Rev.* **1997**, *163*, 253.

(48) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

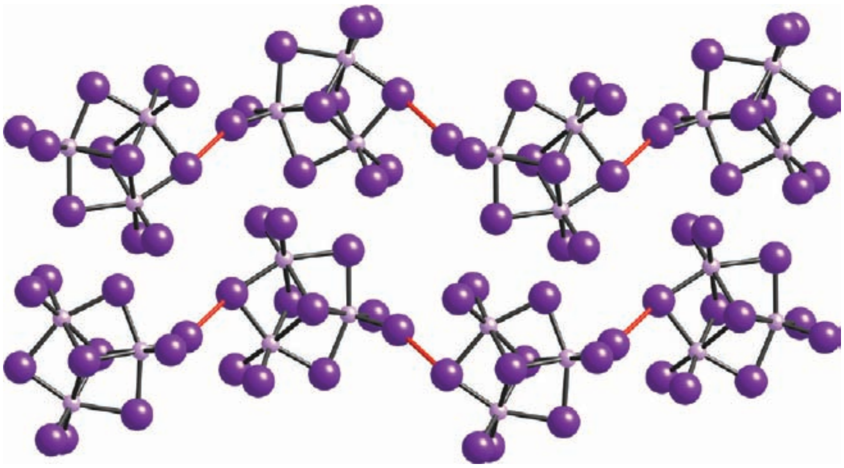

Figure 3. View of two 1-D anionic chains formed by I···I interactions (red lines) between the discrete $[Bi_3I_{11}]^{2-}$ clusters in [M(1,10-phen)]$[Bi_3I_{11}]$ (M = Co (**1**), Fe (**2**), Zn (**3**)). Only the predominant I(10) position is shown. Bi, smaller, pale purple spheres; I, larger, dark purple spheres.

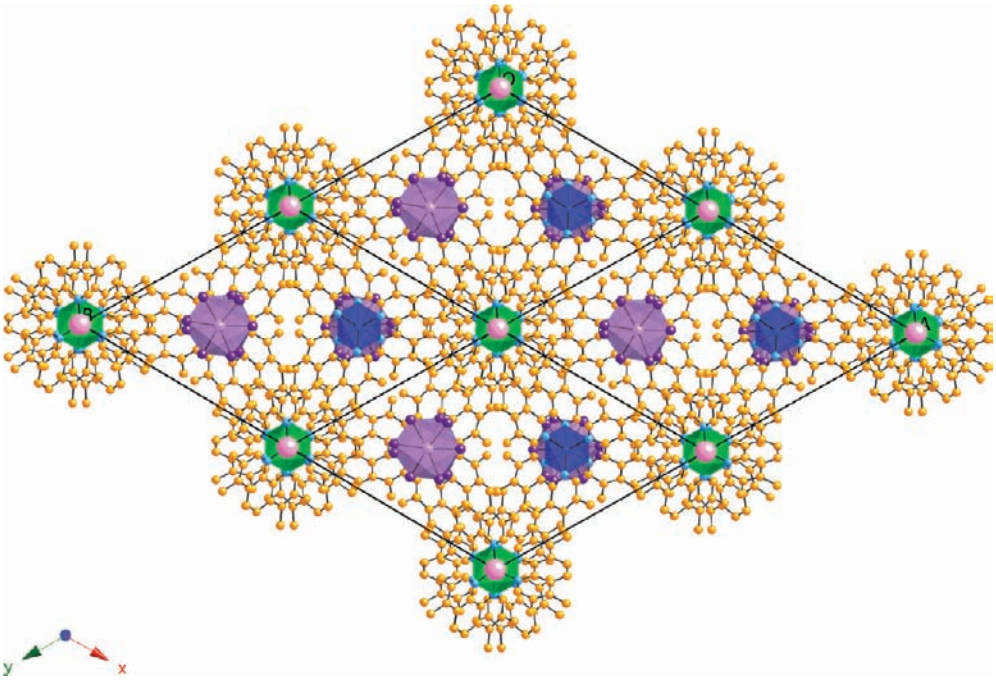

Figure 4. [001] view of the crystal packing in $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (**4**) highlighting the two types of cation/anion columns. Crystallographically different Co centers are differentiated by color. Isolated I^- atoms are differentiated from those part of the iodobismuthate anion by color. Co(1) polyhedra, blue; Co(2) polyhedra, green; isolated I^- atoms, pink; other I atoms, purple; Bi polyhedra, pale purple; N atoms, aqua; C atoms, yellow; H atoms, not shown.

$[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (4). $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ is formed from the reaction of BiI_3, $Co(NO_3)_2 \cdot 6H_2O$, and 3,4,7,8-tetramethyl-1,10-phenanthroline under solvothermal conditions. The compound crystallizes in the trigonal crystal system with the space group $P\bar{3}1c$. The structure exhibits two crystallographically distinct $[Co(TMPhen)_3]^{2+}$ cations (referred to subsequently as Co(1) and Co(2)) in addition to a $[Bi_2I_9]^{3-}$ anion and an I^- anion. Both cations are located on sites of D_3 point symmetry. The tris chelate cations, which can be described as propeller-like, are operated on by the mirror symmetry of the space group resulting in both the Δ and the Λ forms being present in the structure. The $[Bi_2I_9]^{3-}$ anion of the structure, which consists of two BiI_6 octahedra sharing one face, also sits on a site of D_3 crystallographic symmetry, while the I^- anion sits on a site of S_6 symmetry. The $[Bi_2I_9]^{3-}$ anion has been frequently observed in iodobismuthate chemistry,[1,12,16,27,34,49,50] and this species is the only commonly occurring iodobismuthate anion exhibiting face-sharing of BiI_6 octahedra. However, isolated I^- anions are not commonly observed in iodobismuthate chemistry, with the only known examples of this occurring in $[C_6H_5(CH_2)_2NH_3]_4[BiI_6][I] \cdot H_2O$[14] and $[CH_3(CH_2)_3NH_3]_6[BiI_6][I]_2[I_3]$[51] prior to this report of $[Co(TMPhen)_3]_2[Bi_2I_9][I]$. A view of the crystal structure of **4** looking down the crystallographic *c*-axis is shown in Figure 4. Along this direction, the anions

---

(49) Lazarini, F. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 875.

(50) Goforth, A. M.; Hipp, R. E.; Smith, M. D.; Peterson, L., Jr.; zur Loye, H.-C. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *E61*, m1531.

(51) Li, G.-Q.; Xu, G.; Zheng, F.-K.; Guo, G.-C. *Jiegou Huaxue* **2008**, *27* (10), 1275.

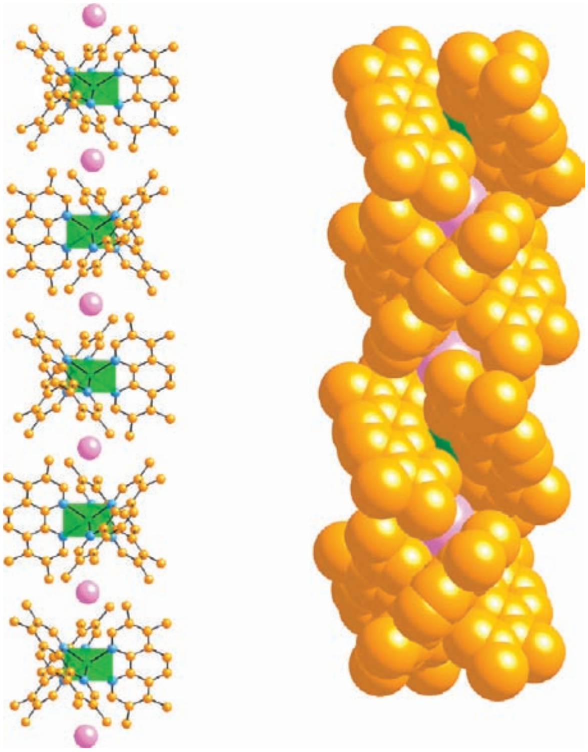

Figure 5. Ball and stick (left) and space-filling (right) views of the Co(2)/I^- chains of $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (**4**). The chains have the repeat sequence Co(2,Δ)···I···Co(2,Λ)···I···Co(2,Δ)···I···Co(2,Λ)···I···. Co(2), green; N, aqua; C, yellow; I, pink. H atoms not shown.

and cations form two kinds of alternating columns. One set of these columns (Figure 5) consists of alternating $[Co(TMPhen)_3]^{2+}$ cations and I^- anions in the sequence Co(2)(Δ)···I···Co(2)(Λ)···I···Co(2)(Δ)···I···Co(2)(Λ)···I···. The second column type (Figure 6) consists of alternating $[Bi_2I_9]^{3-}$ anions and Co(1) cations; however, for this column type, there are two symmetry-related columns distinguished by the handedness (i.e., Δ vs Λ) of the Co cation. These two symmetry-related columns therefore have the repeat sequences Co(1)(Δ)···Bi_2I_9···Co(1)(Δ)···Bi_2I_9··· and Co(1)(Λ)···Bi_2I_9···Co(1)(Λ)···Bi_2I_9···, respectively. The $[Bi_2I_9]^{3-}$ anions and the I^- anions of the structure are physically separated from each other and from themselves by more than 3.96 Å, i.e., more than twice the van der Waals radius of I; consequently, no I···I interactions are observed in $[Co(TMPhen)_3]_2[Bi_2I_9][I]$. Table S9 contains selected interatomic distances and angles for the compound.

[M(2,2′:6,2′′-Terpyridine)$_2$]$_2$[Bi$_2$I$_9$][I] (M = Co (5) or Zn (6)). The isostructural compounds $[M(tpy)_2]_2[Bi_2I_9][I]$ (M = Co (**5**) or Zn (**6**)) crystallize in the monoclinic space group *C*2/*c*. The contents of the asymmetric units are one full $[M(tpy)_2]^{2+}$ cation, half of one $[Bi_2I_9]^{3-}$ anion located on a 2-fold rotation axis, and half of an isolated I^- anion, which is located on a crystallographic inversion center. The isostructural $[M(tpy)_2]_2[Bi_2I_9][I]$ compounds, **5** and **6**, are constitutionally similar to $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (**4**), with the major difference being the presence of a bis-chelate cation involving the tridentate tpy ligand in the former versus the tris-chelate cation involving the bidentate TMPhen ligand in the latter. However, the crystallographic symmetry is very different in the compounds (trigonal $P\bar{3}1c$ in **4** versus monoclinic *C*2/*c* in **5** and **6**), in part due to the absence of cation isomers in **5** and **6**; thus, very different packing arrangements of the constituent species are observed in the compounds. When $[M(tpy)_2]_2[Bi_2I_9][I]$ is viewed along [010], rows of the cations, rows of the $[Bi_2I_9]^{3-}$ anions, and rows of the isolated I^- atoms are observed (Figure 7). No I···I distances in the compounds fall closer than twice the van der Waals radius of I; consequently, no I···I interactions are present in the compounds. Tables S10 and S11 contain selected interatomic distances and angles for compounds **5** and **6**, respectively.

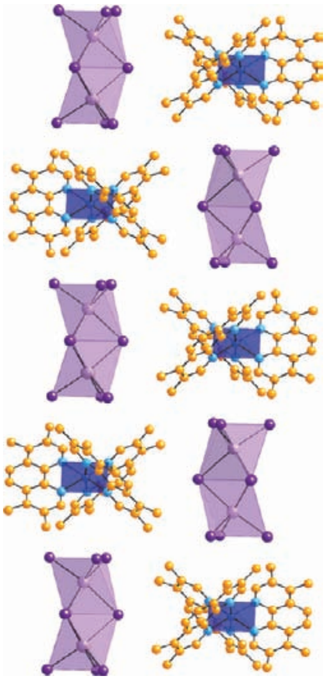

Figure 6. View of the two symmetry-related Co(1)/$[Bi_2I_9]^{3-}$ chains of $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (**4**). One set of chains (left) has the repeat sequence Co(1,Λ)···Bi_2I_9···Co(1,Λ)···Bi_2I_9··· and the other set of chains (right) has the repeat sequence Co(1,Δ)···Bi_2I_9···Co(1,Δ)···Bi_2I_9···. Co(1), blue; N, aqua; C, yellow; Bi, pale purple; I, purple. H atoms not shown.

UV–Visible Spectroscopy. The UV–visible absorption spectra for **1** (blue), **2** (red), and **3** (green) are shown in Figure 8. These spectra were compared to the absorption spectrum of the starting material, BiI_3 (black curve). The onset wavelength of the absorption edge was estimated for each of the three compounds by drawing a best-fit line tangent to the steepest part of the absorbance versus wavelength curve. The energy calculated from this wavelength may be regarded as an estimate of the band gap energy of the compound. The band gap energies so determined were as follows (nm, eV): for **1**, Co (655, 1.9); for **2**, Fe (660, 1.9); for **3**, Zn (640, 1.9). The estimated values of the absorption edges allow classification of these materials as semiconductors, and they are comparable to other reported optical gaps for low-dimensional (i.e., less than two-dimensional) iodobismuthate compounds (∼1.9–2.5 eV),[4,8,9,12–14,51] including several exhibiting I···I interactions that may subtly modulate the optical gap toward lower energies than would be expected for lesser-dimensional, more confined structures by extending the dimensionality of the inorganic component.[4,9] For the starting material BiI_3, the estimated band gap is lower in energy (red-shifted relative to **1**–**3**) at 740 nm, or 1.7 eV, consistent with the higher dimensionality of the two-dimensional semiconducting starting material relative to the zero-dimensional or pseudo-one-dimensional (if I···I interactions are considered) inorganic components of **1**–**3**; the variously reported bandgap for BiI_3 ranges from 1.7–2.2 eV.[52,53]

Thermochromism. In order to investigate the origin of the thermochromic behavior observed in **1**–**6**, crystallographic data

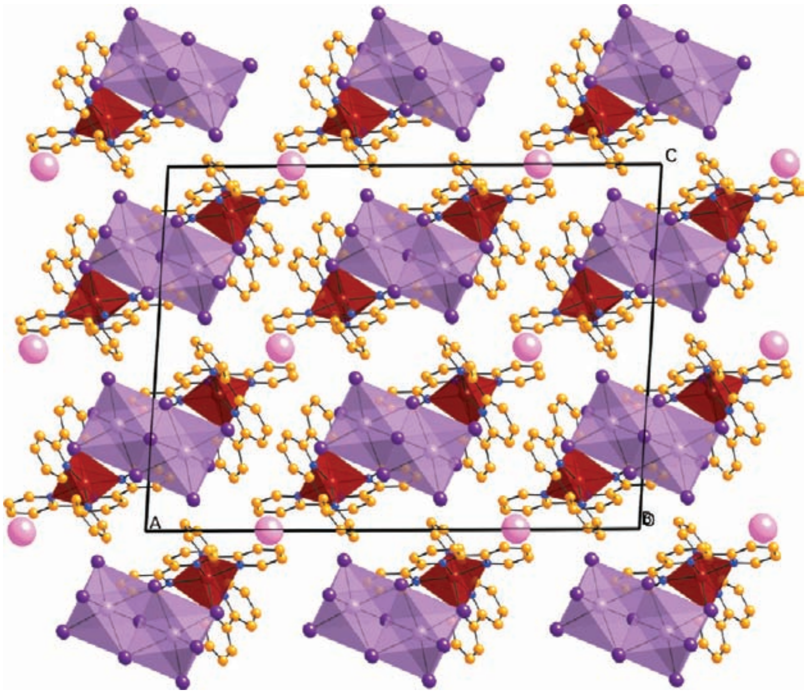

Figure 7. [010] view of the crystal packing in $[Zn(tpy)_2]_2[Bi_2I_9][I]$ (**6**). Isolated I^- atoms are differentiated from those part of the iodobismuthate anion by color. Zn polyhedra, red; isolated I^- atoms, pink; other I atoms, purple; Bi polyhedra, pale purple; N atoms, aqua; C atoms, yellow; H atoms, not shown. $[Co(tpy)_2]_2[Bi_2I_9][I]$ (**5**) is isostructural.

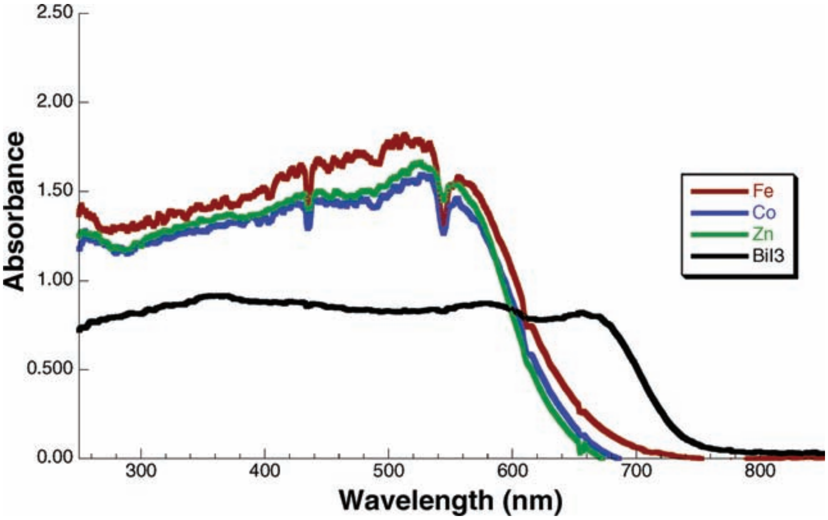

Figure 8. Diffuse reflectance UV−visible absorption spectra for **1** (blue), **2** (red), **3** (green), and BiI_3 (black) taken at room temperature.

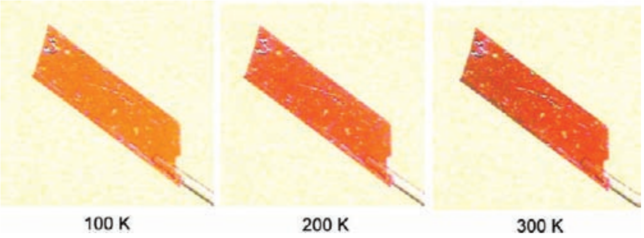
100 K 200 K 300 K

Figure 9. Digital pictures of a mounted single crystal of $[Co(1,10\text{-phen})_3][Bi_3I_{11}]$ (**1**) at different temperatures highlighting the thermochromic behavior of the compound.

were collected on single crystals of **1** at 100(1) K, 150(1) K, 200(1) K, and 294(1) K. Structure transitions or phase changes (generally melting/freezing) are often associated with color changes in other known thermochromic compounds of Bi, including many which are primarily associated with changes in interatomic Bi···Bi distances.[54,55] In contrast, compound **1** (representative of **2**−**6**) does not undergo a phase change upon heating/cooling, and it maintains the same crystal structure at all measured temperatures. The source of the observed, reversible thermochromism is most likely the expansion and contraction of Bi−I, Bi···Bi, and/or I···I interatomic distances within or between the anions, which result in changes in the orbital energy levels associated with the electronic transitions respon-

---

(52) Sobolev, V. V.; Pesterev, E. V.; Sobolev, V. V. *Inorg. Mater.* **2004**, *40*, 878.

(53) Nason, D.; Keller, L. *J. Cryst. Growth* **1995**, *156*, 221.

(54) Ashe, I. A. J. *Adv. Organomet. Chem.* **1990**, *30*, 77.

(55) Spence, R. E. H.; Hsu, D.; Buchwald, S. L. *Organometallics* **1992**, *11*, 3492.

Table 2. Interatomic Distances (Å) at 294 and 100 K and Changes in Interatomic Distances (Å) upon Cooling from 294 to 100 K for Compound **1**[a]

bond description	compound **1**, 294 K	compound **1**, 100 K	change upon cooling[a]
terminal Bi−I			
Bi1 I6	2.9022	2.9059	0.0037
Bi1 I7	2.8845	2.8880	0.0035
Bi2 I8	2.9194	2.9231	0.0037
Bi2 I9	2.8684	2.8769	0.0085
Bi3 I10A	2.8657	2.8702	0.0045
Bi3 I10B	2.9260	2.9200	−0.0060
Bi3 I11	2.8787	2.8829	0.0042
μ_2-bridging Bi−I			
Bi1 I5	3.2249	3.2014	−0.0235
Bi1 I3	3.1478	3.1416	−0.0062
Bi2 I3	3.1959	3.1603	−0.0356
Bi2 I4	3.1665	3.1635	−0.0030
Bi3 I4	3.3040	3.2482	−0.0558
Bi3 I5	3.1264	3.1241	−0.0023
μ_3-bridging Bi−I			
Bi1 I1	3.2280	3.2071	−0.0209
Bi1 I2	3.3291	3.3157	−0.0134
Bi2 I1	3.3018	3.2890	−0.0128
Bi2 I2	3.3192	3.3135	−0.0057
Bi3 I1	3.2592	3.2446	−0.0146
Bi3 I2	3.3412	3.3198	−0.0214
Bi···Bi			
Bi1 Bi2	4.4236	4.2101	−0.2135
Bi1 Bi3	4.2565	4.2157	−0.0408
Bi2 Bi3	4.3653	4.3146	−0.0507
I···I			
I5 I9	3.923	3.903	0.020

[a] (+) denotes an expansion in the interatomic distance upon cooling, and (−) denotes a contraction in the interatomic distance upon cooling.

sible for the observed color. Related polynuclear Cu(I)-halide cluster-based materials (Cu(I) = d^{10}; Bi(III) = $d^{10}s^2$) have been reported to exhibit luminescence thermochromism as a result of changing population of different luminactive excited states (e.g., cluster centered, LMCT-, MLCT- or XLCT-related, X = halide) with changing temperature, which is generally associated with changes in intracluster distances, and sometimes angles, but not wholesale changes in crystal structure.[56−58] While compound **1** does not photoluminesce in the solid state, changes in the bismuth−iodide, bismuth···bismuth, and iodide···iodide distances upon heating/cooling are likely sufficient to cause subtle changes in orbital energies associated with the electronic transitions that contribute to the visible crystal color, thus leading to subtle changes in color with changing temperature. Table 2 reports the changes in the bond lengths upon cooling compound **1** from 294 to 100 K. Changes in most of the bond distances are significantly greater than the associated measurement error (greater than 3× the esd), and most interatomic distances (Bi−I, Bi···Bi, and I···I), including the intra-anion I···I interactions, decrease upon cooling. It is noteworthy that all six of the title compounds and the starting material BiI_3 are thermochromic (BiI_3 changes from black to red upon cooling from room temperature to 77 K) and that only compounds **1**−**3** exhibit I···I contacts less than 4 Å; thus, changes in Bi−I or Bi···Bi distances are more likely to be major contributors to the observed thermochromism. It is possible that future electronic structure calculations may help explain these experimental observations; however, the most extreme change in **1** is an approximately 0.2 Å contraction in a single Bi···Bi distance upon cooling, and three of the four largest contractions are in the Bi···Bi distances. Next to the largest changes, which are in the three Bi···Bi interatomic distances and in a single μ_2-bridging Bi−I bond, the change in the lone I···I interaction is most significant and is a 0.02 Å contraction upon cooling. All bridging Bi−I bonds decreased in length upon cooling while the terminal Bi−I bonds generally increased in length upon cooling; the largest change in the Bi−I bonds was an approximately 0.06 Å contraction upon cooling while the smallest changes in the Bi−I bonds were approximately 0.002−0.003 Å contractions (in the bridging Bi−I bonds) or expansions (in the terminal Bi−I bonds) upon cooling. Of the Bi−I bonding distances, the bridging Bi−I bonds are responsible for the most significant bond changes (avg. bridging (μ_2-, μ_3-) Bi−I (294 K) = 3.1943 Å, 3.2964 Å; avg bridging (μ_2-, μ_3-) Bi−I (100 K) = 3.1732 Å, 3.2816 Å) while the changes in terminal Bi−I bond lengths are smaller in magnitude (avg terminal Bi−I (294K) = 2.8921 Å, avg terminal Bi−I (100 K) = 2.8953 Å).

Conclusions

Six new, mixed-metal iodobismuthate materials were synthesized from 3:3:1 molar ratios of BiI_3:organic ligand:metal nitrate, and these new materials are rare examples of bimetallic halobismuthate materials. The crystal structures of $[Co(1,10\text{-}phen)_3][Bi_3I_{11}]$ (**1**), $[Fe(1,10\text{-}phen)_3][Bi_3I_{11}]$ (**2**), and $[Zn(1,10\text{-}phen)_3][Bi_3I_{11}]$ (**3**), which were synthesized from their respective metal nitrates under the exact same reaction conditions, are isostructural and contain the $[Bi_3I_{11}]^{2-}$ anion, which is a novel example of a rare, face-sharing iodobismuthate anion. Changing the organic ligand of the reaction to TMPhen and varying the reaction conditions slightly resulted in the synthesis of $[Co(TMPhen)_3]_2[Bi_2I_9][I]$ (**4**), which has a different iodobismuthate anion than the compounds synthesized using 1,10-phen. Using tpy as the organic ligand under conditions very similar to those used in the synthesis of the $[M(1,10\text{-}phen)_3][Bi_3I_{11}]$ compounds, $[Co(tpy)_2]_2[Bi_2I_9][I]$ (**5**) and $[Zn(tpy)_2]_2[Bi_2I_9][I]$ (**6**) were the resulting compounds. Compounds **4**−**6**, all of which contain isolated I^- anions, are constitutionally similar though they are based on different organic ligands. Because the reaction conditions were changed little other than the identity of the cation precursors, it may be concluded from this study that the nature of the cation heavily impacts the identity of the inorganic iodobismuthate anion, although other reaction conditions also likely contribute. However, it is reasonable to expect that by choosing other unique cations as charge balancing reagents, additional novel iodobismuthate anions may be observed in the future. Due to the structural diversity in terms of the dimensionality and size of the iodobismuthate anion, this family of materials may someday contribute to our further understanding of size-dependent or other unusual optical properties. Furthermore, the six compounds exhibit thermochromism, as does the starting material BiI_3, and variable temperature crystallographic analysis supports that these changes result from changing interatomic distances within the anions rather than from marked structural transitions or phase changes.

Acknowledgment. Financial support was provided by the National Science Foundation through Grant Numbers CHE-0714555 and CHE-0714439. M.A.T. acknowledges support from a University

---

(56) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625.
(57) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220.
(58) Ford, P. C. *Coord. Chem. Rev.* **1994**, *132*, 129.

of South Carolina Magellan Scholarship. Andrea M. Goforth acknowledges a Career Award at the Scientific Interface from the Burroughs Wellcome Fund (Award 1007294) for support.

Supporting Information Available: Tables of data collection parameters and refinement statistics for compounds **1−6**, tables of selected interatomic distances and angles for compounds **1−6**, calculated and experimental powder X-ray diffraction patterns for compound **1**, CIFs for compounds **1−6** (including CIFs for variable temperature analysis of compound **1**). This material is available free of charge via the Internet at http://pubs.acs.org.

JA108278J