Inorg. Chem. **1996,** *35,* 3709−3712

Tetrahydrofuran Adducts of Bismuth Trichloride and Bismuth Tribromide

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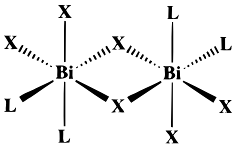
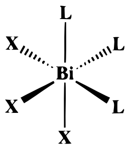
Received December 22, 1995

Bismuth trihalides, BiX_3, are known to form a range of adducts or coordination complexes with neutral two-electron-donor ligands (L) in which up to three ligands may be coordinated to the bismuth center. In fact, compounds are known with the empirical formulas $[BiX_3(L)]$, $[BiX_3(L)_{1.5}]$, $[BiX_3(L)_2]$, and $[BiX_3(L)_3]$ (X = halide), some examples of which are described in refs 1 and 2 and references therein. With particular regard to the last two general types for monodentate L, compounds of the form $[BiX_3(L)_2]$ generally adopt dimeric edge-shared, bioctahedral structures of type **A**, for example $[Bi_2I_6(OPPh_3)_4]$,[3] $[Bi_2Br_6(PMe_2Ph)_2(OPMe_2Ph)_2]$,[4] $[Bi_2Cl_6(L)_4]$ (L = 1-allyl-3-(2-pyridyl)thiourea-*S*,[5] *N*,*N*′-diethylimidazolidine-2-thione-*S*[6]), and $[Bi_2Br_6(PMe_3)_4]$,[2] or a polymeric structure of type **B** as found in the compound $[\{BiCl_3(L)_2\}_x]$ (L = imidazolidine-2-thione-*S*),[7] while compounds of the general formula $[BiX_3(L)_3]$ are found with both *fac* ($[BiCl_3(thiourea)_3]$[8] and $[BiCl_3(dmso)_3]$[9]) and *mer* ($[BiCl_3(L)_3]$; L = 1-phenyl-3-(2-pyridyl)thiourea-*S*,[6] imidazolidine-2-thione-*S*[10]) geometries, as shown in **C** and **D**, respectively.



A



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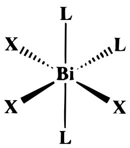

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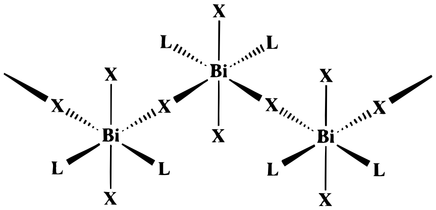

B

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Bi(1)−O(1)	2.635(7)	Bi(1)−O(3)	2.600(8)
Bi(1)−Br(1)	2.628(5)	Bi(1)−Br(1′)	2.685(10)
Bi(1)−Br(2)	2.6834(13)	Bi(1)−Br(3)	2.6623(11)
Bi(1)−O(2)	2.700(7)		
O(3)−Bi(1)−Br(1)	96.0(7)	O(3)−Bi(1)−O(1)	90.6(3)
Br(1)−Bi(1)−O(1)	84.5(2)	O(3)−Bi(1)−Br(3)	85.4(2)
Br(1)−Bi(1)−Br(3)	92.0(2)	O(1)−Bi(1)−Br(3)	174.4(2)
O(3)−Bi(1)−Br(2)	171.3(2)	Br(1)−Bi(1)−Br(2)	92.6(6)
O(1)−Bi(1)−Br(2)	89.1(2)	Br(3)−Bi(1)−Br(2)	95.46(5)
O(3)−Bi(1)−Br(1′)	83.2(8)	O(1)−Bi(1)−Br(1′)	82.2(3)
Br(3)−Bi(1)−Br(1′)	93.5(2)	Br(2)−Bi(1)−Br(1′)	105.4(8)
O(3)−Bi(1)−O(2)	81.6(3)	Br(1)−Bi(1)−O(2)	176.3(5)
O(1)−Bi(1)−O(2)	92.6(2)	Br(3)−Bi(1)−O(2)	90.7(2)
Br(2)−Bi(1)−O(2)	89.7(2)	Br(1′)−Bi(1)−O(2)	163.9(8)

[a] Primed atoms relate to the smaller component of the disorder.

THF (tetrahydrofuran) is a common solvent for reactions involving bismuth trihalides, and herein, we describe the solid-state structures of THF adducts of $BiBr_3$ and $BiCl_3$. Comparisons are made with other analogous bismuth trihalide structures and also with some related structural work on lanthanide trihalide-THF adducts.

Results and Discussion

Crystallization of $BiBr_3$ from THF solution by solvent diffusion from a hexanes overlayer afforded pale yellow crystals of the THF adduct $[BiBr_3(THF)_3]$ (**1**), the structure of which was established by X-ray crystallography; selected bond lengths and angles are given in Table 1. Compound **1** is monomeric in the solid state (Figure 1) and comprises an octahedrally coordinated bismuth atom with the bromine atoms and THF ligands adopting *fac* configurations. The Bi−Br bond distances are all similar, spanning the range 2.628(5)−2.683(1) Å (average Bi−Br 2.658 Å),[11] whereas the Bi−O lengths are somewhat more disparate, ranging from 2.600(8) to 2.700(7) Å (average 2.645 Å). One trend is clear, however, in that the shorter Bi−O distances are *trans* to the longer Bi−Br distances (Table 1).[11] This is an expected observation consistent with the view that the acceptor orbitals of the $BiBr_3$ molecule, which are involved in binding the THF ligands, are Bi−Br σ^* orbitals.[12] Two other examples of bismuth compounds with THF ligands bound *trans* to bromine are also known, *viz.* $[\{BiBr_2Ph(THF)\}_x]$ (Bi−Br = 2.684(1), Bi−O = 2.671(8) Å) and $[BiBrPh_2(THF)]$ (Bi−Br = 2.741(1), Bi−O = 2.589(7) Å).[12] All interbond angles in **1** are close to either 90° or 180°, indicating that the bismuth lone pair has little stereochemical influence, although the average Br−Bi−Br angle (93.4°) is slightly larger than the average O−Bi−O angle (88.3°).[11] A similar situation is seen in the

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(11) In the structure of **1**, the position of Br(1) is disordered, the minor component (labelled Br(1′)) of about one-third occupancy having a Bi−Br distance of 2.685(10) Å. In considering the trend between the observed Bi−Br and Bi−O distances, it is the distance to the major component which has been used. Also, when considering the stereochemical influence of the Bi(III) lone pair, it is the major component to which the discussion refers; in the minor component, the lone pair may be slightly more stereochemically active.

(12) Clegg, W.; Errington, R. J.; Fisher, G. A.; Hockless, D. C. R.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Chem. Soc., Dalton Trans.* **1992**, 1967.

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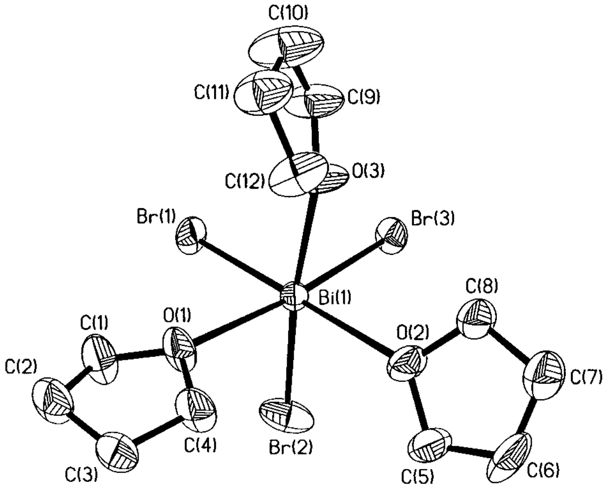

Figure 1. View of the molecular structure of **1** showing the atom-numbering scheme. Ellipsoids are drawn at the 40% level. Hydrogen atoms and minor disorder components are not shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**[a]

Bi(1)−Cl(3)	2.505(3)	Bi(1)−Cl(1)	2.533(2)
Bi(1)−O(1)	2.561(4)	Bi(1)−O(2)	2.619(11)
Bi(1)−Cl(2)	2.634(2)	Bi(1)−Cl(1A)	3.132(2)
Bi(1)−Cl(2A)	3.372(2)	Bi(1′)−Cl(3′)	2.501(3)
Bi(1′)−O(1)	2.551(4)	Bi(1′)−Cl(2A)	2.556(2)
Bi(1′)−O(2′)	2.622(12)	Bi(1′)−Cl(1A)	2.634(2)
Bi(1′)−Cl(2)	3.160(2)	Bi(1′)−Cl(1)	3.338(2)
Cl(1)−Bi(1′B)	2.634(2)	Cl(1)−Bi(1B)	3.132(2)
Cl(2)−Bi(1′B)	2.556(2)	Cl(2)−Bi(1B)	3.372(2)
Cl(3)−Bi(1)−Cl(1)	92.65(9)	Cl(3)−Bi(1)−O(1)	83.12(12)
Cl(1)−Bi(1)−O(1)	78.20(9)	Cl(3)−Bi(1)−O(2)	171.8(3)
Cl(1)−Bi(1)−O(2)	81.2(3)	O(1)−Bi(1)−O(2)	90.2(3)
Cl(3)−Bi(1)−Cl(2)	92.22(9)	Cl(1)−Bi(1)−Cl(2)	81.78(5)
O(1)−Bi(1)−Cl(2)	159.18(9)	O(2)−Bi(1)−Cl(2)	92.4(3)
Cl(3)−Bi(1)−Cl(1A)	93.59(9)	Cl(1)−Bi(1)−Cl(1A)	154.27(4)
O(1)−Bi(1)−Cl(1A)	127.35(9)	O(2)−Bi(1)−Cl(1A)	94.3(3)
Cl(2)−Bi(1)−Cl(1A)	73.05(5)	Cl(3)−Bi(1)−Cl(2A)	94.78(8)
Cl(1)−Bi(1)−Cl(2A)	141.55(5)	O(1)−Bi(1)−Cl(2A)	65.39(8)
O(2)−Bi(1)−Cl(2A)	86.7(2)	Cl(2)−Bi(1)−Cl(2A)	135.38(4)
Cl(1A)−Bi(1)−Cl(2A)	62.56(4)	Cl(3′)−Bi(1′)−O(1)	83.59(13)
Cl(3′)−Bi(1′)−Cl(2A)	93.04(10)	O(1)−Bi(1′)−Cl(2A)	79.83(9)
Cl(3′)−Bi(1′)−O(2′)	174.1(3)	O(1)−Bi(1′)−O(2′)	92.0(3)
Cl(2A)−Bi(1′)−O(2′)	82.2(3)	Cl(3′)−Bi(1′)−Cl(1A)	91.99(10)
O(1)−Bi(1′)−Cl(1A)	160.39(9)	Cl(2A)−Bi(1′)−Cl(1A)	81.35(5)
O(2′)−Bi(1′)−Cl(1A)	90.8(3)	Cl(3′)−Bi(1′)−Cl(2)	93.44(10)
O(1)−Bi(1′)−Cl(2)	126.63(9)	Cl(2A)−Bi(1′)−Cl(2)	153.32(4)
O(2′)−Bi(1′)−Cl(2)	92.4(3)	Cl(1A)−Bi(1′)−Cl(2)	72.58(5)
Cl(3′)−Bi(1′)−Cl(1)	94.86(10)	O(1)−Bi(1′)−Cl(1)	64.52(8)
Cl(2A)−Bi(1′)−Cl(1)	142.24(5)	O(2′)−Bi(1′)−Cl(1)	86.8(3)
Cl(1A)−Bi(1′)−Cl(1)	135.03(4)	Cl(2)−Bi(1′)−Cl(1)	62.69(4)
Bi(1)−Cl(1)−Bi(1B)	112.56(5)	Bi(1′B)−Cl(1)−Bi(1′)	104.39(5)
Bi(1′B)−Cl(2)−Bi(1′)	111.56(5)	Bi(1)−Cl(2)−Bi(1B)	103.05(5)

[a] Symmetry operators: (A) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (B) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$. Primed atoms relate to the smaller component of the disorder.

related *fac* complex $[BiCl_3(dmso)_3]$ (average Cl−Bi−Cl = 95.1°; average O−Bi−O = 85.0°).[9]

Crystallization of $BiCl_3$ from THF/hexanes mixtures afforded colorless crystals of the THF adduct $[BiCl_3(THF)_2]$ (**2**), the structure of which was also established by X-ray crystallography; selected bond lengths and angles are given in Table 2. Unlike **1**, compound **2** has only two molecules of THF coordinated to each bismuth atom, but the structure (Figure 2) is different from the structures represented by **A** and **B**, which have been observed previously for compounds of this stoichiometry. The structure of **2** is polymeric, comprising monomer $BiCl_3(THF)_2$ units in which the coordination geometry around the bismuth center is approximately square-based pyramidal with two *cis* THF ligands and two *cis* chlorines occupying the basal plane and the remaining chlorine in the apical site. These monomer units are then linked together by very asymmetric chlorine bridges such that the apical chlorine and one basal chlorine from one monomer unit form long secondary bonds *trans* to the apical Bi−Cl bond of an adjacent unit, resulting in an overall coordination geometry around each bismuth center that may now be described as pentagonal bipyramidal with one chlorine and one THF ligand in the axial sites and one THF and four chlorines in the equatorial positions, two of the latter with short Bi−Cl bonds and the other two with long Bi−Cl bonds.

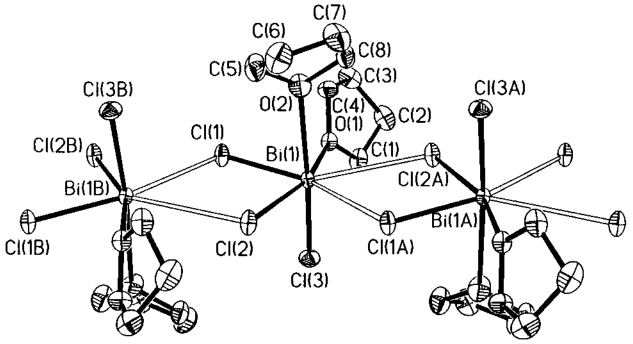

Figure 2. View of three molecular units in the structure of **2** showing the atom-numbering scheme. Ellipsoids are drawn at the 40% level. Hydrogen atoms and minor disorder components are not shown. Symmetry operators: (A) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (B) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

Any detailed discussion of bond lengths and angles is rendered cumbersome, however, in view of the fact that the structure of **2** is disordered. The nature of the disorder places the axial BiCl(THF) (Bi, O(2), Cl(3), and C(5)−C(8)) unit in two alternative positions, one as shown in Figure 2, with primary bonds in the equatorial plane to Cl(1) and Cl(2) and secondary bonds to Cl(1A) and Cl(2A), and the other with primary bonds to Cl(1A) and Cl(2A) and secondary bonds to Cl(1) and Cl(2). This hardly affects the external "surface" of the chain, since one THF is in common and the other has two interpenetrating orientations. Presumably within each chain there is a consistent ordering, but the overall crystal structure with two symmetry-equivalent chains running through each unit cell shows disorder with random distribution of chain direction. Two points worth mentioning, however, are that, as in **1**, the shorter Bi−O distances are associated with the longer *trans* Bi−Cl distances and also that within the equatorial plane the two longer Bi−Cl distances are approximately *trans* to one of the two shorter Bi−Cl bonds, which is probably a reflection of the stereochemical influence of the bismuth lone pair.

An interesting structure for comparison with **2** is a THF adduct of yttrium trichloride, $[YCl_3(THF)_2]$ (**3**), recently described by Sobota *et al.*[13] The structure of **3** is very similar to that of **2** (although not isomorphous), being also polymeric with each yttrium center residing in a seven-coordinate, pentagonal-bipyramidal environment with one chlorine and one THF ligand in the axial sites and the equatorial positions occupied by the remaining THF and four chlorines. The major point of difference, however, is that in **3** the equatorial Y−Cl distances are all much more similar as a result of the chlorine bridges being more symmetric, which is clearly a consequence of the absence of a lone pair of electrons in the yttrium compound.

When BiI_3 was crystallized from THF/hexanes mixtures, well-formed orange crystals were obtained; these were extremely sensitive to loss of THF, immediately turning black on removal

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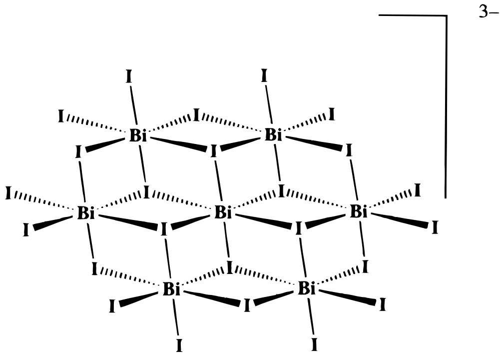
(13) Sobota, P.; Utko, J.; Szafert, S. *Inorg. Chem.* **1994**, *33*, 5203.

from the solvent, and it was not possible to obtain any structural data. A very small number of darker orange crystals, which did not readily lose solvent, did remain, however. These were examined by X-ray crystallography and found to contain the iodobismuthate anion $[Bi_7I_{24}]^{3-}$ with the structure



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The nature of the cation is apparently $[Na_3(THF)_x]^{3+}$, giving an overall formula for the compound $[Na_3(THF)_x][Bi_7I_{24}]$ (**4**). Since we cannot fully characterize the cation, due to the effects of disorder and some uncertainty regarding the space group, the structure will not be discussed further here; the sodium presumably arises from the presence of some sodium iodide in the sample of BiI_3. The anion in **4** is worth reporting, however, since it is an example of a new type of iodobismuthate anion structure.[14]

The black material formed by solvent loss from the orange crystals obtained from BiI_3 in THF was found to be unsolvated BiI_3 by X-ray powder diffraction. The powder diffraction data were of sufficient quality for the structure to be solved, and the results are briefly described here, as the precision and accuracy of the resulting structure determination are significantly better than for the previously published structure of BiI_3, derived also from X-ray powder data (there has apparently been no single-crystal structure reported for BiI_3).[15] The structure of BiI_3 is derived from a hexagonal close-packed arrangement of iodines with the bismuth atoms symmetrically residing in the octahedral interstices such that every other intermediate plane is two-thirds occupied.[16] The two unique Bi−I distances (3.122(7) and 3.109(7) Å) are essentially identical (cf. a value of 3.1 Å reported for both distances in ref 15); bond angles are all close to 90 or 180° and are given in the Experimental Section. The X-ray powder diffraction pattern is shown in Figure 3.

Experimental Section

Synthesis. Both compounds **1** and **2** were obtained in near-quantitative yields as follows. Either $BiBr_3$ or $BiCl_3$ was dissloved in the minimum of freshly distilled, dry, oxygen-free THF (any insoluble material, which is most likely the oxyhalide BiOBr or BiOCl, could be removed at this stage by filtration). About 4−5 times the volume of freshly distilled, dry, oxygen-free hexanes was then layered over the resulting THF solution, and solvent diffusion over a period of days at −30 °C afforded clear crystals of **1** (pale yellow) and **2** (colorless) one each from which were used for the X-ray diffraction studies. After removal of the solvent, and especially after pumping under vacuum, THF is readily lost from the crystals, which then become opaque. Satisfactory elemental analytical data could not therefore be obtained, and so the composition of the bulk sample could not be confirmed by this means. Nevertheless, crystalline **1** and **2** appear homogeneous and the crystals chosen for X-ray diffraction were representative of the sample as a whole in each case.

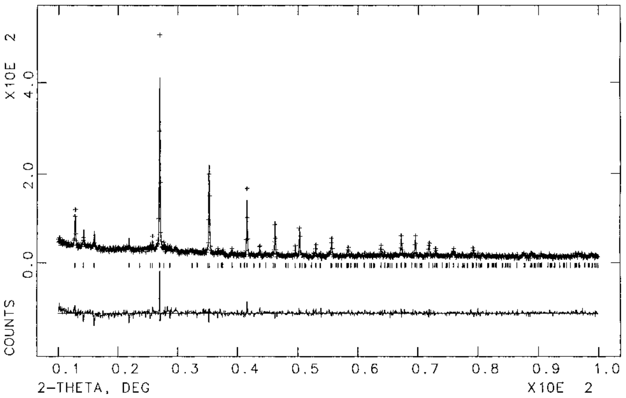

Figure 3. Rietveld profile for BiI_3 showing the fit between observed and calculated data.

Table 3. Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{12}H_{24}BiBr_3O_3$	$C_8H_{16}BiCl_3O_2$
fw	665.0	459.5
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	8.6078(11)	8.018(2)
b, Å	14.459(2)	9.038(2)
c, Å	15.936(2)	18.701(3)
β, deg	104.096(2)	98.70(3)
V, Å^3	1923.7(4)	1339.5(5)
Z	4	4
T, K	160	160
λ, Å	0.710 73	0.710 73
ρ_{obsd}, g cm^{-3}	2.296	2.279
μ, cm^{-1}	154.0	137.4
$R(F_o)^a$	0.0406	0.0390
$R_w(F_o^2)^b$	0.1069	0.1201

^{a} Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$ for "observed" reflections having $F_o^2 > 2\sigma(F_o^2)$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ for all data.

X-ray Crystallography. Crystal data and other information on the structure determinations for **1** and **2** are given in Table 3. Both compounds were investigated at 160 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). For **1**, measurements were made on a Siemens SMART CCD area detector diffractometer; cell parameters were refined from the setting angles of 5301 reflections selected from the complete data set, and intensities were measured from more than a hemisphere of data collected on frames each covering 0.3° oscillation in ω. For **2**, measurements were made on a Stoe-Siemens four-circle diffractometer; cell parameters were refined from 2θ values (20−25°) of 39 selected strong reflections measured at $\pm\omega$ to minimize systematic errors, and intensities were measured from ω/θ scans with an on-line profile-fitting procedure.[17] For both data sets, semiempirical absorption corrections were applied,[18] with an ellipsoidal crystal shape model, and based on the high degree of data redundancy for **1** and on sets of selected equivalent reflections measured at various azimuthal angles for **2**.

The structures were solved by direct (**1**) and heavy-atom (**2**) methods and were refined by full-matrix least-squares on F^2 values for all independent data, with the weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = (2F_c^2 + F_o^2)/3$. An isotropic extinction coefficient x was refined, whereby F_c is multiplied by $(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{-1/4}$. Anisotropic displacement parameters were refined for non-H atoms, and H atoms were constrained with a riding model such that C−H = 0.99 Å, H−C−H = 109.5°, and U(H) = $1.2U_{eq}$(C).

Both structures display some disorder. In **1**, two alternative sites were resolved for Br(1), with occupancy factors 0.63:0.37(6), about

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[14] Fisher, G. A.; Norman, N. C. *Adv. Inorg. Chem.* **1994**, *41*, 233.

[15] Trotter, J.; Zobel, T. *Z. Kristallogr.* **1966**, *123*, 67.

[16] Müller, U. *Inorganic Structural Chemistry*; Wiley: Chichester, U.K., 1992.

[17] Clegg, W. *Acta Crystallogr., Sect. A* **1981**, *37*, 22.

[18] Sheldrick, G. M. *SHELXTL User Manual*; Siemens Analytical X-ray Instruments: Madision, WI, 1994.

0.6 Å apart, and were freely refined; these are labeled Br(1) and Br(1′), respectively. In **2**, two alternative sites were resolved for the axial BiCl(THF) unit (labeled Bi, Cl(3), O(2), and C(5)−C(8) and Bi′, Cl(3′), O(2′), and C(5′)−C(8′)) with occupancy factors 0.546:0.454(2), the remaining THF and two chlorides (involved in bridging) being ordered; refinement of the disorder was assisted by restraints for the THF ligands (similarity of geometry and approximately equal components of anisotropic displacement of atoms along bonds), while the heavier atoms were freely refined.

Programs were standard Siemens (SMART and SAINT) and Stoe (DIF4) control and integration software, Siemens SHELXTL,[18] and local programs. Complete tables of atomic coordinates, geometry, and displacement parameters are available as Supporting Information.

Crystal data for BiI_3: rhombohedral, space group $R\bar{3}$, $a = 7.5117(3)$ Å, $c = 20.700(1)$ Å, $Z = 6$. The structure was refined from X-ray powder diffraction data collected on a Stoe STADI/P transmission system; $\lambda = 1.540\,56$ Å (Cu $K\alpha$). A sample was well ground and loaded into a 0.2 mm diameter Lindemann tube. Data were collected over the range $10° < 2\theta < 102°$ in 0.02° steps, the entire run lasting about 15 h. The starting model for Rietveld refinement was taken from that proposed by Trotter and Zobel.[15] Refinement converged smoothly to agreement factors $R_{wp} = 13.7\%$ and $R_p = 10.7\%$ for 19 variables and 4600 data points (256 reflections) over the range $10° < 2\theta < 102°$. All calculations were carried out using the GSAS program suite.[19]

Refined atomic coordinates for BiI_3 are as follows:

	x	y	z	U(iso), Å^2
Bi	0.0	0.0	0.1675(4)	0.044(3)
I	0.3326(11)	0.3438(11)	0.0799(3)	0.009(1)

Bond lengths: Bi−I, 3.122(7), 3.109(7) Å. Bond angles: I−Bi−I, 177.4(2), 88.1(2), 89.7(3), 91.8(2), 90.5(3)°; Bi−I−Bi, 88.2(2)°.

Acknowledgment. We thank the EPSRC for support and for studentships (C.J.C., J.H., and A.J.S.).

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, bond distances and angles, and data collection and refinement parameters for **1** and **2** (10 pages). Ordering information is given on any current masthead page.

IC951635F

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(19) Larson, A. C.; Von Dreele, R. B. Los Alamos National Laboratory Report No. LA-UR-86-748; Los Alamos National Laboratory, Los Alamos, NM 1987.