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$CuBi_7I_{19}(C_4H_8O_3H)_3(C_4H_8O_3H_2)$, a Novel Complex Bismuth Iodide Containing One-Dimensional $[CuBi_5I_{19}]^{3-}$ Chains

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Introduction

Metal iodides based on components like SnI_2, PbI_2, AuI, or HgI_2 often show interesting electrical or optical properties.[1−6] Here, especially low-dimensional structures can be very interesting. As part of studies of compounds showing such properties, we have investigated the pseudobinary systems $MX-BiI_3$ (M = Cu, Ag, Au). In fact, in view of ternary compounds in these systems little is known. Until now the existence of such phases is deduced from two types of experiments: differential thermal analysis leading to phase diagrams; and X-ray diffraction of powder samples only resulting in cell parameters.[7−9] A characterization of compounds based on complete crystal structures is, with the exception of $CuBiI_4$,[10] missing. Moreover, until now all investigations were carried out at temperatures of 400−600 °C. Under these conditions formation of thermodynamically stable known phases often cannot be prevented. However, in view of novel metastable compounds, significantly lower reaction temperatures are desirable.[11,12]

We report on the reaction of CuI and BiI_3 in diethylene glycol at 140 °C. Under these conditions the novel complex bismuth iodide $CuBi_7I_{19}(C_4H_8O_3H)_3(C_4H_8O_3H_2)$, containing one-dimensional $[CuBi_5I_{19}]^{3-}$ chains, is formed. The preparation and the crystal structure of the compound are described.

Experimental Section

Synthesis. $CuBi_7I_{19}(C_4H_8O_3H)_3(C_4H_8O_3H_2)$ was prepared by mixing 300 mg of BiI_3 (508 mmol) (99.999%, Aldrich) and 15 mg of CuI (73 mmol) (99.999%, Aldrich). This mixture was filled in a quartz tube. A total of 10 mL diethylene glycol (99%, Merck) was added. The quartz tube was thrice evacuated to the vapor pressure of diethylene glycol and flushed with argon. Afterward the quartz tube was heated under argon for 7 days at 140 °C. Brownish-red, air-stable, transparent crystals were produced. The crystals were washed with ethanol to remove diethylene glycol and dried at room temperature in air. A 0.07 × 0.05 × 0.03 mm³ crystal was separated, fixed in a glass capillary, and used to collect the data set. Semiquantitative elemental analyses were performed with the use of an energy-dispersive X-ray (EDX) spectrometry equipped Philips SEM 525R scanning electron microscope; for $CuBi_7I_{19}(C_4H_8O_3H)_3(C_4H_8O_3H_2)$ the Cu/Bi/I ratio was determined to be 0.9/7.1/19.2.

Table 1. Crystal Data and Structure Refinement

chemical formula	$[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)][CuBi_5I_{19}]$
fw	4358.6
space group	$P12_1/n1$
a, Å	16.138(1)
b, Å	18.660(1)
c, Å	26.810(1)
β, deg	95.69(1)
V, Å³	8034(2)
Z	4
temp, °C	22(2)
radiation λ, Å	0.71073
ρ(calcd), g cm^{-3}	3.57
μ(Mo Kα), cm^{-1}	229
R1[a]	0.054
wR2[b]	0.156

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. Denotes value of the residual considering only the reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(F_o^2,0) + 2(F_c^2)]/3$. Denotes value of the residual considering all the reflections.

Table 2. Selected Bi−I Distances (Å) for $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)][CuBi_5I_{19}]$ and $[Li(thf)_4]_4[Bi_5I_{19}]$[15]

	$[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)][CuBi_5I_{19}]$	$[Li(thf)_4]_4[Bi_5I_{19}]$
μ_1-I−Bi	2.87(1)−2.99(1)	2.87−2.92
av μ_1-I−Bi	2.91	2.90
μ_2-I−Bi	2.99(1)−3.43(1)	3.01−3.45
av μ_2-I−Bi	3.18	3.19
μ_3-I−Bi	3.14(1)−3.45(1)	3.20−3.40
av μ_3-I−Bi	3.31	3.32

Crystallographic Studies. A summary of the crystallographic data for $CuBi_7I_{19}(C_4H_8O_3H)_3(C_4H_8O_3H_2)$ is given in Table 1. The data set of the compound was collected on a Siemens Platform/CCD automated diffractometer and was corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares procedures, based on F^2, of the positional and anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).[13] Structural diagrams were performed with KPLOT.[14]

Results and Discussion

The preparation of $CuBi_7I_{19}(C_4H_8O_3H)_3(C_4H_8O_3H_2)$ is performed at low temperatures (140 °C) and yields the pure compound. On the basis of the results of single-crystal structure analysis (Table 1), five bismuth ions are coordinated by iodine as distorted octahedra. These octahedra themselves are edge-shared to form Bi_5I_{19} polyhedra (Figure 1). Such an arrangement was described before as an isolated $[Bi_5I_{19}]^{4-}$ anion in $[Li(thf)_4]_4[Bi_5I_{19}]$.[15] In both cases, the Bi−I distances are very similar and depend on the relevant coordination spheres (Table 2). However, in the title compound the Bi_5I_{19} polyhedra are not isolated but connected via distorted CuI_4 tetrahedra to form parallel chains along [101] (Figure 1). The averaged Cu−I distances are listed in Table 3 and correspond almost to the

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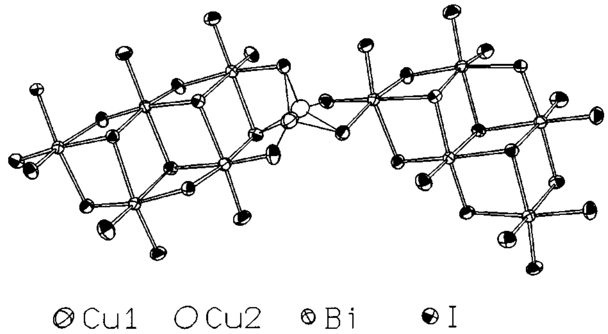

Figure 1. CuI_4 and Bi_5I_{19} polyhedra (anisotropic displacement with 50% probability of finding).

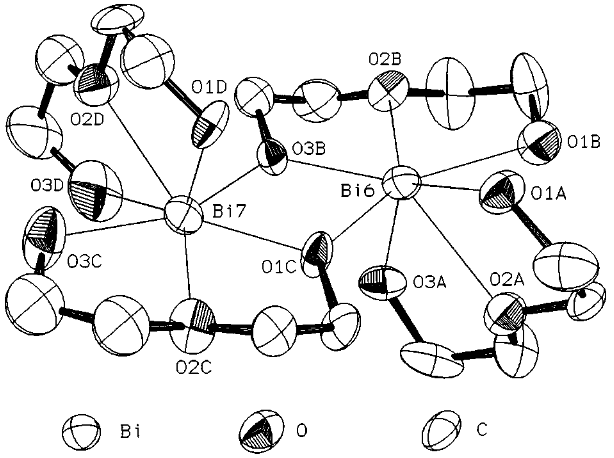

Figure 2. $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$ cation (anisotropic displacement with 50% probability of finding).

Table 3. Selected Cu−I Distances (Å) and Angles (deg) for $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)][CuBi_5I_{19}]$

Cu1−I15	2.61(1)	Cu2−I15	2.62(1)
Cu1−I10	2.63(1)	Cu2−I13	2.64(1)
Cu1−I13	2.70(1)	Cu2−I10	2.66(1)
Cu1−I6	2.79(1)	Cu2−I17	2.92(1)
averaged	2.68	averaged	2.71
I15−Cu1−I6	99.6(3)	I15−Cu2−I17	96.3(4)
I10−Cu1−I13	104.1(3)	I13−Cu2−I17	102.4(5)
I13−Cu1−I6	104.3(3)	I13−Cu2−I10	105.1(5)
I15−Cu1−I10	110.1(3)	I15−Cu2−I10	108.9(5)
I10−Cu1−I6	118.2(3)	I10−Cu2−I17	122.0(6)
I15−Cu1−I13	121.4(3)	I13−Cu2−I15	123.4(6)

situation in CuI (2.62 Å).[16] The $[CuBi_5I_{19}]^{3-}$ chains can be denoted as the one-dimensional anionic part of the structure. In accordance with a second almost tetrahedrically coordinated site between two Bi_5I_{19} polyhedra, a partial disorder of Cu^+ is observed (Figure 1). Because of the two possible CuI_4 tetrahedra being face-shared, the distance between both Cu sites is just 1.50(1) Å. Therefore, only one site can be occupied. This is confirmed by the site occupation factors that were refined as free parameters (Cu1, 0.68(2); Cu2, 0.36(1)). The preferred occupation of the Cu1 site might be due to the fact that, on one hand, the averaged Cu−I distance is closer to the situation in CuI. On the other hand, the angles of the CuI4 polyhedron around Cu1 are closer to an ideal tetrahedron than in the case of the Cu2 site (Table 3).

The cationic part of the structure also includes bismuth. Here, two bismuth ions are complexed by four molecules of diethylene glycol (Figure 2). C−O (1.42−1.45 Å) and C−C (1.52−1.54 Å) distances correspond very well with literature data (1.43 and 1.53 Å, respectively).[17] Each bismuth is surrounded by seven oxygen atoms. The Bi−O distances are listed in Table 4. Obviously, five Bi−O distances (2.19−2.31 Å to O3B, O1C, O1D) are significantly shorter than the eight other (2.36−2.73 Å), the latter including also the oxygen atoms of the ether groups (2.55−2.61 Å to O2A, O2B, O2C, O2D). On the basis of these findings, in the case of the very short bonding to O3B, O1C, and O1D, the oxygen atoms must be assumed to be anionic. In contrast, the significantly longer Bi−O bonding to O1A, O3A, O1B, O3C, and O3D must be assigned to hydroxyl groups. As a result, the cationic part of the structure must be assumed to be $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$.

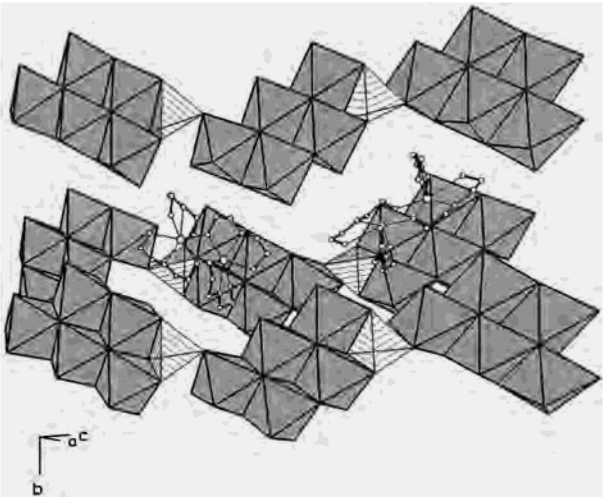

Figure 3. Three-dimensional packing of the $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$ cations and anionic $[CuBi_5I_{19}]^{3-}$ chains (CuI_4 polyhedra, lined; Bi_5I_{19} polyhedra, shaded; $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$ cations, spheres).

Table 4. Selected Interatomic Distances (Å) for the $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$ Cation

Bi6−O1C	2.18(2)	Bi7−O1D	2.19(2)
Bi6−O3B	2.29(2)	Bi7−O3B	2.26(2)
Bi6−O3A	2.36(2)	Bi7−O1C	2.31(2)
Bi6−O2A	2.56(2)	Bi7−O2D	2.55(2)
Bi6−O2B	2.61(2)	Bi7−O2C	2.56(2)
Bi6−O1A	2.61(2)	Bi7−O3C	2.62(2)
Bi6−O1B	2.73(2)	Bi7−O3D	2.72(2)

The three-dimensional packing of the anionic $[CuBi_5I_{19}]^{3-}$ chains and the cationic $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$ is illustrated in Figure 3. The complexed bismuth ions are located between the anionic chains in such a way that each $[Bi_2(C_4H_8O_3H)_3(C_4H_8O_3H_2)]^{3+}$ is surrounded by eight Bi_5I_{19} polyhedra. As a result, locally the packing is close to a CsCl type of structure.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic thermal parameters, and bond length and angles (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org. Further details of the crystal structure investigation are also available from the Fachinformazionzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-411414, the name of the author, and citation of the paper.

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