

MONO- AND BINUCLEAR Bi(III) IODIDE COMPLEXES CONTAINING 2,2'-BIPYRIDYL AND 1,10-PHENANTHROLINE: SYNTHESIS AND STRUCTURE

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Mononuclear complexes TBA[Bi(NN)I₄] (TBA = tetra-*n*-butylammonium, NN = 2,2'-bipyridyl (**1**) and 1,10-phenanthroline (**2**)) are synthesized by the reaction of BiI₃, tetra-*n*-butylammonium iodide, and the corresponding ligand in acetone with subsequent crystallization from a benzene-acetone mixture. By changing the solvent used in crystallization to ethanol, binuclear [Bi₂(NN)₂I₆] complexes (**3** and **4**) are produced. The crystal structure of the compounds is determined by single crystal X-ray diffraction.

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The chemistry of polynuclear iodide complexes of bismuth(III) (iodobismuthates) is currently being intensively developed [1, 2]. The interest in this field of chemistry is due to applied and fundamental aspects; thus, in particular, these compounds could be considered as precursors for BiOI-based photocatalytic materials which have been extensively investigated over the recent years [3-8]. Furthermore, such compounds exhibit thermochromic properties [9].

One of the most fascinating features of iodobismuthates is their structural diversity caused by the characteristic features of the coordination chemistry of both bismuth and iodide ligand. At present, there are iodobismuthates of varying nuclearity (from 1 to 8) [10-22]. Considering these systems to be labile and often extremely sensitive to the synthesis conditions (a counterion [23] and the solvent used [24]) along with their ability to form coordination polymers, one may confirm that a systematic study of iodobismuthates is a rather complicated problem.

According to some researchers, the concept of "construction blocks" cannot be applied to this field of chemistry [2]. Nevertheless, it is supposed that mixed-ligand Bi(III) iodide complexes, especially those with low nuclearity, may play such a role, in particular, in the synthesis of heterometallic iodobismuthate complexes [25-29]. At present there are known several examples of Bi(III) iodide complexes containing N,N-bidentate ligands [30-33] and, at least, one heterometallic compound containing Ag(I) and {Bi(phen)} fragments [34]. Thus, the synthesis of mixed-ligand iodide complexes of Bi(III) can be considered to be a problem of current interest.

In the present work, we have synthesized TBA[Bi(bipy)I₄] (**1**) and TBA[Bi(phen)I₄] (**2**), and have demonstrated the possibility of forming both mononuclear and binuclear ([Bi₂I₆(NN)₂], NN = bipy, phen) complexes depending on a solvent used for crystallization.

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EXPERIMENTAL

All the procedures were carried out in the air. The solvents were purified by the standard procedures, and all reagents were obtained from commercial sources and used without any additional purification. The analyses were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences. The infrared spectra ($4000\text{--}400\text{ cm}^{-1}$, KBr) were recorded using a Scimitar FSC-2000 spectrometer.

Synthesis of TBA[Bi(bipy)I₄] (1). 250 mg (0.423 mmol) of BiI₃ and 156 mg (0.423 mmol) of tetra-*n*-butylammonium iodide (TBAI) were dissolved in 20 ml of acetone. Then, a solution of 66 mg (0.423 mmol) bipy in 1 ml of acetone was added under vigorous stirring. 15 ml of benzene were added to the resulting orange solution. As the solvent was gradually evaporated at room temperature within 24 h, orange crystals of compound **1** formed. The yield was 80%. The elemental composition for C₂₆H₄₄N₃I₄Bi, calculated, %: C 28.0, H 3.98, N 3.77; found, %: C 27.9, H 4.02, N 3.80.

IR, cm⁻¹: 3097 m, 3052 m, 3006 w, 2954 s, 2868 s, 2015 w, 1706 w, 1591 s, 1565 w, 1475 s, 1461 m, 1433 s, 1377 m, 1342 w, 1312 m, 1244 w, 1210 w, 1170 m, 1151 m, 1097 w, 1069 w, 1033 w, 1007 s, 870 m, 805 w, 768 s, 730 m, 643 m, 624 m, 498 w, 449 w, 404 w.

Synthesis of TBA[Bi(phen)I₄] (2). The synthesis procedure was similar to that described above for compound **1**, with only exception: phen·H₂O (84 mg) was added instead of bipy. The evaporation of the solvent resulted in the simultaneous forming of compound **2** and the TBA[Bi(phen)I₄]·0.4C₆H₆ solvate (**2a**), which, according to the data of elemental analysis, completely loses solvate molecules of benzene when the sample is kept for 24 h in the air, and forms also compound **2**. The total yield of (**2+2a**) was 80%. The elemental composition for C₂₆H₄₄N₃I₄Bi calculated, %: C 29.5, H 3.89, N 3.69; found, %: C 29.4, H 3.93, N 3.84.

IR, cm⁻¹: 3045 m, 2956 s, 2928 s, 2896 s, 1620 w, 1587 w, 1571 w, 1514 s, 1465 s, 1378 m, 1344 m, 1315 w, 1219 w, 1141 m, 1098 m, 1031 w, 1006 w, 893 w, 861 w, 847 s, 774 w, 721 s, 637 m, 469 w, 416 m.

Synthesis of [Bi₂(bipy)₂I₆] (3) and [Bi₂(phen)₂I₆] (4). In both cases the procedures were similar to those described above for compounds **1** and **2**, with the exception: 10 ml of ethanol were added instead of benzene. The evaporation of the solvent leads to the simultaneous formation of crystals **1** and **3** or crystals **2** and **4**, respectively. The crystals of **3** and **4** were identified by the crystallographic parameters [32] and [41].

Single crystal X-ray diffraction. The crystallographic data and results of the refinement of the structure are given in Table 1. Single crystal X-ray diffraction was carried out using the Bruker Apex Duo (at 150 K for [**2**]) and Bruker X8 Apex (at 298 K for [**2**]·0.4C₆H₆ and [**1**]) spectrometers (graphite monochromator, MoK_α, λ = 0.71073 Å, φ- and ω-scanning). All the structures were solved by the direct methods and refined by the full-matrix least-square technique in the anisotropic approximation (except the hydrogen atoms) using the SHELXTL program package [43]. The absorption was considered empirically using the SADABS program [44]. The hydrogen atoms were located geometrically and refined by the riding model.

RESULTS AND DISCUSSION

Formation of mono- and binuclear complexes. As it was stated above, mono- (**1**, **2**) and binuclear (**3**, **4**) complexes can be produced by the reaction of BiI₃, TBAI, and the corresponding N,N-ligand in acetone. It is remarkable that the elemental composition of the compounds formed does not depend on the molar ratio of the reagents (in both cases it was 1:1:1). The solvent used for crystallization plays the crucial role: the usage of the acetone-benzene (or toluene) mixture makes it possible to produce pure TBA[Bi(NN)I₄] complexes, while the addition of ethanol results in the simultaneous formation of TBA[Bi(NN)I₄] and [Bi₂(NN)₂I₆]. The mechanism of this phenomenon is not clear. The relationship between mono- and binuclear forms can be estimated as 1:1, although it may be supposed that the relationship can vary. The structures of the binuclear [Bi₂(bipy)₂(μ₂-I)₂I₄] complex and its phen-containing analog have previously been published [32,41], nevertheless, the approaches to the synthesis differ sufficiently from each other, and also from those we have used. The bipy-

TABLE 1. Crystallographic Data and Details of the Diffraction Experiments

Parameter	Compound		
	1	2	2·0.4C₆H₆
Chemical formula	C ₂₆ H ₄₄ BiI ₄ N ₃	C ₂₈ H ₄₄ BiI ₄ N ₃	C _{30,40} H _{46,40} BiI ₄ N ₃
M_r	1115.22	1139.24	1170.48
Crystal symmetry, space group	Monoclinic, $P2_1/c$	Monoclinic, Cc	Monoclinic, $P2_1/c$
Temperature, K	296	296	150
$a, b, c, \text{Å}$	12.526(4), 18.178(6), 16.483(5)	12.102(4), 19.817(7), 15.856(7)	11.3646(3), 20.7656(5), 17.2832(6)
β , deg	104.571(10)	95.922(9)	108.535(1)
$V, \text{Å}^3$	3632(2)	3782(2)	3867.14(19)
Z	4	4	4
μ , mm ⁻¹	8.27	7.95	7.77
Crystal sizes, mm	0.20×0.10×0.05	0.20×0.15×0.10	0.20×0.06×0.06
$T_{\min}; T_{\max}$	0.289; 0.683	0.299; 0.504	0.305; 0.653
Number of measured, unique and observed [$I > 2\sigma(I)$] reflections	26276, 7411, 5841	13106, 6602, 5856	25815, 7910, 6211
R_{int}	0.063	0.035	0.035
Scanning area at θ , deg	$\theta_{\max} = 26.5$; $\theta_{\min} = 2.0$	$\theta_{\max} = 26.4$; $\theta_{\min} = 2.0$	$\theta_{\max} = 26.50$ $\theta_{\min} = 1.6$
Subscript ranges of h, k, l	$-15 \leq h \leq 15$, $-21 \leq k \leq 22$, $-20 \leq l \leq 15$	$-15 \leq h \leq 14$, $-24 \leq k \leq 24$, $-19 \leq l \leq 17$	$-14 \leq h \leq 14$, $-26 \leq k \leq 25$, $-17 \leq l \leq 21$
$R[F^2 > 2\sigma(F^2)]; wR(F^2); S$	0.030; 0.074; 1.00	0.074; 0.221; 1.02	0.042; 0.110; 1.05
$\Delta\rho_{\max}; \Delta\rho_{\min}, \text{e/Å}^{-3}$	0.79; -0.95	2.84; -1.47	2.29; -1.29
Absolute structure parameter	–	0.979(5)	–

Programs used: APEX2 (Bruker-AXS, 2004), SAINT (Bruker-AXS, 2004), SHELXS97 (Sheldrick, 1998), SHELXL97 (Sheldrick, 1998), SHELXTL (Bruker-AXS, 2004), CIFTAB-97 (Sheldrick, 1998).

containing complex was produced by a direct synthesis (BiI₃+bipy in acetonitrile), while the synthesis of the phen-containing complex was nontrivial (phen, BiI₃ and Mn(CH₃COO)₂·4H₂O, a water-ethanol mixture, autoclave). Obviously, the authors of [32] attempted, but unsuccessfully, to produce a heterometallic complex.

In general, the observed effect of the solvent agrees with the previous observations and results stating that Bi(III) iodide complexes, due to the relatively low binding energy of Bi–I and their high lability, are affected by both cation and solvent, which may cause the molecular rearrangement even in a solid [23,24].

Crystal structures. The structures of complexes **1** and **2** consist of TBA cations and [(NN)BiI₄][–] anions. In both cases, the Bi atom is in a distorted octahedral environment consisting of the bidentate N,N-coordinated ligand and four iodide ligands. The earlier publications on complexes containing the [Bi(phen)I₄][–] anion stated that the protonated 1,10-phenanthroline or the Bi(III) cationic complex played the role of the cation, respectively, in the published structures [30,40]. In both cases, acetonitrile was used as a solvent in the synthesis.

In the structure of [**2**]·0.4C₆H₆, the [(phen)BiI₄][–] anion undergoes orientational disordering in order to avoid close I...I contacts in the crystal structure (Fig. 1).

Contrary to that, nonsolvated complexes **1** and **2** do not have similar contacts in a solid, even when iodide ligands are ordered (Fig. 2). In all cases, the C and N atoms of the TBA cations have large atomic displacements, and the attempts to split positions in the refinement of the structure of [**2**]·0.4C₆H₆ lead to a lengthening of the C–C and C–N bond lengths. In the structures of **1** and **2**, the positions of the cation atoms are not split.

The data on the Bi–X and Bi–N bond lengths in such complexes are shown in Table 2.

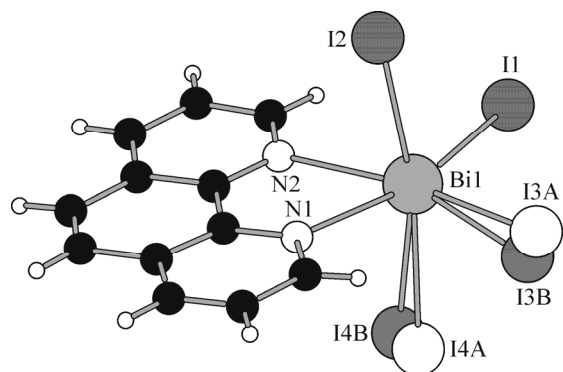


Fig. 1. Structure of the $[\text{Bi}(\text{phen})\text{I}_4]^-$ anion in **2a**.

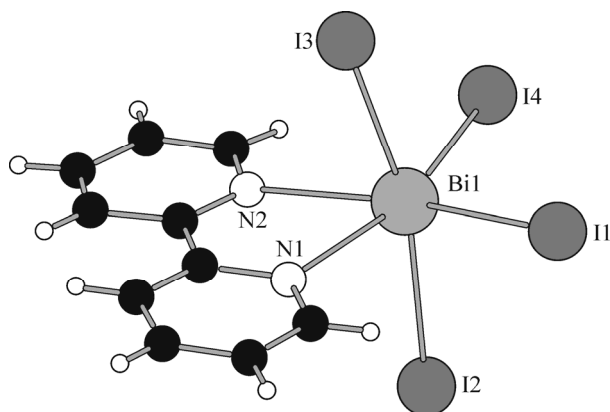


Fig. 2. Structure of the anion of **1**.

TABLE 2. Bond Lengths in the Known Polypyridyl-Halide Complexes of Bi(III)

Complex	Bi–N (av.)	Bi–X (av.)	Bi– μ X (av.)	Reference
$[\text{BiTPCCl}_2]\text{Cl}\cdot 2\text{CH}_2\text{Cl}_2^*$	2.62(5)	2.74(6)	–	[35]
$[\text{BiTPC}][(\text{NO}_3)_2]^*$	2.64(2)	2.74(6)	–	[35]
$[\text{CH}_3\text{Bi}(\text{bipy})\text{Cl}_2]$	2.534(9)	2.694(3)	–	[36]
$(\text{bipyH})[(\text{bipy})\text{BiCl}_3]$	2.48(3)	2.680(6)	–	[37]
$(\text{bipyH})[(\text{bipy})\text{BiCl}_3]\cdot 1,5\text{CH}_3\text{CN}$	2.500(7)	2.680(3)	–	[37]
$[\text{MeBi}(\text{tmeda})\text{Cl}_2]^*$	2.544(12)	2.702(4)	–	[38]
$[(\text{bian})\text{BiCl}_2(\mu\text{-Cl})_2]^*$	2.657(2)	2.5023(17)	2.8732(12)	[39]
$[(\text{phen})\text{BiCl}_3(\text{O-dmsO})_2]\cdot \text{dmsO}$	2.546(8)	2.686(3)	–	[40]
$[(\text{bipy})\text{Cl}_2\text{Bi}(\mu\text{-Cl})_2\text{BiCl}_3(\text{bipy})]$	2.57(3)	2.60(1)	2.752(8)	[41]
$[(\text{phen})_2\text{BiCl}_3]$	2.61(2)	2.661(9)	–	[42]
$[\text{MeBi}(\text{bipy})\text{Br}_2]$	2.500(4)	2.8269(7)	–	[38]
$[\text{MeBi}(\text{phen})\text{Br}_2]$	2.508(6)	2.843(1)	–	[38]
$[\text{MeBi}(\text{tmeda})\text{Br}_2]\cdot \text{THF}^*$	2.515(11)	2.881(4)	–	[38]
$[(\text{phen})(\text{BiBr}_3(\text{O-dmsO})_2)]\cdot \text{dmsO}$	2.571(6)	2.837(1)	–	[40]
$[(\text{bipy})\text{BiBr}_2(\mu\text{-Br})_2\text{BiBr}_2(\text{bipy})]\cdot 2\text{CH}_3\text{CN}$	2.47(1)	2.730(2)	3.00(1)	[41]
$[(\text{phen})\text{BiBr}_2(\mu\text{-Br})_2\text{BiBr}_2(\text{phen})]\cdot 2\text{CH}_3\text{CN}$	2.48(1)	2.717(3)	3.005(3)	[41]
$[(\text{phen})_2\text{BiBr}_3]$	2.61(3)	2.830(4)	–	[37]
$[(\text{phen})_2\text{BiBr}_3]\cdot \text{CH}_3\text{CN}$	2.50(7)	2.81(1)	–	[42]
$[(\text{bipy})_2\text{BiBr}_3]$	2.60(3)	2.825(4)	–	[42]
$[(\text{phen})\text{BiI}_2(\text{O-dmsO})_3][(\text{phen})\text{BiI}_4]$	Cation: 2.53(2) Anion: 2.52(2)	3.008(3) 3.048(3)	– –	[40]
$[(\text{bipy})\text{BiI}_3(\text{O-dmsO})]$	2.56(2)	2.962(4)	–	[40]
$[(\text{bipy})\text{BiI}_2(\mu\text{-Br})_2\text{BiI}_2(\text{bipy})]\cdot 2\text{CH}_3\text{CN}$	2.47(1)	2.920(3)	3.236(2)	[41]
$[(\text{bipy})_2\text{BiI}_3]\cdot \text{CH}_2\text{Cl}_2$	2.64(3)	3.041(3)	–	[42]
$[(\text{phen})_2\text{BiI}_3]\cdot \text{CH}_2\text{Cl}_2$	2.62(2)	3.043(2)	–	[42]
$(\text{Bu}_4\text{N})[(\text{bipy})\text{BiI}_4]$	2.539(4)	3.042(1)	–	[Present article]
$(\text{Bu}_4\text{N})[(\text{phen})\text{BiI}_4]\cdot 0,4\text{C}_6\text{H}_6$	2.546(6)	3.021(3)	–	[Present article]
$(\text{Bu}_4\text{N})[(\text{phen})\text{BiI}_4]$	2.47(3)	3.029(3)	–	[Present article]

* TPC = 1,4,7,10-tetrakis(2-pyridylmethyl)-1,4,7,10-tetraazacyclotetradecane, bian = bis(2,4,6-(trimethyl)phenylimino)acenaphthene, tmeda = N,N,N',N'-tetramethylethane-1,2-diamine.

Thus, the present work shows that mono- and binuclear mixed-ligand complexes can form in the BiI₃-TBAI-NN system, where NN is the polypyridyl ligand. The key factor is the effect of the solvent used to isolate the complexes out of the reaction solution.

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