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Synthesis of Bismuth Complexes from Bismuth Iodide and Ammonium and Phosphonium Salts

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Abstract—The complexes $[Et_2NH_2]_3^+[BiCl_6]^{3-}$ (**I**), $[NH_4]^+[BiI_4(C_5H_5N)_2]^-\cdot 2C_5H_5N$ (**II**), $[Ph_3MeP]_2^+[BiI_5]^{2-}$ (**III**), $[Ph_3MeP]_2^+[BiI_5(C_5H_5N)]^{2-}\cdot C_5H_5N$ (**IV**), $[Ph_3MeP]_3^+[Bi_3I_{12}]^{3-}$ (**V**), $[Ph_3(i\text{-}Pr)P]_3^+[Bi_3I_{12}]^{3-}\cdot 2Me_2C{=}O$ (**VI**), $[Ph_3BuP]_2^+[Bi_2I_8\cdot 2Me_2C{=}O]^{2-}$ (**VII**), and $[Ph_3BuP]_2^+[Bi_2I_8\cdot 2Me_2S{=}O]^{2-}$ (**VIII**) were obtained by reactions of bismuth iodide with ammonium and phosphonium iodides in acetone, pyridine, or dimethyl sulfoxide.

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Numerous complexes with bismuth-containing anions have been synthesized, most of which comprise nitrogen-containing cations and halogen-containing anions with one to eight bismuth atoms [1]. The complexes obtained from ammonium salts and trivalent bismuth halides, containing mononuclear octahedral bismuth-containing anions, have the most trivial structures: $[BiCl_6]^{3-}$, $[BiBr_6]^{3-}$, and $[BiI_6]^{3-}$.

In the present work we studied reactions of bismuth iodide with ammonium and phosphonium salts in order to reveal the effect of the substituents at the nitrogen and phosphorus atoms, solvent, and starting reagents ratio on the structure of the anion in the resulting complex.

It was found that the reaction of bismuth iodide with diethyl ammonium chloride in acetone at room temperature does not form complexes with mixed ligand anions like $[BiCl_3I_3]^{3-}$. At varied starting reagent molar ratios, exclusive formation of diethylammonium hexachlorobismuthate (**I**) was observed:

$$6\,[Et_2NH_2]Cl + BiI_3 \xrightarrow{\text{acetone}} [Et_2NH_2]_3^+[BiCl_6]^{3-} + 3\,[Et_2NH_2]I.$$

I

Probably, the formation of a single bismuth complex is explained by its stability due to a high symmetry of the $[BiCl_6]^{3-}$ anion. Actually, by preliminary X-ray diffraction data the octahedral anion in complex **I** is scarcely deformed (the ClBiCl angles are equal to 174.71°), but the Bi–Cl bond lengths (2.683, 2.877 Å) are slightly larger than the sum of the covalent radii of the constituent atoms (2.57 Å [2]).

The reaction of bismuth iodide with ammonium iodide in pyridine gives, regardless of the starting reagent ratio, complex **II** containing ammonium cations, octahedral $[BiI_4(C_5H_5N)_2]^-$ anions, and solvate pyridine molecules:

$$[NH_4]I + BiI_3 \xrightarrow{C_5H_5N} [NH_4]^+[BiI_4(C_5H_5N)_2]^-\cdot 2\,C_5H_5N.$$

II

The bismuth atom has a slightly distorted octahedral coordination [the axial NBiI and IBiI angles are equal to 167.95(8)°, 168.59(8)°, and 171.46(1)°], and the Bi–N and Bi–I distances are 2.577(3), 2.652(3) and 2.9542(3)–3.0778(3) Å, respectively.

We established that the reactions of bismuth iodide with alkyltriphenylphosphonium halides in different solvents lead to different results at different starting reagent molar ratios. Thus, the reaction of 2 mol of methyltriphenylphosphonium iodide with 1 mol of bismuth iodide in acetone at room temperature results in formation of bismuth complex **III** with a mononuclear anion:

$$2\,[Ph_3MeP]^+I^- + BiI_3 \xrightarrow{\text{acetone}} [Ph_3MeP]_2^+[BiI_5]^{2-}.$$

III

The phosphorus atoms in the methyltriphenylphosphonium cations have a tetrahedral coordination (the CPC angles are 109.42° and 109.52°), and, therewith, the P–C_{Me} bond (1.779 Å) is slightly shorter than the P–C_{Ph} bonds (1.793 Å). The geometry of this anion is an ideal trigonal bipyramid (the Bi–I_{ax} and Bi–I_{eq} distances are 3.048 and 3.003 Å, respectively).

The same reaction in pyridine gave a pyridine solvate of the bismuth complex **IV**.

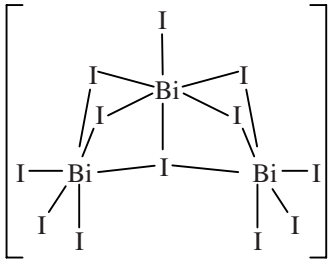
$$2\,[Ph_3MeP]^+I^- + BiI_3 \xrightarrow{C_5H_5N} [Ph_3MeP]_2^+[BiI_5(C_5H_5N)]^{2-}\cdot C_5H_5N.$$

IV

A specific feature of complex **IV** is that it contains both coordinated and solvating pyridine molecules. In the octahedral $[BiI_5Py]^{2-}$ anion, the solvent molecule occupies the sixth position (the Bi···N distance is 2.628 Å, and the N^1BiI^5, I^1BiI^3, and I^2BiI^4 angles are 173.86°, 169.03°, and 172.52°, respectively).

The reaction of equimolar quantities of triphenylmethyl phosphonium iodide and bismuth iodide in acetone results in formation of complex **V** with a trinuclear anion. Each of the terminal BiI_3 groups is linked to the central Bi atom by two μ_2- and one m_3-iodine bridges (the BiBiBi angle is 101.54°):

$$3\,[Ph_3MeP]^+I^- + 3\,BiI_3 \xrightarrow{Me_2C=O} [Ph_3MeP]_3^+[Bi_3I_{12}]^{3-}$$



V

The Bi atoms in $[Bi_3I_{12}]^{3-}$ have a distorted octahedral coordination. The Bi–I distances are 2.882(3)–2.915(3) for monodentate ligands, 3.011(3)–3.426(3) Å for bidentate ligands, and 3.309(3)–3.360(3) Å for a tridentate I(1) atom; the IBiI angles span the range of 80.70(7)°–98.41(9)°. The $Bi^1I^1Bi^2Bi^3$ fragment is planar within 0.030 Å; the BiBiBi angle is 101.54°. The point symmetry group of this anion is close to C_{2v}.

The similar reaction of isopropyltriphenylphosphonium iodide with bismuth iodide gave bismuth complex **VI** with a trinuclear linear bismuth-containing anion, in which terminal Bi atoms are linked to the central one via three iodine bridges:

$$3\,[Ph_3(i\text{-}Pr)P]^+I^- + 3\,BiI_3 \xrightarrow{Me_2C=O} [Ph_3(i\text{-}Pr)P]_3^+[Bi_3I_{12}]^{3-}\cdot 2\,Me_2C=O.$$

VI

In the centrosymmetric trinuclear $[Bi_3I_{12}]^{3-}$ anions, the Bi atoms have an octahedral environment. Each terminal BiI_3 fragment (Bi–I_t 2.8380(8)–2.8995(8) Å) is linked to the central metal atom by three bridging iodine atoms [Bi^1 – $I^{1,2,3}$ 3.3413(8)–3.4164(8) Å]. At the same time, the distances between the central Bi atom and bridging iodine atoms are shorter [Bi^2 – $I^{4,5,6}$ 3.0544(7)–3.0843(7) Å]. The solvate acetone molecules are not coordinated with the bismuth atoms.

It was found that alkyltriphenylphosphonium salts with a longer chain alkyl radical form bismuth complexes of a different type. Thus, the reaction of equimolar quantities of butyltriphenylphosphonium iodide with bismuth iodide in acetone provides complex **VII** with a binuclear anion, in which two octahedral bismuth atoms are linked via two bridging (b) iodine atoms [Bi–I_b 3.1508(7) Å].

$$2\,[Ph_3BuP]^+I^- + 2\,BiI_3 \xrightarrow{Me_2C=O} [Ph_3BuP]_2^+[Bi_2I_8\cdot 2\,Me_2C=O]^{2-}.$$

VII

The Bi and bridging iodine atoms are coplanar with four terminal (t) iodine atoms [Bi–I_t 2.9260(7), 2.9953(6) Å]. The two remaining positions at the bismuth atom are occupied by an iodine atom [Bi–I 2.8531(7) Å] and an *n*-ligand molecule [Bi–O 2.747(6) Å], which are *trans* to each other.

The reaction between butyltriphenylphosphonium iodide and bismuth iodide in DMSO gave complex **VIII** which differs from **VII** only in that it contains coordinated DMSO molecules:

$$2\,[Ph_3BuP]^+I^- + 2\,BiI_3 \xrightarrow{DMSO} [Ph_3BuP]_2^+[Bi_2I_8\cdot 2\,DMSO]^{2-}.$$

VIII

Complex **VIII**, like **VII**, is resistant to moisture and air oxygen, has a well-defined melting point, and is readily soluble in polar organic solvents. The bismuth atoms in $[Bi_2I_8 \cdot 2DMSO]^{2-}$ anion have a distorted octahedral coordination [the axial OBiI and IBiI angles are 176.49(7)° and 164.896(7)°, 171.62(8)°, respectively]. The Bi–O bonds in a crystal of **VIII** [2.507(3) Å]

are stronger than respective bonds in complex **VII** [2.747(6) Å], on account of a stronger donor ability of DMSO compared to acetone. The bismuth–bridging iodine distances in **VIII** are slightly longer [Bi–I_b 3.1961(3), 3.3108(3) Å] than in **VII** [Bi–I_b 3.1508(7) Å], whereas the Bi–I_t bond lengths are almost the same [2.9206(3), 2.9786(3) Å]. The iodine atom opposite to the solvent molecule is spaced by 2.8984(3) Å from the central atom, which is larger than the respective distance in complex **VII** [2.8531(3) Å]. The solvent molecules are *trans* with respect to the Bi_2I_2 group, like in the anion in **VII**.

We found that complex **VIII** is formed quantitatively on recrystallization of compound **VII** from DMSO:

$$[Ph_3BuP]_2^+[Bi_2I_8\cdot 2\,Me_2C{=}O]^{2-}$$

$$\xrightarrow{Me_2C=O} [Ph_3BuP]_2^+[Bi_2I_8\cdot 2\,DMSO]^{2-}.$$

Thus, the structure of the adducts formed in the reactions of bismuth iodide with ammonium and phosphonium salts is defined by the nature of the ammonium and phosphonium salt, solvent, and starting reagent molar ratio.

EXPERIMENTAL

Complex I. A mixture of 0.55 g of diethylammonium chloride, 0.37 g of bismuth iodide, and 30 ml of acetone was allowed to stand at room temperature for 24 h. The solution was filtered and concentrated to a volume of 5 ml. Red crystals formed. Yield 62%, mp 148ºC. IR spectrum, ν, cm^{-1}: 1559 s, 1451 vs, 1387 vs, 1191 s, 1157 s, 1048 vs, 886 s, 837 w, 758 vs, 478 s. Found, %: C 22.04; H 5.37. $C_{12}H_{36}BiCl_6N_3$. Calculated, %: C 22.36; H 5.59.

Complex II. A mixture of 0.15 g of ammonium iodide, 0.59 g of bismuth iodide, and 15 ml of pyridine was stirred at 20°C for 4 h. The reddish orange crystals formed in the solution on concentration were filtered and dried. Yield 81%, mp 88ºC. IR spectrum, ν, cm^{-1}: 2299 w, 2014 w, 1590 s, 1479 m, 1444 m, 1352 w, 1235 w, 1210 m, 1149 m, 1067 s, 1026 m, 1004 s, 937 w, 880 w, 744 vs, 696 s, 617 m. Found, %: C 22.47; H 2.31; N 6.59. $C_{20}H_{24}N_5I_4Bi$. Calculated, %: C 22.84; H 2.28; N 6.66.

Complex III. A mixture of 0.50 g of methyltriphenylphosphonium iodide and 0.37 g of bismuth iodide in 50 ml of acetone was stirred at 20°C for 1 h. The solvent was evaporated for 18 h. Dark claret crystals formed. Yield 96%, mp 192°C. IR spectrum, *ν*, cm^{-1}: 3054 m, 2977 s, 2926 w, 2901 m, 1589 s, 1484 s, 1437 vs, 1338 m, 1333 s, 1315 m, 1187 s, 1163 s, 1108 vs, 1026 m, 998 s, 901 vs, 849 w, 791 w, 746 vs, 718 vs, 688 vs, 539 s, 499 vs, 444 m. Found, %: C 32.08; H 2.34. $C_{38}H_{36}BiI_5P_2$. Calculated, %: C 32.62; H 2.57.

Complex IV. A mixture of 0.50 g of methyltriphenylphosphonium iodide, 0.37 g of bismuth iodide, and 30 ml of pyridine was allowed to stand at room temperature for 24 h. The solution was filtered and concentrated to a volume of 5 ml. Orange crystals formed. Yield 98%, mp 118ºC. IR spectrum, ν, cm^{-1}: 3053 m, 2970 m, 2896 m, 1589 vs, 1481 w, 1446 vs, 1333 s, 1211 s, 1166 s, 1117 vs, 1068 s, 1034 m, 994 s, 901 vs, 847 m, 788 s, 754 vs, 719 s, 685 vs, 616 s, 508 vs, 439 w. Found, %: C 36.79; H 2.72. $C_{48}H_{46}BiI_5N_2P_2$. Calculated, %: C 37.02; H 2.96.

Complex V. A mixture of 0.50 g of triphenylmethyl phosphonium iodide, 0.73 g of bismuth iodide and 15 ml of acetone was stirred under heating until a homogeneous solution formed. The reaction mixture was cooled, and the solvent was slowly evaporated for 24 h at room temperature. Red crystals formed. Yield 99%, mp 126ºC. IR spectrum, ν, cm^{-1}: 2904 w, 1588 w, 1481 m, 1438 s, 1338 w, 1313 w, 1192 w, 1163 w, 1115 s, 998 m, 895 s, 834 w, 781 m, 741 s, 719 m, 686 s, 506 s, 481 m. Found, %: C 22.67; H 1.64. $C_{57}H_{54}Bi_3I_{12}P_3$. Calculated, %: C 22.94, H 1.81.

Complex VI. A mixture of 0.68 g of bismuth iodide, 0.50 g of isopropyltriphenylphosphonium iodide, and 15 ml of acetone was stirred under heating until a homogeneous solution formed. The solvent was slowly evaporated. Dark red crystals of the solvate were obtained. Yield 97%, mp 180ºC. IR spectrum, ν, cm^{-1}: 3055 w, 2977 w, 1705 m, 1588 m, 1140 s, 1117 s, 994 m, 878 w, 749 m, 729 s, 690 s, 529 vs. Found, %: C 25.81; H 2.34. $C_{69}H_{78}Bi_3I_{12}O_2P_3$. Calculated, %: C 26.02; H 2.45.

Complex VII. A mixture of 0.89 g butyltriphenylphosphonium iodide, 1.18 g of bismuth iodide, and 50 ml of acetone was stirred at 20°C for 1 h. The solution was concentrated to a volume of 1 ml. The reddish orange crystals that formed were filtered off and dried. Yield 95%, mp 74°C. IR spectrum, ν, cm^{-1}: 2952 w, 2919 m, 2895 w, 1634 s, 1440 s, 1110 s, 994 w, 729 s, 690 s, 529 m, 503 w. Found, %: C 27.30; H 2.57. $C_{50}H_{60}O_2Bi_2I_8P_2$. Calculated, %: C 27.74; H 2.74.

Complex VIII. A mixture of 1.18 g bismuth iodide, 0.89 g of butyltriphenylphosphonium iodide, and 25 ml of DMSO was stirred at 20°C for 1 h. The solution was concentrated to a volume of 1 ml. The reddish orange crystals that formed were filtered off and dried. Yield 98%, mp 188°C. IR spectrum, ν, cm^{-1}: 2964 w, 2919 m, 2861 w, 1440 m, 1336 w, 1188 w, 1110 s, 1026 s, 987 m, 936 s, 840 w, 734 m, 690 m, 535 m, 497 m. Found, %: C 25.38; H 2.71. $C_{48}H_{60}O_2Bi_2I_8P_2S_2$. Calculated, %: C 25.85; H 2.69.

The IR spectra were recorded on a Shimadzu 1201 FTIR spectrometer in KBr.

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