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Structural Chemistry of Bismuth Compounds. I. Organobismuth Derivatives

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Contents

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Henrik Althaus (center) was born in Duisburg-Rheinhausen, Germany, in 1967. He received his education as a Laboratory Assistant in Chemistry from 1987 to 1990 at the Max-Planck Institut für Kohlenforschung in Mülheim. He studied at the University of Duisburg from 1990 to 1997 and received his degree Diplomchemiker. Since 1997 he has been working on his Ph.D. thesis at the University of Bremen in the group of Professor Breunig. His research interests focus on the chemistry and structure of organoantimony and organobismuth halides.

Hans Joachim Breunig (right) was born in 1945 in Blochwitz, Germany, and studied chemistry at the University of Würzburg. He received his Ph.D. degree from the Technical University Berlin in the group of Professor Herbert Schumann and moved to the University Bremen in 1975 where he is Professor of Inorganic Chemistry. His research interests focus upon the syntheses and properties of organometallic compounds of antimony and bismuth with element–element bonds.

I. Introduction

Bismuth chemistry has received much less attention in comparison with that of N, P, As, and Sb, but the last years have revealed an increasing interest in the investigation of both the inorganic and the organometallic chemistry of the heaviest element of the group 15 elements.[1] There are several fields

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where in relation to fundamental research the chemistry of bismuth has been prompted: (i) bioactivity, i.e., treatment of a variety of gastrointestinal disorders,[2−6] antitumor,[7] antimicrobial and antibacterial activity;[5,8,9] (ii) uses in organic syntheses (e.g., phenylation agent or mild oxidizing agents);[10−12] (iii) industrial uses as precursors in advanced material science (e.g., superconductors, photorefractive systems, sol−gel processes, and chemical vapor deposition techniques),[13−25] catalysts (e.g., Bi−molybdate materials in the SOHIO process for acrylonitrile synthesis and more generally to catalyze amination and oxidation reactions);[26] (iv) heterometallic cluster chemistry, in particular compounds containing Bi−transition metal bonds;[27−29] (v) structural investigation of compounds containing bismuth−bismuth bonds (in dibismuthanes,[30] dibismuthenes,[31] or cyclobismuthine[32]) and bismuth−arene interactions,[33,34] hypervalent bismuth compounds,[35−40] organobismuth(V) derivatives,[41−43] etc.

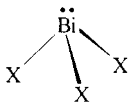
During the past decade the number of Bi compounds structurally characterized by diffraction methods, mainly X-ray crystallography, has considerably increased. The results have pointed out the diversity of Bi coordination chemistry mainly due to the potential for normal covalent as well as coordinative bonds, the latter being the result of the bismuth Lewis acidity.

Bismuth is known to display various oxidation states (the most common being +3 and +5, but formal +1 is also known, for example) and coordination numbers up to 10. So far only two types of Bi(III) compounds have been extensively reviewed, i.e., bismuth halides[44] and bismuth−transition metal[27−29] derivatives, but other classes of bismuth compounds are also of interest, and the structures established so far exhibit a broad range of coordination geometries. This review will focus on the structural aspects of all known crystallographically studied bismuth compounds and will thus bring together for comparison a broad array of structures.

The nature of Bi−element bonding has been previously discussed in relation to structural patterns observed in organometallic and inorganic Bi(III) halides or Bi−transition metal derivatives and will not be presented here in detail. However, some general trends concerning the bonding patterns in bismuth derivatives in relation to the coordination geometries around the metal atom should be emphasized here before starting to discuss the structural features observed in various classes.

The five valence electrons of the bismuth atom may be involved in bonding to other elements in different ways.

For the three-coordinate bismuth in BiX_3 molecules (X = same or different atoms or group of atoms, e.g., most of the triorganobismuthines, cyclobismuthine, and M−Bi bond-containing compounds), the octet rule at bismuth is fulfilled and the resulting trigonal pyramidal geometry (**1**) might be regarded as being consistent with VSEPR theory predictions.[45] On the other hand, this molecular geometry can be described as the result of three covalent Bi−X bonds achieved using the p orbitals of the valence shell. The orbital in which the remaining lone pair of electrons is located has a basically s orbital contribution. This is supported not only by the X−Bi−X angles around the central metal atom (generally close to 90°), but also by the low availability of the lone pair to be used in dative bonds, e.g., complexes of transition metals.



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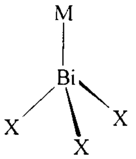

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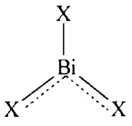
Very few neutral complexes containing a BiX_3 molecule coordinated to a metal center are known,[46] and only $[(OC)_5M(BiPh_3)]$ (M = Cr,[47] Mo, W[48]) complexes were characterized by X-ray diffractometry. These complexes contain a tetrahedral X_3BiM core (**2**), and a degree of hybridization at the Bi atom should be considered. A tetrahedral arrangement around Bi was also observed in the $[(C_5H_5)(OC)_2Fe(BiPh_3)]^+$ cation[49] or in $[Ph_2Bi\{M(CO)_n\}_2]^-$ and $[Bu^iBi\{Fe(CO)_4\}_3]^{2-}$ anions.[50,51] In both cases, the geometry around Bi might be discussed in terms of a dative Bi−M bond (see section C.9.b) and of hybridization (or s orbital contribution) at Bi or, alternatively, the oxidation state at Bi might be considered +5, as suggested by some authors. The last approach is less likely taking into account the presence of a highly oxidizing Bi(V) directly attached to a highly reducing metal carbonyl moiety.

An almost trigonal planar BiX_3 arrangement was found in the inorganic "bismuthinidene" derivative, $ClBi[Mn(CO)_2(C_5H_4Me)]_2$, which contains some multiple bond character in the angular $BiMn_2$ system (**3**).[52] A true bismuth−bismuth double bond was recently described in the first stable dibismuthene compound, 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$−Bi=Bi−C_6H_2-$[CH(SiMe_3)_2]_3$-2,4,6 (**4**), again containing an inert lone pair of electrons at each Bi atom.[31]



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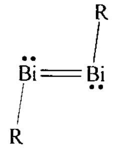

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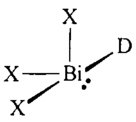
Due to the Lewis acidic character at the Bi center, additional intra- or intermolecular contacts are usually established in the presence of donor molecules or ions, thus increasing the coordination number. According to the "semibonding concept" introduced by Alcock,[53,54] the bonds at the Bi atom might be generally described in terms of ***primary bonds***, i.e., normal covalent bonds with bond lengths close to the sum of the covalent radii for the two elements involved, and ***secondary bonds*** or ***interactions***, with interatomic distances significantly longer than a covalent bond but shorter than the sum of the van der Waals radii for the two elements concerned. For Bi complexes, the interatomic distances for these additional interactions cover a quite large range. Table 1 shows the covalent and van der Waals radii for Bi and elements involved in bonds to the metal atom,[55] as well as the bismuth−element distances estimated from these values, which were used for comparison with the interatomic distances actually found in the discussed compounds.

Table 1. Atomic Radii for Bismuth and Other Elements and the Corresponding Bismuth−Element Distances (Å)[55]

atom X	r_{cov}	$\Sigma_{r.cov}$(Bi,X)	r_{vdW}	$\Sigma_{r.vdW}$(Bi,X)
Bi	1.50	3.00	2.4	4.8
C	0.77	2.27	1.7	4.1
N	0.70	2.20	1.6	4.0
O	0.66	2.16	1.5	3.9
S	1.04	2.54	1.8	4.2
Se	1.17	2.67	1.9	4.3
F	0.64	2.14	1.5	3.9
Cl	0.99	2.49	1.8	4.2
Br	1.14	2.64	1.9	4.3
I	1.33	2.83	2.1	4.5

A trend usually observed is that the secondary bonds lie almost trans to the primary bonds. The trans influence is reflected in the length of the bismuth−element distances, i.e., a shorter secondary bond corresponds to a longer related primary bond, a feature which was considered to be consistent with the use of Bi−X σ^*-antibonding orbitals as acceptor orbitals for a BiX_3 unit.[44,56] In some cases the lengths of secondary and primary bonds are similar, and alternatively, the hypervalent bismuth compounds might be described using the three-center four-electron model,[57] i.e., the use of a single p orbital of bismuth to form two covalent bonds.

With 1−3 donor atoms available for additional interactions, in most cases the resulting coordination polyhedron around the Bi atom becomes ψ-trigonal bipyramidal (seesaw structure) (**5**), ψ-octahedral (square pyramidal) (**6**), or octahedral (**7**), corresponding to 10-Bi-4, 12-Bi-5, and 14-Bi-6 systems, respectively (N-Bi-L designation: N = number of formal valence shell electrons about a Bi atom; L = the number of ligands).[58] However, various degrees of distortion from the ideal polyhedra were reported for particular compounds, e.g., from regular octahedron (**7**) to ψ-pentagonal bipyramid (opened edge) (**8**) or ψ-capped octahedron (opened face) (**9**), and various explanations were given for these distortions.



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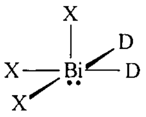

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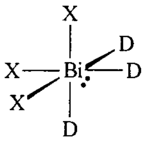

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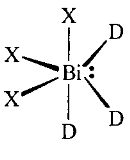

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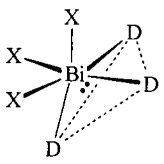

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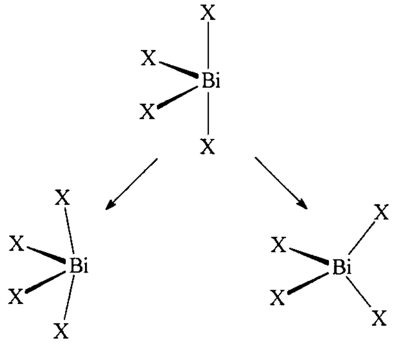
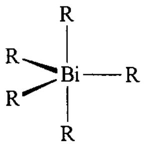
In the cases of four- and five-coordinate bismuth compounds, the geometries generally observed fit with those predicted by the simple VSEPR theory for AB_4E and AB_5E systems, respectively, when a model based on the availability of vacant d orbitals is used to form dsp^3 and d^2sp^3 hybrid orbital sets. Also, the distortions fit with VSEPR theory. Thus, for the AB_4E structure, the equatorial bond angle is less than 120° and the apical groups are displaced toward the equatorial ones as expected for an electrostatic repulsion between the nonbonding lone pair and the bonding pairs of electrons (**10**): Cl−Bi−Cl 175.2° in the chain polymer $[Ph_2BiCl]_n$ and Cl−Bi−N 162.9° in the monomer $[(4\text{-}CH_3C_6H_5)Bi(Cl)(C_6H_4CH_2NMe_2)_2]$,[59,60] O−Bi−O 172° and 159.7° in $[Ph_2Bi\{OC(O)CF_3\}_2]^-$ and $[Bi\{C_6H_4C(CF_3)_2O\}_2]^-$ anions,[61,62] or N−Bi−N 164.8° in $[Bi(C_6H_4CH_2NMe_2)_2]^+$ and O−Bi−O 167.5° in $[Ph_2Bi\{OP(NMe_2)_3\}_2]^+$ cations.[39,63] The constraints imposed by the bidentate ligands in some of the examples given above might account for the strong angular distortion. However, an opposite displacement of the apical groups, i.e., away from the equatorial ones (**11**), was also noted for other 10-Bi-4 compounds, e.g., the monomeric anion $[Cl_2Bi(ML_n)_2]^-$ containing 17-electron organotransition metal fragments attached to bismuth.[64] It is unlikely that the bulkiness of the metal-based ligands on bismuth is the sole reason for this distortion from the usual pseudotrigonal bipyramidal geometry toward a tetrahedral one (e.g., Cl−Bi−Cl angles of 155.6° and 138.5° and M−Bi−M angles of 111.4° and 116.4° in $[Cl_2Bi\{FeCp(CO)_2\}_2]^-$ and $[Cl_2Bi\{MoCp(CO)_3\}_2]^-$, respectively). On the bases of EHMO studies, the authors suggested that π-donation from the organometallic groups in the pseudoequatorial positions may promote the observed structural behavior.[64] An even less distorted tetrahedral environment was reported for the $[Bi\{Co(CO)_4\}_4]^-$ anion (Co−Bi−Co 107.0−112.4°) containing a 10-electron (and therefore "hypervalent") Bi with an apparently stereochemically inactive lone pair.[65,66] The π-acceptor ability of bismuth was also proved by the isolation and structural characterization of analogues of "Menshutkin" complexes of the type (arene)BiX_3 (X = halide or alkoxy groups).[34,67,147,148]



10 **11**

The stereochemical activity of the lone pair at the Bi atom is sometimes questionable. In some cases the lone pair seems to play a considerably smaller role for bismuth than for the more electronegative P, As, or Sb atoms. This is especially obvious for six-coordinate Bi(III) compounds for which several degrees of distortion from the octahedral geometry but also regular octahedra were reported. For example, in the case of inorganic and organometallic bismuth(III) halides and their adducts, there are structures containing regular octahedral coordination as in the $[BiI_6]^{3-}$ anion (stereochemically inactive lone pair at bismuth)[68,69] or exhibiting a C_{2v} distortion as in the $[BiI_4(PMe_2Ph)_2]^-$ anion (possible stereochemically active lone pair localized along one edge of the octahedron resulting in a pseudopentagonal pyramid)[70] or trigonal C_{3v} distortion as in the $[BiCl_6]^{3-}$ anion.[71] Several models, ranging from VSEPR to relativistic molecular orbital calculations, were used to explain the various observed structures, mainly for compounds containing Bi−halide bonds.[21,44,56,71] Moreover, in compounds containing chelating ligands, a small bite might also produce distortions of the coordination geometry. Despite the open questions concerning the role of the lone pair in quite a large number of publications, the stereochemical activity of the lone pair of Bi was given for the observed distortion of the coordination polyhedron, i.e., it was located in an open coordination site, thus completing a coordination geometry suggested by the VSEPR theory. On the other hand, at least two other aspects should also be emphasized: (i) bismuth(III) complexes exhibit coordination numbers up to 10, e.g., Bi(III)−crown-ether adducts,[17,18] and in these cases the attempts to rationalize the coordination polyhedron in terms of a given model raise even more difficulties. (ii) In Bi−transition metal clusters, the bismuth atom may contribute all of its five valence electrons to the bonding in the metal framework.

In compounds containing bismuth in the formal oxidation state +5, the valence shell electrons are all involved mainly in bonds and there is no remaining lone pair at the central metal atom. The most common coordination polyhedron is trigonal bipyramidal, with various degrees of distortion depending on the nature of compound. Thus, for pentaorganobismuth(V) derivatives, the coordination geometries lie between trigonal bipyramidal (**12**) in Me_5Bi[41,72] and square pyramidal (**13**) in Ph_5Bi.[73] Tetrahedral BiC_4 cores (**15**) are observed for bismuthonium $[R_4Bi]^+$ cations, but distortions toward trigonal bipyramidal geometry were noted when donor atoms were present and additional intra- or intermolecular interactions with the central metal atom were established. The Lewis acidic character of the Bi(V) center is also responsible for the possibility of increasing the coordination number to 6, resulting in (distorted) octahedral geometries, e.g., in $[R_6Bi]^-$ (**14**),[41,74] or even more (up to 8 in $[(2\text{-}MeOC_6H_4)_4Bi]^+$, for example[75]).



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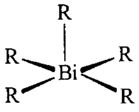

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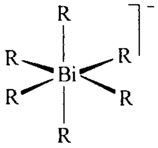

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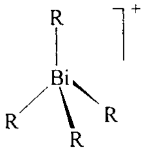

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Generally, the organization of the review will be based on the formal oxidation state of the bismuth atom and the nature of the bismuth−element bonds. It will start with organobismuth compounds exclusively with Bi−C bonds and will continue with derivatives in order of a decreasing number of Bi−C bonds, classified as a function of the nature of the Bi−E bond. A second review will concern inorganic Bi compounds, i.e., without Bi−C bonds. A table format has been usually chosen to summarize the compounds belonging to a particular class, also including some common structural features (e.g., monomeric, dimeric, or supramolecular associations) as well as bond distances and angles around bismuth. A search based on the Cambridge Structure Database as well as the original literature from 1997 to 1998 was used to collect all the available structure determinations by X-ray diffractometry. The structural diagrams were redrawn using the program DIAMOND,[76] on the basis of reported atomic coordinates, and the original atom numbering scheme was usually preserved. In some cases, for clarity and a better view of the coordination environment around bismuth, only parts of the organic groups are represented.

II. Compounds Exclusively with Bi–C Bonds

A. Compounds of the Type R_3Bi and Related Compounds

A general structural feature of tertiary bismuthines of the type R_3Bi and of related compounds is the trigonal pyramidal coordination geometry of the bismuth atom (**16**). This geometry is not particularly surprising because it is in accordance with all popular bonding models. However, a more detailed inspection of the structures of specific molecules reveals interesting variations of the geometric parameters. A list of the bismuthines with known molecular or crystal structures together with the C−Bi−C bond angles and Bi−C bond lengths is given in Table 2. The geometric parameters reflect the different steric requirements of the ligands. Bismuthines with relatively slim ligands (R = CH_3, Ph, 4-MeC_6H_4, C_6F_5, σ-C_5H_5) have bond angles between 90° and 97° and

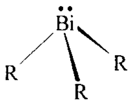

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Table 2. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Triorganobismuthines

	Bi−C	C−Bi−C	ref
Me_3Bi[a]	2.264	96.7	77
$[(Me_3Si)_2CH]_3Bi$	2.306−2.347	102.7−103.0	79
Ph_3Bi[b]	2.237−2.273	92.7−94.7	82
$(4\text{-}MeC_6H_4)_3Bi$	2.25 (av)	93.9−95.3	83
$(4\text{-}Me_2NC_6H_4)_3Bi$	2.22−2.25	93.7−95.6	84
$(C_6F_5)_3Bi$[c]	2.24−2.27	93.4−98.3	85
$(2,6\text{-}F_2C_6H_3)_3Bi$	2.246−2.274	93.3−97.9	86
$[2\text{-}(Me_2NCH_2)C_6H_4]_3Bi$	2.22−2.32	91.4−95.6	87
$[2,6\text{-}(MeO)_2C_6H_3]_3Bi$	2.253−2.278	95.7−101.4	88
Mes_3Bi	2.31−2.32	94.7−107.6	88
$[2,4,6\text{-}(CF_3)_3C_6H_2]_3Bi$	2.356−2.379	105.3−106.5	90
$[2,4,6\text{-}Ph_3C_6H_2]_3Bi$	2.337−2.379	103.7−109.4	91
$(\eta^1\text{-}C_5H_5)_3Bi$	2.34−2.41	91.7−98.0	92
$(4\text{-}MeC_6H_4)_2Bi[C_6H_4(SO_2Bu^t)\text{−}2]$	2.26−2.312	92.8−96.3	93
$O_2S(C_6H_4)_2Bi(C{\equiv}C\text{−}C_6H_4Cl\text{-}4)$	2.211 (alkyne) 2.272; 2.283 (aryl)	87.0 (endocyclic) 90.8; 95.1 (exocyclic)	94
$(biph)_3Bi_2$	2.225−2.284	77.6; 78.2 (endocyclic) 90.9−95.5 (exocyclic)	95
$[(CO)_3Mn(\eta^5\text{-}C_5H_5)]_3Bi$	2.27	93.3	96
$[(CO)_3Cr(\eta^6\text{-}C_6H_5)]_2BiC_6H_5$	2.12−2.26	89−93	97

[a] Gas-phase electron diffraction data. [b] At 143 K. [c] In the adduct $(C_6F_5)_3BiF_2{\cdot}2(C_6F_5)_3Bi$.

Bi−C bond lengths close to 2.27 Å, the sum of the covalent radii of bismuth and carbon. Bulkier ligands [R = $(Me_3Si)_2CH$; 2,4,6-$(CH_3)_3C_6H_2$, 2,4,6-$(CF_3)_3C_6H_2$] may widen the bond angles at the bismuth atom to values between 100° and 107°. In many cases, these ligands are bent away from the base of the trigonal pyramid along the Bi−C axis.

Specific questions arise when homoleptic tertiary aryl bismuthines are inspected. Some of these compounds display considerable distortions of the regular trigonal pyramidal geometry with C_{3v} symmetry of the central BiC_3 unit. The reasons for these distortions are not always well understood. One might expect that the type of rotation of the aryl ligands around the Bi−C axis should be responsible. Aryl rings display enhanced steric requirements mainly in two dimensions. Unequal rotation angles should lead to distortion of the BiC_3 pyramid because the steric repulsion between the aryl ligands should be different, depending on the angles between the ring planes. By contrast, a regular, propeller-like arrangement of the aryl rings should preserve the C_{3v} symmetry of the central BiC_3 pyramid. However, these expectations are not always fulfilled. Another difficulty is to explain why some triarylbismuth compounds have a propeller-like arrangement of the aryl ligands and others do not. In solid-state structures, packing effects may play a major role.

Distortions of the regular trigonal pyramid are expected and occur in triorganobismuth compounds bearing different substituents or in heterocyclic bismuthines. The discussion of structures of specific compounds follows the same order as Table 2, where the compounds are listed according to the type and steric requirements of the ligands.

Only two trialkylbismuthines have been investigated by diffraction methods. Trimethylbismuthine has been studied by gas-phase electron diffraction at 25 °C.[77,78] The C−Bi−C bond angles and the Bi−C bond lengths (see Table 2) are unspectacular. The only reported example of a X-ray crystal structure determination of a trialkylbismuthine has been carried out on $[(Me_3Si)_2CH]_3Bi$.[79] This compound is an excellent example for a bismuthine, where steric effects play an important role. The C−Bi−C angles (102.9°, 103.0°, 102.7°) and the Bi−C bond lengths (2.331, 2.347, 2.306 Å) are large. The bending of the ligands away from the base of the pyramid leads to pairs of dissimilar Bi−C−Si angles (ca. 120°, 106°) at each of the ligands with the larger angles on the side of the ligands nearest to the base of the trigonal pyramid.

Triarylbismuthines have been studied frequently with special focus on the effect of the bulky organic groups. Earlier X-ray work erroneously stated a planar geometry for Ph_3Bi.[80] From the work of Hawley and Ferguson,[81] it became evident that Ph_3Bi has the normal pyramidal geometry with only small deviations from C_{3v} symmetry of the BiC_3 unit (Figure 1). A recent redetermination of the crystal structure at 143 K confirmed the small differences of the Bi−C bond lengths (2.237, 2.268, 2.273 Å) and C−Bi−C bond angles (92.7°, 94.3°, 94.7°).[82] The molecule as a whole possesses no symmetry because of unequal rotation of the phenyl groups about their respective Bi−C bonds. The angles of the planes of the phenyl rings against the plane of the three carbon atoms bonded to the bismuth atom are 38°, 73°, and 42°, each ring being rotated about the appropriate Bi−C bond in the same sense.

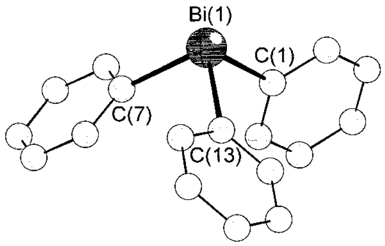


Figure 1. Molecular structure of Ph_3Bi.[82]

Triarylbismuthines with substituted phenyl rings as ligands may be divided into two groups. One group of compounds comprises bismuthines with ligands creating a similar steric situation at the bismuth atom like the phenyl substituent. The compounds (4-$MeC_6H_4)_3Bi$,[83] (4-$Me_2NC_6H_4)_3Bi$,[84] $(C_6F_5)_3Bi$ (in the adduct $(C_6F_5)_3BiF_2{\cdot}2(C_6F_5)_3Bi$, where Bi(V)−F···Bi(III) bridges are present, see also section C.11.),[85] and (2,6-$F_2C_6H_3)_3Bi$[86] belong to this group. An interesting feature of the amino derivative (4-$Me_2NC_6H_4)_3Bi$ is the conjugation of the nitrogen lone pair with the phenyl ring as suggested by the planar geometry of the nitrogen atom.[84] The (2,6-$F_2C_6H_3)_3Bi$ derivative exhibits intramolecular Bi···F contacts (3.115, 3.303 Å) but also two intermolecular Bi···F interactions (3.366 Å) shorter than the sum of the van der Waals radii (3.9 Å), leading to chain polymers in the solid state (Figure 2).[86]

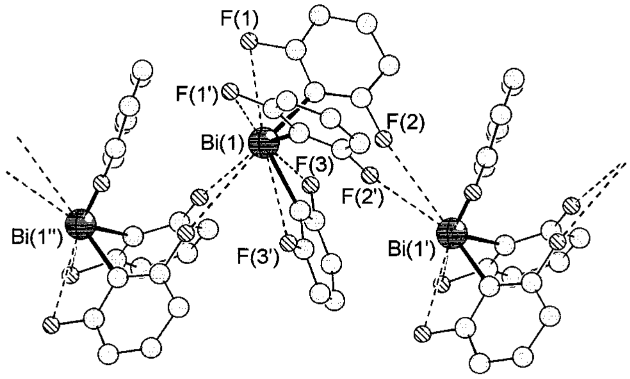


Figure 2. Chain polymeric association in (2,6-$F_2C_6H_3)_3$-Bi.[86]

Particular structural features should be noted in the case of [2-$(Me_2NCH_2)C_6H_4]_3Bi$,[87] which contains ortho-functionalized aromatic ligands with potential ability for additional intramolecular interactions. The crystal contains two very similar, independent molecules. The BiC_3 unit has the normal pyramidal geometry with Bi−C bond lengths and C−Bi−C bond angles similar to those observed for Ph_3Bi. However, secondary intramolecular Bi···N interactions (range 2.97−3.15 Å) are established between all three pendant amino groups and the bismuth center. This results in a very distorted octahedral environment around the metal atom, with a large open face described by the three nitrogen atoms, but the overall C_{3v} symmetry of the molecule is preserved (Figure 3).

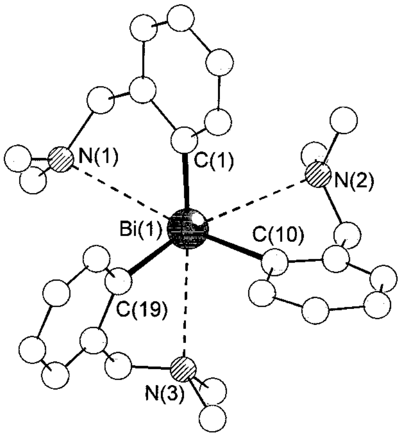


Figure 3. Molecular structure of [2-$(Me_2NCH_2)C_6H_4]_3Bi$.[87]

A second group comprises bismuthines with aryl ligands bearing substituents in *ortho* positions, which display considerable steric effects. One example is [2,6-$(MeO)_2C_6H_3]_3Bi$.[88] The C−Bi−C bond angles of this compound (95.7°, 101.4°, 101.2°) indicate significant distortions from the C_{3v} symmetry of the BiC_3 pyramid. All six oxygen atoms of a molecule exhibit intramolecular through-space interactions to the bismuth center [Bi···O distances lie in the range 2.98−3.41 Å, being inside the van der Waals border (3.9 Å)].

Mesityl groups are sterically even more demanding. In Mes_3Bi,[88,89] the widening of the average bond angles compared to Ph_3Bi is pronounced and there are also considerable distortions from the C_{3v} geometry of the BiC_3 pyramid. A detailed inspection shows that one of the bond angles of Mes_3Bi is very small compared to the other bond angles [C−Bi−C 94.7°, 107.0°, 107.6°]. The individual bond lengths [Bi−C 2.31, 2.32, 2.31 Å] are identical within the experimental error. They are longer than the corresponding values in Ph_3Bi. The steric repulsion leads to bending of the mesityl groups away from the center of the molecule (Bi−C−C 116/127°, 112/128°, 123/117°). The rotation of the mesityl ligands around the Bi−C axis is unequal.

Even more pronounced are steric effects in [2,4,6-$(CF_3)_3C_6H_2]_3Bi$.[90] The bond angles (C−Bi−C 106.1°, 106.5°, 105.3°) are extremely wide, and the bond distances (Bi−C 2.379, 2.367, 2.356 Å) are longer than in any other known tertiary bismuthine. The bending of the aryl ligands is considerable (Bi−C−C 130/116°, 131/116°, 131/114°). The repulsion of the ligands does, however, not result in a major distortion from the C_{3v} symmetry of the BiC_3 pyramid. It is not surprising that short intramolecular Bi···F contacts are present (range 2.87−3.49 Å), but there are also intermolecular Bi···F contacts (3.44 Å) leading to chain polymers in the solid state.

A bismuthine with considerable distortion of the regular pyramidal coordination is [2,4,6-$Ph_3C_6H_2]_3$-Bi,[91] where the range of bond angles (C−Bi−C 104.2°, 103.7°, 109.4°) is wide. The distortion occurs although the bulky aryl groups are arranged in a regular propeller-like fashion. Packing effects and the presence of noncoordinating tetrahydrofuran molecules in the crystal may be responsible for the asymmetry.

One of the most interesting tertiary bismuthines not only from a structural viewpoint is the red crystalline modification of $(^1\eta\text{-}C_5H_5)_3Bi$.[92] This compound is another example for a considerably distorted pyramidal coordination geometry. The metal is directly bonded to the three carbon atoms of the cyclopentadienyl substituents in a monohapto fashion with σ bonds from the metal to the ring carbon atoms. The Bi−C bond lengths (Bi−C 2.34, 2.37, 2.41 Å) are among the largest for tertiary bismuthines, suggesting that bonds between bismuth centers and carbon atoms of the cyclopentadienyl ligands are weaker than those between the bismuth atoms and the phenyl ligands. The bond angles at the bismuth atom are significantly different (Table 2). The molecular packing in the crystal structure of Cp_3Bi is interesting because the bismuth atom of one molecule of Cp_3-Bi is weakly bonded to the cyclopentadienyl ring of

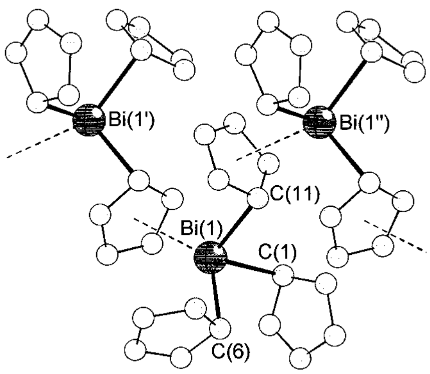


Figure 4. Chain polymeric association in ($^1\eta$-C_5H_5)$_3$Bi.[92]

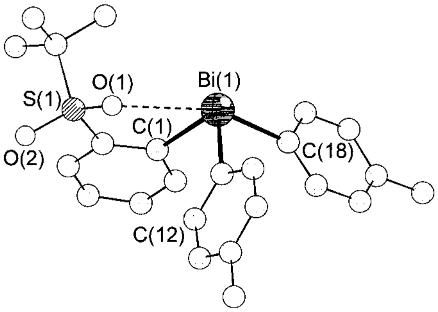


Figure 5. Molecular structure of *p*-$Tol_2Bi(C_6H_4(SO_2Bu^t)$-2].[93]

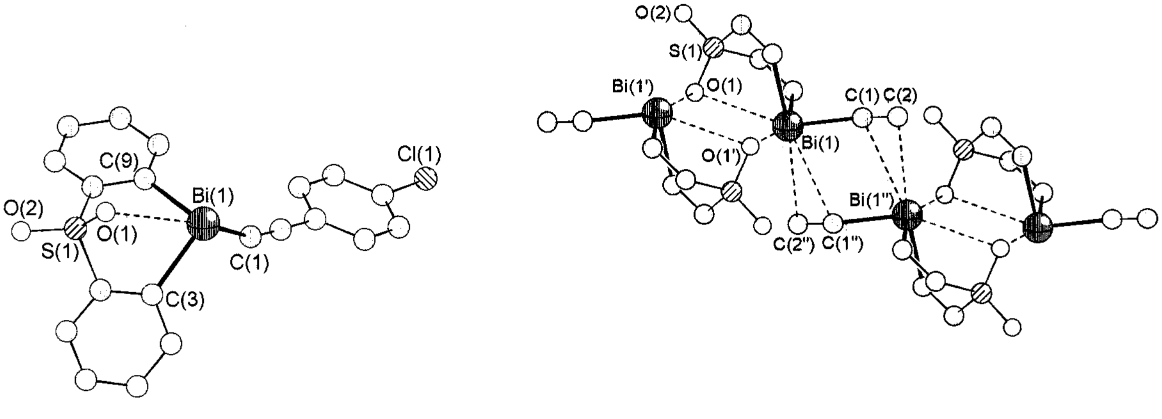
a neighboring Cp_3Bi molecule (intermolecular Bi···C 3.24–3.57 Å) (Figure 4). The intermolecular contacts lead the formation of zigzag chains of the molecules. Interactions of the s-electron lone pair at the bismuth atom in one molecule of Cp_3Bi with the π orbitals of the neighboring molecule may be responsible for the intense red color of the compound.

Only one compound is known as an example of a structure of a tertiary bismuthine of the type $R_2R'Bi$ (R, R′ = aryl), namely, (4-$MeC_6H_4)_2Bi[C_6H_4(SO_2Bu^t)$-2].[93] The intramolecular interaction between one of the oxygen atoms of the Bu^tSO_2 group and the bismuth atom (Bi···O 2.914 Å), opposite an aromatic carbon (C–Bi···O 158°), is a remarkable feature (Figure 5). In view of the different ligands and this Bi···O interaction, it is not surprising that the bond angles at the bismuth atom are not equal (Table 2).

Also, two examples of heterocyclic tertiary bismuthines have been investigated by X-ray diffraction. In $O_2S(C_6H_4)_2Bi(C{\equiv}C{-}C_6H_4Cl$-4), the bismuth atom is a part of a six-membered ring and an alkyne group completes the coordination.[94] The bond length between the bismuth atom and the sp carbon atom is shorter (Bi–C_{alkyne} 2.211 Å) than the bonds between bismuth and the sp^2 carbons (Bi–C_{aryl} 2.283, 2.272 Å). Remarkable features of this compound are a short transannular intramolecular Bi···O distance of 2.979 Å (Figure 6a), and, in addition, a weaker intermolecular Bi···O interaction (Bi···O 3.228 Å) resulting in dimeric associations through O···Bi···O bridges. Also, the fairly marked bending of the acetylene carbon–bismuth bond angle C_{alkyne}–C_{alkyne}–Bi by 160.4° should be noted. The bending is presumably influenced by Bi···C_{alkyne} contacts (3.523 and 3.678 Å) to a neighboring dimeric unit (Figure 6b).

Bismuth atoms as a part of a heterocyclic system are also present in the dinuclear compound (biph)-Bi(biph)Bi(biph) (biph = 2,2′-biphenylene).[95] Here, the Bi–C distances fall within the range reported for other Bi(III) aryl derivatives. The C–Bi–C angles lie in two distinct ranges, namely, 77.6–78.2° and 90.9–95.9°. The smaller values relate to the endocyclic angles and result from the constraints of the chelating 2,2'-biphenylene ligand (Figure 7). There are weak intermolecular Bi···C contacts of 4.7 Å. It is of interest that the molecules are chiral not only in the crystal but also in solution due to the inhibition of the free rotation about the central biphenylene C–C bond.

In two papers, structures of transition metal carbonyl derivatives of tertiary bismuthines with cyclic organic groups on bismuth have been described. One example is $[(CO)_3Mn(\eta^5\text{-}C_5H_4)]_3Bi$ [96] (Figure 8a). The geometry of the bismuth atom is pyramidal, and the $Mn(CO)_3$ groups are in η^5 positions above the planes of the cyclopentadienyl rings. The other example is the complex $[(CO)_3Cr(\eta^6\text{-}C_6H_5)]_2BiC_6H_5$.[97] In this derivative of triphenylbismuth, two of the three phenyl rings are capped with $Cr(CO)_3$ units in a η^6 fashion (Figure 8b). In the complex the geometry of Ph_3Bi is again essentially preserved.



(a) (b)

Figure 6. Molecular structure (a) and intermolecular interactions (b) for $O_2S(C_6H_4)_2Bi(C{\equiv}C{-}C_6H_4Cl$-4) (for clarity, only alkyne carbons and aroma shown in b).[94]

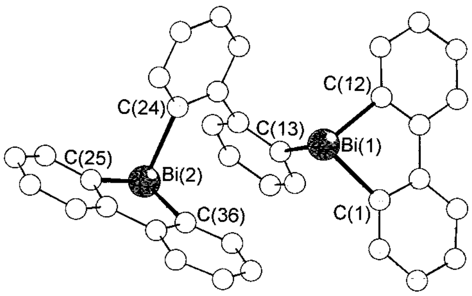
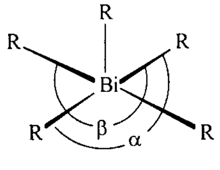


Figure 7. Molecular structure of $(biph)_3Bi_2$.[95]

B. Compounds of the Types R_5Bi, $R_5Bi{\cdot}Donor$, $[R_6Bi]^-$, and a Bismuth Ylide

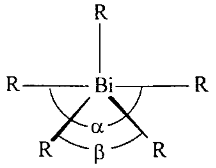
A recent development features the structures of pentamethylbismuth(V) and various pentaarylbismuth(V) derivatives in relation to the colors of the compounds which are unusual for organometallic derivatives of main group metals in the highest oxidation state. Me_5Bi and Ph_5Bi are violet in the crystalline state, but other pentaaryl derivatives are red or yellow. The investigation of the structures has been promoted by the attempt to find a correlation between the colors and the structures.

The coordination geometries of the known R_5Bi compounds lie between the trigonal bipyramidal or square pyramidal arrangement of the organo substituents. The difference of the angles between axial and equatorial bonds, i.e., $\alpha-\beta$ (see diagrams **17** and **18**), is a useful tool for the description of the specific geometry. The $\alpha-\beta$ difference should be 0° in a square pyramid but 60° in a trigonal bipyramid.[98] Many compounds have geometries between these ideal types. An overview of selected geometric parameters, including $\alpha-\beta$ values and colors of pentaorganobismuth(V) compounds with known crystal structures, is given in Table 3.



square pyramid, α−β = 0°

17



trigonal pyramid, α−β = 60°

18

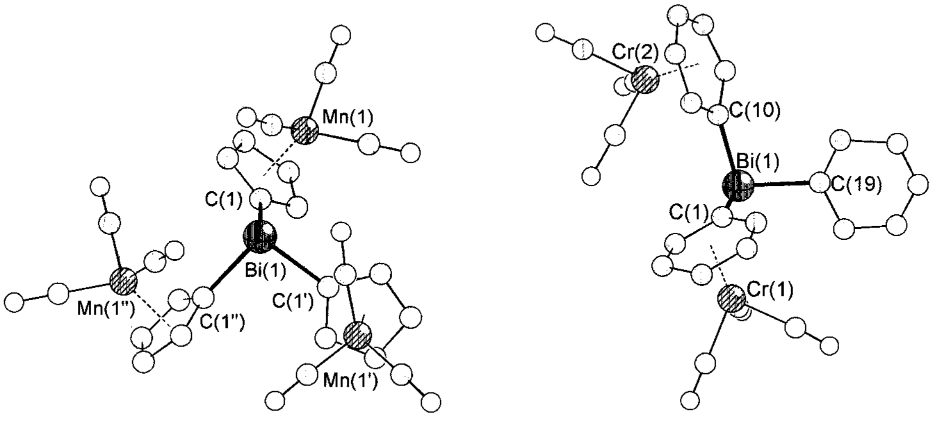
A perfect example of the trigonal bipyramidal arrangement is pentamethylbismuth(V). The structure of the violet crystals was determined at −163 °C. Unlike other trigonal bipyramidal molecules of the type Me_5E ($E = As, P, Sb$), the axial bonds of Me_5Bi are not significantly longer than the equatorial bonds. The repulsion of the axial methyl substituents is possibly responsible for the usual elongation of the axial bonds. In the case of Me_5Bi, the axial bonds are separated by the large Bi atom and hence the repulsion may be diminished (Figure 9).[41,72]

The trigonal bipyramidal structure of Me_5Bi is not rigid in solution. In the ^1H NMR spectrum of Me_5Bi, even at −90 °C the methyl groups are equivalent. This indicates that the methyl groups change positions rapidly, presumably according to the Berry pseudorotation mechanism. Ab initio MO calculations on Me_5Bi suggest that the energy of the square pyramidal configuration is 10.5 kJ mol^{-1} below the energy of the trigonal bipyramidal configuration.[99]

The only example for a pentaarylbismuth(V) derivative with (distorted) trigonal bipyramidal geometry in the crystalline state is the orange compound $(4\text{-}MeC_6H_4)_3(2\text{-}FC_6H_4)_2Bi$ (Figure 10).[100] According to the usual rules for the apicophilicity of the more electronegative ligands in trigonal bipyramidal molecules, the ortho fluorophenyl substituents possess the axial positions.

The violet crystals of Ph_5Bi consist of molecules with an almost regular square pyramidal geometry (Figure 11). The four basal bonds are significantly longer than the axial bond (Table 3). The basal phenyl groups are orientated propeller like, i.e., twisted in the same direction.[73]

Another violet compound with a square pyramidal structure is $Ph_3(2\text{-}FC_6H_4)_2Bi$.[100] The axial position is occupied by one of the phenyl groups. The two phenyl and two *ortho*-fluorophenyl groups in the base are in trans positions. The structure of penta-*p*-tolylbismuth was determined on the violet-red adduct $(4\text{-}MeC_6H_4)_5Bi{\cdot}LiCl{\cdot}2THF$.[85] It may be affected by the presence of THF and LiCl. The coordination is between trigonal bipyramidal and square pyramidal, but closer to the latter.



(a) (b)

Figure 8. Molecular structures of (a) $[(CO)_3Mn(\eta^5\text{-}C_5H_4)]_3Bi$[96] and (b) $[(CO)_3Cr(\eta^6\text{-}C_6H_5)]_2BiC_6H_5$.[97]

Table 3. Geometry and Comparative Interatomic Distances (Å) of Pentaorganobismuth(V) Compounds

	Bi−C$_{axial}$	Bi−C$_{equatorial}$	α−α (deg)	color	ref
Trigonal Bipyramidal Compounds (Ideal: α−β = 60°)					
Me_5Bi	2.28	2.27; 2.23	60	violet	41
$(4\text{-}MeC_6H_4)_3(2\text{-}FC_6H_4)_2Bi$	2.423; 2.358	2.134−2.217	45.4	orange	100
Square Pyramidal Compunds (Ideal: α−β = 0°)					
$(4\text{-}FC_6H_4)_3(C_6F_5)_2Bi$	2.22	2.22−2.44	5.1	yellow	98
$Ph_3(2,6\text{-}F_2C_6H_3)_2Bi$ (molecule I)	2.26	2.25−2.38	11.5	orange	98
(molecule II)	2.23	2.21−2.38	17.0		
Ph_5Bi	2.221	2.322−2.329	13.2	violet	73
$(4\text{-}MeC_6H_4)_3(C_6F_5)_2Bi$	2.18	2.23−2.44	16.0	yellow	98
$(4\text{-}MeC_6H_4)_3(2,6\text{-}F_2C_6H_3)_2Bi$	2.20	2.25−2.34	17.5	orange-red	85
$Ph_3(2\text{-}F{-}C_6H_4)_2Bi$	2.216	2.284−2.363	19.2	violet	100
$(4\text{-}MeC_6H_4)_5Bi{\cdot}LiCl{\cdot}2THF$	2.20	2.28−2.36	26.0	violet-red	85
$Ph_3(biph)Bi$ (molecule I)	2.14	2.23−2.32	28.8	orange-red	85
(molecule II)	2.23	2.18−2.29	21.7		

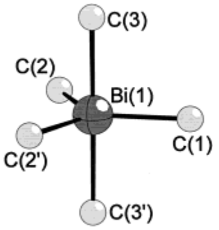


Figure 9. Molecular structure of Me_5Bi.[41]

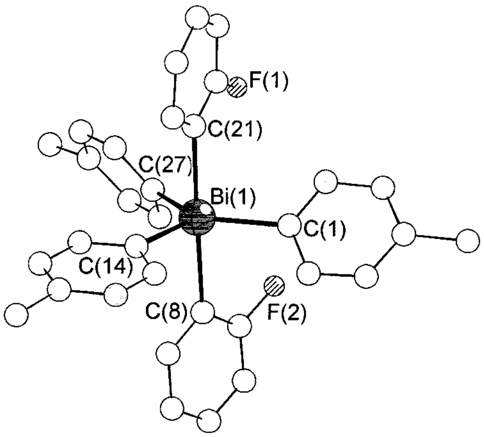


Figure 10. Molecular structure of $(4\text{-}MeC_6H_4)_3(2\text{-}FC_6H_4)_2Bi$.[100]

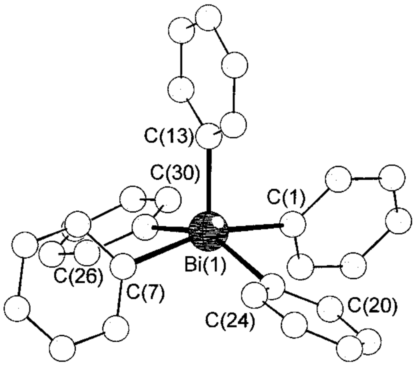


Figure 11. Molecular structure of Ph_5Bi.[73]

In the biphenylene derivative $Ph_3(biph)Bi$, the geometry is also distorted square pyramidal (Figure 12).[85] The crystal contains two independent molecules with different degrees of distortion (Table 3); in both of them the $BiC_{12}H_8$ part of the molecule is almost planar with the 2,2′-biphenylene ligand in a double basal position.

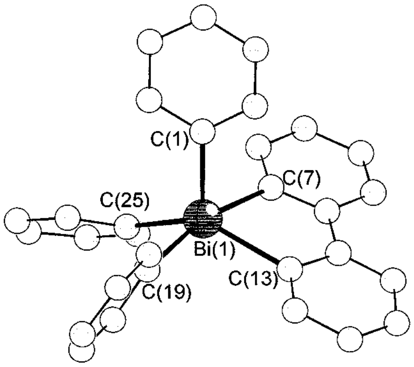


Figure 12. Molecular structure of $Ph_3(biph)Bi$ (molecule I).[85]

More or less distorted square pyramidal arrangements are also adopted in various structures of pentacoordinated bismuth compounds bearing different aryl and fluoroaryl substituents (Table 3). Examples are $(4\text{-}MeC_6H_4)_3(C_6F_5)_2Bi$, $(4\text{-}FC_6H_4)_3(C_6F_5)_2Bi$ (exhibiting the less distorted square planar BiC_5 core),[98] and $(4\text{-}MeC_6H_4)_3(2,6\text{-}F_2C_6H_3)_2Bi$,[85] where the more electronegative pentafluorophenyl or 2,6-difluorophenyl groups occupy basal positions trans to each other. Crystals of $Ph_3(2,6\text{-}F_2C_6H_3)_2Bi$ contain two independent molecules.[98] In both molecules the 2,6-difluorophenyl groups possess basal positions trans to each other. As a general behavior, the Bi−C bonds to the difluorinated or perfluorinated ligands are significantly longer (ca 0.1−0.2 Å) than those to the phenyl or monofluorinated phenyl groups.

The relationships between the structure and color of the pentaorganobismuth compounds are not straightforward.[72] Ab initio calculations on the hypothetical BiH_5 also considering relativistic effects revealed that the relativistic contraction leads to an energetic stabilization of the LUMO where the contribution of a bismuth atomic orbital is important. The HOMO is mainly a ligand orbital. The HOMO−LUMO separation for the tetragonal symmetry of the square pyramidal arrangement should be one-half of that of the trigonal bipyramidal symmetry.[100] One could expect that the violet compounds are square pyramidal, and the yellow or red compounds should be trigonal bipyramidal. The violet color of square pyramidal Ph_5Bi could be explained on the basis of this model. However, as shown in Table 3, Ph_5Bi is an exception and many other pentaarylbismuth derivatives are red or yellow despite the fact that they adopt the (distorted) tetragonal structure in the solid state. On the other hand, Me_5Bi is violet despite its trigonal bipyramidal geometry. These results show that the differences in the electron-withdrawing or electron-releasing effects of the substituents are equally important for the HOMO–LUMO separation. The violet color of Me_5Bi may result from the strong electron-releasing effects of the methyl groups.[72]

When Ph_5Bi is dissolved in pyridine, a blue crystalline 1:1 adduct, $Ph_5Bi{\cdot}NC_5H_5$, with an octahedral structure is formed (Figure 13).[74] The Ph_5Bi moiety has a square pyramidal structure as in the unsolvated molecule, but the angles C–Bi–C between the trans basal phenyl groups are closer to 180° (170.0°, 154.8°). The Bi···N contact is quite long (3.21 Å). From a solution of Ph_5Bi in pyridine, a second crystalline phase of the composition $Ph_5Bi{\cdot}3NC_5H_5$ precipitates. The crystals contain the 1:1 adduct and two additional noncoordinating pyridine molecules.[74]

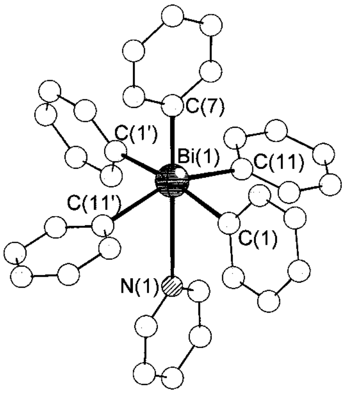


Figure 13. Molecular structure of $Ph_5Bi{\cdot}NC_5H_5$.[74]

An octahedral coordination is also observed in the structure of the homoleptic anions $[Me_6Bi]^-$ (Figure 14) and $[Ph_6Bi]^-$. Both anions are obtained as yellow crystalline lithium salts $Li(THF)_4[Me_6Bi]$[41] and $Li(THF)_4[Ph_6Bi]{\cdot}2THF$,[74] with THF molecules incorporated. In $[Me_6Bi]^-$, the mean Bi–C bond length is 2.33 Å.[41] The Bi–C bond lengths in $[Ph_6Bi]^-$ lie between 2.324 and 2.364 Å, but the octahedral BiC_6 core is slightly distorted as reflected in the C–Bi–C angles (cis C–Bi–C 87.8–92.4°, trans C–Bi–C 177.5–177.9°).[74]

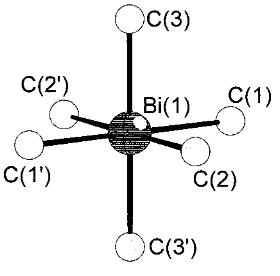


Figure 14. Structure of the $[Me_6Bi]^-$ anion.[41]

Only one bismuth ylide, namely the oxo derivative $Ph_3Bi{=}C[C(O)CH_2]_2CMe_2$, was characterized by X-ray structure analysis (Figure 15).[101] The bismuth atom has a distorted tetrahedral configuration with C_{Ph}–Bi–C_{Ph} and C_{Ph}–Bi=C bond angles in the range 101.6–103.1° and 111.8–119.6°, respectively. The most interesting features of this compound are the carbon–bismuth bonds. The bond length of Bi=C, 2.16 Å, is only slightly shorter than the single-bond length of Bi–C_{Ph} (2.21–2.22 Å). These data indicate a large degree of ionic character as Bi^+–C^- or Bi^+–C=C–O^-, with little double-bond character between bismuth and the ylidic carbon atom.

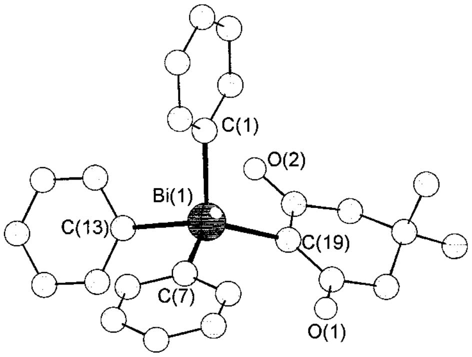
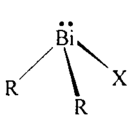


Figure 15. Molecular structure of $Ph_3Bi{=}C[C(O)CH_2]_2CMe_2$.[101]

III. Compounds with Bi–C Bonds and Other Bi–Element Bonds

A. Compounds of the Type R_2BiX (X = Halogen) and $R_2BiX{\cdot}D$ (D = Donor)

The structural chemistry of diorganobismuth(III) halides reflects the Lewis amphoteric character of this class of compounds. There are Lewis acidic sites at the bismuth atoms and Lewis basic centers at the halogen atoms. For this reason, the compounds tend to form coordination polymers in the solid state, with trans bismuth–halogen bonds and ψ-trigonal bipyramidal coordination. The tendency of diorganobismuth(III) halides to achieve this geometry is also observed when donor atoms other than halides are available. It is a general rule that the additional Bi–element dative bond lies trans to the bismuth–halogen bond (**20**), which is significantly lengthened (Table 4) in comparison with the corresponding sum of Bi and halogen covalent radii. In some cases, the bond lengths in the halide–bismuth–donor atom system suggest the formation of a three-center 4-electron bond and the compounds can be described as hypervalent 10-Bi-4 systems. A tendency to increase the coordination number even more at bismuth through a second weak dative interaction, thus resulting in a distorted overall square pyramidal environment (**21**), was also featured in some compounds. This behavior is quite common for organobismuth dihalides for which two strong dative interactions trans to the halogen atoms are often established. Monomeric molecular structures (**19**) occur for diorgano-



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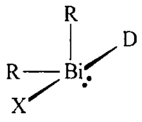

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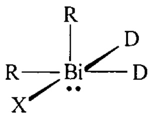

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Table 4. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for R_2BiX (X = Halide) and Their Adducts

		Bi−X[a]	Bi−E[a]	Bi−C	X−Bi−X (or E)	C−Bi−C	ref
Ph_2BiCl[b]	Bi(1) atom	2.763		2.124	175.2 [Cl−Bi(1)−Cl]	101.0	59
		2.746		2.144	175.6 [Cl−Bi(2)−Cl]	102.9	
Mes_2BiBr	Bi(2) atom	2.696; 3.795[c]		2.268; 2.270	156.1 (Br−Bi···Br)	98.0	102
$[2,4,6\text{-}(CF_3)_3C_6H_2]_2BiCl$		2.463		2.338, 2.356		106.9	90
$[(Me_3Si)_2CH]_2BiCl$		2.530		2.273, 2.277		100.7	103
$(1,2,4\text{-}Bu^t{}_3C_5H_2)_2BiCl$		2.63		2.62−2.80			104
$[2\text{-}(Me_2NCH_2)C_6H_4]_2BiCl$		2.667	2.570; 3.047	2.258; 2.264	165.1 (Cl−Bi−N)	95.1	38
$[(2\text{-}NC_5H_4)(Me_3Si)_2C][(2\text{-}NC_5H_4)(Me_3Si)C{=}CHCH_2]BiCl$		2.646	2.485; 2.95	2.23; 2.41	156.7 (Cl−Bi−N)	108.3	105
$(4\text{-}MeC_6H_4)[2\text{-}(Me_2NCH_2)C_6H_4]BiCl$		2.700; 3.94[c]	2.525	2.234; 2.246	162.9 (Cl−Bi−N)	93.7	60
$(4\text{-}MeC_6H_4)[2\text{-}(Bu^tSO_2)C_6H_4]BiCl$		2.556; 3.622[c]	2.592	2.247; 2.288	163.9 (Cl−Bi−O)	94.4	93
$Ph[2\text{-}\{Me_2N(Me)CH\}C_6H_4]BiCl$	*trans* isomer	2.646; 3.696[c]	2.55	2.25; 2.30	162.7 (Cl−Bi−N)	95.6	35
	cis isomer	2.634; 3.717[c]	2.57	2.16; 2.26	161.7 (Cl−Bi−N)	98.0	
$(4\text{-}MeC_6H_4)[2\text{-}(O{=}CMe)C_6H_4]BiBr$		2.746; 3.922[c]	2.519	2.24; 2.26	160.8 (Br−Bi−O)	95.1	36
$(4\text{-}ClC_6H_4)[2\text{-}\{Me_2N(Me)CH\}C_5H_3FeCp]BiI$		2.969; 3.990[c]	2.71	2.19; 2.24	161.4 (I−Bi−N)	95.8	40
$Ph_2BiBr{\cdot}THF$		2.741	2.589	2.229; 2.272	173.5 (Br−Bi−O)	98.2	106
$Mes_2BiBr{\cdot}OSPh_2$		2.749	2.64	2.25; 2.28	176.1 (Br−Bi−O)	107.7	107
$Mes_2BiBr{\cdot}OP(NMe_2)_3$		2.769	2.631	2.24; 2.26	171.7	102.5	107

[a] Bond distances and interactions, X = Cl, Br; E = N, O. [b] Two independent Bi centers are present in the unit cell, and the two Bi−Cl bonds for a bismuth atom are equal. [c] Intermolecular interaction.

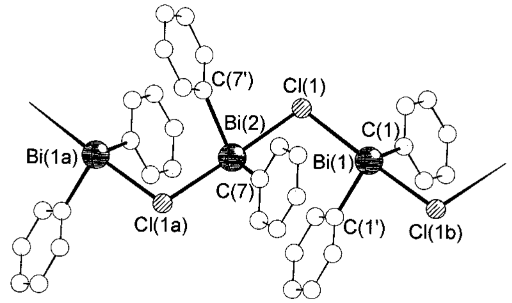


Figure 16. Polymeric association in the crystal of Ph_2BiCl.[59]

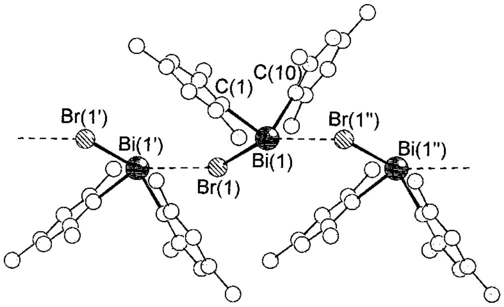


Figure 17. Polymeric association in the crystal of Mes_2BiBr.[102]

bismuth(III) halides only when bulky substituents are used. Diphenylbismuth(III) chloride is an example of a polymeric form.[59] The solid-state structure consists of zigzag chains with bent chloro bridges (Bi−Cl−Bi 100.6°) between the bismuth atoms (Figure 16). The Bi−Cl bond distances within the chain are almost equal, and the Cl−Bi−Cl units are close to linearity. The resulting coordination at the bismuth atoms is ψ-trigonal bipyramidal.

The structure of dimesitylbismuth(III) bromide is midway between the polymeric and monomeric form.[102] The influence of the bulky mesityl substituents leads to distinct molecular units, which are associated through intermolecular Bi···Br contacts (3.795 Å), significantly shorter than the sum of the van der Waals radii (4.35 Å). In the molecular unit, bismuth is in a trigonal pyramidal environment. When the additional Bi···Br interactions are considered, the geometry at the bismuth centers becomes distorted ψ-trigonal bipyramidal, with the halide atoms from the apical positions displaced away from the equatorial ones (Figure 17).

When the bulk of the substituents is further increased like in $[2,4,6\text{-}(CF_3)_3C_6H_2]_2BiCl$[90] and $[(Me_3Si)_2CH]_2BiCl$ (Figure 18),[103] there are no short intermolecular contacts. The crystals consist of monomeric dialkylbismuth halide molecules with a trigonal pyramidal geometry at the bismuth centers (C−Bi−Cl 87.8°, 99.5°; C−Bi−C 106.9° for $[2,4,6\text{-}(CF_3)_3C_6H_2]_2BiCl$ and C−Bi−Cl 95.8, 100.7°; C−Bi−C 100.7° for $[(Me_3Si)_2CH]_2BiCl$, respectively).

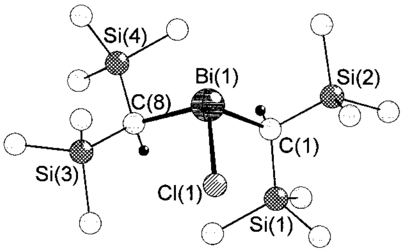


Figure 18. Molecular structure of $[(Me_3Si)_2CH]_2BiCl$.[103]

Monomeric diorganobismuth chloride molecules exist also with substituted cyclopentadienyl groups. One example is the sandwich complex $(1,2,4\text{-}Bu^t{}_3C_5H_2)_2BiCl$ where the ligands adopt approximately η^3-bonding modes, with nonparallel cyclopentadienyl rings (Cp_{cent}−Bi−Cp_{cent} 145.4°) (Figure 19).[104]

Another general method to stabilize monomeric molecular units is to add donors to the bismuth centers, thus increasing the coordination to a ψ-trigonal bipyramidal environment with the donor atoms and the halogen atoms in apical sites.

Especially effective is the use of chelating aryl substituents bearing nitrogen or oxygen donor groups that offer the possibility to form five-membered heterocycles through internal coordination. The most straightforward substituent for this purpose is possibly the 2-(dimethylamino)methylphenyl group. Indeed, monomeric compounds were obtained when two such potential chelating ligands are attached to the bismuth center like in $[2\text{-}(Me_2NCH_2)C_6H_4]_2BiCl$.[38]

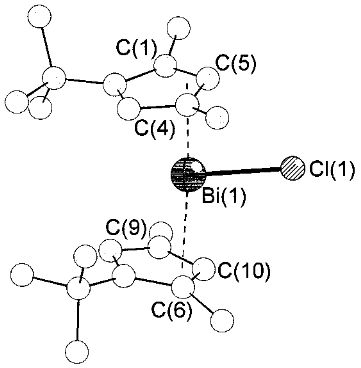


Figure 19. Molecular structure of $(1,2,4\text{-Bu}^t{}_3C_5H_2)_2BiCl$ (for clarity, only the carbons directly attached to C(1), C(4), C(6), and C(9) atoms of the cyclopentadienyl rings are shown for the corresponding Bu^t groups).[104]

Here, one donor nitrogen atom is tightly bound to bismuth trans to the chlorine, thus occupying the apical positions of a distorted, equatorial vacant trigonal bipyramid (N−Bi−Cl 165.1°). The nitrogen atom of the second ligand unit has only a weaker interaction [Bi(1)···N(2) 3.047 Å] with the bismuth atom, being placed in a position trans to the Bi−C bond of the other organic ligand moiety (Figure 20a). The resulting overall environment for the metal atom is square pyramidal (or ψ-octahedral). Instead of amines, the nitrogen atom of a pyridine ring may also coordinate at the bismuth center, i.e., in $[(2\text{-}NC_5H_4)(Me_3Si)_2C][(2\text{-}NC_5H_4)(Me_3Si)C{=}CHCH_2]BiCl$,[105] which contains a four-membered cycle (Figure 20b). The overall structural behavior for this compound is similar to that of $[2\text{-}(Me_2NCH_2)C_6H_4]_2BiCl$, but the distortion of the ψ-trigonal bipyramidal environment is even higher due to the ring constraint. Again, an additional weak, intramolecular Bi···N interaction [Bi(1)···N(2) 2.95 Å] is present.

When only one 2-(dimethylamino)methylphenyl ligand is attached to bismuth as in the *para*-tolyl derivative $(4\text{-}MeC_6H_4)[2\text{-}(Me_2NCH_2)C_6H_4]BiCl$,[60] again a three-center 4-electron bond is formed over the N, Bi, and Cl atoms, which results in a ψ-trigonal bipyramidal geometry of the molecular unit (Figure 21a). However, a closer check of the crystal packing reveals the presence of pairs of enantiomers (the bismuth center is chiral) held together through Bi−Cl···Bi bridges. The additional very weak Bi···Cl intermolecular interaction (3.94 Å, cf. the sum of the van der Waals radii is 4.2 Å) lies trans to the Bi−C bond of the chelating ligands, leading again to an overall square pyramidal environment for both Bi atoms of the dimer association (Figure 21b).

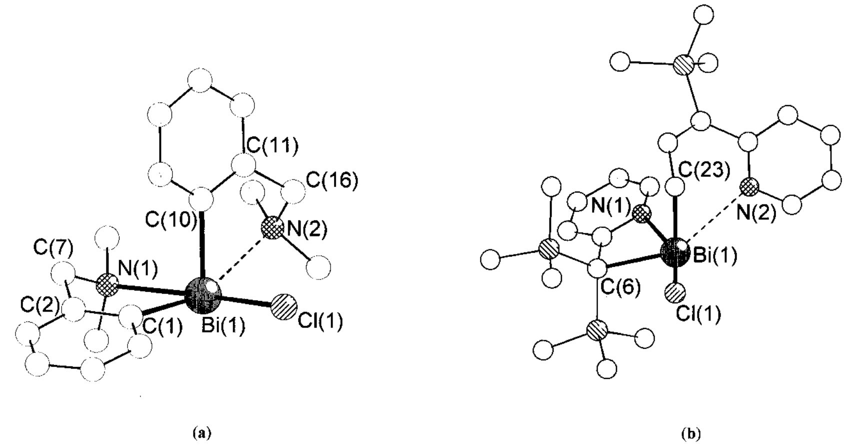


Figure 20. Molecular structure of (a) $[2\text{-}(Me_2NCH_2)C_6H_4]_2BiCl$[38] and (b) $[(2\text{-}NC_5H_4)(Me_3Si)_2C][(2\text{-}NC_5H_4)(Me_3Si)C{=}CHCH_2]BiCl$.[105]

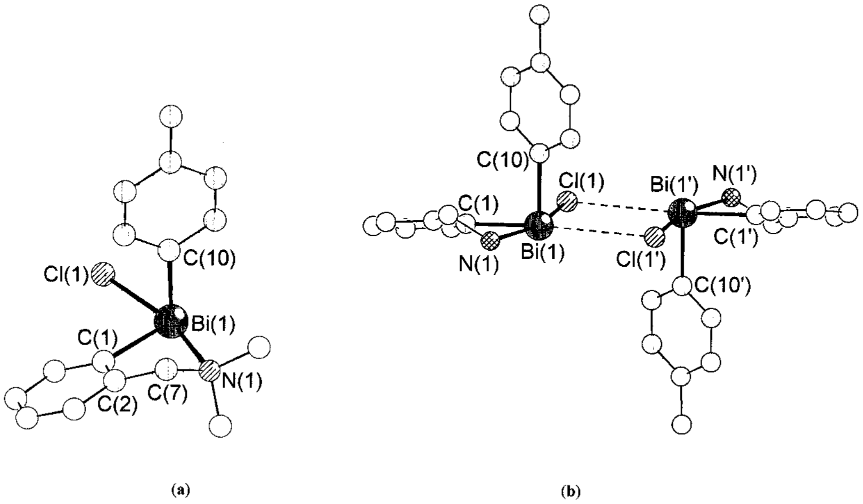


Figure 21. Molecular structure of $(4\text{-}MeC_6H_4)[2\text{-}(Me_2NCH_2)C_6H_4]BiCl$ (a) and the loose dimer association formed in the crystal (b).[60]

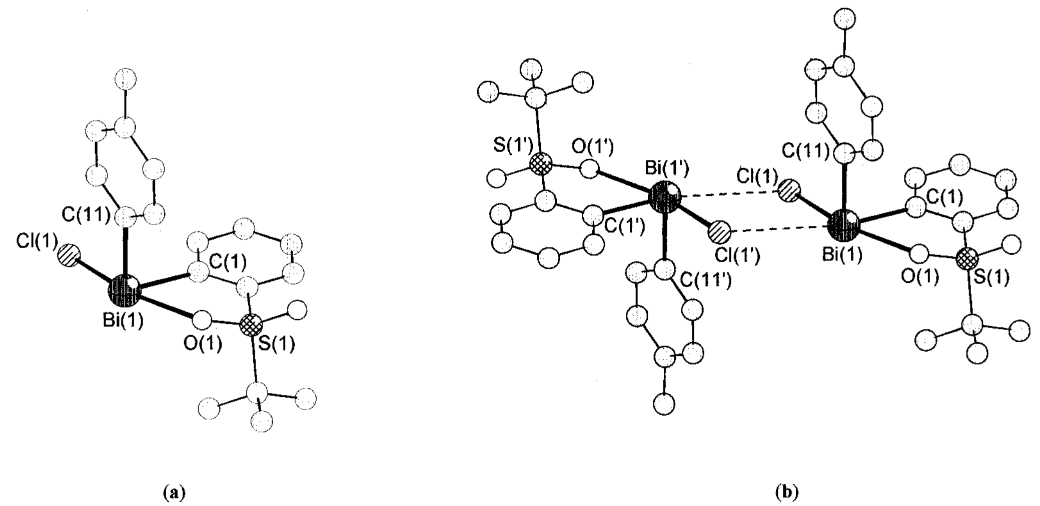


Figure 22. Molecular structure of (4-MeC_6H_4)[2-(Bu^tSO_2)C_6H_4]BiCl (a) and its dimeric association in the crystal (b).

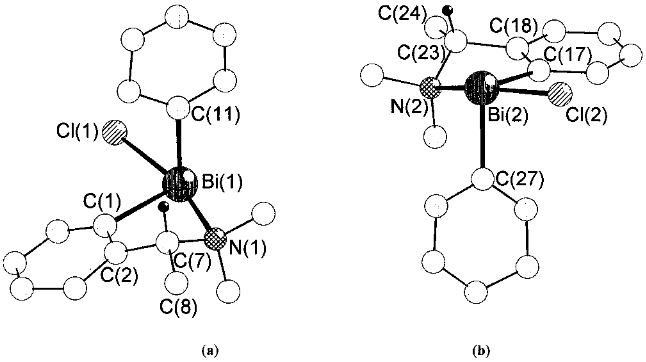


Figure 23. Structure of the trans/cis diastereoisomers of Ph[2-{$Me_2N(Me)CH$}C_6H_4]BiCl.[35]

A similar structural behavior was found for (4-MeC_6H_4)[2-(Bu^tSO_2)C_6H_4]BiCl, which contains a protecting sulfonyl group (Figure 22).[93] The five-membered chelate cycle is coplanar with the chlorine atom and the *ortho*-phenyl group. In the molecular unit the Bi−Cl bond is significantly shorter (2.556 Å) than that in (4-MeC_6H_4)[2-(Me_2NCH_2)C_6H_4]BiCl (2.700 Å)[60] but longer than that in the monomeric, pyramidal [2,4,6-$(CF_3)_3C_6H_2$]$_2$BiCl (2.463 Å).[90] On the other hand, the pairs of enantiomers are held together through stronger Bi···Cl intermolecular interactions (3.622 Å) than in the above amino derivative.

Another example for a diarylbismuth(III) chloride, stabilized by internal nitrogen coordination, is Ar(Ph)BiCl, where Ar = 2-[(R)-1-(dimethylamino)ethyl]phenyl.[35] The molecular structure resembles that of the related amino derivative (4-MeC_6H_4)[2-(Me_2NCH_2)C_6H_4]BiCl,[60] with strong intramolecular Bi−N interactions. However, in this compound both the chelating ligand and the bismuth center are chiral and the asymmetric unit contains a pair of independent molecules with different configuration at the metal atom. The benzylic methyl and equatorial phenyl group are placed in trans (Figure 23a) and cis (Figure 23b) positions, respectively, with respect to the five-membered chelate ring.

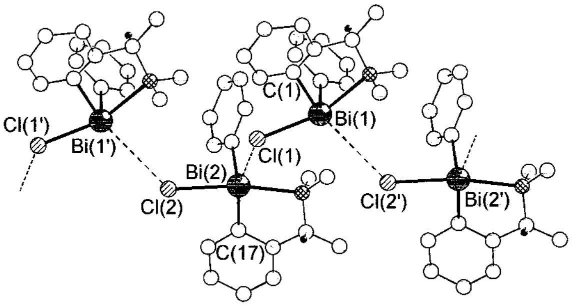


Figure 24. Polymeric association in the crystal of Ph[2-{$Me_2N(Me)CH$}C_6H_4]BiCl.[35]

In the crystal, however, in contrast to (4-MeC_6H_4)[2-(Me_2NCH_2)C_6H_4]BiCl, infinite chains are formed by alternating pairs of the trans/cis isomers linked together through Bi···Cl···Bi bridges, with intermolecular bismuth−chlorine distances of 3.696 and 3.717 Å (Figure 24).

A further example of association in polymeric chains through weak intermolecular bismuth−halogen interactions trans to a bismuth−carbon bond is the hypervalent (4-MeC_6H_4)[2-(O=CMe)C_6H_4]BiBr,[36] which contains an internal coordination of the oxygen atom of an acyl group, thus resulting in a five-membered ring (Figure 25).

Recently, a stereoselective synthesis of the first optically pure diorganobismuth(III) halide, i.e., Ar(4-ClC_6H_4)BiI where Ar = 2-[(*R*)-1-(dimethylamino)ethyl]ferrocenyl, was achieved using the planar chirality of ferrocene, and the molecular structure was established by X-ray diffractometry.[40] The bismuth center has a distorted ψ-trigonal bipyramidal environment, with the nitrogen and iodine atoms in apical positions (N−Bi−I 161.4°) (Figure 26). The strong intramolecular Bi−N coordinative bond is, however, significantly longer (2.71 Å) than those observed in the related chloride derivatives (Table 4). Weak intermolecular Bi···I interactions (3.990 Å) lead to a chain polymeric association of the molecules in the solid state.

Not only the use of bulky organic ligands or intramolecular base coordination but also the addition of external donor molecules may result in a monomeric molecular structure. This behavior was established for various 1:1 adducts of diarylbismuth(III) bromides with monodentate oxygen donor ligands (Table 4). In all the complexes of this type investigated so far by X-ray diffraction, namely, $Ph_2BiBr\cdot$

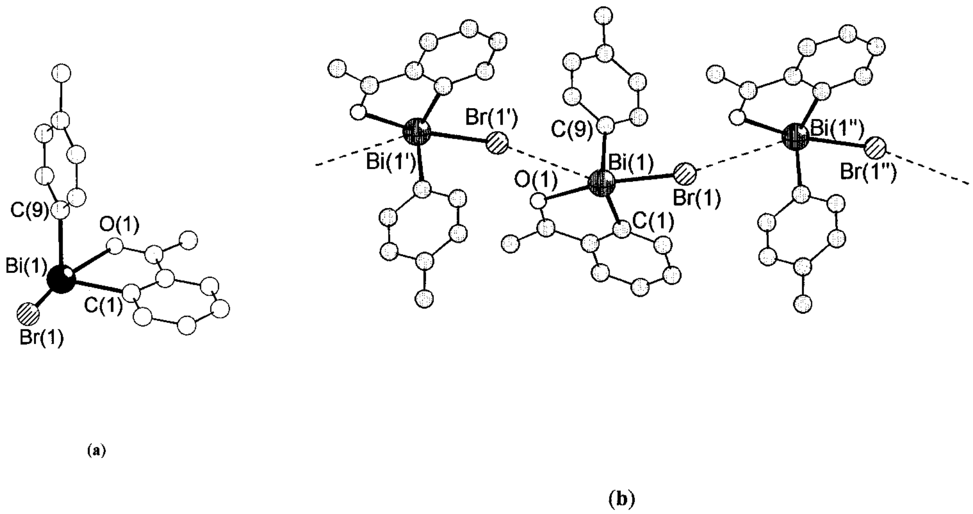


Figure 25. Molecular structure of $(4\text{-}MeC_6H_4)[2\text{-}(O{=}CMe)C_6H_4]BiBr$ (a) and its polymeric association in the crystal (b).[36]

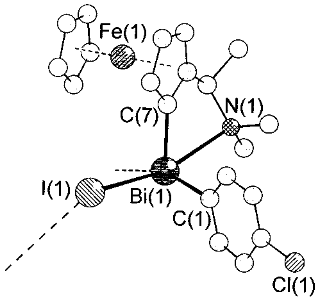


Figure 26. Molecular structure of $(4\text{-}ClC_6H_4)[2\text{-}\{Me_2N\text{-}(Me)CH\}C_5H_3FeCp]BrI$.[40]

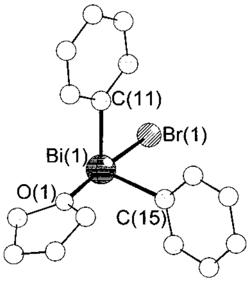
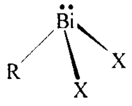


Figure 27. Molecular structure of $Ph_2BiBr{\cdot}THF$.[106]

THF,[106] $Mes_2BiBr{\cdot}OSPh_2$, and $Mes_2BiBr{\cdot}OP(NMe_2)_3$,[107] the coordination at the bismuth centers is enlarged to four, the oxygen atom of the donor ligands and the bromine atom occupying the axial sites of a distorted ψ-trigonal bipyramidal C_2BiBrO core (Figure 27). Significant additional intermolecular Bi···Br interactions, shorter than the sum of the corresponding van der Waals radii, are not present in the crystal of any of these 1:1 adducts.

B. Compounds of the Type $RBiX_2$ (X = Halogen) and $RBiX_2{\cdot}D$ (D = Donor)

The structures of the few organobismuth(III) dihalides or related adducts that have been studied exhibit considerable diversity. As a consequence of the pronounced Lewis acidity of the bismuth centers and the Lewis basic behavior of the halogen substituents, there is a remarkable tendency to form oligomers or polymers with one or both halogen atoms being involved in strong Bi−X−Bi bridges (Table 5). Polymers are formed with slim organic ligands. Sterically protecting organo substituents favor the formation of smaller aggregates, mainly dimers. No monomeric molecular structures (**22**) with three-coordinate bismuth occur for organobismuth(III) dihalides, even when bulky substituents are used. The



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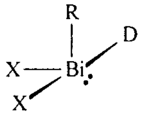

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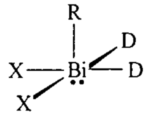

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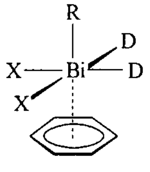

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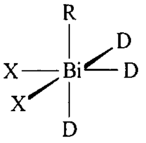

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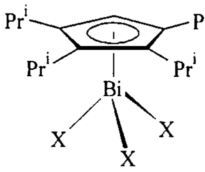

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Lewis acidity of organobismuth dihalides is also responsible for the formation of adducts with oxygen or nitrogen donors, which have different degrees of association as well. The most common coordination geometries around bismuth are ψ-trigonal bipyramidal (**23**) or square pyramidal (**24**) with the Bi−element dative bonds lying trans to bismuth−halogen bonds. In both cases, for some aromatic derivatives additional weak arene···Bi interactions are established, thus increasing the coordination number to 5 and 6, respectively (e.g., **25**).[106,108−110] An octahedral environment around the metal center (**26**) is also achieved through intramolecular coordination in organobismuth dihalides with organic groups bearing a pendant arm with a potential donor. Particular coordination polyhedra, i.e., distorted tetrahedron (**27**), are present in some dimeric (substituted-cyclopentadienyl)bismuth dichlorides.[104]

Examples for extended one-dimensional chainlike structures are alkylbismuth diiodides $RBiI_2$ (R = Me,[21] Et, Bu^n [111]). The bismuth atoms are in a square pyramidal environment, with four iodine atoms form-

Table 5. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for RBiX$_2$ (X = Halide) and Their Adducts

		Bi–X^a	Bi–E^a	Bi–C	X–Bi–X (or E) (trans)	ref
MeBiI$_2^b$	Bi(1) atom	3.087; 3.128		2.29	176.1 (I–Bi–I)	21
	Bi(2) atom	3.086; 3.122		2.26	175.1 (I–Bi–I)	
EtBiI$_2$		3.107; 3.108		2.32	179.0 (I–Bi–I)	111
Bu^{n}BiI$_2$		3.088; 3.134		2.31	178.1 (I–Bi–I)	111
MeBiCl$_2$		2.741; 2.755; 3.648^c		2.225	173.2 (Cl–Bi–Cl)	112
Ph$_2$BiBr		2.880; 2.925		2.247	178.9 (Br–Bi–Br)	113
[2,4,6-Me$_3$C$_6$H$_2$]BiBr$_2^b$	Bi(1) atom	2.619; 2.818; 3.02		2.20	172.4 (Br–Bi···Br)	109
	Bi(2) atom	2.607; 2.808; 3.02		2.25	171.3 (Br–Bi···Br)	
[2,4,6-Ph$_3$C$_6$H$_2$]BiCl$_2$		2.529; 2.530; 3.074^c		2.266	167.8 (Cl–Bi···Cl)	110
CpBiCl$_2$		2.582; 2.643; 3.183; 3.092		2.38–2.92	147.5 (Cl–Bi···Cl)	114
(Pr$^i_4$C$_5$H)BiCl$_2$		2.542; 2.645; 3.138		2.46–2.85		104
(Pr$^i_4$C$_5$H)BiI$_2$		2.911; 3.017; 3.456^c		2.48–2.90		104
(Pr$^i_4$C$_5$H)Bi$_2$Cl$_5$d	Bi(1) atom	2.784; 2.891; 2.891		2.54–2.65		104
	Bi(2) atom	2.469; 2.74; 3.17				
[(Me$_3$Si)$_2$CH]BiCl$_2$·0.5Et$_2$O^b	Bi(1) atom	2.538; 2.704; 2.824	3.557	2.237	160.7 (Cl–Bi–Cl)	103
	Bi(2) atom	2.522; 2.729; 2.852	3.431	2.244	159.4 (Cl–Bi–Cl)	
PhBiCl$_2$·THF		2.543; 2.654; 2.934	2.608	2.266	168.1 (Cl–Bi–Cl) 177.3 (Cl–Bi–O)	108
PhBiBr$_2$·THF		2.684; 2.825; 3.038	2.671	2.281	171.2 (Br–Bi–Br) 177.4 (Br–Bi–O)	106
PhBiI$_2$·THF^b	Bi(1) atom	2.882; 3.056; 3.227	2.808	2.239	172.8 (I–Bi–I)	106
	Bi(2) atom	2.892; 3.079; 3.211	2.813	2.244	175.0 (I–Bi–O) 171.8 (I–Bi–I) 174.9 (I–Bi–O)	
PhBiBr$_2$·OPPh$_3$		2.694; 2.856; 3.143	2.390	2.25	176.0 (Br–Bi–Br) 167.6 (Br–Bi–O)	107
PhBiBr$_2$·dmpu		2.700; 2.829; 3.146	2.34	2.21	176.3 (Br–Bi–Br) 164.8 (Br–Bi–O)	107
PhBiBr$_2$·2dmpu		2.732; 2.765	2.472; 2.564	2.25	169.5 (Br–Bi–O) 172.0 (Br–Bi–O)	107
[2-(Me$_2$NCH$_2$)C$_6$H$_4$]BiI$_2$		2.987; 3.116; 3.243; 3.982^c	2.503	2.239	175.6 (I–Bi–I) 163.9 (I–Bi–N)	38

[a] Bismuth–halogen bond distances and interactions, X = Cl, Br, I; E = N, O. [b] Two independent Bi centers are present in the asymmetric unit. [c] Intermolecular interaction. [d] Two different Bi centers are present in the molecular unit, i.e., Bi(1) = organometallic center, Bi(2) = inorganic center.

ing the base and one alkyl group in the apical site. Each BiI$_4$ basal square shares two trans edges to form straight BiI$_2$ chains, with the organic groups bonded to bismuth on one side of the BiI$_2$ basal plane. Band structure calculations demonstrate that these materials are electronically one-dimensional. For R = Me (two independent bismuth sites corresponding to two symmetry-inequivalent polymeric chains) and Et (only one independent chain in the structure), pairs of chains are formed (interlayer bismuth–bismuth distance of 4.437 and 4.302 Å, respectively) with the organic groups pointing up and down respectively, as shown in Figure 28 for R = Me. By contrast, for R = Bu^n, such pairs are not present. The main difference between the members of this family derives from the stacking of the RBiI$_2$ chains in the three-dimensional structure.[111]

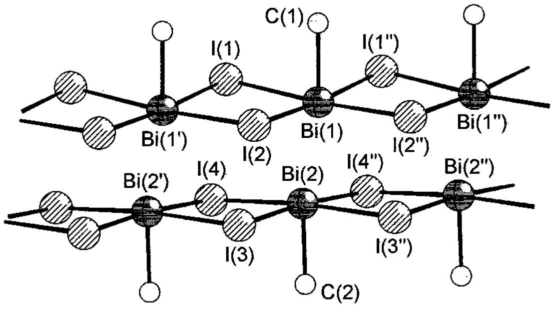
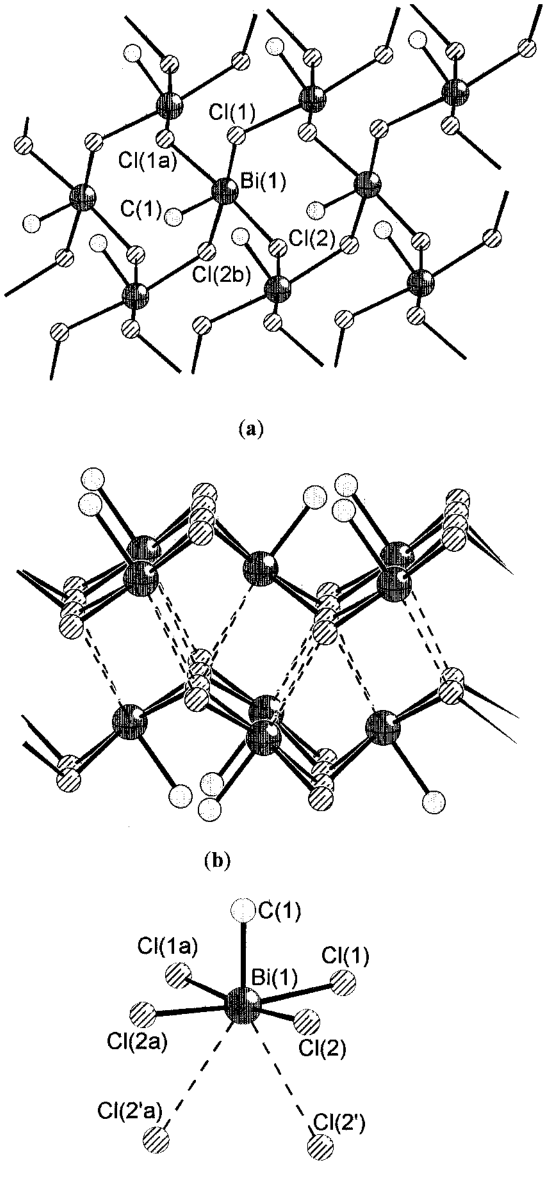


Figure 28. Polymeric association in the crystal of MeBiI$_2$.[21]

Methylbismuth dichloride exhibits a completely different solid-state structure.[112] All chlorine atoms are involved in symmetrical Bi–Cl–Bi leading to a two-dimensional polymer formed by condensed eight-membered Bi$_4$Cl$_4$ rings (Figure 29a), with the methyl groups placed on the same side of the (BiCl$_2$)$_n$ layer. The bismuth atoms are in a square pyramidal environment, with four basal chlorine atoms and an apical methyl carbon atom. In the three-dimensional structure, two such polymeric monolayers are associated through weak interlayer Bi···Cl interactions (3.648 Å) (Figure 29b), thus increasing the coordination number of bismuth atoms to seven (Figure 29c).

Solid PhBiBr$_2$ is a polymer with a rather complex structure.[113] It consists of a chain of Ph$_2$Bi$_2$Br$_6$ dimeric units in which bismuth atoms adopt a square pyramidal local geometry, with the bromine atoms forming the base and the phenyl groups bonding in the apical sites. The two bismuth atoms in the dimer are bonded through two bridging bromine atoms with an angle of 123.4° between the basal planes of the two edge-sharing PhBiBr$_4$ pyramids. The opposite sides of the two basal planes bridge to an adjacent dimer on each corner, leading to an extended one-dimensional chain polymer with the phenyl groups on each successive dimer alternating from side to side of the chain (Figure 30). There are also π–π interactions between the phenyl groups on adjacent chains.[113]

When more sterically demanding organo substituents are used, only one of the halide atoms of the



(a)

(b)

(c)

Figure 29. Monolayer polymeric (a), interlayer association through Bi···Cl interactions (b), and coordination environment for Bi atoms (c) in the crystal of $MeBiCl_2$.[112]

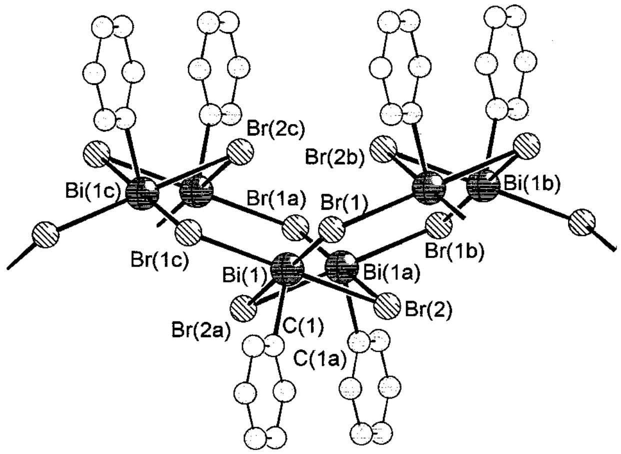


Figure 30. Polymeric association in the crystal of $PhBiBr_2$.[113]

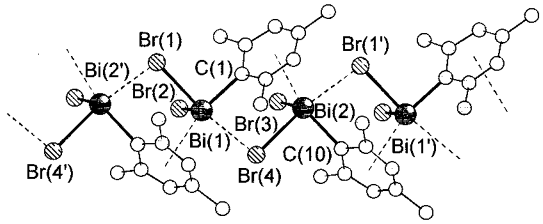


Figure 31. Polymeric association in the crystal of $[2,4,6\text{-}Me_3C_6H_2]BiBr_2$.[109]

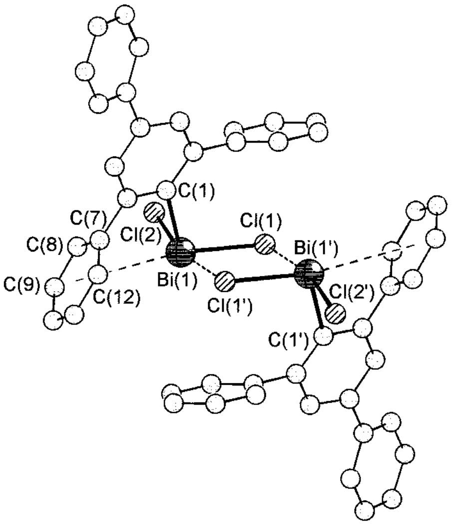


Figure 32. Dimeric association in the crystal of $[2,4,6\text{-}Ph_3C_6H_2]BiCl_2$.[110]

molecular unit is involved in Bi–X–Bi bridges. Thus, the crystals of mesitylbismuth dibromide, $[2,4,6\text{-}Me_3C_6H_2]BiBr_2$,[109] contain two crystallographically independent molecules which build up zigzag chains via strong Bi–Br···Bi bridges. The Bi–Br bond distance is significantly shorter for the terminal bromine (2.619 Å) than for the bridging bromine atom (2.818 Å). Relatively weak η^6-arene···Bi interactions [mean Bi···C 3.48, and 3.59 Å for Bi(1) and Bi(2), respectively] lead to a coordination around the bismuth atoms between the square pyramidal and the trigonal bipyramidal geometry (Figure 31).

With an even more bulky aryl substituent, the association is decreased. The structure of $[2,4,6\text{-}Ph_3C_6H_2]BiCl_2$ consists of molecular units that are associated into dimers with two terminal and two bridging chlorine substituents (Figure 32).[110] Despite the different nature of the chlorine atoms (terminal and bridging), in the molecular unit the Bi–Cl bond distances are equivalent (Table 5). The dimerization brings the bismuth atoms into a close intermolecular contact. The bismuth–bismuth distance is 4.316 Å, which is less than the sum of the van der Waals radii of two bismuth atoms. Also, the intramolecular interactions between the bismuth atoms and the adjacent phenyl groups are remarkable (Bi···C distances in the range 3.01–3.83 Å; *cf.* Σ_{rvdW} C, Bi 4.10 Å). The coordination geometry around bismuth can be described as square pyramidal, with one basal position occupied by the center of the phenyl ring.

π-Bonding from bismuth to the organic ligand is characteristic of the structures of cyclopentadienylbismuth dihalides and related compounds. One example is $CpBiCl_2$ where the organic ligands are in η^2- or η^3-bonded states (Bi−C 2.38−2.92 Å). The crystals consist of $CpBiCl_2$ molecules that are associated into $[(CpBiCl_2)_2]_x$ chains built through Cl−Bi···Cl bridges involving both chlorine atoms of the molecular unit (Figure 33).[114] In the molecular unit the Bi−Cl bond distances are not equivalent (Table 5), their lengths being related to those of the corresponding Bi···Cl semibonding distances in the Cl−Bi···Cl bridges, i.e., shorter Bi−Cl bonds corresponds to longer Bi···Cl distances and vice versa. A particular feature is the presence of an intermolecular Bi···Cl interaction trans to the Cp center (Cp_{center}−Bi···Cl 162.1°), thus leading to a distorted square pyramidal environment (Cl−Bi···Cl 147.5°) with a chlorine atom in the apical position.

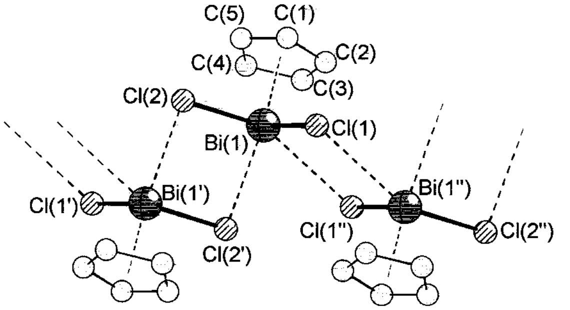


Figure 33. Polymeric association in the crystal of $CpBiCl_2$.[114]

The sterically more protected derivatives $(Pr^i_4C_5H)BiCl_2$ (Figure 34)[104,115] and $(Pr^i_4C_5H)BiI_2$[104] display dimeric structures with two bridging and two terminal halogeno ligands and η^3 coordination of the cyclopentadienyl rings. Again, the Bi−halide bond distance is significantly shorter for the terminal ligand than for the bridging one (Table 5). The coordination geometry around bismuth can be described as distorted tetrahedral, with one position occupied by the center (C_{center}) of the [C(1)C(2)C(5)] system of the cyclopentadienyl ring (Cl−Bi−Cl 82.4−90.6°, C_{center}−Bi−Cl 108.4−148.8° and I−Bi−I 85.3−94.6°, C_{center}−Bi−I 111.0−145.4°, respectively).

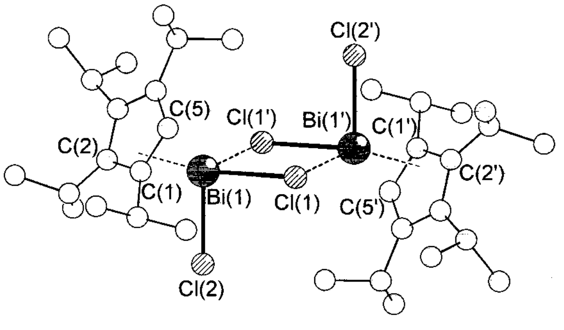


Figure 34. Dimeric association in the crystal of $(Pr^i_4C_5H)BiCl_2$.[104]

The structure of a product with an unusual stoichiometry, $(Pr^i_4C_5H)Bi_2Cl_5$ [it might be considered as a $(Pr^i_4C_5H)BiCl_2 \cdot BiCl_3$ adduct)], was also reported.[104] The crystal contains dimeric units with a central Bi_2Cl_{10} core built from two $BiCl_6$ octahedron sharing an edge. Two $(Pr^i_4C_5H)Bi$ fragments are attached to this core through three chlorine bridges, leading to a framework of two face-sharing cubes (Figure 35) containing three types of chlorine atoms: terminal and μ- and μ_3-bridging halogeno ligands. The cyclopentadienyl rings exhibit a η^5-coordination, and the resulting coordination geometry around bismuth is similar to that observed for the $(Pr^i_4C_5H)BiCl_2$ dimer, i.e., distorted tetrahedral, with one position occupied by the center of the cyclopentadienyl ring (Cl−Bi−Cl 81.9−95.1°, Cp_{center}−Bi−Cl 124.2−128.7°).

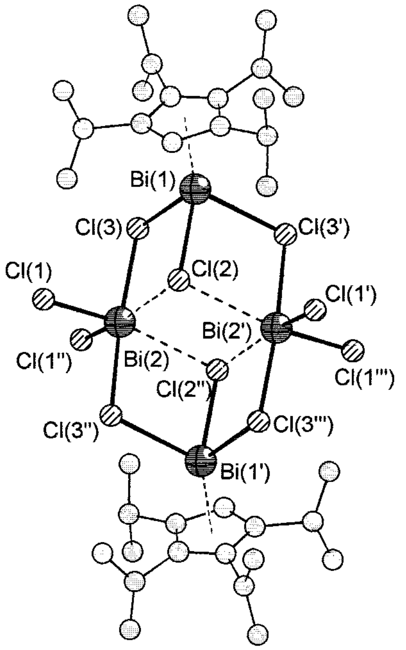


Figure 35. Structure of $(Pr^i_4C_5H)Bi_2Cl_5$.[104]

Adducts of organobismuth dihalides with oxygen donors vary in the type and the length of Bi−O bonds. A relatively loose attachment of diethyl ether in a bridging position between two bismuth atoms is characteristic for the structure of $[(Me_3Si)_2CH]BiCl_2 \cdot 0.5Et_2O$.[103] In the crystal there are polymeric chains with single chloro bridges. The diethyl ether molecules are weakly associated to two neighboring bismuth atoms in the chain, with the oxygen atoms placed trans to the Bi−C bond (Figure 36). When the ether ligands are not considered, the environment of the bismuth atoms is described as ψ-trigonal bipyramidal with the bridging chloro ligands in axial positions and the alkyl groups and the terminal chlorine atoms in equatorial positions.

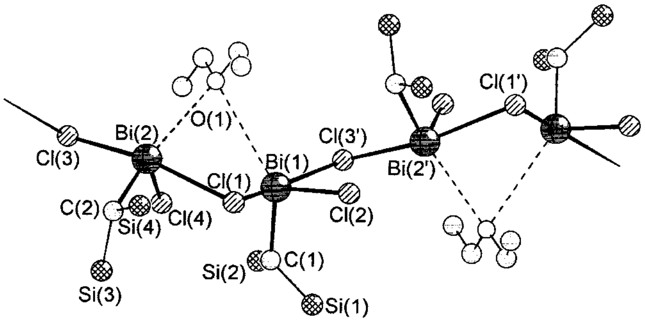


Figure 36. Polymeric association in the crystal of $[(Me_3Si)_2CH]BiCl_2 \cdot 0.5Et_2O$ (the methylic carbons on silicon atoms are not shown for clarity).[103]

The tetrahydrofuran adducts of phenylbismuth dihalides, $PhBiX_2$·THF (X = Cl,[108] Br,[106] I[106]), form one-dimensional chains with a single asymmetrically bridging halide between each pair of adjacent bismuth atoms. As usual, the range of the bismuth–halogen bond lengths for the iodide is smaller than that for the bromide and chloride derivatives. The coordination geometry around the bismuth center is that of a distorted square pyramid with the phenyl groups in the apical position and two cis halides, a bridging halide from an adjacent monomer unit, and the oxygen atom of the THF ligand in the basal plane (e.g., as shown in Figure 37 for X = Br). An interesting feature is the relatively weak η^6-arene···Bi interactions (Bi···Ph_{center} 3.426, 3.472, and 3.541 Å for X = Cl, Br, and I, respectively) between phenyl rings and adjacent bismuth centers. The center of such a phenyl ring is placed trans to the Bi–C covalent bond, thus completing an octahedral environment around the bismuth atoms.

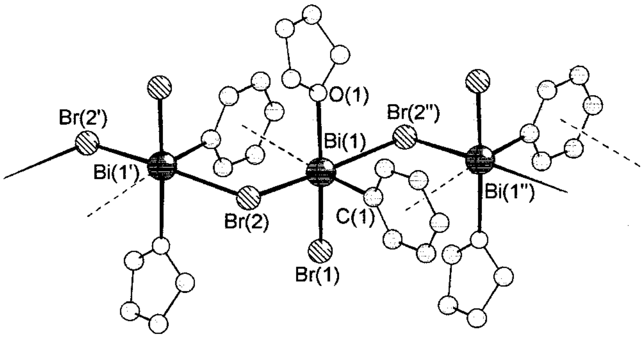


Figure 37. Polymeric association in the crystal of $PhBiBr_2$·THF.[106]

When triphenylphosphine oxide or *N*,*N'*-dimethylpropyleneurea (dmpu) are used as oxygen donor ligands, both the resulting 1:1 adducts $PhBiBr_2$·$OPPh_3$ and $PhBiBr_2$·dmpu exhibit crystallographically centrosymmetric dimeric structures, with two asymmetrically bromine bridges (e.g., as shown in Figure 38 for the dmpu complex).[107] The Bi–O coordinative bond is significantly stronger than in the case of the THF adducts (Table 5). Each bismuth center has a five-coordinate, square-based pyramidal geometry. In both structures a phenyl group occupies the apical site while the four basal positions are occupied by the three bromine atoms, one terminal and two bridging, and the oxygen atom of the coordinated ligand.[107]

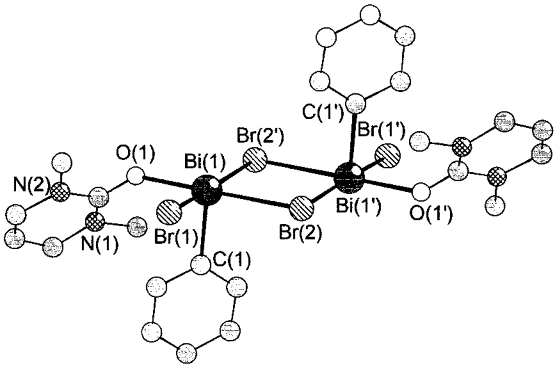


Figure 38. Dimeric association in the crystal of $PhBiBr_2$·dmpu.[107]

The 1:2 adduct $PhBiBr_2$·2dmpu is monomeric, with a square pyramidal geometry around bismuth in which the four basal positions are occupied by two cis bromine atoms and two cis oxygen atoms from the coordinated dmpu ligands (Figure 39).[107]

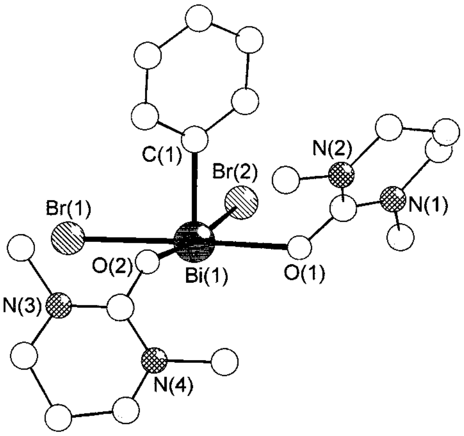
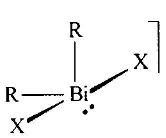


Figure 39. Molecular structure of $PhBiBr_2$·2dmpu.[107]

Intramolecular coordination through nitrogen occurs in the structure of $[2\text{-}(Me_2NCH_2)C_6H_4]BiI_2$.[38] The crystal contains dimeric units with two bridging and two terminal iodine atoms. The terminal iodo ligands interact with bismuth atoms of neighboring dimers to form a polymer of dimers. The geometry at bismuth is distorted square pyramidal with the aryl group in the apical position and three iodine atoms and a nitrogen atom in the basal position.

C. “Ate” Complexes of the Type $[R_nBi_mX_p]^{y-}$ (X = Halogen, Oxygen)

Diorganobismuth(III) compounds of the type R_2BiX (X = halogen or oxoacid radicals) are Lewis acids. The addition of one halide or one anion of an oxoacid results in the formation of ionic “ate” complexes of the type $[R_2BiX_2]^-$ with a ψ-trigonal bipyramidal coordination geometry around the bismuth center (**28**). As a general rule, the organic ligands occupy the equatorial positions and the electronegative halogen or oxygen atoms are placed in the apical sites (Table 6). Due to hypervalent three-center 4-electron bonding, the apical bonds often are elongated compared to normal single bonds. In some cases, additional weak interactions with other donor atoms were observed, which, if considered, lead to very distorted square pyramidal or octahedral coordination geometries. The Lewis acidity of organobismuth(III) compounds of the type $RBiX_2$ (X = halogen or oxoacid radicals) is even more pronounced. Thus, the addition of another halide ligand generally does not



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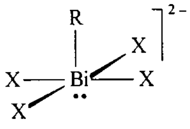

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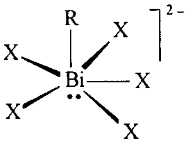

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Table 6. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for $[R_nBi_mX_p]^{y-}$ (X = Halogen, Oxygen) Anions

		Bi–X[a]	Bi–C	X–Bi–X	C–Bi–C	ref
$[Ph_4P][Ph_2BiBr_2]$		2.863; 2.877	2.260; 2.276	177.3 (Br–Bi–Br)	95.9	106
$[(Ph_3P)_2N][(biph)BiCl_2]$		2.702; 2.743	2.230; 2.256	175.1 (Cl–Bi–Cl)	77.6	95
$[Et_4N][Ph_2BiI_2]$		3.052; 3.141 4.085	2.251; 2.294	177.9 (I–Bi–I)	93.6	108
$[Ph_4Bi][Ph_2Bi(O_2CCF_3)_2]$		2.38; 2.41	2.24; 2.26	172 (O–Bi–O)	95	61
$[Et_4N][Bi\{C_6H_4C(CF_3)_2O\text{-}2\}_2]\cdot H_2O$		2.273; 2.306	2.237; 2.249	159.7 (O–Bi–O)	94.1	62
$[Et_4N]_2[Ph_2Bi_2I_6]$	Bi(1) atom	2.945–3.327	2.254	170.9; 172.3 (I–Bi–I)		106
	Bi(2) atom	2.950–3.288	2.266	171.8; 173.4 (I–Bi–I)		
$[Bu^n{}_4N]_2[Ph_2Bi_2Br_6]$		2.742–3.054	2.249	171.8; 176.6 (Br–Bi–Br)		108
$[Me_2NH(CH_2)_3NHMe_2][PhBi(O_2CCF_3)_4]$		2.35; 2.38 (Bi–O) 3.08; 3.21 (Bi···O)	2.19	163.4 (O–Bi–O, *trans*) 164.2 (O–Bi–O, *trans*)		118
$[Me_2NHCH_2CH(OH)CH_2NHMe_2][PhBi(O_2CCF_3)_4]$		2.40; 2.41 (Bi–O) 3.23; 3.33 (Bi···O)	2.25	165.1 (O–Bi–O, *trans*) 167.8 (O–Bi–O, *trans*)		118
$[Me_2NH(CH_2)_4NHMe_2][PhBi(O_2CCF_3)_4]$		2.37; 2.38 (Bi–O) 3.16; 3.26 (Bi···O)	2.22	161.9 (O–Bi–O, *trans*) 165.1 (O–Bi–O, *trans*)		118
$[Me_2NH(CH_2)_2NHMe_2][PhBi(O_2CCF_3)_4]$		2.35–2.62 (Bi–O) 3.15–3.36 (Bi···O)	2.22	52–86 (O–Bi–O, *cis*)[b]		118
$[HPy]_2[PhBi(O_2CCF_3)_4]$		2.36–2.78 (Bi–O) 3.14–3.32 (Bi···O)	2.27	43.7–89.7 (O–Bi–O, *cis*)		118
$[1,4\text{-}(Me_2NH)_2C_6H_4][PhBi(O_2CCF_3)_4]$		2.31–2.91 (Bi–O) 3.16; 3.37 (Bi···O)	2.29	47.4–83.0 (O–Bi–O, *cis*)		118

[a] Bond distances and interactions, X = halogen, oxygen. [b] The lower value corresponds to the oxygen atoms of the chelating ligand, calculated from the published atomic coordinates.

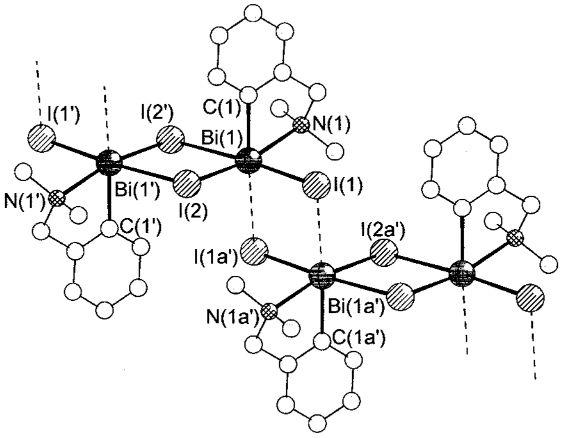


Figure 40. Polymeric association in the crystal of $[2\text{-}(Me_2NCH_2)C_6H_4]BiI_2$.[38]

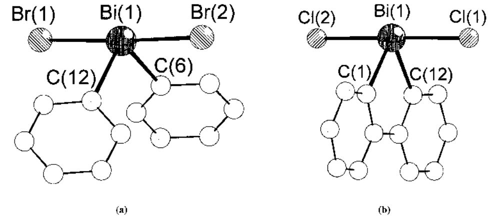


Figure 41. Structure of the anions in (a) $[Ph_4P][Ph_2BiBr_2]$[106] and (b) $[(Ph_3P)_2N][(biph)BiCl_2]$.

lead to monomeric $[RBiX_3]^-$ anions, but instead a dimeric $[RBiX_3]_2{}^{2-}$ species forms through Bi–X–Bi bridges, leading to a square pyramidal coordination geometry around bismuth (**29**). Depending on the countercation, basically square pyramidal or pentagonal pyramidal (**30**) coordination geometries were reported for the $[PhBi(O_2CCF_3)_4]^{2-}$ species. Moreover, for these oxoanions weak Bi···O intramolecular interactions can increase the overall coordination number up to nine.

A representative "ate" complex containing two organic groups attached to bismuth is $[Ph_4P][Ph_2BiBr_2]$ (Figure 41a).[106] It contains monomeric $[Ph_2BiBr_2]^-$ anions with equatorial phenyl groups and apical bromine atoms. Another name for the ψ-trigonal bipyramidal geometry of the anion is a seesaw structure. The angle between the bromine atoms is very close to the ideal value of 180°. The angle between the *ipso* carbon atoms (C–Bi–C 95.9°) is significantly less than the ideal value for a trigonal bipyramid of 120°. Such acute angles are not uncommon in the stereochemistry of heavy main group elements. When the coordination is described as ψ-trigonal bipyramidal, a strong stereochemical effect of the bismuth lone pair on the C–Bi–C angle is implied. However, alternative bonding models based on unhybridized 6p orbitals with the lone pair of electrons at the bismuth center in a 6s orbital appear to be equally appropriate.

A similar monomeric structure was described for the anion of $[(Ph_3P)_2N][(biph)BiCl_2]$ (Figure 41b).[95] In this case the even more acute C–Bi–C angle (77.6°) is obviously the result of the BiC_4 ring constraint.

The monomeric unit of the anion in $[Et_4N][Ph_2BiI_2]$ has a similar structure. However, in the crystal very weak iodine bridges (Bi···I 4.085 Å) trans to Bi–C bonds (C–Bi···I 176.8°) lead to loose dimer associations (Figure 42).[108] If these intermolecular interactions are taken into account, the coordination geometry around the bismuth atoms may be described as

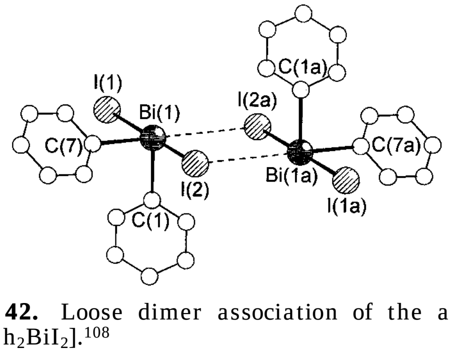


Figure 42. Loose dimer association of the anions in $[Et_4N][Ph_2BiI_2]$.[108]

very distorted square pyramidal, with a carbon atom in the apical position.

A distorted ψ-trigonal bipyramidal coordination can be considered also for the anion of $[Ph_4Bi][Ph_2Bi(O_2CCF_3)_2]$, in which the angle between the *ipso* carbon atoms (C−Bi−C 95°) is again significantly less than 120° and the apical oxygen atoms (O−Bi−O 172°) are displaced toward the equatorial carbon atoms.[61] The Bi−O bond lengths (average 2.40 Å) are longer than the sum of the bismuth and oxygen covalent radii (Table 1), thus supporting the formation of a three-center 4-electron bond. However, the distances between the central metal atom in the anion and the carbonyl oxygens of the trifluoroacetato groups are significantly shorter (Bi···O 3.18, 3.29 Å) than the sum of the bismuth and oxygen van der Waals radii (Table 1). This suggests intramolecular Bi···O interactions resulting in a distorted octahedral environment around the bismuth atom (Figure 43). In addition, a weak intermolecular interaction between a carbonyl oxygen atom and the metal center of the tetraphenylbismuthonium cation is also present (Bi_{cation}···O 3.11 Å).[61]

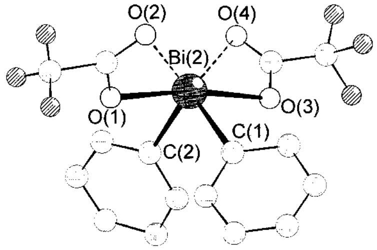


Figure 43. Structure of the anion in $[Ph_4Bi][Ph_2Bi(O_2CCF_3)_2]$.[61]

The higher distortion of the ψ-trigonal bipyramidal coordination, i.e., O−Bi−O 159.7°, in the heterocyclic anion of $[Et_4N][Bi\{C_6H_4C(CF_3)_2O\text{-}2\}_2]\cdot H_2O$ is due to the ring constraints.[62,116] The Bi−O bond distances (2.273, 2.306 Å) in this hypervalent 10-Bi-4 anion are intermediate between the sum of the bismuth and oxygen covalent radii (2.16 Å) and the Bi−O bond lengths (average 2.40 Å) observed for the above $[Ph_2Bi(O_2CCF_3)_2]^-$ anion.[61] The presence of water molecules as crystal solvent results in dimer associations of anions through bridging hydrogen bonds (Figure 44).

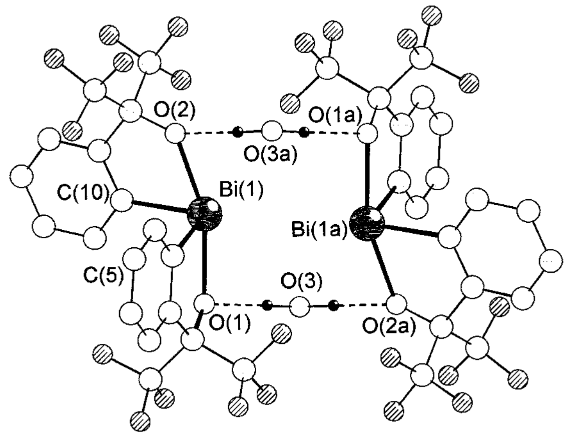


Figure 44. Dimeric association of the anions through hydrogen bonding in $[Et_4N][Bi\{C_6H_4C(CF_3)_2O\text{-}2\}_2]\cdot H_2O$.[62]

The more pronounced Lewis acidity of organobismuth(III) dihalides results in dimeric $[RBiX_3]_2^{2-}$ species with the structure of edge-shared square-based pyramids, instead of monomeric $[RBiX_3]^-$ anions. An example is the ionic species $[Et_4N]_2[Ph_2Bi_2I_6]\cdot Et_2O$ which contains the discrete dimeric $[Ph_2Bi_2I_6]^{2-}$ anion (Figure 45).[106] The phenyl groups are in the apical sites. Two terminal and two bridging iodine atoms occupy the basal sites around each bismuth, with the $Bi-I_{terminal}$ bond distances (2.945−2.972 Å) significantly shorter than the $Bi-I_{bridging}$ bond distances (3.257−3.327 Å). The dihedral angle between the basal planes is 105.2°.

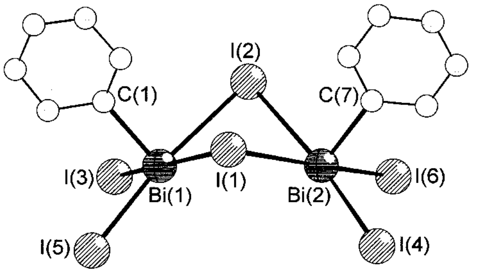


Figure 45. Structure of the anion in $[Et_4N]_2[Ph_2Bi_2I_6]$.[106]

The analogous bromo anion in $[Bu^n{}_4N]_2[Ph_2Bi_2Br_6]$ has a centrosymmetric structure, with the apical phenyl groups trans with respect to an essentially planar Bi_2Br_6 unit (Figure 46).[108] The difference between $Bi-Br_{bridging}$ (3.007, 3.054 Å) and $Bi-Br_{terminal}$ (2.742, 2.756 Å) is again significant.

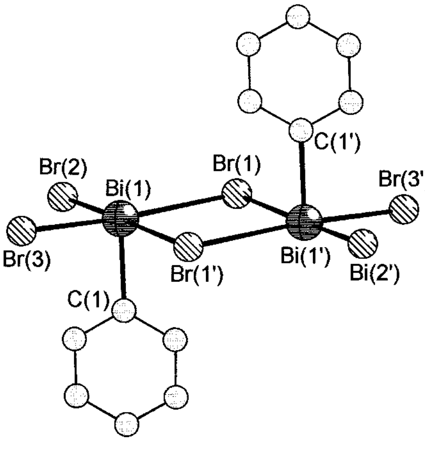


Figure 46. Structure of the anion in $[Bu^n{}_4N]_2[Ph_2Bi_2Br_6]$.[108]

The coordination geometry around the bismuth(III) center in the dianion $[PhBi(O_2CCF_3)_4]^{2-}$ is dependent on the nature of organic diammonium countercation due to the selective hydrogen-bonding interactions between the trifluoroacetato ligand and the cation and the lattice packing forces, respectively.[117,118] Thus, for $[Me_2NH(CH_2)_3NHMe_2]^{2+}$, $[Me_2NHCH_2CH(OH)CH_2NHMe_2]^{2+}$, or $[Me_2NH(CH_2)_4NHMe_2]^{2+}$ as a countercation, a basically square pyramidal $CBiO_4$ core, with the phenyl group in axial position, results. The second oxygen atom of all the four carboxylato groups is placed below the essentially planar BiO_4 unit, resulting in an unusual "cup" structure stabilized by asymmetric bridging N−H···O hydrogen-bonding interactions (Figure 47a). By contrast, the

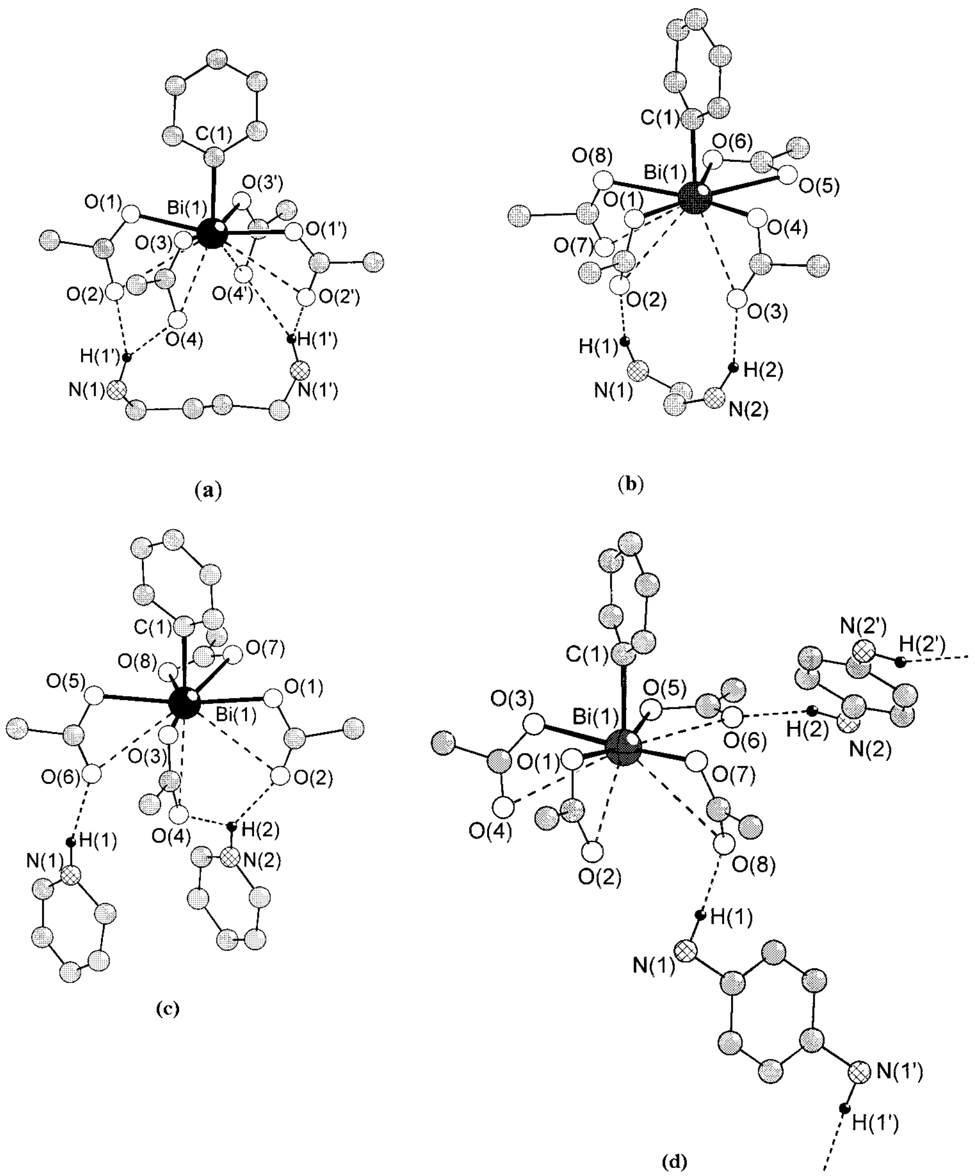


Figure 47. Structures of (a) $[Me_2NH(CH_2)_4NHMe_2][PhBi(O_2CCF_3)_4]$, (b) $[Me_2NH(CH_2)_2NHMe_2][PhBi(O_2CCF_3)_4]$, (c) $[HPy]_2[PhBi(O_2CCF_3)_4]$, and (d) $[1,4\text{-}(Me_2NH)_2C_6H_4][PhBi(O_2CCF_3)_4]$, showing the hydrogen bonding between the cation and the anion.[118]

smaller separation between the two nitrogen atoms in $[Me_2NH(CH_2)_3NHMe_2]^{2+}$ does not allow the formation of hydrogen bonds with all four oxygen atoms, but the two ammonium groups are hydrogen bonded to only two oxygen atoms from cis carboxylato groups. The coordination polyhedron is best described as pentagonal pyramidal, with an asymmetric chelating carboxylato group (Bi−O 2.35, 2.59 Å) in the equatorial plane (Figure 47b) and the forth carboxylato group not involved in a hydrogen bond. A similar $CBiO_5$ coordination core (Bi−O 2.51, 2.78 Å) was also observed for the complex containing protonated pyridine, $[HPy]^+$, as countercations. The Bi−O bond distances for the chelating ligand are longer (2.51, 2.78 Å) than for the previous compound, and all three of the remaining oxygen atoms are involved in hydrogen bonding (Figure 47c). In this case it was suggested that the stacking effect of the aromatic rings in the crystal lattice was the driving force leading to a non-"cup"-like structure, although no separation restriction between the nitrogen atoms is imposed. Indeed, the phenyl rings are placed sandwich-like between the pyridinium rings in an approximately eclipsed configuration. Finally, a basically pentagonal pyramidal coordination geometry was found in the $[1,4\text{-}(Me_2NH)_2C_6H_4][PhBi(O_2CCF_3)_4]$ complex. However, in this case an extended chain polymeric structure is formed as a result of the hydrogen bonding (Figure 47d). The longer Bi−O distance (2.91 Å) for one of the oxygen atoms of the chelating carboxylato group is probably due to the hydrogen bond in which it is involved. For all these "ate" complexes secondary Bi···O intramolecular interactions, shorter than the sum of the bismuth and oxygen van der Waals radii (3.90 Å), are also present (range 3.08−3.36 Å).

D. Cations of the Type $[R_nBiD_m]^{y+}$ (D = Neutral Ligand)

Organobismuth(III) cations may be derived from the six-electron monocation $[R_2Bi]^+$ or the four-elec-

Table 7. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for $[R_nBiD_m]^{y+}$ (L = Neutral Ligand) Cations

	Bi−E[a]	Bi−C	E−Bi−E	C−Bi−C	ref
$[(1,2,4\text{-Bu}^t{}_3C_5H_2)_2Bi][AlCl_4]$		2.648−2.726		172.9 (C_{center}−Bi−C_{center})[b]	119
$[Ph_2Bi\{OP(NMe_2)_3\}_2][BF_4]$	2.358; 2.370	2.239; 2.255	167.5 (O−Bi−O)	93.2	63
$[Ph_2Bi(OPPh_3)_2][BF_4]$,	2.223; 2.223	2.388; 2.389	173.2 (O−Bi−O)	95.8	120
$[Ph_2Bi\{OP(NMe_2)_3\}_2][PF_6]$	2.317; 2.355	2.192; 2.229	172.4 (O−Bi−O)	94.3	120
$[Mes_2Bi\{OP(NMe_2)_3\}_2][PF_6]$	2.35; 2.41	2.21; 2.26	177.2 (O−Bi−O)	108.5	120
$[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Bi][PF_6]$	2.491; 2.509	2.253; 2.259	164.8 (N−Bi−N)	91.6	39
$[PhBi\{OP(NMe_2)_3\}_4][PF_6]_2$	2.32−2.36	2.27	172.5; 174.2 (O−Bi−O)		120

[a] Bond distances, E = oxygen, nitrogen. [b] C_{center} = cyclopentadienyl ring center.

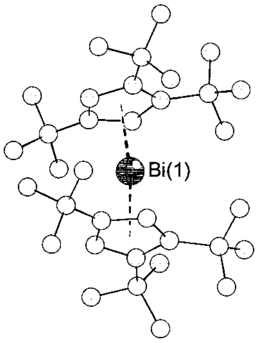
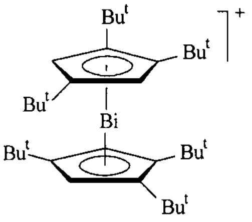


Figure 48. Structure of the cation in $[(1,2,4\text{-Bu}^t{}_3C_5H_2)_2Bi][AlCl_4]$.[119]

tron dication $[RBi]^{2+}$. Such electron-deficient species should possess an extremely high reactivity as Lewis acids. They are unknown in condensed phases. The few known organobismuth cations feature electron-rich species. A bismocenium ion, $[(1,2,4\text{-Bu}^t{}_3C_5H_2)_2Bi]^+$, that may be considered as an 18-electron species was described (**31**), while other known derivatives contain 4-Bi-8 or 5-Bi-10 cations of the type $[R_2BiD_2]^+$ (**32**) or $[RBiD_4]^{2+}$ (**33**) (D = neutral two-electron donor ligand) (Table 7).



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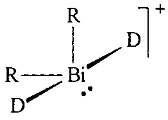

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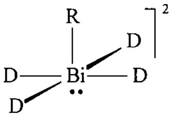

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The bismocenium ion is the cation of the salt $[R_2Bi][AlCl_4]$ (R = $1,2,4\text{-Bu}^t{}_3C_5H_2$).[119] The cyclopentadienyl rings are η^5-coordinated to the metal center with the bismuth−carbon distances in the range 2.648−2.726 Å (Figure 48).[119] The rings are nearly parallel (10.2° inclination of the best planes), and there is only slight bending of the Cp_{center}−Bi−Cp_{center} axis (172.9°).

Discrete $[R_2BiL_2]^+$ cations exist in the salts $[Ph_2Bi\{OP(NMe_2)_3\}_2][BF_4]$,[63] $[Ph_2Bi\{OP(NMe_2)_3\}_2][PF_6]$, $[Ph_2Bi(OPPh_3)_2][BF_4]$, and $[Mes_2Bi\{OP(NMe_2)_3\}_2][PF_6]$.[120] The four structures feature bismuth centers in distorted ψ-trigonal bipyramidal environments with the oxygen atoms of the neutral ligands in the axial sites and the aryl groups in equatorial positions (Figure 49a). In most of these salts there are no close interionic contacts. However, for $[Ph_2Bi(OPPh_3)_2][BF_4]$, a Bi···F distance of 3.533 Å indicates a weak cation−anion interaction (Figure 49b).[120]

Recently, the first structure of a cationic complex stabilized through intramolecular coordination was reported.[39] In the $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Bi]^+$ cation, both nitrogen atoms are strongly coordinated to the metal center (average 2.500 Å). By contrast, in the corresponding chloride, weaker bismuth−nitrogen interactions are established (2.570, 3.047 Å).[38] As expected, the distortion of the ψ-trigonal bipyramidal environment around bismuth in this cation is higher due to the restriction imposed by the intramolecular Bi···N coordinative bonds. A weak intermolecular Bi···F interaction (3.49 Å) is established between the bismuth atom of the cation and a fluorine atom of the $[PF_6]^-$ anion (Figure 50).[39]

The larger C−Bi−C angle in the dimesityl cation, $[Mes_2Bi\{OP(NMe_2)_3\}_2]^+$, might be due to the more bulky nature of the organic groups attached to bismuth. Taking into account the whole series of derivatives containing $[R_2BiD_2]^+$ cations, the molec-

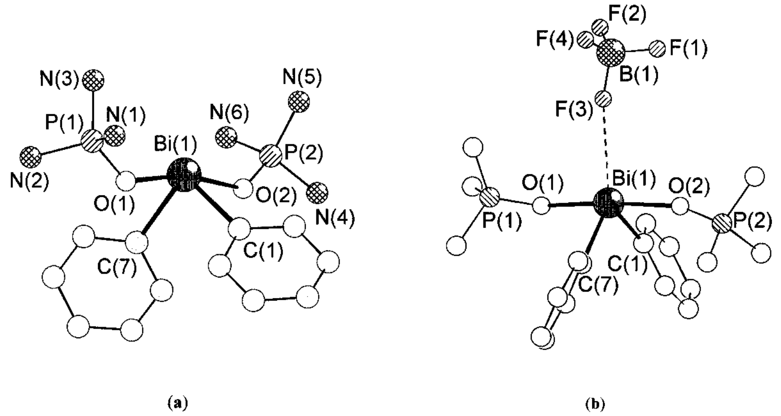


Figure 49. Structure of the cations in (a) $[Ph_2Bi\{OP(NMe_2)_3\}_2][BF_4]$ (for clarity, carbons attached to N atoms are not shown)[63] and (b) $[Ph_2Bi(OPPh_3)_2][BF_4]$ (only ipso carbons on phosphorus atoms are shown).[120]

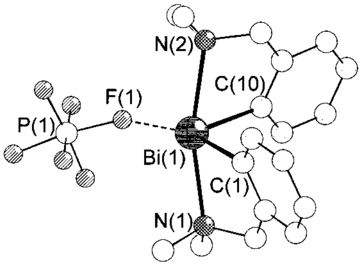


Figure 50. Structure of [{2-(Me_2NCH_2)C_6H_4}$_2$Bi][PF_6].[39]

ular parameters of the C_2BiX_2 cores suggest that the distortion of the ψ-trigonal bipyramidal polyhedron is controlled by a correlation between the magnitude of the C−Bi−C and X−Bi−X angles, i.e., a larger equatorial C−Bi−C angle is related to a larger axial X−Bi−X angle (Table 7).

The only known cation of the type $[RBiD_4]^{2+}$ exists in [PhBi{OP(NMe_2)$_3$}$_4$][PF_6]$_2$.[120] The bismuth center adopts a square-based pyramidal coordination geometry, with the phenyl group in the apical position. In addition, there is an interionic contact between the bismuth atom and a fluorine atom of one of the $[PF_6]^-$ anions (Bi···F 3.28 Å) which lies approximately trans to the phenyl group (C_{ipso}−Bi···F 162°). If this cation−anion interaction is considered as part of the bismuth coordination sphere, the resulting coordination geometry is distorted octahedral (Figure 51).

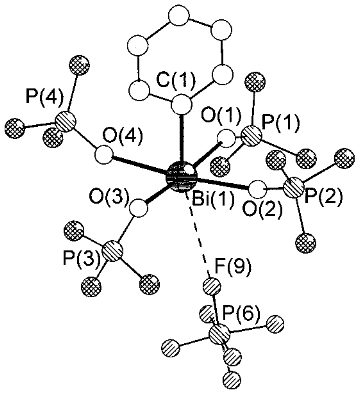
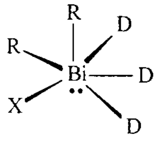


Figure 51. Structure of the cation in [PhBi{OP(NMe_2)$_3$}$_4$]-[PF_6]$_2$.[120]

The strong Lewis acid character of the $[R_nBiD_m]^{y+}$ cations is consistent with the magnitude of the bismuth−element coordinative interactions, which are considerably shorter than in the neutral $R_nBiX_{3-n}D_m$ adducts (for comparison, see Tables 4, 5, and 7).

E. Compounds of the Type R_2BiX (X = O, S, or N Anionic Ligand)

For compounds belonging to this class, a quite general rule is the increase of the coordination number at the bismuth atom either through intermolecular (more often) or intramolecular interactions between the metal atom and a chalcogen or a nitrogen atom. This usually results in more or less distorted ψ-trigonal bipyramidal (**20**) or square pyramidal (**21**) coordination geometries, as also observed for the diorganobismuth(III) halides (see section III.A.). In few cases, even a further increase in the coordination number through weak secondary interactions was observed, thus leading to a distorted pentagonal pyramidal environment around the bismuth atom (**34**). However, some exceptions from this behavior have also been reported, i.e., monomeric compounds containing tricoordinated Bi atoms (**19**). Important interatomic distances and angles for compounds of the type R_2BiX (X = O, S, or N anionic ligand) are listed in Table 8.



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The crystals of $Ph_2BiSePh$ contain discrete monomers;[121] the selenolate ligand acts as a monometallic monoconnective unit (Figure 52). The Bi−Se bond distance is significantly longer (2.704 Å) than in the dinuclear (Mes_2Bi)$_2$Se (2.651 Å),[122] and the bond angles around Bi are smaller than the tetrahedral value (Se−Bi−C 97.4°, 87.4°; C−Bi−C 90.8°), thus indicating a considerable s character of the lone pair of electrons.

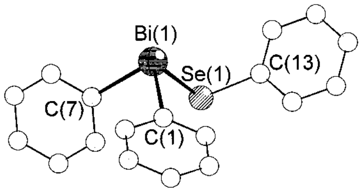
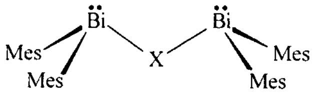


Figure 52. Molecular structure of $Ph_2BiSePh$.[121]

The dinuclear bis(dimesitylbismuth)chalcogenides, (Mes_2Bi)$_2$X (X = O,[122,123] S,[122] Se[122]), containing bulky organic groups attached to the metal atom, exhibit a monomeric structure with a pyramidal geometry of the C_2BiX cores (**35**). The oxide was isolated in solvent-free crystals[123] and cocrystallized with ethanol in a 2:1 ratio.[122] The molecular parameters of the two crystalline forms are quite similar (Table 8), the main difference being the larger Bi−O−Bi angle for the solvent-free derivative.



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Some differences depending on the chalcogen atom bridging the two Bi atoms in the molecular unit should be noted. Thus, the Bi−X−Bi angle decreases significantly when the bridging oxygen (Bi−O−Bi 117.1° for (Mes_2Bi)$_2$O·0.5EtOH[122] and 124.6° for (Mes_2Bi)$_2$O,[123] respectively) is replaced by sulfur (Bi−S−Bi 98.7°) or by selenium (Bi−Se−Bi 91.2°). The intramolecular Bi···Bi distances (3.594,[122] and 3.665 Å[123] for X = O, 3.844 Å for X = S, and 3.79 Å for X = Se) are significantly shorter than the sum of the van der Waals radii (see Table 1). The conformation of the $C_2Bi{-}X{-}BiC_2$ unit is also different: in (Mes_2Bi)$_2$O, the organic substituents occupy trans positions

Table 8. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for R_2BiX Derivatives (X = O, S, or N Anionic Ligand)

		Bi−X[a]	Bi−E[a]	Bi−C	X−Bi−X (or E) (trans)	C−Bi−C	ref
$Ph_2BiSePh$		2.704		2.25; 2.25		90.8	121
$(Mes_2Bi)_2O{\cdot}0.5EtOH$[b]	Bi(1) atom	2.095		2.196; 2.256		97.4	122
	Bi(2) atom	2.117		2.273; 2.293		98.3	
$(Mes_2Bi)_2O$[b]	Bi(1) atom	2.075		2.272; 2.272		98.4	123
	Bi(2) atom	2.064		2.269; 2.280		98.3	
$(Mes_2Bi)_2S$[b]	Bi(1) atom	2.520		2.250; 2.290		98.9	122
	Bi(2) atom	2.545		2.230; 2.325		97.4	
$(Mes_2Bi)_2Se$		2.651		2.265; 2.285		100.6	122
$[2\text{-}(Me_2NCH_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.194	2.62	2.22; 2.236	160.1 (O−Bi−N)	93.3	37
$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.192	2.68; 2.86	2.30; 2.27	158.1 (O−Bi−N)	96.2	37
$[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.193; 2.814	2.536	2.24; 2.25	155.2 (O−Bi−O)	94.4	125
$[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4(CMe_2O)\text{-}2]$		2.134; 3.144	2.566	2.242; 2.241	157.3 (O−Bi−O)	92.1	62
$[2\text{-}(HOCMe_2)C_6H_4]Bi[C_6H_4(CMe_2O)\text{-}2]$[c]	Bi(1) atom	2.323	2.323	2.168; 2.168	158.8 (O−Bi−O)	100.7	62
	Bi(2) atom	2.303	2.334	2.20; 2.210	158.1 (O−Bi−O)	98.4	
Et_2BiOPh		2.382		*d*	179.0 (O−Bi−O)	81.2	126
$Et_2BiOC_6F_5$		2.411		*d*	179.5 (O−Bi−O)	80	126
Me_2BiN_3		2.49; 2.50		2.27; 2.27	169 (N−Bi−N)	96	127
Ph_2BiSCN[c]	Bi(1) atom	2.87; 2.88 (Bi−S)		2.23; 2.27	177.0 (S−Bi−S)	97.1	128
	Bi(2) atom	2.52; 2.53 (Bi−N)		2.19; 2.29	166.2 (N−Bi−N)	96.7	
$Ph_2Bi[S(S)COPr^i]$		2.26; 3.71[e]	3.23 (Bi···S) 3.19 (Bi···O)	2.24; 2.26	161.9 (S−Bi···S)	96	129
$Ph_2Bi[O(O)CCH_2NHCOC_6H_5]$		2.396; 2.484	3.267 (Bi···O) 3.297 (Bi···O)	2.246; 2.250	160.6 (O−Bi−O)	95.1	130
$Ph_2Bi[\{O(O)SMe\}_2N]$		2.397; 2.466		2.238; 2.243	165.4 (O−Bi−O)	93.0	131

[a] Bond distances and interactions, X, E = N, O. [b] For the two nonequivalent bismuth atoms from the molecular unit. [c] Two independent bismuth centers are present in the unit cell. [d] Not given in the original manuscript. [e] Intermolecular interaction.

with respect to the Bi···Bi axis, while in $(Mes_2Bi)_2S$ and $(Mes_2Bi)_2Se$, they exhibit a gauche orientation (Figure 53). In addition, the molecules of $(Mes_2Bi)_2Se$ are weakly associated into dimeric units through intermolecular Bi···Bi interactions (4.634 Å), thus leading to a tetrahedral Bi_4 unit.[122]

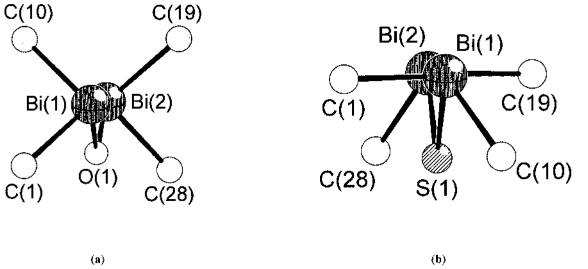


Figure 53. Conformation of the $C_2Bi{-}X{-}BiC_2$ fragment in (a) $(Mes_2Bi)_2O$ and (b) $(Mes_2Bi)_2S$.[122]

The hypervalent compounds $[2\text{-}(Me_2NCH_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O)\text{-}2]$[37,124] and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$[37] exhibit a monomeric structure. For $[2\text{-}(Me_2NCH_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O)\text{-}2]$, the coordination number at the central metal atom is increased through an intramolecular Bi···N interaction and the geometry is described as distorted ψ-trigonal bipyramidal (Figure 54). The oxygen and nitrogen atoms are placed in apical positions. The lone pair of electrons can be considered to occupy an equatorial position, the other ones being occupied by two carbon atoms with a C−Bi−C angle considerably diminished from 120°. The Bi−O bond distance is close to the sum of the covalent radii of bismuth and oxygen atoms. The bismuth−nitrogen distance is longer than expected for a covalent bond but much shorter than the sum of the van der Waals radii of bismuth and nitrogen.

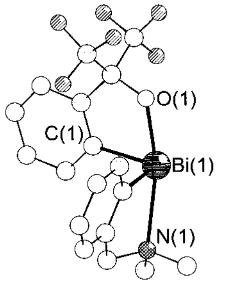


Figure 54. Molecular structure of $[2\text{-}(Me_2NCH_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O)\text{-}2]$.[37]

A related derivative $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ contains two intramolecular Bi···N interactions and, therefore, was described as a 12-Bi-5 compound.[37] The coordination geometry at bismuth is very distorted square pyramidal, or ψ-octahedral, if the lone pair of the metal atom is considered to occupy a position trans to the Bi−C bond of the tridentate ligand (Figure 55). The two nitrogen atoms deviate considerably from the aryl plane with a N−Bi−N angle of 117.6°, and the corresponding Bi−N distances are different, i.e., the length of the Bi−N bond trans to oxygen (O−Bi−N 158.1°) is considerably longer (2.68 Å) than the other one (2.86 Å).

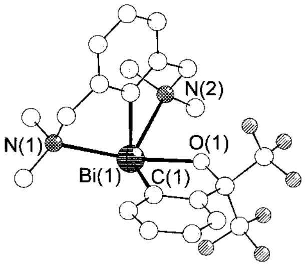


Figure 55. Molecular structure of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$.[37]

For the $[2\text{-}(R''OCR'_2)C_6H_4]Bi[C_6H_4(CR_2O)\text{-}2]$ derivatives, the structure of the monomeric unit is very similar to that of the 2-(dimethylamino)methylphenyl analogue. Here, the oxygen atom of the OR″ group is involved in a strong intramolecular interaction trans to the Bi−O covalent bond, leading to the hypervalent bond system (Figure 56).

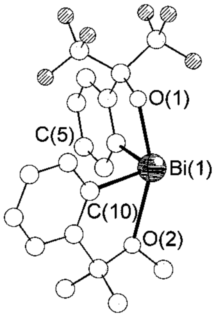


Figure 56. Molecular structure of $[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$.[125]

Some important differences should be noted for particular compounds. Thus, for $[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$[124,125] and $[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4(CMe_2O)\text{-}2]$,[62] the bismuth−oxygen distances are significantly different and the molecular units are associated into dimers through intermolecular Bi···O interactions involving the covalent bonded oxygen atoms (Figure 57). The intermolecular Bi···O interactions are much stronger in the trifluoromethyl derivative (2.814 Å) than in the corresponding methyl analogue (3.144 Å), probably due to the electron-withdrawing effect of the CF_3 groups. If these additional intermolecular interactions are also considered, the coordination geometry around a bismuth atom is better described as very distorted square pyramidal, quite similar to that observed for the 2,6-bis[(dimethylamino)methyl]phenyl analogue described above.

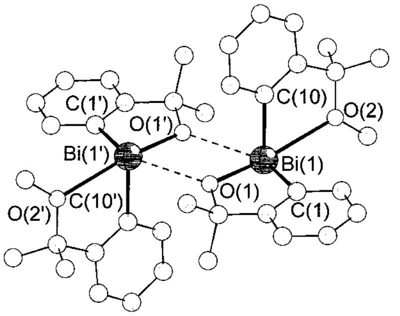


Figure 57. Dimeric association in the crystal of $[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4(CMe_2O)\text{-}2]$.[62]

For the hydroxy derivative, $[2\text{-}(HOCMe_2)C_6H_4]Bi[C_6H_4(CMe_2O)\text{-}2]$,[62] there are 1.5 molecules in an asymmetric unit, with one of them having a crystallographic 2-fold axis. The apical bismuth−oxygen distances in the ψ-trigonal bipyramidal C_2BiO_2 core are equivalent (average 2.32 Å) and significantly longer than a single Bi−O covalent bond. The molecular units are associated into trimers through strong intermolecular O−H···O hydrogen bonds (O···O 2.62, 2.54 Å) (Figure 58), which do not affect the coordination geometry around the bismuth atom.

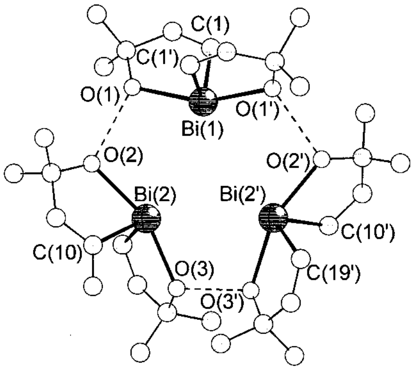


Figure 58. Trimeric association in the crystal of $[2\text{-}(HOCMe_2)C_6H_4]Bi[C_6H_4(CMe_2O)\text{-}2]$ (for clarity, only the aromatic carbons belonging to the Bi−containing rings are shown).[62]

Some general trends for compounds in which aryl substituents on bismuth contain pendant arms with potential donor atoms have to be remarked. Thus, (i) the coordination numbers at the central metal atoms are increased through strong intra- and/or intermolecular interactions, and these derivatives are generally designated as hypervalent 10-Bi-4 and 12-Bi-5 compounds.[37,62,124,125] (ii) The length of the apical bonds is dependent on the nature of the substituents attached to the α-carbon atoms and the electronegativity of the apical groups. (iii) The distortion of the coordination geometry is mainly the result of the small chelate ring angles at bismuth, but some authors have also taken into account the potential repulsive effect of the electron lone pair of the metal atom.

In some diorganobismuth(III) complexes, the increase in the coordination number leading to a ψ-trigonal bipyramidal geometry at the bismuth atom is achieved through intermolecular interactions and results in chain polymers. As a general rule, the apical positions are occupied by electronegative atoms of the ligands while the carbon atoms of the organic groups attached to bismuth are placed in equatorial positions.

In their mass spectra, both Et_2BiOPh and $Et_2BiOC_6F_5$ derivatives showed fragments corresponding to the monomer.[126] However, in contrast to the related monomeric $Ph_2BiSePh$ (see above), the X-ray diffraction studies revealed the two isomorphous compounds to form chiral helical chains with alternating bismuth and oxygen atoms (Figure 59).[126] The

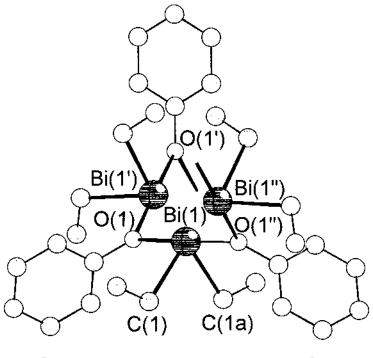


Figure 59. Polymeric association in the crystal of Et_2BiOPh.[126]

ethyl groups are pointed away from the centroid of the spiral, and the C−Bi−C angles have unexpected small values (ca. 80°). The phenoxide ligands behave as bridging groups through equal Bi−O bonds and O−Bi−O angles closed to 180° (see Table 8).

The azido ligands in the Me_2BiN_3 derivative also act as bridging groups involving only their α-nitrogen atoms, but the result is an endless zigzag chain of alternating bismuth and nitrogen atoms (Figure 60) with a planar Bi_nN_n system.[127] The Bi−N distances are equal, and the distortion of the ψ-trigonal bipyramidal geometry around the bismuth atom is reflected by the angular BiN_2 fragment (N−Bi−N 169°). The C−Bi−C angle is significantly larger (96°) in comparison to those observed for the previously mentioned Et_2BiOAr derivatives.[126]

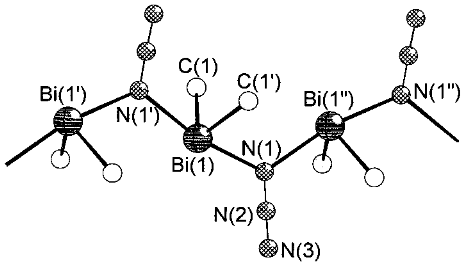


Figure 60. Polymeric association in the crystal of Me_2BiN_3.[127]

An interesting structural pattern was described for diphenylbismuth(III) thiocyanate, $Ph_2BiSCN\cdot 0.5CHCl_3$.[128] Here, a helical chain is formed through 1,3-bridging thiocyanato ligands, but due to the reversed orientation of the thiocyanato group at each bismuth atom (Figure 61), the polymeric chain contains a two-molecule repeating unit, i.e., Bi atoms coordinated to nitrogen atoms of two thiocyanates alternate with Bi atoms coordinated to two sulfur atoms. All bismuth atoms have a ψ-trigonal bipyramidal coordination geometry with equivalent Bi−S and Bi−N bonds, respectively, but with different apical−apical bond angles, S−Bi−S 177.0° vs N−Bi−N 166.2°.

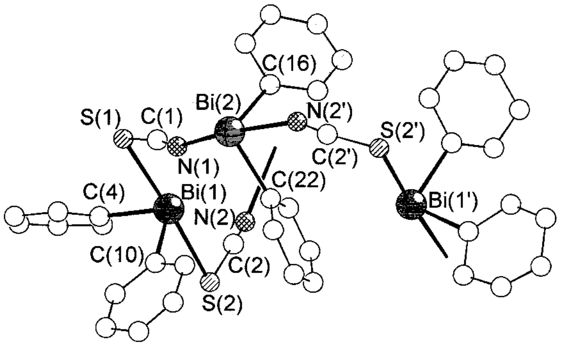


Figure 61. Polymeric association in the crystal of Ph_2BiSCN.[128]

When several donor atoms are present in the inorganic ligand, the coordination number at the bismuth atom is often increased through additional inter- and/or intramolecular interactions which complete the pyramidal arrangement of the three primary covalent bonds at the metal atom. As a consequence, the stereochemically active nature and the coordinative position which might be occupied by the lone pair of electrons at bismuth becomes a subject of discussion. Thus, in the case of (isopropylxanthogenato)diphenylbismuth(III), a polymeric structure is formed as a result of the asymmetric bridging nature of the 1,1-dithio ligand (Figure 62).[129] In the monomer $Ph_2Bi[S(S)COPr^i]$ unit, the Bi−S bond is elongated [Bi(1)−S(1) 2.66 Å] in comparison with the Bi−S bond (2.53 Å) in the monomeric $(Mes_2Bi)_2S$,[122] due to the delocalization over the CS_2 fragment. The second sulfur of the dithio ligand is involved in a weaker intermolecular interaction to the bismuth atom of a neighboring molecule [Bi(1″)···S(2) 3.23 Å], thus leading to a chain polymeric structure. If only these bismuth−sulfur bonds are considered, the coordination geometry can be described as distorted ψ-trigonal bipyramidal, with an apical−apical bond angle S−Bi···S of 161.9° and the equatorial positions occupied by the ipso carbons of the phenyl groups.

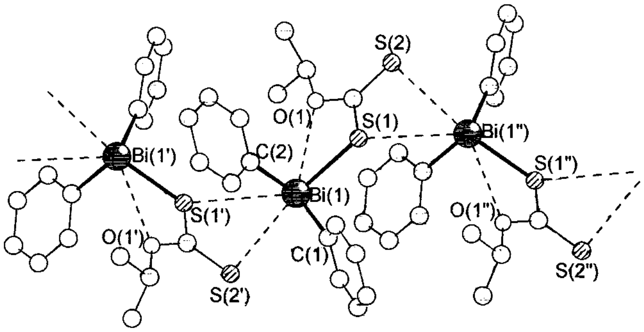


Figure 62. Polymeric association in the crystal of $Ph_2Bi[S(S)COPr^i]$.[129]

A closer check of the cell unit reveals some interesting structural aspects. Thus, two other chalcogen atoms are placed close to a bismuth atom. In the monomeric unit, the interatomic bismuth−oxygen distance, Bi(1)···O(1) 3.19 Å, is significantly shorter than the sum of the van der Waals radii (but longer than the coordinative Bi−O bond observed in the hypervalent bismuth compounds, ca. 2.55 Å). Moreover, the distance to the second sulfur atom of the 1,1-dithio ligand in the neighboring molecule [Bi(1)···S(1′) 3.71 Å] suggests an additional weak secondary interaction. Both of these weak interactions are placed almost in the plane described by the primary Bi(1)−S(1) and Bi(1)−C(1) covalent bonds and the stronger Bi(1)···S(2′) secondary interaction. The result is a pentagonal pyramidal arrangement of the C_2BiOS_3 core ($\Sigma_{\text{eq−eq angles}} = 361°$), distorted mainly due to the restrictions imposed by the small S(1′)···S(2′) and S(1)···O(1) "bite" of the ligand. The bismuth lone pair of electrons, if it is considered stereochemically active, should occupy an axial position trans to the C(2) atom in a ψ-pentagonal bipyramidal environment.

A quite similar structure was described for (*N*-benzoylglycinato)diphenylbismuth(III), $Ph_2Bi[O(O)CCH_2NHCOC_6H_5]$. This compound is polymeric as well, with the carboxylato group of the ligand bridging almost symmetrically two bismuth atoms [Bi(1)−O(3) 2.484, Bi(1″)-O(2) 2.396 Å] (Figure 63).[130] These

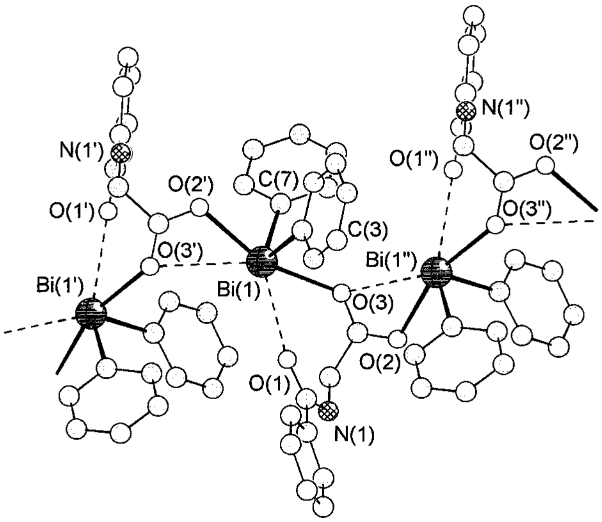


Figure 63. Polymeric association in the crystal of $Ph_2Bi[O(O)CCH_2NHCOC_6H_5]$.[130]

bismuth–oxygen distances are of the same magnitude as those observed in the monomeric hypervalent bismuth derivatives described above. The resulting C_2BiO_2 core has the common distorted *ψ*-trigonal bipyramidal geometry (O–Bi–O 160.6°). Two additional rather strong Bi···O secondary interactions are also present [Bi(1)···O(1) 3.267 Å, Bi(1)···O(3′) 3.297 Å]. This formally increases the coordination number of the metal atom to six, resulting in a C_2BiO_4 core of similar geometry as that observed for the xanthogenato derivative (see above).[129]

The anionic $[H\{O(O)SMe\}_2N]^-$ ("dimesylamido") ligand also acts as a symmetrically bridging group in the diphenylbismuth(III) derivative, but in this case a cyclic dimer, $[Ph_2Bi\{O(O)SMe\}_2N]_2$, containing a 12-membered $Bi_2O_4S_4N_2$ ring, is formed (Figure 64).[131] The bismuth atoms adopt a distorted *ψ*-trigonal bipyramidal geometry, with practically equivalent Bi–O bonds in apical positions (Table 8). No additional bismuth–oxygen and/or bismuth–nitrogen intra/intermolecular interactions were observed in this case.

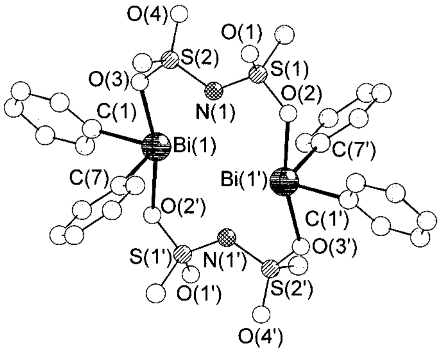
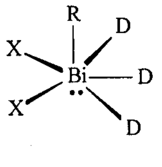


Figure 64. Cyclic dimer structure of $[Ph_2Bi\{O(O)SMe\}_2N]_2$.[131]

F. Compounds of the Type $RBiX_2$ (X = Chalcogenato Ligand)

All of the monoorganobismuth(III) compounds of this class whose structures have been described in the literature contain sulfur ligands able to establish additional intra- and/or intermolecular interactions. This results in either monomeric structures or dimeric/polymeric associations, with various distorted coordination environments around the metal center, e.g., square pyramidal (**24**), octahedral (**26**), pentagonal pyramidal (**36**), or pentagonal bipyramidal (**37**). In



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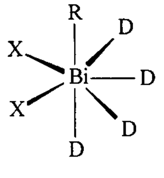

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some cases, the distortion of the coordination polyhedra and the presence of a large free space were considered as possible evidences of the stereochemical activity of the electron lone pair of the bismuth atom. Important interatomic distances and angles for compounds of the type $RBiX_2$ (X = O, S, or N anionic ligand) are listed in Table 9.

Only for $MesBi[S(S)PPh_2]_2$ the cell unit was found to contain discrete molecules with a symmetry plane containing the metal atom and the aromatic ring of the mesityl group attached to bismuth (Figure 65).[102] The dithiophosphinato ligand acts as an anisobidentate unit which results in short (Bi–S 2.662 Å) and long (Bi···S 3.112 Å) bismuth–sulfur distances, with the S···Bi···S angle being considerably larger (131.5°) than the S–Bi–S angle (84.0°). The coordination polyhedron is a distorted square pyramid with the bismuth atom placed 0.333 Å above the basal plane formed by the four coplanar sulfur atoms. The large free space trans to the apical carbon of the mesityl group might be considered to accommodate the stereochemically active lone pair of electrons of the metal atom.

The dithiocarbamato derivative $[2-(2'-Py)C_6H_4]Bi[S(S)CNEt_2]_2$ was also described as monomeric.[132] The dithio ligands are again anisobidentate, but the difference between the cis short and the cis long bismuth–sulfur bond lengths is diminished [$\Delta = (Bi-S)_{long} - (Bi-S)_{short}$ = ca. 0.10 Å, compared with 0.26 Å in $RBi[S(S)CNEt_2]_2$].[132,133] The free space described by the longer Bi–S bonds in the equatorial BiS_4 plane is occupied by the nitrogen atom of the pyridyl group, which is strongly coordinated to the metal atom. The coordination polyhedron was described as *ψ*-pentagonal bipyramidal, with the apical positions occupied by the phenyl carbon atom and the lone pair of electrons. However, long Bi···S intermolecular contacts of 3.876 Å were noted between two neighboring molecules, with this sulfur atom placed trans to the phenyl carbon atom (S···Bi–C 161.1°) (Figure 66). This leads to loose dimeric associations, with sulfur atoms in positions where a stereochemically active lone pair might be assumed.

The solid-state structure of the related dithiocarbamato derivatives $RBi[S(S)CNEt_2]_2$ (R = Me,[133] Ph[132]) differs significantly from that of the above compounds, although in both cases the lattice contains dimeric associations formed through intermolecular Bi···S interactions. The monomeric unit is

Table 9. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for $RBiX_2$ Derivatives (X = Chalcogenato Ligand)

		Bi–X^{a}	Bi–E^{a}	Bi–C	X–Bi–X (or E)	ref
$MesBi[S(S)PPh_2]_2$		2.662	3.112	2.259	152.5 (S–Bi···S, *trans*)	102
$[2\text{-}(2'\text{-}Py)C_6H_4]Bi[S(S)CNEt_2]_2$		2.766; 2.798	2.878; 2.895; 3.876^{b} (Bi···S) 2.553 (Bi–N)	2.263	62.9–78.6 (*cis*)	132
$MeBi[S(S)CNEt_2]_2$^{c}	Bi(1) atom	2.67; 2.70	2.95; 2.98; 3.36^{b}	2.21	63.2–90.7 (*cis*)	133
	Bi(2) atom	2.68; 2.70	2.93; 2.96; 3.27^{b}	2.27	62.6–89.6 (*cis*)	
$PhBi[S(S)CNEt_2]_2$		2.671; 2.676	2.926; 2.942; 3.421^{b}	2.241	63.5–88.0 (*cis*)	132
$PhBi[SC_5H_4NO\text{-}4]_2$		2.653; 2.712	2.51; 2.54; 3.37^{b}	2.26	67.0–81.2 (*cis*)^{d}	134
$PhBi[S(S)COMe]_2$		2.649; 2.670	2.961; 3.079; 3.848;^{b,d} 3.816^{b,d}	2.25	60.5–85.8 (*cis*)^{d}	135
$PhBi(SCH_2CH_2)_2O$		2.560; 2.603	3.440;^{b} 3.509^{b} (Bi···S) 2.97 (Bi···O)	2.25	141.2 (C–Bi···O, *trans*)	135

[a] Bond distances and interactions, X = S; E = N, O, S. [b] Intermolecular interaction. [c] For the two independent molecules present in the unit cell. [d] Calculated from published atomic coordinates.

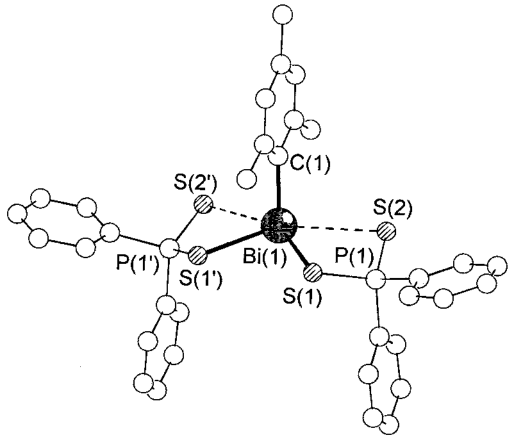


Figure 65. Molecular structure of $MesBi[S(S)PPh_2]_2$.[102]

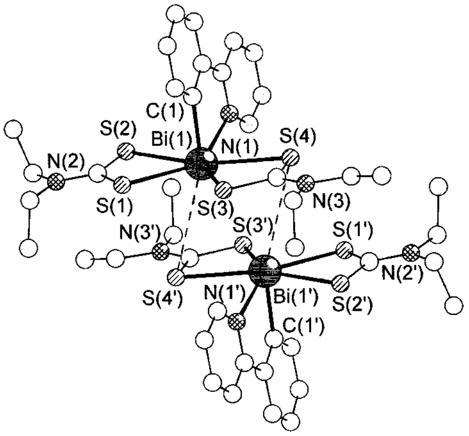


Figure 66. Dimeric association in the crystal of $[2\text{-}(2'\text{-}Py)C_6H_4]Bi[S(S)CNEt_2]_2$.[132]

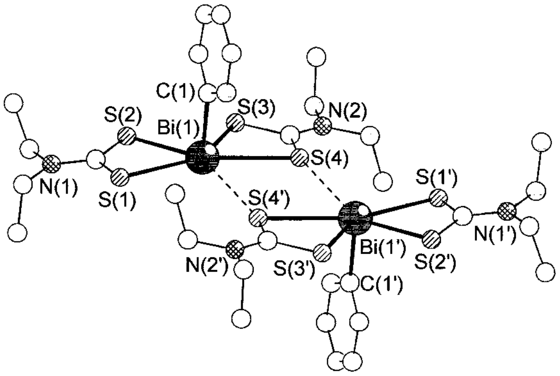


Figure 67. Dimeric association in the crystal of $PhBi[S(S)CNEt_2]_2$.[132]

similar to that of the previous dithiophosphinato derivative, the main difference consisting of the shortening of the intramolecular Bi···S(=C) bond distances (ca. 2.95 vs 3.1 Å). Such a monomeric unit is associated into distinct dimers through additional weaker bismuth–sulfur interactions (3.3–3.4 Å) established with a neighboring independent molecule (R = Me) or centrosymmetrically related one (R = Ph). The weak, intermolecular bismuth–sulfur interaction divides the opened S···Bi···S angle of the molecular unit. The coordination around the bismuth atoms is now distorted pentagonal pyramidal, with the sulfur atoms in the basal plane. The apical C atoms are placed on opposite sites of the Bi_2S_8 system (Figure 67), and again, the free space trans to the apical carbons was suggested to accommodate the lone pair of electrons. It should be noted that the dimeric associations are probably not preserved in solution, e.g., $MeBi[S(S)CNEt_2]_2$ is monomeric in benzene.[133]

The thiolato derivative $PhBi[SC_5H_4NO\text{-}2]_2$ was described as monomeric, with the lone pair presumably occupying a coordination site trans to the *ipso* carbon of the phenyl group.[134] The thio ligands are covalently linked through sulfur and establish strong intramolecular Bi···O interactions (ca. 2.5 Å), leading to a nearly planar BiS_2O_2 moiety with an opened O···Bi···O angle. However, the packing in the unit cell brings two monomeric units in a favorable position to allow weak intermolecular Bi···O interactions (ca. 3.4 Å). This leads to dimeric associations, as observed for the above dithiocarbamato derivative, with a similar distorted pentagonal pyramidal environment for the metal atoms; however, now the fifth equatorial position is occupied by an oxygen atom of the neighboring molecule (Figure 68).

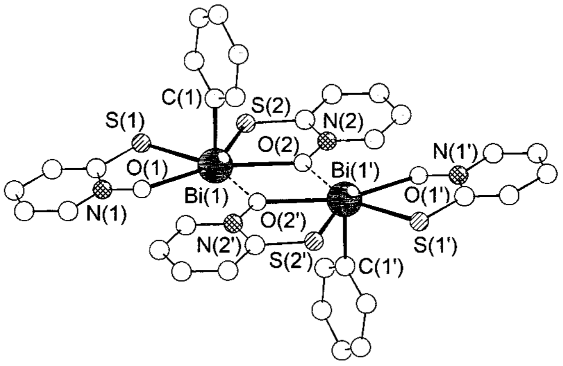


Figure 68. Dimeric association in the crystal of $PhBi[SC_5H_4NO\text{-}2]_2$.[134]

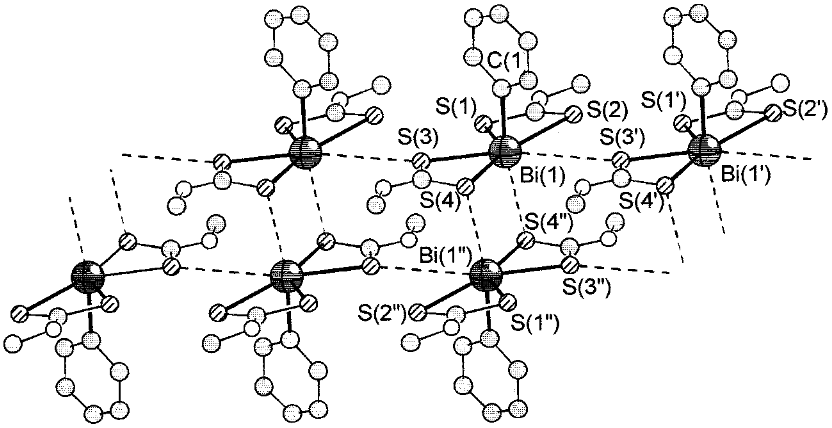


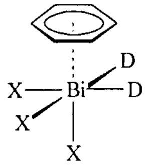
Figure 69. Polymeric association in the crystal of $PhBi[S(S)COMe]_2$.[135]

The molecular unit of the xanthogenato derivative $PhBi[S(S)COMe]_2$ is similar to those of the previously related dithiophosphinato and dithiocarbamato compounds, i.e., anisobidentate dithio ligands, with short and long bismuth−sulfur distances and a large S···Bi···S angle of 155.1°.[135] However, in the crystal, distinct layers are formed as a result of long intermolecular Bi···S contacts of about 3.83 Å (Figure 69): each bismuth atom displays two such weak interactions, one in the equatorial plane dividing the large S···Bi···S angle and the other one trans to the carbon atom attached to the metal atom (C−Bi···S 163.3°). If these interactions are also considered, the coordination geometry is a distorted pentagonal bipyramid.

In the heterocyclic complex $PhBi(SCH_2CH_2)_2O$, the expected pyramidal covalent $CBiS_2$ core is again completed by additional interatomic contacts, i.e., a transannular Bi···O (2.97 Å) and two weak intermolecular Bi···S (3.509 Å, intrachain; 3.440 Å, interchains) interactions, involving only one of the sulfur atoms of the molecular unit.[136] The coordination polyhedron was described as a ψ-monocapped octahedron, a position being occupied by the stereochemically active lone pair of electrons. As a result of these interactions, the crystal structure exhibits a double chain of molecules containing $CBiOS_4$ polyhedra connected through two different edges.

G. Arene Complexes of Bismuth

The structures of adducts of bismuth halides (chlorides, bromides), alkoxides, or carboxylates with neutral arene molecules feature π-complexes where the arenes are coordinated as ligands to the bismuth atoms. Generally, the hapticity is 6, i.e., the bismuth atoms occupy positions above or/and below the center of the arene rings. These complexes are the bismuth analogues of the so-called "Menshutkin" complexes of antimony trihalides with arenes. Bismuth−arene complexes have been known since the 1960s, but the first structures were elucidated only 20 years later. Two distorted coordination geometries around the bismuth atom were generally observed, regardless of the nature of the anionic ligands and the arene molecule, i.e., octahedral (**38** or **39**) and pentagonal bipyramidal (**40**).



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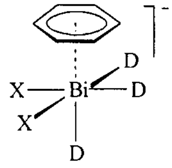

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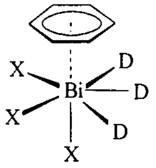

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With one exception, i.e., ionic $[(\eta^6\text{-}C_6Me_6)BiCl_2][AlCl_4]$ which has only two Bi−Cl primary bonds (**39**), in all other compounds investigated by X-ray diffraction some common features concerning the coordination environment of the metal atom can be pointed out. Each bismuth atom has (*i*) three primary (short) bonds and (*ii*) two or three secondary (longer) bonds (or interactions) to halide or oxygen atoms, thus leading to different degrees of association in the crystal, and (*iii*) the C_6 aromatic system is placed trans to a primary Bi−X bond with trans X−Bi···Ar_{center} angles in the range 153.4−168.5°. The Bi−Ar_{center} distances (range 2.72−3.29 Å) reflect the acid−base properties of the arene donors and the bismuth acceptors. The increase of Lewis basicity of the arenes in the series C_6H_6, $Me_2C_6H_4$, $Me_3C_6H_3$, Me_6C_6 as well as an increase of the acidity of the bismuth center (cf. $BiCl_3$ vs $BiCl_2^+$) leads to shorter arene−bismuth bonds. It is also remarkable that the arene−metal bonds are generally shorter for bismuth halide than for antimony halide complexes with arenes. Important molecular parameters for arene complexes of bismuth are listed in Table 10.

The first structurally characterized arene complex of bismuth trichloride was $(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)BiCl_3$.[67,137] The crystals of this complex consist of alternating, crystallographically independent sheets of $BiCl_3$ networks, each of them containing two nonequivalent bismuth atoms [Bi(1), Bi(3) and Bi(2), Bi(4), respectively—see Table 10]. The coordination sphere for the nonequivalent bismuth atoms which build a $(BiCl_3)_n$ sheet is basically octahedral, with three strongly bound chlorine atoms and two, more loosely bound, bridging chlorine atoms occupying five of the coordination sites. The sixth coordination position is screened by an η^6-bound mesitylene molecule. However, Bi(1) and Bi(2) atoms exhibit an additional weaker Bi···Cl interaction (4.050 and 3.879 Å, respectively) which divides the larger cis equatorial Cl−Bi···Cl angle. If these weak interactions are also

Table 10. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Complexes of Bismuth

		Bi−X[a]	Bi−E[a]	Bi−Ar_{center}	X−Bi···Ar_{center} (*trans*)	X−Bi−X (eq, *cis*)	ref
$(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)BiCl_3$[b]	Bi(1) atom	2.465; 2.483; 2.489	3.302; 3.368; 4.050	3.11	167.7[c]	55.8−93.9[c]	137
	Bi(2) atom	2.468; 2.494; 2.501	3.247; 3.436; 3.879	3.10	168.5[c]	56.7−93.3[c]	
	Bi(3) atom	2.455; 2.508; 2.524	3.180; 3.275	2.99	153.4[c]	85.1−95.6[c]	
	Bi(4) atom	2.463; 2.493; 2.503	3.200; 3.283	2.99	154.1[c]	84.9−96.2[c]	
$(\eta^6\text{-}1,2\text{-}Me_2C_6H_4)BiCl_3$[b]	Bi(1) atom	2.442; 2.476; 2.516	3.171; 3.199; 3.768	3.06[c]	153.9[c]	59.9−88.2	138
	Bi(2) atom	2.424; 2.479; 2.531	3.155; 3.261	3.01[c]	165.7[c]	76.3−96.0	
$(\eta^6\text{-}1,3\text{-}Me_2C_6H_4)BiCl_3$		2.424; 2.479; 2.531	3.152; 3.299	2.99[c]	159.1[c]	77.1−101.1	138
$(\eta^6\text{-}1,4\text{-}Me_2C_6H_4)BiCl_3$[b]	Bi(1) atom	2.393; 2.492; 2.493	3.055; 3.312	3.05[c]	163.8[c]	76.5−96.0	138
	Bi(2) atom	2.402; 2.456; 2.479	3.053; 3.200	3.08[c]	161.3[c]	79.5−95.9	
$(\eta^6\text{-}C_6H_6)BiCl_3$[b]	Bi(1) atom	2.444; 2.473; 2.486	3.246; 3.483; 3.578	3.21[c]	167.6[c]	58.0−90.9[c]	139
	Bi(2) atom	2.461; 2.473; 2.481	3.219; 3.415; 3.621	3.10[c]	166.4[c]	56.8−89.9[c]	
$(\mu\text{-}\eta^6\text{-}Me_6C_6)(BiCl_3)_2$		2.404; 2.438; 2.887	2.887; 3.716; 3.716	3.07	168.0[c]	51.0−90.0[c]	140
$(2{\cdot}\eta^6\text{-}C_{16}H_{16})(BiBr_3)_2$d		2.595; 2.663; 2.676	3.325; 3.402	3.09[c]	158.7[c]	78.0−95.5[c]	141
$(2{\cdot}\eta^6\text{-}C_{16}H_{16})(BiBr_3)_2(C_{16}H_{10})$[d,e]		2.587; 2.635; 2.656	3.353; 3.409	3.06[c]	156.6[c]	79.0−94.5[c]	142
$(3{\cdot}\eta^6\text{-}C_{24}H_{24})(BiCl_3)_3(C_6H_6)$[b,f]	Bi(1) atom	2.450; 2.521; 2.523	3.165; 3.230	3.08	166.9[c]	78.7−108.9[c]	143
	Bi(2) atom	2.461; 2.469; 2.498	3.245; 3.529	2.98	162.2[c]	70.5−117.9[c]	
	Bi(3) atom	2.482; 2.516; 2.531	3.131; 3.276	2.99	163.1[c]	72.8−117.4[c]	
$(2{\cdot}\eta^6\text{-}C_{32}H_{32})(BiBr_3)_2(C_6H_5Me)$[g]		2.598; 2.659; 2.668	3.221; 3.419	3.10[c]	164.8[c]	79.8−97.1	34
$(2{\cdot}\eta^6\text{-}C_{16}H_{10})(BiCl_3)_2$e		2.445; 2.511; 2.514	3.154; 3.347; 3.640[c]	3.20[c]	164.6[c]	60.0−88.5	144
$(2{\cdot}\eta^6\text{-}C_{16}H_{10})(BiBr_3)_2(C_6H_4Me_2\text{-}1,4)_{0.5}$[b,h]	Bi(1) atom	2.570; 2.679; 2.695	3.165; 3.494	3.29[c]	158.1[c]	75.5−100.0	145
	Bi(2) atom	2.601; 2.620; 2.670	3.335; 3.369	3.12[c]	161.1[c]	80.3−97.6	
$(2{\cdot}\eta^6\text{-}C_{20}H_{12})_2(BiBr_3)_4(C_{20}H_{12})$[b,i]	Bi(1) atom	2.580; 2.657; 2.691	3.174; 3.363	3.06[c]	161.7[c]	79.2−96.6	146
	Bi(2) atom	2.580; 2.597; 2.676	3.400; 3.450	3.18[c]	156.0[c]	75.3−99.4	
$(\eta^6\text{-}C_6H_5Me)_2[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)]_2$		2.089; 2.136; 2.168	2.555	2.968	167.0	77.7; 90.0	148
$(\eta^6\text{-}C_6H_5Me)_2[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)]_2(C_6H_5Me)_2$		2.088; 2.147; 2.210	2.571	2.958	161.1	76.1; 82.7	148
$(\mu\text{-}\eta^6\text{-}C_6Me_6)[Bi_2(\mu\text{-}O_2CCF_3)_4]_2$		2.387; 2.417		3.05	180	85.9; 91.5[c]	33
$[(\eta^6\text{-}C_6Me_6)BiCl_2][AlCl_4]$		2.433; 2.445[c]	2.946; 3.263; 3.370[c]	2.72	156.2[c]	83.2−92.8	149

[a] Bond distances and interactions, X, E = Cl, Br, O. [b] For the nonequivalent bismuth atoms in the unit cell. [c] Calculated from published atomic coordinates. [d] $C_{16}H_{16}$ = [2.2]paracyclophane. [e] $C_{16}H_{10}$ = pyrene. [f] $C_{24}H_{24}$ = [2.2.2]paracyclophane. [g] $C_{32}H_{32}$ = [2.2.2.2]paracyclophane. [h] $C_{16}H_{10}$ = fluoranthrene. [i] $C_{20}H_{12}$ = perylene.

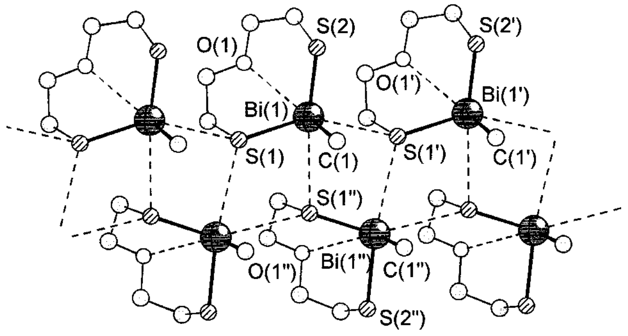


Figure 70. Polymeric association in the crystal of $PhBi(SCH_2CH_2)_2O$ (for clarity, only the carbons bound directly to bismuth atoms are shown).[136]

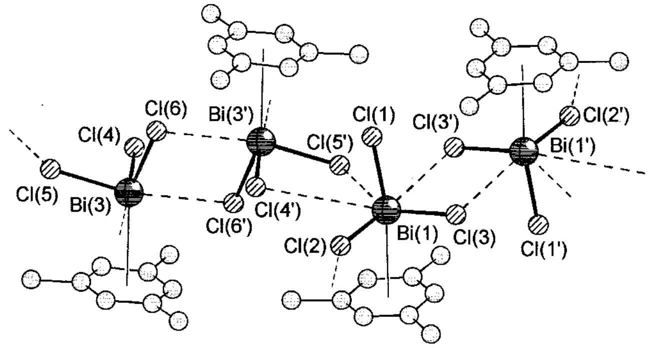


Figure 71. Fragment from one of the two crystallographically independent sheets in the crystal of $(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)BiCl_3$.[137]

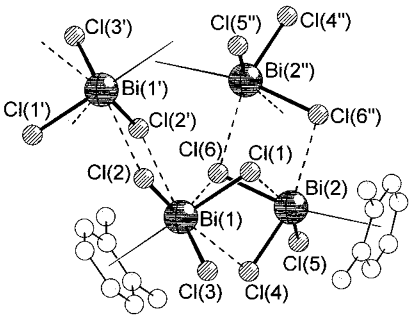


Figure 72. Polymeric association in the crystal of $(\eta^6\text{-}1,2\text{-}Me_2C_6H_4)BiCl_3$.[138]

considered, for each independent sheet one type of bismuth atom might be described as pentagonal bipyramidal, with the arene fragment in an apical position (Figure 71).

The solid-state structures of the three isomeric complexes $(\eta^6\text{-}Me_2C_6H_4)BiCl_3$ ($Me_2C_6H_4$ = *ortho*-, *meta*-, and *para*-xylene) contain different one-dimensional polymeric chains.[138] Thus, in the crystal of the $(\eta^6\text{-}1,2\text{-}Me_2C_6H_4)BiCl_3$ derivative, dimeric arene−$BiCl_3$ units containing four-membered Bi_2Cl_2 rings are formed for both of the two nonequivalent metal centers. These dimeric units are further associated via two shorter [Bi(1)···Cl(4) 3.171 Å and Bi(2)···Cl(1) 3.261 Å] interactions and one longer [Bi(1)···Cl(6) 3.768 Å] bismuth−halogen interactions (Figure 72).[138] Thus, the nature of the chlorine atoms for a $BiCl_3$ unit is different: one terminal and two μ^2-Cl for Bi(1) and two μ^2-Cl and one μ^3-Cl for Bi(2), respectively. The resulting bismuth atom environments are also different, i.e., octahedral for Bi(2) and pentagonal bipyramidal for Bi(1), with the weak Bi···Cl interactions in the equatorial plane.

The crystals of the related $(\eta^6\text{-}1,3\text{-}Me_2C_6H_4)BiCl_3$ and $(\eta^6\text{-}1,4\text{-}Me_2C_6H_4)BiCl_3$ derivatives also contain dimeric arene−$BiCl_3$ units with four-membered Bi_2Cl_2 rings, but in these cases dimeric units are further associated into one-dimensional polymeric chains (Figure 73) only via two weak Bi⋯Cl interactions (Table 10).[138]

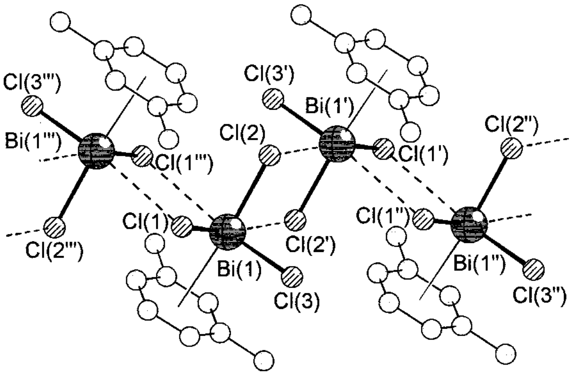


Figure 73. Polymeric association in the crystal of (η^6-1,3-$Me_2C_6H_4$)$BiCl_3$.[138]

The coordination of the arene at Bi is not perfectly centroid but is characterized by ring slippages of 0.41, 0.29, and 0.24 Å for the *ortho*-, *meta*-, and *para*-xylene derivatives, respectively. The direction of this slipping with respect to the arene's methylation sites cannot be understood in terms of electronic influences but was shown to be caused by steric demands.[138]

A very weak bismuth−benzene π-bonding is present in (η^6-C_6H_6)$BiCl_3$.[139] The crystal structure was described as a layer polymer. In the asymmetric unit there are two nonequivalent bismuth atoms which built up a dimeric unit through Bi⋯Cl bridges [Bi(1)⋯Cl(4) 3.246 Å and Bi(2)⋯Cl(1) 3.219 Å]. These dimeric fragments are held together into the layer polymer (Figure 74) through additional weaker Bi⋯Cl(1) bridges (Table 10), all halogen atoms acting as μ^2-bridging ligands. The result is a distorted pentagonal bipyramidal coordination for all bismuth atoms, with three short Bi−Cl bonds, three weaker Bi⋯Cl(1) contacts, and the η^6-benzene ligand in an apical position. The bismuth−carbon distances for both metal centers are significantly longer than those in (η^6-1,3,5-$Me_3C_6H_3$)$BiCl_3$ or (η^6-Me_6C_6)$(BiCl_3)_2$, consistent with a weaker donor character of the unsubstituted benzene ligand.

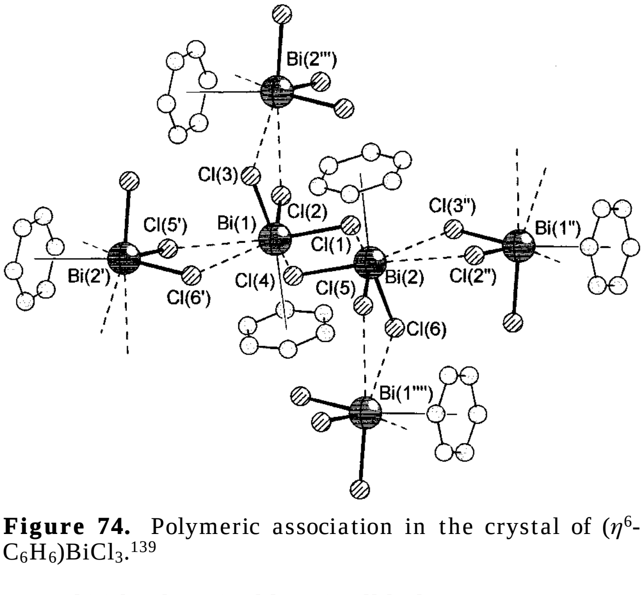


Figure 74. Polymeric association in the crystal of (η^6-C_6H_6)$BiCl_3$.[139]

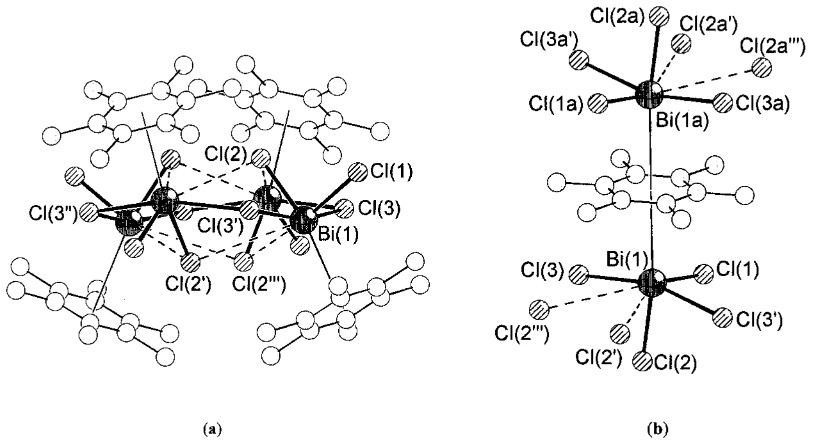
In the crystals of (μ-η^6-Me_6C_6)$(BiCl_3)_2$, the centric η^6 coordination of a C_6 aromatic ligand is further extended in a spectacular way.[67,140] The crystals consist of tetrameric $(BiCl_3)_4$ units each containing four crystallographically equivalent metal centers (Figure 75a) coordinated by a hexamethylbenzene ligand. In the tetranuclear unit, an eight-membered Bi_4Cl_4 is formed through symmetric bridging μ^2-Cl atoms. The magnitude of these Bi−Cl bonds (2.887 Å) and the value of the corresponding Cl−Bi−Cl angle (163.7°) are consistent with a three-center four-electron bond in a hypervalent bismuth atom. Each of the bismuth atoms is also bound to two chlorine atoms at short distances (2.404 and 2.438 Å), one of them acting as a terminal atom. The other one is also involved in two weaker Bi⋯Cl interactions (3.716 Å) to the neighboring bismuth atoms. The result is a bismuth atom surrounded by two Cl atoms at short bond distances, two Cl atoms at longer bond distances, and two Cl atoms involved in weak interactions which occupy the free space between the longer Bi−Cl bonds. The distorted pentagonal bipyramidal coordination of the metal center is completed by a η^6-Me_6C_6 ligand placed in an apical position, trans to the μ^3-Cl atom.

On the other hand the centers of the arene molecules form crystallographic inversion centers with the consequence that an identical bismuth halide unit is found on the other side of the ring (Figure 75b). Hence, the complex can be regarded as an arene complex with an inverted sandwich structure.[67,140] A similar structure was also suggested for the (μ-η^6-Me_6C_6)$(BiBr_3)_2$ analogue, the structure being not fully refined.[140]

The bismuth(III) bromide−[2.2]paracyclophane adduct, ($2\eta^6$-$C_{16}H_{16}$)$(BiBr_3)_2$, exhibits a solid-state structure built up by polymeric linear chains of $BiBr_3$ units interlayered by centrosymmetric hydrocarbon molecules (Figure 76).[141] A $BiBr_2$ unit bridges adjacent bismuth centers so that the coordination is very distorted octahedral with three short and two longer bridging bismuth−bromine bonds. The sixth site is occupied by a benzene ring of the paracyclophane molecule. Compared to other bismuth−arene complexes, this adduct shows higher air and moisture stability which seems to reflect mainly the π-electronic transannular effects.

A ternary [2.2]paracyclophane−BiX_3−arene compound, ($2\eta^6$-$C_{16}H_{16}$)$(BiBr_3)_2$($C_{16}H_{10}$) ($C_{16}H_{10}$ = pyrene), was also described.[142] The crystal structure is similar to that of the above [2.2]paracyclophane adduct, with linear $(BiBr_3)_n$ polymeric chains connected through [2.2]paracyclophane molecules. The resulting two-dimensional network includes pyrene molecules which are not involved in interactions with the metal centers.

In the adduct ($3\eta^6$-$C_{24}H_{24}$)$(BiCl_3)_3$(C_6H_6) ($C_{24}H_{24}$ = [2.2.2]paracyclophane), each aromatic ring of the hydrocarbon is engaged in a centroid (η^6) π-complexation with the $BiCl_3$ units cross-linked by chlorine bridges in a polymeric network (Figure 77).[143] The



(a) (b)

Figure 75. (a) Tetranuclear Bi_4Cl_{12} core and (b) double-side arene coordination in the crystal of $(\mu\text{-}\eta^6\text{-}Me_6C_6)(BiCl_3)_2$.[140]

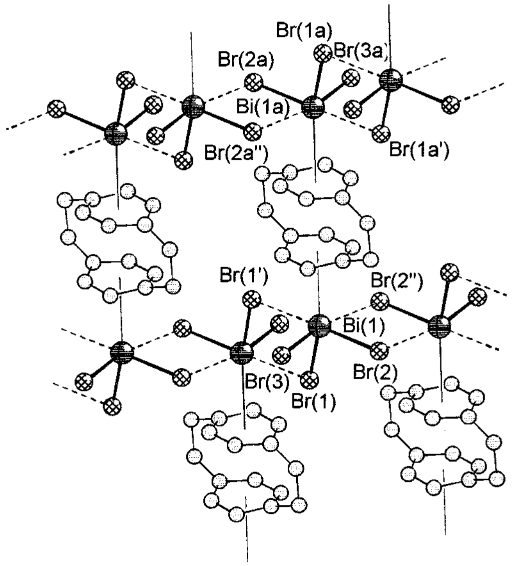


Figure 76. Polymeric association in the crystal of $(2\eta^6\text{-}C_{16}H_{16})(BiBr_3)_2$.[141]

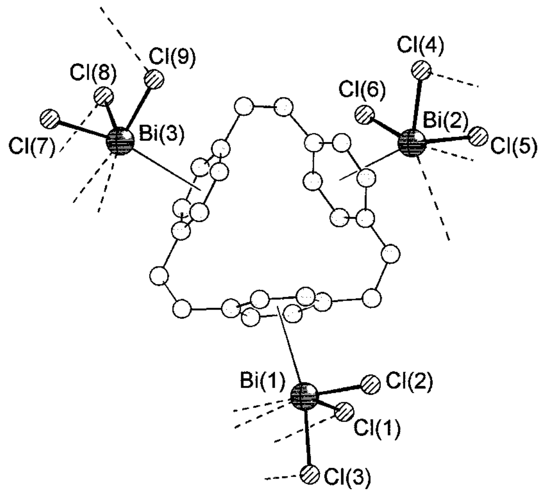


Figure 77. Fragment of the polymeric association in the crystal of $(3\eta^6\text{-}C_{24}H_{24})(BiCl_3)_3(C_6H_6)$ (the benzene molecule is not shown).[143]

coordination geometry for each of the three nonequivalent metal centers is again very distorted octahedral with three short and two longer bridging bismuth−chlorine bonds. π-Complexation is strongly directional with external η^6-coordination, and the benzene molecule is not coordinating.

A complex of an even larger paracyclophane molecule, $(2\eta^6\text{-}C_{32}H_{32})(BiBr_3)_2(C_6H_5Me)$ ($C_{32}H_{32}$ = [2.2.2.2]-paracyclophane), was recently reported.[34] In this charge-transfer compound, the paracyclophane molecule is centrosymmetric and two opposite aromatic rings are involved in external η^6-coordination to bismuth atoms while the toluene molecule acts as solvate. In the crystal, linear $(BiBr_3)_n$ polymeric chains, similar to those observed for the [2.2]paracyclophane adducts,[141,143] are built through asymmetric bridging bromine atoms and connected by the paracyclophane molecules (Figure 78).

The structure of the charge-transfer complex of $BiCl_3$ with pyrene, $(2\eta^6\text{-}C_{16}H_{10})(BiCl_3)_2$, contains two pyramidal $BiCl_3$ units interacting on opposite sides with a centrosymmetrical hydrocarbon molecule.[144] All chlorine atoms are involved in Bi···Cl interactions, thus leading to zigzag $(BiCl_3)_n$ chains interlayered by the organic molecules (Figure 79). The resulting coordination geometry for the bismuth atom is distorted pentagonal bipyramidal with two shorter (3.154, 3.347 Å) and one longer (3.640 Å) Bi···Cl interactions in the equatorial plane.

Another π-complex of a bismuth trihalide with a polycondensed arene is $(2\eta^6\text{-}C_{16}H_{10})(BiBr_3)_2(C_6H_4Me_2\text{-}1,4)_{0.5}$ ($C_{16}H_{10}$ = fluoranthene).[145] The structure is formed by centrosymmetric $(BiBr_3)_4$ built through μ^2-Br and μ^3-Br bridging atoms. Such a tetranuclear unit is interlayered by two fluoranthrene molecules, each of them being involved in two π-donations on the same side of the hydrocarbon molecule plane (Figure 80). There are two types of bismuth atoms bearing one [for Bi(1)] and two [for Bi(2)] unshared halide atoms, respectively, both of them exhibiting a distorted octahedral coordination with an apical position occupied by a benzene ring of the fluoranthene trans to the longest Bi−Br primary bond. The *para*-xylene molecule is not involved in any interactions with bismuth atoms.

A similar structure was described for a complex containing perylene as a π-donor arene system, $(2\eta^6\text{-}C_{20}H_{12})_2(BiBr_3)_4(C_{20}H_{12})$ ($C_{20}H_{12}$ = perylene).[146] In this case the centrosymmetric $(BiBr_3)_4$ unit built through asymmetrically bridging bromine atoms is interlayered by two hydrocarbon molecules. The third one, located on a symmetry center, is not involved in

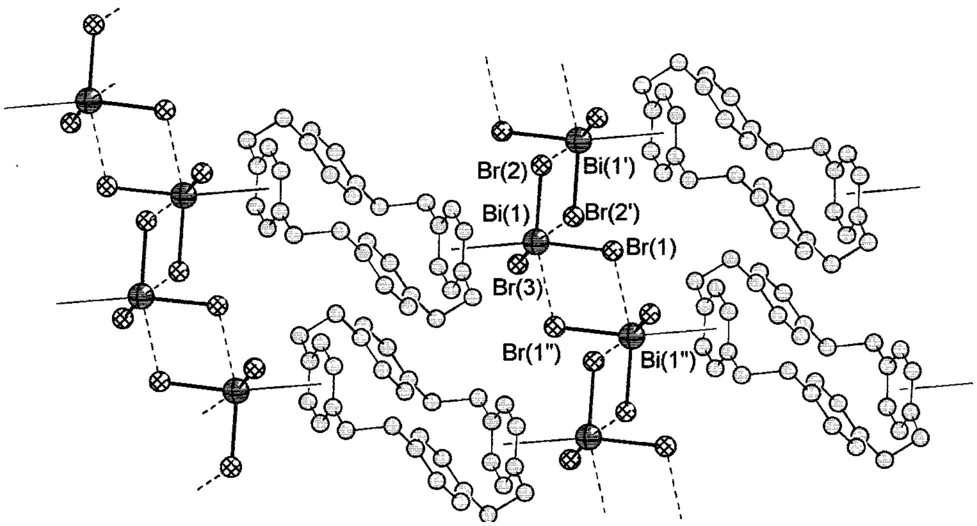


Figure 78. Polymeric association in the crystal of $(2\eta^6\text{-}C_{32}H_{32})(BiBr_3)_2(C_6H_5Me)$ (the toluene molecule is not shown).[34]

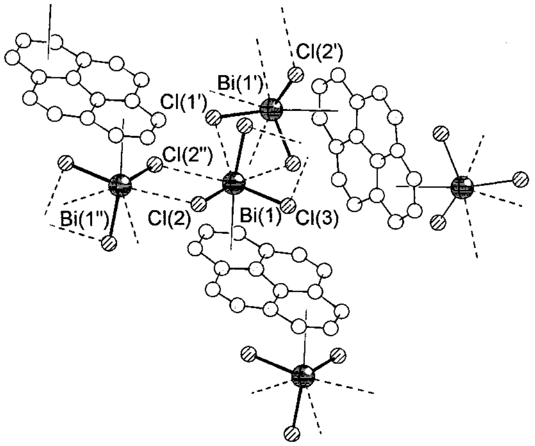


Figure 79. Polymeric association in the crystal of $(2\eta^6\text{-}C_{16}H_{10})(BiCl_3)_2$.[144]

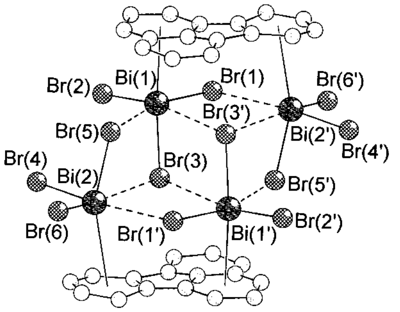


Figure 80. Tetranuclear association in the crystal of $(2\eta^6\text{-}C_{16}H_{10})(BiBr_3)_2(C_6H_4Me_2\text{-}1,4)_{0.5}$ (the *p*-xylene molecule is not shown).[145]

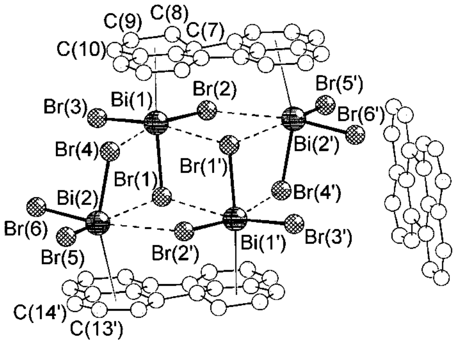


Figure 81. Tetranuclear association in the crystal of $(2\eta^6\text{-}C_{20}H_{12})_2(BiBr_3)_4(C_{20}H_{12})$.[146]

interactions with any metal atom and its plane forms a dihedral angle of 91.2° with that of the π-donor arene molecule (Figure 81). The range for the individual Bi···C distances [3.10–3.68 Å for Bi(1) and 3.10–3.54 Å for Bi(2)], although similar to those observed for other bismuth–arene complexes, was suggested to be consistent with an η^2 rather than η^6 pattern of the π-bonding.

An example of a bismuth–arene π-complex of particular interest is the only compound containing anionic ligands other than chloride or bromide, i.e., the alkoxide $(\eta^6\text{-}C_6H_5Me)_2[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)]_2(C_6H_5Me)_n$ ($n = 0, 2$).[147,148] Two crystalline morphologies differing by the absence or the presence of nonbonded lattice toluene have been investigated by X-ray diffractometry. The geometric parameters of both compounds are essentially the same. There are dimers with a central planar Bi_2O_2 ring built through asymmetric bridging alkoxide ligands. The longer Bi–O interactions (2.555 and 2.571 Å for $n = 0$ and 2, respectively) are comparable with those observed for strong intra- or intermolecular bismuth–oxygen coordinative interactions (see sections III.C or III.E), and therefore, these alkoxides can be considered as hypervalent 10-Bi-4 species [O(1)–Bi(1)-O(2′) 145.4°]. The coordination geometry of the bismuth atom was described as very distorted ψ-octahedral, with a toluene molecule coordinated in an apical position trans to the shorter bismuth–oxygen bond of the μ^2-OR ligand. The fourth equatorial position was suggested to be occupied by the lone pair of electrons, which was considered to be stereochemically active in contrast to the bismuth trihalide–arene complexes.[148] However, a closer check of the interatomic distances around the metal center revealed that for each bismuth atom there are two *ortho*-fluorine atoms establishing Bi···F contacts at distances [Bi(1)···F(1) 3.11 Å, Bi(1)···F(10′) 3.36 Å, for $n = 0$] of the same magnitude as found for some BiR_3 derivatives containing fluorinated phenyl groups as organic ligands (see section III.A). These weak interactions are placed in the equatorial plane in the free place claimed to accommodate the lone pair, and if they are also considered, the resulting coordination geometry can be described as distorted pentagonal bipyramidal (cis equatorial angles around Bi in the range 60.5−90.0°) (Figure 82).

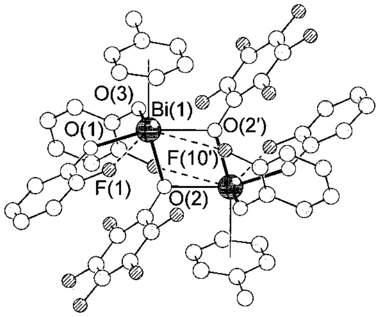


Figure 82. Dimeric association in the crystal of (η^6-C_6H_5-Me)$_2$[Bi(OC_6F_5)$_2$(μ-OC_6F_5)]$_2$.[148]

A very remarkable bismuth−arene adduct, the dark red complex (μ-η^6-C_6Me_6)[Bi_2(μ-O_2CCF_3)$_4$]$_2$, was described recently.[33] This unusual compound is the first example of a carboxylato derivative containing the bismuth atoms in a formal +2 oxidation state, with a Bi−Bi bond (2.947 Å) even shorter than in dibismuthines (see section III.I). The crystal structure contains dinuclear [Bi_2(μ-O_2CCF_3)$_4$]$_2$ units, with two different carboxylato fragments symmetrically bridging the bismuth atoms. The Bi−O bond distances are considerably longer than those observed for the Bi−O covalent bonds in the alkoxide derivative described above (Table 10) but in the range for a single bond in other bismuth−oxygen containing derivatives (see sections III.C and III.E). The coordination sphere of the bismuth atoms is completed by arene molecules placed trans to the Bi−Bi bond on each side of the dinuclear moiety, resulting in an octahedral geometry. The chain polymeric structure with colinear Bi atoms and arene centers (Figure 83) is the result of the π-donation pattern of the Me_6C_6 molecules which exhibit interactions with bismuth atoms on both sides of the aromatic ring. A similar inverted sandwich behavior was also observed for the hexamethylbenzene molecules in the crystal structure of the (μ-η^6-Me_6C_6)($BiCl_3$)$_2$ derivative.[67,140]

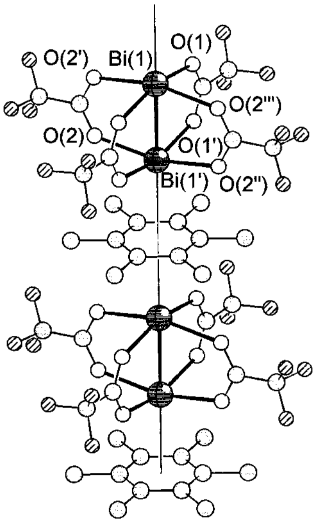


Figure 83. Polymeric association in the crystal of (μ-η^6-C_6Me_6)[Bi_2(μ-O_2CCF_3)$_4$]$_2$.[33]

The shortest Bi−arene distance known was found in the ionic complex formed of [(η^6-C_6Me_6)$BiCl_2$]-[$AlCl_4$].[149] The compound exists as a centrosymmetric dimer in which three of the chlorine atoms of [$AlCl_4$]$^-$ anions are involved in bridges to bismuth atoms (Figure 84). The bismuth atoms have a very distorted octahedral geometry, with two short Bi−Cl bonds and three weaker Bi···Cl interactions and the tilted aromatic rings trans to the shortest Bi···Cl contacts. The bismuth−arene center distance of (2.72 Å) is significantly shorter than in neutral complexes of arenes with $BiCl_3$ (Table 10).

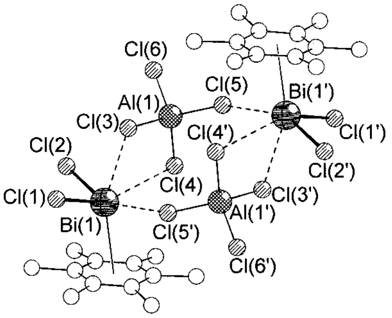


Figure 84. Dimeric association in the crystal of [(η^6-C_6-Me_6)$BiCl_2$][$AlCl_4$].[149]

H. Coordination Complexes of the Type R_nBiX_{3-n}·ML_x

In contrast to the extensive investigation of N, P, As, and Sb donors,[46] very few complexes of tertiary bismuthines BiR_3 are characterized. Only four structures of compounds in which $BiPh_3$ is coordinated to a transition metal center have been reported and discussed in relation to the relative σ and π contributions to the transition metal−bismuth bond.

In the neutral, isomorphous compounds [$(OC)_5M$-($BiPh_3$)] (M = Cr,[47] Mo, W[48]) as well as in the cation of the [(C_5H_5)$(OC)_2$Fe($BiPh_3$)][BF_4] complex,[49] the $MBiC_3$ core is tetrahedral (Figure 85). No Bi···F interactions between the cation and the anion were observed in the latter compound. In the complexes, the Bi−C bond distances are shorter while C−Bi−C

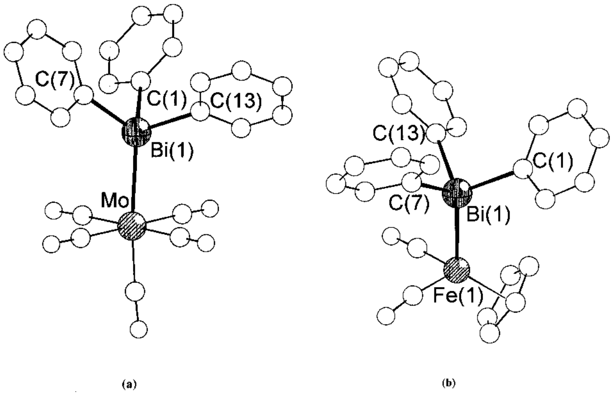


Figure 85. Molecular structure of (a) [$(OC)_5$Mo($BiPh_3$)],[48] and (b) cation in [(C_5H_5)$(OC)_2$Fe($BiPh_3$)][BF_4].[49]

Table 11. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Transition Metal Complexes of $BiPh_3$

	Bi−C	C−Bi−C	Bi−M	M−Bi−C	ref
$[(OC)_5Cr(BiPh_3)]$	2.212−2.222	97.0−101.2	2.705	114.6−123.6	47
$[(OC)_5Mo(BiPh_3)]$	2.213−2.233	95.7−101.7	2.832	114.2−124.5	48
$[(OC)_5W(BiPh_3)]$	2.217−2.234	97.0−102.3	2.829	114.0−123.6	48
$[(C_5H_5)(OC)_2Fe(BiPh_3)][BF_4]$	2.218−2.226	101.1 (av)	2.570	112.6−121.5	49
Ph_3Bi (for comparison)	2.237−2.273	92.7−94.7			82

Table 12. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) in Compounds with Bi−Bi Bonds

	Bi−Bi	Bi···Bi	Bi−C	C−Bi−C	C−Bi−Bi	ref
$Ph_2Bi{-}BiPh_2$	2.990		2.26; 2.28	98.3	90.9; 91.6	151
$(Me_3Si)_2Bi{-}Bi(SiMe_3)_2$	3.035	3.804		92.7[a]	97.4; 92.0	153
$(HC{=}CMe)_2Bi{-}Bi(CMe{=}CH)_2$	2.990	3.66	2.23; 2.24	79.3	88.8; 90.0	30
$(Tbt)Bi{=}Bi(Tbt)$[b]	2.8206		2.290		100.5	31
$[(Me_3Si)_2CH]_4Bi_4$	2.970−3.044		2.33−2.39	79.0−79.9[c]	93.9−109.5	32
$[(HCCMe)_2Bi]_2Fe$		3.69[d]	2.22 (av)	76.4 (av)		30
$(\mu\text{-}\eta^6\text{-}C_6Me_6)[Bi_2(\mu\text{-}O_2CCF_3)_4]_2$	2.947					33

[a] Si−Bi−Si angle. [b] Tbt = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$. [c] Bi−Bi−Bi angle. [c] Inter-ring Bi···Bi contact.

angles are increased in comparison with those observed in free $BiPh_3$ (Table 11). This behavior is consistent with the higher degree of s-character being in the lone pair orbital in triorganobismuthines than in the Bi orbital used in Bi−M bonding. A comparison of the E−M (E = P, As, Sb, Bi) distances within a series comprising both types of complexes suggested the relatively poor π-acceptor properties of the Bi ligand.[47,49]

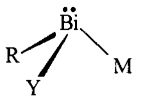
Two other transition metal complexes containing BiR_3 (R = C_5H_5, C_6H_5) ligands, i.e., $[(CO)_3Mn(\eta^5\text{-}C_5H_5)]_3Bi$[96] and $[(CO)_3Cr(\eta^6\text{-}C_6H_5)]_2BiC_6H_5$,[97] which do not contain a Bi−M bond but $\eta^5\text{-}C_5H_5{-}Mn$ and $\eta^6\text{-}C_6H_5{-}Cr$ π-bondings, have also been reported and are described in section II.A.

I. Compounds Containing Bismuth–Metal Bonds

The compounds with known structures containing bismuth−metal bonds can be divided in two classes, i.e., (*i*) compounds with bismuth−bismuth bonds and (*ii*) compounds with bismuth−transition metal bonds. The latter class of compounds has received attention as part of the general interest in main group−transition metal clusters and the results obtained have been periodically reviewed.[27−29] Structures of compounds with bonds between bismuth and other main group metals are unknown.

1. Compounds Containing Bismuth–Bismuth Bonds and Related Compounds

There are very few compounds with known crystal structures in this group. They comprise three dibismuthines, $R_2Bi{-}BiR_2$, a dibismuthene RBi=BiR with a double bond between the bismuth atoms, and a cyclobismuthane, R_4Bi_4. A dibismuth compound with only weak intramolecular Bi···Bi interactions is 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene. The coordination geometry around bismuth atoms is basically pyramidal (**41**, Y = R, Bi; M = Bi) for three-coordinate compounds, with possibilities for an increase of the coordination number through intermolecular Bi···Bi interactions leading to a ψ-trigonal bipyramidal environment (**42**). For two-coordinate bismuth atoms in dibismuthene and η^5-bismolyl ring containing derivatives, the Bi_2C and BiC_2 fragments are angular. Important molecular parameters for derivatives belonging to this class of compounds are listed in Table 12.



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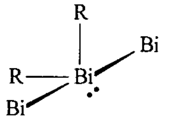

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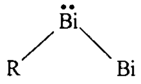

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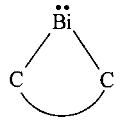

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Interesting aspects of the structures of dibismuthines are the conformation and the possibility of the formation of bismuth chains through alternating Bi−Bi bonds and intermolecular Bi···Bi contacts.

The first crystallographically characterized tetraorganyl derivative of bismuth(II) is tetraphenyldibismuthine, $Ph_2Bi{-}BiPh_2$. The molecule has a staggered trans conformation. The coordination at the bismuth atoms is essentially pyramidal (Figure 86). The bond angles about bismuth are significantly smaller than the tetrahedral value. There are three crystal morphologies for $Ph_2Bi{-}BiPh_2$: a triclinic,[150,151] a monoclinic, and a tetragonal form.[152] In all these crystalline forms the molecules have essentially the same structure. There are no close intermolecular contacts between the bismuth atoms. The color of tetraphenyldibismuthine is yellow.

The dibismuthine $(Me_3Si)_2Bi{-}Bi(SiMe_3)_2$, which does not contain a direct Bi−C bond, has essentially the same molecular structure as tetraphenyldibismuthine with a staggered trans conformation of the substituents.[153] However, the crystal structure is different. There are linear zigzag bismuth chains (Bi−Bi···Bi 169°) with alternating Bi−Bi bonds (3.035 Å) and shortened intermolecular Bi···Bi contacts

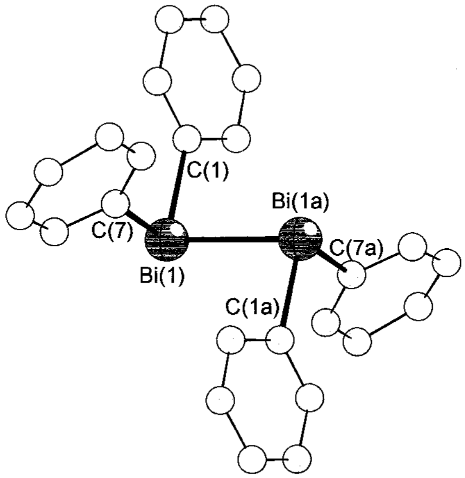


Figure 86. Molecular structure of $Ph_2Bi-BiPh_2$.[151]

(3.804 Å) in the crystalline state (Figure 87). The association leads to a green color of the compounds in the solid state.

An alignment of Bi_2 groups into zigzag chains (Bi···Bi 3.66 Å, Bi–Bi···Bi 166.5°) of bismuth atoms is also characteristic of the structure of 2,2′,5,5′-tetramethyldibismole (Figure 88),[30] which has a staggered trans conformation, as observed for all reported dibismuthines. The color of the crystals is green as well. The Bi–Bi bond distance is identical with that found for tetraphenyldibismuthine, but the C–Bi–C angle is considerably diminished to 79.3° due to ring strain.

A remarkable recent development is the synthesis and crystal structure analysis of the first compound with a Bi=Bi double bond, the dibismuthene (Tbt)-Bi=Bi(Tbt), where Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Figure 89).[31] The compound forms deep purple crystals. The Bi=Bi double-bond length is 6% shorter than that of the Bi–Bi single bond of 2.990 Å in $Ph_2Bi-BiPh_2$. The observed Bi–Bi–C angle of 100.5° is close to 90° and, therefore, consistent with bonding models using nonhybridized 6p orbitals for bonding.

Another recent result is the analysis of the structure of the first cyclobismuthine $[(Me_3Si)_2CH]_4Bi_4$ (Figure 90).[32] It contains a folded four-membered organobismuth ring (fold angles 112.9°; 112.6°), with the alkyl substituents in the all trans positions. The pyramidal Bi_2C core is considerably distorted (angles at bismuth between 79° and 109.5°) due to the bulky substituents at the metal atom and to the ring geometry.

A dibismuth compound where the bismuth atoms are not connected through normal covalent bonds but rather through weak interactions is 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene (Figure 91).[30] The compound adopts a metallocene-like arrangement with a close interring Bi···Bi contact of 3.69 Å. Intermolecular Bi···Bi contacts of the same magnitude are noted in some $[(\mu\text{-RBi})Fe(CO)_4]_2$ complexes (3.783 and 3.664 Å for R = Me and Ph, respectively, as calculated from published atomic coordinates—see section III.I.2).[155,156] The iron atom is π-bonded to two eclipsed η^5-dimethylbismolyl rings. The intraring bond lengths indicate that the bismolyl groups are π-complexed heteroaromatic systems. The bismuth atoms are displaced out of the ring planes away from the iron (average displacement of 0.28 Å).

The shortest Bi–Bi single bond (2.947 Å) was found in the unusual bismuth–arene adduct, $(\mu\text{-}\eta^6\text{-}C_6Me_6)[Bi_2(\mu\text{-}O_2CCF_3)_4]_2$,[33] which is the first example

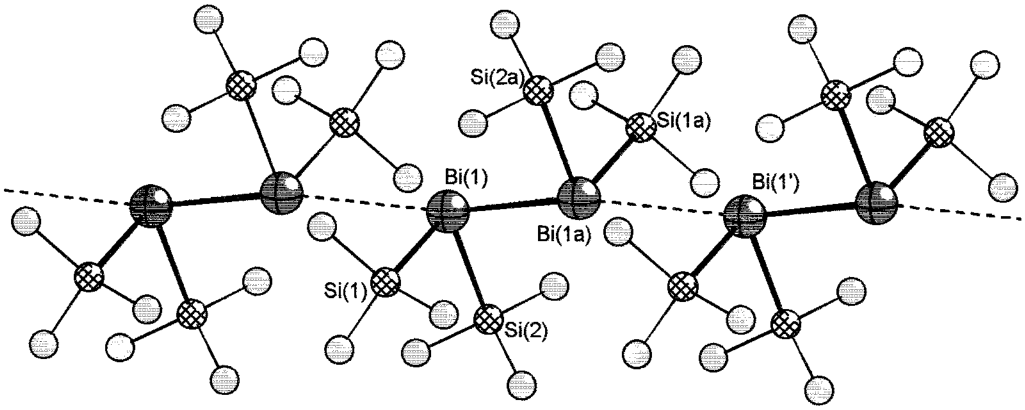


Figure 87. Chain polymeric association in the crystal of $(Me_3Si)_2Bi-Bi(SiMe_3)_2$.[153]

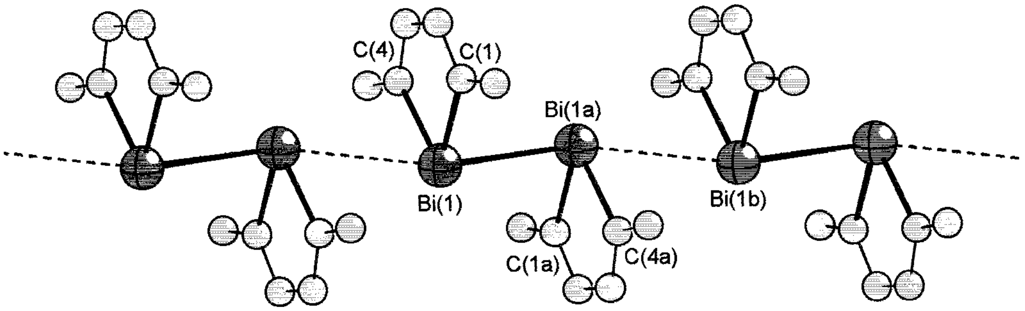


Figure 88. Chain polymeric association in the crystal of $(HC{=}CMe)_2Bi-Bi(CMe{=}CH)_2$.[30]

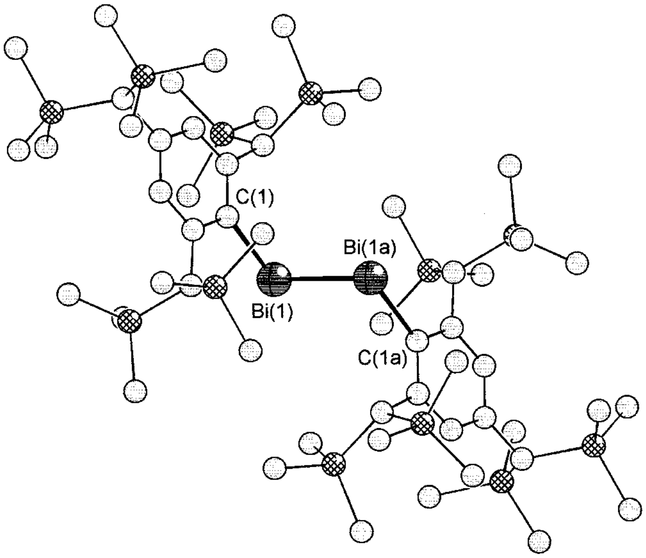


Figure 89. Molecular structure of (Tbt)Bi=Bi(Tbt) (Tbt = 2,4,6-[$(Me_3Si)_2CH]_3C_6H_2$).[31]

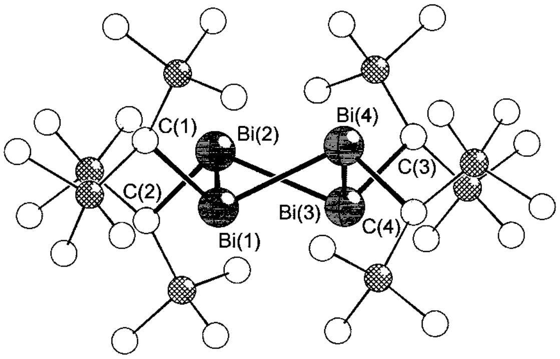


Figure 90. Molecular structure of $[(Me_3Si)_2CH]_4Bi_4$.[32]

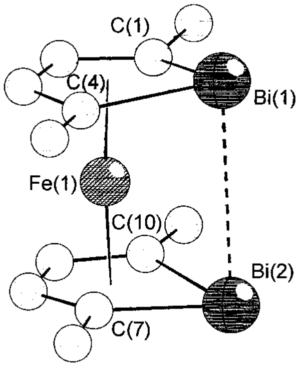
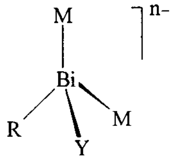


Figure 91. Molecular structure of $[(HCCMe)_2Bi]_2Fe$.[30]

of a carboxylato derivative containing the bismuth atoms in a formal +2 oxidation state. The structure of this remarkable dark red complex was already described in section III.G (Figure 83).

2. Compounds with Bismuth–Transition Metal Bonds

Several types of compounds containing an organometallic BiR_n (n = 1 or 2) moiety attached to a transition metal atom, including neutral and ionic species, have been described. The coordination geometries around the bismuth atom in such compounds are distorted pyramidal (**41**, Y = R, M; M = transition metal), tetrahedral (**45**, anions with Y = R, M; M = transition metal), or ψ-trigonal bipyramidal (**46**). Angular BiC_2 fragments in bismolyl rings (**44**) η^5-coordinated to a transition metal are also known. Important molecular parameters for derivatives belonging to this class of compounds are listed in Table 13.



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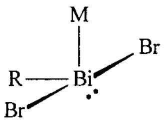

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In three-coordinate Bi–transition metal compounds in which the octet rule at Bi and the 18-electron rule at the transition metal is respected, the Bi–M bond is most appropriately described as a normal covalent bond rather than a dative one and the Bi center usually retains a lone pair. In some cases its stereochemical activity was suggested.[154,157] Neutral complexes in which this lone pair of electrons is involved in dative bonds are not known so far. The increased size of the Bi atom, in comparison to the other group 15 elements, as well as the “inertness” of the lone pair and the bulkiness of the organotransition metal moieties, most likely play major roles in determining the structure formed.[155]

A pyramidal C_2BiM core (type **41**, Y = R) was found in monomeric compounds which contain a Ph_2Bi group bonded to a organotransition metal moiety, i.e., neutral complexes: $Ph_2BiCo(CO)_3(PPh_3)$,[155] $Ph_2BiMn(CO)_5$ (Figure 92),[154] or in the anion of $[(Ph_3P)_2N][Ph_2BiFe(CO)_4]$.[154] The Bi–C bond lengths are similar to those observed in $Ph_2Bi{-}BiPh_2$ or Ph_3Bi, while the M–Bi–C angles, although far from the tetrahedral value, are considerably larger than 90°, as expected for primarily p character bonding to bismuth. Steric repulsions between CO and Ph groups were responsible at least in part for this feature.[154] The lone pair at bismuth was suggested to be stereochemically active in $[(Ph_3P)_2N][Ph_2BiFe(CO)_4]$.[154] The Bi–Fe distance in this compound is, however, of the same magnitude (Table 13) as that observed in $[Et_4N][Ph_2Bi\{Fe(CO)_4\}_2]$[50] and $[Et_4N]_2[Bu^tBi\{Fe(CO)_4\}_3]$.[51] These complexes contain a four-coordinate bismuth atom, and apparently a degree of hybridization might be considered. However, evidences were obtained indi-

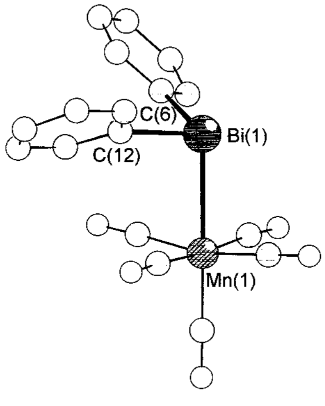


Figure 92. Molecular structure of $Ph_2BiMn(CO)_5$.[154]

Table 13. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) in Complexes Containing Bi−Transition Metal Bonds

	Bi−C	C−Bi−C	Bi−M	Bi···Bi	M−Bi−C	M−Bi−M	ref
$Ph_2BiCo(CO)_3(PPh_3)$	2.25; 2.28	95.7	2.692		100.9; 98.5		155
$Ph_2BiMn(CO)_5$	2.27; 2.23	94.5	2.842		103.3; 99.2		154
$[(Ph_3P)_2N][Ph_2BiFe(CO)_4]$	2.27; 2.32	94.9	2.676		104.0; 101.6		154
$(Ph_2Bi)_2Fe(CO)_4$	2.22; −2.26	94.7; 97.6	2.832; 2.823		100.6; 101.4		154
$[\eta^1\text{-}(HCCMe)_2Bi]Mn(CO)_5$	2.26; 2.25	78.2	2.827		99.8; 97.3		157
$[\eta^5\text{-}(MeCCSiMe_3)_2Bi]Fe(C_5H_5)$	2.23; 2.24	76.6	2.643				159
$[\eta^5\text{-}(HCCMe)_2Bi]_2Fe$	2.22 (av)	76.4 (av)	2.677 (av)	3.69[c]			30
$[(Ph_3P)_2N][Ph_2Bi\{Cr(CO)_5\}_2]$	2.254; 2.263	95.2	2.750; 2.750		103.8−111.8	125.5	50
$[(Ph_3P)_2N][Ph_2Bi\{Mo(CO)_5\}_2]$	2.25; 2.30	94.2	2.882; 2.885		104.2−112.3	125.6	50
$[(Ph_3P)_2N][Ph_2Bi\{W(CO)_5\}_2]$	2.20; 2.23	94	2.891; 2.997		103.9−112	126.2	50
$[Et_4N][Ph_2Bi\{Fe(CO)_4\}_2]$	2.251; 2.262	94.5	2.624; 2.629		106.0−112.2	121.5	50
$[(Ph_3P)_2N][Ph_2Bi\{Cr(CO)_5\}\{Fe(CO)_4\}]$	2.254; 2.260	94.5	2.722 (Cr) 2.630 (Fe)		103.3−112.3	122.3	50
$(\mu\text{-}EtBi)[Mo(CO)_3(C_5H_5)]_2$	2.293		2.994; 2.996		96.7; 107.0	117.8	160
$[(\mu\text{-}MeBi)Fe(CO)_4]_2$	2.28		2.785; 2.787	3.783	104.1; 100.7	98.6	156
$[(\mu\text{-}Bu^iBi)Fe(CO)_4]_2$	2.292		2.786; 2.788		101.5; 101.3	100.7	51
$[(\mu\text{-}PhBi)Fe(CO)_4]_2$	2.25		2.779; 2.793	3.664	103.8	98.3	154
$[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)(\mu\text{-}MeBiW(CO)_2](C_6H_6)$	2.339		2.851−2.881[a]		106.6−111.7	128.5; 129.7[b] 66.3[c]	162
$[Et_4N]_2[Bu^iBi\{Fe(CO)_4\}_3]$	2.32		2.673−2.681		96.7−107.7	112.7−116.4	51
$Ph(Br)BiMo(CO)_3(C_5H_5)$	2.24		2.928		108.1		163

[a] For (C)Bi−W bonds. [b] Exocyclic W−Bi(1)−W angles. [c] Endocyclic W−Bi(1)−W angle.

cating that although Ph_2Bi is a presumably good σ-donor, the availability of the Bi lone pair for dative bonding is too low to result in complexes of Co(I) with bridging Ph_2Bi.[155]

For all three above complexes the Bi−metal distances (Table 13) are characteristic for single bonds. Thus, for example, in $Ph_2BiMn(CO)_5$ the Bi−Mn distance of 2.842 Å is slightly shorter than in the more sterically crowded inorganic $Bi[Mn(CO)_5]_3$ (2.884−2.916 Å)[158] but considerably longer than in the "bismuthinidene" $ClBi[Mn(C_5H_4Me)(CO)_2]_2$ (2.475, 2.483 Å),[52] where multiple-bond character has been attributed to the manganese−bismuth bonds.

A unique example of two Ph_2Bi groups attached to a transition metal atom was found in $(Ph_2Bi)_2Fe(CO)_4$ (Figure 93).[154] In both organobismuth moieties, coordinated to Fe in cis positions, the Bi atoms exhibit a pyramidal coordination geometry. The Bi−Fe bond distances in $(Ph_2Bi)_2Fe(CO)_4$ are considerably longer (average 2.827 Å) than in the $[Ph_2BiFe(CO)_4]^-$,[154] $[Ph_2Bi\{Fe(CO)_4\}_2]^-$,[50] or $[Bu^iBi\{Fe(CO)_4\}_3]^{2-}$ anions,[51] a behavior which might suggest a higher degree of hybridization, although only for $[Ph_2Bi\{Fe(CO)_4\}_2]^-$ the angles around bismuth are close to the tetrahedral value (for comparative data see Table 13). Alternatively, and more likely, the increase in the Bi−Fe bond length might also be produced by steric interactions of phenyl rings with the CO groups. It should also be noted that a phenyl ring attached to Bi(1) has an orientation which allows weak interactions (3.45−3.73 Å, calculated from published atomic coordinates) between Bi(2) and C(11), C(12), and C(16) atoms.

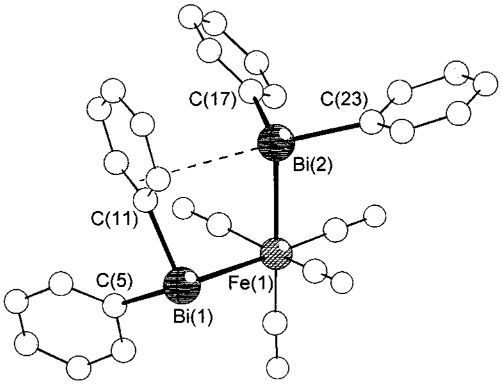


Figure 93. Molecular structure of $(Ph_2Bi)_2Fe(CO)_4$.[154]

A pyramidal C_2BiM core was also found in the $[\eta^1\text{-}(HC{=}CMe)_2Bi]Mn(CO)_5$ complex (Figure 94a) which consists of an almost planar 2,5-dimethylbismolyl moiety acting as an η^1-ligand to a $Mn(CO)_5$ group.[157] As in other complexes containing $M(CO)_n$ moieties, the CO groups are slightly oriented toward the pyramidal Bi atom. The Bi−Mn distance is similar to that of $Ph_2BiMn(CO)_5$.[154] The BiC_4 ring is essentially planar (Bi deviation from the best C_4 plane is 0.086 Å). The bond angles of the heterocyclic moiety are identical to those found in the 2,2′,5,5′-tetramethyldibismole,[30] but the steric repulsion between the ring moiety and the CO groups results in an increase of the Mn−Bi−C angles in comparison

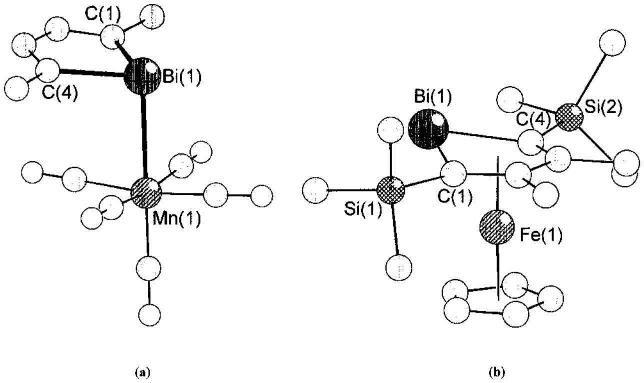


Figure 94. Molecular structure of (a) $[\eta^1\text{-}(HCCMe)_2Bi]Mn(CO)_5$[157] and (b) $[\eta^5\text{-}(MeCCSiMe_3)_2Bi]Fe(C_5H_5)$.[159]

to those corresponding to Bi−Bi−C (88.8° and 90.0°). Again the values of the bond angles around bismuth, considerably smaller than the tetrahedral angle of 109.5°, indicate an s character of the lone pair at Bi. The failure to obtain bismolyl-bridged complexes indicates the inertness of this lone pair of electrons.

The possibility for a bismolyl group to coordinate as an η^5-heteroaromatic ligand was confirmed in the case of two iron derivatives, i.e., $[\eta^5\text{-(MeCCSiMe}_3)_2\text{Bi]Fe(C}_5\text{H}_5)$ (Figure 94b)[159] and $[\eta^5\text{-(HCCMe)}_2\text{Bi]}_2\text{Fe}$.[30] The latter was already briefly mentioned in section III.I.1 in relation with the interring Bi···Bi interactions. The presence of substituents at the carbon atoms of the heterocycle provides steric hindrance which increases the stability of the Bi heterocycle. Both compounds exhibit a metallocene-like arrangement with the carbon atoms of the two cycles lying in parallel planes. The bismuth atom is displaced away from iron above the best C_4 plane in the bismolyl ligand by 0.38 Å in the monobismaferrocene derivative and an average of 0.28 Å in the dibismaferrocene. This behavior appears to be a consequence of simultaneously accommodating the π-bonding to the large heteroatoms and the smaller carbons. A multiple-bond character was suggested for the Bi−C bonds (Table 13) which are, however, longer than the Bi=C double bond of 2.16 Å in a bismuth ylide (see Section II.B).[101]

Four-coordinate bismuth(III) is found in the isoelectronic and isostructural $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ph}_2\text{Bi}\{\text{M(CO)}_5\}_2]$ (M = Cr, Mo, W) derivatives, as well as in $[\text{Et}_4\text{N}][\text{Ph}_2\text{Bi}\{\text{Fe(CO)}_4\}_2]$ and the mixed-transition metal complex $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ph}_2\text{Bi}\{\text{Cr(CO)}_5\}\{\text{Fe(CO)}_4\}]$ (Figure 95).[50] All anions of the type $[\text{Ph}_2\text{Bi}\{\text{M(CO)}_n\}_2]^-$ contain a bridging diorganobismuth moiety and can be considered formally as complexes of the bismuth(I) anion $[\text{BiPh}_2]^-$. The resulting C_2BiM_2 core is of distorted tetrahedral geometry (type **45**, Y = R): the M−Bi−M angle is expanded to 121−126° at the cost of the C−Bi−C angle (94−95°), while the C−Bi−M angles remain in a range (103−112°) close to the ideal tetrahedral value.[50]

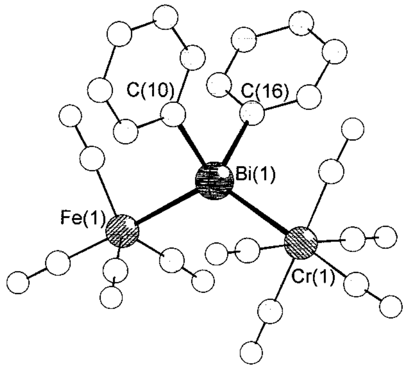


Figure 95. Structure of the anion in $[(\text{Ph}_3\text{P})_2\text{N}][\text{Ph}_2\text{Bi}\{\text{Cr(CO)}_5\}\{\text{Fe(CO)}_4\}]$.[50]

Another dimetallabismuth compound is $(\mu\text{-EtBi})[\text{Mo(CO)}_3(\text{C}_5\text{H}_5)]_2$ in which a monoorganobismuth moiety is bridging two $\text{Mo(CO)}_3(\text{C}_5\text{H}_5)$ fragments (Figure 96).[160] The Bi center is three-coordinate in a trigonal pyramidal environment (type **41**, Y, M = transition metal). The Mo−Bi−Mo angle, although larger than the C−Bi−Mo ones, is diminished in comparison with that observed in the $[\text{Ph}_2\text{Bi}\{\text{Mo(CO)}_5\}_2]^-$ anion,[50] while the Bi−Mo bond distance in the neutral compound is lengthened by about 0.1 Å (Table 13). This is consistent with an influence of the steric effects on both angles and bond lengths in which the two different metal atoms are involved.

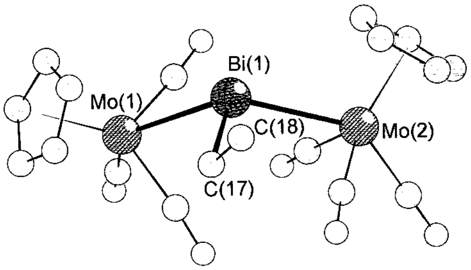


Figure 96. Molecular structure of $(\mu\text{-EtBi})[\text{Mo(CO)}_3(\text{C}_5\text{H}_5)]_2$.[160]

Bridging RBi groups are also present in $[(\mu\text{-RBi})\text{Fe(CO)}_4]_2$ [R = Me,[156] Bu^i,[51] Ph[154]] complexes which contain a planar Bi_2Fe_2 ring. The values of all bond angles around a bismuth atom lie between 90° and the tetrahedral value, thus being consistent with a possible stereochemically active lone pair of electrons. The constraint of the four-membered ring might account for the intermediate length of the Bi−Fe bonds (average 2.786 Å) [between those observed for the related anions (average 2.656 Å) and the neutral $(\text{Ph}_2\text{Bi})_2\text{Fe(CO)}_4$ (average 2.827 Å)], as well as for the short cross-ring Bi···Bi distances (3.635, 3.557, and 3.640 Å for R = Me, Bu^i, and Ph, respectively) (Table 13). The similarity of the molecular structures suggests that apparently the presence of different organic groups has little influence on the ring geometry owing to their trans orientation and little, if any, steric interaction between the organo groups and the CO ligands.

However, a closer check of the cell packing reveals interesting differences. For R = Me and Ph (Figure 97), weak intermolecular Bi···Bi contacts of 3.783 and 3.664 Å (as calculated from published atomic coordinates) are established between neighboring Bi_2Fe_2 rings, thus leading to a supramolecular, chain polymeric association. An interring Bi···Bi contact of the same magnitude (3.69 Å) has been also observed in the dibismaferrocene.[30] By contrast, for R = Bu^i, the bulkiness of the organic groups prevents such intermolecular interactions and no intermolecular bismuth−bismuth contacts shorter than the sum of van der Waals radii (4.8 Å) are observed.

A remarkable compound is $[\text{W}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-Bi}_2)\{\mu\text{-MeBiW(CO)}_5\}](\text{C}_6\text{H}_6)$ (Figure 98).[161,162] The MeBi group might be considered to bridge through single bonds two tungsten atoms of a $\text{W}_2(\text{CO})_8$ fragment and additionally to coordinate to a W(CO)_5 moiety. The length of the three Bi(1)−W bonds is quite similar regardless of the nature of the tungsten atoms. They are slightly longer compared to the coordinative Bi−W bond (2.829 Å) in the $[(\text{OC})_5\text{W(BiPh}_3)]$ complex[48] but significantly shorter than the bismuth−tungsten bonds (2.987−3.001 Å) established by the transverse coordination to the W_2 unit. The distortion

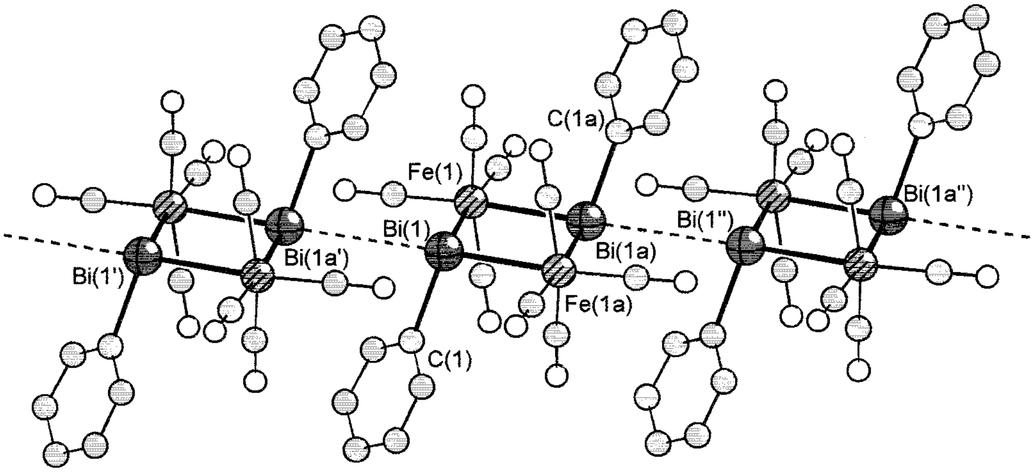


Figure 97. Polymeric association in the crystal of $[(\mu\text{-PhBi})Fe(CO)_4]_2$.[154]

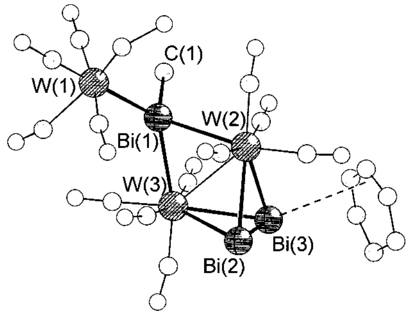


Figure 98. Molecular structure of $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)\{\mu\text{-MeBiW}(CO)_5\}](C_6H_6)$.[162]

of the tetrahedral $CBiW_3$ core (type **45**, Y = transition metal) is due to the restriction imposed by the presence of the W(2)–W(3) bond [endocyclic W–Bi(1)–W 66.3°]. The bismuth–bismuth distance (2.796 Å) suggests a multiple-bond character [cf. 2.821 Å in (Tbt)Bi=Bi(Tbt),[31] see section III.I.1], and the Bi_2 fragment was described as a four-electron donor to the W_2 core. It should also be noted that the benzene molecule incorporated as solvent seems to act as an η^3-ligand. Very weak interactions (3.52–3.74 Å, calculated from published atomic coordinates) are established between Bi(3) of the Bi_2 unit and the aromatic carbon atoms.

In the anion of $[Et_4N]_2[Bu^iBi\{Fe(CO)_4\}_3]$ (Figure 99), a Bu^iBi group is linked to three $Fe(CO)_4$ fragments leading again to a tetrahedral $CBiM_3$ core (type **45**, Y = transition metal).[51] A distortion from a regular tetrahedron, which is small in comparison with the above tungsten complex, might be the result of steric hindrance of the metal carbonyl groups. All the Bi–Fe bond lengths are equivalent and of the same magnitude as that observed for the $[Ph_2BiFe(CO)_4]^-$ anion[154] but somewhat longer than in the iron-containing $[Ph_2Bi\{M(CO)_n\}_2]^-$ anions.[50] A similar behavior may be noted for the Bi–C bond lengths (Table 13).

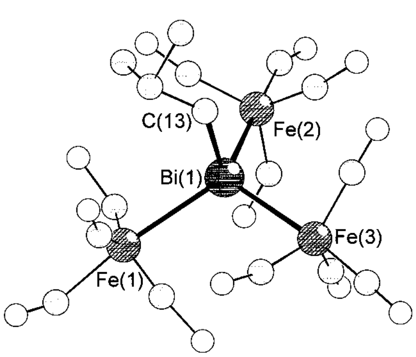


Figure 99. Structure of the anion in $[Et_4N]_2[Bu^iBi\{Fe(CO)_4\}_3]$.[51]

A monoorganobismuth(III) moiety is also found in $Ph(Br)BiMo(CO)_3(C_5H_5)$.[163] The bismuth atom is primarily bonded to three different atoms: a carbon atom of the phenyl group, a bromine atom (Bi–Br 2.891 Å), and the molybdenum atom of the $Mo(CO)_3(C_5H_5)$ moiety. The Bi–Mo bond length is intermediate between those observed in the neutral $(\mu\text{-EtBi})[Mo(CO)_3(C_5H_5)]_2$ (average 2.995 Å)[160] and the $[Ph_2Bi\{Mo(CO)_5\}_2]^-$ (average 2.883 Å) anion.[50] As a consequence of the presence of both Lewis acidic (bismuth atom) and Lewis basic (bromine atom) sites, a strong intermolecular Bi···Br secondary bond (3.033 Å), trans to the Bi–Br primary bond (Br–Bi···Br 161.9°), is established. This results in polymeric zigzag chains with bent bromine bridges (Bi–Br···Bi 129.6°) and bismuth atoms acting as chiral centers (Figure 100). The coordination geometry around the bismuth atoms is distorted ψ-trigonal bipyramidal, with bromine atoms in apical positions and the aromatic carbon and the transition metal atom in equatorial ones.

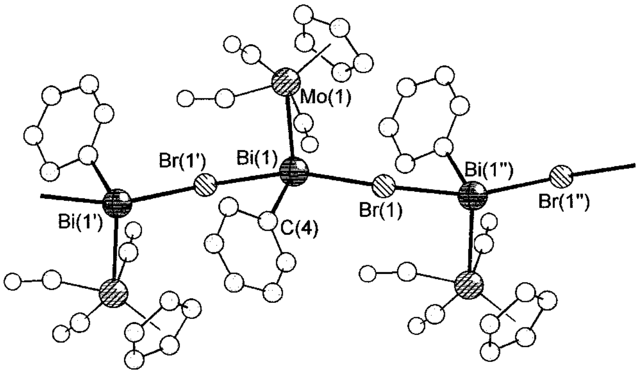
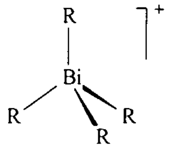


Figure 100. Polymeric association in the crystal of $Ph(Br)BiMo(CO)_3(C_5H_5)$.[163]

J. Compounds of the Type $[R_4Bi]_n^+[X]^{n-}$ and R_4BiX (X = Oxygen- and Halogen-Containing Ligands)

Tetraorganobismuth(V) derivatives with solid-state structures investigated by X-ray diffraction belong to two main types of compounds, i.e., (*i*) ionic derivatives ("bismuthonium" salts), $[R_4Bi]_n^+[X]^{n-}$ and (*ii*) neutral hypervalent compounds, R_4BiX. Most of them are aromatic derivatives. The ionic derivatives exhibit considerable structural diversity mainly due to cation−anion interactions. Few compounds containing tetrahedral $[R_4Bi]^+$ cations (**47**) with no interaction with the counteranion are known. In some cases, four weak cation−anion and/or intra-/intermolecular interactions are centered on the triangular faces of the C_4Bi tetrahedron, with little effect on the magnitude of the C−Bi−C angles (**48**). In some cases only one stronger cation−anion interaction is established trans to a Bi−C bond, thus resulting in various degrees of distortion toward a trigonal bipyramidal environment (**49**). When a phenyl group attached to bismuth has a pendant arm bearing a potentially donor atom, a weak intramolecular interaction is generally established, leading to a further distortion of the coordination geometry (**50**). Neutral tetraarylbismuth(V) compounds exhibit either distorted trigonal bipyramidal (**51**) or octahedral (**52**) coordination geometries. Important molecular parameters for quaternary bismuth(V) derivatives are listed in Table 14.



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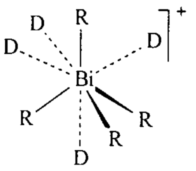

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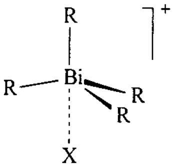

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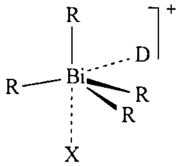

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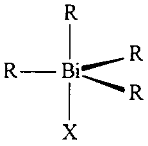

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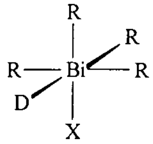

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The first structurally characterized bismuthonium derivative was $[Ph_4Bi][ClO_4]$,[164] which contains an $[R_4Bi]^+$ cation free of any interactions with the counteranion (Figure 101). The degree of distortion of the tetrahedral C_4Bi core is reflected by the C−Bi−C angles ranging between 105° and 112°, close to the ideal tetrahedral value (109.5°). Similar tetraaylbismuthonium cations were described recently for the $[(4\text{-}Me_2NC_6H_4)_4Bi][PF_6]$ and $[(4\text{-}Me_2NC_6H_4)_4Bi]_2[Ag_2Cl_4]$ derivatives, again free of close cation−anion contacts.[84] The former compound is thermochromic and deserves some special comments. At room temperature (23 °C) its color is light green and the crystals belong to the tetragonal space group P4/*n*. At low temperature (−23 °C) the color changes to blue and the crystal unit cell changes to the monoclinic space group $P2_1/n$. The color change is apparently caused by a phase transition.

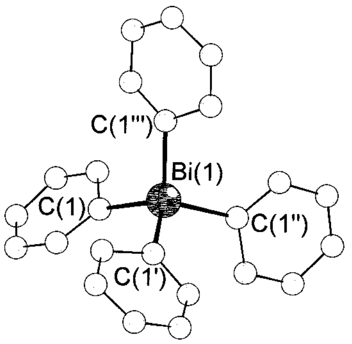


Figure 101. Structure of the cation in $[Ph_4Bi][ClO_4]$.[164]

A large separation (6.752 Å) between the bismuthonium cation and the bromine anion was also noted in $[(2\text{-}MeOC_6H_4)_4Bi][Br]\cdot H_2O$.[75] The C_4Bi core has a similar tetrahedral distortion (C−Bi−C angles in the range 106−115°) as that observed for the above ionic derivatives. The presence of the methoxy groups in *ortho* positions of all aromatic rings in the $[(2\text{-}MeOC_6H_4)_4Bi]^+$ cation allows strong intramolecular Bi···O interactions (Table 14). However, the four oxygen atoms are not all placed above the C_3 faces of the C_4Bi tetrahedron as one would expect for symmetry reasons. Three of the oxygen atoms are indeed capping the triangular faces: O(1), O(3), and O(4) for C(1)/C(8)/C(22), C(1)/C(8)/C(15), and C(8)/C(15)/C(22) systems, respectively, with trans O(1)···Bi(1)−C(15), O(3)···Bi(1)−C(22), O(4)···Bi(1)−C(1) angles of 156.5°, 158.3°, 155.3° (as calculated from published atomic coordinates). The fourth oxygen atom, O(2), is almost coplanar with the Bi(1)/C(1)/C(8) fragment, dividing the corresponding C−Bi−C angle [O(2)···Bi(1)−C(1) 67.4°, O(2)···Bi(1)−C(8) 49.0°], thus leaving the C(1)/C(15)/C(22) face free of any Bi···O interactions (Figure 102a).

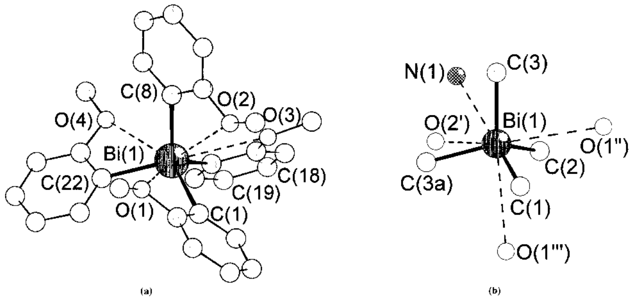


Figure 102. Coordination environment for the cation in (a) $[(2\text{-}MeOC_6H_4)_4Bi][Br]\cdot H_2O$[75] and (b) $[Me_4Bi][O_3SCF_3]\cdot MeCN$.[41]

By contrast, a coordination environment of type **48** (Figure 102b), with all triangular C_3 faces capped by atoms involved in intermolecular interactions, might

Table 14. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Compounds of the Type R_4BiX

	Bi–C	Bi–O	Bi···E or Bi–E[a]	C–Bi···E	C–Bi–C	ref
$[Ph_4Bi][ClO_4]$	2.16[b]				105.1–111.7[b]	164
$[(4\text{-}Me_2NC_6H_4)_4Bi][PF_6]$	2.167–2.194				106.1–112.0	84
$[(4\text{-}Me_2NC_6H_4)_4Bi]_2[Ag_2Cl_4]$	2.14–2.18				106–113	84
$[(2\text{-}MeOC_6H_4)_4Bi][Br]\cdot H_2O$	2.194–2.207		2.968–3.099 (Bi···O)		105.9–114.7	75
$[Me_4Bi][O_3SCF_3]\cdot MeCN$	2.210–2.230		3.31–3.58 (Bi···O)[b] 3.47 (Bi···N)[b]		108.9–112.0	41
$[Ph_4Bi][O_3SC_6H_4Me\text{-}4]$	2.17–2.24		2.77 (Bi···O)	177	98–103 (ax–eq) 113–123 (eq–eq)	61
$[Ph_4Bi][Ph_2Bi(O_2CCF_3)_2]$	2.19–2.23		3.11 (Bi···O)	177	101–109 (ax–eq) 108–120 (eq–eq)	61
$[Ph_3(Me_2C{=}C)Bi][BF_4]$	2.204–2.218 ($Bi–C_{Ph}$) 2.182 ($Bi–C_{alkenyl}$)		3.131 (Bi···F)	178[a]	103.8–107.0 (ax–eq) 109.6–115.3 (eq–eq)	165
$Ph_4BiOC_6F_5$	2.200–2.257	2.544		174.9	96.5–100.5 (ax–eq) 115.9–120.1 (eq–eq)	43
$Ph_4BiOC_6Cl_5$	2.181–2.22	2.543		175.4	97.6–101.5 (ax–eq) 107.8–128.5 (eq–eq)	43
$[Ph_3BiCH_2C(O)Bu^t][BF_4]$	2.19–2.21		2.90 (Bi···O) 3.48 (Bi···F)		102.1–118.4	166
$[Ph_3BiCH_2C(O)Bu^t][O_3SCF_3]$	2.17–2.24		2.93 ($Bi\cdots O_{carbonyl}$) 3.16 ($Bi\cdots O_{triflate}$)		102.6–117.4	167
$[Ph_3BiCH_2CH_2C(O)OPr^i][O_3SCF_3]$	2.206–2.235		3.157 ($Bi\cdots O_{carbonyl}$) 3.140 ($Bi\cdots O_{triflate}$)		101.0–115.5	168
$(4\text{-}MeC_6H_4)_3Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$	2.194–2.266	2.323		169.1	96.6–100.6 (ax–eq) 103.8–133.1 (eq–eq)	169
$(4\text{-}MeC_6H_4)_2(PhC{\equiv}C)Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$	2.193–2.249	2.243		169.4	93.6–108.2 (ax–eq) 108.2–126.8 (eq–eq)	169
$(4\text{-}MeC_6H_4)_2MeBi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$	2.19–2.25	2.328		168.2	94.6–103.0 (ax–eq) 109.5–124.0 (eq–eq)	169
$(4\text{-}MeC_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4(CH_2NMe_2)\text{-}2]$	2.219–2.26	2.313	2.85 (Bi···N)	162.2	94.2–100.4 (ax–eq) 98.5–100.9 (eq–eq)	170
$(4\text{-}CF_3C_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4(CH_2NMe_2)\text{-}2]$	2.228–2.27	2.292	2.878 (Bi···N)	165.4	97.1–100.0 (ax–eq) 100.2–102.3 (eq–eq)	170
$(4\text{-}CF_3C_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4\{C(CF_3)_2OMe\}\text{-}2]$	2.214–2.290	2.275	2.741 ($Bi\cdots O_{methoxy}$)	162.6	97.1–101.9 (ax–eq) 100.2–103.7 (eq–eq)	170

[a] Cation–anion and intra-/intermolecular interactions, E = F, O, N. [b] Calculated from published atomic coordinates.

be considered for $[Me_4Bi][O_3SCF_3]\cdot MeCN$,[41] the only tetraalkylbismuthonium derivative investigated so far by single-crystal X-ray diffraction. Two crystalline modifications, belonging to the monoclinic space groups $P2_1/m$ and $P2_1/c$, respectively, have been isolated, but the differences in the molecular parameters and the ion arrangement are insignificant. The basic C_4Bi core exhibits very small deviations from an ideal tetrahedron as reflected by the C–Bi–C angles (Table 14). All three oxygen atoms of a triflate anion are involved in Bi···O interactions with three different bismuth centers, the cation–anion contacts being considerably longer (Bi···O 3.31–3.58 Å) than the intramolecular Bi···O interactions in the $[(2\text{-}MeOC_6H_4)_4Bi]^+$ cation but still shorter than the sum of the van der Waals radii for bismuth and oxygen.[75] The result is a chain polymeric arrangement with alternate $[Me_4Bi]^+$ cations and bridging triflate anions (Bi···O 3.31 Å), the latter also being involved in interchain cross-contacts (Bi···O 3.58 Å) (Figure 103). In addition, a weak intermolecular Bi···N interaction (Bi···N 3.47 Å) with the acetonitrile solvent molecule completes the O_3BiN tetrahedron, resulting in an overall Bi environment of the type **48** (three D positions are occupied by oxygen atoms).

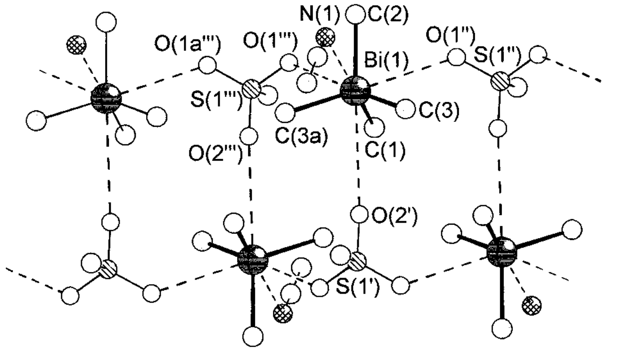


Figure 103. Polymeric association in the crystal of $[Me_4Bi][O_3SCF_3]\cdot MeCN$ (for clarity, the fluorine atoms of the triflate anions are not shown).[41]

For all other quaternary bismuth(V) derivatives, cation–anion and, in some cases, intramolecular interactions lead to distortion of the tetrahedral arrangement toward trigonal pyramidal (type **49**) or octahedral (type **50**) coordination geometries. Thus, in contrast to $[Ph_4Bi][ClO_4]$,[164] for $[Ph_4Bi][O_3SC_6H_4Me\text{-}4]$ a strong Bi···O interaction (Bi···O 2.77 Å) is established between the bismuthonium cation and the tosylate anion, trans to a Bi−C bond in a distorted trigonal bipyramidal C_4BiO core (Figure 104a).[61] A similar situation was noted for $[Ph_4Bi][Ph_2Bi(O_2CCF_3)_2]$: only one of the carboxylato groups of the diphenylbis(trifluoroacetato)bismuthate(III) anion is involved in a weaker Bi···O cation−anion interaction (Bi···O 3.11 Å) (Figure 104b).[61] In $[Ph_3(Me_2C{=}C)Bi][BF_4]$, a Bi···F interaction (Bi···F 3.131 Å), trans to a $Bi{-}C_{phenyl}$, also induced a small distortion of the tetrahedral environment of the alkenyltriphenylbismuthonium cation (Figure 104c).[165] In all these compounds the distortion toward the trigonal bipyramidal geometry of the bismuth center is reflected in opening of the C−Bi−C angles, corresponding to the equatorial sites in comparison with the axial−equatorial ones (Table 14). This behavior is even more evident in tetraphenylbismuth(V) alkoxides, $Ph_4BiOC_6F_5$ (Figure 104d) and $Ph_4BiOC_6Cl_5$,[43] which contain Bi−O bonds of intermediate length between the strongest Bi···O cation−anion interaction in $[Ph_4Bi][O_3SC_6H_4Me\text{-}4]$[61] and a covalent Bi−O bond, as for example in the hypervalent $(4\text{-}MeC_6H_4)_3Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ derivative (Table 14).[169] For these alkoxo derivatives a structure of type **51** can be considered. There are no weak intramolecular Bi···F or Bi···Cl interactions involving the *ortho* halogen atoms, and the packing in the crystal is influenced by weak intermolecular halogen···H interactions (F···H 2.743 Å, and Cl···H 2.895 Å, respectively).[43]

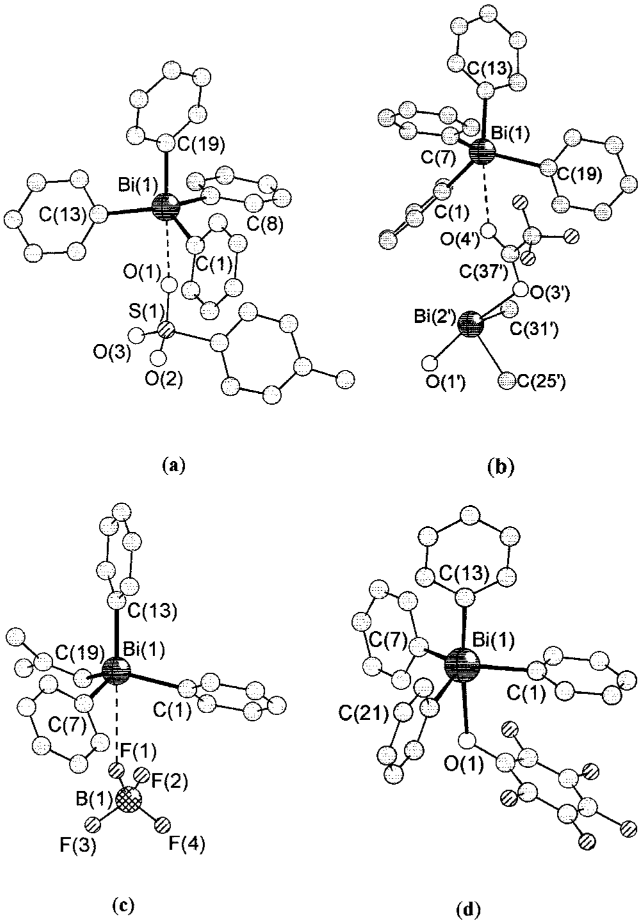


Figure 104. Structure of (a) $[Ph_4Bi][O_3SC_6H_4Me\text{-}4]$,[61] (b) $[Ph_4Bi][Ph_2Bi(O_2CCF_3)_2]$ (only the *ipso* carbons of the phenyl groups and one oxygen of the second carboxylato group of the anion are shown),[61] (c) $[Ph_3(Me_2C{=}C)Bi][BF_4]$,[165] and (d) $Ph_4BiOC_6F_5$.[43]

When a 2- or 3-oxoalkyl group is bound to the metal center in a bismuthonium cation, e.g., $[Ph_3BiCH_2C(O)Bu^t][BF_4]$ (Figure 105a),[166,167] $[Ph_3BiCH_2C(O)Bu^t][O_3SCF_3]$ (Figure 105b),[167] and $[Ph_3BiCH_2CH_2C(O)OPr^i][O_3SCF_3]$,[168] the tetrahedral C_4Bi core is further distorted by a strong intramolecular Bi···O interaction, in addition to the cation−anion Bi···F or Bi···O interactions (type **50**). In all these compounds the C−Bi−C angles opening to the carbonyl oxygen side are significantly larger than the ideal tetrahedral value, while the C−Bi−C angles remote from the carbonyl function are considerably reduced. For $[Ph_3BiCH_2C(O)Bu^t][BF_4]$, the presence of the strong intramolecular interaction might be responsible for the weakening of the cation−anion interaction (Bi···F 3.48 Å, cf. $[Ph_3(Me_2C{=}C)Bi][BF_4]$:[165] Bi···F 3.131 Å). However, for the triflate derivatives the cation−anion interactions are comparable, although the $Bi{\cdots}O_{carbonyl}$ interaction is weaker in $[Ph_3BiCH_2CH_2C(O)OPr^i][O_3SCF_3]$ than in $[Ph_3BiCH_2C(O)Bu^t][O_3SCF_3]$ (Table 14).

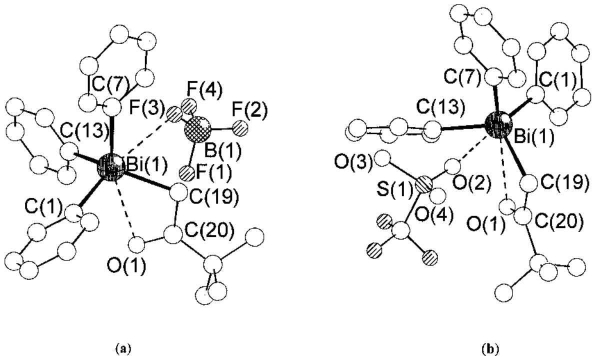
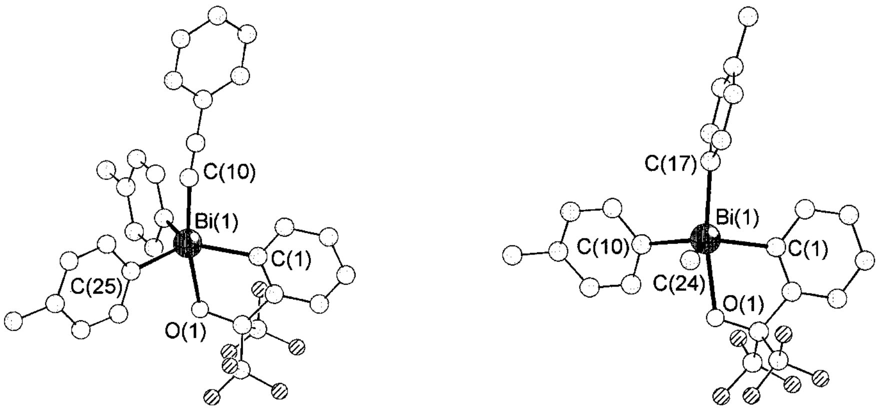


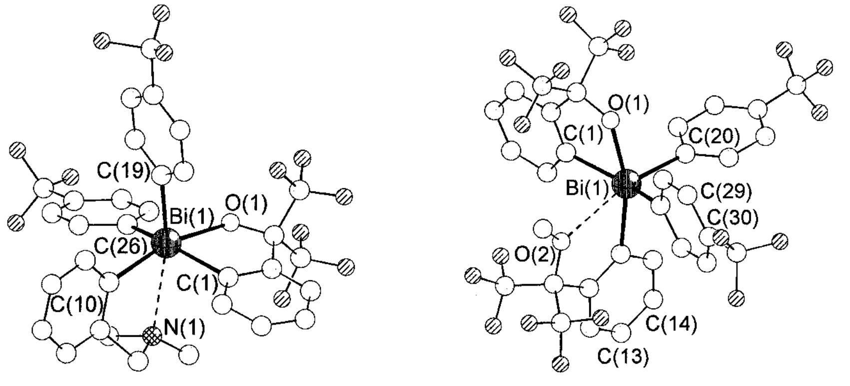
Figure 105. Structure of (a) $[Ph_3BiCH_2C(O)Bu^t][BF_4]$[166] and (b) $[Ph_3BiCH_2C(O)Bu^t][O_3SCF_3]$.[167]

All neutral tetraorganobismuth(V) compounds investigated so far by X-ray diffraction have been obtained using the so-called Martin ligand, which increases the stability due to the formation of a five-membered ring. For these compounds the Bi−O bond distance is close to a covalent bond, which clearly endorses the neutral nature of such molecules. The hypervalent 10-Bi-5 derivatives $(4\text{-}MeC_6H_4)_3Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$, $(4\text{-}MeC_6H_4)_2(PhC{\equiv}C)Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ (Figure 106a), and $(4\text{-}MeC_6H_4)_2MeBi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ (Figure 106b)[169] are five-coordinate species which exhibit a distorted trigonal bipyramidal geometry of the C_4BiO core, as reflected in the angles at the bismuth center (Table 14). The apical−equatorial angles involving the apical carbon atom are between 6° and 23°, larger than the $O{-}Bi{-}C_{eq}$ ones, while the two equatorial−equatorial angles involving the carbon atom of the O-ligand are considerably opened in comparison with the third one. When different organic groups are attached to bismuth, the apical position trans to the oxygen atom is occupied according to the electronegativity of the substituents, i.e., the phenylethynyl or *para*-tolyl groups, the methyl group being placed in an equatorial site.



(a) (b)

Figure 106. Molecular structure of (a) $(4\text{-}MeC_6H_4)_2(PhC{\equiv}C)Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ and (b) $(4\text{-}MeC_6H_4)_2MeBi[C_6H_4C(CF_3)_2O\text{-}2]$.[169]



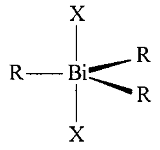
(a) (b)

Figure 107. Molecular structure of (a) $(4\text{-}CF_3C_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4(CH_2NMe_2)\text{-}2]$ and (b) $(4\text{-}CF_3C_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4\{C(CF_3)_2OMe\}\text{-}2]$.[170]

When one of the aromatic ligands on bismuth has a pendant arm bearing donor groups, the coordination number of the metal center is increased through a strong intramolecular interaction, e.g., $(4\text{-}MeC_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4(CH_2NMe_2)\text{-}2]$ (Bi···N 2.85 Å) (Figure 107a), $(4\text{-}CF_3C_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4(CH_2NMe_2)\text{-}2]$ (Bi···N 2.878 Å), and $(4\text{-}CF_3C_6H_4)_2Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2][C_6H_4\{C(CF_3)_2OMe\}\text{-}2]$ (Bi···O 2.741 Å) (Figure 107b).[170] The Bi−O covalent bonds, as well as the Bi···N and Bi···O intramolecular interactions, are weaker than those observed for related bismuth(III) derivatives, e.g., $(4\text{-}MeC_6H_4)[2\text{-}(Me_2NCH_2)C_6H_4]BiCl$ (Bi···N 2.525 Å),[60] $[2\text{-}(Me_2NCH_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ (Bi−O 2.194 Å, Bi···N 2.62 Å),[37] $[2\text{-}(MeOCMe_2)C_6H_4]Bi[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ (Bi−O 2.193 Å, Bi···O 2.536 Å),[125] according to the lower Lewis acidity of the bismuth(V) center. As a result of the intramolecular interaction the neutral, hypervalent 12-Bi-6 derivatives exhibit a distorted octahedral environment around the bismuth atom, with the covalent Bi−O bond and the additional intramolecular interaction in cis positions.

K. Compounds of the Type R_3BiX_2 (X = Halogen)

The structures of the few triorganobismuth(V) dihalides that have been studied belong to the same coordination geometry, i.e., trigonal bipyramidal (**53**), regardless of the nature of the equatorial organic groups and apical halogen atoms. Important molecular parameters for R_3BiX_2 (X = halogen) compounds are listed in Table 15.



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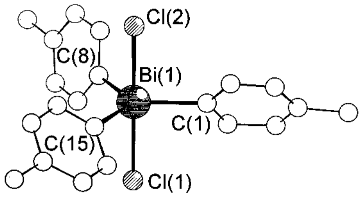


Figure 108. Molecular structure of $(4\text{-}MeC_6H_4)_3BiCl_2$.[169]

Typical examples are Ph_3BiCl_2[171] and $(4\text{-}MeC_6H_4)_3BiCl_2$ (Figure 108).[169,172] The crystals of these compounds contain discrete molecules of distorted trigonal bipyramidal geometry about bismuth. The deviations of the Cl−Bi−Cl angles from 180° (Table

Table 15. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Compounds of the Type R_3BiX_2 (X = Halogen)

		Bi−C	Bi−X	Bi···E[a]	X−Bi−X	C−Bi−C	ref
Ph_3BiCl_2[b]	Bi(1) atom	1.83−2.25	2.530; 2.615		176	113−130	171
	Bi(2) atom	2.00−2.23	2.560; 2.579		175	118−123	
$(4\text{-}MeC_6H_4)_3BiCl_2$		2.19−2.23	2.590; 2.595		176.0	119.1−121.6	169
$(C_6F_5)_3BiF_2\cdot 2(C_6F_5)_3Bi$		2.18−2.19	2.088	2.759[c]	180	118.3−123.4	85
$Me_3BiCl_2\cdot Me_2CO$		2.189−2.207	2.602; 2.617	3.23[d]	177.8	115.3−127.3	41

[a] Intermolecular interaction, E = F, O. [b] Two independent Bi centers are present in the asymmetric unit. [c] E = F, interaction with Bi(1) atoms of the BiR_3 moieties. [d] E = O, as calculated from published atomic coordinates.

15) were suggested to be the result of intramolecular contacts between the halogens and the aromatic rings, which exhibit different rotation from the equatorial C_3Bi plane.[171]

In the case of the centrosymmetric adduct $(C_6F_5)_3BiF_2\cdot 2(C_6F_5)_3Bi$ (Figure 109),[85] the F−Bi−F angle is 180° and the two axial fluorine atoms act as donor ligands for the bismuth(III) atoms (Bi···F 2.759 Å). The distortion from the regular trigonal bipyramid is reflected by the small opening of two of the equatorial C−Bi−C angles (123.4°) at the expense of the third one.

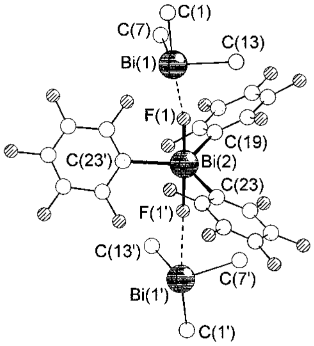


Figure 109. Structure of $(C_6F_5)_3BiF_2\cdot 2(C_6F_5)_3Bi$.[85]

The unique example of a trialkylbismuth(V) dihalide, $Me_3BiCl_2\cdot Me_2CO$,[41] also contains a basically distorted C_3BiCl_2 core. Here, the Cl−Bi−Cl angle (177.8°) is closer to the ideal value, but the trigonal bipyramidal geometry is distorted due to a weak Bi···O interaction (3.23 Å, as calculated from published atomic coordinates), in which the oxygen atom of the acetone solvent molecule is involved (Figure 110). This intermolecular contact is bisecting the largest equatorial C−Bi−C angle (127.3°), and therefore, a distortion toward an octahedral environment might be considered.

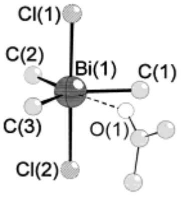
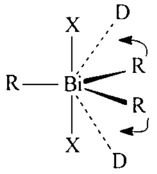


Figure 110. Molecular structure of $Me_3BiCl_2\cdot Me_2CO$.[41]

L. Compounds of the Type R_3BiX_2 (X = Chalcogenato Ligand)

The use of chalcogenato ligands for preparation of compounds of type R_3BiX_2 (X = chalcogenato ligand) is generally restricted to oxygen ligands to prevent reduction of Bi(V) to Bi(III) derivatives. Only arylbismuth(V) derivatives were investigated by X-ray diffraction. Depending on the nature of the ligands, two structural types have been observed, i.e., trigonal bipyramidal coordination with apical oxygen atoms (**53**) for monodentate ligands and various degrees of distortion toward a pentagonal bipyramid (**54** to **55**), depending on the bidentate (chelating) capacity of the anionic ligands. Important molecular parameters for R_3BiX_2 (X = chalcogenato ligand) are listed in Table 16.



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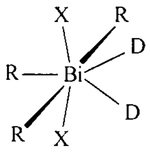

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The structure of the alkoxo derivatives $Ph_3Bi(OC_6F_5)_2$ (Figure 111a) and $Ph_3Bi(OC_6Cl_5)_2$ (Figure 111b)[43] is basically of type **53**; however, some differences should be noted. For the former complex the coordination polyhedron is not distorted; the closest $Bi\cdots F_{ortho}$ contacts of 3.7 Å exhibit no perturbing effect. By contrast, for the pentachlorophenoxy derivative, the trigonal bipyramidal environment about bismuth is considerably distorted and the short $Bi\cdots Cl_{ortho}$ contact of 3.4 Å might account for the decrease of the Cl−Bi−Cl angle (174.1°) and the significant opening of the C(1)−Bi(1)−C(13) angle to 142.6°.

The molecular structures of several carboxylato derivatives, $R_3Bi[O(O)CR']_2$ (Table 16), were reported, and all compounds are monomeric and exhibit similar trends, i.e., distortion of the expected trigonal bipyramidal geometry with apical oxygens toward a pentagonal bipyramidal environment with apical carbons. Both carboxylato ligands in a molecular unit are primarily bonded through one of the oxygen atoms, with the second oxygen atom involved in secondary bonding of variable strength. An almost coplanar $CBiO_4$ system always results (cf. $Ph_3Bi[O(O)CCF_3]_2$,[174] in Figure 112a). There is a direct correlation between the strength of the intramolecular Bi···O interactions and the magnitude of the C−Bi−C angle, i.e., the stronger the secondary bonds, the larger the C−Bi−C angle (Table 16). The carbon atoms are forced to occupy the apical positions in

Table 16. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Compounds of the Type R_3BiX_2 (X = Chalcogenato Ligand)

	Bi−C	Bi−O	Bi···O or Bi−O[a]	O−Bi−O	C−Bi−C	ref
$Ph_3Bi(OC_6F_5)_2$	2.193−2.203	2.212; 2.228		179.4	119.0−121.8	43
$Ph_3Bi(OC_6Cl_5)_2$	2.188−2.209	2.244; 2.250		174.1	103.9−142.6	43
$Ph_3Bi[O_3SC_6H_5]_2$	2.178−2.201	2.276; 2.280	3.129; 3.431	171.8	106.3−135.9	173
$(4\text{-}Me_2NC_6H_4)_3Bi[O(O)CCF_3]_2$	2.00−2.15	2.32	3.16	176	110.9−138	84
$Ph_3Bi[O(O)CCF_3]_2$	2.138−2.185	2.308; 2.309	2.980; 2.981	175.1	109.2−140.6	174
(R,R)/(S,S)-$(4\text{-}Me_2NC_6H_4)_3Bi[O(O)CCH_2CH(OH)CH_3]_2$	2.11−2.20	2.31	2.93[b]	171	107−144	175
(R,R)/(S,S)-$(4\text{-}Me_2NC_6H_4)_3Bi[O(O)CCH(OH)CH_2CH_3]_2$	2.14−2.20	2.27; 2.32	2.90; 2.91[b]	172.3	107.4−144.8	175
$Ph_3Bi[O(O)CH]_2$	2.19−2.23	2.270	2.91	171.6	107.4−145.2	176
$Ph_3Bi[O(O)C(CH_2)_2C_6H_4OH\text{-}4]_2$	2.22−2.229	2.253	2.88	170.1	107.2−145.7	175
$[4\text{-}\{(2\text{-}Py)_2NCH_2\}C_6H_4]_3Bi[O(O)CCH_3]_2$	2.19−2.26	2.19; 2.25	2.80; 2.81	170.6	105−146	84
(R,R)/(S,S)-$(4\text{-}Me_2NC_6H_4)_3Bi[O(O)CCH(CH_2OH)Ph]_2$	2.15−2.29	2.19; 2.30	2.88; 3.03[b]	177	105−147	175
$Ph_3Bi[O(O)C\text{-}C_4H_3O\text{-}2]_2$	2.193−2.215	2.290; 2.301	2.799; 2.813	173.6	104.7−148.2	177
(R,R)/(S,S)-$Ph_3Bi[O(O)CCH(CH_2OH)Ph]_2$	2.21−2.221	2.307	2.80[b]	175.8	105.0−149.9	175
$Ph_3Bi[O(O)C(CH_2)_3OH]_2$	2.21−2.24	2.28; 2.31	2.71; 2.87[b]	174.5	103−150	175
$(4\text{-}Me_2NC_6H_4)_3Bi[O(O)C(CH_2)_3OH]_2$	2.179−2.210	2.287; 2.328	2.78; 2.83	175.7	103.3−152.9	175
$(4\text{-}MeC_6H_4)_3Bi[OC_7H_4O\text{-}2\text{-}NO_2\text{-}5)_2$	2.141−2.391	2.315	2.594	158.2	102.6−154.8	178
$(4\text{-}MeC_6H_4)_3Bi(OC_7H_5O\text{-}2)_2$	2.119−2.215	2.310; 2.317	2.456; 2.498	156.7	99.4−158.8	178

[a] Intramolecular interactions. [b] Calculated from published atomic coordinates.

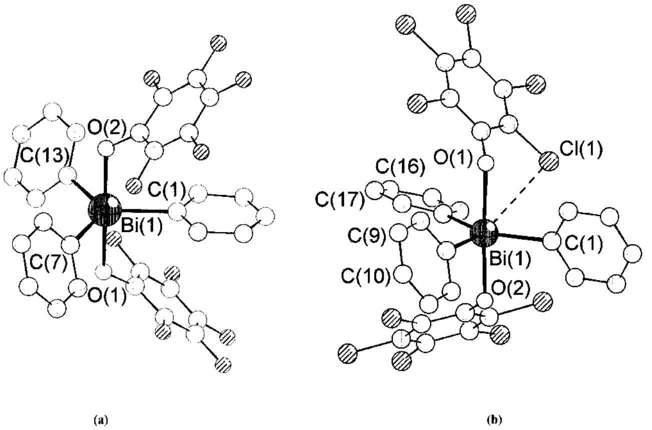


Figure 111. Molecular structure of (a) $Ph_3Bi(OC_6F_5)_2$ and (b) $Ph_3Bi(OC_6Cl_5)_2$.

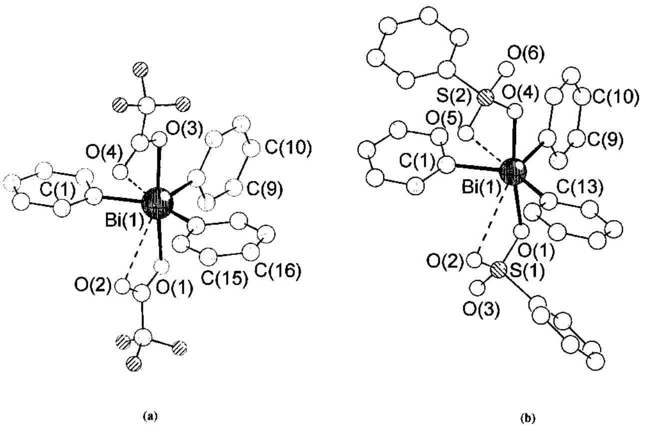


Figure 112. Molecular structure of (a) $Ph_3Bi[O(O)CCF_3]_2$[174] and (b) $Ph_3Bi(O_3SC_6H_5)_2$.[173]

the resulting distorted pentagonal bipyramidal geometry.It should also be noted that the presence of a hydroxyl group in the carboxylato ligand results in hydrogen-bonded extended structures such as double strands and double layers, for example, which however does not involve the metal centers.[175]

The molecular structure of $Ph_3Bi[O_3SC_6H_5]_2$ is similar to that of the related bis(carboxylato) derivatives, the phenylsulfonato moieties acting basically as 1,1-dioxo chelating ligands (Figure 112b).[173] However, the strength of the intramolecular Bi···O secondary interactions is considerably lower than that observed for the large majority of the carboxylato analogues (Table 16).

When 1,2-dioxo ligands have been used, e.g., tropolonato moieties in $(4\text{-}MeC_6H_4)_3Bi(OC_7H_5O\text{-}2)_2$ (Figure 113) and $(4\text{-}MeC_6H_4)_3Bi(OC_7H_4O\text{-}2\text{-}NO_2\text{-}5)_2$,[178] the differences (range 0.15−0.28 Å) between primary and secondary bismuth−oxygen bonds are smaller. As a consequence, the O−Bi−O bond angles (formed by primary Bi−O bonds) are considerably diminished while the C−Bi−C angles have the closest values to the ideal apical−apical and apical−equatorial angles in a pentagonal bipyramid observed for this type of compound.

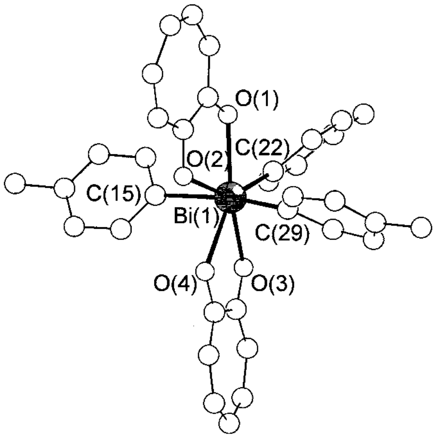


Figure 113. Molecular structure of $(4\text{-}MeC_6H_4)_3Bi(OC_7H_5O\text{-}2)_2$.[178]

M. Miscellanous Compounds Containing $R_3Bi(V)$ Moieties

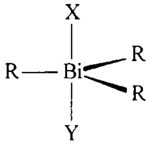
Most of the triarylbismuth(V) derivatives containing two different anionic ligands exhibit a trigonal bipyramidal coordination geometry with various degrees of distortion, regardless of their mononuclear

Table 17. Comparative Dimensional Parameters (interatomic distances, Å, and angles, deg) for Compounds of the Type R_3BiXX' (X = Halogen, Nitrogen; X′ = Chalcogenato Ligand)

		Bi−C	Bi−X/X′	Bi···E[a]	X−Bi−X′	C−Bi−C	ref
$Ph_3BiBr(OC_6F_5)$		2.195−2.220	2.235 (Bi−O) 2.726 (Bi−Br)		176.6	116.9−123.0	43
$Ph_3BiBr(OC_6Cl_5)$		2.189−2.215	2.230 (Bi−O) 2.742 (Bi−Br)		177.8	112.2−131.7	43
$[Ph_3Bi(ClO_4)]_2O$[b]	Bi(1) atom	2.13−2.19	2.065 ($Bi-O_{bridge}$)	2.65 (av, $Bi\cdots O_{perchlorate}$)	168.6[c]	114.7−126.6	179
	Bi(2) atom	2.15−2.26	2.062 ($Bi-O_{bridge}$)	2.655 ($Bi\cdots O_{perchlorate}$)	173.5	112.2−125.7	
$[Ph_3Bi(O_3SCF_3)]_2O$[b]	Bi(1) atom	2.20−2.22	2.039 ($Bi-O_{bridge}$)	2.58 ($Bi\cdots O_{triflate}$)	176.4	112.7−124.4	167
	Bi(2) atom	2.19−2.21	2.091 ($Bi-O_{bridge}$)	2.527 ($Bi\cdots O_{triflate}$)	179.7	113.3−130.5	
$[(4\text{-}Me_2NC_6H_4)_3Bi(Cl)]_2O$[b]	Bi(1) atom	2.14−2.24	2.12 ($Bi-O_{bridge}$)	2.79 (Bi···Cl)	175.9	117−124	84
	Bi(2) atom	2.20−2.24	2.02 ($Bi-O_{bridge}$)	2.77 (Bi···Cl)	179.5	120	
$(4\text{-}MeC_6H_4)_2BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.191−2.201	2.179 (Bi−O) 2.562 (Bi−Cl)		170.0	109.8−124.8	169
$(4\text{-}CF_3C_6H_4)_2BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.19−2.22	2.17 (Bi−O) 2.558 (Bi−Cl)		170.7	107.0−129.1	169
$(4\text{-}MeC_6H_4)_2BiBr[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.20−2.21	2.184 (Bi−O) 2.708 (Bi−Br)		170.1	109.0−126.9	169
$(4\text{-}MeC_6H_4)(4\text{-}CF_3C_6H_4)BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$		2.19−2.21	2.186 (Bi−O) 2.547 (Bi−Cl)		171.2	110.7−124.4	169
Ph_3BiCl(8-oxoquinolinolato)		2.168−2.214	2.230 (Bi−O) 2.742 (Bi−Cl)	2.807 (Bi···N)	175.1	106.2−143.1	61
Ph_3BiCl(2-Me-8-oxoquinolinolato)		2.16−2.29	2.19 (Bi−O) 2.67 (Bi−Cl)	2.71 (Bi···N)	174.5	104.0−150.0	180
$(4\text{-}MeC_6H_4)_2Bi[C_6H_4\{COCH_2CMe_2N\}\text{-}2][NO_2SCF_3]$		2.19−2.23	2.13 ($Bi-N_{imide}$)	2.69 (Bi···N) 2.97 (Bi···O)	163.5[d]	112.0−119.9	42

[a] Intramolecular interaction. [b] Two different Bi centers are present in the molecular unit. [c] Averaged value for the disordered O(1a)/O(2a) positions. [d] $N_{imido}-Bi\cdots N$ angle.

(**56**) or dinuclear (**57**) nature. However, an increaseof the coordination number to six, thus leading to a distorted octahedral environment (**58**), might be achieved through intramolecular coordination. Although such a behavior is consistent with a Lewis acidity of the Bi(V) centers, no examples of associations through intermolecular interactions have been described so far. A basically trigonal bipyramidal geometry was also recently found in a triarylbismuthane imide. However, an additional Bi···O intramolecular interaction might be also considered in this particular compound, thus increasing the coordination number to six (**59**). Important molecular parameters for R_3BiXX' derivatives are listed in Table 17.



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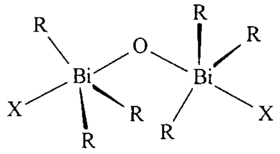

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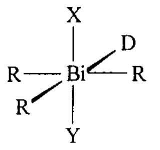

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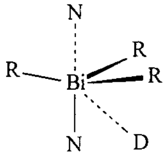

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The coordination environments in the bromo−alkoxo derivatives, $Ph_3BiBr(OC_6F_5)$ (Figure 114a) and $Ph_3BiBr(OC_6Cl_5)$ (Figure 114b),[43] are basically trigonal bipyramidal. The presence of a close $Bi\cdots F_{ortho}$ contact of 3.3 Å (calculated from the atomic coordinates) in the pentafluorophenoxy compound has little effect on the coordination polyhedron. By contrast, the equatorial C−Bi−C angles in the pentachlorophenoxy analogue are considerably perturbed (Table 17), although no shorter $Bi\cdots Cl_{ortho}$ contacts than 3.9 Å are present.

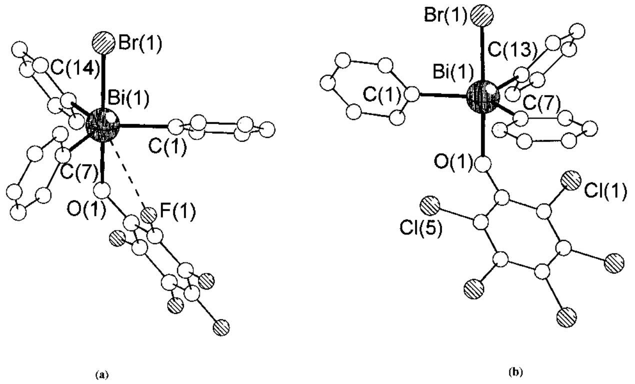

Figure 114. Molecular structure of (a) $Ph_3BiBr(OC_6F_5)$ and (b) $Ph_3BiBr(OC_6Cl_5)$.[43]

The molecular units of the oxo-bridged dinuclear compounds $[(4\text{-}Me_2NC_6H_4)_3Bi(Cl)]_2O$[84] and $[Ph_3Bi(X)]_2O$ [X = ClO_4,[179,181] O_3SCF_3 (Figure 115)[167]] also contain distorted trigonal bipyramidal C_3BiO_2 cores for both bismuth atoms. The Bi−O−Bi angles cover a quite large range (167°, 142.2°, and 134° for the chloro, perchlorato, and triflate derivatives, respectively). Nevertheless, all three derivatives have features in common. Thus, the $Bi-O_{bridge}$ distances are always in the range for covalent bismuth−oxygen single bonds, while the corresponding trans Bi−Cl and Bi−O distances are considerably longer than expected for covalent bonds, probably due to a trans effect induced by the oxo ligand. This behavior

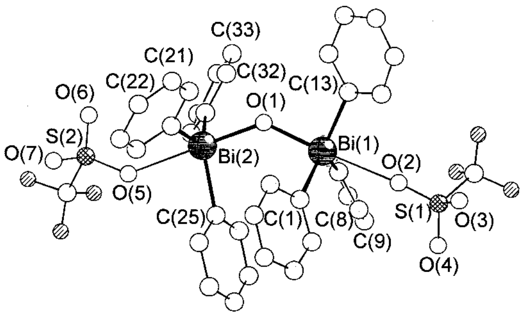

Figure 115. Molecular structure of $[Ph_3Bi(O_3SCF_3)]_2O$.[167]

indicates an intermediate character of these bondings between formal covalent and ionic ones and illustrates the hypervalent nature of these compounds. A certain relation to a tetrahedral configuration at the bismuth centers is suggested by the displacement of the bismuth atoms from the equatorial plane of the trigonal bipyramid toward the bridging oxygen atom (C−Bi−O_{bridge} angle range: 90−97°, 92.1−103.2°, and 92.4−100.4° for X = Cl, ClO_4, and O_3SCF_3, respectively).

Hypervalent 10-Bi-5 derivatives containing the so-called Martin ligand have also been investigated by X-ray diffractometry, i.e., $(4\text{-}MeC_6H_4)_2BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$ (Figure 116), $(4\text{-}CF_3C_6H_4)_2BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$, $(4\text{-}MeC_6H_4)_2BiBr[C_6H_4\{C(CF_3)_2O\}\text{-}2]$, and $(4\text{-}MeC_6H_4)(4\text{-}CF_3C_6H_4)BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$.[169] They exhibit a distorted trigonal bipyramidal geometry around the bismuth, with the halogen and the oxygen atoms in apical positions, thus consistent with the electronegativity of the substituents. The distortion of the coordination polyhedron is mainly due to the five-membered ring constraints, as reflected in the angles at the bismuth center (Table 17). With the exception of the *endocyclic* O−Bi−C angle (ca. 77°, regardless of the nature of the halide and the organic groups attached directly to the metal), all other apical−equatorial angles are larger but close to the 90° value. The crystals of all these compounds contain discrete molecules, and no intermolecular bismuth−halogen interactions were observed.

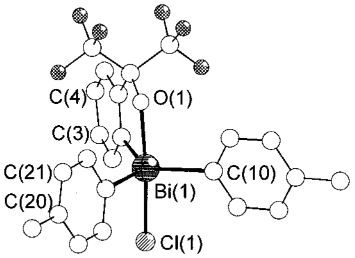

Figure 116. Molecular structure of $(4\text{-}MeC_6H_4)_2BiCl[C_6H_4\{C(CF_3)_2O\}\text{-}2]$.[169]

However, when 8-quinolinolato ligands were used, an increase of the coordination number at the bismuth center through strong intramolecular Bi···N interactions resulted, e.g., Ph_3BiCl(8-oxoquinolinolato) (Bi···N 2.807 Å)[61] and Ph_3BiCl(2-Me-8-oxoquinolinolato) (Bi···N 2.71 Å) (Figure 117).[180] The strength of these interactions is comparable with that observed for tetraarylbismuth(V) derivatives containing a 2-(dimethylamino)methylphenyl group attached to the metal center (see section III.J). The 12-Bi-6 derivatives thus obtained exhibit a distorted octahedral environment around the bismuth atom, with the oxygen and chlorine atoms in apical positions and the Bi···N interactions bisecting the larger cis equatorial C−Bi−C angle.

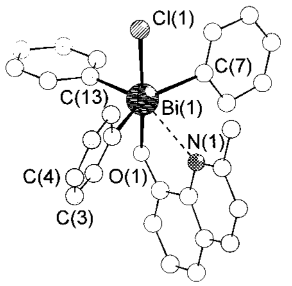

Figure 117. Molecular structure of Ph_3BiCl[2-Me-8-oxoquinolinolato].[180]

The first X-ray structure of a stabilized triarylbismuth imide, $(4\text{-}MeC_6H_4)_2Bi[C_6H_4\{COCH_2CMe_2N\}\text{-}2][NO_2SCF_3]$, was recently reported (Figure 118).[42] The Bi−N_{imide} bond length (2.13 Å) is comparable with known bismuth−nitrogen single bonds in inorganic $Bi(NRR')_3$ complexes (range 2.180−2.189 and 2.12−2.28 Å for R = R′ = Me,[182] Ph[183] or 2.14−2.214 Å for R = 2,4,6-$Bu^t{}_3C_6H_2$, R′ = H[184]), thus suggesting a polarized $Bi^+−N^-$ bond rather than a Bi═N double bond. There is also strong intramolecular coordination of the oxazoline N(2) atom to bismuth (Bi···N 2.69 Å), occupying a position trans to the imido N(1) atom. The resulting coordination geometry can be described as distorted trigonal bipyramidal, with some tetrahedral contribution to the overall geometry, as suggested by the angles at bismuth (range N_{imide}−Bi−C 94.2−107.8°, C−Bi−C 112.0−119.9°), and the displacement of the metal center 0.49 Å from the C_3 equatorial plane. The distortion of the coordination polyhedron is even more increased by the intramolecular coordination of a sulfonyl oxygen atom (Bi···O 2.97 Å) from the widest C−Bi−C side. Both these intramolecular interactions seem to increase the stability of the Bi−N_{imide} bond.

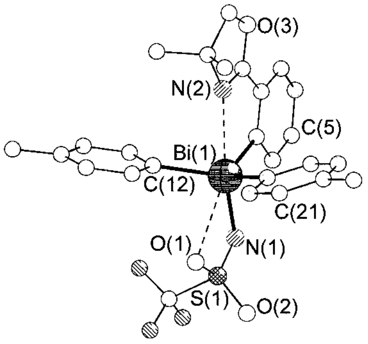

Figure 118. Molecular structure of $(4\text{-}MeC_6H_4)_2Bi[C_6H_4\{COCH_2CMe_2N\}\text{-}2][NO_2SCF_3]$.[42]

IV. Concluding Comments

The overview of the literature on the structure investigations of organobismuth compounds by means of single-crystal X-ray diffraction reflects a considerable recent interest, more than two-thirds of the original contributions on this topic being published after 1990. Although many types of compounds are represented by very few examples, a great structural diversity has been established, namely, in coordination numbers and coordination geometries. Some common features should be emphasized. The Lewis acidic character of many organobismuth compounds leads to an increase in the coordination number of bismuth by anionic ligands or pendant arms of the organic groups attached to bismuth. Consequently, for organobismuth(III) derivatives, coordination numbers higher than three are often achieved through both intra- and/or intermolecular interactions of variable strength. Intermolecular interactions result in the formation of dimers or supramolecular associations. By contrast, for organobismuth(V) compounds, increased coordination numbers mainly through intramolecular interactions have been observed. For compounds in both oxidation states an increase of stability is obtained when strong additional interactions lead to hypervalent bonding systems. Both the coordination geometries and the coordination numbers are severely affected by the bulkiness of the organic substituents. The use of an appropriate organic group attached to the bismuth atom allows one to stabilize even unusual low oxidation states and coordination numbers.

Taking into account the results of the past years, some major achievements in the structural chemistry of organobismuth compounds should be particularly emphasized, e.g., an optically pure diorganobismuth(III) halide,[40] extended polymeric structures of organobismuth(III) dihalides,[21,111−113] π-bonding from bismuth to organic ligands in cyclopentadienylbismuth(III) derivatives,[104,114,115] and bismuth−arene complexes, including the first example of Bi−Bi bond-containing carboxylato compound,[33] a compound containing the Bi=Bi double bond,[31] and a four-membered cyclobismuthine,[32] various organobismuth−transition metal compounds,[29] including η^5-bismolyl complexes,[30,159] methylbismuth(V) derivatives,[41] and a stabilized triarylbismuth imide.[42]

On the other hand there are still many “white areas” challenging future research, e.g., complete series of organobismuth halides, with the same organic groups but different halogen atoms, especially fluorides which are still missing, organobismuth chalcogenides, either monomeric species with Bi=X double bonds or cyclic species, organometallic compounds containing linear Bi_n chains, organobismuth−main group metal compounds, alkylbismuth(V) compounds, other than methyl derivatives.

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