



Phenyl bismuth β -diketonate complexes: Synthesis and structural characterization

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ABSTRACT

The first examples of arylbismuth diketonate complexes are reported. Phenylbismuth(III) bis(hexafluoroacetylacetonate), $\text{BiPh}(\text{hfac})_2$ (**1**) and its adducts $[\text{BiPh}(\text{hfac})_2(\text{L})]$ (Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; L = H_2O (**1a**), Me_2CO (**1b**), THF (**1c**), DMA (*N,N*-dimethylacetamide) (**1d**), DMSO (**1e**), PhCN (**1f**), as well as a mixed hexafluoroacetylacetonate–trifluoroacetate complex, $[\text{BiPh}(\text{hfac})(\text{O}_2\text{CCF}_3)]_2$ (**2**), have been synthesized and characterized. Compound **1** is isolated from the reaction of BiPh_3 with 2 equiv. of Hhfac in dry hexanes. Compound **2** can be synthesized using two different routes: one utilizes the reaction between stoichiometric amounts of **1** and $\text{CF}_3\text{CO}_2\text{H}$, while the second method involves the interaction of the previously described $\text{BiPh}_2(\text{O}_2\text{CCF}_3)$ (**3**) with Hhfac. Crystallographic analysis of the $[\text{BiPh}(\text{hfac})_2(\text{L})]$ adducts reveals a pentagonal pyramidal geometry around the metal center; similarly, the dinuclear $[\text{BiPh}(\text{hfac})(\text{O}_2\text{CCF}_3)]_2$ complex is composed of two distorted pentagonal pyramids connected into dimers by the bridging carboxylate groups. The effect of replacing the Lewis base in the coordination sphere of Bi(III) on the coordination polyhedron and crystal packing is discussed. The ^1H and ^{19}F NMR spectra of the title complexes at room temperature indicate single environments for the hfac group and suggest that they are fluxional in solutions on the NMR time scale. Compounds **1** and **2** are promising starting materials in the chemistry of bismuth(III) and as building blocks for the construction of heterometallic species.

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1. Introduction

Despite of the fact that metal β -diketonates represent one of the oldest and most studied classes of coordination compounds, there is a continuous interest in exploring their synthesis and properties. These compounds are useful in a number of applications, mainly due to their high volatility and solubility in common organic solvents. β -Diketonates proved themselves as very versatile chelating ligands to form stable complexes with almost all metal ions, including such electropositive elements as the alkali-earth [1,2] or lanthanide metals [2,3]. High volatility of metal β -diketonates is associated with an efficient shielding of the positively charged metal ions from the intermolecular interactions by surrounding hydrocarbon or fluorocarbon shells [2]. It is known that in addition to their ability to chelate the metal ions, β -diketonates can also fulfill bridging functions. The degree of oligomerization depends on many factors, including the nature of the metal ion and the electronic and steric effects of the ligands. Large metal ions with pronounced electron deficiency tend to favor bridging linkages over terminal ones, however this tendency is substantially or fully reduced in the presence of Lewis bases.

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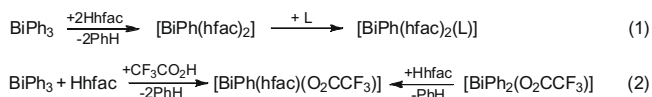
The interest in bismuth(III) β -diketonates has mainly arisen from their utility in different CVD processes. β -Diketonate complexes are usually synthesized by methods similar to those described for the alkoxides [4]. The metathesis reaction of bismuth halides with alkali metal salts of the corresponding diketones has been successfully employed to produce Bi(III) diketonates, however additional purification steps are usually required to remove possible halide contamination. An alternative approach is the acidolysis reaction of triphenylbismuth with β -diketonates. The latter reaction can be performed in an appropriate solvent or solventless. The crystal structures of bismuth(III) β -diketonates have been shown to exhibit considerable diversity. As a consequence of the pronounced Lewis acidity of the bismuth atom and the Lewis basic behavior of the diketonate ligands, there is a remarkable tendency to form oligomers or polymers with one or several bridging atoms. Thus, in two of the most studied bismuth(III) compounds from this class, $\text{Bi}(\text{hfac})_3$ [5] and $\text{Bi}(\text{thd})_3$ [6,7] (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione), the ligands display strong chelating and relatively weaker bridging functions; the latter function is responsible for the assembly of the two complexes into dimers through Bi...O interactions. Recently, new research directions have emerged for bismuth(III) β -diketonate complexes, such as their use in assembly of heterometallic complexes [5] and polynuclear oxo-clusters [8].

While the chemistry of tris-diketonate bismuth complexes is well developed, no data are available on the corresponding arylbismuth diketonate compounds. These compounds are likely formed

as intermediates during the reaction of BiPh_3 with the corresponding β -diketones. However, their isolation may present difficulties due to possible formation of polymeric species. This could be due in part to the large size of Bi(III) (ionic radius 1.03 Å), which allows for high coordination numbers without significant steric constraints, thus favoring the association of Bi(III) centers. In order to control the oligomerization process, one possibility is to use the idea of “solvent control”. In this approach a coordinating solvent forms a stable adduct with the corresponding metal ion, preventing bridging interactions. We attempted to perform the reaction of BiPh_3 with 2 equiv. Hhfac in hexane with subsequent addition of some coordinating molecules. In this paper, we report the synthesis and characterization of phenylbismuth(III) hexafluoroacetylacetonate, (**1**), and its adducts $[\text{BiPh}(\text{hfac})_2(\text{L})]$ (**1a–1f**), as well as a dimeric hexafluoroacetate–trifluoroacetate complex, $[\text{BiPh}(\text{hfac})(\text{O}_2\text{CCF}_3)]_2$ (**2**), obtained by two different synthetic procedures (Scheme 1).

2. Results and discussion

Triphenylbismuth reacts upon reflux with 2 equiv. of hexafluoroacetylacetonate in dry hexanes to produce a yellow solution. Partial removal of the solvent in vacuum and cooling down the concentrated solution to -20°C provides microcrystalline powder of $\text{BiPh}(\text{hfac})_2$ (**1**), as confirmed by spectroscopic and elemental analyses. Attempts to grow single crystals of **1** from non-coordinating solvents were unsuccessful. In the presence of coordinating solvents it turned out that **1** can easily form monoadducts. Thus, yellow crystalline solids of the corresponding adducts **1a–1f** can be isolated from hexanes solution of **1** in the presence of small amounts of H_2O (**1a**), Me_2CO (**1b**), THF (**1c**), DMA (**1d**), DMSO (**1e**), and PhCN (**1f**). Complex **2** was obtained by subsequent addition of 1 equiv. of Hhfac and 1 equiv. of trifluoroacetic acid to BiPh_3 in hexanes. The same compound can be obtained in a lower yield from the reaction of $\text{BiPh}_2(\text{O}_2\text{CCF}_3)$ (**3**) (synthesized as described in [9]) with 1 equiv. of Hhfac (Scheme 1). All isolated β -diketonate complexes appear as yellow–orange, air-sensitive, shiny crystalline solids. They are sparingly soluble in methanol, acetone, dichloromethane and chloroform, but less so in diethylether and hydrocarbons. The newly-synthesized compounds were characterized by IR and NMR spectroscopy as well as by single-crystal X-ray diffraction. The IR spectra exhibit, as expected, the corresponding $\text{C}=\text{O}$ hfac[−] stretches in the range of $1634\text{--}1640\text{ cm}^{-1}$. These bands are at significantly lower energies than those found for free Hhfac (1689 cm^{-1}) and are indicative of β -diketonate chelation to Bi(III). The ^1H and ^{19}F NMR spectra of the isolated complexes at room temperature revealed single environments for the hfac[−] group suggesting that the diketonate ligands are able to undergo ligand exchange processes at a rate that is fast on the NMR time scale. The ortho, meta, and para-protons of the phenyl group are centered at $\sim 8.2\text{--}8.3\text{ ppm}$ (d), $\sim 7.9\text{--}8.0\text{ ppm}$ (t), and $\sim 7.4\text{--}7.5\text{ ppm}$ (t), respectively. The ^1H NMR spectra contain no signals of the di- and triarilated species, which does not support the occurrence of aryl redistribution reactions. Such reactions are commonly encountered in the solution chemistry of arylantimony and arylbismuth complexes [10,11].



Legend Hhfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione;
L = H_2O , Me_2CO , THF, DMA, DMSO, PhCN.

Scheme 1.

The thermal decomposition of the complexes was investigated by TGA and the residues were analyzed by X-ray powder diffraction (XRPD). In all cases, it was found that the compounds undergo thermal decomposition in two or three stages upon heating and do not exhibit any apparent mass loss of the diketonates due to sublimation. The thermogravimetric plots for **1**, **1c** and **1e** (Fig. 1) are qualitatively similar in stages of weight loss up to 550°C . The release of coordinated Lewis base molecules in the adducts is not observed as a separate step. Compound **1** displays a sharp melting point at $82\text{--}83^\circ\text{C}$. The decomposition of **1** proceeds in several steps and is punctuated by an abrupt mass loss ($\sim 62\%$) between 195 and 340°C . The XRPD study of the residue resulted upon thermal decomposition of **1** in Ar probed the formation of a complex mixture with BiOF being a major phase. The formation of BiOF upon thermal treatment of fluorine-containing bismuth(III) compounds has been previously reported in the literature [12,13]. The thermal decomposition of the adducts **1a–1f** somewhat mirrors what was observed for the thermolysis of **1**. In each case, the thermal decomposition of the complex proceeds in several steps with an abrupt mass loss that includes removal of the corresponding neutral ligand. Interestingly, the thermolysis of **1**, **1a–1f** and **2** in air at 550°C for 1 h resulted exclusively in monoclinic $\alpha\text{-Bi}_2\text{O}_3$ (Fig. 2).

The molecular structures of compounds **1a–1f** and **2** were established by single-crystal X-ray diffraction. X-ray quality crystals can be grown directly from the reaction mixtures. All compounds were found to crystallize in the monoclinic crystal system ($P2_1/c$, $P2_1/n$ or $C2/c$ space groups). The $\text{BiPh}(\text{hfac})_2\text{L}$ adducts adopt a pentagonal pyramidal geometry with the metal center coordinated by the phenyl group, two chelating β -diketonate

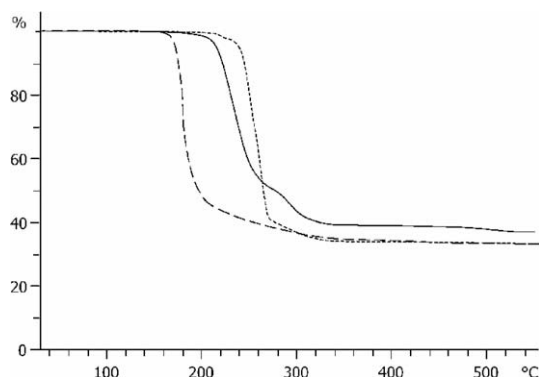


Fig. 1. TGA curves of **1** (—), **1c** (---) and **1e** (.....).

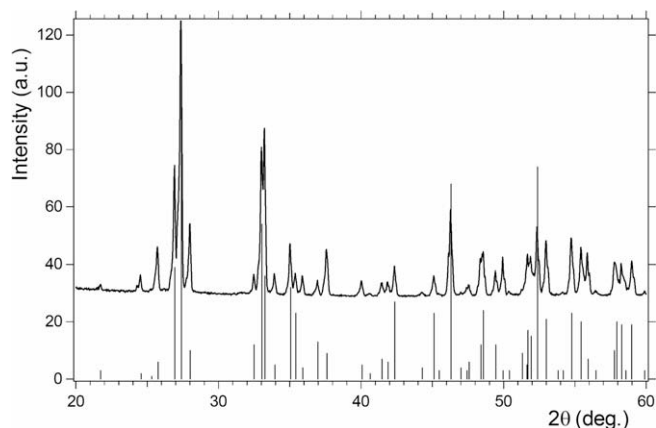


Fig. 2. X-ray powder diffraction pattern of the decomposition product of **1** in air and its comparison to $\alpha\text{-Bi}_2\text{O}_3$ phase, JCPDS No. 00-041-1449.

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