Synthesis and Characterization of New Phenylbis(salicylato)bismuth(III) Complexes

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Compounds with the compositions [BiPh(Hsal)$_2$] (**1a**) and [BiPh(Hsal^{4Me})$_2$] (**1b**) were prepared by the reactions of triphenylbismuth with 2-hydroxybenzoic acid (H_2sal) and 4-methyl-2-hydroxybenzoic acid (H_2sal^{4Me}), respectively, in a 1:2 ratio. The reactions of **1a**,**b** with the bidentate nitrogen donor ligands 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) led to the isolation of the corresponding adducts [BiPh(Hsal)$_2$(phen)] (**2a**), [BiPh(Hsal^{4Me})$_2$(phen)] (**2b**), [BiPh(Hsal)$_2$(bipy)] (**2c**), and [BiPh(Hsal^{4Me})$_2$-(bipy)] (**2d**). Crystallographic analyses of the adducts showed the solids to have monomeric structures with six-coordinate Bi(III). One salicylato ligand is coordinated in a monodentate fashion and the other in a bidentate, chelating manner. The phenol oxygen atoms remain uncoordinated in both cases. The coordination geometry around Bi(III) in **2a**, **2b**·Me_2CO, **2c**, and **2d**·DMF can be described as distorted pentagonal pyramidal with an apical C atom, while the free space trans to the ipso carbon atom of the phenyl group is believed to accommodate a stereochemically active pair of electrons. The ^{1}H data demonstrate that the salicylate ligands are fluxional in solution. It was shown that under different reaction conditions a number of bismuth(III) oligomeric, dimeric, and monomeric complexes are produced, including [$Bi_{38}O_{44}$(Hsal)$_{26}$(Me_2CO)$_{16}$(H_2O)$_2$]·4Me_2CO, [Bi(Hsal^{4Me})(sal^{4Me})(phen)]$_2$·2Me_2CO ([**3**]$_2$·2Me_2CO), [Bi(Hsal^{4Me})$_3$(bipy)]$_2$·4Me_2CO ([**4**]$_2$·4Me_2CO), and [Bi(Hsal^{4Me})$_3$(phen)(MeOH)] (**5**), which attest to a rich chemistry in this system.

Introduction

There has been an increasing interest in the chemistry of bismuth−salicylate complexes, due to their relevance in the treatment of diverse gastrointestinal disorders[1] as well as in the preparation of heterometallic precursors to oxide materials.[2] The salicylate ligand has proven to be versatile, displaying a range of different coordination modes;[2a−d,3] however, there have been no reports on the corresponding organobismuth salicylates, though these compounds are expected to be biomedically relevant. A number of alkyl- and arylbismuth compounds have been tested as efficient antibacterial agents,[1a−e,4] while others have been reported to be cytotoxic.[5] The lack of investigation of these compounds might be attributed to reports that arylbismuth dicarboxylates ArBi(O_2CR)$_2$ are sensitive to redistribution reactions to give Ar_2Bi(O_2CR) and Bi(O_2CR)$_3$.[6] Consequently, the exact composition and sometimes identity of certain arylbismuth species are not known. The synthetic routes to these compounds include exchange reactions of the arylbismuth chlorides with sodium carboxylates, acidolysis of Ar_3Bi, and reaction of arylbismuth alkoxides with the corresponding acids.[6b,7]

In the course of our studies of bismuth complexes with salicylic acid, we have shown that Bi(Hsal)$_3$ can be easily produced via acidolysis of $BiPh_3$ in refluxing toluene.[2c] It was found that the "Bi(Hsal)$_3$" can be trapped and characterized as a 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) adduct. There is an interesting difference in the reactivities of the two amines that leads to [Bi(Hsal)(sal)(phen)·C_7H_8]$_2$ in one case or

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Scheme 1. Synthetic Procedure for 2a−d[a]

$$BiPh_3 + 2\,H_2sal^* \xrightarrow[-\,C_6H_6]{} [BiPh(Hsal^*)_2] \quad (A)$$

$$[BiPh(Hsal^*)_2] + AA \longrightarrow [BiPh(Hsal^*)_2(AA)] \quad (B)$$

[a] Legend: H_2sal^* = 2-hydroxybenzoic acid, 4-methyl-2-hydroxybenzoic acid; AA = phen, bipy.

$[Bi(Hsal)_3(bipy)\cdot C_7H_8]_2$ in the other.[3] Andrews et al. have shown that "$Bi(Hsal)_3$" is accessible via a solvent-free reaction of $BiPh_3$ and salicylic acid.[8] The product of the reaction was reported to be soluble in acetone, and this may be indicative of a different degree of oligomerization as compared to that for "$Bi(Hsal)_3$" synthesized in refluxing toluene.[3] In a continuation of our studies, the reactivity of the former product toward bipy and phen has been investigated. The major products of the reaction proved to be [Bi(Hsal)(sal)(phen)] and [$Bi(Hsal)_3$(bipy)]; however, along with these products small amounts of [$BiPh(Hsal)_2$(phen)] (**2a**) and [$BiPh(Hsal)_2$(bipy)] (**2c**) were detected. The corresponding reactions with 4-methyl-2-hydroxybenzoic acid proceed similarly to give $[Bi(Hsal^{4Me})(sal^{4Me})(phen)]_2\cdot 2Me_2CO$ ([**3**]$_2\cdot 2Me_2CO$) and $[Bi(Hsal^{4Me})_3(bipy)]_2\cdot 4Me_2CO$ ([**4**]$_2\cdot 4Me_2CO$) as the main products, in addition to $[BiPh(Hsal^{4Me})_2(phen)]$ (**2b**) and $[BiPh(Hsal^{4Me})_2(bipy)]$ (**2d**). The formation of phenyl derivatives results from incomplete acidolysis of $BiPh_3$, and the presence of traces of phenylbis(salicylato)bismuth(III) (**1a**) and phenylbis(4-methyl-2-hydroxybenzoato)bismuth(III) (**1b**) is observed in crude products of the solid-state reactions. Using an experimental procedure similar to that for $[Bi(Hsal)(sal)(phen)]\cdot C_7H_8$,[3] the monomeric complex $[Bi(Hsal^{4Me})_3(phen)(MeOH)]$ (**5**) was obtained.

We were able to isolate pure **1a**,**b** by reacting $BiPh_3$ with 2 equiv of 2-hydroxybenzoic acid or 4-methyl-2-hydroxybenzoic acid under anhydrous conditions in boiling acetone. The corresponding diamine adducts **2a**−**d** were prepared by the subsequent addition of the corresponding diamine to solutions of **1a**,**b** (Scheme 1).

Interestingly, when the acidolysis of $BiPh_3$ with salicylic acid is performed in reagent-grade acetone, partial hydrolysis occurs and crystals of the high-nuclear bismuth oxo salicylate cluster $[Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2]\cdot 4Me_2CO$ are produced in high yield. This oxo cluster, along with a Bi_9 oxo cluster, $[Bi_9O_7(Hsal)_{13}(Me_2CO)_5]\cdot 1.5Me_2CO$, has been recently reported by Andrews and co-workers from recrystallization of $Bi(Hsal)_3$ in wet acetone.[9] The same reaction with 4-methyl-2-hydroxybenzoic acid gave a very soluble product which unfortunately has failed to produce X-ray-quality crystals to date.

Results and Discussion

The solid-state reaction of $BiPh_3$ with salicylic acid and some of its derivatives has been examined. The solventless conditions for this reaction previously described in the literature[8] seemed very attractive, because no expensive dry solvents were used; moreover, some of the products of the solid-state reaction display a higher solubility in organic solvents compared to the compounds produced in refluxing toluene. Our initial reactions between the "$Bi(Hsal)_3$" produced from the solid-state reaction and bipy or phen gave [Bi(Hsal)(sal)(phen)] and [$Bi(Hsal)_3$(bipy)], as determined by spectroscopic analyses; however, small amounts of needlelike crystals of **2a**,**c** were also detected. Similar behavior was observed when salicylic acid was replaced with 4-methyl-2-hydroxybenzoic acid. We ascribed the formation of these compounds to the presence of traces of **1a**,**b** in the crude products of the solid-state reaction of $BiPh_3$ with corresponding acids in a 1:3 molar ratio. We noticed that some of the salicylic acid sublimed onto the cold parts of the reaction vessel during this solid-state reaction at 130 °C. The formation of phenylbis(salicylato)bismuth(III) species from the 1:3 reactions was confirmed by NMR spectroscopy. However, their formation can be minimized by using an excess of the corresponding carboxylic acids. In an attempt to isolate phenylbismuthbis(salicylate) species, we treated $BiPh_3$ with 2 equiv of salicylic acid or 4-methyl-2-hydroxybenzoic acid in dry acetone. Dropwise addition of a solution of the acid to $BiPh_3$ in acetone at reflux resulted in formation of clear solutions, which upon concentration and addition of bipy or phen produced **2a**−**d** in good yields upon standing. It is important to maintain anhydrous conditions during the acidolysis of $BiPh_3$ in order to prevent hydrolysis.

Compounds **1a**,**b** and **2a**−**d** are stable in the solid state; however, the solutions tend to decompose upon extended exposure to air, presumably due to hydrolysis. Compounds **1a**,**b** are soluble in Me_2CO, THF, and DMSO but less soluble in alcohols and MeCN. The adducts **2a**−**d** are slightly soluble in Me_2CO but more so in DMF and DMSO. The IR spectra of **1a**,**b** and **2a**−**d** display the phenolic δ(OH) bending peak of the salicylate-type ligands at ∼1250−1255 cm^{-1}, suggesting that the phenol group retains the proton, while the ν_{as}(COO) peaks between 1620 and 1631 cm^{-1} and the ν_s(COO) peaks between 1367 and 1375 cm^{-1} are indicative of a high degree of covalent character in the Bi−O(carboxylate) bonds.[10] The electrospray ionization mass spectra (ESI-MS) of **1a** exhibit two prominent ions at a mass-to-charge ratio (*m*/*z*) of 559.06 and 981.10, with mass and isotope distribution patterns corresponding to $[PhBi(sal)(salH)]^-$ (calculated *m*/*z* of 559.06) or $[Bi_2(Ph)_2(sal)_2(Hsal)]^-$ (calculated *m*/*z* of 981.08) (Figures S1 and S2, Supporting Information). Similarly, the analogous ions $[PhBi(sal^{4Me})(Hsal^{4Me})]^-$ and $[Bi_2(Ph)_2(sal^{4Me})_2(Hsal^{4Me})]^-$ were observed for **1b** at *m*/*z* 587.11 (calculated *m*/*z* of 587.09) and *m*/*z* 1023.17 (calculated *m*/*z* of 1023.14), respectively (Figures S1 and S3, Supporting Information). The ^1H and ^{13}C NMR spectra of **1a**,**b** and **2a**−**d** in d_6-dmso (Figures S4 and S5, Supporting Information) revealed only a single salicylate environment, consistent with fluxional salicylate ligands on the NMR time scale. The spectrum of **1b** in d_6-dmso exhibits the ortho, meta, and para protons of the phenyl group centered at 8.81 ppm (d), 7.92 ppm (t), and 7.37 ppm (t), respectively. The methyl group of the carboxylate ligand displays a singlet at 2.26 ppm, while the signals of the aromatic hydrogens are observed as two doublets at 7.64 and 6.63 ppm and a singlet at 6.67 ppm, while the peak ^1H centered at ∼12.1 ppm suggests a protonated phenoxy group. Complex **1a** displays features in common with **1b**, indicating similar structures for the two complexes in solution. Since there is an overlap of the signals in ^1H NMR spectra for **2a**−**d**, the $^1H-^1H$ COSY experiments provided the assignments of all proton atoms and proved that the signal at 8.7 ppm belongs to the phenyl group (Figure S6, Supporting Information). As in **1a**,**b**, the data revealed a significant downfield shift of the resonance for the *o*-H atoms of the phenyl group, as observed in other organobismuth compounds.[11] In some spectra of crude **2a**−**d** additional very weak signals at

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Table 1. Crystallographic Data for 2a, 2b·Me_2CO, 2c, 2d·DMF, $[3]_2$·$2Me_2CO$, $[4]_2$·$4Me_2CO$, and 5

	2a	**2b**·Me_2CO	**2c**	**2d**·DMF	$[3]_2$·$2Me_2CO$	$[4]_2$·$4Me_2CO$	**5**
formula	$C_{32}H_{23}BiN_2O_6$	$C_{37}H_{33}BiN_2O_7$	$C_{30}H_{21}BiN_2O_6$	$C_{35}H_{34}BiN_3O_7$	$C_{31}H_{27}BiN_2O_7$	$C_{34}H_{29}BiN_2O_9$	$C_{37}H_{33}BiN_2O_{10}$
fw	740.50	826.23	714.47	813.63	748.53	818.57	874.63
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Fdd2$
a (Å)	11.289(2)	11.736(2)	11.8148(7)	11.221(2)	15.979(3)	12.037(2)	29.085(6)
b (Å)	12.720(2)	12.080(2)	19.694(1)	11.789(2)	15.472(3)	14.119(3)	31.861(6)
c (Å)	20.424(3)	14.215(3)	22.990(2)	14.441(3)	12.295(3)	23.159(5)	14.885(3)
α (deg)	74.693(2)	95.21(3)	90	66.93(3)	90	90	90
β (deg)	78.926(3)	111.15(3)	98.299(1)	89.68(3)	108.13(3)	94.55(3)	90
γ (deg)	77.910(3)	113.63(3)	90	69.93(3)	90	90	90
V (Å^3)	2736.8(7)	1655.5(6)	5293.2(6)	1632.2(6)	2888(1)	3923(1)	13794(5)
Z	4	2	8	2	4	4	16
D_{calcd} (g cm^{-3})	1.797	1.658	1.793	1.664	1.721	1.386	1.685
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	223	195	190	298	298	298	298
$2\theta_{max}$ (deg)	56.00	56.64	55.00	56.74	56.60	56.62	56.58
abs. coeff (mm^{-1})	6.492	5.378	6.709	5.454	6.153	4.541	5.175
no. of data collected	9904	6079	12 175	6803	7012	9463	8317
no. of unique rflns	4958	3610	9428	2836	3805	5849	6556
no. of params refined	703	383	811	373	373	349	400
F(000)	1440	816	2768	808	1464	1608	6912
R1 ($I > 2\sigma(I)$)	0.0460	0.0407	0.0363	0.0679	0.0334	0.0415	0.0311
wR2 ($I > 2\sigma(I)$)	0.0940	0.0763	0.0870	0.1636	0.0996	0.1163	0.0710
GOF	0.731	0.865	1.098	0.869	1.034	0.993	1.031
ρ_{fin}(max/min) (e Å^{-3})	1.259/−0.777	0.792/−0.421	0.853/−0.794	1.670/−1.989	1.235/−0.703	2.493/−1.047	0.830/−0.751

∼8.3 (doublet), ∼7.6 and ∼7.3 ppm (pair of triplets) may be observed. The deshielded nature of these signals compared to those of $BiPh_3$ may indicate a possible presence of the diphenylbismuth salicylate species in solutions as a minor impurity.

The molecular structures of compounds **2a**, **2b**·Me_2CO, **2c**, and **2d**·DMF were established by X-ray crystallography. Selected crystallographic data collection and refinement parameters are provided in Table 1. X-ray-quality crystals of **2a**−**c** were grown from acetone, while crystals of **2d**·DMF were obtained from an acetone−DMF solvent mixture. The structure of **2c** was not particularly well determined, due to problems with disorder, as described in the Experimental Section. However, the essential structure was adequately elucidated from the data. **2a**, **2b**·Me_2CO, **2c**, and **2d**·DMF have essentially identical bond lengths and angles around the Bi(III) center but differ slightly in the torsional relationships between their amine and carboxylate rings. As depicted in Figures 1−3 and in Figure S7 (Supporting Information), each hexacoordinate bismuth center is surrounded by two $Hsal^-$, one phenyl, and one amine ligand. The overall geometry of Bi(III) can be described as pentagonal pyramidal, with the stereochemically active pair of electrons in the position trans to the ipso apical carbon of the phenyl group. The base of the pentagonal pyramid is completed by three carboxylate oxygen atoms of one mono- and one bidentate salicylate ligand and two nitrogen atoms of the chelating diamine. The Bi−C bond distances are 2.260(9) (**2a**), 2.255(3) (**2b**·Me_2CO), 2.250(3) and 2.251(2) (**2c**), and 2.250(7) Å (**6**·DMF). Likewise, these values for the Bi−C bond lengths are similar to the values observed for $BiPh_3$ (2.259 Å) and other tris(aryl)bismuthines.[6,12] One carboxylate ligand is aniso-bidentate, while the second one can be considered as monodentate. The carboxylate O atoms were labeled O(X1) and O(X2), where O(X2) was the O atom closest to the phenoxy O atom, which was labeled O(X3). Which O atom of the carboxylate binds to Bi varies, and the numbering scheme serves to highlight this subtle difference in coordination geometries. The atoms Bi(1), O(31), O(21), O(22), N(11), and N(12) in **2a** or Bi(1), O(32), O(21), O(22), N(11), and N(12) in **2b**·Me_2CO and **2d**·DMF are almost coplanar (the sums of the corresponding angles are 358.2(2), 358.3(1), and 358.5(3)°, respectively). The position of the phenyl group in all three complexes is slightly shifted from the perfect perpendicularity (C(11)−Bi(1)−O(carboxylate) angles are in the range 82.7−86.8° and C(11)−Bi−N(diamine) in the range 81.8−87.3°). A stereochemically active lone pair of electrons, localized on the bismuth center, is believed to occupy the position opposite the aryl substituent, as in most of the structurally characterized monoarylbismuth(III) complexes.[7c−f,13,14] The Bi−N bond lengths in **2a**, **2b**·Me_2CO, **2c**, and **2d**·DMF were found in the range of the corre-

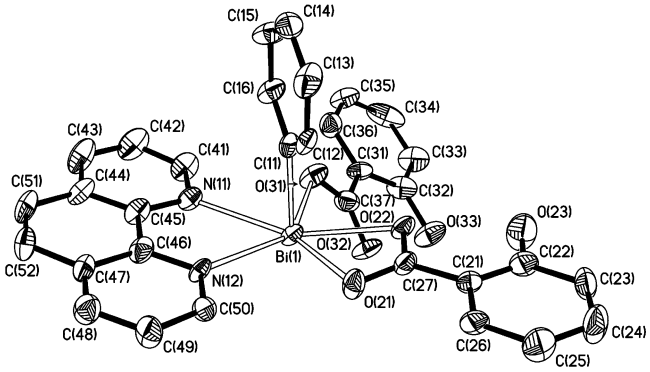

Figure 1. Coordination environment of Bi(III) in **2a** with thermal ellipsoids at the 40% probability level. Only the non-hydrogen atoms are shown. Selected bond lengths (Å) and angles (deg): Bi(1)−C(11) = 2.260(9), Bi(1)−O(21) = 2.551(6), Bi(1)−O(22) = 2.477(6), Bi(1)−O(31) = 2.313(6), Bi(1)−N(11) = 2.544(8), Bi(1)−N(12) = 2.574(7); C(11)−Bi(1)−O(21) = 86.7(3), C(11)−Bi(1)−O(22) = 82.7(3), C(11)−Bi(1)−O(31) = 86.5(3), C(11)−Bi(1)−N(11) = 81.8(3), C(11)−Bi(1)−N(12) = 84.9(3), O(31)−Bi(1)−O(22) = 83.4(2), O(31)−Bi(1)−N(11) = 78.2(2), O(22)−Bi(1)−N(11) = 156.6(2), O(31)−Bi(1)−O(21) = 135.9(2), O(22)−Bi(1)−O(21) = 52.5(2), N(11)−Bi(1)−O(21) = 143.1(2), O(31)−Bi(1)−N(12) = 142.7(2), O(22)−Bi(1)−N(12) = 130.8(2), N(11)−Bi(1)−N(12) = 64.7(2), O(21)−Bi(1)−N(12) = 79.4(2).

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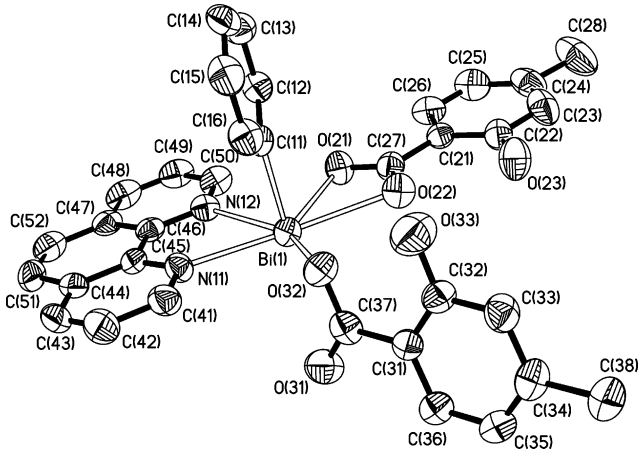

Figure 2. Coordination environment of Bi(III) in **2b**·Me_2CO with thermal ellipsoids at the 40% probability level. Only the non-hydrogen atoms are shown. Selected bond lengths (Å) and angles (deg): Bi(1)−C(11) = 2.255(3), Bi(1)−O(31) = 2.366(4), Bi(1)−O(22) = 2.475(5), Bi(1)−N(1) 2.506(3), Bi(1)−N(2) = 2.553(5), Bi(1)−O(21) = 2.559(5); C(11)−Bi(1)−O(31) = 84.9(2), C(11)−Bi(1)−O(22) = 86.3(2), O(31)−Bi(1)−O(22) 130.2(2), C(11)−Bi(1)−N(11) = 84.3(1), O(32)−Bi(1)−N(11) = 85.2(1), O(22)−Bi(1)−N(1) = 142.2(1), C(11)−Bi(1)−N(12) = 87.3(2), O(32)−Bi(1)−N(12) = 150.0(2), O(22)−Bi(1)−N(12) = 77.9(2), N(11)−Bi(1)−N(12) = 65.2(2), C(11)−Bi(1)−O(21) = 85.4(2), O(32)−Bi(1)−O(21) = 78.9(2), O(22)−Bi(1)−O(21) = 51.6(1), N(11)−Bi(1)−O(21) = 161.7(1), N(12)−Bi(1)−O(21) = 129.3(2).

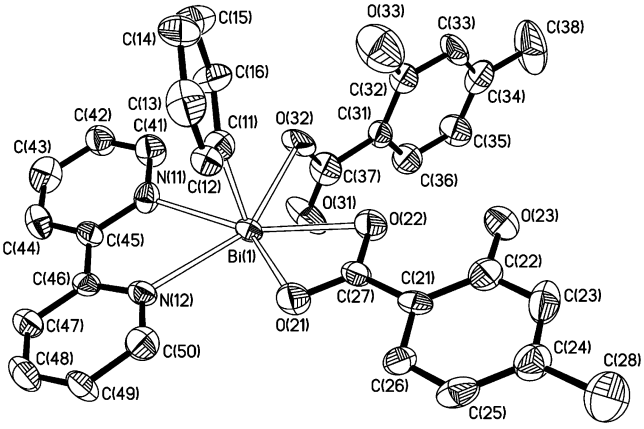

Figure 3. Coordination environment of Bi(III) in **2d**·DMF with thermal ellipsoids at the 40% probability level. Only the non-hydrogen atoms are shown. Selected bond lengths (Å) and angles (deg): Bi(1)−C(11) = 2.250(7), Bi(1)−O(32) = 2.388(8), Bi(1)−O(21) = 2.464(9), Bi(1)−N(11) = 2.490(6), Bi(1)−N(12) = 2.534-(10), Bi(1)−O(22) = 2.594(9); C(11)−Bi(1)−O(32) = 84.1(3), C(11)−Bi(1)−O(21) = 86.8(3), O(32)−Bi(1)−O(21) = 129.3(3), C(11)−Bi(1)−N(11) = 83.9(3), O(32)−Bi(1)−N(11) = 86.3(3), O(21)−Bi(1)−N(11) = 141.9(3), C(11)−Bi(1)−N(12) = 86.2(3), O(32)−Bi(1)−N(12) = 150.5(3), O(21)−Bi(1)−N(12) = 77.7(3), N(11)−Bi(1)−N(12) = 64.9(3), C(11)−Bi(1)−O(22) = 86.2(3), O(32)−Bi(1)−O(22) = 77.5(3), O(21)−Bi(1)−O(22) = 52.1(3). N(11)−Bi(1)−O(22) = 161.8(3), N(12)−Bi(1)−O(22) = 129.6-(3).

sponding distances in $[Bi(S_2CNC_5H_{10})_2(NO_3)(phen)]$ (2.530(8) and 2.534(8) Å),[15a] $[Bi(S_2CNEt_2)I_2(bipy)]$ (2.56(1) and 2.61(1) Å),[15b] or $[BiX_3(bipy)_2]$ and $[BiX_3(phen)(dmso)_3]$ (between 2.49 and 2.60 Å)[15c] and slightly longer than in $[CH_3BiCl_2(bipy)]$ (2.483(9) and 2.486(8) Å)[16a] and [Hbipy][$BiBr_4$(bipy)] (2.45-(3) Å).[16b]

In general, monoarylbismuth(III) compounds contain either halogen substituents[13] or chalcogenato ligands[14] and exhibit considerable structural diversity. The mesityl derivative [BiMes-{S(S)PPh_2}$_2$][14b] contains monomeric molecules, while Bi(2-(2′-Py)C_6H_4){S(S)$CNEt_2$}$_2$][14c] and [BiPh{SC_5H_4NO-2}$_2$][14f] can be described as dimers and [$BiPhBr_2$][13d] and [BiPh{S(S)COMe}$_2$][14e] are polymeric. Trivalent organobismuth compounds with electronegative substituents are good Lewis acids. Thus, most of the $ArBiX_2$ compounds described so far have a high tendency to form oligomeric or polymeric species through Bi−X−Bi bridges. All $PhBi(O_2CR)_2$ species structurally characterized to date, including $[BiPh(ClCH_2CO_2)_2]$,[7c] $[BiPh(O_2CC_6H_2F_3$-3,4,5$)_2]$,[7d] $[BiPh(O_2CCH(CH_3)CH_2GePh_3)_2]$,[7e] and $[BiPh(2$-$C_5H_4N)CO_2)_2]$,[7f] display bridging carboxylate ligands. While the solid-state structures of **1a**,**b** are not available, they may involve bridging carboxylate ligands, as in the aforementioned complexes. The presence of strongly coordinating bidentate ligands, phen and bipy, in **2a**, **2b**·Me_2CO, **2c**, and **2d**·DMF favors the formation of monomeric species.

Salicylate-related ligands have proven to be versatile in binding to Bi(III). Usually the monodeprotonated salicylate ligand chooses an aniso-bidentate coordination mode, while the phenoxy oxygen donor is not involved in coordination. In the compounds **2a**, **2b**·Me_2CO, **2c**, and **2d**·DMF both monodentate and bidentate chelating carboxylate modes occur with significant differences in Bi−O bond distances. In contrast, the doubly deprotonated anion sal^{2-} usually exhibits a bridging mode, either between two bismuth centers, as in [Bi(Hsal)(sal)(phen)·C_7H_8]$_2$,[3] or between Bi(III) and transition metals, as in a range of heterometallic species, including $Bi_2Ti_3(sal)_8(Hsal)_2$,[2c] Bi_2Ti_4-$(sal)_{10}(Hsal)(O^iPr)$·H_2O,[2c] $BiTi_4(sal)_6(O^iPr)_7$,[2b] $Bi_4Ti_4(sal)_{10}(O^i$-$Pr)_8$,[2b] $Bi_8Ti_8(sal)_{20}(O^iPr)_{16}$,[2b] $Bi_2M_2(sal)_4(Hsal)_4(OEt)_4$,[2c] Bi_2M_2-(μ-O)$(sal)_4(Hsal)_4(OEt)_2$·H_2O,[2e] and $BiM_4(\mu$-O$)_4(sal)_4(Hsal)_3$-$(O^iPr)_4$,[2e] where M = Nb, Ta.

As mentioned above, the reaction of Bi(Hsal^{4Me})$_3$, prepared in the solid state, with phen or bipy gave **3** and **4** as the major products. Both compounds were isolated as the dimeric acetone adducts [**3**·Me_2CO]$_2$ and [**4**·2Me_2CO]$_2$, which can be recrystallized from acetone (see the CIF file and Figure S8 in the Supporting Information). In contrast, addition of a methanolic solution of phen to "Bi(Hsal^{4Me})$_3$" prepared in refluxing toluene resulted in formation of a monomeric complex, [Bi(Hsal^{4Me})$_3$-(phen)(MeOH)] (**5**). A comparison of the structures of the newly synthesized bismuth complexes **2a**, **2b**·Me_2CO, **2c**, **2d**·DMF, [**3**]$_2$·2Me_2CO, [**4**]$_2$·4Me_2CO, and **5** with those of the previously described complexes [Bi(Hsal)(sal)(phen)·C_7H_8]$_2$ and [Bi(Hsal)$_3$-

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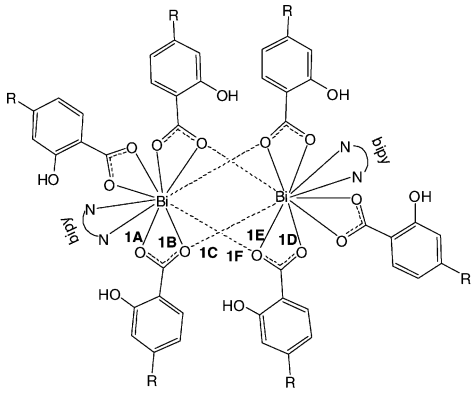
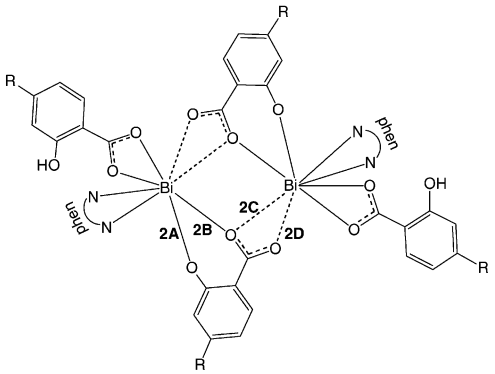
Scheme 2. Coordination Modes of Bridging Salicylate-Type Ligands Observed in (A) bipy Adducts $[Bi(Hsal)_3(bipy)\cdot C_7H_8]_2$ and $[4]_2\cdot 4Me_2CO$ and (B) Phen Adducts $[Bi(Hsal)(sal)(phen)\cdot C_7H_8]_2$ and $[3]_2\cdot 2Me_2CO$ (R = H, Me)



A



B

Table 2. Selected Bi−O Carboxylate Interactions (Å) in the Crystal Structures of Bismuth(III) Diamine Adducts with Salicylate-Type Ligands

	$[4]_2\cdot 4Me_2CO$	$[Bi(Hsal)_3(bipy)\cdot C_7H_8]_2$		$[3]_2\cdot 2Me_2CO$	$[Bi(Hsal)(sal)(phen)\cdot C_7H_8]_2$
1A	2.374(4)	2.348(4)	**2A**	2.115(4)	2.117(4)
1B	2.820(4)	2.870(4)	**2B**	2.263(4)	2.233(4)
1C	2.931(4)	2.906(6)	**2C**	2.838(4)	2.748(4)
1D	2.318(4)	2.309(4)	**2D**	2.922(4)	3.065(5)
1E	2.832(4)	2.794(4)			
1F	3.002(5)	3.222(6)			

$(bipy)\cdot C_7H_8]_2$[3] reveals some interesting features. While the reaction of bismuth salicylate and bipy afforded $[Bi(Hsal)_3(bipy)\cdot C_7H_8]_2$, the use of phen resulted instead in elimination of a molecule of salicylic acid and formation of $[Bi(Hsal)(sal)(phen)\cdot C_7H_8]_2$. A more complex dependence was observed in the case of the corresponding 4-methyl-2-hydroxybenzoates. When the reaction is performed in acetone with "$Bi(Hsal^{4Me})_3$" prepared in the solid state, $[3]_2\cdot 2Me_2CO$ and $[4]_2\cdot 4Me_2CO$ are produced, which exhibit structures (Figure S8) similar to those of $[Bi(Hsal)(sal)(phen)\cdot C_7H_8]_2$ and $[Bi(Hsal)_3(bipy)\cdot C_7H_8]_2$,[3] respectively. Scheme 2 outlines the two structural types with selected Bi(III)−O interactions being presented in Table 2. It should be noted that, in **5**, Bi(III) is coordinated by three bidentate salicylate ligands through carboxylate groups (Bi−O distances range from 2.218(3) to 2.800(4) Å) and two N donors of phen (Bi−N = 2.435(3), 2.545(2) Å), as well as by a weak contact with an O atom of MeOH (Bi···O(MeOH) = 2.929(4) Å) to complete a coordination environment of 9 (Figure 4). As a consequence of the relatively high Lewis acidity of bismuth centers, most of the Bi(III) carboxylates described to date have been dimeric or polymeric; however, in the case of **5**, which contains three carboxylate ligands per Bi(III), the oligomerization is evidently inhibited by the coordination of a methanol molecule. This observation also differs from previous reports that 1:1 adducts of Bi(III) and phen require lower coordination numbers than the corresponding bipy 1:1 adducts.[17] It can be argued that the occurrence of one or the other structural motif results from a slight difference in the electronic properties of the carboxylate ligand coupled with different steric demands resulting from the replacement of one hydrogen atom by a methyl group in the salicylate ion. Crystal-packing forces and hydrogen bonding may play a role as well.[18]

The structural differences between the corresponding organometallic and inorganic salicylate complexes of Bi(III) can be understood from the replacement of the salicylate ligands with the more electron rich phenyl group, which decreases the electrophilicity of the bismuth center. As a result, a lower coordination number for Bi(III) is stabilized, correlating to the appearance in the position trans to the organic groups of a well-defined lone pair of electrons (LPE), which in terms of the valence shell electron pair repulsion (VSEPR) model is considered to be stereochemically active. In many cases where the availability of coordinating sites is limited, oligomerization is often the only way to satisfy the various bonding requirements of bismuth(III) compounds. The tradeoff between oligomeric and mononuclear bismuth(III) species by introducing an aryl

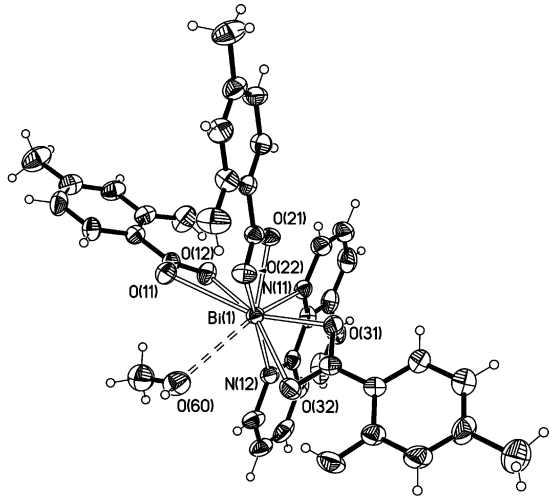


Figure 4. Coordination environment of Bi(III) in **5** with thermal ellipsoids at the 40% probability level. Only the atoms participating in coordination are labeled. Selected bond lengths (Å) and angles (deg): Bi(1)−O(11) = 2.800(4), Bi(1)−O(12) = 2.460(4), Bi(1)−O(21) = 2.318(3), Bi(1)−O(22) = 2.667(4), Bi(1)−O(31) = 2.331-(4), Bi(1)−O(32) = 2.644(4), Bi(1)−N(11) = 2.435(3), Bi(1)−N(12) = 2.545(2), Bi(1)−O(60) = 2.929(4); N(11)−Bi(1)−N(12) = 65.7(1), O(11)−Bi(1)−O(12) = 49.4(1), O(21)−Bi(1)−O(22) = 51.7(1), O(31)−Bi(1)−O(32) = 52.0(1), O(11)−Bi(1)−O(21) = 73.7(1), O(11)−Bi(1)−O(31) = 147.9(1), O(21)−Bi(1)−O(31) = 82.3(2), O(12)−Bi(1)−O(22) = 108.2(1), O(12)−Bi(1)−O(32) = 159.4(1), O(22)−Bi(1)−O(32) = 82.6(1), O(21)−Bi(1)−N(11) = 78.8(1), O(31)−Bi(1)−N(11) 75.8(1), N(11)−Bi(1)−O(12) = 72.2(1), O(21)−Bi(1)−N(12) = 144.5(1), O(31)−Bi(1)−N(12) = 90.0(1), O(12)−Bi(1)−N(12) = 89.1(1), N(11)−Bi(1)−O(32) = 115.6(1), N(12)−Bi(1)−O(32) = 78.1(1), N(11)−Bi(1)−O(22) = 127.7(1), N(12)−Bi(1)−O(22) = 160.4(1).

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substituent (and the resultant diversity in molecular architecture) is an interesting phenomenon which needs additional investigation. The common driving force for the topologies of the structures discussed here is probably the achievement of coordinative saturation of Bi(III), correlated with the role of the LPE.

If the initial reagents used in the acidolysis reaction of $BiPh_3$ are not dry and/or reagent grade acetone is used as a solvent, partial hydrolysis occurs. In the case of H_2sal the reaction eventually produces crystals of the high-nuclearity bismuth(III) oxo-cluster $[Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2]\cdot 4Me_2CO$.[9] Interestingly, Dikarev et al.[19] synthesized and characterized a similar β-diketonate cluster containing 38 Bi(III) atoms, $[Bi_{38}O_{45}(hfac)_{24}]$, where hfac = hexafluoroacetylacetonate(1−). When $BiPh_3$ is treated with H_2sal^{4Me}, a very soluble compound is produced. Despite a lack of X-ray diffraction data for this product, similar hydrolytic reactions appear to be involved, which probably result in a mixture of Bi(III)−oxo compounds. The ESI-MS of the product resulted in a number of ion fragments, including those attributed to the oxo species $[Bi_9O_7(Hsal^{4Me})_{13}(sal^{4Me})]^{2-}$ (*m*/*z* 2053.15, calcd 2053.17) and $[Bi_{10}O_8(Hsal^{4Me})_{14}(sal^{4Me})]^{2-}$ (*m*/*z* 2241.15, calcd 2241.16), along with some other solvated species (Figure S9, Supporting Information). The isotope patterns of these species define doubly charged anions containing 9 or 10 bismuth atoms (Figures S10 and S11, Supporting Information). Solvated $[Bi_{10}O_8(Hsal)_{14}(sal)]^{2-}$ species were found in the ESI-MS of $[Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2]\cdot 4Me_2CO$ as well. The structure of the $Bi_{10}O_8$ cluster can be predicted on the basis of the known arrangement in Bi_9O_7 compounds (Figure 5). These two oxo cores can be presented as a part of a larger class of clusters with a central octahedral $Bi_6(\mu_3\text{-}O)_8$ core with general formula $Bi_6O_4(\mu_3\text{-}OR)_{4-x}(\mu_3\text{-}OBi(OR)_2)_x(OR)_6$ ($x = 0-4$). On the basis of the structural data available in the literature,[20] tetrahedral symmetry is proposed for the $Bi_{10}O_8$ core in $[Bi_{10}O_8(Hsal^{4Me})_{14}(sal^{4Me})]^{2-}$, in which four faces of the core octahedron are capped instead of three, as in the Bi_9 complexes.

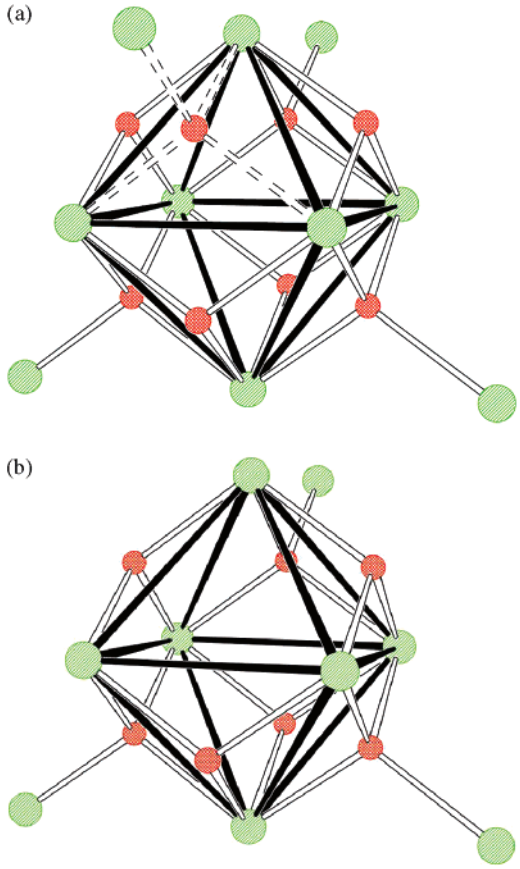

Figure 5. Proposed structures of the cores of (a) $Bi_{10}O_8$ and (b) Bi_9O_7. In Bi_9O_7 six bismuth atoms form an octahedron, seven faces of which are capped by oxide ligands, while the eighth face is capped by a bridging O atom of a carboxylate ligand (not shown). In $Bi_{10}O_8$ four of the eight oxido ligands display μ_4-bridging functions to bind four additional Bi atoms.

Concluding Remarks

The formation of Bi(III) complexes with salicylate-type ligands from the acidolysis reaction of $BiPh_3$ has been examined, and it was found that the outcome of this reaction is highly dependent on reaction conditions. Simple $PhBi(O_2CR)_2$ species (**1a**,**b**) are observed when $BiPh_3$ is treated with H_2sal or H_2sal^{4Me} in a 1:2 ratio in dry acetone. Treatment of **1a**,**b** with the chelating diamine ligands bipy and phen furnishes the monomeric adducts **2a**−**d**. The products of the reaction of bismuth(III) tris(salicylate) complexes with diamine ligands were shown to be highly Lewis acidic, which results in coordination with the O donors of the neighboring molecule to form dimers (as in $[\mathbf{3}]_2\cdot 2Me_2CO$ and $[\mathbf{4}]_2\cdot 4Me_2CO$) or in coordination of solvent molecules (as in **5**). The comparison of the structures of the corresponding organometallic and inorganic salicylate complexes of Bi(III) revealed that the replacement of the salicylate ligands with phenyl groups gives lower coordination numbers and a lower degree of oligomerization. In wet solvent, the acidolysis of $BiPh_3$ is accompanied by partial hydrolysis, and polymetallic bismuth−oxo clusters capped by monodeprotonated salicylate ligands are produced. A Bi_{10} oxo cluster in this system was observed for the first time.

Experimental Section

Materials and Equipment. All of the manipulations were carried out under a dry dinitrogen or argon atmosphere using standard Schlenk and glovebox techniques. Acetone was dried over Drierite and distilled over freshly activated molecular sieves. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. Commercial $BiPh_3$, H_2sal, and H_2sal^{4Me} were dried for 4 h in vacuo and then transferred to the drybox. "Bi(Hsal)$_3$" and "Bi(Hsal^{4Me})$_3$" were prepared by a solid-state reaction of $BiPh_3$ with the corresponding acids, as previously described for the salicylate derivative.[8] NMR spectra were recorded at room temperature in d_6-dmso (containing 0.5% TMS) on Bruker Avance 400 and 500 spectrometers, and the ^1H and ^{13}C chemical shifts are reported to tetramethylsilane (TMS). Mass spectrometric measurements were carried out using a MicrOTOR mass spectrometer (Bruker Daltonics Inc.). The reported infrared data were recorded on a Nicolet 670 FT-IR spectrometer using attenuated total reflectance (Table S2, Supporting Information). Melting points were obtained in sealed capillaries on a Electrothermal melting point instrument. CHN analyses were performed at Galbraith Laboratories.

Typical Procedure for the Preparation of the Complexes: Synthesis of [BiPh(Hsal)$_2$] (1a). $BiPh_3$ (440 mg, 1.0 mmol) was added to a three-neck round-bottom flask while in the drybox under

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N_2. In a separate Schlenk flask salicylic acid (275 mg, 2.0 mmol) was loaded. After the flasks were removed from the drybox and purged with Ar, 200 mL of dry acetone was added into each flask. The three-neck flask containing $BiPh_3$ was heated to reflux, and then the solution of the acid was added dropwise over a period of 3 h. The mixture was stirred at reflux for an additional 1 h, and then the resulting solution was cooled to ambient temperature. The solvent was removed, and the product was washed with dry toluene and diethyl ether and then dried in vacuo. A white solid of **1a** was obtained. Yield: 510 mg, 91%. Anal. Calcd (found) for $BiC_{20}H_{15}O_6$: C, 42.87 (42.43); H, 2.70 (2.60). ^{1}H NMR (d_6-dmso): δ 6.83−6.87 (m, 4H, salH), 7.38 (m, 1H, Ph + 2H, Hsal), 7.78 (d, 2H, Hsal, J = 7.4 Hz), 7.94 (t, 2H, Ph, J = 7.4 Hz), 8.83 (d, 2H, Ph, J = 7.4 Hz), 12.17 (s, 2H, salH, OH). ^{13}C{^{1}H} NMR (d_6-dmso): δ 174.41, 160.70, 137.25, 134.28, 132.38, 130.69, 128.05, 118.58, 117.03, 116.74.

Complex 1b. Complex **1b** was prepared as described for **1a** from $BiPh_3$ (440 mg, 1 mmol) and H_2sal^{4Me} (304 mg, 2 mmol) and was obtained as a pale yellow solid. Yield: 526 mg, 89%. Anal. Calcd (found) for $BiC_{22}H_{19}O_6$: C, 44.91 (44.84); H, 3.25 (2.85). ^{1}H NMR (d_6-dmso): δ 2.25 (s, 6H, $Hsal^{Me}$), 6.63 (d, 2H, $Hsal^{4Me}$, J = 7.3 Hz), 6.67 (s, 2H, $Hsal^{4Me}$), 7.37 (t, 1H, Ph, J = 7.4 Hz), 7.64 (d, 2H, $Hsal^{4Me}$, J = 7.8 Hz), 7.92 (t, 2H, Ph, J = 7.6 Hz), 8.81 (d, 2H, Ph, J = 7.0 Hz), 12.19 (s, 2H, salH, OH). ^{13}C{^{1}H} NMR (d_6-dmso): δ 173.99, 160.17, 144.24, 136.74, 131.81, 130.05, 127.50, 119.17, 116.39, 113.92, 20.79.

Complex 2a. To a solution of **1a** (280 mg, 0.5 mmol) in 10 mL of dry acetone was added via syringe a solution of phen (90 mg, 0.5 mmol) in 8 mL of the same solvent at 25 °C. The mixture was stirred for an additional 30 min, concentrated to approximately half of the initial volume, and left overnight at −20 °C, during which time a white solid deposited in the flask. The product was washed with dry diethyl ether and dried in vacuo to give 326 mg (88%) of the title compound. Anal. Calcd (found) for $BiC_{32}H_{23}N_2O_6$: C, 51.90 (51.52); H, 3.13 (3.32); N, 3.78 (3.99). Mp: 215−217 °C. ^{1}H NMR (d_6-dmso): δ 6.84−6.86 (m, 4H, salH), 7.27 (t, 1H, Ph), 7.37 (m, 2H, Hsal), 7.78 (m, 2H, Hsal), 7.86 (d, 2H, phen), 8.00 (t, 2H, Ph), 8.13 (s, 2H, phen), 8.75 (m, 2H Ph + 2H phen), 9.37 (d, 2H, phen), 12.58 (s, 2H, Hsal). ^{13}C NMR (d_6-dmso): δ 116.55, 117.20, 118.21, 120.45, 124.22, 127.91, 128.32, 130.51, 131.12, 132.24, 133.89, 136.73, 137.34, 149.28, 155.20, 160.68, 173.73.

Complex 2b. A solution of phen (135 mg, 0.75 mmol) in acetone (15 mL) was added to a round-bottom flask containing **1b** (441 mg, 0.75 mmol) in 15 mL of the same solvent at 25 °C. Upon completion of the addition, the reaction mixture was stirred for 30 min and then concentrated to approximately half of the initial volume and kept overnight at −20 °C to give a white solid. The product was filtered, washed with dry toluene and diethyl ether, and dried in vacuo. Yield: 483 mg (84%). Anal. Calcd (found) for $BiC_{34}H_{29}N_2O_6$: C, 52.99 (52.82); H, 3.79 (3.38); N, 3.64 (3.49). ^{1}H NMR (d_6-dmso): δ 2.24 (s, 6H, $Hsal^{4Me}$), 6.68 (m, 4H, $Hsal^{4Me}$), 7.22 (t, 1H, Ph), 7.72 (m, 2H $Hsal^{4Me}$ + 2H phen), 7.76 (t, 2H, salH) 8.00 (2H, d, phen), 8.72−8.76 (m, 2H Ph + 2H phen), 9.37 (d, 2H, phen) 12.32 (s, 2H, $salH^{4Me}$). Mp: 204−206 °C dec.

Complex 2c. The compound was synthesized from **1a** (280 mg, 0.5 mmol) and bipy (78 mg, 0.5 mmol) using the same conditions and procedures as for **2a**. A white solid was obtained (309 mg, 86%). Anal. Calcd (found) for $BiC_{30}H_{23}N_2O_6$: C, 50.29 (50.34); H, 3.24 (3.32); N, 3.91 (3.99). ^{1}H NMR (d_6-dmso): δ 6.77−6.81 (m, 4H, salH), 7.18 (t, 1H, Ph), 7.38 (m, 2H, Hsal), 7.46 (m, 2H, bipy), 7.74 (m, 2H, Hsal), 7.93 (m, 2H Ph + 2H bipy), 8.40 (d, 2H, bipy), 8.71 (d, 2H Ph), 8.81 (d, 2H, bipy), 12.32 (s, 2H, Hsal). Mp: 196−198 °C.

Complex 2d. Complex **2d** was prepared as described for **2b** by the addition of bipy (117 mg, 0.75 mmol) to **1b** (441 mg, 0.75 mmol) in dry acetone. Yield: 453 mg (81%). Anal. Calcd (found) for $BiC_{32}H_{29}N_2O_6$: C, 51.48 (51.94); H, 3.92 (3.98); N, 3.75 (3.61). Mp: 149−151 dec. ^{1}H NMR (d_6-dmso): δ 2.26 (s, 6H, $Hsal^{Me}$), 6.65−6.67 (m, 4H, $Hsal^{4Me}$), 7.36 (t, 1H, Ph), 7.48 (dd, 2H, bipy), 7.62 (m, 2H, $Hsal^{Me}$) 7.95 (m, 2H Ph + 2H bipy), 8.39 (d, 2H, bipy), 8.69 (d, 2H, bipy), 8.78 (d, 2H, Ph), 12.23 (s, 2H, $Hsal^{4Me}$).

Complex 3. The compound [**3**]$_2$·2Me_2CO was obtained in 85% yield by reacting 331 mg (0.5 mmol) of "$Bi(Hsal^{4Me})_3$", prepared by the solid-state reaction described in the literature,[8] and 90 mg (0.5 mmol) of phen in 20 mL of dry acetone. The crude compound obtained by this procedure contains small amounts of **2b**·Me_2CO. Anal. Calcd (found) for $BiC_{31}H_{29}N_2O_7$: C, 49.61 (50.32); H, 3.89 (3.76); N, 3.73 (3.49).

Complex 4. The compound [**4**]$_2$·4Me_2CO was prepared as for [**3**]$_2$·2Me_2CO, using bipy instead of phen. Traces of **2d** were detected in the crude product of the reaction. Anal. Calcd (found) for $BiC_{42}H_{44}N_2O_{11}$: C, 51.23 (52.18); H, 4.73 (3.80); N, 2.99 (3.04).

Complex 5. Compound **5** was obtained using a procedure similar to that described for [Bi(Hsal)(sal)(phen)·C_7H_8]$_2$ by reacting $Bi(Hsal^{4Me})_3$ and phen in dry MeOH.[3] Anal. Calcd (found) for $BiC_{37}H_{35}N_2O_{10}$: C, 50.69 (50.44); H, 4.02 (3.71); N, 3.20 (3.24).

Reaction of $BiPh_3$ with H_2sal in Reagent-Grade Acetone. When the acidolysis reaction of $BiPh_3$ with H_2sal as described for **1a** was performed using reagent grade "wet" acetone, the resulting solution was slightly turbid. Filtration and concentration of the filtrate to approximately 1/10 of the initial volume resulted in a clear solution, which upon standing deposited large colorless crystals of [$Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2$]·4$Me_2CO$ in almost quantitative yield: *Pbca*, a = 31.692(3) Å, b = 31.215(3) Å, c = 31.881(3) Å, V = 31539 (9) Å^3.

Reaction of $BiPh_3$ with H_2sal^{4Me} in Reagent-Grade Acetone. The reaction of $BiPh_3$ with 2 equiv of H_2sal^{4Me} in reagent-grade "wet" acetone produced a very soluble viscous oil. Extended drying in vacuo resulted in the formation of crystals, which unfortunately were not suitable for crystallography.

X-ray Structural Determinations. Single crystals of **2a**, **2b**·Me_2CO, **2c**, **2d**·DMF, [**3**]$_2$·2Me_2CO, [**4**]$_2$·4Me_2CO and **5** suitable for X-ray crystallography were separated as small plates or needles either directly from the aforementioned reactions or recrystallized from the corresponding solvents. X-ray crystallographic data are given in Table 1. The data for **2a**, **2b**·Me_2CO, **2d**·DMF, [**3**]$_2$·2Me_2-CO, [**4**]$_2$·4Me_2CO, and **5** were collected at 298, 223, or 195 K on a Bruker SMART 1000 CCD diffractometer in a hemisphere with 10−30 s exposure times, while the data for **2c** were run on a Bruker SMART[21] CCD system at 190(2) K. The frames were processed with the SAINT software and corrected for Lorentz and polarization effects and absorption using Blessing's method and crystal faces as incorporated into the program SADABS.[22] The structures were solved using direct methods and refined by full-matrix least squares on F^2 using SHELXL.[23] A series of least-squares difference Fourier cycles were required to locate the remaining non-hydrogen atoms. The structure refinement of **2c** was affected by disorder, as indicated by the large anisotropic displacement parameters for several salicylate and phen molecules due to the structure suffering from excessive libration. Disorder ratios were all determined to be 50:50. All non-hydrogen atoms were refined anisotropically, either independently or via EADP commands when they overlapped

(21) SMART (Version 5.04) and SAINT (Version 7.23a); Bruker AXS Inc., Madison, WI, 2002.

(22) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Sheldrick, G. M. SADABS (Version 5.1); Universität Göttingen, Göttingen, Germany, 1997. (c) Sheldrick, G. M. SADABS, Siemens Area Detector Absorption Correction, Version 2006/1; Universität Göttingen, Göttingen, Germany, 2006.

(23) (a) Sheldrick, G. M. SHELXTL, Version 6.1; Universität Göttingen, Göttingen, Germany, 2002. (b) Sheldrick, G. M. SHELXS97 and SHELXL97; Universität Göttingen, Göttingen, Germany, 1997.

another atom (different parts) or due to proximity. In the final difference electron density maps for **2a**, **2b**·Me_2CO, [**3**]$_2$·2Me_2CO, and [**4**]$_2$·4Me_2CO there are peaks larger than 1 e Å^{-3}, but they are generally localized in the vicinity of the heavy atoms and make no chemical sense. Hydrogen atoms were idealized throughout the convergence process.

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Supporting Information Available: CIF files giving crystallographic data for **2a**, **2b**·Me_2CO, **2c**, **2d**·DMF, [**3**]$_2$·2Me_2CO, [**4**]$_2$·4Me_2CO, and **5**, figures giving structures of **2c**, [**3**]$_2$·2Me_2CO, and [**4**]$_2$·4Me_2CO, and some additional information on the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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