Preparation and Characterization of Biologically Active Bismuth(III) Tropolonato Complexes

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Two new types of bismuth(III) tropolonato complexes, nitratobis(tropolonato)bismuth(III) (**1d**) and phenylbis(tropolonato)bismuthin (**1f**), are synthesized and characterized by elemental analysis, ^{1}H-NMR, ^{13}C-NMR, IR spectroscopy, and conductivity measurements. The structures of **1d** and aquabis(4,5-benzotropolonato)bismuth(III) nitrate (**6b**) are confirmed by X-ray structural analyses. Derivatives of tropolone (**2a**) and their bismuth(III) complexes are synthesized and characterized in the same manner. Eight of these compounds are tested against *Helicobacter pylori* (*H.p.*) bacteria, which cause chronic gastritis and peptic ulcus. Most of the bismuth compounds show high in vitro activity against *H.p.*

The stomach bacterium *Helicobacter pylori* (*H.p.*), which was discovered as late as 1983[1], is a pathogenic factor in the ethiology of chronic gastritis and peptic ulcus[1,2]. Today, bismuth complexes such as colloidal bismuth citrate CBS, of which the molecular structure is known[3], are used more frequently in the treatment of these diseases. This was the reason to synthesize bismuth tropolonato complexes and to investigate their biological activity.

The first bismuth tropolonato complexes were synthesized and characterized in 1964 with the help of elemental analysis[4]. At that time, three different bismuth tropolonato complexes were discovered (**1a**, **1b**, **1c**), in which two, three or four tropolone rings are bound to the central bismuth(III) atom (Scheme 1).

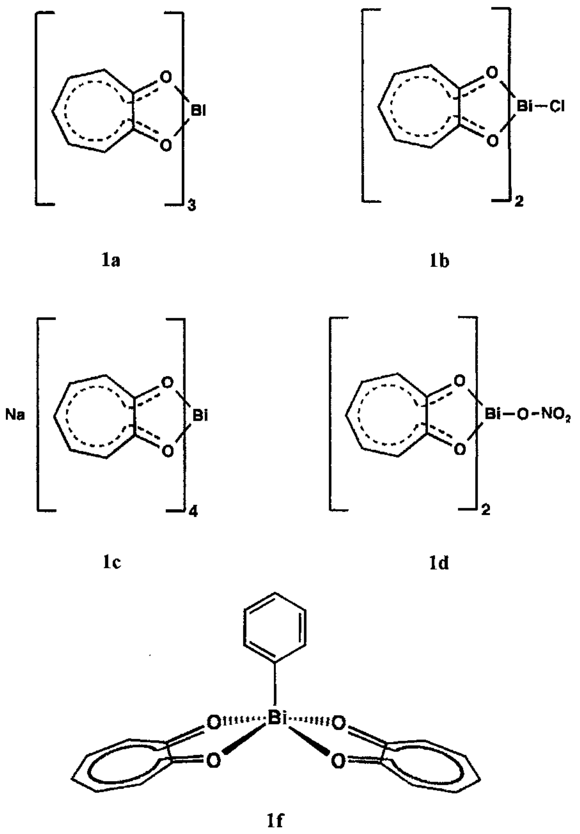
The 6-s orbital in the bismuth(III) cation is fully occupied (lone pair of electrons). The structures of the complexes **1a**–**c** depend on whether or not the lone pair is active. If the lone pair is inactive, then **1a** has an octahedral, **1b** a square-pyramidal or trigonal-bipyramidal and **1c** a square antiprismatic structure[4].

In the project presented here, the complexes **1a** and **1b** are analyzed and characterized by using current analytical methods. In addition, a whole series **2a**–**p** of tropolone derivatives are synthesized (Scheme 2) and converted into the corresponding bismuth tropolonato complexes by applying various working procedures.

Furthermore, two new types of bismuth tropolonato complexes, **1d** and **1f**, are prepared (Scheme 1).

In the investigation of the biological activities of these compounds, seven bismuth(III) tropolonates showed surprising in vitro activities against *H.p.* bacteria.

Scheme 1. Formal structures of the tropolonato complexes **1a**–**d** and **1f**



Results and Discussion

Compound **1a** is obtained by reaction of **2a** with $Bi(NO_3)_3 \cdot 5\ H_2O$ (**3a**) in a mixture of acetone and water.

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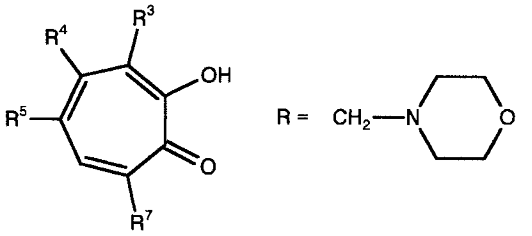
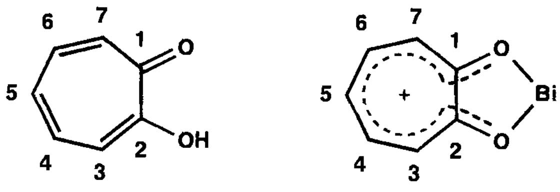
Scheme 2. Synthesized tropolonato derivatives used as chelating ligands



R^3	R^4	R^5	R^7	
H	H	H	H	**2a**
H	CH_3	H	H	**2b**
H	H	CH_3	H	**2c**
CH_3	H	CH_3	CH_3	**2d**
H	C_2H_5	H	H	**2e**
H	$CH(CH_3)_2$	H	H	**2f**
H	C_6H_4		H	**2g**
H	H	NO_2	H	**2h**
H	H	CHO	H	**2i**
Br	H	H	H	**2k**
Br	H	H	Br	**2m**
Br	H	Br	Br	**2n**
CH_2OH	H	CH_2OH	CH_2OH	**2o**
R	H	R	R	**2p**

Compound **2a** is a typical bidentate ligand, resonance-stabilized, and shows aromatic properties. The bismuth tropolonato complex is formed as follows: The proton of the hydroxy group dissociates and the seven-membered tropolone ring is bound to the bismuth(III) cation by the neighboring oxygen atoms. The two equivalent carbon-oxygen bonds have partial double bond character. The three double bonds in the tropolone ring are completely delocalized. Scheme 3 shows the numbering for NMR purposes.

Scheme 3. Numbering of tropolone as a free and as a coordinated ligand



This can clearly be seen from the ^1H- and ^{13}C-NMR spectra of **1a** and **1b**. The ^1H-NMR spectrum of **1a** shows an AA'BB'C spin pattern. In the ^{13}C-NMR spectrum, there are only four signals for the seven carbon atoms, which implies that the atoms C-1 and C-2, C-3 and C-7, C-4 and C-6 are identical. In the FD mass spectrum, the molecular peak is located at $m/z = 572$. Conductivity experiments in DMF show that **1a** has a molar conductivity of $\Lambda_M = 1.5$ S cm^2 mol^{-1}, which implies that the complex is neutral[5]. Table 1 gives a summary of the δ values for the NMR signals of protons and carbon atoms in the complexes **1a**, **b**, **d** and **2a**.

Table 1. NMR signals (δ values) of the protons and carbon atoms in the complexes **2a**, **1a**, **b**, and **d**

^1H-NMR	2-OH	3,7-H	4,6-H	5-H
1 a	-	7.03	7.78	6.98
1 b	-	7.15	7.62	7.11
1 d	-	7.21	7.7	7.22
2 a	-	7.3	7.45	7.09
^{13}C-NMR	1,2-C	3,7-C	4,6-C	5-C
1 a	180.1	127.8	137.5	125.7
1 b	179.7	128.8	137.8	126.8
1 d	179.1	129.5	138.5	128.3
2 a	172.6	124.3	138.4	128.9

Comparing the ^{13}C-NMR spectra of **1a**, **b**, **d** with **2a**, one recognizes that the signals of the carbon atoms 1 and 2 and 3 and 7 are shifted downfield by 6–7 ppm and approximately 3 ppm, respectively. In the bismuth tropolonato complex, the Bi–O bond is formed by the lone pair on the keto oxygen atom. This electron hole is compensated by a strong polarization of the C=O double bond, hence there is a partial positive charge on C-1. This positive charge is evenly distributed between C-1 and C-2 because of the mesomeric resonance relationship of the three conjugated electron pairs in the ring system. The reduction of the electron density on these two carbon atoms is responsible for the downfield shift of 6–7 ppm. The downfield shift of the signals for the carbon atoms C-3 and C-7 is a result of the inductive effects caused by the partial positive charge at C-1 and C-2.

Compound **1b** is formed by reaction of **2a** with **3a** in methanol/H_2O and addition of concentrated hydrochloric acid. The ^1H- and ^{13}C-NMR data show that the tropolone ligands are bound to the bismuth by two equivalent Bi–O bonds. In the FD mass spectra the molecular peak for **1b** is found at $m/z = 486$. This implies that the chlorine atom in the **1b** complex is covalently bound. The conductivity of **1b** in DMSO is 13.9 S cm^2 mol^{-1}. This is a typical value of a neutral complex and also confirms the covalent character of the Bi–Cl bond[5].

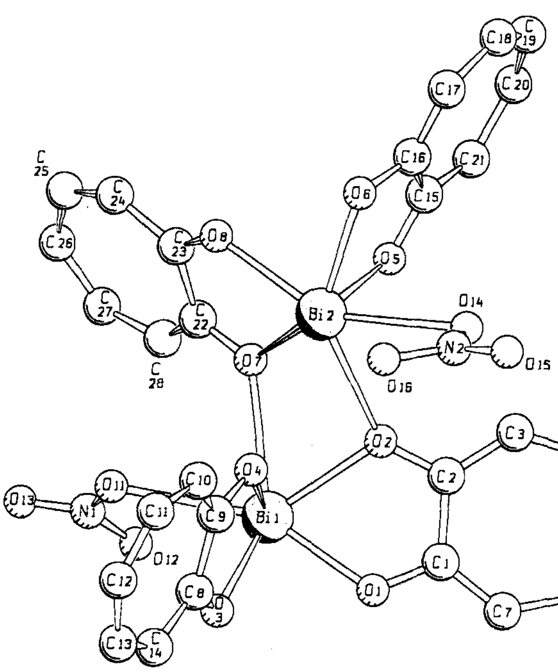
Nitratobis(tropolonato)bismuth(III) (**1d**) is formed when **2a** and **3a** are allowed to react in a ratio of 2:1 in methanol/acetone/H_2O without the addition of acid. The conductivity of **1d** in DMF is 64.3 S cm^2 mol^{-1}, which implies a 1:1 electrolyte[5]. Thus, **1d** is dissociated in a polar solution.

Crystal Structure Analysis of 1d

The structure of **1d** (Figure 1) is the first X-ray structure analysis of a bismuth tropolonato complex.

Both of the tropolonates are coordinated bidentately to the bismuth atom by two Bi–O bonds. In addition, there is a weaker interaction between the bismuth atom Bi1 and the oxygen atom O7 of the adjacent tropolonate, which is firmly coordinated to Bi2. In turn, there is an analogous interaction between Bi2 and O2. This interaction is probably caused by package effects in the solid state. The bonding distances Bi1–O7 (268.8 pm) and Bi2–O2 (266.6 pm) are

Figure 1. SCHAKAL plot of nitratobis(tropolonato)bismuth(III) (**1d**)



distinctly smaller than the sum of their van der Waals radii (360 pm) and should be treated as polar interactions[6,7]. (For the remainder of this text this interaction will be referred to as the Bi–O side interaction.) The lengths of the bismuth-oxygen bonds of the tropolonates which do not have this additional Bi–O side interaction are 217.9–229.8 pm. The bond distances Bi1–O2 (238.4 pm) and Bi2–O7 (237.1 pm) are evidently extended by those additional side interactions of the two oxygen atoms O2 and O7. The bond angles between the two oxygen atoms and the bismuth in the chelate ring also differ, depending on whether one of the oxygen atoms forms a Bi–O side interaction. In the absence of a Bi–O side interaction, the O–Bi–O angles O3–Bi1–O4 and O5–Bi2–O6 are 70.9 and 71.9°, respectively; in the presence of a Bi–O side interaction, however, the bond angle is reduced to 66.7° for O1–Bi1–O2 and to 67.1° for O7–Bi2–O8. One of the nitrate ions is coordinated to the bismuth atom via one oxygen atom (Bi1–O1), the other is coordinated by two of the nitrate oxygen atoms (Bi2–O14, Bi2–O16). Different values for the bond lengths Bi1–O11 (269.4 pm), Bi2–O14 (266.2 pm), and Bi2–O16 (274.0 pm) were determined. These distances are also classified as polar interactions. The coordination of the nitrate ion to the bismuth atom is confirmed by FD mass spectrometry, where a molecular peak is observed at $m/z = 513$. The tropolonate rings without a Bi–O side interaction are lying in a plane spanned by the two bismuth atoms. Their bond angles Bi–O–C are close to 120° of an ideal sp^2 hybrid (i.e. Bi1–O3–C8 118.0, Bi1–O4–C9 117.2, and O4–C9–C8 117°). However, the Bi–O–C angles in the other two tropolonates which have Bi–O side interactions are further away from this value due to distortion (i.e. Bi1–O2–C-2 115.6 and O1–C1–C-2 124°). The coordination spheres of the two bismuth atoms are not identical: Bi1 is surrounded by seven oxygen atoms and Bi2 by six. A closer inspection shows that both spheres are more "open" to one side as an indication of a further pair of inert electrons present in the valence shell of the bismuth atoms.

The reaction of the tropolone derivatives **2b–p** with $BiCl_3$ or $Bi(NO_3)_3 \cdot 5\ H_2O$ (**3a**) produces a number of new complexes which can be classified into three different structure types **4–6**.

Most of the bismuth tropolonate complexes are barely soluble in polar and unpolar organic solvents, so that the recorded ^{13}C-NMR spectra are not always of high quality. Measured chemical shifts of proton and carbon NMR signals are summarized in the Experimental section.

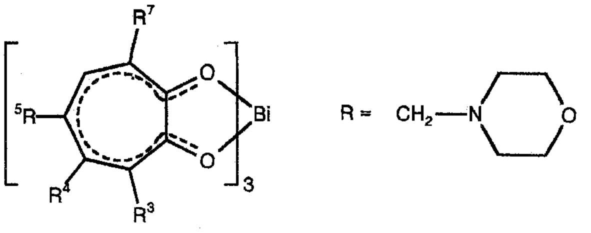
The ^{13}C-NMR spectrum of **6b** shows 11 signals. All the signals have been assigned except those of C-8 to C-11. The molar conductivity measured in DMF is $\Lambda_M = 61.6$ S cm^2 mol^{-1}, and this value lies in the range reported for 1:1 electrolytes[5].

Crystal Structure Analysis of 6b

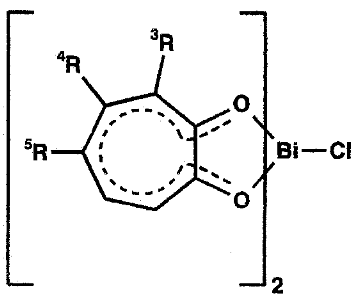
The X-ray structure of **6b** (Figure 2) shows that both the planar 4,5-benzotropolonato ligands are coordinated to the bismuth atom by two oxygen atoms. The four coordinated oxygen atoms (O1, O2, O3, O4) form the base of a distorted pyramid with the bismuth atom in the apical position. The four Bi–O bonds of the chelating ring system have different lengths, their values are in the range of covalent bonds (i.e. Bi1–O1 226.3, Bi1–O2 232.3, Bi1–O3 231.1, Bi1–O4 213.0 pm). The C–C bonds of the tropolonato ring system show alternating bond lengths (i.e. C1–C2 133.5, C-2–C-3 147.8, C1–C7 144.7 pm). This effect is caused by the aromatic system of the condensed benzene ring that prevents delocalization of the double bonds in the tropolonate ring. Further consequences of this fact is the different bond character of the two Bi–O bonds as stated above.

No regular polyhedron is formed by this complex. The coordination sphere is described as follows: The bismuth atom is surrounded by six oxygen atoms. The oxygen atoms O1, O2, O3, O4 are localised below the bismuth central atom, spreading a plane, which is bent towards the diagonal line between O1 and O4 in direction to the central atom. The plane bending is caused by the different bond angles of O1–Bi1–O4 (91.7°) and O2–Bi1–O3 (138.7°). The other bond angles O1–Bi1–O2 (71.2°), O1–Bi1–O3 (78.5°), O2–Bi1–O4 (81.2°), and O3–Bi1–O4 (72.2°) do not differ very much. The atoms O5 and O6 are placed above the bismuth atom. O5 belongs to a coordinated water molecule and is lowered to the edge between O2 and O4, which is proved by the bond angles O2–Bi1–O5 (76.7°) and O4–Bi1–O5 (73.5°). The Bi1–O5 distance of 262.1 pm is in accordance with a polar interaction between the water molecule and the central bismuth atom. The distance of 279.5 pm from the oxygen atom O6 of the nitrato group is evidence of a polar interaction, not of a covalent bond.

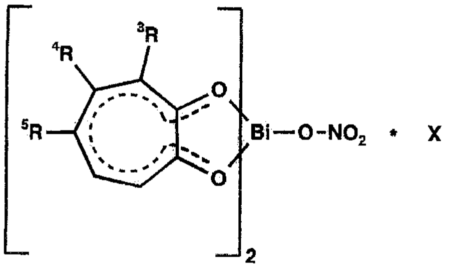
Reaction of **2g** with **3a** in anhydrous methanol produces bis(4,5-benzotropolonato)bismuth(III) nitrate · 1 MeOH



R^3	R^4	R^5	R^7	
H	H	H	H	**1a**
H	CH_3	H	H	**4a**
H	H	CH_3	H	**4b**
CH_3	H	CH_3	CH_3	**4c**
H	C_6H_4		H	**4d**
H	H	NO_2	H	**4e**
H	H	CHO	H	**4f**
Br	H	H	H	**4g**
Br	H	H	Br	**4h**
Br	H	Br	Br	**4k**
CH_2OH	H	CH_2OH	CH_2OH	**4m**
R	H	R	R	**4n**



R^3	R^4	R^5	
H	H	H	**1b**
H	CH_3	H	**5a**
H	H	CH_3	**5b**
H	C_2H_5	H	**5c**
H	$CH(CH_3)_2$	H	**5d**
Br	H	H	**5e**



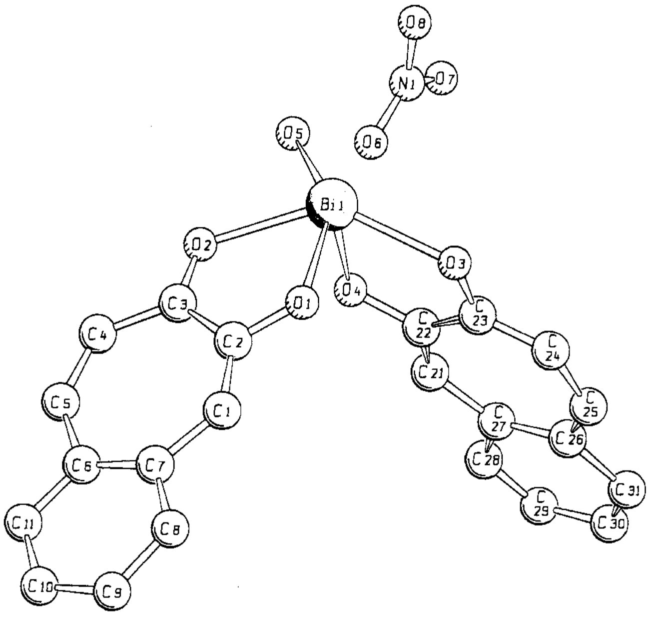
R^3	R^4	R^5	X	
H	H	H	H_2O	**1d**
H	H	CH_3	-	**6a**
H	C_6H_4		H_2O	**6b**[a]
H	C_6H_4		CH_4OH	**6c**[b]

[a] Compound **6b** is a solvate and contains coordinated water molecules.

[b] Compound **6c** is a solvate and contains coordinated methanol molecules.

(**6c**), in which a methanol molecule takes the position of a water molecule in **6b**.

Figure 2. SCHAKAL plot of aquabis(4,5-benzotropolonato)bismuth(III) nitrate (**6b**)



Phenylbis(tropolonato)bismuth (1f)

The reaction of phenylbismuth dibromide with **2a** at −40°C in anhydrous ethanol yields **1f** (Scheme 1). Compound **1f** belongs to a new type of bismuth tropolonato complex – the organobismuth tropolonato complexes. As shown in the formula, two tropolonates are coordinated bidentately by the two oxygen atoms, and, in addition, a phenyl ring is covalently bound to the bismuth atom. The complex is characterized by ^{13}C- and ^{1}H-NMR spectroscopy (see Experimental). The FD mass spectrum shows a molecular peak at $m/z = 528$ and another characteristic peak at $m/z = 451$. The latter corresponds to the bis(tropolonato)bismuth cation without the phenyl ring. The molar conductivity value, $\Lambda_M = 1.1$ S cm^2 mol^{-1}, measured in DMF, shows that **1f** behaves as a neutral complex[5].

IR spectra of all synthesized bismuth complexes are recorded in KBr pellets in a range of 4000−400 cm^{-1}. To verify that no exchange of nitrato groups occurs in the case of the complexes **1d**, **6b** and **6c**, additional IR spectra in Nujol have shown no differences in the positions of the important bands[8]. Valence vibrations of M−O, M−N, M−S, and M−C bonds are expected in a range of 600−200 cm^{-1}[9]. The absorption bands above 600 cm^{-1} are caused by the ligand's valence and deformation vibrations. The range of 4000−600 cm^{-1} is divided into two sectors, one of them is the "fingerprint region" (1500−600 cm^{-1}) containing many bands that characterize the molecule itself. In the other sector (1500−4000 cm^{-1}) the absorption bands of the functional groups appear. Tropolone derivatives show ν(O−H) bands (3300−3000 cm^{-1}) which disappear after complexation of the ligand to the bismuth atom. The δ(O−H) bands (1270−1200 cm^{-1}) also disappear completely[10]. The partial loss of the C=O double bond charac-

Table 2. Minimal inhibitory concentrations (in µl/ml) of the seven bismuth complexes in the agar dilution test

Strain No.	NTCT	4713	4713	4713	4714	4800	4801	4807	4807	Cip
H.p.	11637	8981	9015	9559	8669	4008	4518	3239	3883	101260
1 a	16	-	32	32	*[a]	32	32	64	32	32
1 b	8	8	8	8	8	8	8	16	16	16
4 a	16	16	16	16	16	16	16	16	16	16
4 d	> 512	-	> 512	> 512	*	> 512	> 512	> 512	> 512	> 512
4 e	4	4	4	4	4	4	2	2	4	4
5 a	8	-	16	8	*	8	8	16	8	16
5 c	16	-	32	32	*	16	32	32	32	32
CBS	> 250	> 250	> 250	> 250	> 250	> 250	> 250	> 250	> 250	> 250

[a] This dish contained impurities.

ter after coordination to the bismuth atom is confirmed by the lowering of intensity and downshift of the ν(C=O) bands (1620–1590 cm^{-1}) to lower wave numbers (1600–1550 cm^{-1}). Appearance of ν(C=C) bands in this region prevent a clear assignment of the ν(C=O) bands. Thronton and Hulett were able to assign two ν(Bi–O) bands for **1a**[11]. One of the ν(Bi–O) bands appears in all of the synthesized complexes in a range between 520 and 470 cm^{-1} with medium intensity. The other ν(Bi–O) band, which was expected to appear in a range between 610 and 560 cm^{-1}, could not be determined exactly in all cases because of weakness in intensity. Valence vibration bands of the ligand molecules occur in the same range, so they could overlap this ν(Bi–O) band sometimes or be mistaken for it. For this reason, it is also impossible to assign the weak ν(Bi–Cl) bands for **1b** and **5a–e** to definite values. Absorption bands for N–O vibrations caused by the nitrato group in **1c** and **6a–c** mainly appear in the "fingerprint region" where they are associated with other intensive bands of the molecule. An absolutely certain assignment could therefore not be made either. For further details see Experimental.

In Vitro Activity of the Bismuth Tropolonates Against *H.p.*

Seven of the synthesized complexes are tested against *Helicobacter pylori* in the agar dilution test. In this test, a suspension of the respective complex in 0.1 M NaCl is added to a brain-heart infusion agar in a dish at decreasing concentrations (512–2 µg/ml). The dishes are then infected with *H.p.*, and the bacteria growth is evaluated after a three days' incubation in microaerophilic medium. In each case, ten strains of *H.p.* are tested. Table 2 lists the minimal concentrations (in µg/ml) of the seven bismuth complexes at which no bacteria growth is observed.

The complexes chlorobis(tropolonato)bismuth(III) (**1b**), tris(5-nitrotropolonato)bismuth(III) (**4e**), and chlorobis(4-methyltropolonato)bismuth(III) (**5a**) exhibit a higher activity compared to the standards bismuth citrate, bismuth salicylate, and bismuth nitrate aluminate, which reached minimal concentrations of ≥250 µg/ml.

Experimental

NMR: Bruker AC 200 (TMS as internal standard). – MS: Finnigan MAT 8230. – IR: Bruker IFS 66. – Conductivity meter: WTW LF 191 with Pt electrode LS1/T-1.5. – ICP: Plasma 400 Perkin Elmer. – X-ray: Intensity data for the crystal structures of **1d** and **6b** were collected at room temp. by using a graphite-monochromated Mo-K_{α} radiation on a Siemens Stoe AED II Vierkreis diffraction meter. The X-ray structural analysis was performed with the aid of the SHELXTL-PLUS program by using a Patterson Fourier analysis[12]. The refinement was achieved by the full-matrix least-squares method.

The following compounds were prepared according to literature procedures: 2-hydroxy-2,4,6-cycloheptatriene-1-one (tropolone) (**2a**)[13], 4-methyltropolone (**2b**)[14], 5-methyltropolone (**2c**)[15], 3,5,7-trimethyltropolone (**2d**)[15], 4-ethyltropolone (**2e**)[16], 4-isopropyltropolone (**2f**)[17], 4,5-benzotropolone (**2g**)[18], 5-nitrotropolone (**2h**)[19], 5-formyltropolone (**2i**)[15], 3-bromotropolone (**2k**)[20], 3,7-dibromotropolone (**2m**)[15], 3,5,7-tribromotropolone (**2n**)[21], 3,5,7-tris(hydroxymethyl)tropolone (**2o**)[22], 3,5,7-tris(morpholinomethyl)tropolone (**2p**)[23], phenylbismuth dibromide[24].

Tris(tropolonato)bismuth(III) (**1a**): A solution of **2a** (1.22 g, 10 mmol) in distilled water (250 ml) and acetone (150 ml) was heated under reflux. Finely powdered **3a** (1.45 g, 3.0 mmol) was added to this solution in small portions, and the mixture was stirred vigorously until a clear solution was obtained. The hot solution was filtered and the filtrate concentrated until the solution became turbid. The reaction mixture was cooled slowly down to room temp. The resulting yellow precipitate was filtered off, washed twice with acetone (30 ml) and dried in vacuo over P_4O_{10}. Yield 1.55 g (90%), m.p. >330°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 6.98 (t, J = 9.4 Hz, 3H, 5-H), 7.03 (d, J = 10.9 Hz, 6H, 3,7-H), 7.70 (dd, J = 9.4 Hz, 6H, 4,6-H). – ^{13}C NMR ([D$_6$]DMSO): δ = 125.7 (s, C-5), 127.8 (s, C-3,7), 137.5 (s, C-4,6), 180.1 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1}, 1501, 1421 (C=O and C=C), 565, 494 (Bi–O). – MS (FD), *m/z*: 572 [M$^+$]. – Λ_M = 1.5 S cm^2 mol^{-1} in DMF. – $C_{21}H_{15}BiO_6$ (572.3): calcd. C 44.07, H 2.64, Bi 36.52; found C 44.03, H 2.64, Bi 37.10.

Tris(4-methyltropolonato)bismuth(III) (**4a**): Yield 0.76 g (41%), m.p. 273°C. – ^{1}H NMR (CDCl$_3$): δ = 2.33 (s, 9H, CH$_3$), 6.82 (d, J = 9.7 Hz, 3H, 5-H), 7.09 (d, J = 10.4 Hz, 3H, 7-H), 7.23 (s, 3H, 3-H), 7.24 (t, J = 10.4 Hz, 3H, 6-H). – IR (KBr): $\tilde{\nu}$ = 1585 cm^{-1}, 1500, 1420 (C=O and C=C), 501 (Bi–O). – $C_{24}H_{21}BiO_6$ (614.4): calcd. C 46.92, H 3.45; found C 46.45, H 3.51.

Tris(5-methyltropolonato)bismuth(III) (**4b**): Yield 1.75 g (95%), m.p. 302°C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 2.36 (s, 9H, CH$_3$), 6.96 (d, J = 11.8 Hz, 6H, 3,7-H), 7.37 (d, J = 11.8 Hz, 6H, 4,6-H). – ^{13}C NMR ([D$_6$]DMSO): δ = 24.7 (s, C-8), 128.2 (s, C-3,7), 136.0 (s, C-5), 138.4 (s, C-4,6), 178.8 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}, 1509, 1426 (C=O and C=C), 607, 479 (Bi–O). –

Λ_M = 1.2 S cm^2 mol^{-1} in DMF. – $C_{24}H_{21}BiO_6$ (614.4): calcd. C 46.92, H 3.45; found C 46.64, H 3.41.

Tris(3,5,7-trimethyltropolonato)bismuth(III) (**4c**): Yield 1.50 g (72%), m.p. 275°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 2.16 (s, 18H, 3,7-CH$_3$), 2.35 (s, 9H, 5-CH$_3$), 7.42 (s, 6H, 4,6-H). – ^{13}C NMR ([D$_6$]DMSO): δ = 22.6, 26.0, 136.5, 138.1, 138.6, 175.1. – IR (KBr): ṽ = 1495 cm^{-1}, 1407 (C=O and C=C), 588, 502 (Bi–O). – Λ_M = 1.1 S cm^2 mol^{-1} in DMF. – $C_{30}H_{33}BiO_6$ (698.6): calcd. C 51.58, H 4.76; found C 51.51, H 4.76.

Tris(4,5-benzotropolonato)bismuth(III) (**4d**): A solution of **2g** (0.69, 4.0 mmol) in distilled water (300 ml) and acetone (150 ml) was heated under reflux. A solution of **3a** (0.49 g, 1.0 mmol) in distilled water (10 ml) and glacial acetic acid (10 ml) was slowly added to the former hot solution with vigorous stirring. The acetone was then removed by distillation, and a final volume of 300 ml was obtained. The resulting precipitate was stirred for 1 h under reflux, and the hot suspension was finally filtered. The product was washed twice with acetone (20 ml) and dried in vacuo over P_4O_{10}. Yield 0.64 g (89%), m.p. 265–266°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.13 (d, *J* = 12.3 Hz, 3H, 7-H), 7.44 (t, *J* = 7.0 Hz, 3H, 10-H), 7.49 (s, 3H, 3-H), 7.63 (t, *J* = 7.0 Hz, 3H, 9-H), 7.81 (d, *J* = 8.0 Hz, 3H, 11-H), 7.91 (d, *J* = 7.8 Hz, 3H, 8-H), 8.12 (d, *J* = 12.3 Hz, 3H, 6-H). – IR (KBr): ṽ = 1607 cm^{-1}, 1563, 1505, 1440 (C=O and C=C), 502, 611 (Bi–O). – $C_{33}H_{21}BiO_6$ (722.5): calcd. C 54.86, H 2.93; found C 54.49, H 2.96.

Tris(5-nitropolonato)bismuth(III) (**4e**): Tropolone **2h** (0.52 g, 3.1 mmol) was dissolved in methanol (60 ml) under reflux. Then a solution of **3a** (0.49 g, 1.0 mmol) in distilled water (12 ml) and conc. HCl (1.5 ml) was slowly added to the former solution under reflux. After a few min a yellow precipitate formed. The reaction was maintained under reflux for 2 h, after which time the precipitate was filtered off from the hot suspension. The precipitate was then washed twice with water (10 ml) and acetone (10 ml) and dried in vacuo over P_4O_{10}. Yield 0.49 g (79%), m.p. (dec.) at 330°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 6.98 (d, *J* = 12.5 Hz, 6H, 3,7-H), 8.47 (d, *J* = 12.5 Hz, 6H, 4,6-H). – IR (KBr): ṽ = 1593 cm^{-1}, 1500, 1422 (C=O and C=C), 497, 563 (Bi–O). – $C_{21}H_{12}BiN_3O_{12}$ (614.4): calcd. C 35.66, H 1.71, N 5.94; found C 35.50, H 1.76, N 5.97.

Tris(5-formyltropolonato)bismuth(III) (**4f**): Tropolone **2i** (525 mg, 3.5 mmol) was dissolved in distilled water (70 ml) and acetone (60 ml) under reflux. Then a solution of **3a** (485 mg, 1.0 mmol) in hot methanol (2.5 ml) and conc. HNO_3 (0.8 ml) was added under reflux to the former solution. A yellow precipitate formed immediately. The reaction mixture was stirred under reflux for 30 min. The precipitate was filtered off from the hot suspension, washed once with water/acetone (1:1, 30 ml) and twice with acetone (20 ml) and then dried in vacuo over P_4O_{10}. Yield 0.60 g (91%), m.p. (dec.) 290°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 7.07 (d, *J* = 11.7 Hz, 6H, 3,7-H), 7.94 (d, *J* = 11.7 Hz, 6H, 4,6-H), 9.72 (s, 3H, CHO). – ^{13}C-NMR ([D$_6$]DMSO): δ = 126.0 (s, C-3,7), 130.9 (s, C-5), 139.0 (s, C-4,6), 181.9 (s, C-1,2), 192.3 (s, C-8). – IR (KBr): ṽ = 1698 cm^{-1} (CH=O), 1598, 1516, 1423 (C=O and C=C), 549, 466 (Bi–O). – MS (FD), *m/z*: 657 [M$^+$], 508 [M$^+$ – FT]. – Λ_M = 2.3 S cm^2 mol^{-1} in DMF. – $C_{24}H_{15}BiO_9$ (656.4): calcd. C 43.92, H 2.30, Bi 31.84; found C 43.96, H 2.38, Bi 30.70.

Tris(3-bromotropolonato)bismuth(III) (**4g**): Finely powdered **3a** (485 mg, 1.0 mmol) was added to a solution of **2k** (804 mg, 4.0 mmol) in water (200 ml) and acetone (200 ml). The subsequent workup was similar to that described for **1a**. Yield 0.60 g (74%), m.p. (dec.) 215°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 6.73 (dd, *J* = 10.0 Hz, 3H, 5-H), 7.02 (d, *J* = 10.8 Hz, 3H, 7-H), 7.44 (dd, *J* = 10.0 Hz, 3H, 6-H), 8.15 (d, *J* = 10.6 Hz, 3H, 4-H). – ^{13}C NMR ([D$_6$]DMSO): δ = 123.8 (s, C-3), 128.0 (s, C-5), 130.0 (s, C-7), 137.3 (s, C-4), 140.7 (s, C-6), 175.7 (s, C-2), 177.4 (s, C-1). – IR (KBr): ṽ = 1585 cm^{-1}, 1479, 1401 (C=O and C=C), 589, 518 (Bi–O). – Λ_M = 1.8 S cm^2 mol^{-1} in DMF. – $C_{21}H_{12}BiBr_3O_6$ (809.0): calcd. C 31.18, H 1.50, Br 29.63; found C 31.29, H 1.65, Br 30.07.

Tris(3,7-dibromotropolonato)bismuth(III) (**4h**): Tropolone **2m** (1.13 g, 4.0 mmol) was dissolved in water (80 ml) and acetone (100 ml) under reflux. A solution of **3a** (0.49 g, 1.0 mmol) in methanol (2.0 ml) and conc. HNO_3 (0.7 ml) was then slowly added under reflux to the dibromotropolone solution. A yellow precipitate formed immediately. The solution was heated under reflux for another 30 min. Subsequently, about 40 ml of solvent was distilled off at normal pressure. The precipitate was filtered off, washed twice with water/acetone (1:1, 10 ml) and once with acetone (10 ml). It was then dried in vacuo over P_4O_{10}. Yield 0.93 g (89%), m.p. 233°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 6.47 (t, *J* = 10.6 Hz, 3H, 5-H), 8.14 (d, *J* = 10.6 Hz, 6H, 4,6-H). – IR (KBr): ṽ = 1571 cm^{-1}, 1473, 1390 (C=O and C=C), 497 (Bi–O). – Λ_M = 3.6 S cm^2 mol^{-1} in DMF. – $C_{21}H_9BiBr_6O_6$ (1045.7): calcd. C 24.12, H 0.87, Br 45.85; found C 24.12, H 0.97, Br 45.84.

Tris(3,5,7-tribromotropolonato)bismuth(III) (**4k**): Tropolone **2n** (1.44 g, 4.0 mmol) was dissolved in methanol (25 ml), acetone (20 ml), and distilled water (10 ml) under reflux. Then finely powdered **3a** (0.49 mg, 1.0 mmol) was added with stirring to the obtained solution. A dark yellow precipitate formed immediately. The reaction mixture was stirred lightly for a further 5 h. The precipitate was filtered off from the hot suspension, washed twice with methanol (20 ml) and once with acetone (20 ml), then dried in vacuo over P_4O_{10}. Yield 3.70 g (96%), m.p. 313°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.35 (s, 6H, 4,6-H). – IR (KBr): ṽ = 1599 cm^{-1}, 1477, 1309 (C=O and C=C), 598, 496 (Bi–O). – Λ_M = 8.5 S cm^2 mol^{-1} in DMSO. – $C_{21}H_6BiBr_9O_6$ (1282.4): calcd. C 19.67, H 0.47, Br 56.08; found C 19.74, H 0.55, Br 56.13.

Tris[3,5,7-tris(hydroxymethyl)tropolonato]bismuth(III) (**4m**): Tropolone **2o** (848 mg, 4.0 mmol) was dissolved in distilled water (50 ml) and acetone (50 ml) under reflux. Then finely powdered **3a** (485 mg, 1.0 mmol) was added to the obtained solution. The reaction mixture was stirred under reflux until a clear solution was obtained (ca. 2 min). The hot yellow solution was filtered. Acetone was then removed from the filtrate, and a final volume of ca. 50 ml was obtained. The reaction mixture was cooled to room temp. and then stored at +5°C overnight. The resulting yellow precipitate was filtered off, washed once with water, twice with ether (10 ml) and dried in vacuo over P_4O_{10}. Yield 0.53 g (63%), m.p. (dec.) 275°C. – ^{1}H NMR ([D$_6$]DMSO): δ = 4.35 (s, 12H, 3,7-CH$_2$), 5.28 (s, 6H, 5-CH$_2$), 7.61 (s, 6H, 4,6-H). – IR (KBr): ṽ = 3041 cm^{-1} (OH), 1607, 1499, 1420 (C=O and C=C), 511 (Bi–O). – Λ_M = 2.0 S cm^2 mol^{-1} in DMSO. – $C_{30}H_{33}BiO_{15}$ (842.6): calcd. C 42.77, H 3.95; found C 42.79, H 3.91.

Tris[3,5,7-tris(morpholinomethyl)tropolonato]bismuth(III) (**4n**): Tropolone **2p** (1.68 g, 4.0 mmol) was dissolved in anhydrous ethanol (60 ml) and morpholine (2 ml) under reflux. Then a $BiCl_3$ solution (5 ml, 1.0 mmol) (63.45 mg/ml of anhydrous ethanol) was slowly added to the boiling reaction mixture. A yellow precipitate formed immediately but decomposed after a few min. The reaction mixture was heated under reflux for a further 10 min and then centrifuged while still hot. Excess solvent was decanted, the residue filtered off and the filtrate heated again under reflux for 3 min. The residual solution was then slowly cooled to room temp. while yellow-orange crystalline flakes formed. The precipitate was filtered off, washed with anhydrous ethanol (10 ml), and dried in vacuo over P_4O_{10}. Yield 1.44 g (98%), m.p. 183°C. – ^1H NMR ($CDCl_3$): δ = 2.35 (m, 36H, OCH_2), 3.44 (s, 6H, 5-CH_2), 3.56 (m, 48H, 3,7-CH_2, NCH_2), 7.83 (s, 6H, 4,6-H). – ^{13}C NMR ([D_6]DMSO): δ = 53.3 (s, C-11), 53.6 (s, C-13), 58.3 (s, C-8), 60.2 (s, C-9,10), 66.9 (s, C-14), 67.0 (s, C-12), 133.6 (s, C-5), 136.8 (s, C-3,7), 138.8 (s, C-4,6), 176.2 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}, 1491, 1413 (C=O and C=C), 1116 (C–O–C), 489 (Bi–O). – Λ_M = 1.9 S $cm^2\,mol^{-1}$ in methanol. – $C_{66}H_{96}BiN_9O_{15}$ (1464.5): calcd. C 54.13, H 6.61, N 8.61; found C 53.88, H 6.84, N 8.35.

Chlorobis(tropolonato)bismuth(III) (**1b**): A solution of **2a** (0.43 g, 3.5 mmol) in methanol (8 ml) and conc. HCl (0.2 ml) was heated under reflux. Then **3a** (0.49 g, 1.0 mmol) in conc. HCl (1.5 ml) and methanol (2 ml) was added to the boiling tropolone solution within 3 min. Subsequently, distilled water was added to the clear yellow solution until it became slightly cloudy. The reaction mixture was heated for a further 30 min, during which time the precipitate completely decomposed. It was then slowly cooled to room temp. The yellow precipitate formed was filtered, washed four times with distilled water (20 ml), twice with acetone (20 ml), and dried in vacuo over P_4O_{10}. Yield 0.44 g (90%), m.p. 311–313°C. – ^1H NMR ([D_6]DMSO): δ = 7.11 (t, J = 9.6 Hz, 2H, 5-H), 7.14 (m_c, J = 11.4 Hz, 4H, 3,7-H), 7.62 (dd, J = 9.6 Hz, 4H, 4,6-H). – ^{13}C NMR ([D_6]DMSO): δ = 126.8 (s, C-5), 128.8 (s, C-3,7), 137.8 (s, C-4,6), 179.7 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1591 cm^{-1}, 1506, 1425 (C=O and C=C), 573, 512 (Bi–O). – MS (FD), *m/z*: 486 [M^+], 451 [M^+ – Cl]. – Λ_M = 13.9 S $cm^2\,mol^{-1}$ in DMSO. – $C_{14}H_{10}BiClO_4$ (486.7): calcd. C 34.55, H 2.07, Bi 42.94, Cl 7.29; found C 34.48, H 2.13, Bi 41.50, Cl 7.32.

Chlorobis(4-methyltropolonato)bismuth(III) (**5a**): Yield 0.31 g (60%), m.p. 285–286°C. – ^1H NMR ($CDCl_3$): δ = 2.41 (s, 6H, CH_3), 7.05 (m, 6H, 3,5,7-H), 7.49 (t, J = 10.5 Hz, 2H, 6-H). – IR (KBr): $\tilde{\nu}$ = 1585 cm^{-1}, 1578, 1500, 1420 (C=O and C=C), 562, 512 (Bi–O). – $C_{16}H_{14}BiClO_4$ (514.7): calcd. C 37.33, H 2.74, Cl 6.89; found C 37.45, H 2.86, Cl 7.19.

Chlorobis(5-methyltropolonato)bismuth(III) (**5b**): Yield 0.42 g (82%), m.p. 243–245°C. – ^1H NMR ([D_6]DMSO): δ = 2.39 (s, 6H, CH_3), 7.07 (d, J = 11.5 Hz, 4H, 3,7-H), 7.45 (d, J = 11.5 Hz, 4H, 4,6-H). – ^{13}C NMR ([D_6]DMSO): δ = 24.8 (s, C-8), 128.9 (s, C-3,7), 137.6 (s, C-5), 138.7 (s, C-4,6), 178.3 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1603 cm^{-1}, 1510, 1423 (C=O and C=C), 502, 494 (Bi–O). – $C_{16}H_{14}BiClO_4$ (514.7): calcd. C 37.33, H 2.74, Cl 6.89; found C 37.36, H 3.02, Cl 6.97.

Chlorobis(4-ethyltropolonato)bismuth(III) (**5c**): 4-Ethyltropolone (0.53 g, 3.5 mmol) was dissolved in methanol (15 ml). Yield 0.31 g (57%), m.p. 228–230°C. – ^1H NMR ($CDCl_3$): δ = 1.19 (t, J = 7.5 Hz, 6H, CH_3), 2.61 (q, J = 7.5 Hz, 4H, 4-CH_2), 7.04 (d, J = 10.0 Hz, 2H, 5-H), 7.28 (d, J = 10.8 Hz, 2H, 7-H), 7.43 (s, 2H, 3-H), 7.46 (t, J = 10.8 Hz, 2H, 6-H). – IR (KBr): $\tilde{\nu}$ = 1587 cm^{-1}, 1578, 1498, 1417 (C=O and C=C), 514 (Bi–O). – $C_{18}H_{18}BiClO_4$ (542.8): calcd. C 39.83, H 3.34, Cl 6.53; found C 39.68, H 3.38, Cl 6.89.

Chlorobis(4-isopropyltropolonato)bismuth(III) (**5d**): 4-Isopropyltropolone (0.57 g, 3.5 mmol) was dissolved in methanol (20 ml). Yield 0.21 g (36%), m.p. 285–286°C. – ^1H NMR ($CDCl_3$): δ = 1.20 (d, J = 6.9 Hz, 12H, CH_3), 2.86 (quint, J = 6.9 Hz, 2H, 4-CH), 7.05 (d, J = 9.8 Hz, 2H, 5-H), 7.32 (d, J = 10.5 Hz, 2H, 7-H), 7.47 (t, J = 10.5 Hz, 2H, 6-H), 7.48 (s, 2H, 3-H). – IR (KBr): $\tilde{\nu}$ = 1580 cm^{-1}, 1575, 1496, 1418 (C=O and C=C), 519 (Bi–O). – $C_{20}H_{22}BiClO_4$ (570.8): calcd. C 42.08, H 3.88, Cl 6.21; found C 42.53, H 4.08, Cl 5.96.

Bis(3-bromotropolonato)chlorobismuth(III) (**5e**): $BiCl_3$ (315 mg, 1.0 mmol) was dissolved in methanol (2 ml) and conc. HCl (1.5 ml) under reflux. The obtained solution was slowly added to the boiling solution of **2k** (550 mg, 2.5 mmol) in methanol (8 ml) and conc. HCl (0.2 ml). The reaction mixture was heated under reflux for 10 min. Subsequently, distilled water (17 ml) was added within 10 min. This mixture was heated for a further 30 min. The clear, yellow-orange solution was slowly cooled to room temp. During this time orange needles formed. The precipitate was filtered off, washed with methanol (10 ml), distilled water (10 ml), and then twice with methanol (10 ml). It was dried in vacuo over P_4O_{10}. Yield 0.49 g (76%), m.p. 290°C. – ^1H NMR ([D_6]DMSO): δ = 6.85 (t, J = 10.0 Hz, 2H, 5-H), 7.13 (d, J = 11.0 Hz, 2H, 7-H), 7.58 (t, J = 10.0 Hz, 2H, 6-H), 8.24 (d, J = 10.6 Hz, 2H, 4-H). – ^{13}C NMR ([D_6]DMSO): δ = 123.9 (s, C-3), 128.8 (s, C-5), 130.6 (s, C-7), 137.7 (s, C-4), 141.2 (s, C-6), 175.7 (s, C-2), 177.2 (s, C-1). – IR (KBr): $\tilde{\nu}$ = 1548 cm^{-1}, 1484, 1400 (C=O and C=C), 605, 526 (Bi–O). – Λ_M = 13.0 S $cm^2\,mol^{-1}$ in DMSO. – $C_{14}H_8BiBr_2ClO_4$ (644.5): calcd. C 26.09, H 1.25, Br 24.80, Cl 5.50; found C 26.10, H 1.33, Br 24.69, Cl 5.55.

Nitratobis(tropolonato)bismuth(III) · *H_2O* (**1d**): Tropolone (**2a**) (1.22 g, 10.0 mmol) was dissolved in methanol (100 ml) and acetone (100 ml) under reflux. Finely powdered **3a** (2.42 g, 5.0 mmol) was slowly added to the pale yellow solution. The reaction mixture was heated under reflux until the solution became clear. The solution, which showed a strong yellow color, was filtered, and 150 ml of the solvent was distilled off at normal pressure. The remainder was cooled to room temp. During this time, yellow-orange crystals formed. They were filtered off, washed three times with methanol (30 ml) and dried in high vacuo over P_4O_{10}. Yield 1.40 g (55%); m.p. 271–275°C. – ^1H NMR ([D_6]DMSO): δ = 7.21 (d, J = 11.0 Hz, 4H, 3,7-H), 7.22 (t, J = 9.3 Hz, 2H, 5-H), 7.70 (t, J = 11.0 Hz, 4H, 4,6-H). – ^{13}C NMR ([D_6]DMSO): δ = 128.3 (s, C-5), 129.5 (s, C-3,7), 138.5 (s, C-4,6), 179.1 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1}, 1510, 1413 (C=O and C=C), 588, 522 (Bi–O). – Λ_M = 64.3 S $cm^2\,mol^{-1}$ in DMF. – MS (FD), *m/z*: 513 [M^+], 451 [M^+ – NO_3^-]. – $C_{14}H_{10}BiNO_7$ (513.2): calcd. C 32.76, H 1.96, Bi 40.72, N 2.73; found C 32.79, H 1.97, Bi 38.90, N 2.81.

Bis(5-methyltropolonato)nitratobismuth(III) (**6a**): Yield 2.19 g (81%), m.p. 276–279°C. – ^1H NMR ([D_6]DMSO): δ = 2.45 (s, 6H, CH_3), 7.16 (d, J = 11.7 Hz, 4H, 3,7-H), 7.60 (d, J = 11.7 Hz, 4H, 4,6-H). – ^{13}C NMR ([D_6]DMSO): δ = 24.9 (s, CH_3), 139.3 (s, C-5), 139.5 (s, C-4,6), 177.8 (s, C-1,2). – IR (KBr): $\tilde{\nu}$ = 1604 cm^{-1}, 1515, 1425 (C=O and C=C), 606, 520 (Bi–O). – Λ_M = 63.2 S $cm^2\,mol^{-1}$ in DMF. – $C_{16}H_{14}BiNO_7$ (541.3): calcd.C 35.50, H 2.61, Bi 38.61, N 2.59; found C 35.48, H 2.65, Bi 40.00, N 2.62.

Aquabis(4,5-benzotropolonato)bismuth(III) Nitrate (**6b**): A refluxing solution of **2g** (1.77 g, 10.0 mmol) in distilled water (125 ml) and methanol (350 ml) was added to finely powdered **3a** (2.42 g, 5.0 mmol). The reaction mixture was heated under reflux for 1 h and then centrifugated while still hot. Centrifugation was necessary because it was impossible to filter a colloidal precipitate. The clear, citron-yellow reaction mixture was heated again under reflux. Then it was slowly cooled to room temp., while a yellow crystalline precipitate formed. This precipitate was filtered off, washed with methanol/water (2:1; 30 ml) and dried in vacuo over P_4O_{10}. Yield 1.11 g (57%), m.p. 180°C. – ^1H NMR ([D_6]DMSO): δ = 7.32 (d, J = 12.3 Hz, 2H, 7-H), 7.54 (t, J = 7.1 Hz, 2H, 10-H), 7.64 (s, 2H, 3-H), 7.72 (t, J = 7.1 Hz, 2H, 9-H), 7.91 (d, J = 8.0 Hz, 2H, 11-H), 8.03 (d, J = 7.8 Hz, 2H, 8-H), 8.38 (d, J = 12.3 Hz, 2H, 6-H). – ^{13}C NMR ([D_6]DMSO): δ = 127.2 (s, C-9 or -10), 128.4 (s, C-7), 129.7 (s, C-3), 131.6 (s, C-9 or -10), 132.2 (s, C-8 or -11), 132.6 (s, C-5), 134.2 (s, C-8 or -11), 136.2 (s, C-4), 144.4 (s, C-6), 166.5 (s, C-2), 180.5 (s, C-1). – IR (KBr): $\tilde{\nu}$ = 1597 cm^{-1}, 1568, 1506, 1441, 1383 (C=O and C=C), 512 (Bi−O). − Λ_M = 61.6 S cm^2 mol^{-1} in DMF. − MS (FD), *m/z*: 552 [M$^+$ − NO$_3$ − H$_2$O]. − $C_{22}H_{16}BiNO_8$ (631.4): calcd. C 41.85, H 2.55, Bi 33.10, N 2.22; found C 41.96, H 2.54, Bi 32.90, N 2.31.

Bis(4,5-benzotropolonato)bismuth(III) Nitrate · MeOH (**6c**): Synthesis like **6b** under anhydrous conditions. − $C_{23}H_{18}BiNO_8$ (645.4): calcd. C 42.80, H 2.81, Bi 32.38, N 2.17; found C 42.75, H 2.87, Bi 32.40, N 2.24.

Phenylbis(tropolonato)bismuth(III) (**1f**): A solution of phenylbismuth dibromide (400 mg, 0.9 mmol) in anhydrous ethanol (5 ml) was cooled to −40°C with a dry ice mixture. Then 7.6 ml of a 0.25 M sodium ethanol solution was added within 15 min, during which time the temp. had to be maintained between −30 and −40°C. The mixture was stirred for 30 min. Then a solution of **2a** (230 mg, 1.9 mmol) in anhydrous ethanol (8 ml) was slowly added. The ethanol-dry ice mixture was removed, and the reaction mixture was stirred until the reaction temp. increased to 0°C. Subsequently, distilled water (20 ml) was added to the yellow suspension, and the mixture was stirred for a further 30 min. The precipitate was filtered off, washed twice with ethanol (10 ml), once with ether (20 ml), and dried in vacuo. The crude product was recrystallized from toluene. Yield 0.37 g (78%), m.p. >330°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 6.92 (t, J = 9.2 Hz, 1H, 5-H), 6.9−7.2 (m, 1H, 11-H), 7.08 (d, J = 10.7 Hz, 2H, 3,7-H), 7.41 (t, J = 10.7 Hz, 2H, 4,6-H), 7.59 (t, J = 7.6 Hz, 2H, 10-H), 8.20 (d, J = 6.7 Hz, 2H, 9-H). − ^{13}C NMR ([D$_6$]DMSO): δ = 124.5 (s, C-5), 127.1 (s, C-3,7), 127.4 (s, C-8), 131.5 (s, C-10), 134.9 (s, C-11), 137.6 (s, C-9), 137.6 (s, C-4,6), 180.8 (s, C-1,2). − IR (KBr): $\tilde{\nu}$ = 1591 cm^{-1}, 1501, 1419 (C=O and C=C), 576, 492 (Bi−O). − Λ_M = 1.1 S cm^2 mol^{-1} in DMF. − MS (FD), *m/z*: 528 [M$^+$], 451 [M$^+$ − C$_6$H$_5$]. − $C_{20}H_{15}BiO_4$ (528.3): calcd. C 45.47, H 2.86, Bi 39.56; found C 45.43, H 2.93, Bi 39.84.

Crystal Structure Analysis of Nitratobis(tropolonato)bismuth(III) (**1d**): Tabular crystal from methanol, yellow-orange, 0.15 × 0.5 × 0.6 mm, $C_{28}H_{20}Bi_2N_2O_{14}$, M = 1026.4, rhombic, space group *Pbca*, a = 1460.2(5), b = 1891.2(4), c = 2146.7(4) pm, $\rho_{calc.}$ = 2.30 g/cm^3, V = 5928.2 · 10^6 pm^3, Z = 8, λ(Mo-K_α) = 71.073 pm, μ = 11.9 mm^{-1}, F(000) = 3840, temperature 296 K, range 2Θ = 3−58°, h, k, l: 0 20, 0 26, 0 30, total no. of measured reflections 7440, observed reflections with I 2.5$\sigma(I)$ = 4329. The structure was solved by conventional Patterson and Fourier methods; max. and min. residual electron density: 3.1 and −3.0 eÅ^{-3}. Remarks: High residual electron density at the two bismuth atoms. This is probably the result of the high absorption by the bismuth atoms. The R value was 0.062 (R_w = 0.053).

Crystal Structure Analysis of Aquabis(4,5-benzotropolonato)bismuth(III) Nitrate (**6b**): Tabular crystal from methanol/water, brown, 0.20 × 0.54 × 0.54 mm, $C_{22}H_{16}BiNO_8$, M = 631.4, rhombic, space group *Fdd2*, a = 1886.0(2), b = 2021.0(2), c = 2105.0(2) pm, $\rho_{calc.}$ = 2.09 g/cm^3, V = 8023.4 · 10^6 pm^3, Z = 16, λ(Mo-K_α) = 71.073 pm, μ = 8.81 mm^{-1}, F(000) = 4832, measuring temp. 296 K, range 2Θ = 3−60°, h, k, l: 0 26, 0 28, 0 29, total no. of measured reflections 3176, observed reflections with I 2.5$\sigma(I)$ = 1518. The structure was solved by conventional Patterson and Fourier methods. Max. and min. residual electron density: 1.25 and −0.93 eÅ^{-3}. The R value was 0.042 (R_w = 0.031).

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