



Papers

Dedicated to Prof. Bogdan C. Simionescu
on the occasion of his 75th anniversary

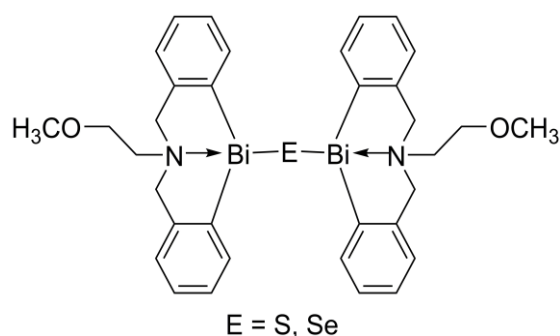
NEW ORGANOBISMUTH(III) COMPOUNDS BASED ON A TETRAHYDRO-DIBENZO[*c,f*][1,5]AZABISMOCINE HETEROCYCLIC FRAMEWORK

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Organobismuth chalcogenides of type $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]_2\text{E}$ [E = S (**1**), Se (**2**)], containing two butterfly-like tetrahydro-dibenzo[*c,f*][1,5]azabismocine heterocyclic frameworks, were prepared and their solution behavior was investigated by multinuclear NMR spectroscopy (^1H , ^{13}C and ^{77}Se , as appropriate) and mass spectrometry. Crystals of $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiO}]_2\text{SeO}$ (**3**) were serendipitously formed during the synthesis of compound **2**. The molecular structure of **3** was determined by single-crystal X-ray diffraction and revealed, besides a strong transannular N→Bi interaction, an additional O⋯Bi interaction involving the oxygen of the $\text{NCH}_2\text{CH}_2\text{OCH}_3$ pendant arm from the organic fragment attached to the metal atom, thus resulting in a 12–Bi–5 hypercoordinate species.



INTRODUCTION

Organometallic complexes of the heavy group 14–16 elements stabilized by intramolecular secondary interactions continue to be of increased importance for several fields, including biology, catalysis and nanomaterials.^{1–4} Antimony and bismuth display in most of their compounds a Lewis acid behavior and, by accepting electron pairs from donor atoms, they form easily hypercoordinated species.^{1,5} Derivatives bearing *C,N*-chelating groups^{5,6} or *N,C,N*-pincer ligands^{3,5} attracted a special attention. In 1988 were reported the first antimony(III) derivatives based

on a *C,N,C*-tetrahydrodibenzo[*c,f*][1,5]azastibocine framework⁷ and one year later organobismuth(III) analogues were also successfully synthesized.⁸

Compounds containing a $\text{RN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{M}$ fragment (R = alkyl, aryl; M = Sb, Bi) were employed in various organic transformations, e.g. one-pot Mannich reactions,^{9,10} allylation,^{11,12} cross-coupling,^{13,14} or addition^{15,16} reactions. Oxides, hydroxides and alkoxides based on a $^t\text{BuN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}$ framework were used as efficient reagents for CO_2 fixation.¹⁷

We reported recently on azabismocine halides of type $\text{RCH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiX}$ (R = C_6H_5 , $\text{C}_6\text{H}_5\text{CH}_2$,

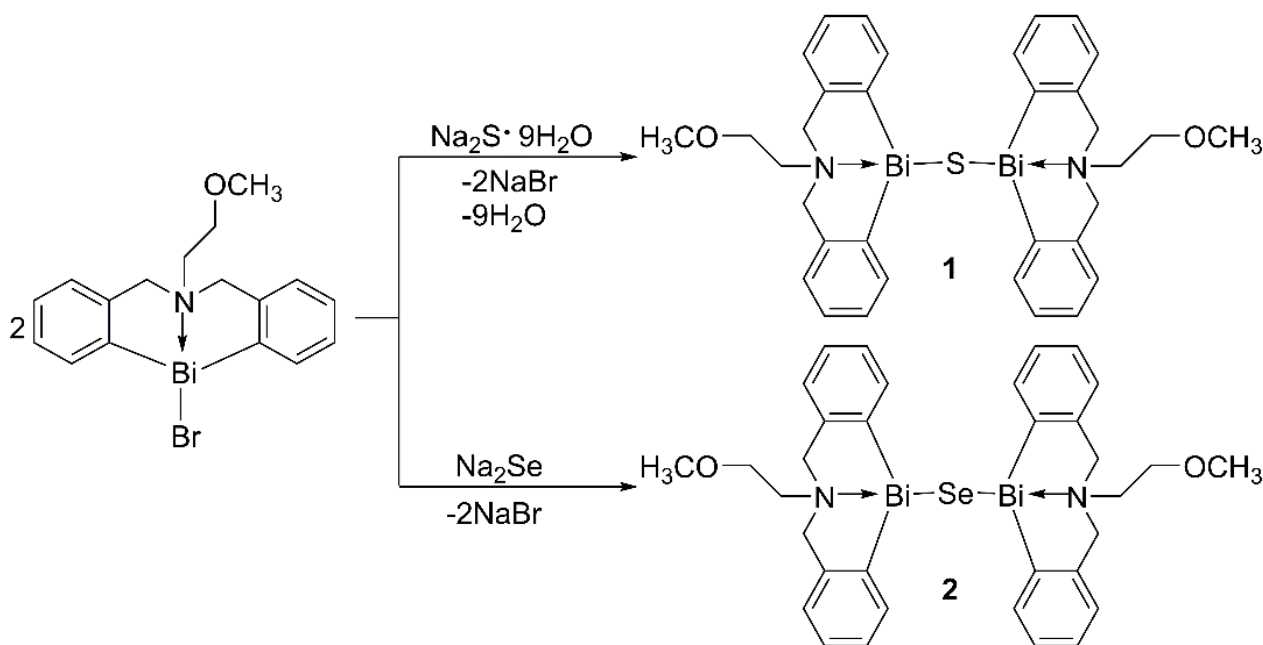
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CH_3OCH_2 ; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$),¹⁸ and the derivatives $\text{RCH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiL}$ [$\text{R} = \text{C}_6\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$,¹⁹ CH_3OCH_2 ;²⁰ $\text{L} = \text{ONO}_2, \text{OSO}_2\text{CF}_3, \text{OSO}_2\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2)$ -4]. Our studies were focused on the solution behavior and the solid-state structure of the investigated compounds. The X-ray diffraction studies evidenced strong $\text{N} \rightarrow \text{Bi}$ transannular interactions in these species based on a heterocyclic butterfly-like tetrahydrodibenzo[*c,f*][1,5]azabismocine skeleton. The bromides $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBr}$ and the derivatives $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiL}$ ($\text{L} = \text{ONO}_2, \text{OSO}_2\text{CF}_3$ or $\text{OSO}_2\text{C}_6\text{H}_4(\text{CH}=\text{CH}_2)$ -4) were employed as efficient catalysts in the oxidation reaction of thiophenol to diphenyldisulfide under mild conditions, showing high conversions and chemoselectivities.¹⁹ As a continuation of our studies we report here about the new bismuth(III) complexes

of the type $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]_2\text{E}$ [$\text{E} = \text{S}$ (**1**), Se (**2**)], as well as the crystal and molecular structure of the serendipitously isolated $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiO}]_2\text{SeO}$ (**3**).

RESULTS

Compounds **1** and **2** were obtained by NaBr elimination in the reactions between $\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBr}$ and the appropriate sodium chalcogenide, Na_2E ($\text{E} = \text{S}, \text{Se}$). In case of compound **1** the commercial $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was used, while the Na_2Se reagent involved in the synthesis of **2** was prepared *in situ*,²² by reacting a mixture of NaBH_4 , NaOH and selenium powder. The synthesis procedures are depicted in Scheme 1.



Scheme 1

Compounds **1** and **2** were isolated as yellow microcrystalline solids, soluble in common organic solvents. The elemental analysis confirmed the identity of these organobismuth(III) chalcogenides. They were investigated by NMR spectroscopy (¹H, ¹³C and ⁷⁷Se, as appropriate) and APCI+ mass spectrometry. Our attempts to grow single crystals of these compounds were unsuccessful. From the reaction mixture resulted in the synthesis of compound **2** we isolated crystals for which the molecular structure determined by single-crystal X-ray diffraction revealed the serendipitous formation of the oxidized species $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiO}]_2\text{SeO}$ (**3**).

DISCUSSION

Spectroscopic characterization

The ¹H and the ¹³C NMR spectra of the two compounds are very similar. They are consistent with the formulation of the desired species, and they suggest the equivalence of the two $\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}$ fragments in a molecule. The aliphatic region of the ¹H NMR spectrum displays the expected multiplicity for the characteristic resonances given by the organic part of the azabismocine skeleton, namely a singlet for the OCH₃ protons, two triplets for the methylene NCH₂CH₂OMe groups and an

AB spin system for the non-equivalent protons of the CH_2N groups attached to the aromatic rings, while the aromatic region displays characteristic multiplet resonances for the four non-equivalent protons in the C_6H_4 moieties. The ^1H NMR spectra gave no evidence for a $\text{MeO} \rightarrow \text{Bi}$ intramolecular interaction in solution, as the CH_2CH_2 protons in the $\text{CH}_2\text{CH}_2\text{OCH}_3$ pendant arm show two triplet resonances and not a multiplet pattern determined by $\text{CH}_\text{A}\text{H}_\text{B}$ protons in each CH_2 group. The ^{13}C NMR spectra display the expected number of singlet resonances, both in the aliphatic and the aromatic region. The ^{77}Se NMR resonance at $\delta = -223.5$ ppm suggests the presence of the Se^{2-} in **2**.²³

The APCI+ mass spectra of the two compounds show the pseudo molecular peaks $[\text{M}+\text{H}^+]$ with low intensity at m/z 957.2352 (5%) (calculated m/z 957.2334) and 1005.1783 (10%) (calculated m/z 1005.1779) for **1** and **2**, respectively. In addition,

the base peaks are present at m/z 462.1257 in **1**, and 462.1264 in **2**, corresponding to the cation $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}^+]$ (calculated m/z 462.1265).

Molecular structure of $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiO}]_2\text{SeO}$ (**3**)

The molecular structure of **3** is depicted in Fig. 1 and relevant interatomic distances and angles are given in Table 1.

Strong transannular $\text{N} \rightarrow \text{Bi}$ interactions are established in both $\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}$ fragments [$\text{N1}-\text{Bi1}$ 2.583(3) and $\text{N2}-\text{Bi2}$ 2.598(4) Å, vs. $\Sigma r_{\text{cov}}(\text{N},\text{Bi})$ 2.19 Å²⁴ and $\Sigma r_{\text{vdw}}(\text{N},\text{Bi})$ 4.20 Å,²⁵ of a similar magnitude as those observed in other related compounds, e.g. $\text{RN}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiL}$ ($\text{R} = \text{CH}_2\text{Ph}$, $\text{CH}_2\text{CH}_2\text{Ph}$, $\text{CH}_2\text{CH}_2\text{OMe}$; $\text{L} = \text{OSO}_2\text{CF}_3$, ONO_2).^{18,19}

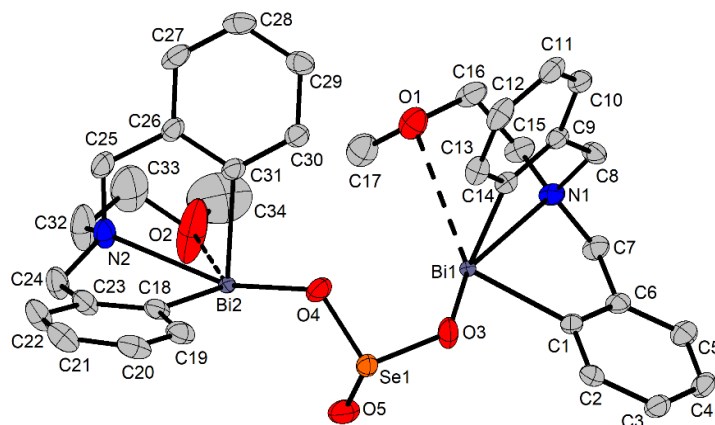


Fig. 1 – Thermal ellipsoids (probability 25%) representation of the molecular structure of $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiO}]_2\text{SeO}$ (**3**). Hydrogen atoms are omitted for clarity.

Table 1

Relevant interatomic distances and angles in $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiO}]_2\text{SeO}$ (**3**)

Bi1–N1	2.5841(1)	Bi2–N2	2.5987(1)
Bi1–O3	2.2655(1)	Bi2–O4	2.2607(1)
Bi1–C1	2.2575(1)	Bi2–C18	2.2550(1)
Bi1–C14	2.2328(1)	Bi2–C31	2.2435(1)
Bi1···O1	3.214(4)	Bi2···O2	3.300(5)
N1–Bi1–O3	149.15(1)	N2–Bi2–O4	147.05(1)
N1–Bi1–C1	71.38(1)	N2–Bi2–C18	71.54(1)
N1–Bi1–C14	73.44(1)	N2–Bi2–C31	72.74(1)
O3–Bi1–C1	86.00(1)	O4–Bi2–C18	88.55(1)
O3–Bi1–C14	88.07(1)	O4–Bi2–C31	84.24(1)
C1–Bi1–C14	94.24(1)	C18–Bi2–C31	96.62(1)
O1–Bi1–N1	61.19(1)	O2–Bi2–N2	61.40(12)
O1–Bi1–O3	136.51(10)	O2–Bi2–O4	138.56(13)
O1–Bi1–C1	132.56(11)	O2–Bi2–C18	131.42(14)
O1–Bi1–C14	72.22(11)	O2–Bi2–C31	81.04(13)
Se1–O3	1.7099(1)	O3–Se1–O4	99.83(1)
Se1–O4	1.7233(1)	O3–Se1–O5	106.99(1)
Se1–O5	1.6343(1)	O4–Se1–O5	103.30(1)

As a consequence, two butterfly-like skeletons are formed, each of them based on two condensed NC_3Bi five-membered rings, and joined by the $\text{O}-\text{Se}(\text{O})-\text{O}$ bridge. The two five-membered rings in each azabismocine fragment are not planar, but folded about the imaginary $\text{C}7\cdots\text{Bi}1 / \text{C}8\cdots\text{Bi}1$, and $\text{C}24\cdots\text{Bi}2 / \text{C}25\cdots\text{Bi}2$ axes, respectively.

The configuration of these NC_3Bi five-membered rings can be discussed in terms of planar chirality,²⁶ induced by the $\text{N}\rightarrow\text{Bi}$ transannular interactions, thus resulting in a racemic mixture of isomers, namely S^1, S^2, R^3, R^4 and R^1, R^2, S^3, S^4 , where the superscript indices 1 and 2 refer to the five-membered rings associated with $\text{Bi}1$, while the superscript indices 3 and 4 refer to those associated with $\text{Bi}2$. The calculated τ values for both Bi atoms ($\tau_{4, \text{Bi}1} = \tau_{4, \text{Bi}2} = 0.82$) suggest a coordination geometry intermediate between a see-saw ($\tau_4 = 0.43$) and a tetrahedron ($\tau_4 = 1.0$).²⁷ In this way, the structure can be described as a 10-*Bi*-4 hypercoordinate species.²⁸ The $\text{CH}_2\text{CH}_2\text{OME}$ groups attached to nitrogen are twisted in such a way that they interact intramolecularly with the bismuth atoms at $\text{O}1\cdots\text{Bi}1$ and $\text{O}2\cdots\text{Bi}2$ distances of 3.214(4)

and 3.30(5) Å, respectively [$\Sigma r_{\text{cov}}(\text{O}, \text{Bi}) 2.14 \text{ \AA}^{24}$ and $\Sigma r_{\text{vdw}}(\text{O}, \text{Bi}) 4.04 \text{ \AA}^{25}$]. If these interactions are considered as well, the coordination geometry about each bismuth atom becomes a distorted square pyramid ($\tau_{5, \text{Bi}1} = 0.27$, $\tau_{5, \text{Bi}2} = 0.26$),²⁹ and the structure can be described as a 12-*Bi*-5 hypercoordinate species, with $\text{O}1$ and $\text{O}2$, respectively, in apices and with $\text{Bi}1$ and $\text{Bi}2$ inside the pyramid, at a distance of 1.01 and 1.03 Å above the best planes $\text{N}1\text{C}1\text{C}14\text{O}3$ and $\text{N}2\text{C}18\text{C}31\text{O}4$, respectively. The selenium atom is surrounded by the three oxygen atoms in a pseudo-tetrahedral coordination geometry, with $\text{O}-\text{Se}$ distances of similar values as those observed in Na_2SeO_3 [1.685(4), 1.703(4) and 1.704(4) Å].³⁰

A close look to the crystal of compound **3** revealed weak intermolecular $\text{H}\cdots\text{O}$ contacts, smaller than $\Sigma r_{\text{vdw}}(\text{O}, \text{H}) 2.70 \text{ \AA}$,²⁵ based on the oxygen atoms in the SeO_3 fragment, *i.e.* $\text{H}11\cdots\text{O}5$ and $\text{H}25\text{B}\cdots\text{O}5$ interactions of 2.67 and 2.59 Å, respectively, which give rise to 2D layers (Fig. 2), which are further connected in a 3D supramolecular network by $\text{H}7\text{B}\cdots\text{O}4$ contacts of 2.64 Å.

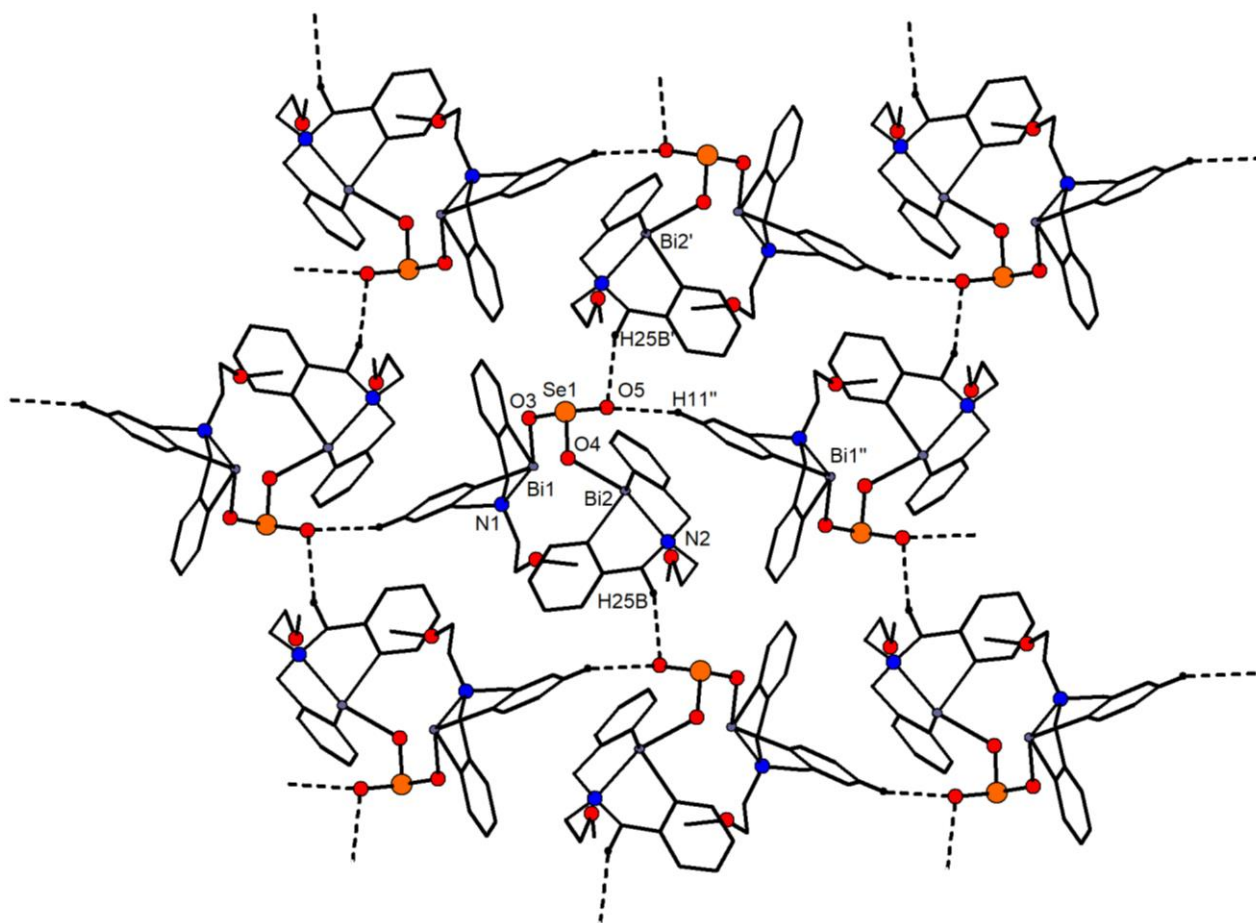
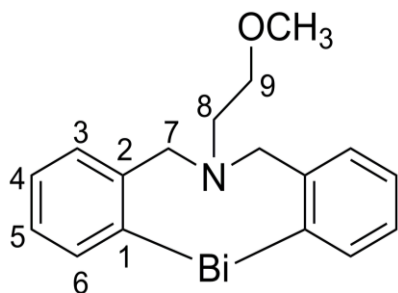


Fig. 2 – A 2D layer in the crystal of **3**. Symmetry equivalent positions $(-1/2+x, 3/2-y, 1/2+z)$ and $(3/2-x, 1/2+y, 3/2-z)$ are given by “prime” and “double prime”, respectively.

EXPERIMENTAL

The starting $\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBr}$ was prepared according to a literature procedure,¹⁸ while all the other reactants were commercially available and used as received from Aldrich. The melting points were measured on an Electrothermal 9200 apparatus. Elemental analyses were performed on a Flash EA 1112 analyzer. The APCI+ mass spectra were recorded on a Thermo Scientific LTQ-Orbitrap XL spectrometer equipped with a standard ESI/APCI source. The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra were recorded on a BRUKER Avance 600 instrument. The ^1H and the ^{13}C chemical shifts are reported in δ units (ppm) relative to the residual peak of the solvent (CHCl_3 , 7.26 ppm) in the ^1H NMR spectra and to the peak of the deuterated solvent (CDCl_3 , 77.16 ppm) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. They are assigned according to the numbering way displayed in Scheme 2. The $^{77}\text{Se}\{^1\text{H}\}$ NMR resonance for compound **2** is reported in δ units (ppm) relative to Me_2Se . The NMR and the mass spectra were processed using the MestReNova software,³¹ and the Thermo Xcalibur software,³² respectively.



Scheme 2 – Numbering scheme for NMR assignments in compounds **1** and **2**.

Synthesis of
 $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]_2\text{S}$ (1**)**

A solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (0.145 g, 1.103 mmol) in water (5 mL) was added dropwise to a solution of $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBr}]$ (0.613 g, 1.102 mmol) in dichloromethane (10 mL). The reaction mixture was left overnight, under stirring. The organic phase was separated and washed with 2×5 mL water and subsequently, the unified water phases were washed with dichloromethane (3×5 mL). The organic phases were dried on anhydrous MgSO_4 . The solvent was removed from the clear solution and the remained yellow solid was washed with hexane (3×5 mL). Yield: 0.42 g (78%). M.p. 122–123°C. Anal. calcd. for $\text{C}_{36}\text{H}_{44}\text{Bi}_2\text{N}_2\text{O}_2\text{S}$ ($M = 986.77$): C 43.82, H 4.49, N 2.84%; Found: C 44.12, H 4.63, N 2.88%. ^1H NMR (CDCl_3 , 600 MHz): δ 2.97 (t, 4H, H_9 , $^3J_{\text{HH}} 5.2$ Hz), 3.01 (s, 6H, CH_3), 3.41 (t, 4H, H_8 , $^3J_{\text{HH}} 5.2$ Hz), AB spin system with $\delta_A 3.95$ and $\delta_B 4.01$, 8H, H_7 , $^2J_{\text{HH}} 14.7$ Hz), 7.23–7.26 (m, 6H, C_6H_4), 7.30–7.34 (m, 4H, C_6H_4), 9.04 (d, 2H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz): δ 56.30 (C_9), 58.48 (CH_3), 62.34 (C_7), 69.93 (C_8), 127.32 (C_3), 127.43 (C_4), 130.29 (C_5), 139.78 (C_6), 146.96 (C_2), 160.65 (C_1).

APCI+ HRMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): m/z (%) 1418.3553(15)/calcd. 1418.3527 [$\text{M} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}^+$], 957.2352(5)/calcd. 957.2334 [$\text{M} + \text{H}^+$], 462.1269(100)/calcd. 462.1266 [$\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}^+$], 256.1695(14)/calcd. 256.1696 [$\text{CH}_3\text{OCH}_2\text{CH}_2\text{NCH}_2\text{C}_6\text{H}_4^+$].

Synthesis of
 $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}]_2\text{Se}$ (2**)**

A solution of NaBH_4 (0.083 g, 2.194 mmol) in 5 mL NaOH (10%) was added dropwise to a suspension of selenium powder (0.043 g, 0.550 mmol) in water (10 mL) and the reaction mixture was boiled under reflux until the formation of Na_2Se . After reaching the room temperature, a solution of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiBr}$ (0.613 g, 1.110 mmol) in dichloromethane (15 mL) was added dropwise and the reaction mixture was left overnight, under stirring. The organic phase was separated and washed with 3×5 mL water and subsequently, the unified water phases were washed with dichloromethane (3×5 mL). The organic phases were dried on anhydrous MgSO_4 . The solvent was removed from the clear solution and the remained yellow solid was washed with hexane (3×5 mL). Yield: 0.41 g (72%) M.p. 128–129°C. Anal. calcd. for $\text{C}_{36}\text{H}_{44}\text{Bi}_2\text{N}_2\text{O}_2\text{Se}$ ($M = 1033.67$): C 41.83, H 4.29, N 2.71%; Found: C 41.78, H 4.34, N 2.79%. ^1H NMR (CDCl_3 , 600 MHz): δ 2.97 (t, 4H, $^3J_{\text{HH}} 5.1$ Hz, H_9), 3.01 (s, 6H, CH_3), 3.41 (t, 4H, H_8 , $^3J_{\text{HH}} 5.2$ Hz), AB spin system with $\delta_A 3.93$ and $\delta_B 4.00$, 8H, H_7 , $^2J_{\text{HH}} 14.7$ Hz), 7.21–7.25 (m, 6H, C_6H_4), 7.27–7.31 (m, 4H, C_6H_4), 9.14 (d, 4H, H_6 , $^3J_{\text{HH}} 7.1$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 600 MHz): δ 56.26 (C_9), 58.47 (CH_3), 62.36 (C_7), 69.92 (C_8), 127.32 ($\text{C}_3 + \text{C}_4$), 130.59 (C_5), 141.63 (C_6), 146.91 (C_2), 156.86 (C_1).⁷⁷Se NMR (CDCl_3 , 400 MHz): δ -223.52 (s). APCI+ HRMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): m/z (%) 1466.2966(7)/calcd. 1466.2971 [$\text{M} + \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}^+$], 1005.1783(10)/calcd. 1005.1779 [$\text{M} + \text{H}^+$], 542.0428(4)/calcd. 542.0430 [$\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{BiSe}^+$], 462.1266(100)/calcd. 462.1265 [$\text{CH}_3\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_4)_2\text{Bi}^+$], 256.1694(5)/calcd. 256.1696 [$\text{CH}_3\text{OCH}_2\text{CH}_2\text{NCH}_2\text{C}_6\text{H}_4^+$].

Crystal structure determination

Single-crystals of **3**, suitable for X-ray diffraction were obtained from a mixture of chloroform/*n*-hexane (1:3, v:v). Details of the crystal structure determination and refinement are given in Table 2.

Data were collected on a Bruker D-8 Venture diffractometer, using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a $\text{I}\mu\text{S}$ 3.0 microfocus source with multilayer optics, at 110 K. The structure was refined with anisotropic thermal parameters for non-H atoms. Hydrogen atoms were placed in fixed, idealized positions and refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the Bruker APEX3 Software Package was used.³³ Intermolecular secondary bonding interactions were found with PLATON.³⁴ The drawings were created with the Diamond program.³⁵

Table 2

X-ray crystal data and structure refinement for compound [CH₃OCH₂CH₂N(CH₂C₆H₄)₂BiO]₂SeO (**3**)

Empirical formula	C ₃₄ H ₃₈ Bi ₂ N ₂ O ₅ Se
Formula weight	1051.59
Temperature (K)	110
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	
<i>a</i> (Å)	8.9909(3)
<i>b</i> (Å)	20.3301(6)
<i>c</i> (Å)	17.7144(6)
<i>α</i> (°)	90
<i>β</i> (°)	90.224(1)
<i>γ</i> (°)	90
Volume (Å ³)	3237.92
<i>Z</i>	4
<i>D_c</i> (g/cm ³)	2.157
Absorption coefficient (mm ⁻¹)	12.023
<i>F</i> (000)	1984.0
Crystal size, mm	0.1 × 0.08 × 0.05
θ range for data collections (°)	2.4770
Reflections collected	87519
Independent reflections	8041
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8041/0/402
Goodness-of-fit on <i>F</i> ²	1.054
Final <i>R</i> indices [<i>F</i> ² > 2σ(<i>F</i> ²)]	<i>R</i> ₁ = 0.0255, <i>wR</i> ₂ = 0.0544
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0304, <i>wR</i> ₂ = 0.0566
Largest diff. peak and hole (eÅ ⁻³)	−2.178 and 3.862

CONCLUSIONS

Organobismuth (III) chalcogenides with azabismocine frameworks of type [CH₃OCH₂CH₂N(CH₂C₆H₄)₂Bi]₂E [E = S (**1**), Se (**2**)] were prepared starting from CH₃OCH₂CH₂N(CH₂C₆H₄)₂BiBr and Na₂E. The ¹H NMR spectra gave no evidence for a MeO→Bi intramolecular interaction in solution, as it was observed in solid state for the serendipitously formed [CH₃OCH₂CH₂N(CH₂C₆H₄)₂BiO]₂SeO (**3**). For this compound the single-crystal X-ray diffraction studies revealed strong transannular N→Bi interactions as well, thus resulting in 12–Bi–5 hypercoordinate species for the two butterfly-like tetrahydro-dibenzo[*c,f*][1,5]azabismocine heterocyclic skeletons.

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Supplementary material. CCDC 2234740 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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