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Synthesis and molecular structure of the novel bismuth(III) sulfonate complex $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$

Abstract: The synthesis of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$ starting from $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$ and 2-(diphenylphosphino)benzenesulfonic acid is presented. $^{31}P\{^1H\}$-NMR experiments confirm the *in situ* oxidation of 2-(diphenylphosphino)benzenesulfonic acid to give 2-(diphenylphosphine oxide)benzenesulfonic acid by heating in dimethyl sulfoxide (DMSO). In the presence of $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$, subsequent formation of single crystals of the title compound is observed. The crystal structure determination reveals that the bismuth atom shows a [5+4] coordination with short Bi−O distances in the range of 2.278(11) to 2.398(11) Å to the oxygen atoms of DMSO and phosphine oxide groups and with longer Bi−O bonds of 2.74(2) and 2.88(2) Å to the chelating sulfonate groups.

Keywords: bismuth; bismuth oxido cluster; phosphine oxide; sulfonate.

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Introduction

Bismuth-containing compounds have been used as medical agents since more than three centuries now (Briand and Burford, 1999; Mehring, 2007; Yang and Sun, 2007). Especially the non-toxic nature of most compounds is one of the major driving forces for the increasing interest in bismuth-containing materials and is mainly a result of the often-observed low solubility of bismuth compounds in aqueous solution. Noteworthy, the so-called bismuth subsalicylate and bismuth subcitrate are used as components in medical formulations such as Pepto-Bismol® and DE-NOL™ (Sun, 2011). Furthermore, bismuth subnitrate and bismuth subsalicylate as additional components in triple and quadruple therapies based on antibiotics and proton pump inhibitors (Dittes et al., 1997; Turel et al., 1998; Phillips et al., 2000; Whitehead et al., 2000; Butcher, 2003) are very active in the eradication of *Helicobacter pylori*, one of the main causes of gastritis and nausea. Andrews et al. (2009) recently demonstrated that water-soluble bismuth complexes based on 5-sulfosalicylic acid exhibit greater activity against *H. pylori* than commercial bismuth subsalicylate. This demonstrates that soluble bismuth sulfonates might be key intermediates in obtaining higher activity against bacteria. In addition to the 5-sulfosalicylate derivatives and the well-known bismuth trifluoromethanesulfonate (Gaspard-Iloughmane and Le Roux, 2004), only a few other bismuth(III) sulfonates such as $[Bi_6O_4(OH)_4(OTf)_6(CH_3CN)_6]\cdot 2CH_3CN$ (TfO^- – triflate) $[Bi_6O_4(OH)_4(O_3SNH_2)_6]$, $[Bi_{18}O_{12}(OH)_{12}(O_3S–Cam)_{18}(H_2O)_2]$ (Cam-SO_3^- — S-(+)-10-camphor sulfonate) and $[Bi_{38}O_{45}(O_3S\text{-}Mes)_{24}(H_2O)_{14}]$ (Mes-SO_3^- — mesitylene sulfonate) have been reported and structurally characterized so far (Arnauld et al., 1997; Sharutin et al., 2002a,b; Andrews et al., 2010, 2012; Miersch et al., 2011b). We report here on the synthesis, crystal and molecular structure of the novel bismuth(III) sulfonate complex $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$, that was obtained upon our attempts to synthesize polynuclear bismuth oxido sulfonates.

Results and discussion

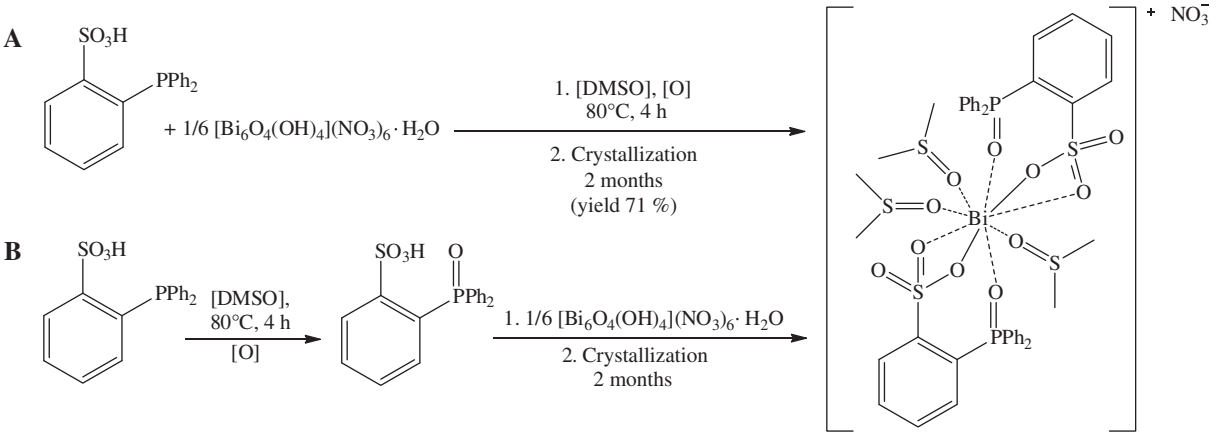
The synthesis of the title compound starts from a dimethyl sulfoxide (DMSO) solution of $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$ (Lazarini, 1979) and 2-(diphenylphosphino)benzenesulfonic acid at a temperature of 80°C. The 2-(diphenylphosphino)benzenesulfonic acid was *in situ* oxidized to the corresponding phosphine oxide. In order to clarify the role of the bismuth oxido cluster in the oxidation process, nuclear magnetic resonance (NMR)-based experiments without adding a bismuth source were carried out. The $^{31}P\{^1H\}$-NMR

signal of a freshly prepared 2-(diphenylphosphino)benzenesulfonic acid solution in $CDCl_3$ is observed at 3.4 ppm. However, in DMSO-d_6, two $^{31}P\{^1H\}$-NMR signals at -11.1 and 34.2 ppm are observed approximately 1 h after dissolution. The latter signal is unambiguously assigned to 2-(diphenylphosphine oxide)benzenesulfonic acid and indicates the oxidation of phosphine to the appropriate phosphine oxide after dissolving the starting compound in DMSO-d_6 at ambient temperature. After heating the NMR tube to 80°C for 4 h, the $^{31}P\{^1H\}$-NMR signal at 34.2 ppm is exclusively observed. An *in situ* NMR experiment in DMSO-d_6 starting from $Bi(NO_3)_3 \cdot 5H_2O$ and 2-(diphenylphosphino) the benzenesulfonic acid shows that bismuth salt decelerates the oxidation of the phosphine group. After 48 h at 80°C, approximately 70% of the phosphine is oxidized to the phosphine oxide and the title compound is formed. This is confirmed by a broad $^{31}P\{^1H\}$-NMR chemical shift at 39.4 ppm (an additional signal at -11.1 ppm is observed for the non-coordinated 2-(diphenylphosphino)benzenesulfonic acid), identical to that observed after the dissolution of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3) \cdot DMSO \cdot 2H_2O$ in DMSO-d_6. A broad $^{31}P\{^1H\}$-NMR signal at approximately 40 ppm is typical for metal-coordinated phosphine oxides (Mecking and Keim, 1996; Levason et al., 2000; Saravanabharathi et al., 2002; Glazier et al., 2004; Farrer et al., 2010).

The same reaction conditions were used in order to modify the periphery of the hexanuclear $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ cluster (Scheme 1). However, we did observe degradation of the cluster to give the mononuclear title compound as observed with a yield of 71% after crystallization.

Our previous investigations towards the functionalization of $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ showed that, in toluene solution, an exchange of the nitrate ligands for trifluoromethanesulfonate to give $[Bi_6O_4(OH)_4(OTf)_6]$ does occur (Miersch et al., 2010). If DMSO is used as a solvent, we did observe a growth of the hexanuclear bismuth oxido cluster to give Bi_{38}-oxido clusters such as $[Bi_{38}O_{45}(NO_3)_{20}(DMSO)_{28}](NO_3)_4 \cdot 4DMSO$, $[\{Bi_{38}O_{45}(NO_3)_{24}(DMSO)_{26}\} \cdot 4DMSO]$ $[\{Bi_{38}O_{45}\text{-}(NO_3)_{24}(DMSO)_{24}\} \cdot 4DMSO]$, $[Bi_{38}O_{45}(OH)_2(p\text{TsO})_8(NO_3)_{12}(DMSO)_{24}](NO_3)_2 \cdot 4DMSO \cdot 2H_2O$ and $[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9] \cdot 2DMSO \cdot 7H_2O$ by adding nitric acid, sodium toluene-4-sulfonate (*p*TsONa) and sodium methacrylate (NaOMc) as additives, respectively (Miersch et al., 2011a,b, 2012). By contrast, under the reaction conditions used here, the chelate effect of the 2-(diphenylphosphine oxide) benzenesulfonic acid favors the degradation of the hexanuclear bismuth oxido cluster $[Bi_6O_4(OH)_4](NO_3)_6$ to give the mononuclear title compound (Figure 1).

$[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3) \cdot DMSO \cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1/m$ with two formula units per unit cell. The cell dimensions are a=9.5436(1) Å, b=18.2414(2) Å, c=15.1817(1) Å, β=90.434(1)° and V=2642.89(4) Å³. The structure shows some disorder of the 2-(diphenylphosphine oxide)benzenesulfonates and the non-coordinating DMSO that was refined properly. The coordination sphere of bismuth shows a [5+4] coordination which results in a square-based pseudo pyramid (Figure 2). The bismuth atom shows five primary Bi−O bonds composed of three monodentate DMSO molecules with short Bi−O bond lengths in the range of 2.278(11) to 2.398(11) Å (Table 1) and of two coordinating oxygen atoms of the phosphine oxides (Bi−O: 2.338(9) Å). The Bi−O bond length of the coordinating phosphine oxide is in the same range as described for the bismuth phosphine oxide complex $[BiI_2\{OP(NMe_2)_3\}_4][I_5]$ reported by Farrugia et al. (1998) (Bi−O: 2.317 Å). The pseudo pyramid is capped by two asymmetrically coordinating and chelating sulfonate groups (Bi−O: 2.74(2)–2.88(2) Å). The Bi−O bond lengths of the sulfonate groups are



Scheme 1 Synthesis of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3) \cdot DMSO \cdot 2H_2O$ by (A) a single step and (B) a sequential approach.

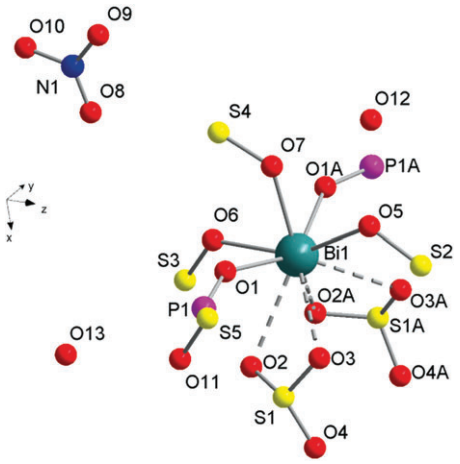


Figure 1 Molecular structure of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$. Symmetry transformations used: A=x, 0.5-y, z. Atomic positions of O2, O3, S1 and P1 are disordered (occupation factor of 0.5). C and H atoms are omitted for clarity.

O(1)–Bi(1)	2.338(9)	O(3′)–Bi(1)[a]	2.88(2)
O(2)–Bi(1)	2.815(19)	O(5)–Bi(1)	2.398(11)
O(2′)–Bi(1)[a]	2.74(2)	O(6)–Bi(1)	2.296(11)
O(3)–Bi(1)	2.81(3)	O(7)–Bi(1)	2.278(11)
O(7)–Bi(1)–O(6)	80.6(4)	O(1)–Bi(1)–O(3)	69.7(7)
O(7)–Bi(1)–O(1)	73.6(3)	O(5)–Bi(1)–O(3)	77.2(7)
O(6)–Bi(1)–O(1)	77.4(2)	O(7)–Bi(1)–O(2)	141.0(4)
O(7)–Bi(1)–O(5)	72.0(4)	O(6)–Bi(1)–O(2)	75.7(4)
O(6)–Bi(1)–O(5)	152.6(4)	O(1)–Bi(1)–O(2)	71.3(5)
O(1)–Bi(1)–O(5)	94.5(3)	O(3)–Bi(1)–O(2)	49.8(7)
O(7)–Bi(1)–O(2′)	136.8(4)	O(7)–Bi(1)–O(3′)	118.5(5)
O(6)–Bi(1)–O(2′)	82.9(4)	O(6)–Bi(1)–O(3′)	126.6(5)
O(1)–Bi(1)–O(2′)	63.9(5)	O(1)–Bi(1)–O(3′)	64.0(5)
O(7)–Bi(1)–O(3)	129.2(5)	O(5)–Bi(1)–O(3′)	69.4(5)
O(6)–Bi(1)–O(3)	122.5(8)	O(2′)–Bi(1)–O(3′)	48.1(5)

Table 1 Selected interatomic distances (Å) and angles (degrees) in $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$.
[a]Atomic positions of O2 and O3 are slightly disordered and have an occupation factor of 0.5.

markedly longer than those reported for the bismuth sulfonate complexes $[Ph_2Bi(O_3S–Mes)]_\infty$, $[Ph_2Bi(O_3S–Cam)]_\infty$, $[PhBi(O_3S–Tol)_2]_\infty$ and $[PhBi(O_3S–Mes)_2]_\infty$, which all show monodentate coordination with Bi−O bond lengths of approximately 2.4 Å (Andrews et al., 2010). Furthermore, one DMSO molecule, one nitrate and two water molecules were found in the unit cell but do not coordinate to the bismuth atom. The infrared spectrum of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$ in the solid state confirms the coordination behavior determined by single-crystal X-ray diffraction. A strong absorption band at 1132 cm^{-1} shows the phosphine oxide coordination to bismuth. The coordination of the sulfonate groups is demonstrated by absorption bands at 1030 cm^{-1} ($\nu_{as}(SO_2)$) and 1262 cm^{-1} ($\nu_s(SO_2)$), and the absorption band at 922 cm^{-1} represents the $\nu_{S=O}$ stretching vibration of coordinated DMSO molecules. A broad and weak absorption band at 3393 cm^{-1} shows the presence of water molecules that are not involved in strong hydrogen bonding. Absorption bands at 1347 and 1068 cm^{-1} are assigned to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ of the nitrate ion.

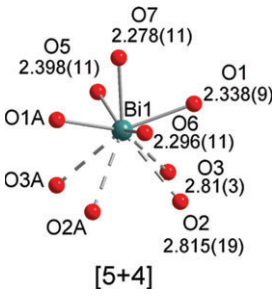


Figure 2 Oxygen coordination environment of the bismuth atom in the title compound. Symmetry transformations used: A=x, 0.5-y, z. Atomic positions of O2 and O3 are slightly disordered and have an occupation factor of 0.5 (Bi(1)–O(2′): 2.74(2) Å; Bi1–O(3′): 2.88(2) Å).

A view along the crystallographic [100]-axis shows channels that accommodate coordinating DMSO molecules, water molecules as well as the non-coordinating molecules of DMSO and nitrate (Figure 3).

Thermogravimetric analysis under nitrogen shows a mass loss within three distinct steps. Up to 120°C, a mass loss of 2.7% is observed which is assigned to the loss of two water molecules (calc. 2.7%). The next step shows a mass loss of 23.2% up to 300°C which is caused by the loss of four DMSO molecules (calc. 23.4%). Up to 800°C, a weight loss of 53.2% is noticed within one step. This is assigned to the decomposition of nitrate and the coordinated organic ligands. Powder X-ray diffraction of the final product shows the formation of elemental bismuth (ICDD 00-044-1246) and bismuth phosphate (ICDD 01-074-1635).

In conclusion, we have shown that the reaction of $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$ with 2-(diphenylphosphino)benzenesulfonic acid in DMSO results in the oxidation of phosphine to the corresponding phosphine oxide and, subsequently, in the degradation of the hexanuclear bismuth oxido cluster to give mononuclear $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$ in 71% yield. Previously, we have demonstrated that the hexanuclear bismuth oxido cluster might be used as a starting material to produce nanoscaled bismuth oxido clusters from DMSO solution. However, in the presence of strongly coordinating chelate ligands, cluster degradation might be observed as shown here.

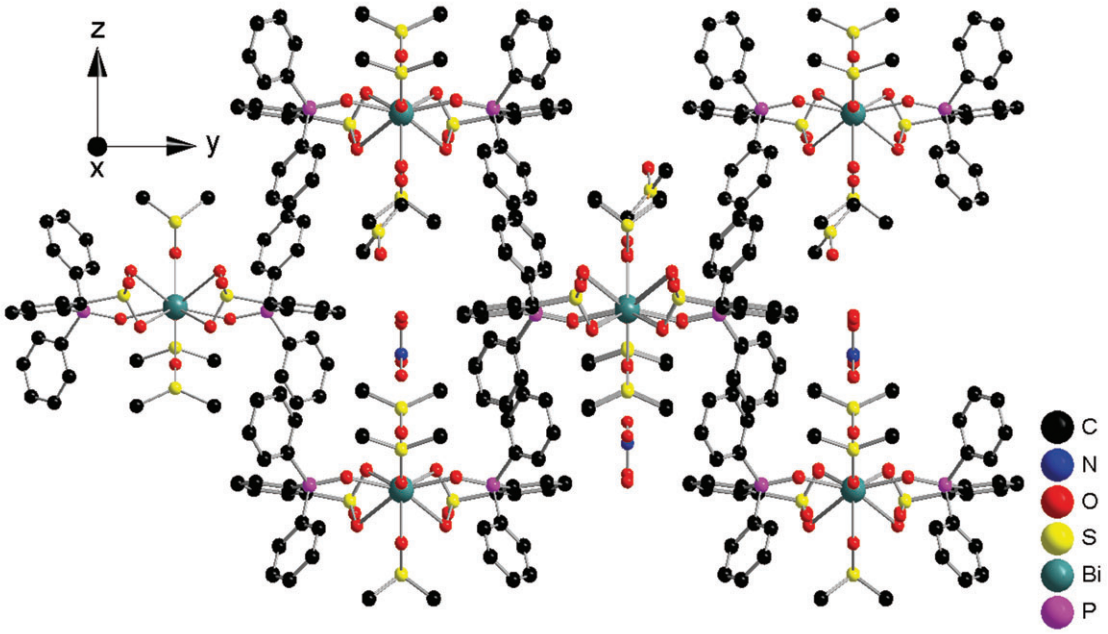


Figure 3 View along [100]-axis of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$. H atoms are omitted for clarity.

Experimental

General

^1H and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker spectrometer (Advance III 500; 500 MHz) (Bruker Corporation, Billerica, MA, USA) at room temperature. Attenuated total reflection infrared spectra were recorded using a Spectromat FTS-165 spectrometer (Bremen, Germany). Thermogravimetric experiments were performed on a METTLER-TOLEDO GmbH (Postfach, Gießen, Germany) TGA/DSC1 1100 system with a UMX1 balance. Melting points were determined on a Büchi Labortechnik GmbH (Essen, Germany) melting apparatus (Melting Point B-540) and are uncorrected. The data set for the single-crystal X-ray diffraction study was collected with Mo Kα radiation (0.71073 Å) on an Oxford Gemini S diffractometer (Agilent Technologies Sales & Services GmbH & Co. KG, Life Sciences & Chemical Analysis, Waldbronn, Germany) at 110 K. All calculations were performed using the SHELXTL program (Sheldrick, 1990). The structures were solved by direct methods and refined by full-matrix least squares on F^2. The CCDC file 901691 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$

The starting material 2-(diphenylphosphino)benzenesulfonic acid was synthesized according to a literature procedure (Schultz and Pfaltz, 2005). Sulfuric acid (819 mg, 2.39 mmol) was added to a solution of $[Bi_6O_4(OH)_4](NO_3)_6\cdot H_2O$ (500 mg, 0.28 mmol) in DMSO at 80°C. The reaction mixture was stirred for 4 h and then cooled to ambient temperature. Slow evaporation of the solvent over a period of 2 months gave $[Bi(C_{18}H_{14}P(O)SO_3)_2(DMSO)_3](NO_3)\cdot DMSO\cdot 2H_2O$ as colorless crystals with a yield of 1.13 g (71%). **M.p.** 103–104°C. **CHN**: $C_{44}H_{56}BiNO_{17}P_2S_6$; C 39.2 (calc. 39.6), H 4.4 (4.2), N 1.2 (1.1) %. **^{1}H-NMR** (500.30 MHz, DMSO-d_6): [δ] 8.14 (m, 1H), 7.77 (m, 1H), 7.67–7.47 (m, 11H), 7.22 (m, 1H), 3.36 (s, H_2O). **^{31}P{^{1}H}-NMR** (202.52 MHz, DMSO-d_6): 39.4 ppm. **IR** [cm^{-1}]: υ 3393 bw, 3050 w, 3015 w, 2971 w, 2920 w, 2852 w, 2361 m, 2344 m, 2168 w, 1587 w, 1484 w, 1435 m, 1347 m, 1262 m, 1182 w, 1132 s, 1123 s, 1090 s, 1068 s, 1030 s, 1007 s, 988 s, 951 s, 922 s, 832 w, 796 w, 779 m, 747 m, 729 m, 720 m, 693 s, 669 m, 610 m, 552 s, 538 m, 529 s, 484 w, 465 w, 442 m, 411 m. *Crystal data:* $C_{44}H_{56}BiNO_{17}P_2S_6$, M=1334.18, crystal size 0.2×0.2×0.2 mm^3, monoclinic, space group $P2_1/m$, Z=2, a=9.5436(1) Å, b=18.2414(2) Å, c=15.1817(1) Å, β=90.434(1)°, V=2642.89(4) $Å^3$, D_c=1.677 g cm^3, $F(000)$=1344, μ(Mo-K_α)=3.702 mm^{-1}, T=110 K, $3.09<2\theta°<26.00°$, completeness to 2θ: 99.6% max./min. residual electron density: 3.191/-5.715 e/$Å^3$. A total of 34,381 reflections collected, 5349 reflections were independent (R_{int}=0.0336). Final R_1=0.0699 ($I>2\sigma(I)$) and wR_2=0.1882 (all data).

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