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Synthesis and Structure of μ-Oxobis[(nitrito)triphenylantimony]

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Abstract — Triphenylantimony dibromide was reacted with sodium nitrite in aqueous acetone to obtain μ-oxobis[(nitrito)triphenylantimony]. According to single-crystal X-ray diffraction data, the Sb atoms in the molecule have a trigonal bipyramidal coordination. The molecule is centrosymmetric, the two Sb atoms are linked with each other by a bridging oxygen atom [the SbOSb angle is 141.8(2)°, and the Sb···Sb distance is 3.7354(5) Å]. The Sb–O_{br} and Sb–O_{term} bond lengths are 1.9768(1) and 2.257(3) Å, and the Sb···O and Sb···N distances are 3.020(4) and 3.070(6) Å, respectively.

It is known that the molecule of μ-oxobis[(nitrato)-triphenylantimony] $[Ph_3(NO_3)Sb]_2O$ (**I**) has a V-like shape [the SbOSb angle is 137.4(2)°] [1]. At the same time, the Sb–O–Sb fragment in "anhydride" molecules may be linear, as in μ-oxobis[(2,5-dimethylbenzene-sulfonato)tri-*p*-tolylantimony] [2]. Note that most structurally characterized Sb(V) compounds of the general formula $(Ar_3SbX)_2O$ are have a V-like structure which, in our opinion, are energetically more favorable because of the additional interaction between the antimony atoms. Actually, the Sb···Sb distances in **I**, $(Ph_3SbCl)_2O$ [3], and $(Ph_3SbI)_2O$ [4] are 3.668, 3.715, and 3.755 Å, respectively, which is much shorter than the sum of the van der Waals radii of antimony atoms (4.40 Å [5]).

We have synthesized μ-oxobis[(nitrito)triphenyl-antimony] $[Ph_3(NO_2)Sb]_2O$ (**II**) and studied its crystal and molecular structure.

Compound **II** was prepared from triphenylanti-mony dibromide and sodium nitrite in aqueous acetone.

$$Ph_3SbBr_2 + 2NaNO_2 \longrightarrow Ph_3Sb(NO_2)_2$$
$$\xrightarrow{H_2O} (Ph_3SbNO_2)_2O$$
II

We found that the antimony atoms in molecule **II** have a trigonal bipyramidal coordination with axial oxygen atoms (Tables 1, 2; see figure). The molecule is centrosymmetric (the inversion center is a bridging oxygen atom) and has a puckered shape [the SbOSb angle is 141.8(2)°], and the distance between the two antimony atoms is 3.7354(5) Å. The Sb–O_{term} bond lengths are 2.257(3) ^A, which is slightly shorter than in molecule **I** [2.264(3) and 2.295(3) Å]. Note that shortening of these distances in **II** is accompanied by lengthening of the Sb–O_{br} [1.9768(1) Å] bond compared with **I** [1.968(3) A]. The distances between the antimony atoms and their nonbonded nitrogen atoms, Sb···N [3.070(6) Å] and Sb···O=N [3.020(4) Å], are

Table 1. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\times 10^3$) in μ-oxobis[(nitrito)tri-phenylantimony] (**II**)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
Sb	1326.6(2)	3482.3(1)	7138.3(1)	50.3(1)
O^1	0	3837(2)	7500	54.0(8)
O^2	2839(2)	3082(2)	6717(2)	73.9(8)
O^3	2955(4)	4114(3)	6128(3)	122(1)
N	3313(5)	3498(3)	6255(4)	108(2)
C^1	5980(3)	3520(2)	5693(3)	56.8(9)
C^2	–1570(3)	4059(2)	5380(3)	68(1)
C^3	–6950(4)	4059(3)	4449(3)	84(1)
C^4	–4960(5)	3537(3)	3851(4)	95(2)
C^5	2680(4)	3010(3)	4160(3)	93(1)
C^6	8240(4)	2996(3)	5079(3)	75(1)
C^7	2257(3)	4301(2)	7970(2)	54.2(9)
C^8	3357(3)	4192(2)	8332(3)	67(1)
C^9	3934(4)	4711(3)	8920(3)	81(1)
C^{10}	3438(4)	5321(3)	9162(3)	79(1)
C^{11}	2356(4)	5436(2)	8814(3)	75(1)
C^{12}	1761(3)	4924(2)	8207(3)	63(1)
C^{13}	1424(3)	2474(2)	7855(2)	53.6(9)
C^{14}	1424(4)	1800(2)	7429(3)	70(1)
C^{15}	1421(4)	1171(2)	7941(3)	78(1)
C^{16}	1437(4)	1199(3)	8865(3)	75(1)
C^{17}	1443(4)	1862(3)	9298(3)	76(1)
C^{18}	1443(3)	2499(2)	8794(3)	66(1)

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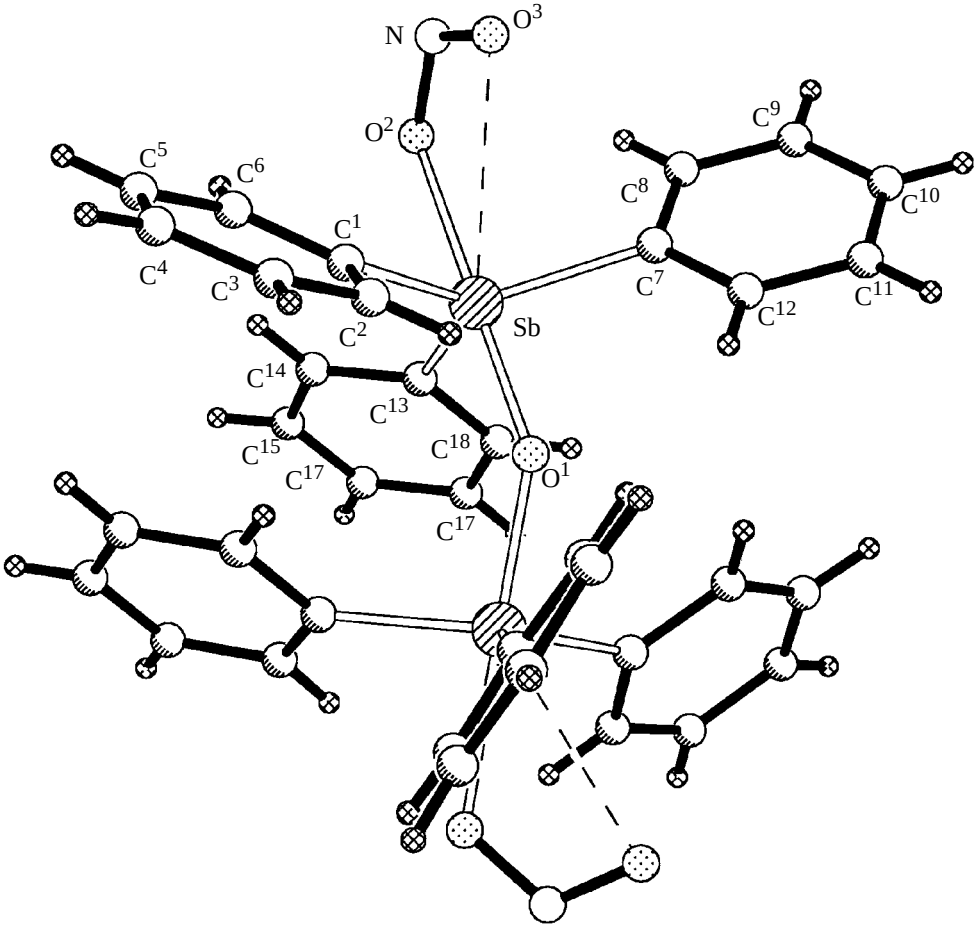
Table 2. Selected interatomic distances and valence angles in μ-oxobis[(nitrito)triphenylantimony] (**II**)

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Sb···Sb'	3.7354(5)	SbO^1Sb'	141.8(2)	$C^4–C^5$	1.369(7)	C^1SbO^3	71.8(1)
$Sb–O^1$	1.9768(1)	O^1SbC^{13}	96.4(1)	$C^5–C^6$	1.382(6)	O^2SbO^3	43.8(1)
$Sb–C^{31}$	2.110(4)	O^1SbC^7	90.6(1)	$C^7–C^{12}$	1.380(5)	NO^2Sb	119.1(3)
$Sb–C^{21}$	2.118(4)	$C^{13}SbC^7$	111.1(1)	$C^7–C^8$	1.391(5)	NO^3Sb	80.9(3)
$Sb–C^{11}$	2.128(4)	O^1SbC^1	92.9(1)	$C^8–C^9$	1.380(6)	O^3NO^2	116.0(5)
$Sb–O^2$	2.257(3)	$C^{13}SbC^1$	119.6(1)	$C^9–C^{10}$	1.363(7)	$C^2C^1C^6$	120.0(4)
$Sb–O^3$	3.020(4)	C^7SbC^1	128.4(1)	$C^{10}–C^{11}$	1.369(6)	$C^1C^2C^3$	119.0(4)
Sb–N	3.070(6)	O^1SbO^2	179.6(1)	$C^{11}–C^{12}$	1.393(6)	$C^4C^3C^2$	121.3(5)
$O^2–N$	1.254(6)	$C^{13}SbO^2$	84.0(1)	$C^{13}–C^{18}$	1.378(5)	$C^3C^4C^5$	119.6(5)
$O^3–N$	1.210(6)	C^7SbO^2	89.4(1)	$C^{13}–C^{14}$	1.380(6)	$C^4C^5C^6$	120.7(5)
$C^1–C^2$	1.379(5)	C^1SbO^2	86.8(1)	$C^{14}–C^{15}$	1.373(6)	$C^5C^6C^1$	119.4(4)
$C^1–C^6$	1.388(6)	O^1SbO^3	135.9(1)	$C^{15}–C^{16}$	1.357(6)	$C^{12}C^7C^8$	119.5(4)
$C^2–C^3$	1.391(6)	$C^{13}SbO^3$	127.4(1)	$C^{16}–C^{17}$	1.367(6)	$C^9C^8C^7$	119.4(4)
$C^3–C^4$	1.357(7)	C^7SbO^3	70.3(1)	$C^{17}–C^{18}$	1.379(6)	$C^{10}C^9C^8$	120.8(4)

The unit cell parameters and the intensities of 2108 unique reflections with $I > 2\sigma(I)$ were measured on a SMART-1000CCD automated diffractometer (λMoK_α radiation, λ 0.71073 Å, 2θ/θ scanning). Monoclinic crystals; at 23°C, *a* 12.650(1), *b* 18.239(2), *c* 14.722(1) Å; β 102.576(2)°, *V* 3315.0(5) $Å^3$, *Z* 4, d_{calc} 1.631 g/cm^3, space group *C*2/*c*. The structure was solved by the direct method and refined by least-



Molecular structure of μ-oxobis[(nitrito)triphenylantimony] (**II**).

squares anisotropically for non-hydrogen atoms to *R* 0.0258 and *RW* 0.0651. The positions of hydrogen atoms were calculated geometrically and refined by the rider model. The coordinates of non-hydrogen atoms are listed in Table 1, and interatomic distances and valence angles, in Table 2. A perspective view of the molecule is given in the figure. Data collection and processing, as well as refinement of unit cell parameters were performed using SMART and SAINT-Plus programs [7]. Structure calculation and refinement were performed using SHELXTL/PC programs [8].

μ-Oxobis[(nitrito)triphenylantimony] (II). A solution of 1.00 g of triphenylantimony dibromide in 10 ml of acetone was added to a solution of 0.27 g of sodium nitrite in 80 ml of water. The precipitate that formed was filtered off, washed with water, dried, and recrystallized from toluene–heptane, 1 : 1. Yield 0.79 g (99%), mp 142°C.

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