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SYNTHESIS AND X-RAY STRUCTURAL INVESTIGATION OF BISMUTH 2-METHYL-8-QUINOLINESELENOLATE $Bi[C_9H_5(CH_3)NSe]_3$

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Bismuth 2-methyl-8-quinolineselenolate, $Bi[C_9H_5(CH_3)NSe]_3$, was synthesized. X-ray analysis was used to determine the structure of this complex. The crystal chemistry of bismuth(III), antimony(III), and arsenic(III) 2-methyl-8-quinolineselenolates and 2-methyl-8-quinolinethiolates was discussed relative to the effect of going from Se to S as the ligand atoms and presence of a methyl group at C-2 of the quinoline system and unshared electron pair of the central atom in the complex.

Keywords: bismuth(III), antimony(III), and arsenic(III) 2-methyl-8-quinolineselenolates and 2-methyl-8-quinolinethiolates, unshared electron pair, X-ray structural analysis.

In a continuation of a systematic study of the structure of inner complexes of 8-hydroxyquinoline, 8-quinolinethiol, and 8-quinolineselenol, we synthesized and determined the structure of bismuth 2-methyl-8-quinolineselenolate, $Bi[C_9H_5(CH_3)NSe]_3$ (**1**). Complex **1** holds interest as a complex of group V *p*-element in an incomplete valence state, in which the interaction of the unshared electron pair and the methyl substituent at C-2 affects the crystal chemistry.

Complex **1** was synthesized as a fine crystalline compound and its cytotoxic activity has been studied [1]. The molecular and crystal structure of complex **1** was determined by X-ray crystallographic structural analysis (Figs. 1 and 2).

The crystal structure of complex **1** consists of neutral asymmetric $Bi[C_9H_5(CH_3)NSe]_3$ complexes. While the bismuth 8-quinolineselenolate molecule (**2**) [2] (space group $R\bar{3}$) has intrinsic three-fold symmetry, the introduction of a 2-CH_3 group into the quinoline system in complex **1** leads to the loss of molecular symmetry and scattering of the lengths of the monotypic bond lengths and valence angles, as well as, especially, to a change in the planarity of the five-membered metallacycles. The selenium and nitrogen atoms of the three 8-quinolineselenol ligands have bidentate (N,Se)-coordination with the bismuth atom and form a distorted octahedron (3Se + 3N) about the central atom (as usual in complexes of arsenic, antimony, and bismuth, symmetrical isomer A [3]. The SeBi(1)N chelate angles (Table 1) vary in a narrow range (±2°) and the mean value $\omega = 70.33°$. The lengths of the major Bi(1)–Se bonds, $l_{av} = 2.698$ Å (Table 1) hardly differ ($\Delta = 0.009$ Å)

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and are slightly less than the sum of the covalent radii of the bound atoms ($R_{\mathrm{Bi}} + R_{\mathrm{Se}} = 2.711$ Å [4]). The length of the Bi–Se bond is in accord with results reported to the Cambridge Crystallographic Data Center (version 5.26). The Bi(1)–Se bonds are arranged approximately at right angles SeBi(1)Se, $\omega = 81.30(2)$-$91.64(2)°$, av. 87.68° and the arrangement of the atoms in (Bi + 3Se) fragment of the complex may be seen as a trigonal bipyramid with the bismuth atom at the apex.

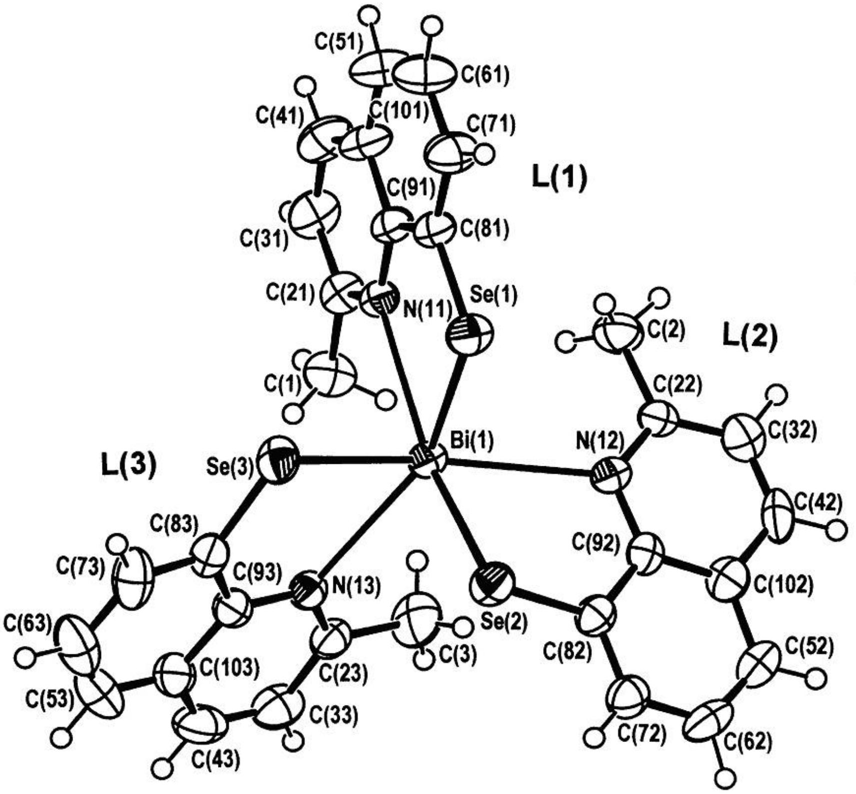

Fig. 1. General view of the molecular structure of complex **1** with designation of the atoms and ligands.

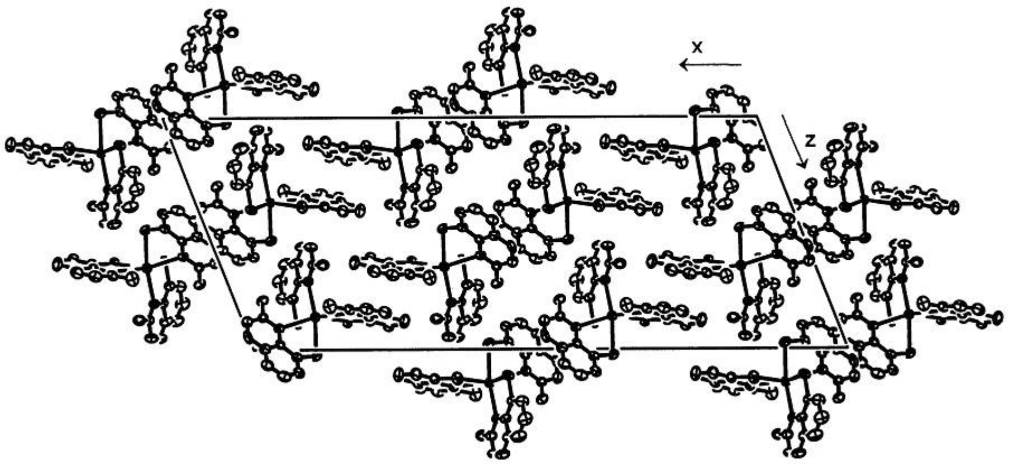

Fig. 2. Projection of the crystal structure of the $Bi[C_9H_5(CH_3)NSe]_3$ complex onto the (010) plane (the hydrogen atoms in complex **1** are not shown).

The weak Bi(1)···N coordination bonds (l_{av} = 2.846 Å) are located in the *trans* position relative to the major Bi(1)–Se covalent bonds and are similar in length (Table 1). The length of these bonds is greater than the sum of the covalent radii of the corresponding atoms ($R_{Bi} + R_N$ = 2.276 Å [4]) and also slightly greater than mean length of the Bi···N bonds in bismuth 8-quinolineselenolate (l = 2.795(5) Å). The NBi(1)N bond angles are close to tetrahedral and the sum of the NBi(1)N angles is 335.40°. The greatest angular deviations (16.7-29.2°) from the ideal octahedral angle (180°) are found for the diagonal SeBi(1)N angles, ω_{av} = 156.7°. The other SeBi(1)N interligand angles lie in the range from 70.07(11) to 88.26(13)°.

The bismuth atom is 1.615(1) Å from the Se(1)/Se(2)/Se(3) face of the octahedron but only -0.829(1) Å from the N(11)/N(12)/N(13) face. These two faces are almost parallel and the dihedral angle between their mean-square planes is 6.9(1)°. There is space for the stereochemically active unshared electron pair perpendicular to the N(11)/N(12)/N(13) plane. The existence of an unshared electron pair in this form is indicated by the three Bi(1)–Se and Bi(1)···N bond lengths and the corresponding valence angles, which are similar in value to each other. Taking account of the unshared electron pair, the coordination polyhedron of the bismuth atom is a centered Ψ-octahedron distorted in the N/N/N face (3Se + 3N + Ψ).

The SeBi(1)N coordination planes of the central atom have approximately perpendicular arrangement; the dihedral angles are 85.16(4)° between the Se(1)Bi(1)N(11) and Se(2)Bi(1)N(12) mean-square planes, 91.47(3)° between the Se(1)Bi(1)N(11) and Se(3)Bi(1)N(13) planes, and 86.47(2)° between the Se(2)Bi(1)N(12) and Se(3)Bi(1)N(13) planes.

The five-membered metallacycles K(1), K(2), and K(3), which contain the L(1), L(2), and L(3) ligands, respectively, have planar configuration. Metallacycle K(1) is virtually planar; the bismuth atom extrudes from the L(1) ligand plane by 0.019(1) Å. Metallacycle K(2) has *envelope* conformation with dihedral angle at the flexure along the Se···N line equal to 28.92(4)°. The bismuth atom extrudes from the metallacycle plane by 1.107(1) Å. Metallacycle K(3) is slightly deformed; the dihedral angle for the flexure along the Se···N line is 172.95(7)° and the bismuth atom extrudes from the plane of the corresponding metallacycle by 0.281(1) Å.

In contrast to complex **1**, all three metallacycles in complex **2** are identical and have *envelope* conformation with dihedral angle for the flexure along the Se···N line equal to 160.2(1)°. The extrusion of the bismuth atom from the planes of the metallacycles is 0.769(3) Å.

TABLE 1. Some Characteristic Bond Lengths and Valence Angles in the $Bi[C_9H_5(CH_3)NSe]_3Bi$ Complex **1**

Bond	l, Å	Angle	ω, deg
Bi(1)–Se(1)	2.702(1)	Se(1)Bi(1)N(11)	71.6(1)
Bi(1)–Se(2)	2.698(1)	Se(2)Bi(1)N(12)	69.9(1)
Bi(1)–Se(3)	2.693(1)	Se(3)Bi(1)N(13)	69.5(1)
Bi(1)–N(11)	2.811(4)	Se(1)Bi(1)Se(2)	91.64(2)
Bi(1)–N(12)	2.850(4)	Se(1)Bi(1)Se(3)	81.30(2)
Bi(1)–N(13)	2.876(4)	Se(2)Bi(1)Se(3)	90.10(2)
Se(1)–C(8)*	1.902(5)-1.909(5)	N(11)Bi(1)N(12)	106.8(1)
Se(1)–C(8) av	1.905	N(11)Bi(1)N(13)	108.1(1)
N(1)–C(2)*	1.322(6)-1.322(8)	N(12)Bi(1)N(13)	120.5(1)
N(1)–C(2) av	1.322	Se(1)Bi(1)N(13)*(diagonal)	150.9 (1)-163.3(1)
N(1)–C(9)*	1.361(6)-1.370(6)	Se(1)Bi(1)N(13) av	156.70
N(1)–C(9) av	1.366	Bi(1)Se(1)C(8)*	101.32(15)-107.09(15)
C(9)–C(10)*	1.404(7)-1.421(6)	Bi(1)Se(1)C(8) av	104.20
C(9)–C(10) av	1.412		

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* The range of values of similar bond lengths and valence angles in ligands L(1), L(2) and L(3).

Comparison of the structure of the five-membered metallacycles in complexes **1** and **2** shows that variations in their planarity are possible for slight changes in the bond lengths (differences in the Bi–Se bond lengths $\Delta = 0.013$ Å, Bi···N bond lengths $\Delta = 0.050$ Å, and Se–C bond lengths $\Delta = 0.003$ Å) and bond angles (differences in the SeBiN valence angles $\Delta = 0.43°$, BiSeC bond angles $\Delta = 0.003°$).

The reason for this finding is the existence of weak Bi···N coordination bonds in the metallacycles in addition to the Bi–Se covalent bonds. These coordination bonds permit some degree of freedom for the arrangement of the quinoline systems to permit formation of intermolecular interaction upon crystallization. We may assume that the flexure of the metallacycles is a consequence of the intermolecular contacts or a π-π interaction.

The quinoline systems of ligand L(3) in the crystal structure of complex **1** partially overlaps with the ring of ligand L(3) of an adjacent molecule related to the former by a center of inversion [[½,½,½]]. The distance between the centroids of the six-membered heterocycles of the quinoline system is equal to 3.639 Å, while the dihedral angle for the flexure along the Se···N line of the corresponding metallacycle is 151.25(4)°. We also find partial overlap of the ring of ligand L(2) with the same ring in the molecule with coordinates ½-x, -½+y, ½-z.

The mean Se(1)–C(8) bond length in complex **1**, $l_{av} = 1.905$ Å, is identical within experimental error to the corresponding value in complex **2** ($l = 1.910(7)$ Å). This bond length is less than the sum of the covalent radii of the corresponding atoms ($R_{Se} + R_C = 1.933$ Å) but, in contrast to 8-quinolineselenolates of transition metals platinum ($l = 1.858(15)$ Å) [5] and palladium ($l = 1.881(4)$ Å) [6], the Se–C bond shows no double bond character.

The quinoline systems are planar to within ±0.04 Å and, in general, have the usual expected structure. The N(1)–C(2) bond lengths ($l_{av} = 1.322$ Å) are greater than for the double bond in complex **2** ($l = 1.301(9)$ Å) but less than the length of the N(1)–C(9) bonds ($l_{av} = 1.366$ Å). The mean C(2)N(1)C(9) angle ($\omega_{av} = 119.6°$) indicates only slight participation of the nitrogen atom in formation of the Bi···N coordination bond. The alternating C(3)–C(4), C(5)–C(6), and C(7)–C(8) bonds ($l_{av} = 1.371$ Å) are shortened. The lengths of the other bonds lie in the range from 1.397(12) to 1.432(7) Å. The mean length of the central bond in the quinoline system C(9)–C(10) ($l_{av} = 1.412$ Å) in complex **1** is not shortened. The CCC angles differ only slightly from 120° (±3.2°).

Atoms C(1), C(2), and C(3) of the methyl groups in complex **1** are 3.703 Å from the central atom. The C(1)/C(2)/C(3) plane is approximately parallel to the Se(1)/Se(2)/Se(3) and N(1)/N(2)/N(3) planes and forms dihedral angles of 15.91(10) and 13.56(10)° with these two planes, respectively.

Table 2 gives the geometrical parameters of the presumed bifurcated intramolecular M(E)···3(H–C Me) hydrogen bond with participation of the unshared electron pair of the central atom in complex **1**. In considering the existence of hydrogen bonding, we should take account of the method used to determine and refine the hydrogen atomic coordinates. The presence of the heavy bismuth atom in complex **1** hinders finding the hydrogen atomic coordinates from the Fourier difference maps. These coordinates were found from geometrical considerations and refined using the "horse and rider" model. Table 2 shows that the positions of the hydrogen atoms in complex **1** correspond to a theoretical conformation of the methyl group, which fails to meet the requirements for the existence of hydrogen bonding since these groups are far from the central atom.

TABLE 2. Geometrical Parameters of the Presumed Bifurcated Intramolecular Hydrogen Bond in Complex $Bi[C_9H_5(CH_3)NSe]_3$ (**1**)

Bond C–H···M	Lengths, Å			Angle C–H···M, deg
	C–H	H···M	C···M	
C(1)–H(46B)···Bi(1)	0.96	3.435	3.678(7)	99.44
C(2)–H(22C)···Bi(1)	0.96	3.362	3.754(8)	106.81
C(3)–H(45B)···Bi(1)	0.96	3.434	3.674(7)	101.43

However, the hydrogen atomic coordinates of the methyl groups in the isostructural complex $Sb[C_9H_5(CH_3)NSe]_3$ [7] with a lighter central atom were localized from the electron density difference map and refined using the "riding" model. The Sb···H distances ranged from 2.894 to 3.011 Å, $l_{av} = 2.939$ Å, while the C–H···Sb angles varied from 136.3 to 140.9°, $\omega_{av} = 138.5°$ and are in accord with the data for intermolecular hydrogen bonding in the structure of $(CN_3H_6)[Sb(Edta)]\cdot 2H_2O$ [8], where the Sb···H distance $l = 3.07$ Å. The existence of a bifurcated intramolecular hydrogen bond M(E)···3(H–C Me) also accounts for the formation of isostructural bismuth, antimony, and arsenic 2-methyl-8-quinolinethiolates [9].

In conclusion, we should note that replacing the Se ligand atoms by S in going from complex **1** to bismuth 2-methyl-8-quinolinethiolate $Bi[C_9H_5(CH_3)NS]_3$ (**3**) [10] does not lead to any significant change in the nature of the bonds or molecular stereochemistry but some change is noted in the long-range order, i.e., the packing of the complexes in the crystal structure (space group $C2/c$ for complex **1**, space group $P2_1/c$ for complex **3**). However, the introduction of a methyl group at C-2 in the quinoline system in the structure of bismuth 8-quinolinethiolate $Bi(C_9H_6NS)_3$ [11] has a significant effect on the molecular level (short-range) leading to change in the coordination polyhedron of the central atom from pentagonal pyramid (3S + 3N) in $Bi(C_9H_6NS)_3$ to distorted octahedron (3S + 3N) in complex **3**. The existence of a weak ring-closing intramolecular hydrogen bond leads to conditional loss of crystal chemical individuality of group V cations, i.e., formation of a series of isostructural bismuth, antimony, and arsenic 2-methyl-8-quinolinethiolates as well as selenolate **1** and thiolate **3**, which are isostructural to each other.

EXPERIMENTAL

Bismuth 2-Methyl-8-quinolineselenolate (1). 50% Hypophosphorous acid (1 ml, 9.7 mmol) was added to a solution of 2,2'-dimethyl-8,8'-diquinolinediselenide (0.2 g, 0.45 mmol) in 3 M hydrochloric acid (2 ml) and maintained for 5 min. Then, saturated aqueous sodium acetate (4 ml, 60 mmol) was added. $Bi(NO_3)_3\cdot 5H_2O$ (0.13 g, 0.27 mmol) was dissolved in a solution of 1 g tartaric acid in 1 ml of 1:1 concentrated hydrochloric acid–water with heating. Saturated aqueous sodium acetate (20 ml, 150 mmol) was added and the mixture was stirred. Water was added to a volume of 20 ml. The bismuth solution obtained was added to the previously prepared solution of the reagent. The dark-yellow precipitate formed was filtered off, washed with water, and dried in the air. The yield of complex **1** was 0.24 g (91%). Found, %: C 41.06; H 2.67; N 4.93. $C_{30}H_{24}BiN_3Se_3$. Calculated, %: C 41.30; H 2.77; N 4.82.

Monocrystals of complex **1** were grown by slow cooling of a hot saturated solution of the complex in chloroform obtained by heating.

X-ray Crystallographic Structural Analysis. The diffraction pattern from a 0.16×0.31×0.34 mm monocrystal of complex **1** was taken at 20°C on an Bruker-Nonius KappaCCD automatic diffractometer by φ and ω scan using MoKα radiation and graphite monochromator to $2\theta_{max} = 60°$. The monoclinic crystals of complex **1** belong to space group $C2/c$. The unit cell parameters: $a = 40.0731(7)$, $b = 8.9120(2)$, $c = 16,9524(4)$ Å, $\beta = 111.2521(9)°$, $V = 5642.4(2)$ Å^3, $Z = 8$, $M_r = 872.4$, $D_x = 2.054$ g/cm^3, $\mu = 10.14$ mm^{-1}. An absorption correction was introduced directly by calculating the transmission factor A using an integral formula after indexing six faces of the crystal polyhedron. The NUMABS program in the maXus program package was used [12]. The molecular structure was found using the heavy atom method and refined by the method of least squares relative to 5716 reflections with $I > 2\sigma(I)$ to $R = 0.0304$ ($wR2 = 0.0840$) anisotropically for the non-hydrogen atoms taking account of the hydrogen atomic coordinates calculated using geometrical considerations. Programs by Mackay [12] and Otwinowski [13] were used.

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