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SYNTHESIS AND STRUCTURE OF BISMUTH 8-QUINOLINE-SELENOLATE $Bi(C_9H_6NSe)_3$

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Bismuth 8-quinolineselenolate $Bi(C_9H_6NSe)_3$ was synthesized. The molecular and crystal structure of this compound was determined by X-ray diffraction structural analysis. The effect of replacing the ligand atoms Se→S and the role of the unshared electron pair on the formation of the coordination polyhedron of the central bismuth atom in bismuth(III) 8-quinolineselenolate and bismuth(III) 8-quinolinethiolate, which are complexes of a Group V p-element in an incomplete valence state was discussed.

Keywords: bismuth chelate compounds, bismuth 8-quinolineselenolate, bismuth 8-quinolinethiolate, unshared electron pair (UEP), X-ray diffraction structural analysis.

Multifaceted systematic studies of chelate compounds of transition and nontransition metals with 8-quinolinethiol (SQu), 8-quinolinol (OQu), and its derivatives have been carried out at the Chelate Compounds Laboratory in the Institute of Inorganic Chemistry at the Riga Technical University headed by Academician Yu. Bankovsky [1]. At the initiative of Academician Bankovsky, studies were undertaken of chelate compounds of 8-quinolineselenol (SeQu), which is a structural analog of 8-quinolinethiol and 8-quinolinol [2-7]. 8-Quinolineselenol, its derivatives, and their complexes hold interest in regard to their possible biological activity.

In systematic studies, the differences in the physicochemical properties of chelate compounds of transition and nontransition elements and the possible use of these compounds have been repeatedly interpreted using X-ray diffraction structural analysis data, leading to an understanding of the role of the chelate-forming M–O, M–S, M–Se, and M–N chemical bonds. Physicochemical and X-ray diffraction data on the M–O, M–S, and M–Se chemical bond nature in chelate compounds of transition metals and conclusions regarding additional M←S π-bonding (direct donor-acceptor π-bond) have been examined in our previous work [8, 9].

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* Dedicated to the memory of Academician Yurii Bankovsky, the founder of the chemistry of 8-mercaptoquinoline (December 22, 1927 – January 28, 2003) on the occasion of the eightieth anniversary of his birth.

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Comparison of the physicochemical properties and structural data of chelate compounds obtained from 8-quinolinol, 8-quinolinethiol, 8-quinolineselenol, and their derivatives is uniquely important in coordination chemistry and comparative crystal chemistry since it shows the effect of substituting one ligand atom (Group VI atoms O, S, and Se) on the properties and structure of both the reagents and corresponding chelate compounds.

Reviews have appeared summarizing the results of our X-ray diffraction structural investigations of $M(SQu)_2$ [10] and $M(SQu)_3$ compounds [11] obtained up to 1998. Analysis of the molecular structure of $M(SQu)_3$ complexes has shown that the metal coordination polyhedron in these compounds is usually a more or less distorted octahedron (3S + 3N) but the spatial arrangement of the sulfur and nitrogen atoms may correspond to two isomers: symmetrical isomer **A** and asymmetrical isomer **B** (Fig. 1) [12].

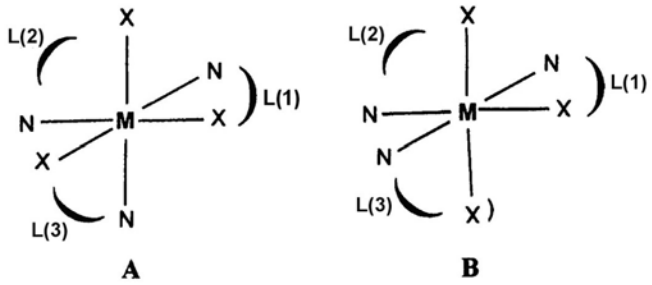
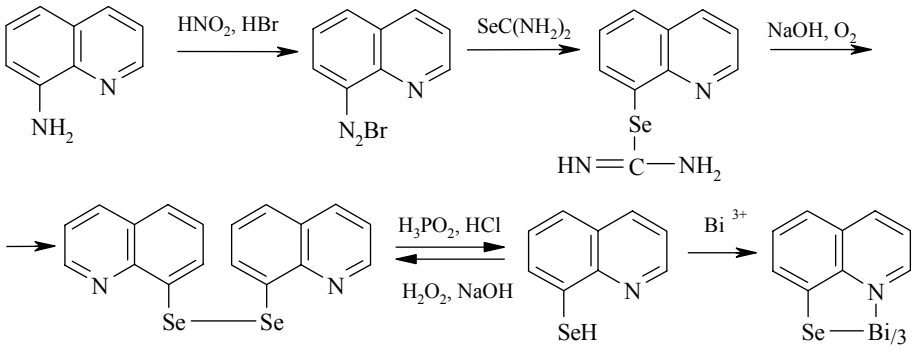


Fig. 1. Isomers of the octahedral environment of the central atoms in complexes $M(SeQu)_3$, $M(SQu)_3$, and $M(OQu)_3$. **A**) symmetrical isomer, **B**) asymmetric isomer; X = O, S, or Se.

The arrangement of the atoms in the coordination nodes of studied 8-quinolinolates, 8-quinolinethiolates, and 8-quinolineselenolates of trivalent metals of Group III (Ga, In, Tl) and Group VIII (Co, Rh, Ir, Fe) corresponds to isomer **B**. The electronic structure of Group V *p*-elements in the incomplete valence state (As, Sb, Bi) accounts for the formation of the metal coordination polyhedron as isomer **A** in the 8-quinolinolates, 8-quinolinethiolates, and 8-quinolineselenolates of these metals [2, 11, 13-16]. The crystal structures of these 8-quinolineselenolates, including bismuth 8-quinolineselenolate, $Bi(C_9H_6NSe)_3$ (**1**) studied in the present work, hold interest in comparative crystal chemistry for clarifying the role of the unshared electron pair (UEP) in formation of the metal coordination polyhedron. It is known [17] that three types of behavior of unshared electron pairs are possible that differ in their effect on the shape of the coordination polyhedron and on the distribution of bond lengths and bond angles: 1) stereochemical activity, i.e., the UEP occupy the site of a ligand (Ψ), 2) complete delocalization of the UEP, and 3) partial stereochemical activity.

Our data for an X-ray diffraction study of the structure of complex **1** when compared to the structural data for bismuth 8-quinolinethiolate, $Bi(C_9H_6NS)_3$ (**2**) [13] permit us to clarify the effect of replacing the ligand atom S→Se on the molecular and crystal structure of these compounds and the state of the UEP in analogous complexes.



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Complex **1** was synthesized in 83.5% yield by the general scheme described in our previous work [6]. The molecular and crystal structure of **1** was established by X-ray diffraction structural analysis.

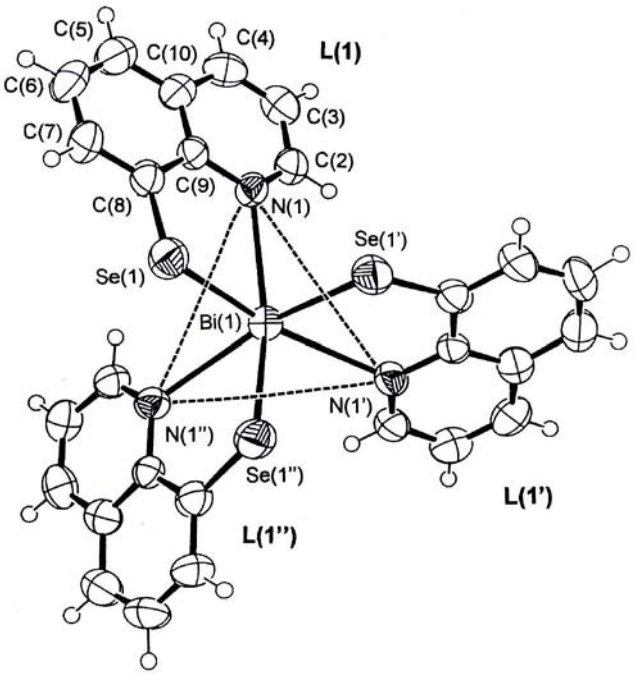

Fig. 2. General view of $Bi(C_9H_6NSe)_3$ with numbering of the atoms. Ligands **L(1), L(1'),** and **L(1")** are identical. The N(1)/N(1')/N(1") face of the octahedral environment of the bismuth atom is noted (3S + 3N + Ψ).

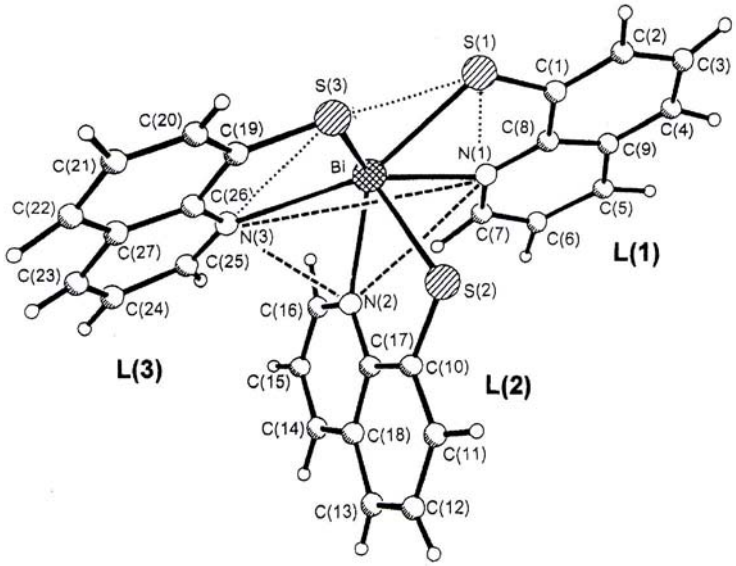

Fig. 3. General view of $Bi(C_9H_6NS)_3$ with numbering of the atoms. The N(1)/N(2)/N(3) plane in the pentagonal environment of the bismuth coordination polyhedron is noted (3S + 3N + Ψ).

The molecular structure of complex **1** (Fig. 2), similar to the structure of complex **2** (Fig. 3 [13]) is a neutral three-ring system. The central bismuth atom in the unit cell of the crystal structure of **1** occupies a special position (0, 0, 0.1659) on a three-fold axis. Thus, the molecule possesses inherent three-fold symmetry. The selenium and nitrogen atoms of the three 8-quinolineselenol ligands have bidentate coordination to the bismuth atom and three identical five-membered –Bi–Se–C–C–N– metallocycles are formed. The structure of the metallocycles is markedly deformed since they are formed by five types of valence bonds. Furthermore, the Se(1)Bi(1)N(1) chelate angle, ω = 70.26(11)° is much smaller and the Bi(1)Se(1)C(8) valence angle (ω = 103.13(19)°) is greater than 90°. The extrusion of the bismuth atom from the Se/C/C/N mean-square planes in the metallocycle is 0.769(3) Å. The bismuth and selenium atoms are extruded from the mean-square planes of the corresponding quinoline rings in opposite directions by 0.556(3) and -0.253(1) Å, respectively. The chelate rings have *envelope* conformation with the dihedral angle between the Se/Bi/N and Se/C/C/N planes equal to 160.2(1)°. The Se/Bi/N coordination planes in complex **1** are arranged approximately perpendicularly at a dihedral angle θ = 85.52(5)°. The dihedral angle between the mean-square planes of the ligands θ = 74.1(1)°. The Bi^{3+} cation has octahedral coordination (3Se + 3N) as a distorted symmetric isomer **A** (see Fig. 1). The lengths of the major Bi–Se bonds, *l* = 2.7109(8) Å (Table 1), corresponds to the sum of the covalent radii of the bound atoms ($r_{Bi} + r_{Se}$ = 2.711 Å [18]). The length of the Bi–Se bond is in accord with the Cambridge Structural Database (Version 5.27, November, 2005). However, we did not detect this bond in the five-membered metallocycles, i.e., this is not a chelate bond. The major angles involving the Bi–Se bond, SeBiSe, ω = 88.11(3)° and the major coordination polyhedron of the bismuth atom is a trigonal bipyramid (Bi + 3Se) with a bismuth at the apex.

The weaker Bi···N coordination bonds are in *trans* position relative to the Bi–Se bonds, *l* = 2.796(5) Å and are slightly longer than those in complex **2**, l_{av} = 2.77°, and in bismuth 2-methyl-8-quinolinethiolate, l_{av} = 2.745 Å [18], and 23% longer than the sum of the covalent radii of the corresponding atoms ($r_{Bi} + r_{Se}$ = 2.276 Å [19]). The NBiN valence angles between weak Bi···N coordination bonds, ω = 112.58(10)°, which are close to the tetrahedral angle 109.5°. The SeBiN interligand angles are 84.93(11)°. The distortion of the octahedral coordination of the bismuth atom is clearly characterized by the diagonal SeBiN angles, ω = 157.44(11)°, which differs from the ideal value of 180°. The sum of valence angles of the type SeBiSe is 264.33°. The sum of the NBiN type angles is 337.74°, which indicates that the Bi···N bonds behavior are strongly displaced and lie approximately in a single plane. The plane of the nitrogen atoms N/N/N, which is seen as a face of the octahedron, is 0.777(5) Å from the central bismuth atom. There is room for a stereochemically active UEP perpendicular to the N/N/N plane. The three equal Bi–Se bonds and the three Bi···N bonds, corresponding valence angles, and the high possible inherent symmetry of a molecule of **1** indicate the existence of an UEP in such a form. The Se/Se/Se plane, which is parallel to the N/N/N plane, is located on the opposite side relative to the central bismuth atom and is at a distance of -1.6156(48) Å from this atom. Taking account of the stereochemically active UEP, the coordination polyhedron of the bismuth atom is a centered Ψ-octahedron (3Se + 3N + Ψ) with distortion in the N/N/N face.

TABLE 1. Characteristic Bond Lengths and Valence Angles in $Bi(C_9H_6NSe)_3$

Bond	*l*, Å	Angle	ω, deg
Bi(1)–Se(1)*	2.7109(8)	Se(1)Bi(1)N(1)*[2]	70.26(11)
Bi(1)–N(1)	2.796(5)	Se(1)Bi(1)Se(1')	88.11(3)
Se(1)–C(8)	1.910(7)	N(1)Bi(1)N(1')	112.56(10)
N(1)–C(2)	1.301(9)	Se(1)Bi(1)N(1')	84.93(11)
N(1)–C(9)	1.384(7)	Se(1)Bi(1)N(1")	157.44(11)
C(9)–C(10)	1.417(9)	Bi(1)Se(1)C(8)	103.13(19)

* *l* Bi(1)–Se(1) = *l* Bi(1)–Se(1') = *l* Bi(1)–Se(1") etc.

*[2] ω Se(1)Bi(1)Se(1') = ω Se(1)Bi(1)Se(1") = ω Se(1')Bi(1)Se(1") etc.

The Se(1)–C(8) bond length in **1**, l = 1.910(7) Å, as in antimony 8-quinolineselenolate, l = 1.911(6) Å [2], is slightly less than the sum of the covalent radii of the corresponding atoms ($r_{Se} + r_C$ = 1.933 Å [19]) but, in contrast to platinum 8-quinolineselenolate (l = 1.858(15) Å [20]) and palladium 8-quinolineselenolate (l = 1.881(4) Å [21]), the Se–C bond has no double bond character.

The quinoline rings are planar to ±0.05 Å and, in general, have the ordinary structure. However, the N(1)–C(2) bond length, l = 1.301(9) Å, is much less than the N(1)–C(9) bond length, l = 1.384(1) Å, and corresponds to a C_{sp^2} = N double bond, l = 1.304 Å, found in furoxane [22]. Such geometry of the pyridine ring taking account of the C(2)N(1)C(9) angle, ω = 119.1(6) 2°, indicates minimal 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 are shortened (av. 1.360 Å). The lengths of the other bonds lie in the range 1.397(12)–1.422(10) Å (Δ = 0.025 Å), l_{av} = 1.414 Å. The central C(9)–C(10) bond of the quinoline system, l = 1.417(9) Å, in complex **1** is not one of the shortened C–C bonds. The CCC angles differ only slightly from 120° (±2.5°).

The bismuth atoms in the crystal structure of **1** (Fig. 4) are found on a three-fold axis in a ···Bi···Bi···Bi··· geometrical series with alternating distances 5.349(7) Å···10.773(7) Å···5.349(7) Å. The shortest Bi···Bi distances are found between the bismuth atoms related by a symmetry center at (0, 0, 0). The N/N/N planes and, thus, the UEP are arranged toward the centers. Direct contacts between the metal atoms are observed when adjacent UEP polyhedra are oriented toward each other [23].

The intermolecular distances correspond to π-π intermolecular contacts. The π-π interaction between centrosymmetrically related quinoline systems of different ligands is characterized by a distance of 4.439 Å between the centroids of the quinoline systems. The distances between the planes containing the quinoline systems are 3.386 Å. This interaction apparently leads to the large flexure of the five-membered metallocycles at the Se···N line.

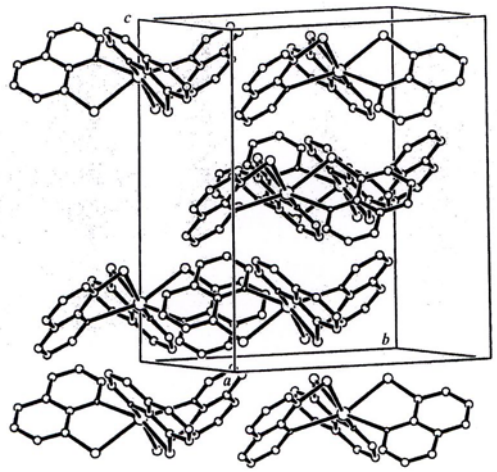

Fig. 4. Fragment of the packing of molecules of complex **1** indicating the edges of the unit cell. Hydrogen atoms are not shown.

The molecular structure of complex **1** is isostructural to antimony 8-quinolineselenolate [2] but differs significantly from the structure of bismuth 8-quinolinethiolate (**2**). The S→Se replacement of ligand atoms in analogous bismuth complexes leads to a change in the type of coordination polyhedron of the central atom. Complex **2** is an exception since the arrangement of the sulfur and nitrogen atoms in the environment of the bismuth atoms does not correspond to isomer **A** (see Fig. 1). Ligands **L(1)** and **L(3)** in complex **2** are located

almost in a single plane, to which the plane of ligand **L(2)** is approximately perpendicular. The corresponding dihedral angles between the 8-quinolinethiol ligands θ = 88.7, 13.6, and 101.5°. The trigonal arrangement of the major Bi–S bonds is retained but the Bi···N coordination bonds are arranged at angles of 76.3, 150.1, and 76.3°. The bismuth atom coordination polyhedron is a distorted pentagonal pyramid (3S + 3N) with a sulfur atom at the apex most strongly bound to the bismuth atom, while the base consists of two sulfur atoms and three nitrogen atoms. The direction of the possible localization of the UEP is approximately perpendicular to pyramid base (2Se + 3N). Taking account of the position of the UEP for the bismuth atom in complex **2**, the coordination polyhedron is a ψ-pentagonal bipyramid (3S + 3N + ψ) with S(2) and the UEP in axial positions (Fig. 3). Two centrosymmetric dimers are formed in the crystal structure of complex **2** in the direction of the UEP through intermolecular contacts Bi···Bi, $l = 3.978$ Å, Bi···S(1'), $l = 3.565$ Å, and Bi···N(1'), $l = 3.492$ Å, which are stronger than for the dimers in complex **1**.

Spectral studies of complexes **1** and **2** in chloroform revealed absorption maxima at 400 nm for complex **1** and at 396 nm for complex **2** [1,4], indicating only slight differences in conjugation between the two complexes.

It was of interest to elucidate the biological properties of complexes **1** and **2**, which are analogous in composition but differ in structure. Professor E. Lukevics and his coworkers have studied the cytotoxicity of a series of complexes of 8-quinolineselenol and 8-quinolinethiol synthesized in our laboratory [6, 24] to evaluate the effect of the ligand on the cytotoxicity of complexes containing M–S and M–Se bonds. Complex **2** was found to have high cytotoxicity in all the tumor cell lines studied but, unfortunately, are also highly toxic relative to normal cells. Complex **1** is efficient relative both to Neuro 2A and melanoma B16.

In conclusion, we note that, in contrast to the other series of analogous palladium [21], mercury [25], and antimony complexes studied [2], the S→Se replacement of ligand atoms in bismuth complexes is accompanied by a radical change in molecular structure, which may be attributed to the effect of the bismuth UEP.

EXPERIMENTAL

Bismuth 8-quinolineselenolate (1) was synthesized according to our previous procedure [6].

X-ray Diffraction Structural Analysis. Monocrystals of complex **1** were grown by slow cooling of a hot saturated chloroform solution of the complex. The diffraction pattern of a 0.15×0.15×0.18-mm monocrystal of complex **1** was taken at 20°C on an Bruker-Nonius Kappa CCD automatic diffractometer with φ- and ω-scanning using MoKα radiation and graphite monochromator to $2\theta_{max} = 60°$. The unit cell parameters of trigonal monocrystals of complex **1** (space group $R\bar{3}$) are as follows for a hexagonal axes: $a = 17.1829(7)$, $c = 16.1223(8)$ Å, $V = 4122.4(3)$ Å^3, $Z = 6$; and for an rhombohedral axes: $a = 7.8541(5)$ Å, $\alpha = 49.863(9)°$, $V = 1374.1(1)$ Å^3, $Z = 2$, $M_r = 830.3$, $D_x = 2.007$ g/cm^3, $\mu = 10.408$ mm^{-1}. An absorption correction was carried out directly by calculating the transmission factor A using an integral formula after indexing 12 faces of the crystal polyhedron. The NUMABS program in the maXus package [26] was used for the calculation. The molecular structure was found by the heavy atom method and refined by the method of least squares for 1851 reflections with $I > 2\sigma(I)$ to $R = 0.0480$ ($wR2 = 0.1319$) anisotropically for the non-hydrogen atoms taking account of the hydrogen atom coordinates calculated geometrically. The programs of Mackay [26] and Otwinowski [27] were used.

The crystallographic data, atomic coordinates, temperature parameters, bond lengths, and valence angles in complex **1** were deposited in the Cambridge Structural Database.

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