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SYNTHESIS AND CRYSTAL STRUCTURE OF A SOLVATE OF ARSENIC 4,6-DIMETHYL-8-QUINOLINETHIOLATE*

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A crystallosolvate of arsenic 4,6-dimethyl-8-quinolinethiolate, $As[4,6\text{-}Me_2C_9H_4NS]_3{\cdot}CHCl_3$ has been synthesized. The molecular and crystalline structures of the compound have been determined by X-ray structural analysis. The influence of the composition and structure of the ligand on the geometry of the coordination environment of the central arsenic atom in the investigated crystal structures of intracomplex compounds of 8-quinolinethiols is discussed.

Keywords: 8-quinolinethiolates, intracomplex arsenic compounds, molecular and crystal structure.

The present study is a continuation of systematic investigations of the structure of intracomplex compounds of 8-quinolinethiol, summarized in [1-3]. Investigation results usually are in agreement with the well established role of the cation in the organization of the crystal structure of the substance. However, among the crystal structures of 8-quinolinethiolates there are groups of ligands, the composition and structure of which influence the geometry of the coordination environment of the cation. The most marked effect on the environment of the cation and also on the physicochemical properties of the corresponding complexes are demonstrated by ligands with a substituent in position 2 of the quinoline nucleus [4]. Thus the presence of a methyl group in this position leads, as a result of steric hindrances, to a tetrahedrally distorted planar environment (2S+2N) for the central atom in 2-methyl-8-quinolinethiolates of palladium and platinum [5, 6] in comparison with the planar centrosymmetric complexes $Pd(C_9H_6NS)_2$ [7] and $Pt(C_9H_6NS)_2$ [8]. In turn, the structural similarity of 2-phenyl-8-quinolinethiolates of transition (Co, Ni) and non-transition (Zn, Hg) metals with the distorted tetrahedral environment (2S+2N) of the central atoms with complex compounds described above, is caused by an intramolecular π-π interaction of the quinoline nucleus of one ligand with the phenyl ring of another ligand of the same complex [9].

It seemed of interest to investigate the effect of composition and structure of the ligand in intracomplex compounds of partial valent *p*-elements of the V group, As(III), Sb(III), and Bi(III), in which the environment of the central atom is determined not only by the nature of the cation, but also by the overall interaction of the lone electron pair (LEP) of the cation and ligand. In the example of the obtained new complex $As(4,6\text{-}Me_2C_9H_4NS)_3{\cdot}CHCl_3$ (**1**) and the previously investigated complexes $As(C_9H_6NS)_3$ (**2**) [10], (**3**) [11],

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*Dedicated to the memory of Academician E. Lukevics.

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$As(4\text{-}MeC_9H_5NS)_3$ (**4**) [12], and $As(4\text{-}MeOC_9H_5NS)_3$ (**5**)*, the effect of the composition and structure of methyl- and methoxy-8-quinolinethiol ligands on the formation of the coordination sphere of the central arsenic atom has been shown.

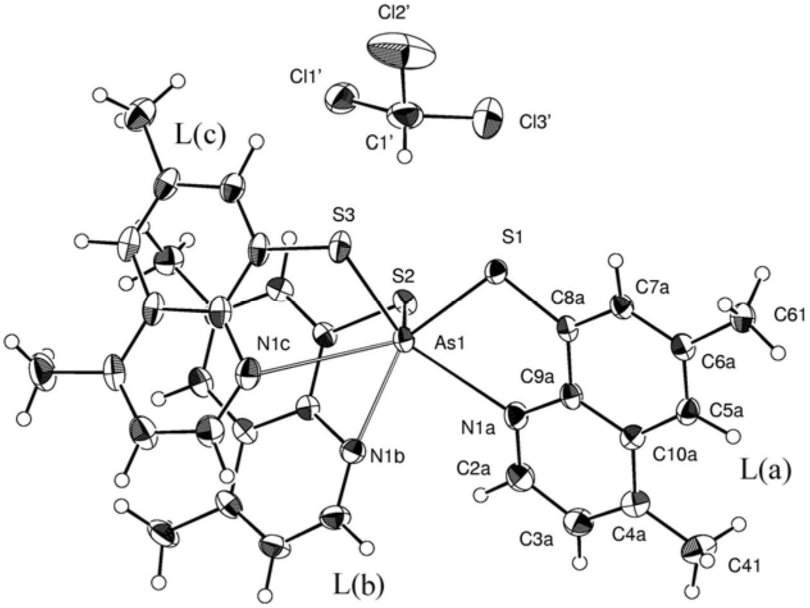

Fig. 1. General view of the $As(4,6\text{-}Me_2C_9H_4NS)_3{\cdot}CHCl_3$ complex with designation of atoms.

TABLE 1. Some Characteristic Bond Lengths (*l*) and Values of Valence Angles (ω) in Complex **1**.

Bond	*l*, Å	Angle	ω, deg.
As(1)–S(1)	2.2699(8)	S(1)–As(1)–N(1a)	75.11(6)
As(1)–S(2)	2.2861(8)	S(2)–As(1)–N(1b)	65.34(5)
As(1)–S(3)	2.3262(8)	S(3)–As(1)–N(1c)	67.38(7)
As(1)···N(1a)	2.637(1)	S(1)–As(1)–S(2)	94.16(3)
As(1)···N(1b)	3.236(1)	S(1)–As(1)–S(3)	82.22(4)
As(1)···N(1c)	3.051(1)	S(2)–As(1)–S(3)	97.25(3)
S(1)–C(8)	1.772	N(1a)–As(1)–N(1b)	75.27(8)
	1.767(2)–1.775(2)*	N(1a)–As(1)–N(1c)	133.60(9)
N(1)–C(2)	1.315	N(1b)–As(1)–N(1c)	67.79(9)
	1.310(3)–1.322(3)*	S(3)–As(1)–N(1a)	156.91(6)
N(1)–C(9)	1.367	S(1)–As(1)–N(1b)	144.06(6)
	1.364(2)–1.372(3)*	S(1)–As(1)–N(1c)	147.75(7)
C(9)–C(10)	1.422	S(3)–As(1)–N(1b)	127.46(6)
	1.420(3)–1.424(3)*	As(1)–Se(1)–C(8)	104.7
			103.5(1)–106.42(8)*

*Limits of variation of lengths of similar bonds and valence angles in ligands L(a), L(b), L(c).

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Compound As[4,6-$Me_2C_9H_4NS$]$_3$ was obtained as a colorless amorphous powder. Recrystallization of the substance from a chloroform–ethanol mixture was accompanied by inclusion of a molecule of chloroform into the crystals. The molecular and crystal structures of the complex As(4,6-$Me_2C_9H_4NS$)$_3$·$CHCl_3$ (**1**) were determined by X-ray structural analysis (Fig. 1).

In the complex the arsenic atom and the sulfur atoms of three ligands form bonds close in lengths to As(1)–S, l_{av} = 2.2941 Å (Table 1). They are somewhat longer than the sum of the covalent radii of the atoms (R_{As}+R_S = 2.28 Å [13]), but somewhat shorter than the mean As–S bond length in the structures of complexes **2-5** (2.3010 to 2.3179 Å [10-12]). The As–S bond lengths are in agreement with the data of the Cambridge Structural Database (version 5.26). The As(1)–S bonds are disposed roughly at right angles S–As(1)–S (ω_{av} = 91.21°), and the disposition of the atoms in the (As(1)+3S) fragment may be characterized as an insignificantly distorted trigonal pyramid with the arsenic atom at the vertex. The As(1) atom deviates from the 3S plane by -1.301(1) Å.

The interatomic As···N distances in complex **1** are different and significantly exceed the sum of the covalent radii of the atoms (R_{As}+R_N = 1.976 Å [13]). The As(1)···N(1a) distance is found to be within the limits of the As···N distances in complexes **2-5**, which correspond approximately to a value between the sums of the covalent and van der Waals radii (r_{As}+r_N = 3.3 [14] and 3.576 Å [15]) and is interpreted as weak coordination bond, which closes the metallacycle. The As(1)···N(1b) and As(1)···N(1c) distances are closer to the sum of the van der Waals radii. It may be considered that in this case closing of the corresponding metallacycles does not occur, in favor of which is also the large deviation of the As(1) atom position from the mean square planarity of the corresponding quinoline nuclei (-1.748(1) (L(b)) and 1.468(1) (L(c)) as distinct from -0.737(1) Å (L(a))). Hence in complex **1**, similarly to complex **2**, one ligand is bidentate (S, N), and the remaining two are monodentate (S). However, as will be shown later, a directed weak second interaction As(1)···N could not be excluded.

The values of the N–As(1)–N angles also differ strongly, Δ = 65.8° (Table 1). The values obtained are in agreement with those in complex **2**, but crucially differ from the approximately tetrahedral angles in complexes **3** and **5** (Table 2) characteristic of the symmetrical isomer of octahedral complexes [16]. In complex **1**,

TABLE 2. Lengths and Configurations of Weak As···N Coordination Bonds in Complexes **1-5**

Complex	Distance As···N, Å	N–As–N angle, deg.	Coordination polyhedron of As atom
1	2.637(1)	67.79(9)	"Swing" (3S + N) or ψ-trigonal
	3.0501(1)	75.27(8)	bipyramid (3S + N + E)
	3.236(1)	133.60(9)	
2*	2.491(4)	73.0(1)	"Swing" (3S + N) or ψ-trigonal
	2.801(4)	87.0(1)	bipyramid (3S + N + E)
	3.422(4)	133.2(2)	
3*	2.641(3)	104.1(1)	Distorted octahedron (3S + 3N)
	2.692(5)	106.3(1)	or one-capped ψ-octahedron
	2.719(4)	109.6(1)	(3S + 3N + E)
4*	2.524(4)	80.8(1)	Trigonal bipyramid (3S + 2N)
	2.672(2)	115.2(2)	or ψ-octahedron (3S + 2N + E)
	2.964(2)	112.8(1)	
5*	2.688(3)	110.12(9)	Distorted octahedron (3S + 3N)
	2.688(3)	110.12(9)	or one-capped ψ-octahedron
	2.688(3)	110.12(9)	(3S + 3N + E)

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*Data on complex **2** are taken from [10], for **3** from [11], for **4** from [12], for **5** from unpublished work by the authors (see footnote on p. 1545).

the sum of the N–As(1)–N angles, equal to 276.6° is the least of all found in complexes **2-5**. The As(1) atom emerged from the plane of 3N by 1.013(1) Å. In the space between the As–N vectors, localization is possible for the stereochemically reactive LEP, which prevents closure of two metallacycles.

The coordination bond As(1)···N(1a) is disposed in an approximately *trans* position to the weaker As(1)–S(3) bond. In accordance with the discussed geometric parameters the coordination polyhedron of the As(1) atom may be characterized as a "swing" (3S+N). However, analysis of all the angle values in the As(1) atom environment (Table 1), taking into account possible weak secondary interactions As(1)···N(1b) and As(1)···N(1c), enabled the disposition of the S(1), S(3), N(1a), N(1b), and N(1c) atoms to be interpreted geometrically as the strongly distorted base of a pentagonal pyramid. In such a case the coordination polyhedron of the As(1) atom is a distorted pentagonal pyramid (3S+3N) with sulfur atom S(2) at the vertex or a ψ-pentagonal bipyramid with sulfur atom S(2) and LEP at the vertices. The deviation of the pyramid base atoms from its mean-square plane was 0.007(1) Å for atom S(1), 0.042(1) for S(3), -0.411(3) for N(1a), 0.699(3) for N(1b), and 0.696(3) Å for N(1c). The central As(1) atom is deviated by -0.037(3) Å from the base of the pyramid, but atom S(2) on the opposite side is deviated by 2.267(1) Å. In the *trans* position the S(2) atom (angle S(2)–As(1)···C(5a) 169.9°) has a shortened contact As(1)···C(5a) (1-*x*, -*y*, 2-*z*) with length of 3.489(2) Å. A pair of contacts As(1)···C(5a) joins the complexes into dimers (Fig. 2). Contact As(1)···H(5a) does not satisfy the criterion for a weak intramolecular hydrogen bond involving LEP proposed in [11].

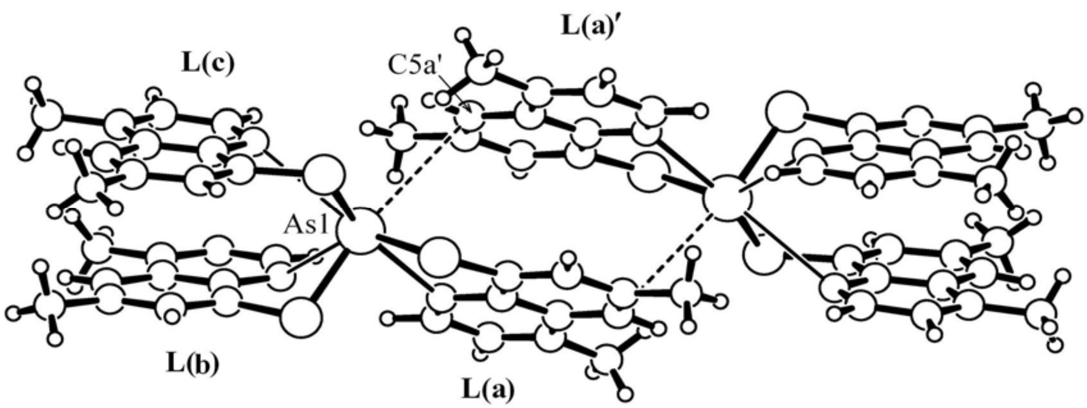

Fig. 2. Dimer of complex **1**.

The dihedral angle between the planes S(1)–As(1)–N(1a) and S(2)–As(1)–N(1b) was 85.78(3)°, between the planes S(1)–As(1)–N(1a) and S(3)–As(1)–N(1c) was 164.56(4)°, and between the planes S(2)–As(1)–N(1b) and S(3)–As(1)–N(1c) was 108.37(3)°. The dihedral angles between the bend of the five-membered rings S, As, N, C, C along the N···S line were 26.22(8)°, 121.07(3)°, 127.7(1)° in the ligands L(a), L(b), and L(c), respectively. The chelate ring –S(1)–As(1)···N(1a)–C(9a)–C(8a)– has an "envelope" conformation, the deviation of the As(1) atom from the mean-square plane carried through the remaining atoms of the ring was -0.928(3) Å.

The S–C bond lengths of complex **1** (Table 1) were insignificantly greater than the standard lengths of a sesqui S–C(sp^2) bond (1.76 Å) [17]. The values of valence angles of the As(1)–S–C(8) type were somewhat less than the value of an ideal tetrahedral angle.

The 4,6-dimethyl-8-mercaptoquinoline molecules have the usual structure (Table 1). The methyl groups are localized in the ligand plane. The structure of the $CHCl_3$ molecule is characterized by the bonds C(1')–Cl close in lengths from 1.741(3) to 1.746(4) Å and values of the valence angles Cl–C(1')–Cl from 109.6(2)° to 111.3(2)°. The $CHCl_3$ molecules are packed as centrosymmetric dimers with intermolecular contacts Cl(1')···Cl(1') (-*x*, 1-*y*, 2-*z*) with a length of 3.481(1) Å ($2r_{\mathrm{Cl}}$ = 3.50 Å [14]).

The general shape of the complex, which is characterized by the dihedral angles between the mean-square plane of the quinoline ligands L(a)/L(b), L(a)/L(c), and L(b)/L(c) equal to 35.9(1)°, 36.2(1)°, and 3.9(1)°, respectively, differs significantly from those of complexes **3-5**. The virtually parallel dispositions of ligands L(b) and L(c) of complex **1** are caused by the π-π interaction of the aromatic systems (distance between the centroids of the heterocycle N(1c), C(2c), C(3c), C(4c), C(9c), C(10c) and of the benzene ring C(5b), C(6b), C(7b), C(8b), C(9b), C(10b) amounts to 3.479 Å).

The complexes $As(4,6-Me_2C_9H_4NS)_3$ in the crystals are packed in layers parallel to the (0 1 0) plane (Fig. 3). The chloroform molecules link the ligands into layers, since the contacts Cl(1')···H(7b) (*x*, *y*, *z*) with geometric parameters Cl(1')···C(7b) 3.841(4) Å, Cl(1')···H(7b) 2.86 Å, Cl(1')···H(7b)–C(7b) 168° in agreement with [18], may be interpreted as weak C–H···Cl hydrogen bonds.

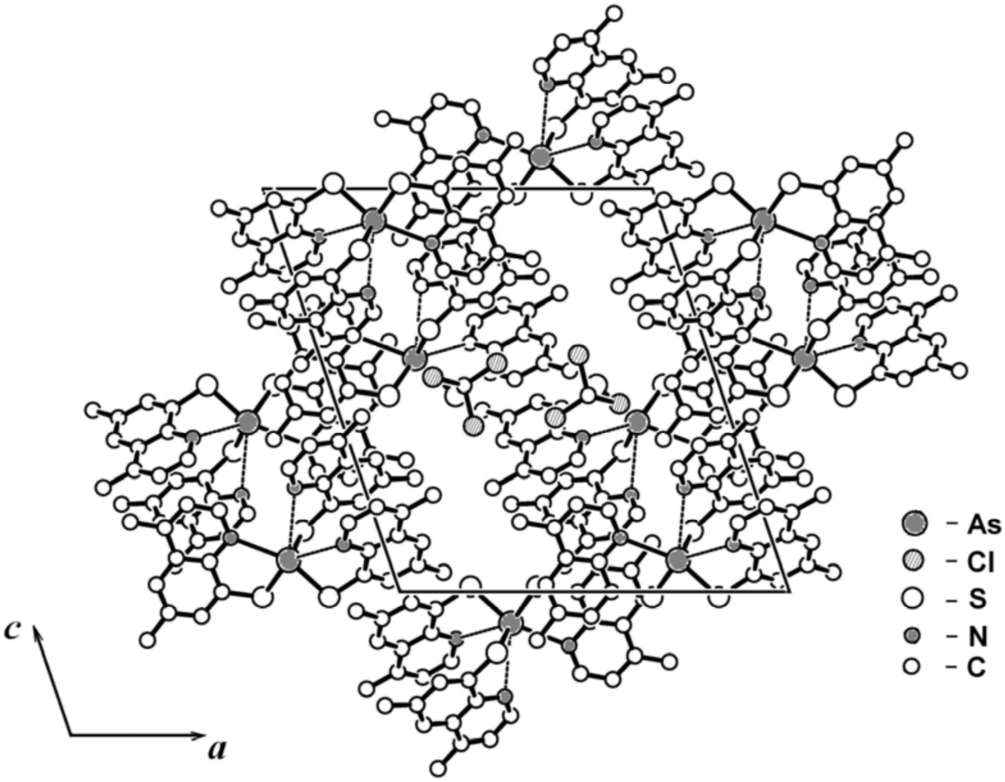

Fig. 3. Complexes **1** packing in crystal structure.

In conclusion, by comparing the investigated intracomplex compounds **1-5** it should be noted that in the molecules described the coordination environment of the arsenic atom depends on the composition and structure of the ligand. Since the structure of the main coordination polyhedron (As+3S) is unchanged, the existing weak coordination As···N bonds determine the type of polyhedron. The lengths and configuration of these bonds may be changed within wide limits both on going from one complex to another and in a single molecule. The presence of methyl substituents in the second and sixth positions of the ligand leads in a complex to the predominant role of weak (As···N, π-π) interactions in the formation of these intracomplex compounds.

EXPERIMENTAL

Synthesis of Complex $As(4,6-Me_2C_9H_4NS)_3$ and Its Solvate (1). 20% Aqueous NaOH was added dropwise to a solution of 4,6-dimethyl-8-mercaptoquinoline (0.50 g, 2.65 mmol) in ethanol (15 ml) and water (3 ml) with heating until the solution acquired a yellow color, after which the mixture was diluted with water to 50 ml. Separately As_2O_3 (0.08 g, 0.40 mmol) was suspended in water (10 ml), 20% aqueous NaOH (several drops) was added and the mixture was shaken until complete dissolution of the solid. The obtained arsenic hydroxide solution was added to the first solution. The reaction mixture was neutralized by adding acetic acid dropwise with stirring until a neutral reaction (pH 7), the precipitated colorless substance was filtered off, washed with water, and air-dried. Yield 0.45 g (88%). Found, %: C 62.04; H 5.12; N 6.63; S 14.92. $C_{33}H_{30}N_3S_3As$. Calculated, %: C 61.60; H 5.17; N 6.54; S 14.96.

Light-yellow monocrystals of solvate **1** were grown from a chloroform–ethanol, 1:1 mixture.

X-ray Structural Analysis of Compound 1. Parameters of the unit cell of the crystal and a diffraction pattern were obtained from a monocrystal of compound **1** of size 0.17×0.16×0.05 mm at -80(2)°C on a Bruker Nonius Kappa CCD automatic diffractometer using scanning by φ and ω (λMoKα-radiation, graphite monochromator) to $2\theta_{max} = 59^o$. Monocrystals of solvate **1** were monoclinic, space group was $P2_1/n$. Crystal lattice parameters: a = 16.4671(2), b = 12.0801(2), c = 17.9947(3) Å, β = 108.7908(7)°, V = 3388.79(9) Å^3, M = 759.116, $F(000)$ = 1552, μ = 1.45 mm^{-1}, ρ_{calc} = 1.488 g/cm^3, Z = 4. The molecular structure of the compound was established by the direct method and was refined by a full-matrix least squares method on 6505 reflections with $I > 3\sigma(I)$ to an R factor = 0.044 (wR_2 = 0.110, $GOOF$ = 1.083) in an anisotropic approximation for the non-hydrogen atoms. The methyl groups hydrogen atoms positions were found from a difference synthesis, the remaining H atoms coordinates were calculated geometrically. The coordinates of the hydrogen atoms were refined with a "rider" model. The programs maXus and Denzo were used [19, 20]. The crystal structure has been deposited in the Cambridge Crystallographic Data Center (CCDC 856937).

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