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# STRUCTURE OF PALLADIUM QUINOLINE-8-SELENOLATE $Pd(C_9H_6NSe)_2$

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*The molecular and crystal structure of palladium quinoline-8-selenolate $Pd(C_9H_6NSe)_2$ has been determined by X-ray structural analysis. The structures of the five-membered metallocycles of palladium 8-hydroxy-, 8-mercapto-, and 8-hydroselenoquinolinates of one type are compared.*

**Keywords:** 8-mercapto-, 8-hydroseleno-, and 8-hydroxyquinolinates, chelate compounds of palladium, molecular structure.

A great number of the complexes of 8-mercaptoquinoline and its derivatives [1] have been synthesized and structurally examined while investigating the metal–sulfur bond in chelate compounds of transition and nontransition elements in the Laboratory of Chelate Compounds of the Institute of Inorganic Chemistry of Riga Technical University. Where possible the results obtained were compared with the structural data of the corresponding 8-hydroxyquinolinates.

To clarify the character of the M–Se(S, O) bond and the overall picture of their dynamics in five-membered isomolecular complexes of one type with ligand atoms of one group (VI), the synthesis and X-ray structural investigations have been continued on chelate compounds of 8-hydroselenoquinoline and its derivatives. Systematic structural investigations on chelate compounds the ligands of which would contain the coordinationally reactive SeH group are not known in the literature. Consequently the main problem was the coordination possibility of selenium(II) as a ligand atom and the experimental determination of the lengths of the M–Se bonds in chelate compounds. Previously we established the molecular and crystal structures of the complexes $Pt(C_9H_6NSe)_2$, $Cd(C_9H_6NSe)_2$ [2], $Zn(C_9H_6NSe)_2$ [3, 4], $In(C_9H_6NSe)_3$ [5], and $Sb(C_9H_6NSe)_3$ [6].

In the present work the synthesis and the results of the X-ray structural investigation of palladium(II) quinoline-8-selenolate $Pd(C_9H_6NSe)_2$ (**1**) are described. Since the crystal structures of palladium 8-mercaptoquinolinate (**2**) [7] and palladium 8-hydroxyquinolinate (**3**) [8] are known, a comparison of the structure of the five-membered metallocycles of one type and consideration of the dynamics of the experimentally found Pd–Se, Pd–S, Pd–O, and Pd–N bond lengths is possible.

The crystal structure of complex **1** consists of neutral centrosymmetric $Pd(C_9H_6NSe)_2$ molecules (Fig. 1). The palladium atoms are disposed at the centers of symmetry [(000)] of the unit cell. They coordinate in a bidentate manner (Se, N) with two quinoline-8-selenol ligands, the chelate angle Se(1)PdN(1) is 85.6(1)°. Surrounding the central palladium is a *trans* square (2Se + 2N). The Pd–Se and Pd–N bonds (Table 1) have a covalent character, since their lengths are less than the sum of the covalent radii of the corresponding atoms ($r_{Pd} + r_{Se} = 2.537$ and $r_{Pd} + r_N = 2.102$ Å [9]. The Se–C(8) bond length = 1.881(4) Å is close to the value of

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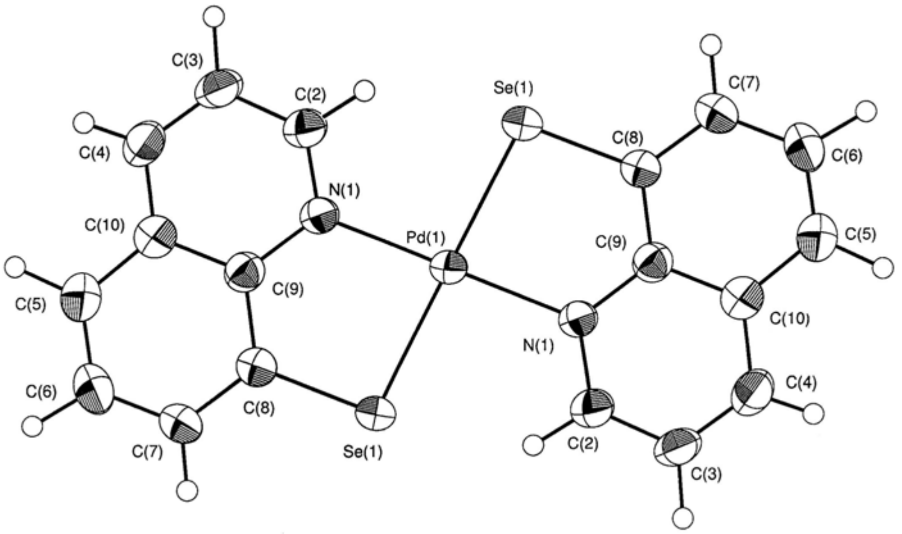

Fig. 1. General form of the $Pd(C_9H_6NSe)_2$ complex with numbering of the atoms.

1.893 Å given in [10] for the $Csp^2$–Se(II) fragment in tetraselenafulvalene. The valence angle PdSe(1)C(8), $\omega = 95.1(1)°$, indicates the octahedral disposition of electrons of the outer shell of the selenium atom and the possibility of additional strengthening of the Se–Pd bond due to π bonding [11].

TABLE 1. Geometric Parameters of the Molecules of the Five-membered Metallocycles in the Isomolecular Complexes **1-3***

| Bond*2 | *l*, Å | | |
|---|---|---|---|
| | **1** | **2** | **3** |
| Pd–X | 2.404(4) | 2.282 | 2.02(2) |
| Pd–N(1) | 2.065(3) | 2.01 | 2.02(2) |
| X–C(8) | 1.881(4) | 1.75 | 1.29(3) |
| C(8)–C(9) | 1.418(6) | 1.44 | 1.48(3) |
| N(1)–C(9) | 1.381(5) | 1.39 | 1.39(3) |
| N(1)–C(2) | 1.330(5) | 1.35 | 1.33(3) |
| Angle | ω, deg | | |
| NPdX | 85.6(1) | 84.0 | 84.1(6) |
| PdXC(8) | 95.1(1) | 102.0 | 112.7(1.8) |
| PdN(1)C(9) | 120.6(3) | 119.0 | 108.0(1.2) |
| XC(8)C(9) | 118.8(3) | 120.0 | 117.2(1.7) |
| N(1)C(9)C(8) | 119.8(4) | 120.5 | 116.9(1.6) |
| C(2)N(1)C(9) | 117.9(4) | 120.0 | 123.3(1.6) |
| C(9)C(8)C(7) | 119.1(4) | 122.0 | 116.6(1.8) |

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* $Pd(C_9H_6NX)_2$: **1** X = Se, **2** X = S, **3** X = O.

*2 The numbering of atoms in complexes **2** and **3** is in agreement with the numbering of atoms in complex **1** (Fig. 1).

The five-membered metallocycles –Pd–Se–C(8)–C(9)–N–, as in complex **1**, were mainly planar within the limits of error (±0.04 Å). The structure of the quinoline rings was normal. The N(1)–C(2) bond length at 1.330(5) Å was significantly less than the N(1)–C(9) bond [1.3581(5) Å] and displays a tendency towards double bond character (length of the $C_{aryl}$–N sesqui bond is 1.333-1.345 Å [10]. The alternating C(3)–C(4), C(5)–C(6), C(7)–C(8) bonds were shortened (mean 1.368 Å). The central C(9)–C(10) bond was lengthened the most [1.42(7)] Å. The CCC angles differed insignificantly (±2.5°) from 120°. The size of the C(2)N(1)C(9) angle at 117.9(4)° confirms the participation of the N atom in the donor–acceptor Pd–N bond. In the crystal structure of complex **1**, from a geometrical point of view, two types of layers are packed. Palladium atoms are disposed in the centers of symmetry [(000)] and between them there is a layer of ligands disposed in a parallel manner (Fig. 2). The shortest intermolecular contacts between the atoms of parallel ligands were C(9)···C(4) (1-*x*, -*y*, 1-*z*) 3.36, C(2)···C(5) (1-*x*, -*y*, 1-*z*) 3.404, and N(1)···C(4) (1-*x*, -*y*, 1-*z*) 3.49 Å. It is not excluded that the shortened cell parameter *a* in complex **1** compared with the parameter in complex **2** reflects the interaction of the atoms Pd···C(5) (*x*, *y*, *z*-1) 3.85, and Pd···C(5) (-*x*, -*y*, 1-*z*) 3.85 Å.

Complex **1** is isostructural with platinum quinoline-8-selenolate, and platinum quinoline-8-thiolate, and also with palladium quinoline-8-thiolate **2** (triclinic system, space group P 1). However the packing of the isomolecular complexes of palladium quinolin-8-olate **3** into the crystal lattice is different (monoclinic system, space group $P2_1/b$). For a comparison of the (Pd + 2Se + 2N), (Pd + 2S + 2N), and (Pd + 2O + 2N) coordination angles and analogous metallocycles in complexes **1-3**, their main geometric parameters are correlated in Table 1. The Pd–N bond lengths in complexes **1-3** (Table 1) are different (Δ 0.055 Å) but their mean value is 2.022 Å and lies on curve *1* (Fig. 3). The weakening of the Pd–N bond in complex **1** is linked with the reduction of the basic properties of the nitrogen atom in quinoline-8-selenol compared with quinoline-8-thiol. A linear dependence exists between the total covalent radii $r_{Pd} + r_{Se}$, $r_{Pd} + r_S$, $r_{Pd} + r_O$ and the covalent radii of the ligand atoms, which is also preserved in the ratio of the Pd–Se, Pd–S, and Pd–O bond lengths found experimentally. Fig. 3, *1* indicates the insignificant lengthening of the Pd–Se(S, O) bonds as a function of the increase of the covalent radius of the ligand atom. The same may be said about the Se–C and S–C bonds, while the O–C bond is shortened significantly (Fig. 3, *2*).

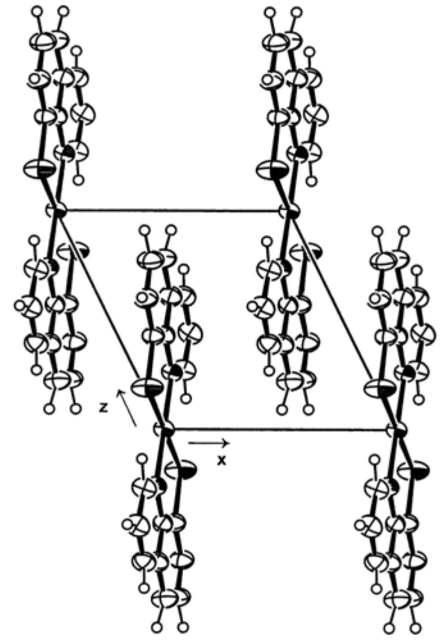

Fig. 2. Projection of the $Pd(C_9H_6NSe)_2$ complex on the *xz* plane.

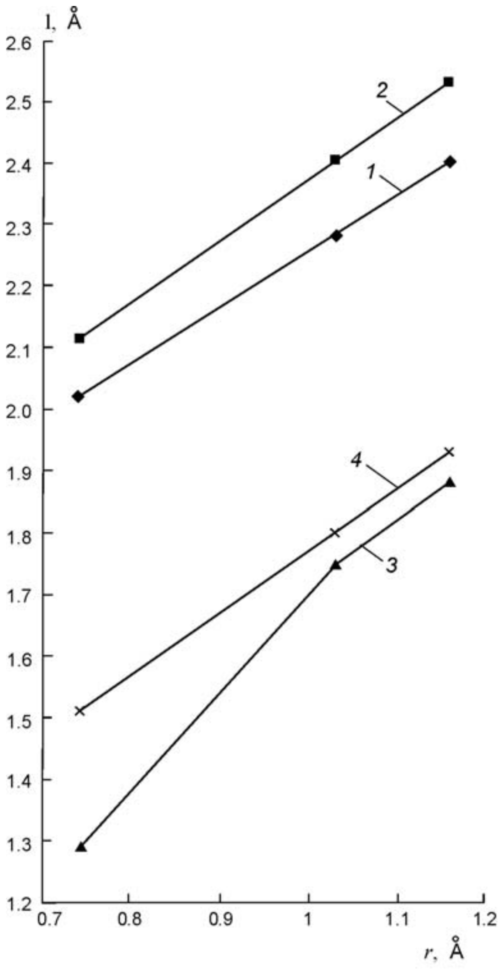

Fig. 3. Dependence of the Pd–Se, Pd–S, and Pd–O bond lengths (*1*), the C–Se, C–S, and C–O bond lengths (*3*) and the totals of the corresponding covalent radii (*2* and *4*) on the covalent radii of the Se, S, and O ligand atoms.

As already mentioned, the C–O bond and the geometry of the Pd–O–C fragment in complex **3** were significantly different. The PdOC valence angle at 112.7° (in difference to the PdSe(1)C(8) 95.1° and PdSC 102°) shows the tetrahedral configuration of the electronic orbitals. The C–O bond length at 1.29 Å is close to the length of the double bond in $C_{aryl}$–$COO^-$ at 1.255 Å [10]. Consequently the ligand oxygen atom participates in a sesqui C-O bond, has a negative charge, but it has free *d* orbitals for interaction with the *d* electrons of the central atom. Consequently the mechanism of formation of the Pd–O bond differs from the formation of the Pd–Se bond in complex **1** and the Pd–S bond in complex **2** in their identical simplicity. In spite of the geometric differences of bond lengths and valence angles (Table 1) the five-membered metallocycles of complexes **1-3** are planar within the limits of experimental error.

Spectral investigations of complexes **1-3** in chloroform revealed an absorption maximum at 505 nm for complex **1**, 485 for complex **2**, and 430 nm for complex **3**, which indicates the increase in the extent of conjugation from complex **3** to complex **1** and the increase in the proportion of π bonding for the ligand atoms S and Se.

Since the structure of complexes **2** and **3** is determined with low precision by the photomethod data, we examined the results of all the investigated 8-mercapto and 8-hydroxy palladium quinolinates containing a centrosymmetric *trans*-square (2S+2N) and (2O+2N) coordination of the palladium atom. The bond lengths in palladium 5-phenylthio [12] and 5-trimethylsilylthio [13] quinolin-8-thiolates were 2.304(2) and 2.294(1) (Pd–S), 2.039(5) and 2.039(3) (Pd–N), 1.730(6) and 1.741(5) Å (S–C) respectively. In palladium 5-methylthio [14] and 2-methyl-5-methylthio [15] quinolin-8-olates the bond lengths were 2.000(3) and 1.9788(5) (Pd–O), 1.994(4) and 2.060(6) (Pd–N), 1.316(5) and 1.296(9) Å (O–C) respectively. These results do not differ significantly from the data for complexes **1-3**.

It should be noted that in the complex palladium 2-methylquinoline-8-thiolate [16], where the sulfur atom is in the *trans* position to nitrogen, the coordination unit of the palladium atom is changed, and is represented by a distorted *cis*-square. This changes the distribution of bond lengths. The Pd–S bonds with an average length of 2.249 Å are shorter, and the Pd–N bonds (mean length 2.126 Å) reach the limits of the sum of the covalent radii. In the trinuclear complex palladium 2-methylthioquinoline-8-thiolate $Pd_3[C_9H_5(SCH_3)NS]_3$ [17], where the coordination unit is a distorted *trans*-square Pd(2S+N+C) with a *trans*-fragment S–Pd–N, the sulfur atom acts simultaneously as a ligand and a bridge atom. The Pd–S distance is 2.307Å on average and is no different from that in complex **2**, but the Pd–N bond is shortened significantly (mean 1.998 Å). Consequently an objective crystallochemical comparison of single-type metallocycles is only possible in a series of analogous isomolecular compounds.

The structure of the coordination unit, a centrosymmetric *trans*-square Pd(2Se+2N) and five-membered metallocycles –Pd–Se–C–C–N–, has been established for the first time. Similar complexes were not discovered in the Cambridge structural data bank.

## EXPERIMENTAL

**Palladium Quinoline-8-selenolate (1)** was synthesized by the procedure of [18].

**X-Ray Structural Analysis.** Monocrystals of complex **1** were grown in pyridine. The diffraction pattern of a monocrystal of **1** of size 0.08 × 0.10 × 0.38 mm was measured at 20°C on a Bruker-Nonius KappaCCD automatic diffractometer with scanning according to φ and ω (Mo*K*α radiation, graphite monochromator) to $2\theta_{max} = 60°$. Monocrystals of **1** belong to the triclinic system, space group *P*1. Cell parameters, $a = 7.2409(3)$, $b = 7.8932(5)$, $c = 7.8953(4)$ Å; $\alpha = 100.701(3)$, $\beta = 115.184(3)$, $\gamma = 92.253(3)°$; $V = 397.68(4)$ Å$^3$; $Z = 1$; $M_r = 520.628$; $D_x = 2.174$ g/cm$^3$; $\mu = 5.74$ mm$^{-1}$. The molecular structure of the compound was established by the heavy atom method and refined anisotropically by least squares from 1828 reflections with $I > 3\sigma(I)$ to $R = 0.040$ ($wR_2 = 0.120$) for the nonhydrogen atoms with allowance for the coordinates of the hydrogen atoms calculated from geometrical considerations. Programs from [19, 20] were used.

The crystallographic characteristics, coordinates of atoms and their temperature parameters, values of bond lengths, and valence angles for complex **1** have been deposited in the Cambridge structural data bank (CSD) under the number CCDC 23567. This information is available at 12, Union Road, Cambridge CB2 1EZ UK [Fax: (internat.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk].

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## REFERENCES

1. Yu. A. Bankovsky, *Chemistry of Chelate Compounds of Mercaptoquinoline and Its Derivatives* [in Russian], Zinatne, Riga (1978), 488 pp.
2. L. Pech, V. Belsky, A. Stash, J. Ashaks, E. Silina, and Yu. Bankovsky, *Latv. J. Chem.*, 237 (2003).
3. E. Silina, J. Ashaks, V. Belsky, A. Stash, L. Pech, and Yu. Bankovsky, *Latv. J. Chem.*, 419 (2001).
4. E. Silina, J. Ashaks, V. Belsky, A. Stash, L. Pech, and J. Bankovsky, *Abs. XX Int. Congress & General Assembly of Union of Crystallography*, Krakov, Poland (2001), p. 267.
5. L. Pech, Yu. Bankovsky, V. Belsky, A. Stash, and J. Ashaks, *Latv. J. Chem.*, 63 (1996).
6. L. Ya. Pech, Yu. A. Bankovskii, E. Ya. Silin', Ya. V. Ashaks, and V. E. Zavodnik, *Zh. Neorg. Khim.*, **45**, 940 (2000).
7. A. Ozola, J. Ozols, and A. Ievins, *Izv. Akad. Nauk LatvSSR, Ser. Khim.*, 662 (1973).
8. C. K. Prout and A. G. Wheeler, *J. Chem. Soc. A*, 1286 (1966).
9. J. Campbell, *Contemporary General Chemistry*, Vol. 1 [Russian translation], Mir, Moscow (1975), 415 pp.
10. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, No. 12, S1.
11. Yu. Bankovsky, *Latv. J. Chem.*, 344 (2002).
12. I. Berzina, V. Belsky, Yu. Bankovsky, G. Jansons, and J. Ashaks, *Latv. J. Chem.*, 533 (1992).
13. Yu. A. Bankovskii, L. Ya. Pech, A. N. Sobolev, and A. P. Sturis, *Zh. Neorg. Khim.*, **39**, 612 (1994).
14. L. Pech, Yu. Bankovsky, I. Berzina, V. Belsky, and J. Ashaks, *Latv. J. Chem.*, No. 3, 19 (1997).
15. L. Pech, Yu. Bankovsky, A. Sobolev, and J. Ashaks, *Latv. J. Chem.*, 147 (1994).
16. L. Pech, Yu. Bankovsky, A. Kemme, E. Silina, J. Ashaks, and A. Sturis, *Latv. J. Chem.*, No. 4, 19 (2000).
17. E. Silin', Yu. A. Bankovskii, V. K. Bel'skii, A. I. Stash, L. Ya. Pech, and Ya. E. Leeis, *Zh. Neorg. Khim.*, **46**, 1317 (2001).
18. J. Ashaks, Yu. Bankovsky, D. Zaruma, I. Shestakova, I. Domracheva, A. Nesterova, and E. Lukevics, *Khim. Geterotsikl. Soedin.*, 905 (2004).
19. Z. Otwinowski and W. Minor, in C. W. Carter & R. M. Sweet (editors), *Methods in Enzymology, Vol. 276, Macromolecular Crystallography*, Pt. A, Academic Press, New York (1997), p. 307.
20. S. Mackay, C. J. Gilmore, C. Edwards. N. Stewart, K. Shankland, maXus, *Computer Program for the Solution and Refinement of Crystal Structures*, Brucker Nonius, The Netherlands, Mac Science, Japan & University of Glasgow (1999).