Chemistry of Heterocyclic Compounds, Vol. 43, No. 1, 2007

SYNTHESIS AND X-RAY STRUCTURAL INVESTIGATION OF ZINC 2-METHYL-8-SELANYLQUINOLINATE. COMPARATIVE CRYSTALLOGRAPHIC ANALYSIS OF THE ZINC 8-SULFANYL-, 8-SELANYL-, AND 2-METHYL-8-SELANYLQUINOLINATE MOLECULES

L. Pech[1], S. Belyakov[2], Ya. Ashaks[1], E. Silina[1], and D. Zaruma[1]

Zinc 2-Methyl-8-selanylquinolinate Zn[C_9H_5(Me)NSe]$_2$ has been synthesized and its structure proved by X-ray analysis. The effect of different ligand atoms (Se or S) and a methyl group in position 2 of the ligand on the geometry of the coordinated zinc atom polyhedron has been studied for zinc 8-sulfanyl-, 8-selanyl-, and 2-methyl-8-selanylquinolinate.

Keywords: intramolecular zinc compounds, zinc 8-sulfanyl-, 8-selenol-, and 2-methyl-8-selanyl-quinolinates, molecular structure, X-ray analysis.

A comparison of the structures of metal complexes with 8-sulfanylquinoline, 8-selanylquinoline, and their derivatives is of interest in revealing the dependence of steric structure on the nature of the ligand atom (S or Se). In this work we have studied the effect of a methyl substituent in position 2 of a quinoline ring on the structure of zinc 2-methyl-8-selanylquinolinate Zn[C_9H_5(Me)NSe]$_2$ [**1**].

Compound **1** has been synthesized by us in 77% yield by the action of 50% hypophosphorous acid on 2,2'-dimethyl-8,8'-diquinolyldiselanyl and subsequent treatment of the 2-methyl-8-selanylquinoline obtained with aqueous solutions of sodium acetate and zinc acetate. The structure of the product **1** has been studied by X-ray analysis and the data obtained compared with analogous data in the literature for zinc 8-selanylquinolinate Zn[C_9H_6NSe]$_2$ (**2**) and zinc 8-sulfanylquinolinate Zn[C_9H_6NS]$_2$ (**3**) [1-3].

The crystalline structures of **1-3** (Figs. 1-3) are composed of the neutral complexes Zn[C_9H_5(Me)NSe]$_2$, Zn[C_9H_6NSe]$_2$, and Zn[C_9H_6NS]$_2$ respectively. The zinc complexes are two ring, intramolecular compounds in which 8-selanylquinoline or 8-sulfanylquinoline are bidentately bound to the central zinc atom *via* the Se(S) and N atoms. The coordinated Zn polyhedra in complexes **1-3** are distorted tetrahedra formed by two nitrogen atoms and two selenium atoms (in **1** and **2**) or two sulfur atoms (in **3**). The bond lengths in the coordinated zinc atom polyhedra in complexes **1-3** are given in Table 1. The distortions of the tetrahedral coordination sphere of the zinc atom are reflected in the valence angles (Table 2).

* Dedicated to Academician E. Lukevics in recognition of his service to organometallic chemistry

[1]Inorganic Chemistry Institute ot the Riga Technical University, Salaspils LV-2169, Latvia; e-mail: nki@nki.lv. [2]Latvian Institute for Organic Synthesis, Riga LV-1006, Latvia; e-mail: serg@osi.lv. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 123-128, January, 2007. Original article submitted January 5, 2006.

 0009-3122/07/4301-0106

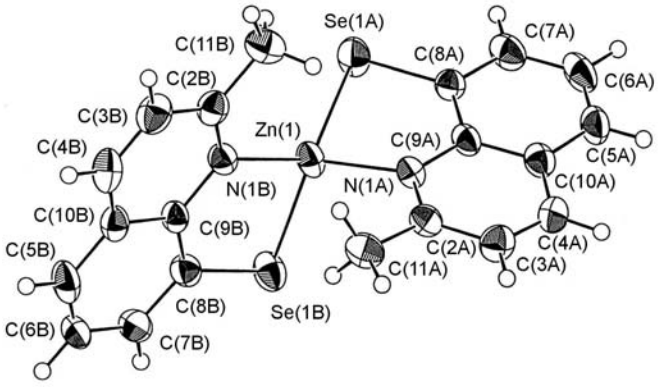

Figure 1. General view of the $Zn[C_9H_5(Me)NSe]_2$ complex (**1**) with atomic numbering.

The interatomic Zn–Se distances in complexes **1** and **2** and also the Zn–S distance in complex **3** point to strong valence bonds between the indicated atoms. Since the mean lengths of these bonds (2.385 in complex **1**, 2.368 in complex **2**, and 2.258 Å in complex **3**) are less than the sum of the corresponding radii R ($R_{Zn} + R_{Se}$ = 2.494, $R_{Zn} + R_S$ = 2.363 Å [4]) the Zn–Se and Zn–S bonds in the complexes **1-3** have a covalent character.

The zinc atom and nitrogen atoms form two bonds with mean Zn–N bond lengths of 2.080 in complex **1**, 2.055 in complex **2**, and 2.052 Å in complex **3**. These values are very close (complex **1**) or equal to (complexes **2** and **3**) the sum of the covalent radii R_{Zn} and R_N (2.059 Å [4]). Hence the Zn–N bonds in the complexes **1-3** have a less marked covalent character when compared with the Zn–Se and Zn–S bonds. Exchange of the selenium atom of the ligand in the complex **2** for a sulfur in the analogous complex **3** has virtually no effect on the length of the Zn–N bond length.

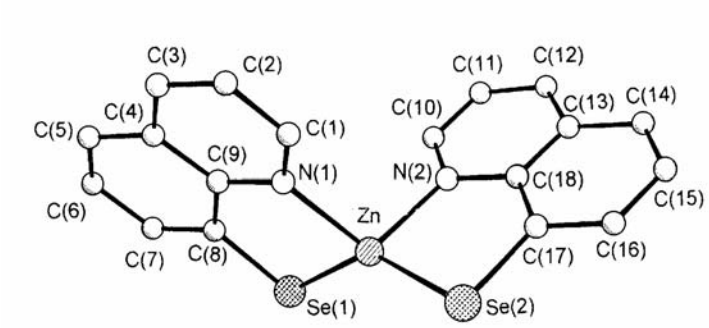

Figure 2. General view of the $Zn[C_9H_6NSe]_2$ complex (**2**) with atomic numbering
(one of the three independent complexes shown).

The lengths of the Se–C bonds in the complexes **1** and **2** do not differ and have a covalent nature since their mean values are equal to 1.903 and 1.908 Å and are markedly less than the sum of the covalent radii for the atoms R_{Se} and R_c (1.933 Å [4]).

The intracyclic chelate angles Se–Zn–N and S–Zn–N are almost linear, their mean values in complexes **1-3** being 89.9, 89.5, and 89.3° respectively. The distortion of the tetrahedral environment of the zinc atom is also characterized by the Se(S)–Zn–S(Se) and N–Zn–N angles between similar bonds. In compound **1** these angles are 124.45(2) and 115.63(9)°, in compound **2** 141.3 and 107.8°, and in compound **3** 139.0(9) and

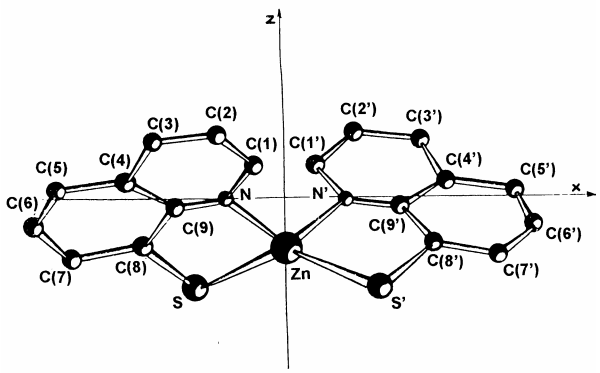

Figure 3. General view of the $Zn[C_9H_6NS]_2$ complex (**3**) with atomic numbering (the Zn atom occupies a specific position on axis 2 and the complex has basic *L*2 symmetry).

114.7(2)°. The remaining interligand Se(S)–Zn–N angles in the coordinated polyhedra of the zinc atom are markedly different to one another and take the values 126.80(7) and 111.82(6)° in complex **1**, 115.1 and 112.0° in complex **2**, and 113. in complex **3**.

The dihedral angles between the coordination planes Se(1A)ZnN(1A), Se(1B)ZnN(1B) in complex **1** and Se(1)ZnN(1), Se(2)ZnN(2) in complex **2** are 91.3 and 88.7° respectively and in compound **3** the angle between the analogous planes S(1)ZnN(1) and S(2)ZnN(2) is 74.7°. These values also indicate a deviation from tetrahedral coordination for the central zinc atom both in zinc 8-selanylquinolinate and, particularly, in the 8-sulfanylquinolinate.

TABLE 1. Bond Lengths (*d*) for the Zn Atom in Compounds **1-3**

Compound **1**	*d*, Å	Compound **2*** [2]	*d*, Å	Compound **3** [3]	*d*, Å
Zn–Se(1A)	2.3790(4)	Zn–Se(1)	2.3659	Zn–S	2.258(1)
Zn–Se(1B)	2.3913(3)	Zn–Se(2)	2.3699		
Zn–N(1A)	2.087(2)	Zn–N(1)	2.059	Zn–N	2.052(3)
Zn–N(1B)	2.074(2)	Zn–N(2)	2.051		

* Mean values for the three independent molecules.

TABLE 2. Valence Angles (ω) for the Zn Atom in Compounds **1-3**

Comound **1**	ω, deg.	Compound **2** [3]*	ω,deg.	CCompound **3** [3]	ω, deg.
Se(1A)ZnSe(1B)	124.45(2)	Se(1)Zn(1)Se(2)	141.3	SZnS'	139.0(1)
N(1A)ZnN(1B)	115.63(9)	N(1)Zn(1)N(2)	107.8	NZnN'	114.7(2)
Se(1A)ZnN(1A)	89.54(6)	N(1)Zn(1)Se(1)	89.6	SZnN (endo)	89.3(1)
Se(1B)ZnN(1B)	90.22(6)	N(2)Zn(1)Se(2)	89.4	SZnN (exo)	113.01
Se(1A)ZnN(1B)	126.80(7)	N(2)Zn(1)Se(1)	115.1		
Se(1B)ZnN(1A)	111.82(6)	N(1)Zn(1)Se(2)	112.0		
ZnSe(1A)C(8A) ⎫ mean ZnSe(1A)C(8A) ⎭	90.62	Zn(1)Se(1)C(8)	91.0	ZnSC(8)	94.6

* * Mean of 3. The dihedral angle between the coordination planes SeZnN (compounds **1** and **2**) and SZnN (compound **3**): θ = 91.26 (compound **1**), 87.5-89.9 (compound **2**), and 74.7 (compound **3**).

The five membered metallocycles in complexes **1-3** are strictly non-planar and form a more or less *chair*-type conformation. In complex **1** the degree of planarity of both metallocycles is markedly different. The metallocycle ligand **B** is approximately planar since the angle of twist of the metallocycle around the Se…N line is 2.0° whereas the angle of twist of the metallocycle ligand **A** is increased to 19.2°. By analysis of the geometry of the molecule of the isostructural compound $Cd[C_9H_5(Me)NSe]_2$ [5] we have proposed that the increase in twist of one of the metallocycles is explained by a π-π interaction of the corresponding centrosymmetric ligand bonds. In complex **1** the distance between the centrosymmetrically bonded ligand planes of the quinoline rings in ligand **A** is 3.470(6) Å which also points to a weak π-π interaction [6]. The distance between the centrosymmetrically bonded planes of the quinoline rings in ligand **B** is 3.625(18) Å and between the closest contacting atoms $C_{2B}…C_{2B'}$ is 3.676(5) Å. The interaction of the quinoline rings on the crystalline projection in structure **1** along the *x* axis (Fig. 4) is shown dotted.

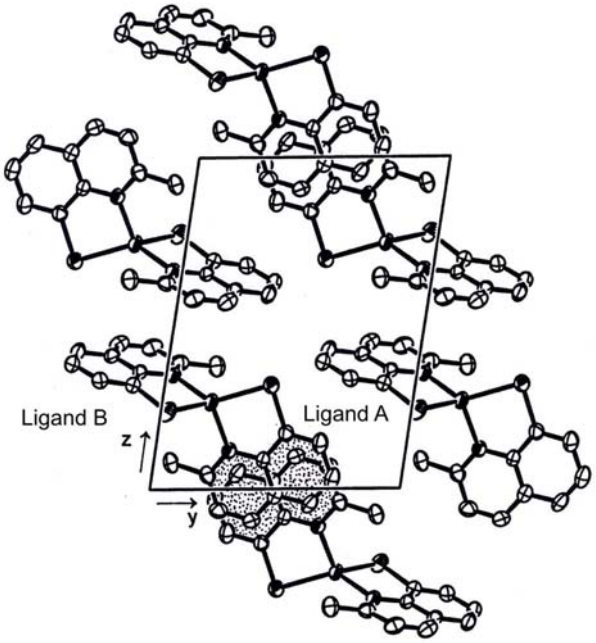

Figure 4. Projection of the crystal structure of the $Zn[C_9H_5(Me)NSe]_2$ (**1**) complex on the *yz* plane

Comparison of the geometry of the molecules $Zn[C_9H_5(Me)NSe]_2$ (**1**) and $Zn[C_9H_6NSe]_2$ (**2**) shows that the introduction of a Me group at the position 2 of the ligand in complex **1** is accompanied by a very small lengthening of the Zn–Se and Zn–N bonds but markedly affects the similar interligand angles: a decrease of the angles SeZnSe from 141.02° (in complex **2**) to 124.45(2)° (in complex **1**) and a small increase in the angles NZnN from 107.8° (in complex **2**) to 115.63(9)° (in complex **1**). The coordination polyhedra of the zinc atoms which appear as more or less distorted tetrahedra (2Se + 2N) are not markedly changed.

EXPERIMENTAL

Zinc 2-methyl-8-selanylquinolinate (1). Ethanol (10 ml) and hypophosphorous acid (50%, 1 ml, 9.7 mmol) were added to a solution of 2,2'-dimethyl-8,8'-diquinolyldiselanyl (0.2 g, 0.45 mmol) in hydrochloric acid (3M, 2 ml) and the reaction mixture was held for 5 min. A saturated, aqueous solution of sodium acetate

(4 ml, 60 mmol) and a solution of $Zn(MeCOO)_2.2H_2O$ (0.09 gm, 0.41 mmol) in water (2 ml)were added to the solution of 2-methyl-8-selanylquinoline obtained. The precipitate yellow product **1** was filtered off, washed with water, and dried in air. Yield 0.16 g (77%). Found, %: C 47.83; H 3.05; N 5.37. $C_{20}H_{16}N_2Se_2Zn$. Calculated, %: C 47.32; H 3.18; N 5.52.

Monocrystals of complex **1** were grown from a solution in chloroform-heptane (1: 1).

X-Ray structural analysis of complex 1. Experimental material for the crystal structure determination of compound **1** was obtained for diffraction with a fine edged, yellow monocrystal of size 0.04×0.25×0.32 mm. The unit cell parameters and intensities of 3049 independent reflections with $I > 3\sigma(I)$ were measured at room temperature on a Bruker-Nonius KappaCCD automatic diffractometer (MoKα radiation, λ = 0.71073 Å). Crystals of compound **1** are triclinic with a = 7.5206(2), b = 10.0679(3), c = 12.7487(4) Å. α = 80.8485(12), β = 86.6889(13), γ = 69.6081(13)°, V = 893.28(5) Å^3, M = 507.652, Z = 2, d_{calc} = 1.887 g/cm^3, space group $P\bar{1}$. The structure was solved by a direct method [7] and refined in a full matrix least squares analysis using the program [8]. The final values of the difference factors were R = 0.042 and R_w = 0.099. The crystallographic parameters, atomic coordinates, and their thermal parameters, bond lengths, and valence angle values for the compound **1** molecule have been placed in the Cambridge structural data bank (CCDC 289468).

The authors thank the Latvian council for science for financing this work (project No. 05.1552).

REFERENCES

1. E. Silina, J. Ashaks, V. Belsky, A. Stash, L. Pech, and Yu. Bankovsky, *Latv. J. Chem,* 419 (2001).
2. L. Pech, J. Ashaks, V. Belsky, A. Stash, E. Silina, and Yu. Bankovsky, *Latv. J. Chem*, 341 (2004).
3. I. Bērziņa, V. Belsky, A. Stūris, J. Ashaks, Yu. Bankovsky, and L. Pech, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 42 (1987).
4. J. A. Campbell, *Chemical Systems.* [Russian translation], Vol. 1, Mir, Moscow (1975), p. 548.
5. E. Siliņa, J. Ashaks, S. Belyakov, L. Pech, and D. Zaruma, *RTU Zinātniskie raksti. Ser. Materiālzinātne un Lietišķā ķīmija*, **11**, 63 (2005).
6. G. Gilli, *Molecules and Molecular Crystals*, in C. Giacovazzo (editor), *Fundamentals of Crystallography*, Oxford University Press (2002), p. 585.
7. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovzzo, A. Guagliardi, G. G. Moliterni, G. Polidori, and R. J. Spagna, *J. Appl. Crystallogr.*, 115 (1999).
8. S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart, and K. Shankland, *maXus Computer Program for the Solution and Refinement of Crystal Structures,* Bruker Nonius, Delft, The Netherlands, MacScience, Japan and Glasgow University (1999).