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SYNTHESIS AND STRUCTURE OF BIS(2-METHYLQUINOLINE-8-SELENOLATO)PLATINUM

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Bis(2-methylquinoline-8-selenolato)platinum was synthesized and studied by X-ray diffraction structural analysis. The diffraction results were compared with the data for bis(quinoline-8-selenolato)platinum, bis(2-methylquinoline-8-thiolato)platinum, and bis(quinoline-8-thiolato)-platinum. The effect of the 2-methyl group on the structure of the complex and its coordination sphere (Pt + 2Se + 2N) was discussed.

Keywords: bis(2-methylquinoline-8-selenolato)platinum, platinum complexes, X-ray diffraction structural analysis.

A systematic X-ray diffraction structural study of quinoline-8-thiolates of divalent transition metals (Pd, Pt, Ni, Cu, and Co) has shown that the presence of a substituent at C-2 of the ligand has the most significant effect on the geometry of the (M + 2S + 2N) coordination unit [1-3].

The coordination polyhedron found in isostructural $M(C_9H_6NS)_2$ complexes (M = Pt [4] and Pd [5]), namely, a centrosymmetric *trans*-square planar (2S + 2N) structure undergoes various types of distortion in going to $M[(2\text{-Me})C_9H_5NS]_2$ complexes (M = Pt [6] and Pd [7]). The structures of ordinarily isostructural complexes of platinum and palladium fundamentally differ. The coordination polyhedron of metal in the $Pt[(2\text{-Me})C_9H_5NS]_2$ complex as well as in other disubstituted platinum complexes such as $Pt[(2\text{-}iso\text{-Pr})C_9H_5NS]_2$ [3] and Pt $(2,7\text{-Me}_2)C_9H_4NS]_2$ [8] is *trans*-square planar (2S + 2N) with a slight pyramidal distortion. The coordination polyhedron of the palladium atom in the $Pd[(2\text{-Me})C_9H_5NS]_2$ is distorted *cis*-square planar (2S +2N). In both cases, the presumed additional π-bonding [9, 10] is favorable for retention of the planarity of the (M + 2S + 2N) coordination unit. The steric hindrance related to the methyl group at C-2 of the ligand in these complexes is removed by large flexures of the five-membered metallacycles along the S···N line (the dihedral angles between the SMN and SCCN planes are up to 30°).

The differences in the coordination of the (M + 2S + 2N) unit in the $M[(2\text{-Me})C_9H_5NS]_2$ complexes of transition metals (M = Ni, Cu, and Co) in comparison with the corresponding quinoline-8-thiolates are related to the different hybrid states of the central atom electrons: centrosymmetric distortion of the octahedral sphere of

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the Ni and Cu atoms (2S + 2N···2S) in $Cu(C_9H_6NS)_2$ [11] and $Ni(C_9H_6NS)_2$ [12] and distorted tetrahedral coordination (2S + 2N) in $Cu[(2,7\text{-}Me_2)C_9H_4NS]_2$ [13], $Ni[(2\text{-}Me)C_9H_5NS]_2$ [14], Ni[(2-*iso*-Pr)$C_9H_5NS]_2$ [15], $Ni[(2\text{-}Ph)C_9H_5NS]_2$ [16], $Co[(2\text{-}Me)C_9H_5NS]_2$ [17], $Co[(2\text{-}SMe)C_9H_5NS]_2$ [17], Co[(2-*iso*-Pr)$C_9H_5NS]_2$ [18], and $Co[(2\text{-}Ph)C_9H_5NS]_2$ [19].

In a continuation of a study of the properties and structure of analogous quinoline-8-selenolates and quinoline-8-thiolates, we used our previous method [20] to synthesis bis(2-methylquinoline-8-selenolato)-platinum $Pt[(2\text{-}Me)C_9H_5NSe]_2$ (**1**) and carried out an x-ray diffraction investigation of this complex.

We should note that the cytotoxic activity of complex **1** and its analog lacking a methyl group at C-2, namely, bis(quinoline-8-selenolato)platinum (**2**) in order to elucidate the effect of ligand structure on this activity [20-22].

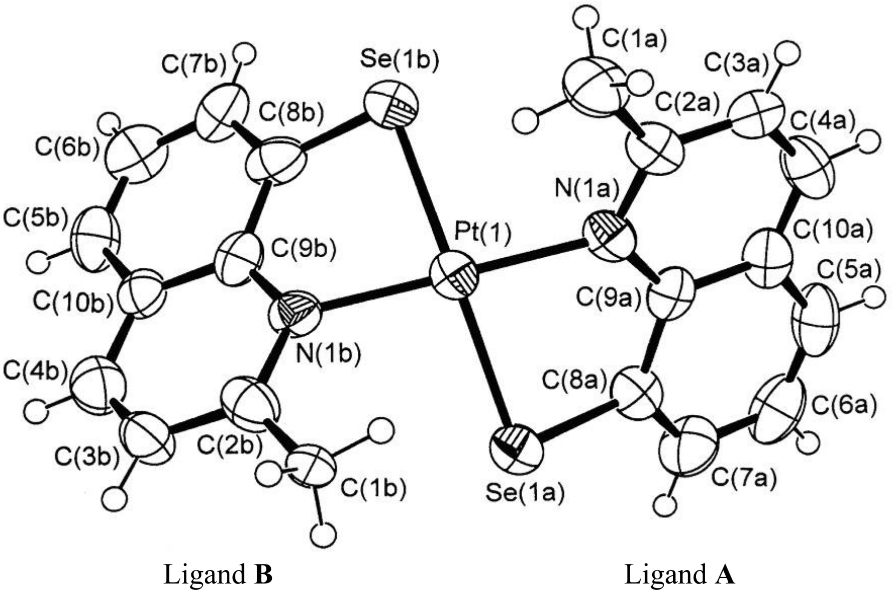

Fig. 1. General view of $Pt[(2\text{-}Me)C_9H_5NSe]_2$ with numbering of the atoms.

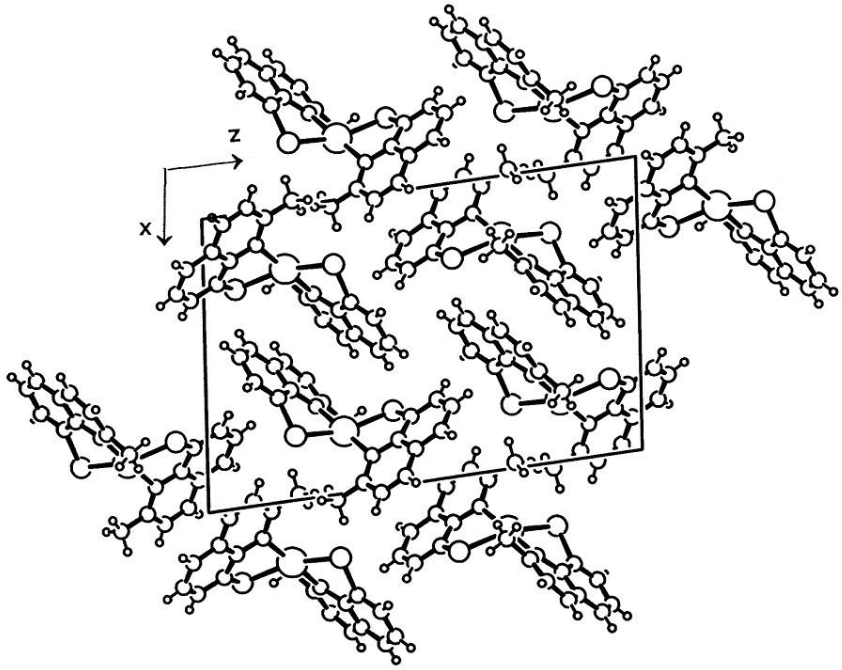

Fig. 2. Projection of $Pt[(2\text{-}Me)C_9H_5NSe]_2$ onto the *xz* plane.

The crystal structure of complex **1** consists of neutral asymmetric Pt[(2-Me)$C_9H_5NSe]_2$ molecules (Fig. 1). The platinum atoms occupy general positions in the unit cell and have bidentate (N,Se) coordination with two nonidentical 2-methylquinoline-8-selenol ligands (**A** and **B**). The SePtN chelate angles ω (see Table 1) are identical within experimental error ($\omega_{av} = 84.0°$). The central platinum atom has slightly distorted *trans*-square planar coordination (2Se + 2N). Covalent Pt–Se ($l_{av} = 2.437$ Å) and Pt–N bonds ($l_{av} = 2.050$ Å) (Table 1) have partial ionic nature since the l_{av} values presented are less than the sums of the covalent radii of the corresponding atoms: $r_{Pt} + r_{Se} = 2.549$ Å and $r_{Pt} + r_N = 2.114$ Å [23]; ionic nature is more pronounced for the Pt–Se bonds. The mean Pt–Se bond in complex **1** is slightly longer than in complex **2** [24] ($\Delta = 0.032$ Å), while the Pt–N bonds in both complexes are equal in length within error of 3σ.

The distortion of the central unit of the complex (Pt + 2Se + 2N) results from a breakdown in its planarity: Pt(1), Se(1a), Se(1b), N(1a), and N(1b) extrude from the mean-square plane of the 2Se + 2N atoms by 0.4145(5), -0.0072(14), -0.0084(15), 0.378(10), and 0.377(10) Å, respectively. The "thickness" of the (Pt + 2Se + 2N) coordination unit is about 0.5 Å. The distortion of the central unit is pyramidal as indicated by the dihedral angle θ between the Se(1a)Pt(1)N(1a) and Se(1b)Pt(1)N(1b) coordination planes equal to 19.97(10)° and the diagonal angles ω Se(1a)Pt(1)Se(1b) = 160.05(5)° and ω N(1a)Pt(1)N(1b) = 178.1(4)°. It is interesting to note a diminished diagonal angle between the stronger Pt–Se bonds. Decreased bond conjugation is reflected in the spectral properties of complex **1**. A marked hypsochromic shift of the absorption maxima is noted for complex **1** in comparison with the maxima of complex **2**: the maxima for complex **1** in chloroform are at 442 and 545 nm, while the maximum for complex **2** is at 588 nm. However, retention of the nominal planarity of the (Pt + 2Se + 2N) coordination unit and unchanged Pt–Se and Pt–N bond lengths in complex **1** as in isostructural Pt[(2-Me)$C_9H_5NS]_2$ (**3**) indicates additional π-bonding in the Pt–Se bond.

The steric hindrance due to the 2-methyl groups in the ligands is compensated by flexures of the five-membered metallacycles at the Se···N line. The dihedral angles between the SePtN and SeCCN planes (Fig. 1) is 30.2(4)° in ligand **A** and 146.1(3)° in ligand **B**. These angles are characterized the deformation of the metallacycles in the structures of quinoline-8-thiolates and quinoline-8-selenolates; the values of these angles are maximal for he studied structures. As a consequence of these angular changes, the planes of the quinoline fragments in complex **1** as in complex **3** are arranged almost perpendicularly (θ = 102.2(3)°) in contrast to planar complex **2** (θ = 180°). It appears that the total steric hindrance due to the 2-methyl group in the ligands has a greater effect of the arrangement of the atoms in the peripheral part of complex **1** and, thus, the packing of this complex in the crystal structure.

The Se–C bond lengths in the ligands of complex **1** (see Table 1) are different ($\Delta = 0.063$ Å, $l_{av} = 1.892$ Å); the mean value is greater than for the analogous bonds in complex **2** ($l_{av} = 1.858(4)$ Å) and is identical to the Csp^2–Se(II) bond length in the compilation of Allen [25]. This value is in accord for the tendency to double bond formation since it is much less than the sum of the covalent radii of the corresponding atoms ($r_{Se}+r_C = 1.933$ Å [23]). The PtSeC bond angle $\omega_{av} = 90.9°$ indicates octahedral arrangement of the electrons in the outer shell of the selenium atom and the possibility of additional π-bonding in the Pt–Se bond.

TABLE 1. Characteristic Bond Lengths (*l*) and Bond Angles (ω) in Pt[(2-Me)$C_9H_5NSe]_2$

Bond	*l*, Å	Angle	ω, deg
Pt(1)–Se(1a)	2.438(2)	Se(1a)Pt(1)N(1a)	84.0(3)
Pt(1)–Se(1b)	2.435(2)	Se(1b)Pt(1)N(1b)	84.9(3)
Pt(1)–N(1a)	2.036(11)	Se(1a)Pt(1)Se(1b)	160.05(5)
Pt(1)–N(1b)	2.063(11)	N(1a)Pt(1)N(1b)	178.1(4)
Se(1a)–C(8a)	1.923(13)	Pt(1)Se(1a)C(8a)	91.6(4)
Se(1b)–C(8b)	1.86(2)	Pt(1)Se(1b)C(8b)	90.2(4)

The quinoline fragments are planar to within ±0.12 Å. The platinum and selenium atoms extrude from the mean-square planes of these fragments in opposite directions: Pt(1) by -0.571(1) Å and Se(1a) by 0.468(1) Å in ligand **A** and Pt(1) by 0.697(1) Å and Se(2) by -0.436(2) Å in ligand **B**.

The structure of the quinoline fragments is ordinary. However, considering the precision in the determination of the bond lengths, we may assume that disproportionation of the N–C(2) (l_{av} = 1.36 Å) and N–C(9) bonds (l_{av} = 1.38 Å) is not observed. The alternating C(3)–C(4), (C5)–C(6), and C(7)–C(8) bonds are shortened (l_{av} = 1.38 Å). The central C(4)–C(9) bond is slightly extended (l_{av} = 1.43 Å) relating to the C–C bond length (l_{av} = 1.40 Å). The greatest departure of some CCC bond angles from 120° is 6°.

We should note that these bond lengths and angles may be inexact due to the poor quality of the monocrystal used. Hence, we did not carry out a graphic quantitative comparison of the experimental and calculated Pt–Se, Pt–S, Pt–O, Se–C, S–C, and O–C bond lengths as in our previous work [24].

The presence of the 2-methyl group in the ligand of complex **1** significantly alters the molecular packing in the crystal structure of this complex. The space group for the crystals of complex **1** is $P2_1/b$, while the space group for the crystals of complex **2** is $P\bar{1}$.

The crystal structure of complex **1** is rather loose. The calculated density is 2.331 g/cm^3 in contrast to 2.550 g/cm^3 for complex **2**. Only a few slightly shortened intermolecular distances were found: C(3a)···C(10a) (1-*x*, -½+*y*, ½-*z*) 3.494 and C(3b)···C(8b) (2-*x*, -*y*, 1-*z*) 3.487 Å.

Analysis of these results indicates that the following trends hold in the series of complexes $Pt[(2\text{-}Me)C_9H_5NSe]_2$ (**1**), $Pt(C_9H_6NSe)_2$ (**2**), $Pt[(2\text{-}Me)C_9H_5NS)_2$ (**3**), and $Pt(C_9H_6NS)_2$ (**4**): 1) the replacement of the ligand sulfur atom by a selenium atom in analogous complexes of a typical platinum transition metal does not cause change in the molecular and crystal structure. Thus, complexes **1** and **3** as well as complexes **2** and **4** are isostructural, 2) the presence of a 2-methyl group in the ligand of complex **1**, as in the case of complex **3**, leads to change in the molecular and crystal structure so that planar centrosymmetric complexes **2** and **4** with a centrosymmetric *trans*-square planar (2Se (or 2S) + 2N) unit crystallize with space group $P\bar{1}$, while asymmetric complexes **1** and **3** with a slight pyramidal distortion of the *trans*-planar (2Se (or 2S) + 2N) unit of the platinum atom and the angular arrangement of the ligands crystallize with space groups $P2_1/c$ and $P2_1/b$, respectively.

EXPERIMENTAL

A sample of bis(2-methylquinoline-8-selenolato)platinum (**1**) was prepared according to our previous procedure [20].

X-ray Diffraction Structural Analysis of Complex 1. Monocrystals of complex **1** were grown by slow cooling from a hot saturated solution in chloroform. The diffraction pattern for a monocrystal of complex **1** was taken at 20°C on a Bruker-Nonius KappaCCD automatic diffractometer with φ and ω scanning up to $2\theta_{max} = 60°$ using Mo*K*α radiation and a graphite monochromator. Monoclinic monocrystals of complex **1** have space group $P2_1/c$. The unit cell parameters: $a = 12.5661(7)$, $b = 7.8072(5)$, $c = 18.6684(12)$ Å, $\beta = 97.328(2)°$, $V = 1816.5(2)$ Å^3, $Z = 4$, $M_r = 637.36$, $D_x = 2.331$ g/cm^3, $\mu = 11.737$ mm^{-1}. The molecular structure of complex **1** was solved by the heavy atom method and refined by the method of least squares using 4086 reflections with $I > 2\sigma(I)$ to $R = 0.0629$ ($wR_2 = 0.1438$) anisotropically for the nonhydrogen atoms taking account of the hydrogen atom coordinates using geometrical considerations. Standard programs were used [26, 27].

The crystallographic data, atomic coordinates, temperature parameters, bond lengths, and bond angles in complex **1** have been deposited at the Cambridge Crystallographic Data Center (CCDC 722430).

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