

Chiral Oligomers

Stepwise Construction of Oligomeric 1,2-Diselenolene Platinum(IV) Complexes**

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The chemistry of selenium-containing ligands has been increasingly studied in the last decade owing to the different properties these ligands have compared to the more common

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sulfur-containing analogues and their potential in various applications.^[1] In the field of molecular conductors, although square-planar transition-metal bis(dithiolene) complexes are widely used as building blocks,^[2–4] bis(diselenolene) analogues are much more scarce, and only recently some examples of Cu^{III}^[5] and Au^{III} complexes^[6] with pyrazine-1,2-diselenolene (pds) ligands,^[6,7] as well as Ni^{II}, Pd^{II}, and Pt^{II} complexes with the maleonitrilediselenolene ligand,^[8,9] were reported. In the complexes with the pds ligand, the redox behavior exhibited is mainly confined to the MSe₄ (M = metal center) units not extending to the ligands.^[5] Thus, it is very attractive to compare complexes of the third-row transition-metal platinum and the pds ligand with the related known complexes. Herein we describe the results obtained following this approach that, in contrast to the well-known square-planar dichalcogenene species, leads to an unprecedented series of tris-, penta-, and hepta-1,2-diselenolene oligomeric complexes of which the mononuclear chiral {Pt^{IV}Se₆} complex **1** and the dinuclear racemic {Pt^{IV}Se₁₀} complex **2** have been isolated as single crystals.

Complex [Pt^{IV}(pds)₃]₂Na₂·6H₂O (**1**) was synthesized by the reaction of pds²⁻ ligand with Pt^{II}Cl₂ (in a 3:1 molar ratio). Single-crystal X-ray diffraction^[10] shows the metal center in an octahedral coordination environment (see Figure 1 a),^[11] with typical Pt^{IV}-Se separations of around 2.46 Å.^[12] Complex **1** crystallizes in the orthorhombic chiral *P*2₁2₁ space group owing to a spontaneous resolution phenomena leading to a conglomerate of crystalline enantiomers.^[13] The three-blade propeller-like structure of **1** in the crystal studied is the anticlockwise *A* enantiomer. Noteworthy, the octahedral geometry around the metal center imposes an arrangement among the blades of the complex that yields a crystal packing of **1** with an orthogonal 3D offset face-to-face (OFF) π stacking (ring intercentroid separations ranging from 3.38 to 3.82 Å). The C-H... π (ring centroid) separations are over 3.70 Å and therefore, an edge-to-face (EF) motif is not considered (typical distances < 2.9 Å).^[14] Interestingly, a *h*₂ helix type (following the disposition of the platinum centers) is formed in each orthogonal direction, with all the stacked aromatic moieties lying inside the helix (see Figure 2). It should be emphasized that the *h*₂ helix type structure is rare as “strictly” 8-fold symmetry cannot exist in the crystal lattice. The efficient packing of **1** may be the driving force leading to the spontaneous resolution observed. The coordination of sodium ions to one nitrogen center of a pyrazine residue and to water molecules of crystallization may also play an important role in preventing a concerted OFF and EF structure.^[5]

When the pds²⁻:Pt^{II}Cl₂ molar ratio was decreased from 3:1 to 2:1 the crystalline product obtained contains a mixture of complex **1**, the dinuclear platinum complex [Pt^{IV}₂(pds)₅]₂Na₂·7H₂O (**2**), and a minor amount of another species that has been ascribed to a trinuclear Pt^{IV} species (**3**, see below). Most of the crystals obtained were dark-red prisms of the three cocrystallized species,^[15] but a few black-plate good quality single crystals of pure **2** were isolated allowing its structure to be solved by X-ray diffraction.^[10] Complex **2** crystallizes in the orthorhombic space group *Pbca* as a racemate. The molecular structure is a dinuclear species with two Pt^{IV} centers in

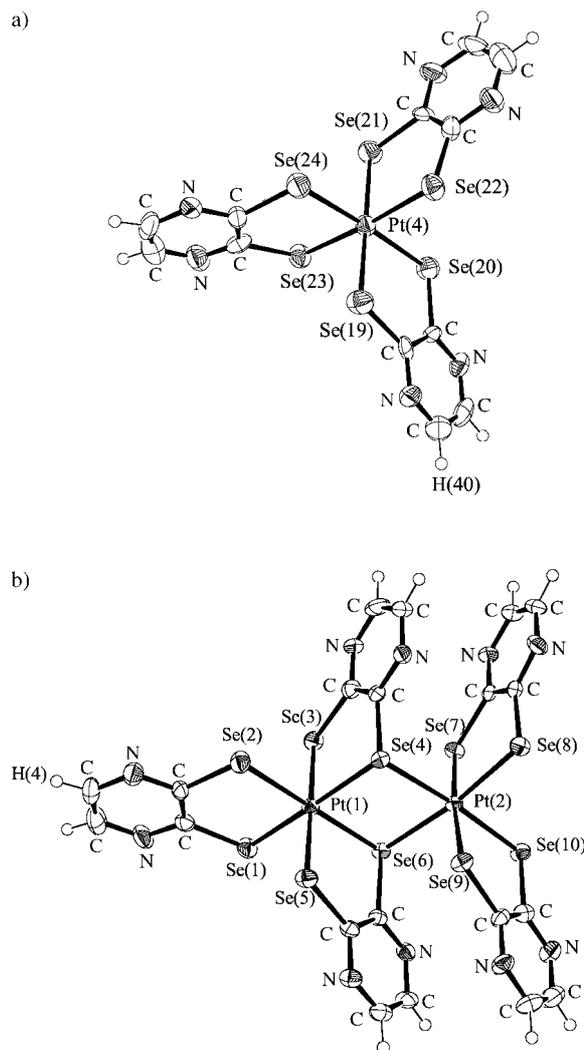


Figure 1. ORTEP structural representation (thermal ellipsoids set at 50 % probability) of the a) monomeric [Pt^{IV}(pds)₃]²⁻ (**1**) and b) dimeric [Pt^{IV}₂(pds)₅]²⁻ (**2**). Selected bond lengths [Å] and angles [°]: a) Pt(4)-Se(19) 2.4514(13), Pt(4)-Se(20) 2.4652(13), Pt(4)-Se(21) 2.4567(13), Pt(4)-Se(22) 2.4618(13), Pt(4)-Se(23) 2.4690(13), Pt(4)-Se(24) 2.4457(13); Se-Pt(4)-Se(*cis*) 86–94 (for Se in *trans*, 176–179); b) Pt(1)-Se(1) 2.4661(6), Pt(1)-Se(2) 2.4598(6), Pt(1)-Se(3) 2.4632(6), Pt(1)-Se(4) 2.4872(6), Pt(1)-Se(5) 2.4708(6), Pt(1)-Se(6) 2.4808(6), Pt(2)-Se(4) 2.5451(6), Pt(2)-Se(6) 2.5539(6), Pt(2)-Se(7) 2.4798(6), Pt(2)-Se(8) 2.4514(6), Pt(2)-Se(9) 2.4599(6), Pt(2)-Se(10) 2.4551(6), Pt(1)···Pt(2) 3.705(1); Pt(1)-Se(4)-Pt(2) 94.819(18), Pt(1)-Se(6)-Pt(2) 94.754(18), Se(4)-Pt(1)-Se(6) 86.559(18), Se(4)-Pt(2)-Se(6) 83.819(18).

octahedral coordination environments and bridged by two selenium atoms. This complex can be considered as the first member of an oligomeric series of compounds constructed by the addition of a Pt(pds)₂ moiety through its coordination to two selenium atoms (which bridge the Pt centers), and which can be generally described as [(Pt^{IV}(pds)₃){Pt^{IV}(pds)₂]_{*n*} dianions. In the case of **2**, the addition of a Pt(pds)₂ moiety yields a five-bladed binuclear structure (Figure 1 b). Indeed, whereas the coordination environment of Pt(1) in **2** is almost unchanged compared to that of the platinum center in **1**, the average Pt(2)-Se_{bridging} bond lengths are longer than those of Pt(1)-Se_{bridging} (2.55 Å versus 2.48 Å) leading to the distorted

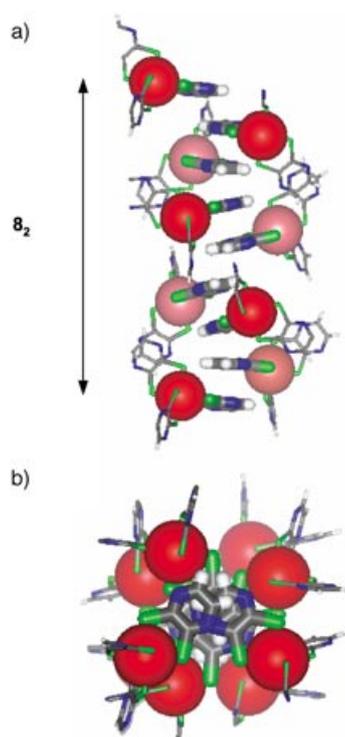


Figure 2. Views of the 8_2 helix-type secondary structure of **1**, a) along its main axis and b) perpendicular to the stacked aromatic rings. Red Pt, green Se, blue N, gray C.

rhombic $\{\text{Pt}_2\text{Se}_2\}$ core of **2**. The enantiomer shown in Figure 1b has Λ and Δ helicities for each platinum stereogenic center (or alternatively M,M). Both M,M and P,P enantiomers are placed in a tail-to-tail fashion within the crystal structure. No significant intermolecular π - π stacking is found (ring intercentroid separations > 4.1 Å), in contrast to the enantiopure **1**. On the other hand, the dimer is further stabilized by the intradimer π - π stacking with intercentroid separations in the range 3.6–3.8 Å. A supramolecular network of 14 water molecules and 4 Na atoms is encapsulated between dimer molecules in a sphere of approximately 10 Å diameter.

The crystalline material isolated using a $\text{pds}^{2-}:\text{Pt}^{\text{IV}}\text{Cl}_2$ molar ratio of 2:1 was fully characterized by ESI-MS, traditional 1D, 2D, and multinuclear NMR spectroscopy.^[15] ESI-MS spectra identify two of the components in the crystalline mixture as **1** and **2** since the peaks with the correct isotopic pattern for the $[\{\text{Pt}^{\text{IV}}(\text{pds})_3\}\text{Na}]^-$ and $[\{\text{Pt}^{\text{IV}}_2(\text{pds})_5\}\text{H}]^-$ ions at $m/z = 927$ and 1571, respectively, were observed. Multinuclear NMR spectroscopy studies reveal that the principal component of the crystalline material is the monomer **1** ($\approx 72\%$, one singlet, symmetrical molecule in solution) followed by the dimer **2** ($\approx 20\%$, five pairs of AB independent spin systems), showing also the presence of a third compound (**3**) ($\approx 8\%$, seven pairs of AB systems).^[16]

To characterize compound **3**, pulse field gradient spin-echo (PGSE) NMR diffusion experiments in solution were performed.^[17–19] The PGSE methods specifically study the correlation between the molecular size of the species (strongly related to friction factors for translational motion)

and their nuclear relaxation rates. Therefore, the decay of signal intensities of each compound can be related to the diffusion rates that in turn, enable the determination of the molecular dimensions in solution. Using CD_3CN as solvent, a quantitative analysis was accomplished by linear regression of the Stejskal–Tanner equation ($\ln(I/I_0) = -\gamma^2 g^2 \delta^2 (\Delta - \delta/3) - D$),^[20] affording self-diffusion coefficient (D) values of $1.070(6) \times 10^{-9}$ for **1**, $0.942(6) \times 10^{-9}$ for **2**, and $0.843(6) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for **3** (Figure 3). According to the Stokes–Einstein

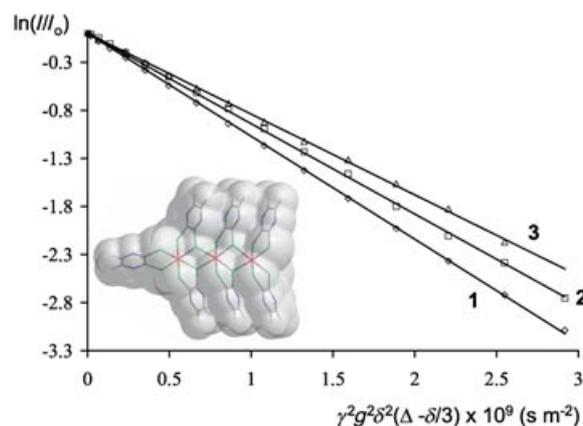


Figure 3. Plot of $\ln(I/I_0)$ versus $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ for the mixture of oligomers **1** (\diamond), **2** (\square) and **3** (\triangle) in CD_3CN at 298 K (I = signal intensity at a given pulsed-field gradient (PFG), I_0 = signal intensity in absence of PFG, γ = gyromagnetic ratio, g = strength of diffusion gradient, δ = length of the diffusion gradient, Δ = time separation between the leading edges of the two diffusion pulsed gradients). The inset shows the solvent accessible surface of the modeled structure of **3**. Red Pt, green Se, blue N, gray C.

equation ($D = kT/6\pi\eta r_H$; where k = Boltzmann constant, T = temperature, and η = solvent viscosity) D is inversely proportional to the hydrodynamic radius (r_H) of the diffusing molecules. Thus, the hydrodynamic radii (r_H) for the hypothetical spheres of **1**, **2**, and **3** are 5.82, 6.61, and 7.40 Å, respectively, yielding the ratios $r_H(\mathbf{2})/r_H(\mathbf{1}) = 1.14$ and $r_H(\mathbf{3})/r_H(\mathbf{1}) = 1.27$. On the other hand, the estimated radii from the X-ray or modeled structures are $r_{\text{STR}}(\mathbf{1}) = 6.50$ Å, $r_{\text{STR}}(\mathbf{2}) = 7.70$ Å and $r_{\text{STR}}(\mathbf{3}) = 8.49$ Å,^[21] affording the ratios $r_{\text{STR}}(\mathbf{2})/r_{\text{STR}}(\mathbf{1}) = 1.18$ and $r_{\text{STR}}(\mathbf{3})/r_{\text{STR}}(\mathbf{1}) = 1.30$. Although the calculated r_H values are smaller than r_{STR} (owing to the assumption of the unrealistic spherical model, since the species have an ellipsoidal disk-like shape), the ratios between them are in excellent agreement. Based on the agreement between NMR PGSE experiments and the X-ray structures, the experimental results point towards a seven-bladed trinuclear structure for compound **3**, $[\{\text{Pt}^{\text{IV}}(\text{pds})_3\}\{\text{Pt}^{\text{IV}}(\text{pds})_2\}_n]$ ($n = 2$), resulting from the addition of a $\text{Pt}(\text{pds})_2$ moiety to **2**. This conclusion is further supported by the seven AB systems seen in the ^1H NMR spectrum.

It should be emphasized that, to our knowledge, no trimeric Pt^{IV} octahedral diselenolene complex has been reported. The compounds $[\{\text{Pt}^{\text{IV}}(\text{pds})_3\}\{\text{Pt}^{\text{IV}}(\text{pds})_2\}_n]$ **1** ($n = 0$) and **2** ($n = 1$) are the first tris- and penta-1,2-diselenolene monomeric and dimeric Pt^{IV} complexes reported. Only one similar mononuclear $\{\text{Pt}^{\text{IV}}\text{Se}_6\}$ octahedral structure has been

reported bearing (Se₄)²⁻ bidentate ligands.^[12] In regard to compound **2**, only a dimeric [Pt^{IV}₂Se₄C₂Cl₂] compound is known,^[22] with a {Pt^{IV}₂Se₂} core have two short and two long equivalent Pt–Se bonds of 2.42 and 2.62 Å, in sharp contrast to the inequivalently distorted rhombic {Pt^{IV}₂Se₂} core found in **2**.

Besides the novelty of the selenium-containing Pt^{IV} complexes reported, a successful use of PGSE studies to characterize oligomeric structures of coordination compounds in solution has been demonstrated, which reveals the PGSE technique to be a powerful alternative when soft characterization by ESI-MS are not applicable, as for complex **3**. The excellent agreement between X-ray diffraction and PGSE in compounds **1** and **2** validates this method, and provides one of the few examples in which this comparison can be made.^[19] These results prompt the application of the PGSE methods to series of supramolecular compounds differing only on size, which opens new possibilities to study the supramolecular interactions in solution. Work is underway to understand the parameters that control the formation of the different five-bladed and seven-bladed oligomers, such as temperature and ligand:metal ratios, and efforts are currently in progress to obtain 1D helical screw-like chiral polymers.

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