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Structural study of Pt(II) and Pd(II) complexes with quinoline-2-carboxaldehyde thiosemicarbazone

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Abstract: Two square-planar complexes, [PtLCl] (1) and [PdCl] (2), were synthesized with quinoline-2-carboxaldehyde thiosemicarbazone ligand (HL), and characterized by IR and NMR spectroscopy and single crystal X-ray diffraction analysis. In both complexes L− is coordinated tridentately via the same donor atom set, while the fourth coordination site is occupied by chloride ion. However, the complexes are not isostuctural due to different types of non-covalent intermolecular interactions. These interactions were analyzed using Hirshfeld surfaces and two-dimensional fingerprint plots.

Keywords: single crystal X-ray diffraction; non-covalent interactions; N-heteroaromatic Schiff base; chelate complexes

INTRODUCTION

During the last decades, thiosemicarbazones have been developed as organic compounds with very diverse pharmacological applications. They showed a broad range of biological activity such as antituberculosis, antiviral, antimalarial and anticancer.1,2 It is assumed that the strong metal-chelating/interacting properties of thiosemicarbazones and interference with the cellular iron and copper homeostasis play an important role in their biological activity.1

Thiosemicarbazones are well known ligands that coordinate to various metal ions in different modes. In general, a bidentate binding mode via N,S donor atom set is the most common one.3,4 However, the chelating capacity of thiosemicarbazones can be enhanced when additional suitable donor atoms are present in the molecule, as in the case of α-N-heterocyclic thiosemicarbazones.3,4 As thiosemi-
carbazones exist as thione-thiol tautomers, they can bind to a metal center in the neutral or the anionic forms. An overview on observed bonding modes for this class of ligands is given in several reviews in literature covering this filed.\textsuperscript{3–5}

Thiosemicarbazone complexes have shown potent biological activity such as anticancer, antibacterial, antifungal, and antiviral owing to their property to diffuse through the semi permeable membrane of the cell lines.\textsuperscript{2,4–6} The enhanced effect of the complexes in comparison to free ligands may be attributed to the increased lipophilicity. Namely, upon coordination to the metal ion, the ligand orient with the lipophilic and aromatic parts outwards, exposing the hydrophobic part to the exterior.\textsuperscript{5} This allows the complex to enter the cell and could explain the reason why complexes result to be more active than the parent ligands.

One line of our previous research has been focused on synthesis, characterization and biological activity evaluation of d-metal complexes with α-N-heterocyclic chalcogensemcarbazones, predominantly derivatives of 2-formylpyridine and quinoline-2-carboxaldehyde.\textsuperscript{7–14} Taking into account that many properties of chemical systems are defined not only by the molecular structure but also by weak intermolecular interactions,\textsuperscript{15,16} herein the synthesis and characterization of Pd(II) and Pt(II) complexes with quinoline-2-carboxaldehyde thiosemicarbazone, with the main focus on solid state structures and main interactions that govern the crystal packings, are reported. Both chosen ions have a d\textsuperscript{8} electronic configuration and almost the same ionic radii; thus, their complexes with the same ligand systems are often isostructural. However, higher basicity of the 5d Pt(II) ion and its extended electronic density in comparison to the 4d Pd(II) ion can often result in stronger M···H−X (X = C, N, O, S) interactions for Pt(II).\textsuperscript{17} These effects can lead to a difference in the molecular structure and especially packing features of the complexes.\textsuperscript{18}

**EXPERIMENTAL**

*Materials and methods*

Thiosemicarbazide (97 %), and quinoline-2-carboxaldehyde (97 %) were obtained from Acros Organics (BVBA, Geel, Belgium), while potassium tetrachloroplatinate(II) (98 %), and potassium tetrachloropalladate(II) (98 %) were obtained from Aldrich (Sigma-Aldrich Chemie GmbH, Steinheim, Germany). All solvents (reagent grade) were obtained from commercial suppliers and used without further purification.

Elemental analyses (C, H, N, S) were performed by the standard micromethods using the ELEMENTAR Vario ELIII C,H,N,S/O analyser, and their results were found to be in good agreement (±0.4 %) with the calculated values. IR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer by the Attenuated Total Reflection (ATR) technique in the region 4000–400 cm\textsuperscript{−1}. Abbreviations used for IR spectra: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. Molar conductivities were measured at room temperature (298 K) on the Crison Multimeter MM41. The NMR spectra were performed on Bruker Avance 500 equipped with broad-band direct probe. All spectra were measured at 298 K in DMSO-\textit{d6}. Chemical shifts are given on δ scale (ppm) relative to tetramethylsilane (TMS) as internal standard for 1H and 13C.
**Synthesis of quinoline-2-carboxaldehyde thiosemicarbazone (HL)**

The ligand was synthesized, as described previously\(^1\) by the condensation reaction of quinoline-2-carboxaldehyde (0.862 g, 5.5 mmol) and thiosemicarbazide (0.500 g, 5.5 mmol) in ethanol (EtOH, 50 mL). The purity of the ligand was checked by elemental analysis and NMR spectroscopy.

**Synthesis of quinoline-2-carboxaldehyde thiosemicarbazonato-N,N,S-chloridoplatinum(II), \([\text{PtLCl}]\) (1)**

Into suspension of HL (0.100 g, 0.44 mmol) in EtOH (10 mL), a solution of K\(_2\)[PtCl\(_4\)] (0.180 g, 0.43 mmol) in 1 mL of water was added. The reaction mixture was refluxed for 1 h. After cooling to room temperature, dark red microcrystals were separated by filtration and washed with cold EtOH. Single crystals of 1 suitable for X-ray diffraction analysis were obtained by slow diffusion of EtOH vapour into DMSO solution of microcrystals. Single crystals of 1 were separated by filtration and washed with cold EtOH.

**Synthesis of quinoline-2-carboxaldehyde thiosemicarbazonato-N,N,S-chloridopalladium(II), \([\text{PdLCl}]\) (2)**

Into suspension of HL (0.050 g, 0.22 mmol) in EtOH (10 mL), a solution of K\(_2\)[PdCl\(_4\)] (0.068 g, 0.21 mmol) in 1 mL of water was added. The reaction mixture was refluxed for 1 h. After cooling to room temperature, orange microcrystals were separated by filtration and washed with cold EtOH. Single crystals of 2 suitable for X-ray diffraction analysis were obtained by slow diffusion of EtOH vapour into DMSO solution of microcrystals. Single crystals of 2 were separated by filtration and washed with cold EtOH.

IR and NMR spectral data and spectra of HL, 1 and 2 are given in Figs. S-1–S-9 of the Supplementary material.

**X-Ray crystallography**

Diffraction data were collected on a Gemini S diffractometer (Oxford Diffraction), equipped with a Mo K\(\alpha\) radiation source (\(\lambda = 0.71073 \, \text{Å}\)) and a Sapphire CCD detector. Data collection strategy calculation and data reduction were performed with the CrysAlisPro\(^20\) Structure was solved by SHELXT,\(^21\) and refined with the SHELXL-2014.\(^22\) The SHELXL\(^23\) was used as a graphical user interface for the refinement procedures. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to C atoms were placed at geometrically idealized positions with C–H distances fixed to 0.93 and 0.96 Å for sp\(^2\) and sp\(^3\) C atoms, respectively. Their isotropic displacement parameters were set equal to 1.2 and 1.5 \(\text{Ueq}\) of the parent sp\(^2\) and sp\(^3\) C atoms, respectively. The hydrogen atoms attached to N atoms were located in difference Fourier map and refined isotopically. Structures were validated with PLATON\(^24\) together with extensive use of Mercury CSD 2020.2.0\(^25,26\) and Cambridge Crystallographic Database (CSD).\(^27\)

A summary of the crystallographic data for crystal structures is given in Table I.

**Hirshfeld surfaces and two-dimensional (2D) fingerprint plots**

For visualization of Hirshfeld surfaces, CIF files were used. Hirshfeld surface visualization, presentation of results as \(d_{\text{norm}}\), shape index, and curvedness, and calculation of 2D fingerprint plots with \(d_e\) and \(d_i\) distances were generated using Crystal Explorer v.17.5.\(^28,29\) The distance from the surface to the nearest nucleus of the atom on the outside of the surface is denoted as \(d_e\), while the distance from the surface to the closest nucleus of the atom on the inside of the surface is denoted as \(d_i\). Surfaces are mapped over a standard color scale, and 2D fingerprint plots are calculated using \(d_e\) and \(d_i\) values in the range 0.4–2.8 Å.
TABLE I. Crystallographic data and refinement parameters for 1 and 2.

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>1</th>
<th>2</th>
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<tr>
<td>Chemical formula</td>
<td>C₁₁H₉Cl₄N₅PtS</td>
<td>C₁₁H₉Cl₄N₅PdS</td>
</tr>
<tr>
<td>Mₜ</td>
<td>459.82</td>
<td>371.13</td>
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<td>Crystal system</td>
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<td>Triclinic</td>
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<td>Space group</td>
<td>P2₁/n</td>
<td>P · 1</td>
</tr>
<tr>
<td>a /Å</td>
<td>11.1555(3)</td>
<td>8.6723(8)</td>
</tr>
<tr>
<td>b /Å</td>
<td>7.1925(2)</td>
<td>8.7320(8)</td>
</tr>
<tr>
<td>c /Å</td>
<td>16.2149(5)</td>
<td>9.5468(9)</td>
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<td>V /Å³</td>
<td>1250.61</td>
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<td>Z</td>
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<td>2</td>
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<tr>
<td>D₀ / Mg m⁻³</td>
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<td>2.011</td>
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<td>Radiation type</td>
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<td>Mo Kα (λ = 0.71073 Å)</td>
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<td>µ / mm⁻¹</td>
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<td>1.886</td>
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<td>Crystal size, mm</td>
<td>0.75 × 0.11 × 0.06</td>
<td>0.42 × 0.16 × 0.05</td>
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Data collection

<table>
<thead>
<tr>
<th></th>
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<td>Absorption correction</td>
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<td>0.859, 0.969</td>
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<td>2749</td>
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<tr>
<td>Observed reflections [I &gt; 2σ(I)]</td>
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<td>2463</td>
</tr>
<tr>
<td>Rint</td>
<td>0.065</td>
<td>0.022</td>
</tr>
<tr>
<td>Range of h, k, l</td>
<td>h = -14→15, k = -8→9, l = -22→18</td>
<td>h = -11→11, l = -12→11</td>
</tr>
<tr>
<td>θ values (°)</td>
<td>θmax = 29.0, θmin = 2.6</td>
<td>θmax = 28.7, θmin = 2.5</td>
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<td>Refinement</td>
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<td>R[F² &gt; 2σ(F²)], wR</td>
<td>0.021, 0.043</td>
<td>0.028, 0.055</td>
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<tr>
<td>R[all data], wR</td>
<td>0.027, 0.045</td>
<td>0.034, 0.059</td>
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<td>Goodness-of-fit (S)</td>
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<td>1.064</td>
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<td>No. of reflections</td>
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<td>2749</td>
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<td>171</td>
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<tr>
<td>No. of restraints</td>
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<td>2</td>
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<tr>
<td>Δρmax, Δρmin / e Å⁻³</td>
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<td>0.40, −0.65</td>
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<tr>
<td>CCDC no.</td>
<td>2044686</td>
<td>2044685</td>
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</table>

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization

By direct reaction of K₂[PtCl₄] or K₂[PdCl₄] with the ligand HL in an equimolar ratio (1 : 1) the corresponding Pt(II) (1) and Pd(II) (2) complexes were obtained (Scheme 1). The mole ratio of the reacting species did not influence the composition of the products. The same products were also obtained by a template reaction of metal salts with quinoline-2-carboxaldehyde and thiosemicarbazide in an equimolar ratio (1 : 1 : 1). Both complexes are soluble at room temperature in
DMSO and DMF, but sparingly soluble at elevated temperature in EtOH. The synthesized complexes are non-electrolytes, as determined by molar conductivity measurements. Elemental analysis showed that the molecules of Pt(II) and Pd(II) complexes contain one deprotonated ligand molecule and a chloride ion. In $^1$H NMR spectra of both complexes H–N3 proton signal (at 11.77 ppm in the ligand) is missing, indicating coordination of the ligand in deprotonated form. The IR spectrum of the free ligand HL exhibits bands at 3393, 3265 and 3146 cm$^{-1}$ arising from asymmetric and symmetric NH$_2$ stretching vibrations. Coordination of azomethine nitrogen to the metal ions in both complexes is suggested by the shift of the ν(C=N) toward higher frequencies (1605 cm$^{-1}$ in HL, 1632 cm$^{-1}$ in 1, 1638 cm$^{-1}$ in 2). As a consequence of the coordination of sulfur atom, the ν(C–S) band in the IR spectra of the complexes is shifted to lower frequencies (816 cm$^{-1}$ in 1 and 817 cm$^{-1}$ in 2) with respect to the metal free ligand (840 cm$^{-1}$). In both complexes coordination via quinoline nitrogen atom can assumed as the ring stretching (1527, 1501 and 1451 cm$^{-1}$) and in-plane (750 cm$^{-1}$) modes of heterocyclic ring are shifted to higher frequencies. The solid state structure of the complexes was elucidated by single crystal X-ray analysis (*vide infra*).

**Scheme 1. Synthesis of Pt(II) and Pd(II) complexes.**

**Molecular structures of 1 and 2**

Complexes 1 and 2 crystallize in the monoclinic $P2_1/n$ and triclinic $P\overline{1}$ space groups, respectively. The asymmetric unit of 1 and 2 contains M(II) ion and one deprotonated ligand coordinated via sulfur atom, quinoline and imine nitrogen atoms (Fig. 1). The fourth coordination site is occupied by chloride ligand. Overlay of the structures shows differences in the value of angles between donor atoms of the ligand (Fig. 1). The coordination geometry around metal centers is slightly distorted square-planar with geometric index of distortion $\tau = 0.10$ for 1 and $\tau = 0.13$ for 2. Due to the similar ionic radii of the metal ions, the lengths of coordination bonds (M–N1, M–N2, M–Cl and M–S) and corresponding bond angles are similar in both complexes (Table II).

**TABLE II. Selected bond lengths and angles for 1 and 2.**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length, Å</th>
<th>Angle</th>
<th>Angle, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1–Cl1</td>
<td>2.3092(10)</td>
<td>N2–Pt1–N1</td>
<td>79.88(12)</td>
</tr>
<tr>
<td>Pt1–N1</td>
<td>2.125(3)</td>
<td>N2–Pt1–S1</td>
<td>84.93(10)</td>
</tr>
<tr>
<td>Pt1–N2</td>
<td>1.946(3)</td>
<td>N1–Pt1–Cl1</td>
<td>106.18(8)</td>
</tr>
<tr>
<td>Pt1–S1</td>
<td>2.2453(10)</td>
<td>S1–Pt1–Cl1</td>
<td>89.16(4)</td>
</tr>
<tr>
<td>Bond</td>
<td>Bond length, Å</td>
<td>Angle</td>
<td>Angle, °</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>Pd1–Cl1</td>
<td>2.3236(8)</td>
<td>N2–Pd1–N1</td>
<td>80.07(9)</td>
</tr>
<tr>
<td>Pd1–N1</td>
<td>2.149(2)</td>
<td>N2–Pd1–S1</td>
<td>84.18(7)</td>
</tr>
<tr>
<td>Pd1–N2</td>
<td>1.964(2)</td>
<td>N1–Pd1–Cl1</td>
<td>108.73(6)</td>
</tr>
<tr>
<td>Pd1–S1</td>
<td>2.2237(8)</td>
<td>S1–Pd1–Cl1</td>
<td>87.04(3)</td>
</tr>
</tbody>
</table>

Fig. 1. Perspective view and labeling of molecular structure of 1 (A) and 2 (B). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. Overlay of molecular structures of 1 (green) and 2 (yellow) (C).

As previously noticed for related thiosemicabazone complexes,³⁻⁵ in 1 and 2 the C1–S1 bond is a much longer than a double bond while the adjacent C1–N3 bond is shorter than a single bond indicating a prevalent thiolate resonance form of coordinated ligand.

Although 1 and 2 have the same geometry, their crystal packings are different. With the exception of nitrogen atoms, there are no classical proton donors, thus crystal packing in both complexes are based mainly on weak non-conventional interactions. An obvious limitation in analysis of non-conventional contacts using tools available in the CSD Mercury²⁵,²⁶ is the application of distance criteria to determine the presence of a contact since interactions can extend beyond sums of van der Waals radii.³²,³³ To gain further insights into the way how molecules of 1 and 2 pack in their crystals we have employed Hirshfeld surface analysis and noncovalent interaction plots (vide infra).

Hirshfeld surface and 2D fingerprint plot analysis

The Hirshfeld surface and 2D fingerprint plot analysis represent important tools in exploring, understanding and describing crystal packing.²⁸,³⁴ The Hirshfeld surfaces mapped over \( d_{	ext{norm}} \) utilize the function of normalized distances \( d_i \) and \( d_e \), where \( d_i \) and \( d_e \) are the distances from a given point on the surface to the nearest atom inside and outside the surface, respectively. The long interatomic contacts,
the contact at van der Waals separations and short interatomic contacts can be seen as the blue, white and red color regions on the $d_{	ext{norm}}$-mapped Hirshfeld surfaces, respectively. Further chemical insight into molecular packing can be obtained using curvedness and shape-index. Interactions can be observed in the shape-index plot as red and blue regions, as well as in the curvature plot as a flat zone in the same position of the surface as in the shape-index plot. On the shape index red-colored regions correspond to an acceptor, while blue-colored regions belong to the donor of an intermolecular interaction.

2D Fingerprint plots, derived form a Hirshfeld surface, are useful method to summarize complex information about intermolecular interactions in a crystal. The color of each point on the plot, corresponding to the relative area of a $(d_e, d_i)$ pair, is recognized as the contribution from different interatomic contacts: blue, green and red correspond to small, moderate and greatest contributions, respectively. An uncolored region indicates no contribution to the Hirshfeld surface.

The Hirshfeld surfaces of the complexes are depicted in Fig. 2, while the pseudosymmetric 2D fingerprint plots are depicted in Fig. 3.
In the crystal structure of 1, each molecule of the complex achieves six types of non-covalent intermolecular interactions/contacts resulting in a three-dimensional (3D) supramolecular structure. On the other hand, each molecule of 2 forms five types of intermolecular interactions. The relative percentage contributions of close contacts to the overall Hirshfeld surfaces in both crystal structures are presented in Table III.

TABLE III. Relative contributions (%) and \( (d_1 + d_e) \) values (Å) of different interaction types in the crystal structures of 1 and 2.

<table>
<thead>
<tr>
<th>No.</th>
<th>Interaction type</th>
<th>Relative contribution, %</th>
<th>( (d_1 + d_e) ), Å</th>
<th>No.</th>
<th>Relative contribution, %</th>
<th>( (d_1 + d_e) ), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N···H</td>
<td>8.6</td>
<td>2.0</td>
<td>1</td>
<td>9.8</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>Cl···H</td>
<td>16.5</td>
<td>2.6</td>
<td>2</td>
<td>16.8</td>
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</tr>
<tr>
<td>3</td>
<td>S···H</td>
<td>11</td>
<td>3.1</td>
<td>3</td>
<td>8.7</td>
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</tr>
<tr>
<td>4</td>
<td>M···H</td>
<td>2.1</td>
<td>3.4</td>
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<td>1.5</td>
<td>3.4</td>
</tr>
<tr>
<td>5</td>
<td>C···H</td>
<td>8.4</td>
<td>4.1</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>6</td>
<td>Cg···Cg</td>
<td>6.2</td>
<td>3.6</td>
<td>5</td>
<td>5.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>

* M = Pt in 1; M = Pd in 2.

The brightness of the red spots on the Hirshfeld surfaces mapped over \( d_{norm} \) can be qualitatively correlated with the strength of intermolecular contact, *i.e.* as potential hydrogen bonds (bright spots), weak interactions (diminutive spots) or short (faint spots) interatomic contacts. The bright-red spots indicated with ‘1’ on the Hirshfeld surfaces mapped over \( d_{norm} \) (Fig. 2) indicate to donors and acceptors of classical hydrogen interactions involving N4 nitrogen atoms as donors and N3 nitrogen atoms as acceptors. The bright-red spots indicated with ‘2’ on the same surfaces point to the chlorine atom Cl1 as double acceptor in
both crystal structures. Corresponding donors however are different. In 1 donors are N4 and C2 atoms, while in 2 donors are C2 and C4. Sulfur atom S1 in 1 is involved in probable short interatomic contact with C11 carbon atom as can be seen from faint spot indicated with ‘3’. In contrast, sulfur atom S1 in 2 is as acceptor in probable weak non classical hydrogen bonding with N4 nitrogen atom as donor, since the spot indicated with ‘3’ is bright red. To examine π–π stacking in the molecular packing, an analysis of the Hirshfeld surface mapped over the shape-index and curvedness properties can be used (Fig. 2). The π–π stacking between the quinoline rings is indicated by the appearance of small blue regions surrounding bright-red spots within the rings (Fig. S-10). The presence of these interactions is also evident as the flat regions around the rings on the Hirshfeld surface mapped over curvedness for both complexes.

The relative contributio

nal packing

Analysis of crystal packing

The packing of molecules in the crystal structure of 1 is depicted in Fig. 4-A. Each molecule of 1 forms a centrosymmetric dimer with a neighbouring molecule via N4–H4B···N3′ (i = - x, 1 - y, 1 - z) hydrogen interaction (D···A = 3.039 Å, <N–H···N = 175.8°). A centrosymmetric dimer is also formed by C5–H5···Pt1′′ (ii = -1 + x, -1 + y, z) weak non-classical hydrogen interaction (D···A = 3.542 Å, <C–H···Pt = 89.9°). These two interactions are responsible for formation of 1-D infinite chains parallel to [110] direction (Fig. 4-B). Coordinated Cl1 atom is a double acceptor involved into two non-classical hydrogen interactions, N4–H4A···Cl1′ (iii = ½ - x, -1/2 + y, 1.5 - z; D···A = 3.385 Å, <N–H···Cl = 141.6°) and C2–H2···Cl1′′ (iv = -1/2 + x, 1.5 - y, -1/2 + z; D···A = 3.527 Å, <C–H···Cl = 161.6°), as depicted in Fig. 4-C. Sulphur atom S1 is involved in weak intermolecular contact C11–H11···S1′′ (v = 1/2 + x, 1.5 - y, -1/2 + z; D···A = 4.156 Å, <C–H···S = 159.7°; Fig. 4-D). Finally, in the crystal packing of 1 there are π–π stacking interactions responsible for formation of dimers (Fig. 4-E) with Cg···Cg′′ distance of 3.60 Å (vi = 1 - x, 2 - y, 1 - z; Cg is the centre of gravity of the pyridine part of the ring).

The packing of molecules in the crystal structure of 2 is depicted in Fig. 5-A. The same N4–H4B···N3′ (i = - x, 1 - y, - z; D···A = 3.009 Å, N–H···N = 175.7°) interactions are responsible for the formation of centrosymmetric dimmers. Each dimer unit is connected to neighboring complex molecule by weak hydrogen interac-
tions involving metal center (C11–H11⋯Pd1ii, ii = 1 - x, - y, 1 - z; D⋯A = 3.369 Å, <C–H⋯Pd = 84.0°), thus forming a chain parallel to [1–1 1] direction (Fig. 5-B).

Fig. 4. Non-covalent interactions in the crystal packing of 1. (A) The packing of molecules in the crystal structure; (B) A chain parallel to [110] direction formed by C–H⋯Pt interactions; (C) C–H⋯Cl and N–H⋯Cl interactions in the crystal structure of 1; (D) C–H⋯S contacts in the crystal structure of 1; (E) π–π stacking interactions.

Fig. 5. Non-covalent interactions in the crystal packing of 2. (A) The packing of molecules in the crystal structure; (B) A chain parallel to [1–1 1] direction formed by C–H⋯Pd interactions; (C) 2D plane, parallel to (021), formed by C–H⋯Cl and N–H⋯S interactions in the crystal structure of 2; (D) π–π stacking interactions.
Although Cl1 atom is also double acceptor in weak hydrogen interactions, as in 1, these interactions involve carbon atoms C2 and C4 (C2–H2···Cl1iii, iii = -1 + + x, y, z; D···A = 3.636 Å, <C–H···Cl = 150.4° and C4–H4···Cl1iii, D···A = 3.653 Å, <C–H···Cl = 153.3°), thus 1D infinite chain parallel to a-axis is formed. This chain is further connected by weak interactions involving S1 atom from adjacent complex molecule (N4–HA···Siv, iv = 1 - x, 1 - y, - z; D···A = 3.542 Å, <N–H···S = 156.2°) thus 2D plane, parallel to (021), is formed (Fig. 5-C). There are also π–π stacking interactions responsible for formation of dimers (Fig. 5-D) with Cg1···Cg2 distance of 3.76 Å (v = 1 - x, - y, 1 - z; Cg1 and Cg2 are the centre of gravity of the pyridine part and benzene part of the quinoline ring, respectively).

**CONCLUSION**

Herein, the synthesis, spectroscopic characterization and single crystal X-ray diffraction analysis of novel square-planar Pt(II) and Pd(II) complexes with quinoline-2-carboxaldehyde thiosemicarbazone is presented. In both complexes the ligand is tridentately coordinated in anionic form via sulfur, quinoline and imine nitrogen donor atoms. The fourth coordination site is occupied by chlorido ligand. Despite similar ionic radii of the metal ions and respective coordination bond lengths, crystal packing of the complexes is different. Detailed analysis of non-covalent interactions revealed that non-classical Cl···H interactions are the most represented in both crystal structures. Coordinated chlorine atom is involved in bifurcated non-classical hydrogen interactions. In both crystal structures one interaction involves imine carbon atom as a donor. However, in the second interaction thioamide nitrogen atom is a donor in the case of 1, while in in the crystal packing of 2, the interaction involves meta carbon atom of pyridine part of the aromatic ring. This might contribute to the differences in crystal packings of the synthesized complexes.

**SUPPLEMENTARY MATERIAL**

Supplementary Material is available electronically from [http://www.shd.org.rs/JSCS/](http://www.shd.org.rs/JSCS/), or from the corresponding author on request.

Additional crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre with quotation numbers CCDC 2044685 and 2044686. They are available free of charge on request via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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ИЗВОД
СТРУКТУРНА СТУДИЈА КОМПЛЕКСА Pt(II) И Pd(II) СА ХИНОЛИН-2-
КАРБОКСАЛЕДЕХИД ТИОСЕМИКАРБАЗОНОМ
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Синтетисана су два квадратно-планарна комплекса, [PtLCl] (1) и [PdLCl] (2), са хинолин-2-карбоксалехид тиосемикарбазонским лигандом (HL), који су окарактерисани IR и NMR спектроскопијом и дифракцијом Х-зрака са монокристала. У оба комплекса L- се координована тридентатно преко истог сете идонорских атома, док је четврто координационо место заузето хлоридним јоном. Међутим, комплекси нису изостуцату због различитих врста нековалентних интермолекуларних интеракција. Ове интеракције су анализирани помоћу Хиршфилдових површин и дводимензионалних графика отисака прстију.

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SUPPLEMENTARY MATERIAL TO

Structural study of Pt(II) and Pd(II) complexes with quinoline-2-carboxaldehyde thiosemicarbazone

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Synthesis of quinoline-2-carboxaldehyde thiosemicarbazone (HL)

Yield: 0.647 g (51 %). IR (ATR, cm⁻¹): 3393s, 3265m, 3146s, 3062m, 3004m, 2979m, 1605s, 1527vs, 1501s, 1451s, 1359w, 1321s; 1281s, 1208w, 1111s, 1060m, 948vw, 925w, 901vw, 867vw, 840m, 773w, 750m. ¹H NMR (500 MHz, DMSO-d₆, δ / ppm): 7.58 (1H, m), 7.72 (1H, m), 7.95 (2H, m), 8.20 (1H, s), 8.31 (2H, m), 8.41(1H, s), 8.43 (1H, s), 11.77 (1H, s). ¹³C NMR (126 MHz, DMSO-d₆, δ / ppm): 118.54, 127.55, 128.25, 128.33, 129.20, 130.33, 136.69, 142.96, 147.75, 154.33, 178.91.

Fig. S-1. IR spectrum of HL.
Fig. S-2. $^1$H NMR spectrum of HL.

Fig. S-3. $^{13}$C NMR spectrum of HL.
**Synthesis of quinoline-2-carboxaldehyde thiosemicarbazonato-N,S-chloridoplatinum(II), \([\text{PtLCl}]\) (1)**

Yield: 0.04 g (42 %). Anal. Calcd. for C\textsubscript{11}H\textsubscript{9}ClN\textsubscript{4}PtS (FW = 459.82): C, 28.73; H, 1.97; N, 12.18; S, 6.97 %. Found: C, 28.39; H, 1.59; N, 11.89; S, 7.23.

IR (ATR, cm\textsuperscript{-1}): 3395\textit{m}, 3287\textit{m}, 3224\textit{w}, 3104\textit{m}, 1632\textit{s}, 1576\textit{m}, 1544\textit{m}, 1516\textit{w}, 1471\textit{vs}, 1442\textit{vs}, 1399\textit{s}, 1317\textit{m}, 1290\textit{m}, 1237\textit{w}, 1206\textit{w}, 1143\textit{m}, 986\textit{w}, 944\textit{vw}, 868\textit{w}, 816\textit{w}, 774\textit{vw}, 745\textit{vw}, 707\textit{w}. \(^1\)H NMR (500 MHz, DMSO-\textit{d}_6, \text{δ} / ppm): 7.70 (1H, t), 7.84 (1H, d), 7.86 (1H, m), 8.05 (1H, d), 8.25 (2H, s), 8.61 (1H, s), 8.74 (1H, d), 9.69 (1H, d). \(^{13}\)C NMR (126 MHz, DMSO-\textit{d}_6, \text{δ} / ppm): 121.24, 126.36, 128.08, 128.69, 129.61, 132.54, 141.73, 147.86, 148.24, 161.82, 185.09. \(A_M\) (1 × 10\textsuperscript{-3} M, DMSO, \(\Omega^{-1}\) cm\textsuperscript{2} mol\textsuperscript{-1}): 2.76.

Fig. S-4. IR spectrum of 1.
Fig. S-5. $^1$H NMR spectrum of 1.

Fig. S-6. $^{13}$C NMR spectrum of 1.
Synthesis of quinoline-2-carboxaldehyde thiosemicarbazono-\(\text{N,N,S}\)-chloridopalladium(II), [PdLCl](2)

Yield: 0.03 g (39 %). Anal. Calcd. for C_{11}H_{9}ClN_{4}PdS (FW = 371.13): C, 35.60; H, 2.44; N, 15.10; S, 8.64 %. Found: C, 35.28; H, 2.52; N, 14.93; S, 8.35 %. IR (ATR, cm\(^{-1}\)): 3422s, 3362s, 3294s, 3127s, 3041m, 2959m, 1598w, 1578w, 1475vs, 1449vs, 1398m, 1320w, 1293w, 1233w, 1158s, 991w, 852w, 817w, 776w, 747w. \(^{1}\)H NMR (500 MHz, DMSO-\(\text{d}_6\), \(\delta\) / ppm): 7.69 (1H, t), 7.83 (2H, m), 8.04 (1H, d), 8.06 (1H, s), 8.11 (1H, s), 8.70 (1H, d), 9.48 (1H, d). \(^{13}\)C NMR (126 MHz, DMSO-\(\text{d}_6\), \(\delta\) / ppm): 121.59, 126.9, 128.43, 128.65, 132.27, 141.28, 147.42, 147.55, 159.17, 182.77. \(\Lambda_{\text{M}}\) (1 × 10\(^{-3}\) M, DMSO, \(\Omega^{-1}\) cm\(^{2}\) mol\(^{-1}\)): 1.98.

Fig. S-7. IR spectrum of 2.
Fig. S-8. $^1$H NMR spectrum of 2.

Fig. S-9. $^{13}$C NMR spectrum of 2.
Fig. S-10. Views of the Hirshfeld surface for 1 (left) and 2 (right) mapped over the shape-index property highlighting blue regions about bright-red spots within the quinoline rings which are highlighted by the white circles.

Fig. S-11. Blue patches on the Hirshfeld surfaces for 1 (left) and 2 (right) with highlighted corresponding M···H interactions.