Poster

Pd(II) and Pt(II) complexes with *N*-benzylphenotiazine – Hirshfeld atom refinement and intermolecular interaction energies

M.G. Bogdanović[1], T.P. Andrejević[2], B.Đ. Glišić[2], D.P. Ašanin[3], M.V. Rodić[1]

[1]University of Novi Sad, Faculty of Sciences, Novi Sad, Serbia, [2]University of Kragujevac, Faculty of Sciences, Kragujevac, Serbia,[3]University of Kragujevac, Institute for Information Technologies Kragujevac, Kragujevac, Serbia.
milica.bogdanovic@dh.uns.ac.rs

Phenothiazine derivatives are widely utilized in medical contexts, with their pharmacological effects contingent upon the specific side chains attached to the phenothiazine nucleus. Moreover, phenothiazine, along with its *N*-alkyl derivatives and metal–phenothiazine complexes, exhibit significant biological activity. Despite the synthesis and characterization of numerous transition metal– phenothiazine complexes, reports detailing their crystal structures remain relatively scarce [1, 2].

We herein report the crystal structure determination with quantum insights via Hirshfeld atom refinement and intermolecular interaction energies on two isostructural complexes of Pd(II) and Pt(II) with *N*-benzylphenotiazine (**L**). Complexes have formulas $[PdL_2Cl_2]\times MeCN$ (**1**) and $[PtL_2Cl_2]\times MeCN$ (**2**) (Fig. 1a), and crystallize in the triclinic space group $P\bar{1}$. The asymmetric unit of both complexes consist of two symmetrically independent molecules, containing two metal atoms (Pd(II) in complex **1** and Pt(II) in complex **2**) at special positions (centers of inversion), two ligand molecules, two chloride anions and one solvent, acetonitrile molecule. The metal atoms are situated in a square-planar environment made up of two sulfur atoms from two **L** molecules and two chloride anions (Fig. 1b). In these complexes, **L** is coordinated as monodentate through sulfur atom of phenothiazine ring.

a) b)

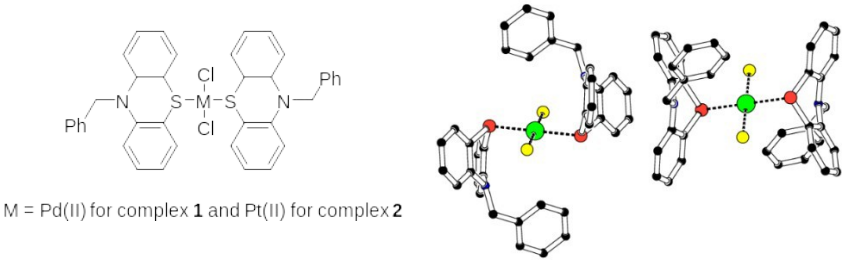

Figure 1. **a)** Chemical structure of complexes and **b)** molecular structure of the complex **1** (solvent molecules are excluded).

During the refinement process, both a conventional independent atom model (IAM) and a quantum crystallographic method known as Hirshfeld atom refinement (HAR) were employed. HAR was carried out successfully using data collected under standard conditions (room temperature and standard resolution) as well as under conditions of elevated resolution and cryogenic temperature. This approach yielded significant improvements in structural geometry and refinement statistics compared to the conventional IAM model, particularly evident in the lower *R* factor values. Notably, the bond lengths for all hydrogen atoms align closely with the standard values typically observed in neutron diffraction. Throughout HAR, all hydrogen atom positions and displacement parameters were refined without constraints. These results indicate the potential of HAR to significantly improve the structural parameters of crystal structures, even with standard data collection procedures, emphasizing its applicability for widespread adoption in small molecule crystallography.

Intermolecular interaction energies are calculated for all intermolecular pairs surrounding the Hirshfeld surface of the central molecule, and valuable insights are obtained through the computation of pairwise interaction energies. This holistic approach, unconstrained by specific atom-atom contacts, offers a deeper understanding of the hierarchy of molecular packing within the crystal from an energetic perspective.

[1] Bell, J. D., Blount, J. F., Briscoe, O. V. & Freeman, H. C. (1968). *Chemical Communications (London),* **24**, 1656.

[2] Filip, I. H., Gál, E., Lupan, I., Perde-Schrepler, M., Lönnecke, P., Surducan, M., & Silaghi-Dumitrescu, L. (2015). *Dalton Trans.,* **44***(2),* 615–629.

This research was supported by the Science Fund of the Republic of Serbia (Grant No. 7730810, Value-added biologics through eco- sustainable routes – BioECOLogics); the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grants No. 451-03-66/2024-03/ 200125 & 451-03-65/2024-03/200125) and German–Serbian joint scientific co-operation project:Application of quantum-crystallographic methods in extended routine X-ray structural analysis of small molecules (Grant No. 337- 00-253/2023-05/12).