

Synthesis and characterization of two novel Schiff base Pd(II) complexes based on 3,5-Diiodo- and 3,5-Dibromosalicylaldehydes

Alina A. Skorynina^{1,*}, Aram L. Bugaev¹, Vera V. Butova¹, Olga A. Burachevskaia¹, Pavel G. Morozov², Igor A. Estrin³, Abdelaziz Aboraia⁴, Evgeny V. Khramov⁵, Alexey A. Veligzhanin⁵, and Alexander V. Soldatov¹

¹The Smart Materials Research Institute, Southern Federal University, Sladkova 178/24, 344090 Rostov-on-Don, Russia

²Department of Chemistry, Southern Federal University, Zorge 7, 344090 Rostov-on-Don, Russia

³Rostov State Transport University, Rostovskogo Strelkovogo Polka Narodnogo Opolcheniya Sq. 2, 344038 Rostov-on-Don, Russia

⁴Physics department, Faculty of Science, Al-Azhar University assiut branch, 71542, Egypt

⁵National Research Centre “Kurchatov Institute”, Ak. Kurchatov Sq. 1, 123182, Moscow, Russia

Received: 1 Jul. 2023, Revised: 22 Sep 2023, Accepted: 22 Oct. 2023.

Published online: 1 Jan. 2024.

Abstract: We report on the synthesis and characterization of the two novel Schiff base Pd(II) complexes based on 3,5-diiodo- and 3,5-dibromosalicylaldehydes. Synthesis was made by the condensation method of these aldehydes with p-Anisidine. The structural features of the complexes were comprehensively analyzed by ¹H nuclear magnetic resonance, X-ray diffraction, optical, vibrational and X-ray absorption spectroscopies. The analysis of experimental data supported by theoretical simulations at the density functional theory level confirmed the formation of the Pd(II) complexes, and provided detailed information on the local environment of the palladium atoms.

Keywords: Palladium complexes, Schiff bases, XANES; EXAFS; UV-Vis

1 Introduction

Palladium (Pd) is one of the most catalytically miscellaneous transition metals used in its different oxidation states and coordination in various industrially relevant reactions. Pd(II) and, less often, Pd(III) complexes, depending on the types of coordinating ligands, find numerous applications from oxidation of hydrocarbons [1-4] to anti-tumor treatment [5-10]. Different Pd(II) Schiff base complexes have been used as catalysts for ethylene polymerization, epoxidation of alkenes [11], carbonylation [12], allylic alkylation [13], Suzuki [14, 15] and Heck [16] reactions.

In heterogenous catalysis, Pd(II) complexes can be created by introducing Pd active sites into porous supports, such as zeolites [17-19], covalent organic frameworks (COFs) [20-24] or metal-organic frameworks (MOFs) [15, 25-31], via organic ligands. In many cases, the functionalization by an organic ligand precedes the introduction of Pd, and the homogenous distribution of the ligands through the support material is crucial. In case the ligand contains a specific element, which can be used as a la-bel-atom, the distribution of the potential Pd-binding sites can be easily probed [27, 32].

Schiff base complexes are also used in biochemistry as antifungal and antibacterial agents [33-36]. Back in 1947, the properties of halogenated salicylaldehydes for antibacterial and antifungal use were investigated [37] and have shown the activity against both fungi and gram-negative and gram-positive bacteria. Later, some of these salicylaldehydes were used in the synthesis of Schiff bases complexes with various bi-valent and trivalent metal atoms, including works with 3,5-dibromosalicylaldehyde [38] and 3,5-diiodosalicylaldehyde [39], where salicylaldehyde derivatives with one or more halogenates in the aromatic ring exhibit antibacterial and antifungal activity. The relevance of the development of such Schiff base compounds is emphasized by re-cent works [40-42] on the synthesis, characterization and study of the antimicrobial activity of Ni(II)-, Cu(II)- and Zn(II)-based complexes with halogenated aldehydes.

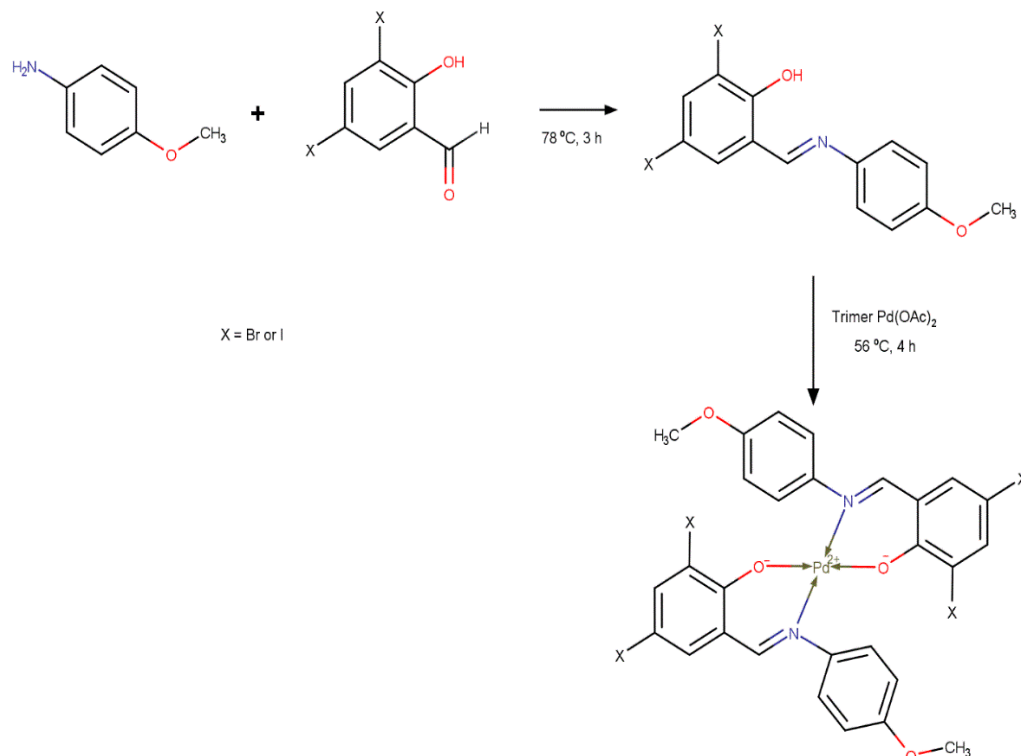
In this work, we have successfully synthesized two novel Schiff base Pd complexes based on 4-Methoxyaniline and aldehydes containing bromine or iodine atoms. The combination of these aldehydes and aniline was chosen for Schiff base synthesis for the first time. The two compounds obtained were extensively characterized by a combination of several methods. Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies were applied to define the functional groups

*Corresponding author E-mail: alinaskorynina@gmail.com

in the synthesized structures. X-ray diffraction (XRD) was used to confirm the formation of new crystalline phase. Molecular electronic transitions were determined from the UV-Vis spectroscopy of Schiff base ligands and the corresponding complexes. Synchrotron-based X-ray absorption spectroscopy (XAS) was used to accurately describe the local atomic environment of palladium atoms in the new systems. Experimental data were supported by density functional theory (DFT) calculations.

2 Result and Discussion

2.1 Local structure of Pd(II) in C1-I and C2-Br



Scheme 1. General procedure for the preparation of newly synthesized compounds.

Scheme 1 demonstrated the proposed scheme for the formation of palladium complexes. To determine the atomic structure of the synthesized complexes, the synchrotron-quality XAS data was collected. The edge position and the shaping of the XANES region indicates Pd(II) sites in a square planar geometry. The Fourier-transformed (FT) EXAFS data also shows the similarity of the local environment of Pd atoms to that in Pd(II) acetate (Fig. 1). Fourier-analysis of EXAFS summarized in Table S1 indicates very close Pd–A distances of ca 2 Å in all studied samples, where A refers to either C, N, or O atoms which are poorly distinguishable by EXAFS (Fig. S1). However, there is a clear difference in both the XANES and EXAFS regions of the complexes from Pd(OAc)₂, while the similarity between the formers indicates that new complexes were formed. Also, the well-defined higher shell contributions observed in EXAFS should originate from the well-ordered carbon atoms of the complexes. Both facts above unambiguously prove the formation of Pd-complexes with aldehydes.

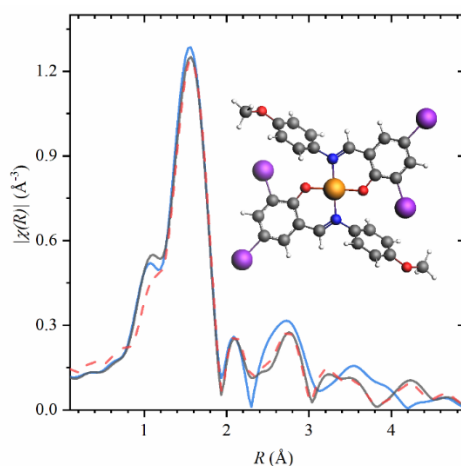


Fig. 1. Pd *K*-edge FT-EXAFS data (phase-uncorrected) for the Pd(OAc)₂ trimer (blue), C1-I (black) and C2-Br (dashed red). DFT-relaxed structure of newly synthesized complexes, where Pd atom is highlighted by gold color, C – grey, H – white, O – red, N – blue and Br or I – purple.

As the next step, we constructed the atomic models of the two complexes based on the initial guess, proposed in Scheme 1 for trans-coordinated complexes with square-planar Pd(II), and two cis-coordinated square-planar Pd(II) complexes. The geometries for the suggested models were relaxed at the DFT level of theory. In both cases, for iodine and bromine containing complexes, the trans-isomers are preferable (Fig. S2), the energy differences between cis- and trans-isomers are 3.9 and 4.5 kcal/mol for C1-I and C2-Br, respectively. The resulting structures (Fig. 1) were used for ab initio simulation of XANES spectra, which reproduced the same changes compared to the simulated Pd(OAc)₂ spectrum, as those observed in the experiment (Fig. 2).

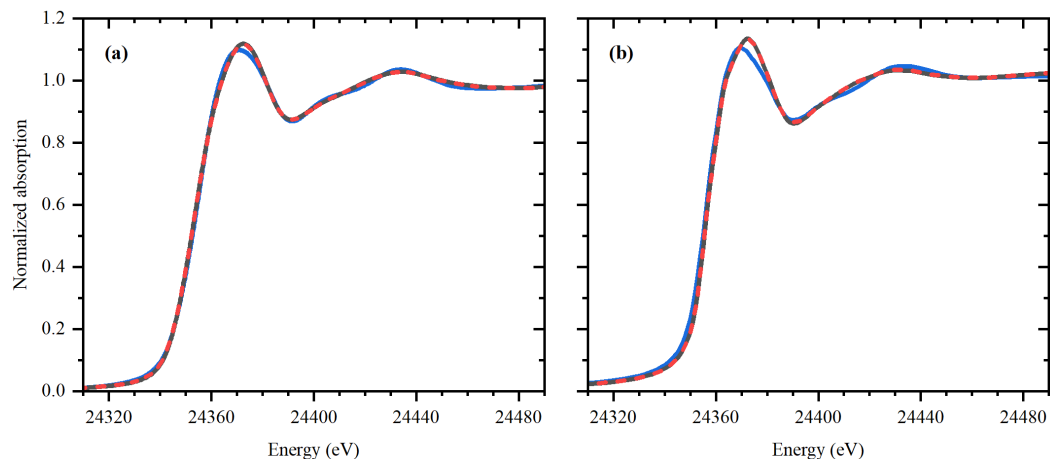


Fig. 1. Experimental (a) and theoretical (b) Pd *K*-edge XANES spectra for trimer of Pd(II) acetate (blue), C1-I (black) and C2-Br (dashed red).

¹H NMR spectroscopy. The main chemical shifts assigned in the ¹H NMR spectra of C1-I and C2-Br are shown in Table 1. The data were recorded in DMSO-d₆ due to its high dissolving power, and the simplicity of its own spectrum. Both spectra (Fig. S3 and Fig. S4) of the complexes are characterized by an overlap of the protons of the methoxy group signal with the signal of the protons of water (δ 3.70 ppm); therefore, the exact value of the chemical shift of these protons has not been established.

Table 1. Chemical shifts (ppm) from ¹H-NMR spectra in DMSO-d₆ of C1-I and C2-Br.

Sample	3H, OCH ₃	2H, 6'-H, 3'-H	2H, 2'-H, 5'-H	1H, H-5	1H, 3-H	1H, N=CH
C1-I	3.70s	6.96d ^a	7.65d ^a	7.80d ^c	7.82d ^c	7.93s
C2-Br	3.70s	6.96d ^b	7.49d ^b	7.57d ^d	7.67d ^d	7.99s

³JHH = ^a 8.9 Hz, ^b 8.8 Hz
⁴JHH = ^c 2.3 Hz, ^d 2.5 Hz

From the gravimetric **elemental analysis**, found atomic ratio of I:Pd in C1-I is equal to 3.79 and Br:Pd = 3.91 in C2-Br, which again confirms the structural models of the complexes.

According to the **powder XRD data analysis**, both complexes were crystallized, with the crystal different from the original ligands (Fig. S5). Both metal complexes are poorly soluble in water but soluble in DMSO.

2.2 Optical and vibrational properties of Schiff base ligands and their Pd(II) complexes

The **UV-Vis** absorption properties of the ligands and their complexes were investigated upon their dissolution in DMSO at room temperature (Table 2). DMSO was chosen as a solvent for UV-Vis mainly because of its transparency in the range above 270 nm, since the calculated optical spectra for the proposed structures have shown that the most significant optical bands in the range of 300–470 nm. Moreover, DMSO is most often used when working with biological and medical objects, because it is less toxic than other common solvents with similar properties, such as HMPA and DMF. Since the most promising and preferable applications of new complexes are the antibacterial and antifungal ones, the characterization should be carried out under similar conditions. The experimental optical absorption spectra were compared with those simulated by DFT. The experimental absorption spectra of the complexes are in agreement with those reported elsewhere [43–46], where Pd(II) is also in square-planar coordination with two oxygen atoms and two nitrogen atoms. In Fig. 3, the calculated electronic transitions are highlighted by vertical lines with the height proportional to the oscillator strength, the theoretical absorption spectra were obtained by applying a Gaussian convolution with a constant full width at half maximum (FWHM) of 30 nm. The calculated wavelengths, vertical excitation energies, oscillator strengths, and percentage contributions of dominant electronic transitions for ligands and complexes are summarized in Table S2, along with the experimental transition wavelengths for comparison. Based on DFT results (Fig. S6), the spectral transitions have been assigned. The lowest energy transition in the Schiff ligands/complexes is an intraligand "phenol/phenoxide-to-imine" charge transfer (ILCT, broad). Then next is $\pi \rightarrow \pi^*$ transitions (with a vibrational progression) on the aromatic rings. The d-d transitions are very weak and broad and are unlikely to be observed as peaks. The Pd-to-imine metal-to ligand-charge transfer (MLCT) is broad and weak, and, since the Pd(II) ions do not oxidize easily, it is at higher energy. The charge transfer between the halogen group and the phenyl ring (XLCT) also at still higher energy.

The optical band gap (E_g) values for the ligands and complexes were estimated from the experimental UV-Vis spectra by the Tauc plot method (Fig. S7). The values obtained for L1-I and C1-I were found to be 2.35 eV and 2.36, respectively. For L2-Br and C2-Br, E_g was determined as 2.28 and 2.38 eV, respectively. Fig. 4 represents the computed energy level diagrams of the boundary molecular orbitals (MO) for the Schiff base ligands and their complexes. The diagrams were constructed from the analysis of the DFT calculation results. The energy gap was evaluated as the difference between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO).

Table 2. The UV-Vis absorption bands (λ_{exp}) and molar attenuation coefficient (ϵ) of the ligands and its Pd(II) complexes in DMSO solution at room temperature.

Sample	λ_{exp} , nm (ϵ , $\times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)				
L1-I	324 (1130.57)	343 (1196.87)	365 (1273.64)	382 (1332.96)	445 (1552.79)
L2-Br	–	343 (1362.78)	365 (1450.19)	383 (1521.71)	446 (1772.02)
C1-I	323 (2416.13)	–	–	–	419 (3134.24)
C2-Br	318 (5671.63)	–	–	–	414 (7383.82)

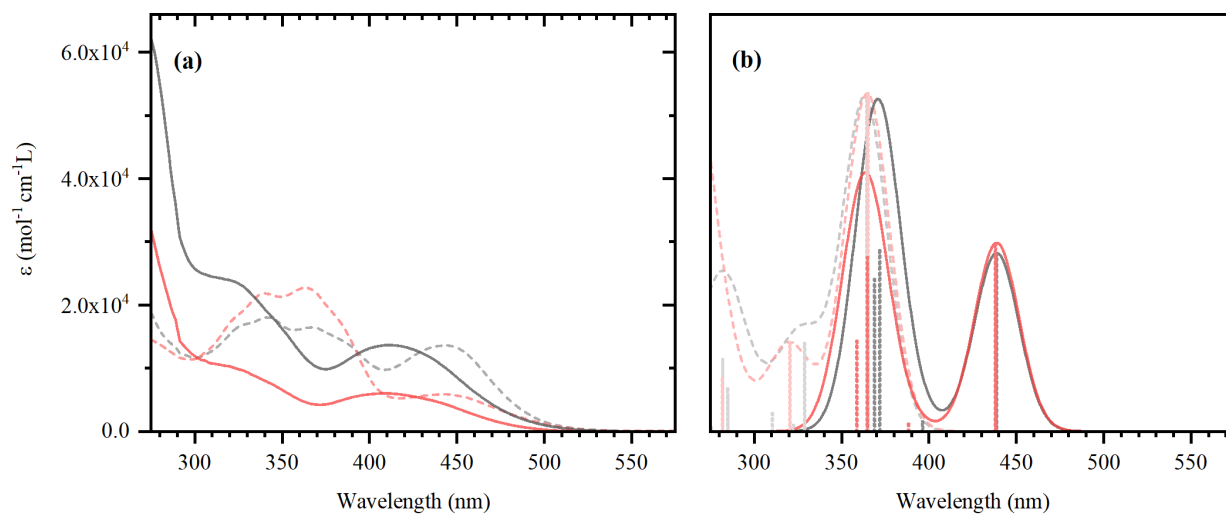


Fig. 2. Experimental (a) and theoretical (b) UV-Vis spectra for ligands (dashed lines) L1-I (light gray) and L2-Br (pink) and complexes (solid lines) C1-I (gray) and C2-Br (red). Vertical bars represent individual calculated electronic transitions with the height proportional to the oscillator strength (the color code is the same as the lines).

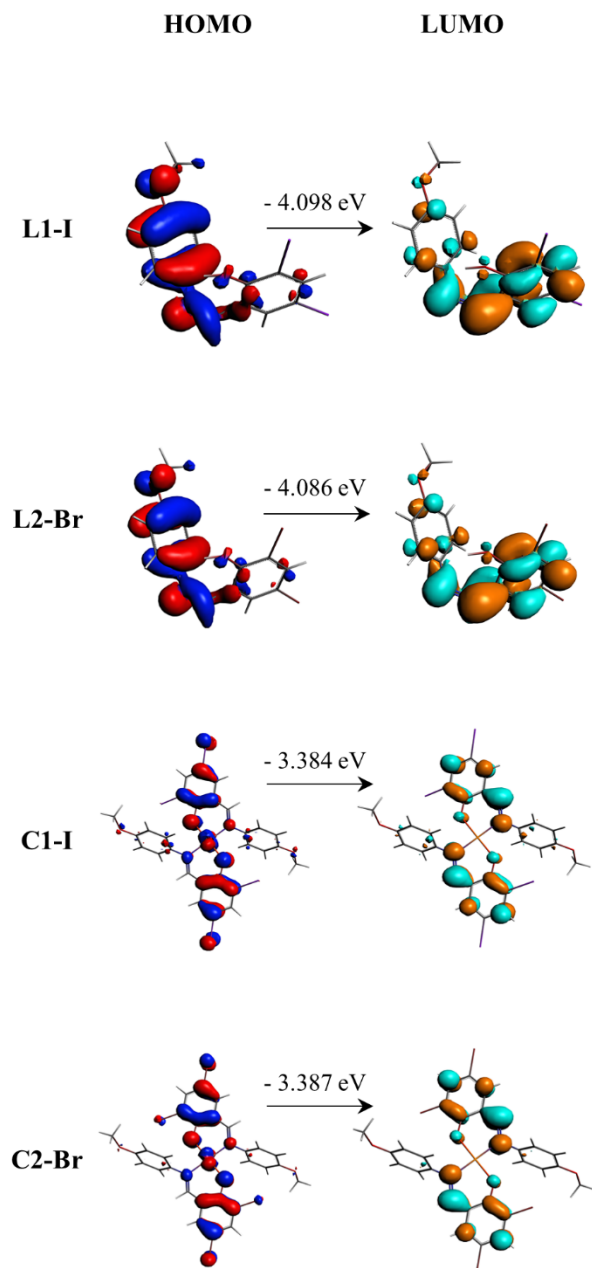


Fig. 3. DFT computed HOMO and LUMO diagrams for ligands and their complexes.

Infrared spectra. To study the vibrational properties, FTIR spectra of the complexes were compared with the FTIR spectra of ligands and computed vibrational spectra (Fig. 4). Both complexes containing bromine and iodine have similar spectra. Strong absorption peaks in the region $1090 - 1520 \text{ cm}^{-1}$ were assigned to the bending C–H modes and stretching C=N, C=C and C=O modes.

Comparing the spectra of the ligands with that of the corresponding metal complexes, no significant shifts were found. The list of bands association is presented in Table 3 together with theoretically calculated vibrational modes. New bands are found in the spectra of the complexes in the $500 - 600 \text{ cm}^{-1}$ region, which are assigned to $\nu(\text{Pd-O})$, and $400 - 500 \text{ cm}^{-1}$ region to (Pd-N) stretching vibrations for metal complexes [47]. The maximum intensity of the absorption band near 1360 cm^{-1} is assigned to C=C stretching vibrations in the aromatic rings together with $\nu(\text{C-O})$.

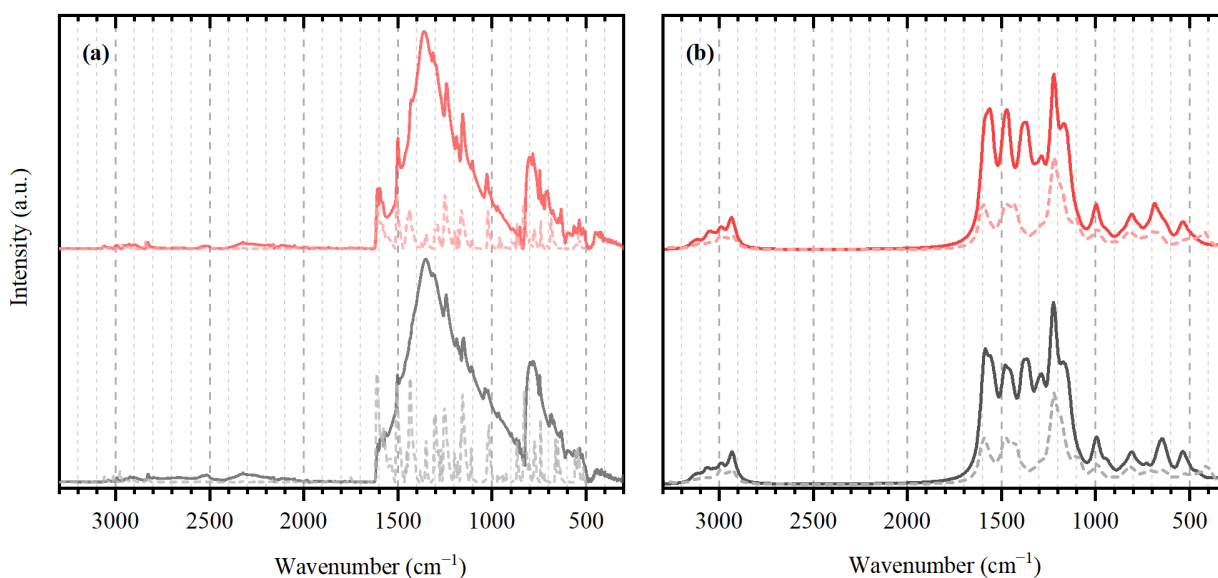


Fig. 4. Experimental (a) and computed (b) FTIR spectra of complexes (solid lines) C1-I (gray) and C2-Br (red) and ligands (dashed lines) L1-I (light gray) and L2-Br (light red).

Table 3. IR frequencies (cm^{-1}) for ligands L1-I, L2-Br, and complexes C1-I, C2-Br.

Assignment	Experimental				Simulated			
	L1-I	L2-Br	C1-I	C2-Br	L1-I	L2-Br	C1-I	C2-Br
$\nu(\text{C-H})$	3066–2895	3084–2870	3074–2843	3078–2856	3126–2914	3130–2910	3122–2916	3123–2915
$\nu(\text{C=N})$	1612–1500	1615–1508	1606–1508	1606–1496	1588–1485	1594–1475	1578–1528, 1365–1303	1578–1538, 1389–1356
$\nu(\text{C=C})$	1612–1500	1615–1508	1606–1508	1606–1496	1588–1485	1594–1475	1578–1528	1578–1538
$\delta(\text{O-H})$	1430–1300	1433–1300			1533–1350	1594–1354		
$\delta(\text{C-H})$	1430–1352	1433–1345	1420–1302	1433–1310	1464–1210	1464–1212	1477–1296	1478–1214
$\nu(\text{C-O})$	1351–1261	1345–1254	1327–1244	1361–1240	1424–1360	1398–1223	1384–1218	1389–1276
$\delta(\text{C=N})$	1153	1159	1149	1149	876	1140	849	853
$\nu(-\text{OCH}_3)$	1016	1021	1030	1028	995	993	995	996
$\delta(\text{C=C})$	1012	1017	1025	1025	985	741	986	986
$\nu(\text{Pd-N})$	–	–	400–500	400–500			849–762	764–717
$\nu(\text{Pd-O})$	–	–	500–600	500–600			643	629–559
$\nu(\text{C-I})$	652	–	632	–	587		579–518	
$\nu(\text{C-Br})$	–	682	–	678		602		628–517

Two Schiff base ligands and their palladium(II) complexes have been successfully synthesized using known condensation technique [47-49], however certain aldehydes and amines chosen for the synthesis were used for the first time. The main feature of the obtained materials is the presence in their structure of metal ions and halogens at once [50]. An extensive study by XAS, NMR, FTIR and UV-Vis spectroscopies made it possible to confirm the formation of complexes, as well as to determine their local features. The correlation of IR spectrometry data with theoretical data is consistent with the results presented for similar complexes in the former studies [42, 46].

Formation of Pd–ligands bonding in complexes significantly changes the electronic spectra since the molecular orbital of the entire molecule changes, which means that charge transfer occurs between its other parts [51, 52].

3 Experimental Procedure

3.1 Synthesis

Schiff base ligands were synthesized by a typical condensation of 4-Methoxyaniline and aldehydes in ethanol [53].

Ligand 1 (L1-I). The solution of 0.12 g (0.98 mmol) 4-Methoxyaniline in 5 mL ethanol was added to the hot solution of 0.37 g (0.98 mmol) 3,5-Diiodosalicylaldehyde in 5 mL ethanol. An orange precipitate was immediately observed. The mixture was boiled for 3 hours. The product was then filtered, washed with boiling ethanol and ether, and dried under vacuum. Final product: orange fine crystalline. Yield: 0.35 g (74%). Melting point (T_{mp}) = 158 °C. Determined molecular weight, %: C 35.40; H 2.50; I 52.50; N 3.30. A chemical formula of the L1-I is $C_{14}H_{11}I_2NO_2$. Theoretical molecular weight, %: C 35.11; H 2.29; I 52.99; N 2.92. Molecular mass (m) = 478.94 g/mol.

Ligand 2 (L2-Br). A solution of 0.14 g (1.14 mmol) 4-Methoxyaniline in 5 mL ethanol was added to the hot solution of 0.32 g (1.14 mmol) 3,5-Dibromosalicylaldehyde in 5 mL ethanol. Three drops of formic acid, acting as a catalyst, were added to the resulting orange solution and refluxed for 4.5 hours. The formed precipitate was separated, washed with ethanol, and recrystallized from 11 mL of ethanol. Final product: orange crystals. Yield: 0.34 g (77%). T_{mp} = 119 °C. Determined molecular weight, %: C 43.90; H 2.40; Br 41.90; N 3.30. A chemical formula of the L2-Br is $C_{14}H_{11}Br_2NO_2$. Theoretical molecular weight, %: C 43.67; H 2.86; Br 41.51; N 3.64. m = 384.94 g/mol.

Complex 1 (C1-I) (2,4-diiodo-6-(((4-methoxyphenyl)imino)methyl) palladium (II) phenolate). The solution of 0.063 g (0.14 mmol) trimer palladium acetate (II) in 4 mL acetone was added to the hot suspension of 0.27 g (0.28 mmol) L1-I in 6 mL acetone. After 10 min of boiling an orange crystalline product was formed. The mixture was boiled for 4 hours. The precipitate was separated, washed with boiling acetone and methanol, and dried in a vacuum. Final product: orange crystals. Yield: 0.22 g (76%). Determined molecular weight, %: C 31.90; H 1.50; I 47.40; N 2.90; Pd 10.50. A chemical formula of the C1-I is $C_{28}H_{20}I_4N_2O_4Pd$. Theoretical molecular weight, %: C 31.66; H 1.88; I 47.78; N 2.64; Pd 10.02. m = 1062.28 g/mol.

Complex 2 (C2-Br) (2,4-dibromo-6-(((4-methoxyphenyl)imino)methyl) palladium (II) phenolate): the solution of 0.073 g (0.15 mmol) trimer palladium acetate (II) in 4 mL acetone was added to the hot suspension of 0.25 g (0.30 mmol) L2-Br in 6 mL acetone. A solution changed its color to red. The mixture was boiled for 4 hours. The precipitate was separated, washed with boiling acetone and methanol and dried in a vacuum. Final product: orange crystals. Yield: 0.2 g (71%). Determined molecular weight, %: C 38.60; H 2.40; Br 36.10; N 3.60; Pd 12.30. A chemical formula of the C2-Br is $C_{28}H_{20}Br_4N_2O_4Pd$. Theoretical molecular weight, %: C 38.46; H 2.29; Br 36.55; N 3.20; Pd 12.17. m = 874.28 g/mol.

3.2 Characterization

Elemental analysis of C, H, N elements were carried out on Carlo Erba TCM 480 equipment using sulfanilamide as a reference. The metal content was determined gravimetrically in the analytical laboratory of the Institute of Physical and Organic Chemistry (SFedU, Rostov-on-Don, Russia). Melting points were measured on a Kofler table.

NMR data. 1H NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer with working frequencies of 250 MHz at 25 °C in d_6 -DMSO.

XRD measurements were carried out on the Bruker D2 PHASER diffractometer in Bragg–Brentano geometry with $Cu K\alpha_{1,2}$ radiation ($\lambda = 1.5406 \text{ \AA}$). X-ray diffraction data were collected in the range from 10 to 50° with 0.05° step and 0.2 s acquisition time.

Pd K-edge XAS spectra were collected at STM beamline of National Research Center “Kurchatov Institute” (Moscow, Russia). Pelletized samples were measured in the transmission mode by step scanning of Si(220) channel-cut monochromator from 24.0 to 25.4 keV. For C1-I and C2-Br samples, 4 scans, taking around 13 min each, were measured and averaged. Pd(II) acetate ($Pd(OAc)_2$) and Pd foil were measured as reference samples. Data processing and the first-shell Fourier-analysis of extended X-ray absorption fine structure (EXAFS) region was performed in Demeter software [54].

FTIR spectra of attenuated total reflectance (ATR) mode were measured on a Bruker Vertex 70 spectrometer equipped with a Bruker Platinum ATR accessory with a diamond crystal. Spectra were collected with resolution of 1 cm^{-1} using a mercuric cadmium telluride (MCT) detector in range from 5000 to 500 cm^{-1} cooled by liquid nitrogen and in range from 5000 to 30 cm^{-1} using deuterated triglycine sulfate (DTGS) detector. Background spectra were collected on air with empty crystal of ATR accessory before each measurement.

UV-Vis spectra were measured on Shimadzu UV-2600 spectrophotometer. An ISR-2600Plus integrating sphere was used for the measurements in diffuse reflectance mode. Two 5-mm quartz cuvettes were filled with a sample dissolved in DMSO and pure DMSO as a reference. The spectral acquisition was performed with a 0.5 nm step in a range 900–190 nm. Atomic models and theoretical vibrational and optical spectra of the synthesized complexes and palladium(II) acetate were obtained in ADF code [55, 56] using Grimme DFT-D4 dispersion correction with the electronegativity equilibrium model in B3LYP Hybrid exchange-correlation (XC) functional and all-electron TZP (Triple Z, 1 polarization function) basic set. Spin-orbit coupling was also considered. Theoretical X-ray absorption near edge structure (XANES) spectra were calculated for the obtained models using a full potential finite difference method implemented in FDMNES code [57]. All calculations were performed with relativistic corrections and the radius of the computational sphere of 7 Å. The energy ranges were limited to 24.27 – 24.48 keV for Pd K-edge.

4 Conclusion

We have successfully synthesized two novel Schiff base complexes with palladium and determined their structure, optical and vibrational properties. Both complexes exhibit 4-coordinated Pd(II) centers bonded with nitrogen and oxygen atoms of the aldehydes, which was unambiguously proven by extensive experimental and theoretical analysis. The use of synchrotron-based X-ray absorption spectroscopy, which is not a widely accessible and frequently used technique to study such complexes, provided unambiguous proof of the 3D local atomic structure around the Pd atoms. MLCT, ILCT, and XLCT transitions in the optical spectra of the complexes were identified. The band gap of the synthesized ligands and their complexes ranges from 2.28 to 2.38 eV but is higher for iodine-containing materials.

An important feature of the complexes obtained is that in addition to Pd, they also contain Br or I, with a ratio of 4:1 in relation to palladium, since the halogenated salicylaldehydes was previously shown to have antiviral and antibacterial properties [38-41]. Another possible application is their use as organic ligands for functionalization of porous supports by Pd for the use in catalysis. In this case, bromine and iodine can be used to track the homogeneity of the ligand distribution prior to the introduction of Pd.

5 Acknowledgments

This research was funded by the RFBR according to project No. 20-32-90078. A.L.B. acknowledges the President's Grant of Russian Federation for young scientists MK-5853.2021.1.2 for the measurement of Pd *K*-edge XANES data. The authors acknowledge the National Research Center "Kurchatov Institute" for providing the beamtime at the STM beamline and the Center for Collective Use "Nanoscale structure of matter" for the laboratory equipment used in the project.

References

- [1] Henry, P., Palladium catalyzed oxidation of hydrocarbons. Springer Science & Business Media: 1979; Vol. 2.
- [2] Negishi, E., Handbook of Organopalladium Chemistry for Organic Synthesis. John Wiley & Sons: New York, 2002; Vol. 1.
- [3] Taylor, M. S.; Jacobsen, E. N., Asymmetric catalysis in complex target synthesis. Proceedings of the National Academy of Sciences of the United States of America 2004, 101, (15), 5368. 10.1073/pnas.0307893101
- [4] Liu, X.; Manzur, C.; Novoa, N.; Celedón, S.; Carrillo, D.; Hamon, J.-R., Multidentate unsymmetrically-substituted Schiff bases and their metal complexes: Synthesis, functional materials properties, and applications to catalysis. Coordination Chemistry Reviews 2018, 357, 144-172. 10.1016/j.ccr.2017.11.030
- [5] Bakr, E. A.; Al-Hefnawy, G. B.; Awad, M. K.; Abd-Elatty, H. H.; Youssef, M. S., New Ni(II), Pd(II) and Pt(II) complexes coordinated to azo pyrazolone ligand with a potent anti-tumor activity: Synthesis, characterization, DFT and DNA cleavage studies. Applied Organometallic Chemistry 2017, 32, (2), e4104. 10.1002/aoc.4104
- [6] Tušek-Božić, L.; Juribašić, M.; Traldi, P.; Scarcia, V.; Furlani, A., Synthesis, characterization and antitumor activity of palladium(II) complexes of monoethyl 8-quinolylmethylphosphonate. Polyhedron 2008, 27, (4), 1317-1328. 10.1016/j.poly.2008.01.002
- [7] Lim, M. C.; Bruce Martin, R., The nature of cis amine Pd(II) and antitumor cis amine Pt(II) complexes in aqueous solutions. Journal of Inorganic and Nuclear Chemistry 1976, 38, (10), 1911-1914. 10.1016/0022-1902(76)80121-2
- [8] Padhye, S.; Afrasiabi, Z.; Sinn, E.; Fok, J.; Mehta, K.; Rath, N., Antitumor Metallothiosemicarbazones: Structure and Antitumor Activity of Palladium Complex of Phenanthrenequinone Thiosemicarbazone. Inorganic Chemistry 2005, 44, (5), 1154-1156. 10.1021/ic048214v
- [9] Zhao, G.; Lin, H.; Ping, Y.; Sun, H.; Zhu, S.; Xuncheng, S.; Chen, Y., Ethylenediamine-palladium(II) complexes with pyridine and its derivatives: synthesis, molecular structure and initial antitumor studies. Journal of Inorganic Biochemistry 1999, 73, (3), 145-149. 10.1016/S0162-0134(99)00009-4
- [10] Taqui Khan, B.; Najmuddin, K.; Shamsuddin, S.; Annapoorna, K.; Bhatt, J., Synthesis, antimicrobial, and antitumor activity of a series of palladium(II) mixed ligand complexes. Journal of Inorganic Biochemistry 1991, 44, (1), 55-63. 10.1016/0162-0134(91)80061-L
- [11] Zhou, X.-G.; Huang, J.-S.; Yu, X.-Q.; Zhou, Z.-Y.; Che, C.-M., Binaphthyl Schiff base complexes of palladium(II). Structures and reactivities toward alkene epoxidation. Journal of the Chemical Society, Dalton Transactions 2000, (7), 1075-1080. 10.1039/A908917I
- [12] Jedlicka, B.; Weissensteiner, W.; Kégl, T.; Kollár, L., Carbonylation (hydroformylation and hydroalkoxycarbonylation) of styrene in the presence of transition metal-ferrocene-based aminophosphine systems. Journal of Organometallic Chemistry 1998, 563, (1), 37-41. 10.1016/S0022-328X(98)00478-1
- [13] Brunner, H.; Deml, I.; Dimberger, W.; Ittner, K.-P.; Reißer, W.; Zimmermann, M., Synthesis of the Stereoisomers of Methohexital by Palladium-Catalyzed Allylation. European Journal of Inorganic Chemistry 1999, 1999, (1), 51-59. 10.1002/(SICI)1099-0682(199901)1999:1<51::AID-EJIC51>3.0.CO;2-Y

- [14] Das, P.; Linert, W., Schiff base-derived homogeneous and heterogeneous palladium catalysts for the Suzuki–Miyaura reaction. *Coordination Chemistry Reviews* 2016, 311, 1-23. 10.1016/j.ccr.2015.11.010
- [15] Rostamnia, S.; Alamgholiloo, H.; Liu, X., Pd-grafted open metal site copper-benzene-1,4-dicarboxylate metal organic frameworks (Cu-BDC MOF's) as promising interfacial catalysts for sustainable Suzuki coupling. *Journal of Colloid and Interface Science* 2016, 469, 310-317. 10.1016/j.jcis.2016.02.021
- [16] Iyer, S.; Kulkarni, G. M.; Ramesh, C., Mizoroki–Heck reaction, catalysis by nitrogen ligand Pd complexes and activation of aryl bromides. *Tetrahedron* 2004, 60, (9), 2163-2172. 10.1016/j.tet.2003.12.012
- [17] Brunel, D.; Bellocq, N.; Sutra, P.; Cauvel, A.; Laspéras, M.; Moreau, P.; Di Renzo, F.; Galarneau, A.; Fajula, F., Transition-metal ligands bound onto the micelle-templated silica surface. *Coordination Chemistry Reviews* 1998, 178-180, 1085-1108. 10.1016/S0010-8545(98)00121-0
- [18] Vercammen, J.; Bocus, M.; Neale, S.; Bugaev, A.; Tomkins, P.; Hajek, J.; Van Minnebruggen, S.; Soldatov, A.; Krajnc, A.; Mali, G.; Van Speybroeck, V.; E. De Vos, D., Shape-selective C–H activation of aromatics to biaryl compounds using molecular palladium in zeolites. *Nature Catalysis* 2020, 3, (12), 1002-1009. 10.1038/s41929-020-00533-6
- [19] Freire, C.; Nunes, M.; Pereira, C.; Fernandes, D. M.; Peixoto, A. F.; Rocha, M., Metallo(salen) complexes as versatile building blocks for the fabrication of molecular materials and devices with tuned properties. *Coordination Chemistry Reviews* 2019, 394, 104-134. 10.1016/j.ccr.2019.05.014
- [20] Segura, J. L.; Mancheno, M. J.; Zamora, F., Covalent organic frameworks based on Schiff-base chemistry: synthesis, properties and potential applications. *Chem Soc Rev* 2016, 45, (20), 5635-5671. 10.1039/c5cs00878f
- [21] Ding, S.-Y.; Gao, J.; Wang, Q.; Zhang, Y.; Song, W.-G.; Su, C.-Y.; Wang, W., Construction of Covalent Organic Framework for Catalysis: Pd/COF-LZU1 in Suzuki–Miyaura Coupling Reaction. *Journal of the American Chemical Society* 2011, 133, (49), 19816-19822. 10.1021/ja206846p
- [22] Hou, Y.; Zhang, X.; Sun, J.; Lin, S.; Qi, D.; Hong, R.; Li, D.; Xiao, X.; Jiang, J., Good Suzuki-coupling reaction performance of Pd immobilized at the metal-free porphyrin-based covalent organic framework. *Microporous and Mesoporous Materials* 2015, 214, 108-114. 10.1016/j.micromeso.2015.05.002
- [23] Biswal, B. P.; Chandra, S.; Kandambeth, S.; Lukose, B.; Heine, T.; Banerjee, R., Mechanochemical Synthesis of Chemically Stable Isoreticular Covalent Organic Frameworks. *Journal of the American Chemical Society* 2013, 135, (14), 5328-5331. 10.1021/ja4017842
- [24] Lin, S.; Hou, Y.; Deng, X.; Wang, H.; Sun, S.; Zhang, X., A triazine-based covalent organic framework/palladium hybrid for one-pot silicon-based cross-coupling of silanes and aryl iodides. *RSC Advances* 2015, 5, (51), 41017-41024. 10.1039/c5ra04433b
- [25] Li, X.; Van Zeeland, R.; Maligal-Ganesh, R. V.; Pei, Y.; Power, G.; Stanley, L.; Huang, W., Impact of Linker Engineering on the Catalytic Activity of Metal–Organic Frameworks Containing Pd(II)–Bipyridine Complexes. *ACS Catalysis* 2016, 6, (9), 6324-6328. 10.1021/acscatal.6b01753
- [26] Reiner, B. R.; Mucha, N. T.; Rothstein, A.; Temme, J. S.; Duan, P.; Schmidt-Rohr, K.; Foxman, B. M.; Wade, C. R., Zirconium Metal–Organic Frameworks Assembled from Pd and Pt P(N)N(N)P Pincer Complexes: Synthesis, Postsynthetic Modification, and Lewis Acid Catalysis. *Inorg Chem* 2018, 57, (5), 2663-2672. 10.1021/acs.inorgchem.7b03063
- [27] Van Velthoven, N.; Henrion, M.; Dallenes, J.; Krajnc, A.; Bugaev, A. L.; Liu, P.; Bals, S.; Soldatov, A. V.; Mali, G.; De Vos, D. E., S,O-Functionalized Metal–Organic Frameworks as Heterogeneous Single-Site Catalysts for the Oxidative Alkenylation of Arenes via C–H activation. *ACS Catalysis* 2020, 10, (9), 5077-5085. 10.1021/acscatal.0c00801
- [28] Bugaev, A. L.; Skorynina, A. A.; Braglia, L.; Lomachenko, K. A.; Guda, A.; Lazzarini, A.; Bordiga, S.; Olsbye, U.; Lillerud, K. P.; Soldatov, A. V.; Lamberti, C., Evolution of Pt and Pd species in functionalized UiO-67 metal-organic frameworks. *Catalysis Today* 2019, 336, 33-39. 10.1016/j.cattod.2019.03.054
- [29] Kamyshova, E. G.; Skorynina, A. A.; Bugaev, A. L.; Lamberti, C.; Soldatov, A. V., Formation and growth of Pd nanoparticles in UiO-67 MOF by *in situ* EXAFS. *Radiation Physics and Chemistry* 2020, 175, 10.1016/j.radphyschem.2019.02.003
- [30] Bugaev, A. L.; Guda, A. A.; Lomachenko, K. A.; Kamyshova, E. G.; Soldatov, M. A.; Kaur, G.; Øien-Ødegaard, S.; Braglia, L.; Lazzarini, A.; Manzoli, M.; Bordiga, S.; Olsbye, U.; Lillerud, K. P.; Soldatov, A. V.; Lamberti, C., Operando study of palladium nanoparticles inside UiO-67 MOF for catalytic hydrogenation of hydrocarbons. *Faraday Discussions* 2018, 208, (0), 287-306. 10.1039/C7FD00224F
- [31] Llabresiamena, F.; Abad, A.; Corma, A.; Garcia, H., MOFs as catalysts: Activity, reusability and shape-selectivity of a Pd-containing MOF. *Journal of Catalysis* 2007, 250, (2), 294-298. 10.1016/j.jcat.2007.06.004
- [32] Van Velthoven, N.; Wang, Y.; Van Hees, H.; Henrion, M.; Bugaev, A. L.; Gracy, G.; Amro, K.; Soldatov, A. V.; Alauzun, J. G.; Mutin, P. H., Heterogeneous Single-Site Catalysts for C–H Activation Reactions: Pd (II)-Loaded S, O-Functionalized Metal Oxide-Bisphosphonates. *ACS Applied Materials & Interfaces* 2020, 12, (42), 47457-47466.

- [33] Ugras, H. I.; Basaran, I.; Kilic, T.; Cakir, U., Synthesis, complexation and antifungal, antibacterial activity studies of a new macrocyclic schiff base. *Journal of Heterocyclic Chemistry* 2006, 43, (6), 1679-1684. 10.1002/jhet.5570430639
- [34] Zoubi, W. A., Biological Activities of Schiff Bases and Their Complexes: A Review of Recent Works. *International Journal of Organic Chemistry* 2013, 03, (03), 73-95. 10.4236/ijoc.2013.33A008
- [35] Siji, V. L.; Sudarsanakumar, M. R.; Suma, S., Synthesis, spectroscopic characterization, and antimicrobial activity of cobalt(II) complexes of acetone-N(4)-phenylsemicarbazone: crystal structure of [Co(HL)₂(MeOH)₂](NO₃)₂. *Transition Metal Chemistry* 2011, 36, (4), 417-424. 10.1007/s11243-011-9485-z
- [36] Arulmurugan, S.; Kavitha, H. P.; Vennila, J. P., Review on the Synthetic Methods of Biologically Potent Benzoxazole Derivatives. *Mini-Reviews in Organic Chemistry* 2021, 18, (6), 769-785.
- [37] Felton, L. C.; Brewer, J. H., Action of Substituted Salicylaldehydes on Bacteria and Fungi. *Science* 1947, 105, (2729), 409-410. doi:10.1126/science.105.2729.409
- [38] Cui, Y.; Dong, X.; Li, Y.; Li, Z.; Chen, W., Synthesis, structures and urease inhibition studies of Schiff base metal complexes derived from 3,5-dibromosalicylaldehyde. *European Journal of Medicinal Chemistry* 2012, 58, 323-331. 10.1016/j.ejmech.2012.09.037
- [39] Xu, S.-P.; Shi, L.; Lv, P.-C.; Fang, R.-Q.; Zhu, H.-L., Synthesis and antibacterial activities of metal(II) complexes with Schiff bases derived from 3,5-diiodosalicylaldehyde. *Journal of Coordination Chemistry* 2009, 62, (12), 2048-2057. 10.1080/00958970902741251
- [40] Kargar, H.; Ardakani, A. A.; Tahir, M. N.; Ashfaq, M.; Munawar, K. S., Synthesis, spectral characterization, crystal structure determination and antimicrobial activity of Ni(II), Cu(II) and Zn(II) complexes with the Schiff base ligand derived from 3,5-dibromosalicylaldehyde. *Journal of Molecular Structure* 2021, 1229, 129842. 10.1016/j.molstruc.2020.129842
- [41] Kargar, H.; Adabi Ardakani, A.; Munawar, K. S.; Ashfaq, M.; Tahir, M. N., Nickel(II), copper(II) and zinc(II) complexes containing symmetrical Tetradentate Schiff base ligand derived from 3,5-diiodosalicylaldehyde: Synthesis, characterization, crystal structure and antimicrobial activity. *Journal of the Iranian Chemical Society* 2021, 18, (9), 2493-2503. 10.1007/s13738-021-02207-x
- [42] Elangovan, N.; Gangadharappa, B.; Thomas, R.; Irfan, A., Synthesis of a versatile Schiff base 4-((2-hydroxy-3,5-diiodobenzylidene)amino) benzenesulfonamide from 3,5-diiodosalicylaldehyde and sulfanilamide, structure, electronic properties, biological activity prediction and experimental antimicrobial properties. *Journal of Molecular Structure* 2022, 1250, 131700. 10.1016/j.molstruc.2021.131700
- [43] Mandal, M.; List, M.; Teasdale, I.; Redhammer, G.; Chakraborty, D.; Monkowius, U., Palladium complexes containing imino phenoxide ligands: synthesis, luminescence, and their use as catalysts for the ring-opening polymerization of rac-lactide. *Monatsh Chem* 2018, 149, (4), 783-790. 10.1007/s00706-017-2119-1
- [44] Blackburn, O. A.; Coe, B. J.; Fielden, J.; Helliwell, M.; McDouall, J. J.; Hutchings, M. G., Nickel(II) and palladium(II) complexes of azobenzene-containing ligands as dichroic dyes. *Inorg Chem* 2010, 49, (20), 9136-50. 10.1021/ic1000842
- [45] Roy, S.; Saha, R.; Mondal, T. K.; Sinha, C., Palladium(II) and platinum(II) complexes of N-((2-pyridyl)methylidene)-6-coumarin and N-((2-hydroxy)benzylidene)-6-coumarin. *Inorganica Chimica Acta* 2014, 423, 52-61. 10.1016/j.ica.2014.07.014
- [46] Khorshidifard, M.; Rudbari, H. A.; Askari, B.; Sahihi, M.; Farsani, M. R.; Jalilian, F.; Bruno, G., Cobalt(II), copper(II), zinc(II) and palladium(II) Schiff base complexes: Synthesis, characterization and catalytic performance in selective oxidation of sulfides using hydrogen peroxide under solvent-free conditions. *Polyhedron* 2015, 95, 1-13. 10.1016/j.poly.2015.03.041
- [47] Mohd Tajuddin, A.; Bahron, H.; Kassim, K.; Ibrahim, W. N. W.; Fun, H. K., Synthesis and Characterization of Palladium(II) Schiff Base and their Catalytic Activities for Heck Reaction. *Advanced Materials Research* 2012, 554-556, 736-740.
- [48] Bhagat, S.; Sharma, N.; Chundawat, T. S., Synthesis of Some Salicylaldehyde-Based Schiff Bases in Aqueous Media. *Journal of Chemistry* 2013, 2013, 909217. 10.1155/2013/909217
- [49] Bartyzel, A., Synthesis, thermal study and some properties of N₂O₄-donor Schiff base and its Mn(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. *Journal of Thermal Analysis and Calorimetry* 2017, 127, (3), 2133-2147. 10.1007/s10973-016-5804-0
- [50] Tajuddin, A. M.; Bahron, H.; Kassim, K.; Nazihah, W.; Ibrahim, W.; Yamin, B., Synthesis and characterisation of palladium (II) Schiff base complexes and their catalytic activities for Suzuki coupling reaction. *Malaysian Journal of Analytical Sciences* 2012, 16, (1), 79-87.
- [51] Kargar, H.; Fallah-Mehrjardi, M.; Behjatmanesh-Ardakani, R.; Bahadori, M.; Moghadam, M.; Ashfaq, M.; Munawar, K. S.; Tahir, M. N., Pd(II) and Ni(II) complexes containing ONNO tetradentate Schiff base ligand: Synthesis, crystal structure, spectral characterization, theoretical studies, and use of PdL as an efficient

- homogeneous catalyst for Suzuki–Miyaura cross-coupling reaction. *Polyhedron* 2022, 213, 115622. 10.1016/j.poly.2021.115622
- [52] Şahin, Ö.; Özdemir, Ü. Ö.; Seferoğlu, N.; Genc, Z. K.; Kaya, K.; Aydiner, B.; Tekin, S.; Seferoğlu, Z., New platinum (II) and palladium (II) complexes of coumarin-thiazole Schiff base with a fluorescent chemosensor properties: Synthesis, spectroscopic characterization, X-ray structure determination, in vitro anticancer activity on various human carcinoma cell lines and computational studies. *Journal of Photochemistry and Photobiology B: Biology* 2018, 178, 428-439. 10.1016/j.jphotobiol.2017.11.030
- [53] Sudhakar, S.; Narasimhaswamy, T.; Srinivasan, K. S. V., Synthesis, characterization and thermal properties of 4,4'-bis(4-n-alkoxybenzoyloxy)benzylideneanilines and bis(4-benzylidene-4'-n-alkoxyaniline) terephthalates. *Liquid Crystals* 2000, 27, (11), 1525-1532. 10.1080/026782900750018690
- [54] Ravel, B.; Newville, M., Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using Iffeffit. *Journal of Synchrotron Radiation* 2005, 12, (4), 537-541. S0909049505012719
- [55] Versluis, L.; Ziegler, T., The determination of molecular structures by density functional theory. The evaluation of analytical energy gradients by numerical integration. *The Journal of Chemical Physics* 1988, 88, (1), 322-328. 10.1063/1.454603
- [56] te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T., Chemistry with ADF. *Journal of Computational Chemistry* 2001, 22, (9), 931-967. 10.1002/jcc.1056
- [57] Joly, Y.; Bunău, O.; Lorenzo, J. E.; Galéra, R. M.; Grenier, S.; Thompson, B., Self-consistency, spin-orbit and other advances in the FDMNES code to simulate XANES and RXD experiments. *Journal of Physics: Conference Series* 2009, 190, 012007. 10.1088/1742-6596/190/1/012007