Article

A New Piano-Stool Ruthenium(II) P-Cymene-Based Complex: Crystallographic, Hirshfeld Surface, DFT, and Luminescent Studies

Mohd. Muddassir *, Abdullah Alarifi and Mohd. Afzal

Catalytic Chemistry Research Chair, Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; arifi@ksu.edu.sa (A.A.); Afzalanalytical@gmail.com (M.A.)

* Correspondence: mmohammadarshad@ksu.edu.sa

Abstract: A new complex $(\text{Ru}(\eta^6\text{-}p\text{-cymene})(5\text{-ASA})\text{Cl}_2)$ (**1**) where 5-ASA is 5-aminosalicylic acid has been prepared by reacting the ruthenium arene precursors $(\eta^6\text{-arene})\text{Ru}(\mu\text{-Cl})\text{Cl}_2$, with the 5-ASA ligands in a 1:1 ratio. Full characterization of complex **1** was accomplished by elemental analysis, IR, and TGA following the structure obtained from a single-crystal X-ray pattern. The structural analysis revealed that complex **1** shows a “piano-stool” geometry with Ru-C (2.160(5)–2.208(5) Å), Ru-N (2.159(4) Å) distances, which is similar to equivalents sister complex. Density functional theory (DFT) was used to calculate the significant molecular orbital energy levels, binding energies, bond angles, bond lengths, and spectral data (FTIR, NMR, and UV–VIS) of complex **1**, consistent with the experimental results. The IR and UV–VIS spectra of complex **1** were computed using all of the methods and choose the most appropriate way to discuss. Hirshfeld surface analysis was also executed to understand the role of weak interactions such as $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}$, $\text{C-H}\cdots\pi$, and vdW interactions, which play a significant role in the crystal environment’s stability. Moreover, the luminescence results at room temperature show that complex **1** gives a more intense emission band positioned at 465 nm upon excitation at 330 nm makes it a suitable candidate for the building of photoluminescent material.

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Keywords: ruthenium(II) p-cymene; Hirshfeld surface; DFT; H-bonding; luminescence

1. Introduction

Ruthenium is an essential class of π -donor metal ions, which exist in various oxidation states such as $\text{Ru}(\text{CO})_4^{2-}$ and RuO_4 [1]. Among them, ruthenium(II) and ruthenium(III) complexes are the most stable and expected to display antitumor activity that is different from those of platinum-based drugs [2], hence their credible importance in therapeutic application [3]. Besides, the low reduction potential, high electron transferability, and increased interaction with heteroatoms make ruthenium superior to other metal ions [4]. Ru(II) complexes have been not only widely used as antibacterial [5], antifungal [6], and antitumor agents [7], but also involves in various steps of organic synthesis and catalytic activity, e.g., α -alkylation [8], hydrogenation, isomerization, reductive elimination [9,10], and C-H activation catalysis, etc. [11]. Nevertheless, the nature of the ligands coordinated to ruthenium ion plays a crucial role in stabilizing various oxidation states via tuning the metallic center’s redox properties [12]. Consequently, lack of stability is a significant concern for ruthenium(II)/(III)-based complexes responsible for its undesired local reactivity. Hence, the complex stability could be improved by inserting a ligand, further stabilizing the molecule. Thereby, improved stability and better reactivity could be achieved.

Hence, the design of new ligands containing different functional groups with electron donor capability should be very interesting for ruthenium metal complexes. Moreover, 5-Aminosalicylic acid (5-ASA) and its derivatives are used as chelating ligands in homo- or heterometallic system of transition metals and lanthanides [13–16]. Metal complex of

5-ASA exhibited a wide range of biological activities and, most notably, in therapeutics to combat many inflammatory diseases such as Crohn's disease and ulcerative colitis [17]. In addition, the structural and spectral characterizations of new half-sandwich ruthenium(II) complexes containing these kind of ligands are of great importance.

In this context, considerably, effort has been paid on the development of organoruthenium complexes having ruthenium–carbon bonds for many years in various fields [18]. There are several metal salts of ruthenium, out of which ruthenium(II) (*p*-cymene) has a special place as it possesses substituted benzene, which in turn stabilizes the molecules through stacking interactions of coordinated aromatic molecules, and thus acts as good model system to study the influence of substituents. Additionally, Ru(II) *p*-cymene complexes have brought a large group of molecules, which show different mechanism of action [19–21]. Hence, the examination of such types of complexes directed their optimistic role as anticancer agent, antibacterial drugs [22–24], alkene polymerization, ring-opening metathesis [25–27], hydrogen transfer catalyst precursors [28,29], olefin oxidation [30,31], and redox-active photosensitizers for solar cells [32–34]. The majority of the application of ruthenium half-sandwich compounds are in the field of biological assay, and other areas are unexplored to understand the mechanism of such complexes fully. In the past few decades, density functional theory (DFT) techniques have been routinely employed to get more insight about the structural and electronic properties of the complexes in lieu of experimental results due to its trustworthy outcomes with thoughtful computational cost in contrast to higher level *ab initio* methods [35–37].

Recently, Malenov and coworker has analyzed the most frequent stacking interactions between aromatic rings of *p*-cymene ligands of transition metal complexes, as well as C–H/ π interactions flanked by methyl substituents by performing DFT calculations, which further establishes the presence of substituents on coordinated aromatic rings that can lead to substantial alterations in the geometries. Moreover, the stacking interactions significantly reinforce the overall networks by generating additional contacts with aromatic rings and thus, provides crucial information for ruthenium-based half-sandwich complexes [38]. Similarly, Chi's group has explored the anion sensing (F^- , Cl^- , NO_3^- , PF_6^- , CH_3COO^- , and $\text{C}_6\text{H}_5\text{COO}^-$) ability of two different dinuclear arene ruthenium complexes using fluorescence titration experiment, which showed a large fluorescence enhancement upon binding to these multicarboxylate anions owing to the hindrance of photoinduced electron transfer process from the ruthenium–arene to the amidic donor in dinuclear arene based ruthenium complexes [39].

Herein, we have synthesized a new ruthenium(II) (*p*-cymene) complex **1** containing 5-ASA as a ligand and structurally characterized using various analytical and spectroscopic techniques and further confirmed by single-crystal X-ray diffraction pattern. DFT calculations at B3LYP/ZORA/D3BJ level are performed on the complex **1** to elucidate the electronic as well as geometrical features and bonding nature of the complex, which recognized that $\text{CH}\cdots\pi$ and H-bonding interactions were involved in the stabilization of the complex. A Hirshfeld surface analysis is also implemented to generate two-dimensional fingerprint plots, which validate the type of weak interactions occurring in the supramolecular network of complex **1**. Furthermore, the emission behavior of complex **1** was studied at room temperature that displayed an intense band at 465 nm that mainly originates from the ruthenium(II) (*p*-cymene) moiety, which could make it a suitable material for the building of photoluminescent material. It is important to note that the emission properties of these kinds of organometallic half-sandwich complexes are sensitive to the substituents on the ligands as reported by others.

2. Experimental

2.1. Starting Materials

Analytical grade reagents and solvents were procured from commercial sources and used without further purification.

2.2. Synthesis

(Ru(η^6 -*p*-cymene)(5-ASA)Cl₂) (1).

To a methanolic solution (10 mL) of (Ru(η^6 -*p*-cymene)Cl₂)₂ (61.2 mg 0.1 mmol), 5-ASA (30.6 mg 0.2 mmol) dissolved in 10 mL methanol was added, and the mixture was stirred at room temperature for 2 h. Thereafter, the solution was kept at room temperature until a red precipitate was formed, which was washed with hexane and then dried. Red color crystals were obtained after they were recrystallized from dichloromethane-ⁿhexane solvent mixture. Yield: 56.6%. Anal. Calc. for C₁₇H₂₁Cl₂NO₃Ru (%) C, 44.45; H, 4.61; and N, 3.05, Found: C, 46.18; H, 4.54; and N, 2.99. Λ_M (1 $\times$ 10^{−3} M, acetonitrile): 17.0 Ω^{-1} cm² mol^{−1} (nonelectrolyte).

The details of X-ray crystal refinement, protocols related to DFT and Hirshfeld surface analyses have been provided in supporting information (See the Supplementary Materials).

3. Results and Discussion

3.1. Synthetic Methodology

Complex **1** has been achieved from the reaction of ruthenium(II) *p*-cymene chloride with 5-ASA ligand in methanol under ambient conditions. The complex is stable towards air and moisture and soluble in most of the organic solvents. The structure elucidation of **1** is established by single-crystal X-ray, ESI-MS, microanalysis, TGA, and IR and NMR (¹H and ¹³C) spectroscopies. Molar conductance value of complex in acetonitrile solution (1 $\times$ 10^{−3} M) at 25 °C suggests its nonelectrolyte nature (17.0 Ω^{-1} cm² mol^{−1}).

3.2. X-ray Structure Investigation

Single crystals suitable for X-ray analysis were attained from the slow evaporation of dichloromethane-ⁿhexane solvent mixture. The structure of the complex **1** is illustrated in Figure 1A. The crystallographic data are listed in Table 1, while the bond distances and bond angles are provided in Table 2. The structure of complex **1** is a ruthenium complex with *p*-cymene and 5-ASA. Each Ru atom coordinates two Cl[−] anions, aromatic ring of *p*-cymene, and 5-ASA through nitrogen atom forming tetrahedral coordination geometry (CN=4). The single crystal X-ray analysis reveals that the complex **1** crystallizes as a monoclinic crystal system with space group *P*2₁/*n*. Only one molecule is present in the asymmetric unit and had a characteristic three-legs piano-stool geometry. A η^6 - π -bonded *p*-cymene arene ring is forming the seat and other three donor atoms (one nitrogen atom of 5-ASA moiety and two chlorine atoms) turns as legs of the stool. The bond lengths between Ru-N and Ru-Cl are 2.159(4) and 2.4005–2.4304 Å, respectively, as reported previously for Ru(II) *p*-cymene complexes [40]. However, Ru-C (*p*-cymene) bond lengths are in the range of 2.160–2.208 Å, consistent with those similar types of mononuclear complexes reported earlier.

Further simplification of a crystal structure to its underlying net in so-called standard representation of the valence-bonded complexes in which all ruthenium atoms and the centers of mass of ligands are nodes of the underlying net [41]. The underlying net can be considered the simplest net that stores the information on the system's overall topology of the structural units chosen according to a chemical vision of the crystal structure, where "simplest" means that the net cannot be more simplified with the secondary simplification procedure. Studying the underlying net, one can abstract from details of complex groups' molecular structure and search for long-range resemblances of complexes of different compositions and architectures.

Such representation shows that no net and structure is consisting of molecular complex groups (Figure 1A, right). It forces us to perform further analysis taking into account H-bonding. In this approach, ruthenium polyhedra is considered as net nodes connected with H-bonds. H-bonded standard representation results into 5-c uninodal underlying net (Figure 1B). The net topology is **tts** with point symbol {3³.4³.5⁴}. This net is two dimensional; the layers parallel the (1 0 -1) planes.

Figure 1. (A) Molecular structure of the complex **1** monomer (left) and standard representation of the group with 1,4M5-1 topology (right). Hydrogen atoms that do not participate in hydrogen bonding are omitted for clarity. (B) Underlying net in standard representation of the H-bonded molecular MOFs corresponds to *tts* topological type. The unit cell of the structure is shown with a blue line. (C) Underlying net in standard representation of the Coulomb or vdW-bonded molecular structures corresponds to *bcu*-x topological type. (D) Density functional theory (DFT)-optimized structures of complex **1**. Thermal ellipsoids were shown at 50% probability. Hydrogen atoms have been omitted for clarity.

Table 1. Crystal structural data and refinement parameters for complex **1**.

CCDC No.	2038452
Formula	$C_{17}H_{21}Cl_2NO_3$ Ru
Formula weight	459.32
Temperature/K	150
Crystal system	Monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	8.6496(15)
$b/\text{\AA}$	12.026(3)
$c/\text{\AA}$	17.285(3)
$\alpha/^\circ$	90.00
$\beta/^\circ$	91.976(6)
$\gamma/^\circ$	90.00
Volume/ $\text{\AA}^3$	1796.9(6)
Z	4
$\rho_{\text{calc}}/\text{mg mm}^{-3}$	1.698
μ/mm^{-1}	9.930
$F(000)$	928.0
Index ranges	$-7 \leq h \leq 10$ $-14 \leq k \leq 15$ $-21 \leq l \leq 19$

$$a: R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|. \quad b: wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP].$$

Standard representation of the Coulomb or vdW-bonded molecular structures is 3D framework. Resulted 14-c uninodal net has *bcu*-x topological type with point symbol $\{3^6.4^8.5^7\}$ as shown in Figure 1C.

We opted the DFT method as an alternative to validate the complex **1** molecular structure. Geometry optimization of complex **1** were performed without symmetry restrictions, and the resulting structures are presented in Figure 1D. Validation of the structural parameters like bond distances ($\text{\AA}$) and bond angles (deg) obtained from X-ray analysis

and theoretical calculation (DFT) has been made for complex **1** (Table 2), which indicates a significant resemblance to each other.

Table 2. Selected bond distances (Å) and angles (degrees) for **1**.

			Complex 1	
			X-ray	DFT
	Ru(1)-Cl(1)		2.4005(16)	2.453
	Ru(1)-Cl(2)		2.4304(14)	2.458
	Ru(1)-N(17)		2.159(4)	2.174
	Ru(1)-C(10)		2.195(5)	2.193
	Ru(1)-C(9)		2.208(5)	2.204
	Ru(1)-C(11)		2.171(5)	2.183
	Ru(1)-C(12)		2.185(5)	2.212
	Ru(1)-C(13)		2.160(5)	2.228
	Ru(1)-C(14)		2.193(5)	2.204
Cl(1)	Ru(1)	Cl(2)	86.89(5)	88.54
N(1)	Ru(1)	Cl(2)	81.78(13)	80.96
N(1)	Ru(1)	Cl(1)	81.41(13)	82.15

3.3. NMR Spectroscopy

Complex **1** shows all the characteristic signals arising from coordinated arene rings and 5-ASA (Figure S1). The resonances due to the 5-ASA ligand are shifted with respect to those of free 5-ASA ascribed to its coordination. The signal of -NH_2 in free 5-ASA appeared at 2.5 ppm as a singlet has been moved to 3.15 ppm confirming its coordination to Ru(II) center. Resonance of η^6 -p-cymene protons appeared as two doublets at 5.8–5.75 ppm. Resonances of methyl groups in η^6 -p-cymene moiety of complex **1** appeared at 1.18–1.17 ppm.

In ^{13}C NMR spectrum, signals at around 206 and 171 ppm corresponds to (-COOH) and (-CO), respectively, in addition to aromatic carbon signals, which appeared at 100.1–124.8 ppm (Figure S2). The η^6 -p-cymene carbon resonances found at 86.3–85.5 ppm corresponds to (C-CHMe_2), 30.6–29.9 ppm belongs to ($\text{CH(CH}_3)_2$), whereas 21.4 ppm corresponds to ($\text{CH(CH}_3)_2$), and 17.8 ppm corresponds to (C-CH_3) in complex **1**. These chemical shift values are consistent with those reported for similar ($\text{Ru}(\eta^6\text{-p-cymene})$) complexes [18].

3.4. IR Spectroscopy

The IR spectra of complex **1** was recorded in the region of $4000\text{--}400\text{ cm}^{-1}$ (Figure 2A,B) and their comparison have been made from calculated frequencies in order to validate the structure. The calculated frequencies in terms of relative intensities and vibrational assignments are in good agreement with the experimental frequencies, as presented in Table 3. The slight deviation observed in the theoretical value arises from the fact that calculations have been carried out in gas phase, while the experimental data have been achieved on an isolated complex in the solid state, which happens to be a typical error for this particular basis set.

The band at 1666 cm^{-1} has been assigned to the symmetric stretching of carboxyl group -C=O with -OH symmetric bend and is computed at 1741 cm^{-1} but the experimental vibration remained undisturbed, indicating that the carboxylate group of 5-ASA is not involved in the coordination to Ru(II) metal ion [16,42]. The other two bands observed at 1623 (DFT: 1684 cm^{-1}) and 1593 cm^{-1} (DFT: 1641 cm^{-1}) are attributed to ring deformation with C=C stretch and C-H bending localized on the 5-ASA ring. The band at 1531 cm^{-1} is assigned to -NH_2 scissoring which is expected by DFT at

1602 cm^{-1} . The stretching vibrations because of C-H (aliphatic and aromatic) group are observed in the range of 2800–3150 cm^{-1} and are theoretically found in the range of 3020–3231 cm^{-1} . The N-H symmetrical and asymmetrical stretching vibrations were observed at 3219 (DFT: 3408 cm^{-1}) and 3285 cm^{-1} (DFT: 3488 cm^{-1}), respectively. The broadening observed at 3350–3500 cm^{-1} has been ascribed to the –OH stretching vibrations [43]. The other calculated IR assignments are given in Table 3, which is consistent with the corresponding experimental values.

The infrared spectrum calculation of these vibrations will help the study these types of ruthenium(II) (p-cymene) and even clarify some experiments and theories of arguing. These results can enhance the characterization and help to discover the contribution of ligand components to these kinds of ruthenium(II) (p-cymene) complexes.

Figure 2. Complex 1 showing (A) IR spectrum, (B) DFT-simulated vibrational spectrum (C) TGA, and (D) experimental and TDDFT (Time-Dependent Density-Functional Theory) calculated UV–VIS spectra (calculated singlet electronic transitions are shown as black vertical bars with height equal to their oscillator strength).

3.5. Thermogravimetric Analysis

The thermogram for complex 1 (Figure 2C) was recorded in the temperature range of 25–800 °C, which shows three steps weight loss pattern. It is observed that the complex 1 loses 32.15% (calculated 33.26%) in the temperature range from 50 to 310 °C designates the removal of 5-ASA. Beyond this temperature, complex 1 starts decomposition. Finally, the TGA curve displayed a plateau around 650 °C, consistent with other previously reported half-sandwich ruthenium (II) (p-cymene) complexes [30].

3.6. Absorption Study

Since we also wanted to investigate the stability of complex 1, after determining the complex's three-dimensional structure in crystalline state, the next step was to define the energy minima conformation thereof. Frontier molecular orbitals (FMO) have an important role for giving an insight into the chemical reactivity's and some of the physical properties. The spectral properties of transition metal complexes are strongly related to the energy of these orbitals. We have performed the TDDFT calculation on complex 1,

at the B3LYP/ZORA/D3BJ level to distinguish their singlet excited states and electronic properties (Figure 2D).

Table 3. Experimental and density functional theory (DFT) calculated IR spectra for complex 1, (wavenumber in cm^{-1}).

Complex 1		
Experimental	DFT	Inference
574	590	Out-of-plane ring deformation
701	740	O-H wagging
743	817	In-plane ring deformation
874	878–925	Ar-CH wagging
999	997	Ar-CH twisting
1026	1027	-CH ₃ rocking
1053	1066	-CH ₃ rocking
1184	1131	Ar-CH rocking
1267	1264	CH twisting
1421	1427	CH scissoring
1492	1497	Ar-C-C asymmetric stretching
1531	1602	-NH ₂ scissoring
1593	1641	C=C stretch and C-H bending
1623	1684	C=C stretch and C-H bending
1666	1741	-C=O symmetric stretching
2870	3020–3040	CH ₃ symmetric stretching
2961	3104–3160	CH Asymmetric stretching
3043	3186–3231	Ar-CH symmetric stretching
3219	3363	Ar-O-H (phenolic) symmetric stretching
3285	3265	-NH ₂ symmetric stretching
3435	3560	O-H (COOH) symmetric stretching

It is evident from Figure 2D that the absorbance tail at 400–500 nm region is influenced by metal-centered and metal-to-ligand charge transfer (¹MLCT) transitions and major contribution is assigned to HOMO-1 → LUMO + 3 excitation. A few ¹MLCT transitions are partially dissociative, since they have considerable contributions from Ru-N (L) σ*-antibonding orbitals. Nearly pure ¹MLCT (Ru→L) states are found in the higher energy (ca. 300–480 nm), assigned to HOMO-3 → LUMO excitation. However, a more pronounced peak at 220 nm is attributed to the mixed ¹MLCT/¹LC (ligand centered) transition, which is in good agreement with the experimental UV–VIS spectrum. The orbital arrangements of computed singlet transitions are shown in Figure 3. Though the simulated spectrum of the title compound in the gas phase has given a reasonable agreement on the band maximum positions with the experiment result, the calculation including solvent effect was also carried out with the expectation of a better match-up between the simulated and the experimental value.

Figure 3. Frontier molecular orbitals (FMO) involved in electronic transitions observed in TDDFT calculated UV–VIS spectrum of complex **1**.

3.7. Hirshfeld Surface Analyses

The Hirshfeld surface is a useful tool for describing the surface characteristics of molecules. To explore the intermolecular interactions as the function of distance (d_e , d_i , d_{norm} , and 2d fingerprint plots) in the crystal system, Hirshfeld surface (HS) analysis was carried out [44]. The HS of complex **1** is mapped over d_{norm} (normalized contact distance), and shape-index and curvedness were generated on an asymmetric unit of the complex **1**. The red, white, and blue color conventions in the d_{norm} images were associated with the distance shorter, equal, and longer than the van der Waals radii, respectively. As shown in Figure 4, d_{norm} was mapped in the color range of -0.2 to 0.8 Å, deep red spots observed in d_{norm} were formed due to shorter contacts indicative of $\text{O} \cdots \text{H}$ interactions, while faint red spots were due to $\text{C} \cdots \text{H}$ interactions. The white zones denote interactions about the van der Waals separation like $\text{H} \cdots \text{H}$ contacts and the blue areas are devoid of close contacts. Beside this, other properties of HS analysis like shape-index and curvedness provides evidence about the weak interactions in the molecular packing. In the shape-index (-1.0 to 1.0 Å) analysis of complex **1**, both the red areas attributing to $\text{C-H} \cdots \pi$ interactions as well as “bow-tie patterns,” which indicated the existence of $\pi \cdots \pi$ stacking interactions. The curvedness points to surface curves electronic density around the molecular contacts. In the d_{norm} surface of complex **1**, blue and white surfaces are more prevailing than red surface, which indicated that the hydrophobic interaction due to the aromatic ring is dominated. The dark red and blue color spots are distribution in the shape index surface that suggested the presence of $\text{C-H} \cdots \pi$ interaction in the complex **1**.

Figure 4. Hirshfeld surfaces mapped with d_{norm} (A), shape index (B), and curvedness (C) for complex **1**.

Further, 2-D fingerprint plots are used for quantitative analysis that can be split into particular atom pair close contacts. The shape index is highly sensitive to very subtle changes in the surface shape; the information conveyed by the shape index are consistent with 2D fingerprint plots. The curvedness is the measurement of “how much shape” there is in a crystal. The flat areas of the surface correspond to low values of curvedness, whereas sharp curvature areas correspond to high values of curvedness and usually tend to divide the surface into patches, indicating interactions between neighboring molecules. The 2D fingerprint plots can be deconstructed to highlight particular atom pair contacts. This deconstruction enables the separation of contributions from different interaction types that overlap in the full fingerprint.

The overall fingerprint plot analysis for complex 1 is given in Figure 5. It exposed that the most significant contribution in the framework comes from $H \cdots H$ interaction (45.30%) of the total HS. However, remaining proportions of $Cl \cdots H$, $O \cdots H$, $C \cdots H$, and $C \cdots C$ interactions include 20.10%, 18.90%, 10.20%, and 4.2%, respectively, of the total HS for each molecule. $H \cdots H$ interactions make up the majority of the Hirshfeld surface, which is consistent with the high proportion of hydrogen atoms in the complex 1. The central spike in the fingerprint plot was due to the $\pi \cdots \pi$ interactions formed between the flanked benzene ring.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number of $H \cdots H$, $Cl \cdots H$, $O \cdots H$, $C \cdots H$, and $C \cdots C$ interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing.

Figure 5. The 2D fingerprint plots for complex 1.

3.8. Photoluminescence Property

The emission profile of ruthenium(II) (p-cymene)-based complexes is of much interest due to their unique emissive nature, originating from the π -arene group, which has ability to tune the photoluminescence properties [45]. The emission studies of ruthenium(II) (p-cymene) complex were monitored at room temperature in acetonitrile, showing an unstructured intense band at 465 nm upon excitation at 330 nm as shown in Figure 6. It seems that the emission largely originates from the ruthenium(II) (p-cymene) moiety. Thus,

it can be concluded that the emission bands of complex **1** is attributed to a metal-ligand charge transfer (MLCT) state. It is important to note that the emission properties of these kinds of organometallic half-sandwich complexes are sensitive to the substituents on the ligands as reported by others [32].

Figure 6. Emission spectra for complex **1** ($\lambda_{\text{ex}} = 330$ nm).

Being a strong luminescence property, complex **1** could have suitable applications as fluorescent material.

4. Conclusions

A new mononuclear $(\text{Ru}(\eta^6\text{-}p\text{-cymene})(5\text{-ASA})\text{Cl}_2)$ complex **1** has been isolated and fully identified by NMR, IR, TGA MS, elemental analysis, UV–VIS spectroscopy. The single crystal X-ray analysis revealed that complex **1** crystallizes in a monoclinic space group $P2_1/n$ and exhibited a usual three-legged piano-stool geometry. The Ru(II) metal ion is coordinated by a nitrogen atom of 5-ASA, two chloride ligands and the p -cymene ligand (with an η^6 coordination mode). The coordination environment around the Ru(II) metal center can be recognized as a distorted octahedron. The presence of two chloride ligands is responsible for the stabilization of the crystal framework. DFT calculations were also performed, revealing the geometric and bond features of the novel complex. Considering all intermolecular contacts during the simplification procedure, we obtain a description of the excellent molecular packing. The strong luminescence property of the complex **1** makes it an ideal candidate as photoluminescent material considering the improved property as reported by others. It should be noted that the reported complex and similar types of such complexes further warrant their use for the development of photoluminescent probe in biological system and sensing application.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4352/11/1/13/s1>, Table S1: The details of X-ray crystal refinement, protocols related to density functional theory (DFT) and Hirshfeld surface analyses; Figure S1: ^1H NMR spectrum of complex **1**; Figure S2: ^{13}C NMR spectrum of complex **1**.

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