



ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2024, 16(3): 349-354
(<http://www.derpharmachemica.com/archive.html>)

Geometric, Electronic Structural Aspects, Stability and Spectroscopic Properties of Ruthenium-octaethylporphyrin Complexes of the Type Ru[OEP]L₂ Where L=NPh₂, NH₃, PH₃, AsH₃-A DFT Study

Dileep D¹, Rajesh R¹, Sivasankar BN¹ and Krishnamoorthy Bellie Sundaram^{2*}

¹Department of Chemistry, Government Arts College, Udhamandalam, Tamil Nadu, India

²Department of Chemistry SF, PSG College of Arts and Science, Coimbatore, Tamil Nadu, India

*Corresponding author: Krishnamoorthy Bellie Sundaram, PSG College of Arts and Science, Udhamandalam, Tamil Nadu, India, Email: bskimo@yahoo.co.in

Received: 08-January-2024, Manuscript no: DPC-24-138413, Editor assigned: 19-January-2024, PreQC No: DPC-24-138413 (PQ), Reviewed: 02-February-2024, QC No: DPC-24-138413, Revised: 17-May-2024, Manuscript No: DPC-24-138413 (R), Published: 14-June-2024, DOI: 10.4172/0975-413X.16.3.349-354

ABSTRACT

Ruthenium is an important element with more than one oxidation states which leads to the diverse structural features and wide range of applications of ruthenium complexes. Here we have studied the geometrical, electronic structure, spectral properties and reactivities of important ruthenium octaethylporphyrin complexes with different ligands like N(Ph)₂ (1), NH₃ (2), PH₃ (3) and AsH₃ (4), F (5), Cl (6), Br (7), I (8). Density Functional Theory (DFT) calculations at BP86/Def2-TZVP level show that the computed molecular geometries are more stable and their metrical parameters are close to the experimentally available similar complexes. The octahedral geometry around ruthenium with axially disposed ligands in these ruthenium porphyrin complexes 1-4 have been confirmed by theoretical DFT (BP86/Def2-TZVP) investigations. Further the spectroscopic and thermochemical properties of these complexes are also in accordance with expected trend. Interestingly the complexes 5 and 6 are not viable from the FMO analysis. Thus this quantum chemical study can lead to design and find out the better ruthenium-porphyrin complexes with different ligands.

Keywords: Ruthenium; Porphyrin; Spectroscopy; DFT; Reactivity descriptors; Molecular orbital

INTRODUCTION

Anticancer agents are main area of research for many of the leading research groups throughout the world. The first of its kind is the success of cisplatin as an effective anticancer agent. Following cis-[PtCl₂(NH₃)₂], many other transition metal complexes as anticancer agents are studied. Photodynamic therapy is an important method now-a-days to treat cancer cells and the method mainly depends on the effective photosensitizer. Among all other transition metal complexes, Ruthenium plays an important role after the first Ruthenium complex TLD1433 as a photosensitizer for Photodynamic Therapy (PDT) in clinical trial in 2017. The structural variation and diverse applications of ruthenium complexes leads to enormous research outputs in the past three decades. Initially it was a great challenge for the ruthenation of porphyrin ring which was reported 50 years before. They have tried this reaction with RuII monocarbonyl complex [Ru(CO)(dmsO)5][PF₆]₂, resulted in ruthenium-porphyrin complex, but due to the labile dimethyl sulphoxide ligand in the complex, the results were neglected. Recently as a proof of concept, 100% ruthenation of tetraphenylporphyrin, for 30 minutes at 140°C is reported using the Ru₃(CO)₁₂ [1]. Porphyrin ligands are also disposed in axial position or in bridging positions in the dimers and trimers of Ruthenium(II) complexes of RuII(OEP)(CO)(H₂PyP3P) (OEP=Octaethylporphyrinato Dianion, H₂PyP₃P=5-pyridyl-10,15,20-triphenylporphyrinato dianion) and their derivatives [2]. Another important application of ruthenium porphyrins is synthesis of new effective molecular junctions. The Ru-TPPdT [5,15-di(p-thiophenyl)-10,20-diphenylporphyrinato]ruthenium(II)(py)₂, with two thiophenyl groups at meso-positions and two pyridine groups at the axial positions of the Ru(II) porphyrin complex, yielded a reliable configuration between metal electrodes and increased spread in conductance when compared to the parent porphyrin [3]. Recent applications include the efficient photo induced energy transfer in porphyrin and metalloporphyrin based nano materials which shows promising candidates for light harvesting in solar cells and optoelectronics [4]. Many of the present day research are mainly based on the implications from the nature and which in turn called as biomimetic. An useful biomimetic study about the functioning of the heme in our human body can be understood by means of biomimetic through modelling. An excellent work of NMR spectroscopic observation on more than hundred thiol ligated ruthenaporphyrin compounds have been reported which can be useful as a model to understand the heme sulphur protein binding interactions [5]. Ruthenation can also be occur at the periphery of the porphyrin ring. The femtosecond dynamics of the cobalt porphyrin with ruthenium bonded in the periphery of porphyrin ring

confirm the efficient electrocatalytic property of this complex when compared to that of the non-ruthenated complex [6,7]. Theoretical investigations based on quantum chemical calculations are crucial in analyzing the potential of molecular junctions. For example computational studies on both meso-substituted porphyrins and beta-substituted metllaporphyrins yielded important results [8-12]. Here we have reviewed and studied the geometrical, electronic structure, spectral properties and reactivities of important octaethyl ruthenium-porphyrin complexes with different ligands like N(Ph)₂ (1), NH₃ (2), PH₃ (3) AsH₃ (4), F (5) and Cl (6). Computational chemistry tools can aid designing new molecules with expected properties by properly choosing the computational level and metal complexes. DFT methods are already proved to help the complete characterization of the newly synthesized molecules and also to study the molecular orbital interactions [13-19]. Computational chemistry tools like DFT methods are successfully used in the mechanistic investigation also. Ruthenium-porphyrin complex catalyzed aziridination of olefins by aryl azides has been studied using the DFT methods [20]. Ruthenium porphyrin complexes can be designed and their viability can be checked and their applications can be tuned with the help of theoretical calculations. Here DFT methods helped to study the ruthenium-porphyrin complexes with different ligands like N(Ph)₂ (1), NH₃ (2), PH₃ (3), AsH₃ (4) F (5), Cl (6), Br (7) and I (8) and to check their viability in laboratory.

Computational details

DFT calculations were carried out using the software ORCA developed by Frank Neese and co-workers [21]. All calculations were performed using the BP86 density functional [22-25] and Def2-TZVP basis set included in the ORCA programme, which is free for academic use. Self-Consistent Field (SCF) calculations were performed using the TIGHTSCF convergence criteria. The geometry optimization was carried out and the resulting geometries are confirmed as minima through the frequency calculations. Pictures of the optimized geometries and the Frontier molecular orbitals are taken using the graphics programme chem craft [26].

MATERIALS AND METHODS

Ruthenium-porphyrin complexes are already known for their catalytic and biological activities. Che and Huang reviewed the synthesis, characterization, reactivity and catalytic activities of ruthenium-porphyrin complexes [27.] Among all three important oxidation states of ruthenium +2, +3 and +4, the complexes most studied for application purposes are with +3 oxidation state followed by +4. Here we have explored the molecular and electronic structural properties of ruthenium(II)-octaethylporphyrin complexes with different ligands. Ruthenated porphyrin complexes are our main interest in this work whereas porphyrin surrounded by ruthenium complex boxes are also proved to be very good candidates, show very good cytotoxicity towards human Me300 melanoma cells and also successfully used in photodynamic therapy [28]. The molecular structure, electronic features, molecular orbital analysis and the thermo chemistry of these Ruthenium(II)-porphyrin complexes are discussed in the following sub-headings.

Molecular structure

The DFT(BP86/Def2-TZVP) optimized geometries of RuP(NPh₂)₂, (1), RuP(NH₃)₂, (2), RuP(PH₃)₂, (3), RuP(AsH₃)₂, (4) (where P=Porphyrin) along with their HOMO and LUMO orbitals are provided in the Figures 1 and 2. All the four complexes are having octahedral geometry with ruthenium atom in the centre of the porphyrin ring along the plane with axially disposed NPh₂/NH₃/PH₃/AsH₃ ligand. The N-Ru-N bite angle of the six membered rings are all close to 90 degrees. The four ruthenium-nitrogen bond lengths of the porphyrine rings are equal in case of 1, 2 and 4 but there is a difference when the ligand is PPH₃ (2.106, 2.106, 2.090, 2.090 Å). The Ru-N distances of the axial ligands in complex 1 are 1.99., 1.990 Å and in complex 2, the bond lengths are 2.128, 2.128 Å. There is a significant increase in Ru-N bonding interaction in complex with NPh₂ ligand when compared to that of NH₃ ligand. The DFT computed axial Ru-N bond lengths in compound 1 are shorter than that experimentally observed value of 2.1085(19) Å for the perfluorinated compound [Ru(F20-TPP)(py)₂] which possess significant Ru-Npy bonding interaction [29]. Further the ligand NPh₂ usually acts as 2e sigma donor and 2e pi donor and the ruthenium also possess vacant d orbital, which lead to the strong Ru-N interaction [30]. The Ru-N bond length with ammonia ligand in compound 2 is closer to the Ru-Npy bond in [Ru(F20-TPP)(py)₂]. The Ru-P bond lengths are 2.898, 2.898 Å in complex 3, when comparing the stability of compounds 2 and 3, the phosphine analogue 3 is more stable and the triphenyl phosphine derivative of the Ruthenium-porphyrin complex is experimentally known and synthesized and characterized well before. The disorder associated with the X-ray diffraction data of this triphenyl phosphine derivative has been overcome by computing the geometrical values at DFT (BP86/def2-TZVP) level and the metrical parameters are listed in the Table 1. Though the optimized geometries of the complexes with halogen substituents in their singlet state F (5) and Cl (6) are resulted in minima in the potential energy surface, the viability of these complexes are not feasible from the FMO analysis. But the geometry optimization of these compounds 5-8 in their triplet state show considerable stability with minimum energy structures and >2 eV LUMO-HOMO energy gap. Figure 3 show the DFT (BP86/Def2-TZVP) optimized geometries of halogen substituted compounds 5-8 in their triplet state RuP(F)₂, (5), RuP(Cl)₂, (6), RuP(Br)₂, (7), RuP(I)₂, (8) (where P=Porphyrin) (Figures 1-3).

Table 1. DFT computed bond parameters for the compounds 1-4. RuP(NPh₂)₂, (1), RuP(NH₃)₂, (2), RuP(PH₃)₂, (3), RuP(AsH₃)₂, (4) (where P=Porphyrin).

Atoms (Bond length Å; bond angles 0)	1	2	3	4
Ru-N _{axial}	1.990 [2.1085(19)] ¹⁵	2.128 [2.1085(19)] ¹⁵	2.898	2.435
	1.99	2.128	2.898;	2.435
Ru-N _{porphyrin}	2.066	2.052	2.106;	2.067
	2.066	2.052	2.09	2.067
N2-Ru1-N4	88.98	90	90.02	90.01
N4-Ru1-N39	90	89.53	90.2	90.22
N5-Ru1-N39	90	90.27	89.76	89.95
N5-Ru1-N3	88.98	90.01	90.02	90.02
N4-Ru1-N5	91.02	89.99	90	89.99

N3-Ru1-N2	91.02	89.99	89.97	89.99
E-Ru-E	180	179.98	179.96	179.95

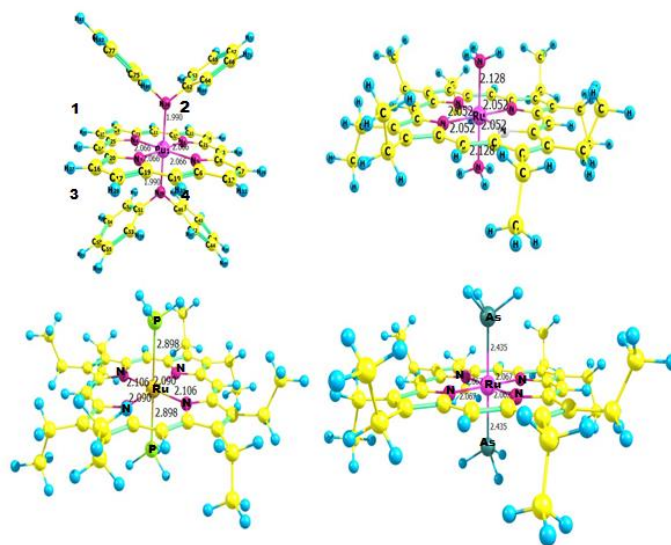


Figure 1: DFT (BP86/Def2-TZVP) optimized geometries of compounds 1-4. RuP(NPh₂)₂, (1), RuP(NH₃)₂, (2), RuP(PH₃)₂, (3), RuP(AsH₃)₂, (4) (where P=Porphyrin).

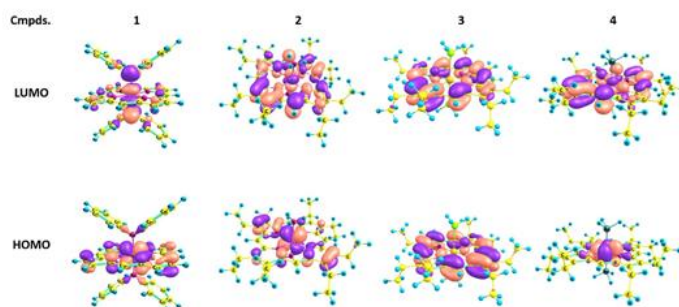


Figure 2: Frontier molecular orbital pictures of compounds 1-4 RuP(NPh₂)₂, (1), RuP(NH₃)₂, (2), RuP(PH₃)₂, (3), RuP(AsH₃)₂, (4) (where P=Porphyrin), obtained from DFT (BP86/Def2-TZVP) optimized geometries.

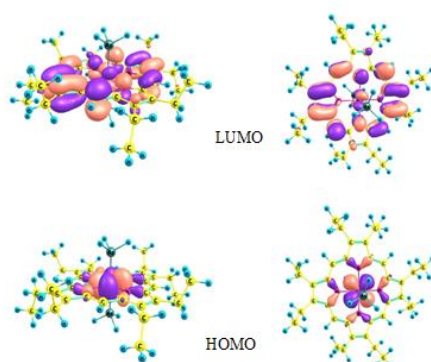


Figure 3: HOMO and LUMO of compound 4 in planar and perpendicular view.

RESULTS AND DISCUSSION

Electronic structure

The experimental viability of the molecules studied is computed by using the HOMO and LUMO energies as suggested by the Koopmanns' theorem. When comparing the stability of compounds 1-4, the phosphine analogue 3 is more stable and the triphenyl phosphine derivative of the Ruthenium-porphyrin complex is experimentally known. The DFT computed ELUMO-HOMO value of 2.0 eV confirming this. When comparing the highest occupied molecular orbitals of the molecules 1, 2 and 4 studied, metal d orbitals only involved mainly in all the HOMOs with minimum contribution from porphyrin nitrogen atoms whereas in the complex 3, the electron density is from porphyrin ring only in the HOMO. The lowest unoccupied molecular orbitals are mainly from porphyrin ring. The conceptual density functional terms usually called as reactivity descriptors are tabulated in the Table 3. The descriptors are computed using the Koopmanns' theorem. From table 3 it is evident that the modelled compounds 2-4 are more stable than the experimentally known ruthenium octaethylporphyrin compound with axially disposed diphenyl amine ligand. Further compound 2 and 4 possess high global electrophilicity index (Table 2).

Table 2: DFT computed $E_{\text{LUMO-HOMO}}$ energies, chemical potential, hardness, softness, electrophilicity, ionization potential and electron affinity for the compounds 1-4. RuP(NPh₂)₂, (1), RuP(NH₃)₂, (2), RuP(PH₃)₂, (3), RuP(AsH₃)₂, (4) (where P=Porphyrin).

Compound	1	2	3	4
HOMO	-4.6686	-3.7156	-4.1871	-4.1708
LUMO	-3.6114	-2.2085	-2.4177	-2.4043
ELUMO-HOMO	1.0572	1.5071	1.7694	1.7665
Chemical potential (μ)	-4.14	-2.9621	-6.6048	-3.2876
Hardness (η)	0.5286	0.7536	0.8847	0.8833
Softness (S)	1.8918	1.327	1.5	1.1321
Electrophilicity (ω)	16.2123	5.8214	24.6543	6.1181
Ionization potential (eV)	4.6686	3.7156	4.1871	4.1708
Electron affinity (eV)	3.6114	2.2085	2.4177	2.4043

The DFT computed frontier molecular orbitals of the metal porphyrins compounds are already used successfully for the prediction of electrical conductance and thermo power of beta-substituted metal porphyrin molecular junctions [30]. The carbene transfer and the hydrogen atom transfer reactions of ruthenium porphyrin complexes bearing quinoid carbene groups are reported and proved as successful catalysts [31].

Spectroscopic data

The ¹H NMR and ¹³C NMR chemical shift values are important parameters in assigning the molecular structure of these ruthenium porphyrin complexes. The DFT (BP86/Def2-TZVP) computed ¹H NMR and ¹³C NMR chemical shift values are presented in Table 3. The DFT computed chemical shift values of phenyl carbon atoms attached to nitrogen atoms are highly shielded and resulted in the upfield shift with the chemical shift values of about -168.7 ppm (Table 3). The DFT computed chemical shift values of eight carbon atoms attached to pyrrolic nitrogen are resonate around -145 (four carbon) and -148 ppm (four carbon) with more shielded nature (Table 3).

Table 3: DFT (BP86/Def2-TZVP) computed ¹H NMR and ¹³C NMR chemical shift values (ppm) for the compound RuP(NPh₂)₂, (1).

¹ H NMR chemical shifts				¹³ C NMR chemical shifts			
24H	-9.608	48H	-6.197	4C	-145.411	38C	-168.722
25H	-8.698	55H	-2.661	5C	-135.656	39C	-123.181
26H	-8.698	56H	-2.661	6C	-148.099	40C	-123.181
27H	-8.973	57H	-5.986	7C	-134.735	41C	-129.323
28H	-8.701	58H	-5.986	8C	-108.339	42C	-129.323
29H	-8.973	59H	-6.197	9C	-108.339	43C	-125.172
30H	-8.973	66H	-2.661	10C	-134.735	49C	-168.722
31H	-9.612	67H	-2.661	11C	-108.261	50C	-123.181
32H	-8.701	68H	-5.986	12C	-108.261	51C	-123.181
33H	-8.973	69H	-5.986	13C	-135.656	52C	-129.323
34H	-8.985	70H	-6.197	14C	-135.656	53C	-129.323
35H	-8.985	77H	-2.661	15C	-134.735	54C	-125.172
44H	-2.661	78H	-2.661	16C	-145.411	71C	-168.722
45H	-2.661	79H	-2.661	17C	-145.411	72C	-123.18
46H	-5.986	80H	-5.986	18C	-148.099	73C	-123.18
47H	-5.986	81H	-6.197	19C	-148.099	74C	-129.323
				20C	-134.735	75C	-129.323

				21C	-145.411	76C	-125.172
				22C	-135.656	71C	-168.722
				23C	-148.099		

DFT (BP86/Def2-TZVP) computations on the ruthenium-porphyrin with halogens F (5), Cl (6) Br (7) and iodine (8), reveal that complexes 5-8 are not showing considerable LUMO-HOMO energy gap when consider as singlet. Whereas they are resulted in more than 2eV LUMO-HOMO energy gap in the triplet state. Ruthenium-porphyrin chemistry is continuously an interesting area of research due to the structural diversity and wider applications [32]. For example, recent synthesis of seven coordinated ruthenium idosylbenzene complex is highly reactive and used for oxygen atom transfer and C-H bond activation reactions (Figure 4).

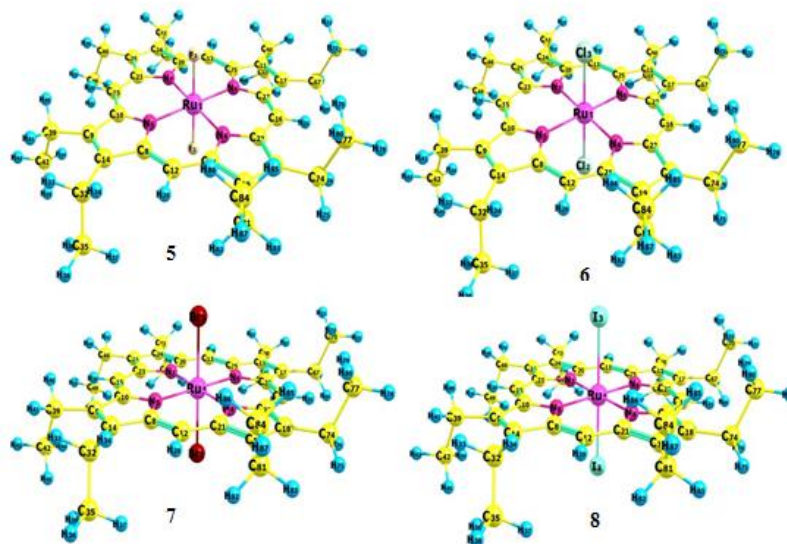


Figure 4: DFT (BP86/Def2-TZVP) optimized geometries of halogen substituted compounds 5-8 in their triplet state RuP(F)₂, (5), RuP(Cl)₂, (6), RuP(Br)₂, (7), RuP(I)₂, (8) (where P=Porphyrin).

CONCLUSION

Density Functional Theory calculations were carried out on the ruthenium-porphyrin compounds RuP[N(Ph)₂]₂ (1), RuP(NH₃)₂ (2), RuP(PH₃)₂ (3) and RuP(AsH₃)₂ (4) to study their geometrical and electronic structural features, stability and spectroscopic properties. The following conclusions were drawn from the present study: Our DFT computations confirm that the stability of these compounds mainly governed by two factors *viz.*, steric factor of the ligand and electronic factor of the porphyrin ring. DFT calculations using ORCA at BP86/def2-TZVP level predict the structural parameters for the compound RuP[N(Ph)₂]₂ (1), are in good agreement with the experimental values. DFT-optimized geometries for the compounds RuP(NH₃)₂ (2), RuP(PH₃)₂ (3) and RuP(AsH₃)₂ (4) resulted in minima in the potential energy surface and the bond parameters are in good agreement with the experimental values of similar compounds. The DFT computed geometries suggesting the possible synthesis of compounds 2-4. DFT computed energetics is really useful in ascertaining the stability of the compounds 1-4 studied. The DFT computed E_{LUMO-HOMO} value of 2.0 eV of the compounds suggests the more stable nature and the viability of the modelled compounds 2-4 when compared to that of experimentally reported ruthenium-porphyrin with diphenyl amine ligand 1. The ¹H and ¹³C, NMR chemical shifts computed at DFT (BP86/Def2-TZVP) level are in close agreement with the experimentally observed values for clusters 1. The DFT computed ¹H, ¹³C NMR and ¹¹B NMR chemical shift values also supporting the octahedral geometries of these ruthenium-porphyrin compounds with axially disposed N(Ph)₂ (1), NH₃ (2), PH₃ (3) and AsH₃ (4) ligands. DFT-optimized geometries and the computed ¹H and ¹³C NMR chemical shift values are very useful in successfully assigning the number and position of the hydrogens and carbon atoms of clusters 1-4. Though the optimized geometries of the complexes with halogen substituents in the singlet state, F (5), Cl (6), Br (7) and I (8) are resulted in minima in the potential energy surface, the viability of these complexes are not feasible from the FMO analysis. Interestingly, the halogen substituted ruthenium porphyrin complexes 5-8 are showing considerable (>2 eV) LUMO-HOMO energy gap in their triplet state. Since the importance of the ruthenium porphyrine compounds as photosensitizers in photodynamic therapy for cancer and also in photo catalysis have been revealed already, the modeled compounds could be synthesized in laboratory and might show potential applications.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

REFERENCES

- [1] Vidal A, Battistin F, Iengo E, et al. Eur J Inorg Chem. **2019**; 24: p. 2883-2890.
- [2] Funatsu K, Kimura A, Imamura T, et al. Inorg Chem. **1997**; 36(8): p. 1625-1635.
- [3] Perrin ML, Martin CA, Prins F, et al. Beilstein J Nanotechnol. **2011**; 2: p. 714-719.
- [4] Haber LH, Karam TE, Siraj N, et al. J Phy Chem. **2020**; 124(44): p. 24533.
- [5] Rebouças JS, Patrick BO, James BR. J Am Chem Soc. **2012**; 134(7): p. 3555-35570.
- [6] Siouani C, Mahtout S, Safer S, et al. J Phy Chem A. **2017**; 121(18): p. 3540-354.
- [7] Yu HZ, Baskin JS, Steiger B, et al. J Am Chem Soc. **1999**; 121(2): p. 484-485.
- [8] Wang N, Liu H, Zhao J, et al. J Phy Chem. **2009**; 113(17): p. 7416-23.

- [9] Noori M, Sadeghi H, Lambert CJ. *Nanoscale*. **2017**; 9(16): p. 5299-5304.
- [10] Cook LP, Brewer G, Wong-Ng W. *Crystals*. **2017**; 7(7): p. 223.
- [11] Li Y, Yao J, Zhong S, Zou Z. *Curr Appl Phys*. **2011**; 11(6): p. 1349-1353.
- [12] Karlström O, Linke H, Karlstrom G, et al. *Phy Rev B*. **2011**; 84(11): p. 113415.
- [13] Nagalakshmi V, Nandhini R, Brindha V, et al. *J Organomet Chem*. **2020**; 912: p. 121-175.
- [14] Krishnamoorthy BS, Kahlal S, Ghosh S, et al. *Theor Chem Acc*. **2013**; 132: p. 1-10.
- [15] K Bharathi, L Beerma, C Santhi, Krishnamoorthy B S, et al. *J Organomet Chem*. **2015**; 792: p. 220-228.
- [16] Bhoopathy P, Subramani K, Krishnamoorthy BS. *Inorg Chem Commun*. **2024**; 12: p. 112583.
- [17] Nandhini R, Krishnamoorthy BS, Venkatachalam G. *J Organomet Chem*. **2019**; 903: p. 120984.
- [18] Drummer S, Madzimbamuto T, Chowdhury M. *Materials*. **2021**; 14(11): p. 2700.
- [19] Arumugam N, Soliman SM, Viswanathan V, et al. *J Mol Struct*. **2023**; 1293: p. 136-189.
- [20] Zardi P, Pozzoli A, Ferretti F, et al. *Dalton Trans*. **2015**; 44(22): p. 10479-10489.
- [21] Neese F. *Wiley Interdiscip Rev Comput Mol Sci*. **2012**; 2(1): p. 73-78.
- [22] Wilk L, Nusair M, Vosko SH. *Can J Phys*. **1981**; 59(4): p. 585-595.
- [23] Becke AD. *J Chem Phys*. **1986**; 84(8): p. 4524-4529.
- [24] Perdew JP. *Phy Rev B*. **1986**; 33(12): p. 8822.
- [25] Che CM, Huang JS. *Coord Chem Rev*. **2002**; 231(1-2): p. 151-164.
- [26] Barry NP, Govindaswamy P, Furrer J, et al. *Inorg Chem*. **2008**; 11(10): p. 1300-1303.
- [27] Xu H, Fan H, Luan Y, et al. *J Am Chem Soc*. **2023**; 145(43): p. 23541-23555.
- [28] Li Y, Chan PW, Zhu NY, et al. *Organometallics*. **2003**; 23(1): p. 54-66.
- [29] Wang HX, Wan Q, Wu K, et al. *J Am Chem Soc*. **2019**; 141(22): p. 9027-9046.
- [30] Wang JS, Li L, Zhong RL, et al. *J Mol Catal*. **2024**; 560: p. 114114.
- [31] Chen TH, Yuan Z, Carver A, et al. *Appl Catal*. **2014**; 478: p. 275-282.
- [32] Wu ZY, Wu N, Zhang QX, et al. *ACS Appl Energy Mater*. **2023**; 6(12): p. 6580-6592.
- [33] Awasabisah D, Gangemi JF, Powell DR, et al. *Transit Met Chem*. **2023**; 1-2.
- [34] Kumar A, Prasad R. *J Iran Chem Soc*. **2023**; 20(8): p. 1997-2004.
- [35] Moura NM, Castro KA, Biazotto JC, et al. *Dyes Pigm*. **2022**; 205: p. 110501.
- [36] Pan Y, Zhou M, Wang R, et al. *Inorg Chem*. **2023**; 62(20): p. 7772-7778.